

Review

The challenge of cyclic and acyclic schiff bases and related derivatives

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Abstract

The use of planar or tridimensional cyclic and acyclic Schiff bases, their polyamine homologues and related derivatives, for the formation of mononuclear and especially polynuclear complexes, is reported.

Attention is devoted to the synthetic pathways and to the structural aspects of the resulting systems, particularly the role of the shape of the coordinating ligands and of the different metal ions in directing the synthesis totally or preferentially towards mono-, di- or poly-nuclear entities.

Special care is paid to compartmental ligands, owing to their ability to bind two or more metal ions in close proximity. The insertion of asymmetry into these ligands provides important diversification of the coordinating sites and allows for different and well defined recognition processes involving specific ions and/or molecules at the adjacent coordinating sites.

New molecular materials, devices and probes for specific recognition and detection in the solid state or solution take advantage of the presence of different metal ions at appropriate distances from each other in a preordered stereochemical environment with variation of oxidation state, magnetic, optical and redox properties. Such polynuclear systems can exhibit unusual reactivity or catalysis.

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1. Introduction

1.1. Macrocyclic and macroacyclic systems

Macrocyclic and macroacyclic compounds have attracted increasing interest owing to their role in the understanding of molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, etc. [1–8].

Many ligands have been designed to mimic the function of natural carriers in recognizing and transporting specific metal ions, anions or neutral molecules and in understanding and reproducing the catalytic activity of metallo-enzymes and proteins [1–8]. In these studies Schiff bases have been extensively employed and a large variety of planar macrocyclic and macroacyclic ligands have been synthesized to ascertain correctly the role of the different donor atoms, their relative position, the number and size of the chelating rings formed, the flexibility and the shape of the coordinating moiety on the selective binding of charged or neutral species [9–11].

The evolution of these Schiff bases has produced macrobicyclic ligands obtained in one-step multiple condensation reactions [8–10]; the cyclic [2+3] Schiff base condensation represents the extension of the [2+2] macrocyclic coordina-

tion systems into the third dimension. In addition to the use in the field of molecular recognition, catalysis and transport, these cage molecules are promising in the stabilization of particular species. The nature and disposition of donor atoms in the rigid cage may enhance the stability of unusual oxidation states in the coordinated transition metal ion, while encapsulation may protect normally labile substrate species. This combination of characteristics will eventually permit moisture sensitive chemistry to be carried out in the protected cavity under room temperature and atmospheric pressure.

Pendant arm macrocyclic or macroacyclic ligands and their metal complexes have also attracted attention [12–15]. Arms bearing additional potential ligating groups have been introduced at both carbon and nitrogen atoms of macrocycles generally based on polyaza- or polyoxa-donor sets, in order to obtain modified complexation properties relative to the corresponding simple macrocyclic or macroacyclic precursors [16–18].

The introduction of specific functionalities at the periphery of the coordinating moiety gives rise to quite sophisticated systems capable of contemporary multi-recognition processes, specific separation and transport processes across membranes or activation and catalysis in a ecocompatible solvents.

For the macrocycles the hole size represents an additional parameter which may influence greatly the ability to discriminate among the different charged or neutral species to be recognized while for the macrocyclic systems interesting properties may arise from their higher flexibility. These ligands have been primarily designed to form 1:1 complexes. The progressive enlargement of the coordinating moiety allowed studies aimed at a deep understanding of physico-chemical properties arising from the simultaneous presence of two or more metal ion in close proximity within the same coordinating moiety.

Attempts to construct *in vitro* systems that mimic the catalytic activity of enzymes have produced increasing attention to compounds that contain cavities of sufficient diameter and depth to form host–guest complexes, such complexes constituting the first intermediate in enzyme-model processes.

A wide variety of different compounds (i.e. cavitands, calixarenes, polyporphyrins, polydentate Schiff bases, poly-aza, poly-oxamacropolycycles) have been designed to throw light on these problems. Cavitands [9] and calixarenes [19–37], widely used since the clarification of the phenol-formaldehyde condensation reaction involved in their systems, represent two examples of macrocyclic systems with an enhanced capability to form stable inclusion complexes with both charged and neutral molecules and to act, after suitable functionalization both at upper and lower rings, as selective catalysts. They corroborate the possibility to design bifunctional or polyfunctional ligands capable to secure contemporary cations and anions at the different functionalities and to insert two- or more equal or different metal ions at suitable distances into their coordinating cavities.

In the past, the major interest was towards the most appropriate synthetic procedures for the preparation of dinuclear complexes and their physico-chemical properties in consequence of the close proximity of two metal ions. In particular the preparation of complexes containing two transition metal ions separated by distances of 3–6 Å is of considerable interest. At these distances, no direct interaction between the metal ions is expected, yet a substrate could interact simultaneously with both ions, and it has been shown that pairs of metal ions at suitable distance and/or with an appropriate structure can mediate certain chemical reactions either better than, or in different manner to isolated centers. Thanks to their peculiar properties, these entities offer the necessary tool for a correct molecular understanding of activation, transport and separation of specific molecules with different complexity, of the selective recognition of neutral or charged species, of the modification of appropriate surfaces, etc. They are currently proposed as essential components in the preparation of suitable devices based on specific molecular assembly.

Starting from simple dinucleating ligands, very complex planar or tridimensional cyclic or acyclic systems have been proposed and prepared using self assembling procedures, recognition processes, template effect, etc. Thus polytopic,

polyfunctional or polymeric systems, containing also lateral groups bearing additional coordinating functions, redox active groups (as ferrocene), or IR active groups (as $\text{Cr}(\text{CO})_3$) have been prepared and studied in detail. Also the use of particular complexes as ligands for further complexation has been successfully used [5,9,10].

The ability of the specific ligand to bind, in appropriate coordination sites, different metal ions is the basic principle for the design of dinucleating or polynucleating ligands.

Many excellent papers have been published during the last two decades on the preparation and properties of dinuclear complexes and the most relevant results have also been reviewed [1–11,38–50]. In particular, attention was devoted to their correlation with the active site of metallo-enzymes and metallo-proteins containing dinuclear metallo entities in order to elucidate the factors that determine the reversible binding and activation of O_2 in various natural oxygen transport systems and mono- and di-oxygenases and to mimic their activity [1–11,38–52]. Macrocyclic and macrocyclic ligands have also been used for the generation of compounds with specific spectroscopic and magnetic properties. Complexes containing magnetic metal centers may exhibit magnetic properties which are not simply the sum of those of the individual ions surrounded by their nearest neighbour ligands. These properties result from both the nature and the magnitude of the interactions between the metal ions within the molecular unit.

Using compartmental ligands, binuclear complexes have been synthesized, where the two metal centers, if paramagnetic, interact with each other through the bridging donor atoms of the ligands in a ferromagnetic or antiferromagnetic way. By changing the type of the ligand, the distance between the two chambers and/or the paramagnetic centers, it is possible to vary considerably the magnetic interaction and, with particular complexes, ferromagnetic interactions have been observed. Thus these complexes may be good building blocks for the preparation of molecular magnets.

Complexes in which a single ligand organizes more than two metal centers into some predetermined arrangement, giving rise to unique behaviour, have been also designed, synthesized and fully characterized.

In these studies Schiff bases deserve a relevant role for several reasons:

- They can be obtained by simple self-condensation of suitable formyl- or keto- and primary amine-precursors. Multiple self-condensation processes give rise to complex planar or tridimensional compounds in one step.
- They generally can contain additional donor groups (O, S, P, etc.) and this makes them good candidates for metal ion complexation and for mimicking biological systems.
- Alternatively they can be obtained by template effect, this procedure directly gives the designed complexes. Moreover, these complexes can undergo transmetalla-

tion reactions when reacted with a different metal salt; this synthetic procedure allows the formation of not otherwise accessible complexes. Template and transmetallation reactions quite often give rise to the designed complexes in high yield and in a satisfactory purity grade.

- (d) They can be functionalized by inserting appropriate groups in the aliphatic and/or aromatic chains of the formyl- or keto- and amine-precursors.
- (e) They can give rise to reductive decomplexation reactions when treated with appropriate reductants with the consequent formation of the corresponding polyamine derivatives less sensitive to hydrolysis and more flexible. These reduced compounds contain NH groups which may be further functionalized by appropriate synthetic procedures.
- (f) The use of particular Schiff bases can exhibit unusual complexation; for instance helicates derivatives have been obtained with imine derivatives containing appropriate chains and/or suitable donor sets.
- (g) They can be linked to an appropriate support (e.g. silica) giving rise to modified catalysts or modified surfaces, bearing well defined molecular assemblies.
- (h) It is well known that other systems are excellent ligands for specific metal ions (i.e. crown ether, macrocyclic thioether, polyaza derivatives, etc.). Thus the fusion of different coordinating entities (i.e. a Schiff base and crown-ether moiety) into a unique ligand can give rise to very interesting systems capable of multiple selective and/or different metal ions recognition processes.

1.2. Aim and structure of the review

In recent papers we reported a comprehensive view on these topics, reviewing the most interesting data available [5,42]. In the present article particular attention is devoted to the most recent progress made in the development of synthetic procedures for the preparation of mono-, di- and poly-nuclear Schiff base complexes and their reduced analogues, together with significant examples of closely related systems, in the study of their physico-chemical properties and in their possible applications.

Special care is devoted to the compartmental ligands, owing to their ability to secure two or more metal ions in close proximity. The insertion of asymmetry into these ligands provides a significant diversification of the coordinating sites and allows different, well defined recognition processes of specific ions and/or molecules at the adjacent coordinating sites and a correct and deep study of the physico-chemical properties arising from these aggregations.

The review basically follows the structure of a previous one published in 1995 [5] and updates the knowledge in this field up to 2002.

It can be divided into two parts. The first part, containing the Sections 2–6, mainly concerns the preparation and properties of the ligands, particularly their ability to act as mono- or poly-nucleating systems, also through additional functionalities that make them di- or poly-topic in nature. The possibility offered by suitable bridging groups to design a chemical pathway, capable of tuning the synthesis from mononuclear to polynuclear complexes and hence to obtain systems with the desired metal nuclearity, is also elucidated. Finally the ability of these systems to give rise to specific recognition, particularly anion recognition, is also considered.

The second part, containing the Sections 7–15, deals with the synthesis and properties of acyclic and cyclic complexes; the presentation follows the different nuclearity of the systems, thus the mononuclear complexes are discussed first, then the dinuclear complexes and finally the polynuclear ones. This offers the possibility to evaluate the different physico-chemical properties arising from the increase in metal nuclearity. The presence of different metal ions, in fact, at appropriate distance from each other, in a preordered stereochemical environment and oxidation state, strongly influences the magnetic, optical and redox properties of these polynuclear systems. Their relevance in obtaining unusual reactivity or catalysis, new molecular materials, devices and probes for specific recognition and detection in the solid state or solution is also considered.

In particular Section 2 is devoted to the role of peculiar formyl- and/or amine-precursors in the synthesis of Schiff bases and related complexes. Moreover the coordination ability of these systems is considered, with a particular emphasis on their ability to give rise to polynuclear systems. Related ligands, containing similar coordination moieties, have been also included in this section in order to give a broader view of the potential of these precursors and also to compare the coordination ability of the different precursors. The self-condensation reaction of these precursors gives rise to cyclic and acyclic Schiff bases which can have different size according to the experimental conditions employed. Moreover the role of the different metal ions as templating agents in directing the synthesis toward a specific Schiff base array is discussed. The parameters influencing ring expansion or ring contraction of the Schiff bases is elucidated. Also the use of transmetallation reactions in the preparation of Schiff bases, especially of those not otherwise obtainable, is reported. The preparation procedures for demetallation of Schiff bases complexes is also considered. Finally the synthetic pathway for obtaining positional isomers and/or migration reactions of specific metal ions from one chamber to another, when compartmental systems are employed, are presented.

In Section 3 the recognition, transport and separation properties of ligands, derived from the addition of specific functionalities to acyclic and cyclic Schiff bases, are taken into consideration. Also the possibility to obtain multiselective coordination processes by tuning the insertion or the

addition of coordinating groups at the periphery of the coordination moiety, is discussed.

Section 4 is especially devoted to macrocyclic and macroacyclic polyamine ligands, derived by reduction of the related Schiff bases, together with their ability to coordinate different metal ions. This allows a comparison of the properties of complexes of these ligands with those derived from Schiff bases containing the same denticity but having a different flexibility.

Section 5 deals with the ability of suitable Schiff bases and especially their reduced analogues to recognize, in addition to specific metal ions, well defined anions, leading to potential applications in hydrometallurgy, detoxification, etc.

Section 6 explains the possibility to tune the chemical synthesis toward mononuclear or polynuclear metal complexes by using ligands containing suitable bridging groups (i.e. phenol or thiosphenol groups) or appropriate spacer groups.

Section 7 deals with the synthesis and the properties of mononuclear complexes. The survey starts off by taking into consideration the complexes derived from [3+2] tridimensional macrobicyclic ligands, followed by those derived from [2+2] and [1+1] planar macrocyclic ligands. Then the complexes with planar asymmetric cyclic and acyclic ligands, containing additional functionalities, are presented.

The preparation of [2+1] planar and [3+1] tridimensional macrocyclic Schiff bases, derived from 2,5-diformylpyrazole, the supervisor diformyl-triptyrrane homologues and acyclic ligands derived from polyether substituted salicylaldehyde derivatives, are discussed. Moreover the related d- and especially 4f-metal ions complexes and their use in biology and medicine is considered. Finally the possibility to tune the synthesis of mononuclear or polynuclear complexes with acyclic [3+1] ligands is reported.

Section 8 is devoted to homo- or hetero-dinuclear complexes with symmetric and asymmetric macrocyclic Schiff bases, mainly [2+2] cyclic complexes derived from the condensation of 2,6-diformyl-4-substituted phenol or 2,6-diformyl-4-substituted thiophenol with facultative polyamines. The related reduced derivatives are also included. Furthermore complexes derived from macrobicyclic ligands or ligands bearing additional different functionalities (mainly as pendant arms) are reported.

Section 9 deals with dinuclear complexes with end-off symmetric or asymmetric and side-off acyclic ligands. The asymmetric ligands revealed that they were very useful tools for the preparation of pure hetero-dinuclear complexes. In several cases the difference of the two adjacent chambers allows the preparation of pure heterodinuclear isomers in one pot without the formation of positional isomers.

In Sections 10 and 11 polynuclear complexes with symmetric and asymmetric macrocyclic ligands are reported, respectively. The possibility to tune the synthesis pathway towards complexes with progressively increasing nuclearity, using the same keto- and amine-precursors, deserves parti-

cular attention. The use of asymmetric compounds offers additional possibilities for selective metal ion recognition at the different donor sets.

Section 12 reports the synthesis and the properties of polynuclear complexes with acyclic ligands derived from substituted salicylaldehyde, 2,6-diformyl-4-methylphenol or related derivatives. Complexes of Schiff bases containing additional auxiliaries, acyclic or cyclic in nature, are also included.

Section 13 takes into consideration Schiff base complexes and their reduced analogues, bearing a progressively increasing number of ferrocene groups. Systems bearing such redox-active groups (i.e. their possibility to give rise to the ferrocene $\rightarrow$ ferrocenium reversible reaction) offer a valid chance to their use as switching agents in complexation–decomplexation processes, making feasible their applications in catalysis, material science, hydrometallurgy and in the design of molecular devices.

In Section 14 the possibility of simple Schiff bases to act as di- or poly-nucleating ligands, through the formation of σ -bonds at the benzene ring, towards specific metal ions (i.e. Pd^{2+} , Pt^{2+}) is discussed. Moreover, a series of polynuclear complexes with giant macrocycles is reported in order to verify the role of the different coordination moiety on the properties of the resulting complexes.

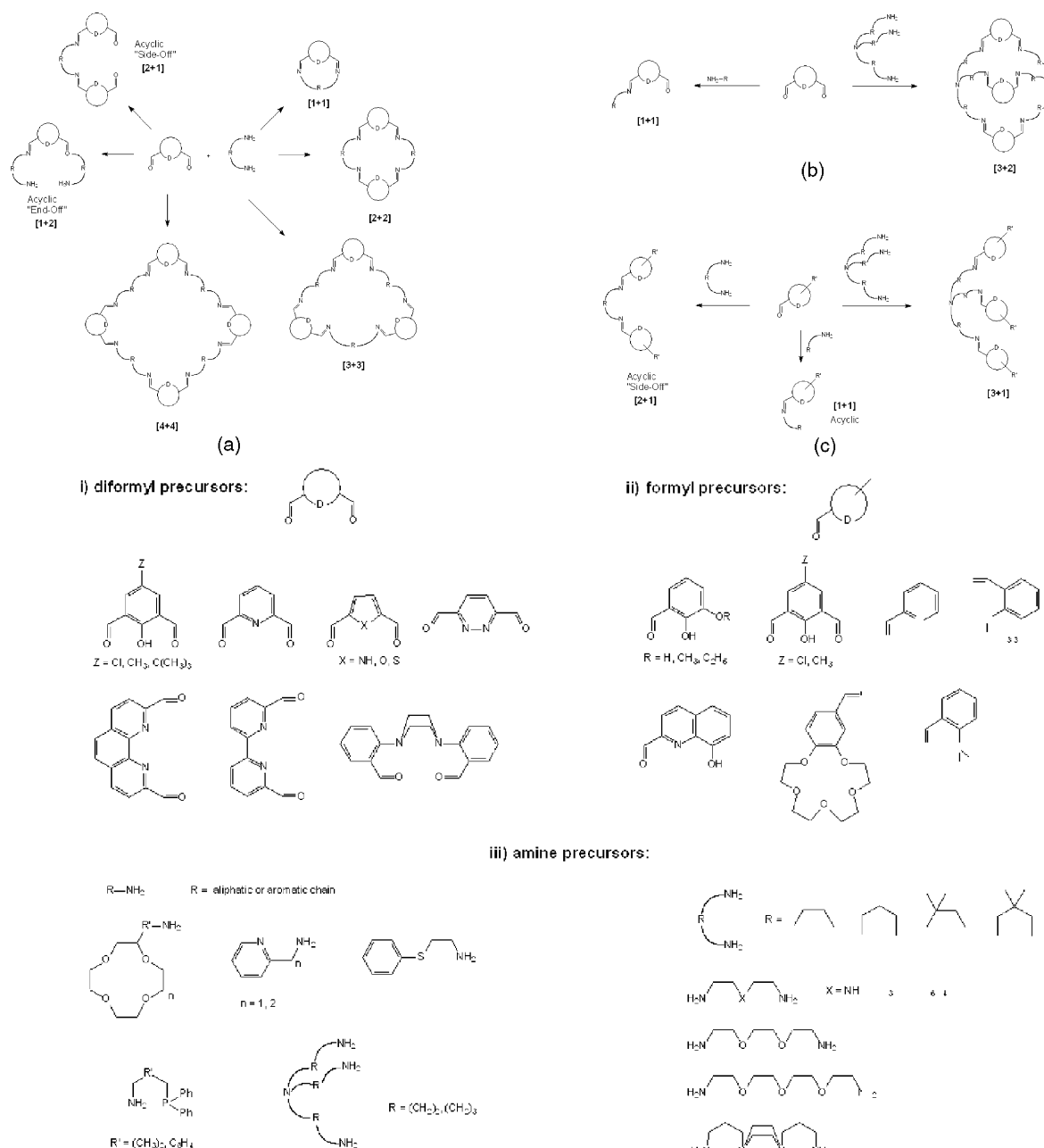
Finally in Section 15 ligands containing oximes and related homo- and hetero-polynuclear complexes are considered. Particular attention is devoted to the relevant magnetic interaction between identical or different paramagnetic centers mediated by the N–O bridges. In this context the possibility to synthesis trinuclear complexes with an almost linear $\text{M}–\text{M}–\text{M}$, $\text{M}–\text{M}'–\text{M}$ or $\text{M}–\text{M}'–\text{M}''$ metal ion assembly is particularly useful for an elucidation of the contribution of the different metal ions to the antiferromagnetic or ferromagnetic behaviour of the resulting complexes. This opens new exciting possibilities in the design of molecular ferromagnets.

2. Schiff bases

2.1. Self condensation by appropriate formyl- and amine-precursors and related polynucleating derivatives

[1+1], [2+1], [1+2] or [3+1] acyclic, [1+1], [2+2], or [3+3] macrocyclic and [3+2] macrobicyclic Schiff bases have been prepared by the well known self condensation reaction of appropriate formyl- or keto- and primary amine-precursors (Scheme 1a and b). Their acyclic or cyclic nature has been proposed especially by IR and NMR spectroscopy and mass spectrometry and often confirmed by single crystal X-ray structural determinations.

Obviously it is much easier to synthesise acyclic systems; in fact, under appropriate experimental conditions, it is possible to obtain the designed ligand in high yield and in a satisfactory pure form directly from the reaction



Scheme 1. Macrocyclic and macroacyclic Schiff bases derived from diformyl- (i), formyl (ii) and amine precursors (iii).

solution. The condensation reactions are simple and generally do not cause the formation of by-products (oligomers or polymers) in a considerable amount especially when precursors bear only one formyl- or primary amine-group

On the contrary it is often difficult to synthesise the designed cyclic Schiff bases; the use of di- or poly-functional precursors can give rise to different condensation products (cyclic or polymeric in nature) with the consequent formation of a variety of by-products which makes the purification of the designed macrocycle very difficult and thus drastically reduces the yield.

The possible instability of the prepared Schiff bases and their tendency to hydrolysis or to suffer additional reactions

causes further problems. Nevertheless many different Schiff bases are available nowadays; they have been well characterized and their coordination properties have been established correctly.

Moreover specific functionalities have been introduced (hydrophobic or hydrophilic groups, aliphatic or aromatic chains containing additional donor atoms, redox- or photo-active groups, etc.) in order to enhance or diversify the coordinating properties and/or the solubility of the resulting compounds in specific solvents.

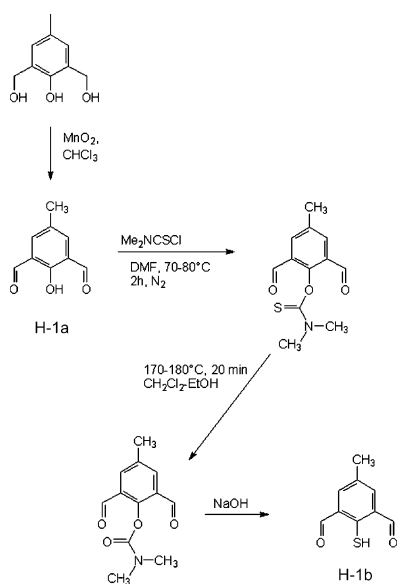
For the synthesis of these Schiff bases a wide range of formyl- and amine-precursors have been used (Scheme 1). Generally the diformyl-precursors have been prepared by

oxidation by MnO_2 , SeO_2 , etc. of the corresponding di(hydroxymethyl) derivatives. The details of the preparation and the physico-chemical properties of several of these compounds have been already reviewed together with their coordination properties [42]. We will refer to them in the following sections, only when necessary. We will be reporting here a brief report on some recent synthesised precursors, not included in previous accounts, together with related polynucleating derivatives.

Recently particular care was devoted in setting up more convenient experimental conditions for the insertion of soft groups such as $-\text{SH}$ (or SeH) instead of $-\text{OH}$ as bridging groups in the polynucleating ligands. Such a modification might be expected to increase the ligand-field strength of the chelating system due to a potential π back-donation and a weaker σ donor ability of RS^- compared to RO^- .

Thus 2,6-diformyl-4-methylthiophenol was derived from 2,6-diformyl-4-chlorophenol in a reproducible way according to Scheme 2 [53,54]. The transformation of 2,6-diformyl-4-methylphenol into the thiophenol analogue needs well defined experimental conditions. It was found that the temperature is crucial; temperature ranges, different from those reported in Scheme 2, can prevent the formation of designed precursors. Thus the preparation of 2,6-diformyl-4-methylthiophenol in considerable quantity has allowed the synthesis of new macrocyclic Schiff bases and related complexes.

Both 2,6-diformyl-4-methylphenol (**H-1a**) or 2,6-diformyl-4-methylthiophenol (**H-1b**) form dinuclear complexes with transition metal salts of the type $\text{M}_2(\text{L})_2(\text{X})_2$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+} ; $\text{X} = \text{Cl}^-$, CH_3COO^- , ClO_4^- ; $\text{H-L} = \text{H-1a}$, **H-1b**) [5,42]. Moreover **H-1a**, when reacted with lanthanide(III) salts, produces the dinuclear complexes $[\text{Ln}_2(\mu\text{-1a})_2(\text{1a})_2(\text{H}_2\text{O}_2)_4](\text{ClO}_4)_2$ and $[\text{Ln}_2(\mu\text{-1a})_2(\text{1a})_4]$ as



Scheme 2. Preparation of 2,6-diformyl-4-methylphenol and 2,6-diformyl-4-methylthiophenol.

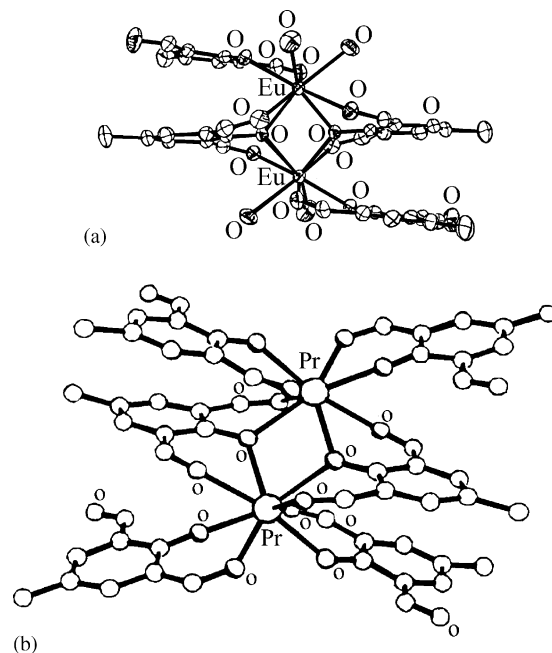


Fig. 1. Structure of $[\text{Eu}_2(\mu\text{-1a})_2(\text{1a})_2(\text{H}_2\text{O}_2)_4]^{2+}$ (a) and $[\text{Pr}_2(\mu\text{-1a})_2(\text{1a})_4]$ (b) (adapted from Ref. [55]).

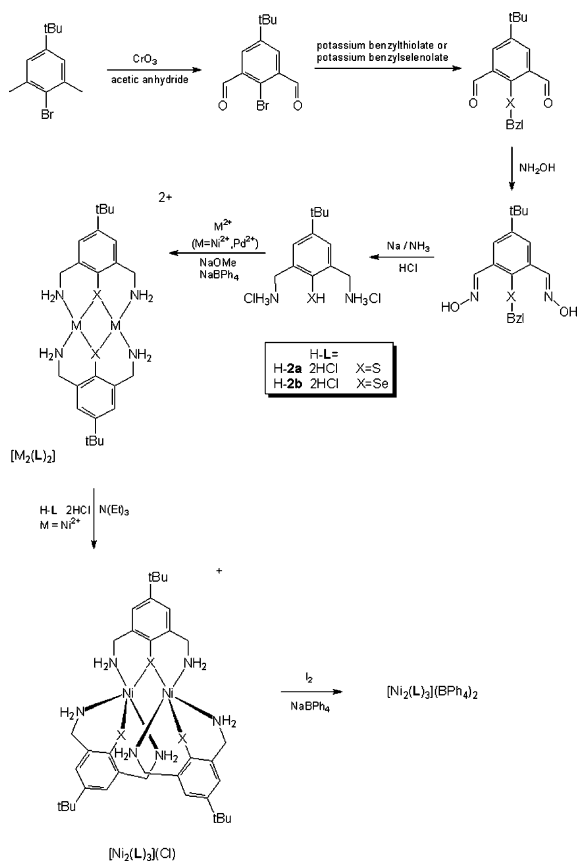
ascertained by X-ray diffractometry respectively for the europium(III) (Fig. 1a) and the praseodymium(III) complexes (Fig. 1b) [55].

In addition to 2,6-di(aminomethyl)-4-methylphenol, prepared in the recent past [54], the similar 4-*tert*-butyl-2,6-di(aminomethyl)thiophenol (**H-2a**) and 4-*tert*-butyl-2,6-di(aminomethyl)selenophenol (**H-2b**) have been prepared according to Scheme 3 [56,57].

The hydrochloride salts of the chalcogenolate ligands **H-2a** and **H-2b** react with equimolecular quantities of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of base to give the air stable dinickel(II) complexes $[\text{Ni}_2(\text{2a})_2](\text{BPh}_4)_2$ and $[\text{Ni}_2(\text{2b})_2](\text{BPh}_4)_2$. Similarly, the reaction of **H-2a** and **H-2b** with $[\text{Pd}(\text{COD})(\text{Cl})_2]$ (COD = cyclooctadiene) and NaOCH_3 in methanol produces, upon addition of NaBPh_4 , $[\text{Pd}_2(\text{2a})_2](\text{BPh}_4)_2$ and $[\text{Pd}_2(\text{2b})_2](\text{BPh}_4)_2$ (Scheme 3).

$[\text{Pd}_2(\text{2a})_2](\text{BPh}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$, isomorphous and isostructural with $[\text{Ni}_2(\text{2a})_2](\text{BPh}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$, consists of well separated molecules of the dipalladium complex and two tetraphenylborate anions. The two solvent molecules of crystallization form hydrogen bonds with nitrogen atoms of the dication but feature no bonding interactions with the palladium ions. The coordination of each palladium(II) ion by two nitrogen and two thiolate sulfur atoms is approximately planar. The two planar PdN_2S_2 units are joined via two bridging thiolate atoms. The $\text{Pd} \cdots \text{Pd}$ distance is $3.084 \text{ \AA}$. In $[\text{Ni}_2(\text{2a})_2](\text{BPh}_4)_2$ the $\text{Ni} \cdots \text{Ni}$ distance is $2.973 \text{ \AA}$ [56] (Fig. 2a).

NMR studies reveal that both complexes $[\text{M}_2(\text{2a})_2](\text{BPh}_4)_2$ ($\text{M} = \text{Pd}^{2+}$, Ni^{2+}) retain their solid-state structure in solution in non-coordinating solvents whereas in CD_3OD



Scheme 3.

or CD_3CN binding of solvent molecules to the dimetallic core yields a paramagnetic species.

All complexes undergo electrochemically reversible one-electron transfer processes in the potential range -1.0 to -0.8 V versus SCE ascribed to metal-centered reductions with formation of mixed-valent $\text{M}^{\text{I}}\text{M}^{\text{II}}$ species $[\text{M}_2(\mathbf{2a})_2]^+$. Further reduction at more negative potentials leads to the neutral $[\text{M}_2(\mathbf{2a})_2]$ species, which are not stable on the time scale of the CV experiment.

The ability of $[\text{Ni}_2(\mathbf{2a})_2](\text{BPh}_4)_2$ to bind substrates is further demonstrated by the facile reaction with another equivalent of H-2a . When a solution of $[\text{Ni}_2(\mathbf{2a})_2]^{2+}$ in acetonitrile is treated with 1 equiv. of $\text{H-2a} \cdot 2\text{HCl}$, an immediate colour change from dark red to pale green is observed, accompanied by formation of $[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$. Although its structure is not yet available, the $[\text{Ni}_2(\mathbf{2a})_3]^+$ cation is assumed to be isostructural to its oxidation product $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$ in $[\text{Ni}_2(\mathbf{2a})_3](\text{BPh}_4)_2$ obtained by reaction of $[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$ with I_2 .

$[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$ is air sensitive while $[\text{Ni}_2(\mathbf{2a})_3](\text{BPh}_4)_2$ is air stable both in the solid state and in solution. Oxidation of $[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$ with I_2 or O_2 affords the same $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$ cation. The oxidation of $[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$ is chemically reversible. Thus, addition of NaBH_4 to a solution of $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$ reforms $[\text{Ni}_2(\mathbf{2a})]^{+}$. Reduction of $[\text{Ni}_2(\mathbf{2a})_3]_2(\text{BPh}_4)_2$ with zinc in DMF also gives $[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$. Finally, addition of

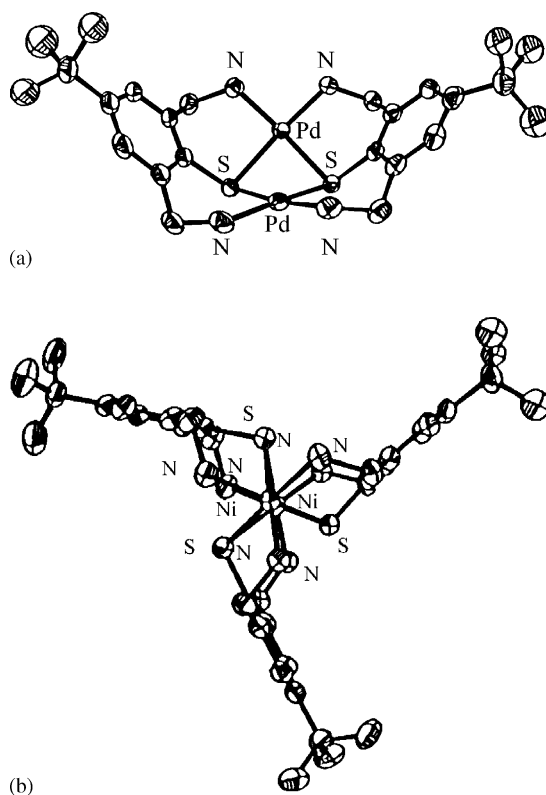


Fig. 2. Structure of $[\text{Pd}_2(\mathbf{2a})_2]^{2+}$ (a) and $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$ (b) (adapted from Refs. [56,57]).

1.0 or 0.5 equiv. of I_2 to a DMF solution of $[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$ or $[\text{Ni}_2(\mathbf{2a})_3]_2(\text{BPh}_4)_2$, respectively, results in the formation of a transient dark green solution tentatively assigned to the species $[\text{Ni}_2(\mathbf{2a})_3]^{3+}$, which is thermally unstable.

$[\text{Ni}_2(\mathbf{2a})_3](\text{BPh}_4)_2$ consists of a discrete, dinuclear $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$ complex cation in which two fac- $\text{N}_3\text{S}_3\text{Ni}$ units are joined by the thiolate sulfur atoms. The dication possesses idealized D_{3h} symmetry. Hence the dication exists as the meso isomer (Λ , D) in the solid state (Fig. 2b). The structural data suggest that this complex is a trapped-valence $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ complex rather than being delocalized.

$[\text{Ni}_2(\mathbf{2a})_3]^+$ and $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$, examined electrochemically in DMF, show that the characteristics of the reduction of $[\text{Ni}_2(\mathbf{2a})_3](\text{BPh}_4)_2$ are essentially the same as those of the oxidation of $[\text{Ni}_2(\mathbf{2a})_3]^+$. On the CV time scale $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$ undergoes two reversible electron-transfer reactions at $E_{1/2} = -0.02$ and $+0.44$ V versus SCE, affording $[\text{Ni}_2(\mathbf{2a})_3]^{2+}$ and the transient dark green trication $[\text{Ni}_2(\mathbf{2a})_3]^{3+}$, respectively. The oxidation of $[\text{Ni}_2(\mathbf{2a})_3](\text{Cl})$ occurs at a relatively low potential, a situation that is consistent with the observation that thiolates are powerful in stabilizing the nickel ion in the trivalent state. Remarkably, the redox potential for the $[\text{Ni}_2(\mathbf{2a})_3]^+ / [\text{Ni}_2(\mathbf{2a})_3]^{2+}$ couple is quite low for a complex that has a positive charge. The majority of the complexes that exhibit potentials at or just below 0 V versus SCE are anions.

Two dinuclear nickel complexes of the tridentate amine-selenolate ligand 4-*tert*-butyl-2,6-di-(aminomethyl)selenophenol, **H-2b** have been synthesized by a procedure similar to that used for the analogous amino-thiolate complexes (Scheme 3) [56,57].

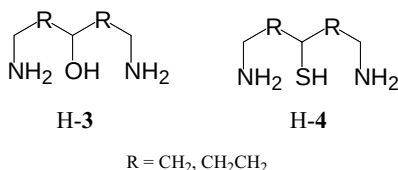
The spectroscopic properties of the thiolate and selenolate complexes are very similar, indicating similar properties of the tridentate amine-chalcogenolate ligands. Moreover, the selenolate and thiolate complexes are isostructural.

The crystal structure of $[\text{Ni}_2(\mathbf{2b})_3](\text{BPh}_4)_2$ confirms the mixed-valent nature of the $[\text{Ni}_2(\mathbf{2b})_3]^{2+}$ dication. $[\text{Ni}_2(\mathbf{2b})_3](\text{BPh}_4)_2$ is isostructural with the amine-thiolate complex $[\text{Ni}_2(\mathbf{2a})_3](\text{BPh}_4)_2$. Both nickel ions are facially coordinated to three amine nitrogen atoms and three bridging selenolate atoms of three $[\mathbf{2a}]^-$ ligands. The N_3Se_3 octahedra around the two nickel ions are different, and consequently, the local symmetry of the $[\text{Ni}_2(\mathbf{2b})_3]^{2+}$ dication is distorted from D_{3h} symmetry.

A metal-centered rather than a ligand-centered oxidation is also supported by infrared spectroscopy. From the apparent distortions from D_{3h} symmetry, $[\text{Ni}_2(\mathbf{2b})_3](\text{BPh}_4)_2$ appears to be a trapped-valence $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ complex. A delocalized species would be expected to have structurally identical nickel sites. The greater extent of distortion in Ni–N and Ni–Se distances at one nickel ion may be due to a Jahn–Teller distortion, which is expected for an octahedral Ni^{III} ion with low-spin d^7 electronic configuration.

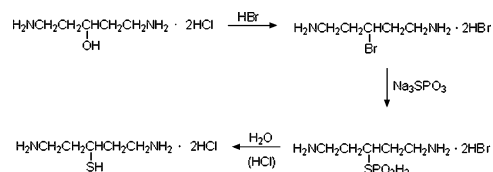
On the CV time scale $[\text{Ni}_2(\mathbf{2b})_3]^+$ undergoes two reversible one-electron oxidations at $E_{1/2}' = -0.15$ and $E_{1/2}^2 = +0.29$ V versus SCE, affording $[\text{Ni}_2(\mathbf{2b})_3]^{2+}$ and the thermally not stable trication $[\text{Ni}_2(\mathbf{2b})_3]^{3+}$, respectively. The EPR spectrum of a powdered sample of $[\text{Ni}_2(\mathbf{2b})_3]^{2+}$ reveals an $S = 3/2$ ground state of the mixed-valent $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ complex.

The potentially dinucleating diamines **H-3** and **H-4** have been extensively used in the formation of macrocyclic or macroacyclic systems [58–60].



1,5-Diamino-3-pentanol (**H-3**, $\text{R} = \text{CH}_2$) was prepared by reduction with NaBH_4 of the corresponding 1,5-diamino-3-pentanone, which was synthesized by reaction of 1,5-dichloro-3-pentanone with potassium phthalimine followed by hydrolysis of the resulting product with HCl. It reacts with transition metal ions forming dinuclear complexes of the type $[\text{M}_2(\mathbf{3})_2]^{2+}$, $[\text{M}_2(\mathbf{3})(\text{Cl})_2(\text{X})]$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+} , $\text{X} = \text{Cl}, \text{OH}, \text{OCH}_3$). Strong antiferromagnetic interactivity operates in the dinuclear copper(II) complexes while the analogous nickel(II) ones are diamagnetic.

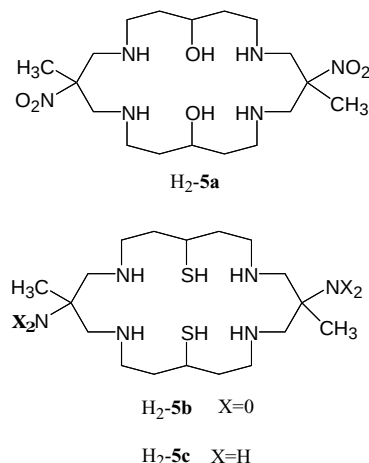
1,5-Diamino-3-pentathiol (**H-4**, $\text{R} = \text{CH}_2\text{CH}_2$), prepared according to Scheme 4, also forms the square planar dia-



Scheme 4.

magnetic homo-dinuclear complexes $[\text{M}_2(\mathbf{4})_2(\text{X})_2]$ ($\text{M} = \text{Ni}^{2+}$, Pd^{2+} ; $\text{X} = \text{Br}^-$, ClO_4^- , NO_3^- , BPh_4^- , NCS^-). Also the diamagnetic cobalt(III) complex $[\text{Co}_2(\mathbf{4})_3](\text{ClO}_4)_3$ was synthesized; the proposed structure is a biocuboctahedron facially joined at the three thiolate sulfur atoms [58,60].

Moreover, in addition to the acyclic [1+2] or cyclic [2+2], [3+3] or [4+4] Schiff bases, obtained by the condensation of **H-3** or **H-4** with the appropriate formyl- or diformyl-derivatives already reported in previous articles [5,42,44,47–49], and/or reported in subsequent sections they can give rise to the macrocycles $\text{H}_2\text{-5a} \cdots \text{H}_2\text{-5c}$ when reacted with formaldehyde and nitroethane in the presence of triethylamine, as confirmed for $[\text{Cu}_2(\mathbf{5a})](\text{ClO}_4)_2$ and $[\text{Ni}_2(\mathbf{5b})](\text{ClO}_4)_2$.



The $[\text{Ni}_2(\mathbf{5b})]^{2+}$ complex cation contains two nickel(II) ions, each bound by two secondary nitrogen and two bridging thiolate donors in essentially planar *cis*- NiN_2S_2 geometries, the donors being part of a [20]-membered macrocyclic ring [60]. The complex is a *syn* isomer, rather than the *anti* isomer found for the analogue $[\text{Cu}_2(\mathbf{5a})]^{2+}$. The two N_2NiS_2 units are not coplanar, but are hinged at the bridging thiolates located on a crystallographic mirror plane, bending down away from the side of the ring where the nitro groups reside. The six-membered rings introduced with nitro substituents during macrocyclization adopt skew-boat conformations, with one oxygen of each nitro interacting axially with a nickel ion. The $\text{Ni} \cdots \text{Ni}$ separation is 3.182 Å (Fig. 3).

A series of similar compounds, inspired by the above precursors, have been successfully used in the formation of di- or poly-nuclear complexes. Thus *N,N'*-tetramethyl-1,3-

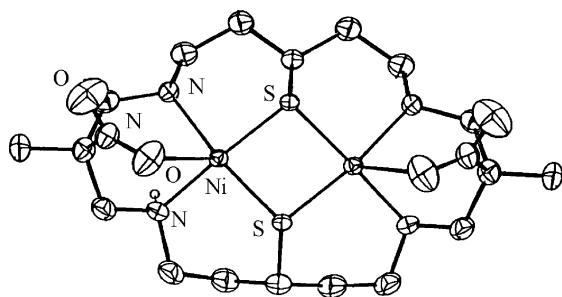
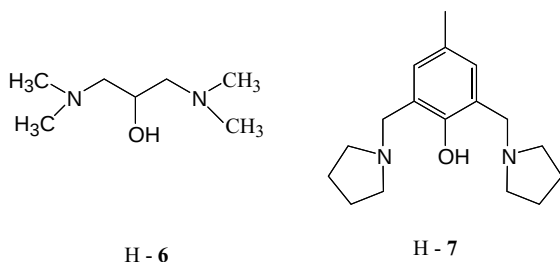


Fig. 3. Views of the cation $[\text{Ni}_2(\mathbf{5b})]^{2+}$ (adapted from Ref. [60]).

diamino-3-hydroxypropane (**H-6**) reacts with CuCl_2 in a 1:1 molar ratio to give $[\text{Cu}_2(\text{H-6})_2(\text{Cl})_4]$ where each copper(II) ion is coordinated by two chlorine atoms and one nitrogen atom and is bridged to the other copper(II) ion by two oxygen atoms [61–63]. The coordination geometry around the copper(II) ion is, therefore, a distorted square pyramid with a chlorine atom as a weakly coordinated axial ligand: the $\text{Cu} \cdots \text{Cu}$ distance is 2.847 Å. The free nitrogen atoms are protonated [61] (Fig. 4a). $[\text{Cu}_2(\text{H-6})_2(\text{Cl})_4]$ has an effective magnetic moment $\mu_{\text{eff}} = 1.14\mu_{\text{B}}$ at 23 °C, attributed to the presence of an antiferromagnetic coupling between the two metal ions.



Reaction of $[\text{Cu}_2(\text{H-6})_2(\text{Cl})_4]$ with $\text{Cu}(\text{OCH}_3)_2$ in a 1:1 ratio in CH_2Cl_2 gives rise to $[\text{Cu}_3(\mathbf{6})_2(\text{Cl})_4]$. This trimetallic compound was also obtained by the reaction of CuCl_2 with $[\text{Na}(\mathbf{6})]$ in tetrahydrofuran. The formation of $[\text{Cu}_3(\mathbf{6})_2(\text{Cl})_4]$ is the direct result of proton removal from the ammonium group in $[\text{Cu}_2(\text{H-6})_2(\text{Cl})_4]$ by the methoxide ligand.

In $[\text{Cu}_3(\mathbf{6})_2(\text{Cl})_4]$ both amino groups of $[\mathbf{6}]^-$ are bonded to copper(II) ions. The oxygen atom in one of the chelating ligands is bonded to three Cu centers [61]. The oxygen atom in the other chelating ligand bridges the copper(II) ions, Cu(2) and Cu(3). The geometry about Cu(3) and Cu(2) is approximately square planar while Cu(1) has a distorted square pyramidal environment [61] (Fig. 4b). The distances between these three metal centers span a considerable range: $\text{Cu}(1) \cdots \text{Cu}(2) = 3.378$ Å, $\text{Cu}(1) \cdots \text{Cu}(3) = 3.027$ Å, and $\text{Cu}(2) \cdots \text{Cu}(3) = 3.200$ Å. The relatively short $\text{Cu}(1) \cdots \text{Cu}(3)$ distance is probably caused by double bridges of oxygen atoms.

$[\text{Pr}_2(\mathbf{6})_2(\text{hfacac})_4(\text{H}_2\text{O})_2] \cdot 2\text{THF}$, where H-hfacac is hexafluoroacetylacetone (Fig. 5a), was obtained from the reaction of $\text{Pr}(\text{hfacac})_3$, **H-6** and H_2O in a 1:1:1 molar ratio in THF. The two praseodymium(III) centers are bridged by two

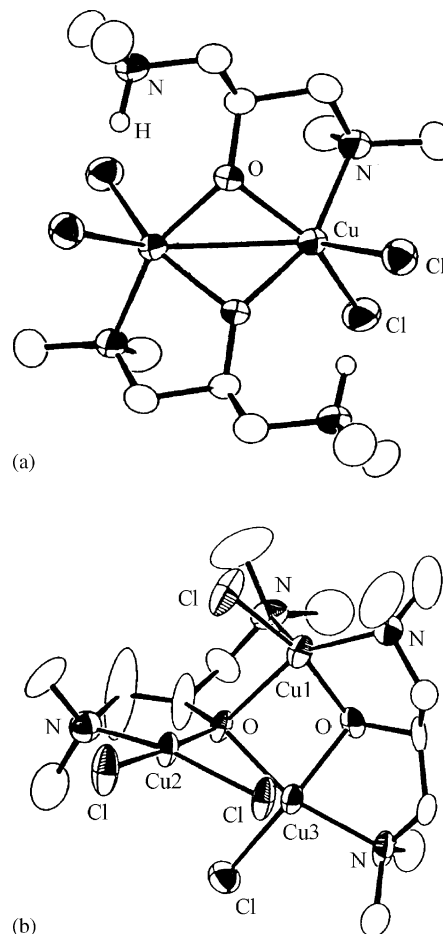


Fig. 4. Structure of $[\text{Cu}_2(\text{H-6})_2(\text{Cl})_4]$ (a) and $[\text{Cu}_3(\mathbf{6})_2(\text{Cl})_4]$ (b) (adapted from Ref. [61]).

oxygen atoms of the ligand $[\mathbf{6}]^-$ with a $\text{Pr} \cdots \text{Pr}$ separation of 3.951 Å. Each praseodymium(III) center is also coordinated by four oxygen atoms of the $[\text{hfacac}]^-$ ligands, two nitrogen atoms of the two ligands $[\mathbf{6}]^-$ and a H_2O molecule. The disordered THF solvent molecule is hydrogen-bonded to the H_2O ligand [62,63].

The heteropolynuclear complexes $[\text{LnCu}(\mathbf{6})_2(\text{hfacac})_2(\text{CF}_3\text{COO})(\text{L})]$ ($\text{Ln} = \text{Pr}^{3+}$, Y^{3+} ; $\text{L} = 2\text{-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato}$) (Fig. 5b), were isolated as blue crystalline products in low yield along with the compound $[\text{LnCu}(\mathbf{6})_2(\text{hfacac})_4(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Pr}^{3+}$) from the reaction of $\text{Cu}(\text{OCH}_3)_2$, $\text{Ln}(\text{hfacac})_3$, and **H-6** in a 1:1:2 molar ratio in THF at 23 °C. These compounds have the same structures in the solid state. The copper(II) and praseodymium(III) ions are bridged by two oxygen atoms from the two $[\mathbf{6}]^-$ ligands with a separation distance of 3.355 Å. The copper(II) center is coordinated by two additional nitrogen atoms, the fifth position of the copper(II) center is occupied by an oxygen atom of a trifluoroacetate ligand. The copper(II) geometry is therefore square pyramidal [62,63].

The trifluoroacetate and 2-methyl-2,4,6-tris(trifluoromethyl)1,3-dioxane-2,4-diolate derive from the decomposi-

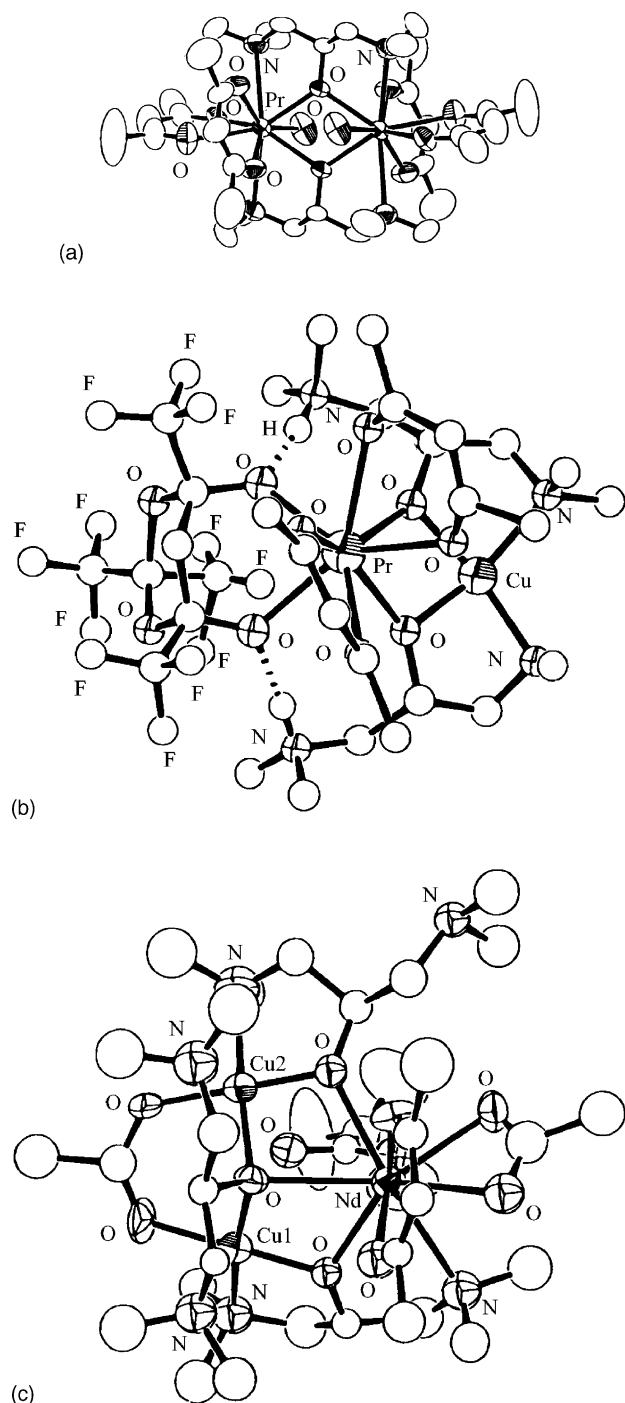


Fig. 5. Structure of $[\text{Pr}_2(\mathbf{6})_2(\text{hfacac})_4(\text{H}_2\text{O})_2]$ (a), $[\text{PrCu}(\mathbf{6})_2(\text{hfacac})_2(\text{CF}_3\text{COO})(\text{L})]$ (b) and $[\text{NdCu}_2(\mathbf{6})_3(\text{hfacac})(\text{CF}_3\text{COO})_2]$ (c) (adapted from Refs. [62,63]).

tion of Hfacac and further reactions promoted by the presence of the metal complex [62,63].

The praseodymium(III) center is surrounded by eight oxygen atoms with four from two hfacac ligands, two from the ligands $[\mathbf{6}]^-$, and two from the ligand L, 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato. The ligand L can be considered as a derivative of 1,3-dioxane-4,6-diol. It has a chair conformation with 4,6-trifluoromethyl groups

occupying the equatorial positions and the two oxygen atoms occupying the axial positions.

The amino groups on the ligand $[\mathbf{6}]^-$ appear to function as a Lewis base to remove the protons on the diol, thereby increasing its nucleophilicity and stabilizing the product. In $[\text{PrCu}(\mathbf{6})_2(\text{hfacac})_2(\text{CF}_3\text{COO})(\text{L})]$, the ligand $[\mathbf{6}]^-$ has a zwitterionic form with one of the amino groups being coordinated to the copper center and the other one being protonated. The protonated amino groups form hydrogen bonds with the two oxygen atoms of the L ligand. The metal centers seem to play an important role in the formation of L because independent syntheses of L in the absence of the metal complexes were unsuccessful. Attempts to free L from the complex by the addition of acids have not been successful perhaps due to the decomposition of L under such conditions.

The copper(II) center is believed to play an important role because the formation of L was not observed when only yttrium or lanthanide complexes were prepared as verified in the synthesis of $[\text{Pr}_2(\mathbf{6})_2(\text{hfacac})_4(\text{H}_2\text{O})_2] \cdot (\text{THF})_2$.

$[\text{NdCu}_2(\mathbf{6})_3(\text{CF}_3\text{COO})_2(\text{hfacac})](\text{H-hfacac}) \cdot (\text{THF})$ (Fig. 5c) was obtained from the reaction of $\text{Nd}(\text{hfacac})_3$ with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and H-6 in a 1:1:3 molar ratio in THF. The trifluoroacetate ligand in this complex is believed again to be one of the decomposition products of the hfacac ligand [62,63].

The three metal ions in $[\text{NdCu}_2(\mathbf{6})_3(\text{hfacac})(\text{CH}_3\text{COO})_2(\text{CF}_3\text{COO})](\text{H-hfacac})(\text{THF})$ are bridged by three $[\mathbf{6}]^-$ ligands through the oxygen atoms in a triangular arrangement, the $\text{Cu} \cdots \text{Cu}$, and $\text{Nd} \cdots \text{Cu}$ distances being 3.165, 3.525, and 3.546 Å, respectively. Each copper center is coordinated by three oxygen atoms and one nitrogen atom with normal bond lengths and an approximate square planar geometry. The oxygen atom of the trifluoroacetate ligand and the nitrogen atoms of a ligand $[\mathbf{6}]^-$ occupy the fifth and the sixth positions of the two copper ions [63,64]. The geometry of the copper(II) ions, has been described as an elongated octahedron. The neodymium(III) ion is surrounded by one nitrogen atom and eight oxygen atoms, three from the ligands $[\mathbf{6}]^-$ two from the acetate ligand, one from the oxygen trifluoroacetate ligand, and two from the oxygens of the hfacac ligand. One of the amino groups of the ligands $[\mathbf{6}]^-$, is not coordinated to any metal center, and its lone pair is oriented away from the complex. Possibly a nitrogen atom forms two hydrogen bonds with the oxygen atoms of the non-coordinating H-hfacac molecule in the lattice. The non-coordinating H-hfacac ligand has the enol form [62,63].

4-Methyl-2,6-bis(pyrrolidin-1-yl-methyl)phenol (H-7), prepared by a Mannich reaction between *p*-cresol, formaldehyde and pyrrolidine, reacts with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or CuBr_2 to form in methanol/water the complexes $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4] \cdot 2\text{CH}_3\text{OH}$ and $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Br})_4]$. Water serves as a source for the μ_4 -oxo ligand [64].

$[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4] \cdot 2\text{CH}_3\text{OH}$ consists of a tetrahedron of four copper(II) ions coordinating a central μ_4 -oxygen atom.

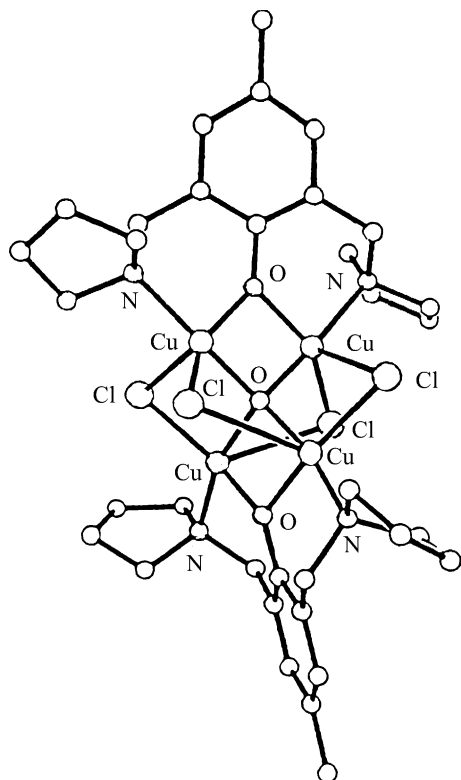


Fig. 6. Structure of $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4]$ (adapted from Ref. [64]).

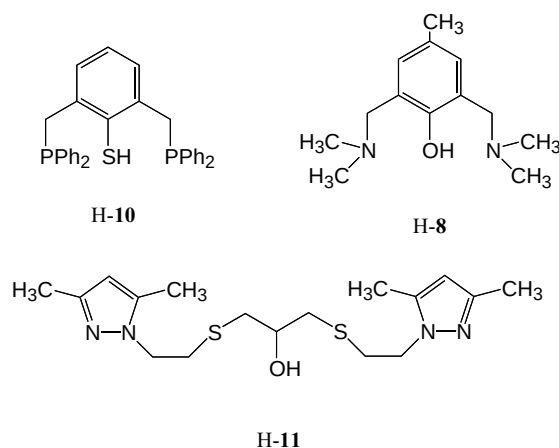
Four edges of the Cu_4 tetrahedron are bridged by chlorine atoms whereas the two remaining ones are bridged by the phenoxo group of the deprotonated ligand $[\mathbf{7}]^-$. The nitrogen atoms of $[\mathbf{7}]^-$ are bound as terminal ligands to each of the copper atoms. Each copper ion is in a NO_2Cl_2 donor set and its coordination geometry is best described as distorted square pyramidal with a chlorine atom at the apex. The chlorine atoms are bridging in such a way that an axial chlorine of the coordination sphere of one copper belongs to the basal plane of another copper (Fig. 6) [64].

The structure of $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Br})_4]$ is closely related to that of the chlorine analogue. The chlorine atoms are replaced by bromine atoms. As in $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4] \cdot 2\text{CH}_3\text{OH}$ the central Cu_4 tetrahedron is strongly distorted. The copper ions are in a NO_2Br_2 environment and their coordination geometry is intermediate between square pyramidal and trigonal bipyramidal. In contrast to the situation in the chlorine complex, the phenolato oxygen atoms are symmetrically surrounded [64].

An antiferromagnetic exchange interaction is operating in both complexes $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4] \cdot 2\text{CH}_3\text{OH}$ and $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Br})_4]$ [64]. Since the average $\text{Cu}-\text{X}-\text{Cu}$ ($\text{X} = \text{Br}$ or Cl) distances are relatively large in $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4] \cdot 2\text{CH}_3\text{OH}$ and $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Br})_4]$, a significant magnetic exchange contribution via this pathway can be excluded. So the only possible pathways allowing a magnetic interaction are $\text{Cu}-\text{O}_{\text{phenolate}}-\text{Cu}$ and $\text{Cu}-\text{O}_{\text{oxo}}-\text{Cu}$. The structures of $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4] \cdot 2\text{CH}_3\text{OH}$ and $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Br})_4]$ can

therefore be reduced to a central Cu_4O_3 core which can be described as two $\mu_4\text{-O}$ -connected Cu_2O_2 rings. The coupling within the dinuclear Cu_2O_2 subunit is expected to be larger than the interdimer exchange interaction via the μ_4 -oxygen atom ($J_{12} = -275 \text{ cm}^{-1}$, $J_{13} = -27.8 \text{ cm}^{-1}$ for $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Cl})_4] \cdot 2\text{CH}_3\text{OH}$, $J_{12} = -261 \text{ cm}^{-1}$, $J_{13} = -21.6 \text{ cm}^{-1}$ for $[\text{Cu}_4(\mathbf{7})_2(\text{O})(\text{Br})_4]$) [64].

2,6-Bis[(dimethylamino)methyl]-4-methylphenol, **H-8**, made quantitatively from 4-methylphenol and an excess of dimethylamine and formaldehyde, yields the mononuclear copper(II) complex $[\text{Cu}(\mathbf{8})_2(\text{H}_2\text{O})]$, when reacted with $\text{Cu}(\text{OCH}_3)_2$ in tetrahydrofuran [65,66], where the copper center has a trigonal bipyramidal geometry with the phenoxo oxygen atoms occupying the axial positions and the water oxygen and the nitrogen atoms occupying the equatorial positions. Moreover, two hydrogen bonds between the H_2O ligand and the two dangling dimethylamino groups occur (Fig. 7).



$[\text{Pr}^{\text{III}}\text{Cu}^{\text{II}}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{hfacac})_3]$ has been obtained from the reaction of $\text{Cu}(\text{OCH}_3)_2$ with **H-8** and $\text{Pr}(\text{hfacac})_3$ in a 1:2:1 ratio via the preliminary formation of the mononuclear compound $[\text{Cu}(\mathbf{8})_2(\text{H}_2\text{O})]$ or from the direct reaction of $[\text{Cu}(\mathbf{8})_2(\text{H}_2\text{O})]$ with $\text{Pr}(\text{hfacac})_3$ in a 1:1 ratio. $[\text{Pr}^{\text{III}}\text{Cu}^{\text{II}}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{hfacac})_3]$ is stable in the solid state but undergoes slow decomposition in solution upon exposure to air. $[\text{Pr}^{\text{III}}\text{Cu}^{\text{II}}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{hfacac})_3]$ is a dinuclear

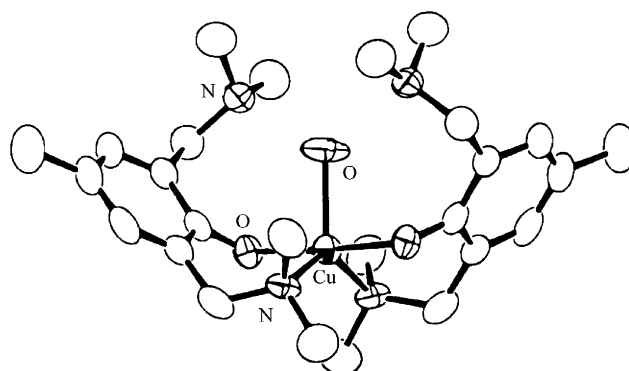
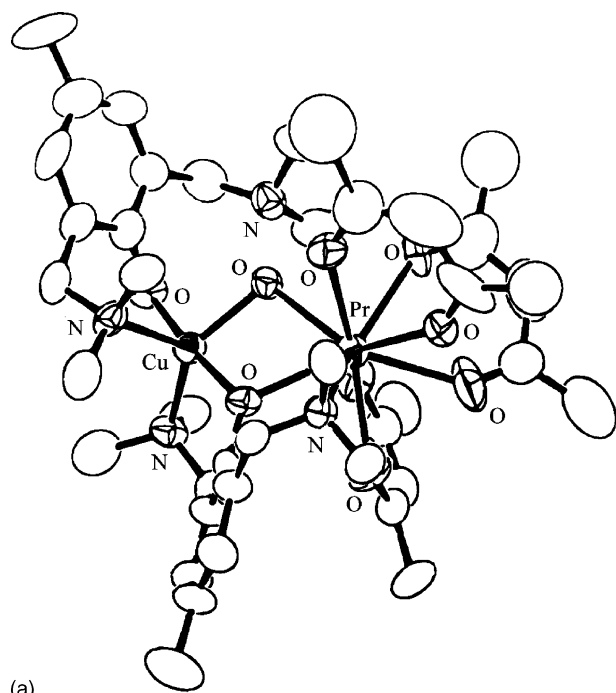
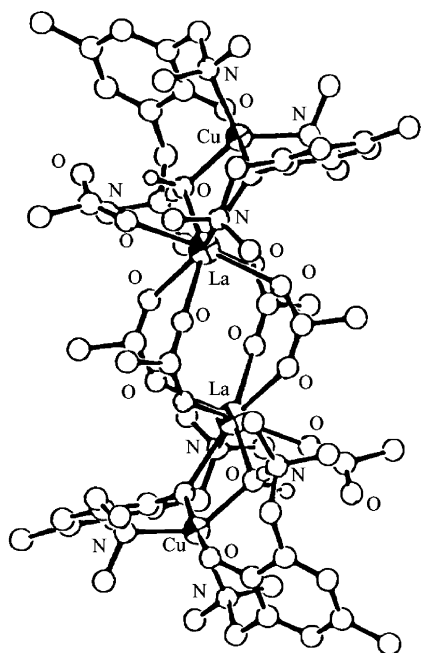


Fig. 7. Structure of $[\text{Cu}(\mathbf{8})_2(\text{H}_2\text{O})]$ (adapted from Refs. [65,66]).



(a)



(b)

Fig. 8. Structure of $[\text{PrCu}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{hfacac})_3]_2$ (a) and $[\text{LaCu}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{CF}_3\text{COO})_3]_2$ (b) (adapted from Refs. [65,66]).

complex where the $\text{Pr}(\text{hfacac})_3$ unit is linked to the copper monomer through a hydroxo and a phenoxo bridge with a $\text{Pr} \cdots \text{Cu}$ distance of 3.538 Å (Fig. 8a). The copper(II) center has a trigonal bipyramidal geometry similar to that of $[\text{Cu}(\mathbf{8})_2(\text{H}_2\text{O})]$. The praseodymium(III) ion is surrounded by one nitrogen and eight oxygen atoms in an irregular polyhedral geometry [65,66].

The structure of $[\text{La}^{\text{III}}\text{Cu}^{\text{II}}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{CF}_3\text{COO})_3]_2$, also obtained via either the reaction of $\text{Cu}(\text{OCH}_3)_2$ with **H-8**

and $\text{La}(\text{CF}_3\text{COO})_3$ in a 1:2:1 ratio or the reaction of $[\text{Cu}(\mathbf{8})_2(\text{H}_2\text{O})]$ with 1 equiv. of $\text{La}(\text{CF}_3\text{COO})_3$, consists of $\text{La}(\text{CF}_3\text{COO})_3$ unit linked to the copper(II) monomer via a hydroxo and a phenoxo bridge with a $\text{La} \cdots \text{Cu}$ distance of 3.556 Å. The Cu(II) center again has a distorted trigonal bipyramidal geometry (Fig. 8b) [65,66].

The hydrogen-bonding pattern in $[\text{LaCu}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{CF}_3\text{COO})_3]_2$, is therefore similar to that in the PrCu homologue. Instead of functioning as a chelating ligand, four of the trifluoroacetate ligands in the LaCu complex act as bridging ligands to link the two dinuclear LaCu units. As a result, the lanthanum(III) center is surrounded by seven oxygen atoms. The structural difference between the PrCu and LaCu compounds is clearly caused by the tendency of the *hfacac* ligand in the PrCu compound to chelate and the tendency of the carboxylate ligand in the LaCu one to bridge [65,66].

$[\text{Cu}_4(\mathbf{8})_2(\mu_4\text{-O})(\text{CF}_3\text{COO})_4]$, synthesized by the reaction of $\text{Cu}(\text{OCH}_3)_2$, **H-8**, $\text{Cu}(\text{CF}_3\text{COO})_2$, and H_2O in a 1:1:1:0.5 ratio in tetrahydrofuran, consists of four copper(II) ions bridged by an oxygen atom in an approximately tetrahedral environment. The oxygen atom of the ligand $[\mathbf{8}]^-$ bridges two copper centers, resulting in two copper $\cdots$ copper distances of 2.930 and 2.933 Å, the other copper $\cdots$ copper distances ranging from 3.155 to 3.379 Å. Each copper center is coordinated by three oxygen atoms and one nitrogen atom. There are considerable deviations of the geometry of the copper center from the ideal square plane, although each CuO_3N portion is essentially planar. The two $\text{Cu}_2\text{O}_4\text{N}_2$ dinuclear units are nearly perpendicular. The fifth position of each copper center is occupied by an oxygen atom of the trifluoroacetate ligands (Fig. 9). The geometry of the copper center therefore has been described as a distorted square pyramid [65,66].

^1H NMR spectra of the tetracopper complex reveals a fluxional behaviour caused by the switching of positions of the weakly bonded carboxylate oxygen atom between two copper centers [65,66].

In $[\text{PrCu}(\text{H-8})(\mathbf{8})(\mu\text{-OH})(\text{hfacac})_3]$, the presence of some degree of antiferromagnetic exchange was supposed [65,66].

The magnetic susceptibility of $[\text{Cu}_4(\mathbf{8})_2(\mu_4\text{-O})(\text{CF}_3\text{COO})_4]$ indicates that the magnetism in the tetracopper complex is dominated by the antiferromagnetic exchange within the dimers ($J_1 = J_2 = -101 \text{ cm}^{-1}$); the interdimer interactions, albeit weaker, are substantial ($J_3 = -45 \text{ cm}^{-1}$, $J_4 = 3 \text{ cm}^{-1}$) [65,66].

2,6-Bis[(dimethylamino)methyl]-4-methylphenol (**H-8**), reacts with *n*-butyl-lithium or sodium hydride in hexane to form $[\text{Li}(\mathbf{8})_3]$ and $[\text{Na}(\mathbf{8})_4]$ [67]. The subsequent reaction of the sodium derivative with an excess of ligand in hexane gives rise to $[\text{Na}(\mathbf{8})(\text{H-8})_2]$ [65,67]. The reaction of the sodium derivative with lutetium or yttrium trichloride in a 3:1 molar ratio and in THF at room temperature forms the hetero-dinuclear complex $[\text{LnNa}(\mathbf{8})_3(\text{Cl})]$ [68] (Scheme 5).

$[\text{Li}(\mathbf{8})_3]$ is a trinuclear entity and contains an almost perfectly planar Li_3O_3 six-membered central ring. Adjacent

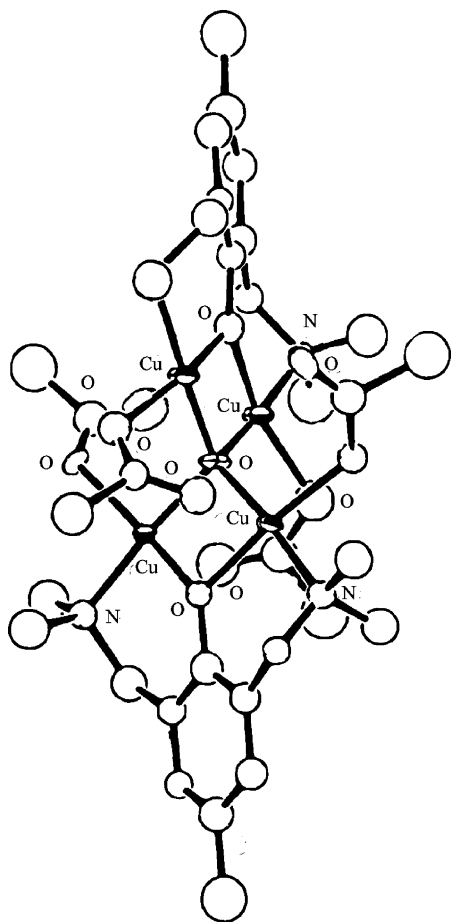


Fig. 9. Structure of $[\text{Cu}_4(\mathbf{8})_2(\mu_4\text{-O})(\text{CF}_3\text{COO})_4]$ (adapted from Refs. [65,66]).

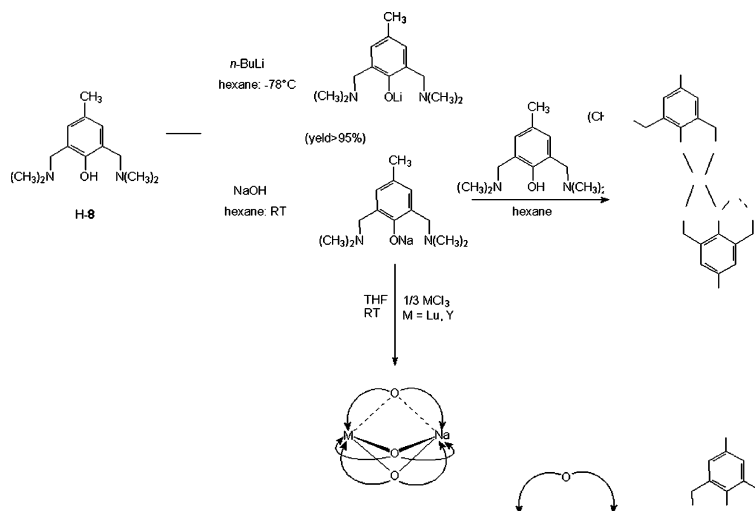
lithium ions are nitrogen coordinated by different $\text{CH}_2\text{N}(\text{CH}_3)_2$ substituents of their mutually oxygen bridging phenolate ligand. The orientation of these ligands with respect to the Li_3O_3 ring results in a propeller-like molecule

with a screw-type chirality. In these molecules each of the 6 equiv. $\text{CH}_2\text{N}(\text{CH}_3)_2$ substituents has inequivalent CH_2N hydrogen atoms and $\text{N}(\text{CH}_3)_2$ methyl groups (Fig. 10a) [67].

The structure of $[\text{Na}(\mathbf{8})]_4$ involves the packing of two discrete tetrameric molecules and two benzene solvate molecules in the unit cell. The tetrameric unit possesses a two-fold rotation axis. The compound shows a tetrameric sodium phenolate with a cubane-like Na_4O_4 core. The sodium ions are five coordinated; they are bonded to three oxygen atoms in the Na_4O_4 core, and to two intramolecularly coordinating tertiary amino groups originating from two phenolate ligands. The tetrameric cluster can be seen as a double dimer in which the two sodium ions of each dimer are bonded with two tridentate pincer-phenolate ligands (Fig. 10b) [67].

$[\text{Na}(\mathbf{8})(\text{H-8})]_2$ consists of two sodium ions, bridged by two phenolate ligands, resulting in a flat $\text{Na}(\mu\text{-O})_2\text{Na}$ unit. Each of the two phenolate ligands coordinates with one of its amino substituents to one of the sodium ions, while its second amino substituents is pendant. The coordination sphere around each sodium ion is completed by an O,N -coordinated neutral H-8 ligand, in which the acidic hydrogen forms a hydrogen bridge with the second amino substituents (Fig. 10c) [67].

$[\text{LuNa}(\mathbf{8})_3(\text{Cl})]$ consists of a seven coordinated lutetium(III) ion surrounded by three phenolate ligands, each bonded through oxygen and coordinating with one of the ortho-amino substituents and the three phenolate oxygen atoms. These binding sites are arranged in such a way that they form a hexadentate coordination pocket for binding of the sodium cation. Chloride, lutetium and sodium lie on a pseudo-three-fold axis, around which the three ligands are arranged (Fig. 11). As a result of the intramolecular coordination of the amino substituents of each bis(amino)-phenolate ligand to two different metal centers (Lu^{3+} and Na^+), the aromatic ring-plane of each ligand is twisted away from



Scheme 5.

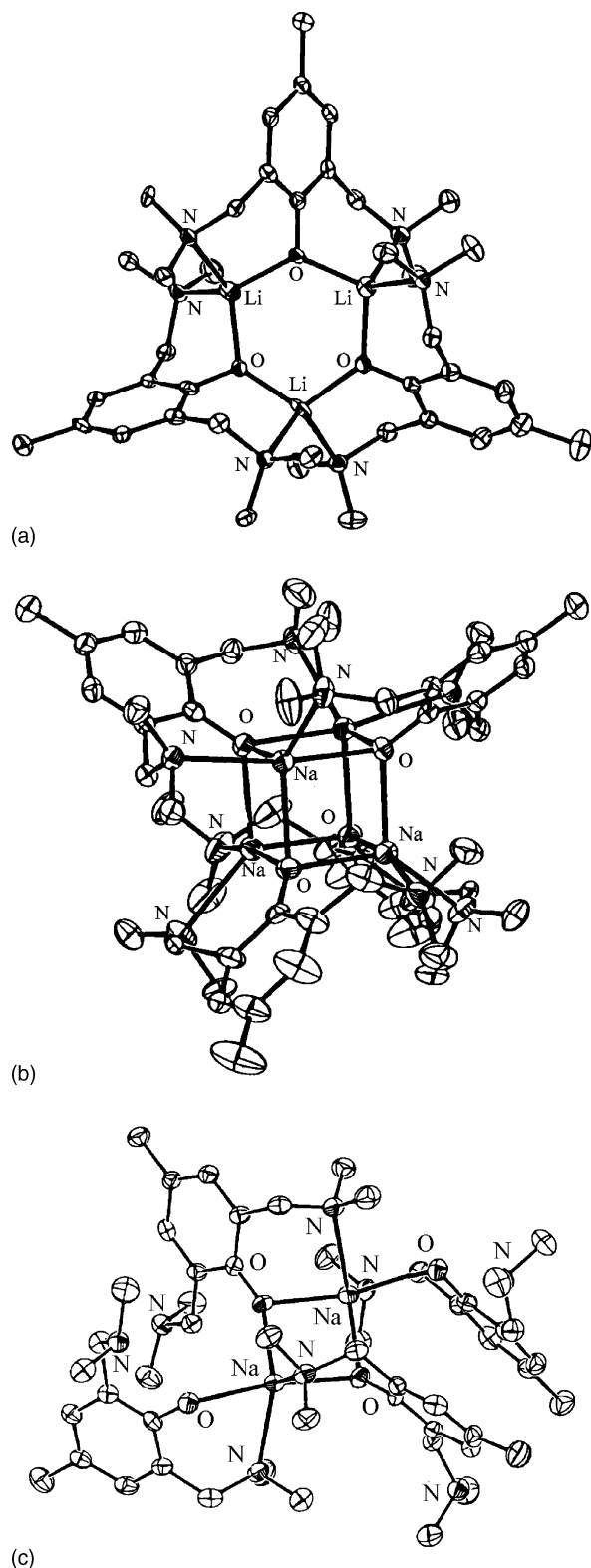


Fig. 10. Structure of $[\text{Li}(\mathbf{8})]_3$ (a), $[\text{Na}(\mathbf{8})]_4$ (b) and $[\text{Na}(\mathbf{8})(\text{H}-\mathbf{8})]_2$ (c) (adapted from Ref. [67]).

position perpendicular to the $\text{Cl}-\text{Lu} \cdots \text{Na}$ vector, resulting in a propeller-like molecule with screw-type chirality. Both enantiomers were present in the measured crystal (Fig. 11) [68].

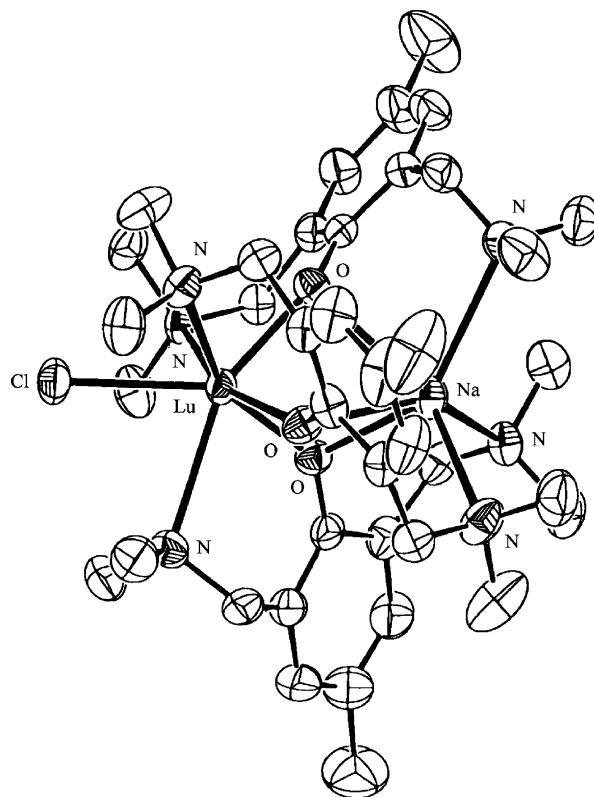
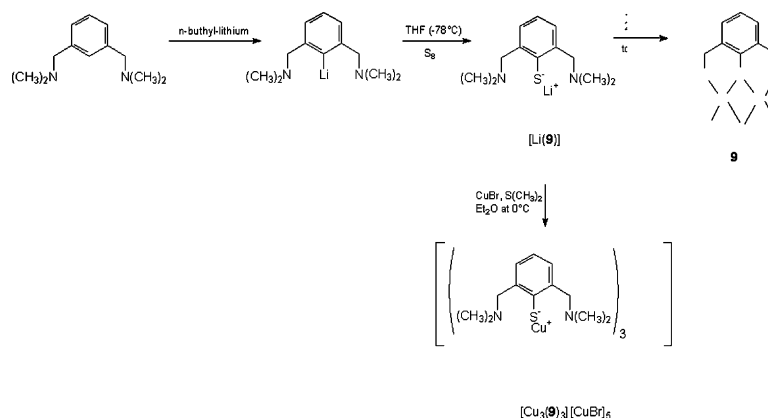


Fig. 11. Structure of $[\text{LuNa}(\mathbf{8})_3(\text{Cl})]$ (adapted from Ref. [68]).

The corresponding thiol derivative **H-9** and related lithium and copper complexes were prepared according to Scheme 6 [69].

$[\text{Li}(\mathbf{9})]$ (Fig. 12) has an hexameric structure based on a central essentially planar Li_6S_6 12-membered ring in which there are alternating Li and S atoms. The central hexagonally shaped Li_6S_6 ring contains arenethiolate sulfur atoms that have a T-shaped geometry. In $[\text{Li}(\mathbf{9})]_6$ the arenethiolate ligands sulfur-bridge between neighbouring lithium centers whose coordination sphere is completed by nitrogen-coordination of two $\text{CH}_2\text{N}(\text{CH}_3)_2$ substituents from different ligand systems. The orientation of the aryl ring in the ligands with respect to Li_6S_6 ring provides an overall propeller-like aggregate with each hexamer having screw-type chirality. Due to crystallographic symmetry both enantiomers are present in the crystal [69].

Reaction of $[\text{Li}(\mathbf{9})]_6$ with 1 equiv. of LiI in toluene leads to the formation of $[\text{Li}_2(\mathbf{9})(\text{I})]_n$ which, initially soluble in toluene, precipitates upon cooling. Crystallization by slow diffusion of pentane into a toluene solution at -20°C (tetrahydrofuran is added to solubilize all material) results in $[\text{Li}_2(\mathbf{9})(\text{I})(\text{THF})_2]$. The structure contains two lithium ions that are bridged by the sulfur atom of the arenethiolate ligand and by one iodide, with one molecule of THF bonded to each lithium. Each lithium coordination sphere is completed by intramolecular nitrogen donor ligation of one dimethylamino group from the ligand **[9][−]** (Fig. 13) [69].

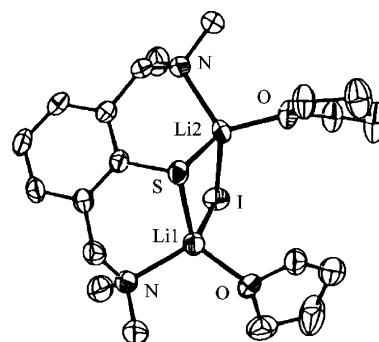
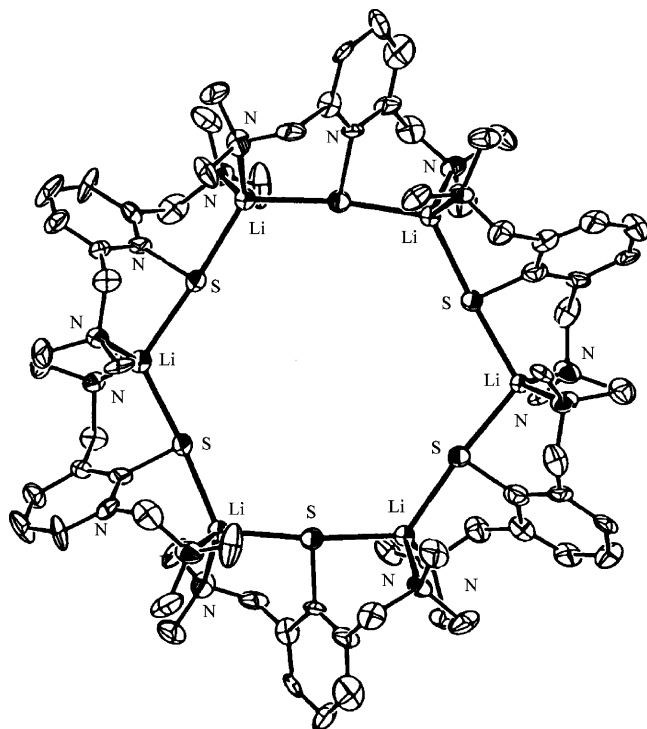
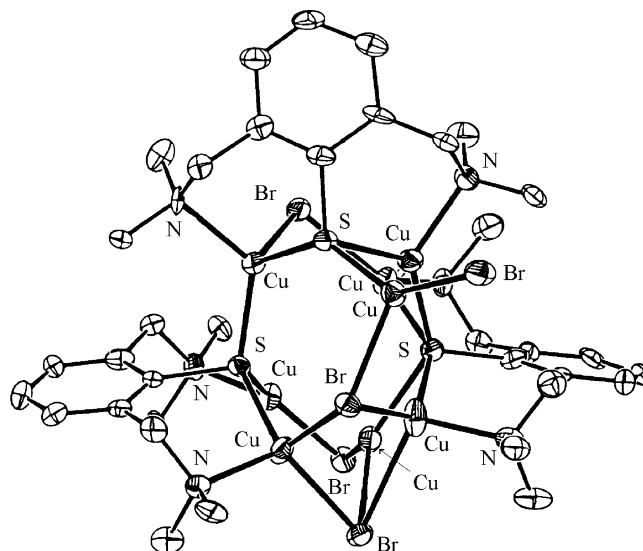


Scheme 6.

The reaction of $[\text{Li}(\mathbf{9})]_6$ with 2 equiv. of $\text{CuBr}\cdot\text{S}(\text{CH}_3)_2$ in Et_2O at 0°C results in the formation of $[\text{Cu}_8(\mathbf{9})_3(\text{Br})_5]$ [69]. The structure of this complex comprises eight copper ions, three arenethiolate ligands and five bromine atoms, with the copper ions arranged in the form of a heavily distorted square antiprism (Fig. 14). In this complex structure, two different modes for bonding of the arenethiolate ligands are present. Two arenethiolate sulfur atoms are μ_3 -bridging over copper ions whereas the sulfur atom of the third arenethiolate ligand is μ_4 -bonded. The bromine atoms are also variously bonded: two bromines are μ_3 -bonded and other two bromine atoms are μ_2 -bonded and one bromine atom is bonded only to one copper ion. The six nitrogen atoms from the arenethiolate ligands all coordinate to a copper atom. As

a result of the different bondings of the arenethiolate ligands, the bromine ions, and the nitrogen coordination, both trigonal planar and tetrahedrally coordinated copper ions are present [69].

By reaction in CH_3CN at room temperature of $[\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$ with 1 equiv. of the phosphinothiolate ligand **H-10**, $[\text{Ir}_2(\mathbf{10})(\text{Cl})_2(\mu\text{-CO})]$ was synthesized in low yield as a

Fig. 13. Structure of $[\text{Li}_2(\mathbf{9})(\text{I})(\text{THF})_2]$ (adapted from Ref. [69]).Fig. 12. Structure of $[\text{Li}(\mathbf{9})_6]$ (adapted from Ref. [69]).Fig. 14. Structure of $[\text{Cu}_8(\mathbf{9})_3(\text{Br})_5]$ (adapted from Ref. [69]).

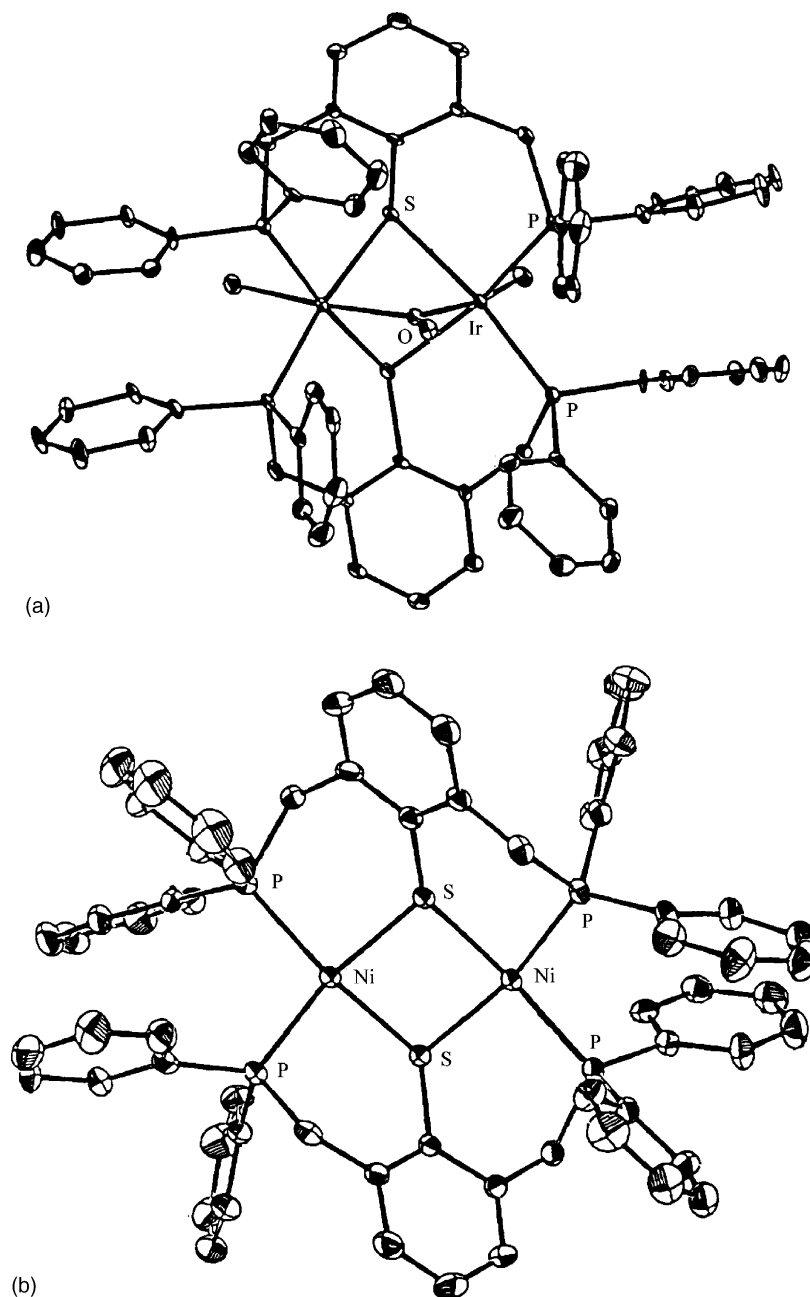


Fig. 15. Structure of $[\text{Ir}_2(\mathbf{10})(\text{Cl})_2(\mu\text{-CO})]$ (a) and $[\text{Ni}_2(\mathbf{10})_2]^{2+}$ (b) (adapted from Ref. [70]).

moderately air stable yellow solid [70]. Both iridium ions are in a pseudo-octahedral environment, the six coordination sites being occupied by two bridging sulfurs, a carbon atom of the bridging CO, a terminal chloride and two phosphorus atoms from different ligands. The $\text{Ir} \cdots \text{Ir}$ distance is 3.103 Å (Fig. 15a).

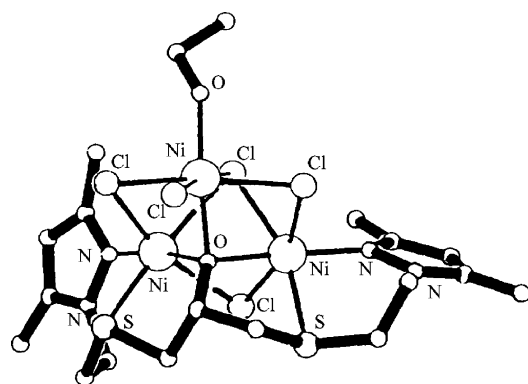
$[\text{Rh}_2(\mathbf{10})(\mu\text{-Cl})(\text{CO})_2]$ was obtained by the reaction of $[\text{Rh}_2(\text{Cl})_2(\text{CO})_4]$ with 1 equiv. of H-**10** in toluene. IR, NMR and FAB spectra suggest a dimeric structure with a bridging chloride ion and two terminal CO ligands [70].

The dimeric dicationic complex $[\text{Ni}_2(\mathbf{10})_2]^{2+}$ was isolated as a brown hexafluorophosphate salt from the reaction of $[\text{Ni}(\text{Cl})_2(\text{PPh}_3)_2]$ with 1 equiv. of H-**10** in CH_3CN at room

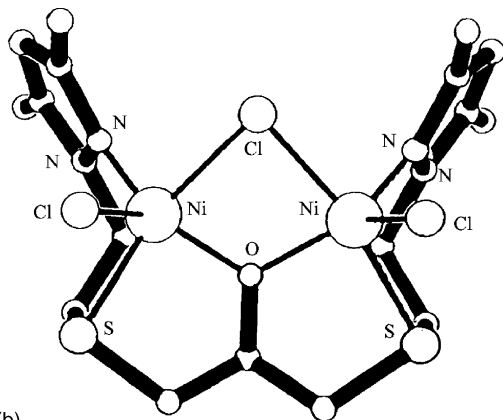
temperature. The geometry at each nickel(II) ion is approximately square planar with a slight fold along the S–S vector providing an overall butterfly type structure. The $\text{Ni} \cdots \text{Ni}$ distance is 3.196 Å (Fig. 15b).

1,9-Bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol (H-**11**) reacts with nickel dichloride in ethanol with the addition of triethylformate (for dehydration) to yield $[\text{Ni}_3(\mathbf{11})(\text{C}_2\text{H}_5\text{OH})(\text{Cl})_5] \cdot 3\text{C}_2\text{H}_5\text{OH}$. When the reaction is performed in acetonitrile the red compound $[\text{Ni}_2(\mathbf{11})(\text{Cl})_3] \cdot \text{CH}_3\text{CN}$ is obtained. With nickel dibromide only the red dinuclear compound could be successfully prepared [71].

The structure of the trinuclear nickel(II) complex (Fig. 16a) shows that all the three nickel ions are bridged



(a)



(b)

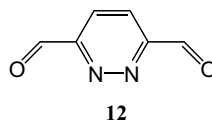
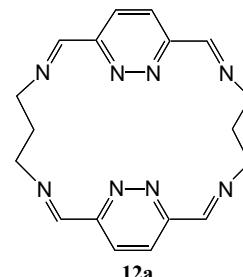
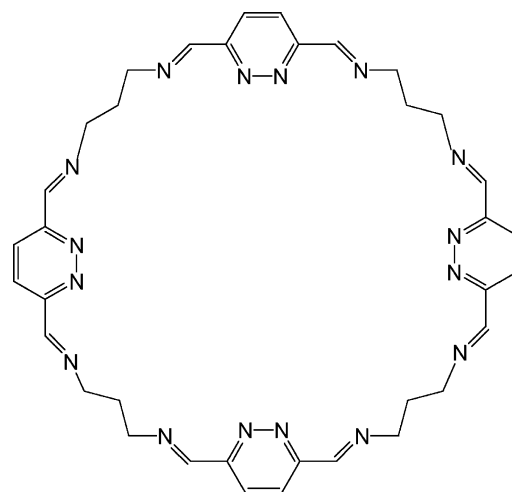
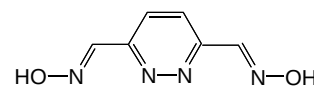
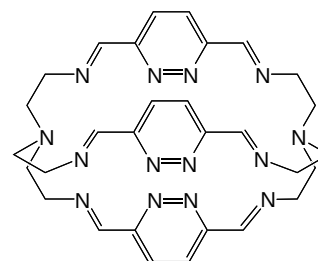
Fig. 16. Structure of $[\text{Ni}_3(\mathbf{11})(\text{C}_2\text{H}_5\text{OH})(\text{Cl})_5] \cdot 3\text{C}_2\text{H}_5\text{OH}$ (a) and of $[\text{Ni}_2(\mathbf{11})(\text{Cl})_3] \cdot \text{CH}_3\text{CN}$ (b) (adapted from Ref. [71]).

by the alkoxide group of the pentadentate ligand. The three nickel ions form an equilateral triangle, with all nickel to nickel distances being only 3.0 Å. Of the five chloride ions, one is μ_3 -bridging to all three nickel ions, three are μ_2 -bridging and one is terminally coordinated. Two of the nickel ions are nearly equivalent and are coordinated in an NSOCl_3 chromophore. The three donor atoms from the ligand are folded around the nickel ions in a meridional fashion. The third nickel ion is distinct and is coordinated in a $\text{trans Cl}_4\text{O}_2$ chromophore, it is bound to the alkoxide oxygen and four of the chloride ions; the sixth coordination site is occupied by the ethanol molecule. The octahedral geometries of all three nickel ions are severely distorted.

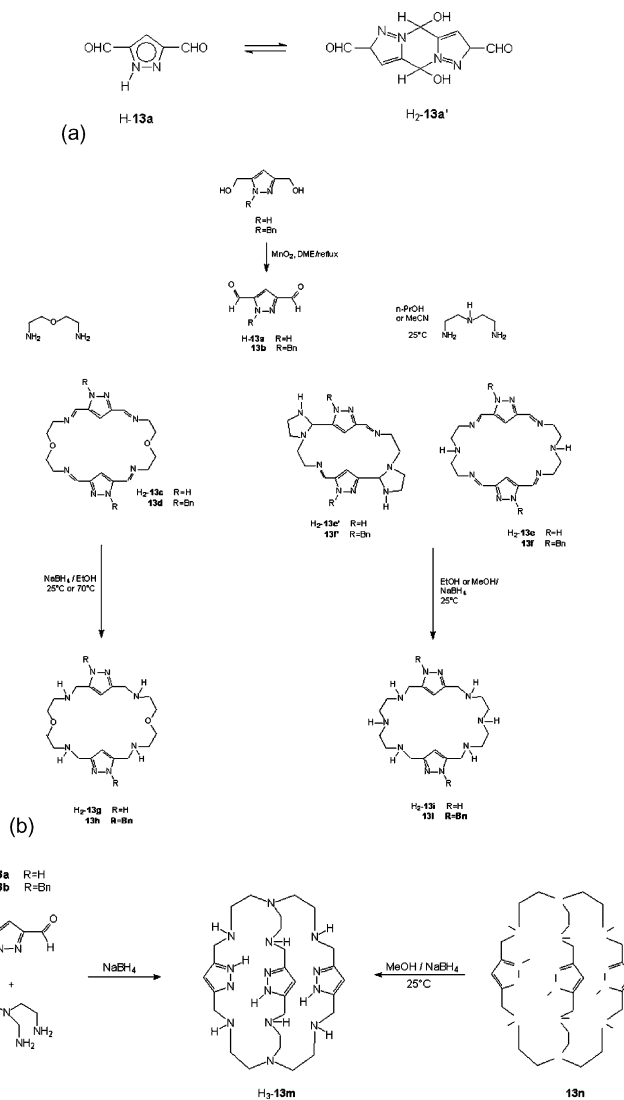
The structure of $[\text{Ni}_2(\mathbf{11})(\text{Cl})_3]\text{CH}_3\text{CN}$ (Fig. 16b) shows the two nickel ions are bridged by the alcoholate group of the ligand and one of the chloride ions. The nickel···nickel distance is 3.26 Å. Both nickel ions are in a five coordination with an NSOCl_2 chromophore. The geometry of the nickel ions is intermediate between a square pyramidal and a trigonal bipyramidal geometry. The ligand is folded around the nickel ion in a way different to that in the trinuclear complex: the nitrogen, sulfur, and oxygen donor atoms are now arranged in a facial conformation [71].

As reported and discussed in a deeper detail in a subsequent section, the diformyl precursor 3,6-diformylpyrida-

zine, **12**, forms the [2+2] **12a** or [4+4] macrocyclic Schiff bases **12b**, when reacted with 1,3-diaminopropane, in the presence of appropriate templating metal ions [72,73]. Also it can give rise to the [1+2] acyclic oxime **12c** or the [3+2] macrobicyclic **12d** when reacted with $\text{NH}_2\text{-OH}$ or tris-(2-aminoethyl)amine, respectively.

**12****12a****12b****12c****12d**

3,5-Pyrazoledicarbaldehyde, **H-13a**, was prepared from 3,5-bis(hydroxymethyl)pyrazole by oxidation with MnO_2 in 1,2-dimethoxyethane (Scheme 7). Starting from 1-benzyl-3,5-bis(hydroxymethyl)pyrazol, and following similar



Scheme 7.

procedure, 1-benzyl-3,5-pyrazoledicarbaldehyde, **13b**, was obtained [74].

3,5-Pyrazoledicarbaldehyde, **H-13a**, is not soluble in chloroform and its ^1H and ^{13}C NMR spectra in $(\text{CD}_3)_2\text{SO}$ show two sets of signal corresponding to a mixture of the monomer **H-13a** and the dimeric species **H₂-13a'**. Also it was observed that in a 0.2 M solution the ratio **H-13a**:**H₂-13a'** increases with the temperature and with dilution. The NMR signals of **H₂-13a'** disappear in highly dilute solutions.

In contrast with this behaviour, 1-benzyl-3,5-pyrazoledicarbaldehyde, **13b**, is soluble in chloroform and other common solvents and presents ^1H and ^{13}C NMR spectra corresponding to a single species.

The dioxo-tetraimine **H₂-13c** was obtained as a crystalline solid by the [2+2] condensation of **H-13a** with 1,5-diamino-3-oxapentane. Further reduction of **H₂-13c** with NaBH_4 in absolute ethanol gave the expected dioxo-tetraazamacrocycle **H₂-13g**.

In contrast with this behaviour, in the [2+2] condensation of **H-13a** with diethylenetriamine in methanol at room temperature, the ^1H and ^{13}C NMR spectra of the solution indicated the presence of more than one species corresponding to a mixture of the tetraimine **H₂-13e** and its contracted imidazoline **H₂-13e'** isomer. The mixture, directly reduced in situ with NaBH_4 , afforded the hexamine macrocycle **H₂-13i** (Scheme 7).

In acetonitrile the [2+2] condensation of **13b** with 1,5-diamino-3-oxapentane or diethylenetriamine at room temperature gave the Schiff base **13d** and the imidazolidine isomer **13f'**, respectively. Further treatment of **13d** and **13f'** with NaBH_4 in ethanol afforded in both cases the desired saturated polyamines **13h** and **13i** [74].

Analogously the condensation of 3,5-pyrazoledicarbaldehyde, **H-13a** and tris-(2-aminoethyl)amine in acetonitrile/methanol and in a 1:0.66 molar ratio afforded the macrocycle **H₃-13m**. The same condensation in methanol followed

by reduction in situ of the resulting Schiff base with NaBH_4 , gave the related polyamine macrobicyclic compound $\text{H}_3\text{-13n}$ (Scheme 7) [74].

The deprotonation of the macrocycles $\text{H}_2\text{-13c}$ or $\text{H}_2\text{-13i}$ with NaOH in anhydrous methanol, followed by reaction with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, afforded the related dinuclear copper(II) complexes as confirmed by the X-ray structure of $[\text{Cu}_2(\text{13i})](\text{ClO}_4)_2$. In this complex the two copper(II) ions are pentacoordinated by five nitrogen atoms forming very distorted square pyramids [74] (Fig. 17a).

Also in $[\text{Cu}_2(\text{13l})(\text{H}_2\text{O})] \cdot (\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$, obtained by reaction of **13l** with copper(II) perchlorate, the coordination geometry around each copper ion is square pyramidal, being the base of the pyramid formed by the three nitrogen atoms of the polyamine bridge, and the nonbenzylated nitrogen of the *N*-benzylpyrazole spacer. The axial position is occupied by a water molecule which is hydrogen bonded to another water molecule. The copper ion almost resides in the equatorial plane of the pyramid. The $\text{Cu} \cdots \text{Cu}$ distance is 6.788 Å. The molecule presents an inversion center, and therefore the water molecules are pointing toward opposite sides of the mean plane defined by the macrocyclic cavity. The benzyl groups are disposed *trans* to each other, pointing also outward from the macrocyclic cavity (Fig. 17b).

The tripodal [3+2] condensation of sodium 3,5-diformylpyrazolate $[\text{Na}(\text{13a})]$ and tris-(2-aminoethyl)amine, in the presence of copper(II) perchlorate as template in different ratios (3:2:2 and 3:2:4) afforded $[\text{Cu}_2(\text{13m})](\text{ClO}_4)_4$ and $[\text{Cu}_4(\text{13m})](\text{ClO}_4)_5$ in which the three pyrazole rings are participating in the complexation as pyrazolate anions. These compounds were directly isolated from the reactions as pure green solids [74].

Starting from the polyaminic cryptand $\text{H}_3\text{-13n}$, $[\text{Cu}_2(\text{H}_2\text{-13n})]^{3+}$, $[\text{Cu}_2(\text{H-13n})]^{2+}$ and $[\text{Cu}_2(\text{13n})]^+$ have been obtained, containing respectively one, two or three pyrazolate units as pyrazolate anions. Treatment of $\text{H}_3\text{-13n}$ with NaOH in 1:3 molar ratio and in methanol at 25 or 78 °C afforded the corresponding mono- or di-pyrazolate salts, which by reaction with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$, respectively gave $[\text{Cu}_2\text{Na}_2(\text{H}_2\text{-13n})(\text{OH})](\text{ClO}_4)_4$ and $[\text{Cu}_2\text{Na}_2(\text{H-13n})(\text{OH})](\text{ClO}_4)_3$ [74].

The structure of $[\text{Cu}_2(\text{H}_2\text{-13n})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$, shows the coordination geometry around each copper(II) ion is square pyramidal, the base of the pyramid being formed by two secondary nitrogens of the bridge and two nitrogen atoms of two different pyrazolate moieties which act as exobidentate ligands. The axial positions are occupied by the bridgehead nitrogen atoms, with distortion being more pronounced in one of the two sites. The $\text{Cu} \cdots \text{Cu}$ distance is 3.960 Å [74].

A ready deprotonation of the two pyrazole fragments of $[\text{H}_2\text{-13n}]^-$ involved in the coordination occurs without requiring any addition of base. However, the pyrazole in the non-coordinating bridge of $[\text{H}_2\text{-13n}]^-$ does not deprotonate, and lies to one side of the macrocyclic cavity. One of the nitrogen atoms of the aliphatic chains is protonated and

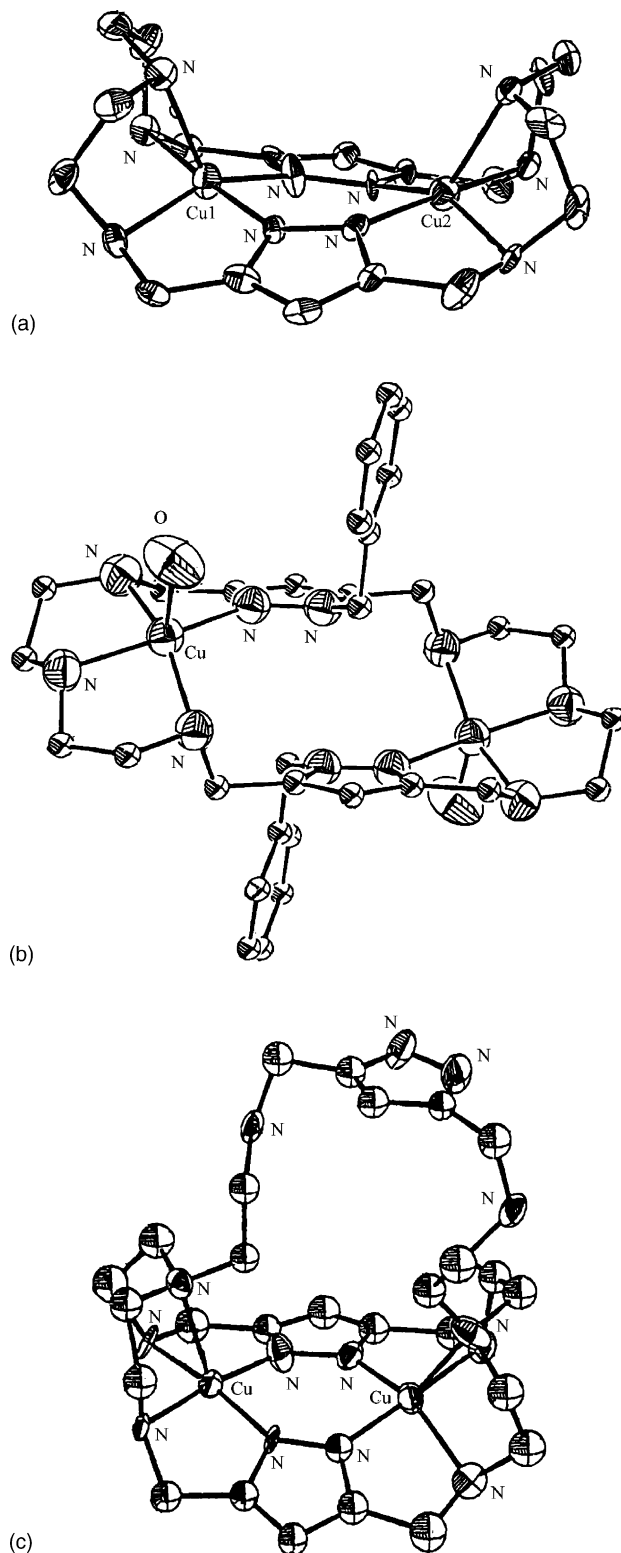


Fig. 17. Structure of $[\text{Cu}_2(\text{13i})]^{2+}$ (a), $[\text{Cu}_2(\text{13l})(\text{H}_2\text{O})_2]^{4+}$ (b) and $[\text{Cu}_2(\text{H}_2\text{-13n})]^{3+}$ (c) (adapted from Ref. [74]).

hydrogen bonded to a water molecule placed at one side of the macrocyclic cavity and further connected to the sp^2 nitrogen of the pyrazole group through an additional hydrogen bond. The other water molecule, which is located

completely outside of the cavity, is hydrogen bonded to an amine nitrogen (Fig. 17c) [74].

The coordination arrangement keeps both copper(II) ions close to one face of the cage leaving enough free room within the cavity to allow the encapsulation of further substrates as exogenous, ligands. The interaction with Cu^{2+} and dopamine of three polyxazacyclopentane $\text{H}_2\text{-13i}$, **13l** and $\text{H}_3\text{-13n}$, containing pyrazole fragments as spacers and the formation of mixed complexes Cu^{2+} -macrocyclic-dopamine has been studied by potentiometric methods in aqueous solution. All three free receptors interact with dopamine in aqueous solution. $\text{H}_3\text{-13n}$ is a receptor particularly interesting with respect to the values of interaction constants over five logarithmic units at neutral pH, which might suggest an encapsulation of dopamine in the macrocyclic cage. All three receptors form mixed complexes Cu^{2+} -L-dopamine. The affinity for the formation of ternary dopamine complexes is particularly high in the case of the binuclear Cu^{2+} complexes of the 1-benzyl derivative **13l** [74].

The 1,4-dihydrazinophthalazine, **14a**, was successfully proposed as an alternative useful precursor in the synthesis of polynucleating systems. The acyclic Schiff bases **14b** and related complexes have been prepared by the reaction with appropriate formyl derivative (i.e. 2-pyridine-2-carbaldehyde, *N*-methylimidazole-2-carbaldehyde) and fully characterized [75].

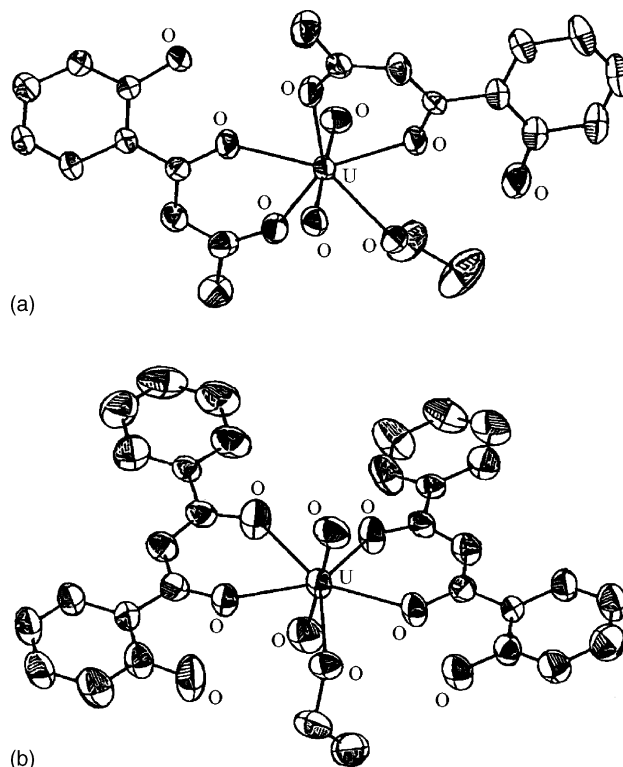
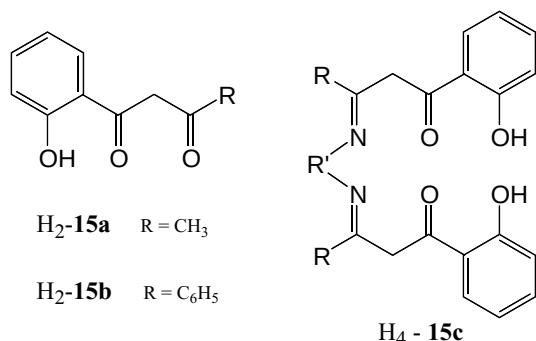
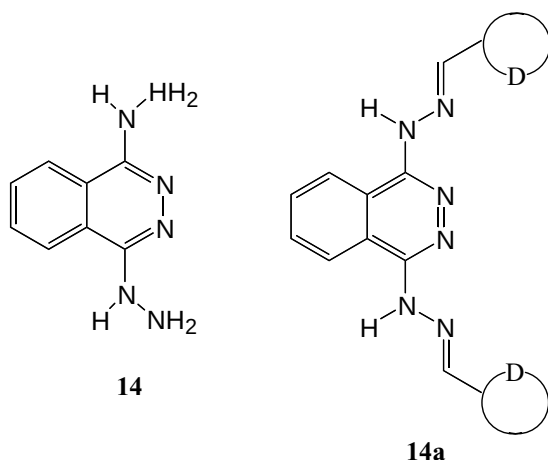


Fig. 18. Structure of $[\text{UO}_2(\text{H-15a})_2(\text{C}_2\text{H}_5\text{OH})]$ (a) and $[\text{UO}_2(\text{H-15b})_2(\text{C}_2\text{H}_5\text{OH})]$ (b) (adapted from Ref. [76]).

The synthesis and the coordination properties of 1-(2-hydroxyphenyl)-1,3-butanedione ($\text{H}_2\text{-15a}$) and 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione ($\text{H}_2\text{-15b}$) have been already reviewed [42,44–49]. They easily form dinuclear complexes of the type $[\text{M}_2(\text{15a})_2(\text{S})_2]$ or $[\text{M}_2(\text{15b})_2(\text{S})_2]$ when reacted with transition metal ions as Cu^{2+} , Ni^{2+} , etc. Recently their reaction with $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in a 2:1 molar ratio to afford $[\text{UO}_2(\text{H-15a})_2(\text{C}_2\text{H}_5\text{OH})]$ and $[\text{UO}_2(\text{H-15b})_2(\text{C}_2\text{H}_5\text{OH})]$ was reported [76]. Both complexes crystallize as seven coordinated monomeric species with a pentagonal bipyramidal geometry about the uranium(VI) ion. The uranyl oxygens occupy the axial positions. Five oxygens make up the equatorially donors, four from two bidentate β -diketophenolate ligands and the fifth from solvent ethanol acting as a ligand to form a puckered pentagon. The ligands are in a *trans*-arrangement in $[\text{UO}_2(\text{H-15a})_2(\text{EtOH})]$ while they have adopted the *cis* form in $[\text{UO}_2(\text{H-15b})_2(\text{C}_2\text{H}_5\text{OH})] \cdot \text{C}_2\text{H}_5\text{OH}$ (Fig. 18a and b) [76]. In solution the two complexes have a fluxional behaviour: variable temperature ^1H NMR spectra indicate that the *cis* and *trans* isomers are in equilibrium for both complexes.

The addition of copper(II) acetate to $[\text{UO}_2(\text{H-15b})_2(\text{C}_2\text{H}_5\text{OH})]$ in ethanol produces the copper(II) mononuclear complex $[\text{Cu}(\text{H-15b})_2(\text{H}_2\text{O})]$, whereas the use of nickel(II) acetate produces a mixture of the mononuclear uranyl(VI) and nickel(II) complexes. In contrast, when manganese(II) acetate was added to an ethanolic solution of the appropriate mononuclear uranyl complex, respectively $[\text{UO}_2\text{Mn}(\text{15a})_2\text{-}$

(C₂H₅OH)·1.5H₂O and [UO₂Mn(**15b**)₂(C₂H₅OH)]·2H₂O were isolated [76]. Conductivity measurements, mass spectra and electronic spectra indicate the occurrence of hetero-dinuclear complexes. Magnetic susceptibility and ESR data confirm the presence of manganese(II). For [UO₂Mn(**15a**)₂(C₂H₅OH)]·1.5H₂O μ_{eff} has a value of 5.41 BM and for [UO₂Mn(**15b**)₂(C₂H₅OH)]·2H₂O the value is 5.92 BM consistent with a high spin 3d⁵ state. In agreement with this the ESR spectra indicate an octahedral MnO₆ coordination. A dimeric structure for [UO₂Mn(**15a**)₂(C₂H₅OH)]·1.5H₂O and a monomeric one for [UO₂Mn(**15b**)₂(C₂H₅OH)]·2H₂O was proposed [76].

These precursors have been engaged in a series of condensation reaction, giving rise to [2+1] acyclic side off systems of the type H₄-**15c** [42,44–50].

A large variety of homo- and hetero-dinuclear complexes have been prepared and their magneto-structural relationship has been discussed and extensively reviewed as well in the recent past [5,42]; thus only the most recent data will be taken into consideration in the present review.

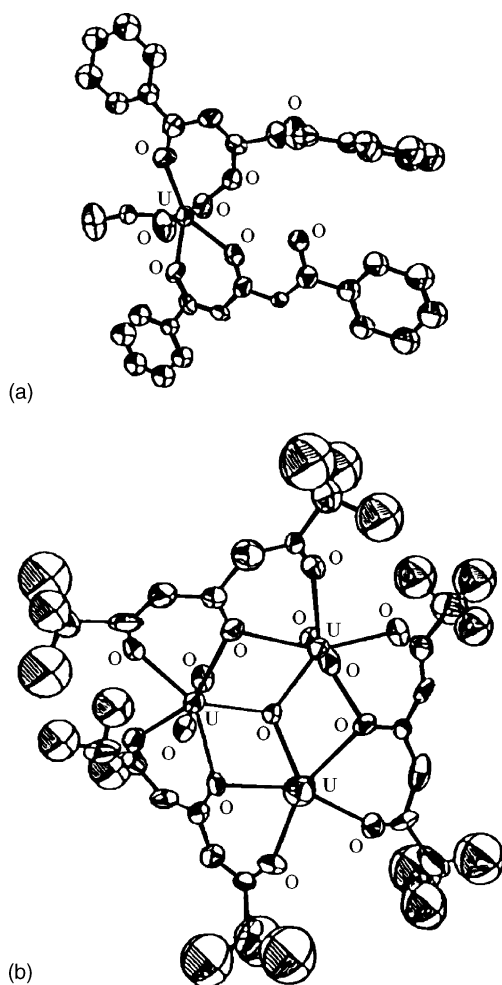
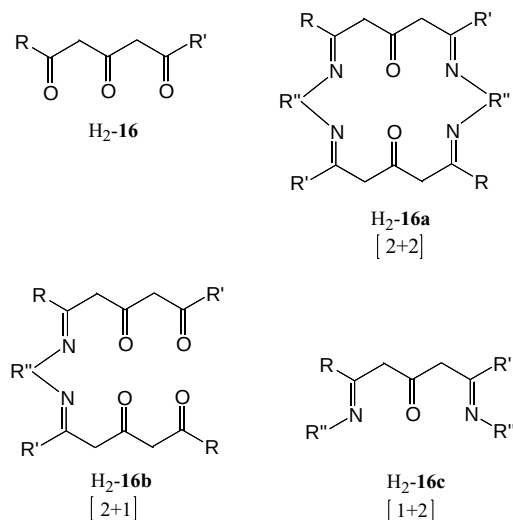


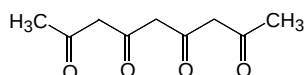
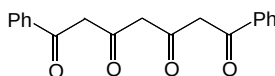
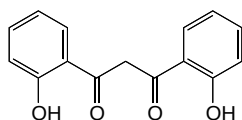
Fig. 19. Structure of bis[UO₂(H-**16**)₂(CH₃OH)] (R = R' = C₆H₅) (a) and [(UO₂)₃(**16**)₃(μ₃O)]²⁻ (R = R' = C(CH₃)₃) (b) (adapted from Ref. [78]).

Many papers have been devoted to the systems of 1,3,5-triketone chelates and to their properties (magnetic, optical, redox, catalytic, etc.), together with those of the related Schiff base complexes [42,49,77]. The triketones H₂-**16** forms, by reaction with transition metal ions, the mononuclear M(H-**16**)₂·nS and especially the homo-dinuclear complexes M₂(**16**)₂·nS while they are not particularly suitable for the formation of dinuclear uranyl(VI) complexes as the seven coordinated pentagonal bipyramidal geometry around this ion imposes constraints on these chelating ligands. On the contrary, no problem arises for the preparation of mononuclear complexes. The structure of the mononuclear uranyl(VI) complex with 1,5-diphenyl-1,3,5-pentanetrione (Fig. 19a) consists of discrete neutral molecules in which the uranium(VI) ion is seven coordinated in the usual pentagonal bipyramidal arrangement [78]. Two triketonate ligands in a *cis*-configuration and one methanolic oxygen atom complete the equatorial pentacoordination. Under somewhat stringent conditions, in the presence of N(C₂H₅)₃, a trinuclear species has been found for bis-(triethylammonium)tris(2,2',8,8'-tetramethyl-3,5,7-nonanetrionato)-μ₃-oxo-tris(dioxouranate) (Fig. 19b). This compound contains a nearly equilateral triangle of UO₂²⁺ ions with a central O²⁻ ion trigonally bonded to the three uranium ions and the terminal oxygen ion bound to one uranium ion. Each uranium ion is seven coordinated in a nearly pentagonal bipyramidal geometry [78].



When reacted with amines they form the [2+2] cyclic H₂-**15a** and acyclic [2+1] side-off H₂-**16b** or [1+2] end-off H₂-**16c** acyclic ligands and related homo- and hetero-dinuclear complexes.

Homotrinnuclear or homo-dinuclear copper(II), nickel(II) and cobalt(II) complexes have been prepared by reaction of 1,3,5,7-heptanetetraone, H₃-**17a** and the appropriate metal salt in methanol-water or acetone-water solution and in the presence of base. Isolation of complexes with two or three metal ions appears to depend on preparative details such as the solvent, temperature and base used [79].

H₃-17aH₃-17bH₃-17c

Magnetic data indicate that the trinuclear copper(II) complex exhibits a reduced magnetic moment due to strong antiferromagnetic interactions, while the binuclear complex exhibits a normal magnetic behaviour, typical of isolated copper(II) ions. The lack of free carbonyl absorptions in the IR spectra of the binuclear complexes supports the conclusion that in the dinuclear compounds the metal ions occupy the external chambers and are separated rather than adjacent to one another in the inner coordination sites.

In the isomorphous heterotrinnuclear bis-[1,7-diphenyl-1,3,5,7-heptanetrionato(3)]-bisdioxouranium (VI)M(II)-tetrapyridine complexes [(UO₂)₂M(17b)₂(py)₄] (M = Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺, Fe²⁺, Mn²⁺) [80,81], two uranyl(VI) ions occupy the terminal coordination positions in the molecules with four ketonate oxygen atoms and one pyridine nitrogen constituting the five equatorial donor atoms in a distorted pentagonal bipyrimidal coordination geometry; the divalent transition metal ion occupies the central position and is bound to four ketonate oxygen atoms, which all act as bridging atoms between the transition metal and uranium atom. In addition pyridine nitrogen atoms occupy the fifth and sixth coordination position above and below the plane of the tetraketones (Fig. 20).

It was suggested that a reasonable precursor to these trinuclear products is the binuclear uranyl(VI) complex

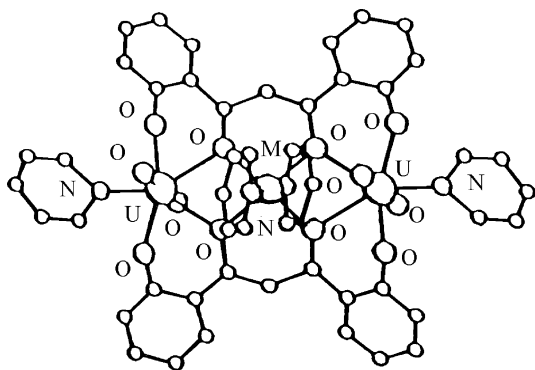


Fig. 20. Structure of [(UO₂)₂M(17b)₂(py)₄] (M = Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺, Fe²⁺, Mn²⁺) (adapted from Refs. [80,81]).

[(UO₂)₂(H-17b)₂(S)₂]. This could explain the ease and specificity with which these heterotrinnuclear complexes are obtained from solutions containing 2:2:1 ratios of ligand: UO₂²⁺:M²⁺ [80,81].

Indeed, attempts were made to prepare 1:1 = UO₂²⁺:M²⁺ and 1:2 = UO₂²⁺:M²⁺ bi- and trinuclear complexes by changing the reaction stoichiometries; however the only products isolated were the [(UO₂)₂M(17b)(py)₄] complexes.

1,3-Bis(2-hydroxyphenyl)-1,3-propanedione (H₃-17c) forms the mononuclear complexes [M(H₂-17c)₂] with divalent transition metal ions [82], where the metal ion is coordinated in a square fashion by two β-diketonic moieties. Usually, the coordinated metal ion fixes two solvent molecules to achieve the hexacoordination around the metal ion [83]. On the contrary, the anionic complex [Li(H₂-17c)₂][−] exhibits a tetrahedral coordination [84], while the chromium(III) and iron(III) compounds present an octahedral coordination around the metal ion [85].

As a result of their structure, only the mononuclear complexes with divalent metal ions are able to afford heterotrinnuclear or homotrinnuclear compounds. These are synthesized by treating the mononuclear precursors with a different or alike metallic salts in a strong basic medium to deprotonate the phenolic groups. The synthetic experimental conditions are critical because mixtures of homotrinnuclear compounds, [M₃(17c)₂] or [M'₃(17c)₂], could be obtained probably because of the strong basic medium employed. Compounds of the formula [(UO₂)₂M(17c)₂(py)₄].2py are synthesized from the corresponding isomeric pure mononuclear precursors [M(H₂-17c)₂] (M = Ni²⁺, Co²⁺, Zn²⁺) by treating them with uranyl acetate in a strong basic medium. The structures of [(UO₂)₂M(17c)₂(py)₄].2py (M = Co²⁺, Ni²⁺) complexes are identical (Fig. 21). The octahedrally coordinated divalent transition metal ion is placed at the crystallographic inversion center. It is coordinated with two pyridine groups in the axial direction and by four oxygen atoms of two β-diketone moieties in the basal plane. The uranyl ions occupy the outer coordination positions with two ketonic oxygen atoms, two phenolic oxygen atoms, and one pyridine nitrogen atom constituting the five equatorial donor atoms in a distorted pentagonal bipyramidal coordination sphere geometry. The ligand molecule and the three metal atoms are essentially

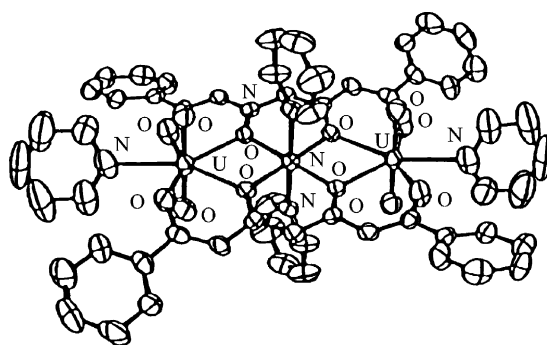
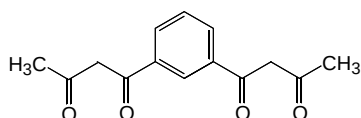
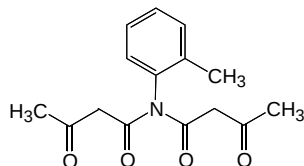
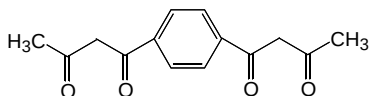
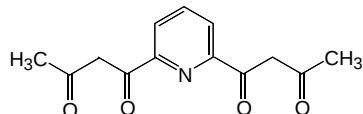
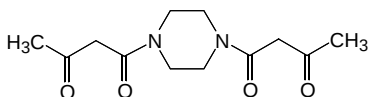


Fig. 21. Structure of [(UO₂)₂M(17c)₂(py)₄] (M = Co, Ni) (adapted from Ref. [85]).

coplanar. Two additional pyridine molecules occupy interstitial lattice positions.

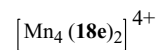
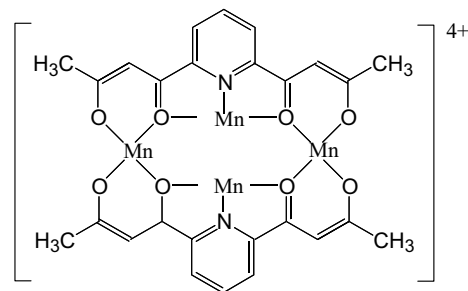
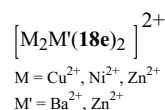
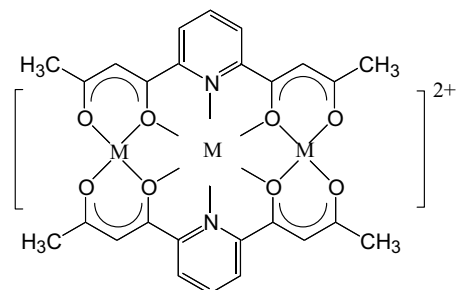
Again the specificity of this controlled synthesis is achieved because the outer positions are the only position accessible to form the unusual seven coordination of the uranium(VI) ions in these compounds. By introduction of slight changes in the experimental conditions, a large series of compounds have been obtained, corresponding to mixtures of homotrinnuclear species [190]. The boiling temperature used and the relatively long time required to dissolve the mononuclear complex in the presence of a large concentration of triethylamine favour reorganization to yield homotrinnuclear complexes. To minimize this reorganization problem, NaH in dry tetrahydrofuran at room temperature was used but no analytically pure heterotrinnuclear complexes were obtained. Surprisingly, when these heterotrinnuclear complexes (CoNiCo, CoZnMn, MnZnMn) are treated with pyridine, outer homo-dinuclear complexes are obtained, leaving a vacancy in the central position [86].

The tetraketones 1,1-(1,3-phenylene)-bis-1,3-butanedione (**H₂-18a**), 1,1-(1,4-phenylene)-bis-1,3-butanedione (**H₂-18b**), 1,4-bis(acetoacetyl)pyperazine (**H₂-18c**), *N*-(*o*-tolyl)diacetoacetamide (**H₂-18d**) and 1,1'-(2,6-pyridyl)-bis-1,3-butanedione (**H₂-18e**) and related Schiff bases have been synthesized and used in the preparation of polynuclear coordination systems [87,88]. The first two ligands offer two isolated β -diketonate moieties and thus the complexes obtained resemble the β -diketonate complexes.

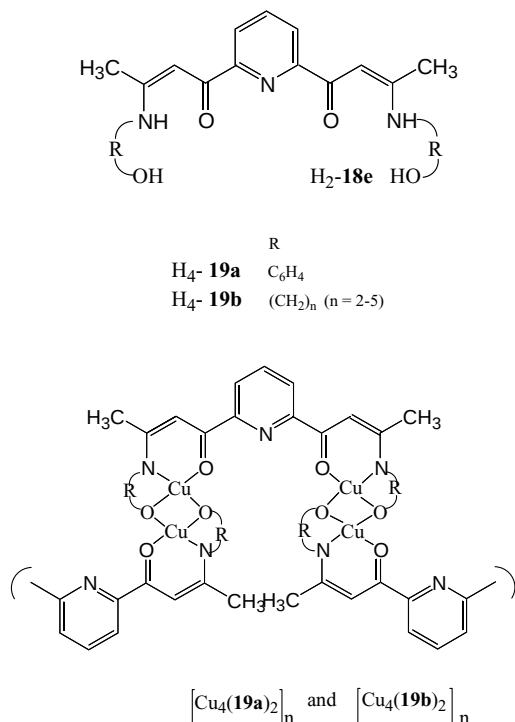
**H₂-18a****H₂-18d****H₂-18b****H₂-18e****H₂-18c**

In *N*-(*o*-tolyl)diacetoacetamide (**H₂-18d**) and 1,1'-(2,6-pyridyl)-bis-1,3-butanedione (**H₂-18e**), the four ketonic moieties are at the appropriate positions to form homo- or hetero-trinuclear complexes in addition to homo-dinuclear complexes, for which the two alternative structures have been proposed [87,88]. The dinuclear complexes can be easily converted into the trinuclear ones by common synthetic procedures. The dinuclear complexes exhibit physico-chemical properties typical of isolated β -diketonato compounds while in the trinuclear species (for instance trinuclear copper(II) complexes), significative antiferromagnetic interactions take place indicating the metal ions are held together in adjacent coordination chambers.

With 1,1'-(2,6-pyridyl)-bis-1,3-butanedione, **H₂-18e**, the discrete trinuclear complexes $[M_2M'(18e)_2]^{2+}$ have been suggested for $M = Zn^{2+}$, Cu^{2+} , Ni^{2+} and $M' = Zn^{2+}$, Ba^{2+} while manganese(II) may form the tetranuclear compound $[Mn_4(18e)_2]^{4+}$ (in addition to the octanuclear $[Mn_8(18e)_6(O)_2]$).



1,1-(2,6-Pyridyl)-bis-1,3-butanedione reacts with a series of hydroxyalkyl- or hydroxyaryl-amines in ethanol to give the Schiff bases **H₄-19a** and **H₄-19b**. By reaction with copper(II) salts, these Schiff bases produce complexes formulated on the basis of their reduced magnetic moments as polymers of the type $[Cu_4(19a)_2]_n$ and $[Cu_4(19b)_2]_n$. In some complexes (containing bromide as anion), the ligand behaves as a neutral entity, the copper ions are coordinated also by bromide ions.



As an extension, the hexaketone 1,3-bis(2-methyl-4,6,8-octanetrione-8-yl) benzene ($\text{H}_4\text{-20}$) and the homo- and hetero-tetranuclear complexes $[\text{Cu}_4(\text{20})_2(\text{py})_4]\text{py}$ and $[(\text{UO}_2)_2(\text{Zn})_2(\text{20})_2(\text{py})_6]$ have been prepared. In the tetra-copper(II) complex two deprotonated ligands and four copper ions form neutral complexes. The four copper ions are grouped into two sets of two with a metal $\cdots$ metal distance of 6.9 Å across the plane of the phenyl groups and an intragroup metal–metal distance of 3.021 Å. The coordination sphere of the copper ions is composed of four ketonate oxygen atoms in the distorted tetragonal pyramid; within the molecule, the pyridines alternate above and below the plane of the ligand (Fig. 22) [89].

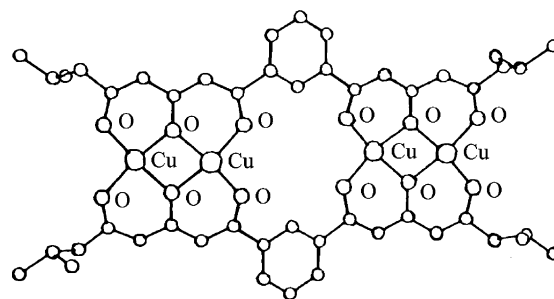
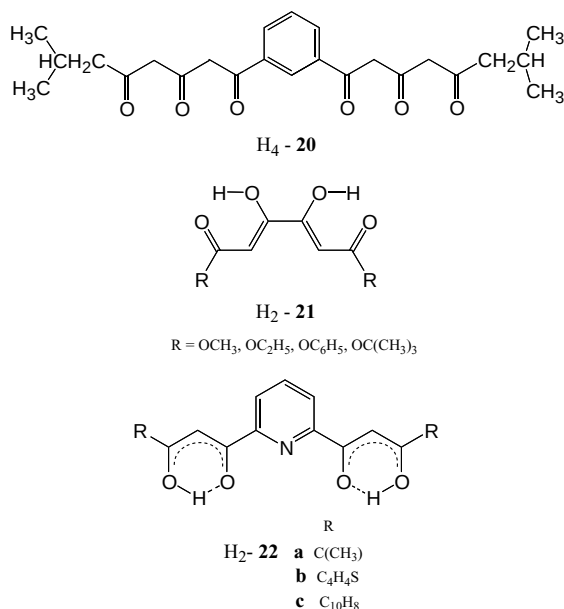


Fig. 22. Structure of $[\text{Cu}_4(\text{20})(\text{py})_4]$ (adapted from Ref. [89]).

Strong magnetic exchange between the copper(II) ions in the binuclear units causes the molecule to be diamagnetic at room temperature. Cyclic voltammetry in pyridine in the range from 0 to 1.2 V yields one quasi reversible wave with $E_{1/2} = 0.8$ V versus SSCE. Chronoamperometric data reveal that this wave is a four-electron transfer process ascribed to two two-electron transfers in non-interacting binuclear centers [89].

Claisen condensation of alkyl acetates or methyl ketones with dialkyl oxalates followed by acidic workup yields the ketipinates $\text{H}_2\text{-21}$ [11]. Reaction of $\text{H}_2\text{-21a}$ ($\text{R} = \text{OC}_2\text{H}_5$) with cadmium or manganese dichloride in methanol in the presence of aqueous ammonia affords the octanuclear complexes $[\text{M}_8(\text{21a})_8] \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Cd}^{2+}, \text{Mn}^{2+}$) [90].

Crystallization of the octanuclear manganese(II) complex $[\text{Mn}_8(\text{21a})_8] \cdot 4\text{H}_2\text{O}$ from hot propanol leads to $[\text{Mn}_8(\text{21a})_8] \cdot (\text{C}_3\text{H}_7\text{OH})_4$ with four coordinated propanol molecules (Fig. 23). Each of the eight manganese ions form the corner of one of two squares of different sizes, but with the same center. The smaller square is turned 45° relative to the larger one. The four outer manganese ions are linked in a μ_1 fashion through the two ester carbonyl oxygen atoms of a set of four ketipinic acid diester dianions, which lie almost in a plane. The two keto oxygen atoms of these four ligands are μ_2 -bound and bridge inner and outer manganese ions. Furthermore, a propanol molecule is coordinated to each of the four outer manganese ions. Four ketipinic acid diester dianions are each bound in a μ_1 fashion through the ester-carbonyl oxygen atoms to one outer and one inner manganese ion. One of the keto oxygen atoms forms a μ_2 bridge between two inner manganese ions, and the other forms a μ_3 bridge to two inner and an outer manganese ion. Thus all eight manganese ions are seven-fold coordinated [90].

Deprotonation of $\text{H}_2\text{-21a}$ with aqueous ammonia in ethanol in the presence of calcium chloride furnishes the octanuclear calcium chelate $[\text{Ca}_8(\text{21a})_8] \cdot (\text{C}_2\text{H}_5\text{OH})_4$, which is isostructural to the cadmium and manganese complexes mentioned above. The coordination ethanol in $[\text{Ca}_8(\text{21a})_8] \cdot (\text{C}_2\text{H}_5\text{OH})_4$ is exchanged on crystallisation from hot alcohols to give $[\text{Ca}_8(\text{21a})_8] \cdot (\text{S})_4$ ($\text{S} = \text{CH}_3\text{CHOHCH}_3, (\text{CH}_3)_3\text{COH}$).

Tetranuclear adamantanoid chelate complexes are formed in a one-pot reaction from dimethyl malonate, methyl-lithium, metal(II) chlorides and oxalylchloride at -78°C

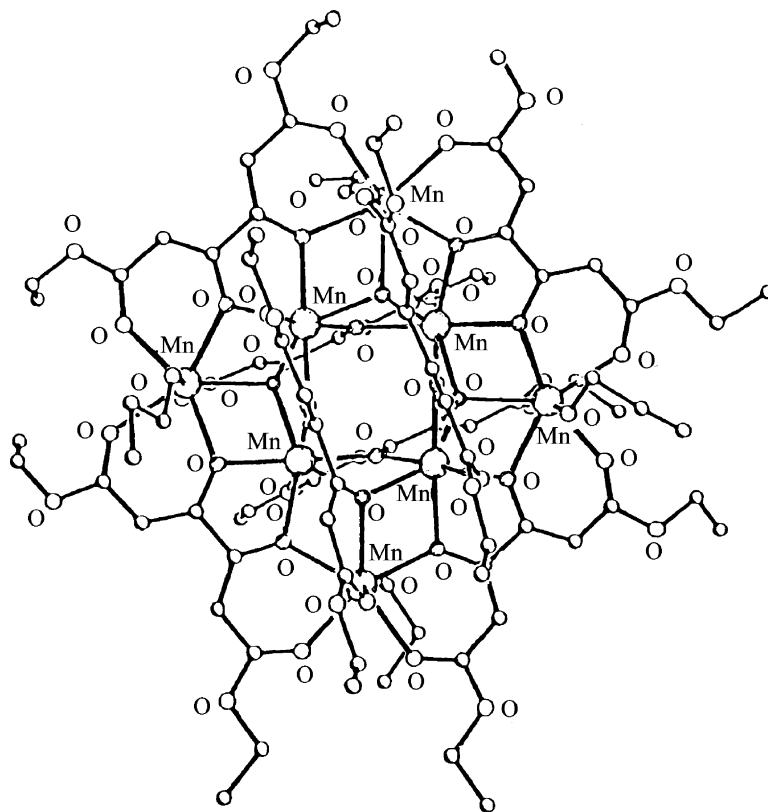


Fig. 23. Structure of $[\text{Mn}_8(\mathbf{21a})_8(\text{C}_3\text{H}_7\text{OH})_4]$ (adapted from Ref. [90]).

in tetrahydrofuran (THF) and subsequent workup with aqueous ammonium chloride. However, this methodology does not work in the case of ethyl acetate and oxalylchloride. Instead, double deprotonation of free $\text{H}_2\text{-21a}$ with methyl-lithium at -78°C in THF and addition of magnesium chloride, followed by workup with aqueous ammonium chloride, furnishes $[\text{NH}_4]_4[(\text{Mg}_4(\mathbf{21a})_6)]$ [90].

$[\text{NH}_4]_4[(\text{Mg}_4(\mathbf{21a})_6)]$ is not a salt in the usual sense, but a tetrahemispheraplex because, on each face of the imaginary tetrahedron constituted by the four magnesium ions, three oxygen atoms are in ideal positions to bind an ammonium ion through three hydrogen bonds [90].

Double deprotonation of $\text{H}_2\text{-21a}$ with sodium hydroxide in a methanolic sodium tetrafluoroborate solution and treatment with copper(II) chloride dihydrate leads to the trinuclear copper-crown ether with an encapsulated sodium ion $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)\}$. Recrystallization of this complex from tetrahydrofuran gave two types of crystals: the double-decker metalla-coronate $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_2\}\cdot\text{THF}\cdot 2\text{H}_2\text{O}$ and the triple decker metalla-crown ether complex $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_3\}\cdot 2\text{THF}$ (Fig. 24a and b) [90].

A common feature of $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_2\}\cdot\text{THF}\cdot 2\text{H}_2\text{O}$ and $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_3\}\cdot 2\text{THF}$ is the neutral, 15-membered trimetalla-crown-6 (15-MC-6) building block. Formal replacement of the three copper(II) centers in the 15-MC-6 fragments of $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_2\}\cdot\text{THF}\cdot 2\text{H}_2\text{O}$ or $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_3\}\cdot 2\text{THF}$ by $\text{C}_2\text{H}_5\text{O}$ bridges leads to the topologically equivalent crown ether 18-crown-6. The three

copper(II) atoms in the 15-MC-6 fragments are linked across the triangular edges by bis(bidentate)diethyl ketipinate dianions. A sodium ion is encapsulated in the center of the 15-MC-6 fragment and charge neutrality is achieved by BF_4^- counterions [90].

In order to accomplish eight-fold coordination of the sodium ions, aggregation of the $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3]\}^+$ monomers furnishes double- and triple-decker metalla-coronates $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_2\}\cdot\text{THF}\cdot 2\text{H}_2\text{O}$ and $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_3\}\cdot 2\text{THF}$. The stacking features are governed by coordination of water molecules. The coordination of water leads to the formation of the dimeric complex $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_2\}\cdot\text{THF}\cdot 2\text{H}_2\text{O}$. In $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_2\}\cdot\text{THF}\cdot 2\text{H}_2\text{O}$ both sides of the stack are totally coordinatively blocked by solvent molecules (THF, H_2O) or counterions as BF_4^- (Fig. 24a). However, without coordination of water, the most suitable ligation around copper(II) and sodium is achieved by the formation of triple-decker metalla-coronate $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_3\}\cdot 2\text{THF}$ (Fig. 24b) [90].

Reaction of $\text{H}_2\text{-22}$ with iron(III) chloride in the presence of potassium, barium, strontium or lanthanum ions yielded $[\text{Fe}_2\text{M}(\mathbf{22})_3]^{n+}$ ($\text{M} = \text{K}^+, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{La}^{3+}$) [91]. Their X-ray structure reveals that the mono-, di- and tri-valent guest cations are encapsulated in the cavity of the bicyclic dinuclear host.

In $[\text{Fe}_2\text{K}(\mathbf{22b})_3](\text{PF}_6)$ the potassium ion is nine coordinated by six oxygen and three nitrogen atoms of the three ligands. The ligands are approximately octahedrally

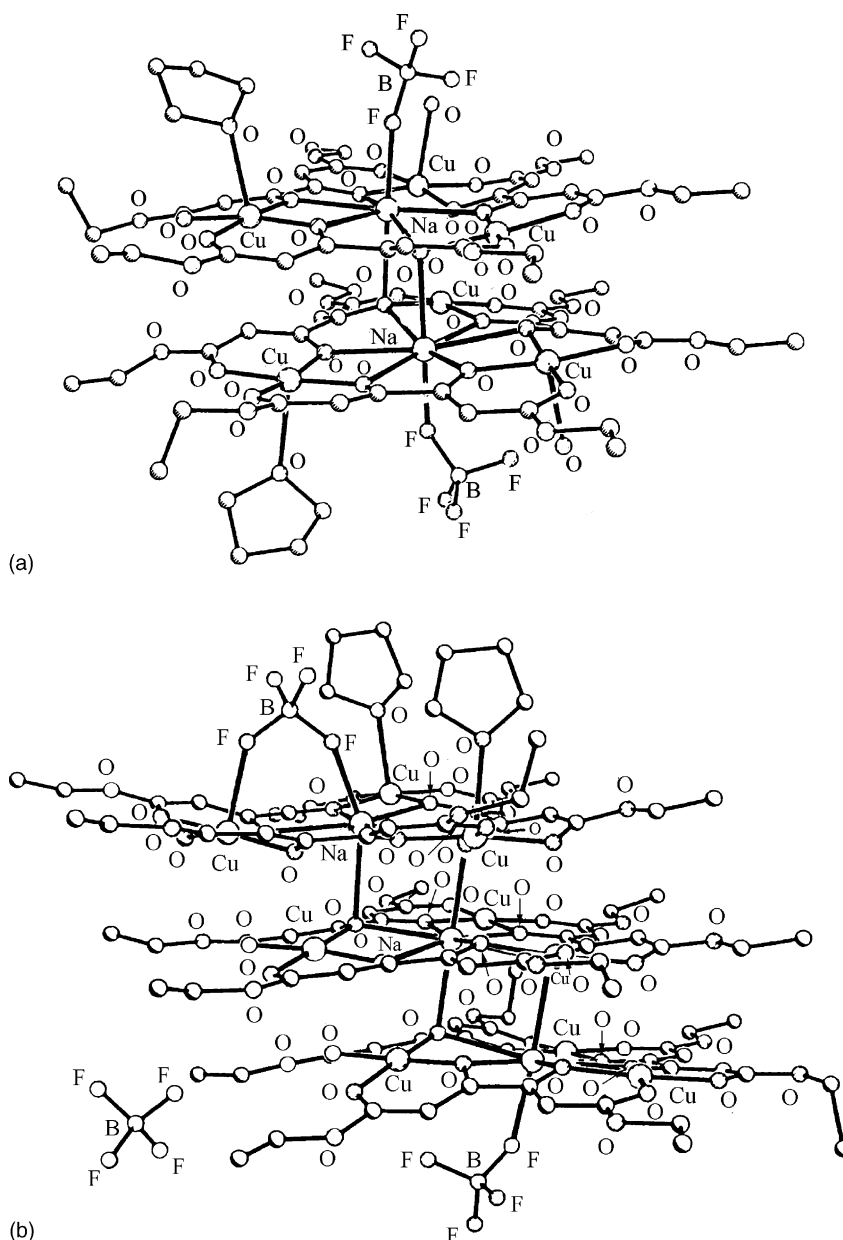


Fig. 24. Structure of double decker metalla-coronate $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_2\} \cdot 2\text{THF} \cdot 2\text{H}_2\text{O}$ and solvent molecules (a) and triple decker metalla-coronate $\{\text{Na}[\text{Cu}_3(\mathbf{21a})_3](\text{BF}_4)_3\} \cdot 2\text{THF}$ (b) (adapted from Ref. [90]).

coordinated to the iron centers in a helical fashion. In the chiral complex of racemic $[\text{Fe}_2\text{K}(\mathbf{22b})_3]^+$ both iron centers are identically coordinated. Therefore $[\text{Fe}_2\text{K}(\mathbf{22b})_3]^+$ is either a (Δ, Δ) -fac or (Λ, Λ) -fac $\{2\}$ -iron cryptate. The iron...iron distance is 7.01 Å (Fig. 25a) [91]. Also in $[\text{Fe}_2\text{K}(\mathbf{22c})_3](\text{PF}_6)$, $[\text{Fe}_2\text{K}(\mathbf{22c})_3]^+$ is a racemic mixture of the helical (Δ, Δ) -fac or (Λ, Λ) -fac $\{2\}$ -iron cryptates. The positive charge of the cluster is compensated by a $[\text{FeCl}_4]^-$ counter ion. Three acetone molecules are additionally present in the unit cell [91].

In $[\text{Fe}_2\text{Ba}(\mathbf{22a})_3]^{2+}$ barium is eleven coordinated by six oxygen and three nitrogen atoms of the three ligands and two additional tetrahydrofuran molecules, situated between each

of the two ligand strands. The solvent molecules coordinate to the guest ion and are located in an almost perfect plane equatorially to the trigonal prism, formed by the oxygen atoms of the ligands. $[\text{Fe}_2\text{Ba}(\mathbf{22a})_3]$ is helical with either (Δ, Δ) -fac or (Λ, Λ) -fac coordinated iron centers, comparable to $[\text{Fe}_2\text{La}(\mathbf{22a})_3]^{3+}$ [91].

Reaction of the doubly negatively charged bis-bidentate ligands $\text{H}_2\text{-22}$ with Mn^{2+} , Co^{2+} , and Cd^{2+} revealed their pentadentate tritopic chelating nature to give the octanuclear bis(triple-helical) chelate complexes $[\text{Mn}_8(\mathbf{22})_6(\text{O})_3]$, $[\text{Co}_8(\mathbf{22})_6(\text{O})_3]$ and $[\text{Cd}_8(\mathbf{22})_6(\text{O})_3]$ [91].

The core of these complexes consists of eight metal(II) ions, forming a two-fold capped, slightly twisted trigonal

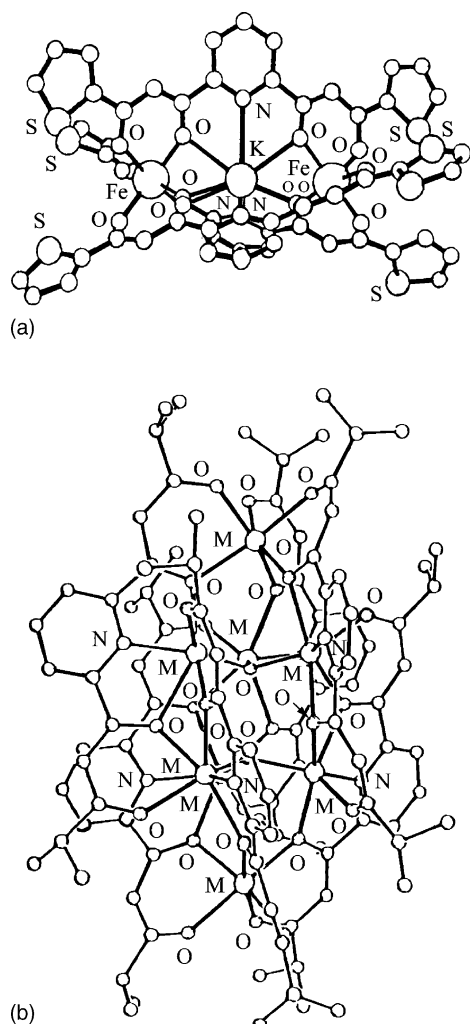
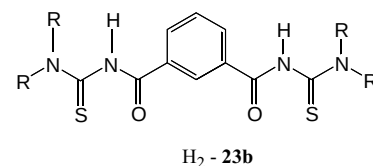
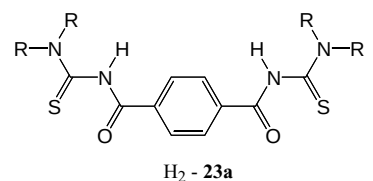


Fig. 25. Structure of the $[\text{Fe}_2\text{K}(\mathbf{22b})_3]^{3+}$ (a) and $[\text{M}_8(\mathbf{22a})_6(\text{O})_2]$ (b) ($\text{M} = \text{Mn}^{2+}$, Co^{2+} , Cd^{2+}) (adapted from Ref. [91]).

prism with a $\mu_3\text{-O}^{2-}$ ion centered in each of the two inner faces. All the six doubly negatively charged pentadentate ligands $[\mathbf{22}]^{2-}$ link to three metal(II) ions. The two antipodal metal(II) ions are coordinated by three μ_1 - and three μ_2 -oxygen chelate atoms of three ligands. However, the six metal centers, constituting the trigonal prism, are coordinated by one pyridylene nitrogen and two μ_2 -chelate oxygen atoms. Distorted octahedral coordination of these six metal(II) ions is achieved by two extra $\mu_3\text{-O}^{2-}$ ions. Consequently, in these neutral, octanuclear, bis(triple-helical) complexes, all the metal(II) ions are octahedrally coordinated (Fig. 25b) [91].

It was suggested that the ligands 3,3,3',3'-tetra-(*n*-butyl)-1,1'-terephthaloylbis(thiourea), $\text{H}_2\text{-23a}$ and 3,3,3',3'-tetraethyl-1,1'-isophthaloylbis(thiourea), $\text{H}_2\text{-23b}$, derived from terephthalic and isophthalic acids, respectively, are ideal for the self-assembly of new metallomacrocyclic complexes. For $\text{H}_2\text{-23a}$ models suggest that only a 3:3 complex appears easily conceivable while for $\text{H}_2\text{-23b}$ only 2:2 and 6:6 com-

plexes appear favourable [92]. Thus treatment of $[\text{Pt}(\text{Cl})_4]^{2-}$ with 1 equiv. of $\text{H}_2\text{-23a}$, leads to the exclusive formation of *cis*- $[\text{Pt}(\mathbf{23a})_3]$, while $\text{H}_2\text{-23b}$ yields only *cis*- $[\text{Pt}(\mathbf{23b})_2]$ [92].



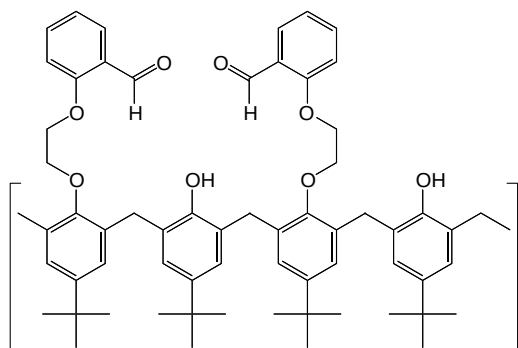
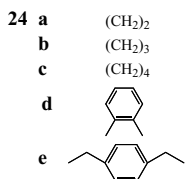
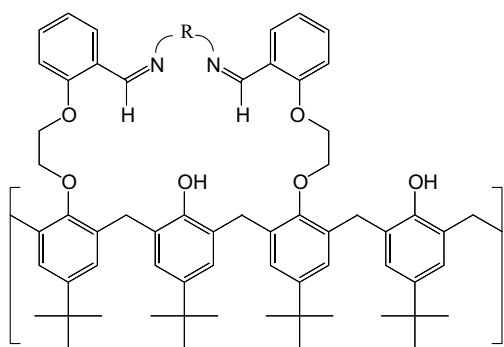
The structures of *cis*- $[\text{Pt}(\mathbf{23a})_3]$ and *cis*- $[\text{Pt}(\mathbf{23b})_2]$ (Fig. 26), shows these complexes to be approximately planar 2:2 and 3:3 metallomacrocyclic assemblies, respectively, with the aromatic rings of the isophthaloyl and terephthaloyl moieties essentially coplanar with the coordination sphere of the platinum(II) ions. In the case of *cis*- $[\text{Pt}(\mathbf{23a})_3]$ however, the macrocyclic ring is somewhat twisted. The coordination sphere of each platinum(II) ion in both *cis*- $[\text{Pt}(\mathbf{23b})_2]$ and *cis*- $[\text{Pt}(\mathbf{23a})_3]$ is also distorted from ideal square planarity [92]. Both metallomacrocycles are somewhat strained, causing a buckling of the assembly from perfect planarity, something which is most evident in the case of the 3:3 complex *cis*- $[\text{Pt}(\mathbf{23a})_3]$ [92].

Calixarenes [93] represent excellent examples of ditopic macrocyclic systems able to form inclusion complexes with both charged species and neutral molecules. The inclusion of neutral molecules [94] and alkylammonium ions [95] occurs mainly in the apolar cavity of these macrocycles which can be enforced by suitable functionalization at the phenolic OH groups (lower rim). On the other hand the attachment of binding groups at the lower rim allows the coordination of different metal ions with high selectivity. Ester and amide derivatives of calix-[4]-arenes in the cone conformation bind sodium and calcium ions very strongly [96] whereas calix-[4]-arene-crown ethers in 1,3-alternate conformation are very selective towards cesium [97] and potassium [98] ions, depending on the ring size. Very recently a calixarene podand with *N,N*-dimethyldithiocarbamoylthio groups which was able to extract transition metal complexes has been reported [99].

The fusion of the Schiff base and calixarene properties into a unique entity can give rise to interesting and versatile systems with very peculiar recognition properties.

Macrocyclic Schiff bases at the lower and upper rim of calix [4] arenes have been reported [100]. Cone-1,3-dialdehyde-25,27-bis[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-tert-butylcalix[4]-arene, $\mathbf{24'}$, obtained from the reaction of *p*-tert-butylcalix[4]arene with 2-(2'-bromoethoxy)-

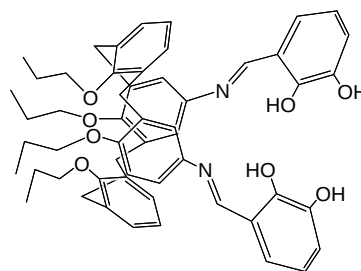
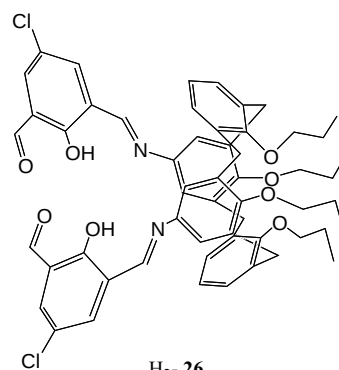
benzaldehyde was refluxed with 1–3 equiv. of the appropriate diamine, $\text{H}_2\text{N}-\text{R}-\text{NH}_2$, in acetonitrile–methanol for 21 h to give the pure Schiff bases **24a–e** [101]. The transformations of the diformyl derivative into the related [1+1] Schiff bases **24a–e** occur with retention of the cone conformation of the *p*-*tert*-butylcalix[4]-arene moiety.

**24'**

An evaluation of the binding efficiencies of **24a–e** was carried out by solvent extraction of metal picrates into dichloromethane under neutral conditions. In the transition metal series, iron(II) and copper(II) ions were extracted more efficiently. Heavy metal cations are extracted with a higher preference for lead(II) ion. In the lanthanide series, there is an extraction selectivity for neodymium(III) and europium(III) ions with **24b** and for europium(III) ion with **24c**. The most efficiently extracted metal ions have been tested with aromatic ligand **24d**, which showed a good extracting power for copper(II) ion only. In methanol solution these Schiff bases form 1:1 complexes only under basic conditions. The phenolic oxygens are deprotonated. The binding ability depends on the length of the Schiff base bridge. Ligand **24b**, which contains a bridge of three carbon atoms, forms the more stable complexes. This ligand pre-

sents the optimal cavity size for the europium(III) ion and for the larger lead(II) ion. The stability of the complexes decreases for the longer bridged ligand **24c** and also for the more rigid aromatic ligand **24d** [102,103].

By [2+1] condensation of 2,3-dihydroxy-benzaldehyde or 2,6-diformyl-4-chlorophenol with 5,17-diamino-25,26,27,28-tetrapropoxy-calix[4]arene in acetonitrile and in 1:2 molar ratio, the acyclic Schiff bases **H₄-25** and **H₂-26** were obtained as orange solids, soluble in most of the common organic solvents [104].

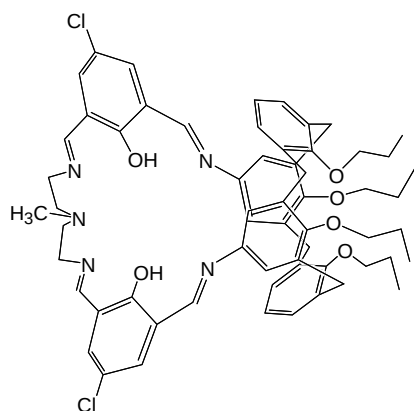
**H₂-25****H₂-26**

H₄-25 reacts in methanol with copper(II) acetate in a 1:1 molar ratio to form the mononuclear brown complex $[\text{Cu}(\text{H}_2\text{-25})]$. The copper(II) ion was proposed to coordinate the inner N_2O_2 site. Moreover, the ascertained flexibility of the cone calix[4] arene moiety might favour the inner coordination of the copper(II) ion [104]. The outer O_2O_2 chamber is too large to accommodate this metal ion and attempts to form the homo-dinuclear complex failed. On the contrary this O_2O_2 site is particularly suitable for f-metal ions and mononuclear complexes were successfully used for the preparation of d–f-hetero-dinuclear complexes [104].

Accordingly $[\text{Cu}(\text{H}_2\text{-25})]$ was used as ligand for the subsequent formation of hetero-polynuclear complexes: by reaction with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the presence of LiOH in a methanol/pyridine solution, a precipitate formulable as $[\text{La}_2\text{Cu}(\text{25})(\text{NO}_3)_2(\text{OH})_2]$ was obtained. The solution, on standing for a prolonged period of time, separated the dinuclear complex $[\text{LaCu}(\text{25})(\text{NO}_3)(\text{H}_2\text{O})(\text{py})]$ [104].

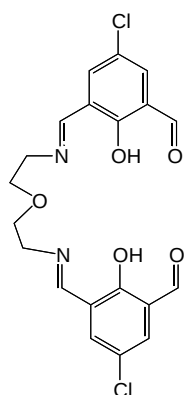
The dinuclear lanthanum(III) complex $[\text{La}_2(\text{27})(\text{NO}_3)_4]$ of the upper bridged calix[4] arene ligand **H₂-27** was obtained by the reaction of **H₄-26** and 1,5-diamino-3-

azamethylpentane in the presence of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, in acetonitrile [104].

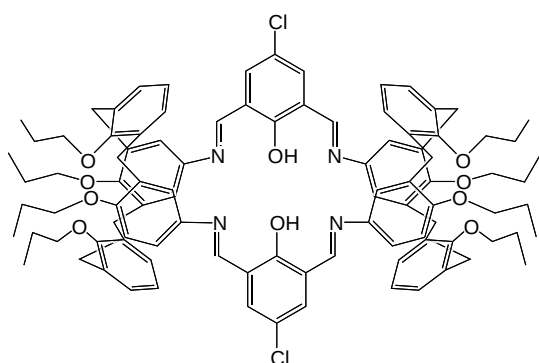


$\text{H}_2\text{-27}$

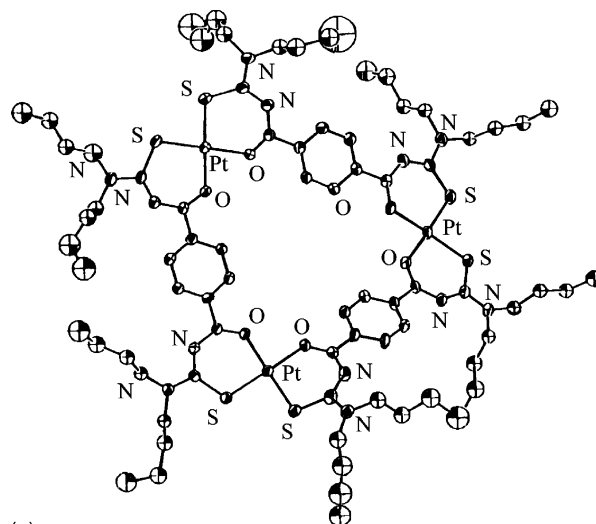
The reaction of the preformed mononuclear complex $\text{La}(\text{H}_2\text{-28})(\text{NO}_3)_3$, obtained by template condensation of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-oxapentane in the presence of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 5,17-diamino-25,26,27,28-tetrapropoxy-calix[4]-arene in ethanol/chloroform, leads to the empty form of a double calix[4]-arene $\text{H}_2\text{-29}$, which evidently derives from the [2+2] condensation of 2,6-diformyl-4-chlorophenol and 5,17-diamino-25,26,27,28-tetrapropoxy-calix[4]-arene [104].



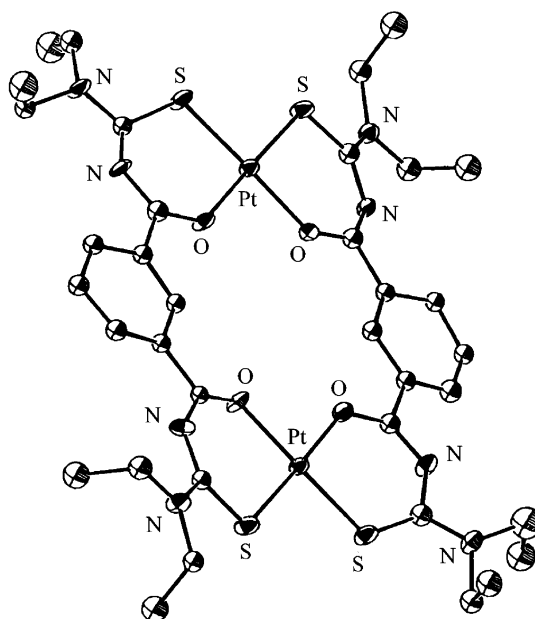
$\text{H}_2\text{-28}$



$\text{H}_2\text{-29}$



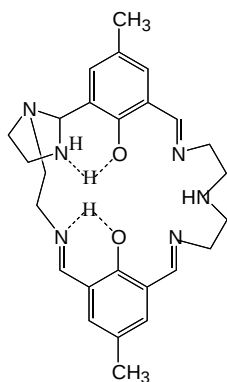
(a)



(b)

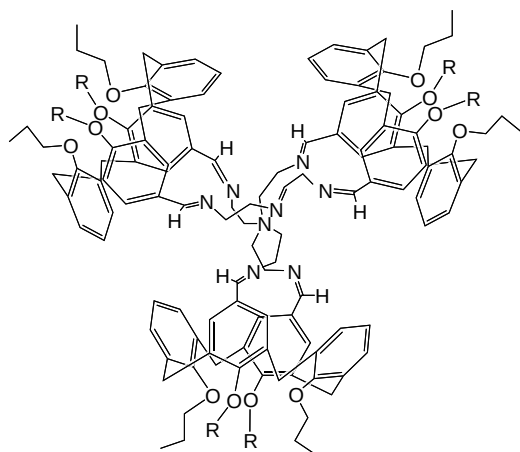
Fig. 26. Structure of $[\text{Pt}(\text{23a})_3]$ (a) and $[\text{Pt}(\text{23b})_2]$ (b) (adapted from Ref. [92]).

This is not a completely surprising result and arises from the lability, owing to hydrolysis, of the Schiff base. In a similar way the reaction of chloro [bis-3-formyl-5-methylsalicylidene]ethylenediaminato]iron(III) with 1,5-diamino-3-azapentane in the presence of the lead(II) ion, followed by the addition of NaNCS , resulted in the formation of the mononuclear iron(III) complex $[\text{Fe}(\text{H}_2\text{-30})(\text{NCS})](\text{ClO}_4)_2 \cdot \text{DMF}$ of the different macrocyclic ligand $\text{H}_2\text{-30}$, supposed to be the [2+2] condensation product between 2,6-diformyl-4-methylphenol and 1,5-diamino-3-azapentane. This result suggests the recombination of the [bis-3-formyl-5-methylsalicylidene]ethylene diamine with 1,5-diamino-3-azapentane in the course of cyclization [105].

H₂ - 30

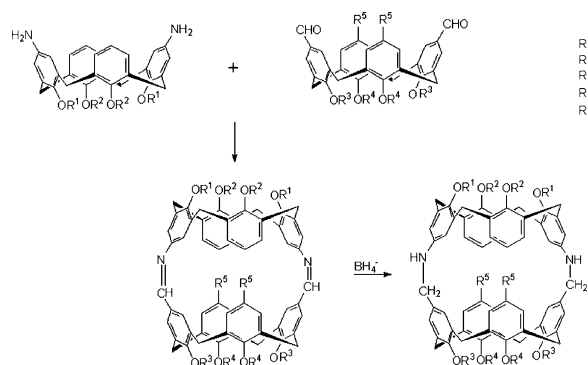
The mononuclear complex [Cu(**29**)] was obtained by condensation of equimolar amounts of 2,6-diformyl-4-chlorophenol and 1,3-diamino-tetrapropoxy-calix[4]arene, in the presence of Cu(ClO₄)₂ as templating agent.

Finally the macrobicyclic ligands **31** (R = H, C₃H₇), containing three calix[4] arene units were obtained by [3+2] condensation in acetonitrile of 5,17-diformyl-25,27-dipropoxy calix[4]-arene or 5,17-diamino-25,26,27,28-tetrapropoxy-calix-[4]-arene [106] with tris-(2-aminoethyl)-amine [104].

**31** (R = H, C₃H₇)

Condensation reaction of calix[4]arenes functionalized at the upper rim in the 5- and 17-positions with amino and formyl groups, respectively, gives a new [1+1] series of head-to-head linked double calix[4]arenes in nearly quantitative yield. The two imine bridges of these [1+1] double calix[4]arenes can easily be reduced with an excess of NaBH₄ at room temperature in a mixture of C₂H₅OH and THF to the corresponding more flexible amines in good yields (Scheme 8) [107].

The X-ray structure analysis unambiguously proves the structure of one the [1+1] reduced Schiff-base, where R^I = R^{II} = R^{III} = R^{IV} = CH₂CH₂CH₃ and R^V = NO₂ in



Scheme 8.

the solid state. Suitable crystals have been obtained by slow diffusion of CH₃OH into a CH₂Cl₂ solution of this macrocyclic amine derivative. Both calix[4]arene moieties of double calix[4]arene derivative adopt a pinched cone conformation in the solid state in which the aromatic nuclei bearing the reduced Schiff base bridges are oriented parallel whereas the remaining aromatic units are flattened. The two calix[4]arene cavities are oriented head-to-head due to the short bridging spacers. The intramolecular N...N distance is 4.39 Å. The two calix[4]arene subunits are slightly twisted around the CH₂NH bridges (Fig. 27) [107].

These highly preorganized double calix[4]arenes complex silver(I) ions ($K_{\text{ass}} = 9.5 \times 10^5 \text{ M}^{-1}$ in CDCl₃); the selectivity of this complexation process was studied by supported liquid membrane transport experiments and chemically modified field effect transistor measurements [107].

The [2+2] macrocycle H-**32c**, able to form complexes of defined stereochemistry with up to four centers on both sides of the molecule, has been prepared by condensation of

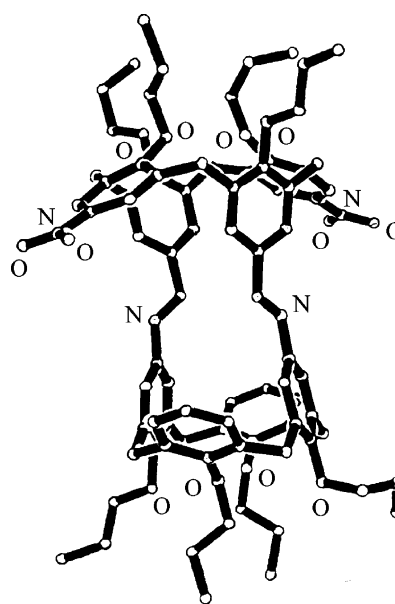
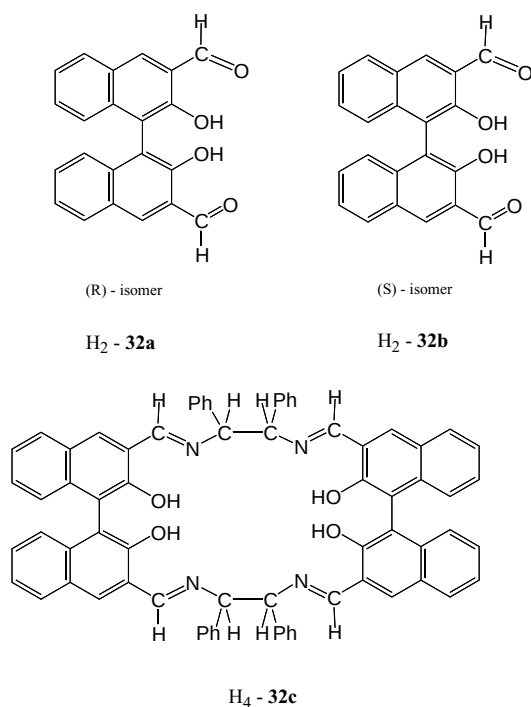


Fig. 27. Structure of the [1+1] double calix[4] arene where R^I = R^{II} = R^{III} = R^{IV} = *n*-Pr and R^V = NO₂ (adapted from Ref. [107]).

2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dialdehyde with (*R,R*)-1,2-diamino-1,2-diphenylethane.

The large-scale synthesis of the racemic diformyl precursor 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dialdehyde is achieved from the commercially available 1,1'-binaphthyl-2,2'-diol. This is first methylated with NaH/dimethylsulphate and then formylated ortho- to the methyl groups with BuLi/DMF/HCl, before the methoxy groups are cleaved with boron trichloride. With this procedure, the dihydroxy-diformyl derivative can be obtained optically pure without laborious recrystallization.

It was found that the (*R*)-dihydroxy-diformyl isomer **H₂-32a** reacts with the above diamine to form polymeric Schiff bases while the (*S*)-isomer **H₂-32b** undergoes condensation with two molecules of diamine to form the [24]-membered [2+2] macrocycle **H₄-32c**, a yellow solid that may be purified by chromatography on silica gel. During the condensation of the (*R*)-diformyl derivative **H₂-32a** with *R,R'*-1,2-diamino-1,2-diphenylethane, the ends of the growing chain are so far apart from one another that the anticipated polymer forms, whereas in the reaction of the (*S*)-diformyl derivative **H₂-32b** with the same diamine, the [2+2] [24] membered ring closes [108].

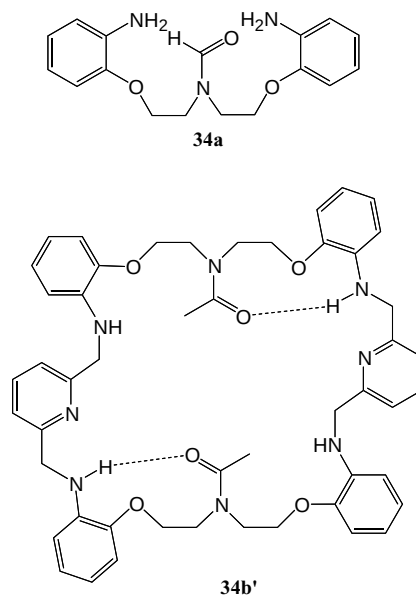


A simple enantiomeric separation exploits the observation that with the given optically active diamine, only the (*S*)-enantiomer **H₂-32b** gives rise to a macrocycle, whereas the (*R*)-enantiomer **H₂-32a** forms a polyimine. When the products of the condensation reaction of (*R*)- and (*S*)-diformyl precursor with the diamine are subjected to column chromatography on silica gel, the macrocycle formed from the reaction of **H₂-32b** with the diamine is eluted with dichloromethane/toluene while the polyimine is left as a residue on

the column. Stirring of the [1+1] macrocycle with hydrochloric acid liberates the (*S*)-diformyl derivative **H₂-32b**, which may then be isolated enantiomerically pure. Compared with similar imines, the [1+1] macrocycle **H₄-32c** has notably enhanced resistance towards hydrolysis, which makes its purification possible by column chromatography on silica [108].

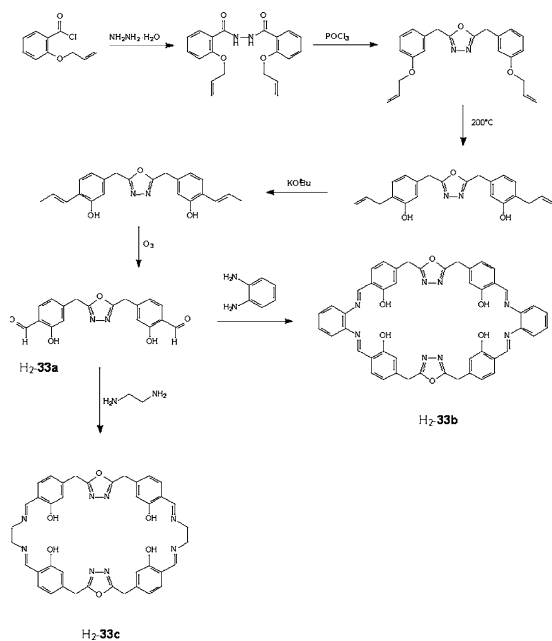
The synthesis of the diformyl derivative **H₂-33a** and the related multidentate 1,3,4-oxadiazole-imine and phenol containing macrocycles **H₂-33b** and **H₄-33c** has been carried out through the reactions of Scheme 9 [109]. In particular, the [2+2] cyclization of the dialdehyde **H₂-33a** and an equimolar amount of either 1,2-benzenediamine or 1,2-ethanediamine in dilute refluxing acetonitrile solutions affords the corresponding macrocycles **H₂-33b** and **H₄-33c**. **H₄-33b** and **H₄-33c** can potentially coordinate two M(II) cations with electron neutrality after deprotonation of the phenol groups. Also these macrocycles can coordinate two additional M'(II) cations with external counterions in an MM'M'M fashion.

The template cyclocondensation of *N,N*-bis[2-(2-amino-phenoxy)ethyl]formamide **34a** with 2,6-diformylpyridine in the presence of Mn(NO₃)₂, followed by reductive demetalation with NaBH₄ of the resulting Schiff base, affords the [2+2] *N,N*-diformylated-[36]-membered N₈O₄ oxa-azamacrocycle **34b** [110].

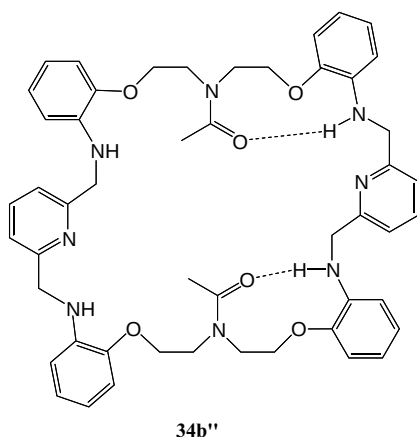


The diamine precursor **34a** has been achieved through the in situ reaction of *o*-nitrophenol Na₂CO₃ and KOH with bis-(2-chloroethyl)amine hydrochloride in hot dimethylformamide. The initial product *N,N*-bis[2-(2-nitrophenoxy)ethyl]formamide was reduced with hydrazine and palladium/carbon in absolute ethanol to provide *N,N*-bis[2-(2-amino-phenoxy)ethyl]formamide [110].

The [2+2] macrocyclic formation was confirmed by the X-ray structure which also revealed the *trans*-arrangement



of the formyl groups, giving rise to the conformer **34b'** (Fig. 28). In solution the two isomers **34b'** and **34b''** are present.



Recently the [26]- or [32]-membered macrocycles **H₄-35a–e** were synthesized by template-induced cyclization (Scheme 10a) of *trans*-(*R,R*)- or *trans*-(*S,S*)-1,2-diaminocyclohexane and an appropriate dialdehyde, prepared from the corresponding aldehydes [111]. In these synthetic procedures, some condensations give rise to a mixture of macrocycles (i.e. [2+2], [3+3] or [4+4] species) while others form exclusively the [2+2] macrocycles. The structure of **H₄-35a**·DMF confirms the [2+2] condensation reaction and shows the four benzene rings to form a well-defined cavity and adopt a 1,3-dialternate conformation with a striking calixarene-like structure. The two opposing face-to-face benzene rings are nearly coplanar and lie 7.57 Å apart and, as a consequence of the preferred 1,3-dialternate con-

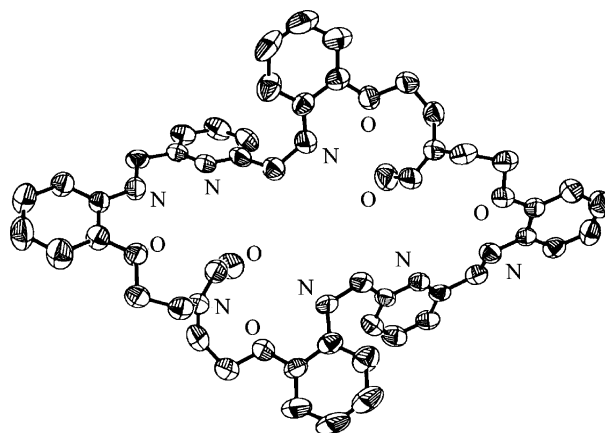


Fig. 28. Structure of **34b'** (adapted from Ref. [110]).

formation, the hydroxy groups are twisted away from the N_2O_2 plane so that hydrogen-bonding between adjacent OH groups is precluded (Fig. 29a) [111].

Although the solid state conformation of **H₄-35a** appears ill-disposed to provide two tetradentate N_2O_2 Schiff base coordination sites, reaction with manganese(III) salts is facile. An addition of a solution of $Mn(CH_3COO)_3$ to solutions of **H₄-35a–e** caused an immediate colour change from yellow to deep brown and the formation of a dinuclear complex. An electrospray mass spectrum of a methanolic solution of the dark brown product obtained by treatment of

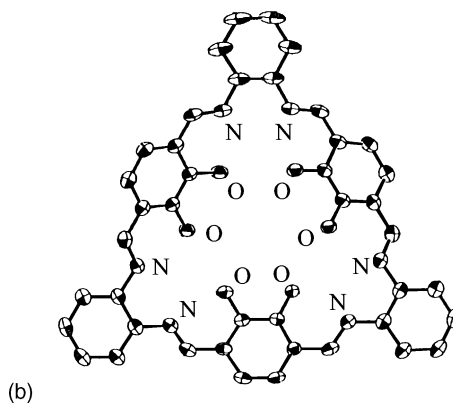
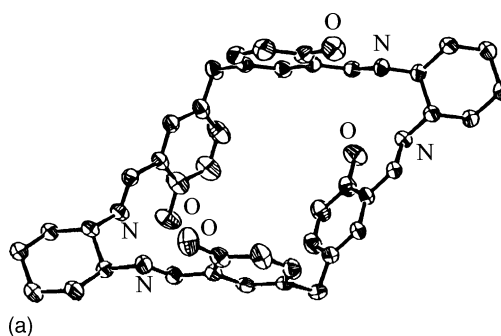
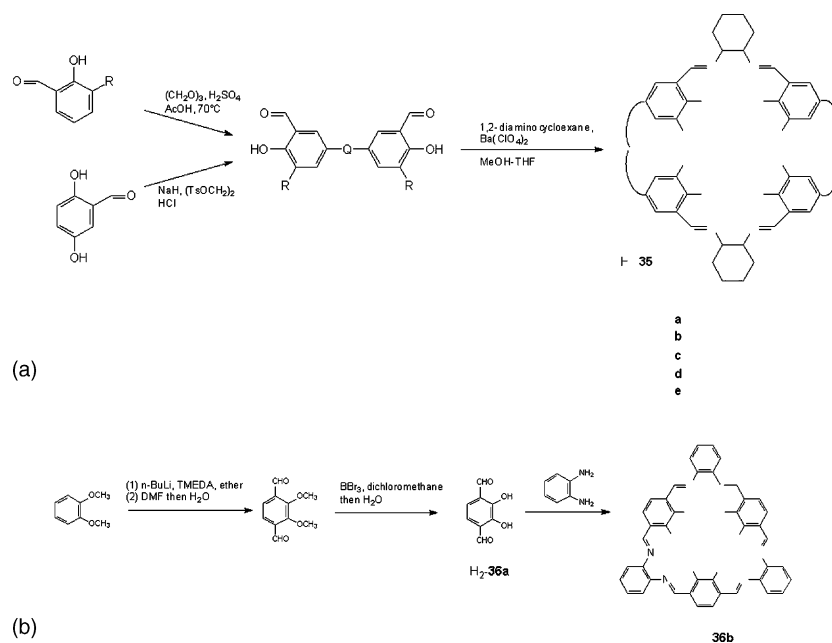


Fig. 29. Structure of **H₄-35a** (a) and **H₆-36b** (b) (adapted from Refs. [111,113]).



Scheme 10.

H₄-**35d** with Mn(CH₃COO)₃ showed strong peaks consistent with the formation of a bimetallic complex.

These manganese complexes show catalytic activity for enantioselective epoxidation of unfunctionalized alkenes in the presence of NaClO (aq) as terminal oxidant. The favourable solubility of the dimanganese complex with H₄-**35d** in CH₂Cl₂ favours the formation of the epoxide product from styrene better than the commonly used [{*N,N'*-bis(salicylideneiminato-ethylenediamine)}manganese(III)] catalyst [112].

2,3-Dihydroxybenzene-1,4-dicarbaldehyde (H₂-**36a**) has been prepared by dilithiation of 1,2-dimethoxybenzene, followed by the reaction with *N,N*-dimethylformamide to give 2,3-dimethoxybenzene-1,4-dicarbaldehyde. Treatment of the resulting compound with boron tribromide afforded 2,3-dihydroxybenzene-1,4-dicarbaldehyde. The related [3+3] macrocyclic compound H₆-**36b** gradually precipitates during the reaction of H₂-**36a** and 1,2-diaminobenzene in acetonitrile at room temperature for 2 weeks [113].

H₆-**36b** has a triangular shape with three apexes of the phenylenediamine. Each hydroxyl group points to a nitrogen atom of the imine forming a strong intramolecular hydrogen-bond network. However, no intermolecular hydrogen bond was observed while the three benzene rings of the phenylenediamine moieties lie on the average plane of the molecule. Four of the six hydroxyl groups stick out on one side of the molecular plane and the other two on the opposite side [113] (Fig. 29b).

Interestingly, [H₆-**36b**]-H₂O-CH₃CN, was obtained from the reaction mixture; in this compound a water molecule is captured in the cavity of the cyclic compound H₆-**36b** [113].

Many acyclic and cyclic Schiff bases, derived from the condensation of the formyl- and amine-precursors of

Scheme 1, have been reported in the recent literature and also reviewed [42]. Here is a brief account of some recent significant examples of the different types of Schiff bases is reported to show the possibility offered by the self-condensation reactions.

As examples of acyclic ligands, the X-ray structure of the [2+1] compounds H₄-**37** and H₂-**37a** derived by the condensation respectively of 2,3-dihydroxybenzaldehyde with 2,2-dimethyl-1,3-propanediamine and 3-methoxy-2-hydroxybenzaldehyde with 1,5-diamino-3-azamethylpentane are reported in Fig. 30a and b [114]. The two symmetric parts of H₄-**37** are in *trans* and mainly governed by hydrogen bondings. A different configuration was found for H₂-**37a**.

The [1+1] cyclic nature of a series of asymmetric compartmental ligands, prepared according to Scheme 11, has been proposed by FAB mass spectrometry and ascertained by X-ray diffractometry (Fig. 31a) [115].

Analogously [2+2] symmetric and asymmetric cyclic Schiff bases have also been prepared and characterized as well, where possible, by X-ray structural determination [115]. When it was impossible to grow good crystals for X-ray determination, mass spectrometry (especially EI, FAB and ESI) was successfully employed in order to obtain indispensable information about the molecular complexity and the correct cyclic nature of these systems. Many Schiff bases with different complexity ([1+1], [2+1], [2+2], [1+1], [2+2], [3+2] etc) have been fully characterized by this methodology [116–122].

When equimolecular quantities of thiophene-2,5-dicarbaldehyde and an α,ω -primary diamine are allowed to react in methanol or ethanol, white or pale yellow powders or crystals of [2+2] macrocycles are obtained. The structure of the macrocycle derived by condensation of 2,5-

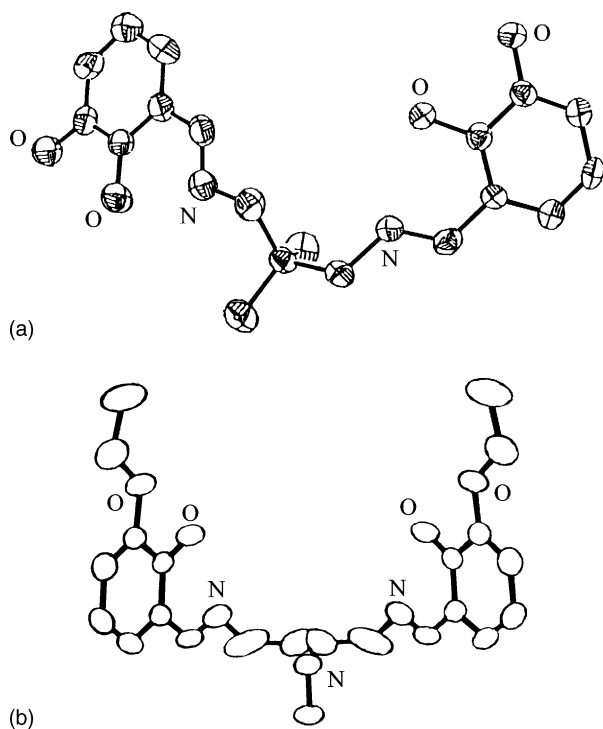


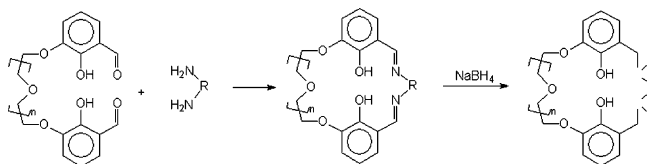
Fig. 30. Structure of H₄-37 (a) and H₂-37a (b) (adapted from Ref. [114]).

diformylthiophene and 1,5-diamino-3-oxapentane confirms the discrete [2+2] nature of these compounds (Fig. 31b) [123].

The reaction of 2,6-diformyl-4Z-phenol (Z = Cl, CH₃) with 1,2-diaminobenzene in alcoholic solution forms the corresponding [2+2] macrocycles which, on the basis of their IR and NMR spectra and X-ray structural analysis, have been formulated as the partially reduced compounds where two C=N groups have been reduced to CH₂-NH groups (Fig. 31c) [115].

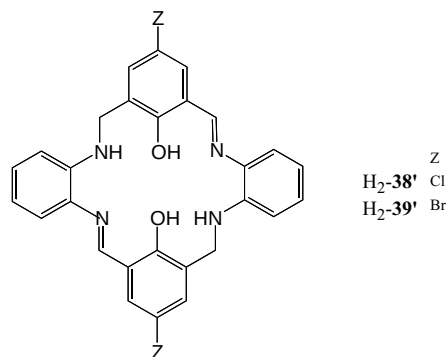
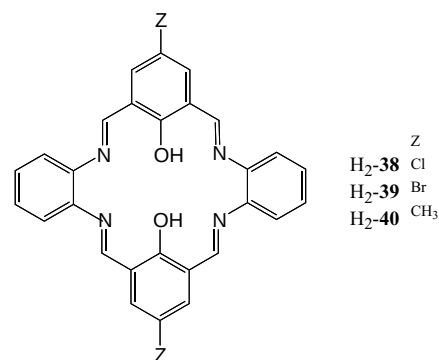
These results document that it is not always possible to obtain the desired macrocyclic Schiff bases by self-condensation of the appropriate precursors. Several systems suffer hydrolysis or follow a different synthetic pathway giving rise to unpredicted species. Recently these synthetic possibilities have been briefly reviewed [42].

Thus the use of a templating agent (i.e. H⁺, Mⁿ⁺, complex systems, etc.) has been introduced in order to eliminate or reduce the formation of unwanted compounds addressing the synthetic pathways toward the designed compound. The subsequent demetallation process gives rise to the designed free Schiff base in a pure form.



Scheme 11.

The template condensation of 2,6-diformyl-4-chlorophenol and 2,6-diformyl-4-bromophenol with 1,2-diaminobenzene, respectively, in the presence of hydrated lanthanide(III) nitrate in acetonitrile affords discrete mononuclear lanthanide(III) complexes of the composition [Ln(H₂-38)(NO₃)(CH₃CN)](NO₃)₂·nH₂O (Ln = Nd³⁺–Tm³⁺ and Y³⁺, except Pm³⁺; n = 1 for Nd³⁺ and Y³⁺, n = 2 for Sm³⁺, Gd³⁺, Sm³⁺, Tb³⁺, Dy³⁺, Ho³⁺ and Tm³⁺ and n = 3 for Eu³⁺ and Er³⁺) and [Ln(H₂-39)(NO₃)(CH₃CN)](NO₃)₂·nH₂O (Ln = Sm³⁺–Tm³⁺ and Y³⁺; n = 2 for Sm³⁺, Dy³⁺, Ho³⁺ and Er³⁺ and n = 3 for Eu³⁺, Gd³⁺, Tb³⁺, Tm³⁺ and Y³⁺). The chloro and bromo substituents on the macrocyclic framework do not affect the template potential of the lanthanide(III) cations [124].



When the Schiff base condensation is carried out in the presence of lanthanide templates in ethanol or methanol either at room temperature or under refluxing condition the diamine–diimine macrocycles H₂-38' and H₂-39' are obtained in the free form.

The macrocycle H₂-40 having methyl substituent on its periphery forms the mononuclear complexes [Ln(H₂-40)(NO₃)(H₂O)](NO₃)₂·nH₂O (Ln = Pr³⁺–Tm³⁺ and Y³⁺) [124]. While H₂-40 forms complexes with coordinated water molecule, the chloro- and bromo substituted macrocycles H₂-38 and H₂-39 form complexes with coordinated acetonitrile under the same experimental conditions [124].

When the condensation of the organic precursors is carried out in the absence of the metal template the diimine–diamine macrocycles are formed in the free form, H₂-38' being formed in 45% yield in methanol and H₂-39' in 29% yield in chloroform, as confirmed by the X-ray struc-

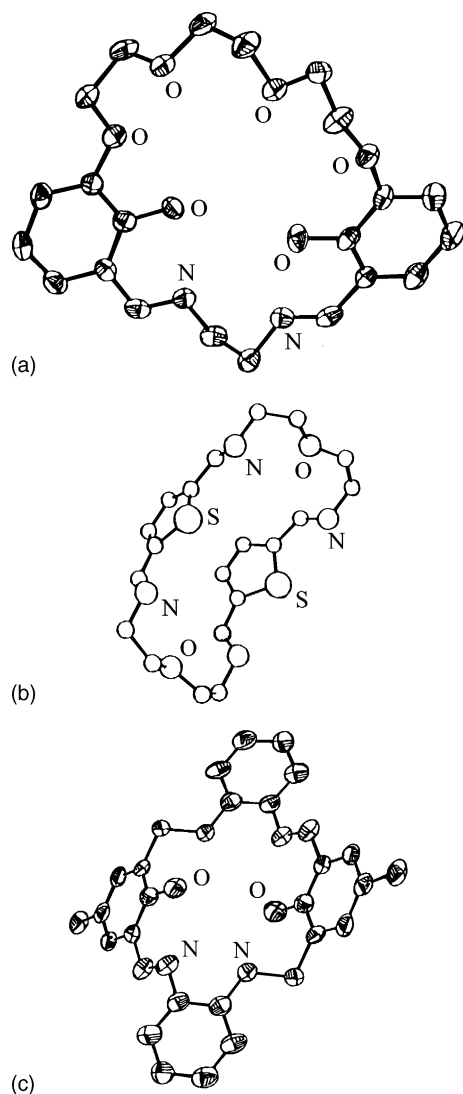
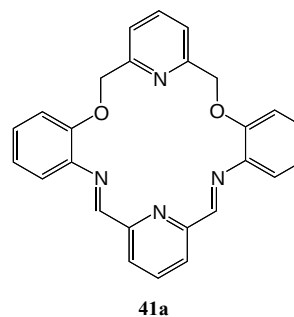


Fig. 31. Structure of the asymmetric [1+1] cyclic Schiff base of Scheme 11, where $n = 2$ and $R = \text{CH}_2\text{CH}_2$ (a), of the [2+2] macrocycles derived by condensation respectively of 2,5-diformyl-thiophene with 1,5-diamino-3-oxapentane (b) and of 2,6-diformyl-4-chlorophenol with 1,2-diamino-benzene (c) (adapted from Refs. [115,123]).

ture of $\text{H}_2\text{-38'}$ (Fig. 31c). On the other hand, when the reaction is carried out in the presence of the metal templates in acetonitrile, complexes of the respective tetraimine macrocycles are formed. The preformed diimine–diamine macrocycles do not form complexes under varying reaction conditions. This indicates the importance of the structural features of macrocycles required to form lanthanide complexes. The imine nitrogen seem to be better donors towards the lanthanide(III) cations than the secondary amine nitrogen.

A similar reduction was observed in the [1+1] condensation reaction of 2,6-bis(2-aminophenoxymethyl)pyridine and 2,6-diformylpyridine in the presence of lanthanide(III) salts [125]. In particular, using $\text{Ln}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ in CH_3CN the designed macrocyclic complexes $[\text{Ln}(\mathbf{41a})(\text{ClO}_4)_3]$ are obtained. Under similar conditions using $\text{Gd}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$

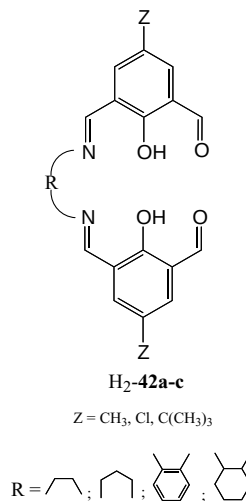
or $\text{Tb}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ and ethanol as a solvent, the reduced macrocycles **41b** is collected.



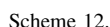
Reduction of **41a** is also observed when the gadolinium or terbium complex is dissolved in ethanol and heated to reflux. The reaction can easily be followed by monitoring the decreasing intensity of the electronic absorption band at 350 nm due to the imine groups. The spectrum of the free reduced macrocycle is obtained after heating at 50 °C for a few hours. The reduction occurs with the europium(III) and samarium(III) complexes as well, but the kinetics are substantially slower.

Electrochemical studies in acetonitrile show that the reduction of the imine groups is favoured when the ionic radius of the lanthanide(III) ions decreases and that a mechanism where a decomplexation of $[\text{Ln}(\mathbf{41a})(\text{ClO}_4)_3]$ followed by a reduction of the free macrocycle **41a** by ethanol with the consequent formation of **41b** and CH_3CHO appears to be the most realistic [125]. Under similar experimental conditions using barium(II) or sodium(I) ions as templating agents **41a** does not suffer reduction to **41b** [126].

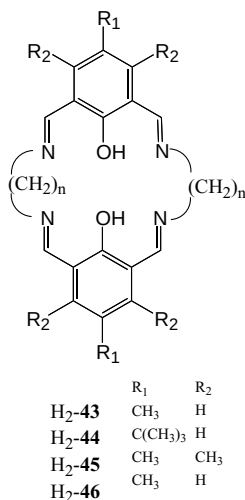
There is also the possibility to obtain the [2+1] acyclic ligand $\text{H}_2\text{-42a-c}$ ($Z = \text{CH}_3, \text{Cl}, \text{C}(\text{CH}_3)_3$) by condensation of 2,6-diformyl-4-substituted phenols with the corresponding diamine in a 2:1 molar ratio.



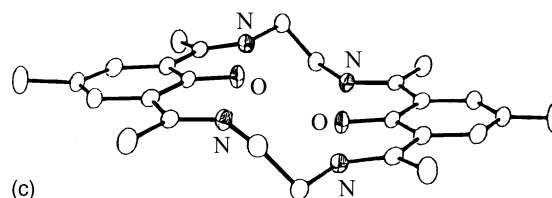
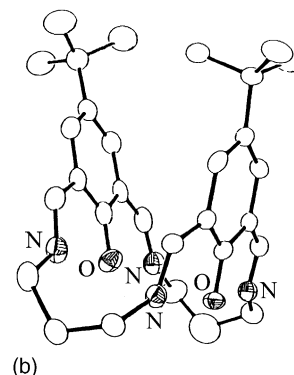
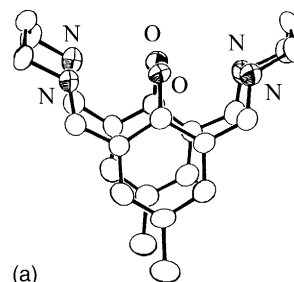
The [2+2] tetraimine macrocycles of Scheme 12, where the lateral sides are formed by different aliphatic chains also



The same condensation reaction in the presence of H^+ as templating agent offers an interesting alternative synthetic strategy for the preparation of pure tetraamine cyclic Schiff bases in one step. Thus the reaction of 1,3-diaminopropane and 2,6-diformyl-4-methyl-phenol in CH_3OH in the presence of 48% HBr , followed by addition of Br_2 , affords the protonated [2+2] macrocycle $[\text{H}_4\text{-}\mathbf{43}](\text{Br})_2$ as a relatively insoluble salt. Metathesis of this salt with NH_4PF_6 or NaBF_4 in CH_3OH gives rise to $[\text{H}_4\text{-}\mathbf{43}](\text{X})_2$ ($\text{X} = \text{PF}_6^-$, BF_4^-).



The protonated Schiff base macrocycle [H₄-**43**](PF₆)₂ adopts a folded conformation with the two phenyl rings involved in inter- and intra-molecular stacking interactions.

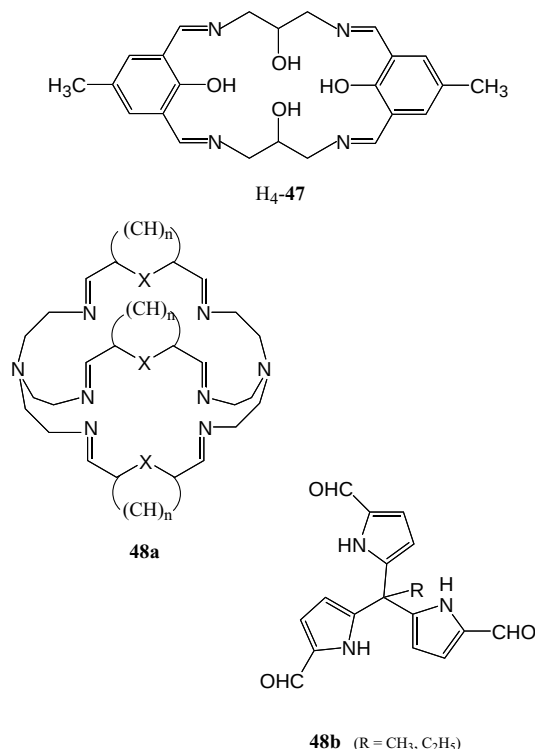


The conformation of [H₄-**43**]²⁺ is reminiscent of calixarenes and of related Schiff base macrocycles, with the phenyl rings folded downwards to leave the nitrogen and oxygen donor atoms on an exposed face (Fig. 32a) [127].

The structure of [H₄-**44**](PF₆)₂ (Fig. 32b), in which the CH₃ group at the 4-position of the phenol moiety has been replaced by a *tert*-butyl group, shows that the conformation of the cation [H₄-**44**]²⁺ is very similar to that observed for [H₄-**43**]²⁺ except that the dihedral angle between the planes of the phenyl rings has increased from 14 to 25° due to the greater steric bulk of the *tert*-butyl groups [127].

The Schiff base condensation of two moles of 2,6-diformyl-4-methyl phenol with two moles of 1,3-diamino-2-

hydroxypropane in the presence of Pb^{2+} , Ba^{2+} , and H^+ resulted in the formation of the [20]-membered Schiff-base macrocycle **H₄-47** [129].



In particular, the reaction of these diformyl and amine precursors in the presence of $\text{Pb}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol yields three products which have been characterised as the mononuclear $[\text{Pb}(\text{H}_4\text{-47})](\text{ClO}_4)_2$, the dinuclear $[\text{Pb}_2(\text{H}_2\text{-47})](\text{ClO}_4)_2$, and the salt of the protonated ligand $[(\text{H}_6\text{-47})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

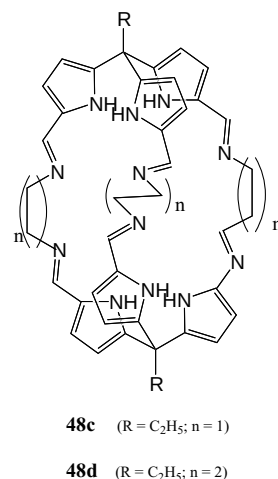
The initial product of the reaction is the binuclear complex; however, if the reaction mixture is allowed to stand for several days the mononuclear complex and ligand salt are obtained and the proportion of the ligand salt increases with time. Pure samples of the mononuclear and dinuclear complexes are quite stable and remain unchanged even after 48 h refluxing in methanol. It seems therefore, that loss of a metal ion from these complexes requires the presence of acid in the solution for the accompanying protonation step to occur. The salt of the protonated ligand can also be prepared directly, by reaction of 2,6-diformyl-4-methylphenol and 1,3-diamino-2-hydroxypropane in the presence of perchloric acid [129].

The cation $[(\text{H}_6\text{-47})(\text{H}_2\text{O})_2]^{2+}$ is folded so that the two resulting parts are almost parallel and are separated by approximately 3.5 Å. The folding of the macrocycle means that each N_2O_2 compartment of the ligand is too small to accommodate a lead(II) ion either within or above the cavity. Since the lead(II) ion is too small to accept any other combination of donors, the most stable product is the ligand salt. The cavity formed by the folding of the macrocycle is occupied by two water molecules, each of which is held in place by a network of short hydrogen bonds (Fig. 33) [129].

The evolution of these cyclic Schiff bases has produced macrobicyclic ligands obtained in one-step multiple condensation reactions [130]. Thus the [3+2] cyclic Schiff base condensation represents the extension of the [2+2] macrocyclic coordination system into the third dimension. In addition to the uses in the field of molecular recognition, catalysis and transport, these cage molecules appear particularly promising in the stabilization of particular species. The nature and disposition of donor atoms in the field cage may enhance the stability of unusual oxidation states in the coordinated transition metal ion [131], while encapsulation may protect normally labile substrate species. It is hoped that this combination of characteristics will eventually permit moisture-sensitive chemistry to be carried out in the protected cavity under room temperature and atmospheric pressure [130,131].

Treatment tris(2-aminoethyl)amine in refluxing alcohol with a series of diformyl derivatives (i.e. 4,4-diformyl-diphenylmethane, isophthalaldehyde, 2,6-diformylpyridine or 2,5-diformylthiophene, 2,5-diformylfuran, etc.) in a 2:3 molar ratio results in the isolation of the bicyclic systems **48a** [130,131]. Several of these compounds have been characterized also by X-ray diffractometry. It is surprising that this multiple self-condensation reaction, apparently difficult, proceeds in a very simple and clear way. Details will be reported in subsequent sections.

The tris formyl-substituted tripyrrols (**48b**) are very interesting precursors in the preparation of the related bis(tripyrrolyl)cryptands by [3+2] condensation with diamines. In particular the triformyl-ethyltripyrrolyl derivative **48b** (R = C₂H₅) reacts with 1,2-diaminoethane or 1,4-diaminobutane in THF to afford **48c** and **48d**. The structure of these macrobicycles evidences the inclusion of one molecule of the amine within the cavity, strongly hydrogen bonded to the nitrogen atoms of the macrocycles (Fig. 34a). NMR experiments show that the inclusion complexes remain intact in CDCl₃. These encapsulated amines can be simply removed by stirring the inclusion compounds in methanol [131].



The reaction of 2,6-diformyl-4-methylphenol and *trans*-(1*R*,2*R*)-cyclohexyldiamine in methanol at room temperature results in the facile formation of the [3+3] condensed optically active, chiral Schiff base macrocyclic ligand **H₃-49** instead of the related [2+2] macrocycle **H₂-49a**. Its [3+3] entity has been inferred especially by FAB mass spectrometry. Reduction of the macrocycle **H₃-49** by NaBH₄, resulted in the formation of the related [3+3] hexaazamacrocyclic derivatives **H₃-50** as evidenced by FAB mass spectrometry and ascertained by an X-ray structural determination on a crystal grown from benzene [132] (Fig. 34b).

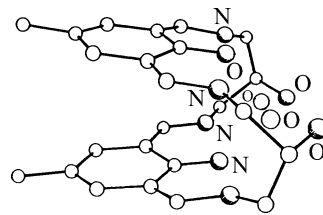
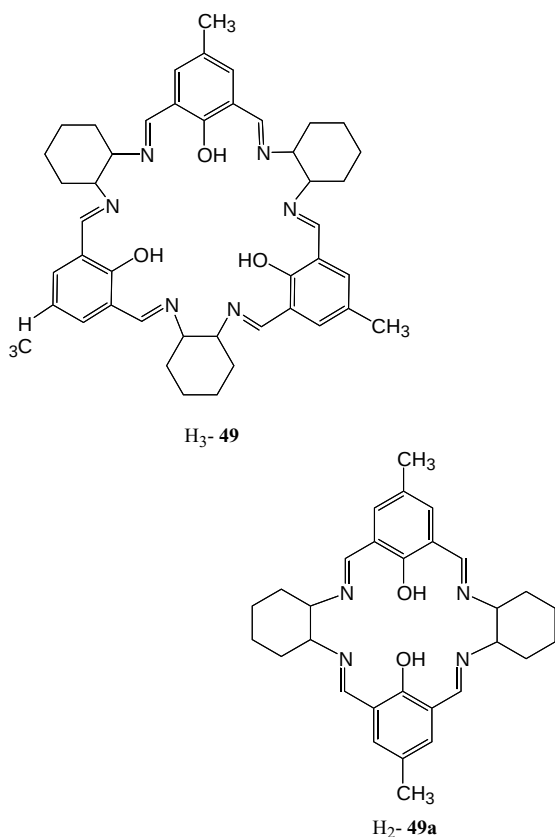


Fig. 33. Structure of $[(\text{H}_6\text{-47})(\text{H}_2\text{O})_2]^{2+}$ (adapted from Ref. [129]).

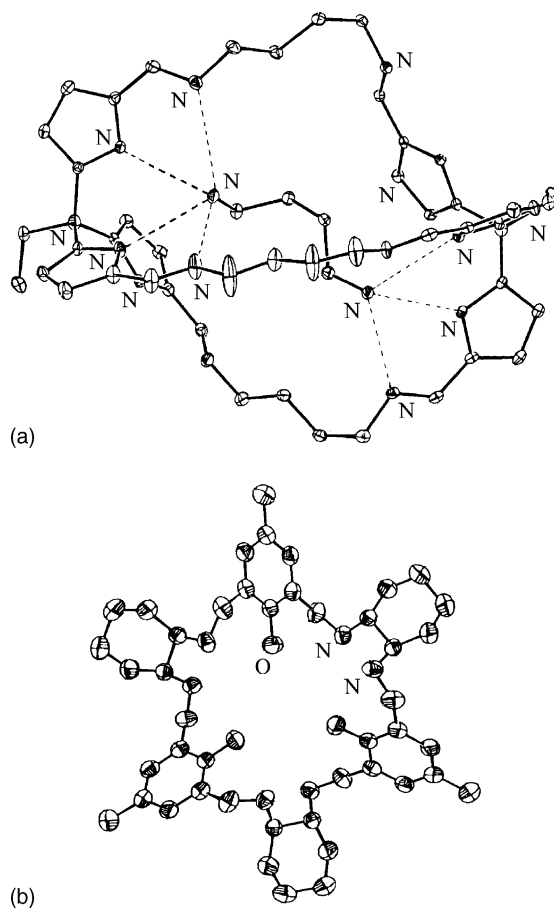


Fig. 34. Structure of **48d** (a) and **H₃-50** (b) (adapted from Ref. [152]).

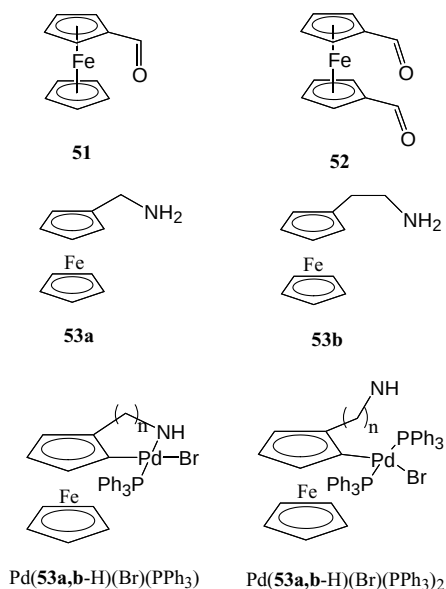
The molecular three-fold symmetry coincides with the crystallographic three-fold axis. The three phenolic-OH groups projected inside the cavity generate 3 equiv. N_2O_2 sub-cavities. The geometry of these sub-cavities appears suitable for metal complexation as the two nitrogen and two oxygen atoms provide appropriate coordination sites. The macrocycle is stabilised by intramolecular hydrogen bonding. The macrocycle has an internal hydrophilic cavity capable of forming hydrogen bonds and an external hydrophobic periphery. The molecules are extended in the *ab* plane with the mean plane of the molecule perpendicular to the *c*-axis. Each molecule is surrounded by six molecules leading to a trigonal network structure. The organisation of the molecules in the *ab* plane is governed by the hydrophobic interaction between the methyl groups of formyl moiety and methylene groups of amine moiety and is not assisted by any

other observable interactions. The stacking in the *c*-axis is maintained by inter-molecular N–H···N hydrogen bonding and supported by weak C–H···O interactions leading to a channel like structure. The three-dimensional trigonal assembly of the macrocycle is maintained by hydrophobic interactions in the *ab* plane and hydrogen bonding along the *c*-axis.

The X-ray structure of the [3+3] reduced macrocycle **H₃-50** suggests that a similar [3+3] macrocyclic structure can occur also for the related Schiff base **H₃-49** [132].

Acyclic or cyclic systems bearing ferrocene- or CrCO₃-groups have been prepared and extensively studied not only for the development of molecular devices but also as carriers for the selective separation of specific metal ions across liquid membranes.

Formylferrocene (**51**) and 1,1'-diformylferrocene (**52**) are excellent precursors in the preparation of these acyclic and cyclic Schiff base containing redox active groups in close proximity to the coordinating moieties. While formylferrocene is commercially available, 1,1'-diformylferrocene must be prepared by reaction of ferrocene with *n*-butyllithium in the presence of *N,N'*-tetramethylethylenediamine and converting the resulting 1,1'-dilithium-ferrocene compound into the formyl derivatives with dimethylformamide [133,136]. Particular care must be devoted to the purity of dimethylformamide to avoid the formation of by-products. Formyl and diformyl ferrocene are respectively, yellow and dark red solids, very soluble in the common organic solvents; they can be recrystallized from hydrocarbons.



52 crystallizes in the solid state such that two molecules (A and B) are located in the asymmetric unit. The major difference between the two molecules lies in the twisting of the cyclopentadienyl (Cp) rings and formyl substituents about the Cp(centroid)–Fe–Cp(centroid) and Cp–COH axes, respectively. In the case of conformer A, the carbon atoms of

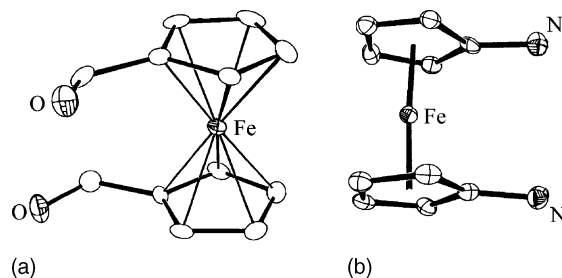


Fig. 35. Structure of one of the two conformers of **52** (a) and **54** (b) (adapted from Refs. [134,135]).

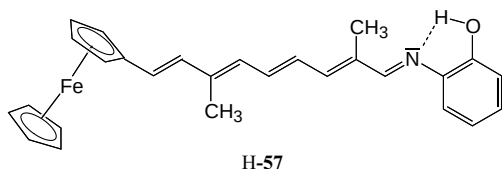
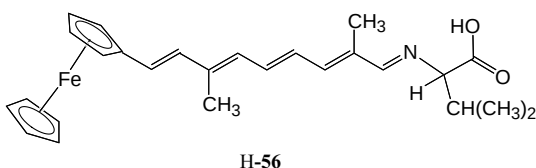
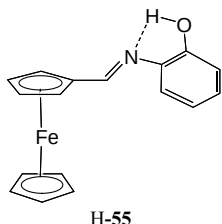
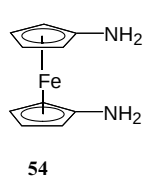
the Cp rings adopt a near eclipsed conformation and the oxygen atoms of both formyl groups, which are nearly coplanar with each Cp ring, point in opposite directions. This contrasts with conformer B in which the carbon atoms of the Cp rings adopt a near staggered conformation in which the oxygen atoms of the formyl substituents, which also lie nearly coplanar with each Cp ring, point in the same direction (Fig. 35a). For comparison, 1,1'-diacetylferrocene crystallizes such that a single conformer is found in the solid state in which the Cp rings of the complex are nearly eclipsed and the oxygen atoms of the acetyl substituents, which are twisted slightly from each Cp ring, are directed in opposite directions. In diacetylferrocene the Cp rings are planar and parallel. The acetyl groups are in the 1,3'-configuration with an average rotation of 4° 4' of the rings from the eclipsed configuration [134].

The primary ferrocenylamines **53a** and **53b** have been obtained by treating $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_3](\text{I})$, respectively, with NaN₃ or NaCN and converting the resulting azide $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{N}_3$ or nitrile ($\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{CN}$) into the appropriate amine by reaction with LiAlH₄ in diethylether [134]. **53a** has been prepared also by converting initially formylferrocene into its oxime by condensation with hydroxylamine, followed by the reduction of the resulting product with LiAlH₄ in tetrahydrofuran [134].

53a and **53b** react with Na₂[PdCl₄] in a 1:1 molar ratio and in methanol at room temperature to form *trans*-[Pd(**53a**)₂(Cl)₂] and *trans*-[Pd(**53b**)₂(Cl)₂]. The same ferrocenylamines, when treated with Pd(CH₃COO)₂ in toluene at room temperature for 19 h followed by the addition of LiBr and the subsequent treatment of the solid formed with PPh₃, give rise to the cyclopalladate complexes [Pd(**53a**-H)(Br)(PPh₃)] or [Pd(**53b**-H)(Br)(PPh₃)] [135] which, by further treatment with an excess of PPh₃ in CHCl₃, suffer an opening of the metallacycle and the coordination of a second phosphine to the palladium(II) with the consequent formation of [Pd(**53a**-H)(Br)(PPh₃)₂] or [Pd(**53b**-H)(Br)(PPh₃)₂] [135].

1,1'-Diaminoferrocene, **54**, was prepared from 1,1'-dilithium-ferrocene which was transformed into 1,1'-dibromoferrrocene by reaction with C₂H₄Br₄ in Et₂O. The dibromo derivative reacts with NaN₃ in the presence of CuI in EtOH/H₂O to form the corresponding 1,1'-diazidoferrrocene. The final reduction of 1,1'-diazidoferrrocene with

H₂ using Pd/C as catalyst in methanol affords **54** [135]. Exposing solutions of 1,1'-diaminoferrocene to air results in rapid oxidation, as evidenced by the appearance of a characteristic dark-green colour; workup is therefore best carried out under nitrogen. Despite its sensitivity in solution, the product is stable as a solid in air for several months at room temperature.



54 undergoes a reversible 1e[−] oxidation in CH₃CN at a potential of −602 mV versus Fc^{0/+}, one of the most negative redox potentials for a ferrocene derivative. The chemical reversibility of this process was confirmed by isolation of the stable, 17-electron [Fe(C₅H₄NH₂)₂]⁺ cation as PF₆[−], CF₃SO₃[−], and TCNE[−] salts [135].

54 crystallizes with two unique molecules in the asymmetric unit. The Cp rings in both molecules are eclipsed, but while in molecule A the NH₂ groups are also eclipsed (1,1'-rotamer), in molecule B they are offset by one-fifth of a turn around the Cp–Fe–Cp axis (1,2'-rotamer). The presence of two distinct rotamers in the same crystal suggests that the rotation around the Cp–Fe–Cp bond is relatively uninhibited and that the solid-state structure is governed mainly by hydrogen bonding and crystal packing forces (Fig. 35b) [135].

A series of 1,1'-N-substituted ferrocenedyl ligands, their reduced analogues and related complexes has been synthesized from 1,1'-diaminoferrocene via Schiff base condensation reaction according to Scheme 13.

The reaction of unsubstituted, mono- or di-substituted salicylaldehyde-ferrocene derivatives (H₂-L) with [Zr(CH₂C₆H₅)₄] afforded the related complexes [Zr(L)(CH₂C₆H₅)₂]. The ¹H and ¹³C NMR spectra of the mono-*tert*-butyl substituted aldimate zirconium(IV) complex, [Zr(L)(C₆H₅)₂], indicate a C_{2v} symmetric structure in solution. This structure was maintained in the solid state where the metal ion resides

in an appropriate octahedral environment comprised of a square planar Schiff base ligand and two benzyl groups located in the axial positions. The benzylic carbons are directed away from the bulky *t*-butyl groups and towards ferrocene. The phenyl groups, on the other hand, are pointed away from ferrocene. The Ferrocene moiety adopts an almost perfectly eclipsed conformation allowing for the two ligand arms to be in the same plane.

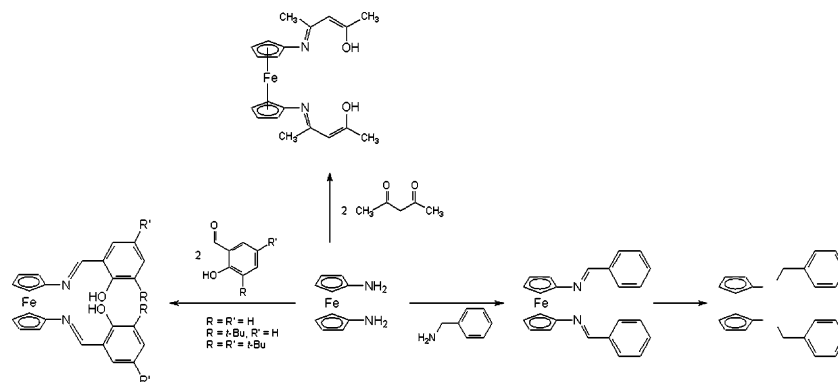
The analogous dibenzyl zirconium(IV) complex with the di-*tert*-butyl substituted aldimine shows a very similar ¹H NMR spectrum.

Attempts to reproduce these results with [Ti(CH₂C₆H₅)₄] led to compounds whose ¹H NMR spectra show a high degree of fluxionality and whose identities remain unknown. Salt metathesis with metal chlorides provided an alternate route to group IV metal complexes. To form the necessary reagents, the salicylaldehyde ligands were deprotonated by [Mg(C₄H₉)₂] in THF affording [Mg(L)(THF)₂]·THF. The ¹H NMR spectra of these complexes are consistent with a C_{2v} symmetric structure in solution. In the solid state the magnesium(II) resides in an approximate octahedral environment composed of the N₂O₂ donor set of the aldimine ligand and two THF molecules [135].

The ability of these magnesium complexes to undergo salt metathesis was assessed by combining [Mg(L)(THF)₂] with [TiCl₄(THF)₂] and ZrCl₄. In both cases the desired [M(L)(Cl)₂] complexes were obtained which, according to their NMR spectra, have structures similar to that of [(Zr(L)(CH₂C₆H₅)₂]. The compounds are sparingly soluble in non-polar solvents and are quite soluble in chlorinated solvents [135].

The reaction of 1,1'-diaminoferrocene with 2,4-pentanedione forms the corresponding ketimine (H₂-L') whose structure shows the ligand arms were almost orthogonal to the plane of the Cp rings. The molecule adopts a staggered conformation with the imine substituents in a *trans* orientation. Each ligand arm is held in a cisoid orientation through an intramolecular N–H···O hydrogen bond. The reaction of H₂-L' with [Zr(CH₂C₆H₅)₄] resulted in the formation of [Zr(L')(CH₂C₆H₅)₂] [135].

The air-sensitive orange 1,1'-diaminoferrocene reacted with excess benzaldehyde to form the burgundy-coloured bis-imine derivative. This was then reduced in situ using lithium aluminium hydride, and following an aqueous work-up with degassed water, the orange, air-sensitive bis-amine derivative L'' was obtained [135]. On reaction of this bis-amineferrocene with [Zr(CH₂C₆H₅)₄], a yellow, air-sensitive oil was formed, which was triturated with pentane to yield [Zr(L''-2H)₂] where according to NMR data all of the benzyl ligands had been displaced give the bis(chelate) zirconium(II) complex. Conversely, reaction of the bis-ferroceneamine with tetrakis(dimethylamino)zirconium, produces the mono-chelate bis(dimethylamino)zirconium(IV) complex. The product, a viscous yellow-orange oil, is soluble in a range of solvents. Both complexes are light and moisture-sensitive materials.



Scheme 13.

The bis-1,1'-salicylaldimineferrocene derivative can potentially bind in a tetradentate fashion, but the reaction with $[\text{Al}(\text{CH}_3)_3]$ reveals a product containing two bidentate bonding modes, i.e. the dinuclear aluminium(III) complex where the two salicylaldimine ligands are oriented *syn*, being only a ca. 17° stagger of the two C_5H_4 rings. The six membered chelate ring has a slightly folded geometry, the aluminium(III) ion lying $0.22 \text{ \AA}$ out of the plane of the other coplanar five atom. The aluminium center has a distorted tetrahedral geometry [135].

Amino-, 1,1'-diamino, aminomethyl- and aminoethyl-ferrocene derivatives give rise to [1+1], [1+2] and [2+1] acyclic Schiff bases when reacted with the appropriate formyl- or diformyl-precursors. Analogously a series of [1+1], [1+2], [2+1] or [3+1] acyclic and [1+1], [2+2] or [3+2] cyclic Schiff bases have been prepared by using formylferrocene or 1,1'-diformylferrocene. They contain one, two, or three ferrocene groups at the periphery of their coordinating moiety and are of the type reported in Scheme 14 [136]. Their properties, together with those of the related reduced analogues or similar compounds (using substituted hydrazine derivatives instead of amine as precursors) will be discussed in detail in a subsequent section.

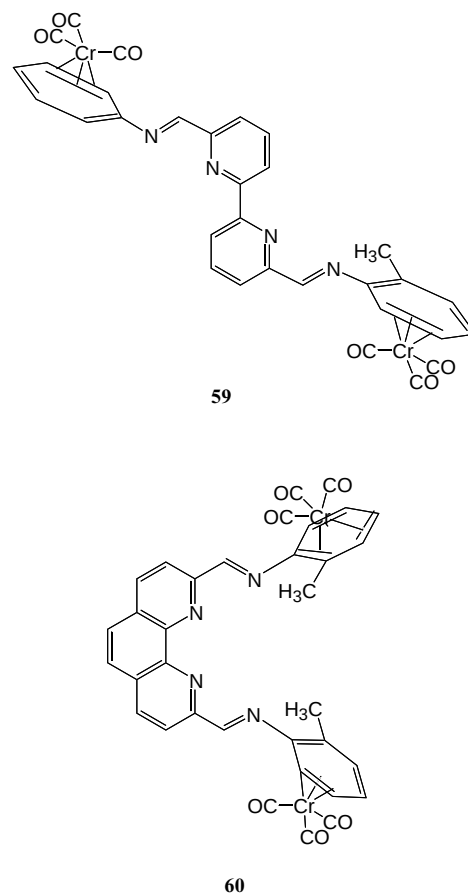
Formylferrocene and 9-ferrocenyl-2,7-dimethylnonatraenal, when react with L-valine or *o*-aminophenol, form the related Schiff bases H-55 ··· H-57 which are hygroscopic and sensitive to light and must be stored in the dark under nitrogen [137,138].

H-55 ··· H-57 react with $[\text{M}(\text{Cl})(\mu\text{-Cl})(\text{PR}_3)_2]_2$ ($\text{M} = \text{Pd}^{2+}$, Pt^{2+}), $[\text{Ir}(\text{Cl})(\mu\text{-Cl})(\text{C}_2\text{H}_5)_2]_2$ and $[\text{Ru}(\text{Cl})(\mu\text{-Cl})(p\text{-cymene})]_2$ in methanol form the mononuclear complexes $[\text{M}(\text{55})(\text{Cl})(\text{L})]$ ($\text{M} = \text{Pd}^{2+}$, Pt^{2+} , $\text{L} = \text{P}(n\text{-Bu})_3$, $\text{P}(\text{Et})_3$, $\text{P}(\text{Ph})_3$, $\text{M} = \text{Ir}^{3+}$, $\text{L} = \text{C}_5\text{H}_5$; $\text{M} = \text{Ru}^{2+}$, $\text{L} = p\text{-cymene}$) $[\text{M}(\text{56})(\text{Cl})(\text{L})]$ ($\text{M} = \text{Pd}^{2+}$, Pt^{2+} , $\text{L} = \text{P}(\text{Et})_3$, $\text{P}(\text{Ph})_3$; $\text{M} = \text{Ir}^{3+}$, $\text{L} = \text{C}_5\text{H}_5$ and $[\text{M}(\text{57})(\text{Cl})(\text{L})]$ ($\text{M} = \text{Pd}^{2+}$, Pt^{2+} , $\text{L} = \text{P}(\text{Et})_3$) as confirmed by the X-ray structure of $[\text{Ir}(\text{55})(\text{Cl})(\text{C}_5\text{H}_5)]$ (Fig. 36) [137,138].

The formation of the iron–chromium heterobimetallic Schiff base ligand 58, containing two different functionalities (i.e. a ferrocene and a chromium tricarbonyl), obtained by condensation of 9-ferrocenyl-2,7-dimethylnonatraen-1-al

with $\eta\text{-anilintricarbonyl-chromium}$ in dichloromethane was proved by single crystal X-ray structure (Fig. 37) [137,138].

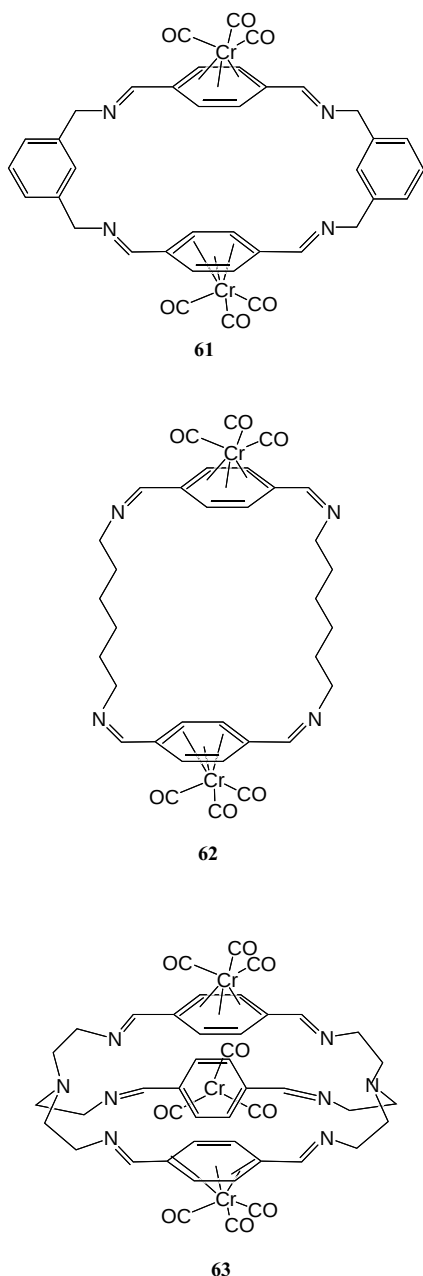
The condensation of 2,2'-bipyridine-6,6'-dicarbaldehyde [139] or 1,10-phenantroline-2,9-dicarbaldehyde [140] with (*o*-toluidine)tricarbonylchromium [141] in refluxing benzene produces the corresponding Schiff base 59 and 60.



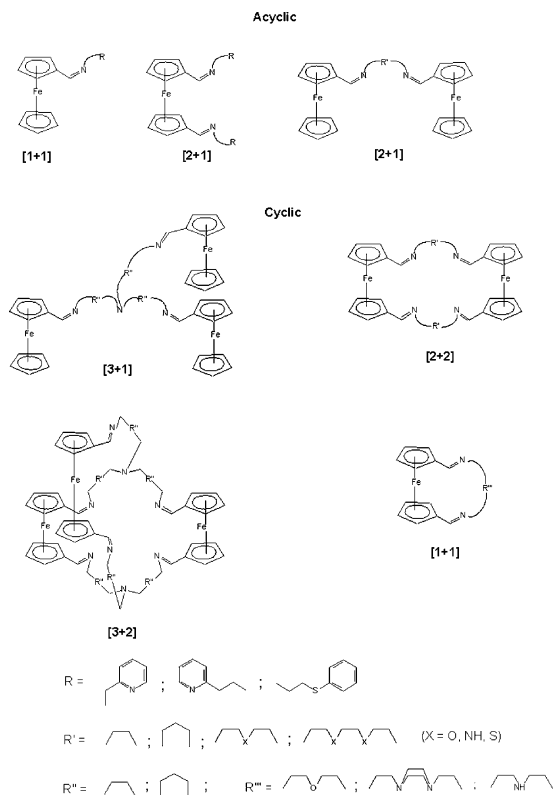
Reaction of 59 with $[\text{Cu}(\text{CF}_3\text{SO}_3)_2] \cdot \text{C}_6\text{H}_6$ in dichloromethane results in an immediate colour change to deep violet followed by precipitation of the complex $[\text{Cu}_2(\text{59})](\text{CF}_3\text{SO}_3)_2$. After purification of the mother liquor by column chromatography, a second deep red complex $[\text{Cu}_2(\text{59})_2](\text{CF}_3\text{SO}_3)_2$ was isolated. Following the same

experimental procedure starting from **60**, complex $[\text{Cu}_2(\mathbf{60})](\text{CF}_3\text{SO}_3)_2$ and $[\text{Cu}_2(\mathbf{60})_2](\text{CF}_3\text{SO}_3)_2$ were isolated [139,142].

Similarly, the reaction of 1,3-bis(aminomethyl)benzene, 1,6-diamineoctane or tris(aminomethyl)amine with 1,4-diformylbenzene tricarbonyl chromium forms the macrocyclic complexes **61** and **62** and the macrobicyclic complex **63** [143].



Condensation of 1,3-bis(aminomethyl)benzene with terephthalaldehyde in anhydrous tetrahydrofuran gave the expected macrocycle which polymerized after a few hours even at low temperature (-30°C). Therefore, the coordination of the tricarbonylchromium subunits leads to a stabilization of the alkylidenamine bonds probably as a result of both electronic and steric effects.



The one-pot cyclization to form **63** does not require high dilution conditions since the expected product precipitates readily from the reaction mixture [143].

Treatment of **63** with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ produces the pentanuclear complex $[\text{Cu}_2(\mathbf{63})](\text{ClO}_4)_2$ (Fig. 38). The hexaimine cavity has an elongated ellipsoidal shape. The two copper atoms are 6.655 Å apart and inside the molecular cavity, whereas the three chromium atoms span a triangle outside the cavity. Each copper(I) ion is similarly coordinated in a distorted tetrahedral fashion to three alkylidenamine nitrogen atoms and to one bridgehead nitrogen atom at longer distance. The geometry about the three chromium atoms is very similar to that of the closely related complex $[\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3]$ [144].

Dendrimers as **64**–**67** have been successfully used as polyamine precursors for the preparation of the related Schiff bases [145]. As an example the hexaimine derivative

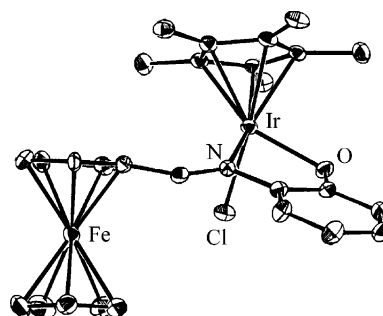
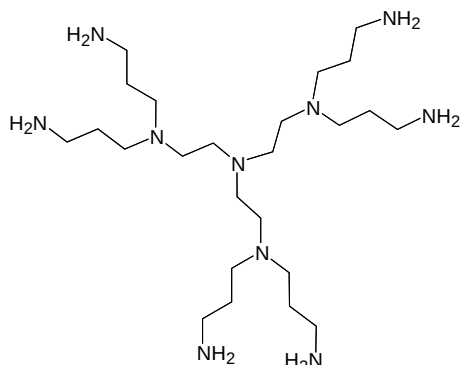
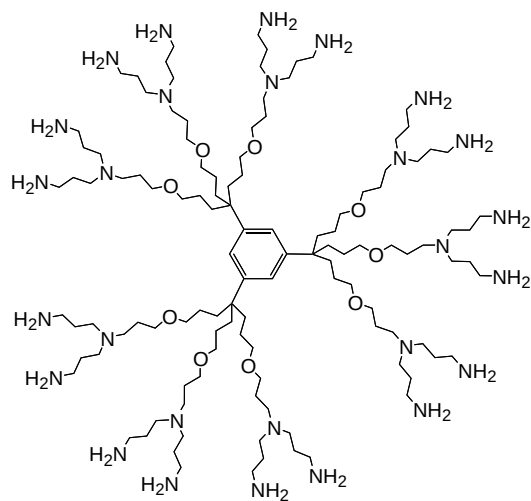
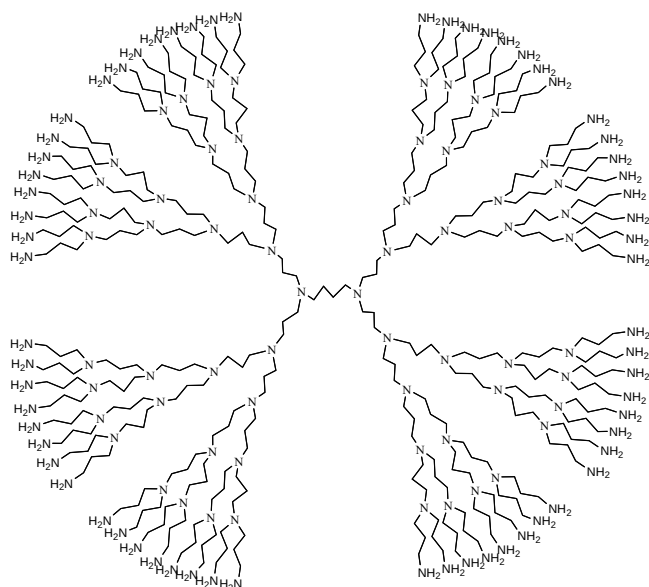
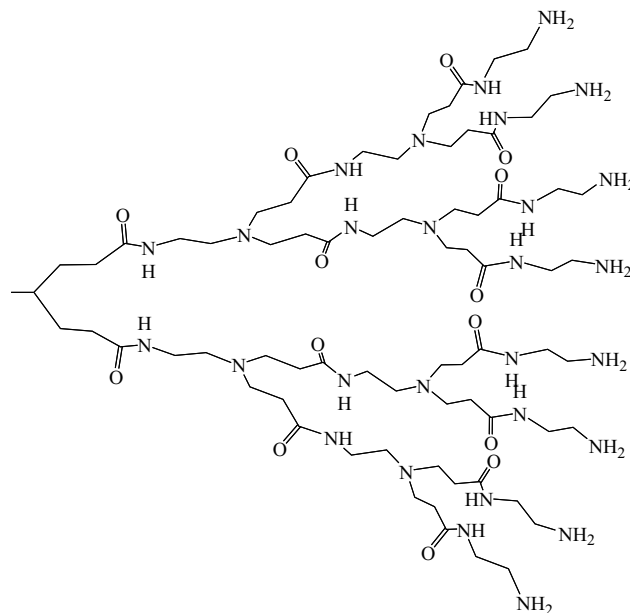
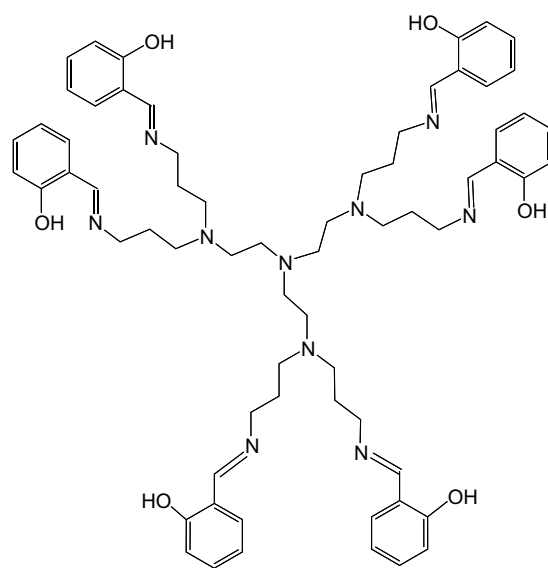


Fig. 36. Structure of $[\text{Ir}(\mathbf{55})(\text{Cl})(\text{C}_5\text{H}_5)]$ (adapted from Ref. [137]).

64, when treated with 2-hydroxybenzaldehyde, gives rise to the hexaimine Schiff base **H₆-68**, which by reaction with cobalt(II) acetate affords the related tricobalt complex [Co₃(**68**)].

**64****65****66****67****H₆-68**

2.2. Ligand flexibility and template ion size

Metal free macrocyclic Schiff bases have been synthesized by self-condensation of functionalized precursors

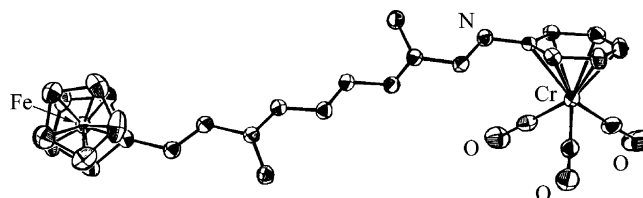


Fig. 37. Structure of **58** (adapted from Ref. [138]).

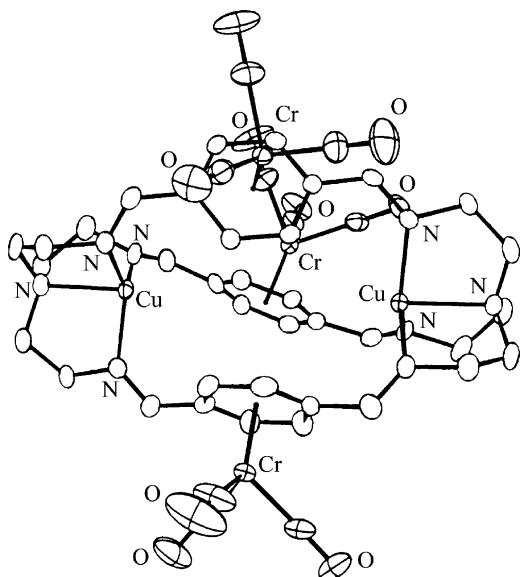


Fig. 38. Structure of $[\text{Cu}_2(\mathbf{63})]^{2+}$ (adapted from Ref. [144]).

bearing appropriate groups (i.e. electron donating substituents) at appropriate position of benzene rings.

It is well known that metal complexes of the cyclic tetraimine **A** of Scheme 15 which have been known for over three decades, are synthesized by the self-condensation reaction of *o*-amino-benzaldehyde in the presence of metal ions. Without metal ion templates, however, the self-condensation reaction produces various polycyclic compounds, including the eight-membered ring macrocyclic compound **B** of Scheme 15 [146].

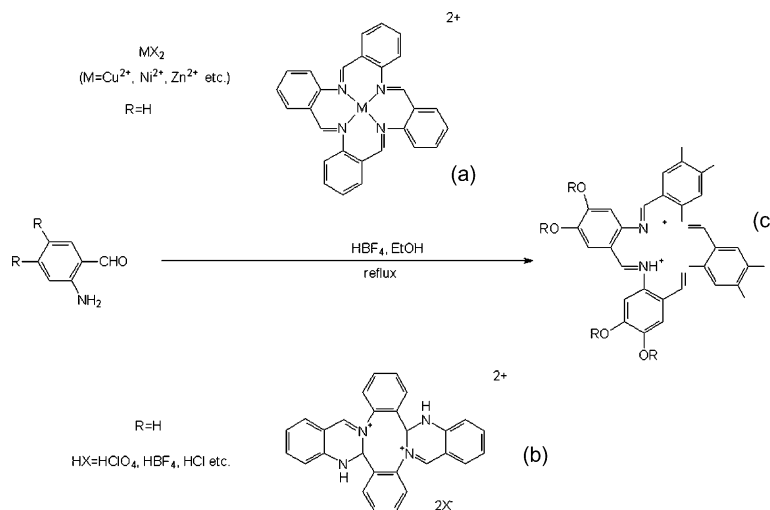
The condensation of the metal free compounds **C** of Scheme 15 was achieved by reaction of dialkoxy-substituted *o*-aminobenzaldehyde using HBF_4 in refluxing ethanol. The electron-donating alkoxy-substituents appears to stabilize the deprotonated core of these macrocyclic entities [147].

These synthetic procedures evidence the essential role of particular metal ions including protons in orienting the preparation pathway. Thus an effective method for the synthesis of macrocyclic complexes involves an in situ approach where the presence of a metal ion markedly increases the yield of the cyclic product. The metal ion plays an important role in directing the steric course of the reaction; this has been termed the metal-template effect [148].

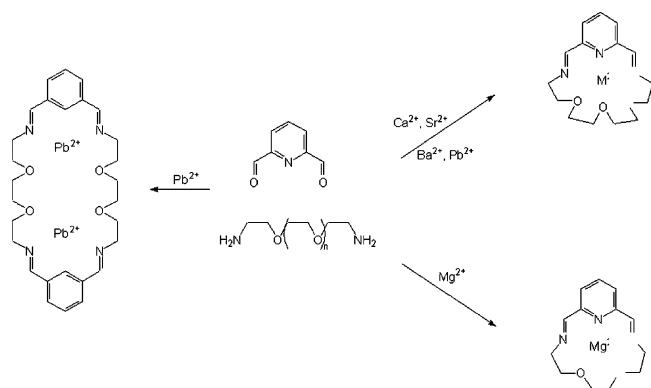
The size of the cation used as a template has proved to be of importance in directing the synthetic pathway in the Schiff base systems as observed for the cyclic condensation of 2,6-diacetylpyridine and respectively, 1,8-diamino-3,6-dioxaoctane or 1,11-diamino-3,7,9-trioxaundecane in the presence of the alkaline earth cations. Only magnesium generates the pentadentate N_3O_2 [1+1] macrocycle but it is ineffective in generating the hexadentate [1+1] N_3O_3 macrocycle which is readily synthesized in the presence of the larger cations calcium, strontium, barium and lead(II). These larger cations, however, generate the [2+2] N_6O_4 macrocyclic derivatives of Scheme 16 [149–151].

The similarity in ionic radii between the alkaline earth metal cations and the lanthanide(III) cations suggested that the latter should also be efficient templating devices, and this has proven to be the case. The actinides, with their high ionic radii and/or unusual coordination geometry can produce and stabilize expanded macrocyclic ligands as in the preparation of superphthalocyanines [152].

For the [2+2] macrocycles the head and the lateral units can be varied with the consequent formation of macrocycles with different donor atoms and/or different cavity size. Moreover with certain precursors (i.e. 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane), [3+3] and [4+4] macrocyclic compounds have been synthesized. The [1+1] condensation of equimolecular amount of 2,6-pyridinedicarboxaldehyde with 1,11-diamino-3,6,9-trioxaundecane, using copper(II) chloride as template, forms by

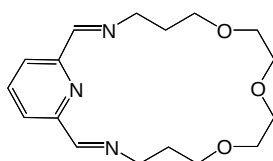
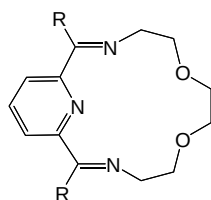
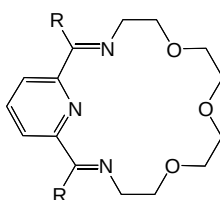


Scheme 15.

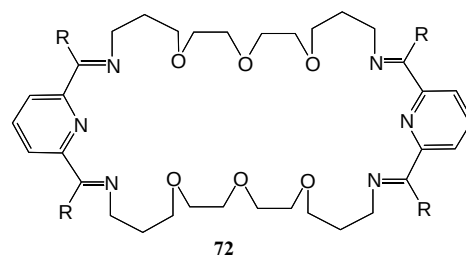
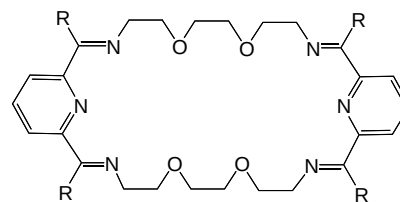


Scheme 16.

the addition of PF_6^- , $[\text{Cu}(\mathbf{69})(\text{Cl})(\text{H}_2\text{O})](\text{PF}_6)$. The [20]-membered macrocycle, **69**, was found to be coordinated to the copper(II) only through the three nitrogen atoms. The copper(II) center nearly has a square pyramidal geometry, with a water molecule occupying an axial site. The first and third oxygens of the polyether bridge are hydrogen-bonded to the water molecule. The copper(II) binding site cooperates with these well-positioned etheric oxygens to make them become excellent H_2O receptors (Fig. 39a). Analogously the reaction of 2,6-diformyl- or 2,6-diacetyl-pyridine with 1,8-diamino-3,6-dioxaoctane in the presence of Cd^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Mg^{2+} , Mn^{2+} , Zn^{2+} forms the [1+1] macrocyclic complexes $[\text{M}(\mathbf{70})]$. In the related [18]-membered [1+1] macrocyclic complexes $[\text{M}(\mathbf{71})]$, the hexadentate macrocycle **71** was approximately planar [153].

**69****70****71**

In the mononuclear nickel(II) complex $[\text{Ni}(\mathbf{72})](\text{PF}_6)_2$ (Fig. 39b), synthesized by making the appropriate diamine, dialdehyde and nickel(II) chloride react in a molar ratio 2:2:1 and precipitating the complex on hexafluorophosphate salt, the hexadentate [2+2] [40]-membered ring macrocycle **72** coordinates only through the nitrogens to the octahedral nickel(II) center. This geometry is similar to that of mononuclear iron, cobalt, and nickel complexes of **73**, however those complexes had to be prepared indirectly by transmetalation of the original dilead complex [153].

**72****73**

These studies prove the possibility of a selective recognition, via coordination to the central metal ion and hydrogen-bonding to the donor atom of the chain not involved in coordination of specific molecules. Thus the complexes can be considered as ditopic systems.

The weak tendency of these d-metal ions to coordinate the polyether oxygens is further made evident by the reaction with [2+1] acyclic or [2+2] macrocyclic ligands derived from the condensation of 2,3-dihydroxybenzaldehyde and 3-methoxy-2-hydroxybenzaldehyde and 2,6-diformyl-4-chlorophenol with 1,8-diamino-3,6-dioxaoctane (Scheme 17). The [2+2] macrocyclic ligand $\text{H}_2\text{-74}$ forms the tetranuclear complexes $[\text{M}_4(\mathbf{74})(\text{OH})_2]^{4+}$ which in solution suffer especially from a tetranuclear-dinuclear transformation [152] with the formation of $[\text{M}_2(\mathbf{74})]^{2+}$. The acyclic ligands $\text{H}_2\text{-75}$ and $\text{H}_2\text{-76}$ form the dinuclear complexes $[\text{M}_2(\mathbf{75})(\text{X})_2]$ and $[\text{M}_2(\mathbf{76})(\text{X})_2]$ which again undergo a partial decomplexation process with the consequent formation of the mononuclear homologues $[\text{M}(\mathbf{75})]$ and $[\text{M}(\mathbf{76})]$ [154].

The [1+1] macrocyclic complexes $[\text{M}(\mathbf{L})(\text{X})_2]$, containing a N_5 donor set ($\text{M} = \text{Cd}^{2+}$, Hg^{2+} , Fe^{3+} , Ag^+ , Pb^{2+} , etc. $\mathbf{L} = \mathbf{77}$, $\mathbf{78}$, $\mathbf{79}$), have been prepared from 2,6-diacetylpyridine and the appropriate tetramine in the presence of the metal salt [155].

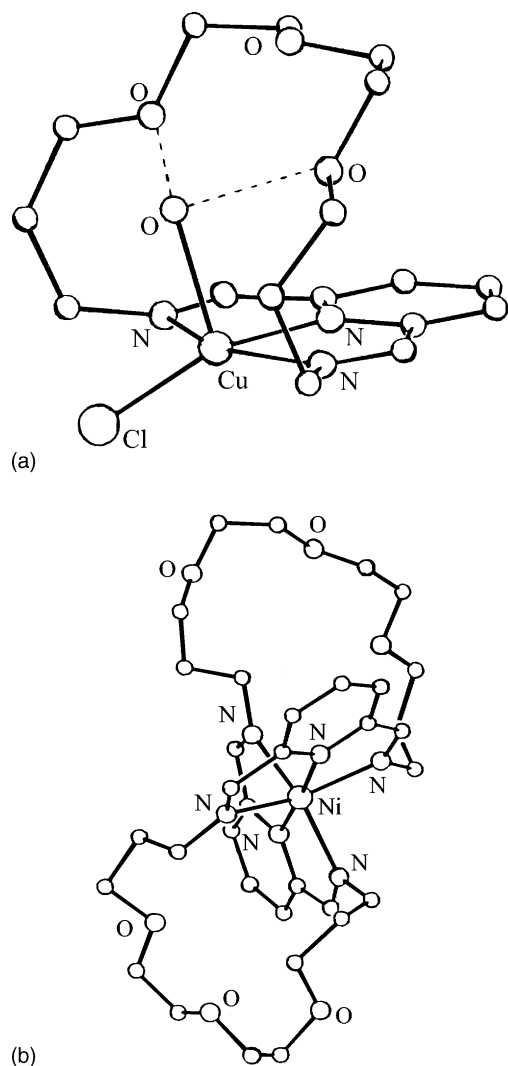
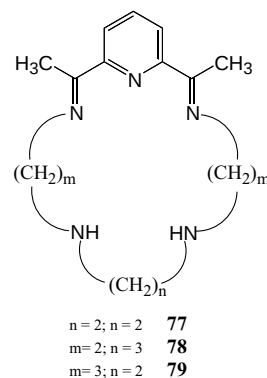


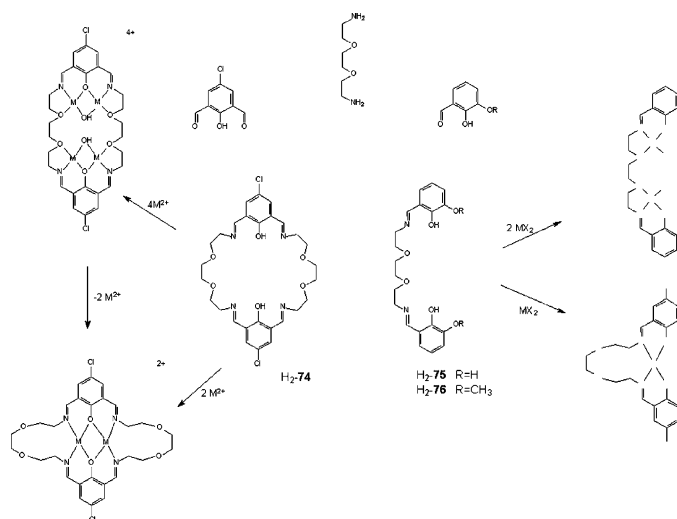
Fig. 39. Structure of $[\text{Cu}(\mathbf{69})(\text{Cl})(\text{H}_2\text{O})]^+$ (a) and $[\text{Ni}(\mathbf{72})]^{2+}$ (b) (adapted from Ref. [153]).



In these complexes the macrocycles define the pentagonal girdle and axial positions are occupied by unidentate ligands. Thus in the structure of $[\text{Fe}(\mathbf{77})(\text{SCN})_2]$ (Fig. 40a) and $[\text{Fe}(\mathbf{78})(\text{SCN})_2]$ (Fig. 40b) the metal ions have distorted pentagonal bipyramidal environments with the thiocyanate ligands in axial positions and the five nitrogen atoms of the macrocycle in equatorial positions. The Fe–N bond lengths and the conformations of the girdles are different in the two molecules as a consequence of the extra CH_2 group in the larger macrocycle **78**. However, both molecules have similar structures to those of the analogous iron(III) complexes $[\text{Fe}(\mathbf{77})(\text{NCS})_2](\text{ClO}_4)]$ and $[\text{Fe}(\mathbf{78})(\text{NCS})_2](\text{ClO}_4)]$ [155,156].

In $[\text{Cd}(\mathbf{78})(\text{Br})][\text{CdBr}_4]$ the polymeric cation $[\text{Cd}(\mathbf{78})\text{Br}]_n^{n+}$ is found in which the cadmium(II) ion is seven coordinated being bonded to five nitrogen atoms and to two bridging Br^- ions. The macrocycle is closely planar and the metal ion is slightly displaced from this plane (Fig. 41a) [155].

The structures of the $[\text{M}(\mathbf{79})(\text{Br})]^+$ cations ($\text{M} = \text{Cd}^{2+}$, Hg^{2+}) are very similar. Both are mononuclear with the metal ion bonded to five nitrogen atoms and a bromine atom. The conformation of the macrocycle is such that the pyridine ring



Scheme 17.

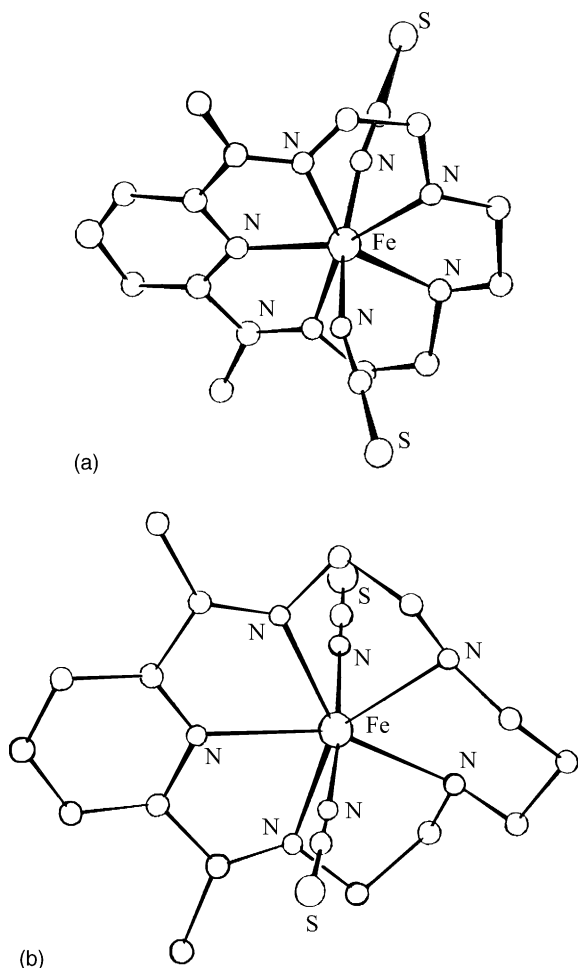


Fig. 40. Structure of $[\text{Fe}(\mathbf{77})(\text{NCS})_2]$ (a) and $[\text{Fe}(\mathbf{78})(\text{NCS})_2]$ (b) (adapted from Refs. [155,156]).

is bent down from the plane of the MN_4 unit. It is similar to that in $[\text{Mn}(\mathbf{79})(\text{NCS})_2]_2$. This folding of the macrocycle leads to one sterically crowded site which is unoccupied in the mercury(II) complexes even by a water molecule and the metal ion remains six coordinated (Fig. 41b). In the manganese(II) complex the smaller angle of fold is in keeping with the attachment of a seventh ligand NCS^- , though at a longer bonding distance than for the NCS^- on the open face [155].

In $[\text{Ag}(\mathbf{79})(\text{ClO}_4)]$ there are two $[\text{Ag}(\mathbf{79})]^+$ cations in the asymmetric unit with similar geometries; the ligands form distorted pentagonal planes [155]. The macrocycle conformation differs from that found in cadmium(II) and mercury(II) homologues where the pyridine nitrogen is displaced from the plane of the other four nitrogens.

In $[\text{Pb}(\mathbf{79})(\text{SCN})](\text{SCN})$ the six-coordinate lead ion is bonded to five nitrogen atoms of the pentadentate macrocyclic ligand and a sulfur atom of a thiocyanate ion, leaving the remaining thiocyanate ligand uncoordinated (Fig. 42) [155].

The condensation of 2,6-diacetylpyridine with 3,6-diox-octane-1,8-diamine in the presence of $\text{Mn}(\text{SCN})_2$ forms the

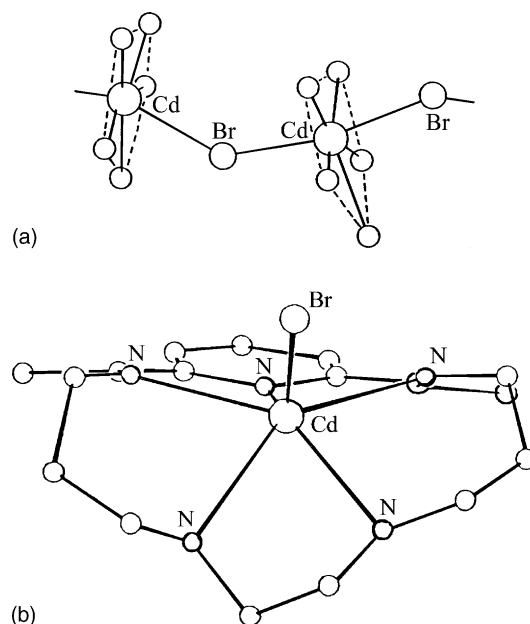


Fig. 41. Structure of $[\text{Cd}(\mathbf{78})(\text{Br})]_n^{n+}$ (a) and $[\text{Cd}(\mathbf{79})\text{Br}]^+$ (b) (adapted from Ref. [155]).

pentagonal bipyramidal complex $[\text{Mn}(\mathbf{70a})(\text{NCS})_2]$ [156], while the same reaction in the presence of $\text{Pb}(\text{SCN})_2$ gives $[\text{Pb}_2(\mathbf{73a})(\text{NCS})_4]$ which contains two seven coordinated lead(II) ions in a [30]-membered, decadentate N_6O_4 macrocyclic ligand [157]. There is a two-fold axis at the center of the [30]-membered macrocycle (Fig. 43) which is non-planar. Each metal ion is bonded to three nitrogens and two oxygens of the macrocycle in the equatorial plane and, above and below this plane, to two thiocyanate sulfur atoms. The $\text{Pb} \cdots \text{Pb}$ separation is $5.227 \text{ \AA}$ [157].

The condensation of either pyridine-2,6-dicarbaldehyde or 2,6-diacetylpyridine with 1,11-diamino-3,6,9-trioxaundecane in 1:1 molar ratio in *n*-butylalcohol leads only resinous gums with properties consistent with oligomeric composition. If, however, the reaction is carried out in the presence of an equimolar amount of $\text{Pb}(\text{SCN})_2$, the

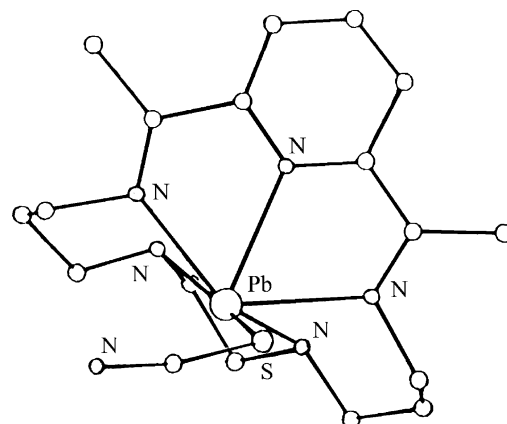
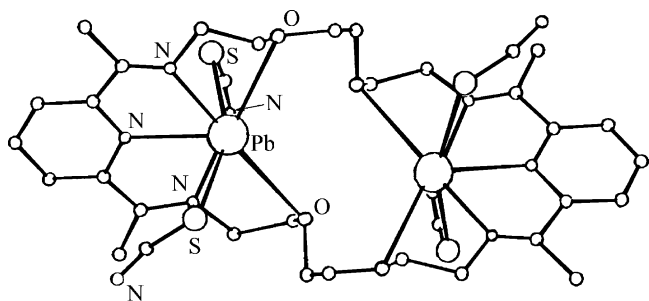


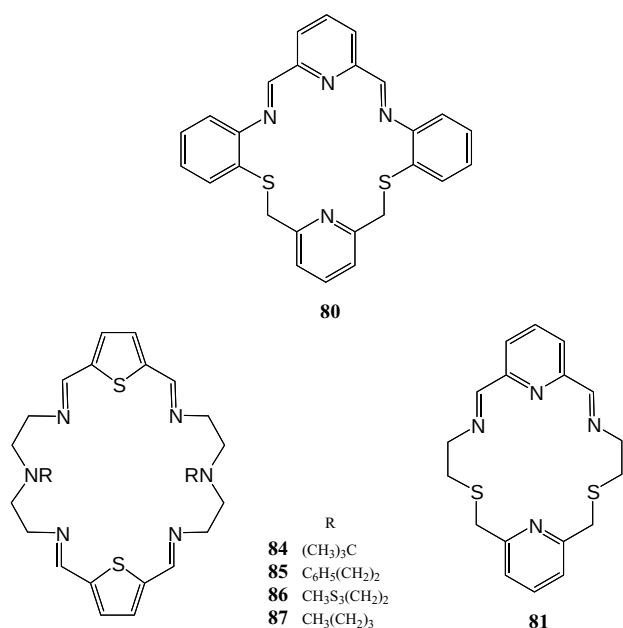
Fig. 42. Structure of $[\text{Pb}(\mathbf{79})(\text{SCN})](\text{SCN})$ (adapted from Ref. [155]).

Fig. 43. Structure of $[\text{Pb}_2(\mathbf{73a})(\text{NCS})_4]$ (adapted from Ref. [157]).

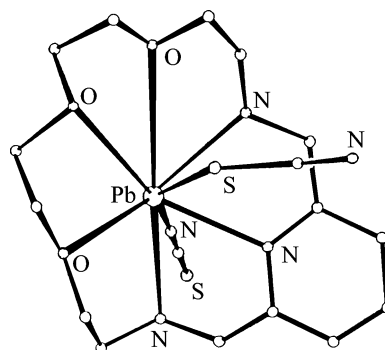
complexes $[\text{Pb}_2(\mathbf{71})(\text{NCS})_2]$ and $[\text{Pb}_2(\mathbf{71a})(\text{NCS})_2]$ are formed in good yield [158].

In $[\text{Pb}_2(\mathbf{71a})(\text{NCS})_2]$ the lead ion is located within the cavity of the macrocycle, while the thiocyanate ions lie above and below the macrocycle mean plane to give an effective eight coordination of the lead. One thiocyanate anion is nitrogen bonded, and the other is sulfur bonded (Fig. 44).

The cyclocondensation of 2,6-bis(2-aminothiophenoxy-methyl)pyridine or 2,6-bis(2-aminothioethoxymethyl)pyridine with 2,6-diformylpyridine in the presence of lead(II), mercury(II), cadmium(II) and silver(I) ions (but not of other ions of comparable radii such as calcium(II) and strontium(II)), afforded 1:1 complexes of the appropriate metal ion with the corresponding [1+1] [18]-membered, potentially hexadentate (N_4S_2), diimine macrocycles **80** or **81** [159].

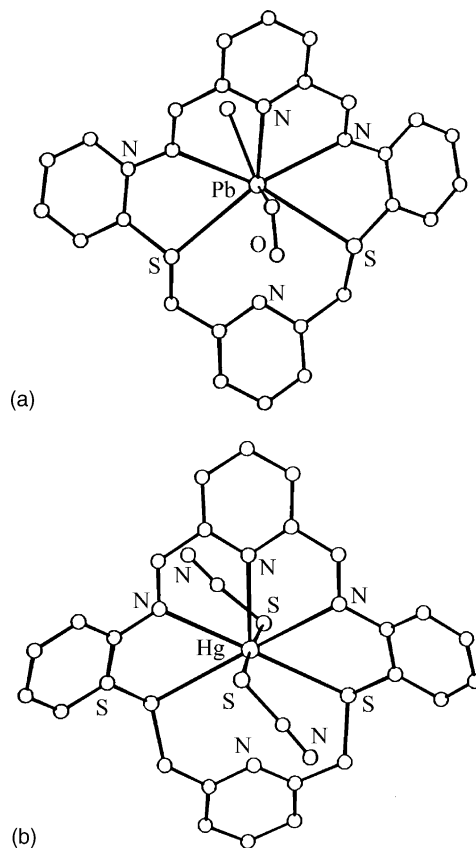


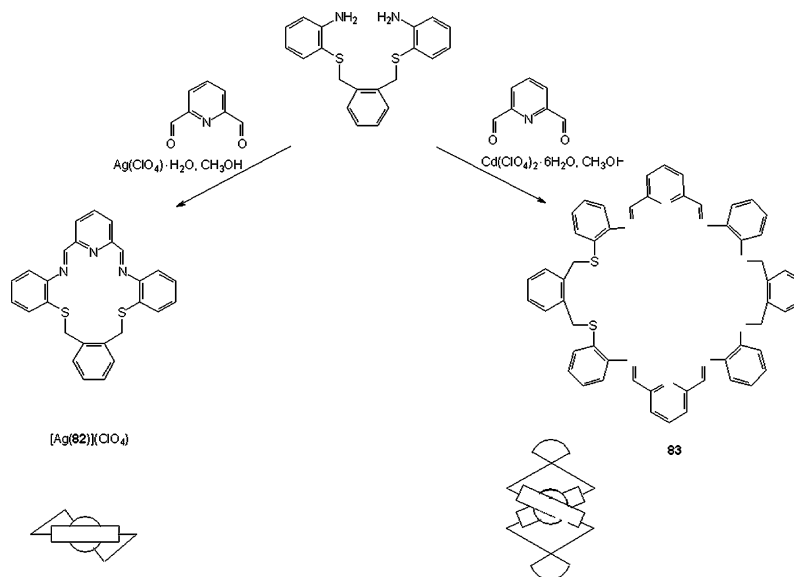
In $[\text{Pb}(\mathbf{80})(\text{CH}_3\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$ the geometry at the lead ion has been described as a very distorted hexagonal bipyramid with **80** occupying five of the six equatorial sites and one pyridine nitrogen remaining uncoordinated; one water molecule and one methanol molecule define the bent axial coordination sites. The lead ion is displaced asymme-

Fig. 44. Structure of $[\text{Pb}_2(\mathbf{71a})(\text{NCS})_2]$ (adapted from Ref. [158]).

trically within the macrocyclic cavity. It is coplanar with the N_3 trimethine end of the ligand, and 0.69 Å out of the mean plane, defined by the five equatorial donor atoms towards the coordinated H_2O (Fig. 45a) [159].

The structure of $[\text{Hg}(\mathbf{80})(\text{SCN})_2] \cdot \text{CH}_3\text{OH}$ is similar to that of the lead(II) analogue. The mercury(II) ion is located asymmetrically within the macrocyclic cavity, being closer to the N_3 trimethine chelating fragment than to the NS_2 chelating fragment. Again the metal geometry is a very distorted nido-hexagonal bipyramid in which the macrocycle occupies five of the equatorial sites once again leaving the pyridyl nitrogen and the sulfur end of the ligand unused;

Fig. 45. Structure of $[\text{Pb}(\mathbf{80})(\text{CH}_3\text{OH})(\text{H}_2\text{O})]^{2+}$ (a) and $[\text{Hg}(\mathbf{80})(\text{SCN})_2]$ (b) (adapted from Ref. [159]).



Scheme 18. Synthesis of macrocyclic single $[\text{Ag}(\mathbf{82})](\text{ClO}_4)$ and double $[\text{Cd}(\mathbf{83})](\text{ClO}_4)_2$ helicates.

thiocyanate anions complete axial sulfur coordination to the mercury (Fig. 45b) [159].

Schiff base condensation of pyridine-2,6-dicarbaldehyde and 2-[(2-[(2-aminophenyl)-sulfanyl]methyl)benzyl]sulfanyl]aniline led to different helical macrocyclic products depending on the template metal ion; a monohelical [1+1] macrocyclic complex was generated in the presence of silver(I) and a double-helical [2+2] macrocyclic complex was generated in the presence of cadmium(II) (Scheme 18) [160]. Remarkably, the larger macrocyclic product is formed with the smaller metal ion template, indicating that the different metal ion affinities for the soft sulfur donors controls the course of the cyclocondensation and generates the monohelical [1+1] complex $[\text{Ag}(\mathbf{82})](\text{ClO}_4)$ with silver(I) and the double-helical [2+2] product $[\text{Cd}(\mathbf{83})](\text{ClO}_4)_2$ with cadmium(II). X-ray structural data obtained for each complex shows that different metal–sulfur interactions are a key feature of the resulting complex [160].

The structure of $[\text{Ag}(\mathbf{82})](\text{ClO}_4)$ confirms the presence of the pentadentate [1+1] cyclocondensation ligand and shows that all the potential donors of the ligand coordinate to the metal ion (Fig. 46a). The coordination geometry in the complex is intermediate between trigonal bipyramidal and square pyramidal and involves a displacement of S donors above and below the N_3 plane of the essentially planar pyridyl-2,6-diimine unit. Such an arrangement produces a single helical species [160].

In contrast, the structure of $[\text{Cd}(\mathbf{83})](\text{ClO}_4)_2$ confirms the generation of the [2+2] N_6S_4 ligand in the presence of cadmium(II) (Fig. 46b). The distorted octahedral N_6 metal environment in the double helical $[\text{Cd}(\mathbf{83})]^{2+}$ cation results from *trans*-meridional coordination of the two pyridyl-2,6-diimine units of the ligand.

The different helicates show a very different behaviour in solution. At room temperature the ^1H NMR spectrum of

$[\text{Ag}(\mathbf{82})](\text{ClO}_4)$ in CD_3CN shows that the complex has effectively two-fold symmetry in solution. The imine proton signal appears as a doublet due to $^{107/109}\text{Ag}-^1\text{H}$ coupling, confirming that the complex is inert to a metal exchange on the NMR time-scale. The singlet observed for the methylene

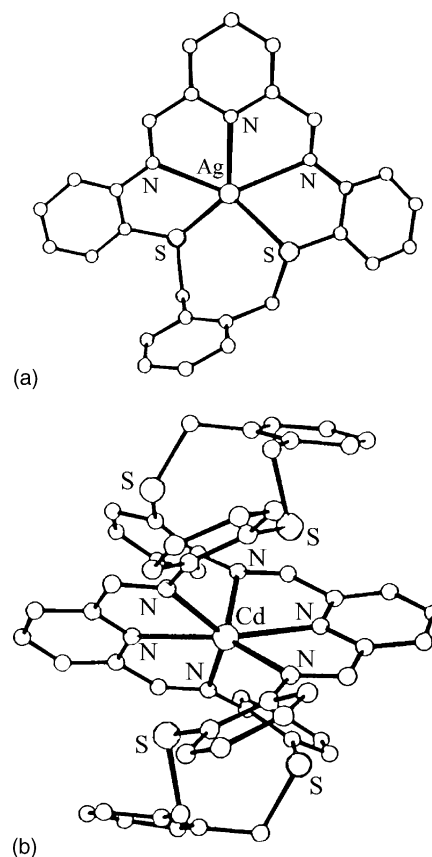


Fig. 46. Structure of the single helicate $[\text{Ag}(\mathbf{82})]^+$ (a) and of the double helicate $[\text{Cd}(\mathbf{83})]^{2+}$ (b) (adapted from Ref. [160]).

protons is attributed to interconversion of enantiomers of the chiral single helicate [160].

In contrast, the room temperature ^1H NMR spectrum of $[\text{Cd}(\mathbf{83})(\text{ClO}_4)_2]$ in CD_3CN shows an AB subspectrum for the methylene protons consistent with retention of molecular helicity in solution. In this case, the spectrum indicates effective four-fold symmetry for the complex. On lowering the temperature, the four-fold symmetry of the complex breaks down and the proton signals of $[\text{Cd}(\mathbf{83})]^{2+}$ broaden (while solvate signals remain sharp). Several resonances are observed to split symmetrically ($\Delta\delta$ ca. 0.6–1.7 ppm) about the positions of the signals at ambient temperature. The widely differing proton environments indicated by these shifts correlate closely with those of the effectively two-fold symmetric solid-state structure. Overall, the low-temperature spectrum is consistent with a C_2 symmetry species, similar to the fully twisted macrocycle array observed in the solid state. Observations of $^{111}/^{113}\text{Cd}$ coupling to the γ -pyridyl protons confirm that the complex is inert to metal exchange throughout the temperature range investigated. The exchange process, that averages these signals at ambient temperature but retains the helicity of the complex and the coordination of the metal, involves an interchange of aromatic ring positions through a concerted slipping of the macrocyclic ring [160].

The reaction between *N,N*-bis(2-aminoethyl)-2-phenylethylamine, *N,N*-bis(2-aminoethyl)-*t*-butylamine and *N,N*-bis(2-aminoethyl)-2-methylthioethylamine, and 2,5-diformylthiophene resulted in the isolation of amorphous orange solids. In the corresponding reaction involving *N,N*-bis(2-aminoethyl)-*t*-butylamine, however, recrystallization of the orange solid from either acetonitrile or acetone resulted in the isolation of the macrocycle **84** [161].

Addition of tetrakis(acetonitrile) copper(I) hexafluorophosphate to a suspension of **84** in either acetonitrile or methanol produced $[\text{Cu}_2(\mathbf{84})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$. In this complex each copper(I) ion is in an approximately tetrahedral environment being coordinated to one tertiary amino- and two imino-nitrogen atoms originating from the macrocyclic ring with the fourth coordination site occupied by the nitrogen of the acetonitrile molecule. There is a further acetonitrile of solvation present in the molecule (Fig. 47). The macrocycle, although reasonably twisted,

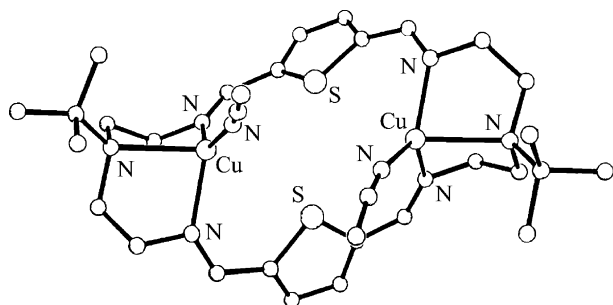


Fig. 47. Structure of $[\text{Cu}_2(\mathbf{84})(\text{CH}_3\text{CN})_2]^{2+}$ (adapted from Ref. [161]).

has not folded to adopt a molecular cleft and consequently the copper...copper separation is quite large. Steric repulsion causes the coordinated acetonitrile molecules to become oriented away from each other and contributes to the large copper–copper separation. The absence of a shared bridging group also contributes to the more open conformation observed [161].

The cyclocondensation of 2,5-diformylthiophene and *N,N*-bis(2-aminoethyl)-2-phenylethylamine, *N,N*-bis(2-aminoethyl)-*n*-butylamine or *N,N*-bis(2-aminoethyl)-*t*-butylamine in the presence of silver(I) salts and tetrabutylammonium hexafluorophosphate or sodium hexafluorophosphate to effect anion exchange and promote crystallisation, yields the homo-dinuclear bibrachial tetraimine Schiff base macrocyclic complexes $[\text{Ag}_2(\mathbf{L})(\text{NO}_3)](\text{PF}_6)$ ($\mathbf{L} = \mathbf{84}, \mathbf{85}, \mathbf{86}$) and $[\text{Ag}_2(\mathbf{87})(\text{PF}_6)_2]$ [162].

In $[\text{Ag}_2(\mathbf{85})(\text{NO}_3)](\text{PF}_6)$ each silver(I) ion is in a distorted tetrahedral environment composed of two imine nitrogen atoms, one tertiary amine nitrogen atom and one oxygen atom originating from the nitrate anion. This oxygen bridges both silver ions leading to a rare example of a dinuclear silver(I) complex containing a unidentate symmetrically bridging nitrate group. The silver...silver separation is 4.161 Å and the hexafluorophosphate anion is not coordinated. The 2-phenylethyl pendant arms are positioned on the same side of the ring, however there is no interaction observed between the π -system of the phenyl rings and the silver ions. The thiophene sulfur atoms are not coordinated. The macrocycle has adopted a bowl-like conformation and not a full cleft conformation, possibly due to the bridging species being exogenous rather than endogenous in origin (Fig. 48a) [162].

$[\text{Ag}_2(\mathbf{84})(\text{BF}_4)_2]$, synthesized from the condensation of 2,5-diformylthiophene and *N,N*-bis(2-aminoethyl)-2-

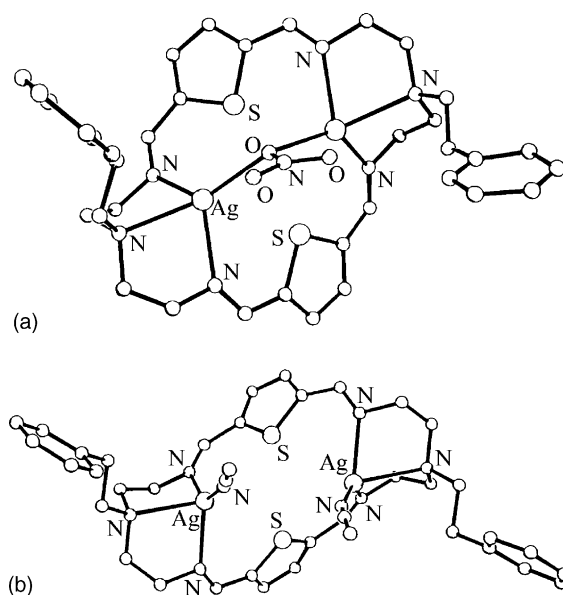


Fig. 48. Structure of $[\text{Ag}_2(\mathbf{84})(\text{NO}_3)]^+$ (a) and $[\text{Ag}_2(\mathbf{84})(\text{CH}_3\text{CN})_2]^{2+}$ (b) (adapted from Ref. [162]).

phenylethylamine in the presence of silver(I) tetrafluoroborate, reacts with tetrakis(acetonitrile)copper(I) tetrafluoroborate in acetonitrile solution under an inert atmosphere to give rise to a mixture of silver(I) and copper(I) species. Attempts to separate the mixture of complexes by recrystallization from acetonitrile and diethyl ether allowed the isolation of the complex $[\text{Ag}_2(\mathbf{84})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2 \cdot \text{CH}_3\text{CN}$. Each silver(I) ion is in a distorted tetrahedral environment and is coordinated by the lateral nitrogen atoms of the macrocycle and an acetonitrile of solvation; this coordination environment was also found in the analogous dicopper(I) macrocycle. The silver(I) ions are 4.920 Å apart. The macrocycle has adopted an even more open conformation and is saucer shaped with both of the coordinated acetonitriles approaching the silver ions from the same side. The thiophene sulfur atoms are non-bonding (Fig. 48b).

A template procedure affords the lead(II) complexes $[\text{Pb}_2(\mathbf{L})(\text{X})_4]$ ($\text{X} = \text{NO}_3^-$, SCN^- , $\text{CF}_3\text{COCH}_2\text{COCF}_3$) with the macrocycles $\mathbf{L} = \mathbf{84}–\mathbf{87}$ [161].

The transmetalation reaction of $[\text{Pb}_2(\mathbf{85})(\text{SCN})_4]$ and $[\text{Pb}_2(\mathbf{86})(\text{SCN})_4]$ in a nitrogen atmosphere in either acetonitrile or methanol with 2 equiv. of tetrakis(acetonitrile) copper(I) hexafluorophosphate gives rise respectively to $[\text{Cu}_2(\mathbf{85})(\text{SCN})](\text{PF}_6)$ and $[\text{Cu}_2(\mathbf{86})](\text{PF}_6)_2$. Transmetalation of $[\text{Pb}_2(\mathbf{85})(\text{NO}_3)_4]$ and $[\text{Pb}_2(\mathbf{87})(\text{NO}_3)_4]$ with tetrakis(acetonitrile) copper(I) hexafluorophosphate affords $[\text{Cu}_2(\mathbf{85})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ and $[\text{Cu}_2(\mathbf{87})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ [162].

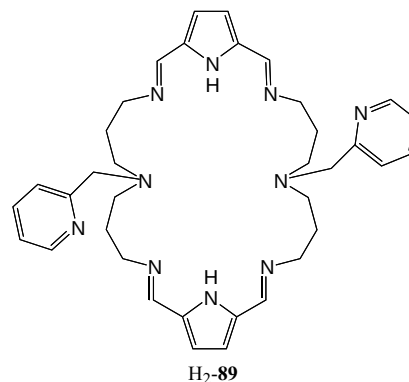
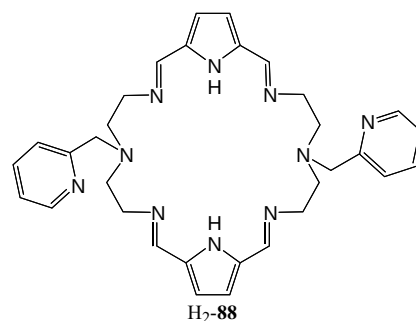
The structure of $[\text{Cu}_2(\mathbf{85})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2 \cdot 0.64 \cdot \text{CH}_3\text{CN}$ (Fig. 49a) shows each copper(I) ion is in a distorted tetrahedral environment composed of two imine nitrogen atoms and one tertiary amine nitrogen atom from the ligand and a nitrogen atom from a molecule of acetonitrile. The copper...copper separation is relatively large, 5.386 Å. The phenyl ethyl pendant arms are oriented upon the same side of the macrocycle and again the macrocycle is not folded. There is an acetonitrile molecule with a partial occupancy of 64% present in the complex.

The structure of $[\text{Cu}_2(\mathbf{87})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$ (Fig. 49b) reveals that the two copper(I) ions are again in distorted tetrahedral environments composed of two imine nitrogen atoms, one tertiary amine nitrogen atom and one acetonitrile nitrogen atom. The copper...copper separation is 5.215 Å and the two acetonitrile molecules are once again oriented away from each other. The *n*-butyl pendant arm groups are oriented on the same side of the macrocyclic ring. The conformation of the macrocycle, although possibly more twisted than $[\text{Cu}_2(\mathbf{84})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2 \cdot 0.64 \cdot \text{CH}_3\text{CN}$, is still not folded into a deep molecular cleft. There is a further acetonitrile of solvation present in the molecule [161]. NMR spectra show the macrocycles have a reasonable degree of conformational flexibility in solution [161].

No reaction was found to have occurred between $[\text{Cu}_2(\mathbf{84})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ and triphenylphosphine while ^1H NMR spectra evidence that the exchange of acetonitrile molecules for carbon monoxide at the copper(I) ions in

the complex $[\text{Cu}_2(\mathbf{84})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ is possible with the formation of three species corresponding to $[\text{Cu}_2(\mathbf{84})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$, $[\text{Cu}_2(\mathbf{84})(\text{CH}_3\text{CN})(\text{CO})](\text{PF}_6)_2$ and $[\text{Cu}_2(\mathbf{84})(\text{CO})_2](\text{PF}_6)_2$. The exchange process appears to be an equilibrium which can easily revert back to the initial complex or to a mixed complex with one copper ion coordinated to an acetonitrile molecule and one coordinated to a carbon monoxide [161].

The cyclocondensation of pyrrole-2,5-dicarbaldehyde and *N,N*-bis(2-aminoethyl)-2-(aminomethyl)pyridine or *N,N*-bis(3-aminopropyl)-2-(aminomethyl)pyridine in the presence of silver(I) nitrate yielded the homo-dinuclear bibrachial tetraimine Schiff base macrocyclic complexes $[\text{Ag}_2(\mathbf{88})]$ and $[\text{Ag}_2(\text{H}_2-\mathbf{89})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$. For the aminopropyl-derived complex sodium perchlorate was added to effect anion exchange and promote crystallisation [163].



In $[\text{Ag}_2(\mathbf{88})]$ each silver(I) ion is in a T-shaped three coordinated environment composed of two imine nitrogen atoms and one nitrogen atom from a deprotonated pyrrolic head group. This leads to an interesting juxtaposition of a five membered chelate ring. A pyrrolic nitrogen atom and one imine nitrogen atom comprise a chelating unit with the non-chelating imine nitrogen atom of the second head-unit providing the third interaction. The silver ions lie slightly above the plane constituted by the three donor atoms (Fig. 50).

The *cis*-imines and pyrrole of each head group are close to coplanar and the silver ions are diagonally disposed within the macrocyclic framework being involved with donor atoms derived from both the head and lateral units (c). This may be compared with the propensity for head-head coordination in the analogous pyridine-derived species (a) and

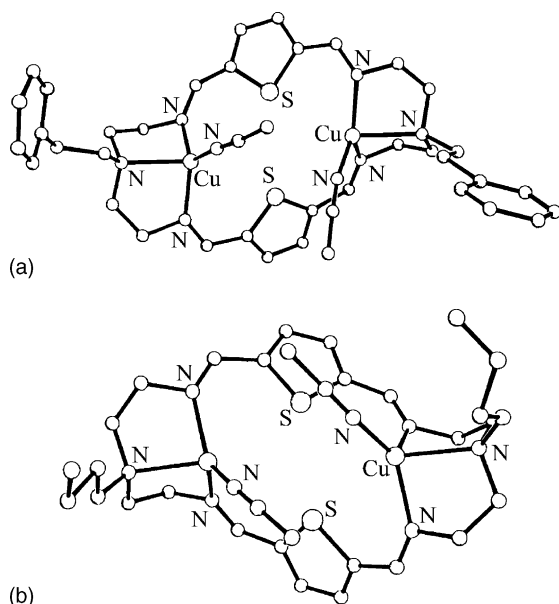
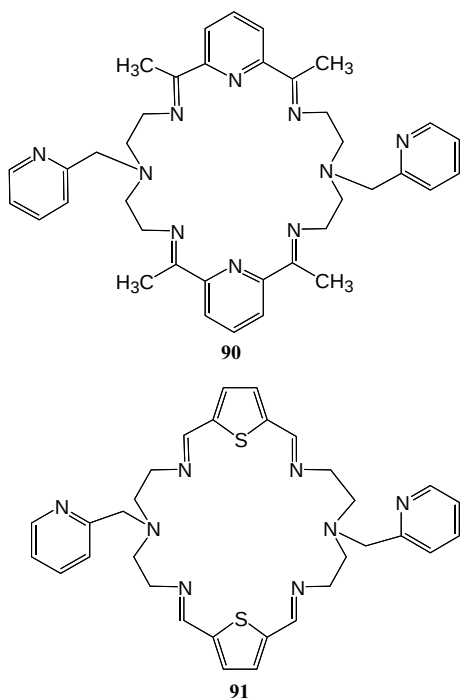


Fig. 49. Structure of $[\text{Cu}_2(\mathbf{85})(\text{CH}_3\text{CN})_2]^{2+}$ (a) and $[\text{Cu}_2(\mathbf{87})(\text{CH}_3\text{CN})_2]^{2+}$ (b) (adapted from Refs. [161,162]).

lateral-lateral co-ordination in the furan and thiophene-derived species (b) where the head-unit serves as an inert spacer (Scheme 19).

In $[\text{Ag}_2(\mathbf{88})]$, unlike the disilver complexes of **90** and **91**, the 2-(aminomethyl)pyridine pendant arms are not coordinated to the metal ions either intra- or inter-molecularly.



The relative planarity of the structure and non-involvement of the pyridine arms in the intermolecular structure can be contrasted with that found for the analogous pyridine-derived complex $[\text{Ag}_2(\mathbf{90})(\text{ClO}_4)_2]$ in which the two metal

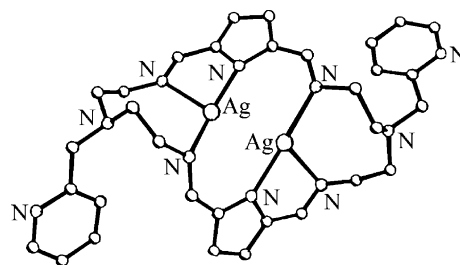
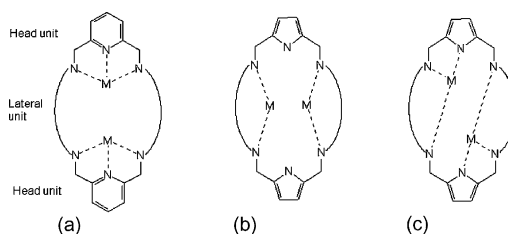


Fig. 50. Structure of $[\text{Ag}_2(\mathbf{88})]$ (adapted from Ref. [163]).



Scheme 19.

ions reside within a clearly defined molecular cleft. The $\text{Ag} \cdots \text{Ag}$ separation is 3.068 Å and each silver(I) ion has its shortest interactions with a pyridine nitrogen atom (ca. 2.38 Å) and the primary pendant pyridinyl atom (ca. 2.40 Å), an intermediate interaction with one imine atom (ca. 2.43 Å) and longer range interactions with the tertiary amine nitrogen atom (ca. 2.57 Å) and the remaining imine nitrogen atom (ca. 2.60 Å). One of the imine nitrogen atoms also provides a symmetric bridge between the two silver ions and this bridge together with weak interactions between the close to parallel pyridine head-units helps to maintain the integrity of the cleft-like structure. Further comparison can be made of the structure of $[\text{Ag}_2(\mathbf{88})]$ with that of $[\text{Ag}_2(\mathbf{91})(\text{NO}_3)](\text{ClO}_4)$ in which the two silver(I) ions were found to be laterally coordinated and separated by 4.56 Å within a much diminished molecular cleft. One silver ion lies in a four coordinated environment formed by the nitrogen atoms of a pendant pyridine group, two imino nitrogen atoms and a tertiary amino nitrogen. The second silver ion has this environment increased by an interaction with a nitrate anion, or a methanol molecule of solvation; the structure is complicated by a disorder problem. This comparison of the disilver complexes of **88**, **90** and **91** clearly shows the differences in co-ordination which can be induced by simply changing the nature of the head group of the macrocycle [163].

It has been shown that in certain copper(I), silver(I) and gold(I) compounds the metal ions are held together in pairs by rigid 1,3-bifunctional bidentate ligands with a $\text{M(I)} \cdots \text{M(I)}$ separation similar to, or shorter than, the intermetallic distances in the metals themselves [163]. This has also been noted for disilver(I) and dicopper(I) complexes of Schiff base derived cryptands and also in complexes of molecular clefts derived from bibrachial tetraimine Schiff base macrocycles. In $[\text{Ag}_2(\mathbf{88})]$ the $\text{Ag} \cdots \text{Ag}$ separation is

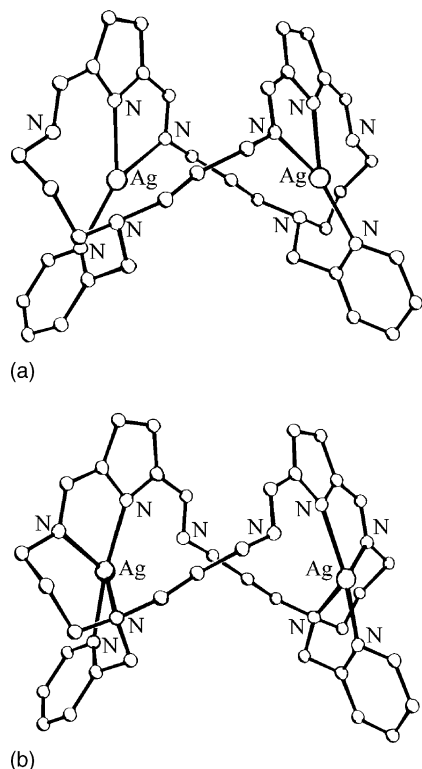


Fig. 51. Structure of the major component (a) and the minor component (b) of $[\text{Ag}_2(\text{H}_2\text{-89})]^{2+}$ (adapted from Ref. [163]).

2.748 Å which is the shortest so far recorded for such an interaction sustained by a macrocyclic ligand [163].

In $[\text{Ag}_2(\text{H}_2\text{-89})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$, expansion of the ligand from a [24–28]-membered ring has allowed the generation of a more cleft-like conformation. In the crystals of $[\text{Ag}_2(\text{H}_2\text{-89})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ a disorder involving the silver atom occurs; a major component (a) having ca. 95% occupancy and a minor component (b) having ca. 5% occupancy have been detected. The silver ions in the major occupancy site are three coordinated in a distorted trigonal planar geometry composed of an imine nitrogen atom, a nitrogen atom from a deprotonated pyrrolic head group and a pendant pyridinyl nitrogen atom (Fig. 51a). The silver ions lie slightly outside of the planes constituted by the three donor atoms. The two silver ions are 5.881 Å apart in this configuration and move to 7.224 Å apart in the minor occupancy configuration. In this latter configuration each silver atom is four coordinated in a distorted tetrahedral geometry composed of an imine nitrogen atom, a nitrogen atom from a deprotonated pyrrolic head group, a pendant pyridinyl nitrogen atom and a tertiary amino nitrogen atom (Fig. 51b).

The pendant pyridine nitrogen atoms are strongly coordinated with the pyrrolic nitrogen atoms tightly held. The remaining nitrogen atoms are less strongly held. The macrocycle is folded so that the pendant pyridine arms approach the silver atoms from opposing sides of the macrocyclic ring.

The relative site occupancy by the silver(I) ions is viewed as indicating a preference of the metal ion for three over four coordination. The perchlorate anions and the acetonitrile of

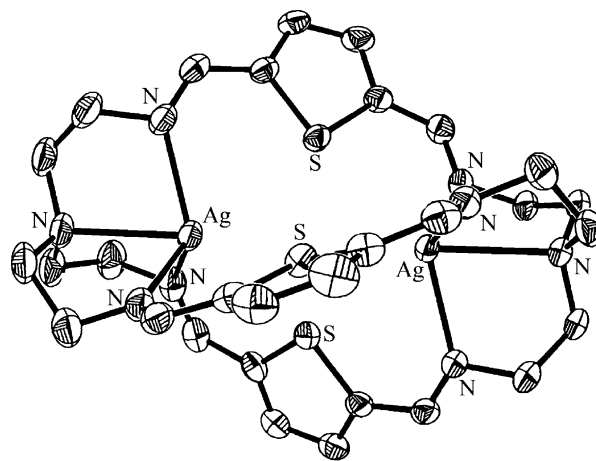
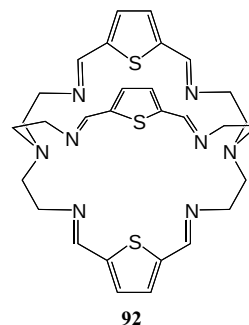


Fig. 52. Structure of $[\text{Ag}_2(\mathbf{92})]^{2+}$ (adapted from Ref. [164]).

solvation are not involved in bonding to the silver ions. Both isomers display a diagonal disposition of the silver ions as found in complex $[\text{Ag}_2(\mathbf{88})]$. An unusual feature of $[\text{Ag}_2(\text{H}_2\text{-89})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ is the presence of the iminium groups which are formed by the shift of the pyrrolic proton to the adjacent imine nitrogen atom [163].

The reaction in methanol of 2,5-diformylthiophene with tris(2-aminoethyl)amine in the presence of silver(I) nitrate in a 2:2:2 ratio gives on cooling to ca. 5 °C shiny yellow crystals of $[\text{Ag}_2(\mathbf{92})](\text{NO}_3)_2 \cdot \text{CH}_3\text{CN}$. The X-ray data, collected at 160 K due to the unstable nature of the crystals, show that the silver(I) ions are encapsulated within the cryptand at either end of molecular cavity (Fig. 52). Each silver ion is in a four coordinated environment within the cryptand cavity, binding to three imino nitrogen atoms and one bridgehead amino nitrogen atom to produce a silver...silver separation of 4.595 Å. The sulfur atoms of the thiophene head units were found to be non-bonding and acting as inert spacers; the geometry around each silver ion is unusual in that all the nitrogen atoms are coordinated on one side of the silver metal ion [164].



92

The cryptands **93** and **94**, generated by template synthesis on silver(I) salts, have been isolated as the disilver complexes $[\text{Ag}_2(\mathbf{93})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ and $[\text{Ag}_2(\mathbf{94})](\text{ClO}_4)_2$. Moreover $[\text{Ag}_2(\mathbf{96})](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared by reaction of **96** and AgBF_4 in $\text{C}_2\text{H}_5\text{OH}$ [165]. $[\text{Ag}_2(\mathbf{93})]^{2+}$, $[\text{Ag}_2(\mathbf{94})]^{2+}$ and $[\text{Ag}_2(\mathbf{96})](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$ retain a trigonal pyramidal nitrogen cap derived site for silver(I) coordination (Fig. 53a–c).

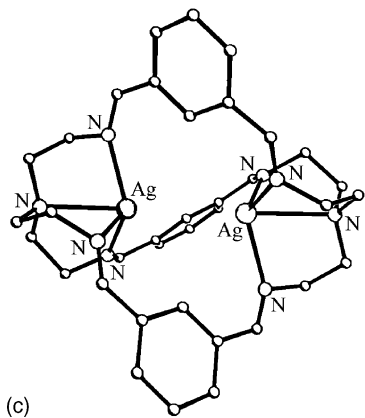
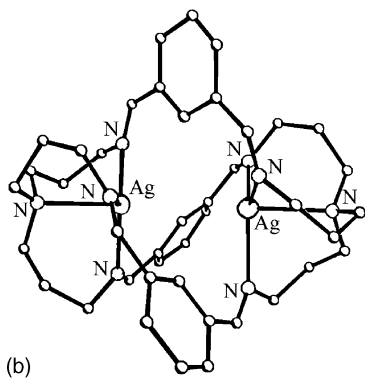
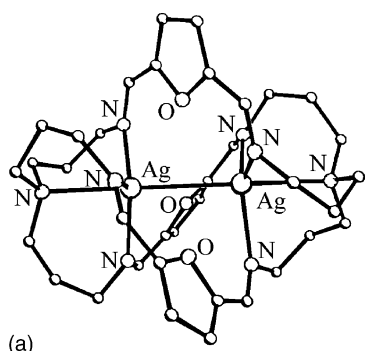
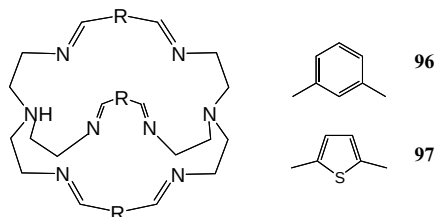
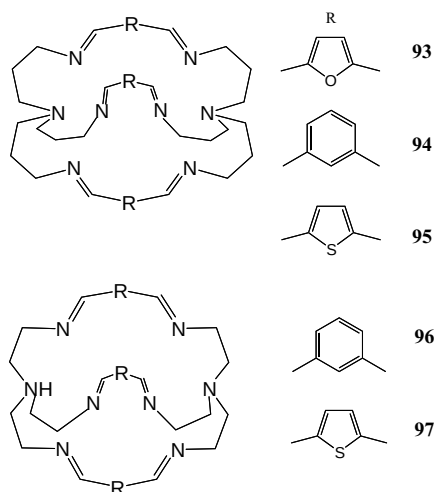
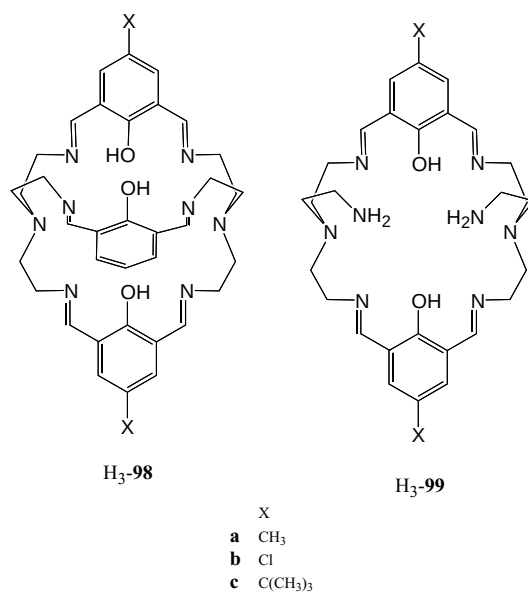


Fig. 53. Structure of $[\text{Ag}_2(\mathbf{93})]^{2+}$ (a), $[\text{Ag}_2(\mathbf{94})]^{2+}$ (b) and $[\text{Ag}_2(\mathbf{96})]^{2+}$ (c) (adapted from Ref. [165]).

Comparing the thiophene-spaced analogues $[\text{Ag}_2(\mathbf{95})]^{2+}$ and $[\text{Ag}_2(\mathbf{97})]^{2+}$ with the *m*-xylyl-spaced pair of cryptates $[\text{Ag}_2(\mathbf{94})]^{2+}$ and $[\text{Ag}_2(\mathbf{96})]^{2+}$, it can be seen that in both cases, the $\text{N}(\text{CH}_2\text{CH}_2\text{N})_3$ derived site presents all four nitrogen atoms to one side of the cation. In the $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{N})_3$ derived site of $[\text{Ag}_2(\mathbf{94})]^{2+}$ the Ag^+ cation lies almost coplanar with the N_3 plane. The other consequence of the greater flexibility of the $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{N})_3$ -cap is that regular trigonal pyramidal angles are achievable within the trigonal plane, and axial to it, in contrast to the $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{N})_3$ -capped cryptate $[\text{Ag}_2(\mathbf{96})]^{2+}$ where significant deviations from the ideal 120 and 90° values are seen.

The observation of less regular trigonal pyramidal geometry in $\text{N}(\text{CH}_2\text{CH}_2\text{N})_3$ -capped cryptates in comparison with the $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{N})_3$ derived analogue is general for dinuclear cryptates and extends even to the analogous podate systems. The $\text{Ag} \cdots \text{Ag}$ separation in $[\text{Ag}_2(\mathbf{94})]^{2+}$ (3.775 Å) exceeds that in $[\text{Ag}_2(\mathbf{96})]^{2+}$ by 0.33 Å and both exceed those in the furan spaced analogues, presumably in response to steric constraints associated with the relatively bulky *m*-xylyl spacer. The relatively long internuclear distance in $[\text{Ag}_2(\mathbf{96})]^{2+}$, would appear to rule out any possibility of $\text{Ag} \cdots \text{Ag}$ bonding [165].

In an attempt to prepare a dinuclear manganese(II) complex with the [2+2] macrocyclic ligand containing pyridine as pendant arms, $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ and pyridine 2-carboxaldehyde in a 1:1 molar ratio were reacted and the resulting Schiff base reduced by an excess of NaBH_4 in ethanol. The subsequent reaction with sodium 2,6-diformyl-4-methylphenol and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ gives rise to the [3+2] macrocyclic Schiff base complex $[\text{Mn}_2(\mathbf{98a})](\text{ClO}_4)_2$ where $\text{H}_3\text{-98a}$ is the [3+2] macrobicycle derived from the condensation of tren and 2,6-diformyl-4-methylphenol [166].



A similar reaction pathway using copper(II), nickel(II), iron(III) and zinc(II) salts affords the designed [2+2]

pendant-armed macrocyclic complexes $[M_2(99a-c)]^{2+}$ [166].

$[M_2(98a-c)](ClO_4)_2$ ($M = Mn^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+}) have been obtained by the transmetalation reaction of $Na_3-98a-c$ with the appropriate metal acetate.

$[Mn_2(98a)](ClO_4)_2$ is a mixed-valence $Mn^{II}Mn^{III}$ complex containing two perchlorate anions. Mn(1) is six coordinated to the macrobicyclic through three imine nitrogens and three phenoxy oxygens, but has less regular geometry than Mn(2) which is also six coordinated in a typically distorted octahedron. Like $[Fe^{II}Co^{II}(98a)](BF_4)_2$ and $[Mn_2(98a)](ClO_4)_2$, all the phenolato oxygen atoms are μ_2 -bridging, and the tertiary nitrogen atoms are not coordinated. The $Mn_2(\mu-O)_2$ bridge is asymmetric. Bond lengths suggest to assign the II^+ state to Mn(2) whereas Mn(1) has been oxidized to the III^+ level (Fig. 54) [166].

Schiff base lateral macrobicycles containing two different binding units, one rigid and unsaturated N_3 or N_2O set and the other flexible and cyclic N_2O_n set linked by two aromatic bridges have been prepared by reaction of the appropriate bibrachial diamines N,N' -bis(aminobenzyl)-1,10-diaza-15-crown-5 (**110a**) or N,N' -bis(aminobenzyl)-4,13-diaza-18-crown-6 (**110b**) and diformyl precursors in the presence of different metal ions as templating agents. The expected cryptands do not form in the absence of the metal ion which is necessary to orient the diamine precursor in a *syn* conformation [167].

The synthetic route to the diamine derivatives **100a** and **100b** involves two key steps, specifically nitrogen-binding of 2-nitrobenzyl chloride to the diaza-crown and subsequent reduction of the NO_2 -groups of the resulting N,N' -bis(2-nitrobenzyl)-diaza-crown to $-NH_2$ groups with hydrazine hydrate in the presence of Pd/C as a catalyst. The synthesis can be carried out in a one-pot procedure by reducing the intermediate N,N' -bis(2-nitro-benzyl)-diaza-crown prepared in situ [167].

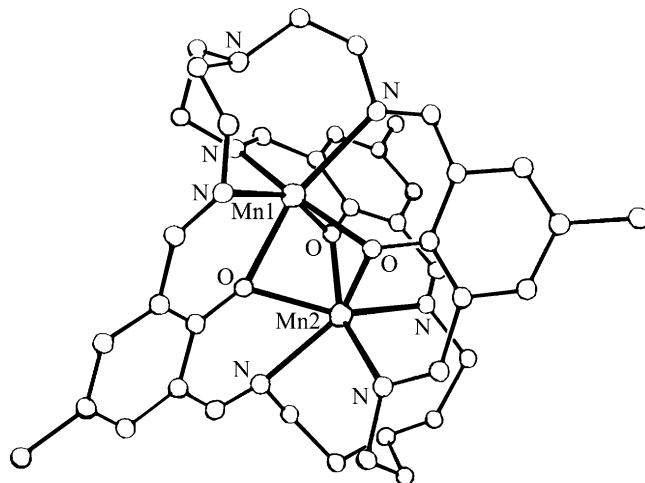
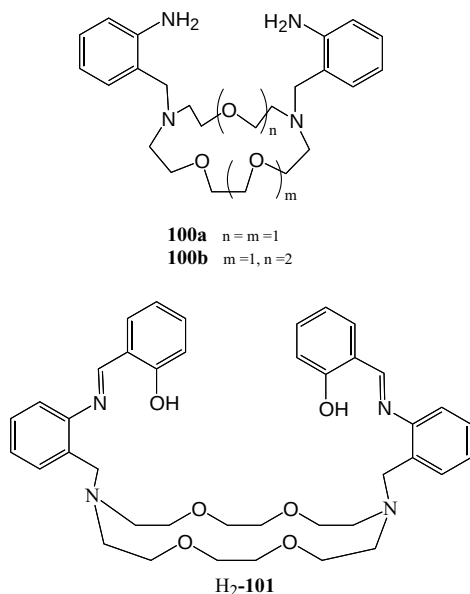


Fig. 54. Structure of $[Mn_2(98a)]^{2+}$ (adapted from Ref. [166]).

In **100a** the arms of the lariat ether are arranged on opposite sides of the crown moiety resulting in an *anti*-conformation. The crystal packing is determined by intermolecular hydrogen-bonds, which involve one proton of the amine group and an oxygen atom of the neighbouring molecule. Weak intramolecular hydrogen-bonds exist between the amine groups and the pivotal nitrogen atoms (Fig. 55a).

Reactions of $M(ClO_4)_2 \cdot nH_2O$ ($M = Pb^{2+}$, Cd^{2+}) with **100a** yielded $M(100a)(ClO_4)_2$. In $[Pb(100a)](ClO_4)_2$ only six of the seven available donor atoms of **100a** are coordinated to the lead(II) ion with one of the aniline pendant arms uncoordinated. The metal ion lies 1.71 Å above the plane defined by the three etheric oxygen atoms and is asymmetrically disposed in respect to the crown ether moiety. The coordination polyhedron at the metal ion has been described as a dodecahedron with two unoccupied sites (Fig. 55b). The presence of these unoccupied sites leads to an empty zone in the coordination sphere of the metal. Both aniline pendant arms are oriented on the same side of the macrocycle plane, resulting in a *syn* conformation, in contrast to the *anti* conformation found for free **100a**. In $[Pb(100a)](ClO_4)_2$ one of the two perchlorate anions is well removed from the complex cation and has no interactions with neighbouring molecules. The second perchlorate anion, however, is involved in both a weak hydrogen-bonding interaction with a hydrogen atom on the non-coordinated pendant amino nitrogen atom. This anion acts as a bridge between the metal ion and the non-coordinated pendant amine group, thereby reinforcing the *syn* conformation present in $[Pb(100a)](ClO_4)_2$.

Also the reaction of **100a** or **100b** with barium salts (perchlorate or thiocyanate) in absolute ethanol gives $[Ba(100a)](X)_2$ and $[Ba(100b)](X)_2$ ($X = ClO_4^-$, SCN^-). $[Ba(100a)(ClO_4)](ClO_4)$, obtained by slow diffusion of diethyl ether into a solution of the complex in acetonitrile (Fig. 55c) contains a BaN_4O_5 core with the seven heteroatoms of **100a** coordinated to the barium ion as well as a

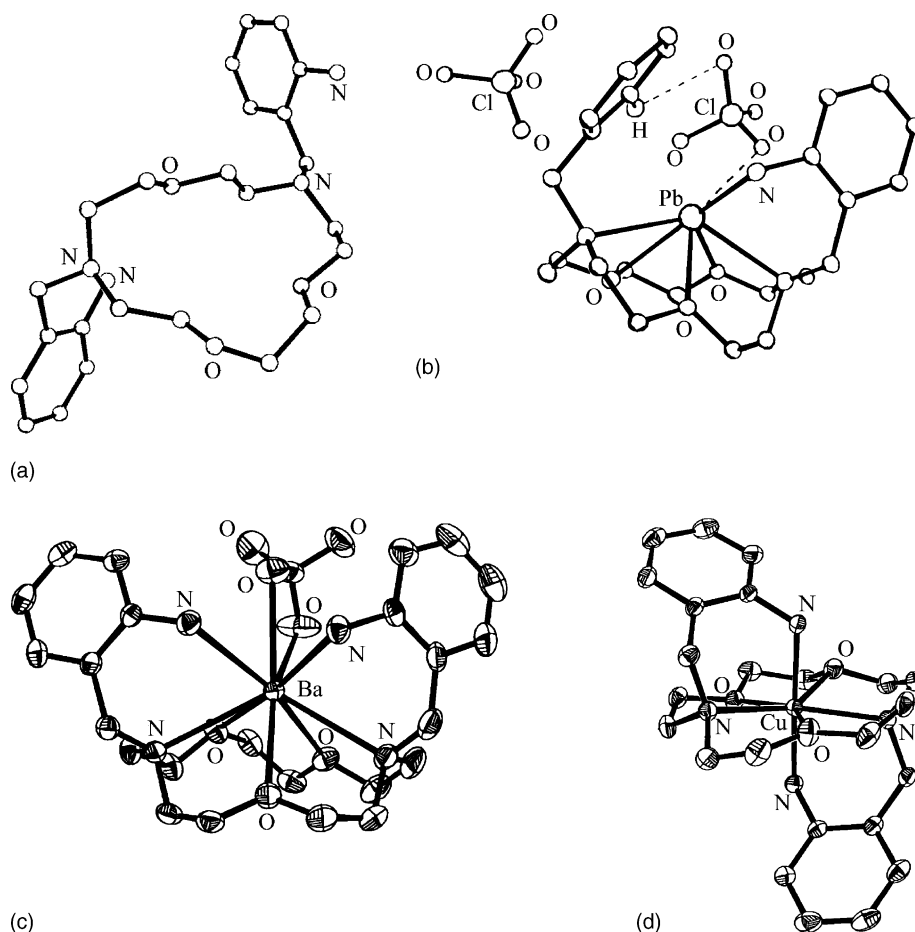


Fig. 55. Structure of **100a** (a), $[\text{Pb}(\mathbf{100a})](\text{ClO}_4)_2$ (b), $[\text{Ba}(\mathbf{100a})](\text{ClO}_4)_2^+$ (c), and $[\text{Cu}(\mathbf{100a})]^{2+}$ (d) (adapted from Ref. [167]).

perchlorate group in a bidentate mode. Both aniline pendant arms are oriented on the same side, resulting a *syn* conformation, unlike the *anti*-conformation found for the free ligand. In this barium compound there are no hydrogen bonds between amine hydrogen atoms and perchlorate groups as occurs in the corresponding lead(II) complex [167].

The reaction of **100a** and **100b** with copper(II) salts in absolute ethanol gives $[\text{Cu}(\mathbf{100a})](\text{X})_2$ and $[\text{Cu}_2(\mathbf{100b})](\text{X})_4$ ($\text{X} = \text{ClO}_4^-, \text{NO}_3^-$) [167]. **100a** is only able to form mononuclear complexes while the larger **100b** is able to form binuclear complexes with copper(II). The impossibility of preparing binuclear complexes with **100a** and/or mononuclear compounds with **100b** evidences the different coordinative properties of both receptors towards copper(II) [167].

$[\text{Cu}(\mathbf{100a})](\text{ClO}_4)_2$ contains a CuN_4O_3 core with the seven heteroatoms of **100a** coordinated to the copper(II) ion which resides in the macrocyclic cavity bound by the three ether oxygen atoms and the two pivotal amino nitrogen atoms of the pendant arms coordinated apically. Thus, the coordination sphere of the copper ion is a distorted pentagonal bipyramid [167] (Fig. 55d).

In $[\text{Cu}(\mathbf{100a})](\text{NO}_3)_2$ the metal ion is also seven coordinated with a distorted pentagonal bipyramidal geometry identical to the one present in $[\text{Cu}(\mathbf{100a})](\text{ClO}_4)_2$ [167].

Reactions of **100b** and salicylaldehyde in the presence of triethylamine and copper(II) perchlorate or nitrate gave $[\text{Cu}_2(\mathbf{101})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Cu}_2(\mathbf{101})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. In $[\text{Cu}_2(\mathbf{101})](\text{ClO}_4)_2$ both copper(II) ions have crystallographically identical coordination environments; each metal ion is placed out of the crown hole but efficiently encapsulated by each pendant arm and is five coordinated being bound to one pivotal nitrogen atom, one phenolate oxygen atom, one imine atom and two ether oxygen atoms [167] (Fig. 56a). The coordination polyhedron around each metal ion is intermediate between a distorted trigonal bipyramid and a square pyramid.

Reaction of $\text{H}_2\text{-101}$, prepared in situ by the condensation of **100b** and salicylaldehyde, with triethylamine and the corresponding hydrated lanthanide perchlorate in 2-propanol led to $[\text{Ln}(\mathbf{101})](\text{ClO}_4)_3$ ($\text{Ln} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}$). Attempts to obtain the expected complexes with the other lanthanide ions (Nd^{3+} to Lu^{3+}) under the same experimental conditions failed, precipitating the corresponding lanthanide hydroxide instead. In all these cases hydrolysis of the Schiff base and protonation of **100b** was also observed [167].

In $[\text{La}(\mathbf{101})](\text{ClO}_4)_3$ the lanthanum ion is coordinated to the ten available donor atoms of the Schiff-base bibrachial lariat ether $[\mathbf{101}]^{2-}$ and almost symmetrically positioned

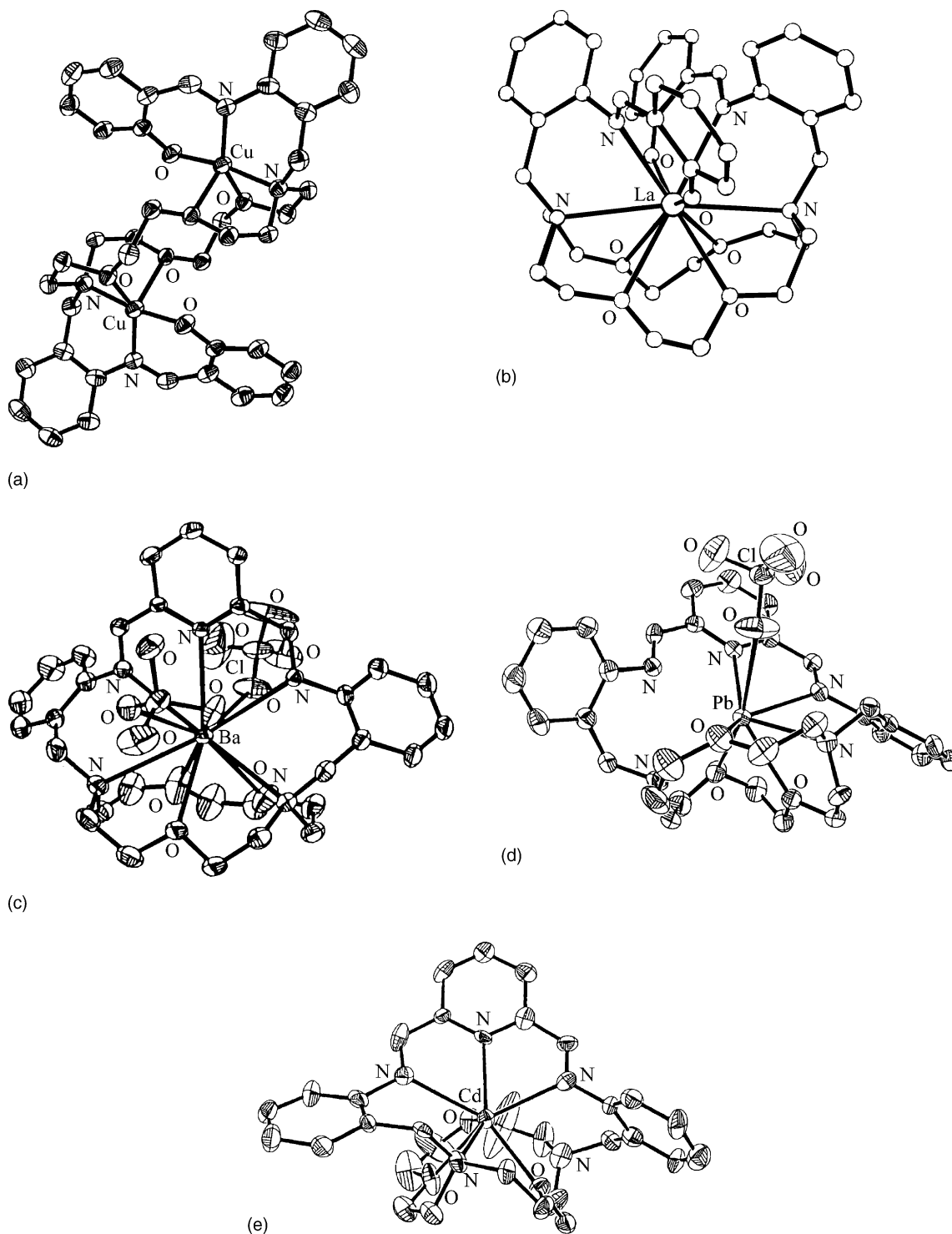


Fig. 56. Structure of $[\text{Cu}_2(\mathbf{101})]^{2+}$ (a), $[\text{La}(\mathbf{101})]^+$ (b), $[\text{Ba}(\mathbf{102a})](\text{ClO}_4)_2$ (c), $[\text{Pb}(\mathbf{102a})]^{2+}$ (d) and $[\text{Cd}(\mathbf{102a})]^{2+}$ (e) (adapted from Ref. [167]).

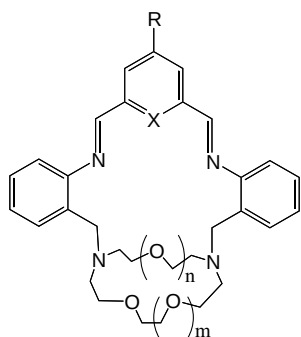
with respect to the ligand cavity. The coordination environment of the metal ion has been described as a distorted tetracapped trigonal prism. Both side arms of the bibrachial lariat ether in $[\mathbf{101}]^{2-}$ are oriented on the same side of the crown moiety, resulting in a *syn* conformation. Likewise, the lone pairs of both pivotal nitrogen atoms are forced to point towards the receptor cavity in an *endo–endo* arrangement.

The *syn* conformation adopted by the lariat ether confers to the complex a chiral structure with two possible optical isomers, labelled as Λ or Δ , indicating either left-handed (Λ) or right-handed (Δ) structural chirality about the two-fold symmetry axis of the complex. It could be surprising that in spite of its chirality the complex crystallises in the $P2_1/n$ space group, which is not chiral. This is because the crystal

contains a racemic mixture of both enantiomers ($Z = 4$, two of them Λ and the other two Δ) centrosymmetrically related (Fig. 56b).

Crystals of $[\text{Ln}(\mathbf{101})](\text{ClO}_4)$ ($\text{Ln} = \text{Ce}^{3+}$, Pr^{3+}) are isomorphous; both complex cations contain the corresponding 10 coordinated lanthanide ion bound to all the donor atoms of the bibrachial lariat ether, similar to the lanthanum complex $[\text{La}(\mathbf{101})](\text{ClO}_4)$ [167]. The conformation of the bibrachial lariat ether in both complexes $[\text{Ln}(\mathbf{101})](\text{ClO}_4)$ ($\text{Ln} = \text{Ce}^{3+}$, Pr^{3+}) is again *syn endo-endo* similar to that present in $[\text{La}(\mathbf{101})](\text{ClO}_4)$ also resulting in structural chirality. However, its fold around the trapped lanthanide ion is different to that found in $[\text{La}(\mathbf{101})](\text{ClO}_4)_2$. This fact is evident because the four oxygen atoms of the crown moiety are not coplanar in $[\text{Ln}(\mathbf{101})](\text{ClO}_4)_2$ ($\text{Ln} = \text{Ce}^{3+}$, Pr^{3+}). In these complexes the coordination polyhedron at the lanthanide ion has been described as a distorted bicapped square antiprism.

The reactions between equimolar amounts of 2,6-diformylpyridine and **100a** or **100b** in the presence of barium perchlorate in absolute ethanol gave $[\text{Ba}(\mathbf{102a})](\text{ClO}_4)_2$ and $[\text{Ba}(\mathbf{102b})](\text{ClO}_4)_2$. Reaction between 2,6-diformyl-4-methylphenol and **100a** also in the presence of barium perchlorate led $[\text{Ba}(\mathbf{102c})](\text{ClO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH}$.



102a $m = n = 1$
102b $m = 1, n = 2$; $R = \text{H}$; $X = \text{N}$
102c $m = n = 1$; $R = \text{CH}_3$; $X = \text{C}-\text{OH}$
102d $m = 1, n = 2$; $R = \text{CH}_3$; $X = \text{C}-\text{OH}$

Successive reactions between 2,6-diformyl-4-methylphenol and **100b** in the presence of barium perchlorate under different experimental conditions did not yield the expected complex of the Schiff base macrobicyclic **102d**. In all cases, the infrared spectra of the products exhibited bands attributable to $\nu(\text{C}=\text{N})$ together with those of carbonyl and/or amine groups indicating the presence of acyclic compounds.

The use of barium thiocyanate to template the above reactions was only effective when the diamine precursor **100b** was employed. Reactions between **100b** and 2,6-diformylpyridine or 2,6-diformyl-4-methylphenol in the presence of barium thiocyanate using absolute ethanol as solvent gave $[\text{Ba}(\mathbf{102b})](\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Ba}(\mathbf{102d})](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$. Infrared and FAB mass spectra provide evidence for the formation of the expected Schiff-base lateral macrobicycles **102b** and **102d** [167].

In $[\text{Ba}(\mathbf{102a})](\text{ClO}_4)_2$ the barium ion is coordinated to the eight donor atoms of the Schiff base lariat macrobicyclic with the metal ion almost symmetrically placed with respect to the ligand. Barium completes its coordination core with three oxygen atoms of the perchlorate groups, one of these groups acting as monodentate whereas the other acts as bidentate. The coordination polyhedron has been best described as an icosahedron with an unoccupied site (Fig. 56c) [167].

Reaction of equimolar amounts of 2,6-diformylpyridine and N,N' -bis(2-aminobenzyl)-1,10-diaza-15-crown-5 (**100a**) in the presence of lead(II) perchlorate in absolute ethanol gave $[\text{Pb}(\mathbf{102a})](\text{ClO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH}$. The same complex can also be prepared by transmetallation reaction using $[\text{Ba}(\mathbf{102a})](\text{ClO}_4)_2$ and lead(II) perchlorate in a 1:1 molar ratio in absolute ethanol solution [167].

Attempted reactions between 2,6-diformylpyridine and **100a** in the presence of cadmium perchlorate under various experimental conditions yielded neither the expected cadmium complex of the Schiff base macrobicyclic nor uncoordinated **102a**. In contrast, a transmetallation reaction between $[\text{Ba}(\mathbf{102a})](\text{ClO}_4)_2$ and cadmium perchlorate in a 1:1 molar ratio gave rise to a yellow analytically pure product $[\text{Cd}(\mathbf{102a})](\text{ClO}_4)_2$ [167].

In the lead complex $[\text{Pb}(\mathbf{102a})](\text{ClO}_4)_2$ the metal ion is asymmetrically positioned in relation to the ligand cavity and only six of the eight available heteroatoms of **102a** are coordinated to it. One pivotal nitrogen atom and one imine nitrogen atom remain only weakly coordinated with long interactions. The coordination sphere of the lead is completed by one oxygen atom of a monodentate perchlorate group and the coordination polyhedron may be described as a dodecahedron with an unoccupied site (Fig. 56d).

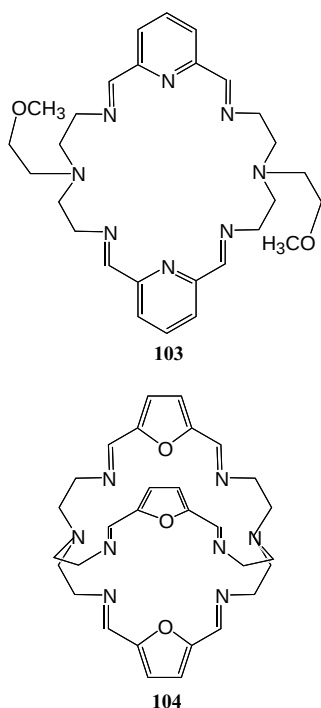
In $[\text{Cd}(\mathbf{102a})]^{2+}$ the cadmium(II) ion resides in a distorted monocapped octahedral N_4O_3 environment, bound by seven of the eight donor atoms of the macrobicyclic receptor; one pivotal nitrogen is rather distant from the metal ion and remains uncoordinated (Fig. 56e).

2.3. Transmetallation, migration and selective demetallation reactions

It has been found that macrocyclic Schiff base complexes may be kinetically labile and that the complexed template ion could be exchanged in many cases with other metal ions present in solution. Thus attention has been focused on the synthesis of macrocyclic complexes by transmetallation reactions to obtain complexes of metal ions which were not effective if fused in the direct template route. Furthermore, when some metal ions were used in the transmetallation reactions, new types of macrocyclic ligands arising from ring expansions or contraction or modification (as a consequence of hydrolysis rearrangement, etc.) were obtained, this depending on the demands and the size of the transmetalling ion.

This approach has been particularly successful when applied to the generation of dinuclear copper complexes of tetraimine Schiff base macrocycles especially starting from barium(II) analogues. Some examples have been already reported in a previous reviews [5,42]. Further examples of this mononuclear barium–dinuclear copper(II) transmetallation reaction are enclosed here.

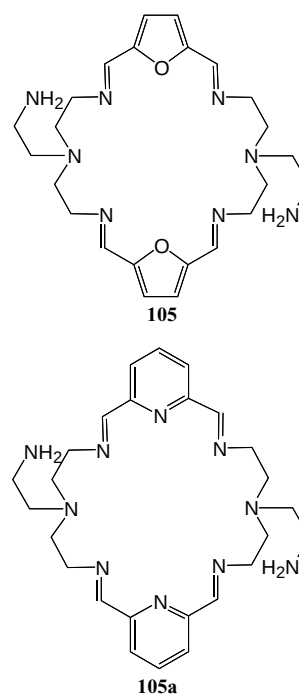
The [2+2] cyclocondensation of *N,N*-bis(2-amino-methyl)-2-methoxyethylamine and 2,6-diacetylpyridine in the presence of barium(II) perchlorate ion was found to be successful and affords $[\text{Ba}(\mathbf{103})](\text{ClO}_4)_2$ [168]. All the 10 donor atoms of the ligand interact with the barium ion which is encapsulated within the macrocyclic ligand. The macrocycle adopts a conformation with approximate C_2 symmetry, defining a molecular cleft between the pyridine diimine units (Fig. 57a).



$[\text{Ba}(\mathbf{103})](\text{ClO}_4)_2$, when treated in refluxing methanol with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, forms $[\text{Cu}_2(\mathbf{103})](\text{ClO}_4)_2$ where the bibrachial macrocycle **103** adopts an open conformation (Fig. 57b) in contrast to the folded cleft-like structure found in the related barium(II) complex. The two copper(II) ions are bound within the pyridine diimine head units of the macrocycle in identical environments related by a crystallographic inversion center. The metal ions are 5.56 Å apart with the donor atoms constituting two isolated coordination sites. The coordination geometry around each copper(II) ion has been described as a severely distorted square based pyramid. The four basal donors are provided by the nitrogen atoms of the macrocyclic ring. The apical site is filled by a longer interaction with the ethereal oxygen donor of the pendant arm [168].

The direct cyclocondensation of 2,5-diformylfuran and tris(2-aminoethyl)amine forms the [3+2] macrocycle **104** [169]. The same reaction in the presence of the appropriate barium salt yields $[\text{Ba}(\mathbf{104})](\text{BPh}_4)_2$ [170]. However, when barium perchlorate was employed as templating agent, the same cyclocondensation gives the [2+2] macrocyclic complex $[\text{Ba}(\mathbf{105})](\text{ClO}_4)_2$. An analogous experiment in the presence of barium nitrate gave only the metal-free **104**, probably because the poor solubility of barium nitrate in the methanol solvent used in the reaction inhibits complex formation [169,170].

Furthermore during attempts to recrystallise the imidazole-bridged dicopper(II) cryptate complex $[\text{Cu}_2(\mathbf{104})(\mu\text{-Im})](\text{ClO}_4)_3$, the macrocyclic complex $[\text{Cu}_2(\mathbf{105})(\mu\text{-Im})](\text{ClO}_4)_3$ was formed [171].



Crystals of $[\text{Ba}(\mathbf{105})](\text{ClO}_4)_2$, formed by vapour diffusion of diethyl ether into a solution of the complex in acetonitrile, show the barium ion is eleven coordinated with all the donor atoms (N_8O_2) of the macrocycle and a monodentate perchlorate completing the coordination. The macrocycle is partially folded to define a molecular cleft with the perchlorate ion coordinating to the barium at the base of this cleft. By comparison with the analogous barium complex of the bibrachial pyridinyl macrocycle **105a** [169], it can be seen that the coordination of this perchlorate causes the cleft to be more open in appearance and both of the tertiary amines are relatively remote from the barium ion. Each furanyldiimine head group is asymmetrically coordinated to barium with one imine nitrogen being more remote than the other; similar pairs are diametrically opposite (Fig. 57c).

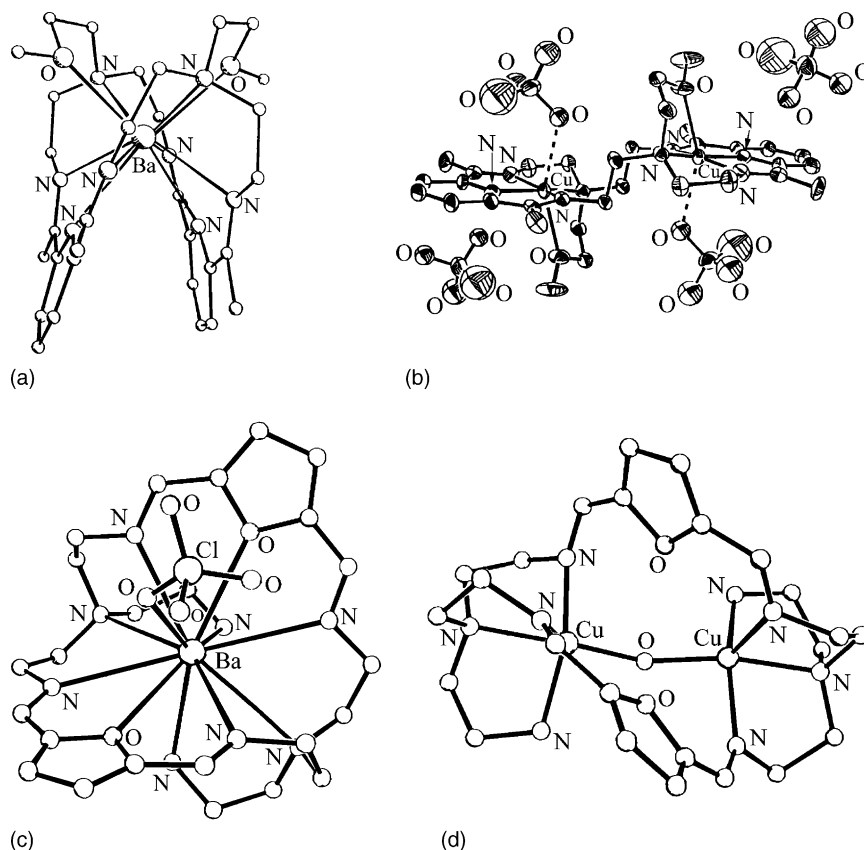
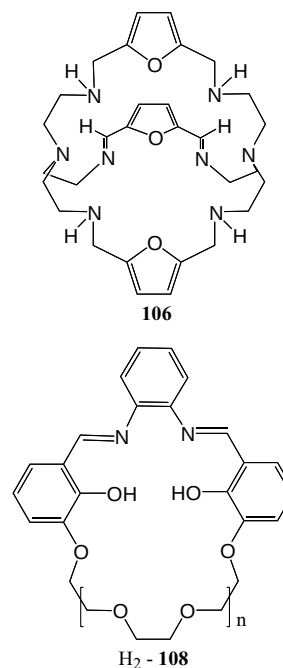


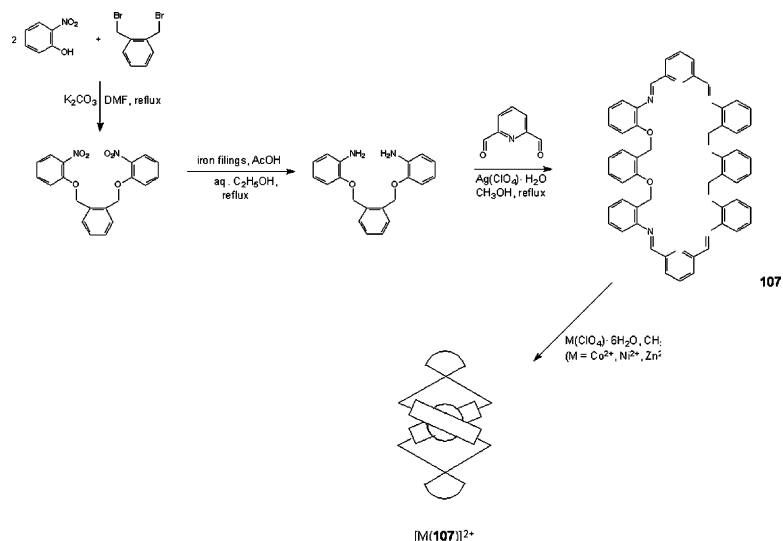
Fig. 57. Structure of $[\text{Ba}(\mathbf{103})]^{2+}$ (a), $[\text{Cu}_2(\mathbf{103})(\text{ClO}_4)_2]$ (b), $[\text{Ba}(\mathbf{105})(\text{ClO}_4)]^+$ (c) and $[\text{Cu}_2(\mathbf{105})(\text{OH})]^{3+}$ (d) (adapted from Refs. [168,169,171]).

A transmetallation reaction occurs when $[\text{Cu}(\text{CH}_3\text{CH})_4](\text{ClO}_4)_2$ is reacted with $[\text{Ba}(\mathbf{105})](\text{ClO}_4)_2$ in methanol. Upon exposure of the resulting solution containing $[\text{Cu}_2(\mathbf{105})](\text{ClO}_4)_2$ to the air, a deep blue colour formed, demonstrating that a redox reaction had taken place and $[\text{Cu}_2(\mathbf{105})(\text{OH})](\text{ClO}_4)_3 \cdot 1.5\text{H}_2\text{O}$ was isolated as deep blue needle-like crystals (Fig. 57d). The structure comprised of two distinct dinuclear macrocyclic units. The two copper(II) ions in each unit are contained within the macrocyclic perimeter and bridged by the oxygen atom of a hydroxide anion. The remainder of the coordination sphere of each copper ion is composed of a tertiary amine nitrogen atoms. The copper coordination polyhedra may be regarded as trigonal bipyramidal with an axial primary amine and imine nitrogen, or as a square-based pyramid with two axial imine nitrogens. The copper...copper separation is 3.742 Å in one unit and 3.736 Å in the other.

The magnetic susceptibility of $[\text{Cu}_2(\mathbf{105})(\text{OH})](\text{ClO}_4)_3 \cdot 1.5\text{H}_2\text{O}$ shows a strong antiferromagnetic interaction ($-2J = 510 \text{ cm}^{-1}$) and the magnetic silence of the compound is confirmed by EPR measurements on the complex as a glass in DMF. The $-2J$ value may be compared with those of 1000 cm^{-1} found for the cryptate complex $[\text{Cu}_2(\mathbf{104})(\text{OH})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ and 865 cm^{-1} found for the related complex $[\text{Cu}_2(\mathbf{106})(\text{OH})](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ in which **106** is the hexamine analogue of **104** [171].



There is also the possibility to transmetallate a dinuclear complex by an appropriate metal salt with the consequent formation of the mononuclear complex where the metal ion adopts a particular configuration. By doing



Scheme 20. Synthesis of Schiff-base macrocyclic helicates.

this synthetic procedure, helicate complexes have been obtained.

A [2+2] cyclocondensation with the formation of the dinuclear silver(I) complex $[\text{Ag}_2(\mathbf{107})]^{2+}$ with the [34]-membered Schiff base **107** has been achieved according to Scheme 20. The transmetalation reaction with $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$) gives rise to the mononuclear helicates $[\text{M}(\mathbf{107})]^{2+}$ [172].

The [2+2] macrocyclic ligand **107** sustains a full double helix in its cobalt(II), nickel(II) and zinc(II) mononuclear complexes (Fig. 58a) and X-ray data confirm that the meridional arrangement of pyridine 2,6-diylidimine units, giving an approximately D_2 metal coordination sphere, acts as a six coordinated nucleus for the development of molecular helicity. The fragment of double helix, initiated by incorporation of such a nucleus in a macrocyclic ligand, is extended by the semi-rigid backbone of the macrocycle, giving a compressed configuration of the inner great ring which corresponds to two helical strands bridged by the methylene carbons. The axis of the double helix, perpendicular to the C_2 axis of the complex, passes through the metal ion and lies close to the bridgehead methylene carbon atoms [172].

The mononuclear complexes $[\text{Co}(\mathbf{107})]^{2+}$, $[\text{Ni}(\mathbf{107})]^{2+}$ and $[\text{Zn}(\mathbf{107})]^{2+}$ are approximately isostructural in the solid state, with the metal ions in very distorted octahedral coordination geometries [172,173].

Both ^1H and ^{13}C NMR spectra of $[\text{Zn}(\mathbf{107})]^{2+}$ in acetonitrile show the complex possesses D_2 symmetry on the NMR timescale. ^1H NMR spectrum of $[\text{Zn}(\mathbf{107})]^{2+}$ at ambient temperature is consistent with the retention of a helically chiral structure for the complex in solution.

^1H and ^{13}C NMR spectra of $[\text{Ag}_2(\mathbf{107})]^{2+}$ in CD_3CN also show resonances corresponding to one quarter of the ligand in the complex. However, while the ^1H NMR methylene subspectrum shows a singlet (A_2) pattern at 298 K, on lowering the temperature it becomes a broad doublet at

253 K before sharpening to resemble a broadened AB multiplet at 233 K. The chemical shift non-equivalence of methylene protons at low temperature is consistent with a chiral structure for $[\text{Ag}_2(\mathbf{107})]^{2+}$, perhaps involving helicity in the macrocyclic ligand, while loss of chirality at higher temperatures corresponds with rapid exchange of metal ions between ligand-coordinated and solvated environments, e.g. $[\text{Ag}(\text{CH}_3\text{CN})_n]^+$ consistent with the lability shown by the disilver complex in transmetalation reactions.

The reaction of α, α' -bis(2-aminophenoxy)-o-xylene with pyridinedicarbaldehyde in the presence of $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ leads to the formation of $[\text{Pb}(\mathbf{107})](\text{ClO}_4)_2$ while $[\text{Cd}(\mathbf{107})](\text{ClO}_4)_2$ was obtained by the transmetalation of $[\text{Ag}_2(\mathbf{107})](\text{ClO}_4)_2$ with a five-fold excess of $\text{Cd}(\text{ClO}_4)_2$ in acetonitrile solution [173].

For $[\text{Cd}(\mathbf{107})](\text{ClO}_4)_2$, metathesis of the anion by an excess aqueous LiSCN yields $\{[\text{Cd}(\mathbf{107})][\text{CdAg}_2(\text{NCS})_6]\}_x$, which is composed by discrete, helically chiral $[\text{Cd}(\mathbf{107})]^{2+}$ cations within an anionic superlattice derived from ribbons of thiocyanate-bridged metals, propagating parallel to the c-axis. The repeat unit of each anionic ribbon comprises two silver(I) ions in S_4 tetrahedral and one cadmium(III) ion in N_6 octahedral coordination environments linked via four μ - and two μ_3 -bridging thiocyanates. In $[\text{Cd}(\mathbf{107})]^{2+}$ the metal ion is coordinated by all the nitrogen donors of the ligand at the center of the double helical array (Fig. 58b). The cadmium coordination geometry is distinctly irregular and although it is best described as distorted octahedral, there appears to be significant interaction with the phenoxy ether donors of the ligand.

In $[\text{Pb}(\mathbf{107})](\text{ClO}_4)_2 \cdot 4\text{CH}_3\text{CN}$ the ligand **107** coordinates to the metal ion in an N_6O_4 environment which encapsulates the metal at the center of its double-helical array and (Fig. 58c) [173].

Despite the considerable differences in metal ion sizes, the lead(II) and cadmium(II) complexes show features in

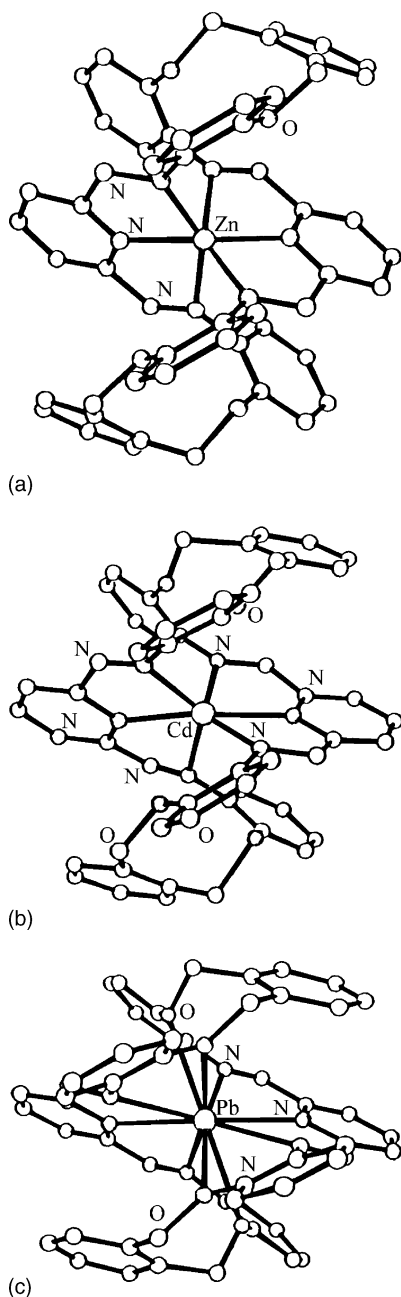


Fig. 58. Structure of $[M(\mathbf{107})]^{2+}$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$), illustrated by $[\text{Zn}(\mathbf{107})]^{2+}$ (a), $[\text{Cd}(\mathbf{107})]^{2+}$ (b) and $[\text{Pb}(\mathbf{107})]^{2+}$ (c). These structures show the compression of the molecular helix on going from $[M(\mathbf{107})]^{2+}$ ($M = \text{Zn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$) to $[\text{Pb}(\mathbf{107})]^{2+}$ (adapted from Refs. [172,173]).

common with the other helicates derived from **107**. The complex cations show idealized two-fold symmetry with the rotation axis lying perpendicular to the helix axis. The double-helical configurations of each complex are stabilized by five intraligand π - π interactions: two iminophenoxy rings lie in offset face-to-face dispositions to one side of each complex, while each pyridyl ring is sandwiched between an *o*-xylene unit and an imino-phenoxy ring. The repetition of these features in complexes of metals of

such different characteristics reiterates the remarkable propensity of **107** for helicate formation.

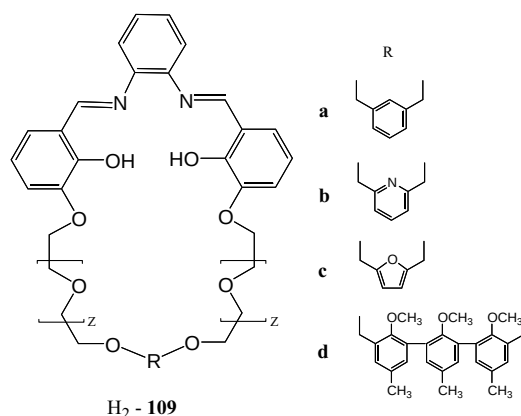
However, while the phenoxy ether donors of **107** are extruded well away from the N_6 metal coordination sphere in $[\text{Zn}(\mathbf{107})]^{2+}$, in $[\text{Pb}(\mathbf{107})]^{2+}$ they effectively swing-in to complete the ten coordinated, N_6O_4 coordination sphere, causing the compression of the double helix. The structure of the cadmium(II) helicate lies between these two extremes with the consequence that its helical pitch lies between that of the other two complexes. The accommodation of ions of different size within the double helical ligand array is analogous to stretching and squashing a spring to, respectively reduce or enlarge its cross-section. Notably, the influence of metal ion size in these systems contrasts with that observed in smaller N_6 macrocyclic complexes, where the pitch of the molecular helix reduces as the ligands wrap more tightly around smaller metal ions. The difference originates in the ambidentate properties of **107** and its ability to enlarge its metal-binding cavity by compressing the double-helical array: in these examples a smooth variation in the secondary structure of the helicate results [173].

When complexes derived from compartmental ligands are employed, the transmetallation reaction can take place also with a change in the coordination chamber for the incoming metal ion. As an example, the reaction of $\text{Ba}(\text{H}_2\text{-}\mathbf{108})(\text{X})_2$ ($\text{X} = \text{ClO}_4^-, \text{CF}_3\text{SO}_3^-, n = 1\text{--}5$) with uranyl(VI) diacetate in refluxing methanol forms the mononuclear uranyl(VI) complexes $[\text{UO}_2(\mathbf{108})(\text{S})]$ ($\text{S} = \text{solvent or neutral monodentate ligands as urea, etc. when present according to the experimental procedure used}$) [174].

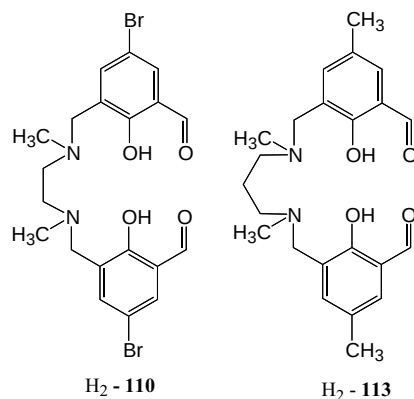
NMR, IR and mass spectra indicate that the uranyl(VI) cation occupies the Schiff base cavity as confirmed by the X-ray structure of uranyl(VI) complex $[\text{UO}_2(\mathbf{108})(\text{urea})]$ ($n = 5$) [174], while in the analogous starting complexes the barium(II) ion is in the polyether coordination chamber. The decomplexation of $\text{Ba}(\text{ClO}_4)_2$ during the complexation of UO_2^{2+} is probably due to the large size of the uranyl(VI) cation. The Ba^{2+} forces the uranyl(VI) ion to coordinate to the Schiff base compartment. The electrostatic repulsion that results from the complexation of UO_2^{2+} causes the decomplexation of the barium ion while the uranyl(VI) ion remains in the Schiff base chamber [174].

This transmetallation and migration reaction is general and a synthetic strategy for the preparation of uranyl(VI) complexes with the ligands $\text{H}_2\text{-}\mathbf{109}$ containing additional groups (i.e. pyridine, furan, xylene) into the crown ether cavity has been reported [174]. For instance the intermediate barium(II) complexes $[\text{Ba}(\text{H}_2\text{-}\mathbf{109b})]^{2+}$ can be reacted with $\text{UO}_2(\text{CH}_3\text{COO})_2$ without prior isolation and purification. Again the X-ray structure of the uranyl(VI) complex $[\text{UO}_2(\mathbf{109b})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ shows that the uranyl(VI) cation is complexed in the Schiff base moiety. The cavity is filled with four water molecules, one of which is coordinated at the fifth position of the uranyl ion. The water molecules are hydrogen bonded to each other and with several of the heteroatoms of the crown ether moiety of the metallo-

macrocycle, including the pyridine nitrogen atom. The encapsulation of water molecules into the cavity of the uranyl(VI) compound demonstrates the potential to complex guest molecules.

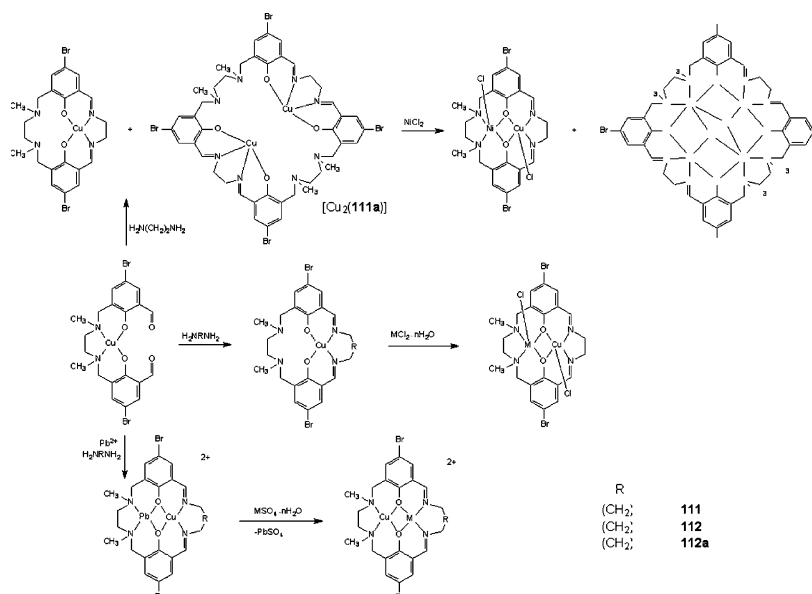
H₂ - 109

A simple or double migration process has been found in the cyclization reaction reported in Scheme 21. The diformyl precursors *N,N'*-dimethyl-*N,N'*-ethylenedi-(5-bromo-3-formyl-2-hydroxybenzylamine) (**H₂-110**), available by the Mannich reaction of 5-bromosalicylaldehyde, *N,N'*-dimethylethylenediamine and formaldehyde in ethanol at the refluxing temperature, reacts with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to form the acyclic complex $[\text{Cu}(\mathbf{110})]$ in an aqueous solution containing potassium hydroxide [175]. $[\text{Cu}(\mathbf{110})]$, when reacted with ethylenediamine in hot DMF, gives the purple complex $[\text{Cu}(\mathbf{111})]$ [175]. A similar reaction with 1,3-diaminopropane or 1,4-tetramethylenediamine in hot methanol gave the cyclic complexes $[\text{Cu}(\mathbf{112})]$ and $[\text{Cu}(\mathbf{112a})]$ [175].

H₂ - 110H₂ - 113

In the acyclic complex $[\text{Cu}(\mathbf{110})]$ the copper(II) ion may be bound at either the $\text{N}(\text{amine})_2\text{O}_2$ site or the O_2O_2 site of the ligand. IR and visible spectra indicate that the copper(II) ion is bound at the $\text{N}(\text{amine})_2\text{O}_2$ site of the acyclic ligand and shifts from the $\text{N}(\text{amine})_2\text{O}_2$ site to the $\text{N}(\text{imine})_2\text{O}_2$ site by the cyclization in the macrocyclic complexes $[\text{Cu}(\mathbf{111})]$, $[\text{Cu}(\mathbf{112})]$ and $[\text{Cu}(\mathbf{112a})]$ (Scheme 21). This is proved by the X-ray structures of $[\text{Cu}(\mathbf{112})]$ and $[\text{Cu}(\mathbf{112a})]$ which demonstrate the formation of macrocyclic complexes with the copper(II) ion at the $\text{N}(\text{imine})_2\text{O}_2$ site. The geometry around the copper(II) ion is essentially planar in both structures. There is a slight distortion of the $\text{Cu}(\text{N}_2\text{O}_2)$ chromophore to tetrahedron (Fig. 59a and b). The trimethylene chain combining the imino nitrogens assumes a chair conformation. The lateral chain involving the amino nitrogens adopts a deformed conformation. The asymmetric nitrogens have *S*- and *R*-configuration, respectively.

$[\text{Cu}(\mathbf{111})]$, $[\text{Cu}(\mathbf{112})]$ and $[\text{Cu}(\mathbf{112a})]$ can incorporate a second metal ion at the $\text{N}(\text{amine})_2\text{O}_2$ site to form the



Scheme 21.

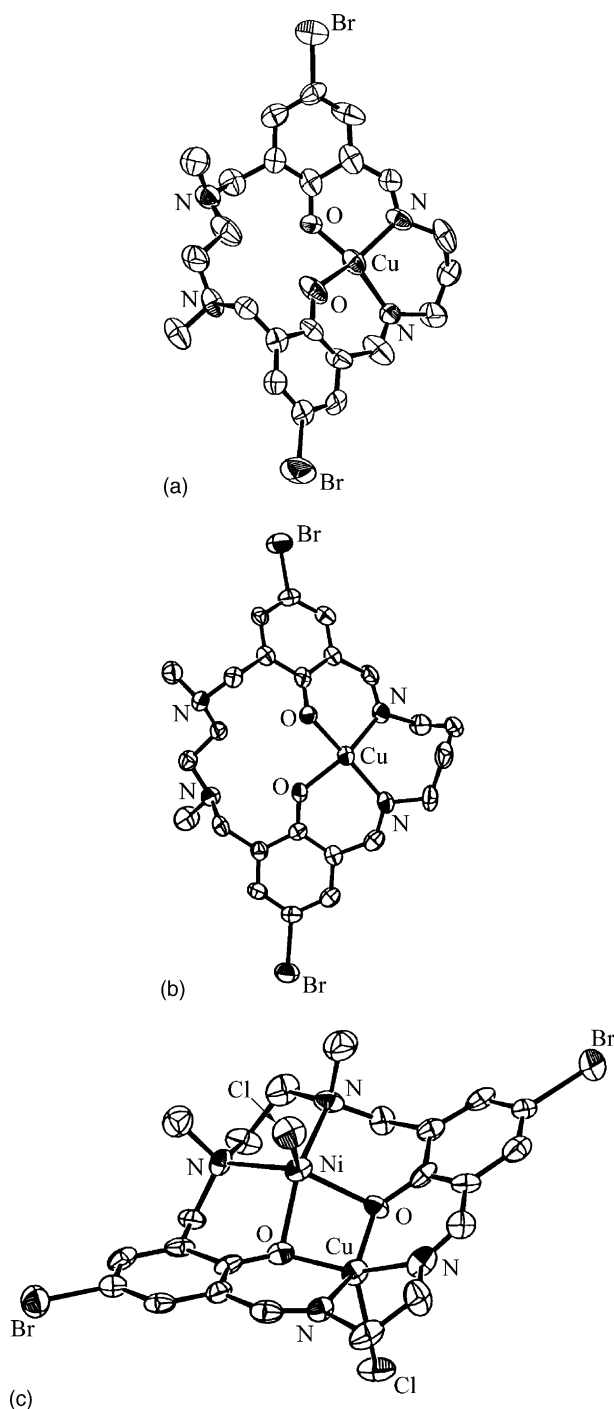


Fig. 59. Structure of [Cu(112)] (a), [Cu(112a)] (b) and [NiCu(111)(Cl)₂] (c) (adapted from Ref. [175]).

homo- and hetero-dinuclear complexes $\text{CuM}(\text{L})(\text{X})_2$ ($\text{L} = \mathbf{111}^{2-}$, $\mathbf{112}^{2-}$, $\mathbf{112a}^{2-}$; $\text{M} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} ; $\text{X} = \text{Cl}^-$, ClO_4^- , etc.). $\text{CuM}(\mathbf{111})(\text{X})_2$ are rather unstable in solution, whereas $\text{CuM}(\mathbf{112})(\text{X})_2$ are stable in DMF and DMSO and can be reduced to the corresponding $\text{Cu}^{\text{I}}\text{M}^{\text{II}}$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+}) and $\text{Cu}^{\text{I}}\text{M}^{\text{I}}$ ($\text{M} = \text{Co}^+$, Ni^+ , Cu^+) complexes which are significantly stable in solution [175].

The structure of $[\text{NiCu}(\mathbf{111})(\text{Cl})_2]$ demonstrates that the copper(II) ion resides in the original iminic site and the nickel(II) ion in the aminic site. The $\text{Ni} \cdots \text{Cu}$ intermetallic separation bridged by the phenolic oxygens is 2.975 Å. Both copper(II) and nickel(II) ions have a five coordinated square pyramidal geometry with a chloride ion at the apex. These two chloride ligands are situated *trans* to each other with respect to the mean molecular plane [175] (Fig. 59c).

The [4+4] macrocycle $\text{H}_2\text{-111a}$ was originally obtained as a by-product in the cyclization of *N,N'*-dimethyl-*N,N'*-ethylenebis(2-aminomethyl-4-bromo-6-formylphenolato)-copper(II), $[\text{Cu}(\mathbf{110})]$, with ethylene diamine (Scheme 21). A solution of 1,2-diaminoethane in methanol, added dropwise to a hot dimethylformamide solution of $[\text{Cu}(\mathbf{110})]$, gives a mixture of $[\text{Cu}(\mathbf{111})]$ and $[\text{Cu}_2(\mathbf{111a})]$. The separation of these two products by fractional crystallization was difficult owing to the very low solubility of the two complexes in organic solvents. The mixture of the complexes was treated with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in methanol to form the $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ complex, $[\text{CuNi}(\mathbf{111})(\text{Cl})_2] \cdot 0.5\text{H}_2\text{O}$, as dark green microcrystals. After removal of this CuNi complex, the solution by diffusion into diethyl ether separated brown crystals of the mixed-metal tetranuclear $\text{Cu}^{\text{II}}_2\text{Ni}^{\text{II}}_2$ complex, $[\text{Cu}_2\text{Ni}_2(\mathbf{111a})(\text{Cl})_2](\text{Cl})_2 \cdot \text{H}_2\text{O}$. FAB mass spectrometry showed signals centered at m/z 1422 and 1387 which are assigned to $\{\text{Cu}_2\text{Ni}_2(\mathbf{111a})(\text{Cl})_3\}^+$ and $\{\text{Cu}_2\text{Ni}_2(\mathbf{111a})(\text{Cl})_2\}^{2+}$, respectively [175].

More recently it was found that $[\text{Cu}(\mathbf{110})]$ reacts with a large excess of ethylenediamine under acid conditions with perchloric acid forming quantitatively $[\text{Cu}_2(\text{H}_2\text{-111a})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ [175]. A mechanism was proposed where the [2+1] acyclic copper(II) complex $[\text{Cu}(\mathbf{110a})]$ was obtained in equilibrium with $[\text{Cu}(\mathbf{110})]$; the further condensation of the two acyclic diformyl and diamino complexes, followed by an migration of the metal ion leads to the formation of $[\text{Cu}_2(\text{H}_2\text{-111a})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. In $[\text{Cu}_2(\text{H}_2\text{-111a})](\text{ClO}_4)_2$ the two copper(II) ions reside in the iminic sites of the macrocyclic ligand, affording a $\{\text{CuN}_2\text{O}_2\}$ chromophore. Two protons exist in the two aminic sites and hydrogen-bonded between the two amine nitrogens. Because of these hydrogen bonds, the complex molecule assumes a U shape with a near-parallel arrangement of the two $\{\text{CuN}_2\text{O}_2\}$ moieties (Fig. 60a) [175].

The mixed complexes $[\text{Cu}_2\text{M}_2(\mathbf{111a})(\text{Cl})_4]$ ($\text{M} = \text{Ni}^{2+}$, Co^{2+} , Zn^{2+}) were obtained by reaction of $[\text{Cu}_2(\text{H}_2\text{-111a})](\text{ClO}_4)_2$ with the appropriate metal chloride in acetonitrile [175].

The structure of the $\text{Cu}^{\text{II}}_2\text{Ni}^{\text{II}}_2$ complex shows each copper(II) ion resides in the $\text{N}(\text{imine})_2\text{O}_2$ site and each nickel(II) resides in the $\text{N}(\text{amine})_2\text{O}_2$ site in the cyclization process. The copper adopts a square pyramidal geometry with a chloride ion at the axial site. The nickel(II) ion has a near octahedral geometry together with two chloride ions in *cis* position. The two chloride ions are involved in a μ_3 -bridge to one copper and one nickel of one dinuclear entity

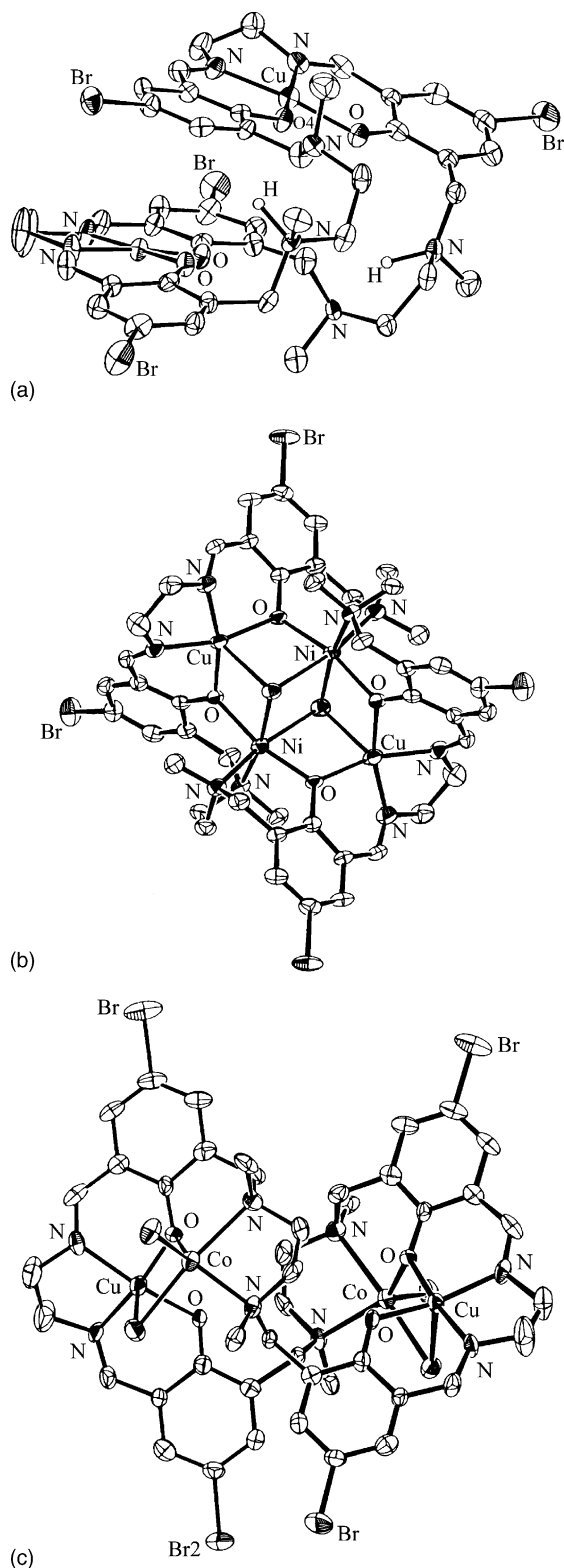


Fig. 60. Structure of $[\text{Cu}_2(\text{H}_2\text{-111a})]^{2+}$ (a), $[\text{Cu}_2\text{Ni}_2(\text{111a})(\text{Cl})_2]^{2+}$ (b) and $[\text{Cu}_2\text{Co}_2(\text{111a})(\text{Cl})_4]$ (c) (adapted from Ref. [175]).

and to one nickel of the other dinuclear entity. The $\text{Cu} \cdots \text{Ni}$ separations range from 3.366 to 3.375 Å. The asymmetric nitrogens have *R*- and *S*-configurations, respectively (Fig. 60b) [175].

The Cu_2Co_2 and Cu_2Zn_2 complexes are isostructural. In $[\text{Cu}_2\text{Co}_2(\text{111a})(\text{Cl})_4] \cdot 2\text{H}_2\text{O} \cdot 2\text{CHCl}_3$ each copper(II) ion resides in the iminic site and has a five coordinate geometry with a chloride ion at the apical position; the chloride ion is involved in the bridge to the adjacent cobalt(II) ion. The displacement of the copper from the basal N_2O_2 least-squares plane toward the apical chloride is 0.123 Å. The cobalt(II) ion is bonded to the phenolic oxygen, the amino nitrogens, the bridging chloride ion and the terminal chloride ion. The geometry about the cobalt(II) ion is intermediate between a square pyramid and a trigonal bipyramid. The $\text{Cu} \cdots \text{Co}$ interatomic separation, bridged by the phenolic oxygen and the chloride ion is 3.272 Å. The two CuCo units in the molecule are separated from one another, providing a dimer-of-dimers structure. The intermetallic $\text{Cu} \cdots \text{Co}$, $\text{Cu} \cdots \text{Cu}$ and $\text{Co} \cdots \text{Co}$ separations are 6.847 Å, 8.000 and 7.119 Å, respectively (Fig. 60c). In the isostructural Cu_2Zn_2 complex for the $\text{Cu} \cdots \text{Zn}$ separation is 3.333 Å, while the intermetallic $\text{Cu} \cdots \text{Zn}$, $\text{Cu} \cdots \text{Cu}$ and $\text{Zn} \cdots \text{Zn}$ separations are 6.899, 7.993 and 7.271 Å, respectively [175].

The magnetic moment of the Cu_2Zn_2 complex, $1.81\mu_{\text{B}}$ per Cu at room temperature, is independent of temperature down to 2 K ($1.79\mu_{\text{B}}$), indicating that the magnetic interaction between the two CuZn units in a molecule is negligibly weak [175]. Cryomagnetic studies for the Cu_2Co_2 complex indicate an antiferromagnetic spin-exchange interaction within each dinuclear $\text{Cu}^{\text{II}}\text{Co}^{\text{II}}$ unit ($J = -9.5 \text{ cm}^{-1}$).

The $\text{Cu}^{\text{II}}_2\text{Ni}^{\text{II}}_2$ complex has a magnetic moment of $5.03\mu_{\text{B}}$ (per Cu_2Ni_2) at room temperature, which decreased with decreasing temperature to a plateau value of $3.3\mu_{\text{B}}$ around 30 K before decreasing to $2.72\mu_{\text{B}}$ at 2 K. On the basis of the crystallographic results, a spin system with 4 equiv. Cu-Ni interactions (J) and one Ni-Ni interaction (J') was considered; the magnetic interaction between the copper ions, 5.735 Å apart, can be neglected. A weak antiferromagnetic interaction between the adjacent copper(II) and nickel(II) ions (-3.5 cm^{-1}) and a weak ferromagnetic interaction between the two nickel(II) ions ($+2.0 \text{ cm}^{-1}$) was found [175].

Moreover, as reported in Scheme 21, a double migration and transmetalation process was observed. X-ray crystallography has established the migration of the copper(II) ion from the $\text{N}(\text{imine})_2\text{O}_2$ site in the CuPb complex to the $\text{N}(\text{amine})_2\text{O}_2$ site in the CuZn complex. The driving force in the initial reaction involving copper(II) and lead(II) ions may be related to the nature of the donor compartments. The copper(II) ion migrates to occupy the relatively rigid $\text{N}(\text{imine})_2\text{O}_2$ site, which provides the more preferred square coplanar environment, and the larger $\text{Pb}(\text{II})$ is then accommodated in the more flexible $\text{N}(\text{amine})_2\text{O}_2$ site. The site selectivity observed in the CuZn complex shows that a reversal of the migratory transmetalation has occurred with the copper(II) ion reverting to the $\text{N}(\text{imine})_2\text{O}_2$ site, which is the smaller copper(II) ion and the $\text{N}(\text{imine})_2\text{O}_2$ site accommodates the larger zinc(II) ion.

The $\text{N}(\text{imine})_2\text{O}_2$ site is also the more flexible and so able to accommodate any distortions imposed at the copper(II)

ion by the Jahn-Teller effect. Similarly, for the other hetero-dinuclear complexes, the copper(II) ion always occupies the N(amine)₂O₂ site and the second metal(II) ion at the N(imine)₂O₂ site.

The reaction of [Cu(**110**)] with 1,3-diaminopropane in the presence of lead(II) perchlorate trihydrate forms [CuPb(**112**)](ClO₄)₂ [176].

The X-ray structure of the analogous benzoate complex [CuPb(**112**)(C₆H₅COO)(DMF)](ClO₄) (Fig. 61a) shows the copper(II) ion resides at the N(imine)₂O₂ site and the lead(II) ion at the N(amine)₂O₂ site, demonstrating that a migratory transmetallation has occurred and that the copper(II) ion is shifted from the N(amine)₂O₂ site to the N(imine)₂O₂ site of the macrocycle in the cyclization process. The two metal ions are bridged by the phenolic oxygens with an intermetallic separation of 3.466 Å. The CuN₂O₂ chromophore involving the aromatic moieties is nearly coplanar. The lead(II) ion at the N(amine)₂O₂ site is significantly deviated from the least-squares N(amine)₂O₂ plane and assumes a seven coordinate geometry together with the bidentate benzoate oxygens and a DMF oxygen. The amino nitrogens have the *R*- and *S*-configuration, respectively, as found for [Cu(**112**)]; the two methyl groups attached to the nitrogen atoms are *cis* to each other. The trimethylene later chain assumes the chair conformation [176].

[CuPb(**112**)](ClO₄)₂ is a good precursor for the formation of the hetero-dinuclear Cu^{II}M^{II} complexes [CuM(**112**)](ClO₄)₂ (M = Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺). The transmetallation of the lead(II) ion for a transition metal(II) ion

has been successfully achieved by the reaction of [CuPb(**112**)](ClO₄)₂ with a metal(II) sulphate salt in acetonitrile. In this reaction the lead(II) ion is eliminated from the reaction mixture as insoluble PbSO₄. In the presence of Na(CH₃COO)·3H₂O, [CuM(**112**)(CH₃COO)](ClO₄) is obtained. In [CuZn(**112**)(CH₃COO)](ClO₄) the copper(II) ion resides at the N(amine)₂O₂ site. The two metal ions are bridged by the two phenolic oxygens and the acetate group, providing a five coordinate geometry for both metal ions. The Cu(N₂O₃) and Zn(N₂O₂) sites are close to square pyramidal. The Cu···Zn separation is 2.942 Å (Fig. 61b). When the formation of hetero-dinuclear complexes is carried out by using a step by step reaction, no migration has been observed. Thus the dinuclear Cu^{II}M^{II} complexes [CuM(**112**)(Cl)₂] (M = Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) have been obtained by reacting [Cu(**112**)] with the appropriate metal(II) chloride in methanol [176].

In [CuNi(**112**)(Cl)₂].CH₃OH (Fig. 61c) and [CuZn(**112**)(Cl)₂].CH₃OH, the copper(II) ion resides in the original iminic site and the nickel(II) or zinc(II) ion reside in the aminic site. The Cu···Ni and Cu···Zn intermetallic separations, bridged by the phenolic oxygens, are 3.008 and 3.135 Å, respectively. In each complex the two metal ions have a five coordinated square pyramidal geometry with further coordination by chloride ion at the apex; the methanol molecule is free from coordination and captured in the crystal lattice [177].

The structure of [CuNi(**111**)(DMF)](ClO₄)₂·CH₃OH, also prepared by transmetallation of [PbCu(**111**)](ClO₄)₂ with

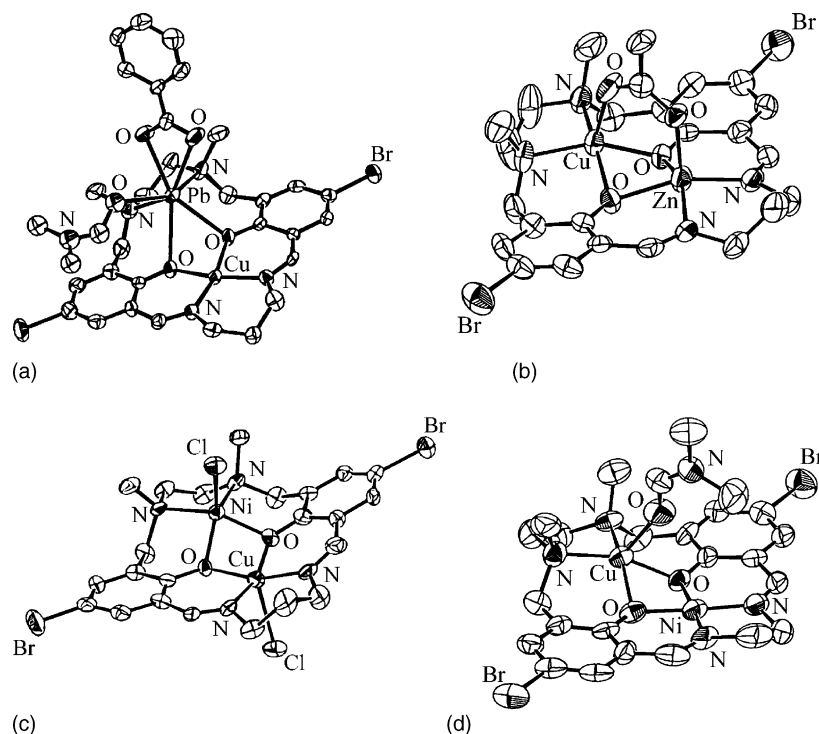


Fig. 61. Structure of [CuPb(**112**)(C₆H₅COO)(DMF)]⁺ (a) [CuZn(**112**)(CH₃COO)]⁺ (b), [CuNi(**112**)(Cl)₂] (c), and [CuNi(**111**)(DMF)]²⁺ (d) (adapted from Ref. [176]).

nickel(II) perchlorate, demonstrates the migration of the copper(II) ion from the iminic site to the aminic one and the accommodation of the nickel(II) ion in the iminic site. The cation is comprised of $[\mathbf{111}]^{2-}$, one copper(II) ion, one nickel(II) ion, and one DMF molecule. The $\text{Cu} \cdots \text{Ni}$ inter-metallic separation bridged by the phenolic oxygens is 2.836 Å. The copper(II) ion has a square pyramidal geometry with a DMF oxygen at the apex while the nickel(II) ion is square planar [177] (Fig. 61d).

N,N' -Dimethyl- N,N' -trimethylenedi(5-methyl-3-formyl-2-hydroxybenzylamine)(H_2 -**113**), prepared by reaction of N,N' -dimethyl-1,3-propanediamine and 3-chloromethylsalicylaldehyde in the presence of triethylamine, always formed $[\text{Cu}_2(\mathbf{113})(\text{ClO}_4)_2]$ even when syntheses were attempted in the stoichiometry of H_2 -**113**/ $\text{Cu}^{2+} = 1/1$ [177]. In the DMF adduct $[\text{Cu}_2(\mathbf{113})(\text{DMF})_2](\text{ClO}_4)_2$ (Fig. 62a), $[\mathbf{113}]^{2-}$ accommodates two copper(II) ions, 3.040 Å apart, in its N_2O_2 and O_2O_2 sites. The geometry regarding the copper(II) ion in the N_2O_2 site is a square pyramid with a DMF oxygen at the axial site. This metal ion is displaced by 0.160 Å from the basal N_2O_2 least-squares plane towards the dimethylformamide oxygen. The copper ion in the O_2O_2 site also has a square pyramidal geometry together with a DMF oxygen at the axial site. It is displaced from the basal plane of 0.51 Å toward the DMF oxygen. The DMF molecules bound to the two copper(II) ions are situated *cis* with respect to the mean molecular plane [177].

The cyclization of $[\text{Cu}_2(\mathbf{113})(\text{ClO}_4)_2]$ with different diamines formed the macrocyclic dinuclear copper(II) complexes $[\text{Cu}_2(\text{L})](\text{ClO}_4)_2 \cdot n\text{S}$ (H_2 -**L** = H_2 -**114a** ··· H_2 -**114e**; $\text{S} = \text{CH}_3\text{CN}$, CH_3OH , H_2O ; $n = 1, 2$) as confirmed by the X-ray structure of $[\text{Cu}_2(\mathbf{114a})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ and $[\text{Cu}_2(\mathbf{114a})](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ [177]. In $[\text{Cu}_2(\mathbf{114a})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (Fig. 62b) the copper(II) ion in the $\text{N}(\text{amine})_2\text{O}_2$ site has a square pyramidal geometry together with the water oxygen at the axial site. The deviation of this metal ion from the basal least-squares plane toward the water oxygen is 0.211 Å. The copper(II) ion in the $\text{N}(\text{imine})_2\text{O}_2$ has a planar geometry. The $\text{Cu} \cdots \text{Cu}$ separation is 2.989 Å.

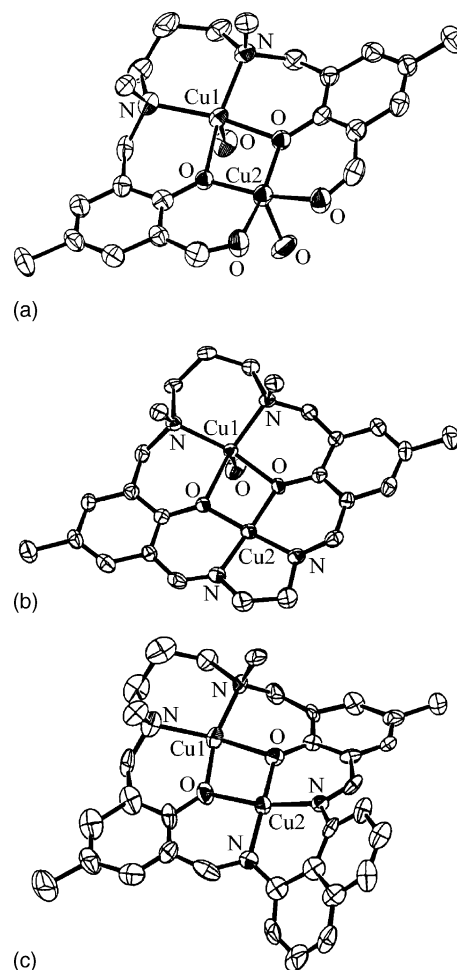
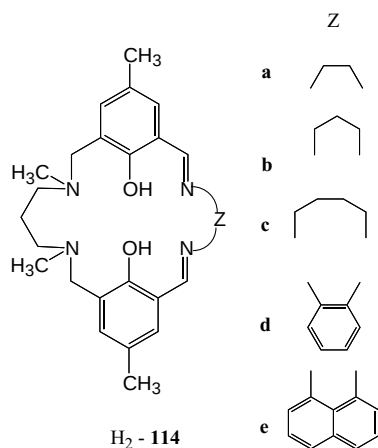


Fig. 62. Structure of $[\text{Cu}_2(\mathbf{113})(\text{DMF})_2]^{2+}$ (a), $[\text{Cu}_2(\mathbf{114a})(\text{H}_2\text{O})]^{2+}$ (b) and $[\text{Cu}_2(\mathbf{114e})]^{2+}$ (c) (adapted from Ref. [177]).

In $[\text{Cu}_2(\mathbf{114e})(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$ the copper(II) ion in the aminic site assumes a nearly planar geometry. The geometry about the copper(II) ion in the iminic site shows a large distortion to tetrahedron [177] (Fig. 62c).

The acyclic $[\text{Cu}_2(\mathbf{113})(\text{ClO}_4)_2]$ and the macrocyclic complexes $[\text{Cu}_2(\mathbf{114a-e})(\text{ClO}_4)_2]$ show a strong antiferromagnetic behaviour, with J values ranging from -252 to -354 cm^{-1} [177].

The macrocyclic complexes can suffer a site selective copper demetallation with the consequent conversion into the mononuclear copper(II) analogues when treated with Na_2S in acetonitrile [177]. The obtained mononuclear complexes can encapsulate NaClO_4 into the aminic site; the final products are $[\text{Cu}(\mathbf{114a})] \cdot 0.8\text{NaClO}_4$, $[\text{Cu}(\mathbf{114b})]$, $[\text{Cu}(\mathbf{114c})] \cdot \text{NaClO}_4$, $[\text{Cu}(\mathbf{114d})]$ and $[\text{Cu}(\mathbf{114e})] \cdot 2.1\text{NaClO}_4$ as confirmed by X-ray structural investigations [177]. Thus in $[\text{Cu}(\mathbf{114b})]$ the copper(II) ion in the aminic site is eliminated while the copper(II) ion in the iminic site has a pseudo tetrahedral geometry (Fig. 63a) [177]. Also in $[\text{CuNa}(\mathbf{114c})(\text{ClO}_4)]$ the copper(II) ion in the aminic site is eliminated and the sodium ion is accommodated in this site (Fig. 63b). The sodium ion has a distorted six coordinated



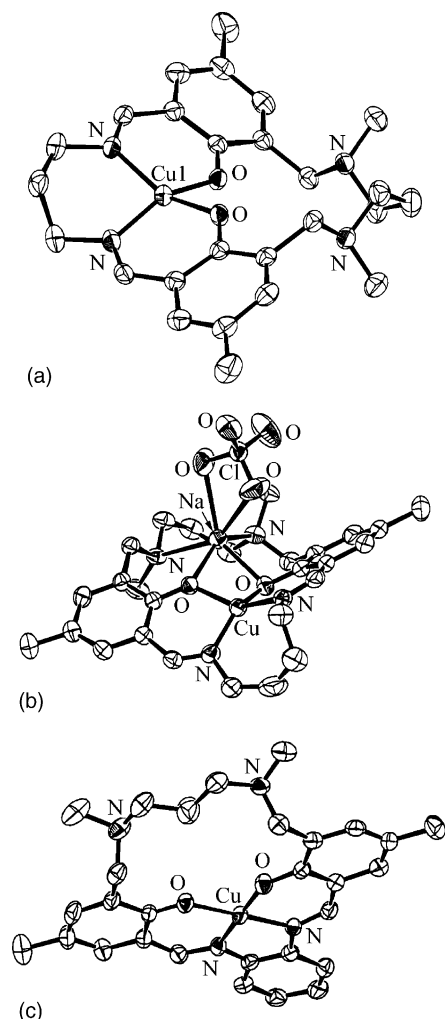
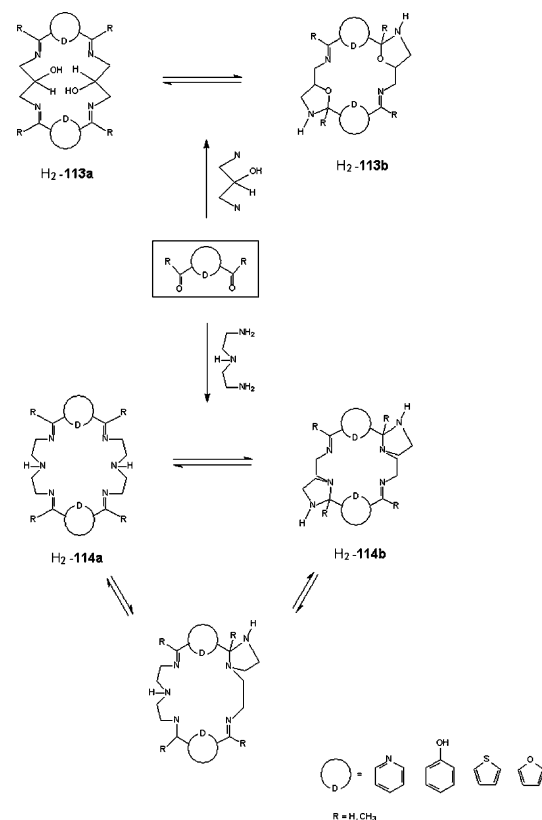


Fig. 63. Structure of [Cu(**114b**)] (a), [CuNa(**114c**)(ClO₄)] (b) and [Cu(**114d**)] (c) (adapted from Ref. [177]).

environment together with a chelating perchlorate group. The geometry about the copper(II) ion in the iminic site is significantly distorted to tetrahedron. The Cu...Na interatomic distance is 3.040 Å: it appears that the aminic site of [CuNa(**114c**)(ClO₄)] has a flexibility for accommodating Na⁺ owing to the elongation in the lateral chain in the iminic site. Finally the structure of [Cu(**114d**)] again demonstrates the selective elimination of the copper(II) ion from the aminic site. The copper(II) ion bound to the iminic site has an essentially planar geometry. The vacant aminic site is expanded so as to reduce a strain within the macrocyclic framework. The molecule except for the -(CH₃)N-(CH₂)₃-N(CH₃)- part in the aminic site forms a good coplanarity [177] (Fig. 63c).

2.4. Ring contraction and ring expansion

A ring contraction of the macrocyclic cavity of Schiff bases, often leading to a stabilization of metal-free ligands, has been observed when there is a functional group (=NH or -OH) available for addition to the imine bond and/or there is



Scheme 22.

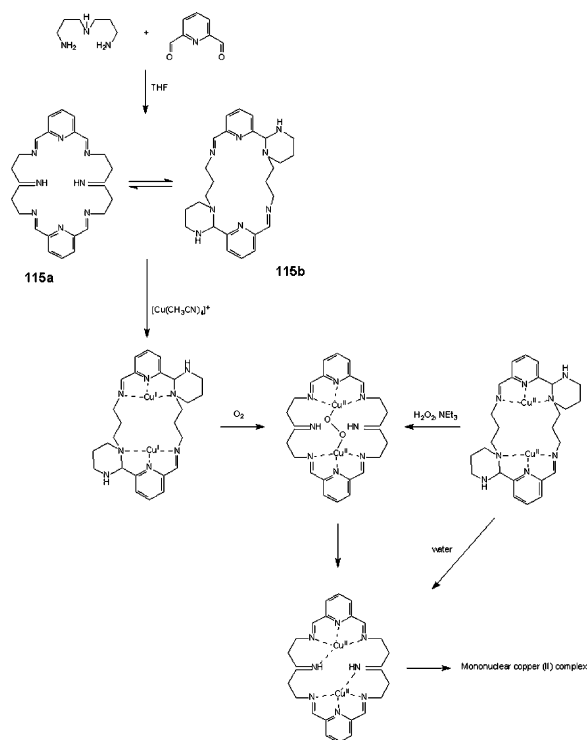
a metal ion too small for the macrocyclic cavity. In this second case the ring contraction causes a smaller, more accommodating cavity for the available metal.

The cyclization reaction of Scheme 22 readily occurs when equimolar amounts of the precursors are reacted in methanol. IR, NMR, mass spectrometry and X-ray diffraction confirm that in the solid state the macrocycles are in the contracted form, while in solution a series of isomers was observed. Moreover, the presence of particular metal ions favours the formation of complexes where the ligand is in the expanded form while other metal ions favour the coordination of the macrocycle in the contracted form [178].

The condensation of pyridine 2,6-dicarbaldehyde with 1,7-diamino-4-azapentane gives rise to the related [2+2] cyclic Schiff base in the [20]-membered contracted form **115b** (Scheme 23) as ascertained by the X-ray structure (Fig. 64a) [179].

This macrocycle reacts with [Cu(CH₃CN)₄](X) (X = ClO₄⁻, PF₆⁻) in CH₃CN/CH₃OH to produce [Cu₂(**115b**)]-(ClO₄)₂, possibly maintaining its contracted form upon coordination [179].

[Cu₂(**115b**)](ClO₄)₂ reacts with O₂ at room temperature and above but not at a low temperature producing an oxygenated intermediate which is gradually converted into a mononuclear complex. During these oxidation processes a conformational rearrangement of the macrocycle from **115b**



Scheme 23.

to **115a** occurs; it is responsible for the slow oxidation of substrates with the copper(I) complex in the presence of O_2 (Scheme 23) [179].

The dicopper(II) complexes, where the ligands are in the ring contracted form, were prepared by reaction of **115b** with CuCl_2 and $\text{Cu}(\text{ClO}_4)_2$. These compounds suffer a conformational conversion into the expanded analogues by the presence of water.

The direct synthesis of the [2+2] metal-free ligand **116** was carried out by cyclo-condensation of thiophene-2,5-dicarbaldehyde with 1,4,7-triazaheptane. The thiophene-containing macrocycle has been shown to exist in solution as a mixture of the [24]-membered ring tetraimine Schiff base **116a** with the corresponding [18]-membered ring-contracted imidazolidinyl isomer **116b** and it is probable that there is an equilibrium between the isomeric forms as was considered for the furan-, pyridine- or phenol-analogue [178].

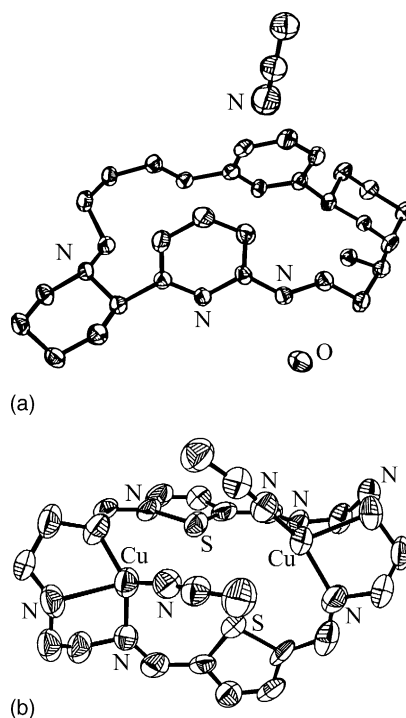
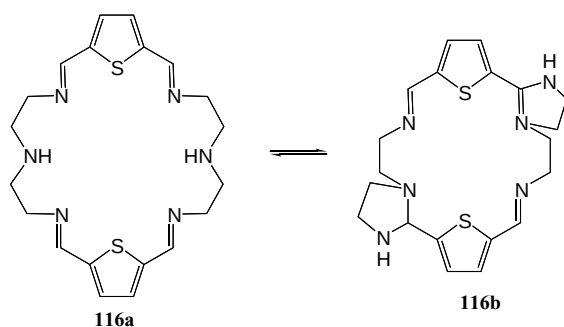


Fig. 64. Structure of **115a** (a) and $[\text{Cu}_2(\text{116a})(\text{CH}_3\text{CN})_2]^{2+}$ (b) (adapted from Refs. [178,179]).

This [2+2] macrocycle reacts with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{BF}_4)$ in anhydrous methanol and under nitrogen to give rise to $[\text{Cu}_2(\text{116a})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$, where each copper(I) ion is in an approximately tetrahedral environment, coordinating to one tertiary amino- and two imino-nitrogen donor atoms originating from the fully expanded macrocyclic ring and with the nitrogen atom from an acetonitrile molecule occupying the fourth coordination site of the copper ion. The thiophene head unit is not involved in coordination, serving as an inert spacer, and so each copper(I) ion is coordinated in a side-on fashion to the lateral units within the macrocycle (Fig. 64b) [179]. The macrocycle displays a fairly twisted arrangement but has folded to present a conformation typical of a molecular cleft, consequently there is a large $\text{Cu} \cdots \text{Cu}$ separation (5.248 Å). The coordinated acetonitrile molecules are directed away from each other due to steric repulsion and their presence helps to restrict the opportunity for the macrocyclic complex to adopt a folded conformation.

The ^1H NMR spectrum of $[\text{Cu}_2(\text{116a})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ gave only one set of signals due to tetraimine macrocycle of the copper complex and so differed significantly from the spectrum of the free macrocycle in which evidence for the presence of the contracted form was noted. It is therefore possible to speculate that in the formation of the complexes, copper(I) reacts preferentially with the ring-expanded form of the macrocycle, thus displacing the isomeric equilibrium in that direction.

Ring expansion and ring contraction have also been observed when no $-\text{NH}$ or $-\text{OH}$ groups are present. Thus

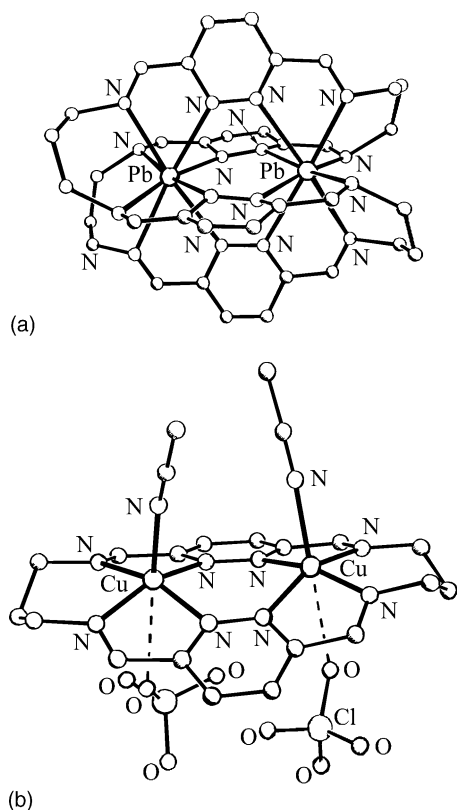


Fig. 65. Structure of $[\text{Pb}_2(\mathbf{12b})]^{2+}$ (a) and $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ (b) (adapted from Refs. [181,182]).

it is possible that there is a ring contraction from a [4+4] to a [2+2] macrocycle. The reaction of 3,6-diformylpyridazine and 1,3-diaminopropane in the presence of lead(II) perchlorate, in dry methanol/acetonitrile at room temperature, yields $[\text{Pb}_2(\mathbf{12b})](\text{ClO}_4)_4$, [180]. The structure analysis reveals that this is a dilead(II) complex of the [4+4] macrocycle (Fig. 65a). The two lead ions lie on the intersection of two mirror planes. They have crystallographically identical coordination environments; each is bound to four pyridazine and four imine nitrogen atoms. The pyridazine head units chelate the two metal ions. The [4+4] macrocycle wraps quite tightly around the two lead ions.

The transmetallation reaction of $[\text{Pb}_2(\mathbf{12b})](\text{ClO}_4)_2$ with $\text{Cu}(\text{ClO}_4)_2$ in acetonitrile forms the dinuclear complex $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ [181]. The FAB mass spectrum shows a cluster of peaks consistent with the presence of $[\text{Cu}_2(\mathbf{12a})(\text{ClO}_4)_2]^+$, thus indicating that the original [4+4] Schiff-base macrocycle had contracted to a [2+2] macrocycle. This ring contraction was confirmed by the X-ray structure of $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ (Fig. 65b) [181]. The two halves of the macrocycle are related by a two-fold rotation axis. The copper(II) ions have distorted square pyramidal geometries: the basal plane consists of two bridging pyridazine nitrogen donors and two imine nitrogen donors, and the copper ions lie 0.317 Å out of this plane towards the apical acetonitrile molecule. A perchlorate ion sits below the remaining face of the macrocyclic complex

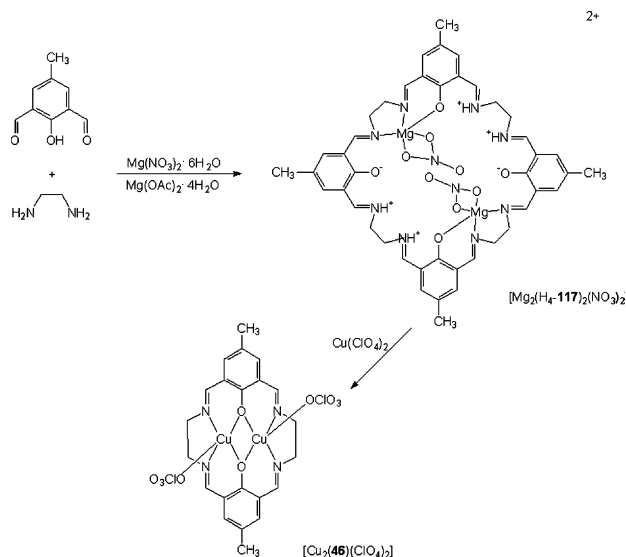
and a weak interaction between an oxygen atom and the copper(II) ion is observed. The macrocycle is fairly flat. The two copper(II) ions are strongly antiferromagnetically coupled ($J = -241 \text{ cm}^{-1}$).

Cyclic voltammetry on $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ in dry CH_3CN revealed two well separated one-electron reduction waves ($E_{1/2} = 0.10 \text{ V}$ and $E_{1/2} = 0.43 \text{ V}$) associated with $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ to $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ to $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ reductions, respectively. Both redox processes are fully reversible. The mixed valence species is reasonably stable ($K_{\text{con}} = 3.8 \times 10^5$).

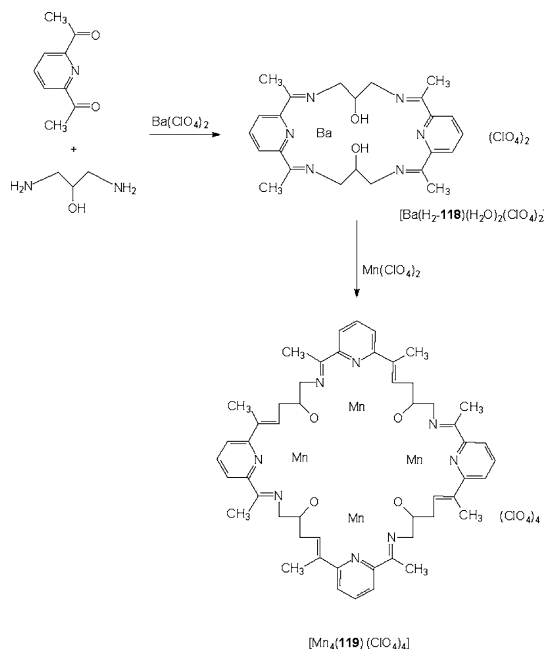
Also the [4+4] macrocyclic magnesium compound $[\text{Mg}_2(\text{H}_4\text{-}\mathbf{117})_2(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, derived from the template reaction involving 4-methyl-2,6-diformylphenol, 1,2-diaminoethane, magnesium acetate and magnesium nitrate, transmetallates with copper(II) perchlorate in the presence of triethylamine originating the [2+2] dinuclear copper(II) complex $[\text{Cu}_2(\mathbf{46})(\text{ClO}_4)_2]$ where the ligand $\text{H}_2\text{-}\mathbf{46}$ is the [2+2] cyclized derivative of 4-methyl-2,6-diformylphenol and 1,2-diaminoethane (Scheme 24) [182]. The reaction between $[\text{Mg}_2(\text{H}_4\text{-}\mathbf{117})_2(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and copper(II) perchlorate in absence of triethylamine affords the copper-deficient species $[\text{Cu}_{1.47}(\text{H}_{1.06}\text{-}\mathbf{46})(\text{ClO}_4)_2]$.

$[\text{Cu}_2(\mathbf{46})(\text{ClO}_4)_2]$ has a centrosymmetric structure with the center of inversion at the middle of the Cu_2O_2 plane. The two square pyramidal copper centers are bridged by the two phenoxide oxygen atoms, and the CuN_2O_2 plane is completed by the two imine nitrogens. The perchlorate ions are transaxially bound above and below the dinuclear centers. The macrocyclic ligand adopts roughly a planar structure in which the two phenyl rings are parallel [182].

The structure of $[\text{Cu}_{1.47}(\text{H}_{1.06}\text{-}\mathbf{46})(\text{ClO}_4)_2]$ shows small but significant differences from those of $[\text{Cu}_2(\mathbf{46})(\text{ClO}_4)_2]$ as the perchlorate ion in its asymmetric unit is distorted over two sites. The metal deficiency in this compound seems to



Scheme 24.



Scheme 25.

arise from a statistical distribution of the diprotonated mononuclear macrocyclic complex $[\text{Cu}(\text{H}_2\text{-46})](\text{ClO}_4)$ and the dinuclear complex $[\text{Cu}_2(\text{46})(\text{ClO}_4)_2]$. The fact that $[\text{Cu}_2(\text{46})(\text{ClO}_4)_2]$ can be isolated by boiling $[\text{Cu}_{1.47}(\text{H}_{1.06}\text{-46})(\text{ClO}_4)_2]$ with water provides support to this view [182].

It is also possible a ring expansion from a [2+2] to a [4+4] macrocycle. The [4+4] macrocyclic tetranuclear manganese(II) complex, $[\text{Mn}_4(\text{119})(\text{ClO}_4)_4]$ has been synthesized by transmetallation reaction by $\text{Mn}(\text{ClO}_4)_2$ of the [2+2] cyclic mononuclear barium(II) complex $[\text{Ba}(\text{H}_2\text{-118})(\text{H}_2\text{O})_2 \cdot (\text{ClO}_4)_2]$, derived from the condensation of 1,3-diamino-2-hydroxypropane and 2,6-diacetylpyridine in the presence of $\text{Ba}(\text{ClO}_4)_2$ (Scheme 25) [183].

In $[\text{Ba}(\text{H}_2\text{-118})(\text{H}_2\text{O})_2 \cdot (\text{ClO}_4)_2 \cdot 0.16\text{H}_2\text{O}]$, the macrocycle is substantially folded and, with the exceptions of the substituent hydroxyl groups, occupies one coordination hemisphere of the barium, with similar length contacts to all six nitrogen atoms. The other coordination hemisphere comprises of five oxygen atoms: the two substituent hydroxyl groups, two water molecules and, at a greater distance, a water molecule of an inversion related complex. The two perchlorate anions are not directly coordinated to the barium ion, but engaged in extended hydrogen bonding to hydroxyl groups and to coordinated water. The asymmetric unit is completed by a partial occupancy water molecule (0.16 per barium). The coordination polyhedron of the barium was suggested to be a square antiprism with two additional sites or a cuboctahedron with two vacant sites (Fig. 66a) [184].

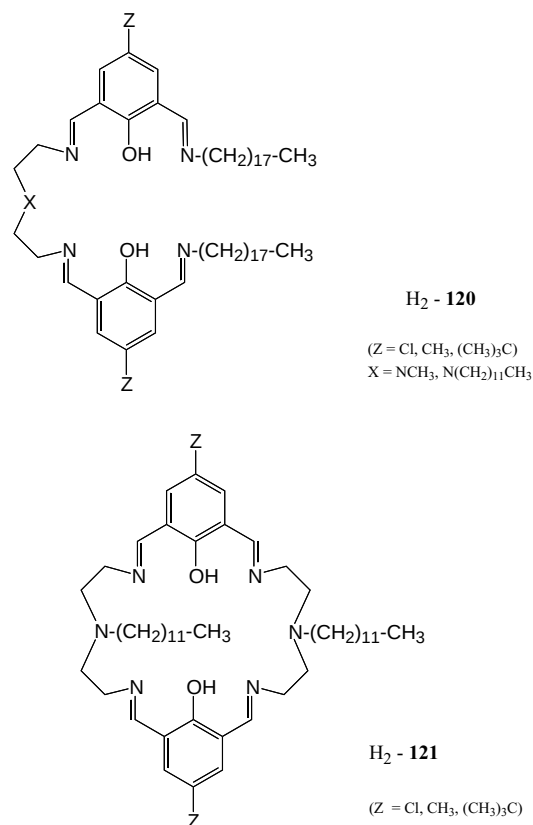
$[\text{Mn}_4(\text{119})(\text{ClO}_4)_4]$ contains the [4+4] ligand utilising all sixteen potential donor atoms to coordinate the four manganese centers (Fig. 66b). The alcohol groups have been

deprotonated and each one bridges three manganese centers, forming the central cubane-type structure $\{\text{Mn}_4(\text{alkoxide})_4\}$. The macrocycle is able to wrap itself around this cluster by virtue of the flexible propane links. Each manganese(II) ion is seven coordinated, bonded to three alkoxide oxygen donors, three nitrogen atoms from a pyridinediimine unit and one perchlorate oxygen. The geometry about each metal center is approximately pentagonal bipyramidal, although the Mn-OCIO_3 distances are rather long. There are also two uncoordinated water molecules for each macrocyclic unit in the lattice [183].

Using the technique of californium 252 plasma desorption mass spectroscopy it was observed that the barium complex does not contain the [4+4] component and hence the larger macrocycle must be formed during the transmetallation reaction with manganese and not in the initial template process [183].

3. Di -or poly-topic systems

The addition of specific functionalities to acyclic or cyclic Schiff bases allows their use in the field of metal ion recognition, transport and separation. Thus the macrocyclic compounds $\text{H}_2\text{-120}$ and $\text{H}_2\text{-121}$ have been successfully proposed for lanthanide(III) ions separation [185].



Also [2+2] tetraimine Schiff bases of the type reported in Scheme 26 have been synthesized and their coordinating

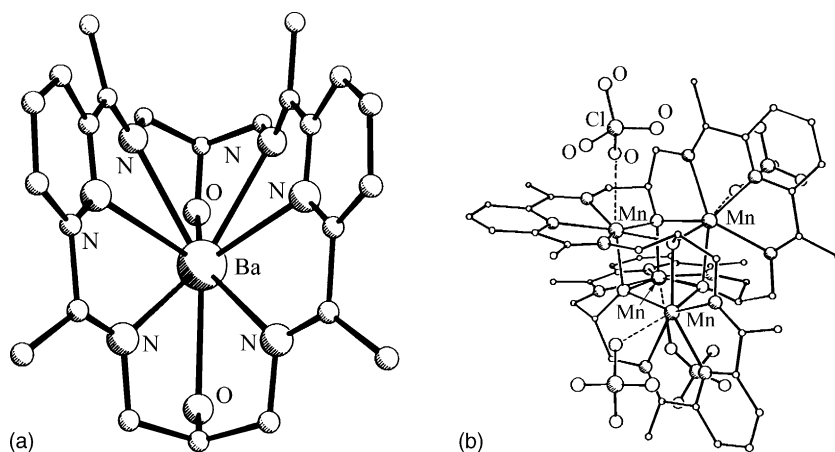
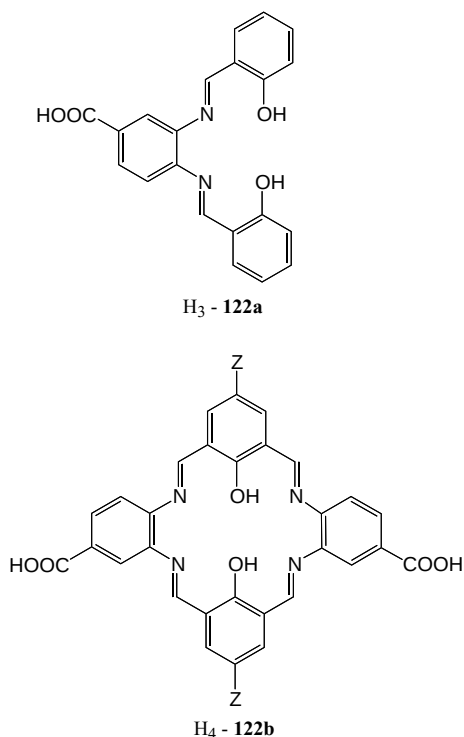


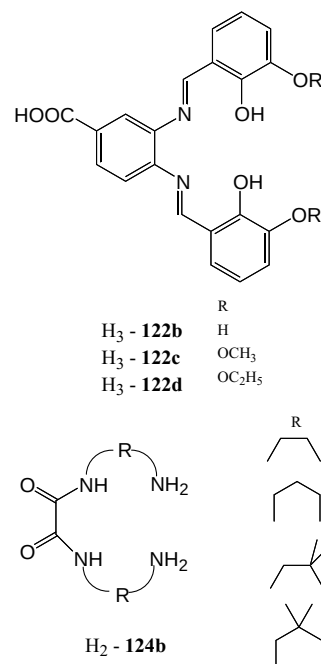
Fig. 66. Structure of $[\text{Ba}(\text{H}_2\text{-118})]^{2+}$ (a) and $[\text{Mn}_4(\text{119})](\text{ClO}_4)_4$ (b) (adapted from Ref. [183]).

properties toward barium(II) or silver(I) ions extensively examined [186].

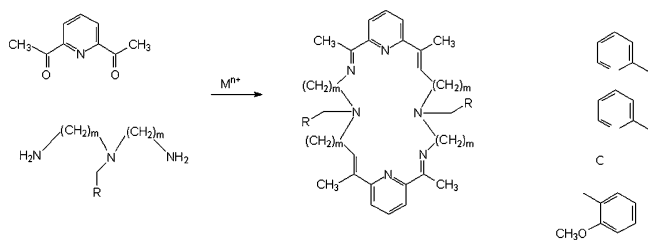
Moreover the insertion of donating groups at appropriate positions of the ligands (i.e. at the periphery of their coordinating moiety) allows contemporary multiple selective coordination processes at the different coordination sites. Thus the reaction of $\text{H}_3\text{-122a}$, derived by the condensation in methanol of salicylaldehyde and 2,3-diaminobenzoic acid in a 2:1 molar ratio, with copper(II) acetate in boiling methanol in the presence of base, affords $\text{Cu}(\text{H-122a})$ where the copper(II) ion resides in the N_2O_2 Schiff bases site. The subsequent reaction with gadolinium(III) salt in the presence of LiOH gives rise to the tetranuclear species $\{\text{Gd}[\text{Cu}(\text{122a})]_3\} \cdot 6\text{H}_2\text{O}$ [187].



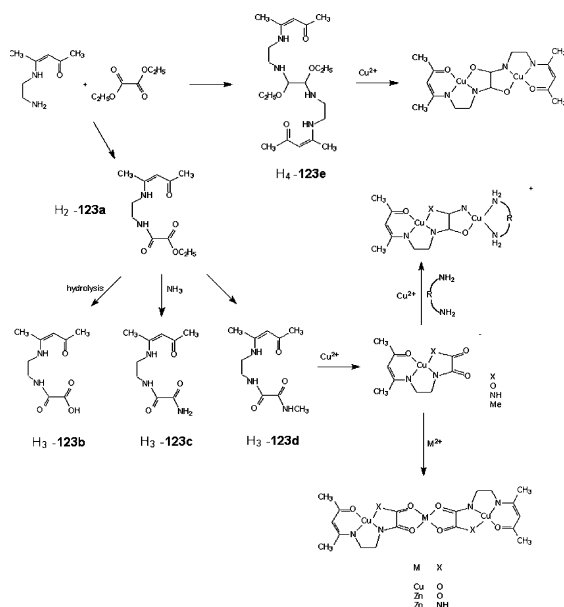
A similar functionalization occurs in the cyclic and acyclic compartmental ligands $\text{H}_4\text{-122b}$ and $\text{H}_3\text{-122c-e}$, derived from the condensation of 2,6-diformyl-4-substituted phenols or 3-substituted-2-hydroxybenzaldehyde with 1,2-diaminobenzene-3-carboxylic acid; again these systems give rise to heteropolynuclear complexes [187].



Among the known polynucleating ligands, attention has been paid to oxalic acid derivatives due to their wide range of possibilities. First, oxalates, oxamates, and oxamides are known to be very efficient in transmitting exchange interaction between magnetic ions in favourable geometries. Furthermore, these ligands are easily altered to give derivatives designed for a particular problem. In some instances, mononuclear precursors can be isolated and subsequently used as chelating ligands towards a second type of metal ion to yield heteropolynuclear species (Scheme 27).



Scheme 26.



Scheme 27.

Depending on the experimental conditions, 7-amino-4-methyl-5-aza-3-hepten-2-one reacts with diethyl oxalate to give either the oxamato derivative H_2 -**123a** or the symmetrical oxamido compound H_4 -**123e**. Interestingly, H_2 -**123a**, can be hydrolyzed to form H_3 -**123b** or can react further with ammonia or a primary amine (i.e. methylamine) yield the unsymmetrical oxamido ligands H_3 -**123c** and H_3 -**123d** [188].

The anionic copper(II) complexes $[Cu(L)]^-$ have been obtained from H_3 -**123b**, H_3 -**123c** and H_3 -**123d**, as established in the case of $Na[Cu(\mathbf{123b})]$ by a structural investigation [188]. In the $[Cu(\mathbf{123b})]^-$ anion, the copper(II) ion is surrounded by two nitrogen and two oxygen atoms. Sodium ions and the water molecules play an important part in stabilizing the structure since they are simultaneously bonded to atoms belonging to different unit cells. The sodium ions are surrounded by either five or six oxygen atoms [188].

The complexes $Na[Cu(\mathbf{123b-d})]$, used as chelating ligands towards a second metal center ($M = Cu^{2+}$, Ni^{2+} , Zn^{2+}), yield homo- or hetero-dinuclear and trinuclear complexes, depending on the nature of M and the mono- or bis-

bidentate behaviour of the second ligand L coordinated to M . If L is a bidentate ligand such as 2,2'-bipyridine (bipy) or a tridentate ligand such as diethylenetriamine (dien), the binuclear complexes $[CuM(\mathbf{123b-d})(L)]^+$ are obtained. The trinuclear complexes $[Cu_2M(\mathbf{123b-d})_2]$ result from the use of H_3 -**123b-d** as a second ligand [188].

On the basis of its symmetrical structure, H_4 -**123e** reacts readily with copper(II) or nickel(II) salts to afford the homodinuclear complexes $[M_2(\mathbf{123e})]$ whatever mole ratio of reactions is used [188].

By slowly adding copper acetate to a mixture of H_4 -**123e** and NaOH in the 1:1:4 ratio, $Na[Cu(\mathbf{123e})] \cdot 2H_2O$ was obtained [188]. The complex, readily soluble in water, may be used to perform the second step of the reaction, i.e. the formation of the neutral dinuclear complexes $[CuM(\mathbf{123e})]$ ($M = Cu^{2+}$, Ni^{2+}) which, being insoluble in water, precipitate.

$[Cu_2(\mathbf{123e})]$ shows a strong antiferromagnetic interactions ($J = -550 \text{ cm}^{-1}$) while $[Ni_2(\mathbf{123e})]$ is diamagnetic. In $[CuNi(\mathbf{123e})]$ the magnetic data, recorded from 300 to ca. 20 K, evidence an isolated copper(II) ion and show that the nickel(II) ion does not contribute to the paramagnetism. The slight decrease of $\chi_M T$ at low temperature is likely attributable to a feeble antiferromagnetic intermolecular coupling ($J = -2.25 \text{ cm}^{-1}$).

EPR and electronic spectroscopy evidence that isomerization occurs upon addition of a second metal ion. Theoretically, EPR offers an easy means to determine the number of nitrogen atoms adjacent to the copper ion through the observation of the superhyperfine (shf) lines resulting from the interaction of the electron with the ^{14}N nuclei ($I = 1$). In the case of $[Cu(\mathbf{123e})]^-$, seven shf-lines are observed with a separation of 13.5 G, indicating that the environment of the copper ion is N_3O , while for $[CuNi(\mathbf{123e})]$, the number of shf-lines decreases to five (separation of 13.2 G) in accordance with the presence of a CuN_2O_2 chromophore. Due to the occurrence of a strong antiferromagnetic coupling, the spectrum of $[Cu_2(\mathbf{123e})]$ displays a broad signal devoid of any structure and centered at $g = 2.089$ [188].

The change of conformation of the oxamido group in going from the mononuclear to the dinuclear complex is further supported by electronic spectra. Indeed, the maximum of absorption suffers a significant shift from ca. 504 nm for the mononuclear species $[Cu(\mathbf{123c})]^-$ and $[Cu(\mathbf{123b})]^-$ to ca. 560 nm for the dinuclear complexes $[Cu_2(\mathbf{123e})]$ and $[CuNi(\mathbf{123e})]$ [188].

$[Cu_2(\mathbf{123b})(\text{bipy})]$, $[Cu_2(\mathbf{123c})(\text{bipy})]$, $[Cu_2(\mathbf{123d})(\text{bipy})]$ and $[Cu_2(\mathbf{123b})(\text{dien})]$ show strong antiferromagnetic interactions, the resulting J values being respectively, -457 , -492 , -495 and -148 cm^{-1} .

Also for the trinuclear copper(II) complex $[Cu_3(\mathbf{123b})_2]$, an antiferromagnetic interaction ($J = -370 \text{ cm}^{-1}$) was found. In order to estimate the interaction between the terminal copper(II) ions in $[Cu_3(\mathbf{123b})_2]$, the magnetic properties of $[Cu_2Zn(\mathbf{123b})_2]$, in which the central ion is the diamagnetic zinc(II) ion, were studied. The proper

conclusion is that the antiferromagnetic interaction between the non-adjacent copper(II) ions is at best very weak ($J = -1.0 \text{ cm}^{-1}$) [188].

The two chiral dinucleating ligands **H₄-123f** and **H₄-123g** have been obtained by grafting a methyl substituent onto one and both diamino arms of **H₄-123e**. These ligands and their related nickel(II) complexes, **[Ni₂(123f)]** and **[Ni₂(123g)]**, exist as a variety of geometrical and optical isomers since, on the one hand, two locations are possible for each substituent and on the other hand, each substituted amino chain comprises an asymmetric carbon. All but one geometrical isomer have been isolated via unequivocal synthetic pathways. Definitive proofs of the existence of all geometrical and optical isomers are gained from an NMR study including 2D and 1D spectra obtained in the presence of a chiral auxiliary. In all cases the five membered ring resulting from coordination of the diamino moiety of the ligands to the nickel ion

adopts a preferred conformation which places the methyl substituent in an axial or pseudoaxial position [188].

When performed in methanol/water the reaction of **Na[Cu(123b)]·1.33H₂O** with **Mn(ClO₄)₂·xH₂O** leads to the formation of the heterotrinnuclear complex **[Cu₂Mn(123b)₂]·5H₂O**. Heating this complex in the solid phase at 80 °C for 24 h affords **[Cu₂Mn(123b)₂]·3H₂O**. A third complex, **[Cu₂Mn(123b)₂]·H₂O**, is obtained by allowing a suspension of **[Cu₂Mn(123b)₂]·5H₂O** in dry acetone to stand for 24 h at room temperature. An interesting complex, **[Cu₂Mn(123b)₂]·4.5H₂O**, results from a slow rehydration of **[Cu₂Mn(123b)₂]·H₂O**. All of these complexes are insoluble in inert solvents. They dissolve readily in the potentially coordinating solvents (dimethylsulphoxide and pyridine), but precipitation of the resulting solutions with diethyl ether yields the solvated species **[Cu₂Mn(123b)₂(DMSO)₂]** and **[Cu₂Mn(123b)₂(py)₄]**, respectively. A suspension of these

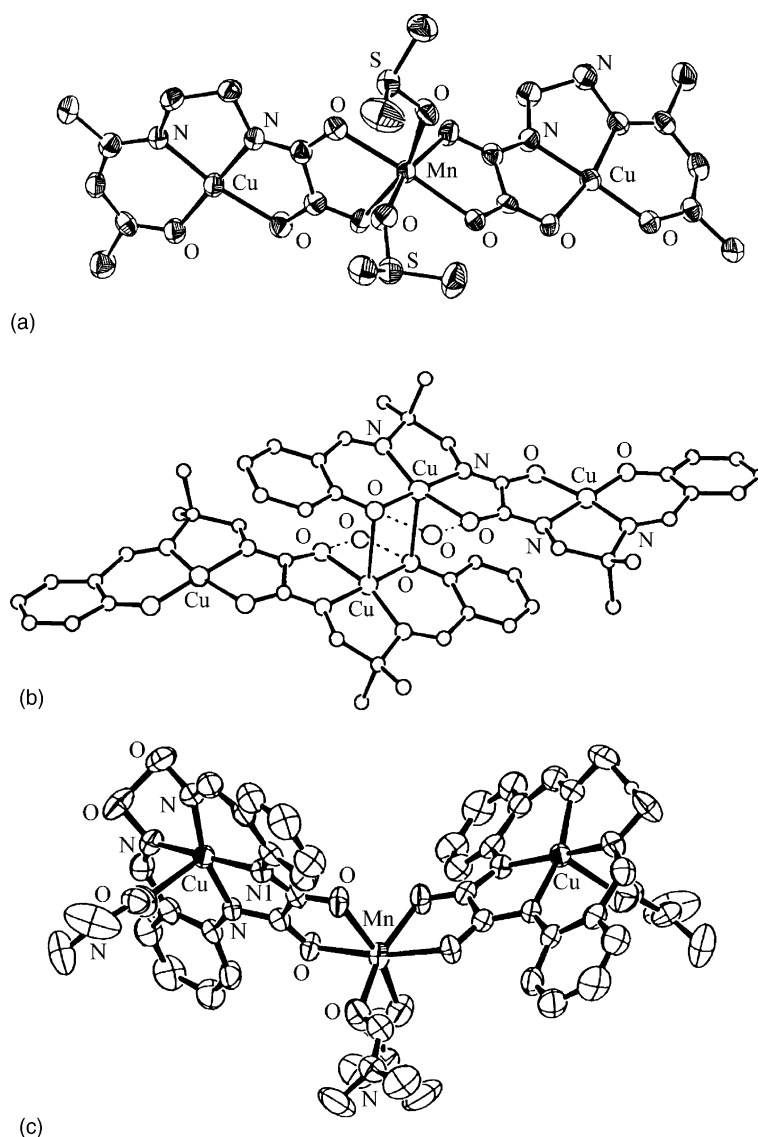


Fig. 67. Structure of **[Cu₂Mn(123b)₂(DMSO)₂]** (a), **[Cu₂(124c)₂]** (b) and **[MnCu₂(H-124i)₂(DMF)₄]** (c) (adapted from Refs. [187,188]).

two complexes in water readily gives $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2] \cdot 5\text{H}_2\text{O}$, which is also recovered if $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2(\text{DMSO})_2]$ or $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2(\text{py})_4]$ are kept in a steam-saturated atmosphere for 3 weeks.

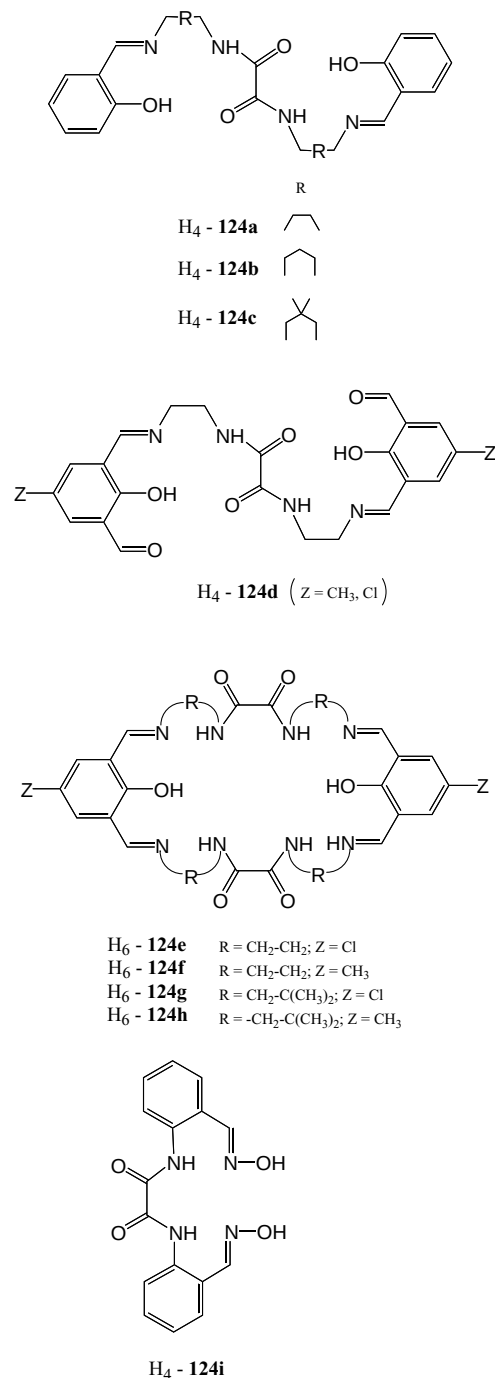
All attempts to obtain crystals suitable for an X-ray diffraction study have failed except in the case of $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2(\text{DMSO})_2]$ (Fig. 67a). The structure consists of neutral trinuclear units, each unit resulting from the complexation of a manganese(II) ion by two $\{\text{Cu}(\mathbf{123b})\}$ subunits and two DMSO molecules. Each copper(II) ion is surrounded by two nitrogen and two oxygen atoms from the ligand $[\mathbf{123b}]^{3-}$. In both cases, the copper environment may be described as square planar. The intramolecular $\text{Cu} \cdots \text{Cu}$ distance is 9.779 Å. The manganese(II) ion is six coordinated by four oxamate oxygen atoms and two oxygen atoms from the DMSO molecules, but the coordination polyhedron is far from having the ideal octahedral geometry. The two DMSO molecules adopt a *cis* geometry [188].

Thermogravimetric analyses confirm that solvent molecules are involved in the structure of all these Cu_2Mn complexes. For $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2(\text{DMSO})_2]$ and $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2(\text{py})_4]$ the loss of two DMSO and four py molecules respectively occurs in the 150–220 °C range. In the $[\text{Cu}_2\text{Mn}(\mathbf{123b})] \cdot n\text{H}_2\text{O}$ series the dehydration process occurs in several steps. For these complexes, one molecule is lost above ca. 220 °C. Below 200 °C, for $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2] \cdot 5\text{H}_2\text{O}$ and $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2] \cdot 4.5\text{H}_2\text{O}$ two overlapping signals were observed at 105 and 135 °C corresponding to the loss of 4 (2+2) and 3.5 (2+1.5) water molecules, respectively, and for $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2] \cdot 3\text{H}_2\text{O}$ one single signal at 135 °C corresponding to the loss of two water molecules. These data suggest that the water molecules involved in the structure of the complexes belong to different types: lattice water, water coordinated to the copper(II) and/or manganese(II) ions, and water hydrogen bonded to the ligand $[\mathbf{123b}]^{3-}$ or to another H_2O molecule.

The $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2] \cdot n\text{H}_2\text{O}$ complexes display the same magnetic behaviour which corresponds to the occurrence of antiferromagnetic Cu–Mn interactions within isolated trinuclear units. The J values are between –29.4 and –33.8 cm^{-1} . Surprisingly the field and temperature dependence of the magnetization for $[\text{Cu}_2\text{Mn}(\mathbf{123b})_2] \cdot 4.5\text{H}_2\text{O}$ confirms that a magnetic phase transition occurs at low temperature and that, below $T_c = 37$ K, the complex displays weak ferromagnetism [188].

The primary amine groups contained in the amino-amide derivatives $\text{H}_2\text{-124'}$ have been engaged in condensation reaction with appropriate formyl precursors, giving rise to Schiff bases which also are excellent di- or poly-nucleating ligands. The [2+1] acyclic $\text{H}_4\text{-124a} \cdots \text{H}_4\text{-124d}$ and [2+2] cyclic Schiff bases $\text{H}_6\text{-124e} \cdots \text{H}_6\text{-124h}$ have been prepared by the reaction of 2-hydroxybenzaldehyde, 2,6-diformyl-4-chlorophenol or 2,6-diformyl-4-methylphenol with the appropriate amino-amide precursor [187]. The [2+2] cyclic nature of $\text{H}_6\text{-124e} \cdots \text{H}_6\text{-124h}$ was inferred by NMR and especially FAB mass spectrometry [187]. $\text{H}_2\text{-124a}$ can form

by reaction with copper(II) salts $[\text{Cu}(\text{H}_2\text{-124a})]$, a good precursor for the synthesis of $[\text{Cu}_2(\mathbf{124a})]$ and especially $[\text{CuNi}(\mathbf{124a})]$. When $\text{H}_4\text{-124'}$ ($\text{R} = \text{CH}_2\text{CH}_2$) is reacted with salicylaldehyde in 1:2 molar ratio and in the presence of lanthanide(III) as templating agent, $[\text{Ln}_4(\mathbf{124a})_3] \cdot n\text{H}_2\text{O}$ is obtained.



N,N' -Bis[(2-amino-2-methyl)propyl]oxamide, obtained by reaction of 1,2-diamino-2-methylpropane and ethyl oxalate in diethyl ether, forms with salicylaldehyde $\text{H}_4\text{-124b}$. The reaction of this Schiff base with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, VOSO_4 or FeCl_3 (also in the presence

of $\text{N}(\text{Et})_3$ produces $[\text{Cu}_2(\mathbf{124b})]$, $[\text{Ni}_2(\mathbf{124b})]$, $[(\text{VO}_2)_2(\mathbf{124b})]$ or $[\text{Fe}_2(\mathbf{124b})(\text{Cl})_2]$ [188], which are very soluble in organic solvents as CH_2Cl_2 or DMSO, slightly soluble in methanol and in H_2O .

The X-ray structure of $[\text{Cu}_2(\mathbf{124b})_2]\cdot\text{H}_2\text{O}$ shows the ligand is in a *trans*-configuration and links each copper(II) ion with one oxygen and one nitrogen atom of the oxamido bridge and one oxygen and one nitrogen atom from the salicyladimine part, forming with each copper(II) ion three chelate rings. A phenolic oxygen atom, belonging to a centrosymmetrically related dinuclear unit, binds axially one copper(II) ion. Thus the coordination environment of the two copper(II) ions is different: one is square planar while the other is square pyramidal with a slight tetrahedral deformation of the basal plane. The intermolecular copper...copper distance (3.288 Å) is significantly shorter than the intramolecular copper...copper separation 5.174 Å and the complex can be considered a tetranuclear entity. The water molecule is not directly linked to a copper(II) ion but forms hydrogen bonds with the two oxygen nitrogens of one N_2O_2 donor set (Fig. 67b) [188].

Magnetic data prove a strong intramolecular antiferromagnetic exchange interaction ($2J = -520 \text{ cm}^{-1}$) and an intermolecular ferromagnetic exchange interaction ($2J = 10 \text{ cm}^{-1}$) for $[\text{Cu}_2(\mathbf{124b})]$. $[\text{Ni}_2(\mathbf{124b})]$ is diamagnetic, while for $[(\text{VO}_2)_2(\mathbf{124b})]$ the magnetic interaction is, at the best, very feeble. The absence of interaction in $[(\text{VO}_2)_2(\mathbf{124b})]$ is not unexpected. Unlike the related copper(II) complex which has $(x^2 - y^2)$ type magnetic orbitals, the magnetic orbitals centered on the square-pyramidal V(IV) ions are of the xy type. An excellent pathway for exchange in the Cu(II) complex results from the fact that the $(x^2 - y^2)$ type orbitals point to the donor atoms of the bridge. In contrast the orbitals on the V(IV) ions are aligned and not directed at the bridging ligand donors. Therefore, no important interaction can be mediated by the bridge. In principle, a direct σ -overlap could be operative but the large separation between the two metal ions suggests this mechanism is not significant. The μ_{eff} value for $[\text{Fe}_2(\mathbf{124b})(\text{Cl})_2]$ (7.42 BM at 280 K) substantiates the presence of high-spin iron(III) ions. As μ_{eff} decreases on decreasing the temperature, there is an antiferromagnetic interaction between the two metal ions ($J = -9.5 \text{ cm}^{-1}$) [188].

The [2+2] macrocycles $\text{H}_6\text{-}\mathbf{124e} \cdots \text{H}_6\text{-}\mathbf{124h}$ ($\text{H}_6\text{-L}$) give rise to $[\text{Ln}_2(\text{H-L})(\text{X})]$ ($\text{Ln} = \text{Y}^{3+}$, La^{3+} , Dy^{3+} , Gd^{3+} ; $\text{X} = \text{NO}_3^-$, CH_3COO^-) when reacted with the appropriate lanthanide(III) salt in a 1:2 molar ratio and in the presence of $\text{N}(\text{Et})_3$. In these complexes the two lanthanide(III) ions reside into the [2+2] macrocyclic cavity. Therefore, they can act as ligands for a further exocyclic complexation of lanthanide(III) or copper(II) ions through the amido $\text{C}=\text{O}$ groups giving rise to homo-polynuclear lanthanide(III) or hetero-polynuclear copper(II)–lanthanide(III) complexes, when reacted, respectively, with an excess of the same lanthanide(III) salt or the appropriate amount of copper(II) chloride [187].

Furthermore, the trinuclear complexes $[\text{MCu}_2(\text{H-}\mathbf{124i})_2(\text{DMF})_4]$ ($\text{M} = \text{Mn}^{2+}$, Ni^{2+} , Co^{2+} , Zn^{2+}) were prepared by reaction of $\text{H}_4\text{-}\mathbf{124i}$ with $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ and NaOH in DMF, followed by the addition of the appropriate metal acetate the molar ratio of the reactants being 1:1:4:1. These isomorphous complexes have an oxamate-bridged trinuclear $\text{Cu}^{\text{II}}\text{M}^{\text{II}}\text{Cu}^{\text{II}}$ structure. Each copper(II) ion resides in a pseudo-macrocyclic framework of $[\text{H-}\mathbf{124i}]^{3-}$ comprised of an oxamate and a hydrogen-bonded dioximate ($=\text{N}-\text{O} \cdots \text{H} \cdots \text{O}-\text{N}=\text{O}$) groups to form the square pyramidal structure $\{\text{Cu}(\text{H-}\mathbf{124i})(\text{DMF})\}$ together with a DMF molecule. Two $\{\text{Cu}(\text{H-}\mathbf{124i})(\text{DMF})\}$ entities coordinate to a manganese(II) ion through the oxamate oxygens to afford a *cis*-octahedral environment about the metal ion together with two DMF oxygens (Fig. 67c). The $\text{M} \cdots \text{Cu}$ intermetallic distances separated by the oxamate bridge are in the order: Cu_2Mn (5.491 Å) $\approx$ Cu_2Co (5.490 Å) $>$ Cu_2Zn (5.385 Å) $>$ Cu_2Ni (5.334 Å).

$[\text{MCu}_2(\text{H-}\mathbf{124i})_2(\text{DMF})_4]$ and ($\text{M} = \text{Mn}^{2+}$, Co^{2+}) a significant antiferromagnetic interaction operates between the adjacent ions. The reaction of $[\text{MnCu}_2(\text{H-}\mathbf{124i})(\text{DMF})_4]$ with $\text{Mn}(\text{ClO}_4)_2$ in acetonitrile in the presence of KOH and 18-crown-6 formed $[\text{MnCu}(\mathbf{124i})(\text{H}_2\text{O})_4]_n$ that has a polymeric structure extended by the dioximate-Mn^{II}-dioximate linkage. It is a weak ferromagnet ($T_c = 5.5 \text{ K}$) exhibiting a weak antiferromagnetic interaction between the ferrimagnetic chains [187].

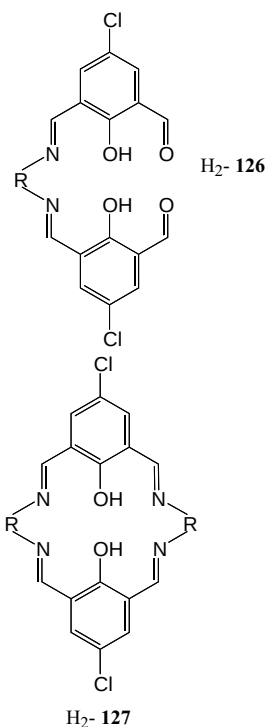
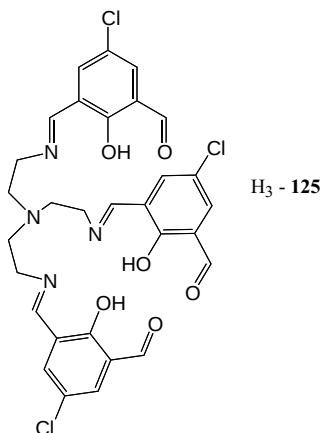
These examples clearly show the remarkable possibilities of multiple specific recognition processes offered by the insertion of additional functionalities to the coordinating moiety of the Schiff base ligands and related complexes.

The fusion of the Schiff bases (or the related reduced polyamine derivatives) and crown-ether properties into a unique entity can give rise to di- or poly-topic ligands with different chambers in close proximity, capable to incorporate well defined metal ions (i.e. transition metal ions) into the Schiff base site and other metal ions (i.e. non transition metal ions) into the crown-ether site. Moreover, anions or neutral molecules can be firmly recognized into one site and a metal ion into the other. The reduced polyamine derivatives bearing crown-ether functionalities offer the additional possibility of protonation–deprotonation processes at the nitrogen atoms, allowing additional different selective recognitions at the two sites. Therefore, acyclic and cyclic systems have been prepared by condensation of the appropriate formyl- or diformyl-precursors and amino derivatives bearing crown-ethers with different cavities. The subsequent reduction of the resulting Schiff bases with NaBH_4 give rise to the corresponding polyamine derivatives [189].

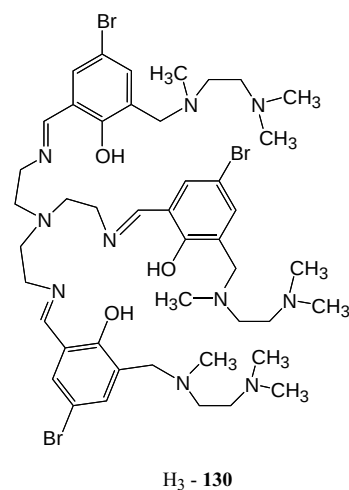
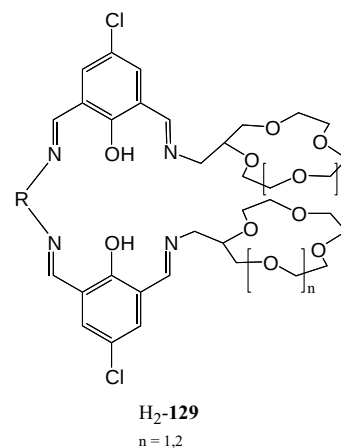
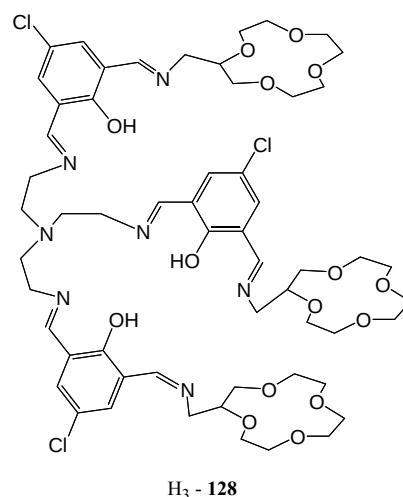
A similar synthetic strategy was also employed for the insertion of other donor systems. The precursors have been conveniently functionalized prior to their condensation reactions.

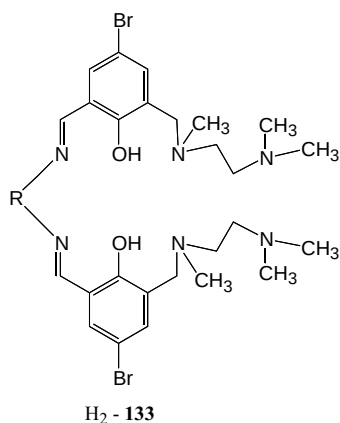
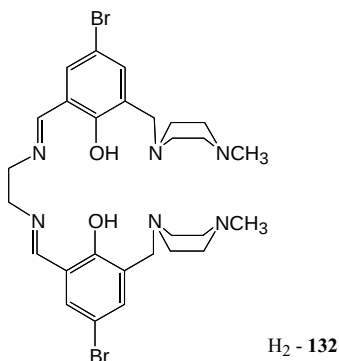
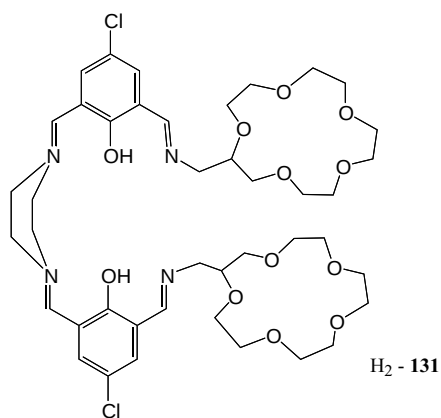
In order to synthesize the functionalized tridimensional or planar compounds derived from 2,6-diformyl-4-chlorophenol, the appropriate formyl precursors $\text{H}_3\text{-}\mathbf{125}$ and $\text{H}_2\text{-}\mathbf{126}$

have been prepared by self condensation and/or the related complexes by template procedure. In particular the condensation reaction in anhydrous acetonitrile of 2,6-diformyl-4-chlorophenol with tris-(2-aminoethyl)amine in a 3:1 molar ratio gives rise to the corresponding tridimensional [3+1] acyclic ligand **H₃-125** with three aldehydic functionalities. The same reaction in methanol affords a compound where the aldehydic functionalities have been transformed into the acetal groups (**H₃-125'**). A similar behaviour was found when 2,6-diformyl-4-chlorophenol was reacted, under the same experimental conditions, with the diamines **H₂-N-R-NH₂** in a 2:1 molar ratio; again the diformyl compounds **H₂-126** are obtained in anhydrous acetonitrile and the diacetal analogues **H₂-126'** in methanol. The experimental conditions employed in the preparation of the acyclic ligands may favour also formation, as by products, of the corresponding symmetric macrocycles **H₂-127**, identical to the genuine [2+2] tetraimine macrocycles synthesized by direct condensation of the appropriate precursors [189].

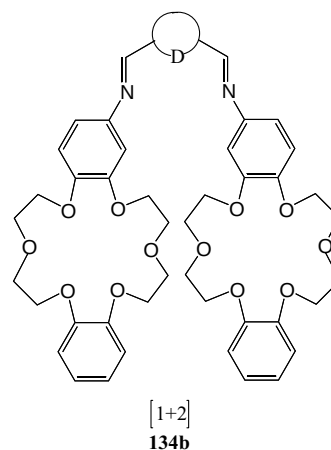
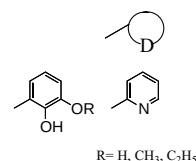
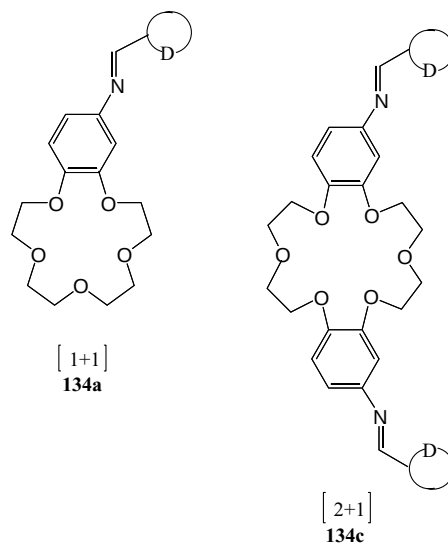


H₃-125, **H₂-126** and/or the related complexes have been engaged in further condensation reactions with 2-aminoethyl-12-crown-4 or 2-aminomethyl-15-crown-5 to give rise to the functionalized Schiff bases **H₃-128** and **H₂-129** and related d- or f-complexes. Moreover, the functionalized ligands **H₃-130**, **H₂-131**, **H₂-132**, **H₂-133** and/or the related d- or f-complexes have been synthesized by condensation of the appropriate formyl- and amine-precursors respectively in the absence or in the presence of the appropriate metal ion [189].



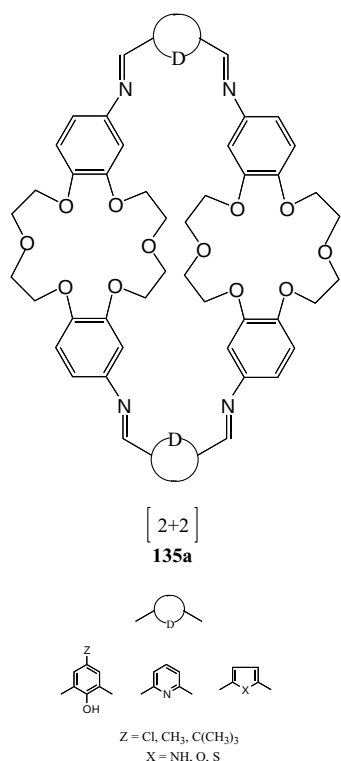


The same approach was employed in the formation of a series of [1+1], [1+2] and [2+1] acyclic and [2+2] cyclic polytopic systems of the type **134a–134c** and **135a**, prepared by the usual self-condensation of the appropriate formyl- (i.e. 2-hydroxy-3-substituted-benzaldehyde, 2-formyl-pyridine, 2-formyl-8-hydroxyquinoline, etc.) or diformyl- (i.e. 2,6-diformyl pyridine, 2,6-diformyl-4-substituted phenol, 2,5-diformylpyrrole, etc.) and amine-precursors (i.e. amino-methyl-crown-ethers, amino-phenyl-crown-ethers, diamino-diphenyl-crown ethers, etc.). The amine analogues have been easily synthesized by reduction of these imine derivatives [189].

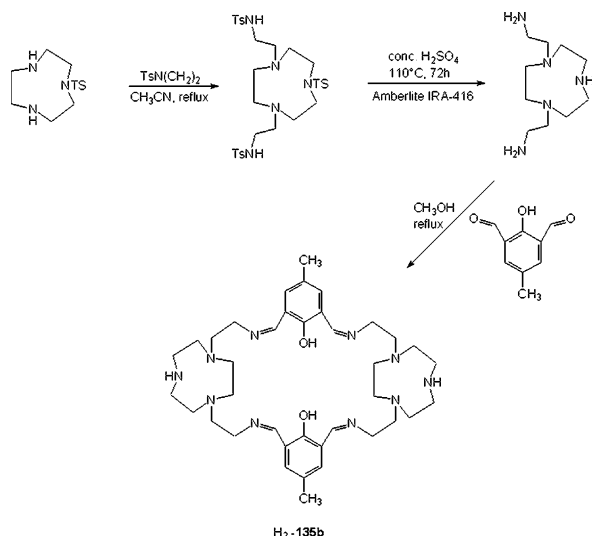


The cofacial binucleating macropolycycle H₂-**135b** has been obtained by direct [2+2] Schiff-base condensation of equivalent amounts of 1,4-bis(2-aminoethyl)-1,4,7-triazacyclononane, and 2,6-diformyl-4-methylphenol in CH₃OH [190]. The amine precursor 1,4-bis(2-aminoethyl)-1,4,7-triazacyclononane was synthesized by reaction of 1-(*p*-tolylsulfonyl)-1,4,7-triazacyclononane with 2 equiv. of *N*-tosylaziridine and subsequent detosylation of resulting product with concentrated sulfuric acid (Scheme 28).

H₂-**135b** is characterized by two large adjacent chambers each with potential N₅O₂ donicity capable of accommodating metal ions with large ionic radii. Reaction of H₂-**135b** with Cd(NO₃)₂·4H₂O and [(CH₃)₄N](OH) in a 1:2:2 molar ratio in CH₃OH-CHCl₃ under reflux gives yellow plate crystals of [Cd₂(**135b**)](NO₃)₂. Each six coordinated cadmium(II) ion is bound to an N₅O donor set within a distorted octahedral environment (Fig. 68a). Each cadmium(II) is coordinated to three nitrogen donors of the triaza



ring, to two imine nitrogen atoms and to one phenolate oxygen. The two N₅O donating chambers of the macropolycycle act, therefore, as isolated donor sets and the phenolate oxygens do not bridge the metal ions. However, the phenolate oxygen donors are involved in a strong hydrogen-bond with a methanol molecule, which is also hydrogen-bonded to the secondary N–H of the triazacyclononane ring to form a six-membered ring including the cadmium(II) ion. Significantly, the two aromatic rings of the macropolycycle are stacked. This face-to-face π – π interaction and additional hydrogen-bonding force the donor atoms of the anionic ligand **[135b)]^{2–}** to assume a



Scheme 28.

peculiar deposition with the phenolate oxygens twisted in opposite directions and each pointing towards an individual metal ion. As a result, the phenolate oxygen donors cannot bridge the cadmium(II) centers, which are, therefore, segregated each within its own N₅O-donor chamber at a Cd···Cd distance of 7.017 Å [190].

Reaction of H₂-**135b** with Y(NO₃)₃·6H₂O in a 1:2 molar ratio under the same conditions affords [Y₂(**135b**)-(OH)][Y(NO₃)₄(CH₃OH)₂(NO₃)₂·2CH₃OH]. The two metal centers in the cation lie within the two N₅O donating chambers of **[135b)]^{2–}** bridged not only by the phenolate oxygen atoms but also by a hydroxy group. Each yttrium(III) ion in [Y₂(**135b**)(OH)]³⁺ is eight coordinated and bound to three nitrogens from the triazacyclononane framework, two azomethine nitrogens, two phenolate oxygens and a hydroxy oxygen. The Y···Y distance is 3.495 Å. The three bridging oxygen atoms in [Y₂(**135b**)-(OH)]³⁺ form an almost equilateral triangle, and the two yttrium(III) ions lie 1.71 Å out of this O₃ plane. Therefore, the coordination polyhedron at each metal ion can best be described as monocapped distorted octahedral [190] (Fig. 68b).

The [2+1] bis- or [3+1] tris(crown-ether)-Schiff base ligands **136** and **137** have been prepared via the condensation of 2 or 3 equiv. of 4-formylbenzo-15-crown-5 with the appropriate diamine H₂N–X–HN₂ or N(C₂H₄NH₂)₃ [190]. Mononuclear copper(I) or silver(I) and heteropo-

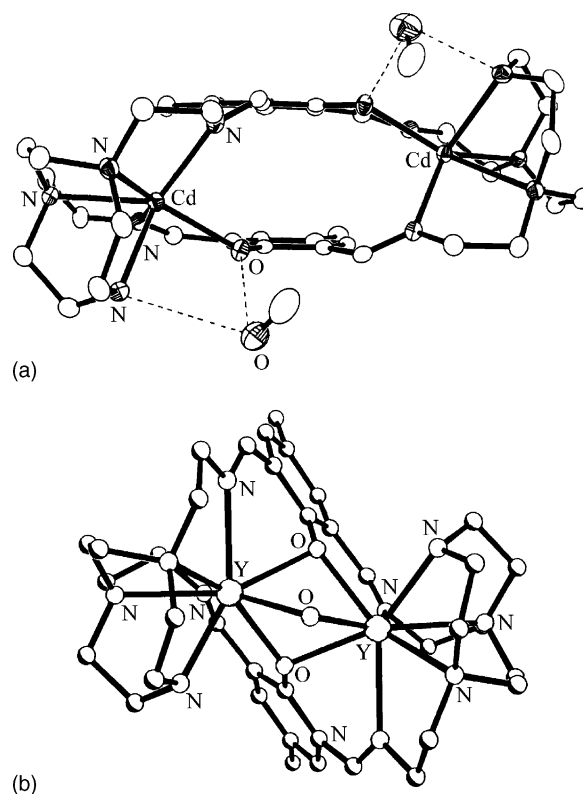
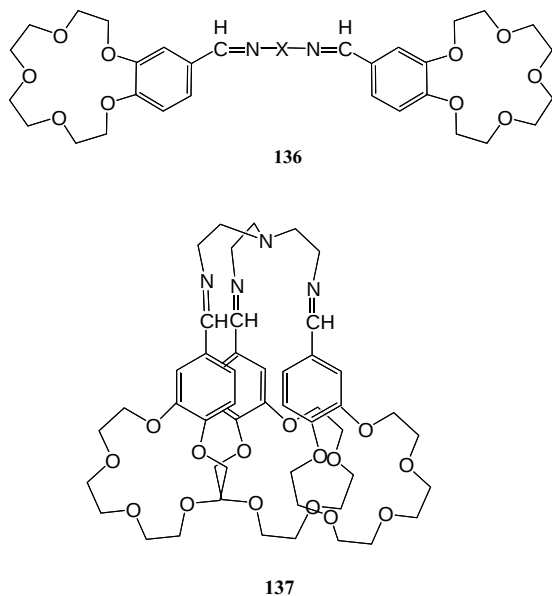


Fig. 68. Structure of [Cd₂(**135b**)]³⁺ (a) and [Y₂(**135b**)(OH)]³⁺ (b) (adapted from Ref. [190]).

lymetallic copper(I)-sodium(I), silver(I)-sodium(I), and copper(I)-potassium(I) complexes have been isolated. The transition metal ion coordinate into the Schiff base moiety while the alkali metal ion prefers the crown-ether chamber [190].

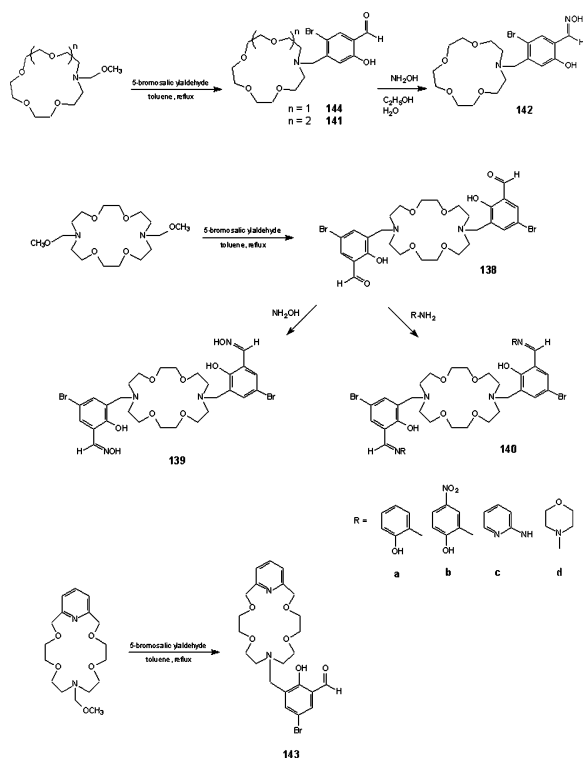


The stoichiometry of **136** where $X = (\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2$ to K^+ guest cations is dependent on the stereochemical requirements of cobound transition metal guests. With tetrahedrally coordinated Ag^+ , the subsequent formation of the intramolecular sandwich complex with K^+ is prevented and the polymetallic complex $[\text{AgK}(\mathbf{136})]_n^{2+}$ results. With the square planar or tetragonally bound copper(II) complex, however, the stereochemical requirements of this transition metal allow the formation of the preferred 1:1 sandwich complex $[\text{CuK}(\mathbf{136})]^{3+}$. In the absence of transition metal ions, Na^+ forms the dinuclear complex $[\text{Na}_2(\mathbf{136})]^{2+}$ while K^+ gives rise to the mononuclear compound $[\text{K}(\mathbf{136})]^+$ [190].

When treated with copper(I) salts **137** gives rise to $[\text{Cu}(\mathbf{137})]^+$ which, in the presence of Na^+ , forms the tetranuclear copper(I)-sodium(I) complex $[\text{CuNa}_3(\mathbf{137})]^{4+}$ [190].

The functionalized formyl-precursors and related oxime or Schiff base derivatives **138–144** have been obtained by reaction of *N*(methoxymethyl)-substituted azacrown-ether with 5-bromosalicylaldehyde, followed by the condensation of the resulting derivatives with hydroxylamine or primary amines (Scheme 29) [191].

Chelating agents bearing 2-hydroxybenzyl functions attached to the azacrown moiety have common structural features, the existence of intramolecular bonds between the phenolic OH groups and nitrogen atoms of the macrocyclic ring. In the case of bis-substituted compounds, this hydrogen bonding leads to opposite side location of aromatic side arms



Scheme 29.

relative to the diazacrown plane as found for **138** in the solid state (Fig. 69). The X-ray structure of **138** shows the molecule lies about a center of inversion which requires that the pendent arms of the ligand are on opposite sides of the diaza-crown ring. There are intramolecular hydrogen bonds linking the phenol oxygens of the sidearms to the nitrogen atoms of the crown ring [191].

Opposite side location of aromatic side arms is likely present in the oxime **139** and Schiff base modified ligands **140a–d** as well. However, conformational changes which bring both phenolic sidearms to one side of the macrocyclic ring have been observed upon complexation. Deprotonation should also facilitate the rotation of aromatics units and promote chelation of the transition metal ions from the same side of the diazacrown plane, especially in case of cations having high deprotonating ability.

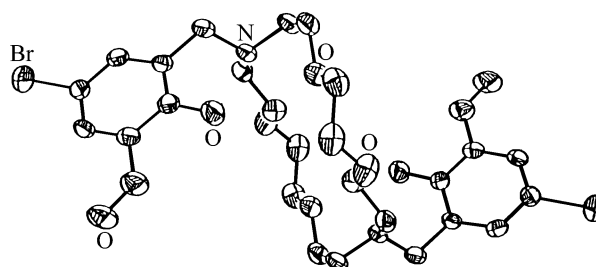


Fig. 69. Structure of **138** (adapted from Ref. [191]).

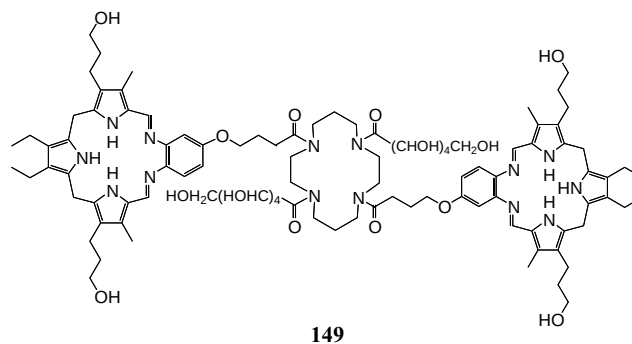
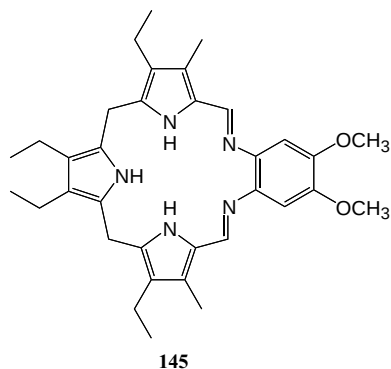
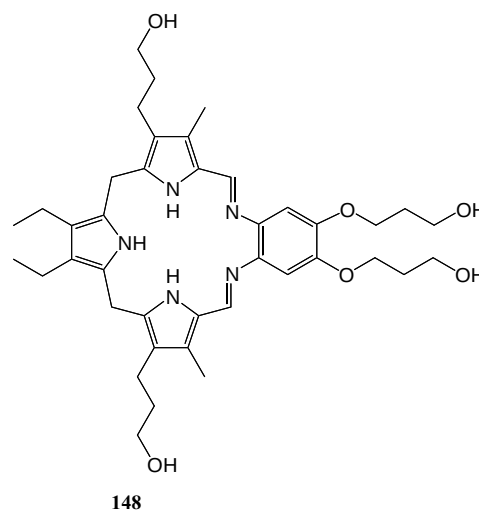
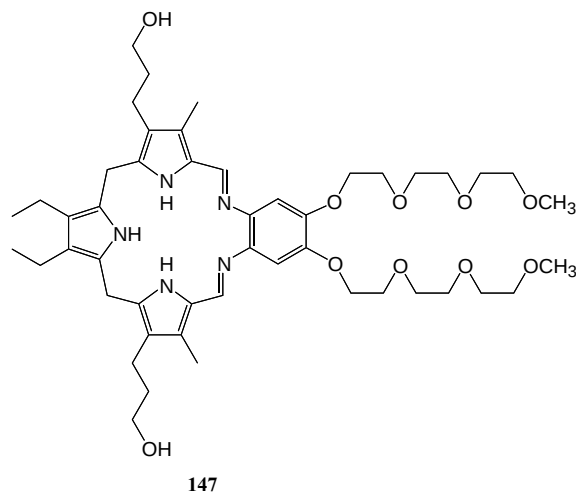
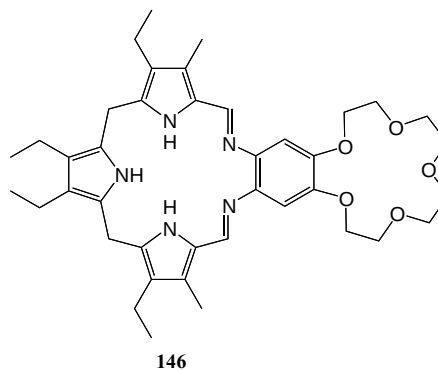
UV–Vis spectra indicate an appreciable interaction of the oximic and Schiff base sidearm-containing ligands with cations, especially with copper(II), zinc(II), cadmium(II) and lead(II) ions, which are able to form chelate complexes with **138–142**.

A study on the complexation of synthesized receptors with a number of alkali, alkaline and transition metal ions, show the potassium complexes with **141** and sodium or potassium complexes with **140** are the most stable ($\log K > 4$) [191].

As compared with parent macrocycles aza-15-crown-5, aza-18-crown-6 and diaza-18-crown-6, **140–142** exhibit increased binding constants for Na^+ and K^+ . This observation indicates a participation of the salicylaldehyde, oxime and Schiff base sidearms in the complexing process. Like most other lariat ethers, K^+/Na^+ selectivity demonstrated by these lariat ether is not as high as that by cryptands. The highest K^+/Na^+ selectivity is observed for **141** which shows $K_{\text{K}}/K_{\text{Na}}$ value of 9.

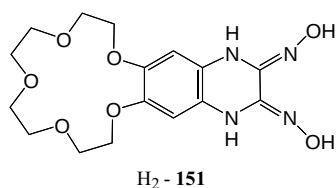
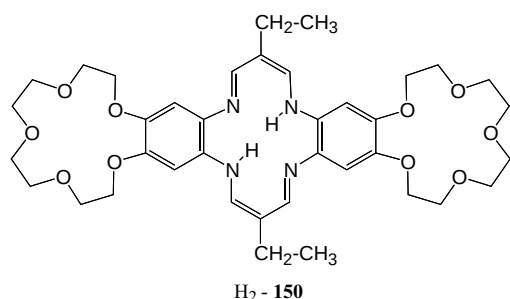
The [15]-membered-ring **144** forms a more stable complex with Na^+ than with K^+ while the [18]-membered-ring **141** forms a more stable complex with K^+ than with Na^+ , indicating that the macroring portions of **144** and **141** play a more important role in cation binding than the salicylaldehyde sidearms. The difference between **144** and **142** is that **144** has salicylaldehyde and **142** an oxime fragment attached to the macrocyclic ring. This difference results in different cation-binding behaviour between **144** and **142**. Macrocycle **144** is selective for Na^+ over K^+ by a factor of 4.1 (ratio of equilibrium constants) while **142** is selective for K^+ over Na^+ by a factor of 1.7. Macrocycle **143** differs from **141** in that pyridine group of **143** is replaced by a $-\text{CH}_2\text{OCH}_2-$ unit in **141**. This structural change results in an increase in K^+ binding by **141** and a small decrease in Na^+ binding. Double-armed **140** shows strong interactions with both Na^+ and K^+ . The phenol substituent on the imine group of **140** is probably an important factor for high Na^+ and K^+ binding constants [191].

Functionalized texaphyrins as **145–149** and their gadolinium(III) complexes have been prepared with the purpose to use them as mri contrast agents [192] and shift reagents for alkali metal ions (especially Na^+) [193].



The solubility of the dinuclear gadolinium(III) texaphyrins complex with **149** was enhanced via the coupling of two gadolinium complexes with a spacer chain consisting of gluconolated 1,4,8,11-tetraazacyclotetradecane. In addition to providing two gadolinium ions per molecule, the space also provides additional binding sites for the chelated metal ion. The system was found to have a longitudinal (T_1) relaxation of ca. $40 \text{ mM}^{-1} \text{ s}^{-1}$ at room temperature, neutral pH, and 500 MHz of applied field. Under the same conditions, the mononuclear gadolinium(III) complex with **148** displayed a relaxation rate of $8 \text{ mM}^{-1} \text{ s}^{-1}$. The augmented relaxivity renders the system of interest as an improved texaphyrin-type mri contrast-enhancing agent. This also suggested that increasing the molecular size influences the per-gadolinium(III)-based relaxivities of the gadolinium(III)–texaphyrin. Thus, the insertion of polymeric functionalization (poly-L-lysine or *s*-gluconolactone) at the periphery of systems as **145–148** considerably increases the water solubility of the gadolinium(III) complexes, substantially enhancing the relaxivity [193].

The tetraaza-[14]-annulene with two crown-5-ethers at 2,3- and 11,12-positions (2,3,11,12-bis(1',4',7',10',13'-pentaaxatridecamethylene)-5,14-dihydro-7,16-diethyl-dibenzo-[b,i] [1,4,8,11]-tetra-azacyclotetradecine), H_2 -**150**, synthesized by cyclization of 2,3-(3',4'-diaminobenzo)-1,4,7,10,13-pentaoxacyclo-pentadecane-2-ene and 2-ethyl-3-ethoxyacrolein in refluxing ethanol for 12 h [194], reacts with copper(II) or nickel(II) acetate in boiling *N,N*-dimethylformamide to give the corresponding metal complex $[\text{M}(\text{150})]$. For the purpose of introducing the alkali metal salts to vacant crown cavities, H_2 -**150** and its complexes were dissolved in chloroform–methanol (4:1, v/v) and a solution of alkali metal or ammonium salt was added in excess. K^+ and NH_4^+ ions formed complexes with the crown ether group in a 1:2 (cation:ether) stoichiometry, while Na^+ formed a 1:1 complex [194].



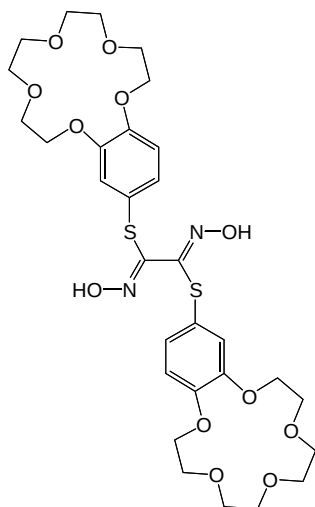
^1H NMR spectra show H_2 -**150** is monomeric in DMSO but dimeric in CHCl_3 . Interestingly the tetraaza-[14]-annulene with crown ether groups is liable to aggregate itself while the tetraaza-[14]-annulene with no crown ether group does not self aggregate: this seems to indicate that the driving force of tetraaza-[14]-annulene aggregation rests on the substituent groups.

The capability of these macrocyclic compounds to complex cations (Na^+ , K^+ and NH_4^+) was studied with the aid of electronic and ESR spectra. The cations (K^+ and NH_4^+), which need two crown ether cavities for complexation, accelerate dimerization of macrocyclic compounds. The copper(I) complex was shown by ESR to dimerize in the presence of added K^+ ions. An addition of Na^+ to the crown tetraaza-[14]-annulene or to its metallo derivatives in chloroform–methanol does not produce any appreciable change in the visible absorption and/or ESR spectra. This indicates that the introduction of the Na^+ ion into crown ether cavities prevents any likely aggregation of the complex due to strong repulsion among the two complexes induced by two Na^+ ions on each complex. ESR spectra indicate that a sandwich aggregation of the two K^+ ions by four crown ether moieties occurs; the K^+ ions are held by the crown ether cavities, so that this complex assumes an axial dimer type [194].

4'-5'-Diaminobenzo-[15]-crown-5 was obtained from benzo-[15]-crown-5 via nitro-, amino-, acetylamino-, acetylamino-nitro-steps as reported [195]. In order to obtain 2,3-bis(hydroxyimino)-1,2,3,4-tetra-hydro-[[15]-crown-5][g]-quinoxaline (H_2 -**151**), this diamino compound was treated with cyanogen di-*N*-oxide, prepared from *anti*-dichloroglyoxime and aqueous sodium carbonate [195]. H_2 -**151** is light-sensitive and its grey colour gradually turns to brown.

The crystalline sodium perchlorate complex of H_2 -**151**, isolated when the corresponding salt and H_2 -**151** were refluxed in ethanol, was more stable than free H_2 -**151**. The dinuclear uranyl complex $[(\text{UO}_2)_2(\text{H-151})_2(\text{OH})_2\cdot\text{H}_2\text{O}]\text{O}$ was prepared from uranyl(VI) diacetate and H_2 -**151** in ethanol. Also H_2 -**151** forms the reddish diamagnetic complex $[\text{Ni}(\text{H-151})_2]$ when reacted with nickel(II) salts. The red solid nickel(II) complexes $\text{NiNa}_2(\text{H-151})_2(\text{X})_2$ ($\text{X} = \text{Cl}^-$, ClO_4^-) were isolated when NaClO_4 was inserted into the crown-ether groups. It is soluble in ethanol, methanol, and chloroform, precluding a polymeric structure. This is apparently due to the bulky crown-ether group which prevents the interaction of metal ions. The reddish brown palladium(II) complex $[\text{PdNa}_2(\text{H-151})_2(\text{Cl})_2]$ was prepared from solutions of $\text{Na}_2(\text{H}_2\text{-151})(\text{Cl})_2$ and $\text{Na}_2[\text{Pd}(\text{Cl})_4]$ in ethanol. In contrast to the nickel(II) complex, the solubility of this compound in solvents such as ethanol, chloroform, dimethyl sulphoxide, and dimethylformamide is very small [195].

Similarly, *S,S'*-bis-(4'-benzo){[15]-crown-5}dithioglyoxime (H_2 -**152**) was prepared by reaction of 4'-mercapto-benzo{[15]-crown-5} with *anti*-dichloroglyoxime in ethanol with an excess of NaHCO_3 as a buffer to neutralize HCl formed during the reaction [196].

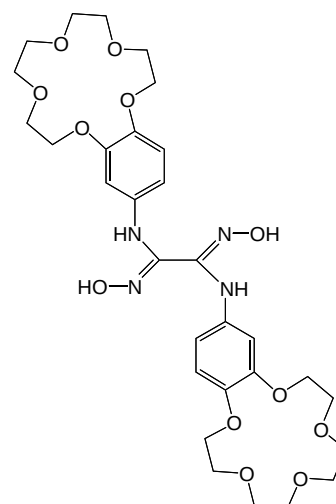
H₂-152

The crystalline lithium chloride, sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate complexes of H₂-152 were isolated by treating H₂-152 with the corresponding salts in ethanol. It was found that two Li⁺ or Na⁺ ions are incorporated into two cavities of H₂-152. In the case of K⁺ and NH₄⁺ ions, however, alkali metal:ligand ratios are definitely 1:1, which unequivocally reflects the effect of the higher diameters of these two cations. Reaction of H₂-152 with nickel(II), palladium(II), and platinum(II) salts gives products with metal:ligand ratios of 1:2. The products obtained from the reaction of copper(II), cobalt(II), and cobalt(III) ions with H₂-152 were highly soluble in ethanol; thus they could only be precipitated as sodium perchlorate complexes. In the nickel(II), palladium(II), platinum(II), copper(II), cobalt(III) complexes of H₂-152, the ligand coordinates through the two nitrogen atoms. The complex [PtNa₄(H-152)₂(Cl)₂](ClO₄)₂ forms six membered chelate rings and co-ordinates through nitrogen and oxygen atoms. [CoNa₄(H-152)₂(PPh₃)(Cl)](ClO₄)₂ and [CoNa₂(H-152)₂(C₅H₅N)(Cl)](ClO₄)₂ have been prepared with triphenylphosphine or pyridine and chloride as axial ligands.

The ion-extraction properties of the nickel(II), palladium(II), and platinum(II) complexes towards lithium, sodium and potassium picrate from aqueous solution to dichloromethane have been measured. Extraction experiments of alkali-metal picrate (Li⁺, Na⁺, K⁺) from aqueous solution into dichloromethane using [Ni(H-152)₂], [Pd(H-152)₂] and [Pt(H-152)₂] show that the percentage extractions for K⁺ (79.3, 99.2 and 15.6, respectively) are the highest and secondly the nickel(II) and palladium(II) complexes exhibits a higher selectivity for K⁺ than the Pt²⁺ complex. The percentage of extractions of Li⁺ are 7.1, 23.6 and 10.2% and of Na⁺ are 8.5, 26.5 and 8.5%. In comparison, the values obtained using [15]-crown-5 are 0.9 for Li⁺, 18.2 for Na⁺ and 33.7% for K⁺. The greater ionic radius of platinum(II) ion than the other d⁸ metal ions might be expected to prevent parallel alignment of the two crown ether units of the same molecule completely to envelope alkali-metal cations. Thus

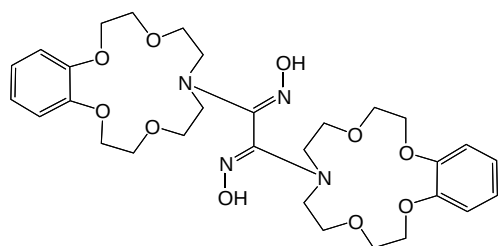
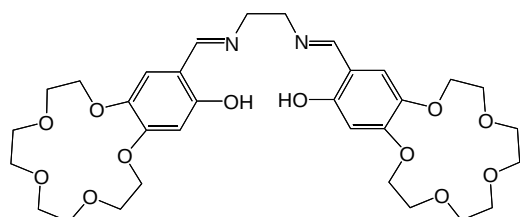
the high extractability of K⁺ ions by the crowned vic-dioxime nickel(II) and palladium(II) complexes can be attributed to the fact that these two compounds exhibit a remarkable capability for forming 1:2 potassium ion-crown sandwich-type complexes. This might be a result of the suitable direction of the crown ether groups for sandwich-type complex formation due to the NN-chelated metal core of the molecule [196].

N,N'-Bis(4'-benzo-{[15]-crown-5}diaminoglyoxime (H₂-153) was prepared by the reaction of 4'-aminobenzo-[15]-crown-5 with *anti*-dichloroglyoxime in the presence of NaHCO₃ added to neutralize HCl formed during the reaction. NaCl was produced as a byproduct, complexed with the crown ether groups, giving rise to the bis(sodium chloride) salt of the ligand, [Na₂(H₂-153)(Cl₂)]. [Na₂(H₂-153)(Cl₂)] reacts with nickel(II), copper(II), cobalt(II), cobalt(III), platinum(II), palladium(II), and uranyl(IV) to give products with metal:ligand ratios of 1:2 or 1:1. The copper(II), nickel(II), and cobalt(II) complexes are of the type [MNa₄(H-153)₂](ClO₄)₄ (M = Cu²⁺, Ni²⁺) and [CoNa₄(H-153)(Cl)](ClO₄)₄; thus they have a metal:ligand ratio of 1:2 and the ligand coordinates through the two nitrogen atoms. [PtNa₄(H-153)₂](ClO₄)₄ and [PdNa₄(H-153)₂](ClO₄)₄ complexes form six membered chelate rings and coordinate through nitrogen and oxygen atoms. [CoNa₄(H-153)₂(L)](ClO₄)₄ has been prepared with L = triphenylphosphine or pyridine, together with a chloride ion, as axial ligands. [Na₂(H₂-153)(X₂)] (X = Cl⁻, ClO₄⁻) reacts with UO₂(CH₃COO)₂·2H₂O to give the complexes [(UO₂)₂-(Na)₄(H-153)₂(OH)₂](X)₄ where a metal:ligand ratio of 1:1 occurs. All these complexes are soluble in water and in the most organic solvents [197].

H₂-153

The crown ether glyoxime derivative H₂-153a, synthesized by the reaction of 2,3,5,6,8,9,11,12-octahydro-1,4,10,13,7-benzotetraoxa-azacyclopentadecine and dichloroglyoxime in ethanol containing an excess of NaHCO₃ as a buffer to neutralize the HCl formed [198,199], gives rise to

the copper(II), nickel(II), palladium(II), cobalt(II), cobalt(III), and platinum(IV) complexes by refluxing a solution of the ligand and the appropriate metal salt in ethanol followed by the gradual addition of an equivalent amount of NaOH dissolved in ethanol, except in the case of the cobalt(III) salt. The nickel(II), palladium(II) and platinum(IV) complexes are isolated as the NaClO₄ free ones [M(H-**153a**)₂] (M = Ni²⁺, Pd²⁺) and [Pt(H-**153a**)₂(ClO₄)₂]. However, the cobalt(II), copper(II) and cobalt(III) complexes were obtained as their tetra(sodium perchlorate) compounds [MNa₄(H-**153a**)₂](ClO₄)₄ (M = Co²⁺, Cu²⁺) and [CoNa₄(H-**153a**)₂(Cl)(C₅H₅N)](ClO₄)₄ [198,199].

H₂ - **153a**H₂ - **154**

15-Formyl-16-hydroxy-2,3,5,6,8,9,11,12-octahydrobenzo-[1,4,7,10,13]-pentaoxacyclo-pentadecine (H₂-**154**) has been synthesized from the corresponding 15-hydroxy substituted crown ether and hexamethylenetetramine in trifluoroacetic acid. Condensation of this formyl derivative with 1,2-diaminoethane gives the corresponding bis(crown ether) substituted ethylenebis(salicylideneimine) ligand H₂-**154** [200].

Cobalt(II), copper(II), nickel(II), and uranyl(VI) complexes of this Schiff base have been prepared from the corresponding metal acetates. Insertion of sodium ions into the crown ether has been accomplished by refluxing H₂-**154** with sodium nitrate in ethanol before the addition of the transition metal ion [200].

The order of the formation constants of the complexes determined by the Calvin Bjerrum pH-titration technique is as follows: [Cu(**154**)] > [UO₂(**154**)] > [Ni(**154**)] > [Co(**154**)]. The tendency of the complex formation in all metal ions is high enough to prevent the precipitation of metal hydroxides up to pH 12. [Co(**154**)] and [Ni(**154**)] are stable only at pH > 6 and dissociate into protonated species at lower pH values [200].

The insertion of crown ether moieties at the periphery of the cobalt(II) Schiff base complex does not lead to a system with an enhanced molecular oxygen-binding properties, even though crown ether groups will increase the electron

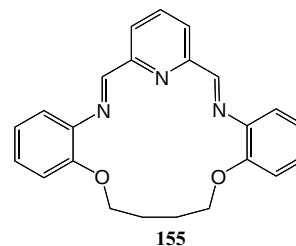
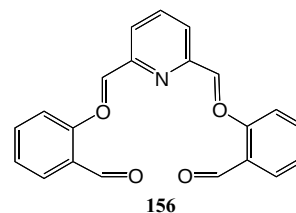
density of the nucleus. No oxygen binding property is observed for [CoNa₂(**154**)(NO₃)₂·4H₂O] [200].

Only the μ -peroxo compound [Co₂(**154**)₂(μ -O₂)-(DMSO)]₂ was obtained in dimethylsulphoxide solution. [Co(**154**)] is paramagnetic (μ_{eff} = 2.43 BM), but its oxygen adduct is diamagnetic. The role of the solvent molecule is undoubtedly to stabilize the Co–O bond by enabling octahedral co-ordination around the metal to be achieved upon oxygenation in solution. When dissolved in chloroform the diamagnetic compound quickly decomposes into paramagnetic species. Even though dimethylformamide was also recommended as a suitable solvent for oxygenation in solution, an octahedral complex with two solvent molecules, [Co(**154**)(DMF)₂], was the only product isolated under similar conditions.

4. Macrocyclic and macroacyclic polyamine ligands

As reported above, it is possible to obtain the designed acyclic or cyclic Schiff bases by self-condensation of the appropriate precursors, if the condensation product is stable to hydrolysis or by template procedure. The corresponding reduced metal free polyamine derivatives has been synthesized by reduction of the Schiff bases or related complexes, quite often in one step, by performing the reduction in situ [5,42].

The non-template reaction of 2,6-bis(2-diformylphenoxy)methylpyridine and 1,5-bis(2-aminophenoxy)-3-oxapentane in absolute ethanol gives the [1+1] macrocyclic Schiff-base **155** as confirmed by the X-ray structure that includes a methanol of solvation hydrogen-bonded to an imine nitrogen (Fig. 70a) [201].

**155****156**

The Schiff base cyclocondensation of 2,6-diformylpyridine and 1,5-bis(2-aminophenoxy)butane in acetonitrile in the presence of the appropriate hydrated metal salt and in 1:1:1 mole ratio gave [Ag(**155**)](ClO₄), [Zn(**155**)](ClO₄)₂·2H₂O, [Zn(**155**)](NO₃)₂, [Cd(**155**)(H₂O)₂](ClO₄)₂ and [Cd(**155**)(NO₃)(CH₃OH)](NO₃) [201].

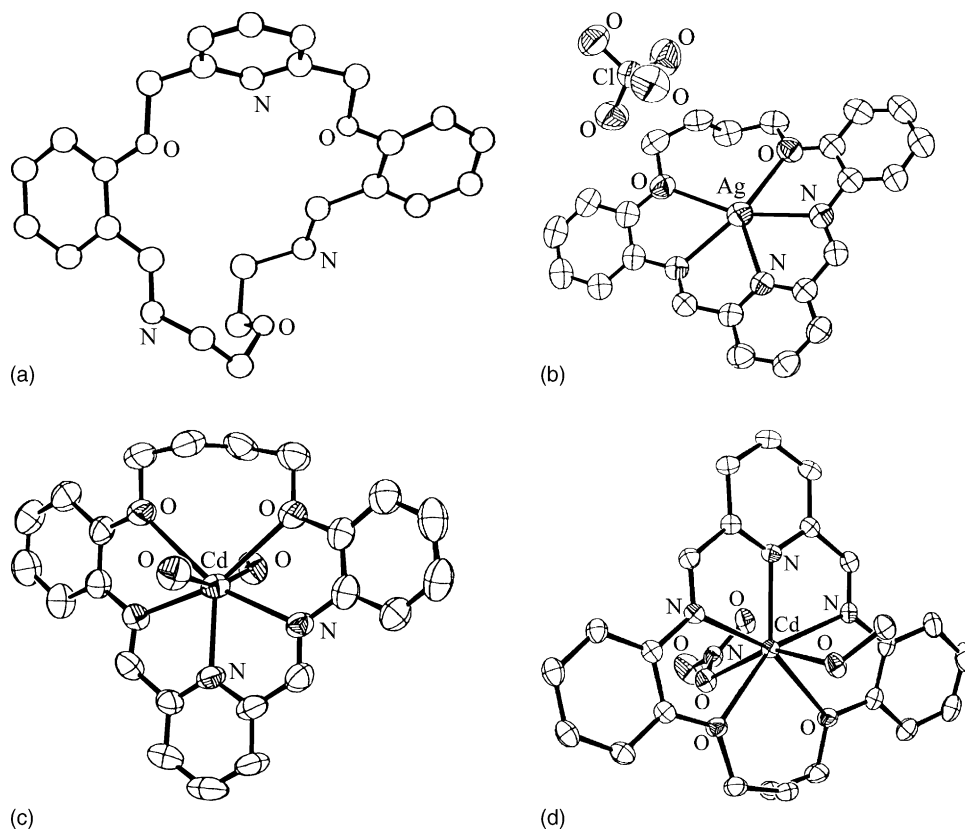


Fig. 70. Structure of **155** (a), $[\text{Ag}(\mathbf{155})](\text{ClO}_4)$ (b), $[\text{Cd}(\mathbf{155})(\text{H}_2\text{O})_2]^{2+}$ (c) and $[\text{Cd}(\mathbf{155})(\text{NO}_3)(\text{CH}_3\text{OH})]^+$ (d) (adapted from Ref. [201]).

In $[\text{Ag}(\mathbf{155})](\text{ClO}_4)$ the silver ion is in a distorted pentagonal planar endomacrocyclic environment, coordinated by all donor atoms of the N_3O_2 macrocyclic ligand (Fig. 70b). In $[\text{Cd}(\mathbf{155})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ the metal ion is in a distorted pentagonal bipyramidal endomacrocyclic environment involving the full donor atom set of the N_3O_2 macrocyclic ligand and the oxygen atoms of two water molecules of solvation. The two oxygen atoms from the water molecules occupy the axial positions of the bipyramid (Fig. 70c). Also in $[\text{Cd}(\mathbf{155})(\text{NO}_3)(\text{CH}_3\text{OH})](\text{NO}_3)$ the metal ion is seven coordinated with a distorted pentagonal bipyramidal geometry arising from coordination by all donor atoms of the N_3O_2 macrocyclic ligand, the oxygen atom of a methanol of solvation and an oxygen atom, from a monodentate nitrate anion; the methanol and nitrate groups are sited *trans* to each other (Fig. 70d).

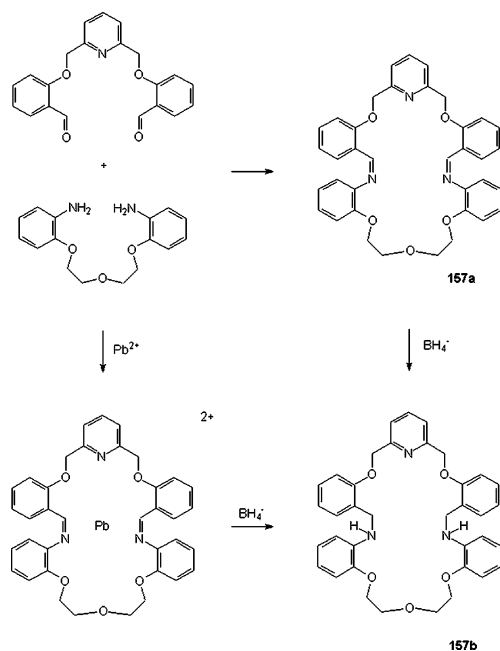
The [1+1] diimine macrocycle **155** in the presence of some metal ions is not stable and suffers hydrolysis; thus when reacted with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in a 1:1 molar ratio and in methanol forms the acyclic complex $[\text{Ce}(\mathbf{156})(\text{N}-\text{O}_3)_3] \cdot 2\text{H}_2\text{O}$ which represents the product of a retro-Schiff base reaction with the consequent formation of the diformyl precursor **156** with accompanying cerium(III) complexation [201]. The acyclic nature of $[\text{Ce}(\mathbf{156})(\text{NO}_3)_3] \cdot 2\text{H}_2\text{O}$ was confirmed by X-ray structure analysis. The cerium(III) ion is ten coordinated, the bonding being provided by oxygen atoms from three symmetrically bidentate nitrate anions

together with two oxygen atoms from the water molecule and one carbonyl oxygen from each **156** ligand. The second carbonyl oxygen atom in each ligand molecule is not coordinated. The coordinated water molecules are involved in hydrogen bonding with a pyridyl nitrogen, and with the non coordinated benzaldehyde oxygen atoms of different molecules [201].

Nevertheless the macrocyclic Schiff base lanthanide(III) complexes $[\text{Ln}(\mathbf{155})(\text{X})_3]$ ($\text{X} = \text{NO}_3^-$, $\text{Ln} = \text{La}^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , Lu^{3+} ; $\text{X} = \text{ClO}_4^-$, $\text{Ln} = \text{La}^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , Eu^{3+}) and $[\text{Pb}(\mathbf{155})(\text{ClO}_4)_2]$ have been prepared by cyclocondensation of 2,6-bis(2-formylphenoxy)methylpyridine and 1,5-bis(2-aminophenoxy)-3-oxapentane in the presence of the appropriate metal salt as templating agent. The nitrate groups are supposed to act as bidentate, the perchlorate groups may be coordinated [202].

Although initially the ligand **157b** was prepared in 30% yield via a lead(II)-templated cyclocondensation of the precursor dialdehyde and diamine followed by an in situ reductive demetallation of the lead(II) Schiff base intermediate $[\text{Pb}(\mathbf{157a})]^{2+}$ by sodium tetrahydroborate, a non-template approach was found to be easier and more effective for the preparation of the [1+1] reduced macrocycle **157b** from the Schiff base **157a** (Scheme 30) [202].

Complexation reactions of **157b** with hydrated lanthanide(III) nitrates (La^{3+} , Lu^{3+}) or perchlorates (La^{3+} , Ce^{3+} ,



Scheme 30.

Pr^{3+}), were carried out in order to investigate the coordination capability of this more flexible and hydrolytically stable ligand towards the lanthanide(III) ions. Only with lutetium(III) nitrate it was possible to obtain a metal complex of formula $[\text{Lu}_2(\mathbf{157b})](\text{NO}_3)_6 \cdot 2.5 \text{ Et}_2\text{O}$; with the lighter lanthanide ions the free macrocycle and unreacted metal salt were recovered [202].

The cyclocondensation of 2,6-diformylpyridine and 1,5-bis(2-aminophenoxy)-3-azapentane in the presence of $\text{Cd}(\text{NO}_3)_2$ or $\text{Cd}(\text{ClO}_4)_2$ gives rise to the complexes $[\text{Cd}(\mathbf{158a})(\text{NO}_3)_2]$ and $[\text{Cd}(\mathbf{158a})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ [202]. The same reaction in the presence of $\text{Zn}(\text{ClO}_4)_2$ affords the dinuclear μ -hydroxy-bridged zinc complex $[\text{Zn}_2(\mathbf{158a})_2(\text{OH})](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN}$ [202].

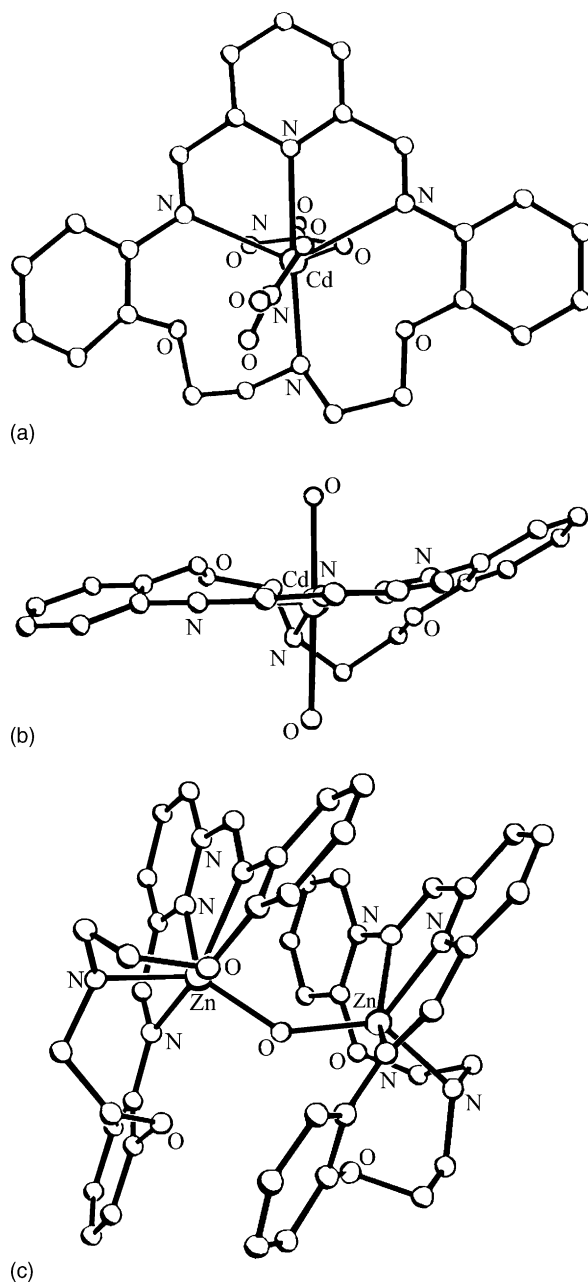
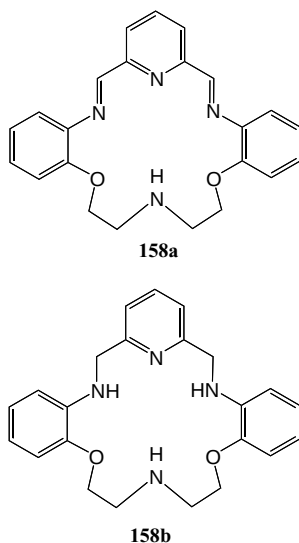


Fig. 71. Structure of $[\text{Cd}(\mathbf{158a})(\text{NO}_3)_2]$ (a), $[\text{Cd}(\mathbf{158a})(\text{H}_2\text{O})_2]^{2+}$ (b) and $[\text{Zn}_2(\mathbf{158a})_2(\text{OH})]^{3+}$ (c) (adapted from Ref. [202]).

In $[\text{Cd}(\mathbf{158a})(\text{NO}_3)_2]$ the seven coordinated metal ion shows a distorted capped trigonal prismatic geometry arising from coordination by the four nitrogen atoms of the macrocycle and three oxygen atoms from monodentate nitrate and an asymmetric bidentate nitrate sited *trans* to the macrocyclic plane (Fig. 71a) [202].

In $[\text{Cd}(\mathbf{158a})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ the six coordinated cadmium(II) ion is in a distorted octahedral geometry arising from coordination by the four nitrogen atoms of the macrocycle, and two oxygen atoms from water molecules sited *trans* to the macrocyclic plane. These oxygen atoms are symmetrically bound. The perchlorate anions are non-coordinating [202] (Fig. 71b).

In $[\text{Zn}_2(\mathbf{158a})_2(\text{OH})](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN}$ the zinc ions are both five coordinated by four macrocycle nitrogen atoms and the bridging oxygen atom of the coordinated hydroxide. The geometry at one zinc ion is a distorted square pyramidal while the other zinc ion shows a significant distortion towards trigonal bipyramidal (Fig. 71c) [202].

The manganese template cyclocondensation of 2,6-pyridinecarboxaldehyde and 1,5-bis(2-aminophenoxy)-3-azapentane in methanol, followed by an in situ reductive

demetallation of the Schiff base macrocyclic manganese(II) complex using excess of sodium borohydride, readily gave the metal-free macrocycle ligand **158b** [202]. The X-ray structure of **158b**, recrystallized from acetonitrile, confirmed the macrocyclic nature of the product (Fig. 72a). The macrocyclic ring is somewhat bent, having a butterfly shape. There is a water of crystallisation weakly hydrogen bonded with one nitrogen atom.

The zinc(II) and cadmium(II) complexes $[\text{M}(\mathbf{158b})(\text{NO}_3)_2]$ or $[\text{M}(\mathbf{158b})(\text{S})_2](\text{ClO}_4)_2$ ($\text{M} = \text{Zn}^{2+}$, $\text{S} = \text{H}_2\text{O}$; $\text{M} = \text{Cd}^{2+}$, $\text{S} = \text{CH}_3\text{CN}$) have been synthesized. In $[\text{Cd}(\mathbf{158b})(\text{NO}_3)_2]$ the metal ion is once again seven coordinated with a distorted capped trigonal prismatic geometry arising from coordination by the four nitrogen atoms of the macrocycle, and three oxygen atoms from a monodentate nitrate and an asymmetric, bidentate nitrate sited *trans* to the macrocyclic plane (Fig. 72b).

In $[\text{Cd}(\mathbf{158b})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ the metal ion is also seven coordinated in a pentagonal bipyramidal geometry formed by the four nitrogen atoms and one ether oxygen atom coordinated in the equatorial plane and the nitrogen atoms of two acetonitrile molecules symmetrically bound in the axial positions. The perchlorate anions are non-coordinating [202] (Fig. 72c).

The macrocycles **159** and **160** have been synthesized directly from an in situ reduction in methanol with excess of sodium tetrahydroborate of the corresponding metal diimine complexes, the lead(II) perchlorate for **159** or the manganese(II) perchlorate for **160** [203].

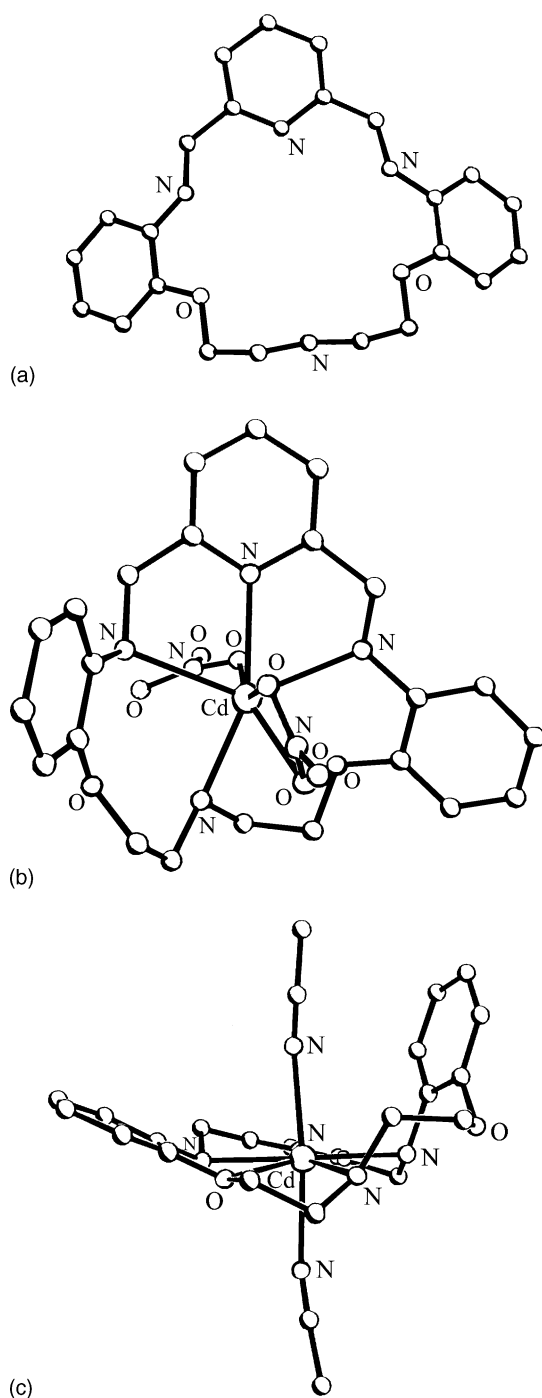
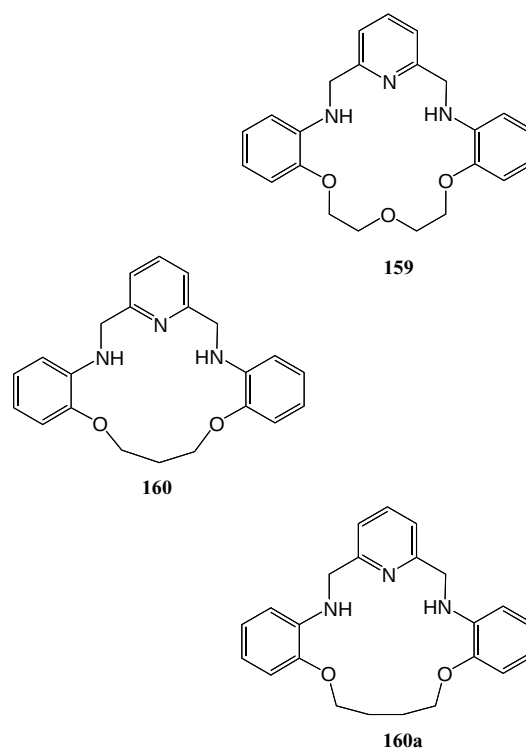


Fig. 72. The structure of **158b** (a), $[\text{Cd}(\mathbf{158b})(\text{NO}_3)_2]$ (b) and $[\text{Cd}(\mathbf{158b})(\text{CH}_3\text{CN})_2]^{2+}$ (c) (adapted from Ref. [202]).



Crystals of **160**, produced by recrystallization of the crude product from acetonitrile, show the macrocycle is bent

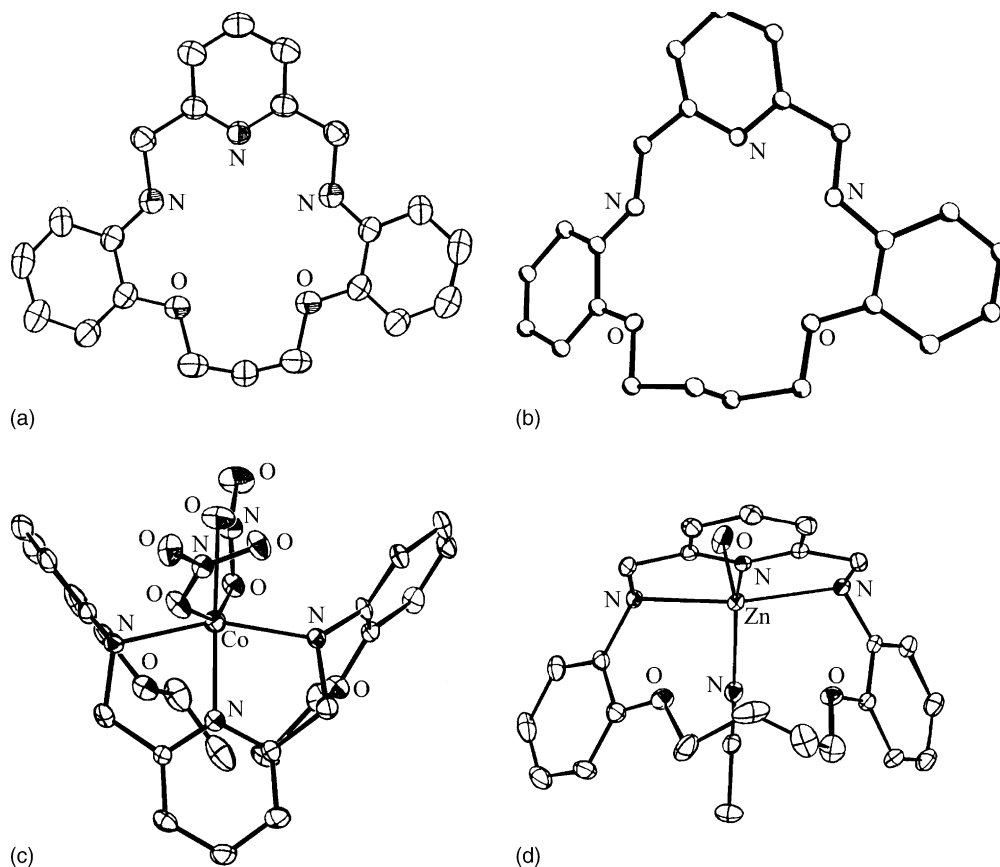


Fig. 73. Structure of **160** (a), **160a** (b), $[\text{Co}(\mathbf{160a})(\text{NO}_3)_2]$ (c) and $[\text{Zn}(\mathbf{160a})(\text{H}_2\text{O})(\text{CH}_3\text{CN})]^{2+}$ (d) (adapted from Ref. [203]).

(Fig. 73a). In $\text{H}_2\text{-160} \cdot 2\text{ClO}_4$, obtained by slow evaporation of a CH_3CN solution of $[\text{La}(\mathbf{160})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, the diprotonated macrocycle is almost symmetrical. The difference between the **160** and $\text{H}_2\text{-160} \cdot 2\text{ClO}_4$ lies in the environments of the nitrogen atoms of the amino groups owing to protonation and to the need to accommodate the perchlorate ions, which are involved in hydrogen bonding interactions with the NH_2 groups.

Reaction between **159** and hydrated lanthanide nitrates or perchlorates in a 1:1 molar ratio gave $[\text{Ln}(\mathbf{159})](\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$) and $[\text{Ln}(\mathbf{159})](\text{NO}_3)_3 \cdot x\text{H}_2\text{O} \cdot y\text{Et}_2\text{O}$ ($\text{Ln} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Lu}^{3+}$). The complexes $[\text{Ln}(\mathbf{160})](\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$) were obtained by reaction of **160** with hydrated lanthanide(III) perchlorates but no complexes have been obtained in the reactions attempted with **160** and lanthanide(III) nitrates, where in all cases the free macrocycle and unreacted metal salts separate out from the reaction medium on cooling to room temperature [203].

Comparison of these results with those obtained for the related diimine macrocycles containing pyridine indicates that reduction of the imine groups increases the ligand flexibility, leading to an enhancement of the complexation capacity of both reduced systems. This effect is especially important at the end of the lanthanide series, with the smaller

lanthanide cations, where flexibility of the ligands is necessary in order to allow the full set of donor atoms from the macrocycle to approach the metal ions.

The results also show that the ligand, derived from 1,5-bis(2-aminophenoxy)-3-oxapentane and containing a pyridine head unit, provides a ligand framework capable of forming more stable lanthanide(III) complexes than when the furan head unit is used. Attempts to synthesize lanthanide complexes of the furan-containing analogue of **159** failed [203].

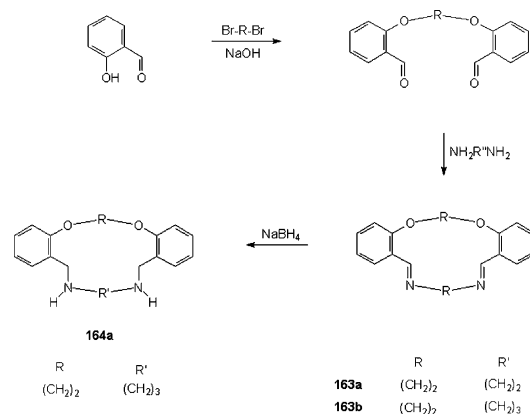
The macrocyclic nature of **160a** prepared by an in situ reduction of the corresponding manganese(II) Schiff base, was ascertained by X-ray diffractometry [203] (Fig. 73b). The ligand is not planar and intramolecular hydrogen bonds are present between amine hydrogens and the nearest ether oxygen atoms. **160a** reacts with cobalt(II), nickel(II), zinc(II) and cadmium(II) nitrate or perchlorate to give $[\text{M}(\mathbf{160a})(\text{NO}_3)_2]$ and $[\text{M}(\mathbf{160a})(\text{ClO}_4)_2] \cdot x\text{H}_2\text{O} \cdot y\text{CH}_3\text{CN}$ ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$) [203]. In $[\text{Co}(\mathbf{160a})(\text{NO}_3)_2]$, grown from CH_3CN , the metal ion is coordinated to the three nitrogen atoms of the donor set. The remaining three coordination sites are occupied by the oxygen atoms from one monodentate and one bidentate nitrate ligand. The ether oxygen atoms of the macrocyclic ligand are not coordinated. The geometry can be described as distorted octahedral, where the three nitrogen atoms of the macrocyclic ligand

are in meridional positions. The fourth coordination position of this plane is occupied by one of the oxygen atoms of the bidentate nitrate ligand. The nitrogen-atom configuration is *R,S* (or *S,R*) [203] (Fig. 73c).

The structure of $[\text{Ni}(\mathbf{160a})(\text{NO}_3)_2]$ is similar to that described above being built up of discrete molecules with the nickel ion coordinated by one macrocyclic ligand through the nitrogen atoms, and through three oxygen atoms of two nitrate molecules. The environment around the metal ion is a distorted octahedron again, with the three nitrogen atoms in meridional positions and one oxygen atom of the bidentate nitrate ligand occupying the fourth coordination position of this plane. The ether oxygen atoms of the macrocyclic ligand are not coordinated. The nitrogen-atom configurations are *R,S* (or *S,R*).

In $[\text{Zn}(\mathbf{160a})(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ the metal ion is in a five coordinated environment in which all three nitrogen donor atoms of the macrocycle are coordinated; the ether oxygen atoms are not coordinated. The coordination sphere is completed by one acetonitrile and one water molecule [203] (Fig. 73d).

A large variety of macrocycles where the shape of the coordination cavity, the number and the type of the donor groups (mainly NH, S, O) have been progressively changed, have been prepared by a procedure similar to that reported in



Scheme 31.

Scheme 31. Their coordinating and selective extracting properties of metal ions from water into organic phase (generally chloroform) was studied and reviewed [42].

The [1+1] cyclic nature of these compounds and the coordination environment about the different metal ions in the related complexes were especially inferred by single crystal X-ray structural determinations as ascertained, for instance, for the macrocycles **161a** (Fig. 74a), **162a** (Fig. 75a) and **162b** (Fig. 76a) [204]. The whole set of

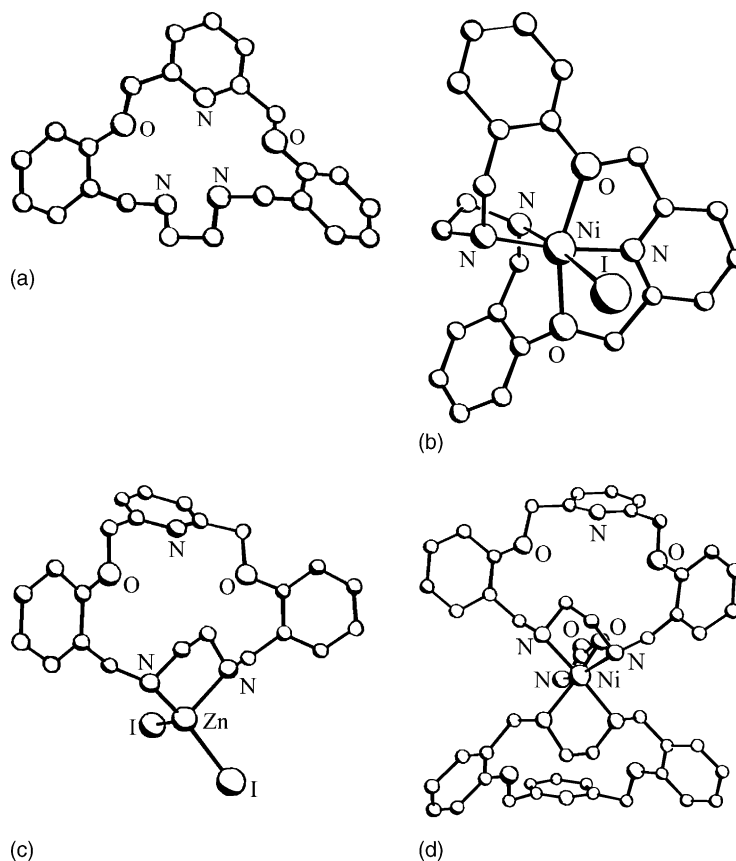


Fig. 74. Structures of **161a** (a) $[\text{Ni}(\mathbf{161a})(\text{I})]^+$ as an example of 1:1 complex with the metal inside the macrocycle (b), $[\text{Zn}(\mathbf{161a})(\text{I})_2]$ as an example of 1:1 complex with the metal ion coordinated exocyclically (c) and $[\text{Ni}(\mathbf{161a})_2(\text{NO}_3)](\text{NO}_3)$ as an example of 1:2 complex with the metal ion coordinated exocyclically to two macrocycles (d) (adapted from Ref. [204]).

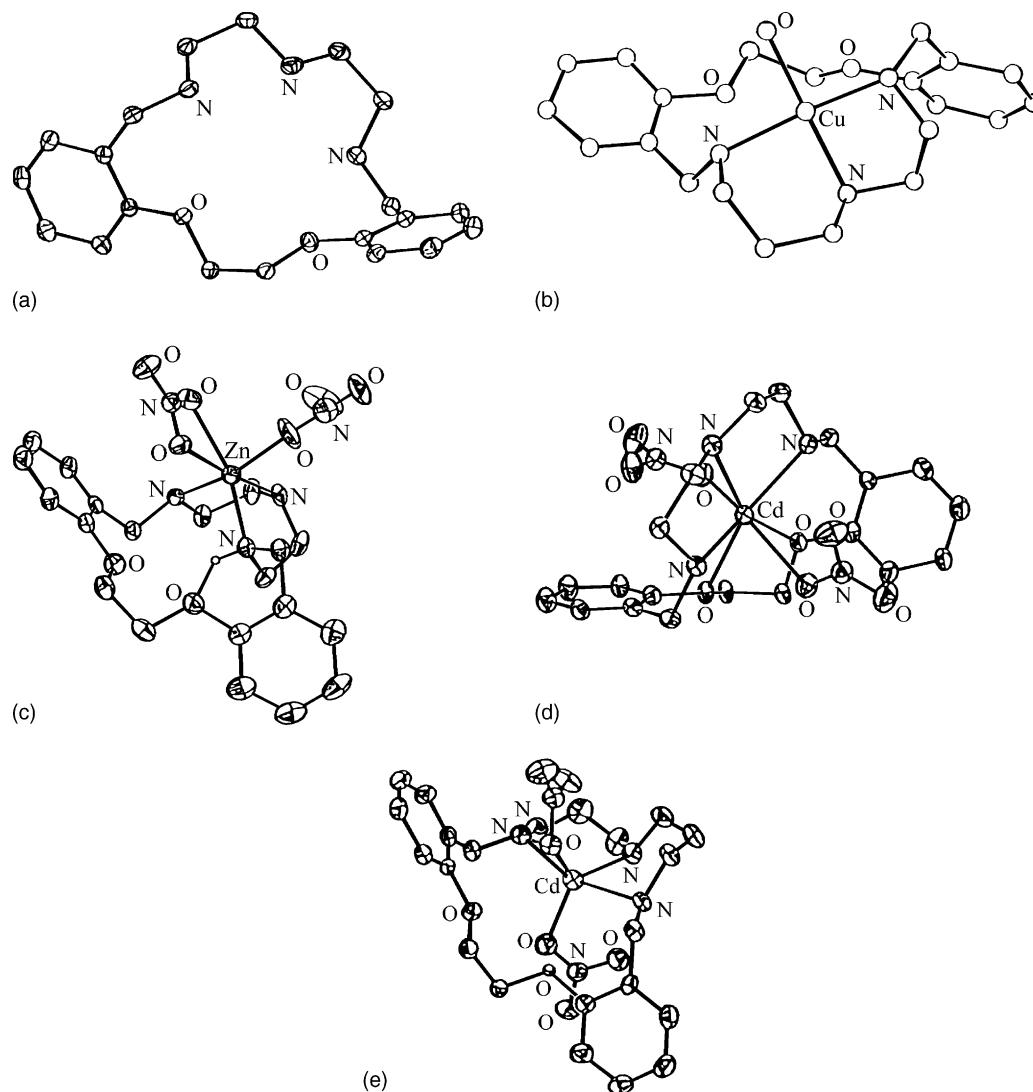
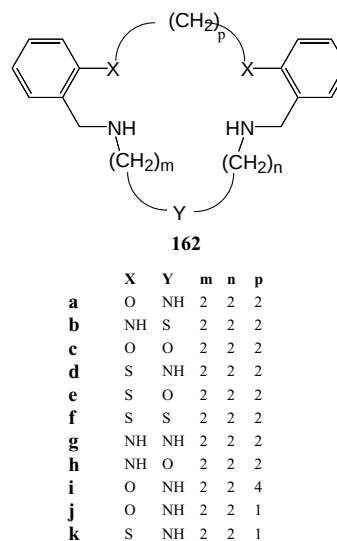
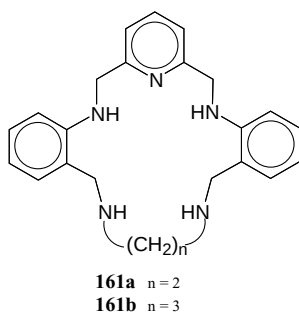


Fig. 75. Structures of **162a** (a), $[\text{Cu}(\mathbf{162a})(\text{H}_2\text{O})]^{2+}$ (b), $[\text{Zn}(\mathbf{162a})(\text{NO}_3)_2]$ (c), $[\text{Cd}(\mathbf{162a})(\text{NO}_3)_2]$ (d), and $[\text{Cd}(\mathbf{162c})(\text{NO}_3)_2]$ (e) (adapted from Refs. [206,207]).

donor atoms, present in these macrocycles or only part of them can be coordinated to a metal ion, this depending on the specific characteristic of the ligand and of the metal ion employed. The metal ion is generally retained in the macrocyclic moiety, but variation of the anion can induce the metal ion to be coordinated exocyclically to the macrocycle via the two secondary amine nitrogen atoms [204].



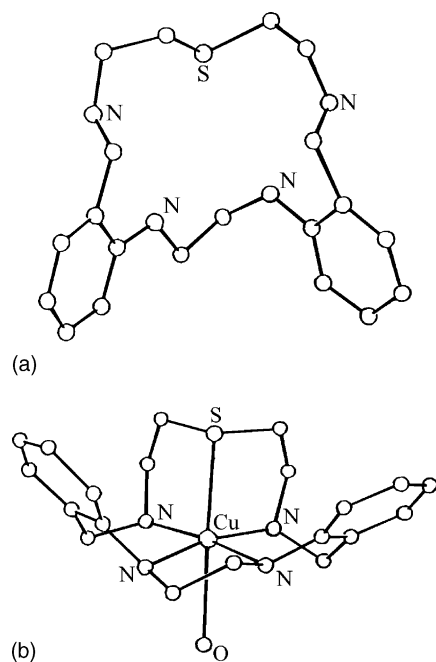


Fig. 76. The structure of **162b** (a) and of $[\text{Cu}(\mathbf{162b})(\text{H}_2\text{O})]^+$ (b) (adapted from Refs. [204,208]).

Copper(II), nickel(II), zinc(II), cadmium(II) and mercury(II) ions react with **161a** or **161b** forming 1:1 and 1:2 species. The metal ion in $[\text{Cu}(\mathbf{161a})(\text{H}_2\text{O})](\text{ClO}_4)_2$ is six coordinated and lies within the folded macrocyclic cavity. The donor set comprises the five macrocyclic donor atoms and a water molecule. Overall, the coordination sphere corresponds to a restricted tetragonal rhombic arrangement [204].

$[\text{Ni}(\mathbf{161a})(\text{I})_2] \cdot \text{CH}_3\text{OH}$ also has all donors of the macrocycle coordinated to the metal ion with an iodide anion occupying the sixth site to yield a distorted octahedral geometry (Fig. 74b) [204].

The metal ions in $[\text{Zn}(\mathbf{161a})(\text{I})_2] \cdot \text{H}_2\text{O}$ and $[\text{Hg}(\mathbf{161a})(\text{I})_2]$ are four coordinated in a tetrahedral geometry and lie outside the macrocyclic cavity. The donor set in each molecule comprises the two secondary amine nitrogen atoms from the macrocycle and the two iodide anions. Thus the coordination of iodide favours zinc(II) and mercury(II) with a tetrahedral geometry at the metal ions (Fig. 74c) [204].

The complex $[\text{Zn}(\mathbf{161a})(\text{NO}_3)](\text{NO}_3)$ has all donors of the macrocycle coordinated to the central metal ion with one oxygen from a nitrate anion occupying the sixth site to yield an approximately trigonal prismatic geometry. The structure of $[\text{Cd}(\mathbf{161a})(\text{NO}_3)(\text{CH}_3\text{OH})](\text{NO}_3)$ shows that the metal ion is seven coordinated in an approximately pentagonal bipyramidal environment consisting of the full donor set of the macrocycle together with one nitrate and a methanol oxygen [204].

The structure of $[\text{Cd}(\mathbf{161b})(\text{ClO}_4)(\text{CH}_3\text{CN})](\text{ClO}_4)$ shows that the metal ion has a coordination environment consisting of the full donor set of the macrocycle together with an

oxygen from a perchlorate anion and an acetonitrile nitrogen [204].

In $[\text{Ni}(\mathbf{161a})_2(\text{NO}_3)](\text{NO}_3) \cdot \text{CH}_3\text{OH}$ the metal ion is six coordinated to the aliphatic nitrogen atoms from the macrocycle, one pair from each ring, and a bidentate nitrate anion. The nickel(II) is therefore complexed in an exomacrocyclic manner (Fig. 74d) [204].

These ligands are compounds of intermediate rigidity. The selective complexation and transport of metal ions may be facilitated by macrocyclic ligands of intermediate rigidity sufficient to present a donor set with a defined geometry to a metal ion but flexible enough to encourage favourable kinetics of metal ion incorporation and release.

In some cases, the stability constants of such complexes have been shown to correlate with the goodness-of-fit of the metal ion for the donor cavity although other mechanisms for discrimination may also operate. Nevertheless, when metal ions are discriminated by a poor fit of the cavity, the possibility exists that the favoured mode of interaction will involve *exo*-macrocyclic complexation using only part of the macrocyclic donor set.

Extraction experiments (water–chloroform) and related transport experiments (water–chloroform–water) were successfully carried out using **161a** and **161b** in the respective chloroform phases which also contained hexadecanoic acid as a counter ion to inhibit bleeding into the aqueous phase of charged species such as the protonated macrocycle and/or the corresponding metal complexes.

For the transport runs, the pH gradient across the cell served to drive the transfer of the metal ions from the source to the receiving phase. In all single-metal extraction and transport studies, the copper(II) ion was favoured over the nickel(II) ion.

The results from these transport and extraction studies parallel each other. In particular the transport results follow the respective $\log K$ values for the individual complexes although it is noted that this need not necessarily be the case. The results from the competitive extraction and transport experiments also follow the above trends and confirm the potential of systems such as these for the discrimination of metals of the present type. Stability constant studies show a stronger complexation to cadmium than to zinc.

The [14–19]-membered macrocyclic Schiff bases **162a–k**, incorporating O_2N_2 , O_2N_3 , O_3N_2 , N_2N_3 , $\text{O}_2\text{N}_2\text{S}$, $\text{S}_2\text{N}_2\text{S}$, S_2N_3 , etc. donor sets, have been obtained by a reaction pathway similar to that reported in Scheme 31 for the macrocycles **163** and **164** [204–206].

The X-ray structure of the [17]-membered O_3N_2 macrocycle **162a** indicates that the macrocyclic hole size is too large to enable simultaneous coordination of all donor atoms of the copper(II), nickel(II) or zinc(II) (Fig. 75a) [206,207].

In $[\text{Cu}(\mathbf{162a})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, the metal ion has a pseudo square-planar coordination geometry with the coordination sphere consisting of the three nitrogen atoms of the macrocycle together with an oxygen from water. The ether

oxygen donors of the macrocycle do not coordinate (Fig. 75b).

In $[\text{Zn}(\mathbf{162a})(\text{NO}_3)_2]$ the macrocyclic ligand adopts an arrangement that removes the ether donors from the coordination sphere. The three nitrogen donors of the macrocycle occupy an approximate facial arrangement around the zinc ion with its overall coordination number being six; the remaining coordination positions are filled by a monodentate and bidentate nitrate ligand (Fig. 75c).

$[\text{Cd}(\mathbf{162a})(\text{NO}_3)_2]$ has a very distorted pentagonal bipyramidal coordination geometry in the solid state with the cadmium(II) ion lying in the cavity of the five equatorial donor atoms of the [17]-membered macrocycle (Fig. 75d); nitrate groups occupy the axial sites and act as monodentate. In the corresponding [19]-membered ring cadmium complex $[\text{Cd}(\mathbf{162c})(\text{NO}_3)_2]$ (Fig. 75e) the ether donors are also outside bonding distance to the metal. The complex contains an approximately planar CdN_3 unit with a ruffled O_2N_3 arrangement. Overall, the coordination number is five with two monodentate nitrates completing the coordination shell.

The interaction of different metal ions with a series of O_2N_3 donor macrocycles gives rise to examples of dislocation behaviour in the coordination patterns of the resulting complexes. Dislocations occur when a gradual change of properties along the ligand series induces a sudden change in coordination behaviour for adjacent complexes in the series. The presence of such dislocations may form a basis for metal ion recognition [206,207].

For the nickel complexes in the solid state and in solution, the results are consistent with the presence of either octahedral or pseudo-octahedral coordination geometries. In solution, the unsubstituted [17]- and [18]-membered O_2N_3 rings appear to adopt a configuration about nickel in which two oxygens and two nitrogens occupy equatorial position while the remaining nitrogen coordinates at an axial site. The remaining axial position is occupied by a halide ion. In contrast, each of the [19]-membered ring complexes are found to adopt a structure different from that of the above complexes. A similar structural dislocation has been induced by introduction of two methyl substituents onto the N_3 -containing backbone of the unsubstituted [17]-membered ring complex. The effects of such structural dislocations are most readily apparent in the stability constants that are 10^3 – 10^5 lower than the remaining complexes. A comparison of the stability constants for the nickel complexes with those for the corresponding cobalt(II) complexes indicates that both series have similar dislocation patterns. In contrast, the copper(II) complexes for which the evidence suggests non coordination of one or both ether oxygens in some complexes, exhibit a different stability pattern [206,207].

When zinc(II) and cadmium(II) ions react with unsubstituted [17–19]-membered macrocycles, the trends in the stabilities for each ion parallel each other for the first two ligands, with the stability constants falling in the order $\text{Cd}^{2+} > \text{Zn}^{2+}$. However, for the [19]-membered ring ligand, a dislocation of the trend is evident for the cadmium(II)

complex but not for the zinc(II) complex: the stability of the cadmium(II) complex is considerably lower than expected, the stability order is now $\text{Zn}^{2+} > \text{Cd}^{2+}$. The origin of the observed dislocation along the cadmium(II) series appears to be crossed from coordination of the ether groups in the [17]- and [18]-membered ring systems to their non-coordination in the [19]-membered ring system. For corresponding substituted ligands derivatives, a similar dislocation pattern is observed and hence the dislocation appears to be primarily a function of ring size for these systems.

These studies illustrate the manner in which minor changes in macrocyclic ligand structure may be reflected by major changes within the coordination spheres of particular complexes and hence can be used to control alternate modes of ligand coordination, a process that can contribute to metal ion recognition by organic substrates [206,207].

As a continuation of these investigations, a study of the interaction of cobalt(II), nickel(II) and copper(II) ions with a much extended series of these ligands, including also sulfur-containing species, where a systematic variation in donor atom pattern and ring size are more clearly designed, has been reported [208].

The X-ray structures of the ligand **162b**, with an N_4S donor set (Fig. 76a), of $[\text{Cu}(\mathbf{162b})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (Fig. 76b), $[\text{Cu}(\mathbf{162d})](\text{ClO}_4)_2$, $[\text{Ni}(\mathbf{162d})(\text{H}_2\text{O})](\text{ClO}_4)_2$, and $\text{Ag}(\mathbf{162d})(\text{ClO}_4)$, with the similar N_3S_2 macrocycle **162d**, and $[\text{Ni}(\mathbf{162e})(\text{H}_2\text{O})(\text{NO}_3)_2]$, with the macrocycle **162e** containing a ON_2S_2 donor set, reveal that all the donor atoms are coordinated to the central metal ions.

In $[\text{Cu}(\mathbf{162b})(\text{H}_2\text{O})]^{2+}$ the ligand adopts a configuration different from that in **162b**; it occupies a square pyramidal arrangement around the copper(II) ion, which also has a water molecule weakly bound in the sixth position. The overall coordination geometry is distorted tetragonal and contains the copper ion slightly displaced from the N_4 equatorial plane towards the axial sulfur donor [208].

A comparison of the structure of the silver(I) and lead(II) complexes with the ligand **162d** shows the silver ion has an irregular five coordinated pentagonal bipyramidal geometry with all donor atoms of the macrocycle coordinated while in the lead(II) complex the metal ion is seven coordinated, being bound to the five donor atoms of the macrocycle and two perchlorate anions which occupy axial positions (Fig. 77a). The coordinated macrocycle adopts a flatter, more open conformation in the lead(II) complex with the metal ion situated above the macrocyclic cavity. This arrangement, together with the significantly longer metal to macrocyclic donor bond lengths found in this complex suggests that the affinity of **162d** for the lead(II) ion is somewhat reduced relative to that for the silver(I) ion [209].

In accordance with the above, the X-ray crystal structure of the silver(I) complex of **162f** where $\text{X} = \text{Y} = \text{S}$ (the ligand showing the highest silver(I)/lead(II) discrimination) confirms that a tight five coordinated geometry is maintained in this complex [210].

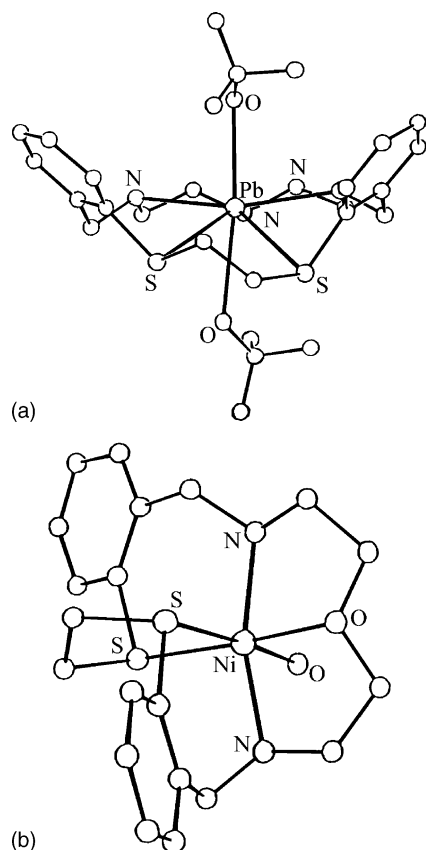


Fig. 77. The structure of $[\text{Pb}(\mathbf{162d})(\text{ClO}_4)_2]$ (a) and $[\text{Ni}(\mathbf{162e})(\text{H}_2\text{O})]^{2+}$ (b) (adapted from Refs. [208,209]).

In $[\text{Ni}(\mathbf{162e})(\text{H}_2\text{O})](\text{NO}_3)_2$ the nickel ion is six coordinated in a distorted octahedral geometry defined by all five donor atoms of the ON_2S_2 macrocycle and a water molecule; the macrocyclic backbone incorporating the NON donor fragment is arranged meridionally (Fig. 77b) [208].

Studies in solution demonstrate for all these complexes the formation of 1:1 complexes and extremely large stability differentials (up to 10^{10} for copper(II)) that may be achieved through structural variation within the ligand framework employed for this study. The contribution of the respective donor atom types to overall complexes stability was found to follow the expected order of $\text{NH}(\text{aliphatic}) > \text{NH}(\text{anilino}) > \text{S} > \text{O}$ [208].

In $[\text{Cu}(\mathbf{162d})(\text{ClO}_4)_2]$, the coordination about the copper(II) ion is square pyramidal with the sulfur atom in the axial site (Fig. 78a) [211]. The similar complex $[\text{Ni}(\mathbf{162d})(\text{H}_2\text{O})](\text{ClO}_4)_2$ displays an octahedral coordination, a water molecule being bound to the central metal ion (Fig. 78b) [211]. In $[\text{Cu}(\mathbf{162d})(\text{H}_2\text{O})]^{2+}$, the 1,4,7-triazaheptane fragment of **162d** is meridionally coordinated, but facially coordinated in $[\text{Ni}(\mathbf{162d})(\text{H}_2\text{O})]^{2+}$ and intermediate in $[\text{Ag}(\mathbf{162d})]^+$ [211].

$[\text{Ag}(\mathbf{162d})(\text{ClO}_4)]$ shows an irregular five coordinated geometry about the metal ion with all donor atoms of the macrocycle coordinated. The macrocycle wraps around the silver ion (Fig. 78c) [211]. In contrast, the structure of the

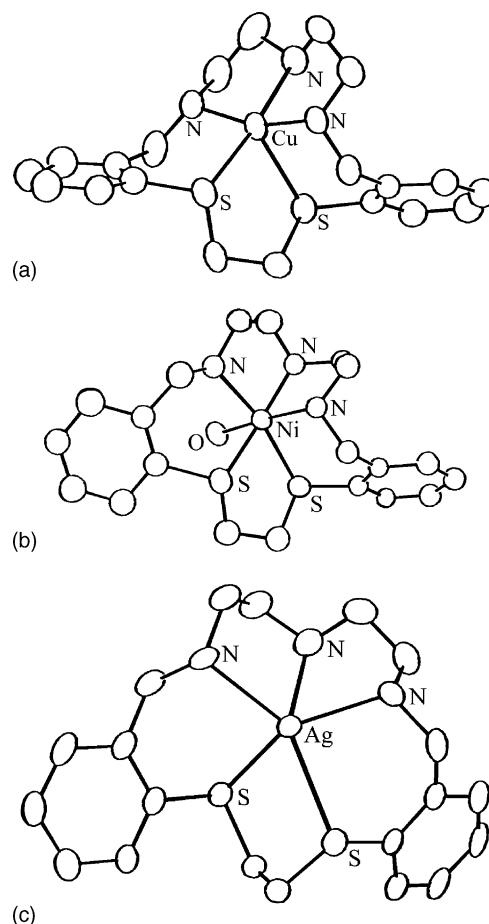


Fig. 78. Structures of $[\text{Cu}(\mathbf{162d})]^{2+}$ (a), $[\text{Ni}(\mathbf{162d})(\text{H}_2\text{O})]^{2+}$ (b) and $[\text{Ag}(\mathbf{162d})]^+$ (c) (adapted from Ref. [211]).

lead(II) complex with **162d** reveals that the metal is seven coordinated, being bound to the five donor atoms of the macrocycle and two perchlorate anions which occupy axial positions. The coordinated macrocycle adopts a flatter, more open, conformation than that occurring in the silver complex with the metal situated above the macrocyclic cavity [211].

The structure of $[\text{Ag}(\mathbf{162e})(\text{ClO}_4)]$ shows that the silver ion is bonded to all five donor atoms of the macrocycle which define a very irregular coordination polyhedron approximating to a trigonal bipyramid (Fig. 79a). The three atoms defining the equatorial sites and the silver atom are coplanar.

The coordination sphere and the configuration of the cyclic ligand in this complex are both quite similar to those in the corresponding silver perchlorate complexes of the related [17]-membered S_2N_3 - and $\text{S}_2\text{N}_2\text{S}$ -donor ligands, **162d** and **162f** [211,212].

The X-ray structure of $[\text{Zn}(\mathbf{162g})(\text{ClO}_4)_2]$ (Fig. 79b) reveals all five donor atoms of the macrocycle are coordinated to the zinc cation, which exhibits a distorted trigonal bipyramidal geometry. The complex cation is strongly hydrogen bonded to the perchlorate anions. In $[\text{Zn}(\mathbf{162h})(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)$ (Fig. 79c) the

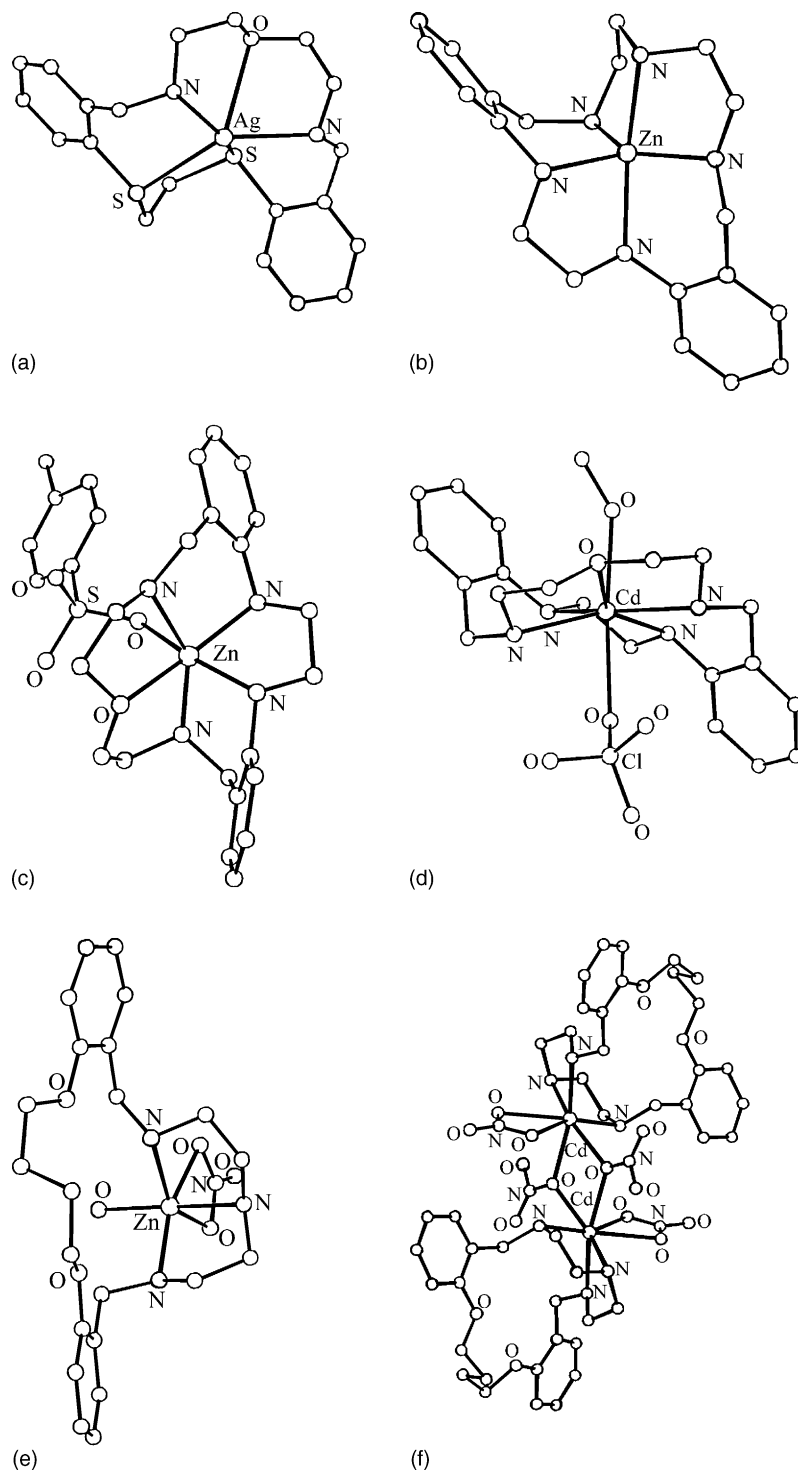


Fig. 79. Structures of $[\text{Ag}(\mathbf{162e})]^+$ (a), $[\text{Zn}(\mathbf{162g})]^{2+}$ (b), $[\text{Zn}(\mathbf{162h})(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)]^+$ (c), $[\text{Cd}(\mathbf{162h})(\text{CH}_3\text{OH})(\text{ClO}_4)]^+$ (d), $[\text{Zn}(\mathbf{162i})(\text{NO}_3)(\text{H}_2\text{O})]^+$ (e) and $[\text{Cd}(\mathbf{162i})(\text{NO}_3)_2]$ (f) (adapted from Refs. [211,212]).

zinc ion is six coordinated with a distorted octahedral geometry made up of all five donor atoms of the N_4O macrocyclic ligand and an oxygen atom of a coordinated 4-toluenesulfonate anion.

For $[\text{Cd}(\mathbf{162h})(\text{ClO}_4)(\text{CH}_3\text{OH})]\text{ClO}_4$ (Fig. 79d) the coordination sphere approximates a pentagonal bipyramid with

the donor atoms of the macrocycle in the equatorial positions while the axial sites are occupied by the oxygen atom of a perchlorate anion and the oxygen atom of a coordinated methanol molecule.

In $[\text{Zn}(\mathbf{162i})(\text{NO}_3)(\text{H}_2\text{O})]\text{ClO}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ the zinc ion is six coordinated with the complex cation exhibiting a

distorted octahedral geometry comprising the three nitrogen donor atoms of the O_2N_3 macrocyclic ligand in a facial arrangement, a water molecule *trans* to a nitrogen atom and the oxygen atoms of a chelating bidentate nitrate anion (Fig. 79e).

In contrast to the zinc complex, $[Cd(\mathbf{162i})(NO_3)_2] \cdot 2C_2H_5OH$ is binuclear with the two cadmium ions separated by 4.17 Å and linked by two single oxygen nitrate bridging across a center of inversion. The cadmium ions are seven coordinated the coordination of each being completed by the three nitrogens of the macrocyclic ligand and a bidentate nitrate ion (Fig. 79f).

The log K values for the respective complexes, determined potentiometrically in 95% methanol show that successive replacement of either nitrogen or oxygen heteroatoms by thioether donors leads to an increasing affinity for silver(I) relative to lead(II), as does the incorporation of an aliphatic NON or NSN donor sequence in the structure. For the [17]-membered system incorporating a S_2N_2S donor set, exceptional discrimination (of the order of 10^9) was observed.

A comparative investigation of the interaction of zinc(II) and cadmium(II) ions with the series of potentially pentadentate macrocycles incorporating nitrogen, oxygen, and/or sulfur donor atoms has been reported [212]. The 1:1 (metal:ligand) complexes have been isolated from the reaction of the metal nitrate in boiling ethanol with the appropriate macrocycle. In the majority of instances lithium perchlorate was added to the reaction solution to induce precipitation of individual complexes as their perchlorate salts. The zinc complexes of **162j**, **162i** and **162k** as well as the cadmium complexes of **162j** and **162k** contain one nitrate and one perchlorate per metal ion, whereas the remaining complexes contain two nitrate anions per complex. The attempted isolation of the zinc(II) and cadmium(II) complexes of most of the macrocycles incorporating less than three nitrogen donors resulted in the separation of protonated ligand salts [212].

FAB mass spectra of these complexes are consistent with the presence of 1:1 (metal to macrocycle) stoichiometries in which one nitrate ion is associated with the complex cation: in each case, a peak corresponding to $[M(\text{macrocycle})(NO_3)]^+$ was observed. These proves together with the conductance data suggest that each of the complexes incorporates at least one nitrate in its coordination shell [212].

Stability constants for the 1:1 (ligand:metal) zinc(II) and cadmium(II) complexes, determined potentiometrically in 95% methanol, show that there is a strong dependence of the respective stabilities on the donor atom set present, with the constants varying by more than eight orders of magnitude along the series. In particular, the magnitude of a particular log K value is strongly influenced by the number of nitrogen donors present, with the contribution to overall stability falling in the order: NH (aliphatic) > NH (anilino). Thus, the [17]-membered ring **162g**, with its N_5 donor set, yields

complexes which are significantly more stable than those of any of the other ligand in the series. Indeed, for all three [17]-membered systems where $X = NH$, the stabilities of the corresponding complexes are consistently higher than their analogues for which $X = O$ or S . The stabilities of the complexes of both metals also show the expected dependence on the nature of the Y donor.

Complexes of the type $[M(\mathbf{163})(X)_2]$, where $M = Cu^{2+}$, Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} ; $X = Cl^-$, Br^- , I^- , NCS^- , ClO_4^- , have been synthesized from a range of [14–17]-membered macrocycles and the X-ray structure solved [209]. Moreover the reduced analogues $M(\mathbf{164})(X)_2$ have been also prepared and fully characterized by X-ray diffractometry, especially those where $R = CH_2CH_2$ and $R' = CH_2CH_2CH_2$ (**164a**).

The structure of $[Co(\mathbf{164a})(NCS)](NCS)$ proves that the cobalt(II) ion is six coordinated in an octahedral environment formed by the N_2O_2 donor set of the macrocycle and the nitrogen atom of a isothiocyanate group (Fig. 80a). In $[Cu(\mathbf{164a})(Cl)](ClO_4)$, the coordination sphere of the copper(II) ion consists of the four donor atoms of the macrocycle together with a chloride ion. The copper ion sits above the hole of the macrocycle which is coordinated in a bent conformation (Fig. 80b) [209].

The nickel(II) dichloride or dibromide complexes $[Ni(\mathbf{164a})(X)_2]$ and the homologous complexes with larger [16]-membered macrocycle have a *trans*-six coordinated structure with the nickel ion contained in the hole of the ligand [213] (Fig. 80c).

$[Zn(\mathbf{164a})(I)_2]$ indicates that the two nitrogen donors of the macrocycle, together with two iodide ions, coordinated to the zinc ion in an approximately tetrahedral arrangement such that the zinc ion lies outside the cavity of the macrocycle. The ether oxygens of the macrocycle do not coordinate [209] (Fig. 80d).

The kinetics of dissociation in acid of a range of nickel(II), copper(II) and zinc(II) complexes of the above [14–17]-membered macrocycles show that for the unsubstituted macrocycles, the kinetic labilities follow the ring size sequence $14 > 15 > 16 < 17$. In agreement with the sequence, hole size considerations suggest that the [16]-membered macrocycle provides the ring of the best fit for nickel in this series of ligands [205,206]. In contrast to the nickel complexes, which show a peak in both the kinetic and thermodynamic stabilities at the [16]-membered ring complex, the copper complexes show no definite ring-size discrimination effects; this difference in behaviour has been discussed in terms of the respective structures of these two sets of complexes. Also for zinc complexes no well defined correlation between macrocyclic size and thermodynamic stability was observed [206,207].

The stabilities of the [16]-membered ring complexes tend to be lower than the corresponding [17]-membered ring system-undoubtedly reflecting, at least in part, the potential for less stable [4]-membered chelate rings in the former. Complexes of the larger rings also tend to be of lower stability than their [17]-membered ring analogues.

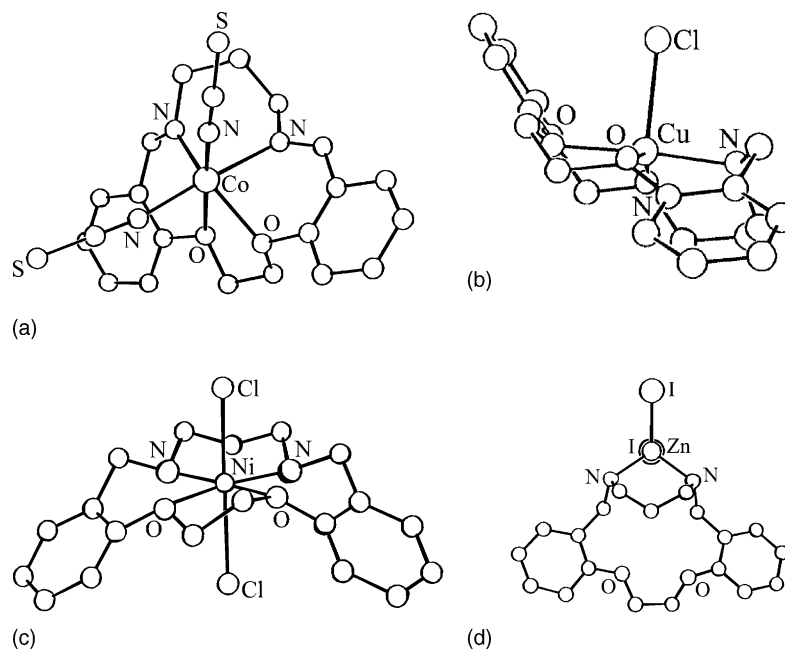
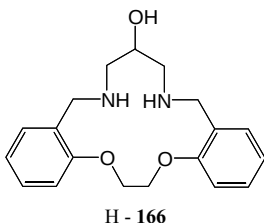
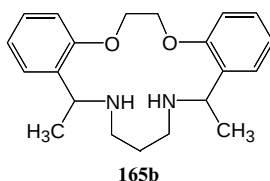
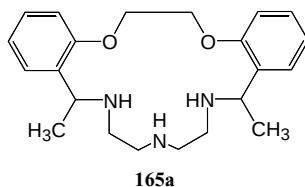


Fig. 80. Structures of $[\text{Co}(\mathbf{164a})(\text{NCS})]^+$ (a), $[\text{Cu}(\mathbf{164a})(\text{Cl})]^+$ (b), $[\text{Ni}(\mathbf{164a})(\text{Cl})_2]$ (c) and $[\text{Zn}(\mathbf{164a})(\text{I}_2)]$ (d) (adapted from Ref. [213]).

Similar macrocyclic ligands, i.e. mixed-donor dibenzo-substituted derivatives incorporating O_2N_3 , O_2N_4 , O_3N_2 , O_3N_3 , O_4N_4 and $\text{O}_2\text{N}_3\text{S}$ donor set [213] or methyl-substituted [15]- and [17]-membered derivatives incorporating N_3O_2 (**165a**) and N_2O_2 (**165b**) donors, have been subsequently prepared by the same synthetic procedures and their interaction with cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II) or silver(I) ions evaluated [213,214].



All ligands form 1:1 (metal:ligand) complexes. The stability of the complexes depends on the type and the extent of donor set and the lengthening of the aliphatic chains. As

expected ether oxygens or tosylated nitrogens show weak donor capacity towards the above mentioned metal ions. The stability of the metal complexes decreases when $\text{CH}_2\text{CH}_2\text{CH}_2$ groups replace CH_2CH_2 groups.

Substitution of a thioether donor for a secondary amine donor leads to an expected reduction in stability for the corresponding zinc(II), cadmium(II) and lead(II) complexes, while the value for the soft silver(I) complex remains essentially unaltered [214].

The binding of silver(I) and lead(II) ions to the [17]- and [18]-membered O_3N_2 ligands has been assessed in $(\text{CD}_3)_2\text{SO}$ by means of ^{13}C NMR spin-lattice relaxation (T_1) studies as well as by observation of the induced chemical shifts of particular resonances on complex formation. Overall, the NMR results correlate well with the observed thermodynamic stabilities of the individual complexes.

As expected from the presence of an additional nitrogen donor in **165a** relative to **165b**, the stabilities of the complexes of the former are in each case significantly higher than those of the corresponding complexes of **165b**. The solution data suggest that the stability order of cobalt(II) < nickel(II) < copper(II) > zinc(II) holds for both ligand systems. The stabilities for the metal complexes of the dimethyl derivatives are either reduced or remain almost unchanged relative to the values for the corresponding complexes of the parent unsubstituted analogues. For the cases where a reduction is evident, this most probably reflects steric influences associated with the additional bulk of the methylated derivatives.

An X-ray crystallographic study of $[\text{Ni}(\mathbf{165a})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (Fig. 81) confirms that the nickel ion is six coordinated, with the complex cation exhibiting a distorted

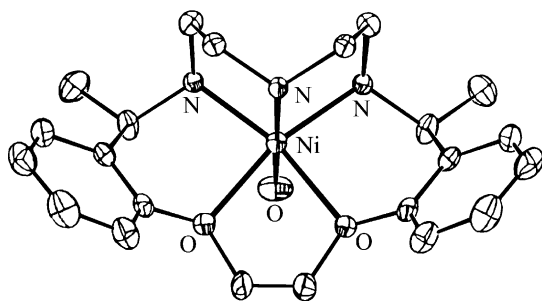


Fig. 81. Structure of $[\text{Ni}(\mathbf{165a})(\text{H}_2\text{O})]^{2+}$ (adapted from Refs. [213,214]).

octahedral geometry defined by all five donor atoms of the O_2N_3 macrocycle (in its meso form) and the oxygen of the water molecule. In this structure the macrocyclic backbone incorporating the N_3 donor fragment is arranged facially. Molecular mechanism modelling of this complex predicts that the observed facial configuration will be favoured over an alternative facial arrangement or a meridional one [213,214].

Using the macrocycle **H-166** the mononuclear complexes $\text{M}(\text{H-166})\text{X}_2$ ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}$; $\text{X} = \text{Cl}, \text{Br}$) and homo-dinuclear complex $\text{Cu}_2(\mathbf{166})(\text{Cl})_2(\text{OH}) \cdot n\text{H}_2\text{O}$ were recovered. $\text{M}(\text{ClO}_4)_2$ and $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$) gave $[\text{M}(\mathbf{166})(\text{X})]$ and FAB mass spectrometry provided evidence for oligomer formation [215].

$[\text{Cu}_2(\mathbf{166})(\text{Cl})_2(\text{OH})] \cdot n\text{H}_2\text{O}$ was proposed to have the exocyclic dinuclear structure shown in Fig. 82a. Attempts

to grow crystals of these species were unsuccessful; however, the complex $[\text{Cu}_2(\mathbf{166})(\text{Cl})_2(\text{OH})]$ was recovered from benzyl alcohol and the structure solved. This not only confirmed the exocyclic homo-dinuclear nature of the complex but also showed that the exogenous hydroxyl group had been replaced by a benzoate anion present in the solvent [215]. The resulting complex $[\{\text{Cu}_2(\mathbf{166})(\mu\text{-C}_6\text{H}_5\text{COO})(\text{H}_2\text{O})(\text{Cl})_2\}_2] \cdot 2\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, comprises a centrosymmetric tetranuclear entity in which each of two pairs of copper ions is coordinated exocyclically by a macrocyclic ligand via two amine nitrogen atoms (one to each copper), and by an oxygen of a deprotonated pendant hydroxyl group which bridges the two coppers; the pair of copper ions is also bridged by a benzoate anion. The coordination sphere of the outer copper of each pair is completed by a terminal chlorine and, more remotely, by a water ligand. The inner two centrosymmetrically related copper ions (one from each pair) are asymmetrically bridged by a pair of chlorine ligands. The $\text{Cu} \cdots \text{Cu}$ distances are 3.489 and 3.391 Å, the latter being between symmetry-related, dichloride-bridged copper ions. Each of the independent copper ions has a five coordinated geometry [215] (Fig. 82b).

The macrocycles, **167**, incorporating *trans*- N_2O_2 or *trans*- N_2S_2 donor atoms, have been prepared by reduction of the related Schiff bases **167a** with $\text{NaBH}_3(\text{CN})$ in acetic acid methanol in order to compare their coordinating properties with those of the related macrocycles containing *cis*- N_2O_2 or *cis*- N_2S_2 (**162** and **163**) [216].

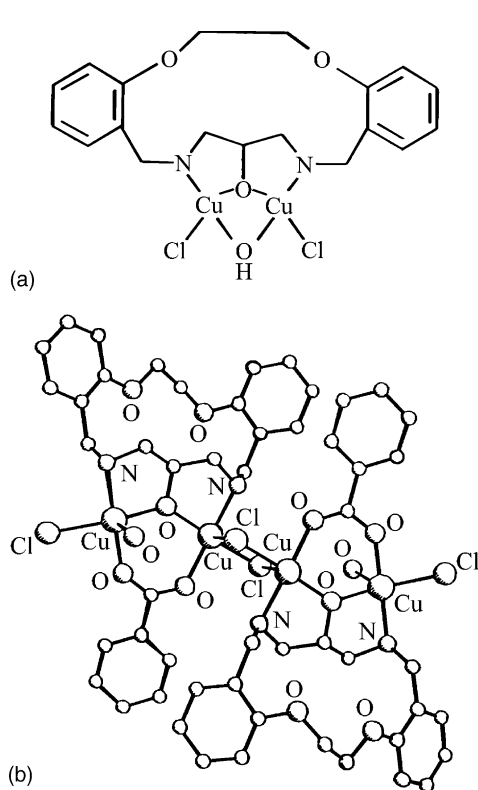
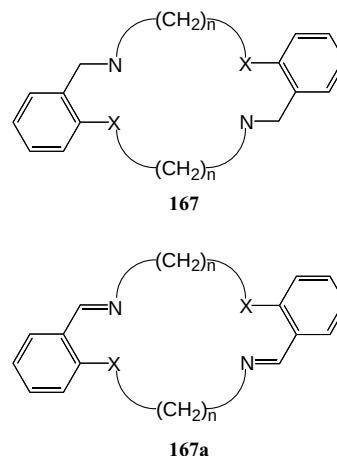


Fig. 82. Proposed structure of $[\text{Cu}_2(\mathbf{166})(\text{Cl})_2(\text{OH})]$ (a) and structure of $[\{\text{Cu}_2(\mathbf{166})(\mu\text{-C}_6\text{H}_5\text{COO})(\text{H}_2\text{O})(\text{Cl})_2\}_2]$ (b) (adapted from Ref. [215]).



Cis- $[\text{Ni}(\mathbf{167a})(\text{SCN})_2] \cdot \text{CH}_3\text{CN}$ ($n = 2$; $\text{X} = \text{NH}$) was obtained by reaction of a methanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and KSCN with a CHCl_3 solution of **167a**. The nickel(II) ion in this complex has an approximate octahedral geometry with three nitrogen atoms from the macrocycle and one nitrogen from a thiocyanato nitrogen ligand occupying the equatorial plane. The axial sites are filled by the remaining nitrogen of the macrocycle and the nitrogen of the second thiocyanato group. The thiocyanato ligands thus occupy mutually *cis* positions in this complex (Fig. 83). *Cis*- $[\text{Ni}(\mathbf{167a})(\text{Cl})_2]$ ($n = 2$; $\text{X} = \text{S}$), shows a similar structure [216].

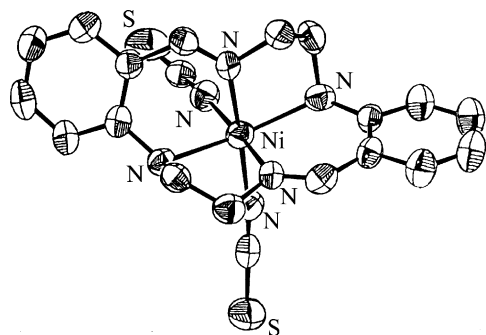


Fig. 83. Structure of *cis*-[Ni(**167a**)(NCS)₂] (adapted from Ref. [216]).

In the complex *trans*-[Ni(**167**)(NCS)₂] ($n = 2$; X = NH), synthesised by reaction of a CH₂Cl₂ solution of **167** and a 1:1 water/methanol solution of NiCl₂·6H₂O and KSCN, the overall geometry is again distorted octahedral with the four nitrogens of the macrocycle coordinating in a planar fashion and the nitrogen bonded thiocyanato ligands occupying the axial sites (Fig. 84). *Trans*-[Ni(**167**)(Cl)₂] ($n = 2$; X = O) shows a similar structure [217].

Comparative investigation of the 1:1 (metal:ligand) complex stabilities of [14]- and [16]-membered derivatives of dibenzo-substituted macrocycles **167** incorporating *trans*-N₂O₂, -N₂S₂ and -N₄ donor sets towards cobalt(II), nickel(II), zinc(II), cadmium(II), silver(I) and lead(II) ions has been carried out with emphasis on the influence of systematic donor atom variation on the respective 1:1 stability constants [216].

A similar comparative investigation of the 1:1 (metal:ligand) complex stabilities of the related series reduced (diamine–tetraamine) macrocycles from [14–16]-membered, *cis*-N₂O₂- and *cis*-N₄ ligand systems towards the same metal ions shows the stability order: Co²⁺ < Ni²⁺ < Cu²⁺ > Zn²⁺ [216].

The observed log *K* values show a dependence on the nature of the donor atom X. Except for the complexes of the soft silver(I) ion, the N₄-donor systems yield more stable complexes than the systems with X = O or S. In the case of the latter pair, the sulfur-containing rings tend to yield

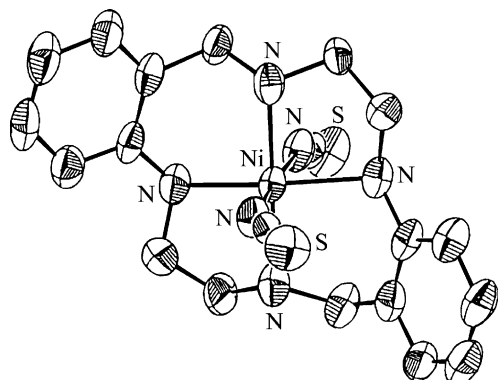
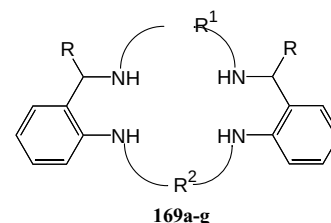
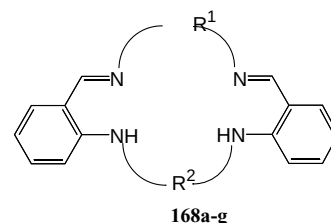


Fig. 84. Structure of *trans*-[Ni(**167**)(NCS)₂] (adapted from Ref. [217]).

somewhat more stable complexes than the corresponding oxygen-containing systems.

The sulfur-containing macrocycles show particular affinity for the silver(I) ion. In this context, both the [14]- and [16]-membered *trans*-N₂S₂ rings show strong discrimination for the silver(I) over lead(II) ion, with stability differentials of the order of 10⁵ in favour of silver(I) being observed in each case [216].

The [1+1] macrocyclic Schiff bases **168a–g**, containing N₄ donor atoms, have been prepared by reaction of the appropriate diformyl-dianilino and polyamine precursors in very high yield (76–84%) under a variety of experimental conditions [218]. The formation of these diimino macrocycles is strongly facilitated by the stabilization of the imine bond by intramolecular hydrogen-bonding. From the reaction of the related dialdehyde, which has no anilino-hydrogen atom, with 1,2-diaminoethane, 1,2-diaminobenzene, and 1,3-diamino-propane the 1:2 linear condensation products [218] were obtained instead of the macrocyclic diimines. These macrocyclic Schiff bases adopt an extended configuration which minimizes nitrogen lone pair-lone pair repulsion.



	R ¹	R ²	R
a	(CH ₂) ₃	(CH ₂) ₂	C ₂ H ₅
b	(CH ₂) ₃	(CH ₂) ₂	C ₄ H ₉
c	(CH ₂) ₃	(CH ₂) ₂	H
d	(CH ₂) ₃	(CH ₂) ₂	H
e	(CH ₂) ₄	(CH ₂) ₂	H
f	(CH ₂) ₅	(CH ₂) ₂	H
g	(CH ₂) ₂	(CH ₂) ₂	CH ₃
	C ₆ H ₄	(CH ₂) ₃	

Structural determination of the macrocyclic Schiff base systems shows that the presence of anilino-hydrogen atoms allows intramolecular hydrogen-bonding which reduces such lone-pair interactions in the centers of the rings. Almost planar hydrogen-bonded units are observed in the X-ray structures of several of these macrocycles [218]. The overall configurations of the macrocycles differ considerably probably to preserve the planarity of the hydrogen bonded units and to minimize contact between the anilino protons in the two halves of the molecules [218].

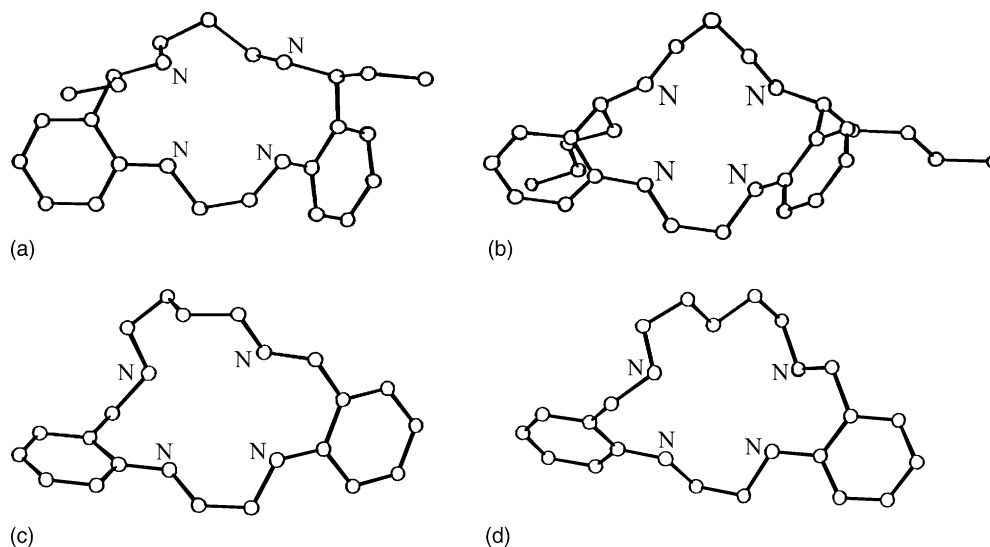


Fig. 85. Structure of **169a** (a), **169b** (b), **169d** (c) and **169e** (d) (adapted from Ref. [218]).

The N_4 macrocycles containing two *o*-iminoanilino units can give neutral magnesium complexes on reaction with 2 equiv. of ethylmagnesium bromide [218] but undergo stereoselective C-alkylation on treatment with an excess of the Grignard reagent [218]. The subsequent hydrolysis affords the meso-diethylsubstituted tetra-amines **169** [218]. The tetra-aza macrocycles ($R = H$) have been prepared by reduction with an excess of $NaBH_4$ of the corresponding diimine precursors [218]. The reductive C-alkylation of **168** to form **169** was also achieved using methyl lithium or *n*-butyllithium [218].

The structure of **169a** and **169b** [218] shows them to be the meso-isomers. Both R groups and the benzylamino N–H bonds are displaced to the same side of the mean plane of the four nitrogen atoms (Fig. 85a and b).

The structures of **169d** and **169e** (Fig. 85c and d), resembling those of **169a** and **169b**, show the two intramolecular hydrogen bonds involve interaction of the anilino hydrogen atoms with the lone pairs on the adjacent benzylamino nitrogen atoms and the geometry of these bonds is constrained by the cyclic nature of the compounds. In **169d** the relevant distances and angle in one half of the macrocycle are strikingly dissimilar to those in the other compounds and in the other half of **169d**, indicating a difference in the hydrogen-bonding pattern for **169d**. Here, one of the intramolecular hydrogen bonds is replaced by a very weak intermolecular hydrogen bond across a crystallographic center of symmetry, between the lone pair of a benzylamino atom and the anilino hydrogen atom of a neighbouring molecule [219].

$[Cd(\mathbf{169d})(Br)_2]_2[CdBr_4]$ (Fig. 86a) consists of two cationic cadmium(II) complexes each coordinated to all four nitrogen donors of the macrocycle and to an axial bromide ligand. These two complexes sandwich a tetrabromocadmiate(II) anion in such a way that two of its bromine atoms are directed towards the cadmium atoms of each cation. The

conformation of the macrocyclic ligand in each complex are markedly different; in that containing Cd(1) the benzo rings are inclined to opposite sides of the N_4 donor plane with the amine hydrogen atoms alternately above and below the plane giving the *R,R,R,R* (or *S,S,S,S*) sequence of absolute configurations of the nitrogen atoms. In contrast, the complex containing Cd(2) has the benzo rings inclined to the same side of the N_4 donor plane as the coordinated bromine atom with the two anilino hydrogen atoms on the same side and the two benzylamino hydrogen atoms on the opposite side giving absolute configurations of *R,S,R,S* (or *S,R,S,R*). These configurations of the ligand are conveniently referred to as *rac* and *meso*, respectively. The *rac* configuration has

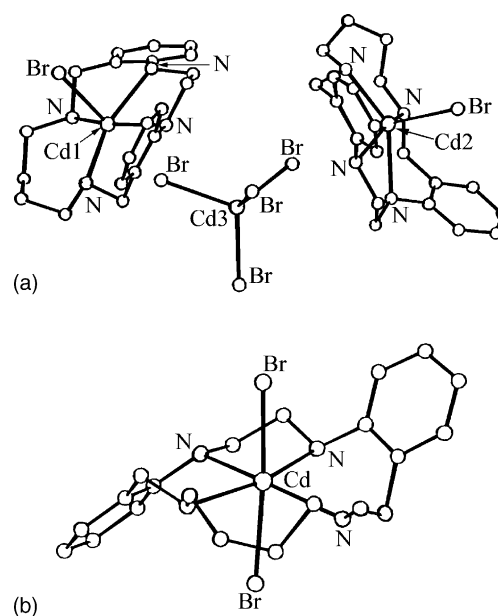


Fig. 86. Structures of $[Cd(\mathbf{169d})(Br)_2]_2[Cd(Br)_4]$ (a) and of $[Cd(\mathbf{169e})(Br)_2]$ (b) (adapted from Ref. [219]).

been observed also in the nickel(II) complexes of **169f** and **169g** and the meso in $[\text{Zn}(\mathbf{169g})(\text{I})](\text{I})$, $[\text{Zn}(\mathbf{169g})(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)$, $[\text{Cd}(\mathbf{169g})(\text{N}_3)](\text{NO}_3)$, and $[\text{Cd}(\mathbf{169b})(\text{NO}_3)](\text{NO}_3)$. The seven membered chelate rings in rac- and meso- $[\text{Cd}(\mathbf{169d})(\text{Br})]^+$ adopt distorted skew and chair conformations, respectively [219].

$[\text{Cd}(\mathbf{169e})(\text{Br})_2]$ (Fig. 86b) consists of a pseudooctahedral geometry in which the cadmium ion is coordinated to all four nitrogen donors of the macrocycle and to two *trans*-axial bromide ligands. The macrocycle conformation differs from that in rac- $[\text{Cd}(\mathbf{169d})(\text{Br})]^+$ in the configurations of the amine hydrogen atoms. Here one of the hydrogen atoms is on the opposite side of the N_4 plane to the others, giving a *R,S,R,R* (or *S,R,S,S*) sequence. The eight membered chelate ring in $[\text{Cd}(\mathbf{169e})(\text{Br})_2]$ contains two disordered carbon atoms giving two alternative twist-boat conformations.

In general terms in the series **169a–g**, increasing ring size has the effect of allowing a cadmium ion to approach closer to the center of the N_4 cavity and to form a six coordinated *trans*-dibromo complex of the largest ring, **169e**. Thus, with the exception of the rac-form of the complex $[\text{Cd}(\mathbf{169d})(\text{Br})]$, the displacement of the cadmium ion from the mean plane of the N_4 -donor set decreases as the ring size increases.

Five coordinated complexes are formed by the [15]-membered macrocycle **169g** and its C-butylated homologue **169b**; transoid coordination of a second nitrate or aqua ligand is apparently sterically hindered by the macrocyclic ligand in these compounds. In the complexes of the [16]-membered macrocycle **169d** a relatively weak interaction

between the cadmium ion and a second (*trans*-axial) bromine atom gives the complex a structure intermediate between five and six coordinated [219].

High-spin complexes of type $[\text{Ni}(\mathbf{169f})(\text{X})_2]$ ($\text{X} = \text{Cl}$, NCS) and $[\text{Ni}(\mathbf{169g})(\text{Cl})_2]$ have been characterised [219]. Moreover the nickel(II) isothiocyanate complexes of **169d–f** were obtained by reaction of the corresponding macrocycle in methanol or methanol-dichloromethane with nickel(II) tetrafluoroborate, followed by addition of potassium thiocyanate. The related dichloronickel(II) derivatives of **169d** and **169e** were obtained by direct reaction of the corresponding macrocycle with nickel(II) chloride in methanol. Reaction of nickel(II) nitrate hexahydrate with **169d** or **169e** in refluxing methanol-dichloromethane yielded the dinitrate complexes. The colours (purple to blue-green) and spectral data for the respective complexes suggested that each contained a high-spin nickel(II) ion in a distorted octahedral geometry [219].

In the nickel(II) thiocyanate complexes of the [15–17]-membered macrocycles (**169c–e**) the nickel ion is equatorially coordinated to all four macrocyclic donor nitrogens with two *trans*-axial, nitrogen bonded thiocyanate ligands. The macrocyclic ligand adopts a step configuration in which the benzo groups are directed to opposite sides of its coordination plane. As an example the structure of $[\text{Ni}(\mathbf{169c})(\text{NCS})_2]$ is reported in Fig. 87a [219].

In the related complexes of **169f** and **169g** the nickel ion lies in the respective mean planes of the macrocyclic donor sets.

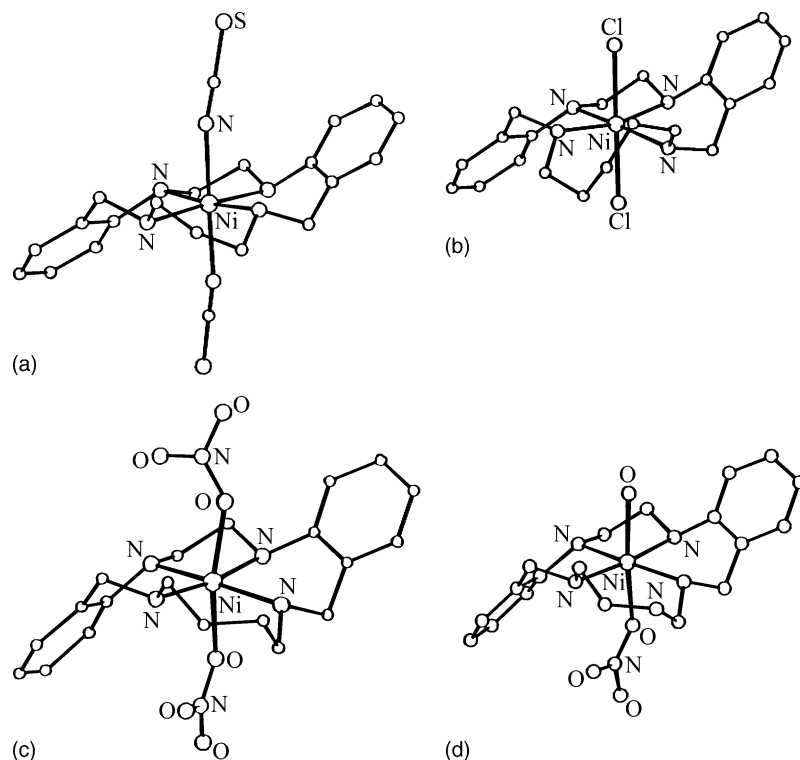


Fig. 87. Structures of $[\text{Ni}(\mathbf{169c})(\text{NCS})_2]$ (a), $[\text{Ni}(\mathbf{169e})(\text{Cl})_2]$ (b), $[\text{Ni}(\mathbf{169d})(\text{NO}_3)_2]$ (c) and $[\text{Ni}(\mathbf{169d})(\text{NO}_3)(\text{H}_2\text{O})]^+$ (d) (adapted from Ref. [219]).

Also in $[\text{Ni}(\mathbf{169e})(\text{Cl})_2]$, as in the thiocyanato complexes, all four nitrogen donors of the macrocycle are equatorially coordinated to the nickel(II) ion, with chlorides filling the apical sites (Fig. 87b).

Slow recrystallization of the nickel(II) nitrate complex of **169d** from methanol yielded crystals containing an equal mixture of two separate complexes $[\text{Ni}(\mathbf{169d})(\text{NO}_3)_2]$ and $[\text{Ni}(\mathbf{169d})(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)$, with the macrocycle being coordinated equatorially and yielding a near-planar donor set in each case. Both complexes contain the nickel ion in a distorted octahedral environment and the coordinated nitrate groups are all monodentate. The metal ion is very close to the best plane in each case (Fig. 87c and d).

The results of these X-ray crystallographic analyses, as well as molecular mechanics studies, have allowed comparison of the effect of change of ring size on the structures of the [14–17]-membered ring complexes with $\text{X} = \text{NCS}^-$. All complexes have similar six coordinated *trans*-isothiocyanate geometries in which the four donors of the macrocycle occupy the equatorial plane. For this series an inverse correlation between in-plane and axial bond lengths around the nickel atoms occurs for the [14–16]-membered ring complexes; the correlation is less apparent in the case of the [17]-membered species. The X-ray and molecular mechanics studies indicate that, as the number of methylene carbons linking adjacent benzylamino nitrogens increases, the corresponding bite angle at the metal increases, with the opposite bite angle decreasing in a (partial) compensatory manner. As a consequence, there is only a minor variation in the planarity of the macrocyclic donor plane along the series [219].

Cyclic voltammetry indicates that formation of the respective nickel(II) species is facilitated by the smaller-ring ligands; the oxidation of the [17]-membered ring

complex is non-reversible and probably ligand based [219].

Thus electronic spectra, crystal structure determinations and molecular mechanics calculations on these complexes indicate that the tendency for the nickel(II) ion to favour octahedral coordination promotes changes in ligand conformation which reduce the lop-sidedness of the N_4 donor set. The planarity of the N_4 donor set is maintained in the nickel complexes, but the distortion to a trapezoidal arrangement of the donors increases steadily as the length of the methylene bridge between the benzyl nitrogen atoms is increased [219].

The dimethyl-substituted macrocycle **169g** is a meso-isomer as revealed by the structure determination of the copper(II) complex, $[\text{Cu}(\mathbf{169g})(\text{DMF})](\text{ClO}_4)_2 \cdot \text{DMF}$. In this complex, the ligand more nearly approaches mirror plane symmetry (Fig. 88a). The copper is pentacoordinated with a pyramidal square environment [218].

$[\text{Zn}(\mathbf{169c})(\text{NO}_3)(\text{H}_2\text{O})]^+$ has a six coordinated structure with the metal ion lying fairly close to the best plane through the four nitrogen donors and with a monodentate nitrate and a water molecule defining apical sites in an approximately octahedral geometry [218] (Fig. 88b). In contrast, the cadmium complexes $[\text{Cd}(\mathbf{169c})(\text{NO}_3)]^+$ and $[\text{Cd}(\mathbf{169b})(\text{NO}_3)]^+$ (Fig. 88c) have only one ligand in addition to the macrocycle in the coordination sphere and have the metal much further displaced from the N_4 planes towards the coordination nitrate ions. The nitrate groups adopt an unsymmetrical bidentate mode of coordination [218]. The structure of $[\text{Zn}(\mathbf{169c})(\text{I})]^+$ confirms a square pyramidal coordination geometry for the zinc(II) ions which is bound by the four nitrogens of the macrocycle and has one axial iodine ligand (Fig. 88d). In all these complexes, the ligands adopt a folded conformation [218].

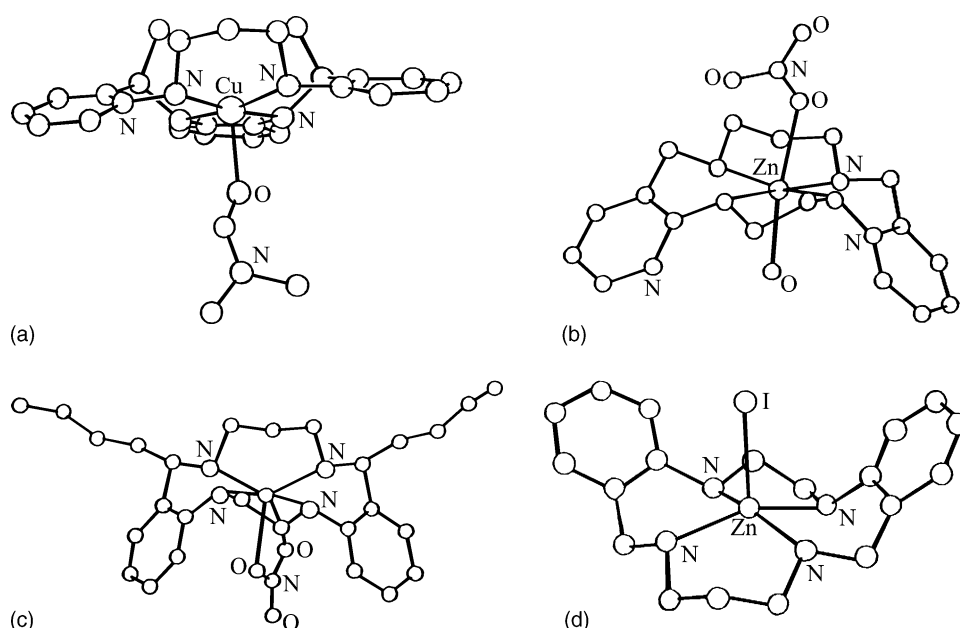
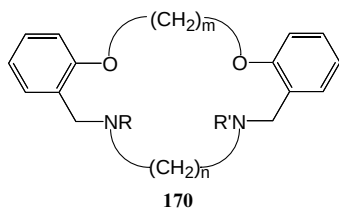


Fig. 88. Structures of $[\text{Cu}(\mathbf{169g})(\text{DMF})]^{2+}$ (a), $[\text{Zn}(\mathbf{169c})(\text{NO}_3)(\text{H}_2\text{O})]^+$ (b), $[\text{Cd}(\mathbf{169b})(\text{NO}_3)]^+$ (c) and $[\text{Zn}(\mathbf{169c})(\text{I})]^+$ (d) (adapted from Ref. [218]).

All N_4 macrocyclic ligands **169** form 1:1 (metal:ligand) complexes in solution with the metal ions mentioned above; the thermodynamic stabilities of the complexes in 95% methanol have been determined. Along one series of [14–16]-membered macrocyclic systems a dislocation in the stability pattern occurs for zinc(II) at the [16]-membered ring complex while, for cadmium(II), the dislocation corresponded to the [15]-membered ring species. As a consequence, there is an enhanced stability difference [$Zn^{2+} > Cd^{2+}$] between the complexes of this latter ring. The observed discrimination shown by the [15]-membered ring is largely maintained when bulk alkyl substituents are appended to carbons adjacent to two of the secondary amine donors; however, the absolute magnitudes of the respective stabilities are decreased because of steric effects. In an extension of this study, it has been found that open-chain analogues show no unusual discrimination between zinc(II) and cadmium(II) ions. Other macrocyclic and open-chain ligands containing only anilino nitrogen donors have been shown to form only very weak complexes with zinc(II) and cadmium(II) ions [218].

The macrocycles **170a–o**, incorporating from [14]- to [17]-membered rings and containing also pendant coordinating groups [220], react with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) nitrate or perchlorate (or in some cases metal nitrate in the presence of lithium perchlorate) in ethanol or methanol to yield the corresponding 1:1 (metal:ligand) complexes [221]. Where soluble, these complexes were either 1:1 electrolytes in methanol or yielded values that fell between those for 1:1 and 2:1 electrolytes. Hence, under the conditions of measurement, significant complex cation–anion association is present in each case [221].



	m	n	
a	4	3	R,R' = CH ₂ CO ₂ H
b	2	2	R,R' = CH ₂ CH ₂ OH
c	2	3	R,R' = CH ₂ CH ₂ OH
d	3	3	R,R' = CH ₂ CH ₂ OH
e	4	3	R,R' = CH ₂ CH ₂ OH
f	2	3	R = H, R' = CH ₂ CH ₂ OH
g	2	2	R,R' = CH ₂ CH ₂ CONH ₂
h	2	3	R,R' = CH ₂ CH ₂ CONH ₂
i	2	2	R,R' = CH ₂ C ₅ H ₄ N
l	2	3	R,R' = CH ₂ C ₅ H ₄ N
m	3	3	R,R' = CH ₂ C ₅ H ₄ N
n	4	3	R,R' = CH ₂ C ₅ H ₄ N
o	2	3	R,R' = CH ₂ C ₅ H ₄ N

The coordination geometry of the nickel ion in [Ni(**170b**)(NO₃)](NO₃) (Fig. 89a) is distorted octahedral involving both nitrogen donors of the macrocyclic ring and two oxygen atoms of the pendant alcohol groups, with

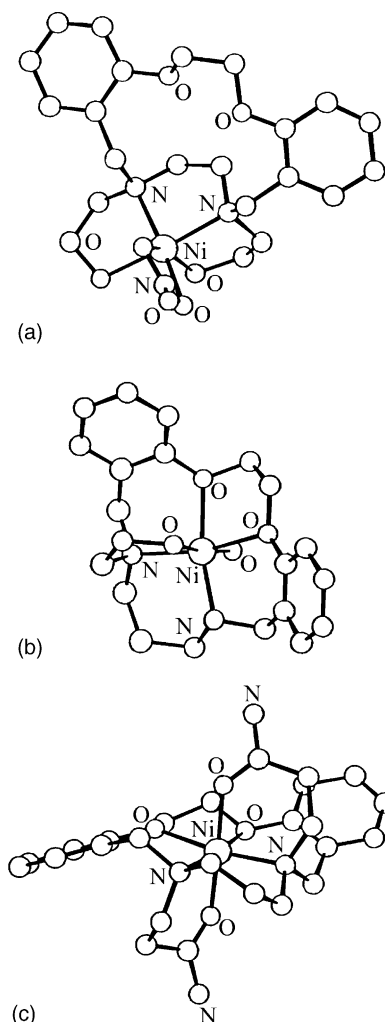


Fig. 89. Structures of [Ni(**170b**)(NO₃)]⁺ (a), [Ni(**170f**)(H₂O)]²⁺ (b) and [Ni(**170h**)]²⁺ (c) (adapted from Ref. [221]).

the fifth and sixth positions being occupied by oxygen atoms from a bidentate nitrate ion. The ether oxygens are not bound to the nickel. The main distortion from octahedral symmetry is associated with the small bite of the coordinated nitrate ion [221].

[Ni(**170c**)(NO₃)](NO₃) and [Ni(**170d**)(NO₃)](NO₃) have similar distorted octahedral structures to that above. Once again the ether oxygen atoms of the respective rings do not coordinate. Comparison of corresponding bond lengths and angles in each structure confirms that they are generally quite similar [221].

In contrast to these structures, [Ni(**170f**)(H₂O)](NO₃)₂ has the metal ion situated in the macrocyclic cavity such that the overall geometry is near octahedral (Fig. 89b). The coordination sphere of the nickel ions consists of two ether oxygen atoms and two nitrogen atoms from the macrocyclic ring (coordinated in a plane) together with oxygen atoms from the single pendant alcohol arm and a water molecule occupying the axial sites. Only one of the ionic nitrate groups shows evidence of disorder [221].

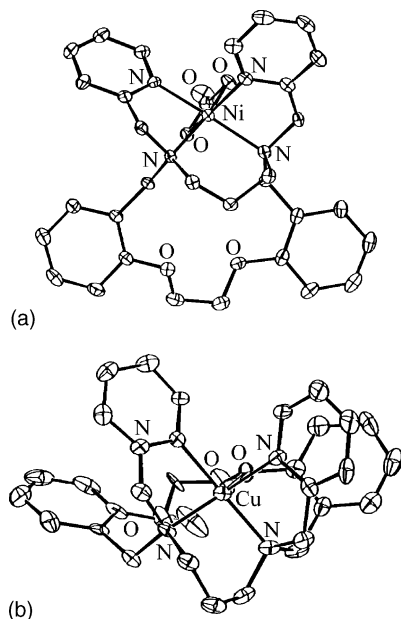


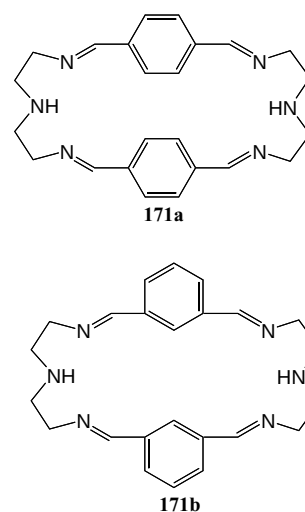
Fig. 90. Structures of [Ni(**170l**)(NO₃)]⁺ (a) and [Cu(**170l**)]²⁺ (b) (adapted from Ref. [221]).

In [Ni(**170h**)](NO₃)₂·0.5H₂O·0.5C₂H₅OH the nickel ion is six coordinated with the complex displaying near-octahedral geometry; the N₂O₂ donor set of the macrocyclic ring is coordinated in the equatorial plane with the carbonyl oxygen atoms of the pendant amide groups coordinated in the axial sites. Unlike the complexes of the bis(hydroxyethyl) derivatives **170b–d** discussed above, neither of the nitrate groups is involved in coordination. For this complex there is evidence for hydrogen-bond formation between a nitrate counter ion and amide hydrogens on adjacent [Ni(**170h**)]²⁺ cations. Namely, the structure consists of two [Ni(**170h**)]²⁺ cations linked by a hydrogen-bonded nitrate group [221] (Fig. 89c).

The structure of the nickel(II) complex [Ni(**170l**)-(NO₃)](NO₃) with the [15]-membered N₂O₂ donor macrocycle containing two pendant 2-pyridylmethyl groups (**170l**) (Fig. 90a) shows only the nitrogens of the macrocyclic ring and the pendant pyridyl nitrogens are coordinated; overall, the coordination geometry is distorted octahedral, with the fifth and sixth positions occupied by a bidentate nitrate group. In contrast, in the copper complex [Cu(**170l**)](NO₃)₂ (Fig. 90b) the four nitrogens and at least one of the two ring ether oxygens are coordinated (there is a long contact with the second); these two oxygens may be considered to displace those of the nitrate chelate found in the nickel complex [221].

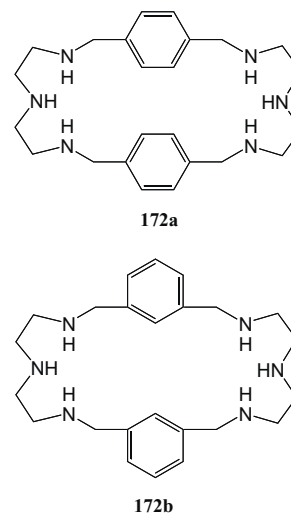
The [2+2] macrocyclic ligands **171a** and **171b**, obtained in high yield from a [2+2] dipodal condensation of iso- or tere-phthalaldehyde and 3-azapentane-1,5-diamine, react with [Cu(CH₃CH)₄]ClO₄ in CH₃CN to give rise to the air stable complexes [Cu₂(**L**)(CH₃CN)₂](ClO₄)₂ (**L** = **171a** and **171b**) where the two distorted tetrahedrally coordinated copper(I) centers are at 7.04 Å distance each other [222].

The copper ions are coordinated by the three nitrogen atoms of the macrocycle and the nitrogen atom of an acetonitrile molecule. Two perchlorate anions do not interact with the metal centers [222] (Fig. 91a).



Dicopper complexes of **171a** are air stable while those of **171b** cannot be isolated in the presence of oxygen because of the rapid oxygenation of the copper(I) centers and subsequent hydroxylation of one of the benzene rings.

Hydrogenation of these [2+2] Schiff base yields the reduction products **172a** and **172b** which form stable dinuclear copper(II) complexes [222]. Thus **172a** forms [M₂(**172a**)(CH₃COO)₂](ClO₄)₂ (Ni²⁺, Cu²⁺ and Zn²⁺), when reacted with 2 equiv. of the appropriate metal acetate in the presence of NaClO₄ [222,223]. [Cu₂(**172a**)(CH₃COO)₂](ClO₄)₂·5H₂O contains two copper(II) ions bound by the dipropylene-triamine units of the [30]-membered macrocyclic ligand. Each copper ion is further coordinated by a bidentate acetate ligand thus achieving overall penta-coordination. The acetate coordination is unsymmetrical. The aromatic rings of the macrocycle are nearly coplanar. The Cu···Cu distance (8.40 Å) probably precludes the incorporation of bridging species [223] (Fig. 91b).



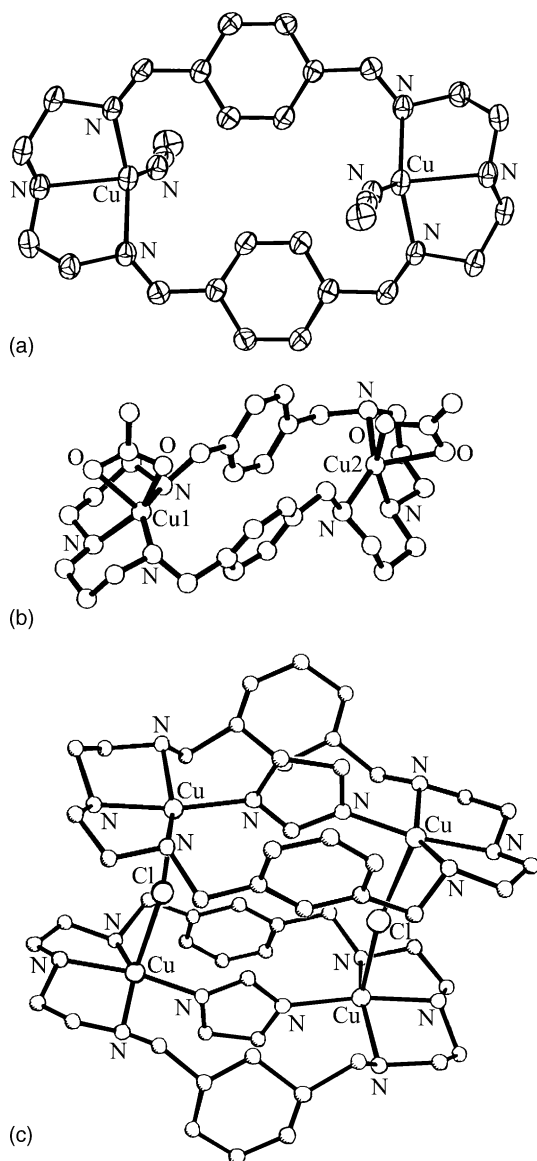


Fig. 91. Structure of $[\text{Cu}_2(\mathbf{171a})(\text{CH}_3\text{CN})_2]^{2+}$ (a), $[\text{Cu}_2(\mathbf{172a})(\text{CH}_3\text{COO})_2]^{2+}$ (b) and $[\text{Cu}_4(\mathbf{171b})(\text{Im})_2(\text{Cl})_2]^{2+}$ (c) (adapted from Refs. [222,224]).

The reaction of copper(II) chloride with **172a** forms $[\text{Cu}_2(\mathbf{172a})(\text{Cl})_2](\text{Cl})_2$ where each copper(II) ion is bound by a dipropylene-triamine unit of the macrocycle and one chloride ion. A second chloride ion is only weakly associated with each copper ion suggesting that the complex is cationic in solution [223].

The tetranuclear complex $[\text{Cu}_4(\mathbf{172b})_2(\mu\text{-Im})_2(\text{Cl})_2](\text{ClO}_4)_4 \cdot 5\text{CH}_3\text{OH}$ (H-Im = imidazole) obtained by reacting a methanolic solution containing imidazole and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with **172b**, consists of 2 equiv. $[\text{Cu}_2(\mathbf{172b})(\text{Im})]^{3+}$ subunits linked by a pair of chloride ions, forming a tetranuclear structure. The $\text{Cu} \cdots \text{Cu}$ separation within a dinuclear entity is 5.106 Å and that between dinuclear entities is 6.052 Å. Between the ClO_4^- ions and

the amino hydrogens around the copper(I) ion in each subunit there exists a weakly intramolecular hydrogen bond (Fig. 91c) [223].

The pH-dependent EPR studies of the tetranuclear complex in frozen 50% aqueous DMSO solution show that the bridged cation $[\text{Cu}_2(\mathbf{172b})(\text{Im})]^+$ exists as a major species in solution over the pH range 7.00–11.5, and the $\mu\text{-Im}$ bridge is broken in the pH range of 7.00–5.20. The molar conductance of this tetranuclear complex indicates that the $\mu\text{-Cl}$ bridge is almost entirely dissociated when dissolved in 1:1 DMSO aqueous solution. However, when chloride ions were gradually added to the solution, a complex with a Cu_4Cl chromophore was successively formed. Magnetic measurements studies on the powder sample reveal that antiferromagnetic interactions are mediated through both $\mu\text{-Im}$ ($J_1 = -26.78 \text{ cm}^{-1}$) and $\mu\text{-Cl}$ ($J_2 = -9.52 \text{ cm}^{-1}$) bridges [223].

$[\text{Cu}_2(\mathbf{172a})(\text{Cl})_2](\text{Cl})_2$ was used in the electrocatalysis of oxygen reduction at the glassy carbon electrode [224]. Electroreduction of oxygen in the borate buffer solution containing $10^{-3} \text{ mol dm}^{-3}$ chloride, pH 7.3, takes place at -0.62 V versus SCE. In the presence of the copper(II) complex with the hexaazamacrocyclic ligand **172a** the overpotential for O_2 reduction is decreased by more than 400 mV. The electrode potential has to be close to the redox potential of $[\text{Cu}_2(\mathbf{172a})(\text{Cl})_2](\text{Cl})_2$ before oxygen reduction can take place. The oxidation counterpart of the voltammetric reduction peak of the copper(II) complex disappears when the ratio of oxygen:complex concentration is higher than 0.5. This indicates that the electrochemically generated reduced form of the binuclear complex is required for the catalytic reduction of oxygen [224].

Voltammetric studies under an argon atmosphere show $[\text{Cu}_2(\mathbf{172c})(\text{Cl})_2](\text{Cl})_2$ undergoes reversible $2e^-$ reduction on glassy carbon, gold and platinum electrodes [224]. Both copper(II) centers of the complex are independently reduced at a similar potential to $[\text{Cu}^{\text{I}}_2(\mathbf{172a})(\text{Cl})_2]$ [223,224]. This binuclear copper(I) complex can be prepared in the thoroughly deoxygenated solution either by reduction of the copper(II) complex or by mixing $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{BF}_4)$ with the ligand and chloride ions. It is stable under argon atmosphere but exhibits high reactivity towards both oxygen and hydrogen peroxide. On the other hand the copper(II) complex itself does not react with oxygen. These observations lead to the suggestion that oxygen is reduced in the presence of the copper(II) complex according to an EC catalytic regeneration mechanism with the copper(I) bimetallic complex acting as the catalyst.

The copper(I) reoxidation signal is absent at ratios $[\text{O}_2]/[\text{Cu}^{\text{I}}_2(\mathbf{172a})(\text{Cl})_4]$ higher than 0.5. The products of oxygen reduction were found to depend on the oxygen:catalyst concentration ratio. At higher ratios, H_2O_2 can be detected by the appearance of an anodic signal close to 0.7 V at pH 9, corresponding to peroxide oxidation. Under excess of the complex no similar peak is detected, which indicates that H_2O_2 is transformed into a different species.

A multistep [2+2] reduction mechanism was proposed which involves oxygen reduction in a two step pathway through hydrogen peroxide to water, the latter being the product at high excess of the catalyst. The reduction of peroxide by copper(I) was found to be slower than that of oxygen.

The electrocatalytic activity exhibited by the complex is unique among the solution soluble copper complexes. These features are attributed to the geometric constraints imposed upon the reactive center by the surrounding rigid macrocyclic framework of the ligand. The electrocatalytic behaviour towards oxygen reduction has not been observed for any other macrocyclic binuclear copper complex. The separation of copper centers in the copper(II) complex is 8.40 Å and the characteristics of the cyclic voltammogram fully support the lack of exchange coupling between the copper centers postulated on basis of the EPR spectrum [224].

The synthesis of the saturated [2+2] macrocycle and analogous [3+2] macrobicyclic via efficient and facile direct condensation of benzene-1,3-dicarboxaldehyde with diethylenetriamine [225] or with tris(2-aminoethyl)amine [218], followed by hydrogenation with NaBH₄, represents a valuable route to pairs of analogous macrocyclic and macrobicyclic ligands [226,227] (Scheme 32).

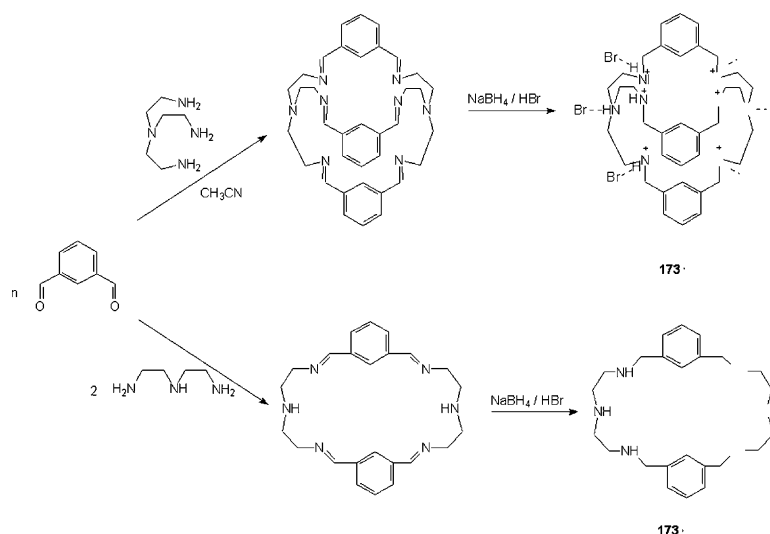
The X-ray structure of the [3+2] macrobicyclic **173**·8HBr (Fig. 92a) [225] shows that the cryptand is associated with three of the bromide anions, which are situated on the cryptand periphery between two of the three bridges but outside the cavity of the cryptand. The structure therefore could be described as [3Br[−], (**173**)(H⁺)₈](Br[−])₅·6H₂O. The octaprotonated cryptand has a Y shape with the three legs being the planes of the phenyl rings. The length of the macrobicyclic cage (distance between the bridgehead nitrogens) is 7.60 Å. The internal central cavity of the cryptand can be described as a sphere of diameter 7.4–7.6 Å. The

protons located at the bridgehead nitrogens point toward the outside of the spherical internal cavity. This cavity is empty and does not contain a solvent molecule. The protonated macrobicyclic exhibits bromide anion binding, but none of the three bromide anions is located inside the internal cavity [225].

The nitrate salt of **173** was prepared by dissolving the free base in CH₃OH and adjusting the pH to 3 by addition of concentrated HNO₃. The tosylate salt of **174** and **173** were prepared by adding a CH₃OH solution of the free base to TsOH. In each case, the product precipitated after stirring at room temperature or after refrigeration [226].

In [(H₆-**173**)(NO₃)₂]·(NO₃)₄·2H₂O two nitrate groups are encapsulated inside the macrobicyclic cavity while the other four nitrates and two water molecule are external (Fig. 92b). In the template compound [H₆-**173**]·(tosylate)₆·8H₂O the six tosylate groups are external with their sulfonate groups pointing into the cavity; the eight water molecules are external [226]. The free macrobicyclic **173**·*n*H₂O, prepared by adding an excess of NaOH to [H₈-**173**](Cl)₈ in water, crystallizes with an encapsulated water and intricate water network (Fig. 92c).

In the [2+2] macrocycle **174**·6HBr there is only one molecule per unit cell with extensive hydrogen bonding among neighbouring molecules. The three nitrogen atoms of each macrocyclic arm are linearly accommodated in a plane which contains the rest of the aliphatic carbons. The planarity is achieved because of a zigzag type of arrangement of successive nitrogen and carbon atoms. The phenyl rings are nearly perpendicular to that plane pointing in opposite directions. All six nitrogens are protonated, and each has one of the two hydrogen atoms directed outside the ring. None of the bromide counter ions are situated inside the macrocyclic cavity. The distance between the xylyl planes is 12.89 Å and the perpendicular width of the cavity is 2.68 Å (Fig. 93a) [226].



Scheme 32.

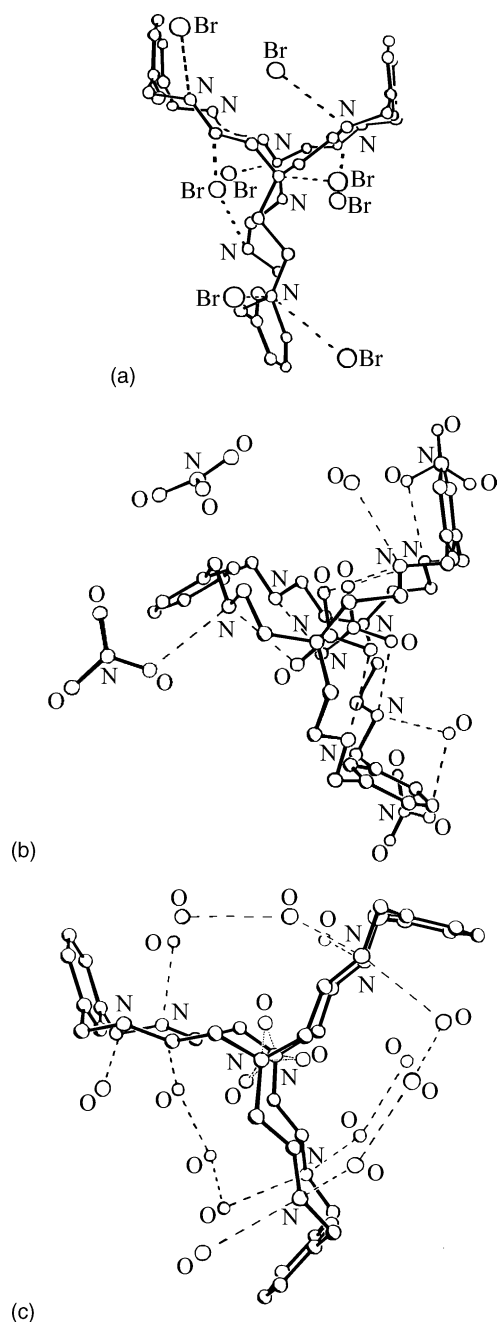


Fig. 92. Structures of **173**·8HBr (a) and **173**·6HNO₃ (b) and **174**·*n*H₂O (c) (adapted from Refs. [225,226]).

[H₆-**174**](NO₃)₆·H₂O and [H₆-**174**](SO₄)₃·5H₂O were obtained by adjusting a methanol solution of **174** with the appropriate acid [226]. Structural results indicate relatively planar macrocycles with *cis* and *trans* orientations of the phenyl groups for [H₆-**174**](NO₃)₆·H₂O and [H₆-**174**](SO₄)₃·5H₂O, respectively and the anions above and below the macrocycle rings [226] (Fig. 93b and c).

Potentiometric studies indicated negligible binding for **174** and nitrate, but high affinity was observed for sulfate. Stronger binding was observed for the cryptand **173** with both nitrate and sulfate [226].

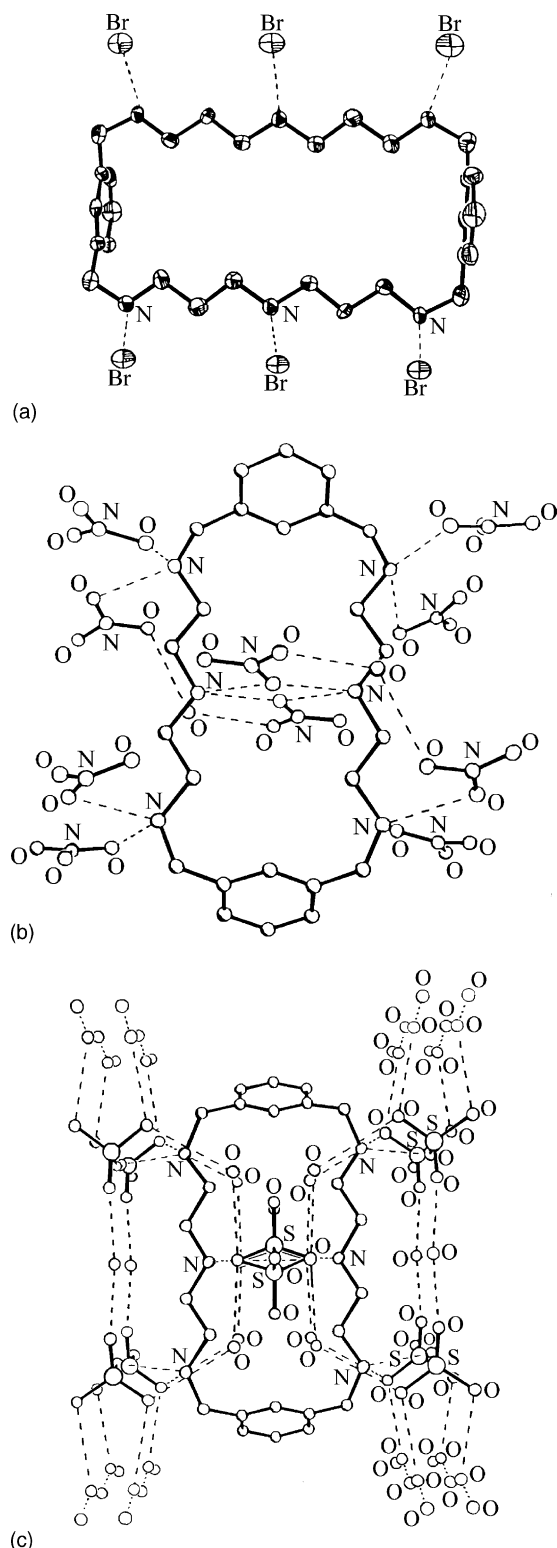


Fig. 93. Structures of **174**·6HBr (a), **174**·6HNO₃·H₂O (b) and **174**·3H₂SO₄·5H₂O (c) (adapted from Ref. [226]).

The binuclear copper(II) complex [Cu₂(**173**)(μ-Im)]-(ClO₄)₃ was prepared by addition of a stoichiometric amount of **173** to a solution of [Cu₂(μ-Im)](ClO₄)₃ by a sequential route without isolation of the unbridged dicopper complex.

In a similar way the hetero-dinuclear copper(II)–zinc(II) complex was synthesized by the reactions of **173** with $\text{Zn}(\text{ClO}_4)_2$ to form the mononuclear complex $[\text{Zn}(\mathbf{173})](\text{ClO}_4)_2$ followed by the subsequent reaction with $\text{Cu}(\text{ClO}_4)_2$ to give rise to the unbridged complex $[\text{CuZn}(\mathbf{173})](\text{ClO}_4)_4$. This hetero-dinuclear species was not isolated but engaged in reaction with imidazole to form $[(\text{CuZn}(\mathbf{173})(\mu\text{-Im}))](\text{ClO}_4)_3$ [227].

In the blue $[\text{Cu}_2(\mathbf{173})(\mu\text{-Im})](\text{ClO}_4)_3$ and the dark blue $[\text{CuZn}(\mathbf{173})(\mu\text{-Im})](\text{ClO}_4)_3$, precipitated in methanol and recrystallized by slow diffusion of ethyl acetate into an acetonitrile solution, each metal ion is pentacoordinated (four nitrogen atoms from **173** and one from imidazolate) in an arrangement intermediate between a trigonal bipyramid and a square pyramid, depending on the metal center. The coordination environment is found to be a slightly distorted trigonal bipyramid for one and metal center and a distorted square pyramidal for the other. The $\text{Cu}\cdots\text{Cu}$ and $\text{Cu}\cdots\text{Zn}$ distances are 5.95 and 5.93 Å, respectively (Fig. 94).

Magnetic measurements and EPR spectroscopy of the dicopper complex have shown an antiferromagnetic exchange interaction with a coupling constant of $-2J = 88 \text{ cm}^{-1}$ [227].

The magnetic behaviour of $\text{Cu}^{\text{II}}\text{Zn}^{\text{II}}$ complex agrees with a one-spin system, the different behaviour found at low temperatures being ascribed to the presence of dicopper and dizinc species as minor products [227]. EPR data of the CuZn complex exhibits the usual line shape for mononuclear Cu(II) complexes indicating a square geometry with a $d_{x^2-y^2}$ ground state. In addition the spectrum exhibits another set of small signals at 1500, 2500, and 3600 G assigned to the $[\text{Cu}_2(\mathbf{173})(\text{im})]^{3+}$ species in agreement with the magnetic measurements. From pH-dependent EPR and electronic spectroscopic studies the two complexes have been found to be stable over the pH ranges 4.5–12 for $[\text{Cu}_2(\mathbf{173})(\mu\text{-Im})]^{3+}$ and 6–10.5 for $[\text{CuZn}(\mathbf{173})(\mu\text{-Im})]^{3+}$.

Electrochemical studies have shown quasi-reversible behaviour in dimethylacetamide solution for the first step of the reduction: $E_{1/2} = -0.27 \text{ V/SCE}$ for the Cu_2 complex

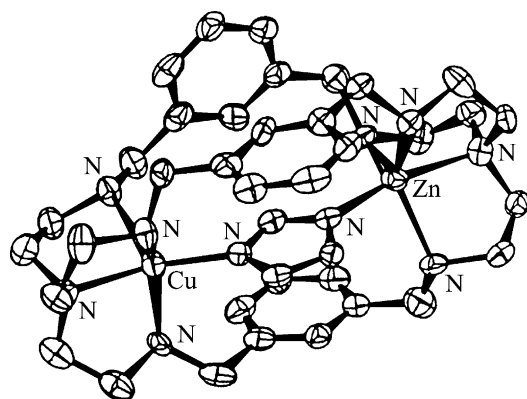
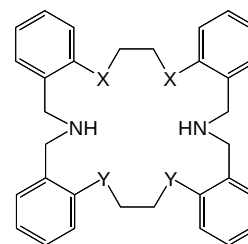


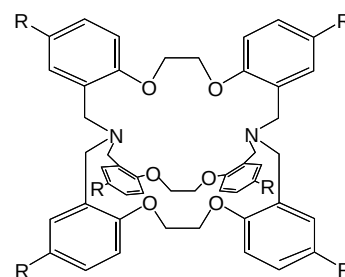
Fig. 94. Structures of $[\text{CuZn}(\mathbf{173})(\mu\text{-Im})]^{3+}$ (adapted from Ref. [227]).

($\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox process) and $E_{1/2} = -0.31 \text{ V/SCE}$ for the CuZn complex ($\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox process). The two complexes catalyze the dismutation of superoxide at biological pH, and the activity survives in the presence of bovine serum albumine. All the results indicate that the Cu_2 and CuZn complexes act as good models for superoxide dismutase [227].

The N_2O_4 macrocycle **176a** and the N_2O_6 macrobicyclic **177a** have been obtained by the synthetic procedure reported in Scheme 33. Using the readily prepared dialdehyde **175a** it is possible to synthesize all precursors necessary to assemble the desired cage molecule **177a** [228].



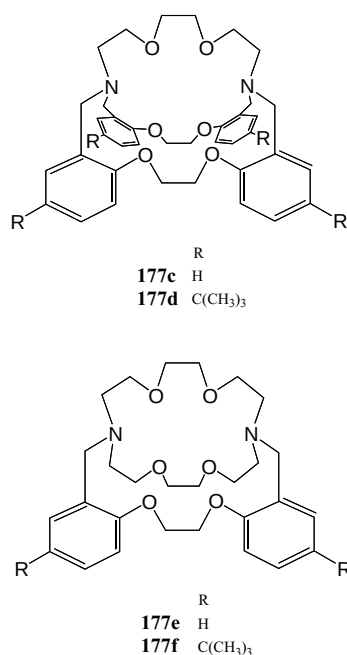
176a $\text{X}=\text{Y}=\text{O}$
176b $\text{X}=\text{O}, \text{Y}=\text{O}$
176c $\text{X}=\text{Y}=\text{S}$



177a $\text{R}=\text{H}$
177b $\text{R}=\text{C}(\text{CH}_3)_3$

The X-ray structure of **177a** shows that the cage adopts a propeller-shaped chiral configuration. The polyhedron defined by the six oxygen atoms approaches D_{3h} symmetry-forming an achiral trigonal-prismatic arrangement of the oxygen atoms. Both the bridgehead nitrogens are configured with their lone pairs projecting away from the macrobicyclic cavity to give an *exo-exo* arrangement. The bridgehead $\text{N}\cdots\text{N}^{\text{I}}$ approach of 5.44 Å is somewhat closer than the across cavity $\text{O}\cdots\text{O}$ distance (mean value 6.83 Å between directly opposite oxygens) so that the macrobicyclic cavity has a spheroidal geometry [228].

The more lipophilic **177b** has been prepared similarly together with the macropolycyclic compounds **177d**–**177g** in order to verify the cryptand flexibility on sodium ion affinity [228]. Attempts to grow crystals of the sodium complexes with these ligands were successful only for $[\text{Na}(\mathbf{177c})](\text{picrate})\cdot\text{CH}_2\text{Cl}_2$. The structure shows that the bridgehead nitrogens adopt *endo-endo* configurations and that these nitrogens are weakly coordinating while all six oxygen donors are coordinated to sodium [228].



The rigidity of the series of cryptands **177**, incorporating an N₂O₆ donor set, has a marked effect on the ability of such species to complex sodium ions. X-ray and associated computational investigations, including molecular mechanics, semi-empirical and ab initio (density functional)

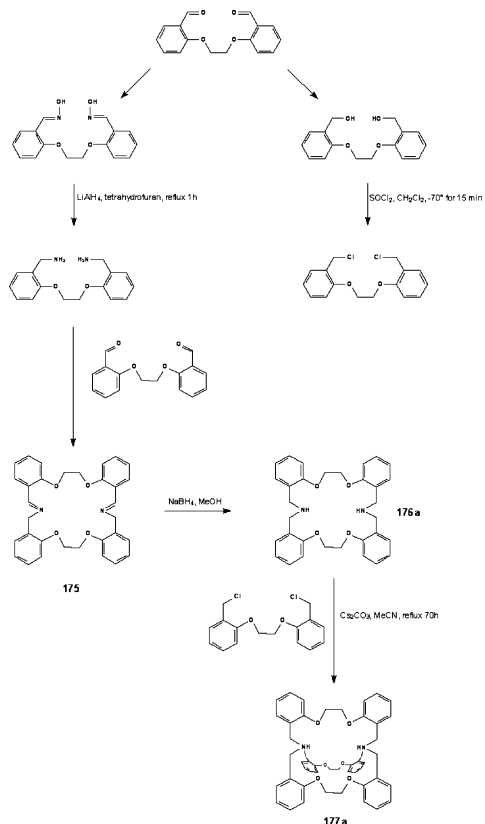
studies, coupled with the results of sodium picrate extraction experiments and NMR studies, have been employed to probe the conformational aspects influencing sodium ion complexation along the ligand series. It is concluded that the ease with which a cryptand is able to adopt an *endo-endo* conformation is an important factor affecting the occurrence of inclusive metal ion binding in these systems [228]. Thus increasing benzylamine incorporation into the macrocycles, i.e. the benzyl substituent on the bridgehead amine atoms, hinders the adoption of an *endo-endo* nitrogen conformation and in doing so impedes metal ion complexation [228].

By a synthetic procedure similar to that reported in Scheme 33 the macrocycles **176b** and **176c** have been prepared and their metal ion recognition ability tested [229]. In particular a comparative potentiometric investigation in 95% methanol of the complexation of these [22]-membered macrocyclic rings (**176a–c**) incorporating mixed O₄N₂, O₂S₂N₂ and N₂S₄ donor-atom sets towards copper(II), silver(I) and lead(II) ions has been made. The introduction of soft sulfur donors into the macrocycle framework increases the discrimination for silver(I) over lead(II) with that incorporating an N₂S₄ donor set showing discrimination of at least 10⁸ in favour of silver(I). Details of the binding of silver(I) and lead(II) to the O₄N₂ and O₂S₂N₂ systems have been assessed in CDCl₃–(CD₃)₂SO (1:4) using ¹³C NMR spin-lattice relaxation (*T*₁) studies as well as observation of the induced chemical shifts of ligand resonances on complex formation. Overall, the NMR results correlate well with the observed thermodynamic stabilities of the individual complexes. Competitive mixed-metal transport experiments across a bulk chloroform membrane have been performed using each of the three macrocycles as the ionophore. For each experiment the source phase contained equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) as their nitrate salts. In each case the silver(I) ion was the only one to exhibit significant transport under the conditions employed, with both macrocycles incorporating sulfur donors being more efficient ionophores than the O₂N₂ donor system [229].

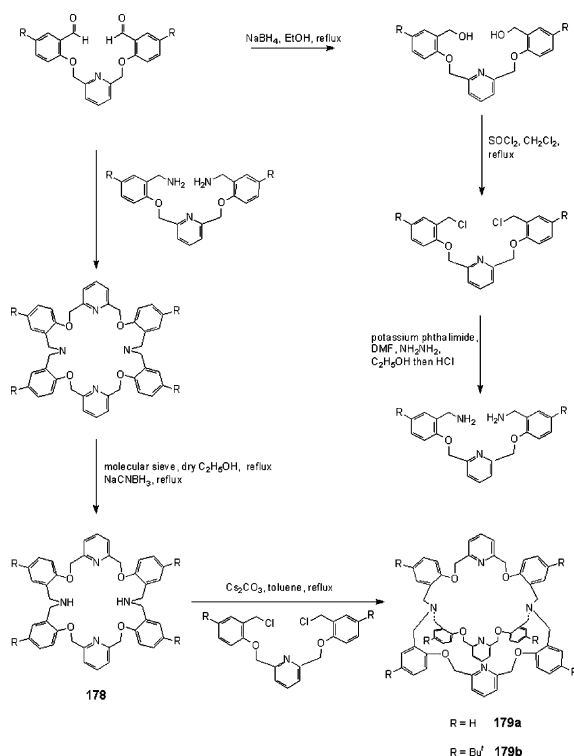
Large macrocycles (**178**) or macrobicycles (**179**), capable of encapsulating organic molecules as benzene were synthesized according to Scheme 34 [230]. Again the dialdehyde is the starting compound for the preparation of all the precursor necessary to obtain **179** via **178**.

Although both **179a** and **179b** were synthesised, the *tert*-butyl derivative **179b** was exclusively employed in subsequent studies because of its considerably enhanced solubility in chloroform and methylene chloride.

The X-ray structure of **179b** (Fig. 95), crystallised from benzene, shows the cage adopts a configuration in which both bridgehead nitrogens are *exo*. The cage has a pseudo three-fold axis passing through the bridgehead nitrogens with the pyridyl rings aligned approximately parallel to this axis such that the pyridyl nitrogens do not point towards the central cavity. A single benzene molecule is a guest within the cavity [230].

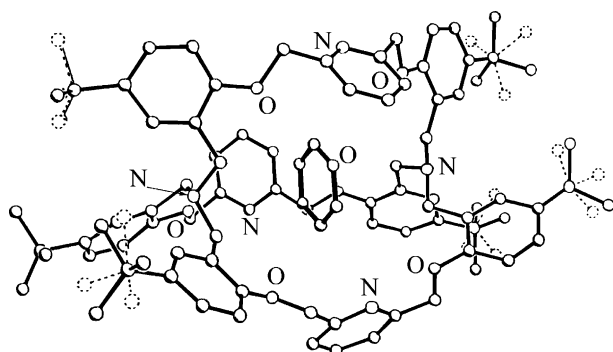


Scheme 33.



Scheme 34.

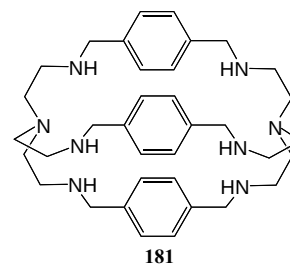
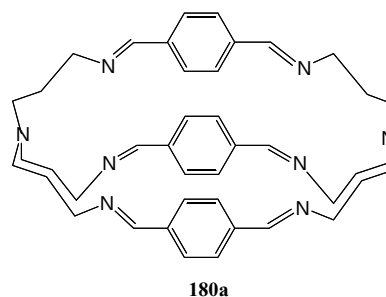
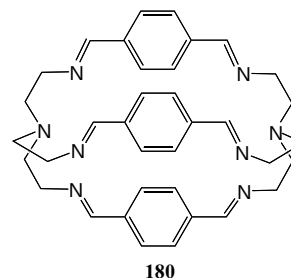
Cryptand **179b** selectively binds certain di- and tri-phenols. Thus, an addition of resorcinol or phloroglucinol to a solution of the cryptand in CDCl_3 results in distinctive shifts in the ^1H NMR signals of both the host **179b** and the guest (resorcinol or phloroglucinol). These include for the cryptand, downfield shifts of the 3- and 4-pyridyl protons and corresponding (but smaller) upfield shifts of the benzylamine methylene protons. The ring protons of the guests appear at higher field in the complexes, consistent with increased electron density on the phenolic oxygens. The observed shifts are consistent with these guests being bound centrally within the cage via stereo-complementary H-bonds between the phenolic protons of the guest and the pyridyl nitrogens of the cage. A parallel experiment using catechol as the potential guest, produced no significant changes in the

Fig. 95. Structure of **179b** (adapted from Ref. [230]).

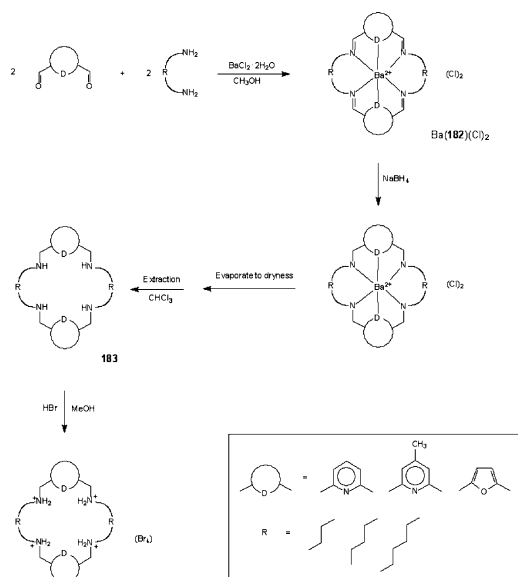
^1H NMR signals of guest or host, attesting to the selectivity, of the binding in the former cases [230].

These systems are large enough to accommodate two metal ions: and the related dinuclear complexes have been prepared and studied. These dinuclear complexes may link the bridging anionic species, thus acting as anionic recognizing systems. Explicatory examples will be included and discussed in a subsequent section.

By tetrahydroborate reduction of the [2+3] condensation product of tris(2-ethylamino)amine with terephthalaldehyde **180** or of the disilver or dilead complexes of **180**, a complete reduction of all six imino functions was obtained and the structure of the resulting octamino cryptand **181** was determined by X-ray diffractometry [231]. This octamino cryptand acts as a host for pairs of protons or first series transition metal cations. Pairs of transition metal cations, coordinated to the amino nitrogen donors, accommodate mono-, bi- or tri-atomic bridging ligands, such as OH^- , imidazolate or azide, generating weak to moderate antiferromagnetic interaction. For the dicopper(II) μ -azido complexes a triplet ground state was suggested, possibly derived from a near linear alignment of the $\text{M}-\text{NNN}-\text{M}$ assembly [231].



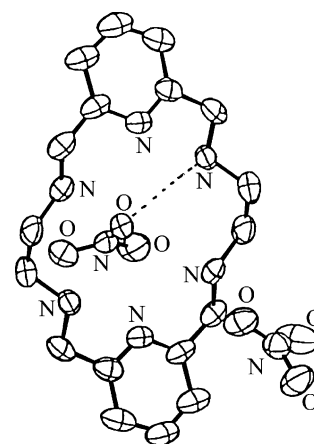
The [2+2] cyclic complexes $\text{Ba}(\mathbf{182})(\text{Cl})_2$, obtained by template procedure (Scheme 35), can also be contemporarily reduced with NaBH_4 and demetallated to form the corre-



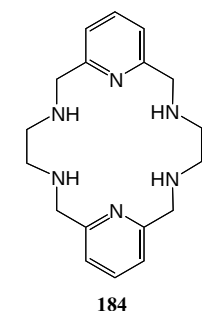
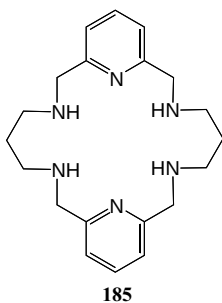
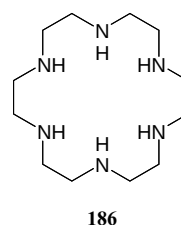
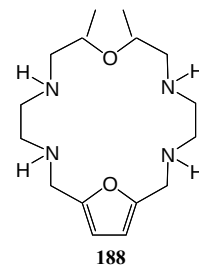
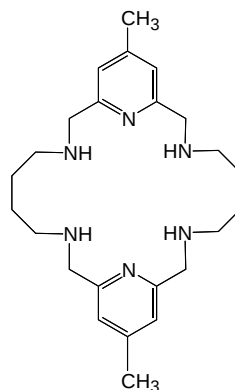
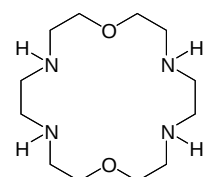
Scheme 35.

sponding [18]-membered macrocyclic ligand **183** containing a saturated amine as lateral unit and pyridine, furan, thiophen, etc. as head unit [231].

$[H_4\text{-}\mathbf{184}](NO_3)_4$ (Fig. 96) consists of discrete centrosymmetric three-ring tetrapositive $[H_4\text{-}\mathbf{184}]^{4+}$ cations and two crystallographically independent nitrate ions [232]. There is a direct and a rather strong intermolecular hydrogen-bond contact between the NH_2^+ groups and the nitrato groups. The nitrate ions have their shortest $H \cdots O$ contact with one ammonium group and a longer contact distance with the ammonium group at the other side of the pyridine ring. The overall conformation of the macrocycle is slightly chair-shaped, and similar to that of $[H_4\text{-}\mathbf{187}](ClO_4)_4$ [233].

Fig. 96. Structure of $[H_4\text{-}\mathbf{184}](NO_3)_4$ (adapted from Refs. [232,233]).

1:1 mononuclear (metal:ligand) nickel(II), copper(II), zinc(II), cadmium(II) and lead(II) complexes were identified with **184** and **185**. Electronic spectral data indicate octahedral six coordination for the complexes of copper(II) and nickel(II) with **184** and **185**. Copper(II) also forms a monoprotonated mononuclear complex and a dinuclear complex with **185**. The metal ion affinities of **184**, compared to those of the fully saturated 1,4,7,10,13,16-hexaazacyclooctadecane **186** by thermodynamic and electronic spectral data, evidence that the larger stability of the copper(II) ion with **184** relative to **186** is entirely due to a more favourable entropy change, indicating that ligand preorganization is the main reason for the increased stability. The metal ion affinity of **185** is lower than that of **184** due to the less exothermic heats of complexation [232].

**184****185****186****188****187****189**

The protonation equilibria of the macrocycles **184**, **186**, **188**, **189** were studied by potentiometric titrations at 25 °C. Four protonation steps were observed for each ligand in the pH ranges 3–12. The protonation mechanism of these macrocyclic ligands, determined by ^1H NMR, is consistent with protonation of only the saturated amine groups in the pH range studied. The formation constants of the complexes of **184** with cadmium(II), magnesium(II), manganese(II), copper(II), zinc(II), cadmium(II), lanthanum(III) and gadolinium(III) ions, determined potentiometrically, follow the order $\text{Ca}^{2+} < \text{La}^{3+} < \text{Mn}^{2+} < \text{Cd}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$, consistent with 1:1 metal ion binding. Furthermore, **184** binds as well or better than its saturated homolog **186**. In contrast, **188** does not bind effectively in comparison to the saturated homolog **189**. The difference in binding may be due to a combination of enthalpic (polarity of ligating groups and steric strain of the ligand and entropic (rigidity of the ligand) contributions [232,233].

The zinc complex of **184** has stability greater than that of the analogous [18]aneN₆ (**186**) complex, suggesting that the macrocycle coordinates through all six nitrogen atoms. $[\text{Zn}(\text{184})][\text{CF}_3\text{SO}_3]_2$, was prepared by reaction of the ligand triflate salt with $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ followed by neutralization with triethylamine. The ^1H NMR spectrum of the complex is consistent with D_2 symmetry in which the ligand is hexacoordinated in a meridional wrap with the pyridine groups twisted relative to each other and the $-\text{CH}_2\text{NHC}_2\text{H}_4\text{NHCH}_2-$ groups forming helical linkages connecting the pyridine groups [233].

The complex was inert to both NH and metal ion exchange in aqueous solution. The right- and left-handed helical enantiomers were resolved by a formation of diastereomers with (+)-tartrate. The CD spectra gave positive and negative Cotton effects at 262 nm corresponding to the pyridine π to π^* transition. The appearance of CD bands indicates that, upon coordination to the zinc(II) ion, a conformationally rigid macrocyclic complex is formed that persists in solution, allowing the separation and isolation of Δ and Λ enantiomeric forms. Racemic $[\text{Zn}(\text{184})][\text{CF}_3\text{SO}_3]_2$ does not give a CD spectrum.

In the crystals of $[\text{Zn}(\text{184})][\text{CF}_3\text{SO}_3]_2$ (Fig. 97) the macrocycle is twisted, with the two pyridine rings oriented 104.5° relative to each other. The twisting of the macrocycle gives rise to two meridional linkages, each incorpor-

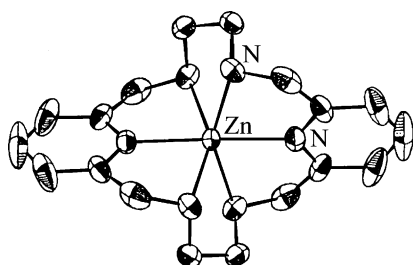


Fig. 97. Structure of $[\text{Zn}(\text{184})]^{2+}$ (adapted from Ref. [233]).

ating one pyridine nitrogen and the two adjacent aliphatic amines. The twist of **184** about the zinc(II) ion gives rise to $\Lambda\delta\delta$ and $\Lambda\lambda\lambda$ isomers. The conformation of the diaminoethane chelate rings within the macrocycle is gauche [233].

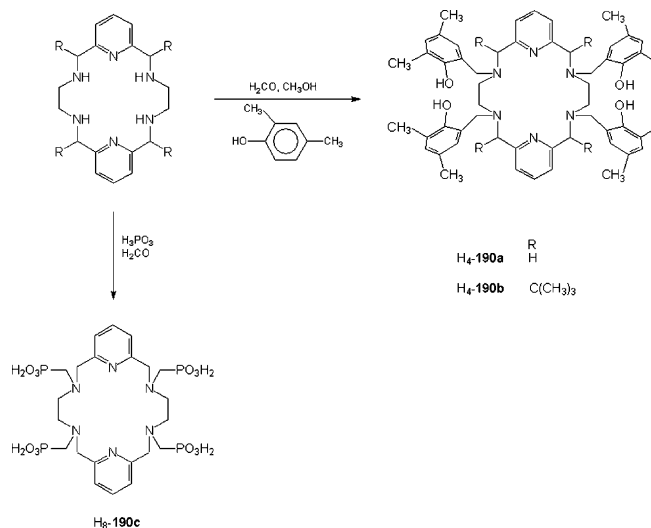
Appropriate functionalization at the NH groups of [2+2] macrocyclic systems introduces further coordinating groups (amine, pyridine, phenol, carboxylic acid, thiol, thioether, etc.) capable to modify the selective properties of the macrocyclic systems. Several synthetic routes have been successfully suggested. Thus substituted derivatives **H₄-190a** and **H₄-190b** were obtained following a Mannich-type reaction according to Scheme 36 [234]. IR and NMR spectra and liquid secondary ion mass spectroscopy evidence that the four ethylene diamine nitrogens are fully saturated. The crystal structure of **H₄-190b** (Fig. 98a) shows the presence of two independent, exactly centrosymmetric, ligand molecules in the crystal and confirms the presence of two different diastereoisomers [234].

The gadolinium(III) complex $\text{Gd}(\text{H}_3\text{-190a})(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_3$, isolated as pure well defined crystals when a methanolic solution of excess gadolinium(III) nitrate was added to a refluxing suspension of the ligand in methanol, shows the presence of a cationic complex $[\text{Gd}(\text{H}_3\text{-190a})(\text{NO}_3)]^+$ in which the ligand adopts a boat conformation, in contrast to the chair conformation observed in the analogous ligand **H₄-190b** in the solid state, with all the nitrogen donors being coordinated [234]. The gadolinium(III) ion has an irregular nine coordinated geometry completed by a bidentate nitrate ligand and the phenolic oxygen atom, of one pendant arm, which forms the shortest metal-ligand bond in the structure. The remaining three pendant arms radiate out away from the metal showing no sign of coordination [234] (Fig. 98b).

The magnetic moment of $[\text{Gd}(\text{H}_3\text{-190a})(\text{NO}_3)](\text{NO}_3) \cdot 3\text{H}_2\text{O}$ was found to be $6.5\mu_B$ at 303 K, lower than the typical value expected for gadolinium(III); no explanation for this was proposed [234].

The relaxivity, R_1 , of $[\text{Gd}(\text{H}_3\text{-190a})(\text{NO}_3)]^+$ was $8.2 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (28 °C, 10 MHz), which is comparable to the relaxivity of $[\text{Gd}(\text{dota})]^-$ ($7.2 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 23 °C, 10 MHz, **H₄dota** = 1,4,7,10-tetraa{acyclodecaoe-1,4,7,10-tetraacetic acid) and better than that of $[\text{Gd}(\text{dtpa})(\text{H}_2\text{O})]^{2-}$ ($5.6 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 23 °C, 10 MHz, **H₅dtpa** = N, N, N^I, N^{II}, N^{III}-diethylenetriamine-pentaacetic acid) [235]. The good relaxivity of $[\text{Gd}(\text{H}_3\text{-190a})(\text{NO}_3)]^+$ can be explained by the fairly exposed gadolinium(III) ion, the coordinating phenolic oxygen being on the opposite side to the coordinating nitrate ion, which allows its easy access to water molecules. However, R_1 was reduced dramatically to $2.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ when the gadolinium(III) complex was in phosphate buffer (pH 6) [234].

The [18]-membered hexaaza macrocycle containing four methylenephosphonate pendant arms **H₈-190c** was prepared by Mannich reaction using a double to triple excess of



Scheme 36.

phosphorous acid and formaldehyde and a 24 h period of reflux. Pure material was obtained by dissolving the crude product in dilute HCl and recrystallising it from ethanol [234] (Scheme 36). The overall conformation of the free hexaaza macrocycle is slightly twisted but is not folded. This conformation arises from the unusual orientation of the pendant arms the phosphonate pendants associated with

one diaminomethylenepyridyl group lying on opposite sides of the macrocycle ring, so that they alternate up and down round the ring. Two of the pendant arms are wrapped across the macrocycle and two are extended outwards [234] (Fig. 98c).

H₈-190c forms a 1:1 stable complex with lanthanum(III) salts. The ¹H NMR spectrum of [La(H₅-198c)] together with its solid state characterisation suggests that the ligand adopts only one of the five possible configurations, i.e. the *SSSS* or *RRRR* configuration [234]. The X-ray structure analysis of [La(H₅-190c)] confirms the *SSSS/RRRR* conformation of the macrocycle indicated by the ¹H NMR studies; both enantiomers are present in the crystal, related by the inversion of the *n*-glide planes, and the *SSSS* conformation is illustrated in (Fig. 98d). The lanthanum ion has the irregular 10 coordinated geometry derived from four oxygen atoms of the four phosphonate pendant arms and six nitrogen atoms of the [18]-membered hexaaza macrocycle. The [La(H₅-190c)] complexes has four coordinated pendant arms [234].

5. Anion recognition by acyclic and macrocyclic systems

The early cryptands, derived from diazapolyoxocrown ethers by the addition of a third polyether strand, generated

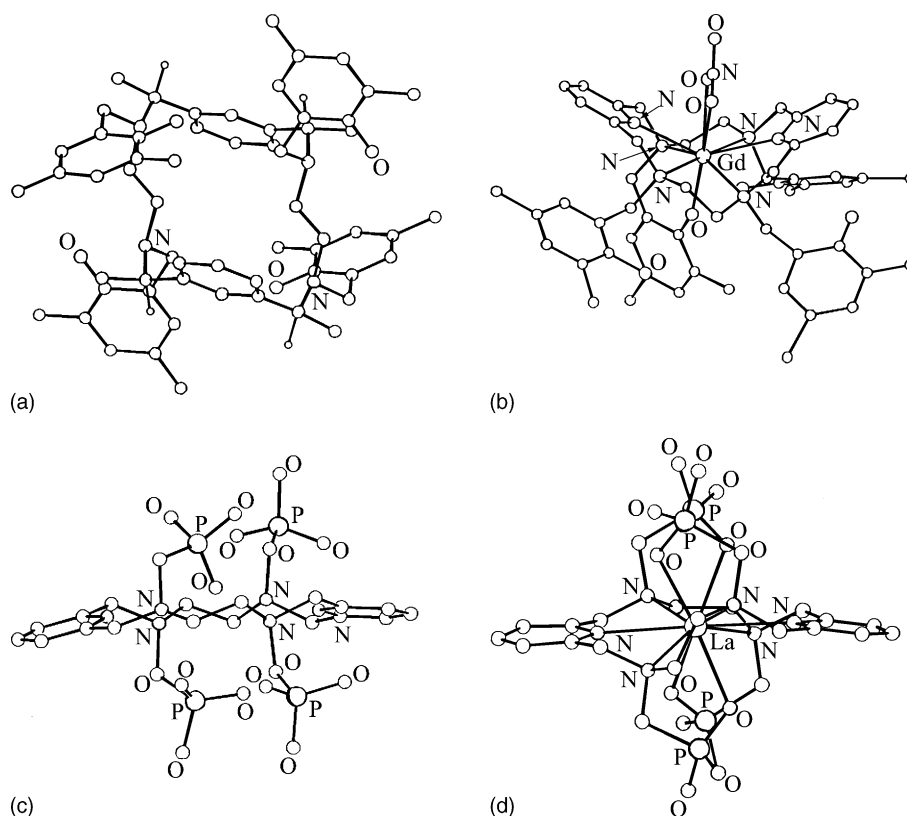


Fig. 98. Structure of **H₄-190b** (a), [Gd(H₃-190a)(NO₃)]⁺ (b), **H₈-190c** (c) and [La(H₅-190c)] (d) (adapted from Ref. [234]).

an invaluable range of applications in the areas of cation recognition, transport and catalysis [236]. The ligands have shown an unrivalled ability to selectively recognize particular alkali metal cations [236,237], permitting their transport through membranes owing to the hydrophilic nature of the exterior of the cryptand within which the polar guest lies concealed [238]. The polyether cryptands surpass crown ethers in their capacity to form stable and selective inclusion complexes and have all enhanced capacity to solubilize polar salts in nonpolar solvents leading to applications [239] in phase-transfer catalysis and anion activation as well as in cation transport and selectivity especially alkali metal cations.

In addition to the alkali metal ions, the polyether cryptands can accommodate other main group cationic guests such as lead(II), cadmium(II) and lanthanide ions [240], but in general, complexation of transition metal ions and heavy main group cations is not most efficiently achieved with neutral ether oxygen donor ligands. The nitrogen donors, whether sp^2 N or sp^3 N, are much better equipped to coordinate transition metal ions and many main Group 3–14 (IIIA–IVA) cations [241]. Several valuable or potentially toxic target cations such as copper(II), silver(II), thallium(I) and mercury(II) ions are expected to be efficiently sequestered by nitrogen donor cryptands (azacryptands), leading to potential applications, for example, in hydrometallurgy or detoxification.

Azacryptands can be readily protonated, which enables them to encapsulate anions, an objective not readily achieved with the analogous oxygen donor hosts. The ability of many of these ligands to encapsulate pairs of cations likewise enables the resultant cryptates to act as metallor-eceptors, hosting bridging anions in cascade fashion [242].

The rapidly growing interest for anion binding and recognition by appropriate receptors in the last years covers a lack of knowledge for these species, of key importance across many fields of chemistry, environment, biology and medicine sciences.

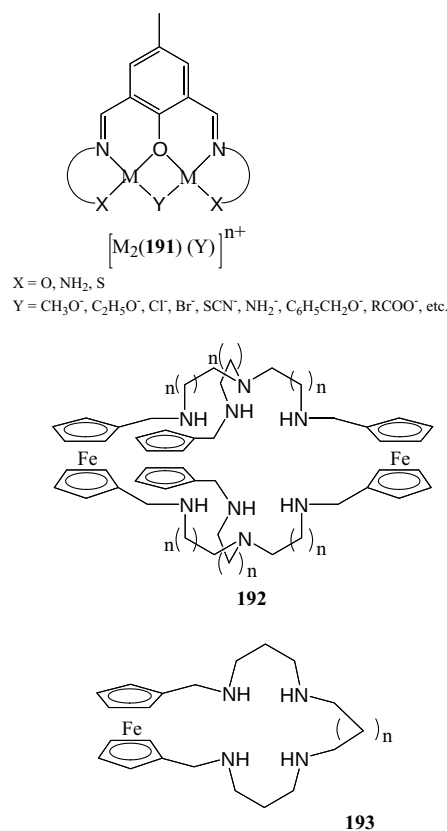
Starting from the design and synthesis of organic receptors for anions, mainly based on hydrogen bonding formation, these investigations rapidly increased and involved a new range of receptors, incorporating metal centers. Moreover, the use of hydrogen-bonding groups in combination with metal centers to produce a wide range of excellent anions receptors was successfully tested [243]. Thus the combination of organometallic or transition metal Lewis and units with amine or amide binding sites (and/or other functionalities) have demonstrated their remarkable utility in these recognition processes of this new class of metal based hydrogen-bonding anion receptors.

Furthermore, the combination of the coordination of a specific anion via the formation of hydrogen bonding with the coordinating system adds significant specificity to the recognition processes [243].

Acyclic, macrocyclic or macrobicyclic dinuclear entities can be considered as suitable systems for binding anions

between the two metal ions; thus they act as binucleating anion receptors.

[1+2] Acyclic Schiff bases complexes of the type $[M_2(191)(Y)]^{n+}$ represent an example of the anion recognition. An evolution of these systems is represented by the dicopper(II) complex that binds phosphate esters and increase their rate of hydrolytic cleavage [243]. This indicates the potential of these systems for the incorporation of catalytic functions as well as anion recognition properties.



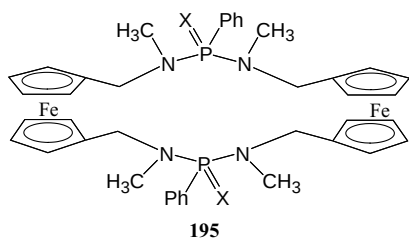
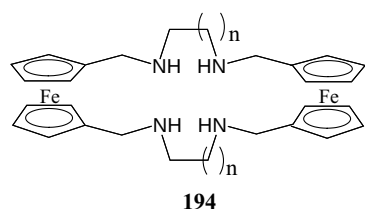
Dinuclear macrocyclic and macrobicyclic Schiff base complexes also bind anions and act as selective receptors and catalysts.

Moreover, the reduced polyamine analogues offer the possibility of anion recognition when they are in the form of dinuclear complexes or when they are protonated. Thus [2+2] macrocycles as **183**, and/or their dinuclear complexes can selectively bind different anions according to the nature of the head and lateral units. Macrobicyclic receptors also as in **173** and related complexes (i.e. dicopper(II), dinickel(II), dizinc(II), etc.) coordinate different anions according to their bite length and/or the ability to act as bridging groups between the two metal ions not according to their size or coordinating tendency.

In the synthesis of these receptors ferrocene moieties were extensively used as redox units capable of sensing anionic guest. For instance, the macrobicyclic **192**, obtained by reduction with $NaBH_4$ of the corresponding [3+2] Schiff

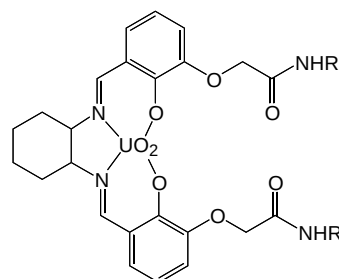
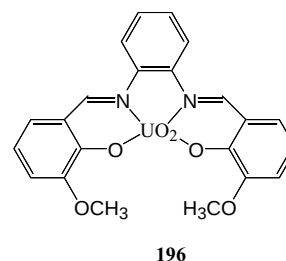
base and easily synthesized in a one pot condensation of 1,1'-diformylferrocene and tris(2-aminoethyl)amine, forms dinuclear copper(II) or zinc(II) complexes. On addition of NaN_3 to the dizinc complex, a solid cascade formation was observed, as indicated by IR investigation of N_3^- stretching frequencies [243].

The anion-binding function of the water-soluble polyaza ferrocene macrocycles (**193** and **194**) [244] operates at pH 7 and below when they are partially protonated. Anions are bound through a combination of electrostatic and hydrogen-bonding interactions, analogous to the organic polyaza receptors discussed earlier. The ferrocene unit is also capable of electrochemically reporting on the binding of biologically important anions such as H_2PO_4^- and ATP^{4-} by means of large ($\cong 100$ mV) cathodic shifts. The binding process of these anions was readily followed using ^{31}P NMR techniques.

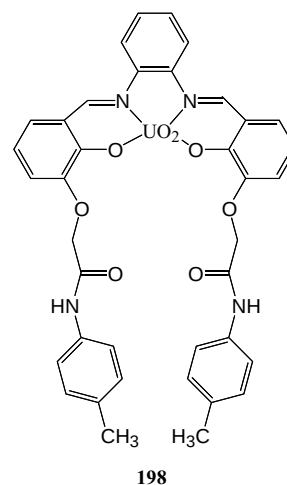


The ferrocenyl-phosphorus macrocycle **195** is capable of binding anions through hydrogen-bonding interactions [245]. This receptor showed an EC (electron transfer followed by chemical reaction) electrochemical response and shifts in the anodic peak potential on the addition of anions. Evidence of dihydrogen phosphate selectivity (over hydrogen sulfate and chloride ions) in dichloromethane was presented. Molecular modelling studies indicated the most stable free receptor conformation had a 5 Å cavity defined by the four inwardly pointing to N–H groups, being exactly the right size for H_2PO_4^- encapsulation.

Uranyl(VI) Schiff base complexes, demonstrated their potential in anion recognition based on coordination to UO_2^{2+} in its equatorial plane to complete the usual pentacoordination and on hydrogen-bonding of the anions at the peripheral functionalities of the ligands. Receptors such as **196**, were observed to bind anions such as chloride with stability constants of 400 M^{-1} in acetonitrile/DMSO (99:1). Crystallographic data showed the chloride ion to be bound to the Lewis acidic uranyl center.



The incorporation of secondary amide functionalities (**197** and **198**) markedly enhanced the binding of anions and, notably, dihydrogen phosphate was bound in polar organic solvents with stability constants as high as 10^5 M^{-1} . This result was remarkable for a neutral receptor system. Crystallographic analysis of **197** with bound dihydrogen phosphate (Fig. 99), showed the anionic guest was bound by a strong bond to the uranium atom and secondary amide hydrogen-bond participation was also observed.



A further modification was the introduction of crown ethers at the end of the side arms creating a ditopic receptor (**199**) [246]. This modification imparted the ability to bind cations and anions simultaneously, introducing an additional electrostatic component to the anion-binding interaction. This receptor exhibited significant transport of hydrophilic KH_2PO_4 through a supported liquid membrane. Electroche-

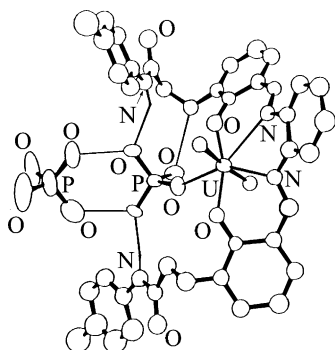
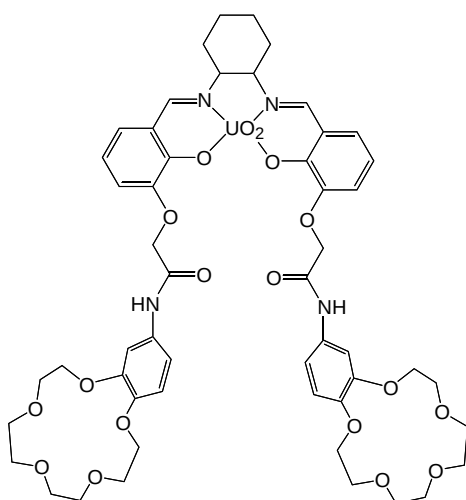


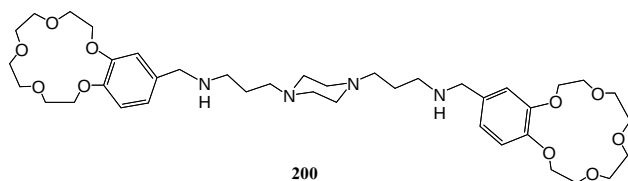
Fig. 99. Structures of the receptor **197** with two bound dihydrogen phosphate anions (adapted from Ref. [246]).

mical studies indicated that H_2PO_4^- perturbed the electrochemistry of the proximate uranyl salene moiety, while the more distantly bound potassium ion left it unperturbed.



199

Crown ethers have also been incorporated into other anion receptors [239,240]. Receptors such as **200** when protonated, simultaneously bind cations in the crown ether rings and anions at the central linker portion (through hydrogen bonding and electrostatic attraction). Chloride binding was probed using ^{35}Cl NMR techniques. Potassium ions formed a 1:1 sandwich complex, while sodium ions formed a complex of 2:1 stoichiometry. No evidence was provided to demonstrate that anion and cation binding were complementary processes.



200

These ditopic [2+1] side-off ligands were also used for the simultaneous recognition and solvent extraction of cations and anions. For instance a chloroform solution of

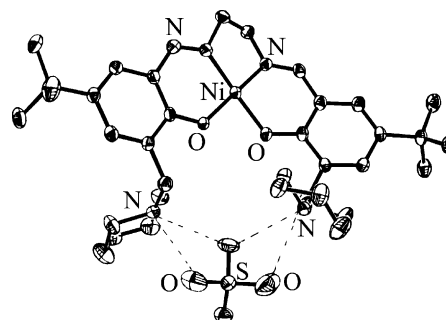
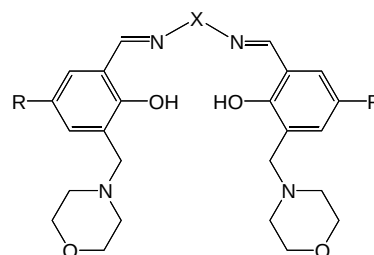


Fig. 100. Structure of $[\text{Ni}(\text{H}_2\text{-202})(\text{SO}_4)]$ (adapted from Ref. [246]).

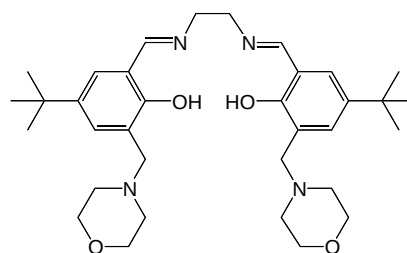
the Schiff bases $\text{H}_2\text{-201}$, contacted with an aqueous solution of CuSO_4 , extracts this metal salt close to 100% [246]. The binding of divalent transition metal ions and their attendant anions was ascertained by X-ray diffractometry on $[\text{Ni}(\text{H}_2\text{-202})(\text{SO}_4)] \cdot 6\text{H}_2\text{O}$ obtained by the reaction of $\text{H}_2\text{-202}$ with $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in methanol [246]. The nickel(II) cation is coordinated in the planar N_2O_2 cavity of the Schiff base moiety. The coordination of the nickel(II) ion has two important effects on the structure of the ligand. The two protons liberated from the phenols of the metal binding site have been transferred to the nitrogen atoms of the pendant morpholine groups and the ligand has been organised to bring the two morpholine groups into close proximity to produce a dicationic binding site for the sulfate anion. This represents an example of cooperativity in which binding of the metal cation directly enhances the binding of the anion. The sulfate dianion is bound by both electrostatic interactions and two separate bifurcated hydrogen bonds, one to each quaternary amine (Fig. 100).



$\text{H}_2\text{-201}$

$\text{R} = \text{CH}_3, \text{C}(\text{CH}_3)_3$

$\text{X} = \text{CH}_2\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}_2, \text{C}_6\text{H}_4, \text{C}_6\text{H}_{10}$



$\text{H}_2\text{-202}$

An X-ray structure of the free ligand shows that in the solid state the torsion around the ethylene linker group places the chelating units in a *trans* configuration and it is therefore not predisposed for complexation [246].

6. From mononuclear to polynuclear systems

It was verified that the phenolic oxygen atoms of the simple open Schiff bases, obtained by reaction of substituted salicylaldehyde with monoamines ($\text{NH}_2\text{-R}$) or diamine ($\text{H}_2\text{N-R-NH}_2$) can act as bridging groups giving rise to dinuclear or polynuclear entities.

The tetradentate Schiff bases $\text{H}_2\text{-L}$, derived from the condensation of salicylaldehyde and 1,2-diaminoethane ($\text{H}_2\text{-207a}$) or 1,2-diaminobenzene ($\text{H}_2\text{-204}$) in a 2:1 molar ratio, react with lanthanide(III) salts to form $[\text{Ln}_2(\text{L})_3]$ where the two lanthanide centers are held together by one of the three deprotonated Schiff bases acting as a bridging ligand via its two phenoxo oxygen atoms [247]. The magnetic properties of the complexes $[\text{Gd}_2(\text{L})_3]$ suggest the presence of an antiferromagnetic interaction in both complexes, the values varying from -0.140 to -0.100 cm^{-1} . These results confirm the presence of oxygen bridges between the two gadolinium centers in the $[\text{Gd}_2(\text{L})_3]$ complexes. Solution studies show that the complexes $[\text{Ln}_2(\text{L})_3]$ are dissociated into the mononuclear species $[\text{Ln}(\text{L})_2]^-$ and $[\text{Ln}(\text{L})]^+$ which have been isolated and characterized [247].

The reaction between salicylaldehyde (or a tin-salicylaldehyde complex precursor) and diethylenetriamine in the presence of lanthanide(III) nitrates yields $[\{\text{Ln}(\text{203})\text{-(NO}_3)_2\}_n \cdot n\text{CH}_3\text{OH}]$ ($n = 0$, $\text{Ln} = \text{Sm}^{3+}\text{-Tb}^{3+}$; $n = 1$, $\text{Ln} = \text{Dy}^{3+}\text{-Lu}^{3+}$) [247].

The X-ray analyses of $[\{\text{Ln}(\text{203})\text{-(NO}_3)_2\}_2]$ ($\text{Ln} = \text{Gd}^{3+}$, Tb^{3+}) show the two structures to be isomorphous. The complexes are dimeric with each cationic center coordinated to all five heteroatoms of **203** and to two oxygen atoms of a bidentate nitrate anion (Fig. 101). One of the phenolate

oxygen atoms of each ligand is binucleating and serves to bridge adjacent centers. Each gadolinium(III) cation is eight coordinated with the ligating atoms forming a distorted bicapped trigonal prism, with the phenolic oxygen and the aminic nitrogen as the capping atoms. The crystallographic center of symmetry lies at the center of the four membered Gd_2O_2 ring. Within this ring the non-bonded $\text{Gd} \cdots \text{Gd}$ distance is $3.81 \text{ \AA}$. Each acyclic Schiff base ligand has an essentially flat conformation; the gadolinium(III) cation and the coordinating atoms are coplanar [247].

The dinuclear complex $[(\text{CuGd}(\text{204})(\text{hfac})_3)]$ (Fig. 102a), synthesized by the combination of a tetrahedrally distorted copper(II) complex $[\text{Cu}(\text{204})]$ with $[\text{Gd}(\text{hfac})_3] \cdot 2\text{H}_2\text{O}$, where $\text{H}_2\text{-204}$ and H-hfac denote *N,N'*-bis(salicylidene)-2-iminobenzylamine and 1,1,1,5,5,5-hexafluoro-acetylacetonate, respectively [248], has the intermolecular metal $\cdots$ metal distances long enough to be regarded as a discrete one. The shortest intermolecular $\text{Cu} \cdots \text{Cu}$, $\text{Cu} \cdots \text{Gd}$, and $\text{Gd} \cdots \text{Gd}$ distances are 6.002 , 7.522 , and $8.507 \text{ \AA}$, respectively, showing that the structure of the present complex consists of a discrete binuclear unit. The copper(II) and gadolinium(III) ions are bridged by the two phenolic oxygens. The $\text{Cu} \cdots \text{Gd}$ distance is $3.248 \text{ \AA}$. The copper(II) ion is bound to the two imino nitrogens and the two phenolic oxygens of the Schiff base. It was observed that a large tetrahedral distortion of the coordinating geometry around copper(II) ion. The gadolinium(III) ion is of eight coordination with six oxygens of three hfac and two phenolic oxygens of the Schiff base. The four atoms forming the bridge CuO_2Gd , do not lie on the same plane. Magnetic data evidence a ferromagnetic spin coupling between gadolinium(III) and copper(II) ions [248].

When $[\text{Cu}(\text{205})]$ is treated respectively with $\text{Ln}(\text{NO}_3)_3$ ($\text{Ln} = \text{Gd}^{3+}$, Er^3) and $\text{Ce}(\text{NO}_3)_3$ in ethanol $[\text{CuLn}(\text{205})\text{-(NO}_3)_3] \cdot \text{C}_2\text{H}_5\text{OH}$ or $[\text{Cu}_2\text{Ce}(\text{205})_2(\text{NO}_3)_3]$ were obtained [249].

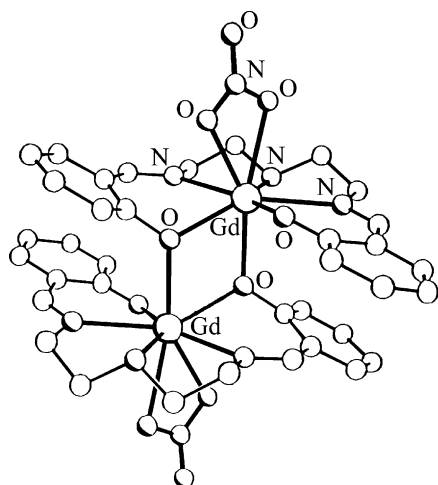
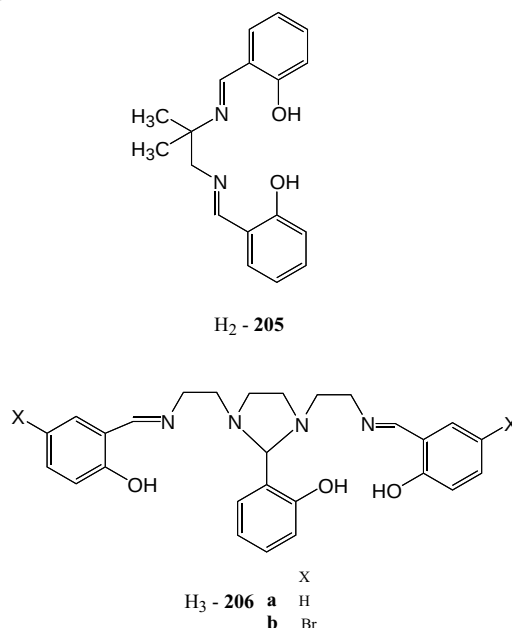


Fig. 101. Structure of $[\text{Gd}(\text{203})(\text{NO}_3)_2]_2$ (adapted from Ref. [247]).



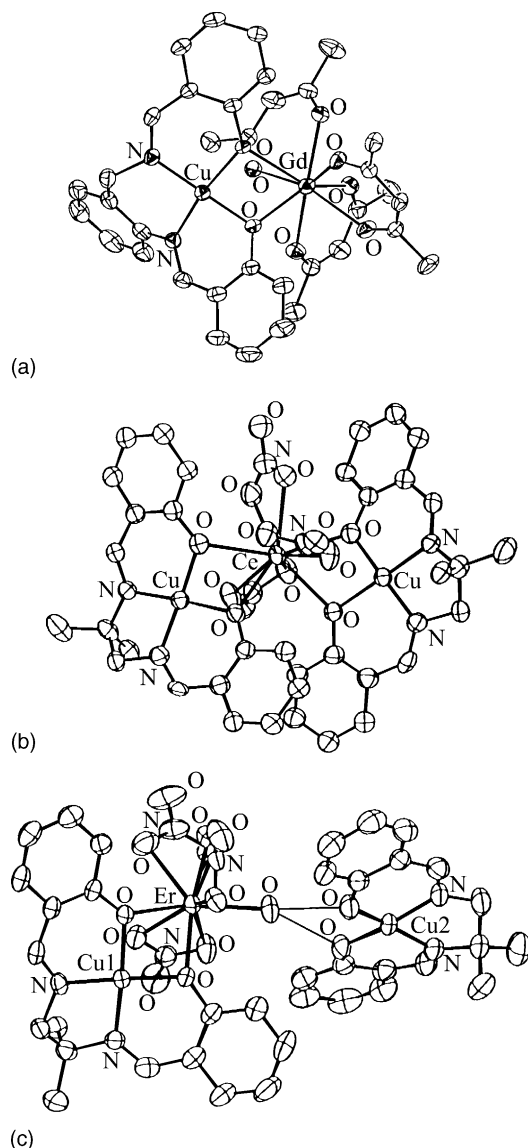


Fig. 102. Structure of $[\text{CuGd}(\mathbf{204})(\text{hfac})_3]$ (a) $[\text{Cu}_2\text{Ce}(\mathbf{205})_2(\text{NO}_3)_3]$ (b) and $[\text{Cu}_2\text{Er}(\mathbf{205})_2(\text{NO}_3)_3(\text{H}_2\text{O})]$ (c) (adapted from Refs. [248,249]).

The structural determination of $[\text{Cu}_2\text{Ce}(\mathbf{205})_2(\text{NO}_3)_3]$ (Fig. 102b) confirms the existence of a trinuclear species. The cerium center is surrounded by two $\{\text{Cu}(\mathbf{205})\}$ entities and three nitrato anions. It is linked to ten oxygen atoms, four coming from the phenolato atoms and six from the nitrate anions. The copper environment can be considered as square planar for it is situated in the mean N_2O_2 coordination plane. The two $\text{Cu} \cdots \text{Ce}$ separations are equal to 3.403 Å. The separations between metal ions belonging to neighbouring molecules are large ($\text{Ce} \cdots \text{Cu} = 6.960$ Å and $\text{Ce} \cdots \text{Ce} = 10.125$ Å) except for the $\text{Cu} \cdots \text{Cu}$ separations, which are shorter (4.186 Å).

A slow evaporation of an acetone solution of $[\text{Cu}(\mathbf{205})]$ and $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ affords $[\text{Cu}_2\text{Er}(\mathbf{205})_2(\text{NO}_3)_3(\text{H}_2\text{O})]$ which comprises a dinuclear $[\text{CuEr}(\mathbf{205})(\text{NO}_3)_3]$ complex and a mononuclear $\{\text{Cu}(\mathbf{205})\}$ entity (Fig. 102c). The two

fragments are linked via a water molecule bonded to the erbium(III) ion and hydrogen-bonded to the phenoxo oxygen atoms of the mononuclear complex. The central part of the dinuclear entity is occupied by the expected CuO_2Er bridging core. The $\text{Cu}(1) \cdots \text{Er}$ separation (3.208 Å) is rather short but the $\text{Cu}(2) \cdots \text{Er}$ separation (5.908 Å) is longer. The separations between metal ions belonging to neighbouring molecules are again large ($\text{Er} \cdots \text{Cu}(1) = 7.158$ and $\text{Er} \cdots \text{Cu}(2) = 7.553$ Å, $\text{Cu}(1) \cdots \text{Cu}(1) = 5.939$ and $\text{Cu}(2) \cdots \text{Cu}(2) = 15.83$ Å). The erbium ion is nonacoordinated to only two oxygen phenolato atoms of the Schiff base ligand and to six oxygen atoms of the three coordinated nitrato anions, the ninth position being occupied by a water molecule. The two copper ions are four-fold coordinated to the equatorial N_2O_2 donors of the Schiff base $[\mathbf{205}]^{2-}$, without any solvent molecule in an axial position. The copper environment can be considered as square planar. Finally, $[\text{Cu}_2\text{Er}(\mathbf{205})_2(\text{NO}_3)_3(\text{H}_2\text{O})]$ is made up of two quasi-independent entities, dinuclear (CuGd) and mononuclear (Cu) fragments and cannot be considered as a genuine trinuclear compound. For $\text{CuGd}(\mathbf{205})_2(\text{NO}_3)_3 \cdot \text{C}_2\text{H}_5\text{OH}$ a ferromagnetic interaction ($J = 3.5 \text{ cm}^{-1}$) was found [249].

The reaction of triethylenetetramine and salicylaldehyde in the presence of $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ in a 4:3:1 ratio yields the unsolvated dinuclear complexes $[\text{Ln}(\mathbf{206a})_2]$ [250]. The crystal structure of $[\text{Sm}(\mathbf{206a})_2]$ confirms the dinuclear sandwich binding in which the pair of samarium(III) ion is trapped between the two chelates to yield an eight-fold square antiprismatic coordination geometry on each samarium(III) ion [250]. The four ligand nitrogen atoms are planar and the two terminal phenolate rings are inclined by ca. 25° to this plane. The ligand is heptadentate, and together with a centrosymmetrically related counterpart utilizes all of their potential coordinating sites (Fig. 103). The two coordination polyhedra are edge linked with an intramolecular $\text{Sm} \cdots \text{Sm}$ separation of 3.917 Å. The shortest interdimer $\text{Sm} \cdots \text{Sm}$ distance is 9.60 Å. An inspection of the packing of the dimers reveals only weak π stacking (3.7 Å interplanar separation) between the terminal phenolate rings of adjacent

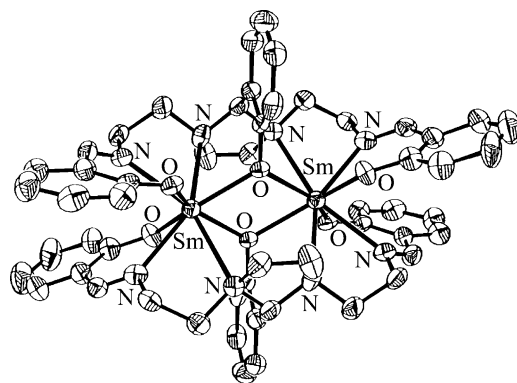
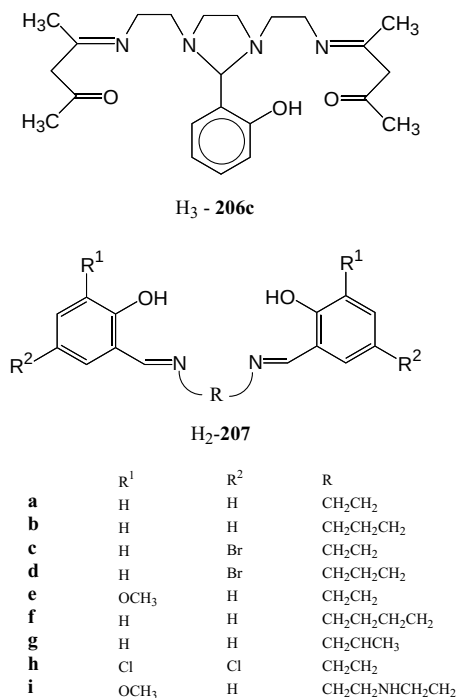


Fig. 103. The dimeric sandwich structure of $[\text{Sm}(\mathbf{206a})_2]_2$ (adapted from Ref. [250]).

molecules, the overall intermolecular interactions being essentially van der Waals in nature.



[La(**206b**)]₂·2CHCl₃, although significantly different from a crystallographic point of view, is also centrosymmetric and the lanthanum(III) ions have a distorted square antiprismatic coordination geometry of roughly similar magnitudes to those found in [Sm(**206a**)]₂ [250].

The similar ligand **H₃-206c** was prepared by condensation of triethylenetriamine with acetylacetone in methanol at 0 °C followed by the addition of salicylaldehyde in a molar ratio 1:2:1. NMR spectral and single crystal X-ray structural characterizations confirm the formation of a five-membered imidazolidine ring as a backbone to have a new type of doubly bridging binucleating ligand system. The structure clearly shows two tetradentate non-planar compartments suitable for binding two of the same, or different metal ions [250].

The homo-dinuclear manganese(III) complexes [Mn₂(μ-**206c**)(μ-X)(H₂O)₂](Cl)₂ (X = Cl, OCH₃, OC₂H₅) were prepared from reactions of manganese(III) ion with **H₃-206c** in presence and absence of bases (alkoxide), following oxidation by air. Each manganese(III) ion is coordinated by the N₂O₂ donor set of one half of the ligand. The phenolate oxygens atom from the middle arm of the ligand acts as an endogenous bridge between the two metal centers. The exogenous alkoxide bridge and terminal water groups complete the coordination sphere and the biotetrahedral structure. The binucleating ligand provides four donor points around each manganese(III) center [250].

In methanol solutions both the Mn^{III}Mn^{IV}/Mn^{III}Mn^{III} and Mn^{III}Mn^{III}/Mn^{III}M^{II} couples are observable for the chloro bridged complex with *E*_{1/2} in the range of +0.49 to −0.13 V

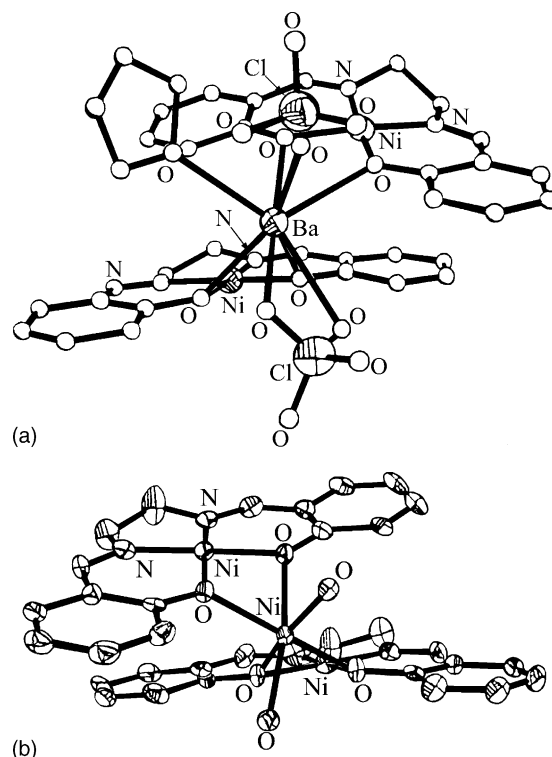


Fig. 104. Structure of [Ni₂Ba(**207a**)₂(ClO₄)₂(THF)] (a) and [Ni₃(**207a**)₂(H₂O)₂]²⁺ (b) (adapted from Ref. [251]).

versus SCE. The calculation of the comproportionation constant (*K*_{com}) from the *E*_{1/2} values clearly point towards the role of the Mn–O(phenolate)–Mn core for thermodynamic stability of the Mn^{III}Mn^{III} complex which is considerably stabilized with respect to the Mn^{III}Mn^{IV} and Mn^{III}M^{II} species [250].

The reaction of [Ni(**207a**)] with M(ClO₄)₂·*n*H₂O (M = Ba²⁺, Ni²⁺) in tetrahydrofuran affords [Ni₂Ba(**207**)₂(ClO₄)₂(THF)] and [Ni₃(**207a**)₂(H₂O)₂](ClO₄)₂ [251]. Two [Ni(**207a**)] units act as oxygen bidentate ligands in both the compounds. The barium ion is coordinated to eight oxygen atoms in a distorted square antiprismatic geometry. The eight-fold coordination is completed by a molecule of tetrahydrofuran, two perchlorate anions acting as bidentate and monodentate oxygen ligands, respectively. In [Ni₃(**207a**)₂(H₂O)₂](ClO₄)₂ the nickel(II) ion, coordinated to two [Ni(**207a**)] complexes, has a distorted octahedral geometry and completes its coordination by linking two water molecules (Fig. 104a and b).

Reaction of manganese(II) carboxylate with the tetradentate Schiff bases **H₂-207** gives rise to mono- and polynuclear species. Thus polymeric chains were observed for [Mn(**207b**)(C₂H₅COO)]_n and [Mn(**207d**)(C₆H₄CH₂COO)]_n (Fig. 105a and b). The first complex shows an *anti-anti* bridging of the manganese centers while the second exhibits a *syn-anti* bridging. Also the second complex contains a dimeric repeat unit due to an alternate 180° twist in the polymeric chain necessitated by steric constraints [251].

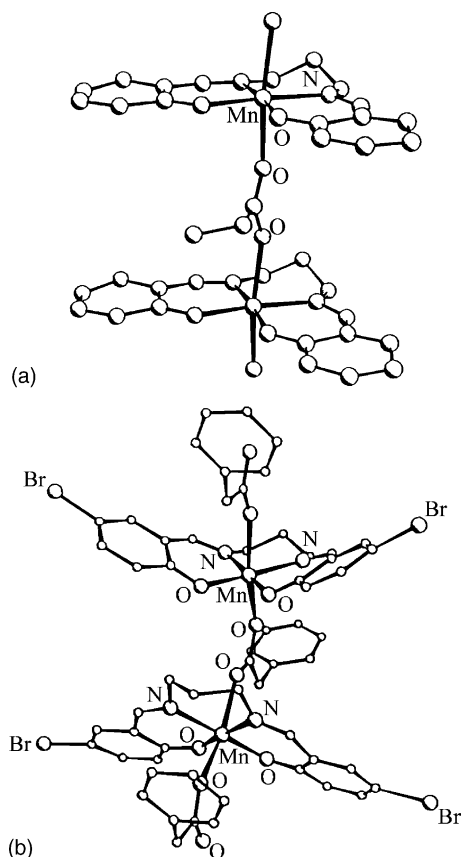


Fig. 105. Structure of $[\text{Mn}(\mathbf{207b})(\text{C}_2\text{H}_5\text{COO})]_n$ (a) and $[\text{Mn}(\mathbf{207d})(\text{C}_2\text{H}_5\text{COO})]_2$ (b) (adapted from Ref. [251]).

$[\text{Mn}(\mathbf{207e})(\text{C}_2\text{H}_5\text{COO})]_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (Fig. 106a) is a dimer in which the manganese centers are linked by phenoxy bridges between one phenolic oxygen atom of each ligand and the metal centers resulting in a $\text{Mn} \cdots \text{Mn}$ separation of 3.485 Å. The planar nature of the ligand, in conjunction with the phenoxy bridges, leaves only one site of each manganese center available for coordination, resulting in the propionate binding in the relatively rare unidentate mode [251]. The manganese(III) ion has a slightly distorted octahedral environment.

The structure of $[\text{Mn}(\mathbf{207e})(\text{C}_4\text{H}_9\text{COO})]_2$ was found to be analogous to that of $[\text{Mn}(\mathbf{207e})(\text{C}_2\text{H}_5\text{COO})]_2 \cdot \text{C}_2\text{H}_5\text{OH}$. The complex was found to exist as a phenoxy bridged dimer, although the linkages were slightly weaker resulting in the slightly longer $\text{Mn} \cdots \text{Mn}$ separation of 3.529 Å [251].

$[\text{Mn}(\mathbf{207a})(\text{C}_3\text{H}_7\text{COO})]$ crystallizes as the dinuclear complex $[\text{Mn}_2(\mathbf{207a})_2(\text{C}_3\text{H}_7\text{COO})(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})](\text{C}_3\text{H}_7\text{COO})$ (Fig. 106b). The manganese ions are situated in the equatorial plane of two phenolic oxygen atoms and two imine nitrogen ions of the $[\mathbf{207a}]^{2-}$ ligand and are bridged by a single $\text{C}_3\text{H}_7\text{COO}^-$ group. Octahedral coordination is completed by an ethanol molecule for one manganese(III) ion and a water molecule for the other manganese(II). The cationic charge of the dinuclear unit $[\text{Mn}_2(\mathbf{207a})_2(\text{C}_3\text{H}_7\text{COO})(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})]^+$ is balanced by an uncoordinated $\text{C}_3\text{H}_7\text{COO}^-$ anion.

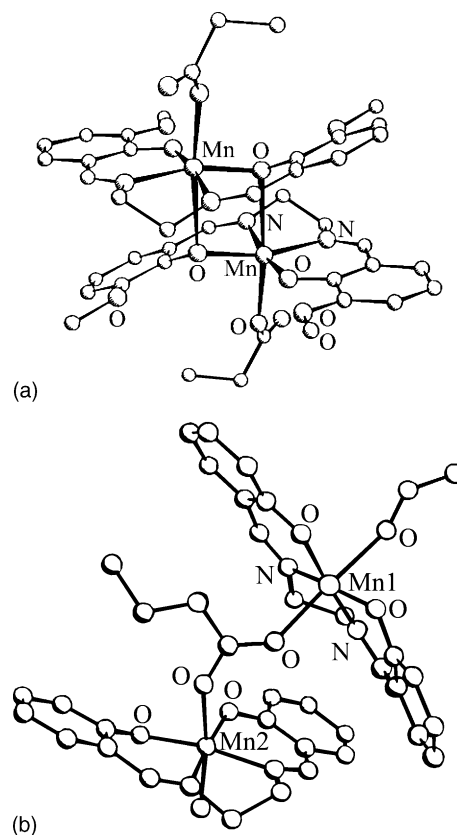


Fig. 106. Structures of $[\text{Mn}(\mathbf{207e})(\text{C}_2\text{H}_5\text{COO})]_2$ (a) and $[\text{Mn}_2(\mathbf{207a})_2(\text{C}_3\text{H}_7\text{COO})(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})]^+$ (b) (adapted from Ref. [251]).

In complete contrast to the aforementioned structure and that of the polymeric acetate complex, $[\text{Mn}(\mathbf{207b})(\text{C}_4\text{H}_9\text{BuCOO})]$ has a monomeric structure.

Also the recrystallization of $[\text{Mn}(\mathbf{208})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ from a dimethyl sulfoxide solution ($[\mathbf{208}]^{2-}$ is the dianion of *N,N'*-bis(3-bromo-5-nitrosalicylidene)-1,2-diamino-(2-methyl)ethane) induces a dimerization with the formation of $[\text{Mn}_2(\mathbf{208})_2(\text{H}_2\text{O})_4(\text{DMSO})_2]$ [252] (Fig. 107) whose structure consists of an N_2O_2 coordination sphere around each manganese(II) ion with capping water and dimethyl sulf-

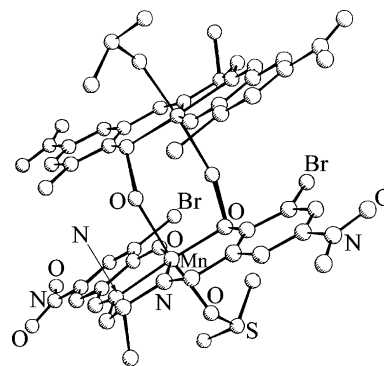


Fig. 107. Structure of $[\text{Mn}(\mathbf{208})(\text{H}_2\text{O})_2(\text{DMSO})]_2$ (adapted from Ref. [252]).

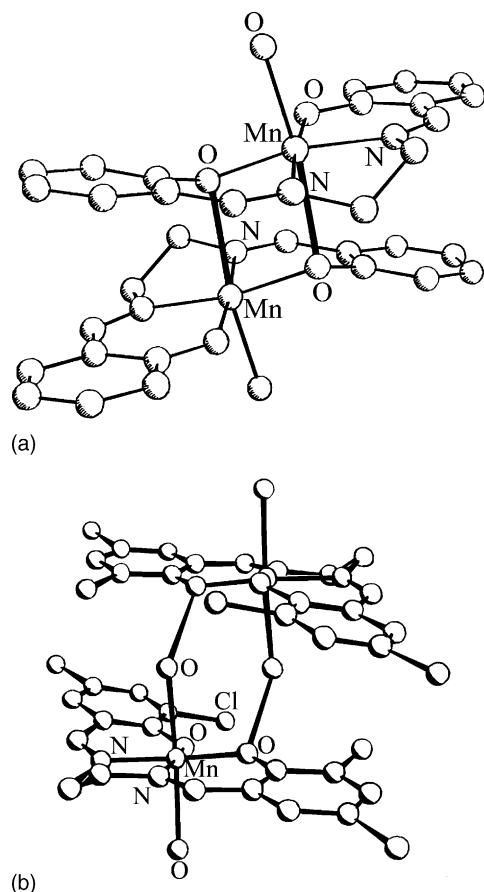


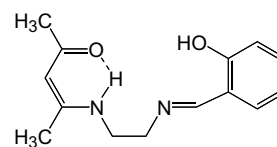
Fig. 108. Structures of $[\text{Mn}(\mathbf{207a})(\text{H}_2\text{O})]_2^{2+}$ (a) and $[\text{Mn}(3,5\text{-Cl-}\mathbf{207h})(\text{H}_2\text{O})]_2^{2+}$ (b) (adapted from Ref. [253]).

oxide groups in the axial positions. The closeness of the water molecules between the manganese(II) moieties leads to the very strong hydrogen bonding and consequently the short $\text{Mn} \cdots \text{Mn}$ separation of 4.6 Å. The dimerization is also facilitated by the strong π -interaction between overlapping ligand orbitals, which leads to the high degree of symmetry observed in the structure [252].

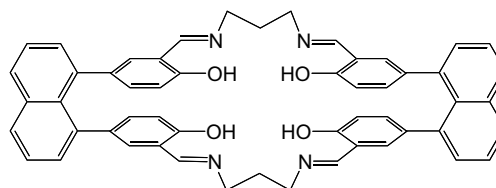
Manganese(III) complexes of the type $[\text{Mn}(\text{L})(\text{H}_2\text{O})]_2^{2+}$ ($\text{L} = \mathbf{204}^{2-}, \mathbf{207}^{2-}$) in aqueous solution liberate dioxygen and reduce *p*-benzoquinone to hydroquinone when irradiated with visible light. The photoactivity is critically dependent on the structure of the ligand, the complex $[\text{Mn}(\mathbf{207b})(\text{H}_2\text{O})](\text{ClO}_4)_2$ being the most active [253].

The dimeric nature of these manganese complexes was also confirmed by X-ray structural determinations of $[\text{Mn}(\mathbf{207a})(\text{H}_2\text{O})]_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Mn}(3,5\text{-Cl-}\mathbf{207h})(\text{H}_2\text{O})]_2(\text{ClO}_4)_2$ [253] (Fig. 108a and b).

In $[\text{Mn}(\mathbf{207a})(\text{H}_2\text{O})]_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, obtained by irradiation of an aqueous solution of $[\text{Mn}(\mathbf{209})(\text{H}_2\text{O})]_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, each $[\text{Mn}(\mathbf{207a})(\text{H}_2\text{O})]_2^{2+}$ moiety is linked to its neighbour across a crystallographic inversion center by two shared phenoxo oxygen atoms which complete a distorted octahedron about each manganese ion. The two manganese ions are separated by 3.361 Å.



H₂ - 209



H₄ - 210

The structure of $[\text{Mn}_2(3,5\text{-Cl-}\mathbf{207h})(\text{H}_2\text{O})_4](\text{ClO}_4)_2$, prepared by the reaction of the disodium salt of the ligand with manganese(II) perchlorate in ethanol followed by a slow evaporation of an isopropyl alcohol solution of the resulting solid, comprises a planar tetradentate Schiff base. The manganese(III) centers are linked via an array of hydrogen bonds between the phenoxo oxygen atoms of the ligand and one of the capping water molecules. This produces a hydrogen bonded di-aqua-bridged structure with a $\text{Mn} \cdots \text{Mn}$ separation of 5.07 Å. The hydrogen bonding along with the steric bulk of the ligands, creates a coordination cleft in which the bridging aqua groups are situated. The combined effect of hydrogen and π -bonding between pairs of molecules could possibly result in the integrity of this dimer remaining in aqueous solution.

An aqueous solution of this complex in the presence of *p*-benzoquinone evolves dioxygen when irradiated with a 500 W tungsten bulb. The coordination cleft of the complex can allow the approach of *p*-benzoquinone and water photolysis to occur on irradiation with visible light (no such photolysis occurs when sterically bulky 2,5-*tert*-butyl-*p*-benzoquinone is employed). Thus the association of manganese ions in clusters is important in water splitting reaction and the tetradentate Schiff bases can offer an useful substrate for the obtainment of complexes capable of undergoing this photochemical process.

When the dinuclear manganese(III) complex $[\text{Mn}_2(\mathbf{210})](\text{ClO}_4)_2$, prepared by the condensation of the appropriate dialdehyde and 1,3-diaminopropane in the presence of manganese(III) as templating ion, was suspended in water with of *p*-benzoquinone at 25 °C and irradiated with a 300 W tungsten lamp over an 18 h period, oxygen evolution was detected. It shows activity as a water splitting complex, although it is not as active as the complexes $[\text{Mn}_2(\mathbf{207a})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ [254].

Reaction in refluxing methanol or water between $[N,N'$ -ethylenebis(salicylaldiminato)]manganese(III)bromide, $[\text{Mn}(\mathbf{207a})(\text{Br})]$, and *N*-4-pyridylglycine or 4-pyridylthioacetic acid gives $[\text{Mn}(\mathbf{207a})(N\text{-4-pyridylglycinate})]$ or $[\text{Mn}(\mathbf{207a})(4\text{-pyridylthioacetate})]$ which exist as infinite

coordination polymers in the solid state [255]. The manganese ions in both of these compounds have octahedral geometries with the Schiff base ligand **[207a]**^{2−} occupying four equatorial sites on the metal ion. One of the axial sites is occupied by a carboxylate oxygen atom and the other by a pyridyl nitrogen atom from an adjacent monomer. This bridging of adjacent monomers by 4-pyridylglycinate and 4-pyridylthioacetate in **[Mn(207a)(N-4-pyridylglycinate)]** and **[Mn(207a)(4-pyridylthioacetate)]**, respectively, results in the formation of infinite polymeric chains within crystals of these materials. Crystals of both complexes also contain waters of hydration, and methanol is also observed in the lattice of **[Mn(207a)(N-4-pyridylglycinate)]** [255]. The manganese ions in both of these compounds are bound to their carboxylate ligands in a *syn* conformation, with the manganese ions significantly out of the planes defined by carboxylate groups.

These polymers are linear ... ABABAB ... chain molecules, derived from two basic components [**A** = {**Mn(207a)**} and **B** = pyridylcarboxylate ligand], where each ligand **B** bridges two neighbouring **A** components in a head-to-tail fashion, i.e. −Mn(OOC-py)Mn(OOC-py)Mn(OOC-py)−. Polymers of both complexes are therefore two component systems containing two standard linkages [a Mn–N(pyridyl) bond and a Mn–O(carboxylate) bond]. The polymer chains are situated on two-fold screw axes within the crystals. Both polymers possess a characteristic undulating backbone structure with adjacent {**Mn(207a)**} units oriented nearly perpendicular to one another within their respective chains (Fig. 109a and b).

The major product, isolated from the reaction of **[Mn(207a)(Br)]** with *N*-(4-cyanophenyl)-glycine in refluxing methanol after recrystallization from water, is the

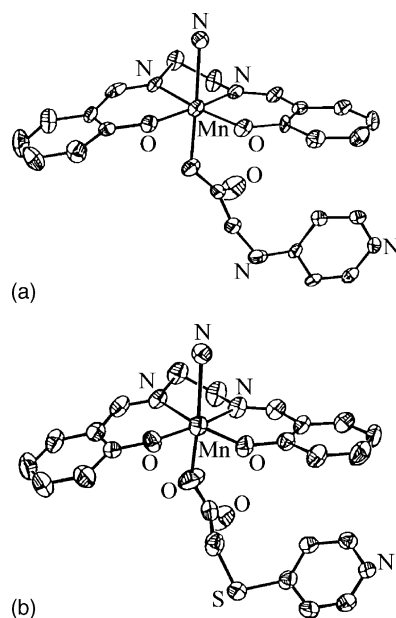


Fig. 109. Structures of **[Mn(207a)(N-4-pyridylglycinate)]** (a) and **[Mn(207a)(4-pyridylthioacetate)]** (b) (adapted from Ref. [255]).

orange-brown **[Mn(207a)(N-(4-cyanophenyl)glycinate)]·1/2H₂O** which contains polymer chains of **[Mn(207a)(N-4-cyanophenylglycinate)]** (polymer A) in intimate association with additional discrete molecules of **[Mn(207a)(H₂O)(N-4-cyanophenylglycinate)]** (polymer B) [255]. Polymer A is based on an octahedral manganese(III) ion with the Schiff base **[207a]**^{2−} occupying four equatorial sites of the metal ion. One of the axial sites in A is filled by a carboxylate oxygen atom (in this case from the glycinate ligand) while the remaining axial site is filled by a second carboxylate oxygen atom from a neighbouring unit to give a polymer backbone based on μ, η^2 -bridged structure, i.e. −Mn[OC(R)O]Mn[OC(R)O][Mn[OC(R)O][−]. The 4-cyanophenyl moiety does not participate in any bonding interactions with the manganese ions [255]. The {**Mn(207a)**} unit is in the stepped conformation. One end of the Schiff base **[207a]**^{2−} is folded toward one axial carboxylate oxygen atom, while the other end of **[207a]**^{2−} is folded toward the other axial carboxylate oxygen atom. The Mn[μ, η^2 -OC(R)O]Mn bridge in A exhibits a *syn-anti* bonding pattern. The four equatorial sites on the metal ion in the polymer B are also involved in bonding to a **[207a]**^{2−} Schiff base ligand, and one of the axial sites is occupied by a carboxylate oxygen atom. The coordination sphere of the manganese ion is completed by the binding of a water molecule to the remaining axial position. The {**Mn(207a)**} units B have a stepped conformation. One end of the **[207a]**^{2−} Schiff base is folded toward the axial carboxylate oxygen atom and the other end is folded toward the water oxygen atom. The metal-carboxylate interaction may be described as having a *syn* conformation.

A synthetic strategy for the achievement of polynuclear Schiff base complexes containing oxocations has been successfully proposed. In particular, compounds containing vanadium–oxygen chains have been prepared by oxidation of **[VO(207a)]** with iodine to produce a mixed vanadium(IV)–vanadium(V) species (Fig. 110a) containing **[VO^{IV}VO^V(207a)₂]⁺** and the counter ion **I₅[−]** [256], or by controlled protonation of **[VO(207a)]** to form **[V(VO)₃−(207a)₄](BF₄)₂** (Fig. 110b), **[{V(VO)(207a)₂]₂O](BPh)₄** (Fig. 110c) and **[{V₂(VO)(207a)₂]₂(I₃)₂** (Fig. 110d) [257].

The interaction in air of vanadyl(IV) chloride or sulfate, 2,6-diformyl-*p*-cresol and 1,2-diaminoethane in methanol yields **[VO₂(211)]₂** an acetal compound of **VO₂⁺** [258]. The X-ray analysis of **[VO₂(211)]₂** reveals the formation of a symmetric oxo bridged dimeric structure with each Schiff base ligand being tridentate and binding to each vanadium center via amine and imine nitrogen and the phenolate oxygen atoms. The coordination at vanadium is distorted octahedral. The dimeric complex, where a V...V distance of 3.08 Å occurs, is further stabilized by a pair of N–H...O hydrogen bonds between one of the amino N–H hydrogen atoms on one ligand and the phenoxy oxygen atom of the other and vice versa. Adjacent dimers are linked via pairs of N–H...O hydrogen bonds between the other amino N–H hydrogen atom of one dimer and the terminal oxo oxygen

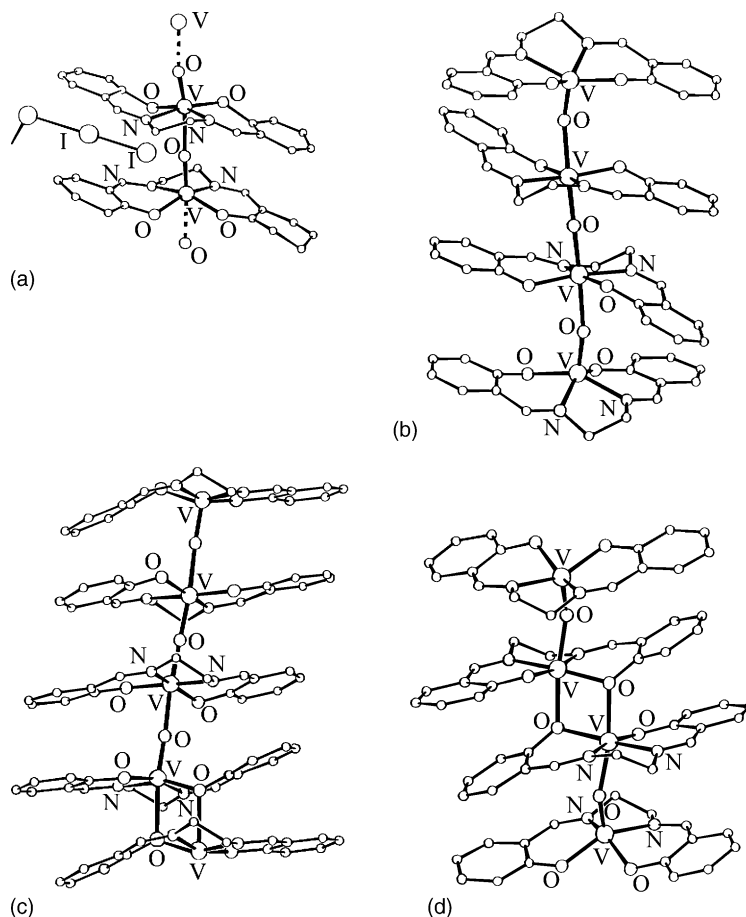
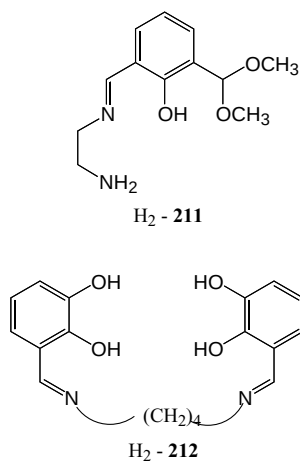


Fig. 110. Structures of $[V^{IV}OVVO(207a)_2]^+$ (a), $[V(VO)_3(207a)_4]^{2+}$ (b), $[{VVO(207a)_2}_2O]^{2+}$ (c) and $[{V_2(207a)_2O}_2]^{2+}$ (d) (adapted from Refs. [256,257]).

atom of another dimer and vice versa to form hydrogen-bonded chains of dimers that extend in the crystallographic *b* direction [258].



When the Schiff base has an appropriate spacer between the two moieties, as in the case of H_4 -**212**, polymeric helical complexes can arise from the flexibility of the ligand [259].

An electrochemical cell $[Cu(+)/CH_3CN + H_4$ -**212**/Pt(-)] yielded powdery $[Cu_2(212)(H_2O)]_n$ and crystalline $[Cu_3(H_2-212)(212)] \cdot 2H_2O$ [259].

The neutral trinuclear complex is formed by two molecules of the coordinated ligand, one tetraanionic, $[212]^{4-}$, the other dianionic, $[H_2-212]^{2-}$, and two water molecules linked by hydrogen bonds to the outer phenolic atoms of $[H_2-212]^{2-}$. The three copper(II) ions are held together by two μ -phenoxo bridges of $[212]^{4-}$. The $Cu(2) \cdots Cu(1)$ distance is 3.413 Å, while the longer $Cu(1) \cdots Cu(3)$ distance, 3.858 Å, seems to be imposed by the spatial arrangement of both ligands and the three metal centers form an isosceles triangle arrangement. The central $Cu(2)$ ion lies within the N_2O_2 inner compartment of $[212]^{4-}$ and is very severely tetrahedrally distorted. The longer, more flexible $(CH_2)_4$ chain allows the ligand to twist and achieve additional coordination to $Cu(1)$ and $Cu(3)$ by means of both outer O_2 donor sets, acting as μ -phenoxo bridges, instead of a more typical binucleating fashion ($N_2O_2 + O_4$) for this type of ligand. Thus $[212]^{4-}$ is clearly behaving as a helicand with three metal-binding domains ($O_2 + N_2O_2 + O_2$) (Fig. 111). As $Cu(1)$ and $Cu(3)$ do not satisfy their coordination numbers with coordination only to $[212]^{4-}$, the

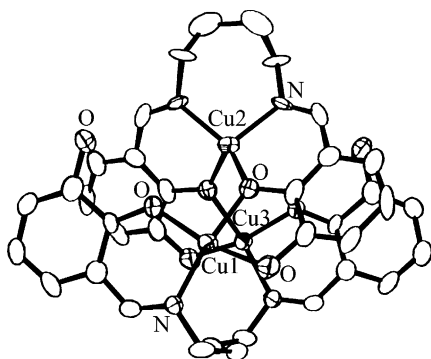
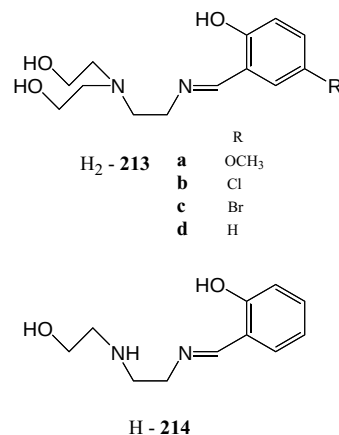


Fig. 111. Structure of $[\text{Cu}_3(\text{H}_2\text{-212})(\text{212})]\cdot 2\text{H}_2\text{O}$ (adapted from Ref. [259]).

other ligand unit $[\text{H}_2\text{-212}]^{2-}$ must complete these coordination numbers. This ligand is bisbidentate and binucleating by use of the double NO donor set of its inner compartment. Thus, the NO_3 environment of Cu(1) and Cu(3) is achieved through the oxygen atoms of $[\text{212}]^{4-}$ while the inner oxygen and nitrogen atoms of $[\text{H}_2\text{-212}]^{2-}$ complete the coordination sphere leading to a slightly distorted square planar coordination environment. The other two potential donor oxygen atoms remain protonated and are uncoordinated, but are linked by hydrogen interactions to solvated water molecules [259].

The polynucleating Schiff bases H-213a–d, prepared in situ by reaction of the appropriate formyl- and amine-precursors, react in methanol with manganese(II) acetate

tetrahydrate in the presence of sodium methoxide in a 1:2:3 ratio under strictly anaerobic conditions to give rise to $[\text{Mn}_2(\text{L})(\text{CH}_3\text{COO})(\text{solv})]_n$ ($\text{L} = \text{213a}^-$, 213c^- , 213d^- ; $\text{solv} = 0.5\text{CH}_3\text{OH}$; $\text{L} = \text{213b}^-$; $\text{solv} = 0.5\text{H}_2\text{O}$) [260]. EPR spectra are characteristic of oligomeric manganese(II) species [261].



The same complexation reactions in the air afforded the hexanuclear complexes, $[\{\text{Mn}^{\text{III}}_3(\text{L})(\text{O})(\text{CH}_3\text{COO})(\text{CH}_3\text{O})_3\}_2]\cdot 2\text{solv}$ ($\text{L} = \text{213a}^-$, $\text{solv} = \text{CH}_3\text{OH}$; $\text{L} = \text{213b}^-$, $\text{solv} = 2\text{H}_2\text{O}$) [260]. The six manganese ions in $[\{\text{Mn}_3(\text{213a})(\text{CH}_3\text{COO})(\text{CH}_3\text{O})_3\}_2]$ are distributed in two μ_3 -oxo-centered trinuclear arrays related through an inversion center situated in the middle of the $\text{CH}_3\text{-O}\cdots\text{OCH}_3$ edge

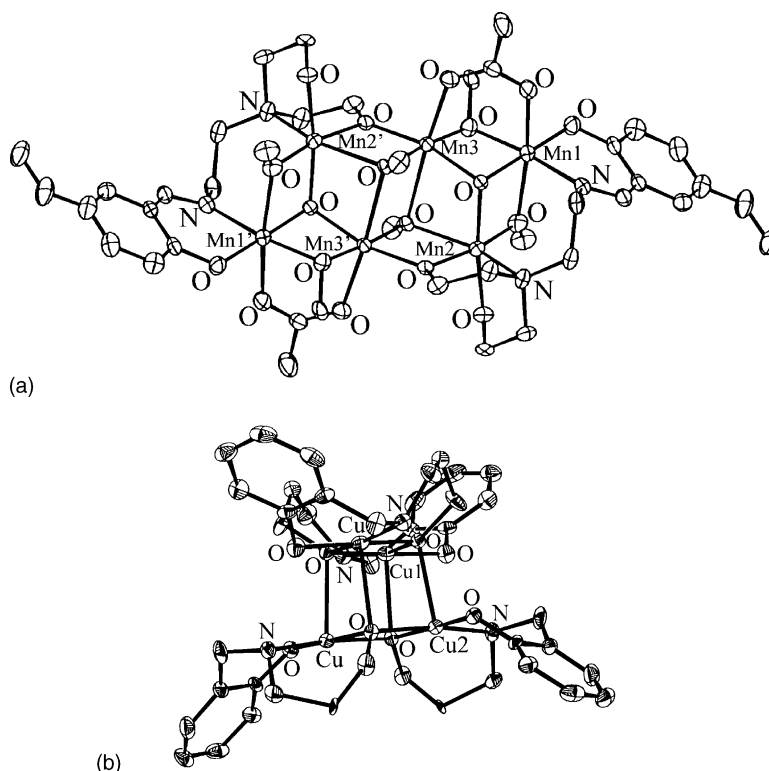


Fig. 112. Structure of $[\{\text{Mn}_3(\text{213a})(\text{CH}_3\text{COO})(\text{CH}_3\text{O})_3\}_2]$ (a) and $[\text{Cu}(\text{214})_4]$ (b) (adapted from Ref. [260]).

shared by the Mn(3) and Mn(3') coordination octahedra (Fig. 112a). This structural arrangement may be viewed as a stacking of six edge sharing coordination octahedra with the external Mn(1) [Mn(1')] coordination octahedra sharing one edge with each of the two adjacent Mn(2) and Mn(3) [Mn(2'), Mn(3')] octahedra, the intermediate Mn(2) [Mn(2')] coordination octahedra sharing one edge with each of the three adjacent Mn(1), Mn(2'), Mn(3) [Mn(1'), Mn(2), Mn(3')] octahedra and the central Mn(3) [Mn(3')] coordination octahedra sharing one edge with each of the four adjacent Mn(1), Mn(2), Mn(2'), Mn(3) [Mn(1'), Mn(2), Mn(2'), Mn(3)] octahedra. Alternatively, this hexanuclear manganese array may be described in terms of four face-sharing Mn_3O_4 incomplete cubane moieties [260]. The magnetic interactions operating in this hexanuclear manganese(III) structure result in a bulk antiferromagnetic behaviour.

2-(Hydroxybenzyl)-propanolamine ($\text{H}_2\text{-214}$), synthesized by the reduction of the corresponding Schiff base using NaBH_4 , when reacted in methanol with equimolar $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ under reflux in the presence of 2 equiv. NaOH , yields dark green crystals of $[\text{Cu}(\text{214})]_4$ after removal of the solvent. The complex contains an alkoxo bridged cubane Cu_4O_4 core (Fig. 112b), which can be understood as a tetramer joined up by two dimers. Four copper(II) ions and four oxygen atoms occupy the alternative vertices of the cube. Each copper(II) ion is coordinated with one deprotonated phenoxo oxygen, one amino nitrogen and three deprotonated bridging alkoxo oxygen atoms to give a distorted square pyramidal geometry. The intradimeric and interdimeric copper...copper distances have the nearly equal values in the range of $3.019 \dots 3.146 \text{ \AA}$. There are four intramolecular hydrogen bonds between the coordinated phenoxo and the amino functionalities. A strong antiferromagnetic interactions between the copper(II) ions occur [260].

$[\text{Mn}_2(\text{215})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]_2$, $[\text{Mn}_2(\text{216})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]_2$, and $[\text{Mn}_2(\text{H-217})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]_2$ ($\text{H}_2\text{-215} = 3\text{-}[\text{((2'-pyridyl)methyl)imino)methyl}]$ benzene-1,2-diol, $\text{H}_2\text{-216} = 3\text{-}[\text{((2-(2'-pyridyl)ethyl)imino)methyl}]$ benzene-1,2-diol, $\text{H}_3\text{-217} = 3\text{-}[\text{((2-(4'-imidazolyl)ethyl)imino)methyl}]$ benzene-1,2-diol), have been synthesized by reaction of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and the appropriate ligand in alcoholic solution under nitrogen [262].

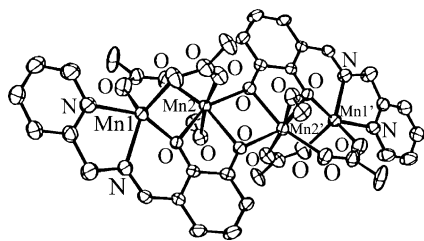
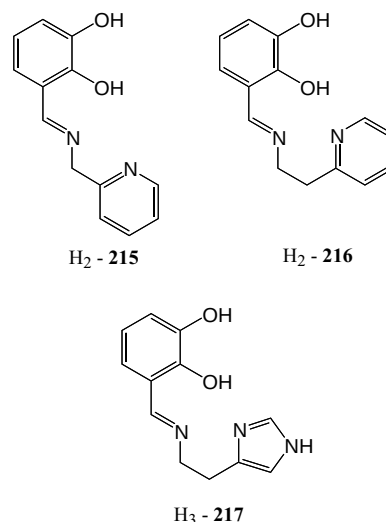


Fig. 113. Structure of $[\text{Mn}(\text{215})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]_2$ (adapted from Ref. [262]).



In $[\text{Mn}_2(\text{215})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]_2$ (Fig. 113) each molecule includes four manganese ions, two $[\text{215}]^{2-}$ ligands coordinated to Mn(1) through two nitrogen and one oxygen of the Schiff base and to Mn(2) through three oxygen atoms, four acetate ligands bridging Mn(1) to Mn(2) and two methanol molecules, the oxygen donors from the methanol ligands supplementing the Mn(2) coordination spheres. The $[\text{215}]^{2-}$ catecholate oxygen atoms are thus simultaneously bridging and chelating. Inside each dinuclear unit, Mn(1) and Mn(2), bridged by two acetate and the oxygen catecholate oxygen atoms, are separated by a distance of $3.413 \text{ \AA}$ while the $\text{Mn}(2) \dots \text{Mn}(2')$ distance resulting from the catecholate oxygen bridges is $3.297 \text{ \AA}$. The arrangement of the four manganese ions whose center of symmetry is located at the center of the $\text{Mn}(2)\text{-O}_2\text{-Mn}(2')$ parallelogram is chair like. The symmetry of the N_2O_3 donor set around the outer Mn(1) is close to a trigonal bipyramid. The imine nitrogen atom of $[\text{215}]^{2-}$ and the acetate oxygen atoms occupy the basal plane while the pyridine nitrogen and phenolate oxygen atoms of $[\text{215}]^{2-}$ are situated at the apices of the bipyramid. The O_6 ligand environment of the inner Mn(2) has been described as a rhombically distorted octahedron, the basal plane of which includes three catecholate and one acetate oxygen atoms [262]. The magnetic behaviour of these complexes indicates an overall antiferromagnetic coupling of the manganese(II) ions. Moreover the EPR spectra at 90 K in DMF/toluene show the interactions operating in the solid state are retained in solution for all these complexes.

$[\text{Cu}(\text{H-218})](\text{ClO}_4)$ and $[\text{Cu}(\text{H-219})](\text{ClO}_4)$ have been prepared by a stepwise reaction procedure. The unsymmetrical ligands were obtained by 1:1 condensation of acetylacetone and ethylenediamine or propane-1,3-diamine under highly dilute conditions. Then 1 equiv. of 4-formylimidazole was reacted with the 1:1 condensation product to produce the unsymmetrical quadridentate ligands $\text{H}_2\text{-218}$ and $\text{H}_2\text{-219}$. Reaction of these ligands with copper(II) perchlorate hexahydrate gave the complexes $[\text{Cu}(\text{H-218})](\text{ClO}_4)$ and $[\text{Cu}(\text{H-219})](\text{ClO}_4)$ [263]. In both

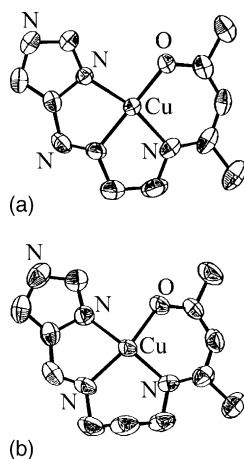
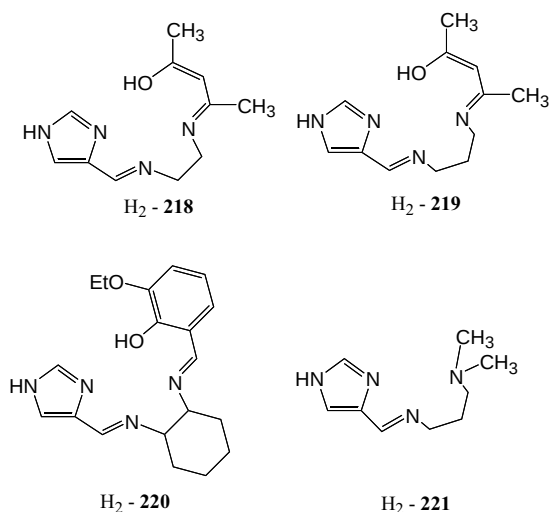


Fig. 114. Structures of $[\text{Cu}(\text{H-218})]^+$ (a) and $[\text{Cu}(\text{H-219})]^+$ (b) (adapted from Ref. [263]).

complexes (Fig. 114a and b) the copper(II) ion assumes a square planar coordination geometry. The saturated five membered chelate ring of $[\text{Cu}(\text{H-218})]^+$ adopts a gauche conformation. The saturated six membered chelate ring of $[\text{Cu}(\text{H-219})]^+$ adopts a boat conformation. A weak hydrogen bond between the imidazole nitrogen atom and the oxygen atom of the perchlorate anion through the imidazole proton is observed in both complexes [263].



$[\text{Cu}(\text{H-218})](\text{ClO}_4)$ reacts with $[\text{Cu}(\text{12-ane-N}_4)]^{2+}$ (12-ane-N₄ = 1,4,7,10-tetraazacyclododecane) or $[\text{Cu}(\text{pyr-N}_3)]^{2+}$ (pyr-N₃ = 2-[2-(2-pyridyl)ethyliminomethyl]pyridine) in the presence of 1 equiv. of triethylamine to give the imidazolate-bridged binuclear copper(II) complexes $[\text{Cu}_2(\text{218})(\text{12-ane-N}_4)(\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}]$ and $[\text{Cu}_2(\text{218})(\text{pyr-N}_3)(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}]$, respectively [263]. Analogously the copper(II) complexes $[\text{Cu}_2(\text{218})(\text{tfacac})_2]$ (tfacac = trifluoroacetylacetonate) and $[\text{Cu}_2(\text{218})(\text{tebima})](\text{PF}_6)(\text{ClO}_4) \cdot \text{CH}_3\text{COCH}_3$ (tebima = tris[2-(*N*-ethylbenzimidazolyl)methyl]amine) have been prepared by the reaction of

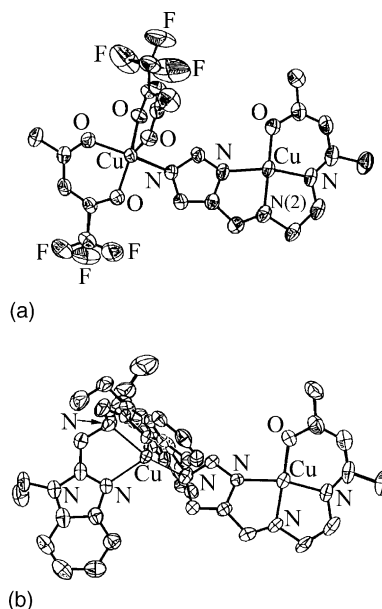


Fig. 115. Structures of $[\text{Cu}_2(\text{218})(\text{tfacac})_2]$ (a) and $[\text{Cu}(\text{218})(\text{tebima})]^{2+}$ (b) (adapted from Ref. [263]).

$[\text{Cu}_2(\text{218})](\text{ClO}_4)$ and $[\text{Cu}(\text{tfacac})_2]$ or $[\text{Cu}(\text{tebima})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the presence of 1 equiv. of triethylamine [263].

$[\text{Cu}_2(\text{218})(\text{tfacac})_2]$ (Fig. 115a) has a discrete imidazolate-bridged binuclear structure and the coordination geometries around the two copper ions are non identical: one copper(II) ion assumes a square planar coordination geometry in which one oxygen atom and three nitrogen atoms of the unsymmetrical quadridentate ligand coordinate to the copper(II) ion, while the other copper(II) ion is five coordinated with the remaining imidazolate nitrogen atom and four oxygen atoms of two trifluoroacetylacetonate ligands. The coordination geometry has been described as slightly distorted square pyramidal, where the basal plane comprises an imidazolate nitrogen atom and three oxygen atoms of trifluoroacetylacetonate ligands and the axial position is occupied by a β -diketonate oxygen. The intramolecular $\text{Cu} \cdots \text{Cu}$ distance is 5.996 Å [263].

In $[\text{Cu}_2(\text{218})(\text{tebima})](\text{PF}_6)(\text{ClO}_4) \cdot (\text{CH}_3)_2\text{CO}$ the imidazolate bridged binuclear cation, $[\text{Cu}_2(\text{218})(\text{tebima})]^{2+}$, shows that the coordination geometries around the two copper(II) ions, 5.996 Å apart, are non identical. One copper(II) ion assumes a square planar coordination geometry while the other copper(II) ion is five coordinated with one tertiary amine nitrogen and three benzimidazole nitrogen atoms of the tripodal ligand tebima and one imidazole nitrogen atom of the neighbouring $\{\text{Cu}(\text{218})\}$ unit. The coordination geometry of this copper(II) ion is intermediate between square-based pyramidal and trigonal bipyramidal. A parallel packing between the planar $\{\text{Cu}(\text{218})\}$ units of two symmetry-related complexes is observed, where the $\text{Cu} \cdots \text{Cu}$ intermolecular distance is 5.351 Å (Fig. 115b). In these binuclear complexes an antiferromagnetic interac-

tion ($-2J = 89.5\text{--}140\text{ cm}^{-1}$) was observed. Electronic and EPR spectra show that an imidazolate-bridged binuclear structure exists even in solution [263].

The above synthetic method has been extended to the preparation of the trinuclear $\text{Cu}^{\text{II}}_2\text{Mn}^{\text{II}}$ complexes $[\text{Cu}_2\text{Mn}(\mathbf{218})_2(\text{tfacac})_2]\cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{Mn}(\mathbf{218})_2(\text{hfacac})_2]\cdot 3\text{H}_2\text{O}$ (hfacac = hexafluoroacetylacetonate), obtained by mixing the mononuclear complexes $[\text{Cu}(\text{H-}\mathbf{218})](\text{ClO}_4)$ and $[\text{Mn}(\text{tfacac})_2]\cdot 2\text{H}_2\text{O}$ or $[\text{Mn}(\text{hfacac})_2]\cdot 2\text{H}_2\text{O}$ in a 1:1 molar ratio [264]. The six coordination around the manganese(II) ion in these heterotrinuclear complexes is presumed to be reached by four oxygen atoms of two β -diketonato ligands and two imidazolate nitrogen atoms from the $\{\text{Cu}(\mathbf{218})\}$ units. Their magnetic behaviour suggests that intra- or/and inter-molecular antiferromagnetic interactions operate ($J = -13$ and -8 cm^{-1}) [264].

In $[\text{Cu}(\text{H-}\mathbf{219})](\text{BPh}_4)$ the copper(II) ion assumes a square planar coordination geometry with a slight tetrahedral distortion. The saturated six membered chelate ring has a chair conformation [263,264].

$[\text{Cu}(\text{H-}\mathbf{219})](\text{BPh}_4)$ deprotonates the imidazole proton in alkaline medium (i.e. in the presence of triethylamine) to produce the imidazolate-bridged polynuclear complex $[\text{Cu}(\mathbf{219})]_n$ [263,264]. The asymmetric unit of the crystal comprises three copper units A, B, and C. The imidazolate nitrogen atom of unit A coordinates to the copper(II) ion of unit B, the imidazolate nitrogen atom of unit B coordinates to the copper(II) ion of unit C, the imidazolate nitrogen atom of unit C coordinates to the copper(II) ion of another unit A*, and such imidazolate bridges are repeated. As a result, an helicoid linear chain structure is produced. The copper(II) ions in all units assume the same square based pyramidal coordination environment with the imidazolate nitrogen atom of the neighbouring copper unit occupying the axial position (Fig. 116).

The magnetic behaviour, analysed on the basis of the Ising model for a one-dimensional infinite chain structure, gives a

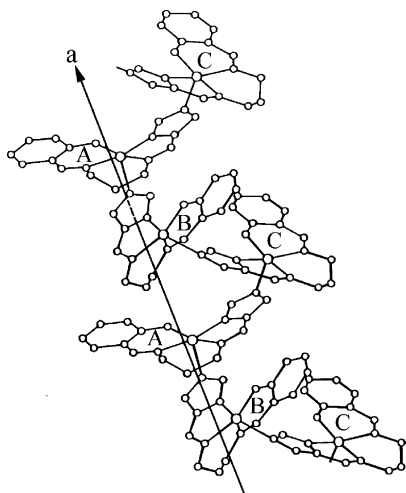


Fig. 116. Structures of $[\text{Cu}(\mathbf{219})]_n$ (adapted from Refs. [263,264]).

relatively small $2J$ value (-30 cm^{-1}) presumably due to the long Cu–N(imidazolate) bond distance and almost perpendicular orientation between the basal coordination and the imidazolate ring plane [263,264].

Analogously the two complexes $[\text{Cu}(\text{H-}\mathbf{220})]^+$ and $[\text{Cu}(\text{H-}\mathbf{221})]^{2+}$ [$\text{H}_2\text{-}\mathbf{220} = N\text{-}3\text{-ethoxysalicylidene-}N^1\text{-imidazol-4-ylmethylenecyclohexane-1,2-diamine}$ and $\text{H-}\mathbf{221} = N\text{-imidazol-4-ylmethylene-}N',N'\text{-dimethylpropane-1,3-diamine}$] undergo deprotonation of the imidazole under basic conditions to give respectively the imidazolate-bridged polymeric $[\text{Cu}(\mathbf{220})]_n$ and the tetranuclear $[\text{Cu}(\mathbf{221})_4](\text{ClO}_4)_4$ complexes [265].

$[\text{Cu}(\mathbf{220})]_n$ assumes an infinite zigzag chain structure, where neighbouring units in the chain are related by a two-fold screw axis along b . Each copper(II) ion assumes a square pyramidal coordination geometry in which the basal coordination plane is occupied by N_3O donor atoms of the quadridentate ligand and the apical site is occupied by an imidazolate nitrogen of an adjacent unit.

$[\text{Cu}(\mathbf{221})_4](\text{ClO}_4)_4$ assumes an imidazolate-bridged cyclic tetranuclear structure in which four copper(II) ions are tetrahedrally arranged. The Cu $\cdots$ Cu distances with linkage through the imidazolate group (6.042, 6.067 Å) are shorter than those without linkage (6.757, 7.124 Å), indicating a distortion of the Cu_4 core from an ideal tetrahedron. Each copper(II) ion assumes a square planar coordination geometry in which three nitrogen donor atoms of the tridentate ligand and the imidazolate nitrogen of the adjacent unit occupy the four equatorial coordination sites (Fig. 117) [265].

The magnetic susceptibility data of $[\text{Cu}(\mathbf{220})]_n$, analysed on the basis of the Ising model for a one-dimensional infinite chain structure, give a J value of -1.8 cm^{-1} , which is smaller than that of $[\text{Cu}(\mathbf{218})]_n$ having an imidazolate-bridged helical linear chain structure ($J = -15\text{ cm}^{-1}$) [265].

The μ_{eff} of $[\text{Cu}(\mathbf{221})_4](\text{ClO}_4)_4$, $1.56\mu_{\text{B}}$ at 290 K, decreases to $0.46\mu_{\text{B}}$ at 44 K. The magnetic data, interpreted on the basis of a model derived from a cyclic tetranuclear structure, give a J value of -60 cm^{-1} [265].

Polynuclear complexes can also be prepared by introducing a spacer in between mononuclear or binuclear well

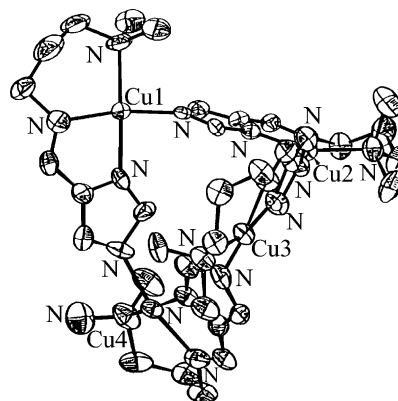
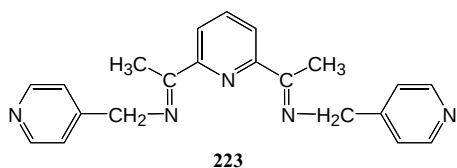
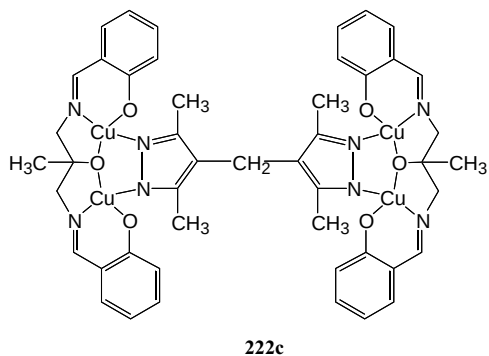
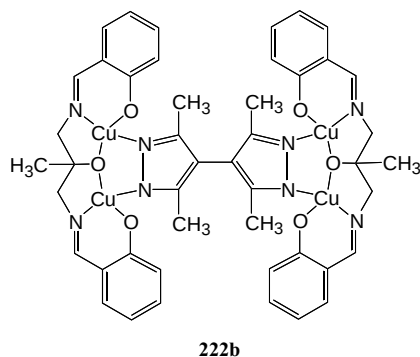
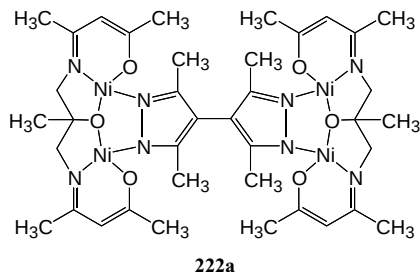


Fig. 117. Structures of $[\text{Cu}(\mathbf{221})_4](\text{ClO}_4)_4$ (adapted from Ref. [265]).

defined entities to study how the degree of coupling, if any, across this spacer is related to size, degree of conjugation, donor atom, etc. By this procedure, very interesting polymeric molecular materials have been proposed.

The reaction of *N,N'*-(2-hydroxypropylene)bis(acetylacetonimine), 4,4'-di-3,5-dimethylpyrazole, nickel salts and KOH in methanol and in a 2:1:4:8 ratio, yielded the red-brown tetranuclear nickel(II) compound **222a** [266]. In a similar way the tetranuclear copper(II) compounds **222b** and **222c** have been synthesized [267].



The molecular structure of the tetranickel(II) complex **222a** confirms the designed pair-of-dimers structure and displays clear twisting around the central single C–C bond brought about by interaction of the 3,3' and 5,5' methyl

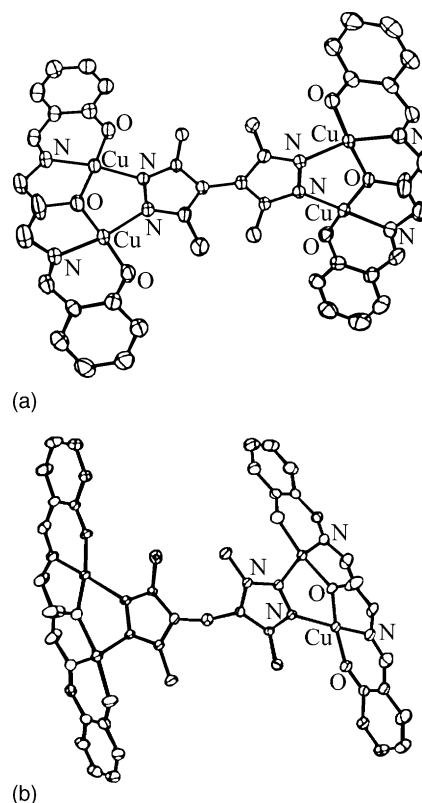


Fig. 118. Structures of **222b** (a) and **222c** (b) (adapted from Ref. [266]).

groups on the pyrazoles. Thus, there is no conjugation between the two pyrazole rings of the compound but there is delocalization within each ring. Each *trans*-NiN₂O₂ chromophore is square planar and the two coordination planes within each dinuclear moiety are not coplanar. The endogenous bridging oxygen atoms are up and down in relation to each other. Owing to the twisting around the central C–C linkage the four nickel ions are not disposed in a flat rectangular array [266].

The dinucleating pentadentate character of the ligand and the pair-of-dimers arrangement, through the incorporation of the dipyrazolate moiety within the exogenous bridge, is clearly evident in the structure of both compounds **222b** and **222c** (Fig. 118a and b). The copper ions are coordinated in slightly distorted square planar arrangements within each dinucleating half of the complex and bridged monatomically by the secondary alkoxo oxygen of the ligand and diatomically by the pyrazolato moiety. The copper...copper intramolecular distances are 3.391 Å in **222b** which are slightly longer than those within **222c** (3.373 Å).

The magnetic behaviour of **222b** is indicative of an intramolecular antiferromagnetic interaction between the copper(II) centers ($2J = -460 \text{ cm}^{-1}$), whilst that of **222c** is characteristic of an antiferromagnetically coupled system with intramolecular coupling in the order of $2J = -380 \text{ cm}^{-1}$ with the presence of a further very weak intermolecular interaction [267].

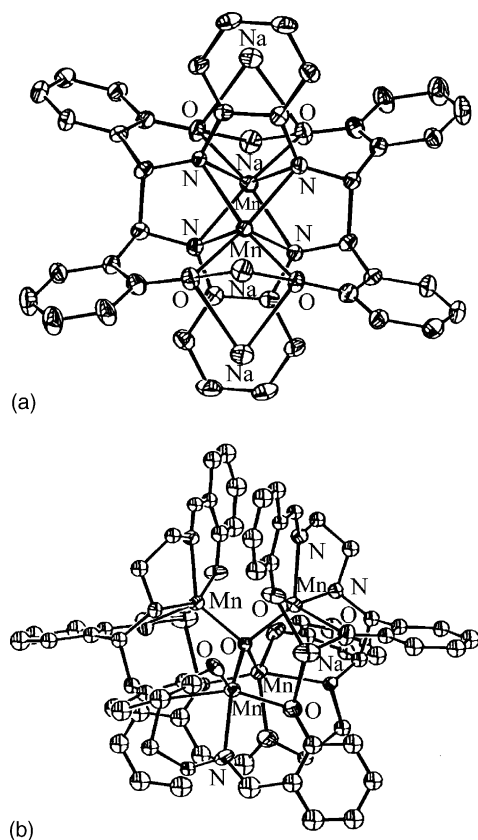
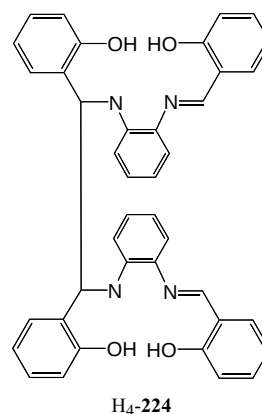


Fig. 119. Structures of $[\text{Mn}_2\text{Na}_4(\mathbf{224})(\text{dme})_6]$ (a) and $[\{\text{Mn}_2\text{Na}_2(\mathbf{225})\}_2(\mu_4\text{-O})(\text{dme})_2]$ (b) (adapted from Ref. [268]).

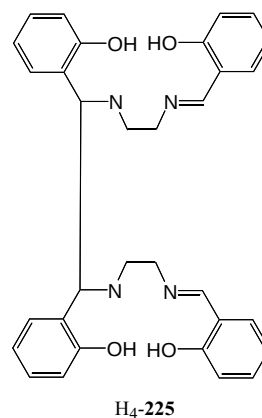
The polynuclear complex $[\text{FeRu}_4(\mathbf{223})_2(\text{bipy})_8(\text{Cl})_4](\text{PF}_6)_6 \cdot \text{H}_2\text{O}$, containing four $[\text{Ru}(\text{bipy})_2(\text{Cl})]^+$ groups attached to the pendant pyridine residues of the bis(2,6-diacetyl-4-methylpyridyliminepyridine) iron(II) complex has been synthesized by reaction of the mononuclear iron(II) compound $[\text{Fe}(\mathbf{223})_2](\text{PF}_6)_2$ with $[\text{Ru}(\text{bipy})_2(\text{Cl})_2] \cdot \text{H}_2\text{O}$ [267].

Polymeric formation via reactions at the coordinated ligands was also observed. $[\text{Mn}(\mathbf{204})]$, when reacted with sodium in tetrahydrofuran/dimethoxyethane (dme), suffers a reduction process with the formation of the manganese(II) dimer $[\text{Mn}_2\text{Na}_4(\mathbf{224})(\text{dme})_6]$ [268]. In this reaction a two-fold reductive coupling of imino groups of adjacent $\{\text{Mn}(\mathbf{204})\}$ units occurs. In the reduced complex the polynucleating ligand $[\mathbf{224}]^{8-}$ contains a [12]-membered planar ring. Two centrosymmetric manganese(II) ions, anchored to the four nitrogen atoms, lie at 1.332 Å from the plane of the N_4 core. The hexacoordination of each manganese ion is completed by two *cis* oxygen atoms. The $\text{Mn} \cdots \text{Mn}$ distance is 2.699 Å. The conformation of the ligand gives rise to cavities which accommodate the four centrosymmetric sodium cations, completing their coordination with dimethoxyethane molecules (Fig. 119a). Magnetic susceptibility data for this reduced Mn_2Na_4 complex show an antiferromagnetic coupling due the μ -amido manganese(II) dimer ($J = -34.6 \text{ cm}^{-1}$).



$[\text{Mn}_2\text{Na}_4(\mathbf{224})(\text{dme})_6]$ undergoes $4e^-$ oxidations when reacted with I_2 by cleaving the two C–C bonds across the dimer to restore the original imino functionalities with the formation of $[\text{Mn}(\mathbf{204})(\text{I})(\text{THF})]$. The two additional electrons come from the oxidation of manganese(II) to manganese(III) [268].

The reduction of $[\text{Mn}(\mathbf{207a})]$ with Na in tetrahydrofuran/dimethoxyethane gives an extremely reactive compound, which was oxidized with traces of O_2 in Et_2O to $[\{\text{Mn}_2\text{Na}_2(\mathbf{225})\}_2(\mu_4\text{-O})(\text{dme})_2]$ [268] (Fig. 119b). The precursor of this complex is the fragment $\{\text{Mn}_2\text{Na}_2(\mathbf{225})_2\}$, where the two $[\mathbf{225}]^{3-}$ ligands are linked by a single C–C bond. $[\{\text{Mn}_2\text{Na}_2(\mathbf{225})\}_2(\mu_4\text{-O})(\text{dme})_3]$ contains a tetrahedral arrangement of four unbridged manganese(III) ions around a central oxo group. The molecule has C_2 symmetry. The two $[\text{Mn}_2(\mathbf{225})_2]$ units are bridged by two sodium cations bonded to the three phenolic oxygens, while a dme molecule acting as a bidentate ligand completes the coordination sphere.



The magnetic susceptibility of $[\{\text{Mn}_2\text{Na}_2(\mathbf{225})\}_2(\mu_4\text{-O})(\text{dme})_2]$, measured from 300 down to 1.9 K, indicated that the ground state is a quintet with a septet at only 6.0 cm^{-1} , a triplet at 19.2 cm^{-1} and many other closely spaced states above 34 cm^{-1} .

Reaction of sodium hydride in tetrahydrofuran (THF) with *N,N'*-*o*-phenylenebis(salicylideneimine), $\text{H}_2\text{-204}$, or

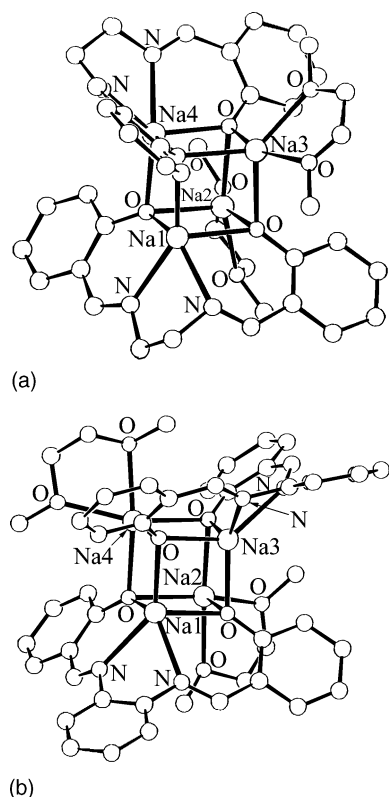


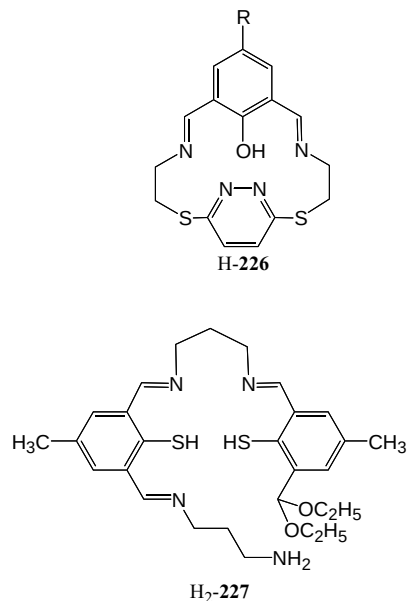
Fig. 120. Structures of $[\text{Na}_4(\mathbf{207a})_2(\text{dme})_2]_2$ (a) and $[\text{Na}_4(\mathbf{204})_2(\text{dme})_2]$ (b) (adapted from Ref. [269]).

N,N' -ethylenebis(salicylideneimine), $\text{H}_2\text{-207a}$, gave the corresponding sodium derivatives $[\text{Na}_2(\mathbf{204})(\text{THF})]_n$ and $[\text{Na}_2(\mathbf{207a})(\text{THF})]_n$. Recrystallization from 1,2-dimethoxyethane gave the stable solvated forms $[\text{Na}_4(\mathbf{204})_2(\text{dme})_2]$ and $[\text{Na}_4(\mathbf{207a})_2(\text{dme})_2]$ (Fig. 120a and b) [269].

The structure of these compounds consists of a discrete cubane skeleton of alternate sodium and oxygen atoms derived from the Schiff base dianion. In the asymmetric unit of $[\text{Na}_4(\mathbf{207a})_2(\text{dme})_2]$ there are two crystallographically independent molecules having very close geometries except for the conformation of the $\text{N}\cdots\text{N}$ five membered chelation rings. There are two kinds of sodium cations, two of them being bonded to the Schiff base only, and the other two completing their coordination sphere with a dme molecule. All of them are five coordinated [269].

It was found that the same ligand can form, under different experimental conditions, mononuclear, dinuclear or polynuclear complexes. As an example the template condensation of 2,6-diformyl-4-methylphenol with 3,6-aminoethanethiolatopyridazine in the presence of copper(II) nitrate and trifluoromethanesulfonate (or triflate) leads to the formation of dinuclear copper(II) complexes of the [17]-membered [1+1] macrocyclic ligand H-226 . The structure of the nitrate complex $[(\text{Cu}_2(\mathbf{226})(\mu_2\text{-CH}_3\text{O})(\text{NO}_3)_2)]$ shows each copper(II) center has four short contacts to an azomethine nitrogen, bridging methoxide and phenoxide oxygens, and a nitrate oxygen, which form a roughly planar

arrangement [270]. The two copper centers are separated by 2.937 Å (Fig. 121a). The axial contacts of these copper ions with the pyridazine nitrogens are weak and the copper ion coordination geometry was considered as predominantly square planar.



By a similar procedure, using $\text{Cu}(\text{NCS})_2$ as metal salt, the mononuclear complex $[\text{Cu}(\text{H-226})(\text{NCS})_2]$ was obtained, whose structure reveals two chemically identical, but crystallographically independent, molecules in the asymmetric unit. The square planar copper(II) center is coordinated in a *cis*-arrangement with two bound isothiocyanates, an imine nitrogen and a phenolic oxygen (Fig. 121b). The quite short $\text{Cu-O}(\text{phenol})$ distances, suggest that the phenolic oxygen has lost its proton, behaving as a phenoxide anion. Since the complex is neutral, the extra hydrogen was found attached to nitrogen [270].

Treatment of $[\text{Cu}_2(\mathbf{226})(\mu_2\text{-CH}_3\text{O})(\text{NO}_3)_2]$ with chloride, azide, thiocyanate, and bromide produces the tetranuclear derivatives $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-CH}_3\text{O})_2(\mu_2\text{-Cl})_2(\text{Cl})_2]$, $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-C}_2\text{H}_5\text{O})_2(\mu_2\text{-N}_3)_2(\text{N}_3)_2]$, CH_3OH , $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-CH}_3\text{O})_2(\text{NCS})_4]\cdot\text{DMF}$ and $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-CH}_3\text{O})_2(\mu_2\text{-Br})_2(\text{Br})_2]\cdot 2\text{H}_2\text{O}$, respectively [270].

Each dinuclear center in $[\text{Cu}_4(\mathbf{226})_2(\mu_2\text{-CH}_3\text{O})_2(\mu_2\text{-Cl})_2(\text{Cl})_2]$ consists of two pseudo-square planar copper ions, separated by 3.066 Å and bridged by phenoxide and methoxide oxygen atoms and bound terminally by azomethine nitrogens and chlorines. This tetracopper complex can best be represented as a dimer, in which the dinuclear halves are joined together by fairly long axial contacts forming a tetranuclear core involving μ_3 -methoxide and μ_2 -chloride bridges and square-pyramidal copper centers. The tetranuclear core can be considered as a pair of cubes connected by a common Cu_2O_2 face, but with one vertex missing on each external face [270] (Fig. 121c).

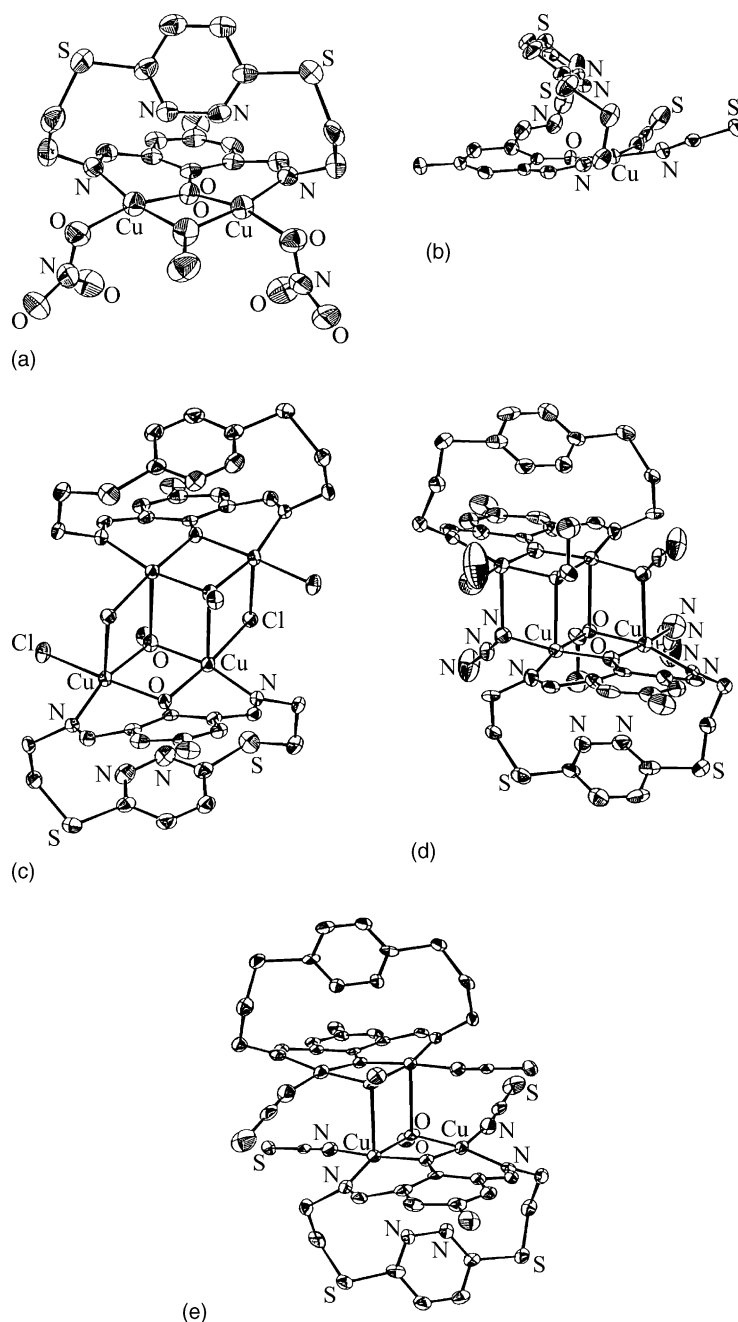


Fig. 121. Structures of $[\text{Cu}_2(\mathbf{226})(\mu_2\text{-OCH}_3)(\text{NO}_3)_2]$ (a), $[\text{Cu}(\text{H-}\mathbf{226})(\text{NCS})_2]$ (b), $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-OCH}_3)_2(\mu_2\text{-Cl})_2(\text{Cl})_2]$ (c), $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-OC}_2\text{H}_5)_2(\mu_2\text{-N}_3)_2(\text{N}_3)_2]$ (d), $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-OCH}_3)_2(\text{NCS})_4]\text{DMF}$ (e) (adapted from Ref. [270]).

The basic structural framework of $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-C}_2\text{H}_5\text{O})_2(\mu_2\text{-N}_3)_2(\text{N}_3)_2]\text{CH}_3\text{OH}$ resembles that of each dinuclear half in $[\text{Cu}_4(\mathbf{226})(\mu_3\text{-CH}_3\text{O})(\mu_3\text{-N}_3)_2(\text{N}_3)_2]\cdot\text{CH}_3\text{OH}$ with two essentially square planar copper centers, separated by 3.039 Å and bridged by a phenoxide oxygen and an ethoxide oxygen and each bound terminally by an azide ligand. In this complex two dinuclear halves associate in a tetranuclear structure: the two dinuclear units are bridged in an axial fashion, with relatively short contacts involving bridging $\mu_2\text{-(1,1)}$ azides and $\mu_3\text{-ethoxides}$. The

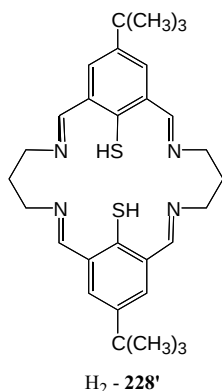
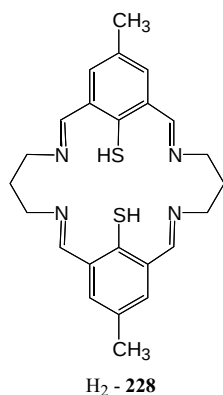
copper centers, therefore, have square pyramidal structures as in $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-CH}_3\text{O})_2(\mu_2\text{-N}_3)_2(\text{N}_3)_2]\cdot\text{CH}_3\text{OH}$ (Fig. 121d) [270].

The basic dinuclear fragment in $[\text{Cu}_4(\mathbf{226})_2(\mu_3\text{-CH}_3\text{O})_2(\text{NCS})_4]\cdot\text{DMF}$, consists of a dinuclear copper(II) center, involving a $\mu_2\text{-phenoxide}$ bridge and a $\mu_2\text{-methoxide}$ bridge. The complex has been described as a tetranuclear structure, with two square pyramidal copper centers bridged axially via the methoxides and involving just terminally bound isothiocyanates. The orientation of the pyridazine

mean planes with respect to the Cu_2O_2 dinuclear centers mean plane, indicates pyridazine nitrogen coordination in all these three tetranuclear structures (Fig. 121e) [270].

Variable temperature magnetic studies evidence for the dinuclear and the tetranuclear complexes strong antiferromagnetic exchange coupling ($-2J > 445 \text{ cm}^{-1}$) within each dinuclear fragment. Weak interdimer ferromagnetic exchange has been proven for the chloro- and bromo-tetranuclear complexes, but for complex $[\text{Cu}_4(\mathbf{226})(\mu_2\text{-C}_2\text{H}_5\text{O})(\mu_2\text{-N}_3)_2(\text{N}_3)_2] \cdot \text{CH}_3\text{OH}$, in which bridging azides link the dinuclear halves, much stronger antiferromagnetic interdimer coupling appears to exist. No interdimer coupling was observed for $[\text{Cu}_4(\mathbf{226})(\mu_2\text{-CH}_3\text{O})_2(\text{NCS})_4] \cdot \text{DMF}$ [270].

A ligand can suffer also an hydrolytic process which gives rise to unpredicted complexes. The reaction of deprotonated 2-sulfanyl-5-methylisophthalaldehyde, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 1,3-diaminopropane in ethanol forms the trinuclear complex $[\text{Ni}_3(\mathbf{227})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ together with the cyclic dinuclear complex $[\text{Ni}_2(\mathbf{228})_2](\text{ClO}_4)_2$ [271].



The IR spectrum of $[\text{Ni}_3(\mathbf{227})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was consistent with imine and acetal formation, and no peaks corresponding to unreacted carbonyl were present. Gold-brown crystals of $[\text{Ni}_3(\mathbf{227})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ were obtained by fractional recrystallization of the crude condensation product from acetonitrile by diethyl ether diffusion. The less soluble $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$ was also isolated from this reaction. However, pure samples of this complex are more readily

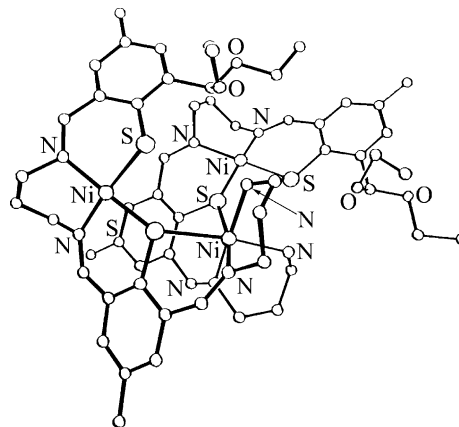
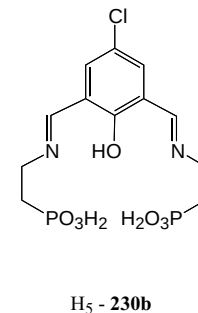
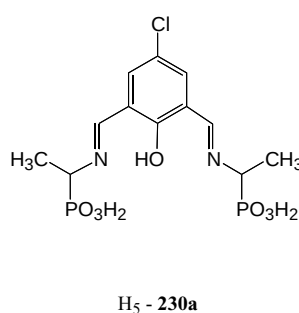
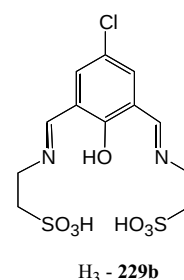
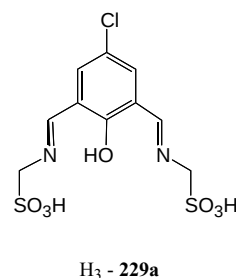


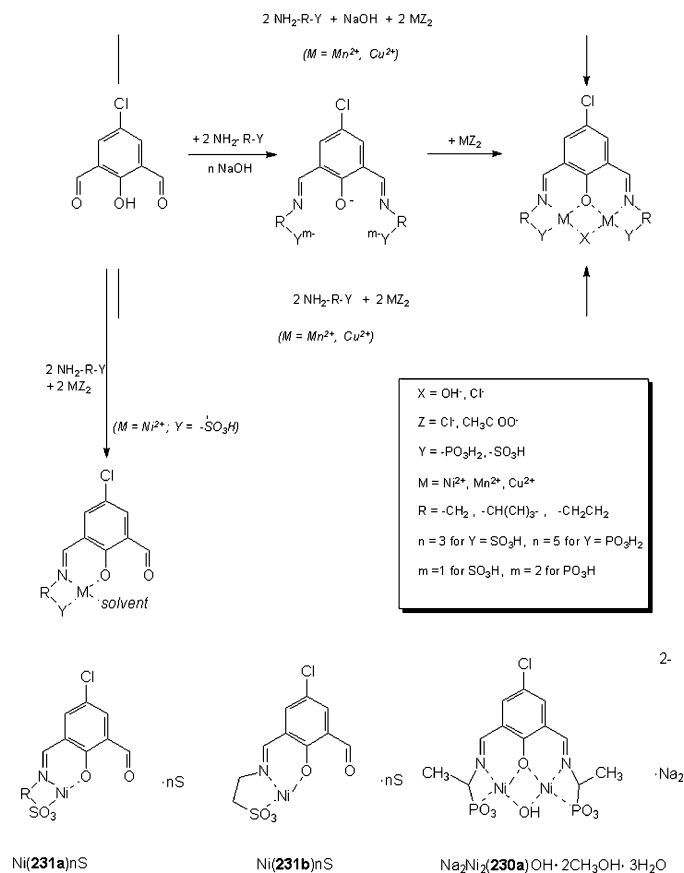
Fig. 122. Structure of $[\text{Ni}_3(\mathbf{227})_2]^{2+}$ (adapted from Ref. [271]).

isolated by carrying out the reaction in propan-2-ol. $[\text{Ni}_3(\mathbf{227})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ is indeed trinuclear, with two peripheral square planar Ni_2S_2 nickel(II) ions and a central octahedral Ni_4S_2 nickel(II) ion, bridging the two mononuclear acyclic units (Fig. 122).

The Schiff bases **H₃-229a**, **H₃-229b**, **H₅-230a** and **H₅-230b** have been prepared as trisodium (for sulfonates) and pentasodium (for phosphonates) salts by reaction of 2,6-diformyl-4-chlorophenol with the appropriate amino acids (aminomethanesulfonic acid, 2-aminoethanesulfonic acid, ($\pm$)-1-aminoethanephosphonic acid and 2-aminoethanephosphonic acid) in alcoholic solution and in the presence of NaOH form mononuclear or polynuclear copper(II), nickel(II) and manganese(II) complexes according to Scheme 37 [272].



Dinuclear complexes have been obtained by reaction of the preformed ligands with the appropriate metal acetate or



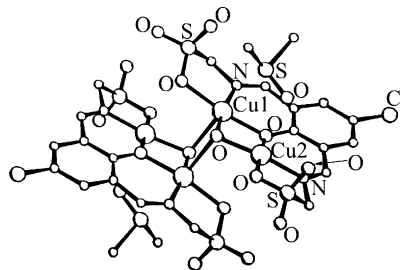
Scheme 37.

chloride. For copper(II) and manganese(II) a template synthesis (without addition of NaOH) can be also used. Both procedures give the same sulfonate derivatives while the phosphonate complexes, obtained by template synthesis, contain two hydrogens instead of sodium. In these complexes the exogenous bridge X is $-\text{OH}$ or $-\text{Cl}$ according to the type of metal salt used; the hydroxo group was found when metal acetates were employed. Nickel(II) gives, by the template procedure, the [1+1] complexes $\text{Ni}(\mathbf{231a}) \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\mathbf{231b}) \cdot 2.5\text{H}_2\text{O}$ and by reaction with the preformed compound $\text{Na}_5(\mathbf{230a}) \cdot 3\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$, the complex $[\text{Na}_2\text{Ni}_2(\mathbf{230a})(\text{OH})] \cdot 3\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$ [272].

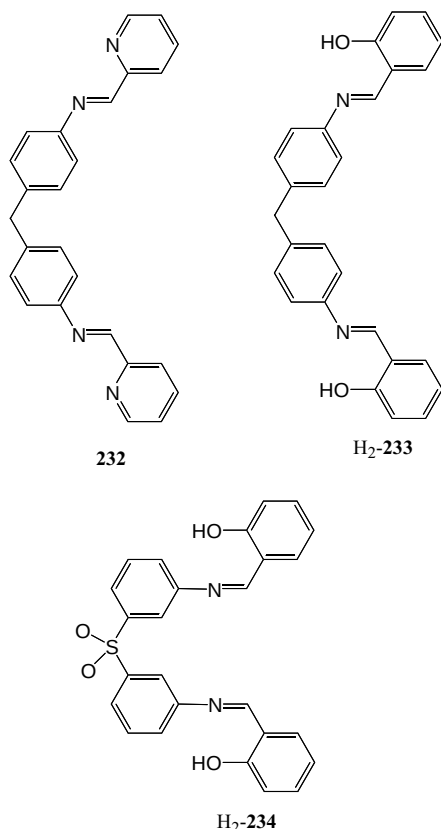
The structure of $[(\text{Cu}_2(\mathbf{229a})(\text{OH}))]$, grown from dimethylsulfoxide solution, shows the complex must be correctly formulated as $\{[\text{Cu}_2(\mathbf{229a})(\text{OH})](\text{DMSO})(\text{H}_2\text{O})\}_2$, the centrosymmetric molecule being formed by two binuclear units, one of which is the crystallographic asymmetric unit. The two binuclear units are parallel and form approximately planar moieties so that the entire molecule adopts a chair configuration. Two independent copper ions are present in the asymmetric unit. One copper ion is five coordinated in the square pyramidal arrangement, being bound to the phenolate oxygen atom, the hydroxo oxygen atom, the sulfonato oxygen and a nitrogen as base atoms, the hydroxo

oxygen atom of the centrosymmetric unit being the axial atom. The other copper ion, which is square planar, is coordinated by three oxygens and one nitrogen atom; this copper ion also makes a contact of 2.58 Å with the oxygen atom of a DMSO molecule (Fig. 123).

Dinuclear triple-helical zinc(II) and copper(II) complexes have been obtained by the Schiff bases **232** and **H₂-233** [273]. $[\text{Zn}_2(\mathbf{232})_3](\text{ClO}_4)_4 \cdot \text{DMF} \cdot 2\text{CH}_3\text{CN}$ contains two zinc(II) ions and three **232** ligands. The building units, particularly the bridging groups $(-\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4-)$, are stacked face-to-face ($\pi \cdots \pi$) and edge-to-face ($\text{CH} \cdots \pi$)

Fig. 123. Structure of $\{[\text{Cu}_2(\mathbf{229})(\text{OH})](\text{DMSO})(\text{H}_2\text{O})\}_2$ (adapted from Ref. [272]).

to each other. Formation of a helix arises from a twisting of these bridging groups. Each zinc(II) ion is six coordinate (Fig. 124a) [273].



H₂-234, prepared by addition of 3,3'-diaminosulfone to salicylaldehyde in ethanol, reacts with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (1:1 molar ratio) in ethanol to form the tetranuclear complex $[\text{Cu}(\mathbf{234})_4]$ (Fig. 124b) [273]. The tetranuclear double helical structure appears to be stabilized by $\text{CH}-\pi$ and $\pi-\pi$ aromatic interactions (3.2–3.9 Å) between the bridging groups ($-\text{C}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4-$). The complex contains four copper(II) ions and four ligands. Two copper(II) ions at the top and bottom of the tetranuclear core adopt a square planar coordination geometry, whereas the two remaining copper(II) ions in the middle adopt a tetrahedral coordination geometry. Each copper(II) ion is coordinated by NO bidentate sites originating from two different ligands. Each ligand interacts with two copper(II) ions with a different coordination geometry. The copper(II) ions lie almost in one plane and in a rhombus arrangement with $\text{Cu} \cdots \text{Cu}$ distances between 4.043 and 7.659 Å. Flexible geometry of copper(II) (square planar or tetrahedral) and the flexible conformational freedom in the ligand lead to $\text{CH}-\pi$ and $\pi-\pi$ aromatic interactions between the bridging groups and the tetranuclear double-helical structure [273].

Zinc(II), nickel(II) and cobalt(II) complexes with **H₂-234**, which are insoluble in most organic solvents, appear to form polymeric structures [273].

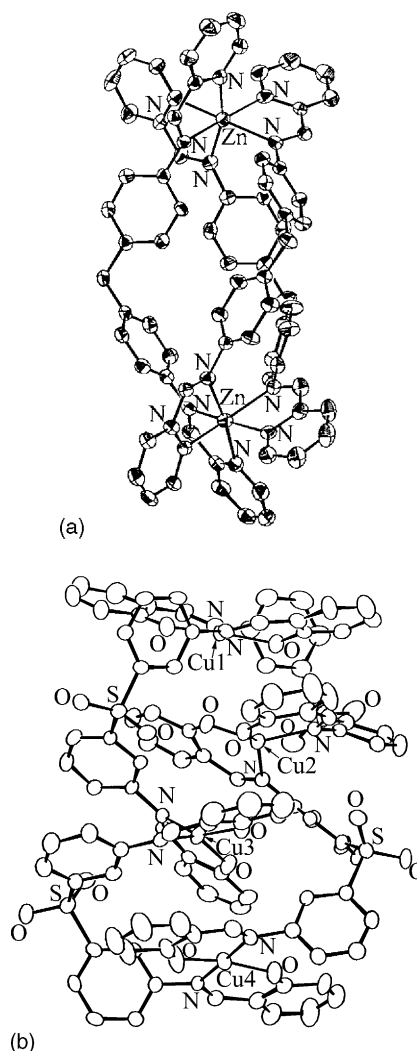


Fig. 124. Structure of $[\text{Zn}_2(\mathbf{232})_3]^{4+}$ (a) and $[\text{Cu}(\mathbf{234})_4]$ (b) (adapted from Ref. [273]).

7. Mononuclear complexes

7.1. [3+2] Macrobicyclic complexes

The formation of mononuclear acyclic and cyclic Schiff base complexes have been achieved with d- and f-transition and non transition metal ions [5,42].

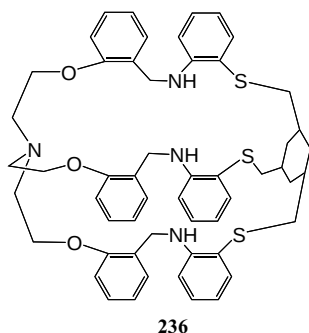
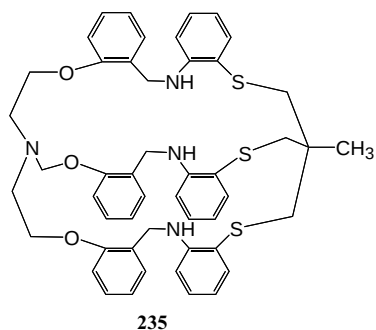
Considerable attention was devoted in recent years to [1+1], [2+2] and [3+2] macrocyclic complexes derived from the template condensation of the appropriate formyl- or keto- and amine-precursors in the presence of lanthanide(III) salts or by transmetallation reaction from the barium analogue [5,42]. These studies have been primarily addressed to the use of these lanthanide(III) complexes as probes for biological systems. The time frame metal- and ligand-exchange kinetics become a major consideration when lanthanide complexes are to be used as probes for biological systems. In dilute aqueous or aqueous-organic solutions required for these systems, which often involve

potentially competing ligands, even a highly stable complex, if labile, may not give reliable results. Therefore a systematic investigation of the conditions leading to the lanthanide macrocyclic synthesis has been undertaken [5,42].

The Schiff base condensation of dicarbonyl and triamine derivatives gives rise to [3+2] azacryptands according to Scheme 38 in high yield under mild conditions without the need for high dilution techniques in a one pot procedure [274].

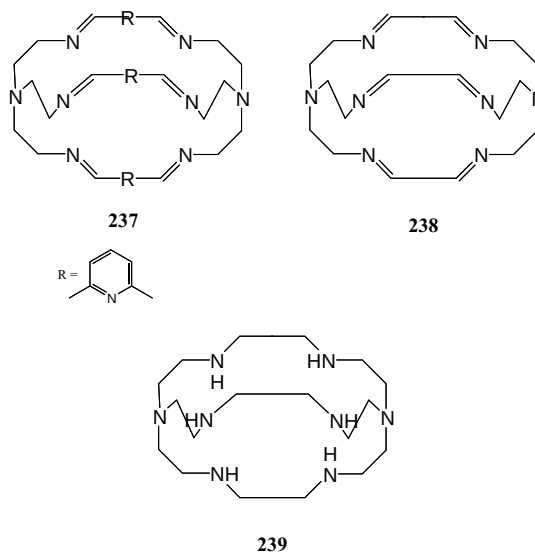
Attempts to replace dialdehydes with diketones in the [3+2] Schiff base condensation reaction normally meet with failure. In only one case so far diketone has been successfully substituted for the dialdehyde normally required for efficient [3+2] condensation; this cryptand product is formed only under acidic conditions, which suggests that the proton may act as template or as catalyst [275]. Their [3+2] cyclic nature was inferred by FAB mass spectrometry and especially by X-ray structural determinations.

The [3+2] Schiff base cryptands can be readily reduced with NaBH_4 or LiAlH_4 to generate the analogous octaaminocryptands [276–279] which, being more chemically robust than their Schiff base precursors, have many advantages as ligands for both cation and anion encapsulation. Large cryptands such as **235** and **236**, generated in their imino form by [1+1] condensation of appropriate trialdehyde with triamine [276,277], are normally reduced in situ to the polyamine form.



Crystals of **237**, obtained by self condensation of tris(2-aminoethyl)amine with 2,6-pyridinedicarboxaldehyde in methanol followed by a recrystallization from methanol containing a small amount of dimethylsulfoxide, show the macrobicycle has a divergent structure. The cavity of the

ligand seems to be a column. The three pyridine nitrogens are located nearly on the circumference. In spite of the necessity for DMSO for the crystallization, no solvent molecules are found around the ligand or in the cavity (Fig. 125a) [280].

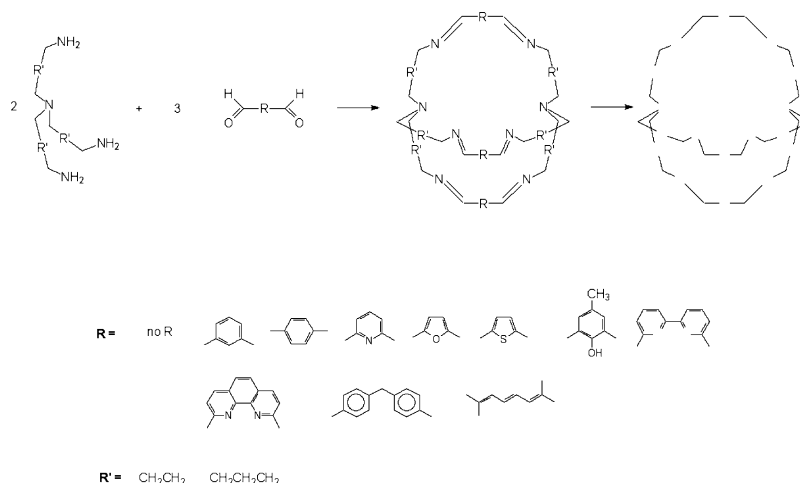


Quite often the metal complexes of these [3+2] cryptands have been prepared by the template procedure, although the reaction of the preformed macrocycle with the appropriate metal salt has been used. Both synthetic procedures give rise to the same complex although generally higher yields are obtained by using the template approach.

The template synthesis of tris(2-aminoethyl)amine and 2,6-diformylpyridine in the presence of BaX_2 ($\text{X} = \text{I}^-$, ClO_4^- , BPh_4^-), produces $[\text{Ba}(\mathbf{237})](\text{X})_2$. The barium complex has a crystallographical C_2 axis through the nitrogen atom in a pyridine ring and the central barium ion. The complex cation also has an approximate trigonal symmetry. Three pyridine nitrogen atoms and six imine nitrogen atoms coordinate to the barium ion (Fig. 125b). The lone pairs of the two tertiary nitrogen atoms at the center of the tris(2-aminoethyl)amine moieties are directed toward the central barium ion, but the Ba-N distance is too long for coordination. The two conformers, convergent and divergent, present respectively in the free ligands and in the barium complex, which can be distinguished by NMR spectroscopy, can be interconverted [280].

The addition of DMSO to a solution of the barium complexes with the **237** ligand causes a change of the conformation from convergent into divergent with the consequent decomplexation of the barium(II) ion. Furthermore, the ligand encapsulates the barium(II) ion again with increase of the barium(II) concentration [281].

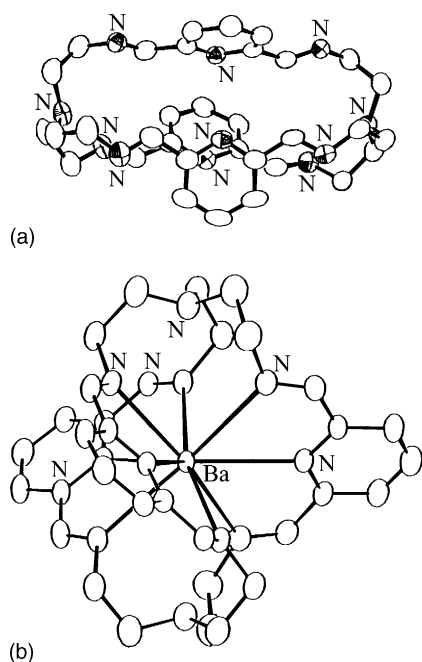
The structure of **104**, obtained by [2+3] condensation of tris(2-aminoethyl)amine and furan-2,5-dicarbaldehyde, shows a three-fold non-crystallographic axis running through the two bridgehead tertiary aminic nitrogens and



Scheme 38.

the eclipsed methylene carbons (Fig. 126). This geometry is achieved by means of a configuration in which only the bridgehead nitrogen lone pairs are directed inside the cavity. The imine functions are in *trans, trans* geometry [282]. There is one solvent water molecule per macrocycle, hydrogen-bonded to imine nitrogens on two adjacent molecules. These hydrogen bonds link the macrocycles in one-dimensional chains throughout the structure [282].

Among the various possibilities presented by this ligand, the candidate most likely for the dynamic process responsible for fluxionality appears to be restricted rotation about the furan carbimine bond, leading to interconversion of the *trans, trans* and *cis, cis* furan dicarbimine configurations.

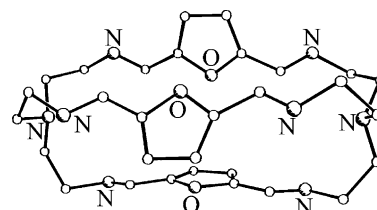
Fig. 125. Structure of **237** (a) and $[\text{Ba}(\mathbf{237})]^{2+}$ (b) (adapted from Ref. [280]).

Experiments involving the barium(II) complex of **104** support the idea of accessible interconversion of *trans, trans* and *cis, cis* isomers. The product of [2+3] template condensation of tris(2-aminoethyl)amine and 2,5-diformylfuran on barium(II) in the presence of BPh_4^- is identical with that obtained by treatment of the free cryptand **104** with barium(II) and BPh_4^- under mild conditions. The ^1H NMR spectrum of $[\text{Ba}(\mathbf{104})](\text{BPh}_4)_2$ suggests a *cis, cis* configuration which is the expected product of template synthesis.

Calcium(II) and strontium(II) complexes have been obtained by the same procedure employed for the barium(II) complex. From NMR data it seems that these smaller ions have the option of occupying alternative coordination sites involving less than the maximum number of available donors.

The ready interconversion of the *cis, cis* and *trans, trans* conformers of **104** means that despite the unfavourable disposition of donor pairs in the solid state, this cryptand should be capable of functioning as a mono- or bi-nucleating ligand for metal cations as well, possibly, as host for small (e.g. triatomic) molecules or anions.

The smallest macrobicyclic ligand **238**, generated by [3+2] condensation of glyoxal with tris(2-aminoethyl)amine, forms 1:1 complexes with transition metal ions as shown for the cobalt(II) and copper(II) complexes although copper(I) and silver(I) can form dinuclear complexes (Fig. 127a–d).

Fig. 126. Structure of **104** (adapted from Ref. [282]).

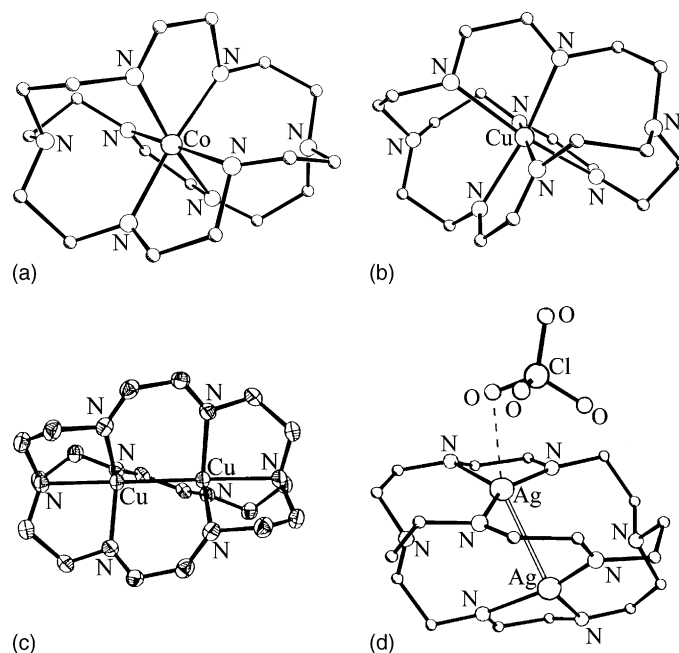


Fig. 127. Structure of $[\text{Co}(\mathbf{238})]^{2+}$ (a) and $[\text{Cu}(\mathbf{238})]^{2+}$ (b), $[\text{Cu}_2(\mathbf{238})]^{2+}$ (c) and $[\text{Ag}_2(\mathbf{238})(\text{ClO}_4)]^+$ (d) (adapted from Ref. [283]).

$[\text{M}(\mathbf{238})](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Pb}^{2+}$, Cd^{2+} , Hg^{2+}) have been prepared by reaction of the bicyclic ligand with the appropriate metal(II) perchlorate in $\text{CHCl}_3/\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{OH}$ solution [283]. In $[\text{Hg}(\mathbf{238})](\text{ClO}_4)_2$ the mercury(II) ion sits at the approximate center of the cryptand ligand and is coordinated to the six imino donors but not to the bridgehead amines (Fig. 128a). The coordination geometry is closer to octahedral than trigonal prismatic.

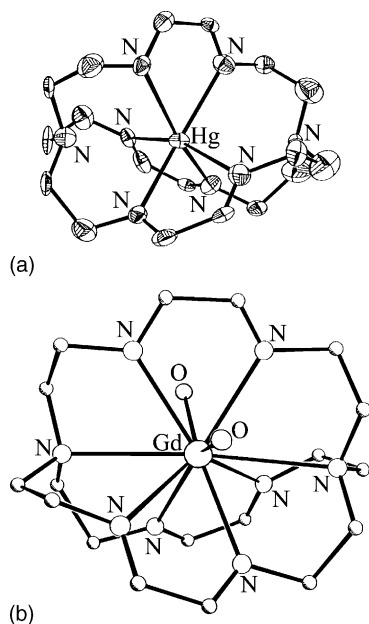


Fig. 128. Structure of $[\text{Hg}(\mathbf{238})]^{2+}$ (a) and $[\text{Gd}(\mathbf{238})(\text{H}_2\text{O})_2]^{2+}$ (adapted from Refs. [283,284]).

Solid state NMR spectra of the mononuclear lead(II), cadmium(II) and mercury(II) and dinuclear copper(I) and silver(I) cryptates of **238** show well resolved coupling between ^{15}N and encapsulated metal ion in the case of dicopper(I) and monocadmium(II) cryptates testifying to high symmetry and strong interaction which also show the largest ^{15}N coordination shifts. Comparison of solution and solid state NMR spectra confirms the existence of decomplexation equilibria in CD_3CN solutions of the disilver(I) but not the dicopper(I) cryptate. The observation of satellite peaks, including separately resolved ^{111}Cd and ^{113}Cd satellites, in CD_3CN solution, confirms the absence of decomplexation equilibria for mercury(II), cadmium(II) and lead(II) cryptates [283].

Complexation of lanthanide(III) ions with the consequent formation of $[\text{La}(\mathbf{238})](\text{ClO}_4)_3$ and $[\text{Gd}(\mathbf{238})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{CH}_3\text{CN}$ is achieved by treating a CH_3CN solution of **238** with the appropriate metal salt under anhydrous conditions. Once formed, however, they do not appear to be susceptible to hydrolysis as they can be recrystallised without deterioration and treatment with basic aqueous solution ($\approx 1\text{ M NaOH}$) fails to cause precipitation on standing over a period of weeks, as does the addition of phosphate, even at acidic pH (4.5). Such chemically robust behaviour can be attributed to kinetic stability against decomplexation, an unusual and potentially valuable property in gadolinium(III) complexes.

In $[\text{Gd}(\mathbf{238})(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, obtained by recrystallisation from $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$, the metal ion is bonded to six nitrogen atoms of the macrobicyclic and two water molecules: the nitrate counter ions are uncoordinated (Fig. 128b) [284]. NMR relaxometry of this cryptate reveals a relaxivity

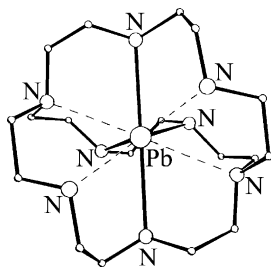


Fig. 129. Structure of $[\text{Pb}(\mathbf{239})]^{2+}$ (adapted from Ref. [285]).

of $5.8 \text{ mM}^{-1} \text{ s}^{-1}$ (at 10 MHz, 298 K and pH 6), which is pH sensitive over the range 4–9 [284].

The octamine azacryptand **239**, conveniently prepared by borohydride reduction of **238**, when treated with $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Pb}^{2+}, \text{Cd}^{2+}$) affords $[\text{M}(\mathbf{239})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ [285].

The X-ray structure of $[\text{Pb}(\mathbf{239})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Fig. 129) shows that the lead(II) cation is unsymmetrically sited within the cryptand, making contacts of around 2.6–2.7 Å to four of the *sec*-amine nitrogen donors, and longer contacts, >2.8 Å to the bridgehead and the other two *sec*-amine nitrogens. The asymmetry among the *sec*-amine nitrogens suggests that the lead lone pair is stereochemically active. Taking the lone pair as a pseudo-coordination site and assuming it to be directed midway between the two long imine distances, the coordination can be regarded either as nine coordinated (if all N–Pb contacts are included) or five coordinated with reasonably good trigonal bipyramidal geometry [285].

Neither cadmium(II) nor lead(II) ions undergo rapid exchange with the solvent environment. The cadmium(II) ion appears more symmetrically placed within the cryptand than the lead(II) ion, whose more complex NMR spectrum suggests that the unsymmetric solid-state structure may persist in solution. The smaller size of the cadmium(II) ion causes the methylene chain to contract about the cation generating a lower degree of conformational mobility than in the lead analogue. X-ray crystallographic measurements thus indicate strong complexation of the lead(II) ion within the cryptand, and NMR spectra suggest a high degree of kinetic stability towards decomplexation [285].

239 reacts with AgX ($\text{X}^- = \text{BF}_4^-, \text{CF}_3\text{SO}_3^-$) in methanol in a 2:1 molar ratio to form $[\text{Ag}_2(\mathbf{239})](\text{X})_2$ where each silver(I) ion is coordinated to one bridgehead nitrogen, as well as to three NH donors, a pair from one strand of the cryptand as well as one each from the third strand. The $\text{Ag} \cdots \text{Ag}$ distance is 2.814 Å [285] (Fig. 130a).

Despite the apparently good coordination stabilization of this four coordinate silver(I) dimer, it is not stable long-term in solution. When the $\mathbf{239}/\text{Ag}^+$ system is allowed to stand for several days in solution, a trinuclear silver(I) cryptate can be isolated the structure of which, as the triflate salt $[\text{Ag}_3(\mathbf{239})](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH} \cdot 0.5\text{Et}_2\text{O}$, is shown in Fig. 130b. In this structure each silver(I) ion is near-linear two coordinated, when close contacts to other silver cations

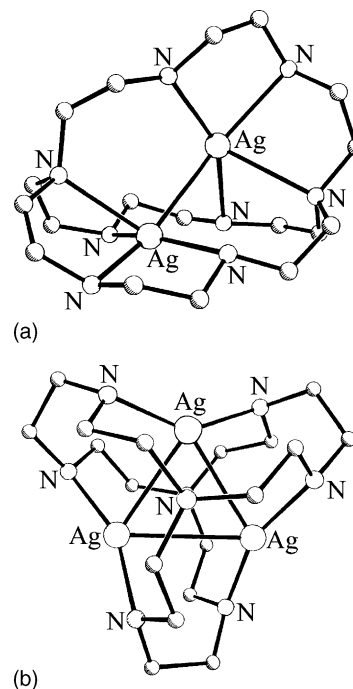


Fig. 130. Structure of $[\text{Ag}_2(\mathbf{239})]^{2+}$ (a) and $[\text{Ag}_3(\mathbf{239})]^{3+}$ (b) (adapted from Ref. [285]).

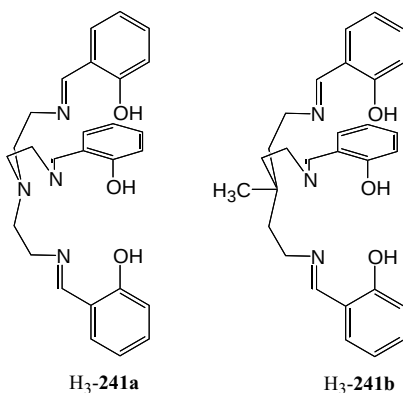
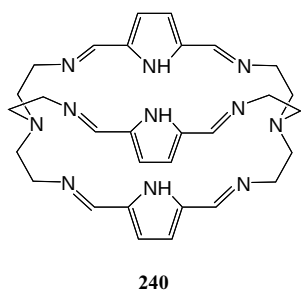
are ignored. The silver(I) ions link together a pair of *sec*-amino donors from two different strands of the cryptand host; the bridgehead nitrogen donors are not involved in coordination. Close contacts to other silver(I) cations at 3.089, 2.849 and 2.854 Å presumably contribute to the stabilization of the trinuclear coordination mode. These three $\text{Ag} \cdots \text{Ag}$ contacts suggest appreciable metal–metal interaction.

The nuclearity of the product depends on the time allowed for rearrangement as well as, to some extent, on the ligand to silver ratio. Below an $\text{Ag}:\mathbf{239}$ stoichiometric ratio of 5:1, clean disilver cryptates were obtained as the initial product with no evidence for the presence of the trisilver cryptate. Thus the trinuclear complex can be obtained starting from the disilver analogue or by reacting under nitrogen in isopropyl alcohol **239** and $\text{Ag}(\text{CF}_3\text{SO}_3)$ in a 4:1 molar ratio [285].

With larger macrobicyclic systems, dinuclear complexes are generally obtained, however alkali ions (i.e. Na^+) form mononuclear species. Thus reaction of **107** or **237** with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ in $\text{CH}_2\text{Cl}_2\text{--CH}_3\text{CN}$ gives $[\text{Na}(\mathbf{107})](\text{ClO}_4) \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ and $[\text{Na}(\mathbf{237})](\text{ClO}_4) \cdot \text{CH}_3\text{CN}$, respectively [286]. Both cations (Fig. 131a and b) show approximate three-fold symmetry about the two bridgehead nitrogens and sodium ion axis and an unsymmetrical placing of the sodium cation. The degree of asymmetry is different in the two structures. Neither the acetonitrile solvent nor the perchlorate anion have any significant interactions with the cations $[\text{Na}(\mathbf{107})]^+$ or $[\text{Na}(\mathbf{237})]^+$. The significant difference between the two structures is that in addition to the sodium

ion there is an extra water molecule within the cavity of the furan system. The overall coordination sphere of each sodium ion is different in $[\text{Na}(\mathbf{107})]^+$ and $[\text{Na}(\mathbf{237})]^+$. The former system is five coordinated with the sodium ion coordinated to three imine nitrogens, one bridgehead nitrogen and the oxygen of the water molecule; there are also three weaker interactions with the furan oxygens. The position of the sodium ion in $[\text{Na}(\mathbf{237})]^+$ is asymmetrical with the metal ion forming bonds with the three pyridine nitrogen atoms and three stronger bonds to three imine nitrogen atoms [286].

$\text{H}_3\text{-240}$ and $\text{H}_3\text{-98a}$, obtained as barium(II) complex by template procedure, reacts with NaX to form $[\text{Na}(\text{H}_3\text{-240})](\text{X})$ and $[\text{Na}(\text{H}_3\text{-98a})](\text{X})$, respectively [286].



^{23}Na NMR studies in methanol for $[\text{Na}(\mathbf{107})](\text{ClO}_4)$ and $[\text{Na}(\mathbf{237})](\text{ClO}_4)$ suggest a slow exchange of the sodium ion between the complexed and uncomplexed sites on the NMR time-scale in this solvent. $[\text{Na}(\text{H}_3\text{-240})]^+$ shows a similar behaviour in that there is a slow exchange of the sodium ion [286].

Although the Schiff base $\text{H}_3\text{-98a}$ may be prepared by [3+2] condensation of 2,6-diformyl-4-methylphenol with tris(2-aminoethyl)amine, a useful method is to carry out the condensation reaction in the presence of Group 1 or 2 cations as templates; through this procedure the macrocycles can be obtained in high yield. The Group 2 cryptates are poorly soluble, so the sodium cryptates $[\text{Na}(\text{H}_3\text{-98a})](\text{X})$ ($\text{X} = \text{BPh}_4^-, \text{ClO}_4^-$) were preferred as starting materials for transmetalation with appropriate metal salts under pH-neutral conditions to give the mononuclear cryptates $\text{M}(\text{H}_3\text{-98a})(\text{X})_2$ ($\text{M} = \text{Pb}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$) [287].

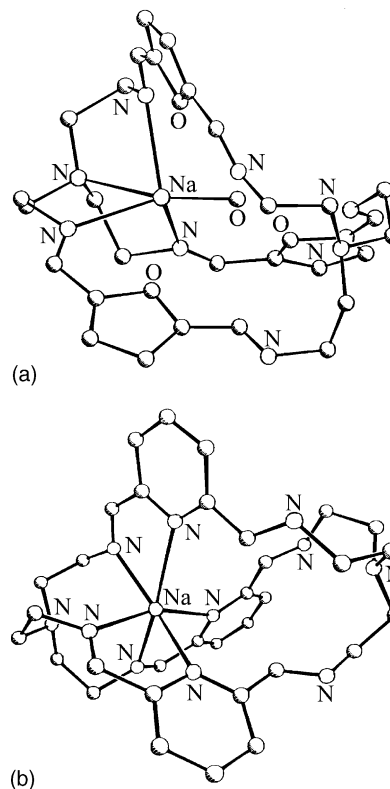


Fig. 131. Structure of $[\text{Na}(\mathbf{107})(\text{H}_2\text{O})]^+$ (a) and $[\text{Na}(\mathbf{237})]^+$ (b) (adapted from Ref. [286]).

^1H NMR spectra showed that the second site is occupied by three protons transferred from phenol to imino nitrogen atoms. Under basic conditions, the protons can be displaced by a second cation forming a dinuclear cryptate. X-ray crystallographic structure determinations have been made for the complexes $[\text{Pb}(\text{H}_3\text{-98a})](\text{BPh}_4)_2$, two forms of $[\text{Cd}(\text{H}_3\text{-98a})](\text{ClO}_4)_2$, and $[\text{Cd}_2(\mathbf{98a})](\text{ClO}_4)_4$.

In the structure of $[\text{Pb}(\text{H}_3\text{-98a})](\text{BPh}_4)_2$ there are two positions for the lead atom with occupancies of 0.87 and 0.13, respectively. The major position is found to one side of the cryptand and is bonded to the three phenoxy oxygen atoms, the three imine nitrogen atoms and a bridgehead nitrogen atom. The minor position is very similar at the other end of the macrobicyclic and also forms close contacts to seven donor atoms. The cryptand can accommodate one lead(II) ion without notable distortion from two-fold symmetry and this leaves two possible positions for the metal ion with the other site occupied by three protons. The coordination geometry of the metal ion has been considered as an irregular capped octahedron with the bridgehead nitrogen in the capping position, the three imine nitrogen atoms in the capped face and the three phenoxy oxygen atoms in the uncapped face [287] (Fig. 132).

For $[\text{Cd}(\text{H}_3\text{-98a})](\text{ClO}_4)_2$ two different solid-state forms (a and b) were isolated under slightly different synthetic conditions. The complex a has a similar structure to that of the monolead complex $[\text{Pb}(\text{H}_3\text{-98a})](\text{BPh}_4)_2$, but here the

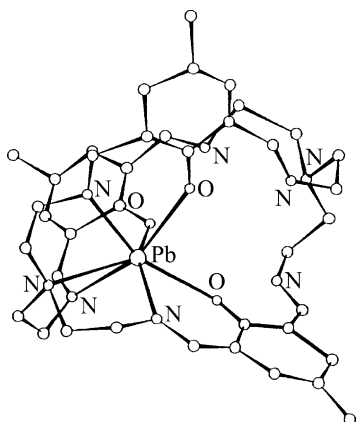


Fig. 132. Structure of $[\text{Pb}(\text{H}_3\text{-98a})]^{2+}$ (adapted from Ref. [287]).

two relative sites have occupancy factors of 0.66 and 0.34, respectively [287]. The structure b exhibits crystallographic C_2 symmetry with one cadmium in the macrocycle disordered over two sites. In general, though, the essential features of the mononuclear complex apparent in a are maintained. In this complex the disorder is over 2 equiv. positions of the metal ion [287].

Transmetallation of $[\text{Na}(\text{H}_3\text{-98a})]^+$ or $[\text{Na}(\text{H}_3\text{-98c})]^+$ with iron(II) or iron(III) salts under aerobic conditions does generate the mononuclear iron(III) complex. Magnetic and spectroscopic data indicate distortion from regular octahedral geometry. The X-ray structure of $[\text{Fe}(\text{H}_3\text{-98a})](\text{ClO}_4)_3 \cdot 0.5\text{CH}_3\text{CN}$ shows a distortion of octahedral coordination geometry towards a trigonal prismatic arrangement (Fig. 133) [287].

The monomanganese cryptates, on the other hand, whether synthesized by transmetallation of the sodium templates with manganese(II) or manganese(III) ions, are obtained in the manganese(II) state. Their coordination geometry is similar to that of the iron(III) analogues, with somewhat less distortion in the $\text{H}_3\text{-98c}$ cryptate [287].

The trigonal distortion revealed in the crystal structures of $[\text{Fe}(\text{H}_3\text{-98a})](\text{ClO}_4)_3 \cdot 0.5\text{CH}_3\text{CN}$, $[\text{Mn}(\text{H}_3\text{-98a})](\text{BPh}_4)_2 \cdot$

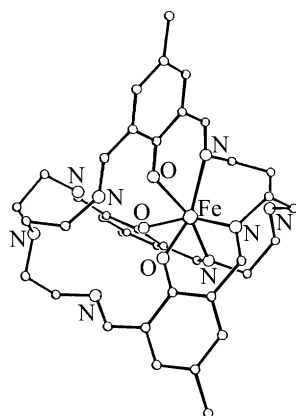


Fig. 133. Structure of $[\text{Fe}(\text{H}_3\text{-98a})]^{3+}$ (adapted from Ref. [287]).

CH_3CN and $[\text{Mn}(\text{H}_3\text{-98c})](\text{ClO}_4)_2$ is acceptable to the d^5 cations, iron(III) and manganese(II), while the reduced iron(II) (d^6) or oxidised manganese(III) (d^4) states have more specific geometric requirements which cannot easily be met within the rigid cryptand framework. Where a ligand with the same donor set lacks the built-in rigidity of the cryptand, no trigonal distortion is enforced, and square-based octahedral or tetragonal sites may be achievable.

Template synthesis of $\text{H}_3\text{-241a}$ and $\text{H}_3\text{-241b}$ on manganese(II) salts generates respectively, the manganese(III) and manganese(IV) complexes $[\text{Mn}(\text{241a})] \cdot 0.5\text{H}_2\text{O}$ and $[\text{Mn}(\text{241b})](\text{ClO}_4)$ [287]. Given the identical donor set across the series of ligands $\text{H}_3\text{-98a}$, $\text{H}_3\text{-98c}$, $\text{H}_3\text{-241a}$ and $\text{H}_3\text{-241b}$, any alteration of redox preference may be attributed to subtle but effective geometric factors. The more flexible podand ligand, $\text{H}_3\text{-241a}$, can provide the tetragonal geometry preferred by manganese(III), while steric restrictions in the smaller N_3 cap of $\text{H}_3\text{-241b}$ enforce Mn-L dimensions appropriate to manganese(IV).

A comparison of iron and manganese monocryptates is instructive in this respect: the +III oxidation state cryptate is isolated starting either from iron(II) or iron(III) salts, unless careful inert-atmosphere conditions are utilized, whereas the + II oxidation state cryptate is the invariable product of reaction with either manganese(II) or manganese(III) salts. The difference has been rationalized in terms of the well-defined geometric requirements of manganese(III), which are unattainable in the cryptand host [287].

NMR and X-ray structural data on $[\text{Tl}(\text{H}_3\text{-98a})](\text{ClO}_4)_3$, obtained by reaction of $[\text{Na}(\text{H}_3\text{-98a})](\text{ClO}_4)$ with $\text{Tl}(\text{NO}_3)_3$, show that the phenolic of groups have been deprotonated with proton transfer to the uncoordinated imine functions [288]. The structure contains $[\text{Tl}(\text{H}_3\text{-98a})]^{3+}$ cations and uncoordinated ClO_4^- anions, and the cation is disordered over two positions (lying at opposite ends of the cryptand host) with relative occupancies of 0.59 and 0.41; in the major component (Fig. 134), the thallium(III) cation sits unsymmetrically in the cryptand cavity, so that one end of the potentially binucleating ligand contains the tripositive cation and the other the three transferred protons. The thallium(III)

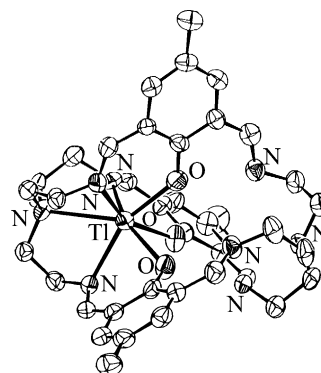


Fig. 134. Structure of $[\text{Tl}(\text{H}_3\text{-98a})]^{3+}$ (adapted from Ref. [288]).

ion is seven coordinated in both positions, with a capped octahedral geometry [288].

Transmetallation of $[\text{Na}(\text{H}_3\text{-98a})]^+$ or $[\text{Na}(\text{H}_3\text{-98c})]^+$ with $\text{Ln}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ yields the mononuclear complexes $[\text{Ln}(\text{H}_3\text{-98a})](\text{ClO}_4)_3 \cdot n\text{H}_2\text{O} \cdot \mu\text{CH}_3\text{OH}$ ($\text{Ln} = \text{Y}^{3+}$, $n = 12$, $m = 0$; $\text{Ln} = \text{Eu}^{3+}$, $n = 3$, $m = 2$; $\text{Ln} = \text{Tb}^{3+}$, $n = 1$, $m = 4$) or $[\text{Ln}(\text{H}_3\text{-98c})(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot n\text{H}_2\text{O} \cdot \mu\text{CH}_3\text{OH}$ ($\text{Ln} = \text{Y}^{3+}$, $n = 8$, $m = 2$; $\text{Ln} = \text{Eu}^{3+}$, $n = 8$, $m = 0$; $\text{Ln} = \text{Tb}^{3+}$, $n = 8$, $m = 0$; $\text{Ln} = \text{Gd}^{3+}$, $n = 0$, $m = 0.5 + 2\text{C}_2\text{H}_5\text{OH}$) [288].

The diamagnetic cryptates $[\text{Y}(\text{H}_3\text{-98c})]^{3+}$ and $[\text{Sc}(\text{H}_3\text{-98c})]^{3+}$ have ^1H NMR spectra similar to those found for the structurally characterised monozinc and monocadmium cryptates of $\text{H}_3\text{-98a}$, suggesting a similar configuration. In particular proton transfer from the coordinated phenoxy oxygen to the uncoordinated imino nitrogen is confirmed. Furthermore, the high degree of resolution of the spectra testifies to the absence of rapid exchange of cations between the solvent and the cryptand host, in other words to kinetic stabilization of the cryptate. ^{45}Sc NMR spectra of $[\text{Sc}(\text{H}_3\text{-98c})]^{3+}$ confirms the absence of scandium exchange between cryptand host and DMSO-d_6 solvent.

There is chemical evidence for kinetic stabilization of the cryptates, in that no precipitation is observed over a period of several days when solutions are treated with aqueous hydroxide or phosphate solutions. Solutions in $\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{OH}$ are stable indefinitely, and crystals for X-ray diffraction studies are obtained by slow evaporation in air over weeks or month.

In the $\text{H}_3\text{-98a}$ series, the triperchlorate salts were unsuitable for X-ray crystallographic studies, but mixed acetate/perchlorate crystals (obtained in an attempt to deprotonate the second coordination site) proved suitable in one case. The structure of $[\text{Gd}(\text{H}_3\text{-98a})(\text{CH}_3\text{COO})](\text{ClO}_4)_2$ (Fig. 135) shows the metal ion is nine coordinated, being bonded to three imino nitrogen atoms and three oxygen donors as well as one bridgehead nitrogen atom and one acetate anion. Despite the difference in coordination number, the structure is remarkably similar to $[\text{Gd}(\text{H}_3\text{-98c})(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 0.5\text{CH}_3\text{OH}$, particularly if the acetate is considered to take up one coordination site. The macrocycle is

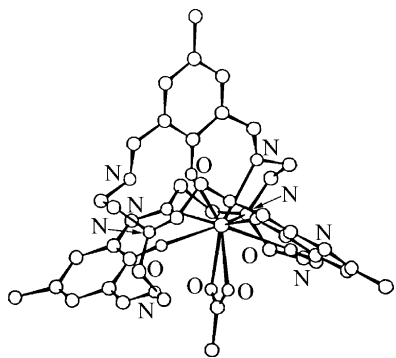


Fig. 135. Structure of $[\text{Gd}(\text{H}_3\text{-98a})(\text{CH}_3\text{COO})]^{2+}$ (adapted from Ref. [288]).

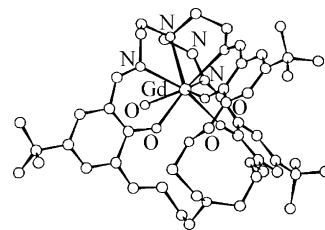


Fig. 136. Structure of $[\text{Gd}(\text{H}_3\text{-98c})(\text{H}_2\text{O})]^{3+}$ (adapted from Ref. [288]).

folded so that the acetate group is directed outside the macrobicycle [288].

The three isomorphous structures of $[\text{M}(\text{H}_3\text{-98c})(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 0.5\text{CH}_3\text{OH}$ ($\text{M} = \text{Y}^{3+}$, Gd^{3+} , Tb^{3+}) show that the metal ion is eight coordinated, being bonded to three imino nitrogens and three oxygen donors from one end of the cryptand, as well as to the bridgehead nitrogen and one water molecule. The geometry of the coordination sphere can be considered as a distorted dodecahedron [288] (Fig. 136). In these cryptates solvate molecules are located in disordered positions in the crystal; on standing in the open air, however, the crystals disintegrate as these solvate molecules are replaced by water.

There is evidence for rapid relaxation in the ^1H NMR spectra of the gadolinium(III) and dysprosium(III) cryptates $[\text{Gd}(\text{H}_3\text{-98a})(\text{CH}_3\text{COO})](\text{ClO}_4)_2$, $[\text{Gd}(\text{H}_3\text{-98c})(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 0.5\text{CH}_3\text{OH}$ and $[\text{Dy}(\text{H}_3\text{-98c})(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot 5\text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$ in that proton or carbon resonances of the ligand are severely broadened. ESR $g \approx 2$ signals are easily observed for the gadolinium cryptates at temperatures near ambient, demonstrating the required slow electronic relaxation. The short residence time likely for the coordinated water molecule, in consequence of strong binding by the remaining cryptand donors and the increased correlation time arising from encryption, may also favour relaxivity enhancement [288]. Thus the relaxivity properties of the cryptate are likely to be of interest in connection with MRI, while the solubility of the present series may be insufficient for *in vivo* use [288].

Reactions between 2,6-diformyl-4-methylphenol and tris(2-aminoethyl)amine in the presence of hydrated yttrium(III) or lanthanide(III) nitrates in a 3:2:2 mole ratio in absolute ethanol for ca. 24 h gave very good yields of the analytically pure products $\text{Ln}_2(\text{H}_3\text{-98a})(\text{NO}_3)_6 \cdot x\text{H}_2\text{O} \cdot \text{ysolv}$ ($\text{Ln} = \text{Y}^{3+}$, La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+}). This reaction was also attempted with samarium(III) and lutetium(III) nitrates but the elemental analyses are not consistent with this formula [289].

Crystals of composition $[\text{Dy}(\text{H}_3\text{-98a})(\text{NO}_3)][\text{Dy}(\text{NO}_3)_5] \cdot 2\text{CH}_3\text{CN}$, grown by slow evaporation of a CH_3CN solution, contain two different structural units, the anion $[\text{Dy}(\text{NO}_3)_5]^{2-}$ and the cation $[\text{Dy}(\text{H}_3\text{-98a})(\text{NO}_3)]^{2+}$. In the anion the dysprosium(III) ion is ten coordinated, being bonded to five bidentate nitrate ions. The oxygens define a

distorted bicapped dodecahedron. In $[\text{Dy}(\text{H}_3\text{-98a})(\text{NO}_3)]^{2+}$ the metal ion is placed asymmetrically at one end of the cavity, and is eight coordinated, being bonded to three imino nitrogen atoms, three phenolic oxygens and one of the bridgehead nitrogen atoms. The eighth position is occupied by one oxygen of a monodentate nitrate ion. The bond distances show a weak interaction between the dysprosium(III) ion and the amine nitrogen in contrast with the strong interaction with the imino nitrogen and phenolic oxygen. The coordination polyhedron has been described as a distorted dodecahedron [289].

The sodium cryptates of $\text{H}_3\text{-98d}$ were synthesized by different sodium templating reactions: $[\text{Na}(\text{H}_2\text{-98d})]$ and $[\text{Na}(\text{H}_3\text{-98d})](\text{ClO}_4)$ were obtained under basic and neutral conditions, in the presence of NaOH and NaClO_4 , respectively. The FAB mass spectrum of $[\text{Na}(\text{H}_2\text{-98d})]$ had only two important peaks at m/z 748 and 726, corresponding to a mononuclear sodium cryptate and a metal-free cryptand, respectively. Only mononuclear products formed under basic or neutral conditions, with 1 or 3 equiv. of the template ions. However, similar sodium template synthesis resulted in binuclear sodium complexes of phenolate-bridged Schiff-base [2+2] macrocycles. This shows that the cavity size selectivity plays an important role in the [2+3] condensation process [290].

The transmetallation of $[\text{Na}(\text{H}_2\text{-98d})]$ with $\text{La}(\text{ClO}_4)_3$ in $\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{OH}$ solution and the subsequent recrystallization of the yellow product from DMF forms $[\text{La}(\text{H}_3\text{-98d})(\text{DMF})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$. The same reaction using $\text{Eu}(\text{NCS})_3$ gives rise to $[\text{Eu}(\text{98d})(\text{H}_2\text{O})][\text{Eu}(\text{H-98d})(\text{NCS})] \cdot 9\text{H}_2\text{O} \cdot 2\text{CH}_3\text{CN} \cdot \text{C}_2\text{H}_5\text{CN} \cdot \text{C}_2\text{H}_5\text{OH}$ [291] whose structure revealed the coexistence in the same crystal of two independent cryptates, together with thirteen solvent molecules. Since there is no dissociated anion in the crystal, the protonated forms of the cryptand ligands can be defined according to the requirement for electrovalence equilibrium for the two independent cryptates. In the same crystal, one cryptate has the tris-deprotonated ligand $[\text{98d}]^{3-}$ and H_2O , another has the bis-deprotonated ligand $[\text{H-98d}]^{2-}$ and NCS^- [291]. In both cryptates, the europium(III) ions have similar eight coordination and the same intracryptand donors N_4O_3 , resulting in two similar distorted dodecahedrons. The macrocyclic ligand presents two different sites, one functioning as host for one europium(III) ion and the other empty (in $[\text{98d}]^{3-}$) or as host for a proton (in $[\text{H-98d}]^{2-}$). The empty site has a cavity size of about 5 Å, capable of encapsulating another metal ion to form a heterodinuclear cryptate [291] (Fig. 137a and b).

The cryptates in $[\text{Eu}(\text{98d})(\text{H}_2\text{O})][\text{Eu}(\text{H-98d})(\text{NCS})] \cdot 9\text{H}_2\text{O} \cdot 2\text{CH}_3\text{CN} \cdot \text{C}_2\text{H}_5\text{CN} \cdot \text{C}_2\text{H}_5\text{OH}$ have highly similar structures. The small differences may arise mainly from the coordination of the second ligands, which provides an oxygen donor in $[\text{Eu}(\text{98d})(\text{H}_2\text{O})]$ and a nitrogen donor in $[\text{Eu}(\text{H-98d})(\text{NCS})]$, respectively. The europium(III) ion in $[\text{Eu}(\text{98d})(\text{H}_2\text{O})]$ has an eight coordinated environment with a N_4O_4 donor set, being isostructural to other lanthanide

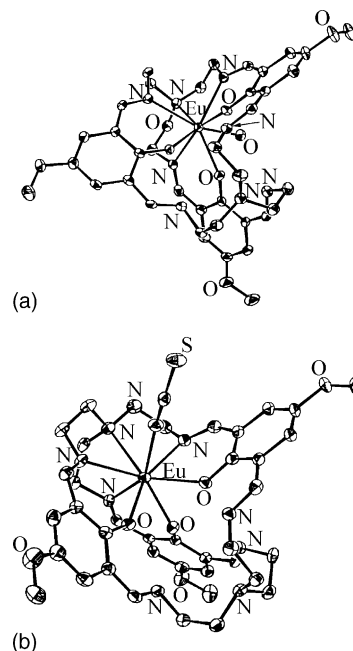


Fig. 137. Structure of $[\text{Eu}(\text{98d})(\text{H}_2\text{O})]$ (a) and $[\text{Eu}(\text{H-98d})(\text{NCS})]$ (b) in $[\text{Eu}(\text{98d})(\text{H}_2\text{O})][\text{Eu}(\text{H-98d})(\text{NCS})]$ (adapted from Ref. [291]).

cryptates while the europium(III) ion of $[\text{Eu}(\text{H-98d})(\text{NCS})]$ is eight coordinated by a N_5O_3 donor set. In $[\text{Eu}(\text{H-98d})(\text{NCS})]$ the Eu-NCS group is nearly linear [291].

$\text{Ln}(\text{H}_3\text{-98a})(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Y}^{3+}, \text{La}^{3+}\text{--}\text{Lu}^{3+}$; $n = 1\text{--}4$), prepared by a one-step condensation of 2,6-diformyl-4-methylphenol and tris(2-aminoethyl)amine in the presence of the appropriate $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [292], consists of the dication $[\text{Ln}(\text{H}_3\text{-98a})(\text{NO}_3)]^{2+}$ and two well-separated nitrate anions; crystal lattices also contain solvent and/or water molecules.

Crystals of $[\text{Nd}(\text{H}_3\text{-98a})(\text{NO}_3)](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $[\text{Eu}(\text{H}_3\text{-98a})(\text{NO}_3)](\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ are isomorphous while $[\text{Ce}(\text{H}_3\text{-98a})(\text{NO}_3)](\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O} \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ is not isomorphous with them and shows different helicity [292]. In the cation complexes, $[\text{M}(\text{H}_3\text{-98a})(\text{NO}_3)]^{2+}$ (Fig. 138a and b), the metal ion is placed asymmetrically at one end of the cavity of the cryptand and is nine coordinated, bound to three imino nitrogen atoms, three phenolic oxygen atoms and one of the bridgehead nitrogen atoms. The distance between the lanthanide ion and the bridgehead nitrogen is considerably higher than those of the lanthanide ion and the imino nitrogen atoms, showing a weak interaction between the amine nitrogen and the lanthanide(III) ion. A progressive decrease on the Ln-donor atom bond distances is observed upon decreasing the ionic radii of the lanthanide ions. The eighth and ninth positions are occupied by two oxygen atoms of a bidentate nitrate anion. The coordination geometry of the metal ion is a slightly distorted monocapped dodecahedron where the oxygen of the coordinated nitrate group is the atom that is capping the dodecahedron [292].

With respect to the conformation that $\text{H}_3\text{-98a}$ adopts in these three lanthanide(III) complexes, the nitrogen atoms of

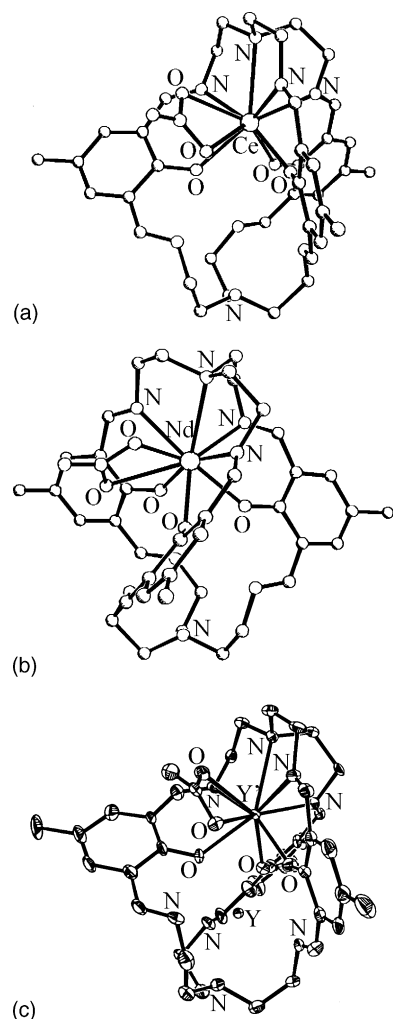


Fig. 138. Structure of $[\text{Ce}(\text{H-98a})(\text{NO}_3)]^{2+}$ (a) $[\text{Nd}(\text{H}_3\text{-98a})(\text{NO}_3)]^{2+}$ (b) and $[\text{Y}(\text{H}_3\text{-98a})(\text{NO}_3)]^{2+}$ (c) (adapted from Ref. [292]).

the imine bonds are on the same side of the aromatic ring in the three chains, what is described as a sss conformation, and not only the coordinated bridgehead nitrogen atom but also the other one that is not involved in the coordination of the metal ion are disposed in *endo*. Likewise, $\text{H}_3\text{-98a}$ is twisted around the axis that passes through both bridgehead nitrogen atoms resembling a triple helix [292].

$[\text{Y}(\text{H}_3\text{-98a})(\text{NO}_3)][\text{Y}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})](\text{NO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{CH}_3\text{CN}$, obtained by a similar procedure [292], contains two different metal structural units, the cation $[\text{Y}(\text{H}_3\text{-98a})(\text{NO}_3)]^{2+}$ and the neutral complex $[\text{Y}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})]$, two well-separated nitrate anions, a molecule of ethanol and a molecule of acetonitrile [292]. In the neutral complex the yttrium ion is bound to nine oxygen atoms, six corresponding to three bidentate nitrate ions, two to two water molecules and one to an ethanol molecule. The coordination polyhedron can be described as a distorted tricapped trigonal prism. In the cation complex there are two positions for the yttrium ion with occupancies of 0.95 and 0.05, respectively. The major position of yttrium(III) ion is found to one side of the cryptand, where it is

bound to the three imino nitrogen atoms, the three phenoxy oxygen atoms and a bridgehead nitrogen atom and completes its coordination sphere with two oxygen atoms of a bidentate nitrate ion. Once, again the coordination geometry around the metal ion can be described as a distorted mono-capped dodecahedron where the oxygen of the coordinated nitrate group is the atom that is capping the dodecahedron. The minor position of the yttrium(III) ion is located at the other end of the macrobicycle, where it also forms close contacts with seven donor atoms of the macrobicycle [292] (Fig. 138c).

In aqueous solution, NMR spectra of the entire series of complexes indicate that they have an effective C_3 symmetry, with the metal ion bound not centered in the cryptand cavity. Moreover, their solution structures show excellent agreement with the X-ray crystal structures of the neodymium(III) and yttrium(III) complexes.

In $[\text{Ba}(\mathbf{242})](\text{ClO}_4)_2$, prepared via the [2+2] cyclocondensation of tris(2-aminoethyl)amine and 2,6-diacetylpyridine in the presence of $\text{Ba}(\text{ClO}_4)_2$ and in a 2:2:1 molar ratio [293], the structure of the cation $[\text{Ba}(\mathbf{242})]^{2+}$ (Fig. 139a) is very similar to that of the $\text{Ba}(\text{ClO}_4)_2$ complex of the corresponding methoxyethyl pendant-armed macrocycle [293]. The macrocycle adopts a folded, or cleft-like, conformation completely encapsulating the metal. The complex is chiral due to the conformation of the five membered chelate rings which can be distinguished as either δ or λ . Furthermore, the arrangement of the chelate rings around the metal ion may produce either one of a pair of distinct helical conformations, Λ or Δ . In the crystal structure both the $\Delta(\delta\delta)$ conformation and the enantiomeric $\Delta(\lambda\lambda)$ conformation are found.

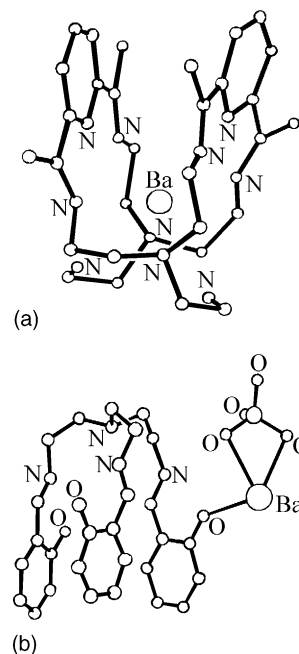
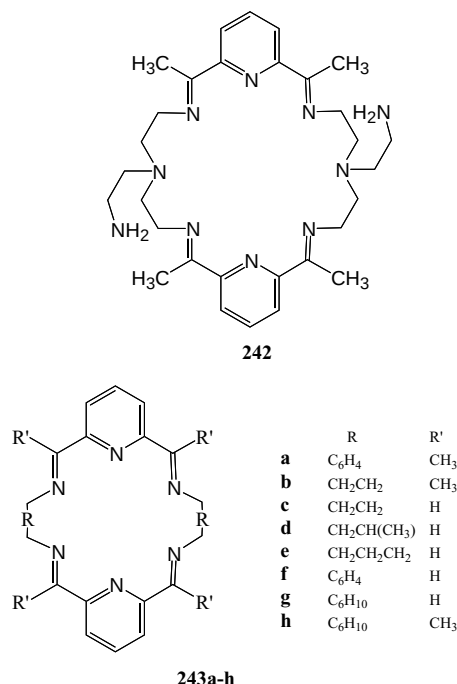


Fig. 139. Structure of $[\text{Ba}(\mathbf{242})]^{2+}$ (a) and $[\text{Ba}(\text{H}_3\text{-241a})_2(\text{ClO}_4)_2]$ (b) (adapted from Ref. [293]).



Functionalization of this barium complex was attempted using salicylaldehyde but it was not possible to isolate a discrete product from the reaction of the barium complex with salicylaldehyde in 1:2 stoichiometric ratio. When an excess of salicylaldehyde was used, two different types of yellow needles were obtained in succession, respectively [Ba(H₃-**241a**)₂(ClO₄)₂] and the tripodal ligand tris[2-salicylideneamino)ethyl]amine (H₃-**241a**) [293].

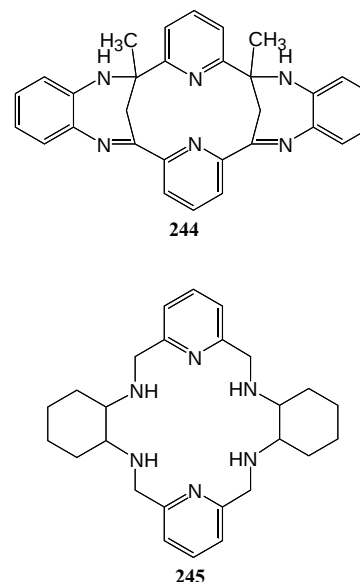
In the structure of [Ba(H₃-**241a**)₂(ClO₄)₂] (Fig. 139b) the ligand bridges adjacent barium cations using two of the three phenolic oxygen atoms so that each barium forms four such Ba–O bonds giving an approximately square, planar coordination geometry. The coordination polyhedron around the barium ion is completed by a pair of centrosymmetrically related, approximately symmetrically bidentate perchlorate anions. The *cis*-conformations of all three salicylideneimine residues permits the formation of internal hydrogen bonds [293].

It is possible that the tripodal products arise from transimination reactions which lead to displacement of the pyridyldiimine head groups from the macrocycle or from hydrolysis of the Schiff base macrocycle followed by formation of the tripod by reaction of salicylaldehyde with tris-(2-aminoethyl)amine [293].

7.2. [2+2] Symmetric macrocyclic complexes

Many papers have been published on the preparation, properties and X-ray structure of lanthanide(III) complexes with the [2+2] macrocycles **243a–h** derived from 2,6-diformyl- or 2,6-diacetyl-pyridine and the appropriate diamine [294]. Using 2,6-diacetylpyridine as diformyl precursor it is easy to obtain the appropriate complexes when R is an aliphatic chain, while it is very difficult to obtain the similar complexes when R = C₆H₄. In this least case the reaction of

1,2-diaminobenzene with 2,6-diacetylpyridine gives rise to the different product **244**, containing one [12]-membered and two [7]-membered inner rings and not a single [18]-membered inner ring as originally supposed [295]. The easy recovery of **244** during attempts to obtain metal complexes of **243a** by template procedures led to the conclusion that steric crowding inhibited the formation of **243a**. This could arise via interaction of the methyl groups with proximal aromatic hydrogen atoms.



The condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene in the presence of lanthanum(III), praseodymium(III) or neodymium(III) nitrate yielded the metal-free tricyclic compound **244** and a metal-free half-cycle. However, minute yields of metal-containing compounds having the general formula [M(NO₃)₃(**243a**)]·H₂O (*n* = 0.5–3.0) could be obtained from the mother liquid after the removal of **244** and of the half-cycle.

The structure of [Pr(**243a**)(NO₃)₂(CH₃OH)](ClO₄)·0.5CH₃OH·0.5H₂O confirms the formation of the designed macrocyclic complexes of **243a** [296] (Fig. 140a). The tetraimine [2+2] macrocycle **243a** coordinates with its six nitrogen atoms to the central metal ion, which is eleven coordinated, being bound also to two bidentate nitrate ions and to the oxygen atom of a methanol molecule. The presence of one nitrate and one methanol group, both coordinated on the same side, causes an asymmetric bonding mode of this nitrate group. The macrocyclic ring is not planar but strongly bent [296].

In contrast, the related template condensation of 1,2-diaminobenzene with 2,6-diformylpyridine in the presence of calcium(II), strontium(II), barium(II) or lead(II) ions readily gives complexes of the [2+2] hexaazamacrocyclic **243f** [297].

In the complexes with **243b** it was verified that, along the series of lanthanide(III) ions, the coordination number decreases. Thus for the lanthanide(III) nitrate complexes with the [2+2] macrocycle **243b** derived from the conden-

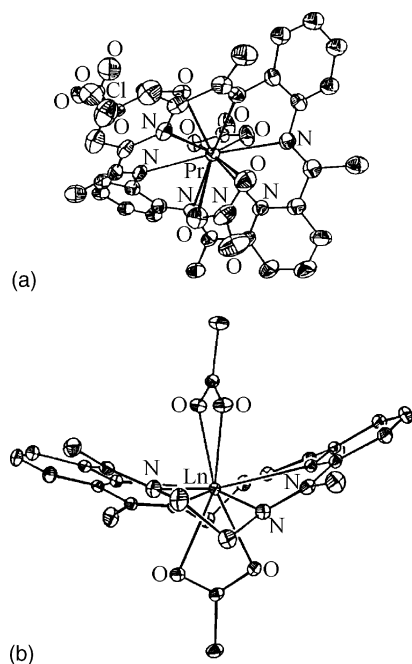


Fig. 140. Structure of $[\text{Pr}(\mathbf{243a})(\text{NO}_3)_2(\text{CH}_3\text{OH})]^+$ (a) and $[\text{Ln}(\mathbf{243b})-(\text{CH}_3\text{COO})_2]^+$ ($\text{Ln} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$) (b) (adapted from Refs. [296,298]).

sation of 2,6-diacetylpyridine and 1,2-diaminoethane, the lanthanum(III) ion is 12 coordinated, the cerium(III) is 11 coordinated and neodymium(III) is 10 coordinated [294].

In addition to the three compounds whose structures were fully determined, the other lanthanide complexes of similar stoichiometries examined showed that the twelve coordinated structure adopted by lanthanum was confirmed by single-crystal cell-dimension determinations to be adopted by cerium also. The 11 coordinated structure adopted by cerium was shown to be adopted also by lanthanum and praseodymium. Crystals of the terbium complex were similarly found to be isostructural with those of the ten coordinated neodymium complex, and although twinning was present in some other cases, giving difficulty with cell-dimension determination, the same structure was proposed for the series Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} and Ho^{3+} . However, single-crystal cell-dimension determination shows that Er^{3+} adopts a different crystal structure, as yet undetermined [294].

The early lanthanides seem to be on the 12–11 coordination borderline in these complexes, and accept compact bidentate nitrate ligands in non aqueous solution, to give a coordination number of twelve, while in aqueous solution, the overall effect is to substitute a coordinated bidentate nitrate ion by a monodentate water molecule [294].

Tetraimine Schiff bases derived from 2,6-diformylpyridine and 1,2-diaminopropane (**243d**) or 1,3-diaminopropane (**243e**) have been isolated for the lanthanides (except promethium) [295].

In order to assess how a decrease in the ionic radius of the lanthanide(III) ions influence the structural feature and

special arrangement of the macrocyclic entity itself, a series of lanthanide(III) complexes with the macrocycle **243b** and different counter anions have been prepared. The Schiff base condensation of 2,6-diacetylpyridine and ethylenediamine in the presence of lutetium(III) acetate followed by precipitation with ClO_4^- , yields $[\text{Lu}(\mathbf{243b})(\text{CH}_3\text{COO})(\text{OH})](\text{ClO}_4)(\text{CH}_3\text{OH})(\text{H}_2\text{O})_n$ [296]. The crystal of this complex consists of two species described as $[\text{Lu}(\mathbf{243b})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{CH}_3\text{OH})(\text{OH})(\text{ClO}_4)$ and $[\text{Lu}(\mathbf{243b})(\text{CH}_3\text{COO})(\text{CH}_3\text{OH})(\text{OH})(\text{ClO}_4)]$. The cation consists of a nine coordinated lutetium(III) ion linked to the six nitrogen donor atoms of the macrocycle, to a bidentate chelating acetate and to either a water or methanol molecule. Non coordinated OH^- and ClO_4^- anions balance the residual cationic charges; clathrated methanol is also present. The lutetium(III) macrocyclic moiety has a folded butterfly arrangement whereas for the related lanthanum(III) and samarium(III) complexes there was only a minor displacement from planarity. The hinging of the macrocycle at the flexible ethylenic side chains is suggested to relieve strain in the cycle, and to minimize repulsion between the hetero-ligands to allow optimum coordination at the metal. As there are non coordinated but potentially strong oxygen donor ligands present it is also suggested that nine is the limit for lutetium coordination in such species. The question remains of whether the folding of the macrocycle is indeed governed by the ionic size of the metal or by the steric requirement of the ligand.

Complexes of the general formula $\text{Ln}(\mathbf{243b})(\text{CH}_3\text{COO})_2\text{Cl}\cdot n\text{H}_2\text{O}$ ($n = 3\text{--}6$) have also been obtained by template procedure. The X-ray structure of $[\text{Ln}(\mathbf{243b})(\text{CH}_3\text{COO})_2](\text{Cl})\cdot 4\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$) shows the complex cations consist of a 10 coordinated metal center linked to the six nitrogen donor atoms of the macrocycle in an approximately equatorial belt and to both oxygen atoms of the acetate groups above and below this belt. The lanthanide(III) ion lies only $+0.039 \text{ \AA}$ from the least-squares plane through the six nitrogen atom; however, the individual nitrogen atoms show large deviations from this plane. This leads to substantial ruffle-angles around the LnN_6 system. Each of the two acetate groups behaves as a bidentate ligand and takes up pseudo-axial positions with mutually staggered coordinated oxygen atoms. The complex cation is not of high symmetry. Rather, the hexadentate macrocyclic ligand takes up a bowl-shaped configuration such that one acetate ligand partially shielded, whereas the other is far more open. The crystal structure is completed by four water molecules of crystallization and a bare chloride ion [298,302] (Fig. 140b).

By the reaction of $[\text{Ln}(\mathbf{243b})(\text{CH}_3\text{COO})_2](\text{Cl})\cdot n\text{H}_2\text{O}$, ($\text{Ln} = \text{Y}^{3+}, \text{Eu}^{3+}$) with an excess of NaNCS , the tris-isothiocyanate complexes $[\text{Ln}(\mathbf{243b})(\text{NCS})_3]$ have been synthesized. The two complexes are isostructural and are composed of two distinct asymmetric units both formed by $[\text{Ln}(\mathbf{243b})(\text{NCS})_3]$ having almost the same ligand conformation. The lanthanide(III) ion is nonacoordinated by six nitrogen atoms of the macrocycle and by the three nitrogen atoms of the thiocyanate groups which behave as

monodentates. The macrocycle is bent in the direction of the singly coordinated ligand [294].

These results show that the considerable contraction in ionic radius occurring along the 4f series does not appreciably affect the ability of the lanthanide(III) ions to act as templating agents for the formation of the [18]-membered macrocycle. The ease and the yield of the metal template macrocyclic synthesis appear to depend more on the counterion present than on the metal ion; good oxygen donor anionic ligands, such as acetate, favour the reaction much more effectively than do chloride and perchlorate [294,296].

NMR spectra show that all six nitrogen donor atoms of the macrocyclic cavity remain coordinated to the metal ion not only for lanthanum(III) but also for the smaller lutetium(III) ion [296].

These examples prove the ability of the lanthanide(III) and yttrium(III) ions to act as templates for the [2+2] Schiff base condensation of 1,2-diaminoethane with 2,6-diacetylpyridine. These complexes are unique among the compounds of the lanthanides in that the metal-macrocyclic entity is extremely inert with respect to release of the metal ion, whereas the exocyclic ligands (anions or solvent molecules) are labile and easily exchangeable. The inertness of the metal-**243b** entity must arise from an especially favourable combination of metal ionic radius, cavity size of the [18]-membered macrocyclic ligand **243b**, and bonding ability of the six nitrogen donor atoms. This suggestion is supported by the observation that the imine macrocycles similar to **243b** but having furan instead of pyridine head-units, are labile and decompose rapidly when dissolved in water.

The [2+2] condensation reaction of 2,6-diformyl- or 2,6-diacetyl-pyridine and ($\pm$)-*trans*-1,2-diaminocyclohexane in the absence of a metal ion, at both low and high dilution, resulted in the isolation of the pure macrocycles **243g** and **243h**, respectively. **243h** adopts a stepped conformation with a parallel pyridine-ring arrangement, the direction of the folding being dictated by the racemic conformation of the cyclohexane. The symmetry-related cyclohexyl rings adopt chair conformations of opposite hand (*S,S*) and *R,R*, respectively [299] (Fig. 141).

Yttrium(III), lanthanum(III), gadolinium(III) and dysprosium(III) nitrate and chloride complexes with the [18]-membered hexaaza-tetraimine macrocycle **243g** containing backbone cyclohexyl units have been prepared by template procedure [298]. The metal complexes of **243g** with nitrate as counter ions were isolated in better yields, but the chloride complexes were more soluble in water and methanol. Crystals of $[\text{Gd}(\mathbf{243g})(\text{H}_2\text{O})_3](\text{Cl})_3 \cdot 3\text{H}_2\text{O}$, grown from methanol, show the gadolinium(III) ion has a nine coordinated geometry (Fig. 142a), the donor atoms being six nitrogens from the macrocycle and three oxygen atoms from coordinated water molecules [299].

Solution studies with radiolabelled ^{90}Y indicated that, in competition with the very strong chelator diethylenetriamine-*N,N,N',N'',N'''*-pentaacetic acid ($\text{H}_5\text{-dtpa}$), a $\{\text{Y}_2(\mathbf{243g})\}$ macrocyclic unit is maintained for 1 h.

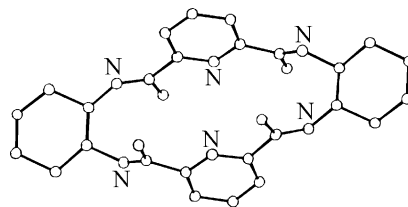


Fig. 141. Structure of **243h** (adapted from Ref. [298]).

The relaxivity of the gadolinium(III) complex $[\text{Gd}(\mathbf{243g})(\text{H}_2\text{O})_3]^{3+}$, is higher than those of $[\text{Gd}(\text{dtpa})(\text{H}_2\text{O})]^{2-}$ and $[\text{Gd}(\text{L})(\text{H}_2\text{O})]^-$ ($\text{H}_4\text{L} = 1,4,7,10\text{-tetraazacyclododecane-}N,N',N'',N'''$ -tetraacetic acid), both of which are currently used as contrast agents in magnetic resonance imaging [299]. Relaxivity measurements R_1 in water (pH 6, 20 MHz, 37 °C) on $[\text{Gd}(\mathbf{243g})(\text{H}_2\text{O})_3](\text{Cl})_3$ gave a value of $11.0 \text{ dm}^3 \text{ mmol}^{-1} \text{ s}^{-1}$ which is very much greater than that of $4.4 \text{ dm}^3 \text{ mmol}^{-1} \text{ s}^{-1}$ for $[\text{Gd}(\text{dtpa})(\text{H}_2\text{O})]^{2-}$. $[\text{Gd}(\mathbf{243g})(\text{H}_2\text{O})_3](\text{Cl})_3$ has also significantly greater relaxivity than that of $[\text{Gd}(\mathbf{243b})(\text{CH}_3\text{COO})_2]^+$ ($9.7 \text{ dm}^3 \text{ mmol}^{-1} \text{ s}^{-1}$, 20 MHz, 30 °C). This appears to be related to the number of water molecules coordinated, but surprisingly luminescence studies of the analogous complex, $[\text{Eu}(\mathbf{243b})(\text{CH}_3\text{COO})_2]^+$, show ready replacement of the acetate ligands by water in aqueous solution. Even in phosphate buffer (pH 6) the relaxivity of $[\text{Gd}(\mathbf{243g})(\text{H}_2\text{O})_3](\text{Cl})_3$ ($4.7 \text{ dm}^3 \text{ mmol}^{-1} \text{ s}^{-1}$) is still comparable to that of

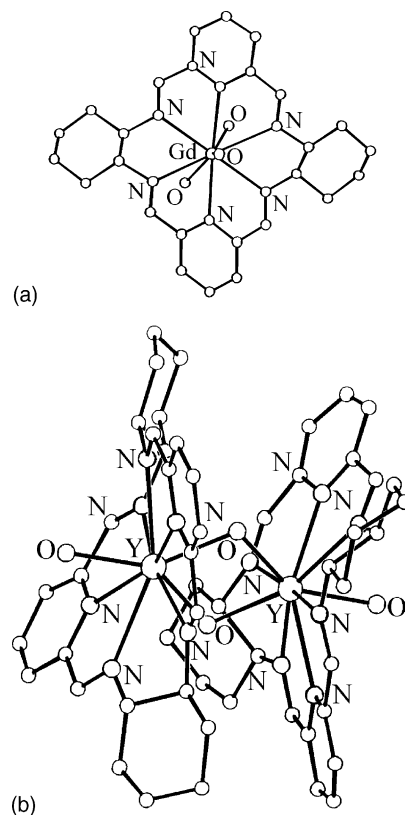


Fig. 142. Structure of $[\text{Gd}(\mathbf{243g})(\text{H}_2\text{O})_3]^{3+}$ (a) and $[\text{Y}_2(\mathbf{243g})_2(\text{OH})_2(\text{H}_2\text{O})_2]^{4+}$ (b) (adapted from Ref. [299]).

$[\text{Gd}(\text{dtpa})(\text{H}_2\text{O})]^{2-}$ in water. These results demonstrate the potential of $[\text{Gd}(\mathbf{243g})(\text{H}_2\text{O})_3](\text{Cl})_3$ as a contrast agent in magnetic resonance imaging [299].

The neodymium(III) and terbium(III) nitrate complexes with the ligand $\text{H}_2\text{-243g}$ are isostructural and the decacoordinated metal cations have a coordination environment composed of four nitrate oxygen atoms and six nitrogen atoms belonging to the macrocycle. These data parallel the NMR studies and show these complexes adapt a helical structure of D_2 symmetry [298,299].

$(\pm)$ -*Trans*-1,2-diaminocyclohexane, 2,6-diformylpyridine and yttrium(III) or neodymium(III) nitrate react in methanol and in a 2:2:1 molar ratio to form the dinuclear complexes $[\text{Ln}_2(\mathbf{243g})_2(\text{OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4$ confirmed by the X-ray structure of the yttrium(III) complex which consists of two independent macrocyclic units connected by two hydroxyl ligands coordinated to the central yttrium(III) ions (Fig. 142b). Each yttrium(III) ion is nine coordinated with six nitrogen donors forming an equatorial set, a water molecule in one axial position and two symmetrically, bridging hydroxyl groups on the other side. The dimeric unit has crystallographic C_2 symmetry with the two water ligands and the two yttrium ions lying on a two-fold axis, so that the two halves within each macrocyclic ring are related by symmetry. Within the dimer the two macrocycles have virtually identical conformations [299].

Both dimeric complexes have the remarkable ability to degrade double-stranded DNA while the corresponding monomeric gadolinium(III), yttrium(III) and dysprosium(III) complexes have no activity. Cleavage most likely involves random attack at single strands, in which closed circular plasmid DNA is initially converted to a nicked DNA intermediate before final cleavage [298,299].

The macrocyclic hexaazatetraamine **245**, obtained in a one-step synthesis by reducing the corresponding tetraimine with NaBH_4 in situ and purifying the brown-yellow oily product by column chromatography, reacts with lanthanide(III), zinc(II), cadmium(II) nitrate or perchlorate in refluxing acetonitrile/dichloromethane to form the corresponding complexes [300]. In $[\text{La}(\mathbf{245})(\text{NO}_3)_3]$ the metal ion shows an eleven coordination. A slight twist is apparent in the conformation of the macrocycle but it is dominated by the folding of the macrocycle away from the two nitrate ligands towards the third. The conformation of the tetraamine is surprisingly similar to the arrangement observed in the less flexible tetraimine structures. For example the fold angle is comparable to that which arises in the tetraimine $[\text{Ce}(\mathbf{243b})(\text{NO}_3)_2(\text{CH}_3\text{OH})]^+$ [300]. In contrast, with softer metal ions of lower coordination requirements, the new hexaazatetraamine ligand adopts a distorted octahedral arrangement of the six nitrogen donor atoms giving the helical chiral macrocyclic complexes $[\text{Zn}(\mathbf{245})]^{2+}$ and $[\text{Cd}(\mathbf{245})]^{2+}$ (Fig. 143a–c).

Two types of conformation are observed for this type of hexaaza-macrocyclic ligand, which may be defined relative to a hypothetical planar arrangement. In a twist-wrap conformation, the ligand wraps round the metal ion by a twisting

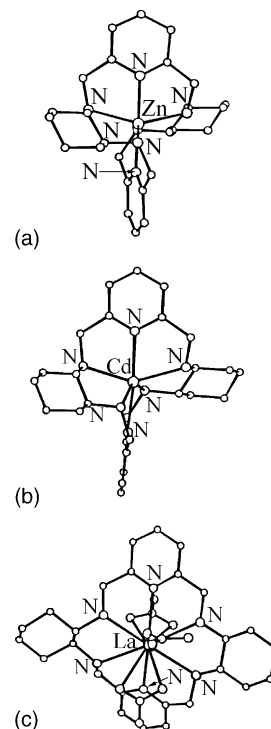


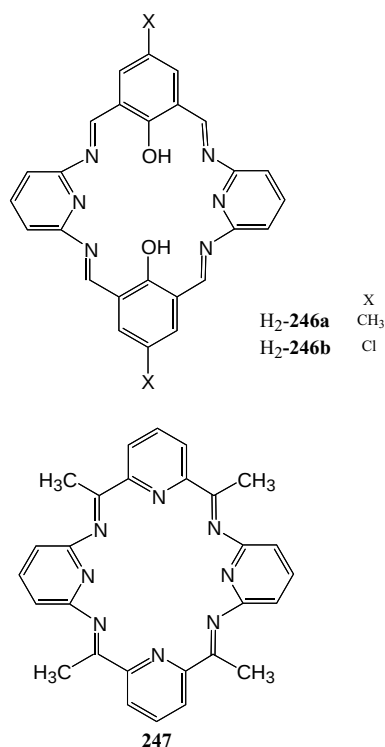
Fig. 143. Structure of $[\text{Zn}(\mathbf{245})]^{2+}$ (a), $[\text{Cd}(\mathbf{245})]^{2+}$ (b) and $[\text{La}(\mathbf{245})(\text{NO}_3)_3]$ (c) (adapted from Ref. [300]).

of the two pyridyl bridge-head units relative to each other, eventually giving a helical conformation in which they are approximately orthogonal. In a twist-fold conformation a slight twisting of the two bridge-heads is accompanied by an overall folding of the great ring of the macrocycle so that the pyridine nitrogen atoms and the metal ion are no longer virtually linear [300].

$[\text{Ln}(\text{H}_2\text{-40})(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$, $n = 1$; $\text{Ln} = \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}$, $n = 2$) and $[\text{Y}(\text{H}_2\text{-40})(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (with the [18]-membered dioxatetraaza macrocyclic ligand $\text{H}_2\text{-40}$) were synthesized by condensation of 2,6-diformyl-4-methylphenol with 1,2-diaminobenzene in the presence of hydrated lanthanide(III) nitrate or yttrium(III) nitrate pentahydrate in dry acetonitrile at room temperature. The condensation of the same organic precursors in the absence of the metal template yields the diimine-diamine macrocycle $\text{H}_2\text{-40'}$ as indicated by the X-ray structure already reported in a previous section [124,301].

Also lanthanide(III) (except Ce^{3+} , Pm^{3+} , Yb^{3+} and Lu^{3+}) and yttrium(III) cations promote Schiff base condensation of 2,6-diaminopyridine and 2,6-diformyl-4-methylphenol leading to the formation of complexes of the [2+2] symmetric macrocycle $\text{H}_2\text{-246a}$. $[\text{Pr}(\text{H}_2\text{-246a})(\text{NO}_3)_2(\text{H}_2\text{O})_3](\text{NO}_3) \cdot 3\text{H}_2\text{O}$, $[\text{Ln}(\text{H}_2\text{-246a})(\text{NO}_3)(\text{H}_2\text{O})_3](\text{NO}_3) \cdot 4\text{H}_2\text{O}$ ($\text{Ln} = \text{La}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$ or Tm^{3+}), $[\text{Eu}(\text{H}_2\text{-246a})(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3) \cdot 5\text{H}_2\text{O}$ and $[\text{Y}(\text{H}_2\text{-246a})(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3) \cdot 5\text{H}_2\text{O}$ have been synthesized by using the respective hydrated metal nitrate as the template, in acetonitrile. When the Schiff base condensation

is carried out in super-dry ethanol or methanol in the presence of hydrated lanthanide(III) nitrate, compounds of undefined composition are obtained [301].



The formation of complexes of both the lighter and heavier lanthanide(III) cations by H₂-40 and H₂-246a by metal template synthesis under the same experimental conditions reflects the ability of these macrocycles to adapt to the geometrical requirements of the metal ions. Nevertheless, in the case of the [18]-membered tetraaza-macrocyclic H₂-40 there is a gradual increase in the yield of the complexes along the lanthanide series, whereas the yield decreases for H₂-246a. It was suggested that the [20]-membered macrocycle H₂-246a is more suitable to synthesise complexes of the larger lanthanides and the [18]-membered macrocycle H₂-40 is more suitable for the smaller lanthanides [301].

For the [20]-membered hexaaza-macrocyclic H₂-246b, lanthanide(III) complexes have been synthesized by the condensation of 4-chloro-2,6-diformylphenol and 2,6-diaminopyridine in the presence of lanthanide(III) nitrates yielding [Ln(H-246b)(NO₃)(H₂O)₂](NO₃)_n·nH₂O (Ln = La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Y³⁺; n = 3 or 4). The formation of lanthanide(III) complexes of 246a and H₂-246b demonstrates the template potential of the lanthanide(III) cations in the assembly of [2+2] symmetric Schiff base macrocycles having pyridine or phenol head units and pyridine lateral units [301].

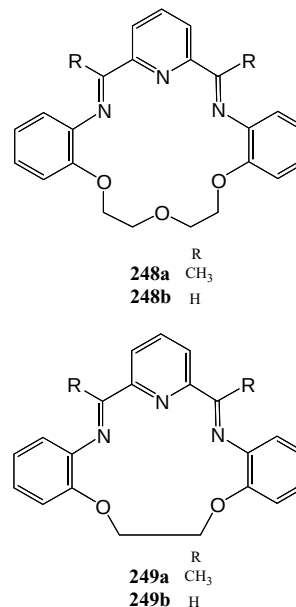
The mononuclear lanthanide(III) complexes of the [20]-membered octaaza macrocyclic Schiff base 247, [La(247)-(NO₃)(H₂O)₃](NO₃)₂·2H₂O, [Ln(247)(NO₃)(H₂O)₂](NO₃)₂·nH₂O (Ln = Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Y³⁺; n = 2 or 3), [Ln(247)(ClO₄)₂(H₂O)](ClO₄)·

3H₂O and [Ln(247)(CH₃COO)₃(H₂O)]·3H₂O (Ln = Eu³⁺ or Tb³⁺) have been synthesized by the condensation of 2,6-diacetylpyridine and 2,6-diaminopyridine in the presence of lanthanide(III) nitrate, perchlorate or acetate as the metal template. [Dy(247)(NO₃)(ClO₄)](NO₃)·H₂O and [Ln(247)(NO₃)(NCS)](NO₃)·H₂O (Ln = Eu³⁺, Tb³⁺) have been synthesized by anion metathesis of the respective (nitrate)(aqua) complex with perchlorate or thiocyanate.

The difference in the size of the lanthanide(III) cations does not affect their template potential in the formation of the complexes H₂-246b and H₂-247. Again this indicates the adaptability of these macrocycles to folding according to the geometric requirements of the metal ions. The formation of complexes of these macrocycles along with coordinated nitrate, perchlorate or acetate and water shows the ability of oxygen donor ligands in stabilizing the lanthanide(III) ions in the macrocyclic frameworks [301].

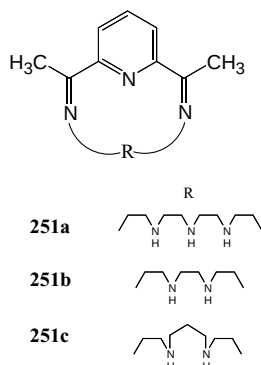
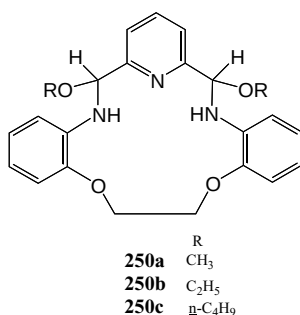
7.3. [1+1] Asymmetric macrocyclic complexes

The condensation of suitable formyl- and/or amine-pre-cursors give rise, under appropriate experimental conditions, to [1+1] asymmetric macrocyclic compounds. Reactions between equimolar amounts of 2,6-diacetylpyridine, 1,5-bis(2-aminophenoxy)-3-oxapentane or 1,2-bis(2-aminophenoxy)ethane and hydrated lanthanide nitrates or perchlorates gave [Ln(248a)](NO₃)₃·xH₂O (Ln = La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺) and [Ln(249a)](ClO₄)₃·xC₂H₅OH (Ln = La³⁺, Ce³⁺), respectively. No analytically pure products in the reactions attempted with holmium(III), erbium(III), thulium(III), ytterbium(III) or lutetium(III) nitrate and praseodymium(III), neodymium(III), europium(III), gadolinium(III), holmium(III) or erbium(III) perchlorate were obtained [302]. Using conductivity data in dimethylformamide for [Ln(248a)](NO₃)₃·xH₂O it is evident that one nitrate ion is coordinated; such coordination is also most likely in the solid state.



The reaction of 2,6-diacetylpyridine and 1,2-bis(2-aminophenoxy)ethane in 1:1 ratio in absolute ethanol gives an off-white unidentified crystalline material. However, lanthanide(III) complexes of the [15]-membered N_3O_2 macrocycle **249a** were prepared by template condensation of 2,6-diacetylpyridine with 1,2-bis(2-aminophenoxy)ethane in absolute ethanol in the presence of $Ln(ClO_4)_3 \cdot xH_2O$ ($Ln = La^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Gd^{3+} , Ho^{3+} , Er^{3+}) [302].

The metal-free macrocycles **250a–c** were obtained as the alcohol adducts when magnesium salts were used as potential templates. The same compounds have been obtained when equimolecular amount of ethanolic solutions of 2,6-diformylpyridine and 1,2-bis(2-aminophenoxy)ethane were mixed and refluxed. The dialcohol addition product crystallised out as fine needles on cooling, and was recrystallised from ethanol.



Transition metal complexes of the pentadentate macrocycle **249b** have been isolated from the Schiff-base condensation of 2,6-diformylpyridine and 1,3-bis(2-aminophenoxy)ethane in methanol in the presence of manganese(II) or zinc(II) perchlorate or nitrate.

2,6-Diacetylpyridine and 1,5-bis(2-aminophenoxy)-3-oxapentane in absolute ethanol form an unidentifiable viscous oil. A template method using strontium(II) was found to provide a useful route to the formation of the metal diimine macrocyclic complex [302].

Equimolar amounts of 2,6-diformylpyridine, 1,5-bis(2-aminophenoxy)-3-oxapentane, and hydrated lanthanide nitrates in refluxing methanol gave $[Ln(248b)](NO_3)_3$ ($Ln = La^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Gd^{3+}). The lanthanum(III) complex crystallizes with 0.5 molecule of solvent [302]. This reaction does not occur with terbium(III), dysprosium(III), ytterbium(III) and lutetium(III) nitrate [302]. The

same condensation reaction in the presence of $Ln(ClO_4)_3 \cdot nH_2O$ in absolute ethanol, produces complexes of general formula $[Ln(248b)](ClO_4)_3 \cdot xH_2O \cdot yEtOH$ ($Ln = La^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Ho^{3+} , Er^{3+}). In the absence of metal salt the [1+1] macrocycle is not formed.

The FAB mass spectra evidence the [1+1] monomeric nature of the complexes, with the macrocycles **248** and **249**. The molar conductance values of the complexes in CH_3CN at 25 °C lie in the range reported for 2:1 electrolytes in this solvent. The perchlorate complexes of La^{3+} , Ce^{3+} , Nd^{3+} and Ho^{3+} have values intermediate between those for 2:1 and 3:1 electrolytes, indicating a weak coordination of the perchlorate anion [302].

When 2,6-diacetylpyridine and facultative polyamines, containing additional donor atoms in the R chain, are reacted in the presence of lanthanide(III) ions, the [1+1] macrocycles of the type **248** or **251** are obtained. $[La(L)](NO_3)_3 \cdot nH_2O$ have been recovered for $L = 248a$ and **251a** while with the macrocycles $L = 251b$ and **251c**, $[La(L)](NO_3)_2(OH) \cdot nH_2O$ are obtained [294].

When $La(SCN)_3$ is used as the template, mixed OH-SCN complexes are obtained throughout, $La(L)(SCN)(OH)_2$ ($L = 248a$, **251c**) and $La(L)(SCN)_2(OH)$ ($L = 248a$, **251a**). The presence of the macrocycle is supported by IR and ^1H NMR studies, and for $[La(248a)(NO_3)_3]$ an X-ray structure is available to confirm the assignment. The lanthanum is centered in the macrocyclic ring, twelve coordinated by the six heteroatoms and the three bidentate nitrate anions, one on one side of the macrocycle and two on the other side [294] (Fig. 144). There appears to be consistency in the twelve coordination of lanthanum in the presence of [18]-membered rings bearing six donor atoms, and three potentially bidentate anions. In $[Ln(248a)](NO_3)_3$, the macrocycle is quite bent, folding away from the hemisphere containing the two nitrate anions and towards that containing the lone nitrate.

The lanthanide complexes are not very stable in water, being similar in behaviour to the complexes derived from 2,5-diformylfuran and diamines and from cyclic polyethers. Metal hydroxide is readily precipitated on dissolution in H_2O ; it is probable that this is begun by initial breaking of the three adjacent ether-lanthanum bonds. The ^1H NMR spectra of $[La(248a)](NO_3)_3$ in acetonitrile solution indicate the integrity of the macrocycle in that medium [294].

The kinetics of decomposition of lanthanide(III) hexaaza macrocyclic Schiff base complexes with **243b**, **c**, **e**, **f**, and **251a** in aqueous solution shows that for a given macrocycle, decomposition of the Schiff base into component amine and carbonyl compound is dependent on which lanthanide ion is used. For the complexes with **243b** the rate of decomposition increases as: $Eu(243b)^{3+} < La(243b)^{3+} < Gd(243b)^{3+} < Tb(243b)^{3+} < Lu(243b)^{3+}$. Decomposition of $La(243b)^{3+}$ is accelerated 78-fold in the presence of a 10-fold excess of ethylenediaminetetraacetic acid and 10-fold in the presence of a 10-fold excess of diethylenetriaminopentaacetic acid (DTPA): In contrast $[Eu(243b)]^{3+}$ decomposes two-fold

more rapidly in the presence of a 10-fold excess of DTPA. Other lanthanum(III) Schiff base macrocycles which feature larger chelate rings, more rigid macrocyclic backbones and removal of two of the imine linkages all decompose more rapidly than does the parent $\text{La}(\mathbf{243b})^{3+}$ complex. These data are useful in the design of kinetically inert macrocyclic lanthanide(III) complexes for biologically relevant applications [302].

The lanthanide(III) and uranyl(VI) complexes $[\text{Ln}(\text{H}_2\text{-}\mathbf{121})(\text{X})_3]$ and $[\text{UO}_2(\mathbf{121})]$ with the functionalized macrocyclic ligands $\text{H}_2\text{-}\mathbf{121}$ have been obtained by reaction of the preformed ligands with the appropriate metal ion or by template procedure. On the contrary the complexes with the acyclic ligands $\text{H}_2\text{-}\mathbf{120}$ have been obtained by a step by step procedure. The diformyl precursor $\text{H}_2\text{-}\mathbf{252}$ and/or the related complexes $[\text{Ln}(\text{H}_2\text{-}\mathbf{252})(\text{X})_3]$ or $[\text{UO}_2(\mathbf{252})]$ have to be prepared as a first step; the IR subsequent condensation with $\text{H}_2\text{N}(\text{CH}_2)_{17}(\text{CH}_3)$ affords $\text{H}_2\text{-}\mathbf{120}$, $[\text{Ln}(\text{H}_2\text{-}\mathbf{120})(\text{X})_3]$ or $[\text{UO}_2(\mathbf{120})]$ [303]. The Schiff bases behave as neutral pentadentate ligands in the lanthanide complexes and as pentadentate dinegative ligands in the dioxouranium(VI) analogues. These functionalized ligands, owing to their solubility and that of related f-containing complexes in organic solvents, can be used for the separation of f-ions. The solubility of the mononuclear complexes depends on the substituent Z and follows the order $-\text{Cl} < -\text{CH}_3 < -\text{C}(\text{CH}_3)_3$. The macrocyclic ligands $\text{H}_2\text{-}\mathbf{121}$ offers the advantage of a single step preparation and, owing to their cyclic nature, of an enhanced, selectivity towards lanthanide ions. They are good extractants for some trivalent lanthanide ions (Dy^{3+} – La^{3+}) from a nitrate medium [185,303].

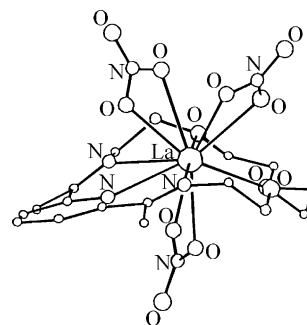
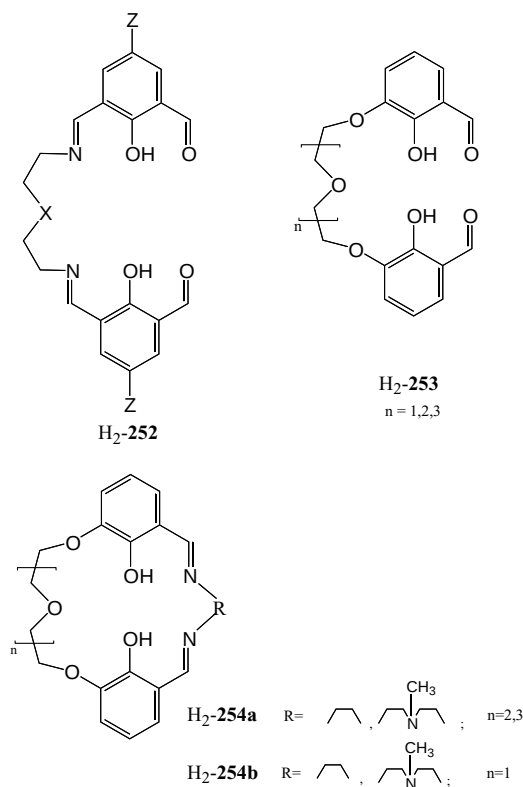


Fig. 144. Structure of $[\text{La}(\mathbf{248a})(\text{NO}_3)_3]$ (adapted from Ref. [294]).

The [1+1] Asymmetric compartmental macrocycles $\text{H}_2\text{-}\mathbf{254}$, containing one N_2O_2 , N_3O_2 or $\text{N}_2\text{O}_2\text{O}_2$ Schiff base and one adjacent O_2O_3 , O_2O_4 or O_2O_5 crown like coordination chamber, have been prepared by self-condensation or by reaction of the appropriate diformyl ($\text{H}_2\text{-}\mathbf{253}$) and amine precursors in the presence of barium(II) salts, followed by a demetalation reaction of the resulting complexes, $\text{Ba}(\text{H}_2\text{-}\mathbf{254})(\text{ClO}_4)_2$, with guanidinium sulfate [304,305].

Their [1+1] cyclic nature was inferred by fast atom bombardment mass spectrometry which mainly leads to the facile production of protonated $[\text{MH}]^+$ and cationized $[\text{MNa}]^+$ species [304]. As reported in a previous section the formation of [1+1] cyclic compounds was confirmed by a single crystal X-ray determination on $\text{H}_2\text{-}\mathbf{254a}$ ($\text{R} = \text{CH}_2\text{CH}_2$, $n = 2$). The two molecules present in the asymmetric unit are chemically identical and comparable in bond distances and angles. The four phenolic hydrogen atoms were not localized in the Fourier difference map but probable hydrogen bonds are present which involve each OH group and the closest iminic nitrogen atom [304] (Fig. 145).

$\text{Ln}(\text{H}_2\text{-}\mathbf{254})(\text{Cl})_3 \cdot n\text{S}$ or $\text{Ln}(\text{H}_2\text{-}\mathbf{254})(\text{NO}_3)_3 \cdot n\text{S}$, $[\text{Ba}(\text{H}_2\text{-}\mathbf{254})](\text{ClO}_4)_2$ and $\text{Ni}(\mathbf{254}) \cdot n\text{S}$ have been prepared by reaction of the preformed ligands with the appropriate metal salt in a 1:1 molar ratio, by template procedure or by reaction of the appropriate acyclic complexes with the desired amine. The template reaction was commonly used, owing to its simplicity and the higher yield of the resulting products. IR

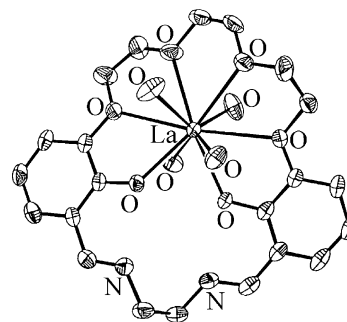


Fig. 145. Structure of $[\text{La}(\text{H}_2\text{-}\mathbf{254a})(\text{H}_2\text{O})_4]^{3+}$ ($\text{R} = \text{CH}_2\text{CH}_2$; $n = 2$) (adapted from Ref. [304]).

data suggest that the complexes may be formulated as $[\text{Ln}(\text{H}_2\text{-254})(\text{Sn})](\text{Cl})_3$ and $[\text{Ln}(\text{H}_2\text{-254})(\text{NO}_3)_3] \cdot n\text{S}$ ($\text{S} = \text{H}_2\text{O}, \text{CH}_3\text{OH}$), respectively [304].

In these complexes the metal ion invariably occupies the O_2O_n crown-like chamber, independently of the shape of the two adjacent coordination sites as confirmed also by X-ray structural investigations on $[\text{La}(\text{H}_2\text{-254a})(\text{H}_2\text{O})_4](\text{Cl})_3$ ($\text{R} = \text{CH}_2\text{CH}_2$, $n = 1$) and $[\text{Ln}(\text{H}_2\text{-254b})(\text{H}_2\text{O})_4](\text{Cl})_3$ ($\text{Ln} = \text{Ce}^{3+}, \text{Dy}^{3+}, \text{Lu}^{3+}$; $\text{R} = \text{CH}_2\text{CH}_2\text{NCH}_3\text{CH}_2\text{CH}_2$; $n = 1$). In particular yellow crystals of $[\text{La}(\text{H}_2\text{-254a})(\text{H}_2\text{O})_4](\text{Cl})_3$, grown from acetonitrile, show the metal ion is ten coordinated in a bicapped square antiprismatic environment; all six oxygen atoms of the outer crown-like site of the ligand are involved in the coordination to the central ion that achieves 10 coordination by the additional bonding of the oxygen atoms of four water molecules. The three chloride ions, which compensate the positive charge of the lanthanum, are not involved in the coordination but in a complicated hydrogen bonding network with the water molecules (Fig. 145) [304].

Crystals of $[\text{Ln}(\text{H}_2\text{-254b})(\text{H}_2\text{O})_4](\text{Cl})_3 \cdot (\text{H}_2\text{O})_n$ ($\text{Ln} = \text{Ce}^{3+}, \text{Dy}^{3+}$ $n = 1$; $\text{Ln} = \text{Lu}^{3+}$ $n = 3$) were obtained from slow evaporation of n -propanol solutions (Fig. 146a and b) [305]. The structures consist of discrete $[\text{Ln}(\text{H}_2\text{-254b})(\text{H}_2\text{O})_4]^{3+}$ cations and three Cl^- counterions with one (Ce and Dy complexes) and three (Lu complex) water molecules trapped in the lattice. The cerium and dysprosium

complexes are isomorphous. Each central metal ion is located in the O_2O_3 crown-like chamber of the macrocyclic ligand and reaches the coordination number of nine by bonding five oxygen atoms of the ligand and four oxygen atoms of the water molecules. The coordination geometry of these complexes is influenced by the ionic size of the central metal ion and by the degree of freedom of the donor oxygen atoms. In fact, only one ether oxygen atom experiences a certain degree of freedom given by the flexibility of the carbon chains, whilst the other two ether oxygen atoms and the two phenolic ones are somewhat constricted by their connection to a benzene ring. The size of the lutetium ion (ionic radii 0.85 Å), when compared to those of the other two ions (ionic radii 1.034 Å for Ce; 0.908 Å for Dy) is probably more suitable to accommodate into the O_2O_3 coordination chamber. This results in a higher stability, as also shown by a greater ease of structure resolution. The coordination geometry of the lutetium complex is well described as either a distorted square monocapped antiprism, or as a distorted tricapped trigonal prism. The coordination geometry of the cerium and dysprosium complexes is better described as a distorted square monocapped antiprism. The butterfly shape adopted by the cyclic ligand around the central ion has two phenyl rings as wings and the reduced dimensions of the lutetium ion allow, in this complex, a more folded position of the benzene wings. In the cerium and dysprosium complexes with a flatter arrangement of the ligand around the metals occurs. The hydrogen bonding network in the crystal structure of these complexes is remarkable and involves the three chloride anions as well as all the coordinated and uncoordinated water molecules [305].

Under particular conditions, the coordination of the chloride ions to lanthanum(III) was forced. Yellow crystals of $[\text{La}(\text{H}_2\text{-254b})(\text{Cl})_3]$ ($\text{R} = \text{CH}_2\text{CH}_2\text{NCH}_3\text{CH}_2\text{CH}_2$, $n = 1$), obtained by recrystallization under nitrogen atmosphere from a tetrahydrofuran/ethanol solution of $[\text{La}(\text{H}_2\text{-254b})(\text{H}_2\text{O})_4](\text{Cl})_3$, reveal that two complex molecules are present in the asymmetric unit together with one molecule of ethanol (Fig. 146c) [306]. Both complex molecules are chemically equivalent and similar in bond distances and angles. In both complexes the lanthanum ion is nine coordinated, being bonded to the three chlorine anions and to all the six oxygen atoms of the ligand ($\text{H}_2\text{-254b}$). The coordination polyhedron is well described as a tricapped trigonal prism. A hydrogen bonding network, in the crystal structure, is present and involves the chloride anions, the $\text{C}_2\text{H}_5\text{OH}$ molecule, iminic nitrogen and the phenyl oxygen atoms.

The mononuclear copper(II), nickel(II), cobalt(II), palladium(II) $[\text{M}(\text{254})]$ and manganese(III) complexes $[\text{Mn}(\text{254})(\text{CH}_3\text{COO})]$ have been obtained by employing a similar procedure. All these complexes recognize Na^+ . When the same reaction is carried out in the presence of NaOH the complexes $[\text{MNa}(\text{254})(\text{CH}_3\text{COO})_2] \cdot n\text{S}$ have been obtained. Moreover the preformed complexes, when reacted

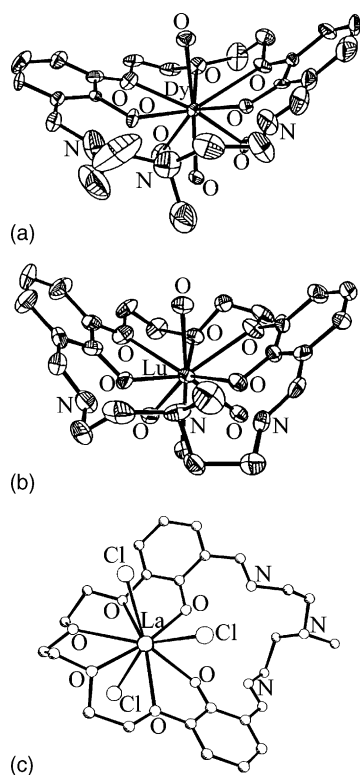
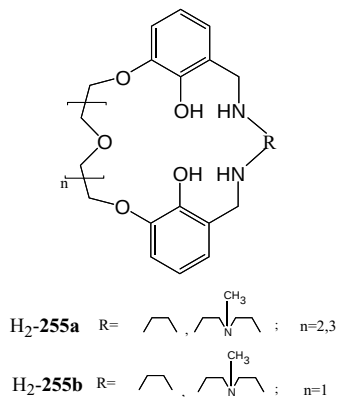


Fig. 146. Structure of $[\text{Dy}(\text{H}_2\text{-254b})(\text{H}_2\text{O})_4]^{3+}$ (a), $[\text{Lu}(\text{H}_2\text{-254b})(\text{H}_2\text{O})_4]^{3+}$ (b) and $[\text{La}(\text{H}_2\text{-254b})(\text{Cl})_3]$ (c) (adapted from Refs. [305,306]).

with Na^+ , again form the hetero-dinuclear complexes $[\text{MNa}(\mathbf{254})(\text{CH}_3\text{COO})]^+$ [306].

Analogously the reduced [1+1] macrocycles $\text{H}_2\text{-255a}$ and $\text{H}_2\text{-255b}$, obtained by reduction with NaBH_4 of the related Schiff bases $\text{H}_2\text{-254a}$, and $\text{H}_2\text{-254b}$, react with copper(II), nickel(II) or cobalt(II) acetate to form $[\text{M}(\mathbf{255})]$ or $[\text{M}(\text{H}_2\text{-255})(\text{CH}_3\text{COO})_2]$.



The manganese(III) complexes $[\text{Mn}(\mathbf{207})(\text{RCOO})]$ have been prepared by the reaction of the ligands $\text{H}_2\text{-207}$ with a stoichiometric quantity of the appropriate manganese(II) carboxylate salt in ethanol under aerobic conditions [307].

$[\text{Mn}(\mathbf{207e})(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$ (Fig. 147a) consists of a manganese(III) center bonded in the equatorial plane by the tetradentate Schiff base. The axial coordination sites of the manganese ion are filled by a water molecule and a unidentate acetate ligand. This mode of coordination of the carboxylate anion was also observed in $[\text{Mn}(\mathbf{207e})(\text{C}_2\text{H}_5\text{COO})]$ and $[\text{Mn}(\mathbf{207e})(\text{C}_4\text{H}_9\text{COO})]$, and this perhaps accounts for the unusual similarity in the fragmentation pattern observed in the FAB mass spectra of these complexes.

With the exception of *i*-propylcarboxylate (*i*-PrCOO) and *t*-butylcarboxylate, (*t*-BuCOO) the carboxylate is always coordinated in the unidentate mode when a methoxy group is ortho to the phenolic oxygen donor.

Both complexes $[\text{Mn}(\mathbf{207d})(t\text{-BuCOO})]$ and $[\text{Mn}(\mathbf{207d})(i\text{-PrCOO})]$ were found to exist as monomeric species in which the Schiff base ligand affords *cis* sites at the manganese(III) center for bidentate chelation of the carboxylate ligands. They consist of extremely distorted octahedral centers (Fig. 147b) [307].

For $[\text{Mn}(\mathbf{207e})(\text{C}_6\text{H}_5\text{CH}_2\text{COO})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, as in $[\text{Mn}(\mathbf{207e})(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$, the coordination sphere of the octahedral manganese center consists of the tetradentate Schiff base ligand in the equatorial plane, with the axial sites filled with the unidentate carboxylate and a water molecule (Fig. 147c). Also $[\text{Mn}(\mathbf{207d})(\text{C}_6\text{H}_5\text{CH}_2\text{COO})(\text{H}_2\text{O})]$ is a monomeric species with a coordination polyhedron similar to that of the other complexes [307].

The addition of *o*-vanillin to an excess of *N,N'*-bis(3-aminopropyl)ethylenediamine in CH_2Cl_2 and in the presence of MgSO_4 affords $[\text{Mg}(\mathbf{207i})]$ where the magnesium-

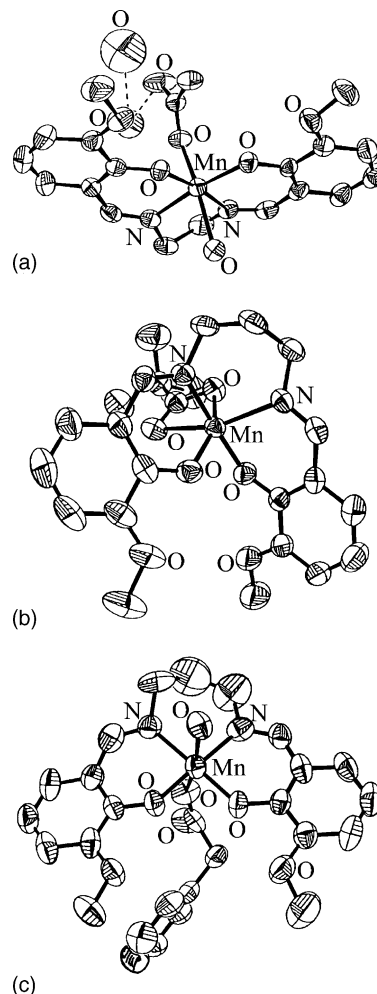


Fig. 147. Structure of $[\text{Mn}(\mathbf{207e})(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$ (a), $[\text{Mn}(\mathbf{207d})(t\text{-BuCOO})]$ (b) and $[\text{Mn}(\mathbf{207e})(\text{C}_6\text{H}_5\text{CH}_2\text{COO})(\text{H}_2\text{O})]$ (c) (adapted from Ref. [307]).

m(II) ion, coordinated inside the Schiff base O_2N_4 site of the compartmental Schiff base $[\mathbf{207i}]^{2-}$, exhibits an octahedral geometry surrounded by four nitrogen atoms in an equatorial plane and two axial oxygen atoms (Fig. 148a). The nearest structural analogue to the magnesium(II) compound is a positively charged gallium(III) complex $[\{1,12\text{-bis}(2\text{-hydroxy-3-methoxybenzyl})\text{-1,5,8,12-tetraazadodecane}\}\text{gallium(III)}]$, $[\text{Ga}(\mathbf{207i}')^+]$, a potent antimalarial agent which selectively targets chloroquinone-resistant organisms and is capable to inhibit directly heme polymerization, [308]. $\text{H}_2\text{-207i'}$, obtained through in situ potassium tetrahydroborate reduction of $\text{H}_2\text{-207i}$, forms $[\text{Ga}(\mathbf{207i}')^+]$ when dissolved in methanol and treated with the hydrated gallium(III) perchlorate. Crystals, grown through slow evaporation of methanol over a period of 2–3 days, show the gadolinium(III) ion is six coordinated in the N_4O_2 compartment involving two phenolate oxygens and four amine nitrogens providing overall octahedral geometry. A minimally distorted octahedral geometry about the central metal ion was found (Fig. 148b) [308].

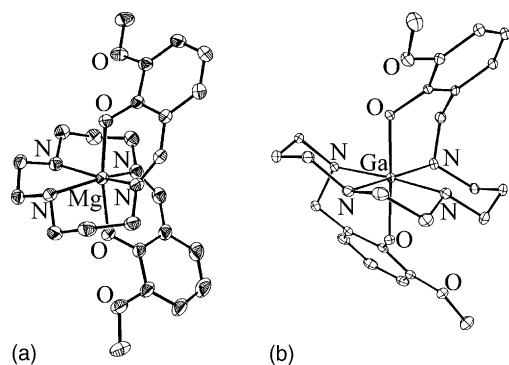


Fig. 148. Structure of $[\text{Mg}(\mathbf{207i})]$ (a) and $[\text{Ga}(\mathbf{207i})]^+$ (b) (adapted from Ref. [308]).

As above reported metallocycles containing an immobilized uranyl(VI) cation have been obtained by a barium(II) templated macrocyclization in methanol of the appropriate dialdehyde and diamine, followed by demetalation of the barium salt with uranyl acetate. The cavity thus created can be occupied by small neutral molecules, which can coordinate to the uranyl cation. The uranyl cation provides a fifth coordination site in the equatorial plane.

The similar uranyl(VI) complexes $\text{UO}_2(\mathbf{254}) \cdot n\text{S}$ have been obtained by reaction of the cyclic Schiff base $\text{H}_2\text{-254}$ with $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in boiling ethanol. Alternatively a template procedure has been used to produce the same uranyl complexes [309]. The linear UO_2^{2+} group coordinates the Schiff base moiety of these ligands: the usual equatorial pentacoordination about the metal ion is reached by the N_3O_2 or N_2O_2 donor set; in this last case a solvent molecule completes the coordination sphere. In the IR spectra of the complexes a very strong band at $1625\text{--}1620\text{ cm}^{-1}$, due to $\nu\text{C}=\text{N}$ can be detected. The presence of the uranyl(VI) group can be easily ascertained by the strong IR band at $915\text{--}890\text{ cm}^{-1}$ due to the $\nu_3\text{ O-U-O}$. No bands due to the presence of acetate groups have been observed. ^1H and ^{13}C NMR spectra corroborate the proposed structures. As an example the ^{13}C NMR spectra of $\text{UO}_2(\mathbf{254b})$ where $\text{R} = (\text{CH}_2)_2\text{NCH}_3(\text{CH}_2)_2$ in $(\text{CD}_3)_2\text{SO}$ at 298 K consists of twelve resonances, five in the aliphatic region and seven in the chemical shift range 115–171 ppm. The degeneracy of the spectra could be explained by a dynamic process which averages the signals of pairs of atoms, in solution on the NMR time scale. Alternatively the complex could be extremely rigid with a planar structure where the ligand has C_{2v} symmetry around the metal ion. More information is provided by the proton spectra which consist of ten resonances: a singlet at low field (relative intensity 1; $\delta = 9.5\text{ ppm}$) for the imino proton, two multiplets in the aromatic region (2.1; 6.6–7.2 ppm), a triplet and a doublet of doublets (1:1, 3.7–3.5 ppm) a multiplet (2; $\sim 4.1\text{ ppm}$), a triplet (2; 4.0 ppm) a triplet and a doublet of doublets (1:1, 3.7–3.5 ppm) and a singlet (1.5; $\delta = -3.1\text{ ppm}$) easily attributable to the methyl group. The complete assignment of the peaks was possible based on a 2D NOESY experiment. At 298 K and by using a

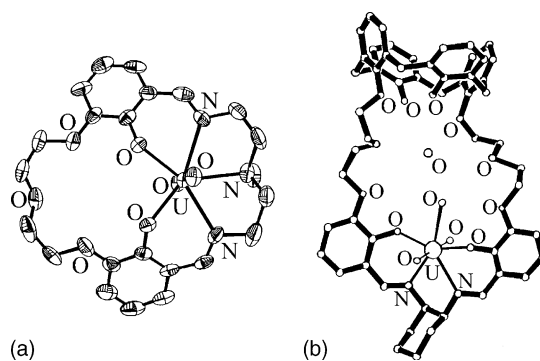


Fig. 149. Structure of $[\text{UO}_2(\mathbf{254b})]$ ($\text{R} = \text{CH}_2\text{CH}_2\text{NCH}_3\text{CH}_2\text{CH}_2$) (a) and $\mathbf{262c} \cdot 2\text{H}_2\text{O}$ (b) (adapted from Refs. [309,312]).

mixing time of 300 ms cross peaks were detected between the protons peak and the resonance at 7.2 and 4.5 ppm, thus allowing the discrimination between the protons of the ethylenediamine group. Finally, a heteronuclear 2D COSY experiment at 298 K has provided the basis for the assignment of the ^{13}C NMR spectra. The low flexibility of the macrocycle in DMSO at room temperature is clearly revealed by the presence in the proton spectra of two triplets and two doublets (ABCD pattern) for the geminal protons of the ethylenediamine groups and of the multiplet and the triplet for the diether bridges originating from a slow conformational interchange. The ethylenediamine groups are extremely rigid, in fact the ethylenic protons can be identified as axial protons (triplets at 5.1 and 3.7 ppm) and equatorial protons (doublet of doublets at 4.5 and 3.5 ppm). This rigidity can be assumed only with the coordination of the uranyl ion in the N_3O_2 cavity of the macrocycle. Thus the NMR spectra are consistent with the presence in solution of a time-averaged planar structure of the complexes of symmetry C_{2v} resulting from rearrangement of the ligand about the metal ion. Despite the similar Ln spectra with the same ligand the NMR spectra of the uranyl complex provide precise information about the coordination mode and position of the metal ion.

The X-ray structure of $[\text{UO}_2(\mathbf{254b})]$ (Fig. 149a) confirms the NMR data, demonstrating that the uranyl(VI) ion is firmly coordinated into the N_3O_2 Schiff base chamber in an equatorial pentagonal environment.

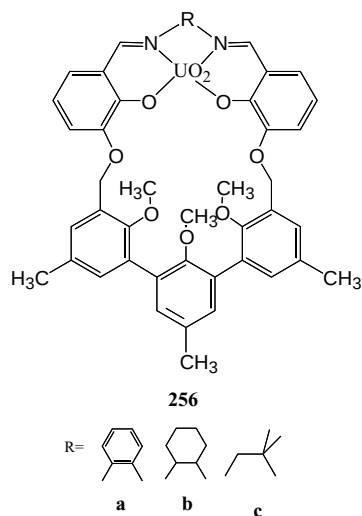
Thus the availability of a series of similar asymmetric cyclic systems, where the two chambers have been progressively enlarged allows one to verify the selectivity of the Schiff base and crown-ether site towards uranyl(VI) ion. Even when employing different synthetic pathways, UO_2^{2+} always prefers the N_2O_2 or N_3O_2 Schiff base site [309,310], in contrast to other 4f metal ions which invariably coordinate in the crown-ether chamber.

When $\text{H}_2\text{-254}$ ($\text{R} = \text{CH}_2\text{CH}_2$) containing a tetradentate N_2O_2 Schiff base site is used, the equatorial pentacoordination environment about UO_2^{2+} offers the possibility to complex neutral molecules. Usually, these complexes are obtained with a solvent molecule filling the cavity. By

introducing different guest molecules that can coordinate to the uranyl ion it is possible to replace the solvent molecule giving rise to $[\text{UO}_2(\mathbf{254})(\text{guest})]$ [309]. Acetone, formamide, acetamide, *N*-methylurea and urea are not able to substitute the water when $n = 2$. Acetone does not substitute water also when the cavity is enlarged while the other solvent do this; the association constant determined by polarography in acetonitrile depends on the ring-size and on the guest used [309].

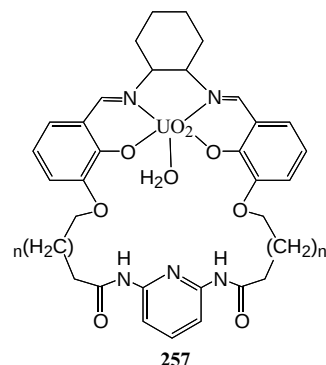
The transmetallation reaction was used for the synthesis of the compounds **109a–c**. Association constants of the complex **109b** determined by ^1H NMR titration experiments in acetonitrile- d_3 , for *n*-propylamine, *n*-butylamine, and *n*-pentylamine are 200, 527 and 966 M^{-1} , respectively. The CH_3 groups of *n*-butylamine and *n*-pentylamine reveal upfield shifts upon complexation. These CH_3 groups are in the shielding zone of the pyridine ring and π – σ attractions are probably responsible for the increase of the complex stability.

The preorganized metallomacrocyclic **256** has been synthesized with different diamines in the N_2O_2 Schiff base unit. The electrophilic UO_2^{2+} cation in combination with a preorganized terphenyl moiety, having additional binding sites, make these compounds selective receptors for NH_3 over primary amines. The selectivity of **256** for ammonia over benzylamine ($K_{\text{ass}}(\text{NH}_3):K_{\text{ass}}(\text{BzNH}_2)$) is 33. ^1H NMR studies with host **256** in CDCl_3 with excess of NH_3 shows the free NH_3 at δ 0.75 ppm and the 1:1 complexed ammonia as a broad singlet at δ 4.10 ppm.

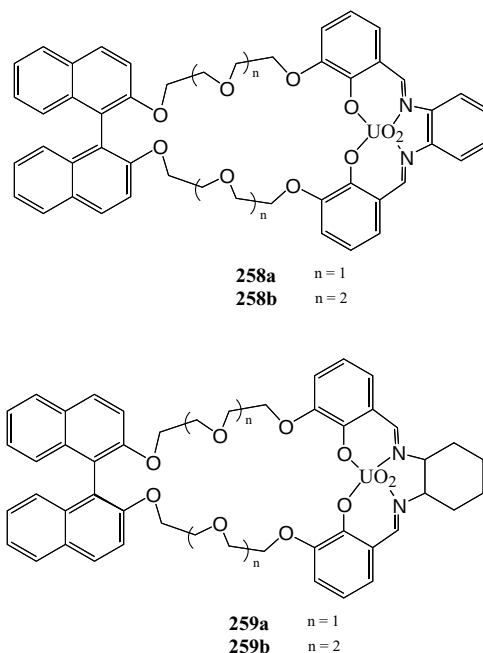


257 has been designed for the complexation of barbiturates. The synthesis was accomplished by barium(II)-templated macrocyclization of the appropriate dialdehyde and *cis*-1,2-cyclohexanediamine, followed by reaction with uranyl acetate. ^1H NMR experiments in CDCl_3 revealed that intramolecular self-complexation takes place and a constant $K_{\text{self-ass}}$ for this process of **257** has been estimated. The association constants of three barbiturates could be determined by ^1H NMR titrations in a mixture of CDCl_3 and $\text{DMSO}-\text{d}_6$ (95:5). The association constants of dimethyl,

diethyl, and ethylphenyl barbituric acid are 112, 97, and 45 l mol^{-1} , respectively. It is obvious that a sterically more demanding barbiturate results in a lower association constant. The host **257** is able to transport barbituric acid through a supported liquid membrane (SLM; *o*-nitrophenyl *n*-octyl ether as solvent with dissolved carrier in a porous polymer support). A flux 3.7 times higher than the blank was observed.

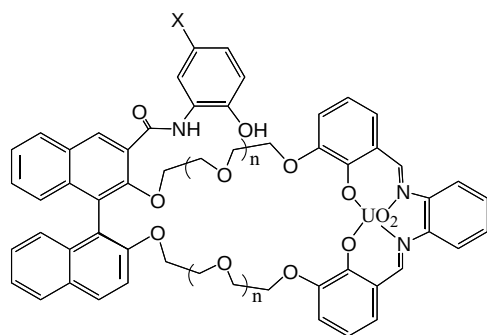


The synthesis of **258** and **259** has been carried out according to the strategy described above with the aim to recognize urea. Solid urea complexes have been isolated by allowing solutions of urea in methanol and **258** and **259** in CH_2Cl_2 to mix by diffusion. IR and FAB mass spectrometry prove that the guest urea is coordinated through the oxygen atom. Urea transport through supported liquid membrane increased by a factor of 14 using **258a** and **258b** as carriers. The carrier **258a** is selective for urea over *N*-methylurea ($\text{flux}_{\text{urea}}/\text{flux}_{\text{N-methylurea}} = 8.2$) [311].

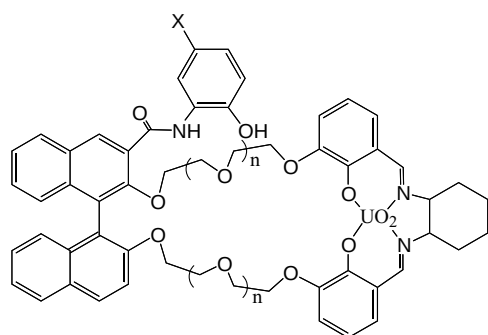


A convergent multi-step synthesis has been developed for the introduction of functional groups at the 3-position of the binaphthyl moiety (**260** and **261**) [311]. By ^1H NMR studies it has been shown that **260a** is present in two forms. One form

is the water complex and the other is the complex with an intramolecular coordination of the hydroxyl moiety to the uranyl cation.

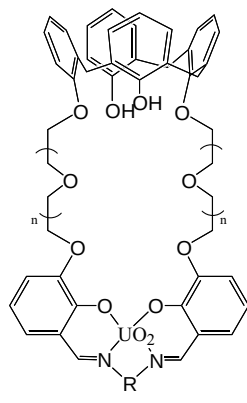


260a $n = 1$
260b $n = 2$



261a $n = 1$
261b $n = 2$

Calix[4]arene have been used as platform for the synthesis of uranyl containing metallocycles (**262a–d**) [312]. The use of calix[4]arene allows an easier introduction of functional groups than the binaphthyl moiety. The crystal structures clearly show the coordination of the guest to the uranyl group. In the structure of **262c**·2H₂O the cavity is filled by a second water molecule which is most likely hydrogen bonded to the host and the other water (Fig. 149b).



262a $R = C_6H_4$ $n = 1$
262b $R = C_6H_4$ $n = 2$
262c $R = C_6H_{10}$ $n = 1$
262d $R = C_6H_{10}$ $n = 2$

In particular, the uranyl(VI) calix[4] based Schiff base crown ether complexes **262a–d**, prepared by template condensation of the appropriate diformyl and diamine precursors in the presence of UO_2^{2+} as templating agent, are lipophilic carriers for neutral molecules [312].

The X-ray structure of the CH₃OH and (CH₃)₂SO complexes of **262a**, obtained by crystallization of **262a** from hot CH₃CN or by diffusion respectively of CH₃OH or (CH₃)₂SO into a solution of **262a**·2H₂O in CH₂Cl₂, shows the usual pentacoordination geometry about the uranyl(VI) group, the fifth equatorial position being filled by one molecule of CH₃OH or (CH₃)₂SO.

As reported in a previous section these complexes have also been used as anion receptors. Thus the uranyl complex **196**, prepared by condensation in methanol of 3-methoxy-2-hydroxy benzaldehyde and 1,2-diaminobenzene in the presence of $UO_2(CH_3COO)_2 \cdot 2H_2O$, reacts with tetrabutylammonium dihydrogen phosphate $[N(Bu)_4][H_2PO_4]$ to form the Schiff base complex $[N(Bu)_4][(196)(H_2PO_4)]$ [313]. In this complex the uranium(VI) ion has an approximate pentagonal bipyramidal coordination, with the two oxygens in apical positions. In the equatorial plane, the fifth coordination position is occupied by an oxygen atom of the dihydrogen phosphate ($H_2PO_4^-$) anion in addition to coordination with the two nitrogens and two oxygens of the Schiff base moiety. In the solid state the complexes are arranged in centrosymmetric pairs (Fig. 150). The core of the dimer consists of two $H_2PO_4^-$ anions which are connected by two short H-bonds. Another H-bond is formed between the $H_2PO_4^-$ anion and a methoxy oxygen of the salophene moiety [313].

In order to obtain anion receptors which contain a combination of both UO_2^{2+} cation and C(O)NH amido functionalities as additional binding sites, the uranyl(VI) complexes **197** have been prepared by template procedure [309,313].

The structure of **197b** contains two independent molecules in the asymmetric unit. The fifth position of the UO_2^{2+}

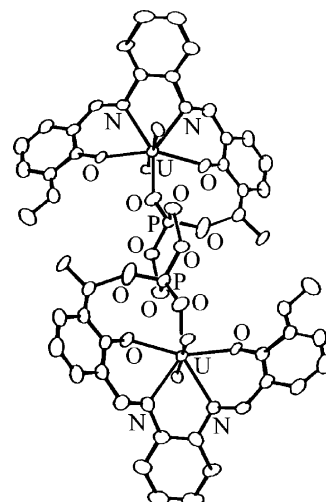
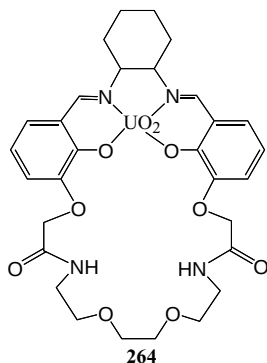
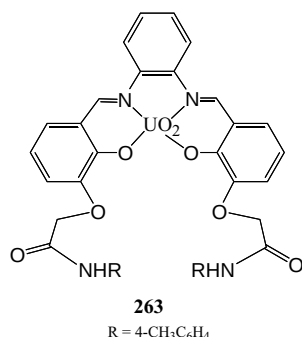


Fig. 150. Structure of $[(196)(H_2PO_4)]_2^{2-}$ (adapted from Ref. [313]).

cation is filled by an oxygen atom of the amide group of a second molecule. In this way, molecules are organized in the solid state as dimers (Fig. 151a). The FAB mass spectrum of **197b** also shows dimer formation, with an intense molecular dimer peak.

The further reaction of these complexes with $[\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$ gives rise to complexes which recognize H_2PO_4^- as confirmed by the structure of **263** with $[\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$ where the $[\text{H}_2\text{PO}_4]^-$ anion is tightly complexed to the UO_2^{2+} center in addition to a H-bond formation with the acetoxy oxygen of the salene moiety (Fig. 151b). However, in this case two additional H-bonds between the amido groups of the ligand and the complexed anion are present which clearly shows the participation of CONH fragments in anion complexation. The H_2PO_4^- complexed to the UO_2^{2+} cation forms a H-bonded associate with the second H_2PO_4^- anion which in this case is not complexed itself by ligand **263**.



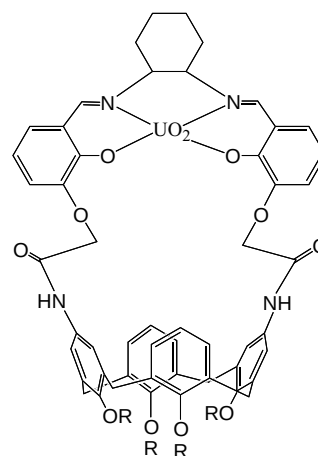
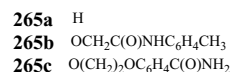
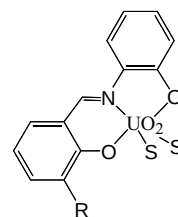
The complex **264** has been obtained by cyclization of the appropriate dialdehyde with *cis*-1,2-cyclohexanediamine in the presence of $\text{Ba}(\text{CF}_3\text{SO}_2)_2$ as a template followed by addition of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ [314].

The stirring of a mixture of **196**, **197a**, **197b**, **263** or **264** and $[\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$ in CH_3CN overnight followed by evaporation of solvent gave the corresponding complex as an orange powder. In the ^1H NMR spectra of all complexes, significant changes of the host were found for the NH amido, the $\text{HC}=\text{N}$, and the $\text{CH}_2\text{C}(\text{O})$ signals which clearly indicate the presence of a guest anion in the cavity. In the ^{31}P NMR spectra of H_2PO_4^- complexes with **196**, **197a**, **197b**, and **264**,

signals of H_2PO_4^- are shifted downfield ($\Delta\delta = 1.9$ – 2.3 ppm) in comparison with free H_2PO_4^- .

In these complexes the uranyl(VI) ion contains only one vacant position; uranyl(VI) complexes where two vacant coordination site for complexation guest are available (**265**) have been prepared by reaction of the corresponding aldehydes (6-substituted-1-hydroxy-2-formylbenzene), *o*-aminophenol, and $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in refluxing CH_3OH . The coordination sphere about the uranyl(VI) group is completed by CH_3OH or H_2O molecules.

Orange crystals **265a** with $[\text{NBu}_4][\text{H}_2\text{PO}_4]$, grown by slow diffusion of diisopropyl ether into a solution of **265a** and a two-fold excess of $[\text{NBu}_4][\text{H}_2\text{PO}_4]^-$ in CH_3CN , show that binding of two H_2PO_4^- anions takes place. Again phosphate anions form H-bonded dimers with phosphates complexed by another molecule of **265a**. At the same time, due to the unique fact that two phosphates are complexed by the UO_2^{2+} cation, molecules of complex $[\text{265a}(\text{H}_2\text{PO}_4)_2]^{2-}$ are organized as a H-bonded ribbon [314].



In the case of the preorganized systems **197b**, **197d**, and **264**, strong ($K_{\text{ass}} > 10^5 \text{ M}^{-1}$ in CH_3CN – DMSO , 99:1) and selective complexation of H_2PO_4^- has been observed. Selectivities of >102 and >103 over Cl^- and HSO_4^- , NO_2^- , and SCN^- , respectively, were obtained for **197b**. The uranyl(VI) complexes **265a**–**c**, in which the Lewis acidic binding center contains two vacant positions for guest coordination, have been designed for complexation of dianions like malonate and succinate with K values of 80 – 460 M^{-1} in DMSO [314].

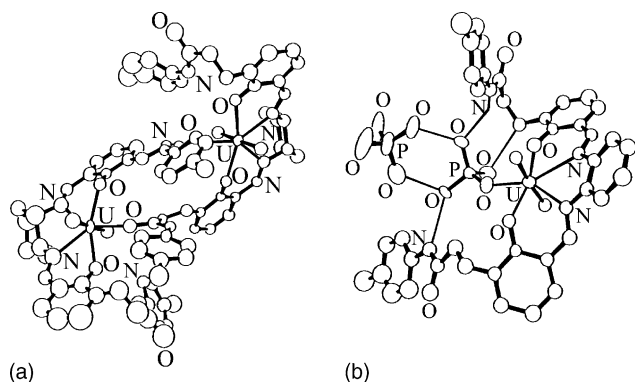


Fig. 151. Structure of [(197b)₂] (a) and [(263)(H₂PO₄)]·(H₂PO₄)₂²⁻ (b) (adapted from Ref. [313]).

The simultaneous complexation of the difunctional uranyl Schiff base complex **199** with cations and with anions was investigated by ¹H NMR spectroscopy, cyclic voltammetry, FAB mass spectrometry and liquid–liquid extraction experiments [313,316]. The complexation of tetrabutylammonium dihydrogen phosphate and potassium picrate was tested, because UO₂²⁺-containing clefts complex H₂PO₄⁻ and bis-[benzo[15]crown-5]ethers bind K⁺ with a high degree of selectivity [313,316].

In dilution experiments with solutions of **199** and [NBu₄][H₂PO₄] in DMSO-d₆ the ¹H NMR signals of the HC=N groups of both the free and complexed ligand were observed at δ = 9.51 and 9.46, respectively. From this experiment an association constant *K*_{ass} of 1.1 × 10³ M⁻¹ was calculated. The contribution of the C(O)NH...H₂PO₄⁻ hydrogen bond to the overall anion complexation can clearly be observed in the ¹H NMR spectrum even in DMSO-d₆ as a solvent, since the N–H signals of the free and complexed **199** appear at δ = 10.47 and 11.21, respectively.

Complexation of K⁺ ions by **199** was studied by picrate (Pic) extraction experiments. For the 1:1 complex [K(**199**)](Pic) a value of log *K*_{ex} = 5.3 was obtained in chloroform [316].

Liquid–liquid extraction (CHCl₃/H₂O) of KH₂PO₄ with the difunctional receptor **199** resulted in 15–20% complex formation (**199**·KH₂PO₄) in the organic phase (according to ¹H NMR spectroscopy). At the same time no extraction of KH₂PO₄ was observed with functionalized UO₂-containing clefts that do not contain cationic binding sites [316].

The complexation of K⁺ and H₂PO₄⁻ ions by **199** was also investigated by cyclic voltammetry in DMSO with 2% HCl and with tetrabutylammonium tetraphenylborate as a supporting electrolyte. Addition of [NBu₄][H₂PO₄] to a solution of **199** causes a clear shift of both cathodic and anodic peaks toward more negative potentials. This effect is accompanied by a systematic increase in the peak separation, from 85 to 100 mV, and by a decrease of the normalized peak heights. These results suggest that a labile, redox-inactive complex is formed with H₂PO₄. Assuming the formation of a 1:1 complex, a *K*_{ass} value of 1.3 ×

10³ M⁻¹ for H₂PO₄⁻ is obtained, which is in a good agreement with the ¹H NMR measurements.

Upon addition of potassium tetraphenylborate to a solution of **199** in DMSO the electrochemical behavior did not change, probably since the crown ether moieties in **199** are situated rather far from the redox-active UO₂²⁺ center. However, an indirect procedure for the determination of complexation constants based on competition between TI⁺ and K⁺ ions gave a *K*_{ass} value of 1.0 × 10² M⁻¹ for K⁺ [313,315,316].

Finally the FAB mass spectrum of the 1:1 complex of receptor **199** and KH₂PO₄, prepared by mixing the host and guest in acetonitrile with 10% water and evaporating the solvent, indicates an intense peak corresponding to [**199** + K⁺]⁺. The corresponding FAB⁻ mass spectrum of the same sample yielded an intense peak for [**199** + H₂PO₄⁻]⁻, while a signal for [**199** + H₂PO₄⁻ + K⁺]⁺ is also present, which clearly proves the complexation of the salt. These data show a significant transport of KH₂PO₄ as a hydrophilic potassium salt through a supported liquid membrane with receptor **199**.

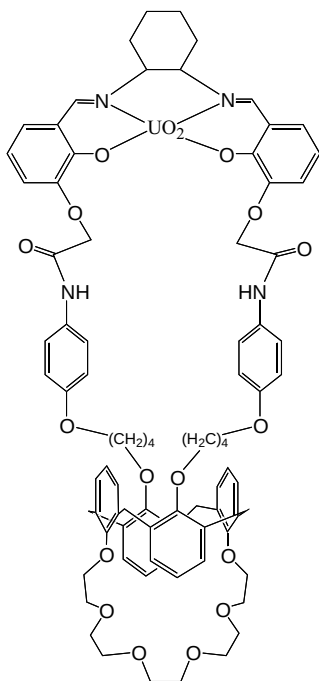
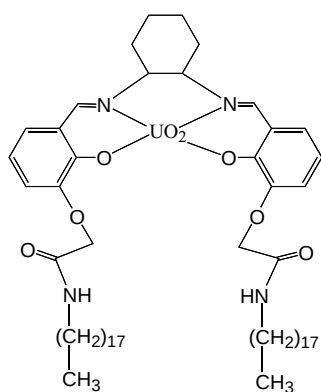
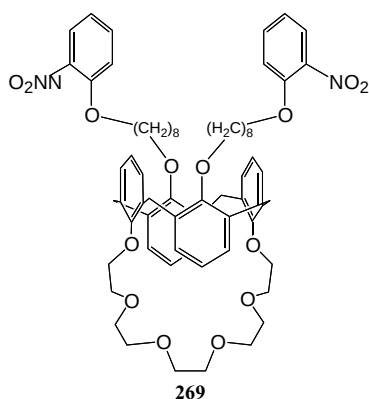
The bifunctional uranyl(VI) complexes **266a** and **266b** contain a calix[4]arene moiety, and a combination of a UO₂²⁺-Lewis acidic center and C(O)NH groups; **266b** contains also four preorganized ester fragments which are known to complex alkali metal cations with a high selectivity for Na⁺ [317]. **266a** and **266b** selectively bind dihydrogen phosphate [H₂PO₄⁻]. From ¹H NMR dilution experiment with [NBu₄][H₂PO₄] in DMSO-d₆ association constants *K*_{ass} of 3.5 × 10² M⁻¹ and 3.9 × 10² M⁻¹ were calculated for **266a** and **266b**, respectively. The contribution of the C(O)NH...H₂PO₄⁻ hydrogen bond interaction to the overall anion complexation can be clearly seen even in polar DMSO-d₆ from a significant downfield shift of the C(O)NH protons of ca. 0.4 ppm upon complexation. Only slight shifts were observed upon dilution experiments with tetrabutylammonium salts of Cl⁻, HSO₄⁻ and ClO₄⁻ anions which indicates their weak binding (*K*_{ass} < 10 M⁻¹) [317].

In the negative FAB mass spectra of the 1:1 complexes of **266a** and **266b** with [Bu₄N][H₂PO₄], prepared by mixing of host and guest in CH₃CN, intense peaks corresponding to [**266** + H₂PO₄⁻]⁻ and [**266b** + H₂PO₄⁻]⁻, respectively, were observed. Moreover, in the positive FAB mass spectrum of the 1:1 complex of **266b** and NaH₂PO₄, prepared by mixing of host and guest in CH₃CN-H₂O, 10:1, an intense peak corresponding to [**266b** + Na⁺]⁺ was observed, while the corresponding negative FAB mass spectrum of the same sample yielded an intense peak for [**266b** + H₂PO₄⁻]⁻, which proves the complexation of both cation and anion in one bifunctional receptor molecule [317].

The simultaneous transport of cations and anions through a supported liquid membrane was successfully carried out with the aid of the bifunctional receptor [318]. The synthetic strategy is based on the attachment of both cation and anion binding sites to the rigid lipophilic calix[4]arene platform.

267 has been used as a carrier to investigate the transport of hydrophilic CsCl and the more lipophilic CsNO₃ across a

supported liquid membrane composed of a porous polymeric support (Accurel) impregnated with *o*-nitrophenyl-*n*-octyl ether. For comparison, the same experiment was performed with the receptors **268** and **269**, which have only either anion or cation binding sites, respectively.

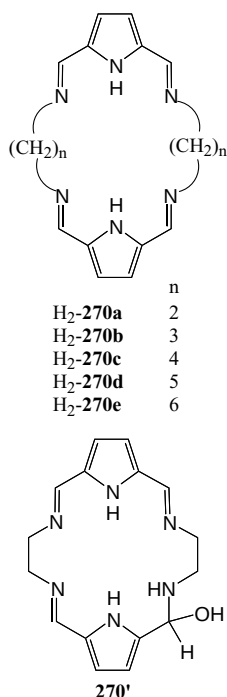
**267****268****269**

The transport processes for CsNO_3 and CsCl are different; NO_3^- is much more lipophilic than Cl^- , and only NO_3^- can easily follow the complexed Cs^+ cation through the hydrophobic membrane, even in the absence of anion carrier. With the cation carrier **269**, a high flux of CsNO_3 ($5.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$) was observed, but the anion receptor **268**, which is not selective for NO_3^- , did not transport CsNO_3 . The flux was very low ($0.02 \times 10^{-1} \text{ mol m}^{-2} \text{ s}^{-1}$) and comparable with the (blank) flux obtained without carrier. Most likely in the case of **269**, only the cation binding site is responsible for the transport.

The transport of CsCl by the monofunctional carriers **268** (anion) and **269** (cation) exhibits low flux values of 0.07×10^{-7} and $0.42 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, respectively. Obviously, when one of the ionic species is complexed, the uncomplexed counterion cannot sufficiently penetrate the lipophilic membrane. However, a significant flux ($1.20 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$) was observed for bifunctional carrier **267** with CsCl , which is much higher than the corresponding fluxes for the monofunctional carriers **268** and **269**. At the same time, carrier **267** showed a surprisingly low flux of CsNO_3 ($0.89 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$) when compared with that observed for cation receptor **269** ($5.50 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$). Thus it was suggested that both anion and cation binding sites of **267** are involved in the complexation and the presence of only an anion or a cation binding site in the receptor molecule is not sufficient for effective transport of a hydrophilic salt such as CsCl . Also this suggests a preference of hydrophilic CsCl over lipophilic CsNO_3 [318]. These results indicate the unique feature of receptors in which both binding sites are covalently linked.

7.4. Macrocyclic complexes derived from 2,5-diformylpyrrole or superior homologues and related systems

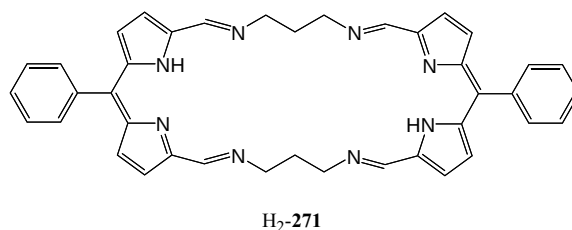
Considerable effort has been devoted to pyrrole containing complexes. Mononuclear and homo-dinuclear copper(II) complexes of macrocyclic Schiff bases have been derived from the condensation of pyrrole-2,5-dicarbaldehyde and α,ω -alkanediamines [319]. In particular μ -alkoxy-bridged copper(II) complexes of pyrrole-2,5-dicarbaldehyde were prepared by reaction of copper(II) acetate, an alcoholic solution of pyrrole-2,5-dicarbaldehyde and a slight excess of KOH. The subsequent reaction of these μ -alkoxy copper(II) complexes with 1,2-diaminoethane or 1,3-diaminopropane forms the related [2+2] macrocyclic complexes [Cu(**270**)] as confirmed by an X-ray structural determination of [Cu(**270b**)] [319]. The copper(II) ion is accommodated at one end of the macrocycle where it is bonded to two pyrrole and two imino nitrogen atoms in a coordination geometry which has a tetrahedral distortion from square planar. Both pyrrole-dicarbimine fragments adopt *cis-trans* conformations of the carbimine fragments. The macrocycle is twisted with the major twist occurring in the region remote from the coordinated copper ion (Fig. 152a).



The use of longer chain diaminoalkanes led to the preparation of the methoxy-bridged dicopper(II) complexes $[Cu_2(270c-e)(OCH_3)_2]$ [319].

Dinuclear complexes were obtained when larger [2+2] Schiff bases (i.e. H_2-271) have been used, as confirmed by the structure of the dimanganese(II) complex $[Mn_2(271)-(CH_3COO)_2(H_2O)]$, prepared by condensation of 2,2'-benzyl-5,5'-diformyldipyrrole and 1,3-diaminopropane in the presence of manganese(II) acetate. The macrocycle is in the dipyrromethene form, which means that the diformyldipyrromethane reactant oxidizes during the course of the Schiff base reaction. Upon complex formation, two of the pyrrole nitrogens deprotonate resulting in a dianionic ligand. The structure (Fig. 152b) reveals a dinuclear metal site with a $Mn \cdots Mn$ separation of 5.40 Å. Each dipyrromethane frag-

ment is coordinated to a manganese ion in a planar fashion and the two planes are almost perpendicular to each other. One acetate forms a *cis, anti* bridge between the two metal ions, while the other is weakly chelated to one of the manganese(II) ions. Additionally, one water molecule is bound to Mn(1) which thus maintains a distorted octahedral geometry and Mn(2) forms a distorted pseudo-seven coordinate complex. The complex catalyzes the disproportionation of H_2O_2 making it a functional model for dimanganese catalase [319].



[2+2] Tetraimine macrocyclic uranyl(VI) complexes **272a–c** and **273** have been prepared in the presence of uranyl(VI) nitrate via a metal template condensation between 3,4-diethyl-2,5-dicarbaldehyde and ethylenediamine, 1,3-propanediamine or 4,5-diamino-1,2-dimethoxybenzene, respectively. This last complex was also prepared by treating the preformed Schiff base with $UO_2(NO_3)_2$ in a methanol/dichloromethane solution and in the presence of N,N,N',N' -tetramethyl-1,8-naphthalenediamine, added to prevent the formation of the dinitrate ligand. These complexes are highly soluble in chloroform and dichloromethane but insoluble in more polar solvents such as H_2O , CH_3OH , and C_2H_5OH [320].

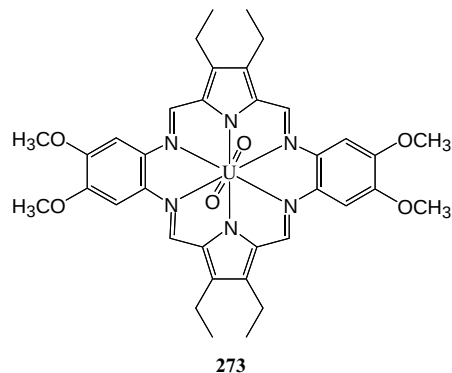
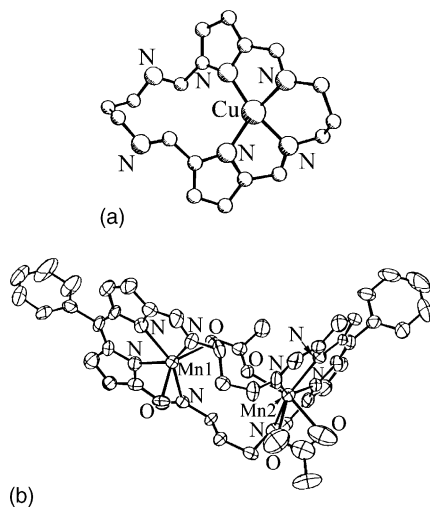
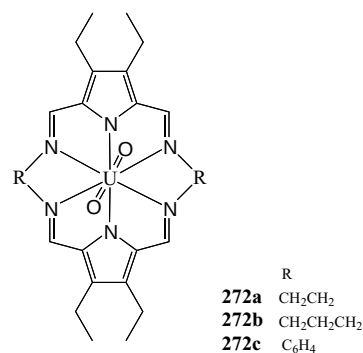


Fig. 152. Structure of $[Cu_2(270b)]$ (a) and $[Mn_2(271)(CH_3COO)_2(H_2O)]$ (b) (adapted from Ref. [319]).

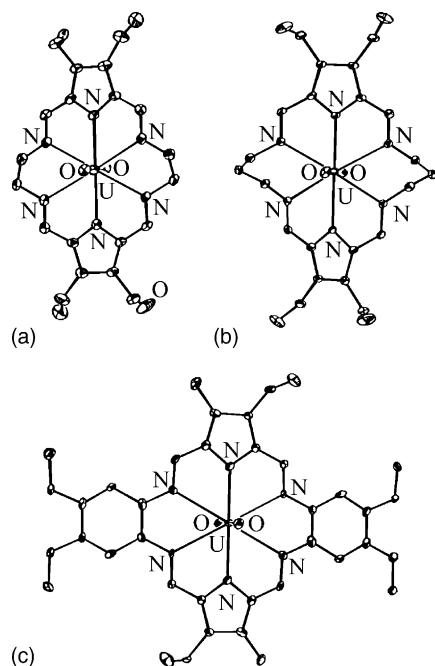


Fig. 153. Structure of **272a** (a), **272b** (b) and **273** (adapted from Ref. [320]).

In **272a** and **272b** derived from 1,2-diaminoethane and 1,3-diaminopropane the uranyl(VI) cation is bound to all six nitrogen atoms, however in a non-planar fashion, in a distorted hexagonal bipyramidal environment (Fig. 153a and b). The ring size of the macrocycle in **272b** is larger than that in **272a**, the nitrogen–uranium bond lengths for **272a** and **272b** are nearly identical [320].

In **273** the uranyl cation is coordinated to the six nitrogen atoms in a planar fashion (Fig. 153c). As a result, in part, of the planarity, the coordination geometry about the uranyl(VI) ion is hexagonal bipyramidal [320].

Instead, the principal difference between **272a** and **272b** is the extent of the twist between the two nearly planar halves of the macrocycle. In **272a**, the imine–pyrrole–imine dihedral angle is 17.5° while in **272b** it is 35.7° . On the other hand, it is near 0° in the analogous complex **272c** and in **273** [320].

The uranyl complex **273** appears to be quite stable, undergoing no apparent decomposition or demetallation when stirred for several hours in a 5:1 (v/v) solution of chloroform and trifluoroacetic acid. In fact, exposure to these conditions leads solely to protonation (not demetallation) as indicated by the fact that adding triethylamine serves to regenerate quantitatively the starting complex as determined by both optical spectroscopy and FAB mass spectrometry. In addition, heating **273** to 300°C fails to effect any apparent decomposition.

272c displays two reversible oxidations at +0.82 and +1.09 V versus ferrocenium/ferrocene in CH_2Cl_2 containing $[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4](\text{PF}_6)$, while **272a** and **272b** display irreversible oxidation waves at +1.22, +1.46 and +1.22 and +1.47 V versus ferrocenium/ferrocene, respectively. **272a–c** also display quasi-reversible uranyl-centered

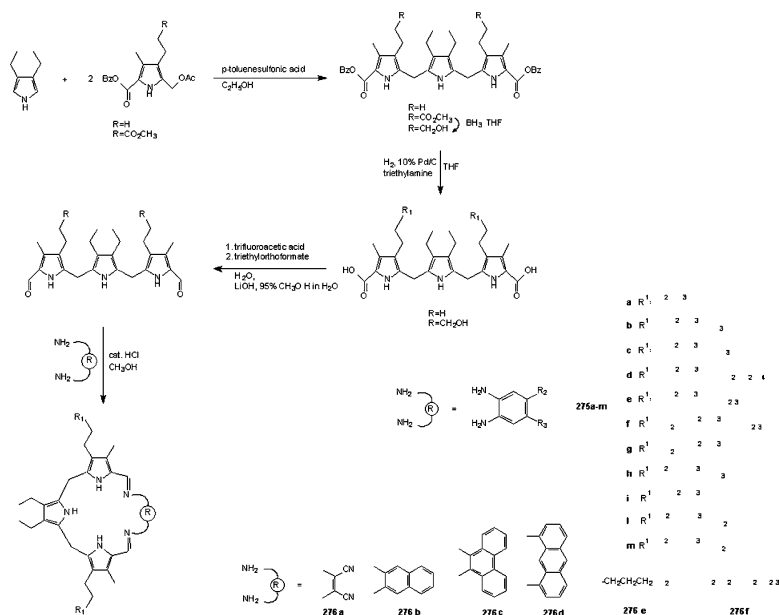
reductions at -0.85 , -1.02 , and -0.96 V versus ferrocenium/ferrocene, respectively. The anodic oxidation waves seen in the CVs for all complexes are presumed to be ligand-based oxidations. In contrast, the cathodic reduction waves for **272a–c** are presumed to involve reduction of the uranyl(VI) cation [i.e. U^{6+} to U^{4+}].

The near-reversibility of the oxidation waves for **272c** as compared to **272a** and **272b** can be rationalized in terms of complex stability under electrochemical oxidations. The presence of four electron donating methoxy substituents on the macrocyclic periphery, as well as, the π -conjugation of the ligand may impart stability to **272c**. For both **272a** and **272b**, the non-planar geometry, macrocyclic flexibility, and lack of a delocalization pathway, destabilizes them towards oxidation. Thus, these electrochemical measurements reveal a degree of increased chemical reactivity in both of these newer complexes (i.e. **272a** and **272b**) that is not present in the parent system **272c**.

The superior homologues are represented by the diformyl tripyrrane precursors **274**. The availability of their efficient synthetic methodology allows the formation of a large variety of tripyrrane-based macrocyclic Schiff bases, by acid catalyzed condensation with appropriate polyamine [321–323] (Scheme 39).

In marked contrast, however, to the dipyrane case above reported no macrocyclic products could be isolated in condensations involving the tripyrrane **274** and diamines when simple basic metal salts (e.g. $\text{Ba}(\text{CO}_3)_2$) were used as potential templates. Nor were any products isolated if the reaction was carried out in boiling benzene or CH_3OH in the absence of a catalyst. Only when an acid catalyst was present and air excluded would the condensations proceed in an acceptable manner. Even then, the yields of **275** and **276** were extremely sensitive to the reaction conditions employed. High yields can however be obtained when salts of large cations (i.e. UO_2Cl_2 and $\text{Pb}(\text{SCN})_2$) are added in stoichiometric quantities to the Schiff base condensations, provided that acid catalysis is also employed. Further treatment with base (i.e. K_2CO_3 or NaHCO_3) allows the formation of metal-free or unprotonated macrocycles [321].

The observation of a doublet for the bridging methylenes in the ^1H NMR of **275a** indicates the presence of diastereotopic protons. This suggests that compound **275a** adopts a conformation in solution in which the macrocyclic ring deviates from planarity. The nonplanar structure of **275a**·HSCN, is due to internal hydrogen bonding to the SCN^- counterion and saturated methylene bridges which preclude conjugation between the central pyrrole and the rest of the macrocycle. The nitrogen atom of the thiocyanate ion is above the mean plane of the five macrocyclic nitrogen atoms and is directed toward the macrocycle cavity. Also it is within H-bonding distance of the various N–H protons (three pyrroles and one the protonated imine). All three pyrrole rings are thus tilted toward the capping anion. Hydrogen bonding also forces pyrroles A and C out of the plane of the



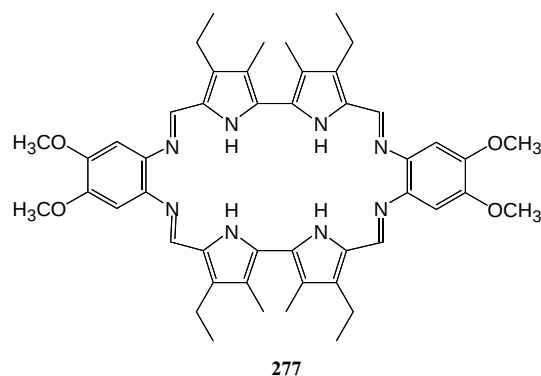
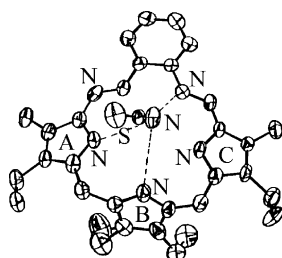
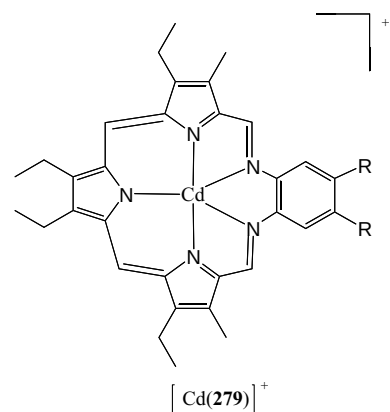
Scheme 39.

phenyl ring. The central pyrrole ring B is tilted away from the pyrrole rings A and C [321] (Fig. 154).

The anthracene-derived Schiff base [(H₂-**276d**)(X))(X) (X = Cl[−], F[−]) was similarly obtained by condensation of **274** and 1,9-diminoanthracene under acid conditions. The subsequent treatment with aqueous NaHCO₃ produces **276d**. Crystals of the diprotonated macrocycle as its mixed chloride tetrafluoroborate salt, [(H₂-**276d**)(Cl))(BF₄), were obtained by slow diffusion of diethyl ether into a solution of dichloromethane/methanol (2:1, v/v) containing [(H₂-**276d**)(Cl)]⁺ and a small excess of ethereal tetrafluoroboric acid. The core of the macrocycle contains a near mirror plane, and the two pyrrole rings A and C of the tripyrrane and the anthracene moiety lie in essentially the same plane (Fig. 155). The central pyrrole ring B is almost perpendicular to this plane; the chloride anion is bound in pseudo square-planar geometry 0.795 Å above the planar portion of the macrocycle with the four inner hydrogen atoms pointing towards it. There is also a hydrogen-bonding interaction between a fluorine atom of the BF₄[−] and the nitrogen of the central pyrrole unit [324].

The diformyl-dipyrrole 4,4'-diethyl-5,5'-diformyl-3,3'-dimethyl-2,2'-bipyrrole reacts with 1,2-diamino-4,5-

dimethoxybenzene under nitric acid catalyzed conditions to form **277**·2(HNO₃)₂, which precipitates from the reaction mixture after several minutes in near quantitative yield. The neutral ligand **277** was obtained by dissolving this salt in CH₂Cl₂ and adding a few drops of triethylamine. Attempts to prepare **277** using other acids were also made. In all cases, the yields of **277** were substantially lower than if HNO₃ were used [325].

**277**Fig. 154. Structure of **275a**·HSCN (adapted from Ref. [321]).

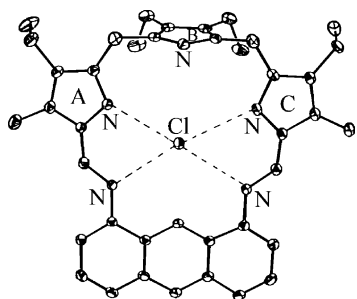


Fig. 155. Structure of $[H_2\text{-}276d](Cl)]^+$ (adapted from Ref. [324]).

X-ray diffraction analysis of single crystals of **277**, obtained by redissolving in CH_2Cl_2 and layering with methanol **277**, revealed a 2:1 complex of methanol (Fig. 156). The methanol molecules lie above and below the macrocycle. The bipyrrole hydrogens, are hydrogen bound to the methanol oxygens. The methanol hydrogen is also involved in a bifurcated hydrogen bond with the imine nitrogen atoms [325].

The expanded porphyrin is formally in its unprotonated neutral free-base form. IR and NMR experiments show that hydrogen bonding remains also in CH_2Cl_2 .

Ethanol, trifluoroethanol, phenol and catechol are also bound to **277**, however with a preference for 1:1 compounds. These data support the hypothesis that certain expanded porphyrins, such as **277**, may be used to chelate neutral substrates both in solution and in the solid state. The high affinity observed for the complexation of certain substrates (e.g. phenol, catechol) suggests that a generalized expanded porphyrin approach could provide the basis for an interesting way to the recognition and binding of neutral substrates, including those substrates such as catecholamines and carbohydrates, that are of obvious biological importance [325].

The possibility to obtain the HSCN salt of **275a** as well as of the mono HCl adduct of the anthracene macrocycle **276d** suggests the use of these and other expanded porphyrins as anion specific chelating agents. The latter nonaromatic system showed some promise as an effective anion carrier and as an anion-specific receptor in solution. In a set of solution-phase transport experiments using a three-phase model membrane system $[Aq^I]\text{-}[CH_2Cl_2]\text{-}[Aq^{II}]$ ($aq =$

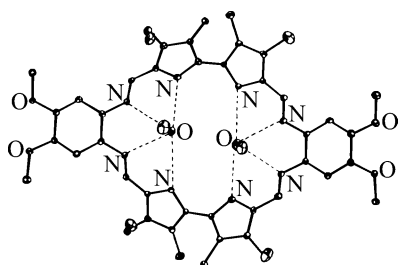


Fig. 156. Structure of $277\cdot 2CH_3OH$ (adapted from Ref. [325]).

aqueous: $Aq^I = 0.5\text{ M HF}$, adjusted to pH 3.2 with NaOH and $Aq^{II} = \text{NaOH}$ at pH 12) **276d**, via the presumed intermediacy of $[(276d)(F)]^-$, was found to accelerate the transport of fluoride ions through the CH_2Cl_2 phase. Roughly 13 h were required in the case of **276d** for the transport of 10 mol.% of the fluoride ions from Aq^I through CH_2Cl_2 to Aq^{II} . During this time the carrier **276d** appeared to be completely stable. However, as expected, a steady decrease in the pH of Aq^{II} from 12 to 5 was observed during this monitoring period. This is consistent with fluoride ion transport by a mechanism in which anions and protons are complexed and transported together by the macrocyclic carrier.

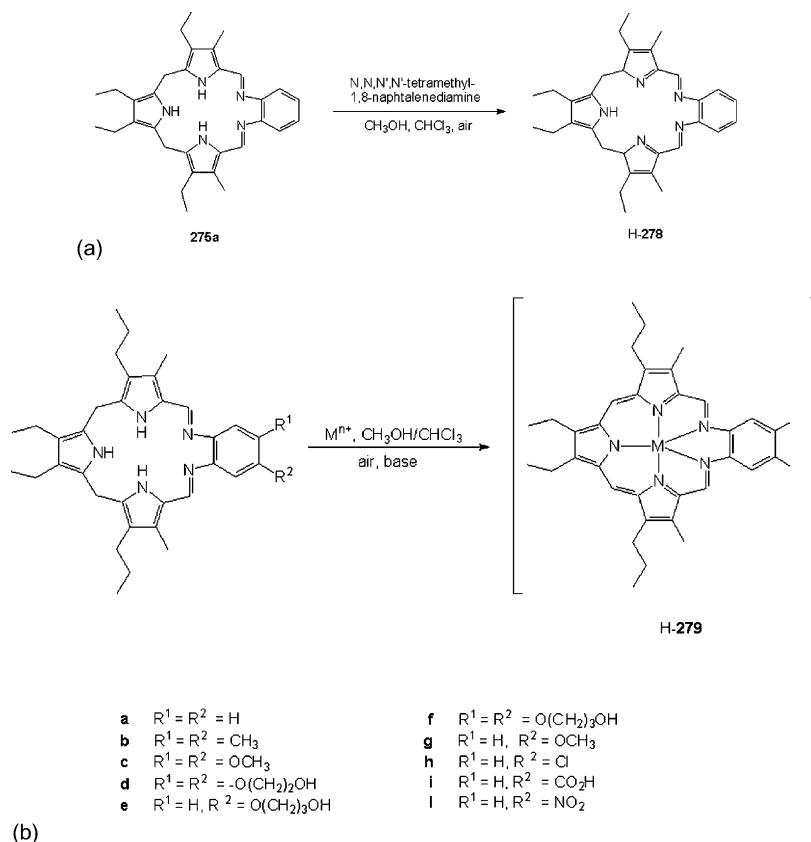
The transport of fluoride ions was found to be strongly inhibited by chloride ions, owing to the formation and/or break-up of a strong, kinetically nonlabile chloride complex. Consistent with this supposition, it was found that macrocycle **276d** is a relatively ineffective chloride ion carrier and only nominally better than **275b** and that chloride ions are bound roughly 14 times more effectively than fluoride ions by the diprotonated macrocycle **276d**. According to these results it was suggested that this expanded porphyrin can serve not only as an effective anion carrier but also as an anion-specific receptor.

A critical feature of these compounds is that they are nonaromatic. As such, they act more as expanded porphyrinogens than as true expanded porphyrins. For instance, they are essentially colorless when pure and moderately unstable toward oxidation.

It was however found that stirring the reduced macrocycle **275a** in air-saturated chloroform methanol with *N,N,N',N'*-tetramethyl-1,8-naphthalenediamine (Proton Sponge, a non-nucleophilic base) provided the free-base aromatic texaphyrin **H-278** in ca. 12% yield (Scheme 40a) [322].

NMR and electronic spectra indicate that the texaphyrin **H-278** may be envisaged as a 22π benzannulene with both 18π - and 22π -electron delocalization pathways. Further evidence of the aromatic nature of **H-278** was provided by the enhanced stability observed for the latter compared to the precursor **275a**. The electronic spectrum is dominated by a Soret-like band at 422.5 nm (60,500), flanked by N- and Q-like bands at higher and lower energies, with the lowest energy Q band at 752 nm (36,400) [325].

Unfortunately, efforts to reproduce and/or generalize the above oxidative chemistry proved difficult. Thus, the direct oxidative insertion of metal cations into the precursor non-aromatic forms (e.g. **275a–l**) was successfully carried out (Scheme 40b) first using cadmium(II) as the templating cation and air as the oxidant. Subsequently, it was discovered that this approach could be used effectively with a number of different reduced texaphyrin precursors and with a wide range of other large cations, including those of the lanthanide series, provided an excess of a *N,N,N',N'*-tetramethyl-1,8-naphthalenediamine is also added to the reaction mixture [322].



Scheme 40.

Thus the green solution obtained by reaction of the reduced macrocycle **275** with CdCl₂ or Cd(NO₃)₂ in air-saturated chloroform–methanol, after a chromatographic purification on silica gel and recrystallization from chloroform–hexane, separates the five coordinated expanded porphyrin chloride or nitrate complexes [Cd(**278**)](Cl) and [Cd(**278**)](NO₃) (as the semihydrates). When the same green solution (in the case of Cd(NO₃)₂) was purified by chromatography on Sephadex, a mixture of crystalline and noncrystalline green solids was obtained. Treatment of this apparently inhomogeneous bulk material with excess pyridine and recrystallization from chloroform–hexane produced the bis(pyridine) complex [Cd(**278**)(py)₂](NO₃) as dark green crystals in essentially quantitative yield. In this complex the central five nitrogen donor atoms of the macrocycle are essentially coplanar and define a near circular cavity which is roughly 20% larger than that found in metalloporphyrins. The cadmium(II) ion lies in the plane of the central N₅ binding core and is seven coordinated, being complexed by two apical pyridine ligands, in a pentagonal bipyramidal configuration (Fig. 157a) [322,323].

A single crystal, isolated from the inhomogeneous solid mixture (Fig. 157b), revealed the six coordinated pentagonal pyramidal cadmium(II) complex [Cd(**278**)(benzimidazole)](NO₃) wherein one of the two possible axial

ligation sites is occupied by a bound benzimidazole with the nitrate counter anion not coordinated to the central cadmium(II) ion. The five donor atoms of the ligand are bound to the cadmium ion, which lies out of the plane of the macrocycle, being displaced by 0.338 Å from the N₅ donor plane toward the coordinated nitrogen of the benzimidazole ligand. In [Cd(**278**)(py)₂](NO₃), the cadmium(II) cation was found to lie essentially within the plane of the macrocycle.

[Cd(**278**)(benzimidazole)]⁺ further differs from [Cd(**278**)(py)₂]⁺ in that, within the crystal lattice, two molecules stack on one another in a face to face fashion, being separated by Van der Waals distances of ca. 3.38 Å. As a result, the alkyl groups in any given molecule are all

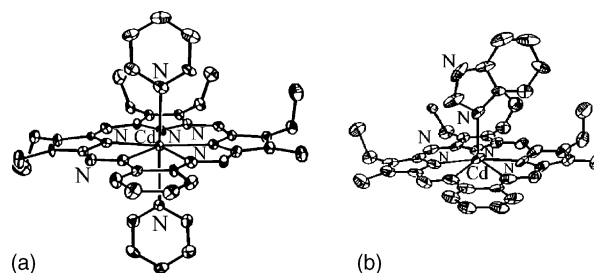


Fig. 157. Structure of [Cd(**278**)(py)₂]⁺ (a) and [Cd(**278**)(benzimidazole)]⁺ (b) (adapted from Ref. [323]).

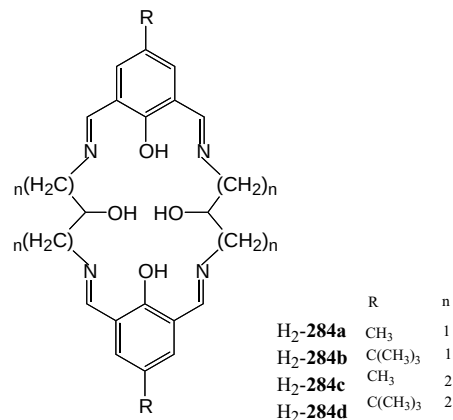
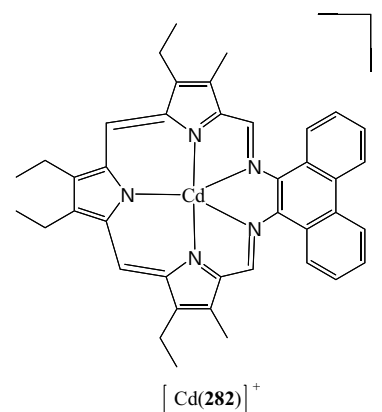
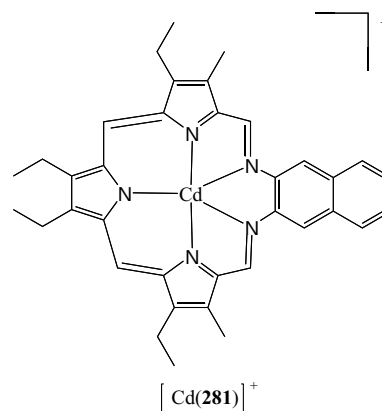
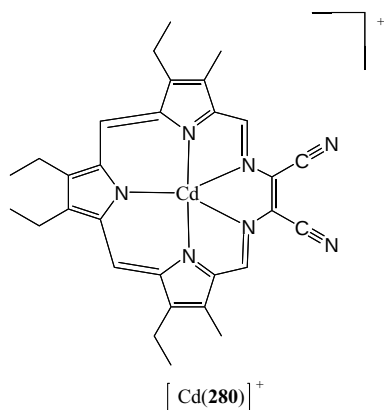
displaced to the benzimidazole-bearing side of the macrocyclic plane. As in the bis(pyridine) structure, however, in $[\text{Cd}(\mathbf{278})(\text{benzimidazole})]^+$ the nitrogen atoms of the macrocycle are all essentially planar. Also in common with $[\text{Cd}(\mathbf{278})(\text{py})_2]^+$, the five ligand nitrogens define a near circular binding cavity with a center-to-nitrogen distance of ca. 2.42 Å.

The benzimidazole was thought to result from electrophilic aromatic deacylation of a tripyrrane α -carbon and subsequent condensation with *o*-phenylenediamine.

Treatment of the remaining inhomogeneous material with pyridine gave only a single crystalline aromatic product, $[\text{Cd}(\mathbf{278})(\text{py})_2]^+$ [322,323].

The ^1H NMR spectrum in CDCl_3 of this bulk material is essentially identical with that of the pure five coordinated complex $[\text{Cd}(\mathbf{278})]^+$ prepared independently but showed the presence of a broad feature at ca. 6.4 ppm and two sharper peaks at 6.81 and 7.27 ppm ascribable to the bound benzimidazole ligand. These diagnostic ligand features are reproduced upon titrating the pure five coordinated complex $[\text{Cd}(\mathbf{278})]^+$ with roughly 3/5 equiv. of benzimidazole. This observation suggests that the bulk material, from which crystals of $[\text{Cd}(\mathbf{278})(\text{benzimidazole})](\text{NO}_3)$ were isolated, consists of a mixture of crystalline and noncrystalline six and five coordinated species and supports the hypothesis that the bound benzimidazole found in $[\text{Cd}(\mathbf{278})(\text{benzimidazole})]^+$ is derived from degradative side reactions associated with the metal insertion and accompanying ligand oxidation. Also it was suggested that in benzimidazole-containing chloroform solutions an extended concentration range exists wherein the pentagonal pyramidal complex $[\text{Cd}(\mathbf{278})(\text{benzimidazole})]^+$ is the primary cadmium-containing species, whereas in the presence of pyridine it is either the unligated complex $[\text{Cd}(\mathbf{278})]^+$ or the coordinatively saturated pentagonal bipyramidal species $[\text{Cd}(\mathbf{278})-(\text{py})_2]^+$ that will dominate in solution [325].

Using the same synthetic procedure cadmium(II) texaphyrins substituted with various electron-donating or electron-withdrawing groups, i.e. $[\text{Cd}(\mathbf{279})]^+$, $[\text{Cd}(\mathbf{280})]^+$, $[\text{Cd}(\mathbf{281})]^+$ and $[\text{Cd}(\mathbf{282})]^+$, have been obtained [326].



The one-electron oxidation and reduction potentials and the energies absorption band maxima (Ω -type band = 754–797 nm) are sensitive to the nature of substituents attached to the phenyl ring of the pentadentate macrocycles. Cyclic voltammetric data revealed that weakly binding counter ions, associated with these monocationic complexes (e.g. ClO_4^- or NO_3^-) dissociate upon one-electron reduction; the reduction peaks are irreversible to quasi-reversible in these cases. However, in the presence of strongly binding chloride ion or nitrogen bases (e.g. pyridine), the reduction process is electrochemically reversible and ligand dissociation does not occur on the cyclic voltammetric time scale. A linear relationship between the frequency of the lowest energy absorption maximum and the difference in potentials for the

first oxidation and reduction processes (1.54–1.40 V) exists in these systems. A similar relationship was also found for those texaphyrin complexes in which the phenyl group is replaced by a naphthyl, phenanthryl, or dicyano group [326].

To date, considerable effort has been devoted to explore the ground- and excited-state optical properties of metallo-texaphyrins, because the texaphyrins absorb strongly in the 720–780 nm spectral region, which is of particular interest in photodynamic therapy (PDT) [327]. In general terms, PDT uses a localizing, light-absorbing dye to bring about the oxygen-dependent, photosensitized destruction of unwanted tissue, such as carcinomas. At present, diamagnetic porphyrins and their derivatives are the dyes of choice for PDT [327] in part because they localize and/or are retained selectively in rapidly growing tissues such as sarcomas and carcinomas. Unfortunately, however porphyrin PDT dyes generally absorb at approximately the same wavelengths as endogenous porphyrins. Thus, the photodynamic effect is drastically reduced. The texaphyrins, on the other hand, absorb in the spectral region where living tissues are relatively transparent (i.e. 700–1000 nm). Thus, they might represent a new type of alternative PDT photosensitizer [328].

The photophysical properties of a number of metallotexaphyrins, containing cadmium(II), samarium(III), lanthanum(III) or lithium(I) have been studied and have revealed three important and near-unique optical properties: strong absorbance in the physiologically important far-red spectral region, high yields for the production of long-lived triplet states, and remarkable efficiency as singlet oxygen producing photosensitizers [328]. Also it was also found that modifying the texaphyrin skeleton would allow for a variation of the lowest energy Q-type band absorption maximum anywhere from 629 to 864 nm without reducing substantially the singlet oxygen quantum yield [328].

To date, several preliminary investigations of the photodynamic activity of the diamagnetic texaphyrins have been carried out [328]. For instance, in one representative *in vitro* study, the cadmium texaphyrin complex $[\text{Cd}(\mathbf{279})]^+$ was found to be very effective in the photoeradication of K562 leukemic cells, being considerably more potent than hematoporphyrin. Importantly, in this and other studies, evidence was also obtained indicating that the macrocycle remained unaffected by the irradiation process. Moreover, the diamagnetic lanthanum and lutetium texaphyrins were found to be photoactive *in vivo* at the 10 $\mu\text{mol/kg}$ level, sufficing to effect a 65% reduction in a murine adenocarcinoma following a single irradiation with 500 J of 746 nm light. Thus it was suggested that these complexes or their analogues could prove useful as PDT sensitizers in a clinical setting [328].

H-275a reacts with samarium(III) and europium(III) salts to form, only in the presence of *N,N',N'',N'''*-tetramethyl-1,8-diaminonaphthalene, a trace quantity of the related complexes while an higher quantity of the neodymium(III) complex was obtained [328]. However spectral evidence suggests that the metal uptake and ligand oxidation were occurring when the macrocycle is treated with numerous other lanthanide(III)

salts. It was found that, at least for samarium(III), europium(III) and gadolinium(III), the very high solubility of the complexes in water, where they appear hydrolytically stable, preclude their extraction into organic solvents.

The expanded porphyrins **H-279b** and **H-279c**, obtained by condensing the appropriate diamine with 2,5-bis[(3-ethyl-5-formyl-4-methylpyrrol-2-yl)methyl]-3,4-diethylpyrrole under acid-catalyzed conditions identical with those used to prepare **H-278** and **H-279a**, when treated with $\text{Gd}(\text{CH}_3\text{COO})_3$, $\text{Eu}(\text{CH}_3\text{COO})_3$ and $\text{Sm}(\text{CH}_3\text{COO})_3$ under reaction and workup conditions similar to those used to obtain $[\text{Cd}(\mathbf{279a})](\text{NO}_3)$, gave the cationic complexes $[\text{Ln}(\mathbf{279b})]^{2+}$ and $[\text{Ln}(\mathbf{279c})]^{2+}$ ($\text{Ln} = \text{Gd}^{3+}$, Eu^{3+} , Sm^{3+}), as their dihydroxide adducts [328]. $[\text{Ln}(\mathbf{279c})]^{2+}$ are high soluble in both chloroform or methanol and moderately soluble in 1/1 (v/v) methanol/water mixtures. These complexes are stable in these solvents. Kinetic studies carried out using a 3.5×10^{-5} M solution of the gadolinium(III) complex with **H-279c** in 1/1 (v/v) methanol/water at ambient temperature, indicate that the half-life for decomplexation and/or decomposition of this complex is 37 days [328].

The reaction pathway above reported was subsequent optimized by heating the ligand **275b** in the presence of $\text{Ln}(\text{NO}_3)_3$ and $\text{N}(\text{Et})_3$ in oxygenated methanol [329]. Yields of the purified metal complexes improved from ca. 25% using the original preparation to ca. 55–70% for all of the heavier lanthanide texaphyrin complexes (Nd^{3+} – Lu^{3+} , except Pm^{3+}). The lighter lanthanide cations (La^{3+} – Pr^{3+}) produced slightly lower yields of complex (ca. 30%). All of these lanthanide(III) complexes with **H-279c** were formulated as 1:1 (metal:ligand) complexes as characterised by mass spectrometry and for the lanthanum(III) and gadolinium(III) complexes also by X-ray crystallography [329].

In $[\text{La}(\mathbf{279c})(\text{NO}_3)_2(\text{CH}_3\text{OH})]$ (Fig. 158a), the metal cation is ten coordinated, being ligated by two bidentate nitrates along with one molecule of methanol. The lanthanum(III) cation is displaced from the N_5 plane by 0.914 Å.

In $[\text{Gd}(\mathbf{279c})(\text{NO}_3)(\text{CH}_3\text{OH})](\text{NO}_3)$ two distinct structures were found in the unit cell (Fig. 158b). In the first structure, the nine coordinated gadolinium(III) ion is ligated by one bidentate nitrate on and two methanol molecules. In the second structure the gadolinium(III) cation was found to be ten coordinate, being surrounded by two bidentate nitrate ions and one molecule of methanol.

The gadolinium(III) complexes $[\text{Gd}(\mathbf{278})]^+$ and $[\text{Gd}(\mathbf{279})]^+$ were somewhat soluble in 3:1 mixtures of water/methanol. However, these complexes proved to be insufficiently soluble in pure water to allow their use as *in vivo* paramagnetic contrast agents. Therefore, the lanthanide(III) complexes and especially the gadolinium(III) texaphyrin derivative that would be soluble at the concentrations required for magnetic resonance imaging (1–0.1 mM), were prepared by appending several hydroxyl substituents around the periphery of the macrocycle. Thus, in a first attempt the disubstituted 1,2-diaminobenzene was prepared according to Scheme 41.

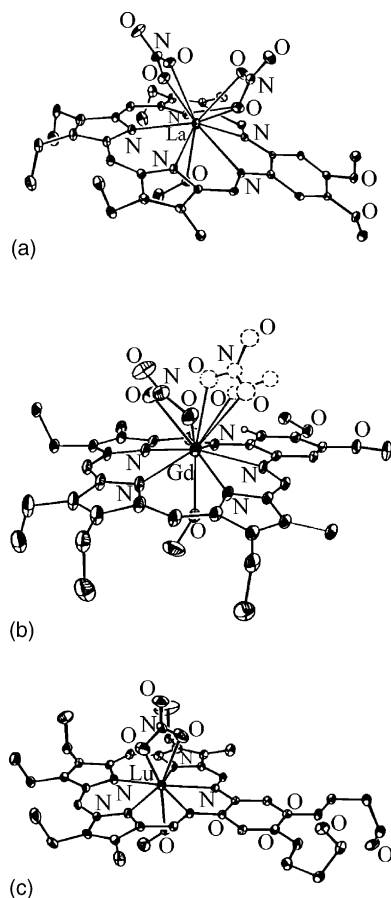


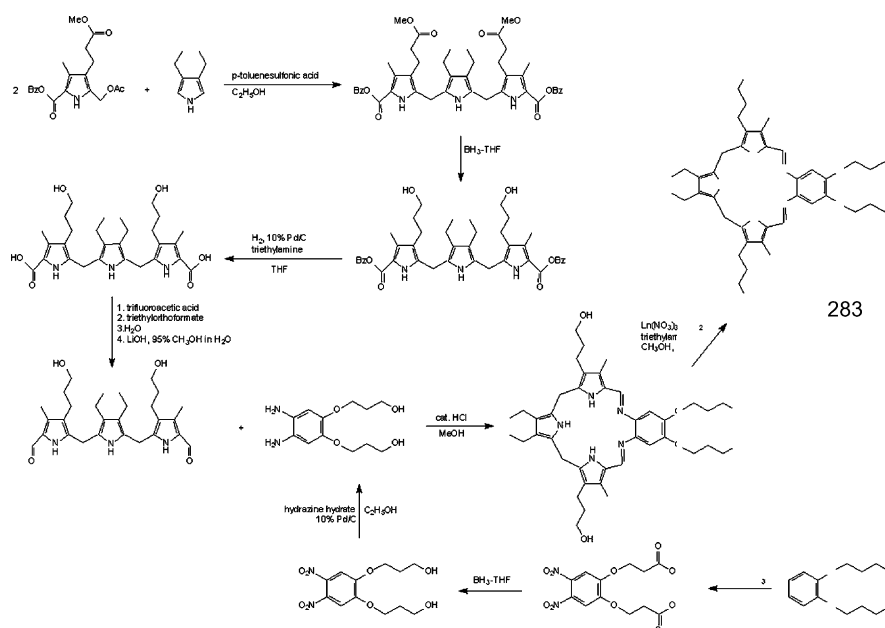
Fig. 158. Structure of $[\text{La}(\mathbf{279c})(\text{NO}_3)_2(\text{CH}_3\text{OH})]$ (a) $[\text{Gd}(\mathbf{279c})(\text{NO}_3)_2(\text{CH}_3\text{OH})]^+$ (also $[\text{Gd}(\mathbf{279c})(\text{NO}_3)(\text{CH}_3\text{OH})_2]^+$ is shown) (b) and $[\text{Lu}_2(\mathbf{279e})(\text{NO}_3)(\text{CH}_3\text{OH})]^+$ (adapted from Ref. [329]).

Acid-catalyzed condensation between 2,5-bis[(3-ethyl-5-formyl-4-methylpyrrol-2-yl)methyl]-3,4-diethylpyrrole and substituted 1,2-diaminobenzene produced the key nonaromatic texaphyrin-type ligand **275e** in quantitative yield. Final oxidative metallation carried out in the presence of $\text{Lu}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ then produced $[\text{Lu}(\mathbf{279e})(\text{NO}_3)_2]$. Unfortunately this is organic soluble not water soluble. In this complex the lutetium(III) cation was found to be eight coordinated (Fig. 158c), ligated by a single bidentate nitrate and one molecule of methanol in addition to the five nitrogen atoms of the macrocycle. The metal ion lies slightly above the plane of the macrocycle being displaced by approximately 0.27 Å from the mean plane of the five nitrogens.

In order to increase the water solubility of these complexes the tetrahydroxylated texaphyrin **H-283** and related complexes were synthesized according to the Scheme 41.

Acid-catalyzed Schiff base condensation between the appropriate dipyrrole and the diamine precursor produced the nonaromatic macrocycle of Scheme 41 in quantitative yield. This macrocycle is quite stable, decomposing only slightly over a period of months when stored in a freezer. Its oxidation and metallation in the presence of 1.5 equiv. of the desired lanthanide(III) salt, triethylamine, and air in boiling methanol produces the deep green complexes $[\text{Ln}(\mathbf{283})]^{2+}$ ($\text{Ln} = \text{La}^{3+}$ – Lu^{3+} , except Pm^{3+}).

The europium(III) and gadolinium(III) complexes with **H-283** are isomorphous. In both cases, the nine coordinated metal cation lies approximately 0.6 Å from the macrocyclic N_5 plane. In addition, each complex contains one bidentate nitrate and two molecules of methanol (top and bottom) (Fig. 159a).



Scheme 41.

Thus the lanthanide complexes are characterised by five coordination from the texaphyrin, a coordinated methanol on one side and at least one symmetrically bidentate nitrate group opposite the methanol. The ten coordinate lanthanum(III) complex [La(**279c**)(NO₃)₂(CH₃OH)] has two bidentate nitrate groups on the same side of the macrocycle. The europium(III) and gadolinium(III) texaphyrins [Ln(**283**)(NO₃)(CH₃OH)₂](NO₃) are nine coordinated species with a bidentate nitrate group and a methanol molecule on the top side of the macrocycle. On the other hand, the lutetium(III) texaphyrin is eight coordinated with only a single bidentate nitrate group chelated to the top side of complex. In an unusual case of disorder, the gadolinium(III) texaphyrin Gd(**279c**)(NO₃)₂ has both nine and ten coordinated species present in the solid state. The geometry of the nine coordinated species is much like that found in [Ln(**283**)(NO₃)(CH₃OH)₂](NO₃), while the ten coordinated gadolinium(III) species is similar to the lanthanum(III) species [La(**279c**)(NO₃)₂(CH₃OH)]. Together, these structures reflect both the decrease in coordination number and the intrinsic contraction in cation size observed as the lanthanide series is transverses. In the analogous terbium(III) dinitrate complex with **283** the metal ion is nine coordinated. The metal center is found to lie 0.595 Å above the mean N₅ plane while being bound by the pentadentate texaphyrin ligand and by a bidentate nitrate group and a pair of transverse ligating methanol molecules (Fig. 159b) [329].

The macrocyclic Schiff base lanthanide(III) complexes Ln(H₄-**284**)(Cl)₃·*n*H₂O have been synthesized by condensation of 1,3-diamino-2-hydroxypropane and 2,6-diformyl-4-methylphenol in the presence of lanthanum(III), cerium(III)

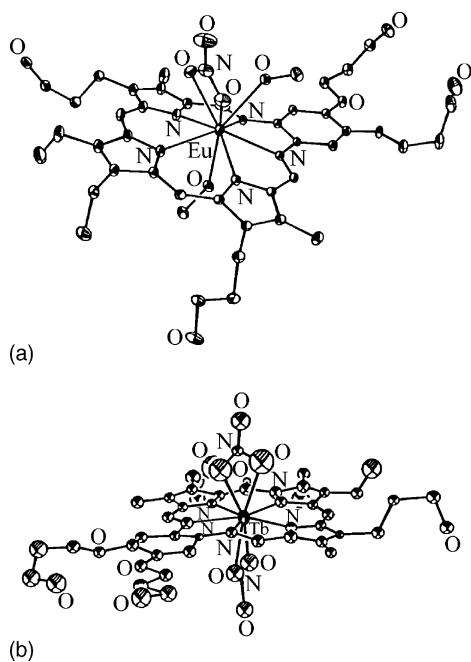


Fig. 159. Structure of [Eu(**283**)(NO₃)(CH₃OH)]⁺ (a) and [Tb(**283**)(NO₃)₂] (b) (adapted from Ref. [329]).

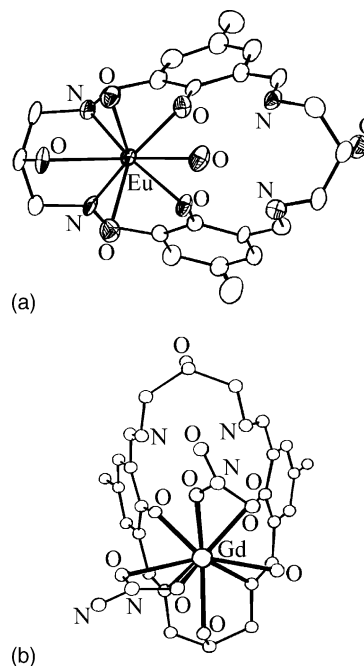


Fig. 160. Structure of [Eu(H₄-**284**)(H₂O)]³⁺ (a) and [Gd(H₄-**284**)(NO₃)₂(H₂O)]⁺ (b) (adapted from Ref. [330]).

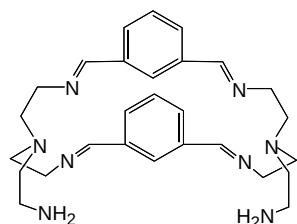
and europium(III) chlorides. The ¹H and ¹³C NMR spectra of the cerium(III) and europium(III) derivatives indicate the unsymmetrical coordination of the lanthanide(III) ions within the macrocyclic ligand H₄-**284**. The crystal structure of the europium(III) complex (Fig. 160a) contains two different complex molecules: in each molecule the europium(III) ion is eight coordinated and the ligand adopts a bent conformation. In the first molecule the europium(III) ion is bound to two nitrogen atoms and three oxygen atoms derived from the macrocyclic ligand as well as to three water molecules, while in the second molecule one of the coordinated water molecules is substituted by a chloride anion [330].

The same reaction of the presence of Gd(NO₃)₃·6H₂O, Sm(NO₃)₃·6H₂O and La(NO₃)₃·5H₂O, yielded [Ln(H₄-**284**)(NO₃)₂(H₂O)](NO₃). In spite of different crystallographic parameters, probably due to the different solvent content of both crystals, the first coordination sphere of the gadolinium(III) and samarium(III) complexes appears identical (Fig. 160b). In both complexes the macrocyclic ligand acts as a pentadentate chelate, binding to only one lanthanide center, which is nine coordinated in the form of a monocapped square antiprism. The nine-fold coordination is completed around the metal center by a monodentate nitrate, a bidentate nitrate and a water molecule.

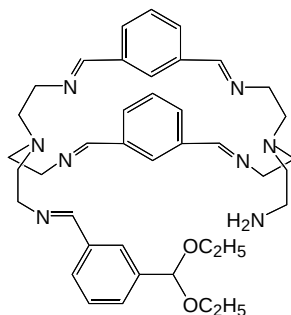
[Cu₂(H₂-**284**)(H₂O)₂](NO₃)₂ was obtained during the reaction of [La(H₄-**284**)(NO₃)₂(H₂O)](NO₃) with copper(II) trifluoroacetate. This transmetalation reaction yields a copper(II) homo-dinuclear complex, in which the Schiff base behaves as a dianionic ligand since the phenol groups appear deprotonated, acting as endogenous bridges between the two

copper(II) centers. The macrocycle ligand adopts an essentially flat structure with the two slightly distorted square pyramidal copper(II) centers bridged by the two phenoxide oxygen atoms, with two imine nitrogen donors completing the CuN_2O_2 plane. The aliphatic alcohol oxygen atoms remain protonated, and do not participate in the coordination to the metal centers. An antiferromagnetic interaction between the copper(II) ion ($2J = -63 \text{ cm}^{-1}$) was observed for this dinuclear copper complex [330].

Many of the Schiff bases complexes reported so far are stable in solutions; this is not however, a general trend: in several cases hydrolysis occurs. For instance, when $[\text{Cu}_2(\mathbf{95})(\text{OH})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ is left for 1–2 days in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ solution in air or in inert atmosphere, $[\text{Cu}_2(\mathbf{285})(\text{OH})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ has been obtained. Hydrolysis of $[\text{Cu}_2(\mathbf{95})(\text{OH})]^{3+}$ is slower in the absence of CH_2Cl_2 and produces the dicopper(II) μ -hydroxo complex of the $[\text{Cu}_2(\mathbf{286})(\text{OH})](\text{BPh}_4)_2 (\text{CF}_3\text{SO}_3) \cdot \text{H}_2\text{O} \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ containing the ring opened ligand **286** [331].



285



286

The octamine cage compound **239**, prepared by the one-pot condensation of tris-(2-aminoethyl)amine and glyoxal (2:3 ratio) in ethanol and subsequent reduction of the $\text{C}=\text{N}$ bond by NaBH_4 in methanol followed by recrystallization from water [332], incorporates nickel(II), copper(II), zinc(II) in aqueous solution by a fast and reversible process. In $[\text{Ni}(\text{H-}\mathbf{239})](\text{ClO}_4)_3$, obtained through crystallization of a solution of the complex at pH 7, one noncoordinated amine is protonated and hydrogen-bonded to a water molecule. Of the eight potential donor atoms, one tertiary and five secondary amine groups are coordinated to nickel(II), whereas the other tertiary nitrogen atom, and the secondary one are far away from the metal center. The latter noncoordinated nitrogen is protonated, the nickel(II) ion is coordinated in a very distorted octahedral arrangement. Both the distorted

octahedral geometry and the electrostatic repulsion between the metal center and the ammonium group are expected to induce a conformational and geometrical strain in the cage framework (Fig. 161) [332].

239 takes up as many as six protons in the pH range 2–12. Both in NaClO_4 and KNO_3 media, the highest protonated form was $[\text{H}_6\text{-}\mathbf{239}]^{6+}$ at pH 2 where the protons are probably bound to the six secondary nitrogen atoms as suggested also on the basis of NMR titration experiments [332].

Least-square fitting of the titration curve in presence of 1 equiv. of nickel(II) ion indicated the formation of two major species: $[\text{Ni}(\text{H-}\mathbf{239})]^{3+}$ and $[\text{Ni}(\mathbf{239})]^{2+}$. $[\text{Ni}(\text{H-}\mathbf{239})]^{3+}$ begins to form at pH 5.5 and reaches the respectable concentration of 70% at pH 7. Then $[\text{Ni}(\mathbf{239})]^{2+}$ forms and is present at 100% from pH 9 [333].

In the case of copper $[\text{Cu}(\text{H}_2\text{-}\mathbf{239})]^{4+}$ forms at a little below pH 3, reaching its maximum concentration at pH 3.5. Then, the major species $[\text{Cu}(\text{H-}\mathbf{239})]^{3+}$ forms and is present at 100% in the 4–8 pH range. $[\text{Cu}(\mathbf{239})]^{2+}$ predominates only in a rather alkaline solution (pH > 10).

The less stereochemically demanding zinc(II) ion displays a behaviour quite similar to that of the genuine nickel(II) and copper(II) ions. In fact, $[\text{Zn}(\text{H}_2\text{-}\mathbf{239})]^{4+}$ forms at pH 5 and reaches a concentration of 50% around pH 6; then, $[\text{Zn}(\text{H-}\mathbf{239})]^{3+}$ is present as the major species over a substantial pH range (7–9) while $[\text{Zn}(\mathbf{239})]^{2+}$ is the dominating species at pH ≥ 9 .

Both $[\text{Ni}(\mathbf{239})]^{2+}$ and $[\text{Cu}(\mathbf{239})]^{2+}$ complexes are labile with respect to demetallation in acidic solution, as demonstrated by the instantaneous decolouration of the violet and blue solution, respectively, on addition of strong acid. It was found that for $[\text{Cu}(\mathbf{239})]^{2+}$ two protons participate in the transition state of the reaction while for the nickel(II) cage complex, the protonation of only one of the coordinated amine groups is sufficient to promote the destruction of the complex. This may be due to the lower intrinsic stability of nickel(II) polyamine complexes than those of copper(II) and to their lack of predisposition toward five coordination.

7.5. Acyclic tridimensional complexes

Polyether substituted salicylaldehyde derivatives (**H-287a–c**) were prepared by reaction of the dianion of 2,3-dihydroxybenzaldehyde with 1-bromo-2-(2-methoxyethoxy)ethane, pentaethyleneglycol monomethylether toluene-

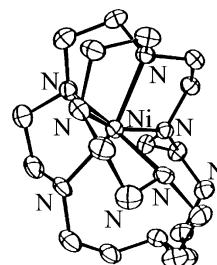


Fig. 161. Structure of $[\text{Ni}(\text{H-}\mathbf{239})]^{3+}$ (adapted from Ref. [332]).

p-sulfonate or hexaethylene glycol monotoluene-*p*-sulfonate, respectively [334]. The condensation of these functionalized salicylaldehydes with tetraethylenepentaamine or with tris(2-aminoethyl)amine in methanol affords the corresponding [2+1] H₂-288 and [3+1] H₃-289 Schiff bases [334].

For the [2+1] condensation products NMR investigations suggest the presence of isomers of the Schiff base H₂-288 (due to imidazolidine ring formation as a consequence of the nucleophilic addition of the two secondary amine functions across adjacent imine bonds) to give H₂-288' and H₂-288''. Treatment of these Schiff bases with sodium borohydride resulted in the reduction of two imine bonds and/or ring opening of the imidazoline five-membered rings, respectively with the consequent formation of H₂-290 [333]. An analogous reduction of H₃-289 affords H₃-291 (Scheme 42).

The preparation of [Gd(289)], by treating H₃-289 with GdCl₃ both in the presence or in the absence of triethylamine, failed, only the starting ligand being recovered. When H₂-288...H₂-291 were successively treated first with stoichiometric quantities of sodium methoxide or with powdered sodium hydroxide in methanol, and then with 1 equiv. of GdCl₃, the complexes [Gd(289)], [Gd(291)], [Gd(288)(Cl)] and [Gd(290)(Cl)] were obtained. The same complexes have been synthesized by template procedure in the presence of the above mentioned quantity of base. The

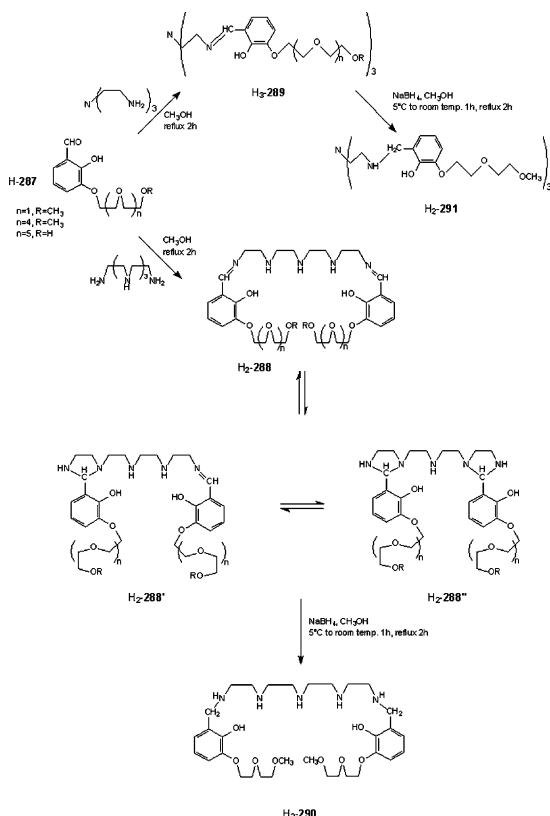
FAB mass spectra of [Gd(289)] and [Gd(291)] show molecular ion peaks at *m/z* values increased by complexation with sodium or with sodium and potassium, respectively. The parent peaks in the FAB mass spectra of the [Gd(288)(Cl)] and [Gd(290)(Cl)] correspond to the molecular ion with loss of chlorine anion [334].

These compounds have been tested as potential MRI contrast agents with some success. Solubility limitations and toxicity remain a problem with the neutral systems studied. Although the animal population studied is too small to allow any firm conclusion to be drawn from these preliminary experiments, in the case of compound [Gd(288)(Cl)] where *n* = 1 and R = CH₃, at least, promising results are obtained. The increase of signal from the liver with this gadolinium(III) complex immediately after contrast injection reflects the enhanced signal from the liver vascular system (arterial + venous) which carries the contrast agent. In addition, the long period of enhancement in liver compared with the enhancement encountered with Gd-DTPA (a pure vascular agent) and the enhancement in the spleen seem to present this product as a potential contrast agent of the reticuloendothelial system [334].

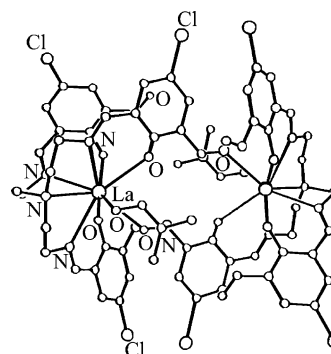
Reaction of H₃-125 with LnCl₃·*n*H₂O (Ln = La³⁺, Gd³⁺, Dy³⁺, Y³⁺; *n* = 6–8) in the presence of NEt₃ afforded [La(125)]·1.5H₂O. The same complexes were obtained when the formyl and the amine precursors were reacted in acetonitrile, using the appropriate lanthanide(III) chloride hydrate as templating agent. When recrystallized from a dimethylformamide/acetonitrile solution, the complexes [Ln(125)(DMF)]₂ were obtained (Ln = La³⁺, Gd³⁺, Y³⁺) [188].

[La(125)(DMF)]₂ is dimeric and centrosymmetric, the inversion center being between the two lanthanum(III) ions that are 8.24 Å apart. Each lanthanum ion is nine coordinated and the coordination polyhedron has been described as a square monocapped antiprism. The two mean planes of the two square bases are almost parallel. The aminic nitrogen atom is the cap of the polyhedron (Fig. 162).

An X-ray powder diffraction investigation of [Gd(125)(DMF)]₂ reveals it is isostructural with the lanthanum(III) analogue. Due to the extremely low solubility of the gadolinium(III) complex in H₂O it was impossible to



Scheme 42.

Fig. 162. Structure of [La(125)(DMF)]₂ (adapted from Ref. [188]).

measure its relaxivity complex although the extensive broadening of the residual HDO water in DMF solution strongly indicates a direct interaction with the metal center, most likely the two coordination sites occupied in the solid state respectively by a formyl and the amidic oxygens are substituted by H₂O in solution. The complex is then monomeric in solution and might be formulated as [Gd(**125**)(H₂O)]₂ [188].

The acyclic planar ligands H₂-**126** react with d- or f-metal ions to form the mononuclear complexes [M(**126**)], [UO₂(**126**)(S)], [Ln(H₂-**126**)(X)₃] (M = Cu²⁺, Ni²⁺; S = H₂O, CH₃OH, CH₃CN; X = NO₃[−], Cl[−]). The same complexes have been obtained by condensation of the formyl and amine precursors in a 2:1 molar ratio and in the presence of the appropriate metal salt. The formation of these compounds shows a solvent-dependent behaviour: complexes containing the formyl or the acetal groups have been obtained respectively in acetonitrile or methanol.

The NMR spectra of La(H₂-**126**)(NO₃)₃ in DMSO-d₆, progressively changes becoming identical in a few minutes to that of the free ligand showing that DMSO is able to substitute the Schiff base in the coordination to the central metal ion when the Schiff base behaves as a neutral ligand. When it acts as a deprotonated ligand, it is firmly bound to the central metal ion and cannot be substituted by strong coordinating solvents.

The mononuclear lanthanide complex [La(**128**)] with the tridimensional functionalized ligand H₃-**128** was synthesized by condensation of [La(**125**)] and 2-(methyamino)-{[12]-crown-4} in alcoholic solution and in a 1:3 molar ratio.

[La(**130**)] was prepared by template reaction of tris-(2-aminoethyl)amine and 4-bromo-2-(dimethylaminoethyl)-methylaminomethyl-6-formylphenol in a 3:1 molar ratio and in the presence of La(NO₃)₃·6H₂O and NaOH as a base. Elemental analyses together with SEM and EDX studies prove the presence of NaNO₃.

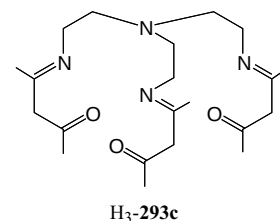
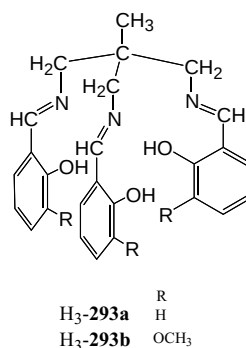
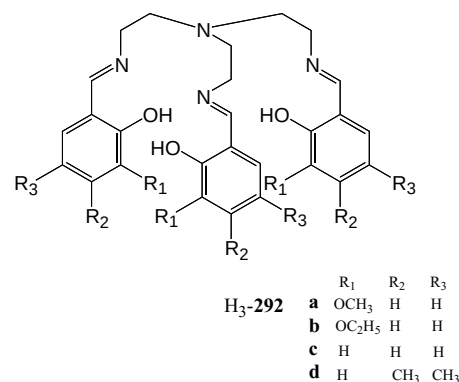
The acyclic ligands H₂-**126** and the related complexes, containing the formyl groups in the acetal form, may also undergo under appropriate experimental conditions further condensation reactions giving rise to functionalized compounds. Thus [UO₂(**126**)(CH₃OH)] or [UO₂(H-**126**)(NO₃)], when reacted with 2-aminoethyl-{[15]-crown-5}, form [UO₂(**129**)(CH₃OH)] (*n* = 2) or [UO₂(H-**129**)(NO₃)] (*n* = 2).

The condensation of the acyclic formyl precursor La(H₂-**126**)(NO₃)₃ with 2-(aminomethyl)-{[12]-crown-4} gives rise to a mixture of the symmetric cyclic complex La(H₂-**127**)(NO₃)₃ (R = CH₂CH₂SCH₂CH₂) and of the designed functionalized complex La(H₂-**129**)(NO₃)₃.

The condensation of 2-methylamino-{[12]-crown-4} with Mn(**126**)(OH), obtained by the reaction in acetonitrile of H₂-**126** with manganese(II) acetate, gives rise to Mn(**129**)(OH). Analogously the square planar complexes [Ni(**129**)] were obtained when the acyclic complexes [Ni(**126**)] was reacted with 2-methylamine-{[12]-crown-4}.

H₂-**131**·H₂O reacts with uranyl(VI) nitrate in a chloroform–methanol solution and in the presence of NaOH to give rise to the complex [UO₂(**131**)]·2NaNO₃·2CHCl₃·3CH₃OH.

Lanthanide(III) salts react with the tridimensional podand ligands H₃-**292a** or H₃-**292b** to form Ln(**292a**)·*n*H₂O or Ln(**292b**)·*n*H₂O (*n* = 1, 2) in the presence of the appropriate amount of base and Ln(H₃-**292a**)(X)₃·*n*H₂O or Ln(H₃-**292b**)(X)₃·*n*H₂O (X = Cl, NO₃[−]; *n* = 1–5) in the absence of base. In Ln(**292a**)·*n*H₂O or Ln(**292b**)·*n*H₂O the metal ion occupies the inner N₃O₃ coordination chamber while in Ln(H₃-**292a**)(X)₃ or Ln(H₃-**292b**)(X)₃, only some oxygen atoms of the external O₃O₃ chamber are involved in the coordination, the other coordination sites about the metal ion being filled by the anions X [188].



Ln(H₃-**292a**)(NO₃)₃ and especially Ln(H₃-**292b**)(NO₃)₃ are not stable in alcoholic solution and suffer a partial hydrolysis when redissolved in these solvents; on the contrary, they are stable in air for a long period of time. Moreover, in coordinating solvents, such as dimethyl sulfoxide, a demetallation reaction occurs and the free ligand H₃-**292a** can be recovered from the solution.

Lanthanide complexes of the tripodal ligands H₃-**292a** and H₃-**292c** have been obtained by deprotonation of the ligands with a strong base as CsOH·H₂O prior to the addition of the lanthanide nitrate or acetate salts [335]. The complexes, once formed, are stable and can be washed with H₂O. The complexation of the lanthanide ion occurs at the N₄O₃ site as confirmed by NMR spectroscopy in DMSO solution. The complexes have been formulated as Ln(**293**)·*n*H₂O

(Ln = La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺, $n = 0-2$). The praseodimium(III) complex contains also methanol as crystallization solvent [335].

[Ni₂(H-**L**)₂] (H₃-**L** = H₃-**293a**, H₃-**293b**) were prepared by reaction of nickel(II) with H₃-**293a** or H₃-**293b** in methanol without the addition of base. When Ni²⁺ was allowed to react with the same tripodal hexadentate ligands in the presence of N(Et)₃ and in a 3:2:6 ratio, the trinuclear [Ni₃(**L**)₂] complexes form [336].

In [Ni₂(H-**293b**)₂], the two independent molecules in the unit cell are linked by hydrogen bonding between phenol and phenolate oxygen atoms. The two phenolate nickel(II) ions, 4.763 Å apart, are in an approximately octahedral environment composed of three facially coordinated imine nitrogen atoms and three phenolic oxygen atoms (Fig. 163a). A small J value ($\cong 1.00$ cm⁻¹ for [Ni₂(H-**293a**)₂], and $\cong 1.02$ cm⁻¹ [Ni₂(H-**293b**)₂]) was found [336].

[Ni₃(**293b**)₂], is a doubly face-sharing, trinuclear, molecule. The coordination geometry around each nickel(II) ion is approximately octahedral. Two terminal nickel(II) ions are coordinated by the hexadentate tripodal ligands, and the central and the terminal nickel(II) ions are bridged by six phenolate oxygen atoms. Thus, the terminal mononuclear units function as tridentate ligands (Fig. 163b).

The terminal nickel(II) ions are crystallographically equivalent, and thus the spin exchange coupling constant for the interactions between the adjacent nickel(II) ions is expressed as $J = J_{12} = J_{23}$. The best fits were obtained with $J = 14.8$ cm⁻¹, $J_{13} = -1.77$ cm⁻¹, and $g = 2.03$ for [Ni₃(**293a**)₂], $J = 15.8$ cm⁻¹, $J_{13} = -2.61$ cm⁻¹, and $g = 2.19$ for [Ni₃(**293c**)₂].

Also the phenolate-bridged heterotrinuclear complexes, [MNi₂(**293b**)₂] (M = Mn²⁺, Co²⁺) have been prepared by

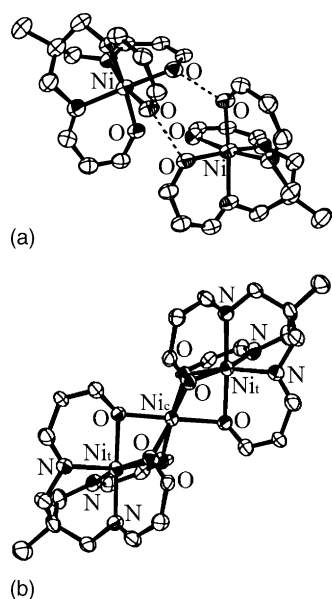


Fig. 163. Structure of [Ni₂(H-**293b**)₂] (a) and [Ni₃(**293b**)₂] (b) (adapted from Ref. [336]).

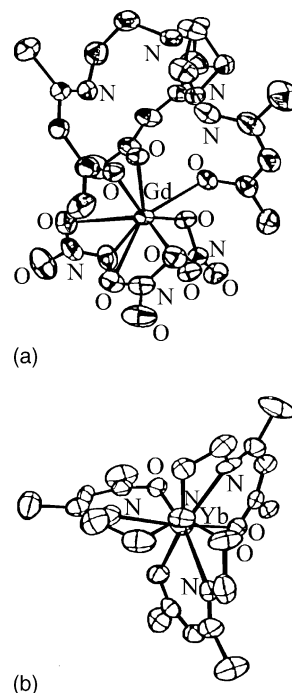


Fig. 164. Structure of [Gd(H₃-**293c**)(NO₃)₃] (a) and of one of the two crystallographically independent [Yb(**293c**)] molecule (b) (adapted from Refs. [335,336]).

the reaction at room temperature of [Ni₂(H-**293b**)₂] and the appropriate metal(II) salt in the presence of triethylamine to avoid transmetalation [336].

H₃-**293c** reacts with LnCl₃· n H₂O or Ln(NO₃)₃· n H₂O, giving rise to Ln(**293c**)· n S or Ln(H₃-**293c**)(NO₃)₃· n S, respectively, in the presence or absence of base [188, 335]. The preparation of [Ln(**293c**)] is more difficult for smaller lanthanide ions; the opposite trend was observed for the Ln(H₃-**293c**)(NO₃)₃ which is more tractable as the lanthanide(III) ion became smaller. Addition of bases to convert Ln(H₃-**293c**)(NO₃)₃ to [Ln(**293c**)] can result in the partial hydrolysis of the ligand.

The structure of [Gd(H₃-**293c**)(NO₃)₃] shows a nine coordinated gadolinium(III) ion, being bond to the three oxygen atoms of H₃-**293c** and to the oxygen atoms of three bidentate nitrate ions (Fig. 164a). The three acidic protons are in three intra molecular N—H···O hydrogen bonds, between the nitrogen and the oxygen atoms on each acetylacetoneimino arm of the H₃-**293** ligand. In this structure the capping tertiary nitrogen atom is tucked in with its lone pair of electrons pointed at the gadolinium(III) ion. The three arms of the ligand form a left-handed screw in approaching the metal ion, although the three nitrates form a right-handed screw in their orientation around the gadolinium(III) ion.

The reaction in ethanol between H₃-**293c** and LnCl₃ gave Ln(H₃-**293c**)(Cl)₃(H₂O) _{n} in which the ligand was tridentate and three more coordination positions were taken up by Cl⁻; these complexes showed decreasing waters of coordination along the lanthanide series. They hydrolyzed slowly over 1

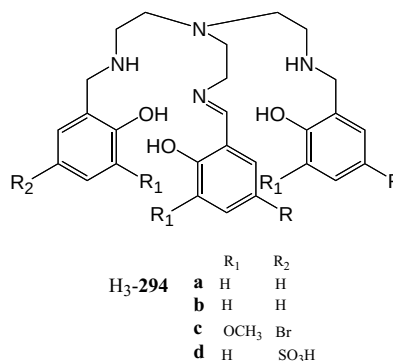
week in aqueous solution, or quickly in refluxing ethanol, to give $\text{Ln}(\text{tren})(\text{Cl})_3(\text{H}_2\text{O})_n$ complexes. They were, however, stable for weeks or months in aprotic solvents. NMR and UV-Vis spectra show that $\text{H}_3\text{-293c}$ is off of the metal ion in DMSO and $\text{C}_2\text{H}_5\text{OH}$ solution because the paramagnetic shifts were very small (<2 ppm) in the praseodymium(III), dysprosium(III) and ytterbium(III) complexes. Furthermore, the chemical shifts for the diamagnetic yttrium(III) complex and the uncomplexed ligand were essentially identical and were quite close to those of the paramagnetic lanthanide complexes [336].

It was impossible to remove HCl from $\text{Ln}(\text{H}_3\text{-293c})(\text{Cl})_3(\text{H}_2\text{O})_n$ with bases such as pyridine or triethylamine. Addition of AgBF_4 gave $[\text{H}_3\text{tren}](\text{BF}_4)_3$ and $\text{Ln}(\text{a-cac})_3$ in addition to AgCl . The highly basic bis-(trimethylsilyl)amido ligand replaces chloride in the starting lanthanide(III) salt using dry tetrahydrofuran as the reaction medium. With these conditions $[\text{Ln}(\text{293c})]$ complexes were reproducibly prepared in good yield. In these complexes the ligand was firmly coordinated to the ion in solution [336].

Single crystals were obtained by sublimation of $[\text{Yb}(\text{293c})]$ (Fig. 164b). Because $[\text{293c}]^{3-}$ can wrap around the ytterbium(III) ion in either a right-handed (Δ) or left-handed (Λ) screw, both enantiomers are present in the unit cell. The structure consists of discrete $[\text{Yb}(\text{293c})]$ units with four molecules of each enantiomer present in the unit cell. Every molecule in the unit cell is essentially independent. The geometry around the ytterbium(III) ion is a monocapped distorted octahedron. The apical nitrogen atom caps the triangular face formed by the other three coordinating nitrogen atoms and the ytterbium(III) ions are displaced 0.63–0.81 Å from the plane of the Schiff base arms. The bond angles suggest that this distortion is a spreading of the N_3 face and a shrinking of the O_3 face of the octahedron.

The related reduced amine phenol ligands $\text{H}_3\text{-294}$ form the mononuclear $\text{Ln}(\text{H}_3\text{-294})(\text{NO}_3)_3$ and the dinuclear $[\text{Ln}(\text{294})]_2$ complexes [337]. $[\text{Ln}(\text{294})]_2$ were prepared from reactions of the appropriate lanthanide(III) ion with $\text{H}_3\text{-294}$ in the presence of excess base (hydroxide or acetate). These complexes could also be prepared from the reaction of lanthanide nitrate with a large excess of $\text{H}_3\text{-294}$ since the amine phenols can act as a base. These homo-dinuclear complexes contain two lanthanide ions, coordinated by a

triply deprotonated N_4O_3 heptadentate ligand. One phenolate oxygen on each ligand acts as a bridge between the two metal centers. Unlike the corresponding heptadentate Schiff base lanthanide complexes, lanthanide complexes with $\text{H}_3\text{-294}$ are very stable under basic or weakly acidic conditions both in the solid state and in solution. Reactions of $\text{H}_3\text{-294}$ with 1 equiv. of $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ salt in the absence of base produce the mononuclear complexes $\text{Ln}(\text{H}_3\text{-294})(\text{NO}_3)_3$, which are quite air-stable and can be easily converted into the dinuclear complexes $[\text{Ln}(\text{294})]_2$ by reacting with 3–4 equiv. of sodium hydroxide.



The dinuclear complex $[\text{Gd}(\text{294a})]_2$ has two identical eight coordinated gadolinium(III) ions, each of which is surrounded by a N_4O_4 donor set (Fig. 165). The two gadolinium(III) centers are bridged by one phenolate oxygen atom from each of the two separate heptadentate ligands. The two gadolinium ions and two bridging oxygen atoms form a planar four-membered ring with a metal...metal separation of 3.984 Å. The geometry around each gadolinium ion can be viewed as a distorted bicapped octahedron. Inspection of the structure of $[\text{Gd}(\text{294a})]_2$ reveals that the heptadentate capability of the ligand has been realized by removing the three acidic phenolic protons, but formation of the unexpected dinuclear complex $[\text{Gd}(\text{294a})]_2$ is probably caused by the higher coordination requirements of lanthanide metal ions and the small cavity in the heptadentate ligand.

Analogously the methoxy derivative $\text{H}_3\text{-294d}$ reacts with $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ in the presence of 3–4 equiv. of sodium hydroxide or acetate to produce the six coordinated complexes $[\text{Ln}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$ ($\text{Ln} = \text{Pr}^{3+}$, Nd^{3+} , Gd^{3+} , Yb^{3+}). In the presence of 6–8 equiv. of sodium hydroxide, the reaction of $\text{H}_3\text{-294d}$ with $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ produces a small amount of $[\text{Gd}(\text{294d})]$ first and then a mixture $[\text{Gd}(\text{294d})]$ and $[\text{Gd}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$. No analytically pure $[\text{Ln}(\text{294a})]$ complexes were isolated from the similar reactions for $\text{Ln} = \text{Pr}^{3+}$, Nd^{3+} , or Yb^{3+} . When more sodium hydroxide (>10 equiv.) was employed, lanthanide hydroxide precipitated. Reactions of $\text{H}_3\text{-294d}$ with 1 equiv. of $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ in the absence of base, produced $[\text{Ln}(\text{H}_3\text{-294d})(\text{NO}_3)_3]$ ($\text{Ln} = \text{Pr}^{3+}$, Nd^{3+} , Gd^{3+} , Yb^{3+}) which are quite air-stable and can easily be converted into $[\text{Ln}(\text{294d})_2](\text{NO}_3)_3$ by reaction with 3–4 equiv. of sodium hydroxide [337].

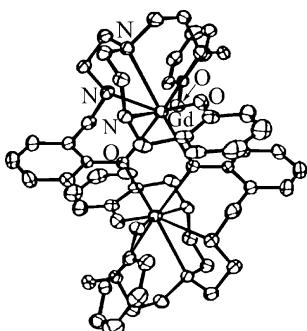


Fig. 165. Structure of $[\text{Gd}(\text{294a})]_2$ (adapted from Ref. [337]).

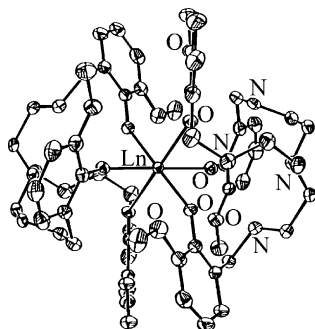


Fig. 166. Structure of $[\text{Ln}(\text{H}_3\text{-294d})_2]^{3+}$ ($\text{Ln} = \text{Pr}^{3+}, \text{Gd}^{3+}$) (adapted from Ref. [337]).

$[\text{Pr}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$ and $[\text{Gd}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$ are isostructural. The complex cation $[\text{Ln}(\text{H}_3\text{-294d})_2]^{3+}$ is centrosymmetric with the two amine phenol ligands facially binding to the metal center in a slightly distorted octahedral coordination geometry (Fig. 166). The coordinated amine phenol ligands are tridentate with three deprotonated phenolate oxygen atoms coordinating to the metal center and the three secondary amine nitrogen atoms protonated. The capping tertiary nitrogen atom is tucked in with its lone pair of electrons pointed at the lanthanide(III) ion. The three arms of one amine phenol ligand form a left-handed screw down the tertiary N–Ln axis while the three arms of the other amine phenol ligand form a right-handed screw [337].

The 3-methoxy groups of the phenyl rings have a profound influence on the coordination behaviour of the N_4O_3 amine phenol ligands towards lanthanide metal ions. In $[\text{Ln}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$, the coordination geometry around the metal center is a trigonally distorted octahedron. The steric hindrance from the 3-methoxy groups of the two coordinated amine phenol ligands prevents the approach of other oxygen donor ligand such as H_2O , and thus the six coordinated bis(ligand) complexes $[\text{Ln}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$ were enforced. Furthermore, the interstrand H-bonds highly stabilize these complexes, making their conversion to either $[\text{Ln}(\text{294d})]$ or $[\text{Ln}(\text{294d})_2]$ complexes very difficult [337].

In $\text{H}_3\text{-294a} \cdot \text{H}_3\text{-294c}$, the three-substituents of the phenyl rings are hydrogens; thus the complexes $[\text{Ln}(\text{H}_3\text{-L})(\text{NO}_3)_3]$ ($\text{H}_3\text{-L} = \text{H}_3\text{-294a} \cdot \text{H}_3\text{-294c}$) can be easily converted into the dimeric complexes $[\text{Ln}(\text{L})_2]$ by adding 3–4 equiv. of a base (acetate or hydroxide). The formation of dinuclear complexes does not cause significant crowding between the two coordinated amine phenol ligands. In $\text{H}_3\text{-294d}$ the hydrogen atoms at 3-positions of the phenyl rings are replaced by three bulky methoxy groups [337].

Owing to steric hindrance $[\text{Ln}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$ cannot be easily converted to either $[\text{Ln}(\text{294d})]$ or $[\text{Ln}(\text{294d})_2]$ under similar conditions.

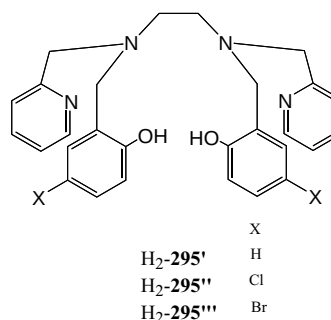
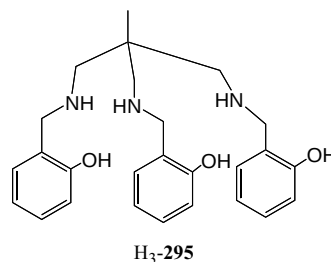
The steric effects of three methoxy groups are also seen in the reaction of a lanthanide nitrate with 1 equiv. of $\text{H}_3\text{-294d}$. For large metal ions such as praseodymium(III) and neodymium(III), the coordination of a tridentate $\text{H}_3\text{-294d}$ ligand to the metal center does not cause significant crowding

between the three 3-methoxy groups and the three bidentate nitrate anions and the complexes $[\text{Ln}(\text{H}_3\text{-294d})(\text{NO}_3)_3]$ are formed. For gadolinium(III) and ytterbium(III) complexes, the steric hindrance from 3-methoxy groups prevents the approach of all three bidentate nitrate anions; therefore, the coordination of the second tridentate $\text{H}_3\text{-294d}$ ligand becomes favourable and six coordinated bis(ligand) complexes $[\text{Ln}(\text{H}_3\text{-294d})_2](\text{NO}_3)_3$ are formed.

The water soluble $\text{H}_3\text{-294e}$ coordinates in water lanthanide(III) ions ($\text{La}^{3+}, \text{Nd}^{3+}, \text{Gd}^{3+}, \text{Ho}^{3+}, \text{Yb}^{3+}$) [337] in a tridentate fashion through the three phenolate oxygen atoms to give mono- and bis(ligand) complexes. The bis-complexes are proposed to be seven coordinated, containing one bound water while the mono complexes are proposed to have a coordination number of eight or nine [337].

The formation constant in aqueous solution for the 2:1 complex $\text{H}_3\text{-294e}:\text{Ln}^{3+}$ is larger than that of the 1:1 complex, and this is believed to be an entropic effect based on the desolvation of the 1:1 complex because of steric crowding. The ligand is highly selective for the heavier lanthanides, and this has been determined to be an enthalpic effect which agrees well with the electrostatic nature of lanthanide(III) bonding [337].

The room temperature addition of the tripodal amine phenol ((1,1,1-tris(2-hydroxybenzyl)amino)methyl)ethane, $\text{H}_3\text{-295}$, prepared by the reduction of the appropriate Schiff base with BH_4^- , to methanolic solutions of $\text{NiX}_2 \cdot 6\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{PF}_6^-, \text{ClO}_4^-, \text{BPh}_4^-$) afforded $[\text{Ni}(\text{H}_2\text{-295})](\text{X})$. $[\text{Ni}(\text{H}_2\text{-295})](\text{PF}_6)$ has a room temperature solid-state magnetic moment of $3.04\mu_B$, which is consistent with a d^8 octahedral species. If, however, the reaction mixtures are allowed to stand for longer periods of time (>2 h; $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{ClO}_4^-$) the dinuclear complexes $\text{Ni}_2(\text{H}_2\text{-295})_2(\text{X})_2$ precipitate as ascertained for $[\text{Ni}_2(\text{H}_2\text{-295})_2(\text{Cl})](\text{Cl})$, which was structurally characterized [338].



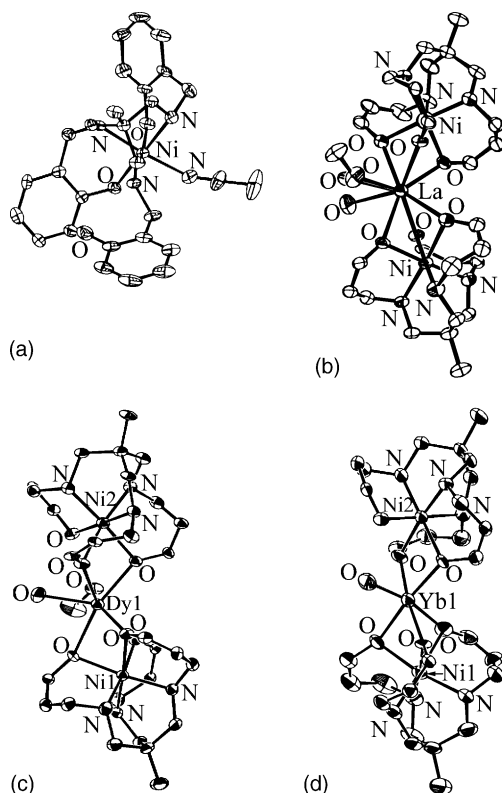


Fig. 167. Structure of $[\text{Ni}(\text{H}_2\text{-295})(\text{CH}_3\text{CN})]^+$ (a), $[\text{LaNi}_2(\text{295})_2(\text{CH}_3\text{OH})_{1/2}(\text{CH}_3\text{CH}_2\text{OH})_{1/2}(\text{H}_2\text{O})]^+$ (b), $[\text{DyNi}_2(\text{295})_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})]^+$ (c) and $[\text{YbNi}_2(\text{295})_2(\text{H}_2\text{O})]^+$ (d) (adapted from Ref. [338]).

The structure of $[\text{Ni}(\text{H}_2\text{-295})(\text{CH}_3\text{CN})](\text{PF}_6) \cdot 2.5\text{CH}_3\text{CN} \cdot 0.5\text{CH}_3\text{OH}$ revealed that the nickel(II) ion has an octahedral geometry, its coordination sphere being defined by one phenolato, one phenol, and three amine functions from the ligand $[\text{H}_2\text{-295}]^-$. The sixth site is occupied by a CH_3CN solvent molecule. The coordination environment has been described as a distorted octahedron. The third ligand phenol OH is neither deprotonated nor coordinated to the nickel(II) center (Fig. 167a).

The $[\text{Ni}(\text{H}_2\text{-295})]^+$ moiety can be deprotonated and used as an encapsulated ligand for a variety of lanthanide(III) ions in a bicapped fashion to generate $[\text{LnNi}_2(\text{295})_2](\text{ClO}_4) \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}^{3+}$, Pr^{3+} , Nd^{3+} , Gd^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Yb^{3+}). The amount of base added to the reaction mixtures is important; if even slight excesses are employed the LnNi_2 complexes cannot be isolated.

$[\text{LaNi}_2(\text{295})_2(\text{CH}_3\text{OH})_{1/2}(\text{CH}_3\text{CH}_2\text{OH})_{1/2}(\text{H}_2\text{O})]\text{ClO}_4 \cdot 0.5\text{CH}_3\text{OH} \cdot 0.5\text{CH}_3\text{CH}_2\text{OH} \cdot 4\text{H}_2\text{O}$ contains an eight coordinated lanthanum(III) ion bonded to two $[\text{295}]^{3-}$ ligands, acting as tridentate with respect to the lanthanum(III) ion and hexadentate with respect to one nickel(II) ion. Each $[\text{295}]^{3-}$ ligand encapsulates a nickel(II) ion via its three amine and three phenolato functions, rendering each nickel(II) coordination sphere approximately octahedral. All six phenols are deprotonated and form bridging bonds between the nickel(II) and lanthanum(III) ions. Two solvent mole-

cules occupy the remaining coordination sites on the lanthanum(III) ion. The $[\text{LaNi}_2(\text{295})_2(\text{CH}_3\text{OH})_{1/2}(\text{CH}_3\text{CH}_2\text{OH})_{1/2}(\text{H}_2\text{O})]^+$ cation is not linear. The geometry of the lanthanum(III) ion has been described as a D_{4d} square antiprism, distorted toward a C_{2v} bicapped octahedron. The $\text{Ni} \cdots \text{La}$ distances are 3.1900 and 3.1533 Å [338] (Fig. 167b).

The structure of $[\text{DyNi}_2(\text{295})_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})](\text{ClO}_4) \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ shares some similarities with its lanthanum(III) analogue. The cation contains a dysprosium(III) ion with two $[\text{Ni}(\text{295})]^-$ units coordinated to it. The dysprosium(III) ion is seven coordinated, being bonded by two $[\text{Ni}(\text{295})]^-$ complex ligands, one bidentate and one tridentate. Each $[\text{295}]^{3-}$ ligand encapsulates a nickel(II) ion via its three amine and three phenolato functions, which results in each nickel(II) ion having approximately octahedral geometry. All of the phenolato functions are deprotonated; only five of them, however, bridge between the nickel(II) and dysprosium(III) ions. One of the phenolato oxygen atoms has a very long interaction and hence is not formally bonded to the dysprosium(III) ion. One methanol and one water molecule occupy the remaining coordination sites on the dysprosium(III) ion. The DyNi_2 cation is not linear. The geometry of the dysprosium(III) ion was described as capped trigonal prismatic [338] (Fig. 167c).

$[\text{YbNi}_2(\text{295})_2(\text{H}_2\text{O})](\text{ClO}_4) \cdot 2.58\text{H}_2\text{O}$ was found to be very similar in the solid state to the dysprosium(III) analogue. The ytterbium(III) ion has a six coordination sphere with a distorted octahedral geometry being bonded to two $[\text{Ni}(\text{295})]^-$ ligands. One $[\text{Ni}(\text{295})]$ is tridentate and the other bidentate with respect to the ytterbium(III) ion; the sixth coordination site is occupied by a water molecule. All of the phenolato functions are deprotonated; only five of them, however, are bridging between the nickel(II) and ytterbium(III) ions. One of the phenolato oxygen atoms is not bonded to the ytterbium(III) ion. Each $[\text{295}]^{3-}\text{Ni} \cdots \text{La}^-$ ligand encapsulates a nickel(II) ion via its three amine and three phenolato functions; hence, each nickel(II) ion has approximately octahedral geometry. The $\text{Ni} \cdots \text{Yb}$ distances are 2.908 and 3.270 Å [338] (Fig. 167d).

The magnetic behaviour of the LaNi_2 complex is consistent with the presence of two magnetically isolated octahedral nickel(II) centers. A small antiferromagnetic coupling may occur in the DyNi_2 complex while in YbNi_2 there is a clear evidence of antiferromagnetic exchange between the ytterbium(III) and the nickel(II) ions. The exchange coupling in the YbNi_2 complex is stronger than that in the DyNi_2 analogue, leading to the general conclusion that the strength of d^n-f^n coupling between nickel(II) and lanthanide ions is determined, at least in part, by the size of the lanthanide ion, increasing with decreasing size [338]. The nature of the d^n-f^n interactions observed here contrasts with that reported for the Cu(II)Ln(III) systems, where either antiferromagnetic or ferromagnetic exchange may be observed depending on the f^n configuration [338].

The lanthanide(III) complexation of the potentially hexadentate ligand $\text{H}_2\text{-295}' \cdots \text{H}_2\text{-295}''$ results in three types of

complexes, depending on the base used in the reactions and the size of metal ion. When 2 equiv. of sodium hydroxide were used as a base with 1 equiv. each of lanthanide(III) salt and ligand, smaller lanthanide(III) ions (Dy^{3+} – Lu^{3+}) formed the neutral mononuclear complexes $[\text{Ln}(\mathbf{295}')(\text{NO}_3)]$ [339]. When similar reactions were performed with larger lanthanide(III) ions (La^{3+} – Gd^{3+}), monocationic complexes $[\text{Ln}_2(\mathbf{295}')_2(\text{NO}_3)]^+$ were produced. Some complexes contained water molecules in their coordination spheres [339]. The third type of monocationic trinuclear complexes $[\text{Ln}_3(\mathbf{295}')_2(\text{X})_n(\text{CH}_3\text{OH})]^+$, where X = bridging CH_3COO^- and bidentate ligands NO_3^- , CH_3COO^- , ClO_4^- and the total of n is 4, were formed when the same reactions were carried out with at least 2 equiv. of sodium acetate as a base [339].

$[\text{Ln}(\mathbf{295}')(\text{NO}_3)]$ and $[\text{Ln}_2(\mathbf{295}')_2(\text{NO}_3)](\text{NO}_3)$ can be easily converted to $[\text{Ln}_3(\mathbf{295}')(\text{X})_n(\text{CH}_3\text{OH})]^+$ by adding 2–3 equiv. of sodium acetate and 1 equiv. of $\text{Ln}(\text{NO}_3)_3$ or LnCl_3 or just by adding 1 equiv. of the desired lanthanide acetate. The resulting complexes $[\text{Ln}_3(\mathbf{295}')_2(\text{X})_n(\text{CH}_3\text{OH})]^+$ have the same formulation as those produced from the reactions of 1 equiv. of the desired lanthanide(III) salt, 1 equiv. of ligand, and 2–3 equiv. of sodium acetate. The conversion to $[\text{Ln}_3(\mathbf{295}')(\text{X})_n(\text{CH}_3\text{OH})]^+$ is only successful when the acetate anion is present.

The magnetic moments of some complexes, measured at room temperature show the lanthanide(III) ions are magnetically dilute; a very weak exchange ($-J = 0.045 \text{ cm}^{-1}$) was found in an encapsulated dimer of an amino phenolato gadolinium(III) complex.

$[\text{Yb}(\mathbf{295}')(\text{NO}_3)]$ consists of one ytterbium(III) ion, one hexadentate $[\mathbf{295}']^{2-}$ ligand, and one bidentate nitrate. The eight coordinated ytterbium(III) ion shows a distorted dodecahedron coordination geometry [339] (Fig. 168).

$[\text{Pr}_2(\mathbf{295}')_2(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)$ shows the presence of two praseodymium ions, one hexadentate ligand $[\mathbf{295}']^{2-}$ with only terminal phenolate oxygen atoms, another $[\mathbf{295}']^{2-}$ with two phenolate oxygen atoms bridging between the two praseodymium ions and one bidentate nitrate bound at one praseodymium ion; thus the coordination numbers of the two metal ions are eight and nine, respectively. The geometry around one praseodymium ion has been described as a distorted cube, while the geometry around the other praseodymium ion is closest to a monocapped square antiprism (Fig. 169a) [339].

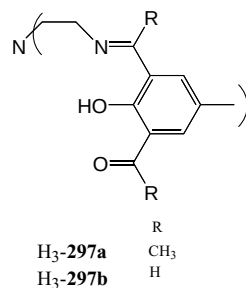
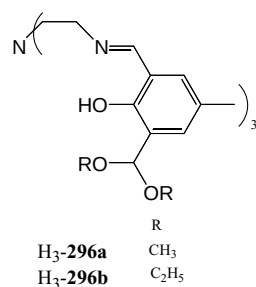
$[\text{Gd}_2(\mathbf{295}')_2(\text{NO}_3)](\text{NO}_3)$ shows a dinuclear $[\text{Gd}_2(\mathbf{295}')_2(\text{NO}_3)]^+$ unit different from its praseodymium congener in that three phenolate oxygen atoms bridge the two gadolinium(III) ions. One gadolinium ion is coordinated by the hexadentate $[\mathbf{295}']^{2-}$ ligand in which there is one bridging phenolate oxygen, and also two bridging phenolate oxygen atoms from the second ligand; thus, the coordination number of this gadolinium(III) ion is eight and the coordination geometry is a distorted square antiprism. The other gadolinium(III) ion is coordinated to the bridging phenolate oxygen, the second hexadentate ligand with its two bridging phenolate oxygen atoms and one bidentate nitrate. The

coordination number of this gadolinium(III) ion is nine and its geometry has been described as a distorted tricapped trigonal prism [339] (Fig. 169b).

The X-ray structural analysis of trinuclear $[\text{Gd}_3(\mathbf{295}''')_2(\text{CH}_3\text{COO})_4(\text{CH}_3\text{OH})](\text{ClO}_4)$ shows the presence of three gadolinium(III) ions, two $[\mathbf{295}''']^{2-}$ ligands with all phenolate oxygen atoms forming bridges, one methanol molecule, two bidentate acetates, one bridging acetate and another tridentate bridging acetate, where one of the acetate oxygen atoms is bound to two gadolinium(III) centers. The geometry around the nine coordinated Gd(1) is distorted monocapped square antiprism. Gd(2) has eight oxygen atoms in a distorted bicapped trigonal prismatic coordination sphere thus. The coordination environment around Gd(3) is exactly the same as that around Gd(1) [339] (Fig. 169c).

The X-ray structure of $[\text{Sm}_3(\mathbf{295}')_2(\text{CH}_3\text{COO})_2(\text{NO}_3)_2(\text{CH}_3\text{OH})](\text{NO}_3)$ (Fig. 169d) shows the presence of three samarium(III) ions, two $[\mathbf{295}']^{2-}$ ligands with all four phenolate oxygen atoms forming bridges, one methanol molecule, two bidentate nitrate groups on two samarium(III) centers, and two bridging acetate groups. Sm(1) and Sm(3) are nine coordinated in a monocapped square antiprismatic geometry, while Sm(2) is coordinated to seven oxygen atoms. The geometry around this center has been described as a distorted monocapped trigonal prism [339].

Reaction of 3 equiv. of 2,6-diformyl-4-methylphenol with 1 or 2 equiv. of tris-(2-aminoethyl)amine in refluxing CH_3OH leads to the formation of a yellow product in high yield. X-ray diffraction study of crystals grown by slow evaporation of a DMSO/ CH_3OH solution of this yellow product reveals the tripodal Schiff base ligand, $\text{H}_3\text{-296a}$ (Fig. 170a). Each arm contains four potential binding sites, an imine nitrogen, phenolic oxygen and two acetal oxygens, the latter being formed by reaction of a formyl group with methanol used as solvent during synthesis [340].



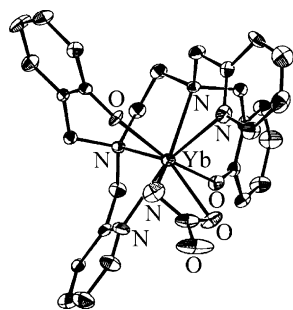


Fig. 168. Structure of $[\text{Yb}(\mathbf{295}')(\text{NO}_3)]$ (adapted from Ref. [339]).

Use of ethanol as a solvent leads to $\text{H}_3\text{-296b}$ in which ethoxides rather than methoxides are present in the acetal. Condensation of 2,6-diacetyl-4-methylphenol with tris(2-aminoethyl)amine leads to $\text{H}_3\text{-297a}$ in which the ketone is retained [340].

Reaction of $\text{H}_3\text{-296a}$ with hydrated $\text{Ln}(\text{ClO}_4)_3$ in CH_3OH forms of bright yellow solids which can be crystallised from $\text{CH}_3\text{NO}_2/\text{Et}_2\text{O}$ ($\text{Ln} = \text{La}^{3+}$, Pr^{3+}) or $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ ($\text{Ln} = \text{Y}^{3+}$). The lanthanum and praseodymium complexes are isostructural and each crystallises as $[\text{Ln}(\text{H}_3\text{-296a})\text{-(H}_2\text{O)}](\text{ClO}_4)_3 \cdot 3\text{CH}_3\text{NO}_2$. The cation shows ten coordination with six acetal and three phenolic oxygens of $\text{H}_3\text{-296a}$ and an additional water molecule, bound to the metal center (Fig. 170b). The ligand is completely reorganised from the conformation observed in the metal-free structure. The coordination polyhedron at the lanthanide(III) ion has been described as an icosahedron [340].

$[\text{Y}(\text{H}_3\text{-296a})](\text{ClO}_4)_3 \cdot 3\text{CH}_3\text{CN}$ contains a nine coordinated metal center in a tricapped trigonal prismatic coordination geometry (Fig. 170c). The lower coordination number compared to the lanthanum(III) and praseodymium(III) complexes is consistent with the smaller ionic radius

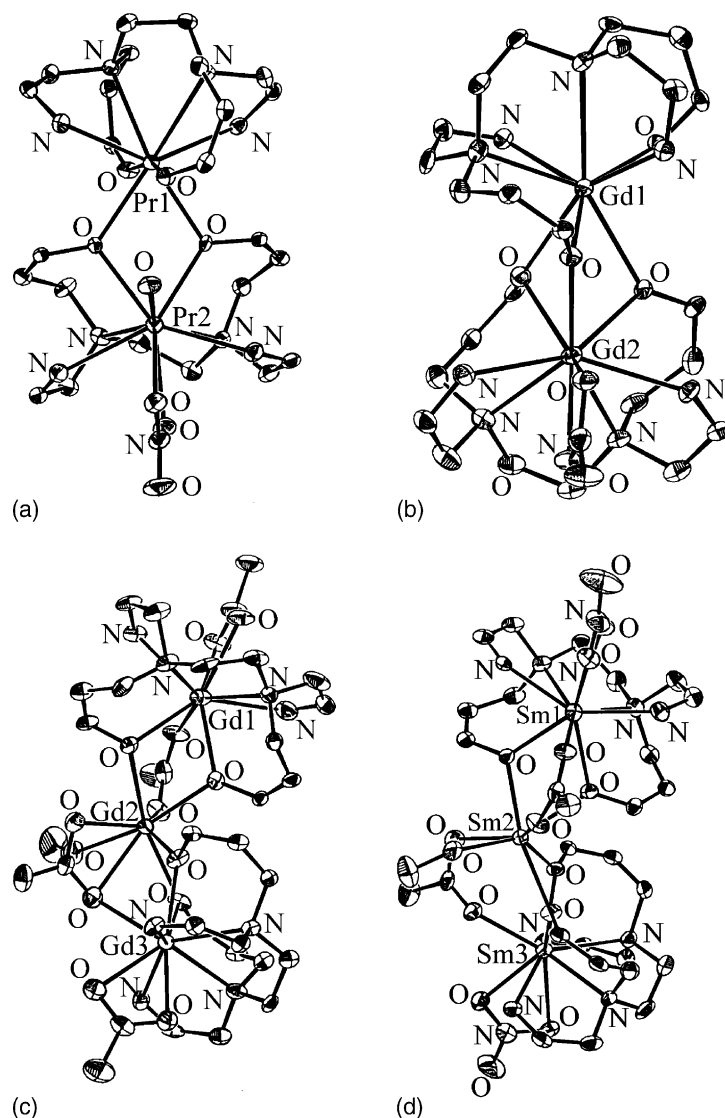


Fig. 169. Structure of $[\text{Pr}_2(\mathbf{295}')_2(\text{NO}_3)(\text{H}_2\text{O})]^+$ (a), $[\text{Gd}_2(\mathbf{295}')_2(\text{NO}_3)]^+$ (b), $[\text{Gd}_3(\mathbf{295}'')_2(\text{CH}_3\text{COO})_4(\text{CH}_3\text{OH})]^+$ (c) and $[\text{Sm}_3(\mathbf{295}')_2(\text{CH}_3\text{COO})_2(\text{NO}_3)_2]^+$ (d) (adapted from Ref. [339]).

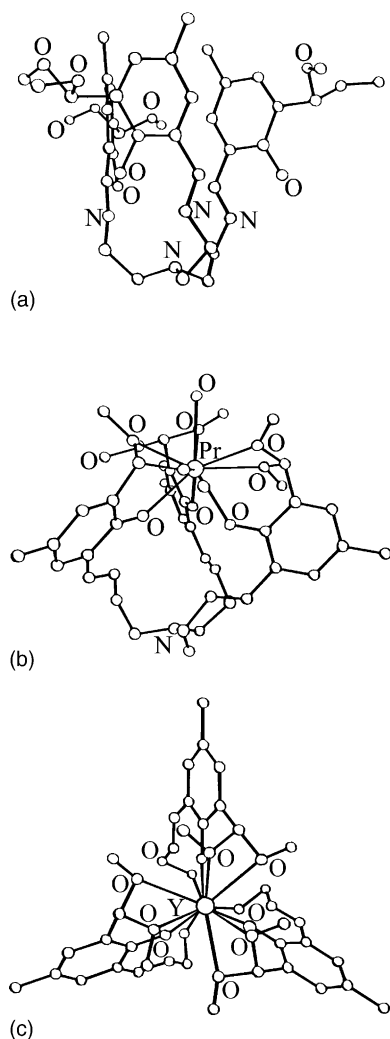


Fig. 170. Structure of $\text{H}_3\text{-296a}$ (a), $[\text{Pr}(\text{H}_3\text{-296a})(\text{H}_2\text{O})]^{3+}$ (b) and $[\text{Y}(\text{H}_3\text{-296a})]^{3+}$ (c) (adapted from Ref. [340]).

of yttrium(III) compared with lanthanum(III) or praseodymium(III) ions [340].

These complexes form hetero-dinuclear complexes when reacted with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Addition of 3 equiv. of dipropylamine to a 1:1 molar solution of $[\text{La}(\text{H}_3\text{-296a})(\text{H}_2\text{O})](\text{ClO}_4)_3$ and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in CH_3CN gives $[\text{LaNi}(\text{296a})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (Fig. 171a). The ligand $[\text{296a}]^{3-}$ uses all twelve potential donor atoms to encapsulate a six coordinated nickel(II) ion and a ten coordinated lanthanum(III) ion. The nickel(II) ion is bound to the three imine nitrogen donors and the three phenolic oxygens. The coordination geometry about the nickel(II) ion is different from an ideal octahedron. The three phenolic oxygen atoms are shared with the lanthanum(III) ion, which has a ten coordination geometry very similar to that in $[\text{La}(\text{H}_3\text{-296a})(\text{H}_2\text{O})](\text{ClO}_4)_3$. Therefore a face is shared by the 3d and 4f metal ions leading to a $\text{Ni} \cdots \text{La}$ distance of 3.355 Å [340]. Similar products have been obtained for other 4f metals investigated ($\text{Ln} = \text{Gd}^{3+}$, Er^{3+} or Pr^{3+}) when treated with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

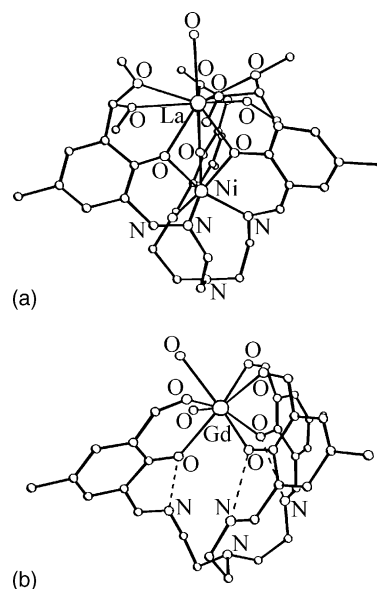
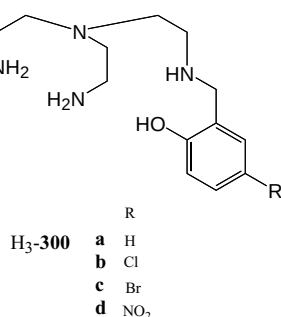
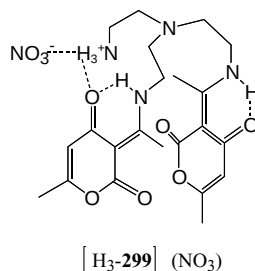
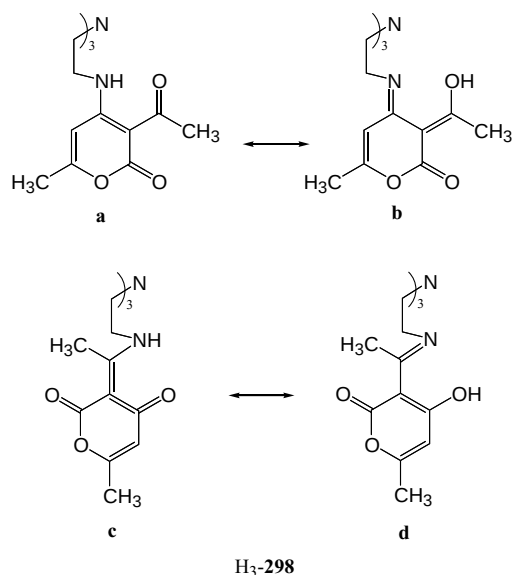


Fig. 171. Structure of $[\text{LaNi}(\text{296a})(\text{H}_2\text{O})]^{2+}$ (a) and $[\text{Gd}(\text{H}_3\text{-297b})(\text{H}_2\text{O})_2]^{3+}$ (b) (adapted from Ref. [340]).

The problem associated with addition of a transition metal salt to lanthanide complexes of $\text{H}_3\text{-296a}$ become much more serious when copper(II) salts are utilized. The second trigonally compressed octahedral cavity is incompatible with the requirements of the d^9 metal ion. All reactions produced compounds which do not contain both metals, and there is no indication from mass spectrometry that heterobimetallic complexes are formed. For example, reaction of $[\text{Gd}(\text{H}_3\text{-296a})(\text{H}_2\text{O})](\text{ClO}_4)_3$ with $\text{Cu}(\text{ClO}_4)_2$ gives crystals of the mononuclear gadolinium complex $[\text{Gd}(\text{H}_3\text{-297b})(\text{H}_2\text{O})_2](\text{ClO}_4)_{2.83}\text{Cl}_{0.17}$. The structure demonstrated that incorporation of a second metal ion has failed and that the ligand has been modified, with the acetal groups hydrolysed (Fig. 171b) to form aldehydes. Therefore in order to reach a satisfactory coordination number at the gadolinium ion, two water molecules are also present [340].

The reaction of tris(2-aminoethyl)amine with dehydroacetic acid may give rise, because of the resonance forms available to dehydroacetic acid, to the different compounds $\text{H}_3\text{-298a-d}$ [341]. NMR and X-ray structural determinations proved that the condensation reaction did occur at the acetyl side chain, excluding the possible existence of ring carbonyl derivatives $\text{H}_3\text{-298a}$ and $\text{H}_3\text{-298b}$ and showing that the compound is in the tautomeric enamine-ketone form $\text{H}_3\text{-298c}$. $\text{H}_3\text{-298}$ can be hydrolyzed, losing one arm, to form $[\text{H}_3\text{-299}](\text{NO}_3)$ in a wet methanol solution of $\text{Yb}(\text{NO}_3)_3$. The X-ray structure shows the two arms were found in the tautomeric enamine-keto form with the hydrogen located on the nitrogen atom. The nitrate group hydrogen bonds to the ligand through one of the primary amine hydrogens. The two Schiff base arm of the ligand are quite delocalized.



The dryness of the solvents, as well as the selection of the metal ion was found to be crucial to the preparation of complexes: only the praseodymium(III) and neodymium(III) complexes $\text{Ln}(\text{H}_3\text{-298}) \cdot 0.5\text{NaNO}_3 \cdot 1.5\text{H}_2\text{O}$ could be prepared from the reaction of $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ with **H₃-298** and 3 equiv. of anhydrous sodium acetate in a mixture of absolute ethanol, chloroform and methanol. The complexes demetallated in methanol and DMSO. The inability to prepare other lanthanide complexes, and the instability of the praseodymium and neodymium complexes are consistent with a lack of flexibility in the ligand backbone due to the exocyclic ring double bond, and the weaker basicity of the exocyclic keto-oxygen on the conjugate chelate ring [341].

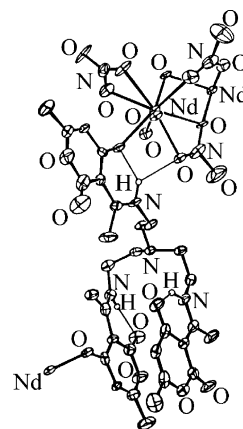


Fig. 172. One unit of the polymeric complex $[\text{Nd}(\text{H}_3\text{-298})(\text{NO}_3)_3]_n$ (adapted from Ref. [341]).

Although characterization of the bulk samples of the lanthanide complexes gave the formulation $\text{Ln}(\text{H}_3\text{-298}) \cdot 0.5\text{NaNO}_3 \cdot 1.5\text{H}_2\text{O}$, the X-ray single crystal diffractometry gave the polymeric structure with the empirical formulation $[\text{Nd}(\text{H}_3\text{-298})(\text{NO}_3)_3]_n$. The two neodymium(III) ions form a dinuclear center through four bridging nitrate groups, and these neighbouring dinuclear centers are linked together by the ligands to build a polymer in a three dimensional array. Each neodymium ion is coordinated by nine oxygens, and the geometry around each of the metal ions is a monocapped square antiprism and the $\text{Nd} \cdots \text{Nd}$ distance is 4.06 Å. Among the nine oxygen atoms coordinated to the neodymium ion, two exocyclic keto-oxygen atoms are from two separate ligands. The other seven oxygen atoms are from three kinds of nitrate ligands: one is the bridging (unidentate, unidentate) between two neodymium ions through the two oxygen atoms, the second is a simple bidentate nitrate to one neodymium ion and the third is a nitrate which bridges the two neodymium(III) ions with one oxygen atom, while the other oxygen atom is only coordinated to one neodymium(III) ion (Fig. 172).

$[\text{La}(\mathbf{300a})_2](\text{CF}_3\text{SO}_3)_3$, supposed to be an intermediate in the reaction of the tris(2-aminoethyl)amine lanthanum(III) complex $\text{La}(\text{tren})_2(\text{CF}_3\text{SO}_3)_3$ with salicylaldehyde, was obtained at lower salicylaldehyde ratio (1:1). In $[\text{La}(\mathbf{300a})_2](\text{CF}_3\text{SO}_3)_3$ the lanthanum(III) ion is coordinated by eight nitrogen atoms and two oxygen atoms. In the presence of an equimolar amount of lanthanum(III) and gadolinium(III) salts and under the condition of $\text{Ln}:\text{tren}:\text{salicylaldehyde} = 1:2:1$ ($\text{Ln} = \text{La}^{3+}, \text{Gd}^{3+}$), $[\text{La}(\mathbf{300a})_2](\text{CF}_3\text{SO}_3)_3$ was preferentially precipitated from the mixture, while the gadolinium(III) complex remained in the solution [342].

Also the reaction between zinc(II) tetrafluoroborate and tripodal ligands of the type **H₃-292** proceeds in acetonitrile at room temperature with partial hydrolysis of the imine bonds, leading to the yellow-orange cationic complexes $[\text{Zn}(\mathbf{300b-d})(\text{BF}_4)]$ [342]. Crystals of $[\text{Zn}(\mathbf{300c})(\text{BF}_4)]$ grown from acetonitrile-diethylether reveal a pseudo-

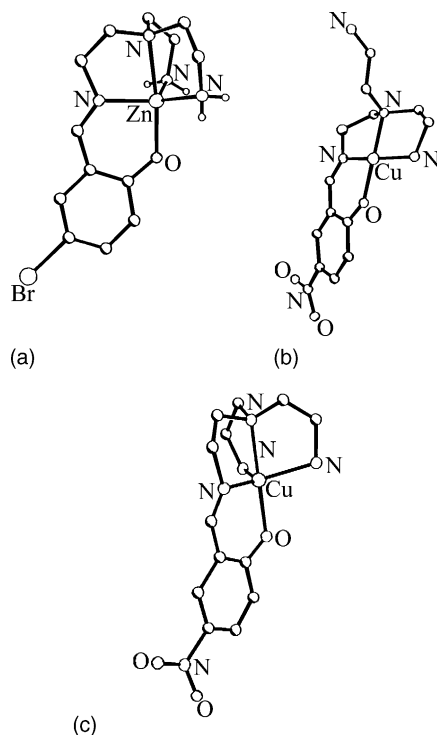


Fig. 173. Structure of $[\text{Zn}(\mathbf{300c})]^+$ (a), $[\text{Cu}(\text{H-}\mathbf{300d})]^{2+}$ (b) and $[\text{Cu}(\mathbf{300d})]^+$ (c) (adapted from Refs. [342,343]).

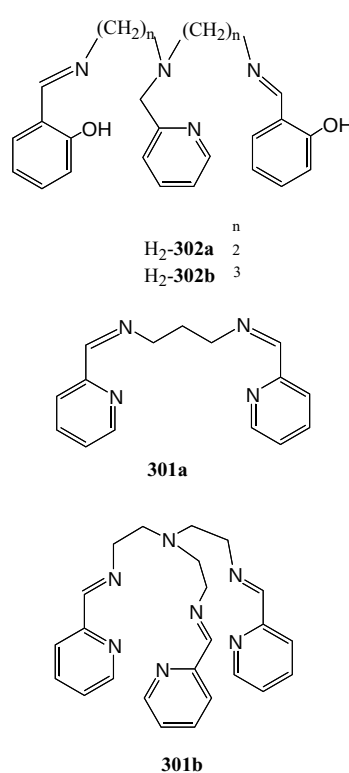
trigonal bipyramidal arrangements at the zinc ion (Fig. 173a) comprising two aminoethyl nitrogen atoms and an imine group in the trigonal plane, the apical positions being occupied by the tripodal nitrogen atom and the oxygen of the salicylidene moiety.

Copper(II) perchlorate hexahydrate also promotes partial hydrolysis of the same tripodal ligands in methanol under ambient conditions, with the consequent formation of $[\text{Cu}(\text{H-}\mathbf{300b-d})](\text{ClO}_4)_2$ [342]. The copper(II) coordination sphere of $[\text{Cu}(\text{H-}\mathbf{300c})](\text{ClO}_4)_2$ (Fig. 173b), which crystallises with one molecule of methanol solvate, comprises tertiary and primary nitrogen atoms, respectively, and the nitrogen and the oxygen atoms of the chelating salicylidene moiety in a distorted square planar arrangement; the nitrogen atom of the unbound arm is protonated, and disposed away from the metal center due to charge effects [342,343].

$[\text{Cu}(\mathbf{300d})](\text{ClO}_4)$ (Fig. 173c), which crystallises from the mother liquor with one molecule of methanol solvate, has the same geometry at the copper ion as the zinc(II) ion in $[\text{Zn}(\mathbf{300c})](\text{BF}_4)$; the unbound protonated aminoethyl arm of $[\text{Cu}(\text{H-}\mathbf{300d})](\text{ClO}_4)_2$ has been deprotonated and coordinates to the copper ion giving a trigonal bipyramidal N_4O donor set at the metal ion. The perchlorate counter ion in $[\text{Cu}(\mathbf{300d})](\text{ClO}_4)$ is not involved in hydrogen bonding with the neutral NH_2 groups of the cationic complex [342,343].

An alternative approach to the non template preparation of Schiff bases is their preparation by self-condensation of the appropriate precursors in aprotic solvent (i.e. toluene) using activated molecular sieves. By this procedure the

tetradentate **301a** and heptadentate **301b** Schiff bases and related cadmium(II) complexes have been prepared [342].

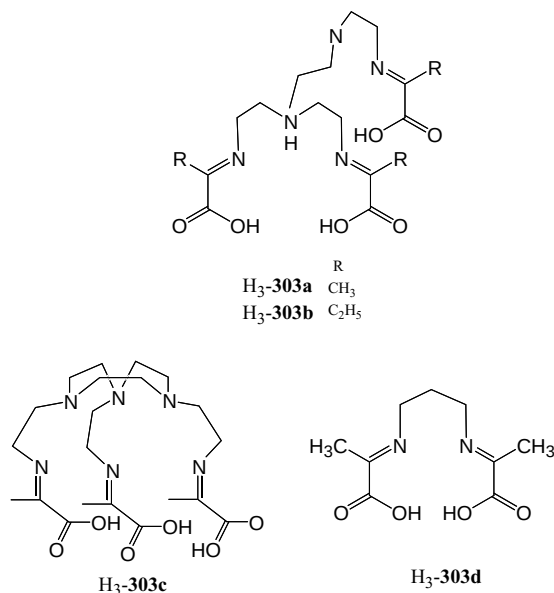


$[\text{Cd}(\mathbf{301a})_2(\text{ClO}_4)_2]$ is formed by coordination of two **301a** podands into a single cadmium ion. Due to its flexible nature **301a** acts as a pseudo-macrocyclic tetradentate ligand, thus resulting in a sandwich-type of eight-coordinated 1:2 complex. It crystallized in an acentric space group and the ligand assumes a helical arrangement around the cadmium(II) ion. The radius of cadmium(II) ion is too small to bind all eight spatially neighbouring nitrogen atoms in a symmetrical cubic coordination, thus creating a twist of approximately 64° between the lower and upper ligand [342,343]. Solution studies of $[\text{Cd}(\mathbf{301a})_2](\text{ClO}_4)_2$ in $\text{CHCl}_3/\text{DMSO}$ (10:1) and pure DMSO suggest a reorientation of **301a**, owing to its flexible nature, with the consequent formation of a four coordinated cadmium(II) complex.

The complexation of cadmium(II) nitrate with **301b**, investigated by NMR, supports the formation of the highly symmetrical helical six coordinated podate $[\text{Cd}(\mathbf{301b})](\text{NO}_3)_2$.

$\text{H}_2\text{-}\mathbf{302a}$ and $\text{H}_2\text{-}\mathbf{302b}$, prepared by reaction with 2-chloromethylpyridine of the Schiff base derived from salicylaldehyde and 1,5-diamino-3-azamethylpentane or 1,7-diamino-4-azamethylpentane, form the trinuclear copper(II) complexes $[\text{Cu}_3(\mathbf{302a})_2](\text{ClO}_4)_2$ and $[\text{Cu}_3(\mathbf{302b})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ when reacted with copper(II) salts in the presence of triethylamine. The trinuclear nature of the cation $[\text{Cu}_3(\mathbf{302b})]^{2+}$ was confirmed by an X-ray structural determination [344].

Reaction of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ with tris(2-aminoethyl)amine and the sodium salt of an α -ketocarboxylic acid afforded the trinuclear species $[\text{Ln}_2\text{Na}(\mathbf{303a})]^+$ and $[\text{Ln}_2\text{Na}(\mathbf{303ba})]^+$ which, on removal of Na^+ , aggregate further in CH_3OH to yield the neutral eight coordinated cyclic tetranuclear species $[\text{Ln}_4(\mathbf{303a})_4]$ ($\text{Ln} = \text{Yb}^{3+}, \text{Y}^{3+}$), and the linear polymer $[\text{Y}_2(\mathbf{303b})_2(\text{CH}_3\text{OH})]$ with alternating eight and nine coordinated yttrium(III) centers: recrystallization of $[\text{Ln}_2\text{Na}(\mathbf{303a})]^+$ from H_2O affords the nine coordinated mononuclear species $[\text{Ln}(\mathbf{303a})(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Sm}^{3+}, \text{Gd}^{3+}$) [345].



The tetrameric yttrium(III) (Fig. 174a) and ytterbium(III) complexes $[\text{Ln}(\mathbf{303a})_4]$ are isostructural with one carboxylate group from each ligand bridging to the next metal center. Since the two halves of the tetramer are related by an inversion center, the four metal ions are exactly planar, forming a parallelogram. The lanthanide(III) centers are eight coordinated, bound by the heptadentate tripodal ligand and an additional carboxylate oxygen of an adjacent complexed ligand. The tetrameric structure is surrounded by independent CH_3OH and H_2O solvent molecules, which are involved in intermolecular hydrogen bonding. Electrospray mass spectrometry suggests that the ytterbium(III) tetramer does exist, at least in part in aqueous solution.

In contrast, $[\text{Y}_2(\mathbf{303b})_2(\text{CH}_3\text{OH})]$ is a linear polymer (Fig. 174b). The complex aggregates via a bridging carboxylate group linking metal centers. The yttrium(III) centers alternate between eight coordinated and nine coordinated respectively, with the ninth coordination site filled by a CH_3OH molecule. These linear polymeric chains are hydrogen bonded to each other and to CH_3OH molecules. The remarkable differences in structure between $[\text{Y}_2(\mathbf{303b})_2\text{MeOH}]_x$ and $[\text{Y}(\mathbf{303a})_4]$ show how an apparently minor change of an organic substituent remote from the metal centers can have a dramatic effect on the observed structure.

In $[\text{Ln}(\mathbf{303a})(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Sm}^{3+}, \text{Gd}^{3+}$) (Fig. 174c) the tripodal, heptadentate Schiff base ligand coordinated to a nine coordinated samarium(III) or gadolinium(III) center. The two remaining coordination sites on the metal(III) center are occupied by two H_2O molecules, each positioned

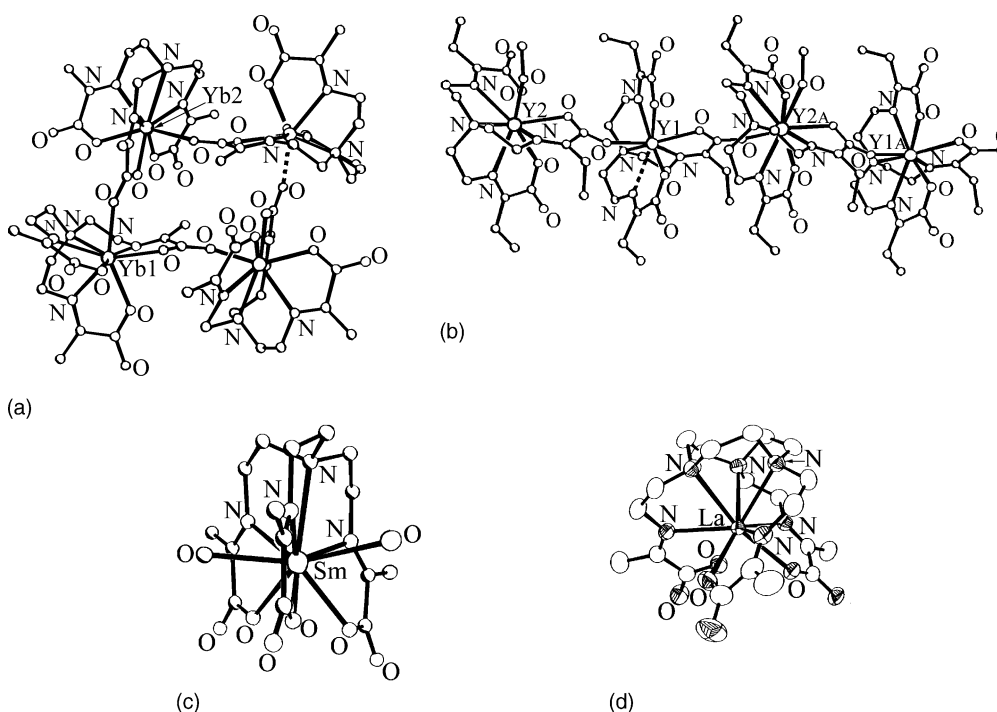


Fig. 174. Structure of $[\text{Yb}_4(\mathbf{303a})_4]$ (a), $[\text{Y}_2(\mathbf{303b})_2(\text{CH}_3\text{OH})]$ (b), $[\text{Sm}(\mathbf{303a})(\text{H}_2\text{O})_2]$ (c), and $[\text{La}(\mathbf{303c})]$ (d) (adapted from Ref. [345]).

between two tripod arms. Each arm of $[\mathbf{303a}]^{3-}$ shows a high degree of planarity allowing effective conjugation of the imine with the carboxylate groups and stabilizing the imine moiety.

The tripodal ligands $\text{H}_3\text{-}\mathbf{303a}$ and $\text{H}_3\text{-}\mathbf{303b}$ are heptadentate, whereas the lanthanide(III) ions are usually of eight or nine coordination. It is therefore necessary for the lanthanide(III) centers to include additional donors in their coordination spheres. $[\text{Y}_2(\mathbf{303b})_2(\text{CH}_3\text{OH})]$ is crystallised from CH_3OH , in which the best donors available are the carboxylate oxygens of neighbouring complexes, resulting in the observed oligomeric structures. However, $[\text{Ln}(\mathbf{303a})(\text{H}_2\text{O})_2]$ is crystallised from H_2O which is itself a good donor, resulting in a monomeric complex. In conclusion, aggregation in the above systems appears to be controlled by Na^+ cations, by solvent, and by variation in the tripodal polychelate as illustrated by the formation of mononuclear, cyclic tetranuclear and polymeric complexes.

Reaction of tris(2-aminoethyl)amine with 3 equiv. of sodium pyruvate in the presence of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ followed by an addition of excess Et_2O affords a white solid of stoichiometry $[\text{Mn}(\mathbf{303a})]\text{Na}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ which, by dissolution in CH_3OH followed by slow diffusion of Et_2O , gives rise to $[\text{Mn}_2\text{Na}_2(\mathbf{303a})_2(\text{CH}_3\text{OH})_4] \cdot 2\text{CH}_3\text{OH}$ and $\{[\text{Mn}_2\text{Na}_4(\mathbf{303a})_2\text{Cl}_2 \cdot 13\text{H}_2\text{O}]\}_\infty$.

The polymer $\{[\text{Mn}_2\text{Na}_4(\mathbf{303a})_2\text{Cl}_2 \cdot 13\text{H}_2\text{O}]\}_\infty$ consists of complex anions, $[\text{Mn}(\mathbf{303a})]^-$ in which the manganese(II) ion lies on a crystallographic three-fold axis and is bound to $[\mathbf{303a}]^{3-}$ via three carboxylate oxygen donors, three imine donors and, at a longer range, the bridge-head tertiary nitrogen donor, to give an overall seven coordinate manganese(II) center. Significantly, an infinite polymeric sheet of sodium ions bridge carboxylate oxygen donors of adjacent layers of $[\text{Mn}(\mathbf{303a})]^-$ units. The sodium centers bind additionally to solvent water molecules, to give five and six coordinate sodium ions. The chloride anions and remaining solvent water molecules are uncoordinated and are themselves sandwiched between $[\text{Mn}_2\text{Na}_4(\mathbf{303a})_2]$ layers.

In the tetranuclear cluster $[\text{Mn}_2\text{Na}_2(\mathbf{303a})_2(\text{CH}_3\text{OH})_4] \cdot 2\text{CH}_3\text{OH}$, two sodium cations are bound to carboxylate oxygens from two $[\text{Mn}(\mathbf{303a})]^-$ anions. The sodium cations also bind two bridging and two terminal CH_3OH molecules, giving overall six coordination at sodium ions [345].

Slow diffusion of Et_2O into a solution of $[\text{Mn}(\mathbf{303a})]\text{Na}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ in a 1:1 mixture of CH_3OH and H_2O results in crystals of both the polymer $\{[\text{Mn}_2\text{Na}_4(\mathbf{303a})_2(\text{Cl})_2 \cdot 13\text{H}_2\text{O}]\}_\infty$ and the tetranuclear cluster, $[\text{Mn}_2\text{Na}_2(\mathbf{303a})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$, whose structure is analogous to that of $[\text{Mn}_2\text{Na}_2(\mathbf{303a})_2(\text{CH}_3\text{OH})_4] \cdot 2\text{CH}_3\text{OH}$ but with solvation of sodium cations in the former being by H_2O rather than CH_3OH [345].

When BF_4^- is used in place of Cl^- , a solid precipitates with a $\text{Na}^+:\text{Mn}^{2+}$ ratio corresponding to 95–98%. It has not yet been possible to grow crystals of this product suitable for X-ray diffraction, but crystals of the nickel(II) analogue $\{[\text{Ni}_2\text{Na}_4(\mathbf{303a})_2(\text{BF}_4)_2]\}_\infty$, synthesized via reaction of

tris(2-aminoethyl)amine with sodium pyruvate and $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in CH_3OH followed by recrystallization from $\text{CH}_3\text{OH-Et}_2\text{O}$, shows a layered polymeric sandwich structure similar to $\{[\text{Mn}_2\text{Na}_4(\mathbf{303a})_2(\text{Cl})_2 \cdot 13\text{H}_2\text{O}]\}_\infty$, although the presence of BF_4^- in the nickel(II) complex leads to BF_4^- anions binding to three sodium cations within the sodium layer. The arms of $[\mathbf{303a}]^{3-}$ helicate about the nickel(II) ions, approximately octahedrally coordinated by three imine nitrogen donors. In contrast to the manganese(II) centers in $\{[\text{Mn}_2\text{Na}_4(\mathbf{303a})]\text{Cl}_2 \cdot 13\text{H}_2\text{O}\}_\infty$, the nickel(II) ions do not interact strongly with the bridgehead amine nitrogen donors. The sodium cations in the nickel(II) complex are extensively disordered and interact with the carboxylate centers and BF_4^- anions, with no coordinated solvent molecules. Within the sodium layer, there are vacant sites surrounded by six carboxylate oxygens [345].

On the contrary only the mononuclear lanthanide(III) complexes $[\text{Ln}(\mathbf{303c})]$ ($\text{Ln} = \text{La}^{3+}, \text{Sm}^{3+}, \text{Y}^{3+}, \text{Yb}^{3+}$) have been obtained by the condensation of 1,4-tris(2-aminoethyl)-1,4,7-triazacyclononane with sodium pyruvate in the presence of lanthanide(III) ions as the templating agent [345]. $[\text{Y}(\mathbf{303c})]$, $[\text{La}(\mathbf{303c})]$ and $[\text{Sm}(\mathbf{303c})]$ are isostructural. In each the lanthanide(III) center is nine coordinated, using all nine donor atoms of the ligands, namely the three amino nitrogen donors of the macrocycle, the three imino nitrogen donors and the three carboxylate oxygen donors. The coordination geometry about the lanthanide center is slightly distorted tricapped trigonal. The presence of 1,4,7-triazacyclononane as a capping moiety forces the lanthanide(III) ion to assume a trigonal prismatic structure as the macrocyclic nitrogen donors impose the first triangular face. The other triangular face of the prism is formed by the carboxylic oxygens with the imine nitrogens capping the three rectangular faces of the prism (Fig. 174d) [345].

NMR studies on the diamagnetic yttrium(III) and lanthanum(III) complexes and on the paramagnetic ytterbium(III) and samarium(III) complexes indicate that $[\mathbf{303c}]^{3-}$ imposes a very rigid coordination cage around the metal center [345].

The evolution of a mononuclear complex into a polynuclear system can be obtained also by simple reaction with a metal ion. Thus reaction of 1,3-diaminopropane with sodium pyruvate and $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Ni}^{2+}, \text{Mn}^{2+}$) in methanol under reflux results in the formation of $[\text{M}(\mathbf{303d})(\text{CH}_3\text{OH})_2] \cdot 2\text{CH}_3\text{OH}$ [345]. Slow codiffusion of methanolic solutions of $[\text{Ni}(\mathbf{303d})]$ and $\text{La}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ results in the growth of brown crystals of the heptanuclear complex $[\text{Ni}_6\text{La}(\mathbf{303d})_6](\text{ClO}_4)_3$, where a lanthanum(III) ion is located at the center of the octahedral cage formed by 6 equiv. $[\text{Ni}(\mathbf{303d})]$ moieties, and is bound by an icosahedron of twelve carboxylate groups, two from each $[\text{Ni}(\mathbf{303d})]$ unit. The octahedral nickel(II) centers are bound equatorially by $[\mathbf{303d}]^{2-}$; the axial sites are occupied by the carboxylate oxygen atoms of two neighbouring $[\text{Ni}(\mathbf{303d})]$ units. Thus, each $[\text{Ni}(\mathbf{303d})]$ unit is joined to four other $[\text{Ni}(\mathbf{303d})]$ units such that the six nickel(II) centers lie at the

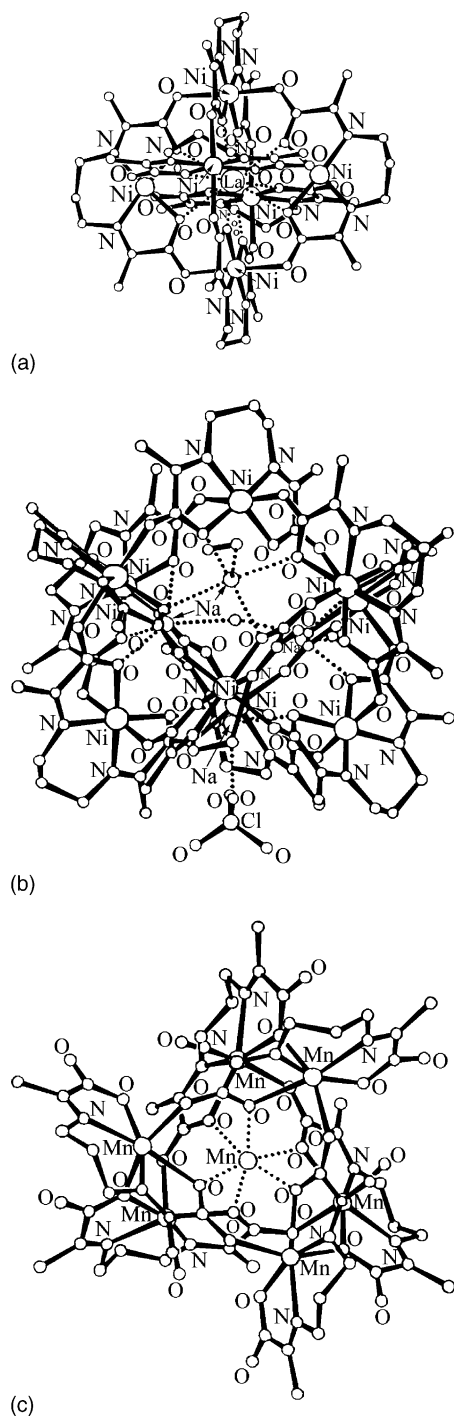


Fig. 175. Structure of $[\text{Ni}_6\text{La}(\mathbf{303d})_6]^{3+}$ (a), $[\text{Ni}_9\text{Na}_4(\mathbf{303d})_9(\text{H}_2\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)]^{3+}$ (b) and $[\text{Mn}_7(\mathbf{303d})_6(\text{H}_2\text{O})_{2.25}(\text{CH}_3\text{OH})_{0.75}]^{2+}$ (adapted from Ref. [345]).

vertices of a near-perfect octahedron with the lanthanum(III) ion at its center (Fig. 175a) [345].

By contrast, crystallization of $[\text{Ni}(\mathbf{303d})]$ from $\text{CH}_3\text{OH}/\text{Et}_2\text{O}$ in the presence of NaClO_4 yields purple crystals of $[\text{Ni}_9\text{Na}_4(\mathbf{303d})_9(\text{H}_2\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{Et}_2\text{O} \cdot 6.5\text{-CH}_3\text{OH} \cdot 0.15\text{H}_2\text{O}$ where four sodium(I) cations are encapsulated within a nine membered $\{\text{Ni}(\mathbf{303d})\}_9$ cage

(Fig. 175b). All the nickel(II) centers are octahedral, with the equatorial sites bound by $[\mathbf{303d}]^-$ and the axial sites bound by the carboxylate oxygen atoms of neighbouring complexes. The nickel(II) centers are arranged in a tricapped trigonal prism, although connection of the nickel(II) centers of adjoining $[\text{Ni}(\mathbf{303d})]$ units gives a polyhedron with three square faces and eight triangular faces, with each $[\text{Ni}(\mathbf{303d})]$ moiety connected to four other $[\text{Ni}(\mathbf{303d})]$ fragments. All the carboxylate oxygen atoms are orientated inwards, encapsulating a core of four sodium cations of which two are five coordinate and two are four coordinate. A water molecule is also bound within the Na_4 core and a ClO_4^- anion and a CH_3OH molecule protrude through two of the square faces of the $\{\text{Ni}(\mathbf{303d})\}_9$ cage to bond to the sodium(I) core [345].

Crystallization of $[\text{Mn}(\mathbf{303d})]$ from $\text{CH}_3\text{OH}/\text{Et}_2\text{O}$ in the presence of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ gave colourless, cube-shaped crystals of the heptanuclear complex $[\text{Mn}_7(\mathbf{303d})_6 \cdot (\text{H}_2\text{O})_{2.25}(\text{CH}_3\text{OH})_{0.75}](\text{ClO}_4)_2 \cdot 1.75\text{CH}_3\text{OH} \cdot 0.5\text{H}_2\text{O}$ where all seven manganese(II) centers are approximately octahedral with six outer manganese(II) centers bound by $[\mathbf{303d}]^{2-}$ in the equatorial plane and an interstitial manganese(II) center bound by six carboxylate oxygen atoms from surrounding $[\text{Mn}(\mathbf{303d})]$ units. The $[\text{Mn}(\mathbf{303d})]$ units are joined to three neighbouring units, with the axial sites on the manganese(II) centers bound either by carboxylate oxygens atoms of neighbouring $[\text{Mn}(\mathbf{303d})]$ complexes or terminal H_2O molecules. Connection of the manganese(II) centers of adjoining $[\text{Mn}(\mathbf{303d})]$ units gives a twisted Mn_6 trigonal prismatic cage in which only one carboxylate oxygen donor from each $[\text{Mn}(\mathbf{303d})]$ unit binds to the interstitial manganese(II) ion (Fig. 175c) [345].

8. Dinuclear complexes with macrocyclic ligands

Dinucleating macrocyclic and/or macroacyclic compounds have been extensively studied since these structural units are thought to be involved in a variety of biochemical and industrial processes. Complexes which contain two metal ions separated by distances of 3.5–6 Å are of considerable interest because at these distances no direct interaction between the metal ions is expected, yet a substrate could interact simultaneously with both ions [5,42].

Dinuclear complexes have been successfully used in the activations of small molecules (especially oxygen). The simultaneous presence of two metal ions at a suitable distance from each other is a pre-requisite for the formation of an activation space necessary for the coordination of oxygen and/or of organic substrates and for their subsequent oxidation. It was found that pairs of clusters of metal ions are sometimes capable of mediating certain chemical reactions either better or in a different way than do isolated centers [5,42].

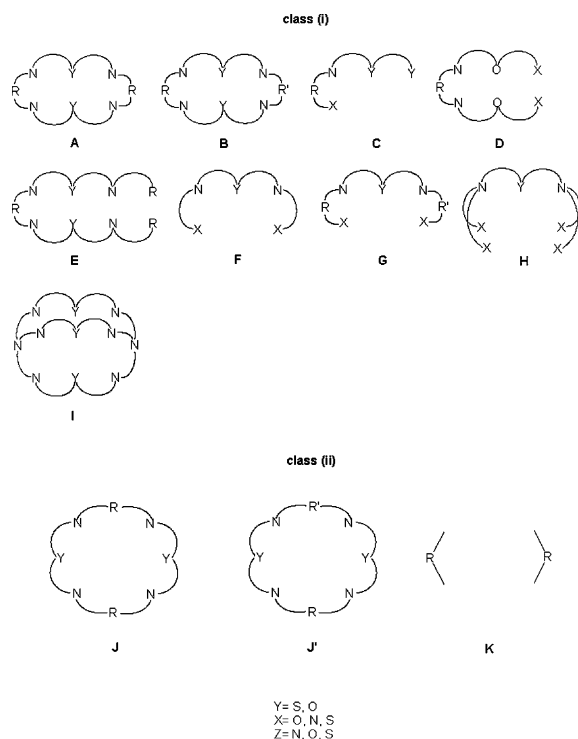
Also dinucleating macrocyclic and macroacyclic ligands can generate compounds with specific spectroscopic and magnetic properties. It was found that complexes containing

magnetic metal centers exhibit magnetic properties which are not simply the sum of those of the individual ions surrounded by their nearest neighbour ligands. These properties result from both the nature and the magnitude of the interactions between the metal ions within the molecular unit. Using compartmental ligands, binuclear complexes can be synthesized where the two metal centers, if paramagnetic, can interact with each other through the endogenous and/or the exogenous bridges in a ferromagnetic or antiferromagnetic way. By changing the type of ligand, the distance between the two chambers and/or the paramagnetic centers, it is possible to vary considerably the magnetic interaction, and particular complexes are good models for the preparation of a molecular ferromagnet. Thus the organization provided by an appropriately designed binucleating ligand may confer unusual structural features and or magnetic, optical, catalytic properties.

According to a recent classification the binucleating ligands which can form complexes with metals sharing at least one donor atom of ligands containing adjacent sites in which the central donor atom provides a bridge, have been collectively termed compartmental ligands (class i).

To a second class of binucleating ligands belong to the coordinating systems which give rise to complexes in which the donor atoms are not shared, thus deriving from ligands having isolated donor sets (class ii).

Ligands suitable to give the most appropriate structural arrangement of the metal ions for obtaining the above-mentioned properties are reported in Scheme 43.



Scheme 43.

Compounds A are symmetric macrocycles derived from [2+2] condensation of suitable diformyl- and polyamine precursors. Compounds B are [2+2] asymmetric macrocycles derived by condensation of functionalized diformyl derivatives and different polyamines. Compounds C are [1+1] acyclic ligands. Compounds D are side-off acyclic ligands in which a [1+2] condensation occurs. Compounds E are also side-off systems derived from D by a further condensation with primary amines when X is a carbonyl group, while compounds F or G are end-off symmetric and asymmetric acyclic ligands in which a [2+1] condensation occurs (in the related metal complexes, Y provides an endogenous bridge; a further exogenous bridge may be provided by a mono- or bidentate anion); compounds H are polypodal acyclic ligands and compounds I are [3+2] bicyclic systems. The chains R and R' can contain additional donor atoms (NH, S, O, PPh, etc.) producing a multiplicity of different compartments. Compounds J, J' and K contain remote chambers; in J and J' the compartments are connected by aliphatic or aromatic chains while in K the two macrocycles are constrained in a stack configuration while the asymmetric systems can be prepared in one step reaction, in the asymmetric systems must be prepared by a step by step procedure.

Thus many modifications have been made on the basic structure such as the provision of different lateral chains, also by introducing additional donor atoms, and the partial or full reduction of the azomethine linkage eventually followed by the insertion of further functionalization bearing donor groups at the aminic nitrogens as pendent arms.

The symmetric legating systems give rise to homo-dinuclear complexes and, under specific experimental conditions, to mononuclear complexes; these compounds, however, can easily be transformed into the homo-dinuclear analogues. Therefore unsymmetrical modifications of the symmetric systems are of paramount relevance in the formation of hetero-dinuclear complexes. The type and the extent of dissymmetry introduced in the coordinating moiety can influence and modify considerably the coordination selectivity of the two sites allowing the formation of pure hetero-dinuclear species, not otherwise accessible.

The prepared legating systems have been widely studied by IR, NMR and mass spectrometry. This last technique revealed its relevant role, especially in the absence of single crystal X-ray structure, in determining the size of these systems, particularly the nature of the macrocycles (i.e. [1+1], [2+2], [3+3] [4+4], or other cyclic or polymeric condensation products).

8.1. Homodinuclear complexes with symmetric macrocyclic ligands

8.1.1. Complexes with [2+2] compartmental ligands derived from 2,6-diformyl-4-substituted phenol and functionalized polyamines

In 1970, the first [2+2] homo-dinuclear complexes with symmetric macrocyclic ligands (the so-called Robson-type

complexes) were prepared by template reaction of 2,6-diformyl-4-methylphenol and 1,2-diaminoethane or 1,3-diaminopropane in the presence of the appropriate metal salt [346]. Since that time many Robson type-complexes have been prepared and their physico-chemical and structural properties reported and adequately reviewed [5,42]. Therefore in the present review only the most recent explication examples of this [2+2] cyclic complexation are inserted.

Sodium 2,6-diformyl-4-methylphenolate forms with 1,3-diaminepropane the [2+2] macrocyclic Schiff base complex $[\text{Na}_2(\mathbf{43})]$ which readily undergoes transmetallation by $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to produce $\text{Zn}_2(\mathbf{43})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. The nitrate complex was similarly prepared from $\text{Zn}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ and the azido complex was prepared by forming the acetato complex first and then reacting this complex with sodium azide [347]. $[\text{Zn}_2(\mathbf{43})(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$ consists of two independent pairs of dinuclear zinc complexes each, possessing a center of symmetry between the metal ions. Two perchlorate counter ions and two water molecules are associated with each bimetallic macrocyclic dication. Each molecule comprises a [2+2] deprotonated Schiff base macrocycle $[\mathbf{43}]^{2-}$. One molecule contains two six coordinate zinc(II) ions with an intermetallic distance of 3.166 Å. The coordination geometry of the zinc ion is derived from four N_2O_2 macrocyclic ligand donors, a water molecule and a more distant monodentate perchlorate anion and may be regarded as distorted octahedral. The metal coordination geometry for the other molecule may be considered as distorted square pyramidal, derived from four N_2O_2 macrocyclic ligand donors and a water molecule, the perchlorate anion being in a more remote position. A $\text{Zn} \cdots \text{Zn}$ distance of 3.177 Å was found. Water molecules are involved in intra- and inter-molecular hydrogen bonding (Fig. 176a) [347].

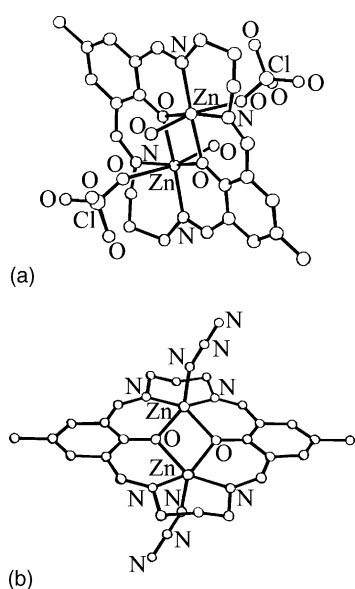


Fig. 176. Structure of $[\text{Zn}_2(\mathbf{43})(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$ (a) and $[\text{Zn}_2(\mathbf{43})(\text{N}_3)_2]$ (b) (adapted from Ref. [347]).

In $[\text{Zn}_2(\mathbf{43})(\text{N}_3)_2]$ (Fig. 176b) each zinc ion is coordinated by a symmetrically bridged pair of phenolate oxygen atoms and by two imino-nitrogen atoms, and carries a terminal azide ligand. The zinc $\cdots$ zinc separation is 3.333 Å and each zinc has a square-based pyramidal coordination geometry, with mutually *cis*-basal bridging oxygens and the azido nitrogen in the axial site at a greater displacement. There are no significant intermolecular contacts, and no opportunities for hydrogen bonding.

$[\text{Ni}_2(\mathbf{43})(\text{CH}_3\text{CN})_4]^{2+}$, prepared by reacting $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ with $[\text{H}_4\text{-}\mathbf{43}]^{2+}$ in CH_3CN and in the presence of $\text{N}(\text{Et})_3$, shows two octahedral nickel(II) centers, coordinated to two imine nitrogen donors, two bridging phenoxy oxygen donors and two axial CH_3CN ligands; the macrocycle is essentially flat with only the middle carbons of the propylene chains deviating from the ligand plane. The Ni $\cdots$ Ni separation is 3.136 Å; this is similar to the Cu $\cdots$ Cu distance (3.091 Å) found in $[\text{Cu}_2(\mathbf{43})(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ and the Fe $\cdots$ Fe distance (3.117 Å) found in $[\text{Fe}_2(\mathbf{43})(\text{imidazole})_4]^{2+}$ where the metal centers are also in octahedral environments and located in the ligand plane [348]. The non-linearity of the Ni- CH_3CN groups and the relative instability of the complexes are caused by unfavourable steric interactions of the axial ligands (Fig. 177a).

In $[\text{Ni}_2(\mathbf{45})](\text{PF}_6)_2$ the reduction of size by replacing $\text{CH}_2\text{CH}_2\text{CH}_2$ with CH_2CH_2 linkers afford a square planarity at each nickel(II) center and a Ni $\cdots$ Ni distance of 3.024 Å [128,348] (Fig. 177b). Therefore it appears possible to control the stereochemistry of the metal ion in the resultant complex by control of the ring size of the macrocycle.

Reaction of $[\text{H}_4\text{-}\mathbf{45}](\text{PF}_6)_2$ with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in the presence of $\text{N}(\text{Et})_3$ affords two binuclear copper(II) species, the green $[\text{Cu}_2(\mathbf{45})(\text{CH}_3\text{COO})](\text{PF}_6)$ and the brown $[\text{Cu}_2(\mathbf{45})](\text{PF}_6)_2$, the former being the major product. Recrystallization of the crude product from acetonitrile/diethylether yields single crystals of both complexes. In the structure of $[\text{Cu}_2(\mathbf{45})(\text{CH}_3\text{COO})]^+$ (Fig. 178a) the two copper(II) ions adopt a square pyramidal geometry with each being coordinated to two imino nitrogens, two phenoxy

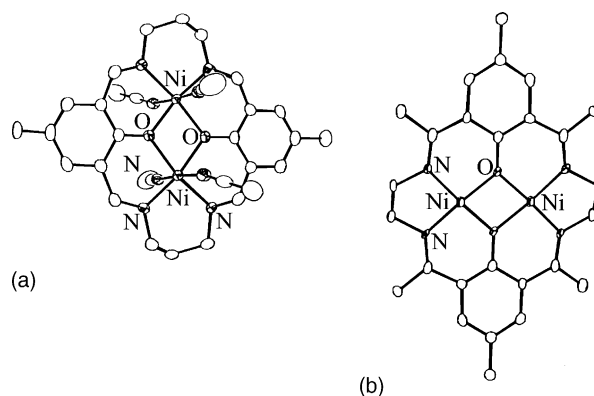


Fig. 177. Structure of $[\text{Ni}_2(\mathbf{43})(\text{CH}_3\text{CN})_4]^{2+}$ (a) and $[\text{Ni}_2(\mathbf{45})]^{2+}$ (b) (adapted from Refs. [128,348]).

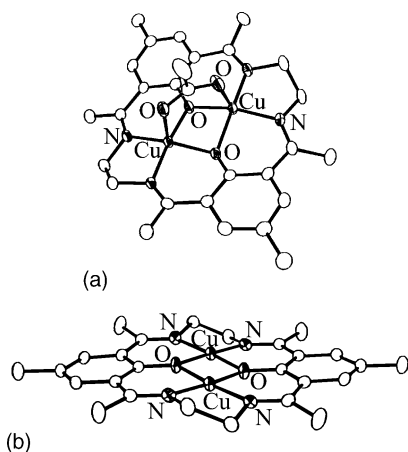


Fig. 178. Structure of $[\text{Cu}_2(\mathbf{45})(\text{CH}_3\text{COO})]^+$ (a) and $[\text{Cu}_2(\mathbf{45})]^{2+}$ (b) (adapted from Ref. [128]).

oxygens, and to an oxygen of the bridging acetate. The $\text{Cu} \cdots \text{Cu}$ separation is 2.824 Å. Both copper(II) ions lie slightly out of their N_2O_2 basal plane. The macrocycle adopts a more buckled conformation than in its protonated form. The structure of $[\text{Cu}_2(\mathbf{45})]^{2+}$ shows (Fig. 178b) that in this species each copper(II) center is coordinated in a square planar fashion by an N_2O_2 donor set from the macrocycle. The $\text{Cu} \cdots \text{Cu}$ separation (2.897 Å) is similar to that found in $[\text{Cu}_2(\mathbf{45})(\text{CH}_3\text{COO})]^+$. The structures of $[\text{Cu}_2(\mathbf{45})]^{2+}$ and $[\text{Cu}_2(\mathbf{45})(\text{CH}_3\text{COO})]^+$ prove that $[\mathbf{45}]^{2-}$ enforces a marginally smaller $\text{Cu} \cdots \text{Cu}$ separation than in comparable systems with $[\mathbf{43}]^{2-}$. $[\text{Cu}_2(\mathbf{45})(\text{CH}_3\text{COO})]^+$ and $[\text{Cu}_2(\mathbf{45})]^{2+}$ can be interconverted: suspension of $[\text{Cu}_2(\mathbf{45})(\text{CH}_3\text{COO})](\text{PF}_6)$ in ethanol followed by the addition of HPF_6 results in the quantitative generation of $[\text{Cu}_2(\mathbf{45})](\text{PF}_6)_2$ [128].

$[\text{H}_4\text{-}\mathbf{43}](\text{BF}_4)_2$ affords $[\text{M}_2(\mathbf{43})]^{2+}$, when reacted in CH_3CN with MCl_2 ($\text{M} = \text{Pt}^{2+}, \text{Pd}^{2+}$) or $[\text{Pd}(\text{CH}_3\text{COO})_2]_3$ in the presence of a 10-fold molar excess of $\text{N}(\text{Et})_3$, and $[\text{Rh}_2(\mathbf{43})(\text{Cl})_4]^{2+}$ when reacted with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of 2 equiv. of TIPF_6 .

In $[\text{Pd}_2(\mathbf{43})](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$ (Fig. 179) each square planar palladium(II) center is coordinated by two oxygen and two nitrogen donors of the macrocycle. The $\text{Pd} \cdots \text{Pd}$ distance is 3.151 Å. In contrast to the folded conformation of

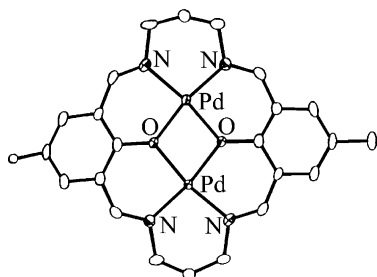


Fig. 179. Structure of $[\text{Pd}_2(\mathbf{43})]^{2+}$ (adapted from Refs. [128,348]).

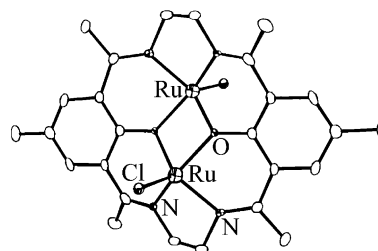


Fig. 180. Structure of $[\text{Ru}_2(\mathbf{45})(\text{Cl})_2]$ (adapted from Ref. [128]).

the protonated ligand $[\text{H}_4\text{-}\mathbf{43}]^{2+}$, the macrocycle in $[\text{Pd}_2(\mathbf{43})]^{2+}$ is planar, thus removing the possibility of intramolecular π interactions between phenyl rings. However, intermolecular stacking of the phenyl rings occurs in the solid state to give a staggered array of cations [128,348].

Reaction of the [2+1] side-off ligand, derived by the condensation of 2,6-diacetyl-4-methylphenol and ethylenediamine in a 2:1 molar ratio, with $[\text{RuCl}_2(\text{PPh}_3)_3]$ affords a red-brown compound, possibly the mononuclear acyclic ruthenium(II) complex which, by further reaction with 1,2-diaminoethane in the presence of $\text{Zn}(\text{CH}_3\text{COO})_2$ and $[\text{Ru}(\text{Cl})_2(\text{PPh}_3)_3]$, affords $[\text{Ru}_2(\mathbf{45})(\text{Cl})_2]$. Each ruthenium(II) metal center is five coordinated, being bound to two imine nitrogens, two bridging phenoxo oxygens and one chloride ligand. Each symmetry-equivalent ruthenium(II) center lies 0.790 Å out of the N_4O_2 plane with the ruthenium(II) centers mutually *anti* with respect to the macrocyclic ligand. Thus, the hole size of the macrocycle appears to be too small for the relatively large ruthenium(II) centers (Fig. 180) [128].

No complexes have been prepared when 2,6-diformyl-4-methylphenol is used as formyl precursor; this may reflect the results that decarbonylation of 2,6-diformyl-4-methylphenol can occur in the presence of ruthenium(II) [349]. Brief boiling of equimolecular proportions of 2,6-diformyl-4-methylphenol and $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ in ethanol or benzene in the presence of 1 equiv. of a primary amine, which appears to be essential for the reaction, affords the dark violet diamagnetic complex of Fig. 181. Identical results are obtained by using the preformed Schiff base in place of

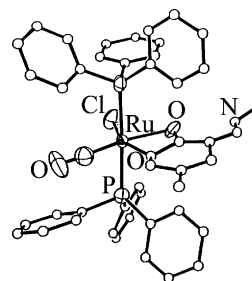


Fig. 181. Structure of the ruthenium(II) complex derived from the decarbonylation-metallation of 2,6-diformyl-4-methylphenol in the presence of methylamine (adapted from Ref. [349]).

2,6-diformyl-4-methylphenol + RHN_2 ($\text{R} = \text{CH}_3$, C_2H_5 , $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$, C_2H_5 , $p\text{-C}_6\text{H}_4\text{CH}_3$), proving that the active species is the Schiff base. The ruthenium complex shows the $\text{RuP}_2\text{C}_2\text{ClO}$ coordination unit is severely distorted from octahedral geometry; the two phosphorus ligands are *trans* and the ring and carbonyl carbon atom *cis*. Thus a decarbonylative metalation of the Schiff base occurs. A protonation of the azomethyne function was indicated also by IR and NMR data [128,349].

The template condensation of 2,6-diformyl-4-methylphenol, 1,3-diaminopropane in the presence of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ forms $\text{Pb}(\text{H}_2\text{-43})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, which reacts with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in methanol and in the presence of NaClO_4 to give rise to $[\text{Fe}(\text{H}_2\text{-43})(\text{H}_2\text{O})(\text{Cl})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. This mononuclear iron(III) complex, when treated under nitrogen with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and CH_3COONa in CH_3CN , turns into the mixed valence dinuclear complex $[\text{Fe}_2(\text{43})(\mu\text{-CH}_3\text{COO})_2](\text{ClO}_4)_4$ [350] which has a centrosymmetric structure; the center of inversion is at the middle of the $\text{Fe}_2(\mu\text{-O})_2$ plane. The crystallographic symmetry in $[\text{Fe}_2(\text{43})(\mu\text{-CH}_3\text{COO})_2](\text{ClO}_4)_4$ indicates that the iron sites are equivalent and the compound is valence-delocalized as corroborated also by electronic and Mossbauer spectra which prove that $[\text{Fe}_2(\text{43})(\mu\text{-CH}_3\text{COO})_2](\text{ClO}_4)_4$ is a valence delocalized complex showing a fast electron delocalization rate. Magnetic data show a ferromagnetic interaction ($J = 17 \text{ cm}^{-1}$) for this complex [350].

Macrocyclic dicopper(II) complexes have been prepared by condensation of 2,6-diformyl-4-substituted phenols and various linked diamine in the presence of the appropriate copper(II) salt [319]. In $[\text{Cu}_2(\text{43})(\text{H}_2\text{O})_2](\text{F})_2 \cdot 2\text{CH}_3\text{OH}$ the macrocyclic complex adopts an essentially flat structure with the two square pyramidal copper centers bridged by the two phenoxide oxygen atoms, with quite large Cu-O-Cu angles. The copper centers are separated by $3.118 \text{ \AA}$. Two water molecules occupy axial positions in a *trans* arrangement and the copper centers are displaced towards the waters by $0.208 \text{ \AA}$ from the mean N_2O_2 basal plane. The fluoride ions and methanol molecules occupy lattice sites, with the water molecules from separate macrocyclic complexes and the methanol molecules hydrogen bonded to the fluoride ions in an arrangement in which two water molecules and two fluoride ions form an eight membered ring between each adjacent pair of macrocyclic units. This hydrogen-bonding framework links the macrocyclic complexes in a stepped, *trans*-axial linear chain.

$[\text{Cu}_2(\text{304})(\text{Cl})_2][\text{Cu}_2(\text{304})(\text{H}_2\text{O})_2](\text{Cl})(\text{ClO}_4) \cdot 5.5\text{H}_2\text{O}$ contains two different molecules in the unit cell. The neutral dinuclear macrocyclic complex (Fig. 182a) has two highly distorted square pyramidal copper centers bridged by the phenoxide oxygens. The $\text{Cu} \cdots \text{Cu}$ separation is $3.115 \text{ \AA}$. The effect of the C_4 chain linking the azomethine nitrogen donors and the resulting seven-membered chelate ring is to twist the two phenolic residues and the copper basal planes. The coordination geometry at each copper is best described as distorted square pyramidal.

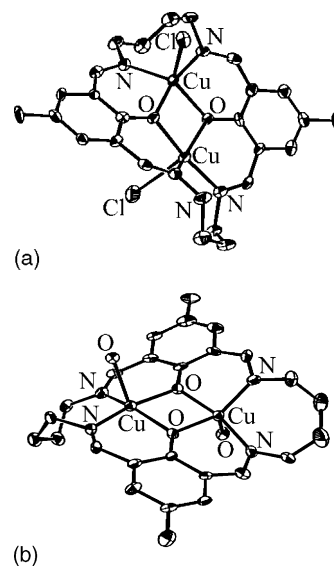


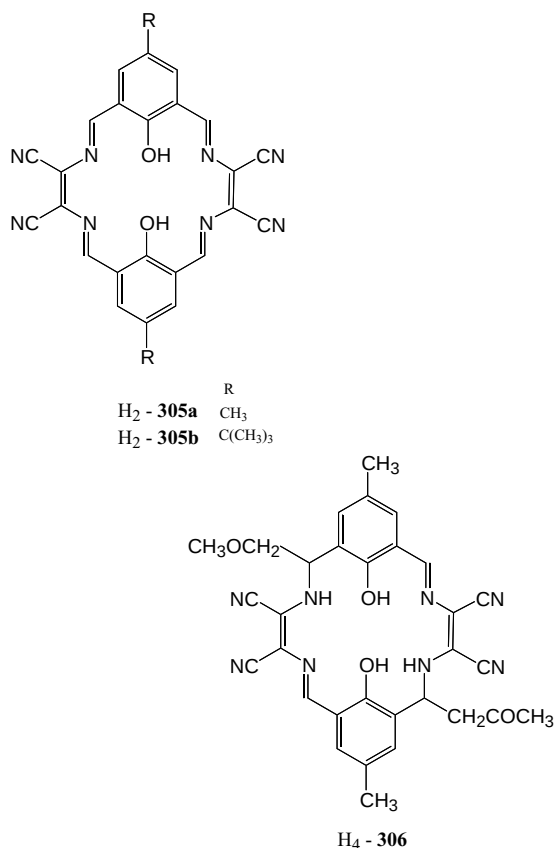
Fig. 182. Structure of $[\text{Cu}_2(\text{304})(\text{Cl})_2]$ (a) and $[\text{Cu}_2(\text{304})(\text{H}_2\text{O})_2]^{2+}$ (b) present in of $[\text{Cu}_2(\text{304})(\text{Cl})_2][\text{Cu}_2(\text{304})(\text{H}_2\text{O})_2](\text{Cl})(\text{ClO}_4) \cdot 5.5\text{H}_2\text{O}$ (adapted from Ref. [350]).

A similar situation prevails for the cation $[\text{Cu}_2(\text{304})(\text{H}_2\text{O})_2]^{2+}$ (Fig. 182b). The two distorted square pyramidal copper centers are separated by $3.102 \text{ \AA}$ and bridged by the two phenoxide oxygen atoms. Axial contacts to the two water molecules are somewhat shorter than the axial chlorine contacts found in the other molecule. A similar twisting of the ligand itself occurs because of the large size of the butane bridging fragment between the azomethine nitrogens. The copper basal coordination planes are again severely distorted, with displacements of the donor atoms around the two copper atoms from their respective mean plane. Copper ions themselves are displaced toward the coordinated water molecule by $0.220 \text{ \AA}$. The coordination geometry at the copper centers has been described as distorted square pyramidal.

The structural features of $[\text{Cu}_2(\text{45})(\text{H}_2\text{O})_2](\text{BF}_4)_2$ are essentially the same as those reported previously [5,42] with two square pyramidal copper centers occupying the macrocyclic cavity with an almost planar basal array of donors.

All these compounds show that strong or moderate net antiferromagnetic interactions occurs between the paramagnetic centers.

Template condensation of 2,6-diformyl-4(R)-phenols ($\text{R} = \text{CH}_3$, $\text{C}(\text{CH}_3)_3$) with diaminomaleonitrile in the presence of copper(II) perchlorate in methanol after extended refluxing leads to the formation of the [2+2] macrocyclic complexes $[\text{Cu}_2(\text{305a})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{305b})](\text{ClO}_4)_2$. The compounds can be recrystallized from methanol, ethanol, DMF or nitrobenzene. Recrystallization of $[\text{Cu}_2(\text{305a})](\text{ClO}_4)_2$ from acetone leads to the different macrocycle complex $[\text{Cu}_2(\text{306})] \cdot \text{CH}_3\text{COCH}_3$ resulting from the addition of two acetone molecules across two imine linkages of the complexes macrocycle $[\text{Cu}_2(\text{305a})](\text{ClO}_4)_2$ as ascertained by an X-ray structural investigation [351].



In $[Cu_2(\mathbf{306})] \cdot CH_3COCH_3$ the macrocycle is not flat but shows a convex shape with the two acetonyl groups, projected onto the same face of the molecule. The dinuclear center has a very small $Cu \cdots Cu$ separation (2.788 Å) with a basal ligand array at each copper which is almost planar (Fig. 183). In $[Cu_2(\mathbf{306})] \cdot CH_3COCH_3$ a moderate antiferromagnetic coupling is operating [351].

$[Cu(\mathbf{307})(DMSO)]$ results from the recrystallization of $[Cu_2(\mathbf{305})](ClO_4)_2$ from dimethyl sulfoxide; this is reasonably due to an hydrolytic attack of H_2O present in the undried solvent, at two adjacent coordinated imine groups. The driving force for this reaction could be, in part, the inherent strain in the parent macrocyclic complex but also the result of the enhanced electrophilic character at the azomethine carbon centers, associated with the presence

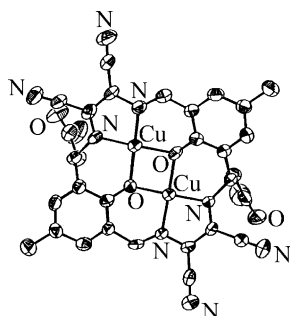
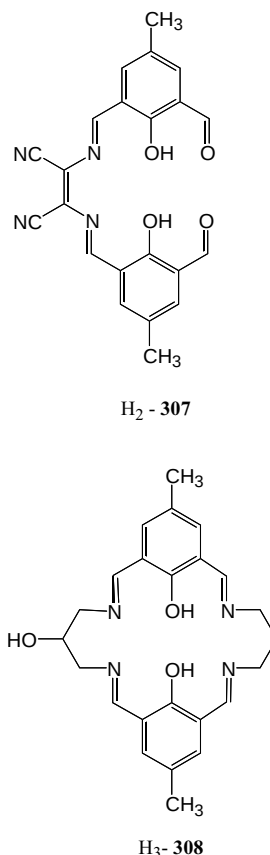


Fig. 183. Structure of $[Cu_2(\mathbf{306})]$ (adapted from Ref. [351]).

of the electron-withdrawing nitrile groups. The same derivative can be prepared by condensing 2,6-diformyl-4-methylphenol and diaminomaleonitrile in a 2:1 molar ratio and in the presence of a copper(II) salt. The copper atom is square-pyramidal with an axially bound DMSO. There is a slight displacement of the copper atom toward the DMSO oxygen [351].



The template condensation of 2,6-diformyl-4-methylphenol or 2,6-diformyl-4-*tert*-butylphenol with 1,3-diamino-2-hydroxypropane in the presence of copper(II) salts in methanol/ethanol produces dinuclear copper(II) complexes of the [20]-membered, potentially octadentate macrocyclic ligands H_4 -**284a** and H_4 -**284b**. These [2+2] macrocycles do not involve endogenous alkoxide and phenoxide bridges simultaneously and do not accommodate four metal centers, unlike the [24]-membered macrocycles derived from 1,5-diamino-3-hydroxypentane (H_4 -**284c**, H_4 -**284d**). This is undoubtedly associated with the small cavity size in H_4 -**284a** and H_4 -**284b**. These dinuclear complexes can also be prepared by transmetallation techniques, reacting the lead(II) or barium(II) complexes of the macrocycles H_4 -**284a** or H_4 -**284b** with the appropriate copper(II) salts [352].

The use of copper(II) chloride as templating agent in the above condensation reactions resulted in the formation of a polymeric product of undefined composition. With copper(II) thiocyanate as templating agent, the protonated ligand salt $[H_6\text{-}\mathbf{284a}](NCS)_2 \cdot 2H_2O$ was produced, rather

than a copper(II) complex. Thus the complexes $[\text{Cu}_2(\text{H}_2\text{-284a})(\text{Cl})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{H}_2\text{-284a})(\text{NCS})_2]$ were prepared by reaction of $[\text{Pb}_2(\text{H}_2\text{-284a})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{H}_2\text{-284a})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ with excess copper(II) chloride and thiocyanate, respectively [352].

Template condensation of 2,6-diformyl-4-methylphenol or 2,6-diformyl-4-*tert*-butylphenol with 1,3-diamino-2-hydroxypropane in the presence of copper(II) acetate and excess azide ions in methanol produced the polymeric copper(II) complexes $[\text{Cu}_2(\text{H}_2\text{-284a})][\text{Cu}_2(\text{N}_3)_6] \cdot 1.5\text{CH}_3\text{OH}$ and $[\text{Cu}_2(\text{H}_2\text{-284b})][\text{Cu}_2(\text{N}_3)_6]$. The complex $[\text{Cu}_2(\text{H}_2\text{-284a})][\text{Cu}_2\text{Cl}_4]$ was derived by template condensation of 2,6-diformyl-4-methylphenol and 1,3-diamino-2-hydroxypropane in the presence of copper(I) chloride but clearly involves an oxidation to give the mixed-oxidation-state species [352].

In $[\text{Cu}_2(\text{H}_2\text{-284a})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ (Fig. 184a) each copper ion is five coordinated, bonded to two imine nitrogen atoms and two endogenous phenolate oxygen bridges in the basal plane, with a methanol oxygen or perchlorate oxygen occupying the fifth, axial positions. The geometry around each copper is slightly distorted square pyramidal [352].

$[\text{Cu}_2(\text{H}_2\text{-284a})][\text{Cu}_2\text{Cl}_4]$ (Fig. 184b) has a polymeric structure with a fairly flat macrocyclic cation, involving two

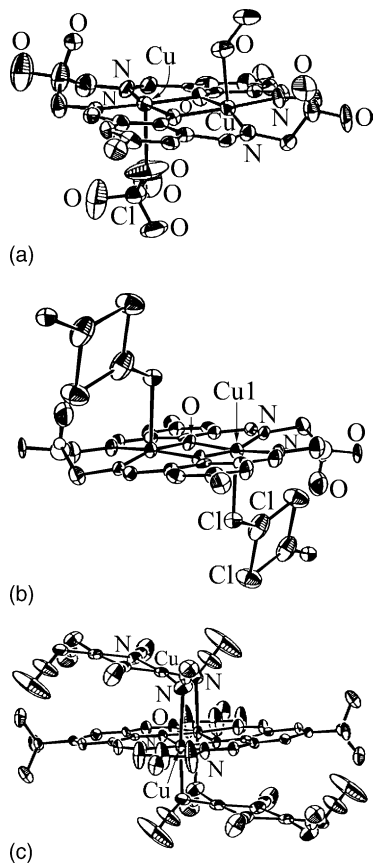


Fig. 184. Structure of $[\text{Cu}_2(\text{H}_2\text{-284a})(\text{CH}_3\text{OH})(\text{ClO}_4)]^+$ (a), $\{[\text{Cu}_2(\text{H}_2\text{-284a})][\text{Cu}_2\text{Cl}_4]\}_n$ (b) and $\{[\text{Cu}_2(\text{H}_2\text{-284b})][\text{Cu}_2(\text{N}_3)_6]\}_n$ (c) (adapted from Ref. [352]).

square-pyramidal copper(II) ions bridged by phenoxide oxygen atoms. The cations are in turn bridged in a *trans*-axial fashion by the flat, asymmetric $[\text{Cu}_2\text{Cl}_4]^{2-}$ anion, which involves two copper(I) ions [352].

In $[\text{Cu}_2(\text{H}_2\text{-284b})][\text{Cu}_2(\text{N}_3)_6]$ (Fig. 184c) the binuclear cation has two copper(II) centers bridged internally by phenoxide oxygen atoms and no coordination of the secondary alcohol groups. Each copper center is six coordinate, with nitrogen atoms from terminal azide groups on the $[\text{Cu}_2(\text{N}_3)_6]^{2-}$ anion acting as axial ligands. The structure consists of an alternating, stepped, chain of interconnected dinuclear macrocyclic cations $[\text{Cu}_2(\text{H}_2\text{-284b})]^{2+}$ bridged axially through 1,1-azide interactions to the dinuclear $[\text{Cu}_2(\text{N}_3)_6]^{2-}$ anions. The basal donor set (N_4O_2) of the macrocyclic cation is very close to planar.

Room-temperature magnetic moments and variable temperature magnetic studies indicate strong intradimer anti-ferromagnetic exchange ($-2J = 675\text{--}902\text{ cm}^{-1}$) and also extended exchange in the azide anion bridged polymers [352].

Electrochemical properties of the dinuclear cations show sequential one-electron-transfer steps at negative potentials ($E_{1/2}^1 = -0.93$ to -0.96 V ; $E_{1/2}^2 = -1.32$ to -1.35 V (vs ferrocenium/ferrocene) due to the formation of $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ species [352].

In $[\text{Mn}_2(\text{H}_2\text{-284a})(\text{CH}_3\text{COO})_2] \cdot 2\text{CH}_3\text{OH}$, obtained by a synthetic procedure similar to that employed for the similar copper(II) derivatives, each manganese ion is coordinated to two imine nitrogen donors and two bridging phenolate groups from the macrocycle. The coordination sphere is completed by a bidentate acetate ligand. The metal ions are therefore six coordinated but their irregular geometry may be described as square pyramidal, with the acetate group as axial ligand. The manganese ions are $0.77\text{ \AA}$ on either side of the mean plane of the N_2O_2 macrocyclic donors and the $\text{Mn} \cdots \text{Mn}$ distance is $3.34\text{ \AA}$ [353] (Fig. 185).

In the related dimanganese(III) complex $[\text{Mn}_2(\text{H-308})(\text{CH}_3\text{COO})](\text{ClO}_4)$ [353] (H-308 is the asymmetric macrocycle ligand bearing OH group on one lateral chain resulting from the two step condensation of 2,6-diformyl-4-methyl phenol with 1,3-diaminopropane and 1,3-diamino-2-hydroxypropane [322]) the acetate group acts as bridge between two dinuclear units affording five-coordination

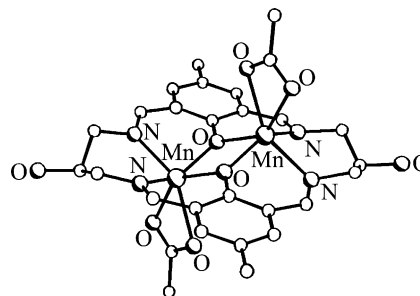


Fig. 185. Structure of $[\text{Mn}_2(\text{H}_2\text{-284a})(\text{CH}_3\text{COO})_2]$ (adapted from Ref. [353]).

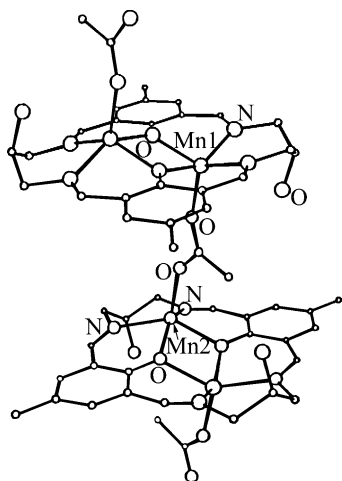


Fig. 186. Structure of $[\text{Mn}_2(\text{H-308})(\text{CH}_3\text{COO})]^+$ cation chain (adapted from Ref. [353]).

around each manganese(II) ion and forming a chain structure. In this complex the deviation of the manganese ion from the basal N_2O_2 plane is 0.61 Å (Fig. 186).

Magnetic moments support an high spin electronic configuration of the manganese(II) ions and show that the two paramagnetic centers are weakly interacting each other, the sign and magnitude of each J_{ij} are sensitive to small change in dinuclear core structure so that the overall magnetic interaction varies from ferromagnetism to antiferromagnetism [353].

$[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})_2]$ and $[\text{Mn}_2(\mathbf{43})(\text{C}_6\text{H}_5\text{COO})_2]$, prepared under anaerobic conditions in alcoholic solution, are air stable in the solid state and in DMF or DMSO solution; they show one quasi-reversible couple at ca. +0.29 V (versus SCE) assigned to the one-electron oxidation process, $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}/\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ [353]. Moreover the oxidation of $[\text{Mn}(\mathbf{43})(\text{CH}_3\text{COO})_2]$ with Br_2 forms the mixed-valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ complex $[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})(\text{Br})_2]\cdot\text{H}_2\text{O}$ [353].

In $[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})_2]$ two manganese(II) ions are bridged by two phenolic oxygens of the macrocycle with a $\text{Mn}\cdots\text{Mn}$ separation of 3.367 Å. A bidentate acetate group affords a six coordinated geometry around each manganese(II): the resulting geometry about the manganese(II) is much distorted from a regular octahedron (Fig. 187a).

In $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$, prepared by reaction of the appropriate diformyl and diamine precursors in the presence of $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ in methanol under nitrogen (Fig. 187b), the macrocycle $[\mathbf{304}]^{2-}$ accommodates two manganese(II) ions within its two N_2O_2 metal-binding sites, providing a centrosymmetric dinuclear core with the nearly coplanar MnO_2Mn skeleton bridged by the two phenolic oxygens. The pair of manganese ions are further bridged by two acetate groups above and below the dinuclear skeleton. Thus, the configuration about each manganese(II) ion is described as a distorted octahedron with the N_2O_2 donor set of the macrocycle in the equatorial plane and the oxygens of

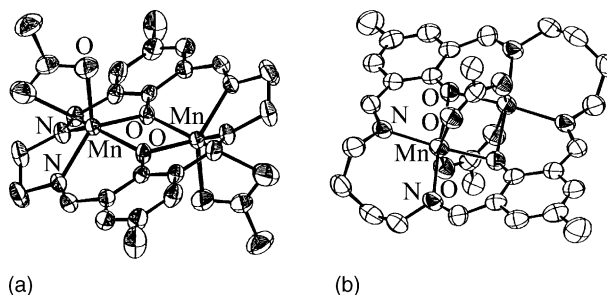


Fig. 187. Structure of $[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})_2]$ (a) and $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$ (b) (adapted from Ref. [354]).

the acetate groups in the axial sites. The $\text{Mn}\cdots\text{Mn}$ separation is 2.978 Å. The macrocyclic entity, except for the lateral chain part, assumes good coplanarity with an inversion center at the center of the dinuclear skeleton MnO_2Mn [354].

The core structure of $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$ differs from that of $[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})_2]$. In the latter complex each manganese(II) ion deviates from the basal N_2O_2 plane by 0.75 Å because of the mismatch between the cavity size and the ionic radius of the manganese(II) ion, and a bidentate acetate group occupies the open space to provide a distorted six coordination about the metal ion.

Cryomagnetic studies (4.2–300 K) indicate for $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$ a significantly strong antiferromagnetic interaction ($J = -5\text{ cm}^{-1}$) while that in $[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})_2]$ is very weak and ferromagnetic ($J = +0.4\text{ cm}^{-1}$) [354].

The EPR spectrum of the electrolysed solution (frozen at liquid-nitrogen temperature) shows a six line hyperfine structure and a weaker 10-line hyperfine structure, characteristic of a mixed-valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ complex comprised of essentially uncoupled manganese(II) and manganese(III) ions [354].

The electrochemical properties $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$, studied by cyclic voltammetry in DMF (platinum electrode), shows one pseudo-reversible couple near +0.35 V versus SCE which is assigned to the $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}/\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ process based on coulometry studies at +0.33 V.

The CAT-like activity of $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$ is low relative to that of $[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})_2]$. It has been shown that the bidentate acetate group of $[\text{Mn}_2(\mathbf{43})(\text{CH}_3\text{COO})_2]$ is substitution labile in aqueous dimethylformamide and this site is available for the accommodation of hydrogen peroxide in the catalase-like reaction. $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$ shows a small electric conductivity in aqueous DMF (DMF-water, 4:1, v/v). This indicates considerable inertness of the bridging acetate group and explains the low catalytic activity of $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$ at the initial stage of the H_2O_2 decomposition reaction. Dissociation of the bridging acetate group, however, may occur with time as indicated by the gradual increase in the O_2 evolution rate. Probably $[\text{Mn}_2(\mathbf{304})(\text{CH}_3\text{COO})_2]$ catalyses the disproportionation of H_2O_2 by the same mechanism proposed for $[\text{Mn}_2(\mathbf{43})-$

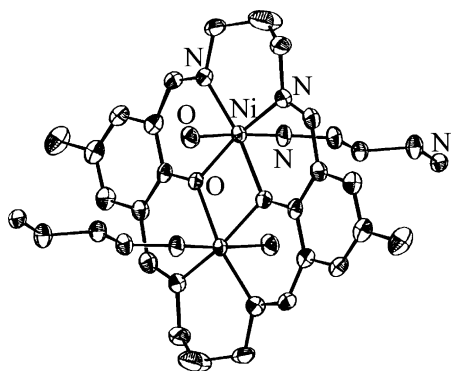


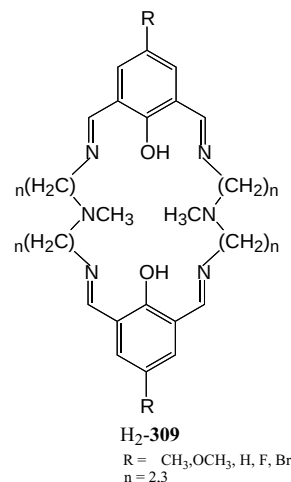
Fig. 188. Structure of $[\text{Ni}_2(\mathbf{43})(\mu\text{-H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{H}_2\text{O})_2]_n^{2+}$ (adapted from Ref. [356]).

lecularly bridged by a phenoxide oxygen atom and intermolecularly bridged by 1,3-diaminopropane. The chain is isolated by ClO_4^- anions and water molecules which are found in the interchain space. There are two perchlorate anions and four water molecules present in each dimeric unit. Hydrogen bonds between the perchlorate group and water molecules and between water molecules are present. Thus nickel(II) dimers are intermolecularly bridged by diaminopropane ligands in an end-to-end fashion. In each dimer the nickel(II) centers are coordinated by two phenoxide oxygen atoms and two imino nitrogen atoms completing the NiN_2O_2 basal plane. Each of the nickel(II) ions achieves a distorted octahedral configuration through the axial coordinations of water and the diaminopropane ligand, which are *trans* to each other. The interesting feature of this structure is that the diaminopropane not only acts as an axial ligand but also bridges the two crystallographically inequivalent dimers. Each dimer has a centrosymmetric structure with a center of inversion at the middle of the Ni_2O_2 plane. The macrocyclic N_2O_2 donor atoms form an exact plane from which the nickel ion is displaced above and below by 0.079 Å. The intradimer distance between two nickel ions is 3.156 Å while the distance between two nickel ions bridged by diaminopropane was found to be 8.79 Å. The bridging behaviour of diaminopropane gives a chain of dimers that propagates in the *ac* diagonal plane. The interesting feature of this compound is the bridging behaviour of 1,3-diaminopropane in an end-to-end fashion. Nickel ions are placed in a distorted octahedral environment [365].

The magnetic properties of the compound reveal a moderately strong intramolecular antiferromagnetic coupling ($J = -30 \text{ cm}^{-1}$) and a weak intermolecular ferromagnetic coupling ($J' = 2 \text{ cm}^{-1}$) [356]. For this complex it was suggested that the nature and magnitude of exchange coupling with the superexchange pathway is dominated by the $d_{x^2-y^2}$ orbital and p_x and p_y orbitals of oxygen of the $^3\text{A}_{1g}$ ground state of this nominally octahedral Ni(II) coordination, while the origin of ferromagnetism between the dimers should be through the d_z^2 orbital.

The macrocyclic size has been enlarged and/or the density increased to incorporate identical or different d and/or

f-metal ions. Using ligands as $\text{H}_2\text{-309}$, the complexes $[\text{M}_2(\mathbf{309})]^{n+}$, $[\text{UO}_2\text{M}(\mathbf{309})]^{n+}$ or $[\text{MM}'(\mathbf{309})]^{n+}$ have been prepared and their properties studies [357].



The complexes $[\text{Mn}_2(\mathbf{309})(\text{R}'\text{COO})](\text{ClO}_4)$ ($\text{R}' = \text{CH}_3$ or XC_6H_4 where $\text{X} = \text{H}, 4\text{-CH}_3\text{O}, 4\text{-CH}_3, 4\text{-Br}, 4\text{-Cl}, 4\text{-F}, 4\text{-NO}_2, 2\text{-CH}_3\text{O}, 2\text{-CH}_3, 2\text{-Br}, 2\text{-Cl}, 2\text{-F}, 2\text{-NO}_2$ and $\text{R}' = \text{XYC}_6\text{H}_3$ where $\text{XY} = 2,4\text{-(NO}_2)_2, 3,4\text{-(NO}_2)_2, 2\text{-Cl-4-NO}_2$; $\text{R} = \text{CH}_3$ and $n = 2$) were synthesized by template condensation of *N,N*-bis(2-aminoethyl)methylamine, 2,6-diformyl-4-methylphenol, $\text{R}'\text{COONa}$ and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The X-ray structure of $[\text{Mn}_2(\mathbf{309})(\text{CH}_3\text{COO})](\text{ClO}_4)$ ($\text{R} = \text{CH}_3$; $n = 2$) shows the macrocyclic Schiff base acts as an octadentate N_6O_2 ligand and an acetate anion bridge the two manganese(II) ions, which are coordinated also by two bridging phenolic oxygens and three nitrogens. The whole coordination geometry around each manganese ion is roughly octahedral but several deformed [357].

The crystal structure of $[\text{Mn}_2(\mathbf{309})(2\text{-O}_2\text{NC}_6\text{H}_4\text{COO})](\text{ClO}_4)$ ($\text{R} = \text{CH}_3$; $n = 2$) (Fig. 189) reveals that the asymmetric unit of the triclinic unit cell contains two crystallographically independent complex cations $[\text{Mn}_2(\mathbf{309})(2\text{-O}_2\text{NC}_6\text{H}_4\text{COO})]^+$ with slightly different conformations attributed to the crystal packing effect, two perchlorate anions and one $(\text{CH}_3)_2\text{NCHO}$ solvate molecule [357].

Electrochemical measurements of these complexes revealed that both the substituents of the phenol ring and those on the ligating acetate effectively control the redox properties of the manganese(II) center [357]. Such fine-

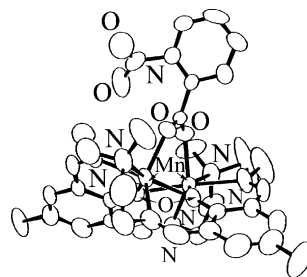


Fig. 189. Structure of $[\text{Mn}_2(\mathbf{309})(2\text{-NO}_2\text{-C}_6\text{H}_4\text{COO})]^+$ ($\text{R} = \text{CH}_3$; $n = 2$) (adapted from Ref. [357]).

tuning of redox properties may be useful to construct functional modes on manganese-containing redox enzymes.

The cyclic voltammograms of $[\text{Mn}(\mathbf{309})(\text{R}'\text{COO})](\text{ClO}_4)$ showed two reversible waves in the range 0.1–1.0 V (versus ferrocenium/ferrocene couple, in acetonitrile-0.1 mol dm⁻³ NEt_4ClO_4), corresponding to $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}/\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ couples. The half-wave potentials ($E_{1/2}^1$ and $E_{1/2}^2$) showed systematic changes for the various bridging benzoates, similar to the acetate based complexes $[\text{Mn}_2(\mathbf{309})(\text{CH}_3\text{COO})](\text{ClO}_4)$.

Bis(2-aminoethyl)methylamine, $\text{MnX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, Br^- , ClO_4^-) and 2,6-diformyl-4-methylphenol form in boiling methanol in the presence of NaX ($\text{X} = \text{ClO}_4^-$, N_3^- , SCN^-) the dinuclear manganese(II) complexes $[\text{Mn}_2(\mathbf{309})(\text{X})](\text{ClO}_4)$ [357]. In $[\text{Mn}_2(\mathbf{309})(\text{Cl})](\text{ClO}_4)$ ($\text{R} = \text{CH}_3$, $n = 2$) the two manganese ions are bridged by the two phenolic oxygens from the macrocycle and the chloride. The overall structure of the $\{\text{Mn}_2(\mathbf{309})\}$ unit is similar to that of $[\text{Mn}_2(\mathbf{309})(\text{CH}_3\text{COO})](\text{ClO}_4)$ with highly deformed octahedral coordination to each manganese ion. The shorter $\text{Mn} \cdots \text{Mn}$ distance is attributed to the presence of the m_2, h^1 -bridging chloride in place of the m_2, h^2 -bridging acetate in $[\text{Mn}_2(\mathbf{309})(\text{CH}_3\text{COO})](\text{ClO}_4)$. From the comparison of the two structures it may be supposed that the $\{\text{Mn}_2(\mathbf{309})\}$ unit should be sufficiently rigid to retain the structural similarity in these complexes, and that all the compounds $[\text{Mn}_2(\mathbf{309})(\text{X})](\text{ClO}_4)$ should contain the binuclear cations with similar structures, with the $\{\text{Mn}_2(\mathbf{309})\}$ core and the bridging X anion [357] (Fig. 190).

The catalase activity of $[(\text{Mn}_2(\mathbf{309})(\text{X}))](\text{ClO}_4)$ ($\text{X} = \text{Cl}^-$, Br^- , N_3^- , SCN^- , CF_3COO^- , CH_3COO^- , Cl_3CCOO^-) was examined by adding an acetonitrile solution of H_2O_2 to a CH_3CN solution of the complex at 25 °C and measuring volumetrically the amount of evolved oxygen. The rate of O_2 evolution was initially zero, rapidly increased to reach a maximum and then gradually decreased. The presence of a lag period before reaching the maximum rate was also noted in a parallel investigation using $[\text{Mn}_2(\mathbf{310})(\text{C}_6\text{H}_5\text{COO})_2(\text{NCS})]$ [357] where, however a distinct two-stage character of the time course was observed which seems absent when $[\text{Mn}_2(\mathbf{309})(\text{X})](\text{ClO}_4)$ are used [357]. Moreover, a colour change of the reaction mixture containing $\text{Mn}_2(\mathbf{310})(\text{C}_6\text{H}_5\text{COO})_2(\text{NCS})$ occurs from yellow to purple, which strongly indicated the formation of a $\text{Mn}^{\text{IV}} = \text{O}$

species, whereas all solutions containing $[\text{Mn}_2(\mathbf{309})(\text{X})](\text{ClO}_4)$ remained yellow, which suggests that the high-valent manganese species, if ever formed, are short-lived and immediately reduced to the pale-coloured manganese(II) species. A comparison of the maximum rates of O_2 evolution (V_{max}), measured for these compounds $[\text{Mn}_2(\mathbf{309})(\text{X})](\text{ClO}_4)$ confirms that the oxidation potentials are not important in determining V_{max} . Instead, it seems that the nature of the bridging anion X^- is closely related with V_{max} the more basic X^- is, the smaller the activity. Nevertheless complexes where $\text{X} = \text{N}_3^-$ and SCN^- , have higher activity than the complex where $\text{X} = \text{CF}_3\text{COO}^-$ in spite of the greater basicity of X^- because in these compounds X^- should bind perhaps in a m_2, h^1 -manner and therefore less tightly. Examination of the two series, $[\text{Mn}_2(\mathbf{309})(\text{CH}_3\text{COO})](\text{ClO}_4)$ ($\text{R} = \text{CH}_3$, $n = 2$; $\text{R} = \text{Br}$, $n = 2$; $\text{R} = \text{CH}_3$, $n = 3$) and $[\text{Mn}_2(\mathbf{309})(\text{CF}_3\text{COO})](\text{ClO}_4)$ ($\text{R} = \text{CH}_3$, $n = 2$; $\text{R} = \text{Br}$, $n = 2$; $\text{X} = \text{CH}_3$, $n = 3$) reveals that the compounds where $\text{X} = \text{CH}_3\text{COO}^-$ or CF_3COO^- and $n = 3$ have much lower activity; it is possible that the $(\text{CH}_2)_3$ chains in these complexes should allow the more stable conformation of the $\{\text{Mn}_2(\mathbf{309})\}$ core which should bind X^- more tightly. It was proposed that dissociation of X^- is involved in the rate-determining step in the catalytic decomposition of H_2O_2 by $[\text{Mn}_2(\mathbf{309})(\text{X})](\text{ClO}_4)$. This is quite reasonable as these complexes have six coordinate (saturated) manganese centers, in contrast with $[\text{Mn}_2(\mathbf{310})(\text{C}_6\text{H}_5\text{COO})_2(\text{NCS})]$ which has five coordinate manganese centers. This important difference might have led to the apparently different behaviour of the two series of compounds [357].

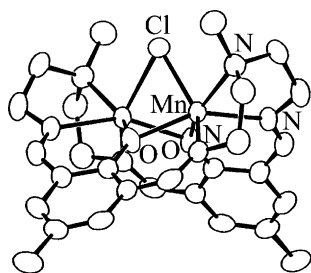
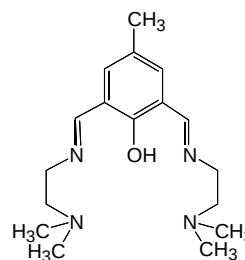
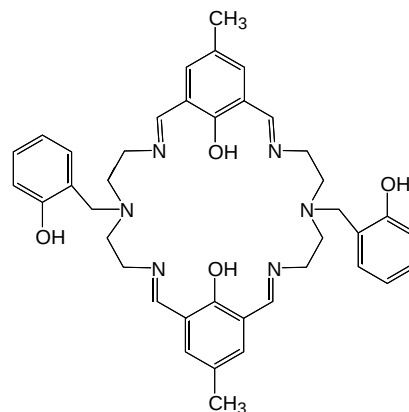


Fig. 190. Structure of $[\text{Mn}_2(\mathbf{309})(\text{Cl})]^+$ ($\text{R} = \text{CH}_3$; $n = 2$) (adapted from Ref. [357]).



H-310

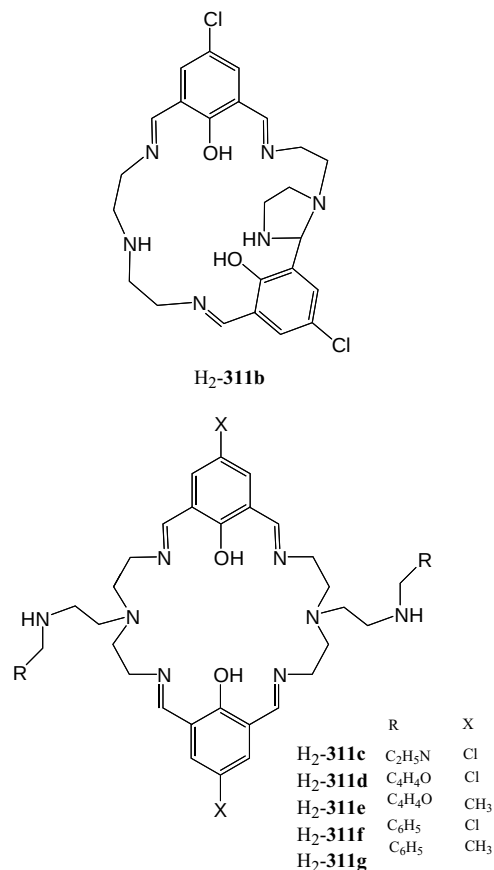


H4-311a

Similarly to previously reported acetate or halide bridged complexes $[\text{Mn}_2(\mathbf{309})(\text{Cl})](\text{ClO}_4)$ and $[\text{Mn}_2(\mathbf{309})(\text{CH}_3\text{COO})](\text{ClO}_4)$, the benzoate complexes $[\text{Mn}_2(\mathbf{309})(\text{R}'\text{COO})](\text{ClO}_4)$ effectively catalysed disproportionation of hydrogen peroxide. When an H_2O_2 solution (8.35 mol dm^{-3}) in CH_3CN (1 cm^3) was added to a solution of $[\text{Mn}_2(\mathbf{309})(\text{R}'\text{COO})](\text{ClO}_4)$ ($5 \times 10^{-3} \text{ mol dm}^{-3}$) in CH_3CN (10 cm^3), gaseous dioxygen was evolved and hydrogen peroxide was almost completely consumed. After completion of the reaction, the starting complex was recovered in 77% yield. These results show that the $\{\text{Mn}_2(\mathbf{309})(\text{R}'\text{COO})\}$ core serves as a very effective and robust device for evolution of dioxygen [357]. The initial maximum rate of O_2 evolution was determined for various benzoate complexes $[\text{Mn}_2(\mathbf{309})(\text{R}'\text{COO})](\text{ClO}_4)$. Since it has been reported that an addition of base causes acceleration of manganese-catalysed O_2 evolution, experiments in the presence of 2,4,6-trimethylpyridine were also performed. It was found that the acetate based complexes $[\text{Mn}_2(\mathbf{309})(\text{CH}_3\text{COO})](\text{ClO}_4)$ showed increasing activity with increasing acidity of the corresponding acid CH_3COOH . It was proposed that dissociation of the bridging $\text{R}'\text{COO}^-$ group is involved in the rate-determining step (the more acidic the acid, the less basic is the conjugate base, and therefore more readily it dissociates). However, with $[\text{Mn}_2(\mathbf{309})(\text{R}'\text{COO})_2](\text{ClO}_4)$ the situation is more complicated; in the presence of 2,4,6-trimethylpyridine, the activity increases with increasing acidity of $\text{R}'\text{CO}_2\text{H}$, while in the absence of 2,4,6-trimethylpyridine the activity decreases with increasing acidity of $\text{R}'\text{CO}_2\text{H}$; it reaches a minimum at $\text{p}K_a \approx 2$, and then rises again for stronger acids ($\text{p}K_a < 2$).

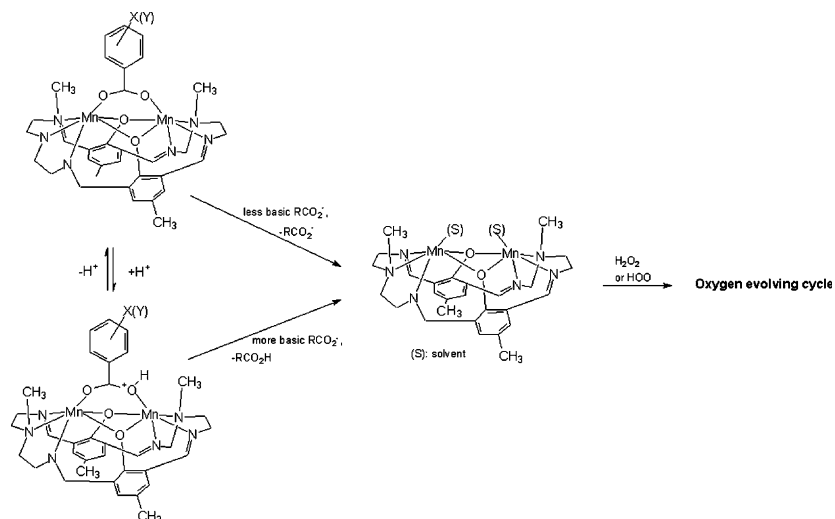
In order to interpret these results, the effect of protonation of the complex upon dissociation of the bridging carboxylate was taken into account. The complex $[\text{Mn}_2(\mathbf{309})(\text{R}'\text{COO})]^+$ acts as Brønsted base, as shown by pH measurements (glass electrode) in aqueous acetonitrile. It is likely that in those complexes with a more basic RCO_2^- group (i.e. larger $\text{p}K_a$) which is reluctant to dissociate, protonation of the complex is necessary prior to dissociation of the carboxylate. In such circumstances, the O_2 evolving reaction has two pathways (Scheme 45): in the region of $\text{p}K_a < 2$, one pathway is prevailing, in which the reaction rate increases for less basic carboxylate; and on the contrary, in the region of $\text{p}K_a > 2$, another pathway becomes dominant, in which the rate decreases for less basic carboxylate. The effect of 2,4,6-trimethylpyridine is to suppress the lower path by consuming H^+ and to accelerate the overall reaction by generation HO_2^- from H_2O_2 [358].

The reaction between sodium 2,6-diformyl-4-X-phenolates ($\text{X} = \text{CH}_3, \text{Cl}$) and *N,N*-bis(2-aminoethyl)-2-hydroxybenzylamine followed by in situ transmetallation with $\text{Cd}(\text{ClO}_4)_2$, $\text{Mn}(\text{ClO}_4)_2$ or $\text{Fe}(\text{ClO}_4)_3$ resulted in the production of $[\text{Cd}_2(\text{H}_2\text{-}\mathbf{311a})](\text{ClO}_4)_2$, $[\text{Mn}_2(\text{H}_2\text{-}\mathbf{311a})](\text{ClO}_4)$ and $[\text{Fe}(\text{H}_2\text{-}\mathbf{311b})(\text{Cl})](\text{ClO}_4)_2$, respectively [358].



In the dinuclear cadmium(II) complex, $[\text{H}_2\text{-}\mathbf{311a}]^{2-}$ is a [26]-membered [2+2] Schiff base macrocycle with two pendant arms being forced to point toward one side of the macrocycle. Two cadmium(II) ions were bridged by two m -phenoxy oxygen atoms on the macrocycle. The coordination geometry of each cadmium(II) ion can be considered as a highly distorted octahedron, possibly imposed by steric requirements. The six coordinate sphere of each metal ion includes two imine groups, one tertiary nitrogen which is connected to a pendant arm, two phenolic oxygen atoms as well as one hydroxyl group from the pending phenolic moiety. Two metal atoms are separated by a distance of 3.42 Å. The deprotonation of the hydroxyl groups of the attaching phenolic arm appears not to take place, consistent with IR and ^1H NMR spectra (Fig. 191a) [358].

In $[\text{Mn}_2(\text{H}_2\text{-}\mathbf{311a})](\text{ClO}_4)$ each manganese(II) ion is six coordinated with a N_3O_3 unit composed of two imino nitrogen atoms, one tertiary nitrogen atom, two phenolic oxygen atoms as well as one oxygen atom from one of the pending phenolic groups. The phenolic oxygen atom of each pendant arm is bound to the adjacent manganese ion and two pendant groups are on the same side of macrocycle, forcing the ring highly twisted and two phenoxy heads of the macrocycle almost vertical each other. The two manganese ions, 3.324 Å apart, are in a similar coordination sphere but with a slight difference. They are bridged by two phenoxy oxygen atoms on the macrocyclic skeleton. One proton is in one of these phenoxy groups of the macrocyclic framework



Scheme 45.

(Fig. 191b) [358]. The magnetic data in the 4–300 K range indicate a weak antiferromagnetic interaction between the two manganese(II) ions ($J = -2.6 \text{ cm}^{-1}$). Cyclic voltammograms of this complex are consistent with a one-electron oxidation process relative to form $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ species [358].

In $[\text{Fe}(\text{H}_2\text{-311b})(\text{Cl})](\text{ClO}_4)_2$ the resulting compartmental ligand is a [21]-membered asymmetric [2+2] Schiff base macrocycle, of which the coordination hemisphere includes two imine groups and one secondary amine nitrogen atom as well as two phenolic groups. The complex is a mononuclear

and six coordinated iron(III) species that has a distorted octahedral geometry around the iron ion. The equatorial plane is composed of two phenoxy oxygen atoms, one imine nitrogen atom and the adjacent secondary amine nitrogen atom, while two apical positions are occupied by the other imine nitrogen atom and a chloride anion. The macrocyclic Schiff base acts as a neutral chelating ligand (Fig. 191c) [358].

$[\text{M}_2(\text{311c})](\text{ClO}_4)_2$ ($\text{M} = \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$), have been prepared via the cyclocondensation between sodium 2,6-diformyl-4-chlorophenolate, and *N*-(2-methylenepyridinyl)tris(2-aminoethyl)amine and the subsequent transmetal-

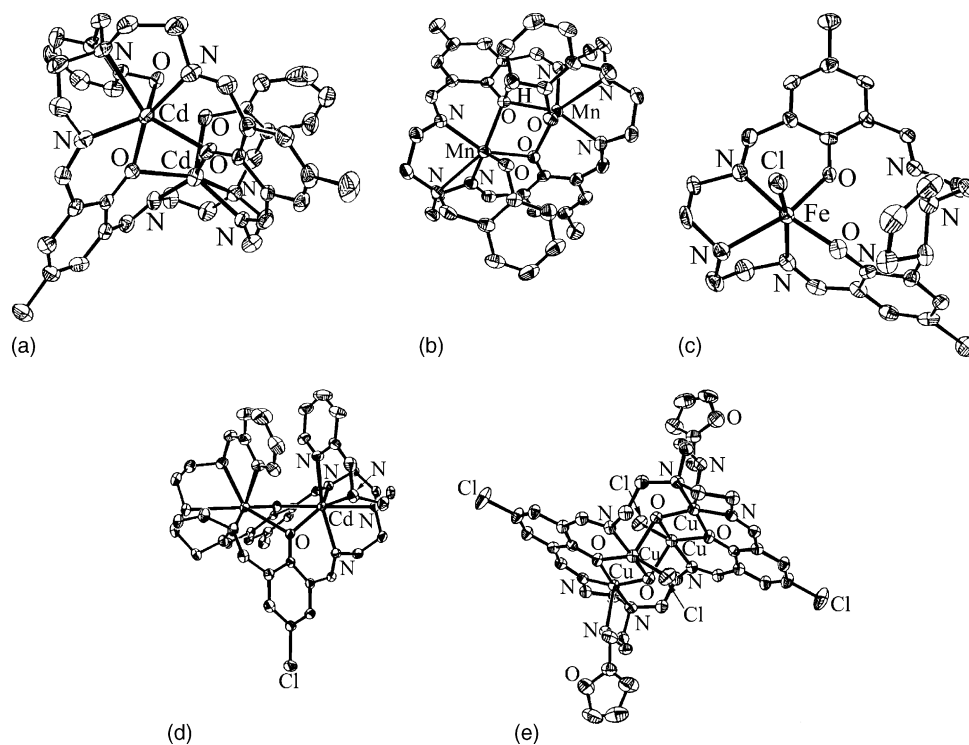


Fig. 191. Structure of $[\text{Cd}_2(\text{H}_2\text{-311a})]^{2+}$ (a), $[\text{Mn}_2(\text{H-311a})]^+$ (b), $[\text{Fe}(\text{H}_2\text{-311b})(\text{Cl})]^{2+}$ (c), $[\text{Cd}_2(\text{311c})]^{2+}$ (d) and $[\text{Cu}_4(\text{311d})(\text{Cl})_2(\text{OH})_2]^{2+}$ (e) (adapted from Ref. [358]).

lation with metal perchlorates [358]. The nitrogen-functionalized polyamine was prepared by the condensation of equal molar amount of tren with 2-formylpyridine in low concentration to avoid the side product of 1:2 or 1:3 Schiff bases. The C=N double bonds were then completely reduced by an excess of NaBH₄.

In [Mn₂(**311c**)](ClO₄)₂ the two nitrogen donor atoms in each arm are bonded to one metal ion, while the bridgehead nitrogen atom (tertiary nitrogen) is non-bonding owing to steric hindrance. Thus an uncommon eight membered chelating ring has been produced. In the [Mn₂(**311c**)]²⁺ cation, each manganese(II) ion is six coordinated by two phenoxy oxygen atoms, two imine nitrogen atoms one secondary amine nitrogen atom and a pyridine nitrogen atom from the pendent arm. The configuration of the metal ion in this complex is a distorted octahedron [358].

Also in [Cd₂(**311c**)](ClO₄)₂ the two pendant arms attach to the metal ions on the same side of the macrocycle. The significant difference in coordination chemistry between [Cd₂(**311c**)](ClO₄)₂ and [Mn₂(**311c**)](ClO₄)₂ is that each cadmium(II) ion is coordinated by all of the ligating atoms including the tertiary nitrogen atom in one of the two chambers of the macrocycle. Each cadmium(II) ion is seven coordinated by two phenol oxygen atoms, two imine nitrogen atoms, one tertiary nitrogen atom, one secondary amine nitrogen atom and a pyridine nitrogen atom from the pendent arm. The coordination sphere of the metal ion has been described as a highly distorted pentagonal bipyramid (Fig. 191d) [358].

In [Mn₂(**311c**)](ClO₄)₂ the two high spin manganese(II) ions show a very weak antiferromagnetic interaction ($J = -2.26 \text{ cm}^{-1}$).

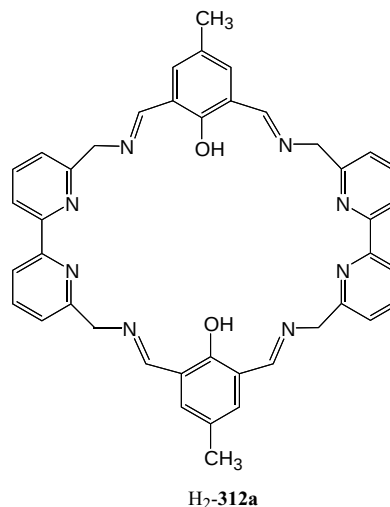
The CAT-like activity of [Mn₂(**311c**)](ClO₄)₂ to catalyze the disproportionation of H₂O₂ into H₂O and O₂ is lower than that of [Mn₂(**43**)](CH₃COO)₂. It has been reported that the dissociation of the bridging carboxylate is involved in the rate-determining step, and the activity of macrocyclic manganese complexes is largely dependent upon the nature of the bridging ligands. In [Mn₂(**311c**)](ClO₄)₂, the two donors atoms in each pendent-arm are chelated to the adjacent metal ion suggesting that full dissociation, in order to generate vacant sites for binding of H₂O₂, would be difficult [358].

[Mn₂(H-**311a**)](ClO₄) exhibits a high activity for catalyzing the reaction of H₂O₂ to O₂ [358]. A comparison of the catalytic behaviour of [Mn₂(H-**311a**)](ClO₄) and [Mn₂(**311c**)](ClO₄)₂ shows that the H₂O₂ decomposition rate and the conversion largely depend upon the nature of the pendant arm of the macrocycles and the electronic nature of the manganese ion. One mole of [Mn₂(H-**311a**)](ClO₄)₂ could convert 112 moles of H₂O₂ in about 2 min, meanwhile one mole of [Mn₂(H-**311a**)](ClO₄) could convert 343 mole of H₂O₂ in the same time. Therefore, the catalytic activity of the title complex is compatible to that of the most efficient macrocyclic dinuclear manganese(II) complex reported [358].

The condensation of sodium 2,6-diformyl-4-X-phenolate (X = Cl, CH₃) with the reduced 1:1 Schiff base of 2,2',2''-

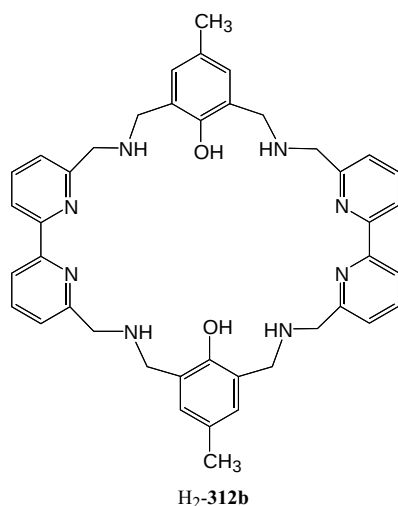
tris(aminoethyl)amine and 2-formylfuran (or benzaldehyde) followed by in situ transmetallation with copper(II) perchlorate results in the production of tetranuclear copper(II) complexes of [2+2] macrocyclic Schiff bases with functional pendant arms (H₂-**311d** ··· H₂-**311g**) [358]. In [Cu₄(**311d**)(Cl)₂(OH)₂](ClO₄)₂ a chair-shaped Cu₄O₄ core is composed of two kinds of crystallographically independent copper(II) ions, each of which possesses a distorted square pyramidal configuration. The four metal ions are in an approximate parallelogram. Two pendant arms, bonding in a monodentate fashion to their adjacent metal atoms, lie in the *trans* position to the macrocycle. All metal ions are bound within the macrocyclic framework, however, there are two sets of coordination environments around the copper ions. In one coordination environment the copper(II) ion is located in a plane consisting of an imine nitrogen one phenoxide oxygen, one amine nitrogen and a hydroxide ion, the axial position is occupied by the secondary amine nitrogen on the arm. But for the other copper(II) coordination environment the plane is composed of one hydroxide ion, an imine nitrogen, one-phenoxide oxygen and a chloride anion and the corresponding axial position is taken by the other hydroxide ion. The axis of the pyramid of the two copper ions beside one phenolic moiety is opposite to that of the remaining two copper ions near the other phenolic ring. Two pendant arms point in opposite directions away from the macrocycle, in which two furan rings, not bonding to the metal atoms, are parallel to each other. The four metal ions are connected by two *m*-phenol oxygen atoms and by two *m*₃-hydroxo groups which are situated in the chamber of the macrocycle. The interatomic distance between the crystallographically independent copper(II) ions are 3.059 and 3.326 Å, respectively (Fig. 191e). Strong antiferromagnetic interactions between the copper(II) ions occur [358].

Condensation of equimolar amount of 2,6-diformyl-*p*-cresol and 6,6'-bis(aminomethyl)-2,2'-dipyridyl in the presence of La(CH₃COO)₃·*n*H₂O as a template agent, leads to a tetraimine Schiff base macrocyclization forming the dinuclear lanthanum complex [La₂(**312a**)(CH₃COO)₄] [359].



The structure of $[\text{La}_2(\mathbf{312a})(\text{CH}_3\text{COO})_4] \cdot 4\text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$ (Fig. 192a), formed by recrystallization of $[\text{La}_2(\mathbf{312a})(\text{CH}_3\text{COO})_4] \cdot 10\text{H}_2\text{O}$ in CH_3CN , reveals entrapment of a pair of lanthanum(III) cations in the twin [18]-membered coordination compartments of the [30]-membered macrocycle $[\mathbf{312a}]^{2-}$. Both lanthanum ions lie within the macrocycle and are bridged by the two phenolate oxygen anions. Each lanthanum ion is decacoordinated, being bound to two phenolate oxygens, two dipyrindyl nitrogens, and two Schiff base nitrogens and four acetate oxygens. The coordination polyhedron has been described as an extended double dodecahedron of D_2 symmetry. The four acetonitrile and three water molecules are within hydrogen bonding distance of acetate oxygen atoms that are accessible to the La_2O_2 core. The $\text{La} \cdots \text{La}$ distance is 4.147 Å [359].

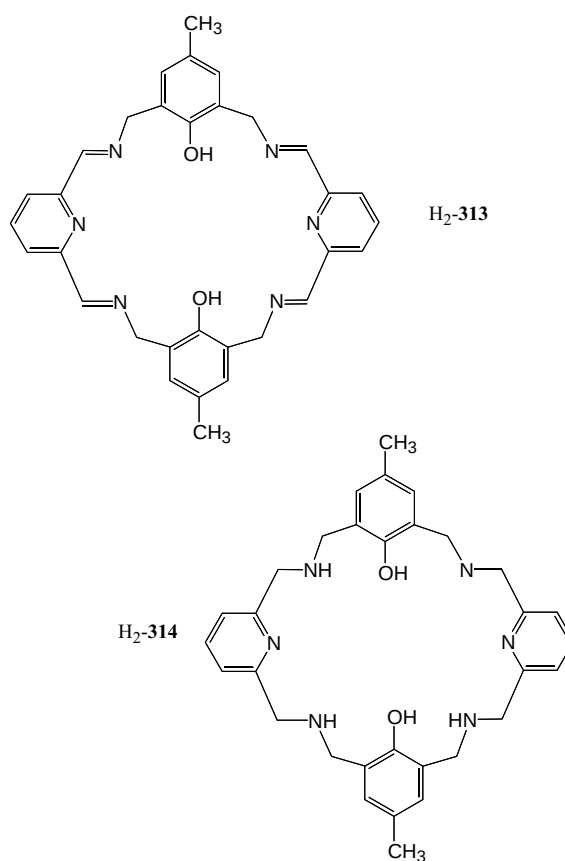
Hydrogenation of $[\text{La}_2(\mathbf{312a})(\text{CH}_3\text{COO})_4]$ with NaBH_4 and NaBH_3CN in methanol gave the metal-free macrocycle $\text{H}_2\text{-}\mathbf{312b}$ which was isolated with the use of diethylenepentacetic acid to remove the lanthanum ion in aqueous solution [359].



All the eight nitrogen atoms of the macrocycle $\text{H}_2\text{-}\mathbf{312b}$, obtained as octahydrosulfate salt, are protonated, including the four bipyridine nitrogens. The $[\text{H}_{10}\text{-}\mathbf{312b}]^{8+}$ cation adopts a three-layer stair-like arrangement with two phenol aromatic rings in the middle, separating two bipyridine aromatic rings on the left top and the right bottom, respectively. The macrocycle is contracted by internal hydrogen bonding with four HSO_4^- and two water molecules inside the macrocycle, and with four HSO_4^- and six water molecules outside the macrocycle (Fig. 192b) [359].

The self condensation between 2,6-bis(aminomethyl)-*p*-cresol and 2,6-diformylpyridine in methanol leads to the formation of the [2+2] macrocyclic Schiff base $\text{H}_2\text{-}\mathbf{313}$. Hydrogenation of this Schiff base produced the related saturated macrocycle $\text{H}_2\text{-}\mathbf{314}$, which was extracted

with an organic solvent from aqueous solution under alkaline condition. The free ligand $\text{H}_2\text{-}\mathbf{314}$ was converted to both the hydrochloride and hydrobromide salts. Crystalline $\text{H}_2\text{-}\mathbf{314} \cdot \text{H}_2\text{O} \cdot 7\text{HBr}$ suitable for X-ray structure determination was obtained under very acidic conditions (48% HBr with $\text{C}_2\text{H}_5\text{OH}$). The crystal structure data provide clear evidence of the [2+2] nature of this macrocycle. All six nitrogen atoms are protonated and a hydronium ion is also present. The macrocycle adopts a low symmetry conformation with no intramolecular stacking effect between its aromatic rings. The macrocycle is associated directly with three bromide anions, which are located close to the cavity of the macrocycle. The four other bromide anions are situated on the periphery of the macrocycle, apparently with charge attraction to one or two protonated sites, but are outside the cavity [359] (Fig. 192c).



The condensation of equimolar amounts of 2,6-diformyl-*p*-cresol and diethylenetriamine in the presence of $\text{Pb}(\text{SCN})_2$ leads to the [2+2] Schiff base macrocyclization forming the dinuclear lead complex. Hydrogenation of this [2+2] Schiff base complex with sodium tetrahydroborate in methanol followed by acidification with H_2SO_4 to remove the lead(II) ion as PbSO_4 , gave the corresponding air stable reduced macrocycle $\text{H}_2\text{-}\mathbf{314a}$ [359].

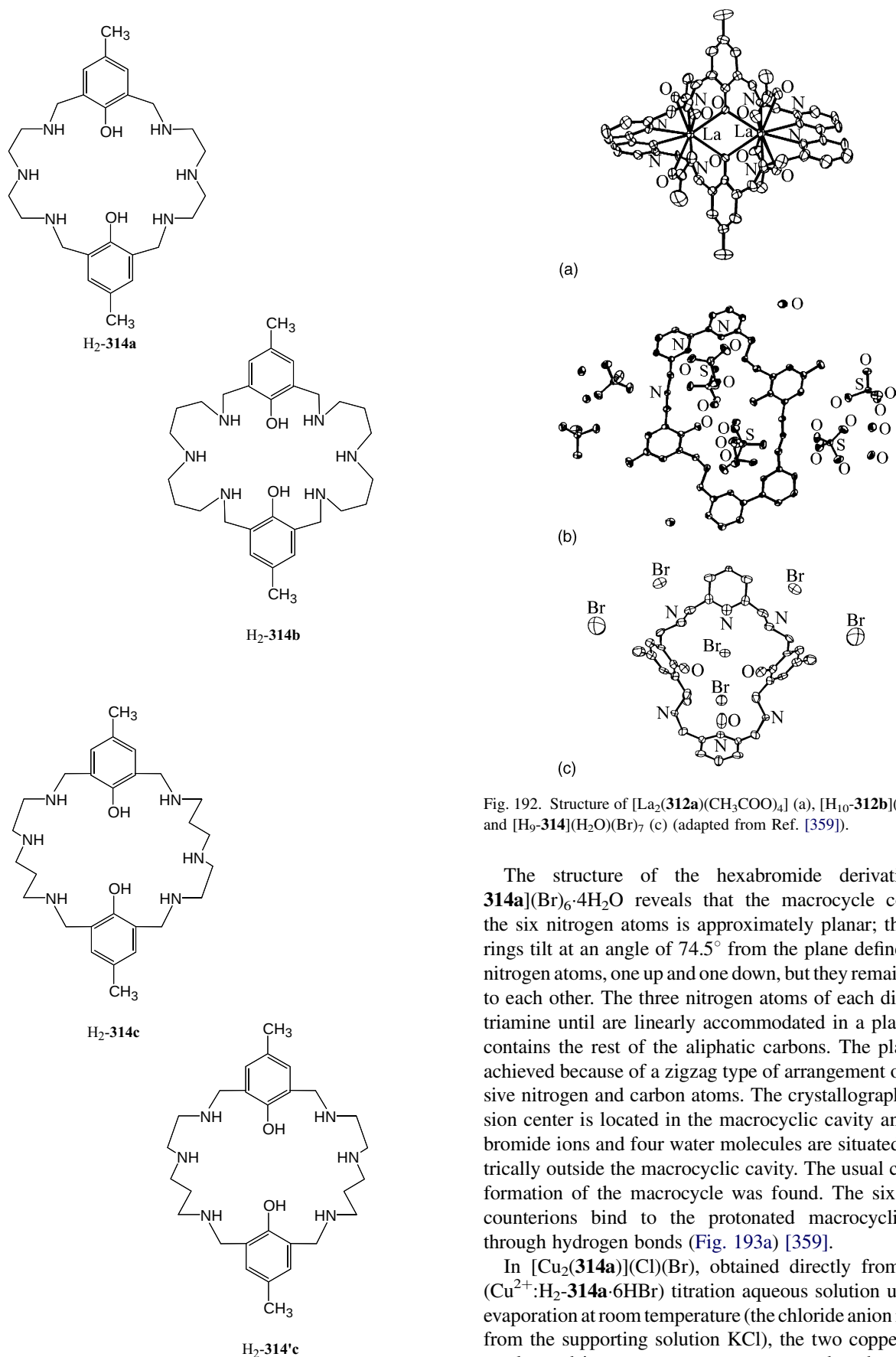


Fig. 192. Structure of [La₂(**312a**)(CH₃COO)₄] (a), [H₁₀-**312b**](HSO₄)₈ (b) and [H₉-**314**](H₂O)(Br)₇ (c) (adapted from Ref. [359]).

The structure of the hexabromide derivative [H₈-**314a**](Br)₆·4H₂O reveals that the macrocycle containing the six nitrogen atoms is approximately planar; the phenol rings tilt at an angle of 74.5° from the plane defined by the nitrogen atoms, one up and one down, but they remain parallel to each other. The three nitrogen atoms of each diethylene-triamine until are linearly accommodated in a plane which contains the rest of the aliphatic carbons. The planarity is achieved because of a zigzag type of arrangement of successive nitrogen and carbon atoms. The crystallographic inversion center is located in the macrocyclic cavity and the six bromide ions and four water molecules are situated symmetrically outside the macrocyclic cavity. The usual chair conformation of the macrocycle was found. The six bromide counterions bind to the protonated macrocyclic ligand through hydrogen bonds (Fig. 193a) [359].

In [Cu₂(**314a**)](Cl)(Br), obtained directly from the 2:1 (Cu²⁺:H₂-**314a**·6HBr) titration aqueous solution upon slow evaporation at room temperature (the chloride anion is derived from the supporting solution KCl), the two copper(II) ions are located in separate compartments and each of them is

coordinated to three amino nitrogens from two diethylene-triamine units and one phenolic oxygen which defines a planar coordination polyhedron. The macrocyclic ligand serves as the N_3O donor to each copper ion. The intramolecular $Cu \cdots Cu$ separation is 5.36 Å. The macrocycle skeleton adopts a distorted conformation to make its cavity suitable for accommodation of metal ions [359] (Fig. 193b).

Also in $[Ni_2(314a)(H_2O)_2](Br)_2 \cdot 2H_2O$ obtained directly from the titration aqueous solution with KCl at $a = 8$ upon evaporation at room temperature for several days [359], each nickel(II) ion is coordinated to three amino nitrogens, two bridged phenolic oxygens and oxygen from a water molecule. The coordination number of the nickel(II) ions is six, which defines a slightly distorted octahedral coordination geometry [359] (Fig. 193c).

The specific spectroscopic and magnetic properties of the lanthanide(III) ions have made them essential components in the preparation of new materials and ideal as probes in studies of biological systems. These investigations have been often carried out with the help of macrocyclic ligands. It has been shown that it is possible to introduce two

lanthanide ions into a macrocyclic cavity; for instance, the Schiff bases obtained by condensation of 2,6-diformyl-4-substituted phenols with the facultative diamines ($NH_2-(CH_2)_2-X-(CH_2)_2-X-(CH_2)_2-NH_2$; ($X = NH, O$), provide a coordination moiety large enough (H_2 -74, H_2 -315, H_2 -316) to allow the preparation of homo- and hetero-dinuclear complexes [360,361]. In particular, the homo- and hetero-dinuclear lanthanide(III) complexes $Ln_2(74)(NO_3)_4 \cdot nH_2O$ ($Ln = La, Pr, Sm, Eu, Gd, Tb, Dy$; $n = 1, 2$) and $Ln^1Ln^2_{2-x}(74)(NO_3)_4 \cdot H_2O$ ($Ln^1Ln^2 = LaSm, LaGd, LaDy, LaEu, DyGd, DyEu, GdEu, GdTb, EuTb, LaTb$; $n = 1, 3$), have been synthesized and their possible structure and the interaction between the metal ions have been inferred from spectroscopic, mass spectrometry and magnetic data together with scanning electron microprobe analyses.

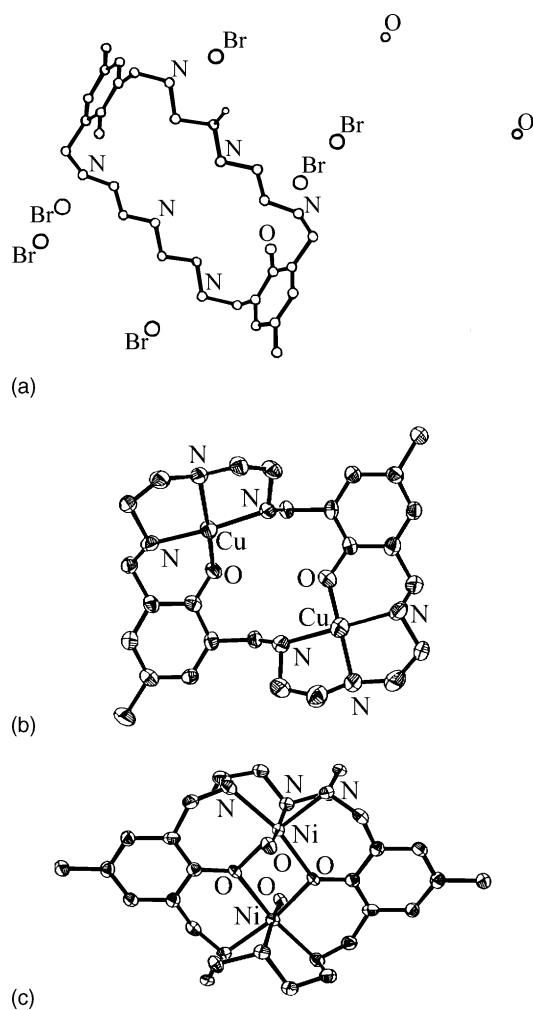
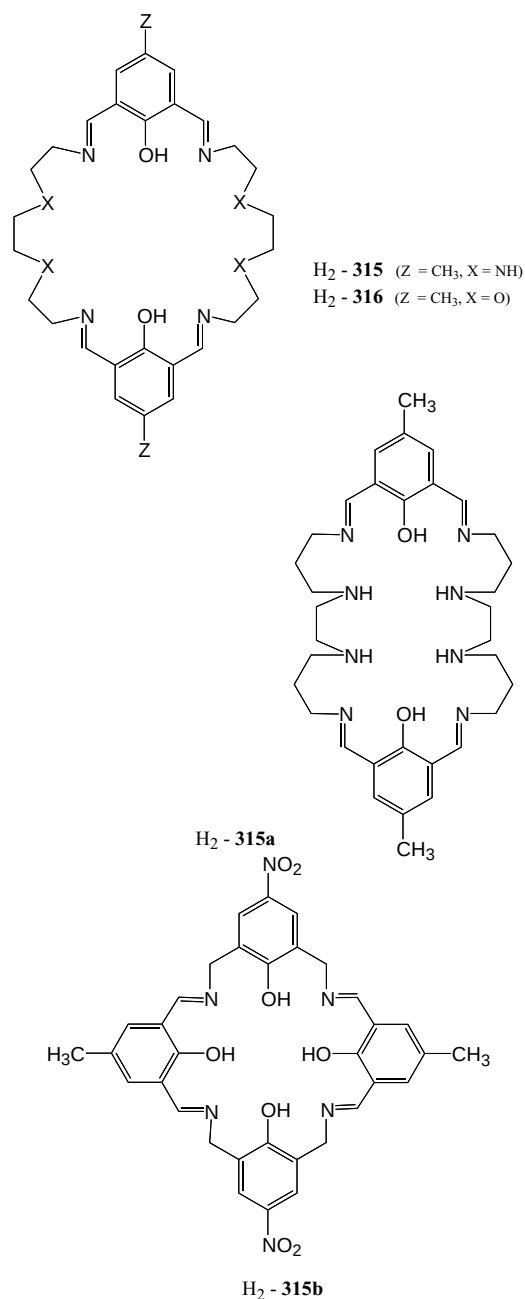


Fig. 193. $[H_8-314a] (Br)_6 \cdot 4H_2O$ (a), $[Cu_2(314a)]^{2+}$ (b) and $[Ni_2(314a)-(H_2O)_2]^{2+}$ (c) (adapted from Ref. [359]).



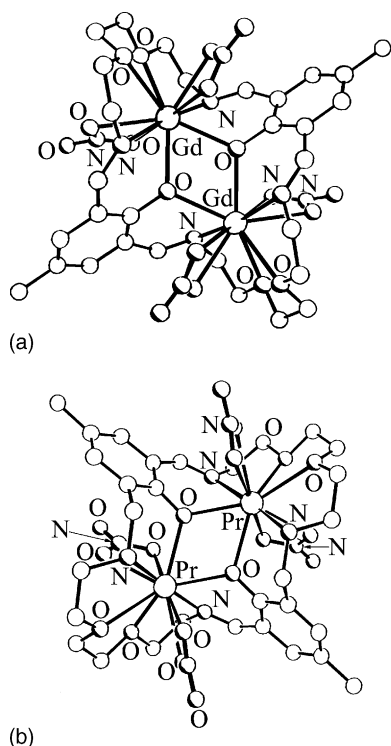


Fig. 194. Structure of $[\text{Gd}_2(\mathbf{316})(\text{NO}_3)_4]$ (a) and $[\text{Pr}_2(\mathbf{318a})(\text{NO}_3)_4]$ (b) (adapted from Ref. [363]).

The homo-dinuclear complex $[\text{Gd}_2(\mathbf{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ has a propeller conformation with approximate non-crystallographic D_2 symmetry with a crystallographic two-fold axis passing through the center and normal to the mean plane of the macrocycle. Both gadolinium ions lie within the macrocycle and are bridged by the two phenolate oxygen atoms. Each gadolinium ion is ten coordinated being bound to two nitrogen and two oxygen atoms of the macrocycle, four nitrate oxygens and two phenolate oxygen atoms [361] (Fig. 194a).

With these hetero-dinuclear complexes, the study of the energy transfer from the ligand to the two different lanthanide ions inside the macrocycle and from one lanthanide ion to other is feasible. Such energy transfer has been well defined especially for the complex $\text{EuTb}(\mathbf{74})(\text{NO}_3)_4$ [360]. The processes, absorption of the ligand $\rightarrow$ energy transfer to the europium(III) $\rightarrow$ Emission, have been studied also for the mononuclear europium(III) nitrate complex with the macrocycle obtained by condensation of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-azapentane [332].

Spectroscopic investigations on hetero-dinuclear species have quantified the ligand to lanthanide(III) and terbium(III) to europium(III) energy transfers also for an evaluation of the intermetallic distance [330]. The reported Gd $\cdots$ Gd distance (3.97 Å) for the complexes $\text{Gd}_2(\mathbf{316})(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ is considerably shorter than estimated for the similar complexes with $\text{H}_2\text{-74}$. Moreover, in the EuEu complex with $\text{H}_2\text{-316}$ the lifetime is much shorter than the lifetime reported for the complex with $\text{H}_2\text{-74}$. It was suggested that the

different R-substituent may induce a different conformation of the ligand and hence different Ln $\cdots$ Ln distances [360,361].

The series of these hetero-dinuclear lanthanide(III) complexes has been subsequently enlarged and the composition of compounds of the type $[\text{Ln}_{1-x}\text{Eu}_x]_2(\mathbf{316})(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ and $[(\text{Eu}_{1-x}\text{Tb}_x)_2(\mathbf{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ inferred by neutron activation analyses [361]. It was suggested that formation of $[\text{LnEu}(\mathbf{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ is more favourable than that of $[\text{LnTb}(\mathbf{87})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$. In both cases the cation discrimination index, computed as the ratio of probabilities of lanthanide(III) incorporation into the crystalline hetero-lanthanide compounds, is in favour of the larger lanthanide(III) ion [361,362].

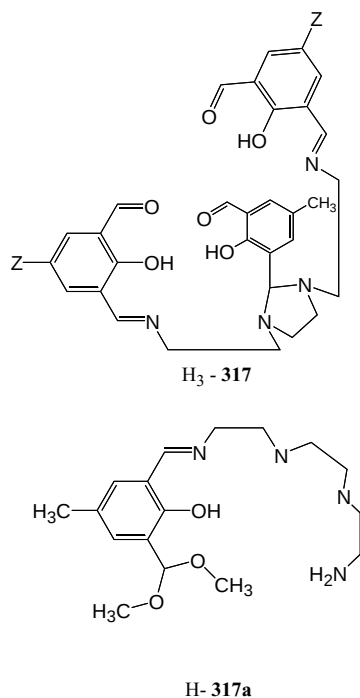
The homo-dinuclear lanthanide(III) complexes $[\text{Ln}_2(\text{H}_2\text{-315a})(\text{NO}_3)_x(\text{H}_2\text{O})_y](\text{NO}_3)_z \cdot n\text{H}_2\text{O}$ (Ln = La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Dy^{3+} ; $x = 3, 4$; $y = 0, 1$; $z = 2, 3$; $n = 1\text{--}4$) and $[\text{Ln}_2(\mathbf{315a})(\text{NO}_3)_x](\text{NO}_3)_y \cdot n\text{H}_2\text{O}$ (Ln = Tb^{3+} , Ho^{3+} , Er^{3+} ; $x = 2, 3$; $y = 1, 2$; $n = 1, 2$) of the [34]-membered octaza macrocycle $\text{H}_2\text{-315a}$ have been synthesized by the condensation of 2,6-diformyl-4-methylphenol with 1,2-bis(3-aminopropylamino)ethane in the presence of hydrate lanthanide(III) nitrates. $\text{H}_2\text{-315a}$ coordinates as neutral ligand with La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} and Dy^{3+} and as dianionic ligand with Tb^{3+} , Ho^{3+} and Er^{3+} [361].

Also the homo-dinuclear lanthanide complexes $[\text{Ln}_2(\text{H}_2\text{-315b})(\text{NO}_3)_2(\text{CH}_3\text{CN})](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ (Ln = La^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} or Dy^{3+} ; $n = 3, 4$ or 5) of the [24]-membered tetraimine $\text{H}_4\text{-315b}$ have been synthesized by the condensation of 2,6-diformyl-4-methylphenol and 2,6-bis(amino-methyl)-4-nitrophenol in the presence of hydrated lanthanide(III) nitrates [361]. In every complex two bidentate chelating nitrate and one molecule of acetonitrile are coordinated to the central metal ion. The two protons of $\text{H}_4\text{-315b}$ are dissociated upon coordination. When the condensation is carried out in the absence of metal templates, polymeric products of undefined composition are obtained. The complexes are appreciably soluble in DMSO and DMF but sparingly soluble in ethanol, methanol and chloroform. The ligand sensitized europium(III) emission observed in the dinuclear europium(III) complexes, indicates electronic energy transfer from the macrocycle to the metal ion [361].

Luminescence decay dynamics of the $[(\text{Sm}_{1-x}\text{Eu}_x)_2(\mathbf{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ and $[\text{Pr}_{1-x}\text{Tb}_x]_2(\mathbf{316})(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ systems ($0 < x < 1$) reveal two microscopic environments for the europium(III) and terbium(III) which were attributed to homo-dinuclear molecules $[\text{Ln}_2(\mathbf{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ (Ln = Eu^{3+} , Tb^{3+}) (slow component) and heterobinuclear molecules $[\text{SmEu}(\mathbf{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ and $[\text{PrTb}(\mathbf{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ (fast component). The luminescence decay rate constants for intramolecularly coupled EuSm and PrTb pairs are 8200 and $12,500 \text{ s}^{-1}$ which yield coupling constants of 2.9×10^{-53} and $4.7 \times 10^{-53} \text{ m}^6 \text{ s}^{-1}$, respectively, when dominant dipolar interactions are assumed. No exchange interactions are evident despite the presence of a phenolate

selectivity shared by the heteroatoms only ~ 4 Å apart. The ratio of EuEu to EuSm cation pairing selectivity constants of 1:1.5 (expected ratio for random pairing is 1:2) supports the intervention of molecular recognition processes favouring the homo- to hetero-paired species in the ion pairing events leading to $[\text{Sm}_{1-x}\text{Eu}_x]_2(\mathbf{316})(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ compounds [361].

In $[(\text{Ln}_2)(\mathbf{315})(\text{NO}_3)_4] \cdot n\text{H}_2\text{O}$ one metal ion can be leached out of $[\mathbf{315}]^{2-}$; this is accompanied by hydrolysis of $[\mathbf{315}]^{2-}$ to 2,6-diformyl-*p*-cresol in water. In mildly acidic alcoholic solutions (with limited amounts of water) partial hydrolysis of $[\mathbf{315}]^{2-}$ occurs along with condensation at the adjacent secondary nitrogen sites. This is proved by the isolation (from a mixture of several products) and characterization by single crystal X-ray crystallography of mononuclear praseodymium and neodymium complexes of a 3:1 zwitterionic Schiff base $[\text{H}_n\text{-}\mathbf{317}]^{(n-3)+}$ [361].



In the case of praseodymium the complex crystallizes as $[\text{Pr}(\text{H}_3\text{-}\mathbf{317})(\text{NO}_3)(\text{OH})_2(\text{ClO}_4)_2 \cdot \text{NaNO}_3 \cdot 2\text{H}_2\text{O}]$ with three of the four nitrogen sites likely protonated and coordination to praseodymium(III) afforded by the three phenolic and three aldehyde sites of $[\mathbf{317}]^{3-}$, a bidentate nitrate anion and an hydroxyl group. The coordination polyhedron of praseodymium(III) ion has been described as a distorted monocapped dodecahedron. $[\mathbf{317}]^{3-}$ is constituted by three molecules of 2,6-diformyl-*p*-cresol and one molecule of triethylenetetramine which utilizes two primary and a pair of adjacent secondary amino groups for condensation with the carbonyls.

In the case of neodymium, the complex appears to crystallize as $[\text{Nd}(\text{H}_3\text{-}\mathbf{317})(\text{NO}_3)(\text{OH})_2(\text{NO}_3)_2]$ with three of the four nitrogen sites of $[\mathbf{317}]^{3-}$ likely protonated and the

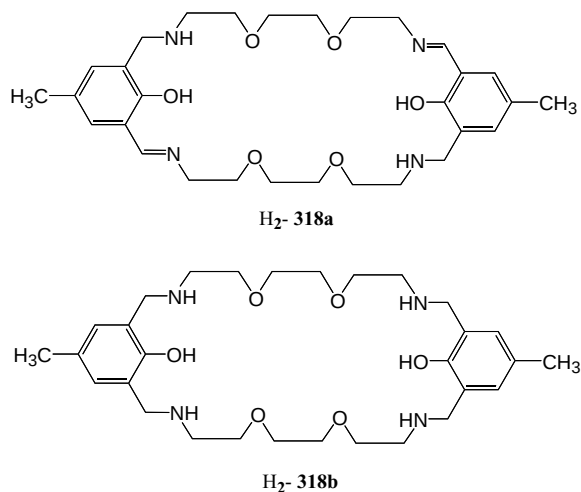
neodymium(III) coordination polyhedron made up of the three phenolate and three aldehyde sites of $[\mathbf{317}]^{3-}$ as well as a bidentate nitrate anion and a water molecule. The neodymium(III) coordination polyhedron is a distorted monocapped dodecahedron [361].

The acid catalyzed condensation of 2,6-diformyl-*p*-cresol and diethylenetetramine at low temperature with $\text{Pr}(\text{NO}_3)_3$ as template agent, produces the complex $\text{Pr}(\mathbf{317})(\text{NO}_3)_2 \cdot \text{CH}_3\text{OH}$, where the non-condensed carbonyl group has been acetylated under mild acid conditions [361].

Compounds of lanthanum and neodymium, isolated from more acid solutions, have a water molecule substituting a methanol molecule to give $\text{Ln}(\mathbf{317a})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

The decacoordination about praseodymium(III) is constituted by one phenolate oxygen, an imine nitrogen and three amino nitrogen atoms from the Schiff base, two bidentate nitrate anions from the Schiff base, two bidentate anions and a molecule of methanol. This decacoordination has been described as a distorted D_{4d} bicapped square antiprism or as a distorted bicapped dodecahedron of D_2 symmetry [361].

The metal-free reaction between 3,6-dioxo-1,8-octanediamine and 2,6-diformyl-*p*-cresol leads to the formation of the related [2+2] macrocycle $\text{H}_2\text{-}\mathbf{316}$. Reduction of this Schiff base with sodium tetrahydroborate is expected to yield the corresponding macrocyclic phenolate amine $\text{H}_2\text{-}\mathbf{318b}$. However, when $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ salts are added to the methanolic reaction products, no solid complexes are deposited over 1 day and intractable products are obtained when the solvent is evaporated off. The nearly colourless methanolic solutions of the tetrahydroborate reduction products gradually become yellow and then orange with the subsequent formation of large crystals of $[\text{Ln}_2(\mathbf{318a})(\text{NO}_3)_4] \cdot 1.2\text{CH}_3\text{OH}$ ($\text{H}_2\text{-}\mathbf{318a}$ represents the partially reduced macrocycle). Without the $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ salts the tetrahydroborate reduction solutions remain light yellow for a long time, but when the solvent is evaporated, IR spectra of the oils show absorption features due to the oxidation product $>\text{C}=\text{N}-$ [363].



Also the reductive amination of $H_2\text{-316}$ with sodium cyanotrihydroborate in the presence of lanthanide(III) nitrates, products either pure dinuclear complexes $[\text{Ln}_2(\text{318a})(\text{NO}_3)_4]$ or a mixture of the lanthanide(III) complexes $\{\text{Ln}[\text{B}(\text{OCH}_3)_4(\text{NO}_3)_2(\text{CH}_3\text{OH})_2]\}$ and $[\text{Ln}_2(\text{H}_2\text{-318a})(\text{NO}_3)_4] \cdot 1.2\text{CH}_3\text{OH}$ [363].

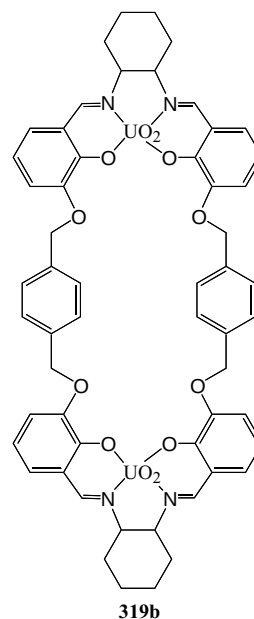
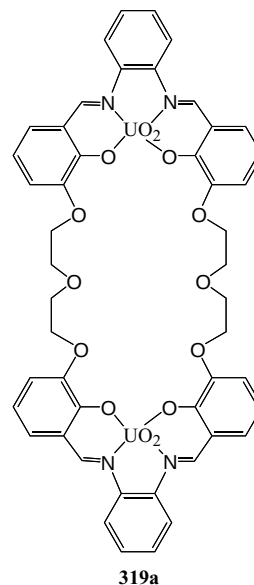
The lanthanide complexes with $H_2\text{-318b}$ appear less stable than the corresponding complexes with $H_2\text{-318a}$ and show a remarkable tendency to evolve into the partially oxidized complexes.

The structure of $[\text{Pr}_2(\text{318a})(\text{NO}_3)_4] \cdot 1.2\text{CH}_3\text{OH}$, confirms the formation of the partially reduced macrocycle. It reveals entrapment of a pair of praseodymium(III) cations in the twin 18-membered coordination cavities of the compartmental macrocycle and two sets of *trans* carbon-nitrogen linkages corresponding to $-\text{CH}=\text{N}-$ and $-\text{CH}_2-\text{NH}-$. The molecular structure of $[\text{Pr}_2(\text{318a})(\text{NO}_3)_4] \cdot 1.2\text{CH}_3\text{OH}$ shows a geometry very similar to that of the $[\text{Gd}_2(\text{316})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$. Each praseodymium(III) cation is ten coordinated, being bound by two bidentate nitrate anions, two phenolate oxygens, two ether oxygens, and one imine and one amine nitrogen atoms. The coordination polyhedron can best be described as a dodecahedron of C_{2v} symmetry. The methanol solvent molecules are not involved either in coordination to the praseodymium(III) centers or in hydrogen bonding to the complex [363] (Fig. 194b).

$[\text{Tb}_2(\text{318a})(\text{NO}_3)_4] \cdot 1.2\text{CH}_3\text{OH}$ and $[(\text{La}_{0.97}\text{Tb}_{0.03})_2(\text{318a})(\text{NO}_3)_4] \cdot 1.2\text{CH}_3\text{OH}$ exhibit strong $\text{Tb}^{3+}({}^5\text{D}_4 \rightarrow {}^7\text{F}_j)$ emission sensitized by the singlet state of $[\text{318a}]^{2-}$ at both 77 and 295 K. No $\text{Tb}^{3+}-\text{Tb}^{3+}$ self-quenching or N-H trapping effects are observed at 77 K (decay rate is 598 s^{-1}); the coordination cavities of $[\text{318a}]^{2-}$ are therefore potentially good hosts for Tb^{3+} in luminescent diagnostic agents. At room temperature the complex decay kinetics of Tb^{3+} in $\text{Tb}_2(\text{318a})(\text{NO}_3)_4 \cdot 1.2\text{CH}_3\text{OH}$ are similar to those of $\text{Tb}_2(\text{316})(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$. But for the dilute complex, $(\text{La}_{0.97}\text{Tb}_{0.03})_2(\text{318a})(\text{NO}_3)_4 \cdot 1.2\text{CH}_3\text{OH}$, unusual thermal equilibration of the ligand triplet and $\text{Tb}^{3+} {}^5\text{D}_4$ states occurs at room temperature; the ligand-to- Tb^{3+} energy-transfer rate is $\approx 4.36 \times 10^4 \text{ s}^{-1}$, while Tb^{3+} -to-ligand back-energy-transfer is $\approx 7.1 \times 10^4 \text{ s}^{-1}$ [363].

The [2+2] dinuclear macrocyclic uranyl complexes **319a** and **319b**, have been found to recognise and form strong 1:1 solution complexes with terephthalate, succinate and fumarate dianions in $(\text{CD}_3)_2\text{SO}$; weaker interactions between these hosts and the shorter malonate and monoanionic benzoate were observed [364]. Both metallomacrocycles showed the strongest complexation with the terephthalate dianion; H_2PO_4^- anion was also bound quite strongly in $(\text{CD}_3)_2\text{SO}$ by both receptors with the formation of 1:2 host-guest complexes. The 1:2 complex **319a**- H_2PO_4^- was prepared by stirring **319** with 2 equiv. of $[\text{NBu}_4][\text{H}_2\text{PO}_4]$ in acetonitrile, followed by evaporation of the solution. The obtained complex was fully characterized by NMR and FAB mass spectra. Selectivity of almost a decade was found for triphosphate over H_2PO_4^- by both **319a** and **319b**, suggest-

ing that preorganisation of the Lewis acid sites in mutual proximity offers a slight advantage in the binding of a single linear dianion over that of two monoanions [364].



8.1.2. Complexes with [2+2] compartmental ligands derived from 2,6-diformyl-4-substituted-thiophenol

The easy preparation of 2,6-diformyl-4-methylthiophenol and the minimization of the difficulties of incorporating thiolate donors into Schiff base macrocycles, thus allowing the formation of thiolate bridged complexes of controlled nuclearity and avoiding the uncontrolled production of disulfides, opened interesting possibilities to shed light on the structure and mechanism of action of thiolate-containing metalloprotein clusters. In addition the properties of these

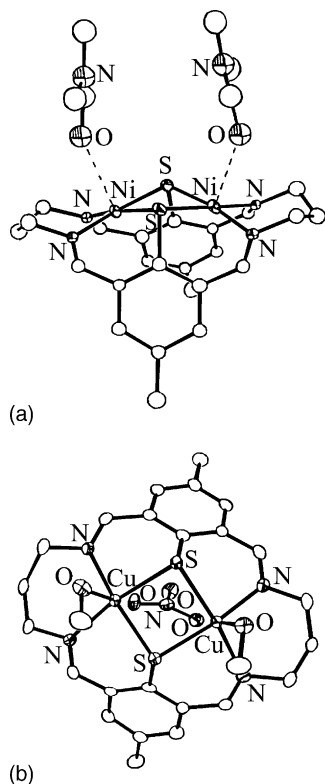


Fig. 195. Structure of $[\text{Ni}_2(\mathbf{228})]2\text{DMF}]^{2+}$ (a) and $[\text{Cu}_2(\mathbf{228})(\text{CH}_3\text{OH})_2(\text{NO}_3)]^+$ (b) (adapted from Refs. [128,365]).

complexes are expected to provide an interesting contrast to those of complexes of widely used phenol and pyridine head units which contain much harder donors.

The reaction of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with 2,6-diformyl-4-methylthiophenol and 1,3-diaminopropane in CH_3CN in the presence of NH_4PF_6 gives $[\text{Ni}_2(\mathbf{228})](\text{PF}_6)_2$ in low yield. Attempted synthesis by template methods of the copper(II) analogue $[\text{Cu}_2(\mathbf{328})]^{2+}$ invariably failed, possibly owing to redox side-reactions occurring during the template process, the reaction of copper(II) with thiolate leading to the potential formation of copper(II) and disulfides. Thus, template synthesis of $[\mathbf{228}]^{2-}$ around the redox-inert zinc(II) ion followed by transmetalation with the appropriate metal ions was successfully tested. Reaction of $\text{Zn}(\text{CH}_3\text{COO})_2$ with 2,6-diformyl-4-methylthiophenol and 1,3-diaminopropane gives rise to $[\text{Zn}_2(\mathbf{228})(\text{CH}_3\text{COO})]^{+}$, which transmetalates with nickel(II) ion to afford $[\text{Ni}_2(\mathbf{228})]^{2+}$ and with copper(II) ion to afford $[\text{Cu}_2(\mathbf{228})]^{2+}$ in high yield [128,365].

The X-ray structure of $[\text{Ni}_2(\mathbf{228})](\text{PF}_6)_2 \cdot 2\text{DMF}$ (Fig. 195a) shows each nickel(II) ion bound to two bridging thiophenolate sulfur donors and two imine nitrogen donors; additional interactions with oxygen donors from two DMF molecules are observed. The coordination geometries at the nickel(II) centers are distorted square planar with the nickel(II) ions displaced by approximately 0.1 Å out of the least-squares plane defined by the N_2S_2 donor set. The $\text{Ni} \cdots \text{Ni}$

distance is 3.163 Å. In order to accommodate the coordination geometries about the nickel(II) ions in $[\text{Ni}_2(\mathbf{228})]^{2+}$, the macrocycle $[\mathbf{228}]^{2-}$ adopts a folder conformation.

The recrystallization of $[\text{Ni}_2(\mathbf{228})]^{2+}$ from CH_3NO_2 affords $[\text{Ni}_2(\mathbf{228})]^{2+} \cdot \text{CH}_3\text{NO}_2$ which shows the CH_3NO_2 solvate molecule sitting inside the cleft formed by the folded $[\mathbf{228}]^{2-}$ macrocycle.

The related nickel(II) complex incorporating pendant OH groups (having a $\text{CH}_3\text{CHOHCH}_2$ chain instead a $\text{CH}_2\text{CH}_2\text{CH}_2$ one) has also been synthesized and shows a similar configuration and conformation to the nickel(II) complexes of $[\mathbf{228}]^{2-}$ [128,365].

$[\text{Cu}_2(\mathbf{228})(\text{CH}_3\text{OH})_2(\text{NO}_3)](\text{PF}_6)$ shows (Fig. 195b) two copper(II) centers each bound to two nitrogen-donors and bridged by two thiolate donors of the compartmental macrocycle. The coordination about each copper(II) ion is completed by one oxygen donor atom from CH_3OH . The conformation of the thiolate macrocycle is very similar to that observed for the corresponding nickel(II) complexes with a $\text{Cu} \cdots \text{Cu}$ separation of 3.264 Å. Interestingly, one NO_3^- counter anion occupies the cleft formed by the folded macrocycle [128,365].

Reaction of *S*-(2,6-diformyl-4-methylphenol)dimethylthiocarbamate with NaOH and $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ followed by the addition of 1,3-diaminopropane in propanol gives rise to $[(\text{Zn}_2(\mathbf{228})(\text{H}_2\text{O})_2)(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}]$ or $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$. Attempts to prepare $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$ in ethanol resulted in the formation of the trinickel complex $[\text{Ni}_3(\mathbf{227})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ of the related acyclic ligand $[\mathbf{227}]^{2-}$ in addition to the expected cyclic complex $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$. When more concentrated solutions were employed, the yield of the acyclic complex $[\text{Ni}_3(\mathbf{227})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ is considerably improved [271,366].

For the dizinc(II) complex the reaction was performed using an excess of $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$; the use of stoichiometric quantities of reagents led to the coprecipitation of hydroxide species together with $[(\text{Zn}_2(\mathbf{228})(\text{H}_2\text{O})_2)(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}]$. For $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$ cocrystallisation with NaClO_4 occurred but an analytically pure product was obtained by washing the crystals with a large volume of water followed by water-methanol (1:1). $[\text{Ni}_2(\mathbf{228})]^{2+}$ can also be obtained, as a triflate salt, from $[(\text{Zn}_2(\mathbf{228})(\text{H}_2\text{O})_2)(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}]$ by transmetalation with $\text{Ni}(\text{CF}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ in acetonitrile and subsequent crystallisation from the reaction mixture by diethyl ether diffusion.

In $[(\text{Zn}_2(\mathbf{228})(\text{H}_2\text{O})_2)(\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}]$ (Fig. 196a) the asymmetric unit consists of two independent dizinc(II) macrocyclic complexes; no major differences are observed between the two molecules. In each case the zinc ions have a $\text{N}_2\text{S}_2\text{O}$ trigonal bipyramidal coordination to two imine nitrogen atoms, two bridging thiolate sulfur atoms and a water molecule. The macrocycles in both molecules are not flat but rather adopt a stepped conformation consistent with a trigonal bipyramidal geometry at the zinc atoms. In each case the trigonal plane consists of one thiolate donor, one imine donor and the bound water molecule. Despite the

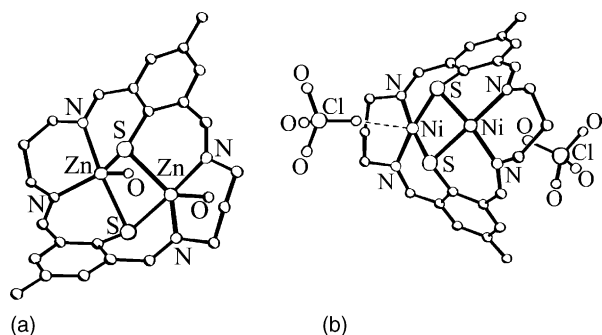


Fig. 196. Structure of one of the two independent cations of $[\text{Zn}_2(\mathbf{228})(\text{H}_2\text{O})_2]^{2+}$ (a) and of $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$ (b) (adapted from Ref. [366]).

slight differences in the macrocycle step conformation of the two molecules, very similar coordination is observed for all four zinc ions, as well as very similar $\text{Zn} \cdots \text{Zn}$ separations. π – π Interactions are observed both between the molecules within the asymmetric unit and between adjacent symmetry-related molecules and result in chains of π -stacked molecules.

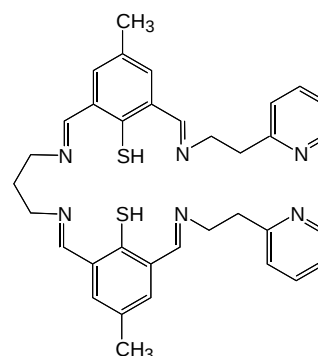
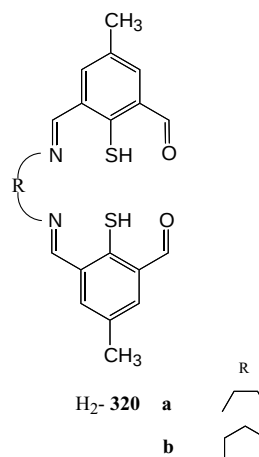
Also in $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$ (Fig. 196b) there are two dinickel(II) macrocyclic complexes in the asymmetric unit. Differences between the two molecules are minor. In both cases the nickel ions have a N_2S_2 square planar environment and lie close to the N_2S_2 plane. Inside each dinuclear unit one nickel(II) interacts weakly with the oxygen atoms of perchlorate ions [366].

Weak axial interactions were observed for both nickel ions in the related complex $[\text{Ni}_2(\mathbf{228})](\text{PF}_6)_2 \cdot 2\text{DMF}$ [367]. The macrocycles are distinctly bowled; despite this difference in macrocycle conformation the coordination of the nickel ions is very similar in both molecules. In addition, the N_2S_2 square planes intersect at very similar angles for both molecules and the $\text{Ni} \cdots \text{Ni}$ and $\text{S} \cdots \text{S}$ separations are very similar. π – π Interactions are observed both between the molecules within the asymmetric unit and between adjacent symmetry-related molecules and result in a network of π -stacked molecules.

Cyclic voltammetry studies in acetonitrile indicate that $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$ undergoes two one-electron oxidations, the first reversible and the second quasi-reversible ($E_{1/2} = 0.93$ V, peak separation 67 mV; $E_{1/2} = 1.38$ V, versus Ag/AgNO_3 (0.01 M), peak separation 80 mV) [366]. $[\text{Zn}_2(\mathbf{228})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ shows a completely different behaviour undergoing an irreversible two-electron oxidation at a similar potential suggesting that a substantial structural change occurs on oxidation. One possibility is that the change might be the result of disulfide formation [366].

The acyclic nickel(II) complexes $[\text{N},\text{N}'\text{-ethylene(6-formyl-4-methyl-2-methyliminatothiophenolato)}]\text{nickel(II)}$, $[\text{Ni}(\mathbf{320a})]$, and $[\text{N},\text{N}'\text{-propane-1,3-diyl(6-formyl-4-methyl-2-methyliminatothiophenolato)}]\text{nickel(II)}$, $[\text{Ni}(\mathbf{320b})]$, were prepared by the template reaction of *S*-(2,6-diformyl-4-methylphenol)dimethylthiocarbamate with 1,2-diami-

noethane or 1,3-diaminopropane in the presence of nickel(II) salts [367].



In $[\text{Ni}(\mathbf{320b})]$ the ligand binds one nickel ion at the N_2S_2 site. The geometry at the nickel(II) ion is approximately square planar but the molecule as a whole has a chair conformation. There is no evidence for an axial interaction between the nickel(II) ion in one molecule with sulfur atom in an adjacent molecule (Fig. 197a).

The presence of two aldehyde groups in $[\text{Ni}(\mathbf{320a})]$ and $[\text{Ni}(\mathbf{320b})]$ makes these complexes candidates for further derivation. The condensation reaction of the aldehyde groups of $[\text{Ni}(\mathbf{320b})]$ with the amine groups of two 2-(2-aminoethyl)pyridines gives rise to the diamagnetic nickel complex, $[\text{N},\text{N}'\text{-propane-1,3-diyl(6-(N-2-ethylpyridyl)iminomethyl)-4-methyl-2-methyliminatothiophenolato}]\text{nickel(II)}$, $[\text{Ni}(\mathbf{321})]$, as a brown crystalline product [367]. The asymmetric unit contains one molecule of $[\text{Ni}(\mathbf{321})]$ and an acetonitrile solvate molecule (Fig. 197b). There are no significant interactions of the acetonitrile molecule with the complex molecule. The nickel ion is coordinated to both thiophenolate sulfur atoms and to the two imine nitrogen atoms on the inner N_2S_2 site of the ligand in an approximately square planar coordination geometry.

The condensation of $[\text{Ni}(\mathbf{320b})]$ with 1,3-diaminopropane gave the dinickel complexes of two different macrocycles: the [2+2] macrocycle $\text{H}_2\text{-228}$ and the [4+4] macrocycle $\text{H}_4\text{-322}$ $[\text{Ni}_2(\mathbf{228})](\text{ClO}_4)_2$, was prepared by reaction of $[\text{Ni}(\mathbf{320b})]$ with 1 equiv. of nickel(II) perchlorate and 1,3-

diaminopropane in methanol/dimethylformamide while the reaction of $[\text{Ni}(\mathbf{320b})]$ with 1,3-diaminopropane carried out in acetonitrile in the presence of PdCl_2 with the aim to form the corresponding hetero-dinuclear complex gave the $[4+4]$ macrocyclic dinickel complex $[\text{Ni}_2(\mathbf{322})]$ [367,368] whose structure (Fig. 197c) can be seen as formed by two $[\text{Ni}(\mathbf{320b})]$ complexes linked by two propylenediamine units. The complex is bowl shaped; the interatomic $\text{Ni} \cdots \text{Ni}$ distance is 11.4 Å.

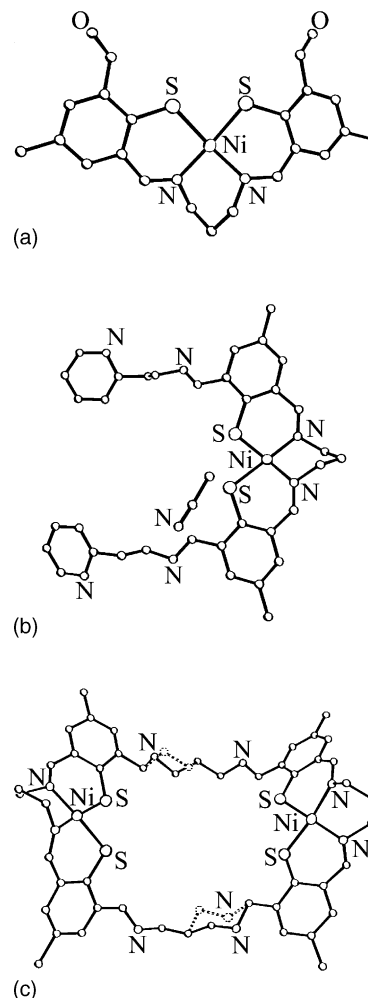
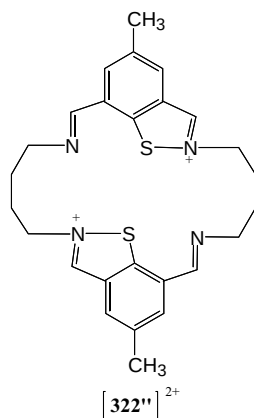
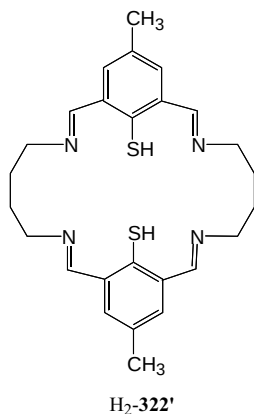
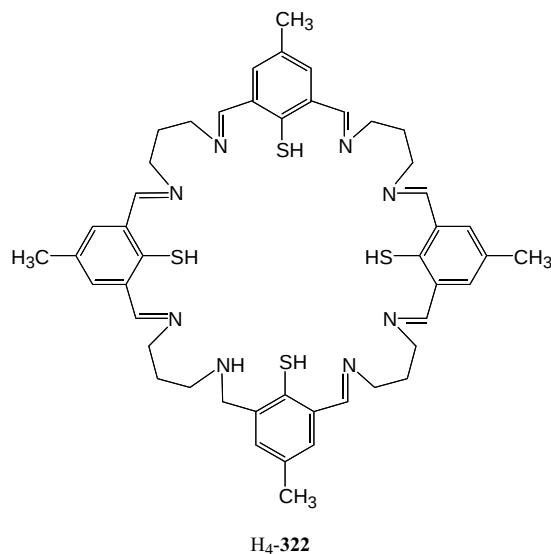
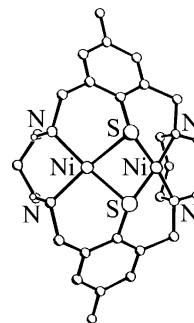
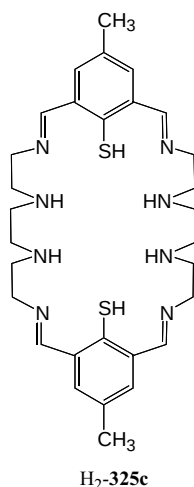
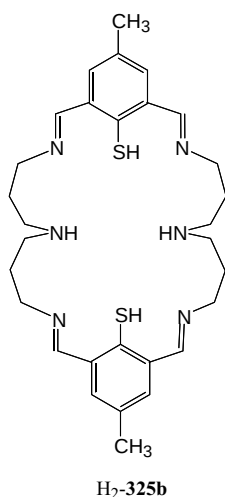
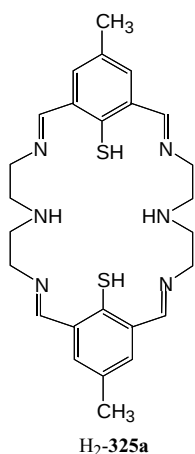
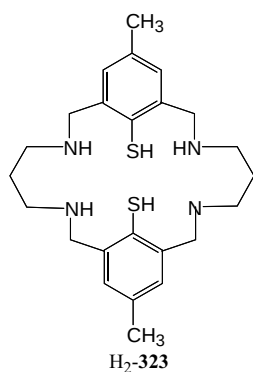


Fig. 197. Structure of $[\text{Ni}(\mathbf{320b})]$ (a), $[\text{Ni}(\mathbf{321})]\text{CH}_3\text{CN}$ (b) and $[\text{Ni}_2(\mathbf{322})]$ (c) (adapted from Refs. [367–369]).

The reduction of $[\text{Ni}_2(\mathbf{228})(\text{ClO}_4)_2]$ with sodium borohydride results in the formation of the dinickel(II) dithiolate amine macrocyclic complex $[\text{Ni}_2(\mathbf{323})(\text{ClO}_4)_2]$ where the nickel(II) ions have an N_2S_2 square planar environment (Fig. 198). In addition to the folding of the two phenyl planes, the ligand exhibits a second folding at right angles to the first, which leads to a bowl-shaped complex overall. This additional fold is possible in $[\text{Ni}_2(\mathbf{323})(\text{ClO}_4)_2]$ because of the change from conjugated trigonal imine groups in $[\text{Ni}_2(\mathbf{228})(\text{ClO}_4)_2]$ to flexible tetrahedral amine groups in $[\text{Ni}_2(\mathbf{323})(\text{ClO}_4)_2]$. The $\text{Ni} \cdots \text{Ni}$ separation is 3.02 Å. The bowl created by the macrocyclic ligand distinguishes the two axial sites on the nickel atoms, producing an inside and outside surface. All of the amine hydrogen atoms point in the same *cis* direction with respect to the macrocyclic bowl [367,368]. The addition of an excess of NaSCN to $[\text{Ni}_2(\mathbf{323})(\text{ClO}_4)_2]$ caused removal of the nickel(II) ions on the complex and formation of a simple salt [366].

Fig. 198. Structure of $[\text{Ni}_2(\text{323})]^{2+}$ (adapted from Refs. [367,368]).

The cyclic voltammograms show that in both $[\text{Ni}_2(\text{323})](\text{ClO}_4)_2$ and $[\text{Ni}_2(\text{228})](\text{ClO}_4)_2$ four separate one-electron steps are readily identified: the dinickel(II) complexes can be oxidised in two steps or reduced in two steps. From EPR studies and comparisons with related square planar dinickel and dizinc thiolate complexes, these processes are believed to be largely metal-centered (i.e. $\text{Ni}^{\text{I}}\text{Ni}^{\text{I}} \rightleftharpoons \text{Ni}^{\text{I}}\text{Ni}^{\text{II}} \rightleftharpoons \text{Ni}^{\text{II}}\text{Ni}^{\text{II}} \rightleftharpoons \text{Ni}^{\text{II}}\text{Ni}^{\text{III}} \rightleftharpoons \text{Ni}^{\text{III}}\text{Ni}^{\text{III}}$). The mixed-valent forms of the complexes, prepared by electrochemical oxidation or reduction, exhibit axial EPR spectra consistent with metal-based nickel(III) or nickel(I) species respectively. In the former, g values are 2.02 and 2.20 and in the latter, 2.01 and 2.08. These values are consistent with those derived for the oxidised and reduced forms of the nickel(II) ion with equatorial tetraaza donors. Interestingly the potentials at which the two sequential oxidation processes occur do not vary much with the change from imine to amine nitrogen donors. In contrast the potential of the two sequential reduction processes differ significantly: there is a substantial shift to more negative potentials on changing from imine to amine nitrogen donors, owing to a reduction of π -acceptor ability. A second feature is that the two waves have a greater ΔE , corresponding to a mixed-valent species $[\text{Ni}_2(\text{323})]^+$ more stable with respect to disproportionation. The dramatic differences in the reductive processes of $\text{Ni}_2(\text{323})(\text{ClO}_4)_2$ when compared with $\text{Ni}_2(\text{228})(\text{ClO}_4)_2$ are not reflected in the oxidative processes [368].

$[\text{Ni}_2(\text{322}')](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN} \cdot 1/4 \cdot \text{H}_2\text{O}$, $[\text{Ni}_2(\text{322}')](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ and $[\text{Ni}_2(\text{228})](\text{CF}_3\text{SO}_3)_2$ were prepared by reaction of the appropriate precursors in the presence of nickel(II) salt [366]. Moreover the red-black complexes $[\text{Ni}_2(\text{322}')](\text{NCS})_2$ and $[\text{Ni}_2(\text{228})](\text{NCS})_2$ were prepared by the addition of 2.2 equiv. of NaSCN to acetonitrile solutions of $[\text{Ni}_2(\text{322}')](\text{ClO}_4)_2$ and $[\text{Ni}_2(\text{228})](\text{CF}_3\text{SO}_3)_2$, respectively [366].

The asymmetric unit of $[\text{Ni}_2(\text{322}')](\text{ClO}_4)_2$ contains four dinickel(II) dithiolate macrocycles which, despite lacking crystallographic symmetry, are reasonably similar to each other and form a star which is templated on a perchlorate ion (Fig. 199). Each nickel(II) ion is square planar in each macrocycle one of the two nickel atoms interacts very weakly with the central perchlorate ion. The folding is optimal for the formation of a large number of favourable

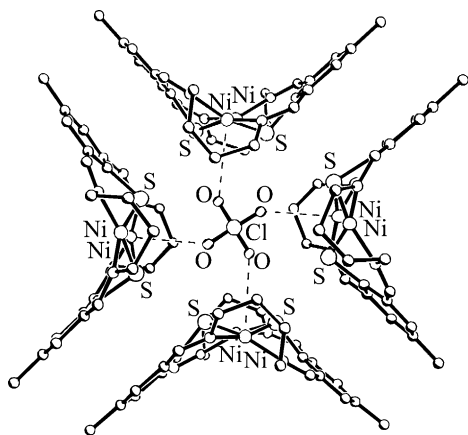


Fig. 199. Perspective view of the four $[\text{Ni}_2(\mathbf{322}')]^{2+}$ cations and one ClO_4^- anion in $[\text{Ni}_2(\mathbf{322}')](\text{ClO}_4)_2$ (adapted from Ref. [366]).

π - π interactions both between phenyl rings and within the asymmetric unit [366].

Interestingly in $[\text{Ni}_2(\mathbf{322}')(\text{NCS})_2]$ both thiocyanate ions bind to one nickel ion, giving it a distorted octahedral geometry overall whilst the other nickel ion remains square planar. $[\text{Ni}_2(\mathbf{322}')(\text{NCS})_2]$ is folded in the same way as $[\text{Ni}_2(\mathbf{322}')](\text{ClO}_4)_2$ (Fig. 200a).

Also in $[\text{Ni}_2(\mathbf{228})(\text{NCS})_2] \cdot \text{CH}_3\text{CN}$ [366] one nickel(II) ion remains square planar whilst the other is distorted octahedral and coordinated to both thiocyanates [366]. The smaller ring size of $[\mathbf{228}]^{2-}$ is still sufficient to accommodate the high-spin nickel(II) ion (Fig. 200b). However, there is sufficient ring strain induced by the change in spin state to promote Schiff base hydrolysis by traces of moisture and ring opening, as the major product of the reaction with NaSCN is shown by IR spectroscopy to be a ring opened product [366].

Two one-electron oxidations and two one-electron reductions are a feature of the electrochemistry of these nickel(II) complexes with H_2 - $\mathbf{322}'$, H_2 - $\mathbf{228}$ and H_2 - $\mathbf{323}$ in CH_3CN ; curiously the potentials for the oxidation processes are almost invariant whereas those for the reduction processes vary. EPR spectroscopy shows that the first one-electron reduction process and the first one-electron oxidation pro-

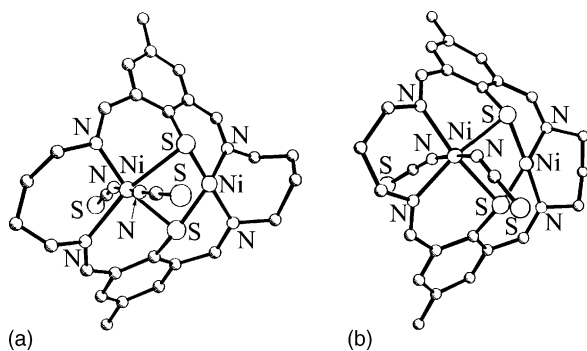


Fig. 200. Structure of $[\text{Ni}_2(\mathbf{322}')(\text{NCS})_2]$ (a) and $[\text{Ni}_2(\mathbf{228})(\text{NCS})_2]$ (b) (adapted from Ref. [366]).

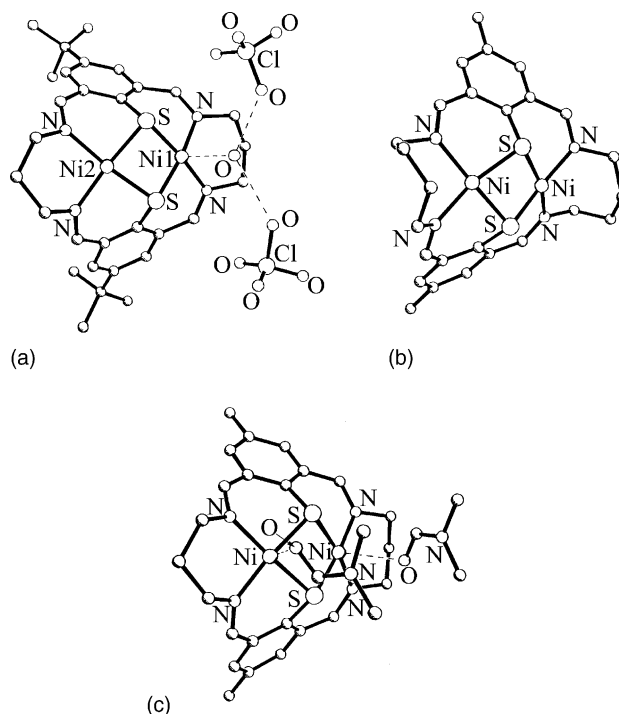


Fig. 201. Structure of $[\text{Ni}_2(\mathbf{228}')](\text{ClO}_4)_2$ (a), $[\text{Ni}_2(\mathbf{322}')]^{2+}$ (b) and $[\text{Ni}_2(\mathbf{228})(\text{DMF})_2]^{2+}$ (c) (adapted from Ref. [366]).

cess are metal centered. Spectroelectrochemical studies and redox titrations indicate that a purplish-coloured complex is produced by one-electron oxidation of $[\text{Ni}_2(\mathbf{228})]^{2+}$. In these complexes the two one-electron oxidation processes are relatively insensitive to the changes made to the ligand but are sensitive to changes in solvent (CH_3CN versus DMF versus CH_3NO_2). In contrast the reduction processes are significantly influenced by changes to the ligand but are relatively insensitive to changes in solvent (CH_3CN versus DMF). A change in the nitrogen donors from imines to amines made the potentials more negative, while increasing the size of the macrocyclic cavity made the potentials slightly less negative. The formally nickel(I) centers are expected to be square planar; hence this can explain the lack of solvent dependency [366].

Each nickel(II) ion within the dinuclear unit in $[\text{Ni}_2(\mathbf{228}')](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O} \cdot 0.5(\text{C}_2\text{H}_5)_2\text{O}$ and $[\text{Ni}_2(\mathbf{322}')](\text{CF}_3\text{SO}_3)_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ is in a square planar N_2S_2 environment. $[\text{Ni}_2(\mathbf{228}')]^{2+}$ adopts a bowl shape while $[\text{Ni}_2(\mathbf{322}')]^{2+}$ is folded [366] (Fig. 201a and b).

The chemical and electrochemical oxidation of $[\text{Ni}_2(\mathbf{228}')](\text{ClO}_4)_2$ show that it is possible to obtain a dinuclear $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ complex. In particular using cerium(IV) ammonium nitrate as oxidant, $[\text{Ni}_2(\mathbf{228}')] [\text{Ce}(\text{NO}_3)_6]$ was recovered that shows an electronic spectrum very similar to those containing a $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ species. This black complex slowly changes in DMF and converts into $[\text{Ni}_2(\mathbf{228}')](\text{NO}_3)_2 \cdot 2\text{DMF}$. In this complex the two nickel(II) ions show a $\text{N}_2\text{S}_2\text{O}$ coordination environment, being bonded also to the oxygen atom of a DMF solvent molecule (Fig. 201c).

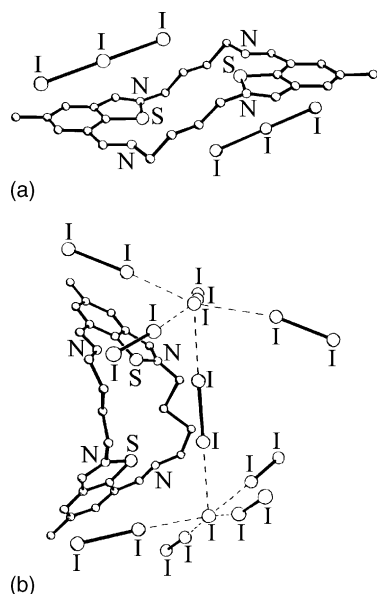
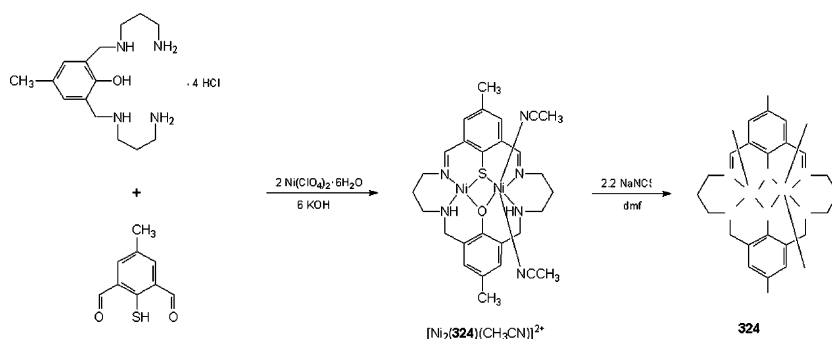


Fig. 202. Structure of $[\mathbf{322''}](\text{I}_3)_2$ (a) and $[\mathbf{322''}](\text{I}_2)(\text{I}_2)_5$ (b) (adapted from Ref. [366]).

Possibly the two nitrate anions result from the decomposition of $[\text{Ce}(\text{NO}_3)_6]^{3-}$.

The oxidation of $[\text{Ni}_2(\mathbf{322'})](\text{CF}_3\text{SO}_3)_2$ with an excess of I_2 in CH_3CN affords red crystals of $[\mathbf{322''}](\text{I}_3)_2$ and brown crystals of $[\mathbf{322''}](\text{I}_2)(\text{I}_2)_5$ (Fig. 202a and b). In both cases a ligand oxidation has occurred to form two five membered isothiazole ring within each macrocycle. In $[\mathbf{322''}](\text{I}_3)_2$ the macrocycle adopts a stepped conformation with the two phenyl rings parallel each other the anion $(\text{I}_3)^-$ originates from the reaction of I_2 with I^- formed during the ligand oxidation reaction. In $[\mathbf{322''}](\text{I}_2)(\text{I}_2)_5$ the macrocycle adopts a bowl shape with the two aromatic ring almost perpendicular each other. Two iodide ions act as the anions [366].

The structure of $[\text{Ni}_2(\mathbf{324})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$, prepared according Scheme 46 [369], reveals that the two nickel(II) ions have differing environments despite the fact that the macrocycle is potentially capable of providing identical N_2OS binding sites. One nickel(II) ion is square planar whereas the other is octahedral with two acetonitrile solvent molecules completing the coordination sphere [369].



Scheme 46.

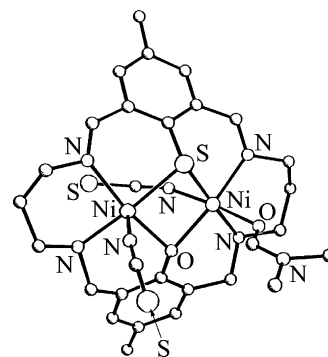


Fig. 203. Structure of $[\text{Ni}_2(\mathbf{324})(\text{NCS})_2(\text{DMF})]$ (adapted from Ref. [369]).

Cyclic voltammetry has revealed one-electron oxidation processes at 0.9 and 1.3 V versus SCE [Pt electrode, CH_3CN , $0.1 \text{ mol dm}^{-3} \text{N}(\text{Et})_4(\text{ClO}_4)$]; the first oxidation is chemically irreversible whilst the second is chemically quasi-reversible (peak separation = 65 mV at 100 mV s^{-1}) [369].

The addition of 2.2 equiv. of sodium thiocyanate to an acetonitrile solution of $[\text{Ni}_2(\mathbf{324})(\text{CH}_3\text{CN})]^{2+}$ causes precipitation of a solid which on recrystallization from DMF/diethylether yields $[\text{Ni}_2(\mathbf{324})(\text{NCS})_2(\text{DMF})]$ (Scheme 46). In this complex the nickel(II) ions are bound by an identical donor set (N_2OS) of macrocycle yet adopt differing stereochemistry (Fig. 203). One nickel(II) ion is octahedral, binding one thiocyanate ion and a dimethylformamide molecule to the axial sites, whilst the other is square pyramidal, binding one thiocyanate ion only [369]. $[\text{Ni}_2(\mathbf{324})(\text{NCS})_2(\text{DMF})]$ shows a magnetic moment of $4.5 \mu_B$ at room temperature.

Reaction of $[\text{Ni}_2(\mathbf{324})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ with an excess of thiocyanate ions also yields $[\text{Ni}_2(\mathbf{324})(\text{NCS})_2(\text{DMF})]$: further thiocyanate ions are not bound at the vacant axial site of the high-spin nickel(II) ion or replace the DMF molecule on the other nickel(II) ion [369].

The dizinc macrocyclic complexes $[\text{Zn}_2(\mathbf{L})](\text{CF}_3\text{SO}_3)_2$ ($\text{H}_2\text{-L} = \text{H}_2\text{-325a}$, $\text{H}_2\text{-325b}$, $\text{H}_2\text{-325c}$) have been obtained by hydrolysis of *S*-(2,6-diformyl- α -methylphenol)-dimethylfithiocarbamate with NaOH, followed by reaction with the appropriate diamine in the presence of zinc(II) template ions [370]. Molar conductance measurements showed that all

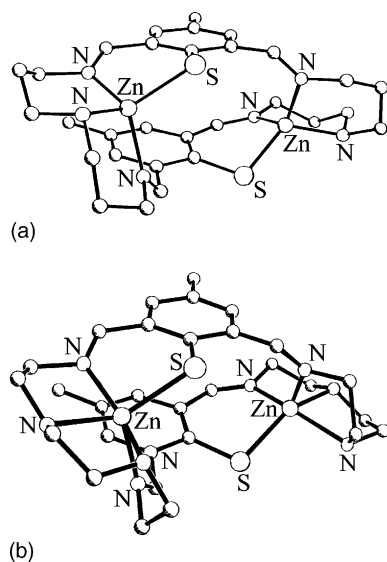


Fig. 204. Structure of $[\text{Zn}_2(\mathbf{325b})]^{2+}$ (a) and $[\text{Zn}(\mathbf{325c})]^{2+}$ (b) (adapted from Ref. [370]).

three complexes are 2:1 electrolytes in freshly prepared CH_3CN solutions. The complexes with $\text{H}_2\text{-}\mathbf{325b}$ and $\text{H}_2\text{-}\mathbf{325c}$ are stable in both CH_3CN and CH_3OH solutions for weeks and single crystals formed from diethylether diffusion into these solutions. In contrast the complex with $\text{H}_2\text{-}\mathbf{325a}$, dissolved in CH_3CN , CH_3OH or DMF, forms an insoluble cream compound within minutes, where the macrocycle has opened to relieve ring strain. Presumably this is caused by the short lateral chains present in the $[\mathbf{325a}]^{2-}$ macrocycle struggling to accommodate the desired folding of the macrocycle. In contrast to $[\text{Zn}_2(\mathbf{325a})]^{2+}$, the longer lateral chains in complexes $[\text{Zn}_2(\mathbf{325b})]^{2+}$ and $[\text{Zn}_2(\mathbf{325c})]^{2+}$ greatly facilitate the desired folding of the macrocycle and hence these complexes do not ring open in solution. The structure of $[\text{Zn}_2(\mathbf{L})](\text{CF}_3\text{SO}_3)_2$ ($\text{H}_2\text{-}\mathbf{L} = \text{H}_2\text{-}\mathbf{325b}$ and $\text{H}_2\text{-}\mathbf{325c}$) (Fig. 204a and b) reveals that the two thiolate donors within each macrocycle do not bridge the metal ions. Rather, in each case the macrocycle twists over on itself, utilizing the flexibility of the lateral chain, such that the two phenol rings form favourable $\pi\text{-}\pi$ stacking interactions [370]. In these complexes the zinc(II) ions are tetrahedral and five coordinate, respectively, in contrast with $[\text{Zn}_2(\mathbf{228})(\text{H}_2\text{O})_2]$ where the two zinc(II) ions are trigonal bipyramidal [366,370].

$\pi\text{-}\pi$ Interactions exist between the two aromatic rings within the macrocyclic unit. Intermolecular $\pi\text{-}\pi$ interactions are also observed and lead to the molecules packing together in chains. The two triflate anions hydrogen bond to the two secondary amines. ^1H and ^{13}C NMR spectra are consistent with the maintenance of the solid-state structure in solution. Cyclic voltammetry studies in CH_3CN show that $[\text{Zn}_2(\mathbf{325a})](\text{CF}_3\text{SO}_3)_2$ undergoes an irreversible, approximately two-electron, oxidation at $E_{\text{pa}} = +1.03$ V versus 0.01 M AgNO_3/Ag [370].

Silver(I)-templated cyclocondensation of pyridine-2,6-dicarbaldehyde and 3-oxa-1,5-diaminopentane yields the

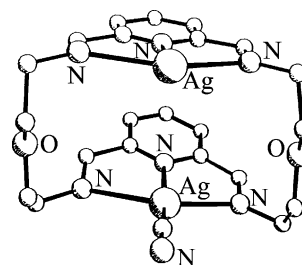


Fig. 205. Structure of $[\text{Ag}_2(\mathbf{326})(\text{CN})]^+$ (adapted from Ref. [371]).

dinuclear silver(I) complex $[\text{Ag}_2(\mathbf{326})(\text{CN})](\text{ClO}_4) \cdot 0.275 \text{H}_2\text{O}$ [371] that is polymeric with cyano-linked dimers being further associated through silver $\cdots$ silver interactions. In particular the asymmetric unit of the crystal structure comprises two silver(I) ions which are coordinated to the two pyridyl-diimine head units of a fully folded macrocycle, in which the pyridyl fragments lie approximately parallel, and approximately eclipsed. The intramolecular silver $\cdots$ silver separation is 4.290 Å. There is no interaction with the oxygen atoms of the two 3-oxapentane chains which link the two approximately parallel and planar units and there are no bridging imino-functions. Also present in the complex are a perchlorate anion, a low occupancy water molecule of crystallisation, and a cyano ligand which coordinates to one silver(I) ion in a site lying *trans* to the pyridyl nitrogen (Fig. 205).

8.1.3. Complexes derived from [3+2] macrobicyclic tridimensional ligands

As above reported on the mononuclear complexes, by using a one pot procedure it is possible to obtain high yields of several symmetric hexamine Schiff base cryptands despite the apparent need for six simultaneous condensations. Yields may be improved by the use of a template. Many of the metal-free Schiff base ligands show surprising long-term stability in the solid state when pure. This efficient tripod-coupling-capping reaction has been used for generation of cryptands derived from tris(3-aminopropyl)amine as well as tris(2-aminoethyl)amine caps [64] and those incorporating spacer units ranging from a two-carbon link to a 9-carbon link in the diphenyl-methane-linked cryptand or as many as 16-carbon links in some carocryptands [372,373]. In only one case so far has a diketone been successfully substituted for the dialdehyde normally required for efficient [2+3] condensation; this cryptand product is formed only under acidic conditions, which suggests that the proton may act as template or as catalyst. Attempts to replace dialdehydes with diketones in the [2+3] Schiff base condensation reaction normally meet with failure.

Once the three-dimensional skeleton is assembled, the Schiff-base cryptands can be readily reduced with NaBH_4 or LiAlH_4 to generate the related octaaminocryptands which, being more chemically robust than their hexa-Schiff base analogues, have many advantages as ligands for both cation and anion encapsulation.

In many free cryptand or cationic ligands, particularly amine systems, hydrogen bonding is important in deciding the details of the solid-state conformation, which presumably is also true for solution conformations. These cages frequently crystallize with many molecules of water solvate and extensive hydrogen-bond networks are built up [372]. Typical is $239.8\text{H}_2\text{O}$, in which each NH is hydrogen bonded to a water molecule and hence to the rest of the network [372].

Binding one or more metal ions in a hexaimino cryptand requires significant reorganization; the N_3 triangle contracts, and the imine nitrogen rotates so that the lone pair can be directed into the cavity. It is this requirement that imparts chirality to the system and goes some way toward explaining why binuclear systems are generally helical even though there is no requirement for both N_3 sets to bind the same metal ion.

The structure of **106** and **173**, obtained by reduction of the corresponding [3+2] cyclic hexamine derivatives **96** and **104**, demonstrates the [3+2] cyclic nature of these derivatives (Fig. 206a and b). In particular **106**, obtained by recrystallization from 1:4 CHCl_3 :hexane lies on a three-fold axis, which runs through the two bridgehead nitrogens. A single water molecule is encapsulated within the cryptand, disordered over equivalent positions about the three-fold axis and moderately strongly hydrogen bonded to the bridgehead nitrogen atoms, which are 5.407 Å apart. The planes of the furan rings are directed tangentially to the three-fold axis of the molecule. The protons on the secondary amines are directed into the clefts between the strands of the cryptand and are not involved in any hydrogen bonding. Crystals of **173** obtained by recrystallization from 1:1 hexane–ether show the asymmetric unit contains two independent, but very similar molecules. Each cryptand has pseudo-three-fold symmetry with the phenyl groups arranged tangentially to the main axis of the molecule and the amine protons directed into the cavity. The cavity is long and narrow but there is no indication of any intramolecular interactions across it. The structures of **173** and **106** show that while the conformation adopted is not fully preorganized for complexation, relatively minor alterations of torsion angles will convert it to a conformation capable of complexation [373].

106 and **173**, together with the analogous aminocryptands containing space host as 1,4-benzene, pyridine or thiophene, exhibit effective complexation of transition ions in aqueous solution, due to good preorganization revealed by comparison of X-ray structures of free ligands and cryptates.

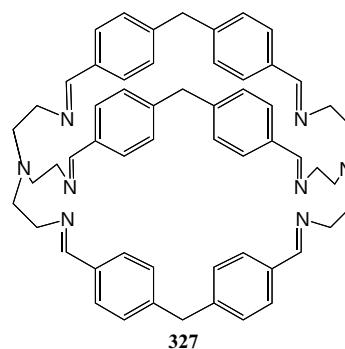
Complexation and protonation equilibria in aqueous solution for the aminocryptand ligands **106** and **173** indicate that stability constants for Ni^{2+} , Cu^{2+} , Co^{2+} and Zn^{2+} are relatively high [373].

With the furan- and pyridine-spaced hosts, both mono- and binuclear cryptates exist in aqueous solution, whereas the *m*- and *p*-xylyl-spaced analogues generally restrict themselves to monocoordination of cationic guests. The best complexation properties are seen with the pyridine

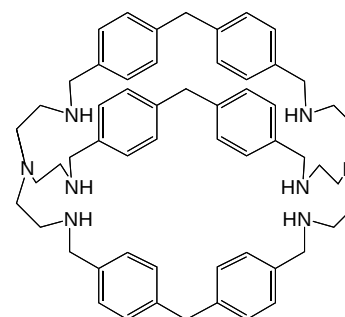
spaced ligand whose stability constants for copper complexation are the highest of any cryptand so far examined. Both pyridine or furane containing spacer ligands show useful selectivity. Studies with the furan-spaced cryptand show that at pH 5 all the copper(II) ions are coordinated while the zinc(II) ions are still 100% free [373].

[3+2] Polyaminic systems, obtained by reduction of the [3+2] macrobicyclic ligands **48**, can selectively recognize different anions in consequence of the different head units. Thus when the head units are diphenylmethane, the resulting amino cryptand acts as receptor for dicarboxylic anions when protonated, and displays chain-length dependent structural selectivity towards the guest dicarboxylates. Structural characterization of the most strongly bound (terephthalate) anion cryptate shows that the strong selectivity for this anion against other aliphatic dicarboxylates is partly explained by hydrogen-bonding complementarity and partly by hydrophobic effects. When the head unit is the small CH_2CH_2 an excellent recognition has been demonstrated for the fluorine anion encapsulated within the cryptand $[\text{H}_6\text{-239}]^{6+}$. Using furan or pyridine as head units the encapsulation respectively of ClO_4^- or SiF_6^{2-} was demonstrated by X-ray structure determinations.

For instance the condensation of 4,4'-diformyl(diphenylmethane) and tris-(2-aminoethyl)amine in CH_3CN forms the almost pure macrobicycle **327**, which may be reduced with LiAlH_4 in tetrahydrofuran to the aminocryptand **328** [373]. Treatment of the Schiff base **327** with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ or AgPF_6 forms $[\text{Cu}_2(\text{327})](\text{ClO}_4)_2$ or $[\text{Ag}_2(\text{327})](\text{PF}_6)_2$ [373].



327



328

The macrobicyclic hexamine **327** has an elongated ellipsoidal shape possessing a ternary symmetry axis through the

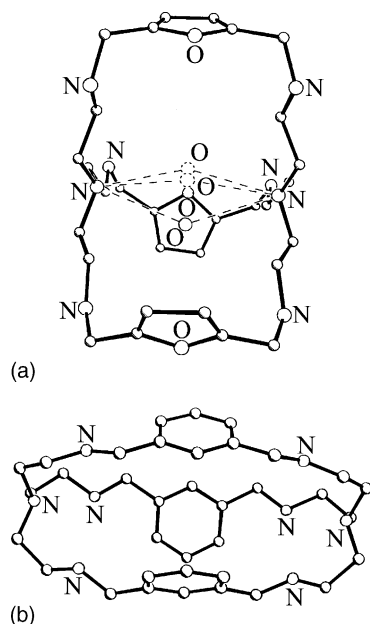


Fig. 206. Structure of **106** (a) and **173** (b) (adapted from Ref. [373]).

bridgehead nitrogens (Fig. 207). In $[\text{Cu}_2(\mathbf{327})]^{2+}$ two copper(I) ions are contained inside the molecular cavity, each bound by one of the tripodal amine, triimine N_4 subunits located at the poles of the ligand (Fig. 208).

The complexation induces drastic changes in the conformation of the macrobicyclic: the bridgehead N–C bonds are staggered in the free ligand, but are eclipsed in the dicopper complex. The approximate symmetry is D_3 (one ternary axis, with three two-fold axes perpendicular to it and passing through the methylene bridges) for the free ligand, but the cryptate loses its ternary axis while exhibiting an approximate mirror plane. The cations attract the imino-nitrogens so that their average N–N distance, 4.4 Å in the free

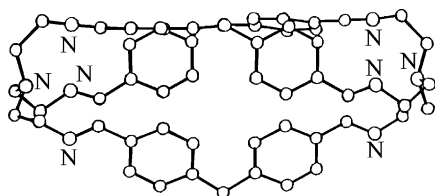


Fig. 207. Structure of **327** (adapted from Ref. [373]).

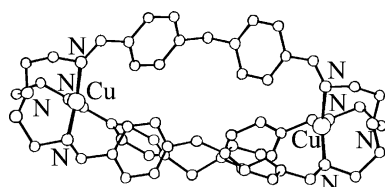
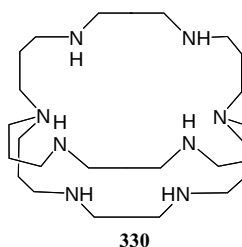
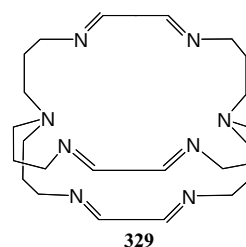


Fig. 208. Structure of $[\text{Cu}_2(\mathbf{327})]^{2+}$ (adapted from Ref. [373]).

macrobicyclic, decreases to 3.4 Å in the complex. The two tetracoordinated copper(I) cations are situated at each end of the macrobicyclic 11.07 Å apart. The coordination polyhedron has a shape with the copper cation lying 0.2 Å outside the tetrahedron formed by the four nitrogens, towards the centers of the cavity.

The series of small aza cages, generated by the Schiff-base [2+3] condensation method from tris(2-aminoethyl)amine and the two-carbon-spaced precursor dialdehyde (glyoxal), have demonstrated the capacity to accommodate a pair of cations, (i.e. silver or copper ions), held in close proximity by the constraints of the ligand [372,374,375]. Within the hexaimino cages **238** and **329** the most stable redox state for the dicopper ions is Cu^ICu^I , as found for $[\text{Cu}_2(\mathbf{238})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{329})](\text{ClO}_4)_2$ [372,275] (Fig. 209a and b). The $\text{Cu} \cdots \text{Cu}$ distances are 2.42 and 2.93 Å, respectively. The cryptates readily undergo one-electron oxidation with mild oxidizing agents such as Ag^+ to generate the mixed $\text{Cu}^I\text{Cu}^{\text{II}}$ complexes $[\text{Cu}_2(\mathbf{238})]^{3+}$ and $[\text{Cu}_2(\mathbf{329})]^{3+}$.



In the analogous octamino derivative **239** and **330**, the Cu^ICu^I oxidation state is not stable, presumably because of the harder nature of the donors and attempts to generate them results only disproportionation and precipitation of copper metal. In this case only in $[\text{Cu}_2(\mathbf{239})]^{3+}$ and $[\text{Cu}_2(\mathbf{330})]^{3+}$ have been obtained [372,374,375]. EPR spectroscopy demonstrates complete delocalization of the unpaired electron over both copper nuclei in these complexes [374,375].

The structure of the dicopper[1.5]cryptate, $[\text{Cu}_2(\mathbf{329})](\text{ClO}_4)_3$, synthesized by a template procedure in the presence of copper(I) ion followed by silver(I) oxidation, confirms the close approach of the copper nuclei within the cryptate ligand cage (Fig. 209c) with a $\text{Cu} \cdots \text{Cu}$ distance of 2.412 Å [372]. The larger cap present in **329** allows the noninteracting copper(I) cations to relax back into the N_3 imino plane, while in the analogous average-valence system

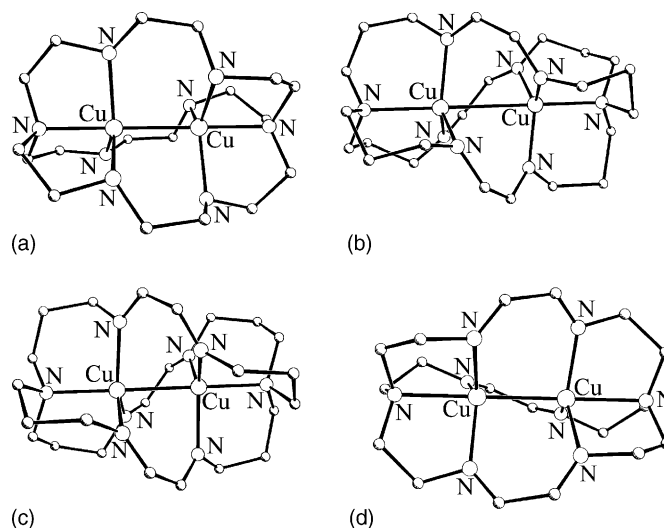


Fig. 209. Structure of $[\text{Cu}_2(\mathbf{238})]^{2+}$ (a), $[\text{Cu}_2(\mathbf{329})]^{2+}$ (b), $[\text{Cu}_2(\mathbf{239})]^{3+}$ (c) and $[\text{Cu}_2(\mathbf{330})]^{3+}$ (d) (adapted from Refs. [372,374,375]).

the copper cations are pulled toward one another by the interaction of the one-electron bond. A similar structure and oxidation state was found for the mixed-valence copper complexes $[\text{Cu}_2(\mathbf{239})(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}]$ and $[\text{Cu}_2(\mathbf{239})(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$ derived from the reaction of **239** with an excess of copper(II) diacetate or dinitrate in methanol, over the course of several days [374].

In $[\text{Cu}_2(\mathbf{239})(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$ the cation $[\text{Cu}_2(\mathbf{239})]^{3+}$ exhibits a very short $\text{Cu} \cdots \text{Cu}$ distance (2.364 Å). Each copper ion is in a trigonal bipyramidal environment, with very similar apical and equatorial $\text{Cu}-\text{N}$ distances. The $[\text{Cu}_2(\mathbf{239})]^{3+}$ cation of $[\text{Cu}_2(\mathbf{239})(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}]$ possesses a slightly elongated ligand structure and an increased $\text{Cu}-\text{Cu}$ distance of 2.415 Å. The observed structural differences between $[\text{Cu}_2(\mathbf{239})(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}]$ and $[\text{Cu}_2(\mathbf{239})(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ are presumably due to the strong hydrogen-bonding interactions observed between the acetate counterions and the secondary amines of **239**. In both structures, the two copper ions are pulled towards each other, out of the plane defined by the three equatorial nitrogen atoms indicating a net bonding interaction between the copper centers [374] (Fig. 209d).

$[\text{Cu}_2(\mathbf{239})(\text{CH}_3\text{COO})_3 \cdot 6\text{H}_2\text{O}]$ shows a magnetic moment ($\mu_{\text{eff}} = 1.7$ BM) typical of a complex with a single unpaired electron and follows the Curie–Weiss behaviour ($T = 5$ – 350 K, $\mu_{\text{eff}} = 1.8$ BM, $\theta = -8$ K). The room temperature solution EPR spectra of $[\text{Cu}(\mathbf{239})(\text{X})_3 \cdot n\text{H}_2\text{O}]$ ($\text{X} = \text{NO}_3^-$, CH_3COO^-) displays an isotropic seven-line signal (9.46 G, CHCl_3 , 300 K, $g = 2.12$, $A = 75 \times 10^{-4} \text{ cm}^{-1}$). This signal becomes asymmetric when frozen due to overlapping g and g' signals, but remains essentially unchanged down to 20 K. The similarity of EPR parameters for $[\text{Cu}_2(\mathbf{239})(\text{X})_3 \cdot n\text{H}_2\text{O}]$ and $\text{Cu}_2(\mathbf{238})(\text{X})_3 \cdot n\text{H}_2\text{O}$ [375], despite the different coordination sites, supports the hypothesis that these signals arise from direct electron transfer between the two copper centers. The q-band EPR spectrum clearly shows that the well-

resolved seven line signal cannot be due to overlapping signals from isolated copper(II) centers [375]. The visible region electronic spectra exhibit two intense absorbance maxima, attributed to a charge transfer within the $\text{Cu}(1.5)-\text{Cu}(1.5)$ center. Moreover MO calculations revealed a direct σ -bonding interactions between the copper centers [374,375].

A treatment of **104** with copper(I) under a nitrogen atmosphere easily generated the dicopper(I) cryptate as a red microcrystalline solid, stable in air as the solid and in solution. The X-ray structure of $[\text{Cu}_2(\mathbf{104})(\text{BF}_4)_2]$ reveals a trigonal pyramidal coordination about the copper(I) ions. The two copper(I) atoms are coordinated by the tren derived caps [376] (Fig. 210a). Treatment of **104** with Cu^{2+} in undried ethanol generates $[\text{Cu}_2(\mathbf{104})(\text{OH})(\text{X})_3]$ ($\text{X} = \text{ClO}_4^-$, PF_6^-), a strong antiferromagnetic coupling ($-2J = 965 \text{ cm}^{-1}$) operates between the two copper(II) ions [376].

The reduced analogue **106** forms with copper(I) perchlorate $[\text{Cu}_2(\mathbf{106})(\text{ClO}_4)_2]$ which is rapidly oxidized to copper(II) in air. It also reacts with CO to form $[\text{Cu}_2(\mathbf{106})(\text{CO})_2](\text{BF}_4)_2$. Treatment of **106** with copper(II) salts in the presence of base gave the μ -hydroxo-dicopper(II) complexes $[\text{Cu}_2(\mathbf{106})(\text{OH})]^{3+}$ in good yield as bright green needles. Physico-chemical data suggest a trigonal bipyramidal coordination about the copper(II) ion as confirmed by an X-ray structural determination of $[\text{Cu}_2(\mathbf{106})(\text{OH})(\text{CF}_3\text{SO}_3)_3]$ which shows that the $\text{Cu}-\text{O}-\text{Cu}$ link is virtually linear with a $\text{Cu} \cdots \text{Cu}$ distance of 3.9 Å (Fig. 210b). A strong antiferromagnetic coupling is operating which makes virtually diamagnetic this compound [376].

The synthesis of $[\text{Cu}_2(\mathbf{93})]^{2+}$, by transmetallation of the disilver(I) analogue, needs a large excess of copper(I) salts and a prolonged reflux. Where mild conditions were used, very little if any dicopper(I) product is obtained and the main

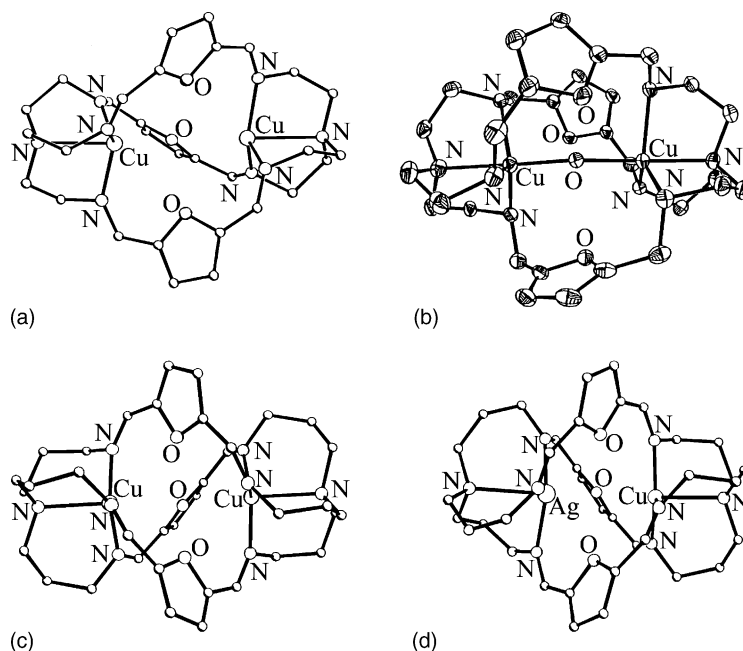


Fig. 210. Structure of $[\text{Cu}_2(\mathbf{104})]^{2+}$ (a), $[\text{Cu}_2(\mathbf{106})(\text{OH})]^{3+}$ (b), $[\text{Cu}_2(\mathbf{93})]^{2+}$ (c) and $[\text{CuAg}(\mathbf{93})]^{2+}$ (d) (adapted from Refs. [376,377]).

trasmetalation product is the hetero-dinuclear cryptate $[\text{CuAg}(\mathbf{93})]^{2+}$ [377] (Fig. 210c and d).

Also the pyrrole-based cryptand $\text{H}_3\text{-240}$ forms $[\text{Cu}_2(\mathbf{240})](\text{BF}_4)$ when treated with $\text{Cu}(\text{BF}_4)$ under inert atmosphere [377]. One electron oxidation yields a localized mixed-valence dicopper cryptate of the singly deprotonated ligands and two electron oxidation a dicopper(II) cryptate of the triply deprotonated ligand. The X-ray structure of $[\text{Cu}_2(\mathbf{240})](\text{ClO}_4)$ shows that the cation has no internal symmetry and the geometry at each copper is irregular: one copper is four-coordinate, distorted toward tetrahedral from square planar while the other copper approximates to square pyramidal coordination geometry. Neither bridgehead nitrogen is coordinated to copper, but the three pyrrole nitrogens and the paramagnetic centers may be considered unbridged, as the magnetic susceptibility results indicate. The $\text{Cu} \cdots \text{Cu}$ distance is 3.006 Å (Fig. 211) [377].

237 does not form with copper(II) salts in the absence or in the presence of base the designed complex while on treatment with the same copper(I) salts, followed by rapid

reduction of volume, produces the dark brown crystalline product $[\text{Cu}_2(\mathbf{237})](\text{X})_2$ ($\text{X} = \text{ClO}_4^-$, BF_4^-). The template strategy was unsuccessful [378].

In $[\text{Cu}_2(\mathbf{237})]^{2+}$ (Fig. 212) two symmetry-related copper(I) ions are bound within the cavity, each coordinated to three imine nitrogen donors, displaced by 0.63 Å from the mean plane of the three imine nitrogen atoms towards the center of the cavity. There are weaker interactions with the bridgehead amine, one of the pyridine nitrogen donors and the second copper atom. In addition, there may be some interaction with the remaining pyridine nitrogen atoms. Neither the perchlorate anions nor the dichloromethane solvate molecules show any interaction with the cation. The $\text{Cu} \cdots \text{Cu}$ distance is 3.038 Å [378].

Cyclic voltammetry of $[\text{Cu}_2(\mathbf{237})](\text{BF}_4)_2$ shows a pair of overlapped quasi-reversible waves, with oxidation components at −110 and +12 mV versus ferrocenium/ferrocene. A DMF solution of this complex, left open to atmosphere for

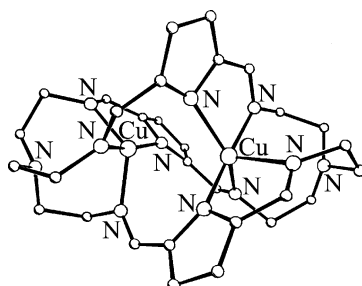


Fig. 211. Structure of $[\text{Cu}_2(\mathbf{240})]^+$ (adapted from Ref. [377]).

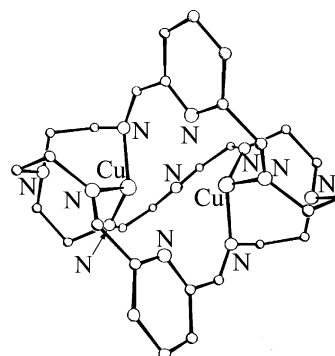
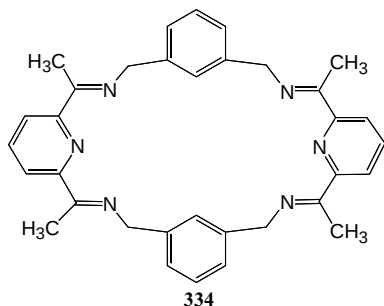
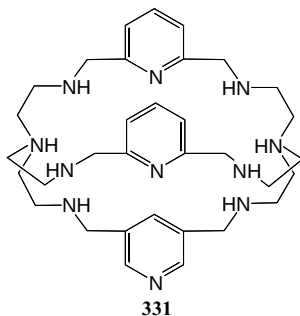


Fig. 212. Structure of $[\text{Cu}_2(\mathbf{237})]^{2+}$ (adapted from Ref. [378]).

several day and monitored over that period of time by EPR spectroscopy shows, that the ligand has been modified by hydrolysis. Also these measurements indicate that copper(II) is not favoured as a guest within this cryptand, and even dicopper(I) is not long-term stable. The one-electron oxidized mixed valence form of the cryptate (i.e. $[\text{Cu}_2(\mathbf{237})](\text{BF}_4)_3 \cdot 4\text{H}_2\text{O}$) exists, but may have a too transient existence in solution to be of value for practical purposes, e.g. in catalysis.

The oxidation state preferences of copper within the amine and imine hosts are markedly different. Thus the dicopper(I) cryptates $[\text{Cu}_2(\mathbf{237})](\text{BF}_4)_2$ and $[\text{Cu}_2(\mathbf{237})](\text{ClO}_4)_2 \cdot \text{CH}_2\text{Cl}_2$ are readily obtained, but the analogous copper(I) complex within the reduced derivative **331**, is so easily oxidized that it was impossible to obtain copper(I) salts of acceptable purity. On the other hand the dicopper(II) cryptate $[\text{Cu}_2(\mathbf{331})](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ was readily obtained by reaction of **331** with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{CN}$. The subsequent recrystallization from $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{CN}$ affords $[\text{Cu}_2(\mathbf{331})](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN}$ [378].



EPR and magnetic susceptibility measurements on $[\text{Cu}_2(\mathbf{331})](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN}$ alike testify to the presence of a weak interaction between the copper(II) ions ($-2J \approx 25 \text{ cm}^{-1}$).

In contrast to the results obtained on $[\text{Cu}_2(\mathbf{237})](\text{BF}_4)_2$ electrochemistry indicates that the copper centers in $[\text{Cu}_2(\mathbf{331})](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN}$ undergo redox more or less independently of each other; just a single fairly broad two-electron quasi-reversible wave is seen. These data testify the increased thermodynamic stability of the copper(II) oxidation state within the saturated azacryptand [378].

Neither magnetic nor electrochemical properties suggest a particularly efficient mode of communication between the

copper centers in $[\text{Cu}_2(\mathbf{331})](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN}$. This presumably derives largely from the absence of a bridging ligand, which limits interaction to the through-space dipole–dipole mechanism. Attempts of incorporation of a bridging ligand, (i.e. imidazolate and pyrazolate) failed; however, with azide in appropriate stoichiometry the green microcrystalline product $[\text{Cu}_2(\mathbf{331})(\text{N}_3)](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ was formed. IR and EPR data indicate a low symmetry site for azide, either terminal, 1,1-bridged or bent 1,3-bridged. There is no indication of a linear 1,3-bridging assembly.

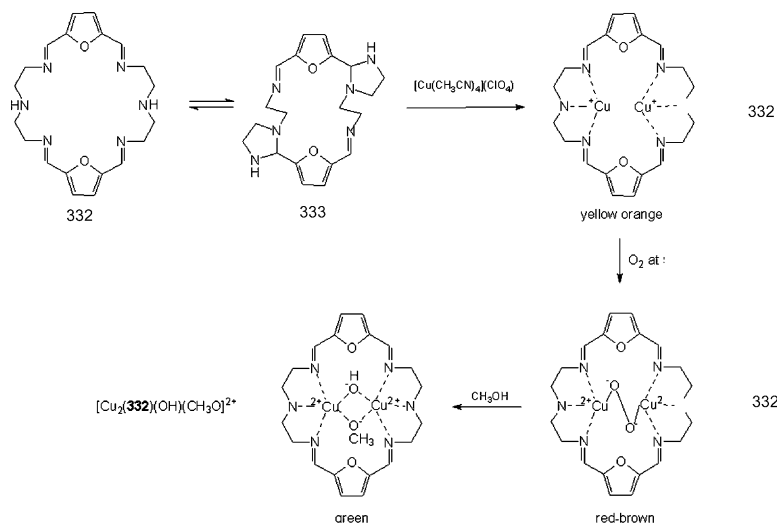
For this diazido complex a negligible magnetic interaction operates between the copper(II) ions ($-2J = 2 \text{ cm}^{-1}$). This is lower than the antiferromagnetic coupling constant observed for $[\text{Cu}_2(\mathbf{331})](\text{ClO}_4)_4 \cdot \text{CH}_3\text{CN}$ and represents a low value even for unsymmetrically bridged azide [378], so it seems clear that if a bridge exists, it is long and weak. The absence of any $[\text{Cu}_2(\mathbf{331})(\text{N}_3)]$ or $[\text{Cu}(\mathbf{331})(\text{N}_3)]$ peaks in the FAB-mass spectrum is further proof of weak coordination of the azido ligand.

However, the presence of azide has an effect on the electrochemistry. A pair of quasi-reversible waves centered around -680 and -855 mV versus ferrocenium/ferrocene replace the single two-electron wave seen for the unbridged dicopper(II) complex. The azide link assists electronic communication between the copper centers so that the assembly undergoes redox in the two sequential steps: $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\mathbf{331})(\text{N}_3)] \rightleftharpoons [\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(\mathbf{331})(\text{N}_3)] \rightleftharpoons [\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\mathbf{331})(\text{N}_3)]$ [378].

The condensation of furan-2,5-dicarboxaldehyde and 1,4,7-triazaheptane in acetonitrile forms the [2+2] macrocycle **332** [379]. As reported in a previous section this ligand, having two secondary NH groups that may undergo addition reactions with adjacent imine groups suffers a ring contraction reaction. ^1H NMR spectra indicate the presence of more than one compound in solution, which is attributed to the ability of the ligand to adopt more than one structural conformation, thus resulting in a mixture of isomers (**332** and **333** of Scheme 47).

The reaction of **332** with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ and the subsequent oxygenation reaction of the resulting dinuclear copper(I) complex is reported in Scheme 47 [379].

Oxygen uptake and UV-Vis spectra indicate that $[\text{Cu}_2(\mathbf{332})](\text{ClO}_4)_2$ reacts with O_2 at 5°C and at pH 9 in the presence of a borax buffer to give the red brown peroxo-bridged dicopper(II) dioxygen adduct $[\text{Cu}_2(\mathbf{332})(\text{O}_2)]^{2+}$. Further bubbling of oxygen through the solution produces complete degradation to an inert green product. Attempts at deoxygenation by vacuum cycling showed the oxygenation process to be irreversible after sufficient time had been allowed to complete the degradation process. The X-ray structure of this green decomposition complex $[\text{Cu}_2(\mathbf{332})(\text{OH})(\text{CH}_3\text{O})](\text{ClO}_4)_2$ (Fig. 213) shows that the four coordinated environment around each copper(II) ion involves one imine nitrogen and one secondary nitrogen of the macrocycle as well as one hydroxy and one methoxy group. The latter two groups are common bridging groups



Scheme 47.

between the two copper(II) centers. The geometric configuration of the coordination sphere has been described as a distorted square planar arrangement. The separation distance between the metal ions is 2.96 Å.

The overall reaction pathway therefore (Scheme 47), involves the formation of [Cu₂(332)]²⁺. Addition of oxygen to this complex produces [Cu₂(332)(O₂)]²⁺ which has lifetime of 3–4 h at 5 °C but is eventually converted to a copper(II) complex containing both hydroxy and methoxy bridging groups with the ligand unchanged throughout the process. The fact that an oxygen complex, albeit of limited lifetime, forms in this case instead of oxygen insertion into the aromatic group is due to the fact that the oxygen of the furan is close to the bridging peroxo group and there is no electron-donating group nearby to react with the coordinated dioxygen, as was the case for the peroxo-bridged binuclear copper(I) complex containing *m*-xylyl connecting groups in the ligand [379].

The use of [Cu₂(332)]²⁺ in performing oxidation reactions with hydroquinones, phenols, catechols, ascorbic acid, and 3,4-dimethylaniline in a 3:1 mixture of methanol and acetonitrile was tested [379,380]. It has been determined that the dioxygen complex [Cu₂(332)(O₂)]²⁺ catalytically converts hydroquinones to the corresponding benzoquinones, ascorbic acid to dehydroascorbic acid, and phenols to their 1,4-benzoquinones and diphenoquinones, in the presence of

excess dioxygen. Turnover numbers range between 5 and 20 h⁻¹. Under the same conditions 4-*tert*-butylcatechol was transformed to the γ -lactone of the corresponding muconic acid ester, 3,5-di-*tert*-butylcatechol was oxidised to the corresponding 1,2-benzoquinone, and 3,4-dimethylaniline was converted to 3,4-nitrosobenzene, all with turnover numbers of less than 1. These reactions were found to occur under stoichiometric conditions as well. Hydroquinones, phenols and ascorbic acid, but not catichols and 3,4-dimethylaniline were also found to be oxidized, under stoichiometric conditions, by a dinuclear copper(II) complex, prepared from the 2:1 stoichiometric reaction between CuCl₂ and 332 in methanol. The rates for the stoichiometric oxidations were determined to be 5–100 times greater for copper(I)-dioxygen oxidations than for corresponding copper(II) oxidations. On the basis of these observations, a catalytic scheme based on the copper(I) complex as the initial active species was proposed. The following steps are suggested: (i) formation of a dinuclear copper(I)-dioxygen adduct, (ii) oxidation of the substrate by the dioxygen adduct with simultaneous formation of a copper(II) dinuclear complex, and (iii) oxidation of the substrate by the copper(II) complex to produce a copper(I) dinuclear complex and the oxidation product of the substrate [380].

The reaction of 2,6-diacetylpyridine with *m*-xylylenediamine in the presence lead(II), strontium(II), barium(II), silver(II), copper(II) or nickel(II) ions failed to give the desired [2+2] macrocycle and led instead to insoluble polymeric material. The addition of a bridging ligand (i.e. imidazole), added during the synthesis of the macrocycle results in a dramatic increase in macrocyclization. In the synthesis, imidazole serves as an initial template to first define the metal–metal separation and geometry, forming a secondary template {M(μ -Im)M} which finally acts as a template for macrocyclization. Thus the formation of any such bridged dinuclear complex {M(μ -Im)M} could be considered a template reaction since the bridge serves to

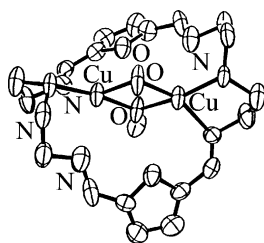


Fig. 213. Structure of [Cu₂(332)(OH)(CH₃O)]²⁺ (adapted from Ref. [379]).

orient two metal ions in defined geometries working against entropy. Although the precise order of events in the mechanism cannot be determined, it is certain that both metal ions and the bridging imidazole must be present before macrocyclization will occur. Evidence of the existence of the $\{\text{Cu}(\mu\text{-Im})\text{Cu}\}$ moiety prior to macrocyclization was obtained from a solution EPR spectrum at room temperature of a mixture of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and imidazole in CH_3OH [381].

In the synthetic procedure, equimolar amounts of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ or $\text{Ni}(\text{CF}_3\text{SO}_3)_2$, imidazole, diketone, and diamine in CH_3OH led to the formation of $[\text{Cu}_2(\mathbf{334})(\mu\text{-Im})](\text{CF}_3\text{SO}_3)_3$ or $[\text{Ni}_2(\mathbf{334})(\mu\text{-Im})](\text{CF}_3\text{SO}_3)_3$, respectively, after 12 h at room temperature. Although only 1 equiv. of imidazole is required in the final complex, it is likely that a second equivalent of imidazole serves as a base for formation of the dicopper imidazolate moiety [381].

A variety of bridging ligands were studied with $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in order to ascertain the generality of the method and the specificity of imidazole as the initial template. Pyrazole, and urea failed to serve as appropriate template for the reaction while copper(II) acetate and nickel(II) acetate yield stable macrocyclic complexes, thus serving as templates for the macrocyclization process. By this procedure $[\text{Ni}_2(\mathbf{334})(\mu\text{-CH}_3\text{CO}_2)_x](\text{CH}_3\text{CO}_2)_{4-x}\cdot 6\text{H}_2\text{O}$ was obtained, which acts as a modest catalyst for hydrolysis of *p*-nitrophenyl acetate [381].

334 can be obtained by extraction of the metal ions from the complexes using concentrated aqueous edta. During the entire extraction process, it was necessary to handle the macrocycle under nitrogen atmosphere and to use degassed solvents. Benzene is an excellent solvent for extracting the compound while chlorinated solvents decompose it. The macrocycle reforms, by reaction with $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and imidazole, $[\text{Cu}_2(\mathbf{334})(\mu\text{-Im})](\text{CF}_3\text{SO}_3)_3$, its dimeric nature as well as the existence of a bridging imidazolate being confirmed by X-ray investigations. In the cation $[\text{Cu}_2(\mathbf{334})(\mu\text{-Im})]^{3+}$ the two copper ions are located 5.92 Å apart. Each copper(II) ion is similarly coordinated to three nitrogen atoms of the macrocycle and to one nitrogen of the imidazolate ligand giving an overall square planar N_4 environment. In addition, axial positions of both coppers are occupied by weakly coordinated H_2O or CF_3SO_3^- oxygen atoms. However, one copper ion is located further away from its mean N_4 plane compared to the other copper ion probably because of the absence of an extra oxygen ligand in the sixth position (Fig. 214). Magnetic and EPR data show that the two copper(II) ions are weakly antiferromagnetically coupled ($-J = 19.3 \text{ cm}^{-1}$). Electrochemical studies indicate a single quasi-reversible two-electron reduction of the copper(II) ions at $E_{1/2} = -435 \text{ mV}$.

Contrasting reactivities of *N,N*-bis(2-aminoethyl)-2-phenylethylamine and *N,N*-bis(3-aminopropyl)-2-phenylethylamine with 2,6-diacetylpyridine in the presence of silver(I) ions were observed. Changing the 2-amino alkyl groups of the alkylamine from ethyl to *n*-propyl provides a change

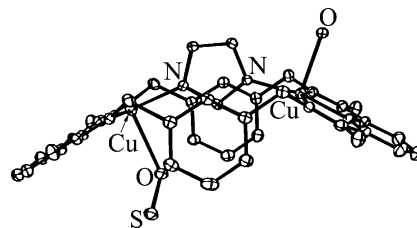


Fig. 214. Structure of $[\text{Cu}_2(\mathbf{334})(\mu\text{-Im})]^{3+}$ (adapted from Ref. [381]).

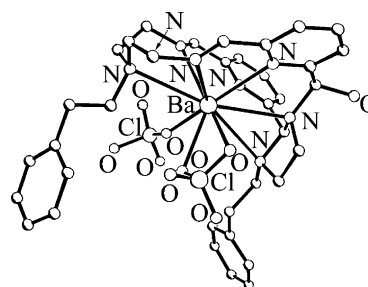
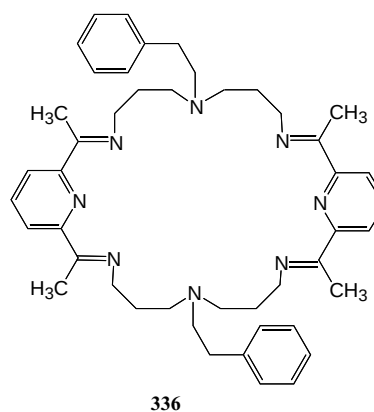
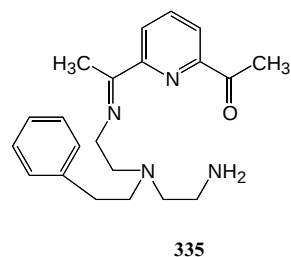
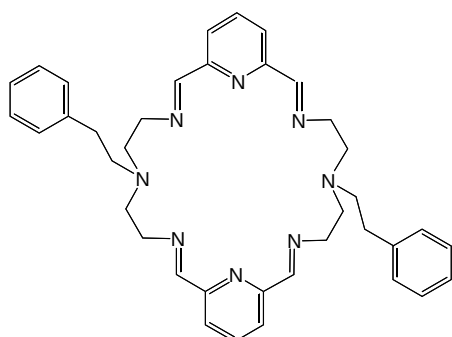


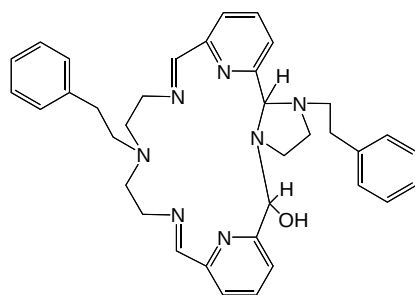
Fig. 215. Structure of $[\text{Ba}(\mathbf{338})](\text{ClO}_4)_2$ (adapted from Ref. [382]).

from the [1+1] acyclic mononuclear silver(I) complex $[\text{Ag}(\mathbf{335})](\text{ClO}_4)$ to the [2+2] dinuclear silver(I) compound $[\text{Ag}_2(\mathbf{336})](\text{ClO}_4)_2$ [382]. The same [2+2] cyclocondensation in the presence of lead(II), barium(II) or lanthanide(III) cations failed [382]. Moreover the similar [2+2] cyclocondensation of 2,6-diformylpyridine and *N,N'*-bis(2-aminoethyl)-2-phenylethylamine in the presence of barium(II) perchlorate in CH_3CN at room temperature forms the expected [24]-membered macrocyclic complex $[\text{Ba}(\mathbf{337})](\text{ClO}_4)_2$ and the [18]-membered macrocyclic complex $[\text{Ba}(\mathbf{338})](\text{ClO}_4)_2$ as ascertained by X-ray diffractometry (Fig. 215) [382].



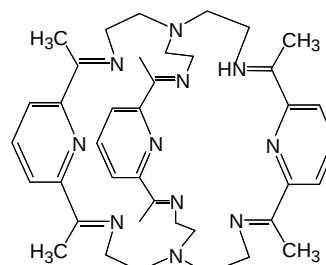


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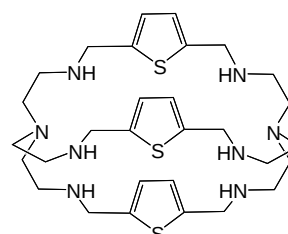


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The reaction of the diprotonated cryptand $\text{H}_2\text{-339}\cdot 2\text{BF}_4$, prepared by the [3+2] cyclocondensation of 2,6-diacetylpyridine and tris(2-aminoethyl)amine in the presence of hydrochloric acid followed by filtration into a solution of sodium tetrafluoroborate in methanol, forms with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{BF}_4)$ in methanol the dinuclear copper(I) complex $[\text{Cu}_2(\text{339})](\text{BF}_4)_2$ [383]. The structure (Fig. 216) shows that both the integrity of the cryptand and the unusual *trans-trans* conformations of the dicarbimine functions found in the protonated cryptand are retained in the structure of the complex. The dimetallic cryptand possesses crystallographically imposed C_{3h} symmetry, with each copper(I) ion and each tertiary amine nitrogen lying on the C_3 axis and the pyridyl nitrogens and their *para*-C–H groups lying on the mirror plane, thus the remainder of each asymmetric unit comprises only half of one of the arms of the cryptand and a single tetrafluoroborate anion. Each copper(I) ion is coordinatively saturated being bonded to four nitrogen atoms in an approximately trigonal pyramidal geometry. Each copper ion is displaced by 0.185 Å from the plane through the imino nitrogen atoms in a direction away from the bridgehead tertiary nitrogen. The copper···copper separation is 6.250 Å but there is no evidence for any electron density lying between the metals within the cavity. The copper separation is well in excess of that reported (3.04 Å) for the dicopper(I) complex $[\text{Cu}_2(\text{237})](\text{ClO}_4)_2$, in which **237** is the [3+2] Schiff-base cryptand derived from pyridine-2,6-dicarbaldehyde and tris(2-aminoethyl)amine. The structures of the complexes differ significantly and in $[\text{Cu}_2(\text{237})](\text{ClO}_4)_2$ each copper is coordinated to three imino nitrogen atoms while the bridgehead nitrogen atom is more distant. Each copper(I) ion is described as being three coordinated and the dicarbimine functions in this complex are in *cis-cis* conformations.



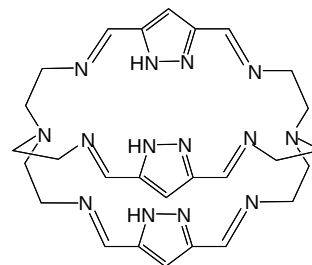
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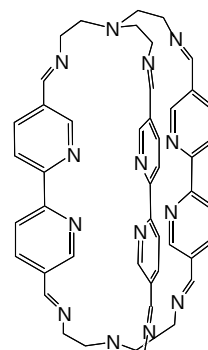
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A further comparison may be made with the structure of $[\text{Cu}_2(\text{104})](\text{BF}_4)_2$ in which the cryptand is derived from furan-2,5-dicarbaldehyde and tris(2-aminoethyl)amine. Here the copper ions, 4.2 Å apart, are four coordinated interacting with the bridgehead nitrogen atom and three imine nitrogen atoms. The conformations of the dicarbimine functions are again *cis-cis* and the furan oxygen atom is non-coordinating.

The reaction of $\text{Cu}(\text{BF}_4)_2$ with the diprotonated cryptand $\text{H}_2\text{-339}\cdot 2\text{BF}_4$ in methanol gives the dinuclear complex, $[\text{Cu}_2(\text{242})](\text{BF}_4)_4\cdot 3\text{H}_2\text{O}$. Hydrolytic cleavage of one dicarbimine bridge of the cryptand has occurred to give a bibracchial tetraimine Schiff base macrocyclic ligand.



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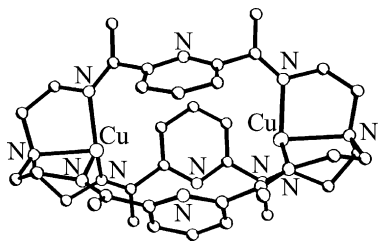


Fig. 216. Structure of [Cu₂(339)]²⁺ (adapted from Ref. [383]).

The recrystallization of this dinuclear complex from ethanol/acetonitrile gave crystals of [Cu₂(242)](BF₄)₄·0.33CH₃CN·0.25H₂O [383]. The ring opening of the Schiff base cryptand, caused by scission of one pyridinyl diimine unit, has occurred such that the dicopper(II) moiety is held inside a cleft. The cation [Cu₂(242)]⁴⁺ possesses an approximate two-fold axis of symmetry, and as a result of coordination the organic ligand is folded in such a way that the two pyridinyl units are nearly parallel with stacking distances of 3.23 Å. Each copper environment is best described as distorted trigonal bipyramidal (Fig. 217a) [383].

[Mn₂(242)(CH₃COO)](BF₄)₃·CH₃CN·0.5C₂H₅OH was obtained by the reaction of equimolar amount of H₂-339·2BF₄ and manganese(II) acetate in methanol/acetonitrile and in the presence of sodium tetrafluoroborate and triethylamine, followed by the recrystallization of the crude product from acetonitrile/ethanol [384]. Again a single ring-opening of the Schiff base cryptand has occurred to yield a carboxylato-bridged dinuclear manganese(II) complex of the bibrachial tetraimine Schiff base macrocycle 242. The macrocycle accommodates two manganese(II) ions, each of which is coordinated to five nitrogen atoms, three from a pyridine dicarbimine head unit, one from a tertiary amino group, and one from the pendant aminoethane residue. The

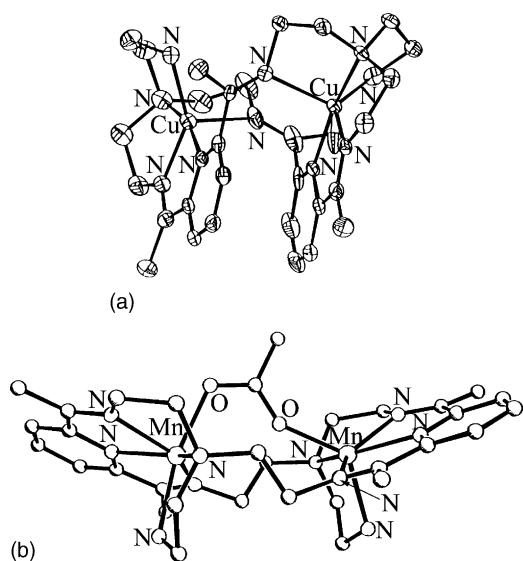


Fig. 217. Structure of [Cu₂(242)]⁴⁺ (a) and [Mn₂(242)(CH₃COO)]³⁺ (b) (adapted from Refs. [383,384]).

two manganese ions are thus located at opposite ends of the [24]-membered macrocycle which has a semiopen, concertina-like conformation. The metal···metal separation is 4.82 Å. The metal ions are singly bridged in an unusual syn-anti manner by an acetato ligand (Fig. 217b) [384].

Magnetic measurements over a temperature range show that [Mn₂(242)(CH₃COO)](BF₄)₃·CH₃CN·0.5C₂H₅OH follows the linear Curie behaviour only at temperatures above 10 K, which indicates the presence of a small exchange interaction ($J = -0.37 \text{ cm}^{-1}$) through the single bridging acetate group. EPR spectra at 4 K in toluene/acetonitrile glass and in solid state, very similar and typical of weakly coupled manganese(II) derivatives, strongly indicate that the complex retains the acetato bridge in solution [384].

Unlike the furan-based cryptand 104, the thiophene-based cryptand 97 is not readily made by direct condensation but can be synthesized via the silver(I) template method in near-quantitative yield as [Ag₂(97)](CF₃SO₃)₂. 95 is similarly made, generating [Ag₂(95)](ClO₄)₂. Transmetalation of [Ag₂(97)](CF₃SO₃)₂ with either copper(I) or copper(II) salts generates the dicopper(I) complexes [Cu₂(97)](CF₃SO₃)₂ or [Cu₂(97)](BF₄)₂. More satisfactory the same complex can be obtained via direct template [385].

In [Ag₂(97)](CF₃SO₃)₂ the two silver(I) ions are encapsulated within the macrocycle at the two ends. The geometry around the metal ions is unusual as all four nitrogen atoms are on one side of the metal. If the long contacts between the silver ions and the thiophene sulfur atoms are considered, the metal coordination sphere would resemble a seven coordinate capped octahedron with the bridgehead nitrogen in the capped position, the three imine nitrogen atoms in the capped face and the three sulfur atoms in the uncapped face. The Ag···Ag distance is 4.65 Å and the N···N bridgehead distance 9.69 Å (Fig. 218a).

Also in [Ag₂(95)](ClO₄)₂ (Fig. 218b) the silver(I) ions are four coordinated; each forms three bonds to the imine nitrogens with a longer contact to the bridgehead nitrogen. The positions of the two silver(I) ions relative to the imine plane are not identical: one silver, like the silver ions in [Ag₂(97)](CF₃SO₃)₂, sits inside the plane formed by the three imine nitrogens so that all four nitrogen donors are on side of the metal cation; the other silver is not in the N₃ plane but slightly off it in the opposite direction so that it lies

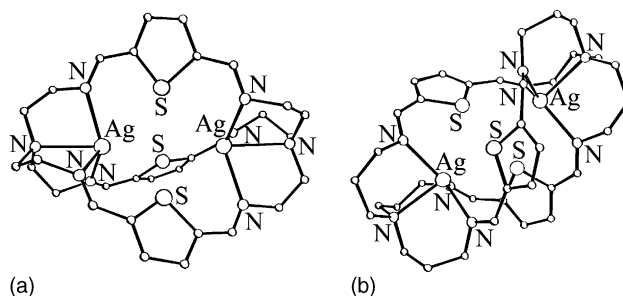


Fig. 218. Structure of [Ag₂(97)]²⁺ (a) and [Ag₂(95)]²⁺ (b) (adapted from Ref. [385]).

between the bridgehead atom and the three imino donors. The silver(I) ions in $[(\text{Ag}_2(\mathbf{95}))(\text{ClO}_4)_2]$ lie closer to the N_3 plane than in $[(\text{Ag}_2(\mathbf{97}))(\text{CF}_3\text{SO}_3)_2]$. Both the $\text{Ag} \cdots \text{Ag}$ (5.004 Å) and $\text{N} \cdots \text{N}$ bridgehead distances (≈ 9.962 Å), however, are longer than in $[(\text{Ag}_2(\mathbf{97}))(\text{CF}_3\text{SO}_3)_2]$.

In $[\text{Cu}_2(\mathbf{97})(\text{CF}_3\text{SO}_3)_2]$ each cation sits on a two-fold rotation axis which passes through the sulfur atom in one of the thiophene rings and bisects the Cu–Cu vector. There is an approximate, non-crystallographic three-fold axis passing through the copper and bridgehead nitrogen atoms of each cation. Although the cations are very similar, there are some subtle differences which can probably be ascribed to packing effects. In each case the copper ion is co-ordinated to the three imine nitrogen atoms and is displaced by ca. 0.5 Å from the plane of the three donors towards the center of the cavity. The copper ions and bridgehead nitrogen atoms interact weakly. There are no significant cation–cation interactions and the triflate anions do not interact with the cation. Although $[(\text{Ag}_2(\mathbf{97}))(\text{CF}_3\text{SO}_3)_2]$ and $[\text{Cu}_2(\mathbf{97})(\text{CF}_3\text{SO}_3)_2]$ are not isostructural, no major differences of coordination site geometry or cryptand conformation with each other are observed. Thus both **97** cryptates have metal ions sited outside the N_3 plane, displaced toward the center of the cavity, while in the **97** cryptate the cations have relaxed back into the N_3 plane with consequent increase of the $\text{Ag} \cdots \text{Ag}$ internuclear distance.

In order to achieve the dicopper(II) state, the hexamine ligand **97** was reduced to the octaamino ligand **340**, anticipating that the harder sp^3 -nitrogen donors would stabilise the higher oxidation state, while the greater flexibility of **340** would simultaneously ensure less restrictive coordination site geometry. On treating **340** with copper(I) salt the air-sensitive cream solid $[\text{Cu}_2(\mathbf{340})(\text{ClO}_4)_2]$ was isolated which acquired a greenish colour on standing in air over a period of weeks, but within minutes in solution. When **340** is treated with copper(II) perchlorate under basic conditions $[\text{Cu}_2(\mathbf{340})(\text{OH})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}]$ is obtained. The temperature dependence of the magnetic susceptibility reveals a magnetic exchange parameter of $2J = -72 \text{ cm}^{-1}$; this is less than one tenth with respect to that found where the copper(II) paramagnets are linearly disposed and is possibly due to a non-linearity of the singly bridged $[\text{Cu}_2(\text{OH})]^{3+}$ assembly.

Moreover, a single triatomic imidazolate or azido bridge is readily accommodated between the copper(II) ions. Moderate antiferromagnetic interaction ($-2J = 112 \text{ cm}^{-1}$) is exhibited in the *m*-imidazolate dimer $[\text{Cu}_2(\mathbf{340})(\mu\text{-Im})(\text{CF}_3\text{SO}_3)_3]$, and there is EPR spectral evidence of thermal accessibility of the excited triplet state. The mono-azido-bridged complex $[\text{Cu}_2(\mathbf{340})(\text{N}_3)(\text{ClO}_4)_3]$, having spectroscopic properties characteristic of a collinear Cu–NNN–Cu assembly, was obtained on treatment of $[\text{Cu}_2(\mathbf{340})(\text{OH})]^{3+}$ with 1 equiv. of NaN_3 .

$\text{H}_6\text{-96} \cdot 6\text{NO}_3 \cdot 2\text{H}_2\text{O}$, containing a bridging *m*-phthalaldehyde spacer, has been isolated by an anion exchange reaction of AgNO_3 with the hydrochloride salt of **96** [385]. While

four of the nitrates were associated via predominantly electrostatic and hydrogen bonding interactions outside of the macrocyclic cavity, crystallographic results indicated a unique encapsulation of two nitrate ions within the bicyclic cavity in an eclipsed conformation. The C_3 symmetry of the bicycle presents an ideal environment for hydrogen bonding interactions with the incorporated anions. The environment about each of the internal nitrates is almost identical. Both of the nitrate nitrogen atoms exhibit rather short interactions with the apical nitrogens of the macrocycle. Of major importance to the stabilization of the structure, are the hydrogen bonding contacts between the trigonally oriented macrocycle amines and the internal nitrate oxygen atoms. Each of these oxygens exhibits an asymmetric bifurcated hydrogen bond between two of the protonated macrocyclic amines, which ties them firmly in place inside the cavity. Four additional nitrates and two water molecules lie outside the macrocyclic cavity [385]. Thus **96** is a receptor capable of binding two discrete anionic guests within a single cavity. The almost ideal D_{3h} geometry and the trigonal positioning of the protonated amines serves to tie-back the nitrate oxygen atoms via hydrogen bonding, which allows for a substantial reduction in anion–anion repulsion [385].

96 fails to template on metal cations, instead it crystallises out in the metal-free form. Once formed, however, the cryptand can be treated with silver(I) or copper(I) salts in an ethanol/acetonitrile solution to give the binuclear cryptates $[(\text{Ag}_2(\mathbf{96}))(\text{CF}_3\text{SO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}]$ or $[(\text{Cu}_2(\mathbf{96}))(X)_2 \cdot n\text{H}_2\text{O}]$ ($X = \text{ClO}_4^-$, $n = 2$; $X = \text{BF}_4^-$, $n = 3$) in high yield. Indeed, the copper(I) cryptate can be obtained by a pseudotemplate method, provided that addition of the copper(I) salt is delayed until the triamine and dicarbonyl have reacted together for 15 min [386].

$[\text{Cu}_2(\mathbf{96})(X)_2 \cdot n\text{H}_2\text{O}]$ requires no inert atmosphere protection in either dimethylformamide or CH_3CN . Indeed, even treatment of $[\text{Cu}_2(\mathbf{96})(X)_2 \cdot n\text{H}_2\text{O}]$ with silver(I) ion as the oxidising agent fails to generate any copper(II). However, the free cryptand may be treated with hydrated copper(II) perchlorate to give the $[\text{Cu}_2(\mathbf{96})(\text{OH})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]$. No EPR spectrum is observable. Magnetic susceptibility measurements confirm the virtual diamagnetism of this complex ($-2J \approx 800 \text{ cm}^{-1}$), suggesting efficient antiferromagnetic exchange such as that existing in $[\text{Cu}_2(\mathbf{104})(\text{OH})]^{3+}$ where a linear {Cu–OH–Cu} assembly encapsulated within the cryptands takes place. For $[\text{Cu}_2(\mathbf{96})(\text{N}_3)(\text{CF}_3\text{SO}_3)_3]$, where a collinear disposition of the bridging link exists, only weak ferromagnetic interaction is observed [386].

The incorporation of bulkier bridging links such as imidazolate between the copper(II) cations in **96** were not successful [386].

$[\text{Cu}_2(\mathbf{96})(\text{OH})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]$ and $[\text{Cu}_2(\mathbf{96})(\text{N}_3)(\text{CF}_3\text{SO}_3)_3]$ are not stable long term in solution. When $[\text{Cu}_2(\mathbf{96})(\text{OH})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]$ is left for 1–2 days in CH_3CN particularly in the presence of CH_2Cl_2 , the dicopper complexes of the partially hydrolysed ligand **285** or **286** can be isolated. In $[\text{Cu}_2(\mathbf{285})(\text{OH})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]$, this

metal-assisted hydrolysis has resulted in the splitting off of an isophthalaldehyde molecule. The same blue product is obtained under inert atmosphere conditions, showing that this is a simple hydrolysis. The hydrolysis of $[\text{Cu}_2(\mathbf{96})(\text{OH})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]$ proceeds more slowly in the absence of CH_2Cl_2 . Under these conditions, the dicopper(II) μ -hydroxo complex $[\text{Cu}_2(\mathbf{286})(\text{OH})(\text{BPh}_4)_2(\text{CF}_3\text{SO}_3) \cdot \text{H}_2\text{O} \cdot 0.5\text{EtOH}]$ of the ring-opened ligand **286** where just one imine function has been hydrolysed and solvent addition accompanying ring opening generates a terminal acetal function, can be crystallised out by addition of BPh_4^- [386].

The macrocycle **286** has adopted a U-shaped configuration, containing the pair of copper(II) cations within the cleft. Both cations are in a distorted trigonal bipyramidal coordination geometry using all available nitrogen donors including one each (amino- or imino-nitrogen) from each of the pendant arms, with a bridging OH completing the coordination sphere. The Cu–O(H)–Cu angle is 166.1° and the Cu...Cu separation 3.89 Å. The pair of U-terminal aromatic rings are stacked, at an approximate separation of 3.4 Å, which presumably contributes to the stabilisation of this configuration. The acetal terminus of the pendant is directed away from the ligand cavity and makes no short intermolecular contact. Antiferromagnetic exchange in $[\text{Cu}_2(\mathbf{285})(\text{OH})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}]$ is very similar to that in $[\text{Cu}_2(\mathbf{286})(\text{OH})(\text{BPh}_4)_2(\text{CF}_3\text{SO}_3) \cdot \text{H}_2\text{O} \cdot 0.5\text{C}_2\text{H}_5\text{OH}]$.

The ready hydrolysis of dicopper(II) complexes of **96** emphasises the unsuitability of this relatively strained hexaimine host for Lewis-acid guests such as copper(II), and draws attention to the possibility of replacing **96** by the octaamine derivative **173** where all six imino functions are hydrogenated. This ligand, easily prepared by borohydride reduction of **95**, readily coordinates copper in both oxidation states. Under inert atmosphere conditions, the colourless dicopper(I) complex $[\text{Cu}_2(\mathbf{173})(\text{ClO}_4)_2]$ is obtained, which rapidly acquires a green colour in solution or more slowly in the solid state on exposure to the atmosphere. Treatment of **173** with copper(II) salts under mildly basic conditions generates pale blue crystals of the μ -hydroxo dicopper(II) complex $[\text{Cu}_2(\mathbf{173})(\text{OH})(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}]$.

Magnetic susceptibility measurements on $[\text{Cu}_2(\mathbf{173})(\text{OH})(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}]$ confirm the lack of strong antiferromagnetic interaction ($-2J$ @ 46 cm^{-1}), suggesting that the $[\text{Cu}_2(\text{OH})]^{3+}$ assembly held within **173** is not linear. The dimethylformamide glass EPR spectrum confirms the presence of a weakish interaction.

Electronic and EPR spectra together with the magnetic behaviour suggest the azide ligand in $[\text{Cu}_2(\mathbf{173})(\text{N}_3)](\text{CF}_3\text{SO}_3)_3$ is linearly coordinated between copper(II) ions, encapsulated within the azacryptate ligand. In addition, magnetic susceptibility measurements show the presence of a ferromagnetic interaction ($2J \approx 25\text{ cm}^{-1}$).

The imidazolate-bridged complex $[\text{Cu}_2(\mathbf{173})(\text{Im})](\text{ClO}_4)_3$, on the other hand, shows a moderately strong antiferromagnetic interaction: a $-2J$ value of 88 and 111 cm^{-1} was found. The electronic spectrum shows a

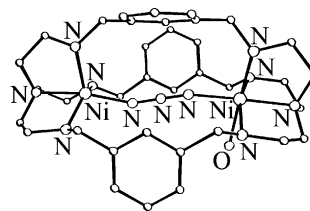


Fig. 219. Structure of $[\text{Ni}_2(\mathbf{173})(\text{N}_3)(\text{H}_2\text{O})]^{3+}$ (adapted from Ref. [391]).

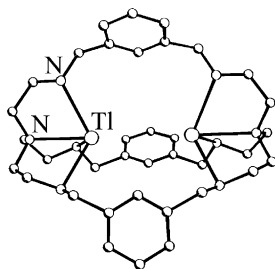
single d–d transition band at 710 nm suggesting a coordination geometry intermediate between square pyramidal and trigonal bipyramidal as confirmed by the structure of $[\text{Cu}_2(\mathbf{173})(\mu\text{-Im})](\text{ClO}_4)_3$ [227,386].

$[\text{Ni}_2(\mathbf{173})(\text{N}_3)(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$, $[\text{Ni}_2(\mathbf{173})(\text{N}_3)](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$, $[\text{Co}_2(\mathbf{173})(\text{N}_3)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ and $[\text{Mn}_2(\mathbf{181})(\text{N}_3)](\text{CF}_3\text{SO}_3)_3$ have been prepared by reaction of the macrobicyclic polyaza derivatives with the appropriate metal salt in the presence of NaN_3 in ethanol or ethanol/acetonitrile [391].

In $[\text{Ni}_2(\mathbf{173})(\text{N}_3)(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_3 \cdot 2\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ a 1,3-azido bridge links the two nickel(II) ions which are 6.270 Å apart (Fig. 219); the nickel ions are each coordinated to the bridgehead nitrogen atom, three amine donors and the azide. One nickel ion has an additional coordinated water and is, therefore, six coordinated. Its geometry is quite irregular with the metal ion displaced out of the tren cap towards the center of the cryptand. The other nickel ion is five coordinated, displaced from the cap and has a geometry intermediate between square pyramidal and trigonal bipyramidal.

$[\text{Ni}_2(\mathbf{173})(\text{N}_3)(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$ and $[\text{Ni}_2(\mathbf{173})(\text{N}_3)](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ show a ferromagnetic coupling between the two nickel(II) ions with a small interdimer antiferromagnetic interaction (respectively $2J = 11.82\text{ cm}^{-1}$ and $2J' = -0.75\text{ cm}^{-1}$ and $2J = 7.72\text{ cm}^{-1}$ and $2J' = -0.95\text{ cm}^{-1}$). The cobalt(II) and the manganese(II) complexes, on the contrary, present an overall antiferromagnetic coupling between the two metal ions ($-2J = 4.1$ and 12.1 cm^{-1} , respectively) [391].

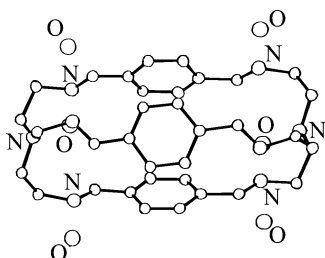
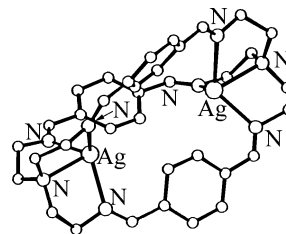
Potentiometric titration experiments on aqueous solutions containing **173** and Ni^{2+} in a 1:2 molar ratio indicate the existence of the monometallic $[\text{Ni}(\text{H}_2\text{-173})]^{4+}$ and the dimetallic species $[\text{Ni}_2(\mathbf{173})]^{4+}$ and $[\text{Ni}_2(\mathbf{173})(\text{OH})]^{3+}$ [392]. At pH values >9.5 only dimetallic species exist in solution, clearly proposing the $\mathbf{173}/2\text{Ni}^{2+}$ system as a receptor for bidentate anions. A spectrophotometric titration at this pH with NaN_3 (0.1 M HClO_4/N -methylpiperazine buffer) indicates the uptake of one azide ion per molecule of ligand. Moreover, after 24 h green crystals of $[\text{Ni}_2(\mathbf{173})(\text{N}_3)_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ precipitated. IR spectra on the solid show two distinct azide bands, centered at 2021 and 2186 cm^{-1} , due respectively to N_3^- anion and an almost linear $\text{Ni}^{\text{II}}\text{N}^-\text{N}^-\text{Ni}^{\text{II}}$ disposition as confirmed by the X-ray structure which parallels that found for $[\text{Ni}_2(\mathbf{173})(\text{N}_3)_2](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ [392]; one pseudo-octahedral nickel(II) ion and the other nickel(II) ion in a distorted

Fig. 220. Structure of $[Tl_2(173)]^{2+}$ (adapted from Ref. [393]).

trigonal bipyramidal environment inside **173** are linked together by a bridging azide. The second azide anion present in the crystal is non-coordinating, acting as a mere counter ion [392].

NMR studies in the solid state and in solution on the thallium(I) complex $[Tl_2(173)](CF_3SO_3)_2$, synthesized by reaction of the preformed ligand with $Tl(CH_3COO)$ in the presence of $Li(CF_3SO_3)$ [393], suggest a simple and symmetric structure where each thallium(I) cation occupies the site defined by the N_4 cap. The structure of the complex, obtained using synchrotron radiation, shows the thallium ion is coordinated to the bridgehead nitrogen and to three secondary amine groups; it is displaced from the plane of the secondary amines by 1.087 Å towards the center of the cavity and the $Tl \cdots Tl$ distance is 4.375 Å (Fig. 220). The ligand host is fully extended to accommodate the pair of large spherical cations, and there is no helicity of cryptand strands. The structure is thus of unusually high symmetry for a cryptate. **173** enforces approach of encapsulated thallium(I) ions to just within 4.4 Å; despite this relatively large separation, strong $Tl \cdots Tl$ interaction is observed and the aromatic proton of the bridging link exhibits a large through-space coupling to the pair of equivalent thallium(I) nuclei [393].

The [2+3] condensation in methanol/acetonitrile of tris(2-aminoethyl)amine with terephthalaldehyde at room temperature forms the bicyclic hexaimino Schiff base **180**·6H₂O [388] which shows a divergent confirmation in which all six imine nitrogen atoms form hydrogen bonds to the water molecules positioned outside the macrocycle [387] (Fig. 221). In addition, each water molecule is hydrogen-bonded to two of the others and therefore links macrobicycles.

Fig. 221. Structure of **180**·6H₂O (adapted from Ref. [387]).Fig. 222. Structure of $[Ag_2(180)]^{2+}$ (adapted from Ref. [387]).

The conformation of the macrocycle is strikingly different from that found in $[Ag_2(180)]^{2+}$ where the two silver ions are encapsulated within the macrocycle and each bonded to four nitrogen atoms [387]. In $[Ag_2(180)](CF_3SO_3)_2$, obtained by template condensation of the precursors in the presence of $AgNO_3$ and $Li(CF_3SO_3)$, the lone pairs on the imine nitrogen atoms were necessarily pointing towards the metal ions. The cryptand adopts a convergent form. The trigonal disposition of aromatic rings in this conformation allows for good access to the coordination site, while steric protection is only moderate. In the cation $[Ag_2(180)]^{2+}$ two silver ions are encapsulated at a distance of 6.06 Å apart and are bonded to a bridgehead nitrogen atom and to the three methylene nitrogen atoms (Fig. 222).

Despite the easy formation of disilver(I) complexes, **180** shows considerable reluctance to accommodate transition metal ion guests except in the presence of further ligands. Dicopper(I) complexes are, however, readily obtained on treatment of **180** with either copper(I) or copper(II) salts. The structure of $[Cu_2(180)](CF_3SO_3)_2 \cdot C_2H_5OH$, obtained by slow evaporation of the green solution derived by mixing **180** with $Cu(CF_3SO_3)_2$ in ethanol, is identical with that of $[Ag_2(180)](CF_3SO_3)_2$ so the copper(I) coordination site can be inferred to be the distorted tetrahedron revealed for the silver(I) ion. Evidently, the coordination preferences of copper(I) ions rather than copper(II) ions are satisfied by the sites presented in the convergent form of **180**.

180, treated with copper(II), nickel(II) or cobalt(II) ions in the presence of thiocyanate ions, forms $[M_2(180)(NCS)_4] \cdot nH_2O$. In these complexes the donor set of each metal ions contains no more than two of the possible four cryptand donor atoms in addition to the pair of nitrogen terminal thiocyanate. No magnetic interaction is operating between the paramagnetic centers in these complexes. $[Ni_2(180)-(NCS)_2](ClO_4)_2$ contains five or six coordinated metal ions, not interacting each other. Also in this complex terminal nitrogen bonded thiocyanate groups are present [387].

The condensation in acetonitrile of 1,4-naphthalenedicarbaldehyde and tris(2-aminoethyl)amine in a 3:2 molar ratio give rise to **341**. The same reaction, carried out in the presence of silver(I) or copper(I) ions, affords the related dinuclear complexes [388].

In the free ligand the molecule has a pseudo C_3 axis lying through the bridgehead nitrogen atoms. Each diimino

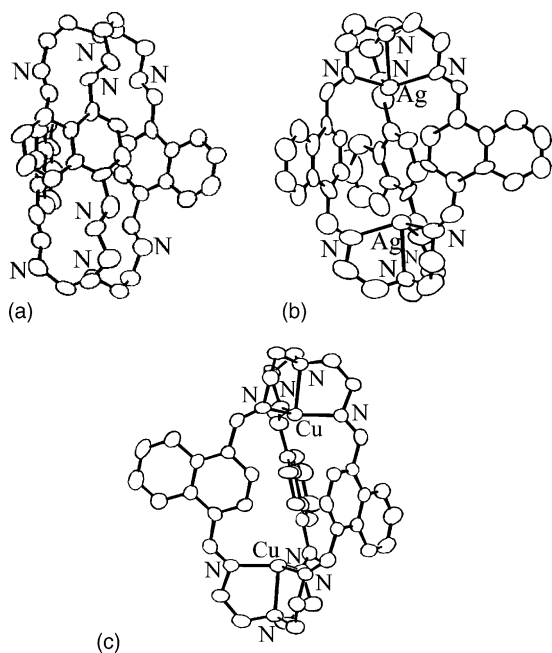


Fig. 223. Structure of **341** (a), $[\text{Ag}_2(\mathbf{341})]^{2+}$ (b) and $[\text{Cu}_2(\mathbf{341})]^{2+}$ (c) (adapted from Ref. [388]).

naphthylene group is parallel to the pseudo C_3 axis, and has an unsymmetric *anti* structure. One water molecule and one acetonitrile molecule are involved in the unit cell. No interactions have been found between the solvent molecules and the ligand. One of the naphthalene planes is parallel to a naphthalene plane of the neighbouring molecule, and a quarter part of the fused ring is overlapped, with a distance between the rings of 3.54 Å (Fig. 223a).

In $[\text{Ag}_2(\mathbf{341})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 5\text{CH}_3\text{OH}]$ (Fig. 223b) each bis(iminomethyl)naphthalene has a symmetric *syn* structure. The two silver(I) ions are encapsulated into two $\text{N}(\text{CH}_2\text{CH}_2\text{N})_3$ moieties of the ligand, and show a distorted trigonal pyramidal geometry. The silver(I) cryptate has a pseudo C_3 -axis which runs through the two bridgehead nitrogen atoms whose distance (10.85 Å) is not different from that of the free ligand (10.80 Å).

In $[\text{Cu}_2(\mathbf{341})(\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}]$ (Fig. 223c) the coordination geometries around the copper(I) ions are similar to those in the silver(I) cryptate. However, the extent of distortion from an ideal trigonal pyramidal is relatively small in the copper(I) complex. The most remarkable structural difference between the copper(I) and silver(I) cryptates is found in the orientation of the naphthalene rings. Since one of the naphthalene rings has been found to be bent to a high degree, C_3 symmetry is completely lost in the copper(I) cryptate. A similar structure was found in $[\text{Cu}_2(\mathbf{341})(\text{I}_6)_2 \cdot \text{H}_2\text{O}]$. NMR spectra of the silver(I) and copper(I) cryptates indicate a D_3 symmetry and a fluxional behaviour of the ligand in each complexes.

The mixed valence silver(I)–silver(III) diperchlorate cryptate $[\text{Ag}_2(\mathbf{180a})(\text{O})(\text{ClO}_4)_2]$ was proposed to originate from the template reaction of the precursors in the presence

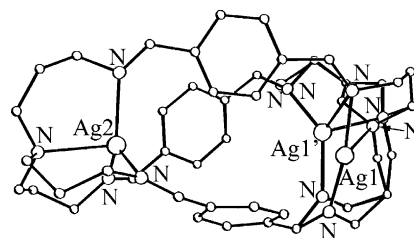


Fig. 224. Structure of $[\text{Ag}_2(\mathbf{180a})]^{2+}$ (the two site occupancy of one silver(I) ion, respectively Ag(1) and Ag(1'), is evidenced) (adapted from Ref. [389]).

of oxygen [389]. From the crystal structure of the complex cation a different coordination environments of the two silver ions was suggested. One silver ion coordinates to one bridgehead nitrogen and three imino nitrogens has a distorted tetrahedral environment while the other silver ion coordinates to two imino nitrogens but also bonds to one oxygen ions, in a trigonal-planar fashion [389]. A subsequent X-ray investigation at 123 K showed the compound is the disordered dinuclear silver(I) complex $[\text{Ag}_2(\mathbf{180a})(\text{ClO}_4)_2]$ [389]. There are two components having approximately 78 and 22% occupancy. The fully ordered silver ion has approximately trigonal pyramidal coordination geometry. It is bonded to three imine nitrogen atoms in the trigonal plane. The major occupancy site of the second silver ion lies at the edge of the cryptand cavity and shows rather irregular atoms geometry. It is coordinated to two imine nitrogens, the bridgehead amine, and, via a rather long interaction, to one oxygen atom of a perchlorate counterion (Fig. 224).

The octaamino ligand **181**, prepared by tetrahydroborate reduction of disilver or dilead complexes of the corresponding Schiff base cryptand **180**, or in somewhat lower overall yield by direct reduction of the free ligand **180**, when treated with 2 equiv. of $\text{M}(\text{CF}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{2+}$, Fe^{2+}) in the absence of exogenous coordinating ions, forms only the tetraprotonated salt $[\text{H}_4(\mathbf{181})](\text{CF}_3\text{SO}_3)_4$. The structure (Fig. 225) indicates four intermolecular hydrogen bonds between NH groups on the cation and oxygen atoms of the triflates. In addition, there are two intramolecular hydro-

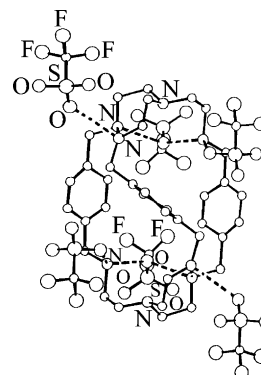


Fig. 225. Structure of $[\text{H}_4\text{-}\mathbf{181}][\text{CF}_3\text{SO}_3]_4$ (adapted from Ref. [390]).

gen bonds in the cation between two aminic nitrogen atoms [390].

With $M = \text{Co}^{2+}$, Ni^{2+} or Cu^{2+} , dinuclear complexes were obtained. The cobalt(II) complexes took the form of $\mu\text{-OH}$ dimers with both ClO_4^- and CF_3SO_3^- counter ions. However, with the copper(II) complexes the nature of the cryptate depends on the counter ion: the $\mu\text{-OH}$ triperchlorate $[\text{Cu}_2(\mathbf{181})(\mu\text{-OH})](\text{ClO}_4)_3$ and the unbridged tetratri-flate $[\text{Cu}_2(\mathbf{181})](\text{CF}_3\text{SO}_3)_4$ have been obtained. This is in contrast to the situation with the related Schiff base **180**, where only the dicopper(I) cryptate was obtained in the absence of coordination anion. With nickel(II) nitrate $[\text{Ni}_2(\mathbf{181})](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ is obtained, with some indication in the infrared spectrum of counter ion coordination [390].

For $[\text{Co}_2(\mathbf{181})(\text{OH})](\text{CF}_3\text{SO}_3)_3$ and $[\text{Co}_2(\mathbf{181})(\text{OH})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ a five coordination was suggested, presumably achieved via coordination of the three secondary amino nitrogen-donors, $\mu\text{-OH}$ and a counter ion or H_2O molecule. A weak interaction between the two cobalt(II) ions was observed. $[\text{Cu}_2(\mathbf{181})(\text{OH})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ shows a medium-weak antiferromagnetic interaction ($-2J = 80 \text{ cm}^{-1}$) while magnetic susceptibility measurements on $[\text{Ni}_2(\mathbf{181})](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ show little temperature variation over the range 200–80 K, as expected for an isolated nickel(II) ion. The electronic spectrum suggests O_h coordination for the nickel(II) ion, which appears to require bridgehead nitrogen or counter ion coordination [390].

Using pyrazole no pyrazolate-bridged complexes have been formed, instead $\mu\text{-OH}$ species were found. On the contrary imidazolate was accepted as bridging ligand by both dicobalt(II) and dicopper(II) complexes. The similarity of the electronic spectra of $[\text{Co}_2(\mathbf{181})(\mu\text{-Im})](\text{CF}_3\text{SO}_3)_3$, $[\text{Co}_2(\mathbf{181})(\text{OH})](\text{CF}_3\text{SO}_3)_3$ and $[\text{Co}_2(\mathbf{181})(\text{OH})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ suggest that a five coordinated geometry exists also for the larger bridge.

Magnetic susceptibility measurements do not indicate greater interaction via $\mu\text{-imidazolate}$ than $\mu\text{-OH}$, in either the dicobalt or the dicopper ($-2J = 65 \text{ cm}^{-1}$) case.

In $[\text{M}_2(\mathbf{181})(\text{N}_3)](\text{X})_3$ ($M = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Cu^{2+} ; $\text{X} = \text{CF}_3\text{SO}_3^-$, ClO_4^-) where azide ion acts as an exogenous bridge between transition metal ions encapsulated within the ligand, it was suggested that the azide ion might be sterically constrained between the cations in perhaps near-linear $\text{M}-\text{NNN}-\text{M}$ geometry. For the dicopper(II) $\mu\text{-azido}$ complexes the combination of a large zero-field splitting in the EPR spectrum and a near Curie-law dependence of magnetic susceptibility on temperature seems to suggest a triplet ground state [390].

Also the proton-ionizable azacryptand ($\text{H}_3\text{-342}$), deriving from [2+3] condensation of 3,5-diformyl pyrazoledicarbaldehyde with tren, generates both di- and tetracopper(II) cryptates on treatment with the appropriate stoichiometric amount of copper(II) salt [394].

The macrobicyclic tris-bipyridine Schiff base **343**, obtained under mild conditions and high yield by one-pot

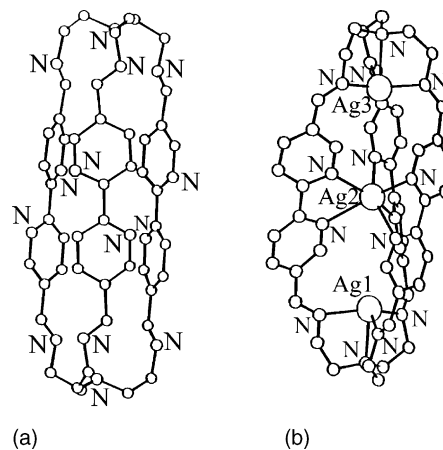
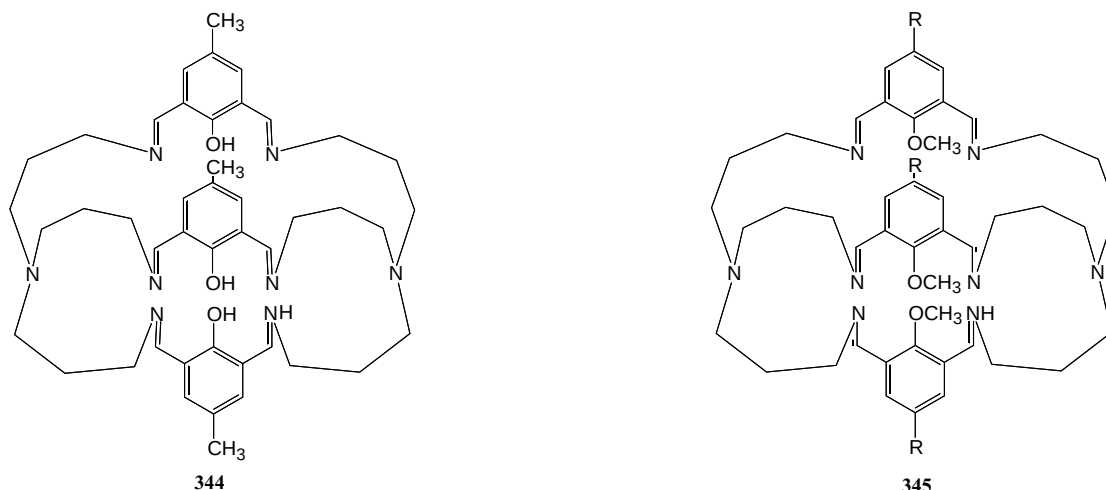


Fig. 226. Structure of **343** (a) and $[\text{Ag}_3(\mathbf{343})]^{3+}$ (b) (adapted from Ref. [395]).

condensation of tris(2-aminoethyl)amine with 5,5'-diformyl-2,2'-bipyridine [395] was subsequently reduced with Pd/H_2 to the related macrobicyclic polyamine. The dinuclear copper(I) $[\text{Cu}_2(\mathbf{343})]^{2+}$ and trinuclear silver(I) complexes $[\text{Ag}_3(\mathbf{343})]^{3+}$ were prepared from **343** and two- or three-fold molar amounts of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{BF}_4)$ or AgBF_4 , respectively. The ^1H NMR spectra of these complexes were markedly different from those of the free ligand **343**, all signals being shifted downfield.

343 and $[\text{Ag}_3(\mathbf{343})]^{3+}$ (Fig. 226a and b) show that the distances between the bridgehead nitrogen atoms are about the same in the two cases. The C_3 symmetry of the free ligand changes to nearly D_3 symmetry in the complex. Whereas in the free ligand the bipyridine subunits show the most favored *anti* conformation, which minimizes lone-pair repulsion, all nitrogen atoms are turned inside in the trinuclear compound for complexing the central silver(I) ion in an almost octahedral way. The coordination sphere around the central silver(I) ion can be regarded as a distorted octahedron, that around each of the two other silver(I) ions has a heavily distorted trigonal pyramid.

$[\text{Cd}_2(\mathbf{344})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot 0.5\text{CH}_3\text{OH}$, synthesized by [2+2] Schiff base condensation of tris(3-aminopropyl)amine with sodium 2,6-diformyl-4-methylphenolate in the presence of cadmium(II) perchlorate and in a 2:3:2 molar ratio, is stable and does not suffer hydrolysis [396]. In the complex cation $[\text{Cd}_2(\mathbf{344})]^{2+}$ each cadmium(II) ion is enclosed within the polyazamacrocycle and coordinated by amino nitrogen of the side chain and imino nitrogens of the tertiary amine. Each of two oxygen atoms of the phenoxy groups bridges the two cadmium ions. The complex has crystallographic C_2 symmetry. Each cadmium(II) ion lies in a N_4O_2 coordination environment and possesses a distorted octahedral geometry. The amino nitrogen and imino nitrogens occupy the equatorial positions, one phenoxy oxygen deviates downwards to the equatorial plane, the tertiary nitrogen and another phenyl oxygen occupy the approximately axial positions. The $\text{Cd} \cdots \text{Cd}$ distance is $3.17 \text{ \AA}$ [396] (Fig. 227a).



The silver(I) complexes $[\text{Ag}_2(\mathbf{345})](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0-4$), synthesized by template condensation in ethanol of tris-(3-aminopropyl)amine with 5-R-2-methoxy-1,3-phenylenedialdehyde ($\text{R} = \text{CH}_3\text{O}$, CH_3 , Br), possess similar spectroscopic features [397]. The complex where $\text{R} = \text{CH}_3\text{O}$ presents a basket structure for the cation $[\text{Ag}_2(\mathbf{345})]^{2+}$ in which both silver(I) centers possess three coordinated environments. Each silver ion locates at the top of a trigonal pyramid distorted from a planar triangle composed of one bridgehead tertiary nitrogen and two imino nitrogens. Only two bridging chains of the cryptand coordinate to the metals, another does not. The internuclear $\text{Ag} \cdots \text{Ag}$ distance is 7.468 Å (Fig. 227b).

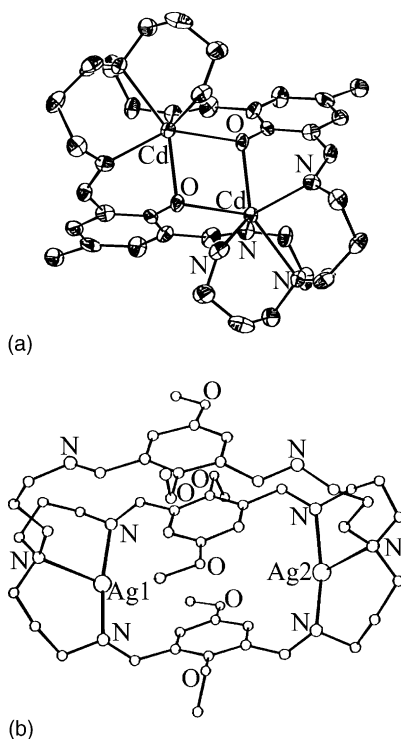


Fig. 227. Structure of $[\text{Cd}_2(\mathbf{344})]^{2+}$ (a) and $[\text{Ag}_2(\mathbf{345})]^{2+}$ ($\text{R} = \text{CH}_3\text{O}$) (b) (adapted from Refs. [396,397]).

$[\text{Ln}(\text{H}_3\text{-}\mathbf{98a})(\text{NO}_3)](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}^{3+}$, Eu^{3+} , Gd^{3+} , Dy^{3+} , Yb^{3+}) and $[\text{Ln}_2(\mathbf{98a})(\text{NO}_3)_2](\text{NO}_3) \cdot n\text{H}_2\text{O} \cdot n\text{C}_2\text{H}_5\text{OH}$ ($\text{Ln} = \text{Tb}^{3+}$, Dy^{3+} , Yb^{3+} , Lu^{3+}) have been prepared by reaction of tris(2-aminoethyl)amine 2,6-diformyl-4-methylphenol and the appropriate lanthanide(III) nitrate respectively in a 2:3:1 and 2:3:2 molar ratio and in the absence or presence of 3 equiv. of $\text{N}(\text{Et})_3$ [398].

In $[\text{Dy}(\text{H}_3\text{-}\mathbf{98a})(\text{NO}_3)](\text{NO}_3)_2 \cdot 2\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ (Fig. 228a) the cation $[\text{Dy}(\text{H}_3\text{-}\mathbf{98a})(\text{NO}_3)]^{2+}$ contains a DyN_4O_5 core with the metal ion asymmetrically placed at one end of the cavity of the macrobicyclic receptor and bound to seven of the eleven heteroatoms of the ligand, three imino nitrogen atoms, one of the bridgehead nitrogen atoms and the three phenolic oxygen atom, as well as to a bidentate nitrate group. A proton transfer from the coordinated phenoxy oxygen atoms to the imine nitrogen atoms has occurred. The coordination polyhedron has been described as a slightly distorted monocapped dodecahedron with the oxygen of the coordinated nitrate group capping the dodecahedron. The macrobicycle $\text{H}_3\text{-}\mathbf{98a}$ is twisted around the axis that passes through both bridgehead nitrogen atoms, forming a triple helical arrangement, and it adopts an sss *endo-endo* conformation, with the nitrogen atoms of the imine bonds being on the same side of the aromatic ring in the three chains and the bridgehead nitrogen lone pairs directed towards the central cavity [398].

In $[\text{Dy}_2(\mathbf{98a})(\text{NO}_3)_2](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (Fig. 228b) both dysprosium(III) ions are positioned in the cavity of the anionic Schiff base macrobicyclic receptor $[\mathbf{98a}]^{3-}$ and have crystallographically identical coordination environments; each is nine coordinated, being bound to one bridgehead nitrogen atom, three azomethine nitrogen atoms, two oxygen atoms of a bidentate nitrate group and to the three μ -phenolate oxygen atoms. The presence of the phenolate groups allows the ions to be situated in close proximity. The coordination polyhedron around each metal ion has been described as a monocapped distorted dodecahedron. The anionic macrobicyclic receptor $[\mathbf{98a}]^{3-}$ also adopts the sss *endo-endo* conformation, which in this case is necessary

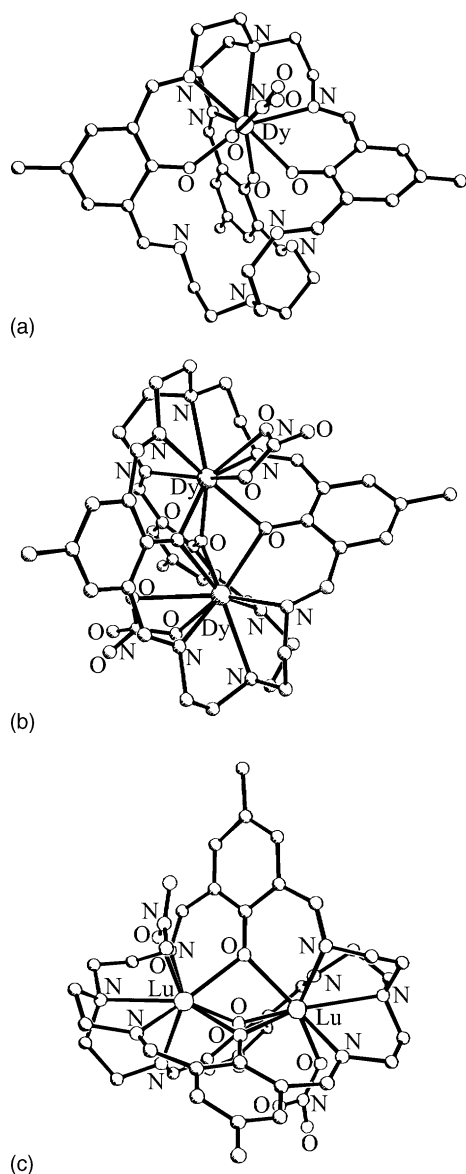


Fig. 228. Structure of $[\text{Dy}(\text{H}_3\text{-98a})(\text{NO}_3)_2]^{2+}$ (a), $[\text{Dy}_2(\text{98a})(\text{NO}_3)_2]^+$ (b) and $[\text{Lu}_2(\text{98a})(\text{NO}_3)_2]^+$ (c) (adapted from Ref. [398]).

for the complexation of both metal ions into its cavity, and again is twisted. The macrobicyclic cavity is clearly more elliptical in this bimetallic cryptate than it is in the mononuclear complex [398].

The structural analysis of the dinuclear lutetium cryptate confirmed the presence of two metal ions in the cavity of the anionic Schiff base macrobicyclic receptor $[\text{98a}]^{3-}$. Each lutetium(III) ion is bound to one bridgehead nitrogen atom, three imino nitrogen atoms, and to the three μ -phenolate oxygen atoms. Eight coordination is completed by one oxygen of a monodentate nitrate ion and the coordination polyhedron has been described as distorted dodecahedron. The distances between lutetium ions is 3.447 Å [398]. The cryptand adopts a conformation resembling a triple helix twisting around a pseudo C_3 -axis which runs through the two

bridgehead nitrogen atoms. Both metal ions deviate from this axis; nevertheless, the deviation is so slight that the symmetry of the cryptate can also be described as three-fold. The distance between the bridgehead nitrogens is 8.65 Å (Fig. 228c). The dinuclear structure is retained in solution as indicated by the proton NMR spectrum in $(\text{CD}_3)_2\text{SO}$.

High resolution laser-excited emission spectra of the mononuclear europium(III) cryptate point to the presence of a single site with low symmetry for the metal, while lifetime measurements in H_2O and D_2O solutions allowed us to estimate the number of bound water molecules, $q = 1$. Both mononuclear and dinuclear ytterbium(III) cryptates display strong emission upon excitation through the ligand electronic levels, the spectrum of the binuclear complex being consistent with the presence of two ytterbium(III) ions in different coordination environments. Proton NMR profiles for the mononuclear gadolinium(III) complex, measured in the temperature range 5–37 °C, show that the relaxivity is mainly limited by fast rotation; this compound is stable towards acid-catalysed decomposition in aqueous solution only at $\text{pH} > 5.5$ [398].

The two cadmium ions in $[\text{Cd}_2(\text{98a})](\text{ClO}_4)_2$, obtained by reaction of $[\text{Na}(\text{H}_3\text{-98a})](\text{BPh}_4)$, with $\text{Cd}(\text{CH}_3\text{COO})_2$ in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ and in the presence of NaClO_4 and AgClO_4 to eliminate BPh_4^- , can be considered to be six or seven coordinated. In addition to the bonds to three imine nitrogen atoms and to three oxygen atoms there is a weak interaction to the bridgehead amine nitrogen (Fig. 229).

The more flexible octaamino cryptate, derived by the reduction of $\text{H}_3\text{-98a}$, forms a structurally characterized dizinc(II) complex (Fig. 230).

The reaction in $\text{CH}_3\text{OH}/\text{CHCl}_3$ of $\text{H}_4\text{-346}$, synthesized by the condensation of 5-chlorosalicylaldehyde and 1,4,8,11-tetrakis-(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane, with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ forms $[\text{Mn}_2(\text{346})(\text{CH}_3\text{COO})_2] \cdot 2\text{CCl}_3$ [399]. The complex has the crystallographic inversion center at the center of the cyclam ring moiety of the ligand. The amine nitrogens of the cyclam ring moiety do not take part in any coordination of the manganese ion. The ligand coordinates to each manganese(III) ion with two imine

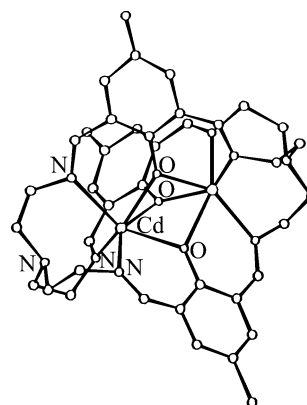


Fig. 229. Structure of $[\text{Cd}_2(\text{98a})]^+$ (adapted from Ref. [398]).

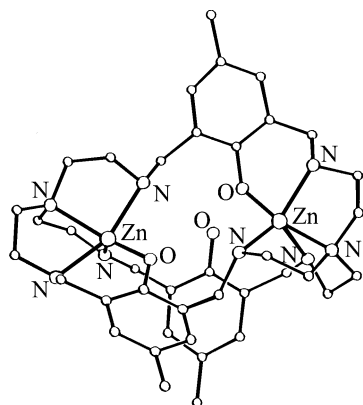


Fig. 230. Structure of the dizinc(II) complex with the octaminophenolate cryptand derived from the reduction of $H_3\text{-98a}$ (adapted from Ref. [372]).

nitrogen atoms and two phenol oxygen atoms of the two pendant groups in a *cis*- β fashion and the acetate ion acts as a bidentate ligand forming a distorted octahedron. An unique aspect of this dinuclear complex is an axial compression of the manganese(III) octahedra [399] (Fig. 231). Electronic and magnetic data indicate little antiferromagnetic coupling between the metal ions [399].

8.1.4. Complexes with compartmental ligands containing 3,6-diformyl-pyridazine as head units

As reported above in a previous section, the [2+2] or [4+4] Schiff-base macrocycles **12a** and **12b** are readily formed from the 3,6-diformylpyridazine and 1,3-diaminopropane using lead(II) ions as templates, the two different macrocycle sizes depending on the reaction conditions employed. Specifically, a 1:1:1 ratio of 3,6-diformylpyridazine:1,3-diaminopropane:lead(II) perchlorate resulted in the formation of the [2+2] macrocyclic complex $\text{Pb}_2(\text{12a})(\text{ClO}_4)_4$ whereas a 2:2:1 ratio gave the [4+4] macrocyclic complex $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$. In both cases the complexes were obtained in good yield and purity [400].

In the absence of added reagents no interconversion between $[\text{Pb}_2(\text{12a})](\text{ClO}_4)_4$ and $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$ is observed. However, when 3,6-diformylpyridazine and 1,3-diaminopropane are added to $[\text{Pb}_2(\text{12a})](\text{ClO}_4)_4$ ring expan-

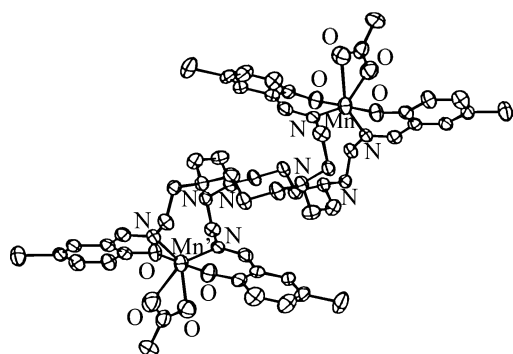


Fig. 231. Structure of $[\text{Mn}_2(\text{346})(\text{CH}_3\text{COO})_2]$ (adapted from Ref. [398]).

sion to the [4+4] complex $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$ is observed. Likewise, the reverse reaction, addition of lead(II) ions to $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$, leads to ring contraction and formation of $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$. Hence the product is simply determined by the reagent ratios employed, and is due to the effect these ratios have on the position of the product equilibrium $2[\text{Pb}_2(\text{12a})]^{4+} \leftrightarrow [\text{Pb}_2(\text{12b})]^{4+} + 2\text{Pb}^{2+}$. At high dialdehyde-diamine to lead(II) ratios the equilibrium favours $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$ where all the lead(II) ions can be wrapped up by the large macrocycle, whereas at low ratios $[\text{Pb}_2(\text{12a})](\text{ClO}_4)_4$ is favoured over a mixture of $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$ and solvated lead(II) ions [400].

No crystals of $[\text{Pb}_2(\text{12a})](\text{ClO}_4)_4$ have been obtained to date so the macrocycle conformation and the geometry about the lead ions is as yet unknown. However, $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$ crystallises well and the structure analysis reveals that it is a dilead(II) complex of the [4+4] macrocycle [400].

The transmetalation of $[\text{Pb}_2(\text{12b})](\text{ClO}_4)_4$ with 4 equiv. of manganese(II) perchlorate and an excess of NaSCN led to the formation of $[\text{Mn}_2(\text{12a})(\text{NCS})_4]$. The same product was also obtained by an analogous transmetalation of $[\text{Pb}_2(\text{12a})](\text{ClO}_4)_4$ [400].

The structure of $[\text{Mn}_2(\text{12a})(\text{NCS})_4]$ (Fig. 232a) reveals that on transmetalation the macrocycle ring had contracted from [4+4] to [2+2]. The resulting dimanganese(II) complex of **12a** binds a total of four thiocyanate ions in an unsymmetrical manner. All bind via the nitrogen atom only, three in a terminal fashion whilst the fourth bridges the two manganese(II) ions as predicted from the analysis of the

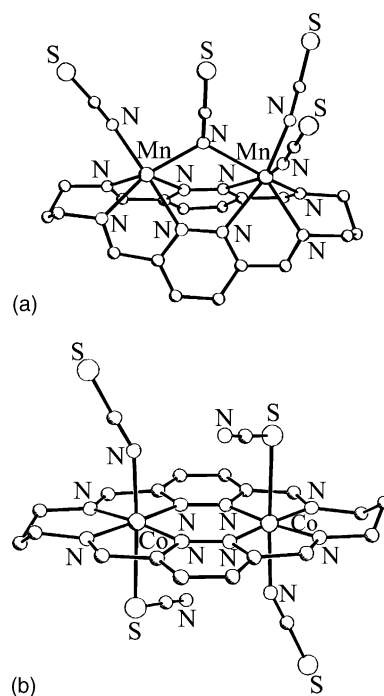


Fig. 232. Structure of $[\text{Mn}_2(\text{12a})(\text{NCS})_4]$ (a) and $[\text{Co}_2(\text{12a})(\text{NCS})_2(\text{SCN})_2]$ (b) (adapted from Ref. [400]).

infrared spectrum. One manganese is seven coordinated, binding three thiocyanate ions, whereas the other manganese is six coordinated with only two co-ordinated thiocyanate ions. Irregular geometries are observed for both atoms. The bridging thiocyanate is not equally shared but rather is bound more tightly to the six coordinate manganese atom. The polydentate [2+2] macrocycle is bent; each manganese atom occupies the apex of an approximate square pyramid formed by its four macrocycle donor atoms. This leaves a whole side of one manganese ion available to accommodate the three thiocyanate donor atoms [400].

The FAB mass spectrum of the green complex $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2](\text{ClO}_4)_2$, synthesized via transmetallation of $[\text{Pb}_2(\mathbf{12b})](\text{ClO}_4)_4$ with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile, shows a cluster of peaks consistent with the presence of $[\text{Cu}_2(\mathbf{12a})(\text{ClO}_4)_2]^+$, thus indicating that the original [4+4] Schiff base macrocycle had ring contracted to a [2+2] macrocycle. This ring contraction was confirmed by an X-ray structural determination of crystals grown by diethylether diffusion into an acetonitrile solution of $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2](\text{ClO}_4)_2$ [181,400]. The temperature dependence of the magnetic susceptibility of $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2](\text{ClO}_4)_2$ is typical of that expected for a strongly antiferromagnetically coupled complex ($J = -241 \text{ cm}^{-1}$).

Cyclic voltammetry, carried out on $[\text{Cu}_2(\mathbf{12a})(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2](\text{ClO}_4)_2$ in dry CH_3CN , reveals two well separated fully reversible one electron reduction waves ($E_{1/2} = 0.10 \text{ V}$ and $E_{1/2} = 0.43 \text{ V}$) associated with $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ to $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ to $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ reductions, respectively. The mixed valence species is reasonably stable ($K_{\text{com}} = 3.8 \times 10^5$).

The transmetallation of $[\text{Pb}_2(\mathbf{12b})](\text{ClO}_4)_4$ with cobalt(II) perchlorate in CH_3CN yields, after vapour diffusion of diethyl ether into the air stable solution, dark red crystals of $[\text{Co}_2(\mathbf{12a})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$. Again the FAB mass spectrum has a cluster of peaks consistent with the presence of $[\text{Co}_2(\mathbf{12a})(\text{ClO}_4)_3]^+$ thus indicating that the original [4+4] Schiff base macrocycle $\mathbf{12b}$ had ring contracted to the [2+2] macrocycle $\mathbf{12a}$. This ring contraction was confirmed by the X-ray structure of $[\text{Co}_2(\mathbf{12a})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ [400].

Moreover, cyclic voltammetry on $[\text{Co}_2(\mathbf{12a})](\text{ClO}_4)_4$ in dry CH_3CN reveals two one-electron reduction waves at remarkably high potentials ($E_{1/2} = -0.11$ and -0.33 V , versus $\text{Ag}/0.01 \text{ M AgNO}_3$) plus two one-electron oxidation waves at positive potentials ($E_{1/2} = +0.87$ and $+1.06 \text{ V}$, versus $\text{Ag}/0.01 \text{ M AgNO}_3$). The two reduction waves are tentatively assigned to $\text{Co}^{\text{II}}\text{Co}^{\text{II}}$ r $\text{Co}^{\text{II}}\text{Co}^{\text{I}}$ and $\text{Co}^{\text{II}}\text{Co}^{\text{I}}$ r $\text{Co}^{\text{I}}\text{Co}^{\text{I}}$ reductions and the two oxidation waves to be $\text{Co}^{\text{II}}\text{Co}^{\text{II}}$ r $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$ and $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$ r $\text{Co}^{\text{III}}\text{Co}^{\text{III}}$ oxidations [400]. The two reductions and the two oxidations all occur in separate one electron steps: in the case of the reductions they are separated by 220 mV ($K_{\text{com}} = 5.24 \times 10^3$) whereas the oxidations are separated by 190 mV ($K_{\text{com}} = 1.63 \times 10^3$). Hence the mixed-valent redox products are moderately stable. Spectroelectrochemical studies of the reduction processes indicate the existence of an intervalence charge

transfer band in the mixed-valent $\text{Co}^{\text{I}}\text{Co}^{\text{II}}$ complex, with the growth of a broad band centered at 965 nm as the first electron is added to $[\text{Co}_2(\mathbf{12a})(\text{MeCN})_4](\text{ClO}_4)_4$, followed by bleaching of this band as the second electron is added. In contrast, oxidation of $[\text{Co}_2(\mathbf{12a})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ does not result in a long wavelength absorption, so in this case the mixed-valent state appears to be valence localised [400].

The dicobalt(II) complex $[\text{Co}_2(\mathbf{12a})(\text{NCS})_2(\text{SCN})_2]$ is readily crystallized in quantitative yield by diffusion of an acetonitrile solution of $[\text{Co}_2(\mathbf{12a})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ into a solution of sodium thiocyanate. The structure, determined at 160 K, shows that the cobalt(II) ions have distorted octahedral geometries where the basal plane consists of two bridging pyridazine nitrogen donors and two imine nitrogen donors. The axial sites are occupied by two thiocyanate anions, one bound through the nitrogen atom and the other through the sulfur atom. Like $[\text{Co}_2(\mathbf{12a})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$, the macrocycle in $[\text{Co}_2(\mathbf{12a})(\text{NCS})_2(\text{SCN})_2]$ is very flat with only the central alkyl carbon atoms of the lateral groups displaced substantially from the macrocyclic plane. The pyridazine ring plane and the basal plane of the cobalt atoms are almost coplanar (Fig. 232b). An antiferromagnetic interaction between the two metal ions occurs ($2J = -11.7 \text{ cm}^{-1}$) [400].

$\mathbf{12d}$, readily made by reaction in alcoholic solution of 3,6-diformylpyridazine with tris(2-aminoethyl)amine, shows (Fig. 233a) a divergent conformation which permits stabilising face-to-face π - π stacking intercryptand interactions involving two of the three aromatic rings. There is no evidence of intracryptand π - π interactions. In comparison with the *p*-phenylene analogue where the imino groups in each strand are mutually *trans*, a conformation which allows the ligand to form hydrogen bonds to six water molecules, $\mathbf{12d}$ is solvent free and adopts a conformation where the imino functions are mutually *cis*, but *trans* to the pyridazine ring CN groups. Despite this the N...N bridgehead distances in the two cryptands are remarkably similar at 10.49 Å [74]. The ^1H NMR spectrum of $\mathbf{12d}$ in CD_2Cl_2 illustrates mobility of conformation at ambient temperature [74].

$\mathbf{12d}$ is able to encapsulate two silver(I) ions, when reacted with AgX ($\text{X} = \text{ClO}_4^-$, CF_3SO_3^-) giving rise to $[\text{Ag}_2(\mathbf{12})](\text{X})_2$. The same complexes have been obtained by template procedure [74]. The convergent conformation adopted in $[\text{Ag}_2(\mathbf{12})](\text{ClO}_4)_2$ (Fig. 233b) leaves the imino groups in each strand *cis* to each other and to the pyridazine-nitrogen atoms. This generates an unusual six coordination for the silver(I) ion. The N...N bridgehead distance (10.50 Å) is identical within experimental error to that in the uncoordinated cryptand $\mathbf{12d}$. The ^1H NMR spectrum of $[\text{Ag}_2(\mathbf{12d})](\text{ClO}_4)_2$ demonstrates mobility of conformation down to ca. -50°C [74].

When $\mathbf{12d}$ is reacted with $\text{Co}(\text{BF}_4)_2$ in methanol $[\text{Co}(\mathbf{12d})](\text{BF}_4)_2$ is obtained [74]. In the cation the mutually *trans* disposition of the imino functions in the unsymmetrical mononuclear cryptate $[\text{Co}(\mathbf{12d})]^{2+}$ enables efficient coordination of the cobalt(II) ions in a six coordinated geometry

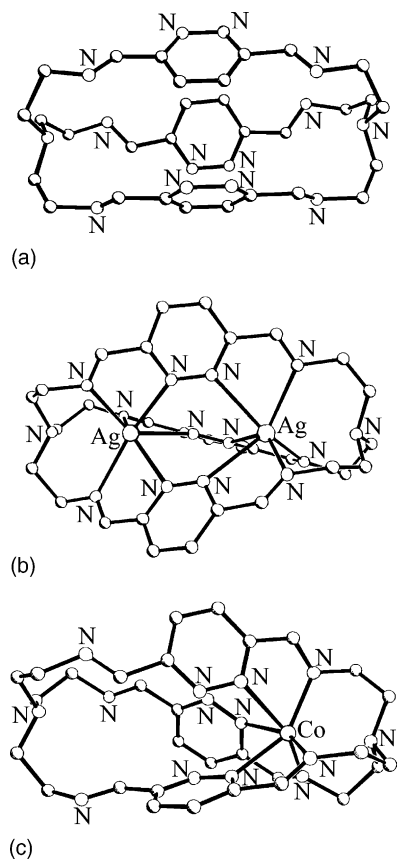


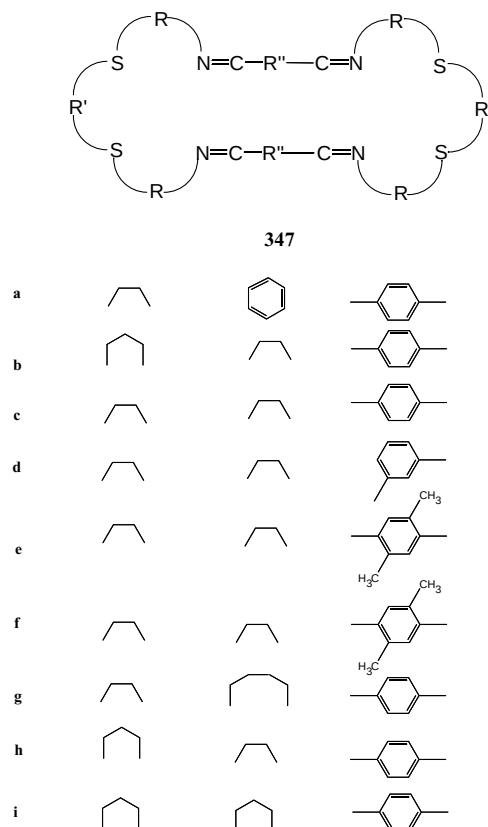
Fig. 233. Structure of **12d** (a), $[\text{Ag}_2(\mathbf{12d})]^{2+}$ (b) and $[\text{Co}(\mathbf{12d})]^{2+}$ (c) (adapted from Ref. [74]).

intermediate between O_h and D_{3h} . The *cis*, *trans* geometry adopted by the three strands of the host in this monocobalt cryptate can presumably be altered to the energetically similar all-*cis* geometry required for dicoordination upon addition of a second less stereochemically demanding and/or perhaps less charged cation. This mononuclear cryptate may thus represent a useful synthon for the generation of heterobinuclear cryptates [74]. Electrochemical studies established that the **12d** effectively stabilised the cobalt(II) ion [74] (Fig. 233c).

8.1.5. Complexes derived from macrocycles containing different functionalities

The addition of stoichiometric amounts of terephthalaldehyde to acetonitrile solutions of 3,7-dithia-1,9-diaminononane or 1,2-bis(1-aminothiophenyl)ethane affords respectively the [2+2] macrocycles **347a** and **347b** which are high symmetrical according to ^1H and ^{13}C NMR spectra. They react with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1:1) to produce $[\text{Cu}_2(\mathbf{347a})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{347b})](\text{ClO}_4)_2$ [401]. The basic structural properties of these two dicopper(I) compounds are rather similar (Fig. 234a and b). The two N_2S_2 donor sets are both tetrahedrally coordinated to the copper(I) centers; the two bridging para-substituted phenyl rings are parallel, about 3.5 Å apart, indicative of a

stabilization by π -stacking; the dihedral angles between the bridging phenyl rings are about 80° , resulting in a double helical arrangement of the ligand backbone. $[\text{Cu}_2(\mathbf{347a})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{347b})](\text{ClO}_4)_2$ have Λ configurations (both compounds crystallize as racemates; there are two crystallographically independent molecules in the asymmetric unit of $[\text{Cu}_2(\mathbf{347a})](\text{ClO}_4)_2$). The distance between the two copper(I) centers is about 7.8 Å in both compounds [401].



NMR data show that the ligands do not have an helicate but an open structure while the complexes are chiral in solution and kinetically inert on the NMR time scale.

There are two possible effects contributing to the stabilization of the helical arrangement of the macrocyclic rings. Namely, the preference of copper(I) for tetrahedral coordination geometry and π stacking of the phenyl rings. The solution structures of the free ligand **347b** and the related dicopper(I) complex $[\text{Cu}_2(\mathbf{347b})](\text{ClO}_4)_2$, deduced from ^1H NMR spectroscopy, indicate that stabilization by π stacking alone is not sufficient to induce helicity [401].

Cyclic voltammetry studies in CH_3CN of $[\text{Cu}_2(\mathbf{347a})](\text{ClO}_4)_2$ indicate that, due to the $\text{Cu}\cdots\text{Cu}$ separation of about 7.8 Å, both copper(I) centers behave largely independently. The oxidation from Cu^{I} to Cu^{II} at a potential of $E_{1/2} = 1.34$ V (verses NHE) is independent of the scan rate (0.1–2 V s^{-1}). The E_p value of 55 mV indicates the presence of a reversible electron process. The stabilization of Cu^{I} by a tetrahedral arrangement of thioether and imine donors is indicated by the highly positive redox potential [401].

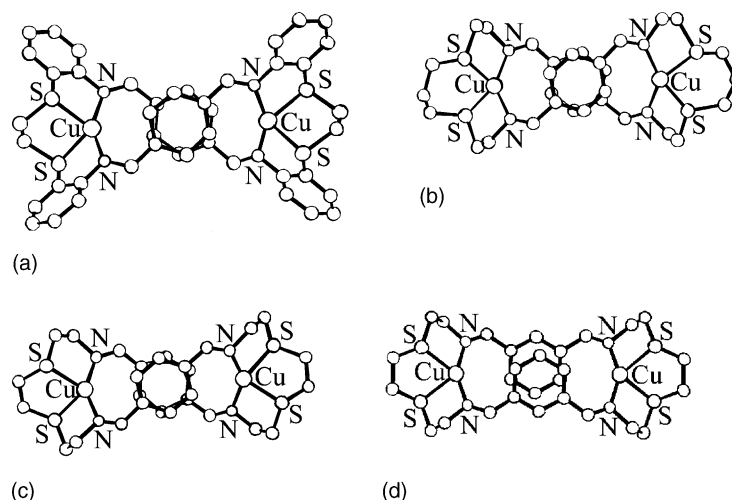


Fig. 234. Structure of $[\text{Cu}_2(\mathbf{347a})]^{2+}$ (a), $[\text{Cu}_2(\mathbf{347b})]^{2+}$ (b), $[\text{Cu}_2(\mathbf{347c})]^{2+}$ (c) and $[\text{Cu}_2(\mathbf{347d})]^{2+}$ (d) (adapted from Ref. [401]).

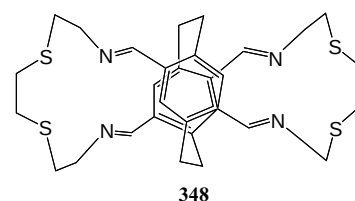
Analogously, the addition of stoichiometric amounts of *tere*- or *iso*-phthalaldehyde to solutions (CH_3CN or toluene, respectively) of 1,8-diamino-3,6-dithiaoctane yields the isomeric compounds **347c** and **347d**. Addition of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ to **347c** and **347d** in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1:1) produces the air-stable complexes $[\text{Cu}_2(\mathbf{347c})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{347d})](\text{ClO}_4)_2$ [401] which belong to two different structural types. While $[\text{Cu}_2(\mathbf{347c})](\text{ClO}_4)_2$ occurs in the chiral twisted figure-of-eight loop form, also found for all other dicopper(I) compounds with the same type of ligand, $[\text{Cu}_2(\mathbf{347d})](\text{ClO}_4)_2$ exhibits a new type of folding with a chiral squeezed figure-of-eight loop conformation. The common structural features of $[\text{Cu}_2(\mathbf{347c})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{347d})](\text{ClO}_4)_2$ are the similar, distorted tetrahedral coordination geometries of the copper(I) centers and a parallel arrangement of the two benzene rings. The difference in the folding of the two macrocycles leads to a slightly larger $\text{Cu} \cdots \text{Cu}$ distance for $[\text{Cu}_2(\mathbf{347d})](\text{ClO}_4)_2$ (8.15 versus 7.83 Å) (Fig. 234c and d).

^1H NMR data show an open cyclic structure of the ligands while the complexes with the twisted and squeezed figure-of-eight loop geometries are kinetically inert on the NMR timescale. This indicates that metal ion coordination is an important driving force for the ligand folding [401].

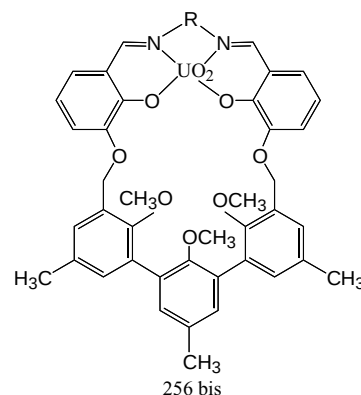
The cyclic voltammogram of the helicate $[\text{Cu}_2(\mathbf{347c})](\text{ClO}_4)_2$ shows a reversible oxidation wave due to copper(II), centered at +1.067 V versus normal hydrogen electrode (NHE) ($\Delta E = 587$ mV; scan rate range 10–100 mV s^{-1}). Oxidation of $[\text{Cu}_2(\mathbf{347d})](\text{ClO}_4)_2$ is irreversible (quasi-reversible after the addition of the ferrocene standard), with the oxidation wave centered around +1.18 V versus NHE. The voltammograms indicate that, in both compounds, the two copper(I) centers each at a distance of ca. 8 Å behave independently. The soft donor sets and the tetrahedral coordination geometry stabilize the reduced form of the dinuclear complexes [401].

Subsequently a series of nine large [2+2] macrocyclic ligands with two N_2S_2 (thioether and Schiff base imine)

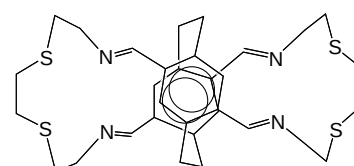
binding sites each, with different bridges between the donor atoms of each site (ethylene, *o*-xylylene, propylene, butylene) and different spacer groups between the two binding sites (*p*-xylylene, 2,5-dimethyl-*p*-xylylene, 2,5-dimethoxy-*p*-xylylene), (**347e–i**) and a similar [1+2] ligand with a preorganized double-helical geometry, based on a paracyclophane spacer group (**348**), have been prepared together with their copper(I) complexes [401].



348



256 bis



348 bis

The yellow or yellow-orange dicopper(I) complexes are generally obtained by reaction of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ with the appropriate ligand. These dicopper(I) compounds are stable when exposed to air and humidity and are generally more stable in acetonitrile than in nitromethane.

Electrochemical data of the dicopper(I) compounds, in nitromethane and acetonitrile, indicate a single reversible reduction wave, indicating that, as expected from the copper···copper distance of ca. 8 Å, there is no metal–metal interaction.

The solid state structures of the dicopper(I) complexes have two tetrahedral copper(I) site, separated by ca. 8 Å, and a figure-of-eight loop configuration of the ligand with a parallel arrangement of the two substituted benzene spacer groups (benzene···benzene distance of ca. 3.5 Å). All the dicopper(I) compounds have the same double-helical configuration (twisted ting figure-of-eight loop) [401].

The most prominent effect in the whole series is that of the variation of the chelate ring size (in **347a–i**) in nitromethane, where the reduction potential shifts from 1370 to 1300 and to 1200 mV (versus NHE) upon reduction of the central chelate ring on each copper center from seven- to six to five-membered, i.e. the larger cavities stabilize the large copper(I) ions. In acetonitrile, the potentials of these three compounds vary only marginally (in fact, in acetonitrile the reduction potentials are roughly constant over the whole series of compounds, except for the preorganized ligand **348**), indicating that, in acetonitrile, the redox active species are structurally very similar. A possible interpretation is that in all these molecules some of the donor groups of the macrocyclic ligands are substituted by acetonitrile molecules, leading to unstrained, structurally similar dicopper(I) compounds [401].

^1H NMR spectroscopy indicates that the structures in solution of the dicopper(I) complexes of the [32–36]-membered macrocyclic ligands (**347a–i**) are similar to the solid-state structures, i.e. figure-of-eight loop double-helical structures.

8.2. Homodinuclear complexes with asymmetric macrocyclic ligands

A mixed-valence dinuclear manganese(II, III) complex has been prepared by the condensation of the sodium salt of 2,6-diformyl-4-methylphenol and $[N,N'$ -bis(2-aminoethyl)] aminoacetic acid, subsequently transmetallated with $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The structure of this complex shows that the macrocyclic ligand formed is not the [2+2] symmetric H_4 -**349a** but the asymmetric H_3 -**349b** [402]. In particular, the resulting complex $[\text{Mn}_2(\text{349b})(\text{H}_2\text{O})_3](\text{ClO}_4)_2$ is a $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ species coordinated to the asymmetric macrocyclic ligand [**349b**] $^{3-}$ bearing a single carboxylic arm. In the complex cation, $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{349b})(\text{H}_2\text{O})_3]^{2+}$, two manganese ions are bridged by two phenoxy oxygen atoms. One manganese has a six coordinated N_2O_4 unit, in an elongated octahedral geometry, composed of two imine nitrogen and

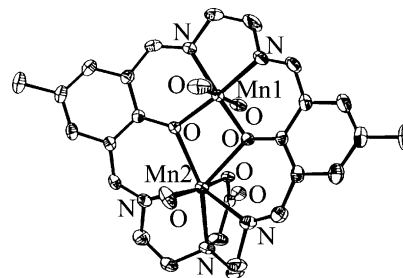
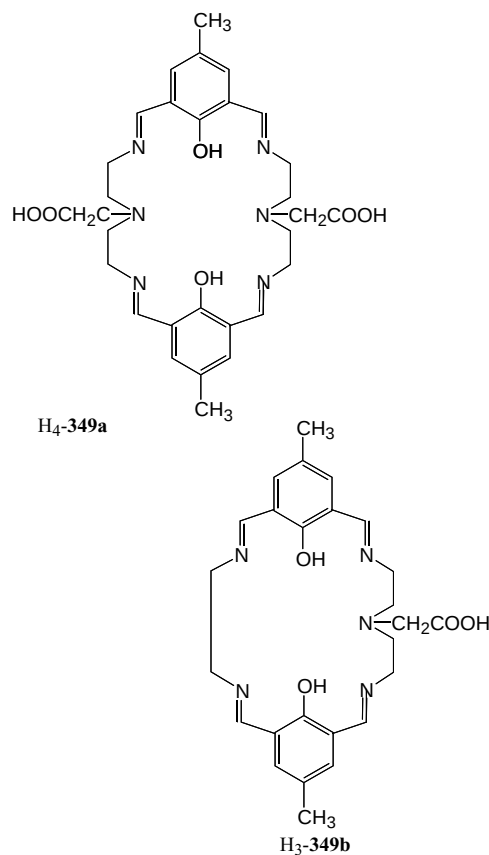
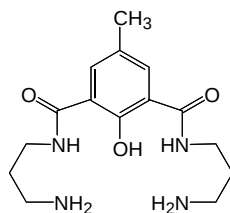
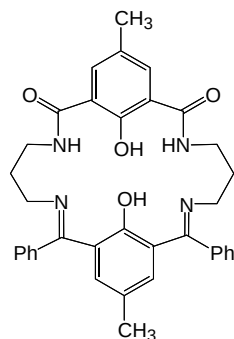
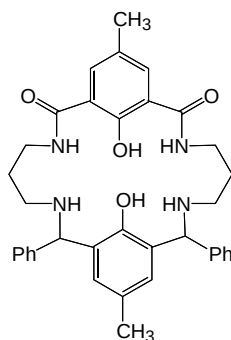


Fig. 235. Structure of $[\text{Mn}_2(\text{349b})]^{2+}$ (adapted from Ref. [402]).

two phenolic oxygen atoms as well as two water molecules, whereas the other manganese has a seven coordinated N_3O_4 in a distorted pentagonal bipyramidal with structural parameters typical of a manganese(II) ion unit, composed of two imine nitrogen atoms, one adjacent secondary amine nitrogen atom, two phenolic oxygen atoms and one water molecule as well as one oxygen atom of the carboxylate group (Fig. 235) [402]. An antiferromagnetic interaction ($J = -147 \text{ cm}^{-1}$) operates from room temperature to 50 K; the increase of μ_{eff} to $9.3\mu_{\text{B}}$ from 70 to 18 K and decrease to $8.5\mu_{\text{B}}$ from 18 to 6 K has been explained as the decreasing of effective moments below 50 K is due to the zero field splitting, and the increasing of effective moments is due to the weak ferromagnetic interaction between two manganese ions [402].



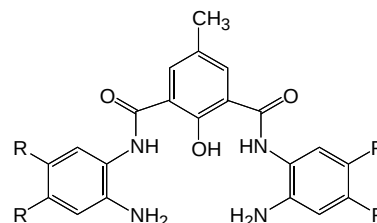
The condensation of dimethyl-2-hydroxy-5-methylbenzene-1,3-dicarboxylate and 1,3-diamino-propane forms **H₃-350a**, which on treatment in water with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NaOH gives the complex $[\text{Cu}_2(\text{350a})(\text{OH})] \cdot \text{H}_3\text{-350a}$ [403].

**H₃-350a****H₄-350b****H₄-351**

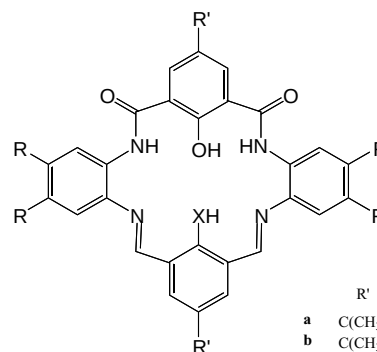
$[\text{Cu}_2(\text{350b})]$, obtained by refluxing a mixture of $[\text{Cu}_2(\text{350a})(\text{OH})] \cdot 2\text{H}_3\text{-350a}$ and 4-methyl-2,6-dibenzoylphenol (1:3 molar ratio) in CH_3OH , can be demetallated

by treating it with H_2S in CH_2Cl_2 . The resulting macrocyclic Schiff base, **H₄-350b**, obtained from $\text{CH}_3\text{OH}/\text{Et}_2\text{O}$, can be reduced to the corresponding cyclic amine **H₄-351** with NaBH₄. The reduced macrocycle is highly soluble in a large number of organic solvents. When it is recrystallized from CH_3OH the hydrated species $[\text{H}_4\text{-351} \cdot \text{H}_2\text{O}]$ is obtained which is soluble only in solvents as DMSO and DMF [403]. The structure of $[\text{H}_4\text{-351} \cdot \text{H}_2\text{O}]$ shows the formation of an inclusion complex and confirmed the asymmetric structure of the macrocycle as indicated by its ^1H and ^{13}C NMR spectra [403].

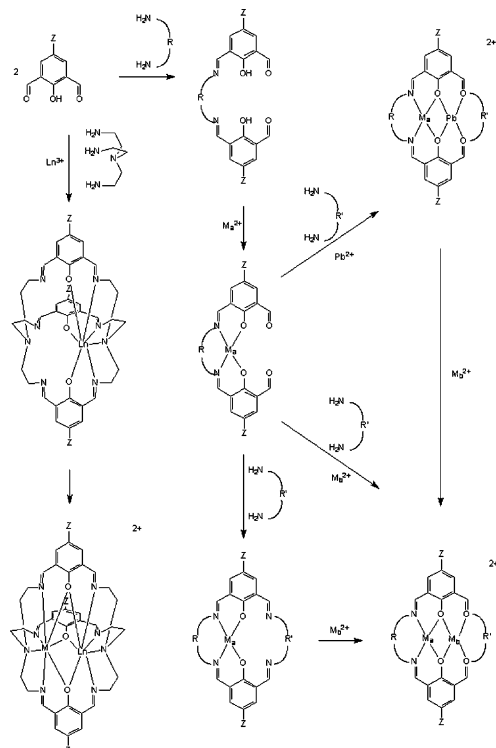
The acyclic, potentially binucleating amide-containing ligands, **H₃-352a** and **H₃-352b**, have been synthesized by reacting of 4-methylphenol-2,6-diacetylchloride with an excess of 1,2-diaminobenzene or 1,2-diamino-4,5-dimethylbenzene, respectively [404]. 4-Methylphenol-2,6-diacetylchloride was obtained by oxidation of 2,6-diformyl-4-methylphenol to the corresponding diacid followed by chlorination with SO_2Cl_2 .



H₃-352a R = H
H₃-352b R = CH₃

**H₄-353**

	R'	R'	X
a	C(CH ₃) ₃	H	O
b	C(CH ₃) ₃	CH ₃	O
c	CH ₃	H	O
d	CH ₃	CH ₃	O
e	C(CH ₃) ₃	H	O
f	C(CH ₃) ₃	CH ₃	O
g	CH ₃	H	O
h	CH ₃	CH ₃	O
i	CH ₃	H	S

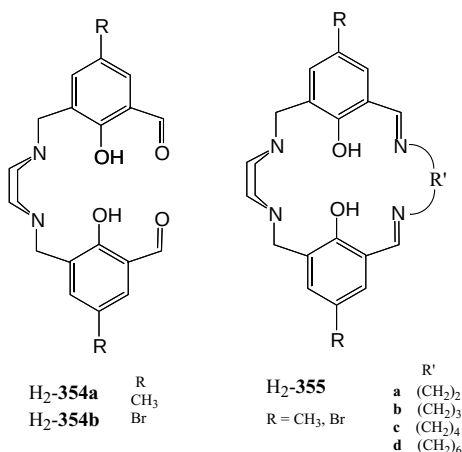


Scheme 48.

Dicopper(II) complexes, $[\text{Cu}_2(\text{352a})(\text{X})]$ ($\text{X} = \text{CH}_3\text{-COO}^-$, OH^-), have been made from **H₃-352a** but the analogous nickel complexes could not be prepared and no complexes with either copper or nickel could be prepared from **H₃-352b**.

The room temperature magnetic moments (1.3 BM per copper atom for $[\text{Cu}_2(\text{352a})(\text{CH}_3\text{COO})]$ and 1.4 BM per copper atom for $[\text{Cu}_2(\text{352a})(\text{OH})]$) indicate that antiferro-

The manganese(III) complexes $[\text{Mn}_2(\mathbf{355})](\text{X})_2$, where $\text{H}_2\text{-}\mathbf{355}$ represents the macrocyclic ligands with dissimilar coordination environments one containing two azomethine nitrogen and two phenoxide oxygen donor atoms and the other with two saturated piperazine nitrogen and two phenoxide oxygen donor atoms, have been prepared by the reaction in air of $\text{H}_2\text{-}\mathbf{354a}$ or $\text{H}_2\text{-}\mathbf{354b}$ and the appropriate diamine in the presence of MnX_2 ($\text{X} = \text{Cl}, \text{Br}$) [405]. The diformyl precursors $\text{H}_2\text{-}\mathbf{354a}$ and $\text{H}_2\text{-}\mathbf{354b}$ were synthesized by the introduction of two molecules of 4-substituted 2-formylphenol at the 1 and 4 positions of a piperazine molecule by an acid-mediated Mannich reaction [405].



In these macrocyclic complexes two reduction couples $[\text{Mn}^{\text{III}}\text{Mn}^{\text{III}} \text{ r } \text{Mn}^{\text{II}}\text{Mn}^{\text{III}} \text{ r } \text{Mn}^{\text{II}}\text{Mn}^{\text{II}}]$ were observed for all the complexes in the negative potential region: the first one electron reduction is observed around -0.90 V and the second around -1.30 V. In the positive potential region (0.00 to $+1.00$ V) two oxidation couples are observed for all the complexes $[\text{Mn}^{\text{III}}\text{Mn}^{\text{III}} \text{ r } \text{Mn}^{\text{II}}\text{Mn}^{\text{IV}} \text{ r } \text{Mn}^{\text{IV}}\text{Mn}^{\text{IV}}]$. The mixed valence species $\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}$ and $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ were confirmed by EPR spectra, the first one electron reduction occurs at the manganese(III) ion coordinated to unsaturated nitrogen atoms and second at the ion coordinated to the

saturated nitroge atoms. The first one electron reduction of the metal center is influenced mainly by the macrocyclic ring size while the second one electron reduction potential has less variation with increase in alkyl chain length. It takes place at the manganese(III) ion present in the pyperazine compartment. The structural variation in the imine nitrogen compartment (variation in the chain length) has very little effect on the coordination geometry of the pyperazine nitrogen compartment. Therefore it is reasonable to believe that the degree of geometrical distortion around the pyperazine coordinated to the manganese(III) ion is less than that around the imine coordinated to the manganese(III) ion. So the second electron reduction is less sensitive to the variation in the alkyl chain length [405].

The complexes with H₂-**355** containing the electron withdrawing substituent Br at the para position to the phenoxide oxygen in the phenyl ring, are reduced at lower negative potentials compared with those containing the electron donating substituent CH₃. This is due to the electron withdrawing group decreasing the electron density at the manganese(III) ion [406]. All the axial chloro complexes are reduced at higher cathodic potentials than those of the axial bromo complexes. This has been ascribed to the higher basicity of the chloride than the bromide ion [405].

The oxidation potential of the metal center is influenced by the axial halogen atom. The axial bromo complexes were oxidized at more positive potentials than those of the axial chloro complexes. Unlike the first reduction potential of the metal center the first oxidation potential does not vary much with increase in the macrocyclic ring size. It takes place at the metal center present in the pyperazine nitrogen compartment. The increase in the ring size may not have much influence on this compartment. The size of the oxidized manganese(IV) ion is smaller than that of the manganese(III) ion, however the size of the reduced manganese(II) ion is greater than that of manganese(III) ion. This increase may result in more stereochemical change around the metal center. Hence the first reduction potential varies considerably with the ring size [405].

H₂-**354** reacts with copper(II) acetate in 1:1 molar ratio to form [Cu(**354**)] which by condensation with another mole of alkanediamine in the presence of a copper(II) salt leads to the formation [Cu₂(**355**)]²⁺ [406].

Cyclic voltammetry in DMF in the negative potential range shows these complexes are sensitive to the macrocyclic structure and the electron-inductive nature of the substituents at the para positions of the benzene rings. For all the complexes two quasi-reversible waves, assigned to successive one-electron reductions at the metal centers, $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$, were observed. The first reduction potential shifts anodically as the size of the macrocycle increases (**355a** to **355d** for $\text{R} = \text{CH}_3$ and **355a–c** for $\text{R} = \text{Cl}$). The replacement of a electron-releasing methyl group by an electron-withdrawing chlorine atom shifts the first reduction to more positive potentials. For the dicopper(II) ion complexes with H_7 -**355a–d** ($\text{R} = \text{CH}_3$)

no oxidation wave was observed at positive potentials. The stability of the mixed-valence $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$ complexes increases with increasing macrocycle size; it also proves that an electron-withdrawing substituent at the aromatic ring of the ligand system relatively destabilises the mixed-valence $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$ state. At negative potentials (–1.3 to –1.5 V) the $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ species undergoes a further reduction and copper metal is deposited on the electrode.

Cryomagnetic investigations (80–300 K) reveal a weak antiferromagnetic spin exchange between the copper(II) ions in each complex ($J = -85$ to -195 cm^{-1}) [406].

8.3. Heterodinuclear complexes with macrocyclic ligands

8.3.1. Complexes with compartmental symmetric and asymmetric ligands derived from 2,6-diformyl-4-methyl phenol

Heterodinuclear complexes with symmetric or asymmetric cyclic ligands have been prepared by a step by step procedure of the type reported in Scheme 48.

The mononuclear dysprosium(III) cryptate, synthesized by metal-template condensation between 2,6-diformyl-4-chlorophenol and tris(2-aminoethyl)amine in 3:2 mol ratio and in the presence of hydrated dysprosium(III) nitrate in methanol under reflux for 3–4 h, reacts after the addition of an excess of CaH_2 and filtration of the solution with copper(II) perchlorate in refluxing $\text{CH}_3\text{OH}/\text{DMF}$ to form the dinuclear $\text{Dy}^{\text{III}}\text{Cu}^{\text{II}}$ complex. Slow diffusion of diethyl ether into an acetonitrile solution of the complex gave red prismatic crystals of $[\text{DyCu}(\mathbf{98b})(\text{DMF})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ [407]. In the crystals the dysprosium(III) ion is located at one end of the cavity and is eight coordinated with the bridgehead nitrogen, the three imino nitrogens, the three μ -phenolate oxygens and the oxygen atom of DMF. The coordination polyhedron has been described as distorted dodecahedral. The other end of the cavity is occupied by the copper(II) ion. Three μ -phenolate oxygen and three imino nitrogen atoms coordinate to copper(II), forming a distorted octahedron. The $\text{Dy} \cdots \text{Cu}$ distance is $3.255 \text{ \AA}$ [407] (Fig. 236).

Heterodinuclear complexes $[\text{M}_A\text{M}_B(\mathbf{43})]^{2+}$, where $\text{M}_A = \text{Ni}^{2+}$, $\text{M}_B = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , have been prepared by a two-step synthesis, based on the reaction of metal acetates with mononuclear nickel complex. The control over metal insertion is achieved simply by changing acidity of the reaction medium. Thus, in the first step, the one-pot formation of mononuclear nickel complex, one of the coordination compartments is blocked by protonation of inner phenolate groups. In the second step acetate ion deprotonates phenolate groups and makes the second compartment available for the coordination of another metal ion. The mild reaction conditions prevent scrambling of the two metal ions and thus, clean formation of hetero-dinuclear species is observed. Thus $\text{Ni}(\text{H}_2\text{-}\mathbf{43})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, by reaction with $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol, produces $[\text{NiZn}(\mathbf{43})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. In a similar way $[\text{NiM}(\mathbf{43})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cu}^{2+}$, Co^{2+} , Fe^{2+} , Mn^{2+}) were synthe-

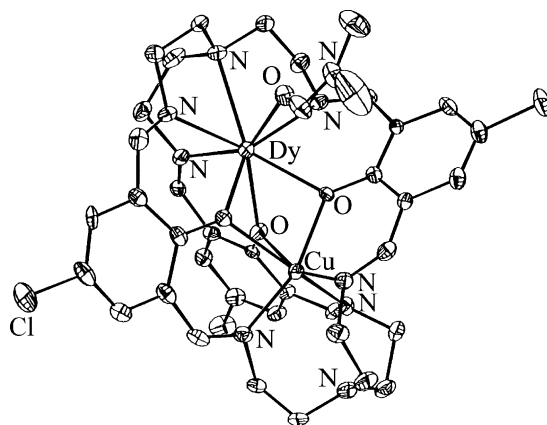


Fig. 236. Structure of $[\text{DyCu}(\mathbf{98b})(\text{DMF})]^{2+}$ (adapted from Ref. [407]).

sized; for the hetero-dinuclear complexes containing Co^{2+} , Fe^{2+} and Mn^{2+} a nitrogen atmosphere was used [408].

Disappointingly, the method used to synthesize the hetero-dinuclear complexes containing nickel(II) has not allowed to obtain every combination of the first row transition metal ions within the macrocycle $\text{H}_2\text{-}\mathbf{43}$. The main obstacle proved to be the availability of the starting mononuclear complexes of the $[\text{M}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ type. Thus attempts to synthesize $[\text{Co}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ and $[\text{Zn}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ under the conditions used in the synthesis of $[\text{Ni}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ led to the relevant homo-dinuclear complexes. The relatively best results were obtained when the protonated free ligand was reacted with metal salts in methanol. This approach is best exemplified by mononuclear cobalt(II) complex $[\text{Co}(\text{H}_2\text{-}\mathbf{43})](\text{Br})_2$ which, although not obtained in the analytically pure form, was synthesized in high yield from $\text{H}_2\text{-}\mathbf{43} \cdot 2\text{HBr}$ and CoBr_2 . The identity of the complex is confirmed by its mass spectrum showing a peak at m/z 231.5 corresponding to $[\text{Co}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ and a peak at m/z 462.3 corresponding to $[\text{Co}(\text{H}-\mathbf{43})]^+$ [408].

The $[\text{Co}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ moiety is much less stable than $[\text{Ni}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ and decomposes in water solution to give $[\text{Co}_2(\mathbf{43})]^{2+}$ and organic fragments. This decomposition process explains the difficulty in obtaining and purifying $[\text{Co}(\text{H}_2\text{-}\mathbf{43})]^{2+}$ complexes. It seems that geometric requirements of nickel(II) ion, together with its kinetic properties, enable easy formation of mononuclear complex, while cobalt(II) and zinc(II) ions tend to form, under the same conditions, thermodynamically more stable dinuclear complexes.

When nickel(II) acetate is added to a D_2O solution containing $[\text{Co}(\text{H}_2\text{-}\mathbf{43})](\text{Br})_2$, the clean ^1H NMR spectrum of the $[\text{CoNi}(\mathbf{43})]^{2+}$ complex can be measured (almost identical to that of $[\text{NiCo}(\mathbf{43})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$). Thus the hetero-dinuclear $\text{Ni}^{\text{II}}\text{Co}^{\text{II}}$ complex is obtained with reversed order of metal ion insertion. Similarly, when zinc(II) acetate is added to a D_2O solution containing $[\text{Co}(\text{H}_2\text{-}\mathbf{43})](\text{Br})_2$, the spectrum of mononuclear complex disappears and new signals at 427.2, 138.3, 29.31, 24.60, 14.71, 14.21 and

−0.83 ppm are generated, indicating the formation of the $[\text{CoZn}(\mathbf{43})]^{2+}$ complex [408].

Electrospray mass spectrometry is a useful tool for the identification of the hetero-dinuclear nature of these complexes. Generally, peaks due to $[\text{M}_A\text{M}_B(\mathbf{43})]^{2+}$ and to $[\text{M}_A\text{M}_B(\mathbf{43})\text{ClO}_4]^+$ have been and can also prove the presence (or the absence) of homo-dinuclear impurities.

The formation of complexes with symmetric compartmental ligands has also been achieved by a step by step procedure that implies the bonding of the second metal ion at the O_2O_2 site of the desired acyclic complex.) $^{2+}(\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+})$ have been prepared and characterized [409].

A trend towards increasing antiferromagnetic interaction is observed in the series; $-J = 30$ for CuMn , $-J = 71$ for CuFe and $-J = 103 \text{ cm}^{-1}$ for CuNi . For the corresponding CuCu complex a larger exchange integral of $-J = 294 \text{ cm}^{-1}$ is obtained [410].

Electrochemical studies on these hetero-dinuclear complexes show that the magnetic interaction between the metal ions has little effect upon the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox potential. The mixed-valence $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$ complex is stabilized by 140 mV ($3.2 \pm 0.8 \text{ kcal mol}^{-1}$) relative to the heterobimetallic $\text{Cu}^{\text{I}}\text{M}^{\text{II}}$ species and the stabilization is ascribed to electronic delocalization in the mixed-valence complex. No significant electronic delocalization is suggested for the $\text{Cu}^{\text{I}}\text{M}^{\text{II}}$ complexes from their consistent $\text{Cu}^{\text{II}}\text{M}^{\text{II}}/\text{Cu}^{\text{I}}\text{M}^{\text{II}}$ potentials [410].

The hetero-dinuclear copper(II)-lanthanide(III) complexes, $\text{CuLn}(\mathbf{46})(\text{NO}_3)_3(\text{H}_2\text{O})_n$ ($n = 2$ for $\text{Ln} = \text{Nd}^{3+}$ and $n = 1$ for $\text{Ln} = \text{Eu}^{3+}$ and Gd^{3+}), were synthesized by the reaction of the acyclic complex $[N,N'$ -bis(3-formyl-5-methylsalicylidene)ethylenediaminato]copper(II) and ethylenediamine in the presence of lanthanide(III) ion as a template. In the CuGd complex cryomagnetic susceptibility data support ferromagnetic spin-coupling between copper(II) and gadolinium(III) ions ($J = +2.1$). The fluorescence intensity of the europium(III) ion decreases drastically upon forming the CuEu complex [410].

However, these methods can give rise to scrambling reactions with the consequent formation of homo-dinuclear complexes in addition to the hetero-dinuclear analogues, transmetallation processes, etc. which cause heavy problems to the synthesis of the desired complex. To overcome these problems a template reaction was proposed where lead(II) is used in the second step of the cyclization. This synthetic procedure gives rise to trinuclear macrocyclic $\{\text{M}_A^{\text{II}}\text{Pb}^{\text{II}}\text{M}_A^{\text{II}}\}$ complexes with different combinations of lateral chains. The subsequent transmetallation of the lead(II) with a transition metal ion, M_B^{II} , to give dinuclear $\{\text{M}_A^{\text{II}}\text{M}_B^{\text{II}}\}$ complexes was successfully performed by using M_B^{II} sulfate salts [410].

Dinuclear $\text{Ni}^{\text{II}}\text{Mn}^{\text{II}}$ and $\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}$ complexes, soluble in polar organic solvents such as DMF, DMSO and acetonitrile and stable towards molecular oxygen both in solid state and in solution, of the general formula $[\text{MMn}(\text{L})]\text{ClO}_4)_2$ ($\text{H}_2\text{-L} =$

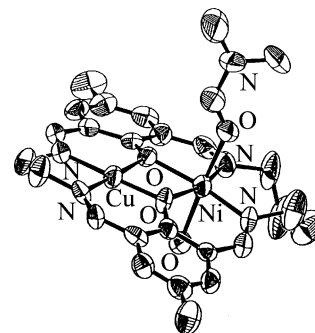
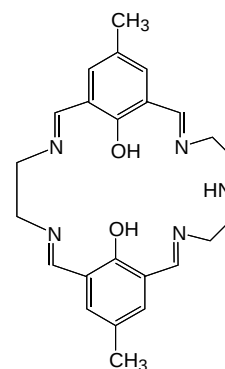
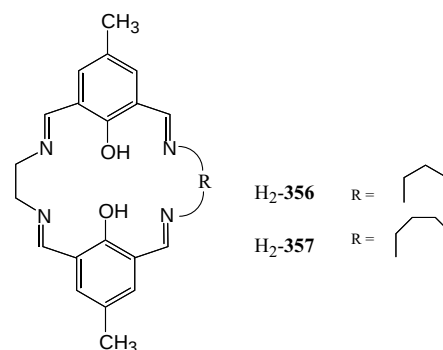


Fig. 237. Structure of $[\text{CuNi}(\mathbf{357})(\text{H}_2\text{O})(\text{DMF})]^{2+}$ (adapted from Ref. [410]).

$\text{H}_2\text{-356}$, $\text{H}_2\text{-357}$ and $\text{H}_2\text{-43}$; $\text{M} = \text{Ni}, \text{Cu}$) have been obtained as solvates by reaction of suspension respectively of $[\text{M}_2\text{Pb}(\mathbf{356})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, $[\text{M}_2\text{Pb}(\mathbf{357})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ or $[\text{M}_2\text{Pb}(\mathbf{43})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ in dry CH_3CN with a methanol solution of manganese(II) perchlorate hexahydrate and manganese(II) sulfate hexahydrate [411]. The same procedure affords also $[\text{MCo}(\mathbf{356})(\text{DMF})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$ ($\text{M} = \text{Cu}^{2+}, \text{Ni}^{2+}$) [412]. Similarly $[\text{Cu}_2\text{Pb}(\mathbf{357})_2](\text{ClO}_4)_2$ reacts with nickel(II) sulfate and nickel(II) perchlorate in acetonitrile to form $[\text{CuNi}(\mathbf{357})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ which, when recrystallized from DMF, forms $[\text{CuNi}(\mathbf{357})(\text{DMF})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{DMF}$ [410] (Fig. 237).



$\text{H}_2\text{-358}$

In the complex cation $[\text{CuNi}(\mathbf{357})(\text{H}_2\text{O})(\text{DMF})]^{2+}$, the copper(II) and nickel(II) ions are doubly bridged by the phenolic oxygens of the macrocycle with a $\text{Cu} \cdots \text{Ni}$

separation 3.038 Å. The copper(II) ion resides at the N₂O₂ site of the ethylene lateral chain and assumes an essentially planar geometry. The nickel(II) ion resides at the N₂O₂ site of the tetramethylene lateral chain and assumes a pseudo-octahedral geometry, together with one DMF and one water molecule at the axial sites of the high-spin nickel(II) ion. The tetramethylene lateral chain adopts a folded conformation [410].

The complex [CuNi(357)](ClO₄)₂·H₂O may also contain a six coordinated nickel(II) ion where the axial donor groups may be a water molecule and a perchlorate ion.

A cryomagnetic study suggests a strong antiferromagnetic interaction between the copper(II) and nickel(II) ions ($J = -90 \text{ cm}^{-1}$) in [CuNi(357)](ClO₄)₂·H₂O. The energy separation between the spin-doublet ground state and the spin-quartet excited state ($-3J = 270 \text{ cm}^{-1}$) is large enough to allow thermal population only of the spin-doublet ground state at 80 K [410].

In [NiMn(356)(DMF)₂](ClO₄)₂·DMF the nickel(II) and manganese(II) ions are bridged by the two phenolic oxygens of [356]²⁻ with a Ni···Mn separation of 3.145 Å. The nickel(II) ion resides at the N₂O₂ coordination site with the ethylene lateral chain and assumes a nearly planar geometry. The manganese(II) ion resides at the N₂O₂ site with the trimethylene chain and assumes a six coordinated geometry together with two DMF oxygens. The surrounding about the manganese(II) ion is fairly distorted from a regular octahedron. The manganese(II) ion is deviated by 0.982 Å from the least squares plane defined by the N₂O₂ donor set because of the mismatch between the cavity size and the ionic radius of manganese(II) ion. Two DMF molecules coordinated to the manganese(II) ion are *cis* to each other. The macrocycle [356]²⁻ is nearly coplanar but bent at the phenoly oxygens O···O edge (Fig. 238a) [411].

The structure of [NiMn(357)(DMF)₂](ClO₄)₂ is essentially similar to that of [NiMn(356)(DMF)₂](ClO₄)₂ and has

a Ni···Mn separation of 3.111 Å. The geometry about nickel(II) ion at the site of the ethylene lateral chain is nearly planar. The manganese(II) ions at the site of the tetramethylene lateral chain has a distorted six coordinated geometry together with two DMF oxygens in *cis* [411].

The magnetic moments of the Ni^{II}Mn^{II} complexes ($\mu_B = 5.87\text{--}5.84$) are very close to the spin-only value for five unpaired electrons ($5.92\mu_B$) and consistent with the spin state Ni^{II} ($S = 0$)–Mn^{II} ($S = 5/2$). The magnetic moments of Cu^{II}Mn^{II} complexes are subnormal at room temperature and decrease with decreasing temperature, suggesting antiferromagnetic interaction between the copper(II) and high-spin manganese(II) ions (J ranging from -23 cm^{-1} to -37 cm^{-1}). Because of the antiferromagnetic interaction, these complexes showed no EPR signal at liquid nitrogen temperature.

The M^{II}Mn^{II} complexes ($M = \text{Ni}^{2+}, \text{Cu}^{2+}$) are electrochemically converted to M^IMn^{II} and M^{II}Mn^{III} complexes which have been characterized by visible spectroscopy.

The absence of CAT-like activity of these Ni^{II}Mn^{II} and Cu^{II}Mn^{II} complexes is due to the high Mn^{II}/Mn^{III} potential which cannot be achieved with H₂O₂ [411].

In [CuCo(356)(DMF)₂(H₂O)](ClO₄)₂ the [CuCo(356)]²⁺ entity forms a near coplane. The copper(II) ion resides at the N₂O₂ site with the ethylene lateral chain and assumes a square pyramidal geometry together with the DMF oxygen at the axial site. The cobalt(II) ion resides at the N₂O₂ site of the trimethylene lateral chain and assumes a pseudo-octahedral geometry together with the water and DMF oxygens at the axial positions. The DMF molecules attached to the copper(II) and the cobalt(II) ions are *trans* to each other with respect to the molecular coplane. The Cu···Co intermetallic separation is 2.998 Å [412] (Fig. 238b).

The room temperature magnetic moment for the Ni^{II}Co^{II} complexes with [356]²⁻ are common for high-spin cobalt(II), the nickel(II) ion being, in these compounds, diamagnetic. The CuCo complexes on contrary show a strong antiferromagnetic interaction between the two metal ions [412].

The cyclic voltammograms of the Ni^{II}Co^{II} complexes show two quasi-reversible couples attributable to the step-wise reductions: Ni^{II}Co^{II} $\rightleftharpoons$ Ni^ICo^{II} $\rightleftharpoons$ Ni^ICo^I. The Ni^ICo^{II} and Ni^ICo^I complexes were prepared in solution by coulometry and characterized by visible spectroscopy. The unusual electrochemical behaviour of the Cu^{II}Co^{II} complexes of [356]²⁻ and [357]²⁻ at the electrode suggests a scrambling or site exchange of the metal ions. In particular for the complex [CuCo(357)]²⁻ the electrochemical data suggest a site exchange of the metal ions may occur with the consequent formation of a coordination-position isomer possessing the cobalt ion at the site of the ethylene lateral chain and the copper ion at the site of the tetramethylene chain. Based on these studies it is shown that rare Ni^ICo^I complexes can be produced using [356]²⁻ and [357]²⁻ and a Cu^ICo^I complex using [43]²⁻ in bulk solution, though the spin state of the Co^I in each complex remains to be clarified [412].

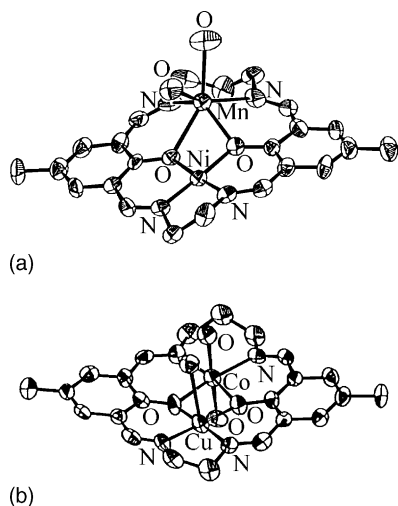


Fig. 238. Structure of [NiMn(356)(DMF)₂]²⁺ (a) and [CuCo(356)(DMF)₂(H₂O)]²⁺ (b) (adapted from Refs. [411,412]).

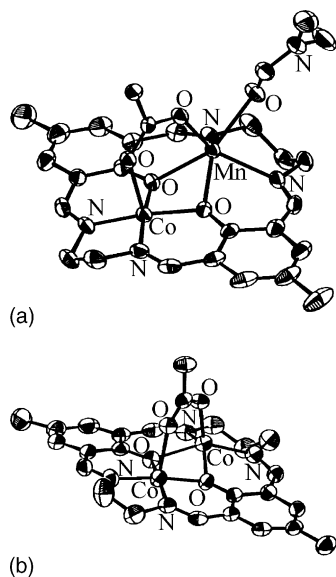


Fig. 239. Structure of $[\text{CoMn}(\mathbf{356})(\text{CH}_3\text{COO})(\text{DMF})]^+$ (a) and $[\text{Co}_2(\mathbf{356})(\text{CH}_3\text{COO})]^+$ (b) (adapted from Ref. [413]).

The trinuclear $\text{Co}^{\text{II}}\text{Pb}^{\text{II}}\text{Co}^{\text{II}}$ complexes, $[\text{Co}_2\text{Pb}(\mathbf{356})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ and $[\text{Co}_2\text{Pb}(\mathbf{357})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ were converted into the dinuclear $\text{Co}^{\text{II}}\text{M}^{\text{II}}$ perchlorate complexes $[\text{CoMn}(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{DMF}$, $[\text{CoMn}(\mathbf{357})(\text{CH}_3\text{COO})](\text{ClO}_4)$, $[\text{Co}_2(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$, $[\text{Co}_2(\mathbf{357})(\text{CH}_3\text{COO})](\text{ClO}_4)$, $[\text{CoZn}(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$, and $[\text{CoZn}(\mathbf{357})(\text{CH}_3\text{COO})](\text{ClO}_4)$ by reaction with $\text{MSO}_4 \cdot n\text{H}_2\text{O}$, $\text{M}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ and sodium acetate in methanol. All the synthetic operations were carried out in a nitrogen atmosphere because the complexes are all air-sensitive [413].

In $[\text{CoMn}(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{DMF}$ (Fig. 239a) the cobalt(II) and manganese(II) ions are bridged by the phenolic oxygens of the macrocycle and the acetate oxygens in the *syn-syn* mode. The $\text{Co} \cdots \text{Mn}$ intermetallic separation is 3.108 Å. The cobalt(II) ion in the smaller site assumes a square pyramidal geometry with the N_2O_2 site of the macrocycle on the base and the oxygen of the acetate bridged at the apical site. The manganese(II) ion in the larger site has a six coordinated geometry being coordinated also by the oxygen of the bridging acetate group and the oxygen of the DMF ligand. These exogenous oxygen donor atoms are situated *cis* with respect to the mean plane defined by the N_2O_2 set of the macrocycle. The *cis* six coordinated geometry arises from the mismatch between the large ionic radius of manganese(II) and the cavity size of the salt site. The $\text{Co} \cdots \text{Co}$ separation in the stack is 3.808 Å.

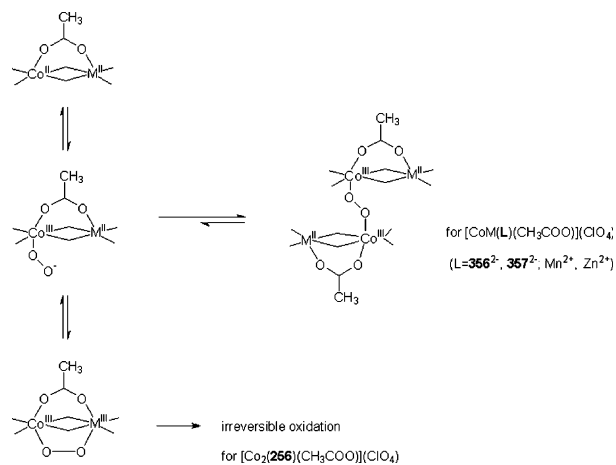
The dinuclear core of $[\text{CoMn}(\mathbf{357})(\text{CH}_3\text{COO})](\text{PF}_6) \cdot \text{DMF}$ is essentially similar to that of $[\text{CoMn}(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$, with the cobalt(II) ion in the smaller site and the manganese(II) ion in the larger site. The $\text{Co} \cdots \text{Mn}$ intermetallic separation, bridged by the phenolic oxygens and the acetate oxygens in the *syn-syn* mode, is 3.120 Å. The geometry about the cobalt(II) ion is square pyramidal

with the acetate oxygen at the axial site. The manganese(II) ion has a *cis* six coordinated geometry with respect to the acetate donor oxygens. The deviation of manganese(II) ion (0.874 Å) from the basal least-squares plane defined by the N_2O_2 donor set is smaller than that for $[\text{CoMn}(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$ because of the large cavity of the site where $\text{R} = \text{C}_4\text{H}_8$ relative to the site where $\text{R} = \text{C}_3\text{H}_6$. In the bulk, the two $[\text{CoMn}(\mathbf{357})(\text{CH}_3\text{COO})]^+$ cations stack with each other at the open face of the smaller N_2O_2 entity. The $\text{Co} \cdots \text{Co}'$ separation in the stack is 3.855 Å [413].

$[\text{Co}_2(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$ and $[\text{CoZn}(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$ are isostructural. The two cobalt(II) ions are bridged by the phenolic oxygens of the macrocycle and the acetate oxygens in the *syn-syn* mode at an intermetallic separation of 2.972 Å. The cobalt(II) ion in the smaller site assumes a square pyramidal geometry together with the oxygen of the acetate bridge at the apical site while the cobalt in the larger site has a five coordinated geometry along with the acetate oxygen of the bridging acetate group. The geometry about the metal ion has been described as a distorted square pyramid with the N_2O_2 donor atoms of the macrocycle on the base and the acetate oxygen at the apex. One cobalt deviates 0.53 Å from the basal least-squares plane toward the acetate oxygen. In the bulk the complex has a dimer structure formed by two $[\text{Co}_2(\mathbf{356})(\text{CH}_3\text{COO})]^+$ cations stacked at the open face of the smaller $\text{Co}(\text{N}_2\text{O}_2)$ entity with a $\text{Co} \cdots \text{Co}$ separation of 3.804 Å [413] (Fig. 239b). In $[\text{CoM}(\mathbf{L})(\text{CH}_3\text{COO})](\text{ClO}_4)$ ($\mathbf{L} = \mathbf{356}^{2-}$, $\mathbf{357}^{2-}$) an antiferromagnetic exchange operates.

These complexes resemble each other in redox behaviour and show an irreversible or quasi-reversible couple at -0.3 V (versus Ag/Ag^+) and a reversible couple at ~ -1.3 V. The two waves are ascribed to the cobalt(II) in the smaller salen-like site; the zinc(II) ion is electrochemically inert, and manganese(II) and cobalt(II) ions in the larger sites where $\text{R} = \text{C}_3\text{H}_6$ or C_4H_8 , are hardly reduced at the available potential. The wave at ~ -0.3 V is attributed to the $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ process. The cobalt(III) ion generally prefers an octahedral geometry, and the poor reversibility of the wave is related to the geometrical change at the cobalt center in the redox process. The couple at ~ -1.3 V can be attributed to the $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ process. The good reversibility of the process can be understood because both low-spin cobalt(II) (d^7) and cobalt(I) (d^8) prefer an axially distorted geometry [413].

$[\text{CoM}(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$ ($\text{M} = \text{Mn}^{2+}$, Zn^{2+}) and $[\text{CoM}(\mathbf{357})(\text{CH}_3\text{COO})](\text{ClO}_4)$ ($\text{M} = \text{Mn}^{2+}$, Co^{2+} , Zn^{2+}) reversibly bind O_2 in DMF at 0°C while irreversible oxidation occurs at room temperature. EPR spectra show the manganese(II) ion does not change during the oxidation process. Thus the oxygenated species have been formulated as $[\{\text{Co}^{\text{III}}\text{Mn}^{\text{II}}(\mathbf{L})(\text{CH}_3\text{COO})\}_2(\text{O}_2^{2-})]^{2+}$ ($\mathbf{L} = [\mathbf{356}]^{2-}$, $[\mathbf{357}]^{2-}$) $[\text{Co}_2(\mathbf{356})(\text{CH}_3\text{COO})](\text{ClO}_4)$ is also oxygenated at 0°C with the formation of the peroxo dimer $[\{\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{356})(\text{CH}_3\text{COO})\}_2(\text{O}_2^{2-})]^{2+}$ which is not stable



in solution. A mechanism was proposed where an equilibrium between peroxo- and super-oxo complexes takes place in solution [413]. The oxygenation and oxidation behaviour of the $\text{Co}^{\text{II}}\text{M}^{\text{II}}$ complexes is summarized in Scheme 49. The reactivity of the $\text{Co}^{\text{II}}\text{M}^{\text{II}}$ complexes toward molecular dioxygen at the cobalt center is influenced by the neighbouring metal(II) ion and the $\text{Co}^{\text{II}}\text{M}^{\text{II}}$ core structure [413].

The macrocycle **H₂-358** has an additional amine nitrogen on one lateral chain to provide a N_2O_2 four coordinating and a N_3O_2 five coordinating site. The complexes $[\text{CuPb}(\text{358})]^{2+}$, differing in the counter anion and solvation, have been prepared by condensation of the copper(II) diformyl-ethylene-diimine acyclic complex with 1,5-diamino-3-azapentane in the presence of lead(II) salts. In $[\text{CuPb}(\text{358})(\text{CH}_3\text{COO})](\text{BPh}_4) \cdot \text{CH}_3\text{CN}$ the copper(II) ion is at the four coordination site and adopts a nearly planar geometry. The lead(II) ion assumes a six coordination with two phenolic oxygens, three nitrogens, and an acetate oxygen. The acetonitrile is free from coordination (Fig. 240a) [419].

The same stepwise template reaction using nickel(II) and lead(II) ions at the different stages of cyclization was successfully applied to the synthesis of $[\text{NiPb}(\text{358})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. Presumably the nickel(II) ion is located at the four coordination site and assumes an essentially planar configuration as supported by the diamagnetic behaviour of this complex. The lead(II) ion occupies the five coordination site of the macrocycle [414].

The transmetallation in methanol of $[\text{NiPb}(\text{358})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ by transition metal(II) sulfates forms the hydrated or solvate complexes $[\text{NiM}(\text{358})](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$).

The cyclic voltammograms of the $\text{Ni}^{\text{II}}\text{M}^{\text{II}}$ complexes show a $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ reduction at -1.0 to -1.1 V versus SCE. The oxidation of the iron(II) ion in the $\text{Ni}^{\text{II}}\text{Fe}^{\text{II}}$ complex occurs at $+0.43$ V whereas the oxidation of the manganese(II) ion of the $\text{Ni}^{\text{II}}\text{Mn}^{\text{II}}$ complex and the cobalt(II) ion of the $\text{Ni}^{\text{II}}\text{Co}^{\text{II}}$ complex does not occur up to $+1.3$ V [414,415].

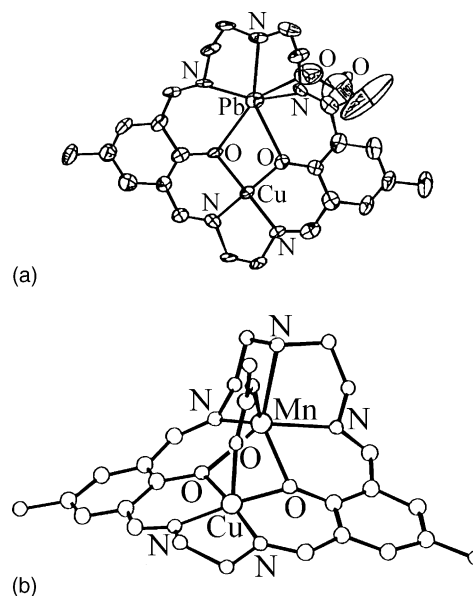


Fig. 240. Structures of $[\text{CuPb}(\text{358})(\text{CH}_3\text{COO})]^+$ (a) and $[\text{CuMn}(\text{358})(\text{CH}_3\text{COO})]^+$ (b) (adapted from Refs. [414,415]).

Also the $\text{Cu}^{\text{II}}\text{Pb}^{\text{II}}$ complexes with **H₂-358** are good precursors for the formation of the $\text{Cu}^{\text{II}}\text{M}^{\text{II}}$ complexes ($\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$). $[\text{CuMn}(\text{358})(\text{CH}_3\text{COO})](\text{BPh}_4)$ has a dinuclear core bridged by an acetate group. The copper(II) ion is bonded to the N_2O_2 four coordination site and assumes a square pyramidal geometry with an acetate oxygen at the apical site. The manganese(II) ion has a distorted octahedral geometry derived from the N_3O_2 site and a bridging acetate oxygen [414,415] (Fig. 240b).

$[\text{CoM}(\text{358})(\text{CH}_3\text{COO})](\text{ClO}_4)$ and $[\text{CoM}(\text{358})(\text{NCS})](\text{ClO}_4)$ ($\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$), $[\text{NiCo}(\text{358})](\text{ClO}_4)_2$ and $[\text{CuCo}(\text{358})](\text{ClO}_4)_2$ have been prepared by transmetallation of $[\text{Co}_2(\text{358})_2](\text{ClO}_4)_2$ with the appropriate metal salt [412,415].

In $[\text{CoMn}(\text{358})(\text{CH}_3\text{COO})](\text{ClO}_4)$, the cobalt(II) ion resides at the N_2O_2 site and the manganese(II) ion resides at the N_3O_2 site. The two metal ions are bridged by the phenolic oxygens of the macrocycle and the acetate group in the $\eta^1:\eta^1$ mode. The geometry about the cobalt ion is square pyramidal with two nitrogens and two oxygens of the macrocycle on the basal plane and one oxygen of the acetate group at the apex. The manganese at the N_3O_2 site assumes a distorted six coordination. Because of the donation of the amino nitrogen, the metal ion cannot reside within the basal N_2O_2 cavity; it deviates 0.78 Å from the basal least-squares plane toward the acetate oxygen. The acetate oxygen and the amino nitrogen are situated *cis* to each other. The manganese(II) ion is in a distorted trigonal prismatic geometry, where one triangular face is defined by the three nitrogen donor atoms and the other face by the three oxygen atom. $[\text{CoFe}(\text{358})(\text{CH}_3\text{COO})](\text{ClO}_4)$ and $[\text{Co}_2(\text{358})(\text{CH}_3\text{COO})](\text{ClO}_4)$ have an essentially similar core structure (Fig. 241a) [415].

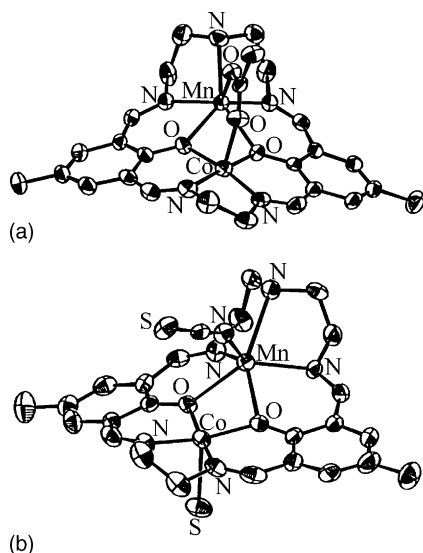


Fig. 241. Structures of [CoMn(358)(CH₃COO)]⁺ (a) and [CoMn(358)-(NCS)]⁺ (b) (adapted from Ref. [415]).

The complexes [CoM(358)(NCS)](ClO₄) (M = Mn²⁺, Fe²⁺, Co²⁺) are isomorphous. In [CoMn(358)(SCN)](ClO₄) the dinuclear core has the cobalt(II) ion at the N₂O₂ site and the manganese(II) ion at the N₃O₂ site. The Co···Mn intermetallic separation doubly bridged by the phenolic oxygens is 3.175 Å. A intermolecular bridge of the isothiocyanate group, forming a bond to the manganese(II) ion through its nitrogen and to the cobalt(II) center of the adjacent molecule through its sulfur to provide an infinite chain extended by Mn–NCS–Co linkages (Fig. 241b). Thus the cobalt(II) ion at the N₂O₂ site assumes a square pyramidal geometry with the two nitrogen and the two oxygen atoms of the macrocycle at the basal plane and the sulfur of the thiocyanate group at the apex. The manganese(II) ion at the N₃O₂ site assumes a distorted six coordinated geometry together with the nitrogen of the thiocyanate group. The geometry about the manganese(II) ion is similar to that in [CoMn(358)(CH₃COO)](ClO₄) and has been depicted as a distorted trigonal prism. Because of the intermolecular bridge of the thiocyanate group, the cobalt at the N₂O₂ site and the manganese at the N₃O₂ site are deviated by 0.14 and 0.74 Å, respectively, in the opposite direction [415].

Each complex has a magnetic moment close to each spin-only value, proving a high-spin state of the cobalt(II) ion in the acetate complexes and a low-spin state in the thiocyanate complexes [415].

[CoMn(358)(CH₃COO)](ClO₄) and [Co₂(358)(CH₃COO)](ClO₄) have similar cyclic voltammograms and show a reversible couple at ~ -1.55 V versus Ag/AgClO₄ (0.01 M) and a quasi-reversible couple at ~ -0.35 V, assigned to the Co^I/Co^{II} and Co^{II}/Co^{III} processes, respectively. The Mn^{II}/Mn^{III} process does not occur in the available potential due to the distorted geometry about the manganese(II) ion and the long manganese(II)–L bond distances. [CoFe(358)(CH₃COO)](ClO₄) has another reversi-

ble wave at +0.05 V, assigned to the Fe^{II}/Fe^{III} process. This wave appears at low potential because of the electronically preferred d⁵ configuration of the iron(III) ion [415].

Also [CoMn(358)(SCN)](ClO₄)₂ and [Co₂(358)(SCN)]-ClO₄ resemble each other in cyclic voltammogram and show a reversible couple due to the Co^I/Co^{II} process at ~ -1.25 V and an irreversible couple due to the Co^{II}/Co^{III} process at ~ -0.23 V.

The potential for the acetate complexes [CoM(358)-(CH₃COO)]⁺ (-1.57 to -1.51 V) is about 0.3 V lower relative to those of the thiocyanate complexes [CoM(358)(SCN)]⁺ (-1.27 to -1.23 V). This reflects the different spin states of the cobalt(II) ion, indicating that the high-spin cobalt(II) ion in [CoM(358)(CH₃COO)]⁺ is hardly reduced compared to the low-spin cobalt(II) ion in [CoM(358)(SCN)]⁺ [415].

The air-sensitive [N,N'-ethylenedi(3-formyl-5-methylsalicylidene)aminato]cobalt(II) reacts with diethylenetriamine in the presence of lead(II) perchlorate trihydrate in a nitrogen atmosphere to give [CoPb(358)(CH₃OH)](ClO₄)₂·CH₃OH [416]. In this complex the cobalt(II) and lead(II) ions are bridged by the phenolic oxygens, with the a Co···Pb separation of 3.468 Å. The cobalt(II) ion resides at the N₂O₂ site of the macrocycle and assumes a square pyramidal geometry together with the methanol oxygen at the axial site. The lead(II) ion at the N₃O₂ site has a seven coordinated geometry together with two perchlorate oxygens. The lead(II) ion is 1.38 Å deviated from the least-squares plane defined by the two phenolic oxygen and the two iminic nitrogens because of its large ionic radius. The deviation of the lead(II) ion from the basal N₂O₂ plane and the coordination of two perchlorate groups to the lead(II) ion provide a large cavity above the cobalt(II) ion, allowing the coordinative incorporation of one methanol molecule in the cavity (Fig. 242a). Two CoPb complexes stack at the Co(N₂O₂) entity with the average interatomic separation of 3.5 Å [416].

The axial methanol ligand was readily released under a reduced pressure. In the open air the methanol-free complex formed the dioxygen adduct [CoPb(358)(O₂)](ClO₄)₂ with a concomitant colour change from orange to dark brown. The same dioxygen adduct was obtained when the mono-methanol adduct was allowed to stand in open air. The dioxygen adduct shows an isotropic EPR signal of a narrow band width at $g \sim 2.01$, typical of a superoxocobalt(III) complex though the cobalt hyperfine structures are not resolved. The room-temperature magnetic moment of the dioxygen adduct is 1.89 μ_B that is also consistent with the Co(III)–O₂–formalism. When heated at 80 °C in vacuo, the dioxygen-adduct was converted into [CoPb(358)](ClO₄)₂. Thus this Co^{II}Pb^{II} complex acts as a reversible O₂-carrier in solid state, while it does not show such oxygenation in solution at room temperature. In fact the dioxygen adduct was deoxygenated in acetonitrile or DMF [416].

[CoPb(358)(CH₃OH)](ClO₄)₂ reacts with nitrogen monoxide to give the nitrosyl complex [CoPb(358)-

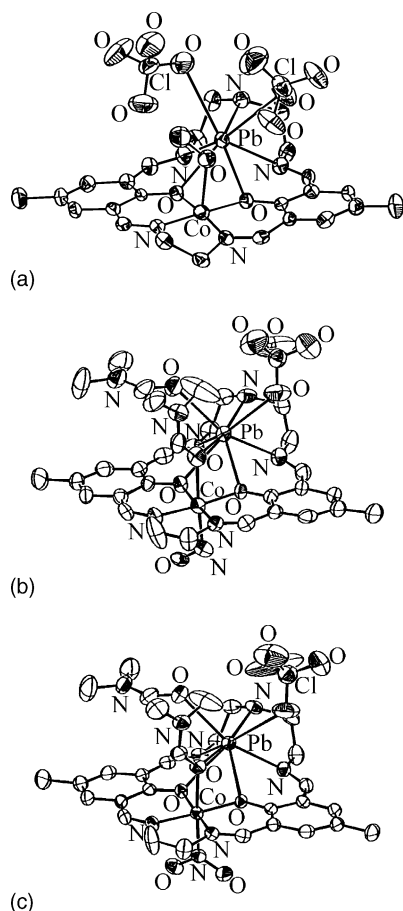


Fig. 242. Structures of $[\text{CoPb}(\mathbf{358})(\text{CH}_3\text{OH})](\text{ClO}_4)_2$ (a), $[\text{CoPb}(\mathbf{358})-(\text{NO})(\text{DMF})_2](\text{ClO}_4)]^+$ (b) and $[\text{CoPb}(\mathbf{358})(\text{NO}_2)(\text{DMF})_2](\text{ClO}_4)]^+$ (c) (adapted from Refs. [416,417]).

$(\text{NO})(\text{DMF})_2(\text{ClO}_4)](\text{ClO}_4)$ where the cobalt(III) ion resides in the N_2O_2 site and the lead(II) ion in the N_3O_2 site. The two metal ions, 3.511 Å apart, are doubly bridged by the phenolic and DMF oxygens [417]. The geometry about the cobalt(II) ion is pseudo-octahedral, with the two nitrogens and the two oxygens of the macrocycle on the equatorial plane and the nitrosyl nitrogen and the bridging DMF oxygen at the axial positions. The lead ion in the N_3O_2 site cannot reside within the cavity and has an eight coordinate geometry together with one bridging and one terminal DMF oxygen and one perchlorate oxygen (Fig. 242b). $[\text{CoPb}(\mathbf{358})(\text{NO})(\text{DMF})_2](\text{ClO}_4)]$ is oxidized with molecular oxygen to the nitro complex $[\text{CoPb}(\mathbf{358})(\text{NO}_2)(\text{DMF})_2](\text{ClO}_4)]\text{ClO}_4$ which has a dinuclear core very similar to that of the nitrosyl complex. The $\text{Co}\cdots\text{Pb}$ separation, triply bridged by the two phenolic oxygens and a DMF oxygen, is 3.537 Å. The cobalt(II) ion assumes a pseudo octahedral geometry with the N_2O_2 donor atoms of the macrocycle on the basal plane and the bridging DMF oxygen and the nitro nitrogen at the axial sites. The basal plane defined by the two oxygen and the two nitrogen atoms form a good coplane with very small deviations of the atoms. The eight coordinated geometry of the lead ion is formed by the N_3O_2 donors

of the macrocycle, by one bridging and one terminal DMF oxygen and one perchlorate oxygen (Fig. 242c).

NMR spectra, indicate that the DMF-bridged dinuclear cores of the nitrosyl and of the nitro complexes are retained in solution [417].

Heterodinuclear $\text{M}^{\text{II}}\text{Pb}^{\text{II}}$ complexes of $[\mathbf{358}]^{2+}$, having the cobalt(II), iron(II) or manganese(II) ion at the N_2O_2 site, are of particular interest because they are reactive towards molecular dioxygen [418]. At lower temperature in solution ($<20^\circ\text{C}$), the CoPb complex suffer an oxygenation reaction to form a peroxo complex $[\{\text{CoPb}(\mathbf{358})\}_2(\text{O}_2)](\text{ClO}_4)_4$ [418]. In this case, two oxygenation modes are possible with respect to the CoN_2O_2 plane, i.e. at the same side as the Pb(*syn*) or on the opposite side to the Pb(*anti*). Based on NMR spectroscopy of the peroxo complex, which lacks C_2 symmetry, the *syn* structure of the peroxo complex is proposed where the free rotation of the two $\{\text{CoPb}(\mathbf{358})\}$ entities with respect to the $\text{Co}-\text{O}-\text{O}-\text{Co}$ linkage is prohibited. The formation of the *syn* structure of the peroxo complex is supported by recognizing that the $\{\text{Co}^{\text{III}}(\text{OH})\text{Pb}\}$ complex, resulting from the hydrolytic substitution of the peroxo group ($\text{Co}^{\text{III}}-\text{O}-\text{O}-\text{Co}^{\text{III}} + 2\text{H}_2\text{O} = 2\text{Co}^{\text{III}}(\text{OH}) + \text{H}_2\text{O}_2$), has a *syn* core with a strong bonding interaction between the hydroxo oxygen and the neighbouring lead(II) ion. Based on this fact and together with the $\text{Pb}-\text{O}(\text{methanol})$ interaction in $[\text{CoPb}(\mathbf{358})(\text{CH}_3\text{OH})](\text{ClO}_4)_2$, it is inferred that the oxygenation in the *syn* mode is facilitated by a $\text{Pb}-(\text{O}_2)_2-\text{Pb}$ bonding interaction and this interaction prohibits the free rotation of the two CoPb entities with respect to the peroxo bond.

$[\text{FePb}(\mathbf{358})(\text{NCS})(\text{DMF})(\text{ClO}_4)]$, prepared by the reaction between $[\text{bis}(3\text{-formyl-5-methylsalicylidene})\text{ethylene-diaminato}]\text{iron(II)}$ and 1,5-diamino-3-azapentane in the presence of lead(II) ion followed by the addition of an equimolar amount of NaNCS [105], has a dinuclear $\text{Fe}^{\text{II}}\text{Pb}^{\text{II}}$ core bridged by the two phenolic oxygens with a $\text{Fe}\cdots\text{Pb}$ intermetallic separation of 3.438 Å (Fig. 243a). The iron(II) ion resides in the N_2O_2 site and assumes a square pyramidal geometry with an isothiocyanate nitrogen at the axial site. The basal N_2O_2 donor atoms form a near coplane. The lead(II) ion in the N_3O_2 site has a seven coordinate geometry with one DMF oxygen and one perchlorate oxygen at the axial sites. The N_3O_2 donor atoms resides on a near coplane. The geometry about lead can be regarded as a distorted pentagonal bipyramid with a DMF oxygen and a perchlorate oxygen at the axial sites. The magnetic moment at room temperature is $5.06\mu_{\text{B}}$. The complex behaves as a 1:1 electrolyte in DMF: the $\text{Fe}-\text{NCS}$ bond is retained but the perchlorate group is free from coordination [105].

Two distinct core structures have been recognized for the $\text{M}^{\text{II}}\text{Pb}^{\text{II}}$ complexes of $[\mathbf{358}]^{2+}$. In one core, the lead(II) ion is largely displaced from the mean molecular plane, owing to the mismatch between the ionic radius of the lead(II) ion and the cavity size of the N_3O_2 site and the axial ligand attached to M^{2+} is situated *syn* with respect to the lead ion. In another

core, the axial ligand attached to M^{2+} is situated *anti* with respect to the displaced lead ion. The *syn* core is found for $[\text{CoPb}(\mathbf{358})(\text{CH}_3\text{OH})(\text{ClO}_4)_2]$ and $[\text{CoPb}(\mathbf{358})(\text{OH})(\text{CH}_3\text{CN})_2]^{2+}$ and the *anti* core for $[\text{CoPb}(\mathbf{358})(\text{NO})(\text{DMF})_2(\text{ClO}_4)]^+$ and $[\text{ZnPb}(\mathbf{358})(\text{CH}_3\text{OH})(\text{DMF})(\text{ClO}_4)]^+$ [105]. The core structure of $[\text{FePb}(\mathbf{358})(\text{NCS})(\text{DMF})(\text{ClO}_4)]$ can be depicted as an intermediate between the *syn* and *anti* core, indicating that the two cores can be interconverted through an intermediate core. The *syn* and *anti* cores occur when the metal in the N_2O_2 site resides within the N_2O_2 cavity and hence the N_3O_2 site has little flexibility to accommodate the large lead(II) ion within its N_3O_2 cavity. When M^{2+} in the N_2O_2 site is largely displaced from the N_2O_2 plane, the N_3O_2 site has considerable flexibility for accommodating the lead(II) ion within its N_3O_2 cavity, providing the intermediate core [105] (Fig. 243b).

A DMF solution of $[\text{FePb}(\mathbf{358})(\text{NCS})(\text{DMF})(\text{ClO}_4)]$ undergoes an immediate colour change from red to yellow upon exposure to air, giving rise to $([\text{FePb}(\mathbf{358})(\text{NCS})(\text{DMF})(\text{ClO}_4)]_2(\text{O}))$. The infrared spectrum of the oxidized complex is very similar to that of the starting complex, except for a new strong band at 845 cm^{-1} , assigned to the $\nu_{\text{as}}(\text{Fe}-\text{O}-\text{Fe})$ mode. The complex behaves

as a 2:1 electrolyte in DMF. In the range 50–300 K an antiferromagnetic interaction operates ($-J = 90.6\text{ cm}^{-1}$), compatible with an oxo-bridged diiron(III) complex [105].

The acyclic complex $[N,N'$ -di(3-formyl-5-methylsalicydene)ethylenediaminato]cobalt(II), when reacted with 3-thia-1,5-pentanediamine respectively in the presence of copper(I) or lead(II) ions in methanol, forms the complexes $[\text{CoCu}(\mathbf{359})(\text{ClO}_4)\cdot 5\text{DMF}]$ or $[\text{CuPb}(\mathbf{359})(\text{ClO}_4)_2]$ where the cobalt(II) is of low spin [419]. $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\mathbf{359})(\text{ClO}_4)]$ was prepared similarly [414]. In $[\text{Co}^{\text{II}}\text{Cu}^{\text{I}}(\mathbf{359})(\text{ClO}_4)\cdot 5\text{DMF}]$ (Fig. 244a) the cobalt(II) ion resides in the N_2O_2 site and the copper(I) ion in the $\text{N}_2\text{O}_2\text{S}$ site. The perchlorate group and the DMF molecules are free from coordination and are captured in the crystal lattice. The $\text{Co}\cdots\text{Cu}$ intermetallic separation bridged by the two phenolic oxygens is $3.355\text{ \AA}$. The cobalt(II) ion has a planar geometry; also the copper(I) ion in the $\text{N}_2\text{O}_2\text{S}$ site has a planar four coordinate geometry found by two phenolic oxygens and two imine nitrogens. The thioether atom on the lateral chain is located at an axial site of the copper(I) center but the $\text{Cu}-\text{S}$ separation ($3.075\text{ \AA}$) is too large to be considered as a coordination bond. The copper(I) ion is displaced by $0.106\text{ \AA}$ from the least-squares plane toward

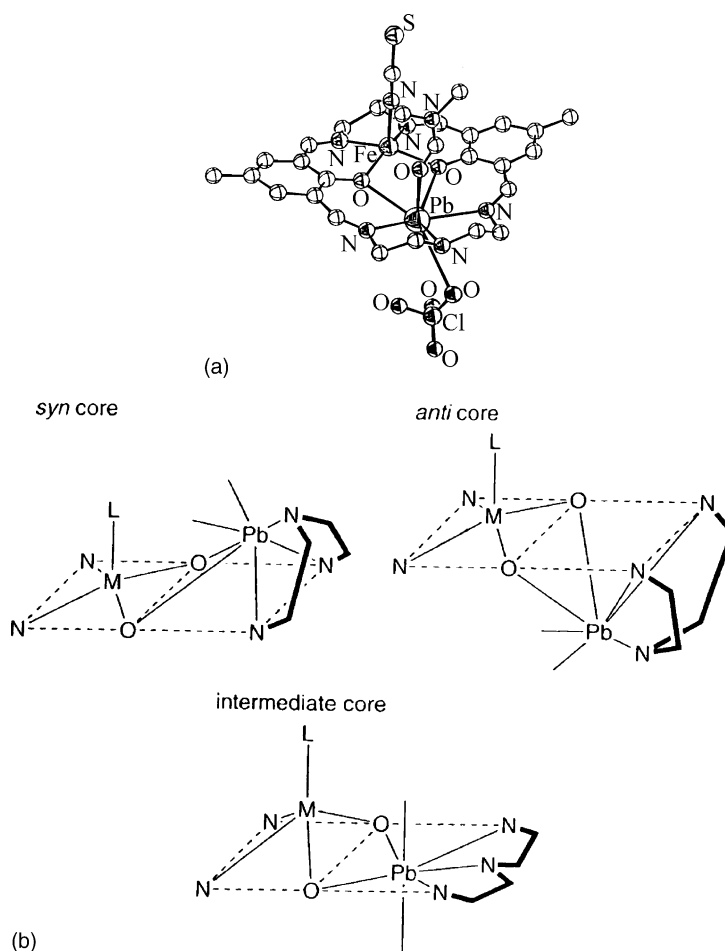
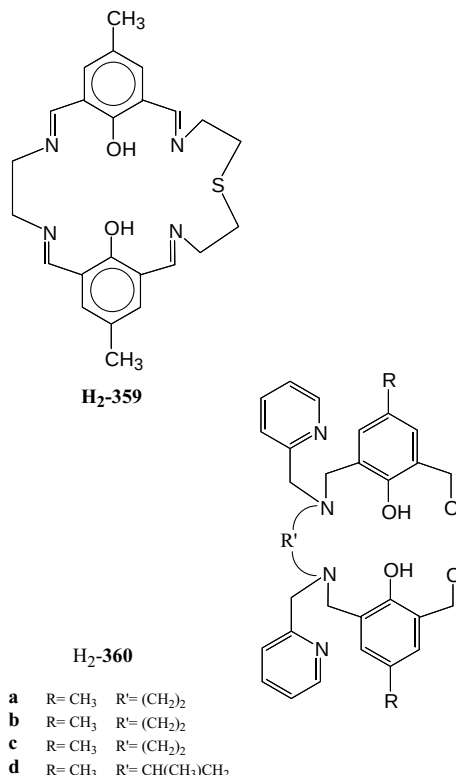


Fig. 243. Structure of $[\text{FePb}(\mathbf{358})(\text{NCS})(\text{DMF})(\text{ClO}_4)]$ (a) and the *syn*, *anti* and intermediate core structure about the MPb complexes (b) (adapted from Ref. [105]).

the sulfur. It must be emphasized that the configuration of the $\{\text{CuN}_2\text{O}_2\}$ chromophore is largely distorted from a regular square [419].



$[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\mathbf{359})]\text{ClO}_4 \cdot 5\text{DMF}$ (Fig. 244b) has a dinuclear core similar to that for the $\text{Co}^{\text{II}}\text{Cu}^{\text{I}}$ complex. The two metal ions, bridged by the phenolic oxygens, are 3.364 Å apart. The copper(II) in the N_2O_2 site has an essentially planar geometry. The thioether atom on the lateral chain is positioned at an axial site of the copper(I), but the Cu–S separation is very large [419].

In $[\text{CoPb}(\mathbf{359})(\text{DMF})_2](\text{ClO}_4)_2$ (Fig. 240c) the cobalt(II) ion resides in the N_2O_2 site and the lead(II) ion in the $\text{N}_2\text{O}_2\text{S}$ site; the $\text{Co} \cdots \text{Pb}$ intermetallic separation is 3.37 Å. The cobalt(II) ion has a square pyramidal geometry with a DMF oxygen at the axial site; it is displaced by 0.12 Å from the basal least-squares plane toward the axial DMF oxygen. The lead(II) ion has apparently a six coordinated geometry along with a DMF oxygen. The DMF oxygen at the axial site of the cobalt(II) ion forms a bridge to the lead(II) ion; thus the lead ion can be regarded as seven coordinated. Such a bridge of the axial donor atom to the adjacent lead(II) ion has been found in the related $\text{Co}^{\text{II}}\text{Pb}^{\text{II}}$ and $\text{Co}^{\text{III}}\text{Pb}^{\text{II}}$ complexes [419].

A comparison of the cyclic voltammetry in DMF of $[\text{CoCu}(\mathbf{359})]\text{ClO}_4 \cdot 5\text{DMF}$, $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\mathbf{359})]\text{ClO}_4$ and $[\text{CoPb}(\mathbf{359})](\text{ClO}_4)_3$ indicates a $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ process in the $\text{N}_2\text{O}_2\text{S}$ site at similar potentials (–0.25 and –0.26 V, respectively). The $\text{Co}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Co}^{\text{II}}\text{Pb}^{\text{II}}$ complexes show the $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ process at different potentials (–1.30 and –1.02 V, respectively). The $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ process of the $\text{Co}^{\text{II}}\text{Cu}^{\text{I}}$ complex is irreversible and shows only an anodic peak at +0.8 V.

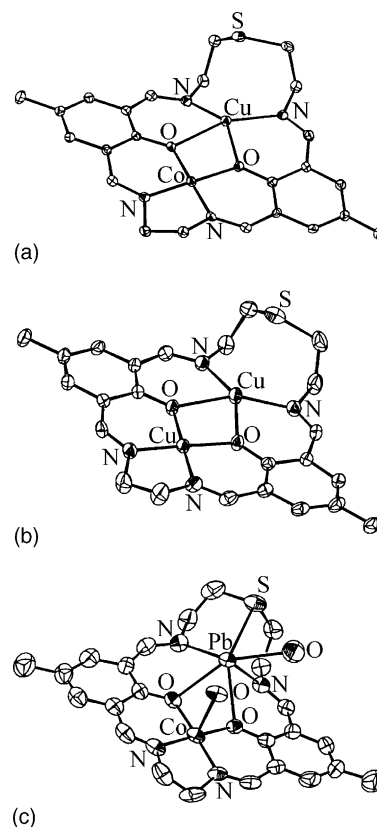


Fig. 244. Structures of $[\text{Co}^{\text{II}}\text{Cu}^{\text{I}}(\mathbf{359})]^+$ (a), $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\mathbf{359})]^+$ (b) and $[\text{Co}^{\text{II}}\text{Pb}^{\text{II}}(\mathbf{359})(\text{DMF})_2]^{2+}$ (c) (adapted from Ref. [419]).

The $\text{Co}^{\text{II}}\text{Cu}^{\text{I}}$ complex in DMF is very sensitive to oxygenation and is oxidized at –50 °C. The $\text{Co}^{\text{II}}\text{Pb}^{\text{II}}$ complex is oxygenated at 0 °C to form a peroxo dimer ($\text{Pb}^{\text{II}}\text{Co}^{\text{III}}\text{—O—O—Co}^{\text{III}}\text{Pb}^{\text{II}}$): the high sensitivity of the $\text{Co}^{\text{II}}\text{Cu}^{\text{I}}$ complex to dioxygen has been explained by the irreversible oxidation to a $\text{Co}^{\text{III}}\text{Cu}^{\text{II}}$ species through an intramolecular-type peroxo complex ($\text{Co}^{\text{III}}\text{—O—O—Cu}^{\text{II}}$). Thus $\text{Co}^{\text{II}}\text{Cu}^{\text{I}}$ complex is exceptionally reactive toward dioxygen so as to be converted into a $\text{Co}^{\text{III}}\text{Cu}^{\text{II}}$ species. This fact strongly suggests an interplay of the cobalt(II) and copper(I) ions in the oxygenation providing an intramolecular m-peroxo complex $[\text{Co}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{359})\text{—}(\text{O}_2^{2+})]^+$. The intramolecular peroxo complex must be equilibrated with the peroxo dimer $[\{\text{Co}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{359})\}_2\text{—}(\text{O}_2^{2+})]^{4+}$ through the superoxo cobalt complex $[\text{Co}^{\text{III}}\text{Cu}^{\text{I}}(\mathbf{359})(\text{O}_2^-)]^+$. The instability of the intramolecular m-peroxo species of the $\text{Co}^{\text{II}}\text{Cu}^{\text{I}}$ complex is notable. The oxidation of the copper(I) ion accompanies a large configuration change about the metal ion, from the distorted $\{\text{Cu}^{\text{I}}\text{N}_2\text{O}_2\}$ to a planar $\{\text{Cu}^{\text{II}}\text{N}_2\text{O}_2\}$; this facilitates the hydrolytic (or solvolytic) replacement of the peroxo group [419].

The reaction of $[N,N'$ -bis(3-formyl-5-methylsalicylidene)ethane-1,2-diaminato] copper(II) with 1,5-diamino-3-thiapentane and $\text{Pb}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ethanol and in the presence of HClO_4 , gives rise to $[\text{Cu}(\mathbf{359})]$ [419]. In this condensation reaction the lead(II) ion, employed with the aim to form the corresponding hetero-dinuclear complex, plays an essential role in the formation of the macrocycle

despite the lack of the ion in the product, because the non-template reaction between [*N,N'*-bis(3-formyl-5-methylsilylidene)ethane-1,2-diaminato] copper(II) and 3-thiapentane-1,5-diamine gave a tarry material. The involvement of the non-stoichiometric amount of perchloric acid suggests the formation of two complexes in this reaction $[\text{Cu}(\mathbf{359})]$ and $[\text{Cu}(\text{H}_2\text{-}\mathbf{359})](\text{ClO}_4)$. The reaction mixture, acidified to $\text{pH} \approx 3$ with perchloric acid, forms the diperchlorate salt $[\text{Cu}(\text{H}_2\text{-}\mathbf{359})](\text{ClO}_4)_2$ [419]. This complex, by reaction with $\text{M}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$) in methanol and in the presence of triethylamine followed by the addition of sodium thiocyanate, produces $[\text{CuM}(\mathbf{359})(\text{NCS})_2] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$); the corresponding complexes with $\text{M} = \text{Mn}^{2+}$ or Fe^{2+} were not precipitated. On the other hand, the 1:1 reaction of $[\text{Cu}(\text{H}_2\text{-}\mathbf{359})](\text{ClO}_4)_2$ and copper(II) perchlorate, in the presence of triethylamine forms the homo-dinuclear complex $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$. Similarly, the reaction of $[\text{Cu}(\text{H}_2\text{-}\mathbf{359})](\text{ClO}_4)_2$ with copper(I) perchlorate in the open air produces the $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ complex $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$. Apparently the $\text{N}_2\text{O}_2\text{S}$ donor site of $[\mathbf{359}]^{2-}$ has a high affinity for both copper(II) and copper(I) ions. It is also noteworthy that the copper(I) oxidation state is much stabilized in $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$, as judged from the stability towards molecular oxygen, probably due to donation from the thioether sulfur to the copper(I) ion [419].

The X-ray analysis of $[\text{CuZn}(\mathbf{359})(\text{NCS})_2] \cdot \text{DMF}$ reveals a discrete CuZn dinuclear structure with the macrocycle $[\mathbf{359}]^{2-}$. The copper(II) ion resides at the N_2O_2 site and assumes a square pyramidal geometry with the nitrogen and oxygen donor atom of the macrocycle at the basal plane and the nitrogen atom of a thiocyanate ion at the apex (Fig. 245). The copper(II) ion is 0.29 Å from the basal least-squares plane towards the apical nitrogen atom. The zinc(II) ion occupies the N_2SO_2 site and also assumes a square pyramidal geometry with the nitrogen and the oxygen atoms at the basal plane and the nitrogen of the thiocyanate ion at the apex. The deviation of the zinc ion from the basal least-squares plane towards thiocyanate nitrogen is 0.36 Å. The two isothiocyanato nitrogens, bound to the copper and zinc ions, are *trans* towards each other with respect to the macrocycle. The macrocycle forms a near coplane.

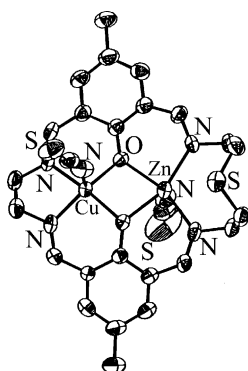


Fig. 245. Structure of $[\text{CuZn}(\mathbf{359})(\text{NCS})_2]$ (adapted from Ref. [419]).

$[\text{CuM}(\mathbf{359})(\text{NCS})_2] \cdot \text{H}_2\text{O}$ behaves as 1:1 electrolytes in DMF. It is likely that the thiocyanate ion weakly bonded to the copper(II) ion is dissociated in DMF. $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)$ behave respectively as 2:1 and 1:1 electrolytes in DMF [419].

$[\text{Cu}(\text{H}_2\text{-}\mathbf{359})](\text{ClO}_4)_2$, $[\text{CuZn}(\mathbf{359})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)$ have a magnetic moment characteristic for one unpaired electron while $[\text{CuCo}(\mathbf{359})(\text{NCS})_2]$, $[\text{CuNi}(\mathbf{359})(\text{NCS})_2]$ and $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$ show a subnormal magnetic moment at room temperature, suggesting an antiferromagnetic spin-exchange interaction within each molecule ($J = -32 \text{ cm}^{-1}$ for CuCo, -90 cm^{-1} for CuNi and -440 cm^{-1} for Cu_2) [419]. $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$ shows a very strong antiferromagnetic interaction relative to the similar dinuclear copper(II) complex containing a NH group instead of S ($J = -62 \text{ cm}^{-1}$).

The solution EPR spectra of $[\text{Cu}(\text{H}_2\text{-}\mathbf{359})](\text{ClO}_4)_2$, $[\text{CuZn}(\mathbf{359})(\text{SCN})_2]$ and $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)$ are typical of planar or axially distorted copper(II) compounds. Thus, the spin is localized in the mixed-valence $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ complex. $[\text{CuCo}(\mathbf{359})(\text{NCS})_2]$ showed no EPR signal at liquid-nitrogen temperature, probably owing to the magnetic interaction between the copper(II) and cobalt(II) ions. Similarly, $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$ is EPR silent because of the strong antiferromagnetic interaction between the two copper(II) ions.

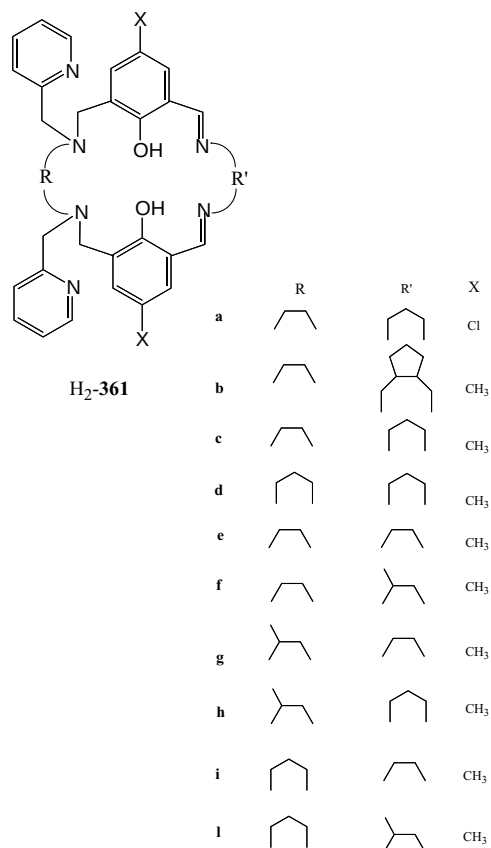
$[\text{CuNi}(\mathbf{359})(\text{NCS})_2]$ shows fairly well resolved EPR signals when measured as a frozen DMF solution at liquid-nitrogen temperature. The spectrum is regarded as an axial pattern with $g_{\text{II}} \approx 2.1$ and $g_{\perp} \approx 2.2$ despite very poor resolution of the g_{II} component. The order $g_{\perp} > g_{\text{II}}$ corresponds to an axially distorted d^9 configuration with one unpaired electron in the d_z^2 orbital [419]. The energy separation between the spin-singlet ground state and spin-quartet excited state for $[\text{CuNi}(\mathbf{359})(\text{NCS})_2]$ ($S_{\text{Ni}} = 1$) ($-3J = 246 \text{ cm}^{-1}$) shows that the thermal population of the spin-quartet excited state is negligibly small at liquid-nitrogen temperature and the EPR signals observed for the CuNi complex arise from the spin-doublet ground state. In general spin coupling through $d_{x^2-y^2}(\text{Cu})-d_{x^2-y^2}(\text{Ni})$ in a $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ complex is strongly antiferromagnetic as demonstrated for many dinuclear copper(II) complexes as well as for $[\text{CuNi}(\mathbf{359})(\text{NCS})_2]$, one unpaired electron remaining in the $d_z^2(\text{Ni})$ orbital (local *x* and *y* axes are taken as along the donor atoms in the equatorial plane). The observed spectral feature $g_{\perp} > g_{\text{II}}$ is in accord with this, but the broad g_{II} feature, probably due to the copper nucleus, suggests the delocalization of one unpaired electron over the CuNi core.

$[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$ shows a reversible couple at +0.07 V (versus SCE) and a quasi-reversible couple at -1.02 V , assigned to the stepwise reduction processes $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$, respectively. Essentially the same cyclic voltammogram was obtained for $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)$ (+0.09 and -1.01 V). The $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ complex of $[\mathbf{358}]^{2-}$ shows corresponding reduction waves at -0.35 and -1.09 V in DMSO. In spite of the different solvents in the electrochemical measurements, $[\text{Cu}_2(\mathbf{359})](\text{ClO}_4)_2$

shows the first reduction (of the copper(II) ion at the N_2O_2S donor site) at a significantly higher potential. The positive shift of the reduction potential and the good reversibility of the first wave are indicative of the stabilization of the copper(I) oxidation state at the N_2O_2S site, effected by the coordination of thioether sulfur [419].

8.3.2. Complexes derived from asymmetric compartmental ligands containing additional donor auxiliaries

The introduction of a donor auxiliary to each amino nitrogen provides new macrocycles having a potentially six coordinated aminic N_4O_2 site and a four coordinated iminic N_2O_2 site. Such macrocycles, having two pyridyl auxiliaries attached to the amino nitrogens, were prepared by condensation of the acyclic dialdehyde precursors $H_2\text{-}360$ or their mononuclear metal complexes with the appropriate diamine to give the mononuclear complexes $[M(\mathbf{361})]$ ($M = Zn^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}$, etc.) [420–422]. The further reaction with a second different metal ion M'^{n+} allows to the formation of the hetero-dinuclear complexes $[MM'(\mathbf{361})]^{n+}$. The preparation of acyclic diformyl derivative is the most relevant goal of the entire preparative pathway. In a first approach a nine-step synthesis was successfully proposed. By this procedure compounds with different aliphatic chains have been synthesized [420–422].

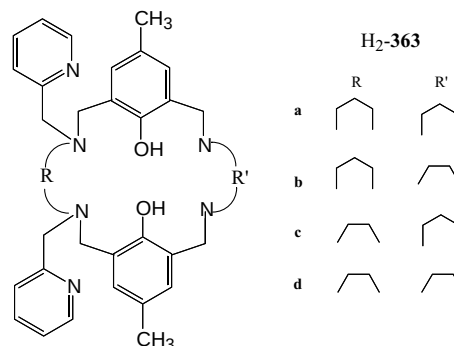
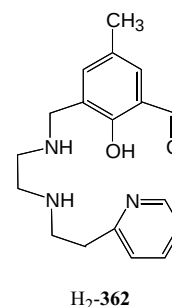


In an alternative simpler method, the ligands bearing picolyl pendant arms on the amine nitrogen donors have been synthesized via the Mannich condensation in alcoholic

solution of 5-substituted salicylaldehyde, formaldehyde and N,N' -bis(2-pyridylmethyl)-1,2-diaminoethane [423] and purified by column chromatography; alternatively the zinc(II) or nickel(II) complexes can be prepared in situ by the addition of the metal acetate and 2 equiv. of triethylamine to the ethanol solution of the unpurified diformyl derivatives. The neutral mononuclear acyclic complexes precipitate from the solution. H_2S gas has been successfully used for the demetallation of $[Zn(\mathbf{360a})]$. This method, however, does not work for $[Zn(\mathbf{360b})]$. The most successful procedure for isolation of $H_2\text{-}360b$ uses the precipitation of insoluble zinc(II) oxalate upon treatment of $[Zn(\mathbf{360b})]$ with an equivalent amount of $H_2C_2O_4$ in a two-phase water/chloroform system. The protonated ligand, in the form of its tetrabromozincate salt $[H_6\text{-}360b][(ZnBr_4)_2]$, can also be isolated, by treating an ethanol suspension of $[Zn(\mathbf{360b})]$ with HBr gas.

In the structure of $[H_6\text{-}360b][(ZnBr_4)_2 \cdot 2H_2O]$, the cation is tetraprotonated on all four nitrogen atoms and shows an extended conformation, probably arising from repulsions between the four positively charged atoms. The structure is stabilized by intramolecular stacking interactions between the pyridine and phenolic rings (Fig. 246). $H_2\text{-}360b$ reacts with $M(CH_3COO)_2 \cdot 4H_2O$ ($M = Cu^{2+}, Ni^{2+}$) to form $M(\mathbf{360b})$ and with $CrCl_2$, in the presence of air and KOH as base source, to give rise to $[Cr(\mathbf{360b})(Cl)]$ [423].

Attempts to incorporate a second metal ion into the O_2O_2 compartment of these mononuclear complexes failed. In an attempt to isolate the homo-dinuclear nickel(II) complex from the reaction of $[Ni(\mathbf{360b})]$ with $Ni(ClO_4)_2$, the compound $[Ni_2(\mathbf{362})](ClO_4)_2$ was isolated, possibly originated by a retro-Mannich rearrangement in consequence of a decomposition of the acyclic ligand $H_2\text{-}360b$ [423].



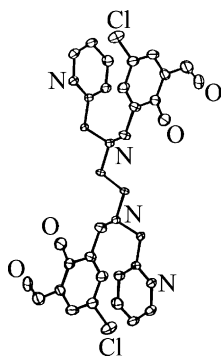


Fig. 246. Structure of $[H_6\text{-}360b]^{4+}$ (adapted from Ref. [423]).

Mononuclear nickel(II) and zinc(II) complexes are obtained when the related acyclic complexes $[M(360)]$ are reacted with diamine; on the contrary the chromium(III) acyclic complex gives rise to the acyclic acetal derivative in methanol and the expected cyclic complex in DMF. The structure of the mononuclear $[Zn(H_2\text{-}361a)](ClO_4)_2 \cdot 1/2CH_3CN$ shows the ligand is significantly distorted. The zinc(II) ion is pseudo-octahedrally coordinated to two amine nitrogen donors, two phenolic oxygen donors and two *trans* pyridine nitrogens; the two Schiff base nitrogens in the open site of the ligand are presumed to be protonated. The cavity at the unfilled site of the ligand has diagonal distances of 3.957 Å suitable for a second 3d transition metal ions. Although the main N_2O_2 ligand unit is reasonably planar and the zinc ion is not displaced out of the plane ZnN_2O_2 , the $Zn-N(py)$ directions are far from perpendicular to this plane (Fig. 247). This is due to the pendant arms being shorter than ideal. The structure of $[Ni(H_2\text{-}361a)](ClO_4)_2$ is similar to that of the zinc analogue, where a much smaller twist than the corresponding zinc(II) complex occurs [423].

The reaction of $[Ni(H_2\text{-}361a)](ClO_4)_2$ with nickel(II) acetate in the presence of 2 equiv. of triethylamine gives rise to $[Ni_2(361a)](ClO_4)_2$. Similarly, reaction of $[Cr(361a)-(Cl)]$ with copper(II) chloride produces $[CrCu(361a)](Cl)_3$. In the latter case, no dichromium or dicopper complexes were formed, confirming the absence of scrambling of different metal ions [423].

Slow addition of the chiral diamine (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane to the acyclic mononuclear complexes gives the desired macrocyclic complexes salts $[M(H_2\text{-}361b)](PF_6)_2$ ($M = Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}$),

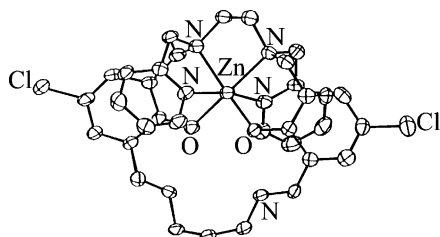


Fig. 247. Structure of $[Zn(H_2\text{-}361a)]^{2+}$ (adapted from Ref. [423]).

isolated as their bis-(hexafluorophosphate) salts. The acetic acid generated serves to catalyze Schiff base formation and also provides protons for the N_2O_2 site [424].

The mononuclear copper(II) complex is more difficult to prepare in pure form; the bimetallic species $[Cu_2(361b)]-(PF_6)_2$, and a side product often formed concomitant with the desired product. Under appropriate conditions the formation of the homo-dinuclear copper complex could be suppressed. The cobalt(III) complex $[Co(H_2\text{-}361b)](PF_6)_3$ was prepared in high yield by oxidation of the cobalt(II) complex $[Co(H_2\text{-}361b)](PF_6)_2$ with ferrocenium hexafluorophosphate in acetonitrile solution. Attempts to oxidize the mononuclear manganese(II) complex by this method failed [424].

The macrocyclic complexes of the divalent metal ions are 2:1 electrolytes in acetonitrile solutions and the cobalt(III) complex is a 3:1 electrolyte. The ^1H NMR spectra of $[Zn(H_2\text{-}361b)(H^+)_2]^{2+}$ and $[Co(H_2\text{-}361b)]^{3+}$ indicate that a single diastereomer is formed in each case and that the structures possess C_2 symmetry, where the two pyridine ligands are *trans*-disposed. This C_2 symmetric structure and the presence of a single diastereomer induced by the chiral diamine is also likely to obtain for the other monometallic complexes. NMR data are consistent with the N_2O_2 site hydrogen-bonded structure [422].

$[Mn(H_2\text{-}361b)](PF_6)_2$ contains a manganese(II) ion in the N_4O_2 site. A highly twisted structure is observed in which the phenolic fragments are skewed one above and one below the mean macrocyclic plane. The macrocyclic cavity defined by the two phenolic oxygen atoms and the two imine nitrogen atoms is large. The four potential donor atoms lie essentially in one plane. The absolute configuration about the manganese(II) in $[Mn(H_2\text{-}361b)]^{2+}$ is Λ (Fig. 248a) [422].

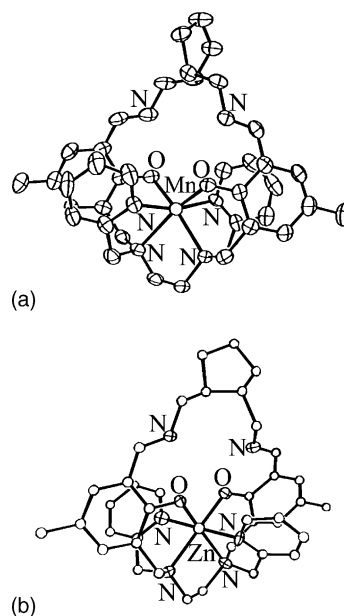


Fig. 248. Structures of $[Mn(H_2\text{-}361b)]^{2+}$ (a) and $[Zn(H_2\text{-}361b)]^{2+}$ (b) (adapted from Refs. [422,424]).

Also in $[\text{Zn}(\text{H}_2\text{-361b})](\text{PF}_6)_2$ the zinc(II) ion is bound in the N_4O_2 site of $\text{H}_2\text{-361b}$. The topological chirality is Δ , opposite to that found for the manganese(II) complex (Fig. 248b) [424]. In this zinc(II) complex the ligand $\text{H}_2\text{-361b}$ assumes a less twisted conformation where the phenoxide groups are roughly in the mean macrocyclic plane. The macrocyclic cavity of the mono zioic(II) complexes is somewhat contracted compared to the manganese(II) structure. Hydrogen bonding is believed to exist across two phenolic and two iminic nitrogen atoms. Three of the atoms defining this cavity, two phenolic oxygens and one iminic nitrogens, lie approximately in the macrocyclic plane, whereas the fourth atom, the other iminic nitrogen, is projected out of the plane, accounting for the differences in diagonal distances and breaking the C_2 symmetry of the molecule in the crystal. The ^1H NMR spectrum, however, indicates a C_2 symmetric structure, which implies either that a different conformation exists in acetonitrile solution than in the crystal or that the diimine moiety is rapidly oscillating in solution.

The heterobimetallic complexes $[\text{CoM}(\text{361b})(\text{Cl})](\text{PF}_6)_2$ ($\text{M} = \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$) were isolated by adding an ethanol solution containing the appropriate metal acetate and LiCl to an acetonitrile solution of $[\text{Co}(\text{H}_2\text{-361b})](\text{PF}_6)$. The corresponding $\text{Co}^{\text{III}}\text{Cu}^{\text{II}}$ complex, $[\text{CoCu}(\text{361b})](\text{PF}_6)_3$, was isolated without the chloro ligand [424]. In acetonitrile the chloro complexes were found to be 2:1 electrolytes, indicating that the chloro ligand is bound to the metal ion in these solutions while the copper complex was found to be a 3:1 electrolyte. Since cobalt(III) forms very stable and stereochemically inert complexes, all of the heterobimetallic complexes have the second metal exclusively in the Schiff base site and preserve the C_2 symmetric structure of the original $[\text{Co}(\text{H}_2\text{-361b})]^{3+}$ complex. The C_2 symmetric of the diamagnetic $[\text{CoZn}(\text{361b})]^{3+}$ complex prepared in acetone by the addition of silver triflate to a solution of $[\text{CoZn}(\text{361b})(\text{Cl})]^{2+}$ was confirmed by ^1H NMR.

In $[\text{CoCu}(\text{361b})(\text{CH}_3\text{CN})](\text{PF}_6)_3$ the cobalt(III) ion is six coordinated and has a C_2 symmetric structure with *trans*-disposed pyridine ligands. Also this complex has the twisted phenoxide groups lying roughly in the mean macrocyclic plane and one of the imine nitrogens is projected out of the macrocyclic plane. The acetonitrile ligand is loosely bound to the Schiff base site copper(II) ion. This five coordinated copper(II) center resembles a distorted trigonal bipyramid (Fig. 249a). The absolute configuration of the molecule was determined by X-ray diffraction and the topological chirality about the cobalt(III) is Δ . This is opposite to what was found for $[\text{Mn}(\text{H}_2\text{-361b})]^{2+}$ but is the same as was observed for $[\text{Zn}(\text{H}_2\text{-361b})]^{2+}$.

$[\text{MCu}(\text{361b})]^{2+}$ ($\text{M} = \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$) as well as the dicopper complex were prepared by adding a 1,4-dioxane solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to an acetonitrile solution containing $[\text{M}(\text{H}_2\text{-361b})](\text{PF}_6)_2$ and triethylamine [424]. $[\text{CoCu}(\text{361b})](\text{PF}_6)_2$ is air sensitive in solution and its preparation required the rigorous exclusion of oxygen. On

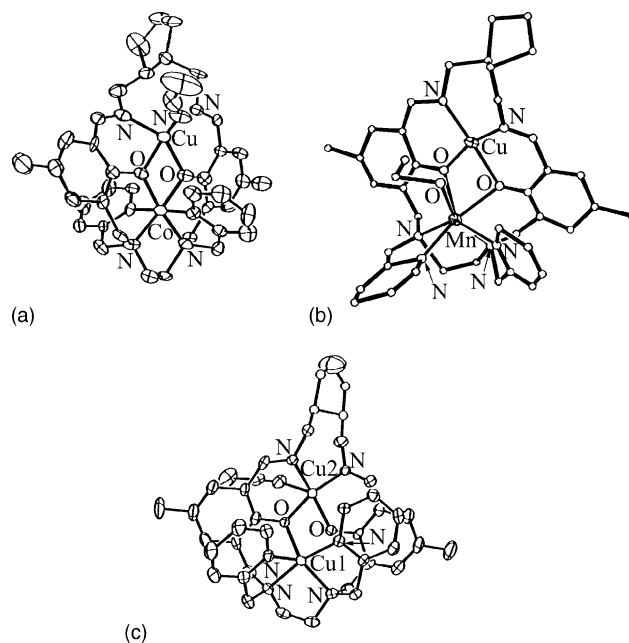


Fig. 249. Structures of $[\text{CoCu}(\text{361b})(\text{CH}_3\text{CN})]^{3+}$ (a), $[\text{MnCu}(\text{361b})(\text{C}_2\text{H}_5\text{OH})]^{2+}$ (b) and $[\text{Cu}_2(\text{361b})(\text{CH}_3\text{CN})]^{2+}$ (c) (adapted from Refs. [423,424]).

the contrary, it is stable in air as the solid. The air sensitivity of $[\text{CoCu}(\text{361b})]^{2+}$ contrasts with the air stability of $[\text{Co}(\text{H}_2\text{-361b})]^{2+}$ in solution [424].

An addition of an ethanol solution of $\text{Mn}(\text{CH}_3\text{COO})_2$ to an acetonitrile solution of $[\text{Mn}(\text{H}_2\text{-361b})]^{2+}$ did not result in the formation of the dimanganese complex. Rather, the monometallic starting material was recovered [424]. The formation of $[\text{Mn}_2(\text{361b})(\text{Cl})](\text{PF}_6)$ can be achieved by the addition of LiCl and 2 equiv. of triethylamine. In a similar way $[\text{Ni}_2(\text{361b})(\text{Cl})](\text{PF}_6)$ was prepared. Once isolated as yellow crystals the dimanganese(II) complex is air-stable. Aerated solutions of $[\text{Mn}_2(\text{361b})(\text{Cl})]^+$ however, gradually turn into $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{H}_2\text{-361b})(\text{Cl})_2](\text{PF}_6)$ and, after slow evaporation of the solvent, green needles can be isolated. $[\text{CuZn}(\text{361b})(\text{Cl})](\text{PF}_6)$ was prepared in a manner analogous to that described for the dimanganese complex [424].

Spectroscopic and X-ray data on $[\text{MnCu}(\text{361b})(\text{C}_2\text{H}_5\text{OH})](\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$ are consistent with the presence of an equal mixture of $[\text{MnCu}(\text{361b})(\text{C}_2\text{H}_5\text{OH})](\text{PF}_6)_2$ and $[\text{MnCu}(\text{361b})(\text{CH}_3\text{COO})](\text{PF}_6)$. Two molecules are present in the unit cell which contains only three PF_6^- ions. Both of the manganese(II) ions in the N_4O_2 site are seven coordinated [424]. The ligand adopts an unsymmetrical structure with both of the pyridine ligands coordinating to manganese(II) ion on one side of the mean macrocyclic plane. The seventh ligand (ethanol or acetate) coordinates the manganese(II) adjacent to the two *cis*-disposed pyridine ligands. The larger radius of spin-free manganese(II) presumably allows the metal to achieve seven coordination. The copper(II) ion in this complex is four coordinated [423,424] (Fig. 249b).

In $[\text{Cu}_2(\mathbf{361b})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ (Fig. 249c) the copper(II) ion in the Schiff base site forms a distorted square pyramidal structure while the copper(II) in the other site adopts a distorted square pyramidal geometry by breaking a bond to one of the phenolic oxygen atoms. In order to accommodate both metals, the macrocyclic ligand assumes a configuration with the pyridine groups *cis* to each other [424].

An addition of 2 equiv. of $\text{M}(\text{CH}_3\text{COO})_2$ ($\text{M} = \text{Zn}^{2+}$, Co^{2+} , Mn^{2+}) to $\text{H}_2\text{-360a}$ followed by reaction with either ethylenediamine or *o*-phenylenediamine yielded intractable products; the same procedure employing the larger 1,3-diaminopropane formed the homo-dinuclear complexes which by addition of NH_4PF_6 , have been recovered as crystalline products with varying amounts of solvent of crystallization. The subsequent addition of chloride ions gave $[\text{M}_2(\mathbf{361c})(\text{Cl})](\text{PF}_6)$ [424,425].

The cyclization of $[\text{M}(\mathbf{360a})]$ with 1,3-diaminopropane under acid catalysis, followed by the addition of the second metal salt in a 1:1 molar ratio, represents a useful alternative pathway for the synthesis of homo- and especially hetero-dinuclear complexes. The complexes containing cobalt(II) or manganese(II) were inert to O_2 in the solid state but displayed variable reactivity in acetonitrile solution. Exposure of $[\text{ZnMn}(\mathbf{361c})(\text{Cl})]^+$ and $[\text{Mn}_2(\mathbf{361c})(\text{Cl})]^+$ to air in acetonitrile caused the yellow solutions to turn brown, the latter complex reacting faster. After air was bubbled through the solution of the dimanganese(II) precursor for 24 h, the mixed-valence complex $[\text{Mn}_2(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})](\text{PF}_6)$ was isolated as brown-black crystals [424,425]. This complex contains a manganese(III) ion in the N_2O_2 site and a manganese(II) ion is retained in the closed site. The same $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ complexes can be prepared by the addition of ferrocenium in the presence of Cl^- ions to the dimanganese(II) precursor. Attempts to prepare a $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ species by the addition of amounts in excess of 2 equiv. of ferrocenium yielded the same $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ product, suggesting that the oxidation of the manganese(II) ion in the N_4O_2 site is more difficult after the manganese(II) ion in the N_2O_2 site has been oxidized.

When exposed to O_2 in CH_3CN , $[\text{ZnMn}(\mathbf{361c})(\text{Cl})]^+$ gives a brown powder which consists of the starting material and probably MnO . Addition of varying equivalents of $[\text{Fe}(\text{Cp})_2]^+$ to a solution of $[\text{ZnMn}(\mathbf{361c})(\text{Cl})]$ led to the same products. $[\text{ZnCo}(\mathbf{361c})(\text{Cl})]^+$ and $[\text{Co}_2(\mathbf{361c})(\text{Cl})]^+$ species were essentially inert to O_2 in acetonitrile solutions. Under similar conditions $[\text{Co}_2(\mathbf{361c})]^{2+}$ slowly darkened over several days but no clean products could be isolated.

As expected, the dizinc complex is not a catalyst for epoxidation and the dicobalt species shows marginal catalytic activity. The manganese species, however, are effective catalysts; $[\text{ZnMn}(\mathbf{361c})(\text{Cl})]^+$, where the manganese(II) ion resides in the N_2O_2 site, and the corresponding complex $[\text{MnZn}(\mathbf{361c})(\text{Cl})]^+$ where the manganese(II) ion is in the N_4O_2 site show similar catalytic activity, suggesting that the manganese(II) ion in the N_4O_2 site dissociates one of the

pyridyl ligands to open a site for forming the catalytically active oxo species.

The dimanganese species are the most effective catalysts. The two dimanganese complexes lead essentially to the same product ratios, and both catalysts consume 90% of the substrate. It seems probable, therefore, that the same catalytically active intermediate is being generated from the two dimanganese catalytic precursors. The fact that the mixed-valent dimanganese complex has a much faster initial rate may reflect the greater ease of attaining the catalytically active species for the mixed-valent catalyst precursor. At the midpoint of reaction, both catalysts have similar rates. All of the catalysts become ineffective after a varying number of turnovers, which is probably associated with the destruction of the ligand. A comparison of the catalysis using the similar mononuclear Schiff base complex $[\text{Mn}(\mathbf{207b})]$ with the two dimanganese complexes indicates that the bimetallic systems produce catalysts which have greater turnover numbers, different product ratios and faster rates.

Although the monomeric species $[\text{Zn}(\mathbf{360a})]$ and $[\text{Co}(\mathbf{360a})]^+$ have a C_2 symmetrical arrangement of the chelate arms, the bimetallic macrocyclic complexes $[\text{Mn}_2(\mathbf{361c})(\text{Cl})](\text{PF}_6)$, $[\text{Co}_2(\mathbf{361c})(\text{Cl})](\text{PF}_6)$, $[\text{Co}_2(\mathbf{361c})](\text{PF}_6)_2$ and $[\text{Mn}_2(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})](\text{PF}_6)$ (Fig. 250a–d) have an unsymmetrical arrangement of ligands at the N_4O_2 site where both pyridyl ligands lie on the same side of the mean molecular plane. In all of the structures, the N_4O_2 site resembles a trigonal prismatic structure, whereas the N_2O_2 site is square pyramidal or square planar. In the case of the mixed-valence structure $[\text{Mn}_2(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})](\text{PF}_6)$ the manganese(III) ion in the N_2O_2 site is octahedral while the N_4O_2 site resembles a trigonal prismatic geometry having one disconnected phenolic bridging ligand. $[\text{Co}_2(\mathbf{361c})(\text{Cl})](\text{PF}_6)$ and $[\text{Mn}_2(\mathbf{361c})(\text{Cl})](\text{PF}_6)$ ions are isostructural. The unsymmetrical structures are not caused by the presence of chloro group in the N_2O_2 site as indicated by the fact that the $[\text{Co}_2(\mathbf{361c})(\text{Cl})]^+$ and $[\text{Co}_2(\mathbf{361c})]^{2+}$ ions have similar unsymmetrical structures. Thus there is an inherent feature of the binucleating macrocyclic ligand that causes the asymmetry. This, in turn, forces the phenolic groups to adopt a conformation where these bridging groups lie on the same side of the mean macrocyclic plane. As a consequence, these transmitted steric imperatives cause both of the pyridyl ligands to dispose themselves to the same side of the mean molecular plane opposite to that of the phenolic groups. It was suggested that to obtain a symmetrical N_4O_2 site structure where one pyridyl ligand lies above and the other below the mean macrocyclic plane, the bite angles associated with the ethylenediamine and/or trimethylene diimine links are required to be expanded [424,425].

The homo- and hetero-dinuclear complexes $[\text{Co}_2(\mathbf{361b})]^{3+}$ and $[\text{CoM}(\mathbf{361b})]^{3+}$, derived from the chiral ligand $\text{H}_2\text{-361b}$ with the cobalt(III) ion in the N_4O_2 site and the copper(II), nickel(II), cobalt(II) or manganese(II) ions in the N_2O_2 Schiff base site and $[\text{CuM}(\mathbf{361b})]^{2+}$ with copper(II) ion in the N_2O_2 Schiff base site and copper(II),

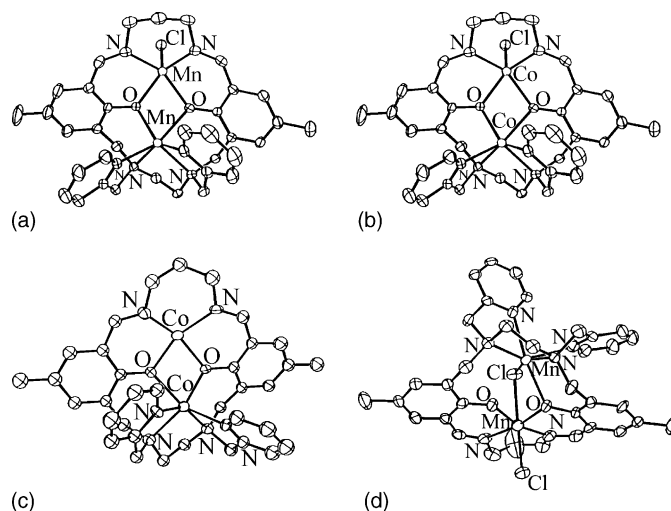


Fig. 250. Structures of $[\text{Mn}_2(\mathbf{361c})(\text{Cl})]^+$ (a), $[\text{Co}_2(\mathbf{361c})(\text{Cl})]^+$ (b), $[\text{Co}_2(\mathbf{361c})]^{2+}$ (c) and $[\text{Mn}_2(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})]^+$ (d) (adapted from Refs. [424,425]).

nickel(II), cobalt(II) or manganese(II) ion in the N_4O_2 site, give magnetic moments which are less than the total spin-only values owing to antiferromagnetic coupling between the two contiguous paramagnetic ions [424,425].

The magnetic moment of $[\text{Cu}_2(\mathbf{361b})]^{2+}$ exhibits spin-spin coupling at 20 °C but at 77 K no EPR signal is observed. This suggests that the electrons are paired and that a singlet state obtains at low temperatures. The spectrum of the $[\text{NiCu}(\mathbf{361b})]^{2+}$ complex also shows evidence of metal-metal interaction. When there is interaction between the $S = 1/2$ state of the copper(II) ion and the $S = 1$ state of high spin nickel(II) ion, two states are generated, a doublet and a quartet. Since the magnetic moment of the $[\text{NiCu}(\mathbf{361b})](\text{PF}_6)_2$ complex is near the spin-only value for the bimetallic system, this indicates that there is extensive population of the quartet state at room temperature. For $[\text{Cu}(\text{H}_2\text{-}\mathbf{361b})]^{2+}$, $[\text{CuZn}(\mathbf{361b})(\text{Cl})]^+$, $[\text{CuZn}(\mathbf{361b})]^{2+}$, $[\text{Cu}_2(\mathbf{361b})]^{2+}$, $[\text{ZnCu}(\mathbf{361b})]^{2+}$, $[\text{NiCu}(\mathbf{361b})]^{2+}$, $[\text{CoCu}(\mathbf{361b})]^{3+}$, the EPR spectra at 77 K in acetonitrile/toluene glasses indicate that $[\text{Cu}_2(\mathbf{361b})]^{2+}$ may exist as a spin-paired singlet, whereas the spectrum of $[\text{NiCu}(\mathbf{361b})]^{2+}$ exhibits the spin-interacting doublet state. The EPR spectra, used to monitor both inter- and intra-molecular metal site scrambling of these complexes, show that no scrambling can be detected.

The electronic absorption spectra for $[\text{Co}^{\text{III}}\text{M}^{\text{II}}(\mathbf{361b})]^{3+}$ complexes indicate distorted trigonal bipyramidal N_2O_2 site metal geometries, whereas the copper(II) ions in the $[\text{MCu}(\mathbf{361b})]^{2+}$ complexes generally have distorted four or five coordinate structures.

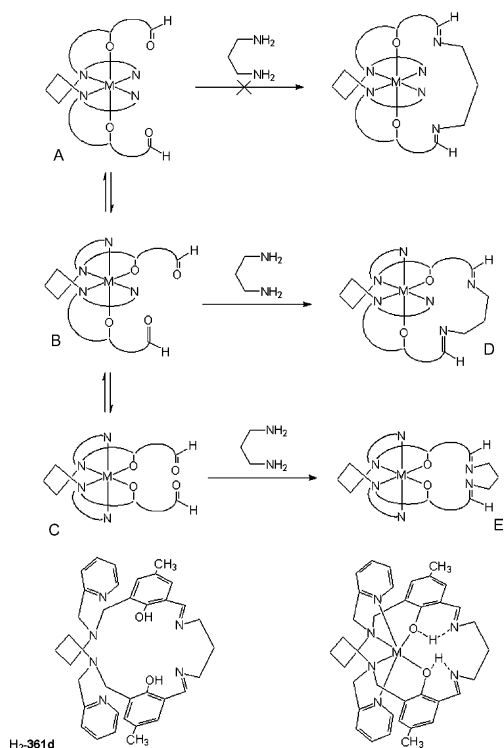
Cyclic voltammetry of a series of copper(II) complexes of the type $[\text{CuM}(\mathbf{361b})]^{2+}$ and of cobalt(III) complexes of the types $[\text{CoM}(\mathbf{361b})(\text{Cl})]^{2+}$ and $[\text{CoM}(\mathbf{361b})]^{3+}$ show that the potentials of the invariant metals are dependent on the nature of the neighbouring metal. Whereas some of these variations could be due to structural differences in the bimetallic series, metal-metal interaction may also influence the redox prop-

erties of the invariant copper(II) and cobalt(III) ions in these complexes [420].

$\text{H}_2\text{-}\mathbf{361d}$, containing two larger trimethylenediamine units, has been synthesized in order to avoid the preparation of the complexes with the two pyridine groups *cis*-, as found in the above reported complexes, and to favour *trans*-structures [421]. For the preparation of this macrocycle, the related acyclic diformyl-precursor $\text{H}_2\text{-}\mathbf{360c}$ had to be prepared first [421]. $\text{H}_2\text{-}\mathbf{360c}$, an oil purified by isolation of its insoluble neutral monozinc complex $[\text{Zn}(\mathbf{360c})]$, reacts with $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ to give the neutral insoluble cobalt(II) complex $[\text{Co}(\mathbf{360c})]$, which could be oxidized to the soluble cobalt(III) monocationic complex $[\text{Co}(\mathbf{360c})]^+$ with ferrocenium hexafluorophosphate in acetonitrile. The ^1H NMR spectrum of the diamagnetic cobalt(III) complex indicated that three topological isomers were present, two of which were C_2 symmetrical and one unsymmetrical, in the ratio = 7:3:1. The isomer in lowest proportion is the unsymmetrical C_1 isomer with *cis*-pyridines and *cis*-phenolates. The C_2 symmetrical isomers correspond to the one with *trans* pyridines and the one with *trans* phenolates, although it was not possible to determine which was predominant (Scheme 50). $[\text{Zn}(\mathbf{360c})]$ is likely to consist of a mixture of topological isomers [424].

Formation of the macrocycle $\text{H}_2\text{-}\mathbf{361d}$ by template condensation of $\text{H}_2\text{-}\mathbf{361c}$ with 1,3-diaminopropane requires that topological rearrangement occur. Cyclization is unlikely to occur with the isomer **A** of Scheme 50 but can occur with the isomers **B** and **C**. In addition, the cyclized product **D** is likely to be less stable than **E** and could convert to **E**.

When either of the zinc(II) or cobalt(II) dialdehyde complexes of type **A–C**, $[\text{M}(\mathbf{360c})]$, are reacted in ethanol with 1 equiv. of trimethylenediamine and 2 equiv. of acetic acid followed by the addition of PF_6^- , the cyclic complexes $[\text{M}(\text{H}_2\text{-}\mathbf{361d})](\text{PF}_6)_2$ are formed. In $[\text{Zn}(\text{H}_2\text{-}\mathbf{361d})](\text{PF}_6)_2$ the cation $[\text{Zn}(\text{H}_2\text{-}\mathbf{361d})]^{2+}$ has an essentially C_2 symmetry with *trans*-disposed pyridine ligands (Fig. 251a).



Scheme 50.

The trimethylenediamine link of the N_4O_2 site has a skew conformation, the phenolic residues are in a highly twisted array, and the trimethylenediamine fragment is skewed and disposes the iminic nitrogen atoms not involved in coordination above and below the mean macrocyclic plane. The two protons reside in the Schiff base cavity as shown by ^1H NMR spectra which confirm the existence of a single isomer with a C_2 symmetry also in solution [421].

The complexes $[\text{M}(\text{H}_2\text{-361d})](\text{PF}_6)_2$ are excellent precursors for the mild synthesis of hetero-dinuclear complexes under basic condition and in the presence of the appropriate metal acetate. By this procedure $[\text{Zn}_2(\text{361d})(\text{CH}_3\text{COO})](\text{PF}_6)$, $[\text{Zn}_2(\text{361d})(\text{Cl})](\text{PF}_6)$, $[\text{ZnCu}(\text{361d})](\text{PF}_6)_2$, $[\text{ZnCo}(\text{361d})(\text{Cl})](\text{PF}_6)$, $[\text{CoZn}(\text{361d})(\text{Cl})](\text{PF}_6)$, $[\text{CoCu}(\text{361d})](\text{PF}_6)_2$, and $[\text{Co}_2(\text{361d})(\text{Cl})](\text{PF}_6)$ were prepared. Apart from the copper containing complexes, the others required a chloride or acetate ligand in order to obtain pure crystalline compounds. In some cases triethylamine was added in order to complete the reaction.

The ^1H NMR spectrum at 25°C in CD_3CN of $[\text{Zn}_2(\text{361d})(\text{CH}_3\text{COO})](\text{PF}_6)$ is indicative a C_2 symmetric structure which is lost at -45°C . It was suggested that at 25°C the acetate ligand is rapidly exchanging between the two axial sites of the zinc(II) ion in the N_2O_2 site, giving a time-averaged C_2 structure. Cooling slows the exchanging, which results in the appearance of a spectrum consistent with an unsymmetrical structure. In CD_2Cl_2 the ^1H NMR spectrum of this complex indicates an unsymmetrical structure. $[\text{Zn}_2(\text{361d})(\text{Cl})](\text{PF}_6)$ in either CD_3CN or CD_2Cl_2

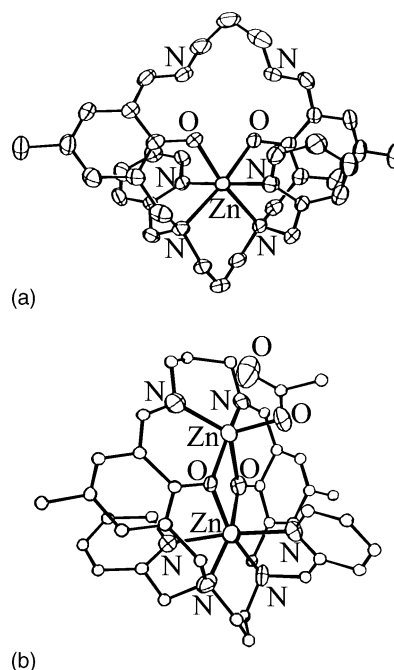


Fig. 251. Structures of $[\text{Zn}(\text{H}_2\text{-361d})]^{2+}$ (a) and $[\text{Zn}_2(\text{361d})(\text{CH}_3\text{COO})]^+$ (b) (adapted from Ref. [421]).

solutions gives ^1H NMR spectra consistent with an unsymmetrical structure at 25°C , but upon the addition of AgPF_6 to remove the coordinated chloride the ^1H NMR spectrum becomes consistent with a C_2 symmetric molecule. These results indicate that the structure of the dizinc complexes in solution contain *trans*-disposed pyridine ligands which lie above and below the mean macrocyclic plane. This conclusion was confirmed by the structure of $[\text{Zn}_2(\text{361d})(\text{CH}_3\text{COO})](\text{PF}_6) \cdot \text{CH}_3\text{OH}$ (Fig. 251b) where the C_2 symmetrical structure of the N_4O_2 site is retained and the general twisted ligand structure resembles that observed in the monometallic complex, $[\text{Zn}(\text{H}_2\text{-361d})]^{2+}$. The modest angle changes from mononuclear to homo-dinuclear complexes are apparently accommodated by ligand conformational adjustments without requiring the heavy structural changes that are observed for the related bimetallic complexes. As a consequence of the highly twisted structure of the N_2O_2 site in the monometallic complex, the zinc(II) ion in the N_2O_2 site is in a distorted trigonal bipyramidal environment.

Very little dissociation of the fifth ligand coordinated to the N_2O_2 site metal appears to occur in acetonitrile solutions because all of the $[\text{M}_a\text{M}_b(\text{361d})(\text{X})](\text{PF}_6)$ ($\text{X} = \text{CH}_3\text{COO}^-$, Cl^-) complexes are 1:1 electrolytes. The copper-containing complexes $[\text{MCu}(\text{361d})](\text{PF}_6)_2$ are 2:1 electrolytes. Thus the symmetrical broad ^1H NMR signals observed for $[\text{Zn}_2(\text{361d})(\text{CH}_3\text{COO})](\text{PF}_6)$ in CD_3CN at 25°C cannot be interpreted in terms of extensive acetate dissociation. When 10% D_2O is added to the CD_3CN solutions of $[\text{Zn}_2(\text{361d})(\text{CH}_3\text{COO})]^+$ and $[\text{Zn}_2(\text{361d})(\text{Cl})]^+$, ^1H NMR spectra indicate a C_2 symmetry consistent with the dissocia-

tion of the acetate and chloride ligands, respectively. The room temperature magnetic moments suggest that there is only weak spin-coupling between the electrons on the two metal ions.

Electronic spectra indicate that the copper(II) ion is in a distorted four coordinate environment in $[\text{ZnCu}(\mathbf{361d})]^{2+}$ while the cobalt(II) ion is octahedral in $[\text{CoZn}(\mathbf{361d})(\text{Cl})]^+$ and five coordinated in $[\text{ZnCo}(\mathbf{361d})(\text{Cl})]^+$.

$[\text{Co}(\text{H}_2\text{-}\mathbf{361d})](\text{PF}_6)_2$, $[\text{CoCu}(\mathbf{361d})](\text{PF}_6)_2$ and $[\text{CoM}(\mathbf{361d})(\text{Cl})](\text{PF}_6)$ ($\text{M} = \text{Zn}^{2+}$, Co^{2+}) are not oxidized by ferrocenium. Thus the cobalt(III) in the six coordinated site of $[\mathbf{361d}]^{2-}$ is unstable, owing to the inability of $[\mathbf{361d}]^{2-}$ to adjust cobalt(III) bond lengths.

The variation of the $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ couple in the N_4O_2 site appears to depend on the structure, of the neighbouring metal ion in the N_4O_2 site and possibly on the charge of the complex. The structural effect is exemplified by the relative ease of oxidation by ferrocenium of the $[\text{Co}(\text{H}_2\text{-}\mathbf{361d})]^{2+}$ and $[\text{Co}(\text{H}_2\text{-}\mathbf{361c})]^{2+}$ complexes. Ferrocenium ion readily oxidizes the latter to the stable $[\text{Co}(\text{H}_2\text{-}\mathbf{361c})]^{3+}$ complex whereas the former is not oxidized under the same conditions. $[\text{Co}(\text{H}_2\text{-}\mathbf{361c})]^{2+}$ gives a highly irreversible wave, which makes impossible to evaluate a reliable $\text{Co}(\text{III})/\text{Co}(\text{II})$ couple but the ferrocenium oxidation clearly indicates a potential more negative than that for $[\text{Co}(\text{H}_2\text{-}\mathbf{361d})]^{2+}$. This difference was ascribed to an inability of the $[\mathbf{361d}]^{2-}$ structure to adjust to the shorter bond lengths of cobalt(III) complexes over the corresponding cobalt(II) complexes. In the complexes derived from $[\mathbf{361c}]^{2-}$ the ethylenediamine chelate accommodates the cobalt(III) ion better than the larger trimethylenediamine chelate in $[\mathbf{361d}]^{2-}$ [421].

The above synthetic procedure was used in the preparation of the similar macrocycles $\text{H}_2\text{-}\mathbf{361e}\text{--}\mathbf{I}$, where the different aliphatic chains R and R' have been inserted into the lateral units in order to investigate the influence of the chelate ring size on the ligands binding stereochemistry [422].

Reaction of the appropriate dialdehyde precursor ($\text{H}_2\text{-}\mathbf{360a}$, $\text{H}_2\text{-}\mathbf{360c}$, $\text{H}_2\text{-}\mathbf{360d}$) with zinc(II) and cobalt(II) acetate leads to the formation of very insoluble neutral acyclic complexes which, when reacted with diamines in the presence of 2 equiv. of acetic acid, give the monometallic macrocyclic complexes $[\text{M}(\text{H}_2\text{-}\mathbf{361e}\text{--}\mathbf{I})]^{2+}$. NMR data indicate that two protons lie in the Schiff base cavity.

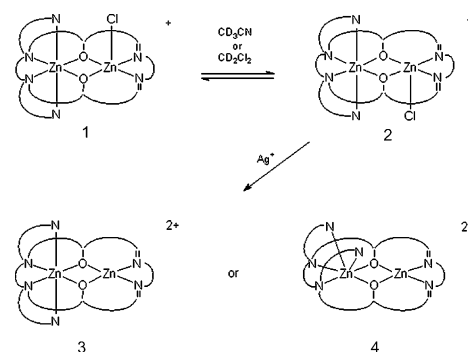
The cobalt(II) complexes containing a five membered chelate linked at the N_4O_2 site were oxidized to the cobalt(III) complexes $[\text{Co}(\text{H}_2\text{-}\mathbf{361})](\text{PF}_6)_3$ with ferrocenium hexafluorophosphate while the complexes with a six membered chelate linked at the N_4O_2 site could not be oxidized. ^1H NMR spectra of the cobalt(III) complexes indicate that all have the C_2 symmetric topology in which the pyridines are disposed *trans*. The complexes containing the $-\text{CH}(\text{CH}_3)\text{CH}_2-$ chain consist of one topological isomer indicating that this chain induces the formation of the Δ -topological isomer exclusively.

The complexes $[\text{Zn}_2(\text{L})(\text{Cl})](\text{PF}_6)$ ($\text{H}_2\text{-L} = \text{H}_2\text{-}\mathbf{361c}$, $\text{H}_2\text{-}\mathbf{361d}$, $\text{H}_2\text{-}\mathbf{361i}$), $[\text{CoZn}(\text{L})(\text{Cl})](\text{PF}_6)_2$ ($\text{H}_2\text{-L} = \text{H}_2\text{-}\mathbf{361c}$, $\text{H}_2\text{-}\mathbf{361e}$, $\text{H}_2\text{-}\mathbf{361g}$ and $\text{H}_2\text{-}\mathbf{361h}$) and $[\text{CoZn}(\text{L})(\text{Cl})](\text{PF}_6)$ ($\text{H}_2\text{L} = \text{H}_2\text{-}\mathbf{361d}$, $\text{H}_2\text{-}\mathbf{361i}$) incorporating zinc chloride in the N_2O_2 site were prepared under mild conditions by adding ZnCl_2 to solutions of the appropriate $[\text{M}(\text{H}_2\text{-}\mathbf{361})]^{n+}$ complexes in the presence of triethylamine [422].

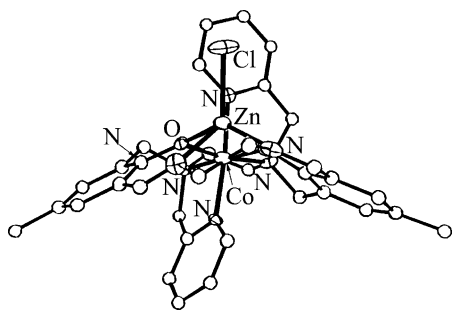
Acetonitrile solutions of $[\text{Zn}(\text{H}_2\text{-}\mathbf{361g})]^{2+}$ and $[\text{Zn}(\text{H}_2\text{-}\mathbf{361h})]^{2+}$ are configurationally stable for 2 weeks as indicated by the constancy of their ^1H NMR spectra at 25°C . The complexes $[\text{Zn}(\text{H}_2\text{-}\mathbf{361f})]^{2+}$ and $[\text{Zn}(\text{H}_2\text{-}\mathbf{361l})]^{2+}$ were isolated as roughly equal mixtures of the two topological isomers. The ratio of these isomers remains constant in CD_3CN solutions for each complex [422].

The ^1H NMR spectra in CD_3CN or CD_2Cl_2 of the three dizinc(II) complexes of $\text{H}_2\text{-}\mathbf{361c}$, $\mathbf{361d}$ and $\text{H}_2\text{-}\mathbf{361i}$ are consistent with the existence of the equilibrium depicted as $\mathbf{1} \rightleftharpoons \mathbf{2}$ of Scheme 51 where the Cl^- ion interchanges from one side or the mean macrocyclic plane to the other. In CD_3CN solutions this process is fast on the ^1H NMR time scale, giving a broad, approximately symmetrical spectrum. In CD_2Cl_2 solutions this interchange occurs more slowly or not at all and results in an unsymmetrical spectrum. Removal of the bound Cl^- ligand with silver(I) ions leads to the production of species which give ^1H NMR spectra that indicate symmetrical species of the type $\mathbf{3}$ or $\mathbf{4}$ of Scheme 51, the latter of which achieving C_s symmetry on the ^1H NMR time scale through conformational fluxionality.

When the stereochemically rigid cobalt(III) ion is present in the N_4O_2 site, the ^1H NMR spectra on monometallic complexes bearing an ethylenediamine link at the N_4O_2 site strongly suggest that all of these monometallic cobalt(III) complexes have the pyridines disposed *trans*. The further incorporation of zinc(II) will not change the overall stereochemistry. The ^1H NMR spectra of $[\text{CoZn}(\text{L})(\text{Cl})](\text{PF}_6)_2$ ($\text{H}_2\text{-L} = \text{H}_2\text{-}\mathbf{361c}$, $\text{H}_2\text{-}\mathbf{361e}$, $\text{H}_2\text{-}\mathbf{361g}$, $\text{H}_2\text{-}\mathbf{361h}$) in CD_3CN solutions at 25°C are sharp and suggest that Cl^- ligand interchange in these complexes is slow compared to that in the dizinc(II) analogues. The ^1H NMR spectrum of $[\text{CoZn}(\mathbf{361c})(\text{Cl})]^{2+}$ at 25°C indicates an unsymmetrical structure consistent with the presence of the $\text{Zn}\text{--}\text{Cl}$ frag-



Scheme 51.

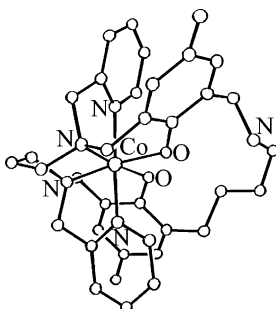
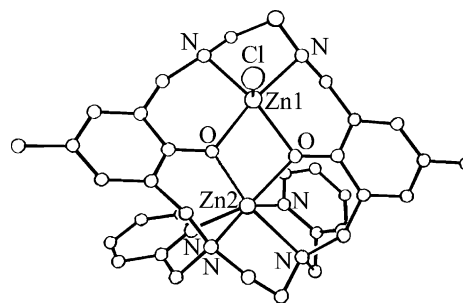
Fig. 252. Structure of $[\text{CoZn}(\mathbf{361e})(\text{Cl})]^{2+}$ (adapted from Ref. [422]).

ment, which removes the two-fold axis of symmetry. Upon removal of the chloride ligand with silver(I) ions, the spectrum is consistent with a C_2 symmetric structure. The preparation of $[\text{CoZn}(\mathbf{361e})(\text{Cl})]^{2+}$ by ferrocenium ion oxidation of the Co(II) complex, $[\text{CoZn}(\mathbf{361e})(\text{Cl})]^+$, gives a product with an identical ^1H NMR spectrum; this suggests that the cobalt(II) precursor has the same topology as the cobalt(III) product [425].

In $[\text{CoZn}(\mathbf{361e})(\text{Cl})](\text{PF}_6)_2$ the zinc(II) ion lies above the N_2O_2 plane. The cavity of this Schiff base macrocycle is too small to accommodate the zinc(II) ion into its mean plane (Fig. 252). The topology about the cobalt(III) ion is that expected with *trans*-disposed pyridines [422].

The reduced mononuclear complexes $[\text{M}(\text{H}_2\text{-L})](\text{PF}_6)_2$ ($\text{H}_2\text{-L} = \text{H}_2\text{-363a}$, $\text{H}_2\text{-363b}$, $\text{H}_2\text{-363c}$ and $\text{H}_2\text{-363d}$ for $\text{M} = \text{Zn}^{2+}$, Co^{2+} and $\text{H}_2\text{-263c}$ and $\text{H}_2\text{-263d}$ for $\text{M} = \text{Mn}^{2+}$) and $[\text{Co}(\text{H}_2\text{-L})](\text{PF}_6)_3$ ($\text{H}_2\text{-L} = \text{H}_2\text{-363c}$ and $\text{H}_2\text{-363d}$), have been obtained by slow addition of 1 equiv. of NaBH_4 in ethanol to a solution of the appropriate mononuclear diimine derivative $[\text{M}(\text{H}_2\text{-361})]^{n+}$ in acetonitrile at 5°C . The cobalt(II) and manganese(II) complexes are O_2 sensitive in acetonitrile solutions but appear to be stable to dioxygen in the solid state [426].

$[\text{Co}(\text{H}_2\text{-363b})](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$ (Fig. 253) shows *trans* disposed pyridine ligands oriented perpendicular to the mean macrocyclic plane. The conformation of the N_4O_2 site link is skew rather than chair as required for the *trans* disposition of the pyridine ligands. The rest of the ligand displays considerable conformational twisting.

Fig. 253. Structure of $[\text{Co}(\text{H}_2\text{-363b})]^{2+}$ (adapted from Ref. [426]).Fig. 254. Structure of $[\text{Zn}_2(\mathbf{363d})(\text{Cl})]^+$ (adapted from Ref. [426]).

The subsequent addition to the mononuclear complex $[\text{M}(\text{H}_2\text{-361})]^{n+}$ of the appropriate metal salt in the presence of LiOH produces the corresponding dinuclear complexes. By this procedure the complexes $[\text{Zn}_2(\mathbf{363a-d})(\text{Cl})](\text{PF}_6)$ were prepared; the analogous dicobalt(II) complexes were also prepared with all ligands except for $\text{H}_2\text{-363d}$. These complexes proved to be more soluble and more difficult to crystallize than their imine analogues.

In $[\text{Zn}_2(\mathbf{363d})(\text{Cl})](\text{PF}_6)$ (Fig. 254) the pyridine groups are *cis*-disposed. Both sets of the aliphatic amine groups, are in the meso (*R,S*) configuration. Both zinc ions lie out of the mean macrocyclic plane. Both zinc coordination geometries are distorted from the usual six and five coordinated geometries [426].

All of the complexes $[\text{Co}^{\text{II}}(\text{H}_2\text{-363a-d})]^{2+}$ are oxidized by ferrocenium ion to give stable cobalt(III) complexes and it is concluded that the rigidity of the imine ligands prevents the ligand from adjusting to the stereochemical demands of cobalt(III) when the six coordinated site contains the larger $\text{CH}_2\text{CH}_2\text{CH}_2$ link in the imine systems. This stereochemical hindrance is relaxed in the more flexible amine systems. Ferrocenium ion oxidation of the bimetallic amine complexes, $[\text{Co}_2^{\text{II}}(\mathbf{363})(\text{Cl})]^+$, leads only to the formation of the mixed oxidation state complexes $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{363})(\text{Cl})]^{2+}$ where the cobalt(III) ion is in the six coordinated site. Unlike the imine dicobalt(II) complexes which are unreactive to dioxygen, the amine ligand dicobalt(II) complexes readily react with dioxygen to give the mixed oxidation state complexes, $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mathbf{363})(\text{Cl})]^+$, where the cobalt(III) ion occupies the four coordinate site. The inability to form stable dicobalt(III) complexes with these amine ligands, despite the fact that each site is capable of supporting the cobalt(III) states, is ascribed to various forms of coupling between the metals in the two sites: mechanical coupling which refers to ligand constraints, through-space electrostatic interactions between metals, and through-bond coupling which refers to covalent interaction between the metals via the bridging ligands [426].

The N_4O_2 site occupancy for cobalt(III) and the N_2O_2 site occupancy for cobalt(II) were supported by a series of chemical reactions. Addition of LiOH followed by CoCl_2 to the independently prepared cobalt(III) complexes $[\text{Co}^{\text{III}}(\text{H}_2\text{-363})](\text{PF}_6)_3$ gave the mixed oxidation state

products $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{363})(\text{Cl})](\text{PF}_6)_2$ which were identical to the species prepared by ferrocenium oxidation $[\text{Co}_2^{\text{II}}(\text{H}_2\text{-}\mathbf{363})(\text{Cl})](\text{PF}_6)_2$. Further, heating the mixed oxidation products in water gave the monometallic cobalt(III) complexes. It thus appears that after the N_4O_2 site cobalt ion is oxidized, the N_2O_2 site cobalt(II) is not oxidized by ferrocenium ions. This was confirmed by the fact that ferrocenium ions did not oxidize the N_2O_2 site cobalt(II) in the prepared mixed oxidation state complexes.

The oxidation of both cobalt(II) ions of $[\text{Co}_2^{\text{II}}(\mathbf{363})(\text{Cl})](\text{PF}_6)_2$ to $[\text{Co}_2^{\text{III}}(\mathbf{363})(\text{NO})(\text{Cl})](\text{PF}_6)_2$ was attempted with NOPF_6 . However an addition of 1 equiv. of NOPF_6 to alkylnitrile solutions of $[\text{Co}_2(\mathbf{363a})(\text{Cl})](\text{PF}_6)$ and $[\text{Co}_2(\mathbf{363c})(\text{Cl})](\text{PF}_6)$ led to the formation of the mixed oxidation state complexes $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{363a})(\text{Cl})]^{2+}$ and $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{363c})(\text{Cl})]^{2+}$, respectively. Treating these mixed oxidation state complexes in water led to the isolation of the N_4O_2 site monometallic cobalt(III) complexes.

When either of the complexes $[\text{Co}_2(\mathbf{363a})(\text{Cl})](\text{PF}_6)$, $[\text{Co}_2(\mathbf{363b})(\text{Cl})](\text{PF}_6)$ or $[\text{Co}_2(\mathbf{363c})(\text{Cl})](\text{PF}_6)$ is dissolved in CH_2Cl_2 , acetone or acetonitrile at 25°C and exposed to atmospheric oxygen for ~ 2 h, visible-near-IR spectra in all cases show that metal oxidation occurred. In all cases transitions in the 960–1000 nm region, indicative of N_4O_2 site cobalt(II), were observed. Hence the reaction with dioxygen, in contrast to ferrocenium oxidation, leads to the oxidation of the N_2O_2 site cobalt(II) ion. Prolonged exposure to dioxygen does not lead to the oxidation of the N_4O_2 site cobalt(II) ion.

An addition of acetic acid to an acetonitrile solution of the product of oxidation of $[\text{Co}_2^{\text{II}}(\mathbf{363c})(\text{Cl})](\text{PF}_6)$ by dioxygen led to the isolation of the mixed oxidation state complex, $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mathbf{363c})(\text{CH}_3\text{COO})(\text{CH}_3\text{CN})](\text{PF}_6)_2$. Similarly, oxidation of $[\text{Co}_2(\mathbf{363b})(\text{Cl})](\text{PF}_6)$ by O_2 in CH_2Cl_2 led to low-yield precipitation of a product possessing all of the spectroscopic characteristics expected of a mixed oxidation state dicobalt system with the cobalt(III) ion in the N_2O_2 site. These N_2O_2 site cobalt(III)- N_4O_2 site cobalt(II) complexes when heated in water are transformed to monometallic complexes of the type $[\text{Co}^{\text{III}}(\text{H}_2\text{-}\mathbf{363})]^{3+}$.

The presence of the cobalt(III) ion in one of the sites appears to inhibit the oxidation of the cobalt(II) in the other site. Thus the oxidation of the dicobalt(II) amine complexes with ferrocenium, NO^+ , and O_2 led to the oxidation of one of the cobalt ions, the site occupancy of which is dependent on the oxidant [427].

$[\text{Fe}(\text{H}_2\text{-}\mathbf{361c})](\text{PF}_6)_2$, $[\text{Fe}(\text{H}_2\text{-}\mathbf{361d})](\text{PF}_6)_2$ and $[\text{Fe}(\text{H}_2\text{-}\mathbf{361i})](\text{PF}_6)_2$, prepared by condensation of the appropriate diformyl precursor with $[\text{Fe}(\text{py})_4(\text{Cl})_2]$ which in turn can be cyclized with a diamine in the presence of acetic acid to form the monometallic diprotonated complex, gives rise to the corresponding amine complexes by BH_4^- reduction [427]. Unlike the corresponding imine complexes, these amine complexes are extremely air sensitive as solids, and their yellow CH_3CN solutions are oxidized by O_2 upon exposure to air to give deep blue solutions.

The diiron(II) complex $[\text{Fe}_2(\mathbf{361c})(\text{Cl})](\text{PF}_6)_2$, prepared by reaction of $[\text{Fe}(\text{H}_2\text{-}\mathbf{361c})](\text{PF}_6)_2$ with $[\text{Fe}(\text{py})_4(\text{Cl})_2]$, is indefinitely air stable in the solid state and in CH_3CN . Its 25°C magnetic moment ($7.09\mu_{\text{B}}$), indicates a slight magnetic exchange between the iron(II) ions [427].

Reaction of $[\text{Fe}(\text{H}_2\text{-}\mathbf{361c})](\text{PF}_6)_2$ with $\text{VCl}_3 \cdot 3\text{THF}$ in CH_3CN in the presence of triethylamine leads to the formation of orange crystals, indefinitely stable in air in the solid state, of $[\text{FeV}(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})]\text{PF}_6$. In this complex a chloro bridge exists between the two metal ions. As a consequence, one of the phenolate oxygen atoms is not bonded to the iron ion. The pyridine ligands are *cis* disposed so that the iron ion is coordinated in a distorted octahedral structure. The vanadium ion is also in an octahedral environment which is less distorted than for the case of the iron ion (Fig. 255a) [426,427].

$[\text{FeV}(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})](\text{PF}_6)_2$, suspended in CH_3CN and allowed to react with 2,4,6-trimethyliodosobenzene, forms green crystals of $[\text{FeVO}(\mathbf{361c})](\text{PF}_6)_2$. The same complex is isolated when $[\text{FeV}(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})](\text{PF}_6)_2$ is dissolved in CH_3CN and exposed to O_2 over a period of days. Similarly addition of 1 equiv. of ferrocenium ion to $[\text{FeV}(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})](\text{PF}_6)_2$ in CH_3CN followed by exposition of the resulting solution to moisture produces $[\text{FeVO}(\mathbf{361c})](\text{PF}_6)_2$. Addition of 2 equiv. of ferrocenium to $[\text{FeV}(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})]^{2+}$ gives the same product with 1 equiv. of ferrocenium ion remaining. In $[\text{FeVO}(\mathbf{361c})]^{2+}$ the pyridine ligands are *cis* disposed, while both phenolate oxygen atoms bridge both metals. The V–O bond is directed *trans* to the *cis* pyridine ligands. The iron(II) ion is in a distorted octahedral structure while the vanadium(IV) ion is pentacoordinate [427] (Fig. 255b).

$[\text{Fe}(\text{H}_2\text{-}\mathbf{361c})]^{2+}$ is rapidly oxidized by 1 equiv. of ferrocenium in CH_3CN to the corresponding iron(III) phenolate

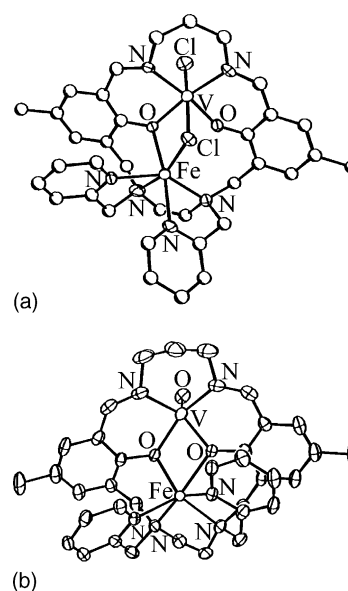


Fig. 255. Structure of $[\text{FeV}(\mathbf{361c})(\mu\text{-Cl})(\text{Cl})]^{+}$ (a) and $[\text{FeVO}(\mathbf{361c})]^{2+}$ (b) (adapted from Ref. [427]).

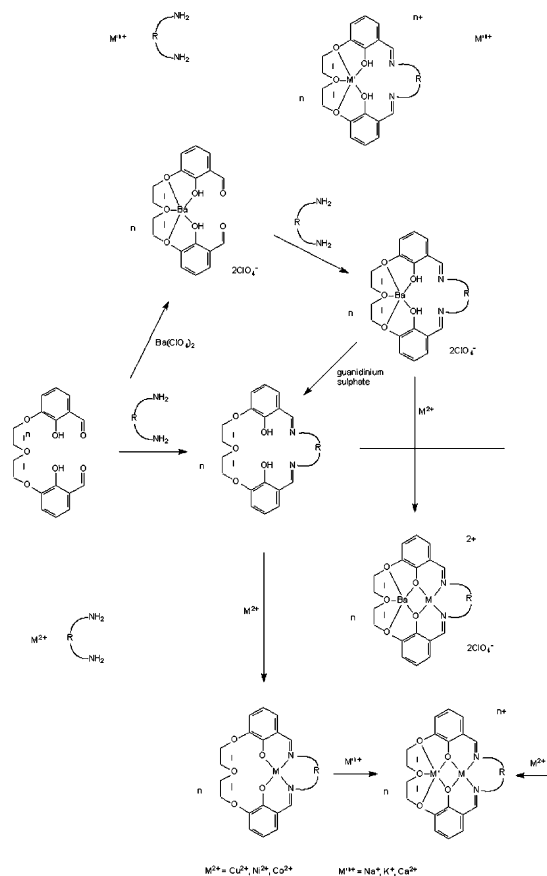
complexes, while $[\text{Fe}(\text{H}_2\text{-361i})]^{2+}$ is not oxidized under the same conditions. This behaviour is analogous to that observed with the corresponding cobalt(II) complexes, where ferrocenium only causes oxidation when the CH_2CH_2 link is present in the N_4O_2 site. Similarly, all of the mononuclear iron(II) amine complexes are immediately oxidized by O_2 irrespective of whether a CH_2CH_2 or $\text{CH}_2\text{CH}_2\text{CH}_2$ link is present in the N_4O_2 site.

The addition of 1 equiv. of ferrocenium ion to either $[\text{Fe}_2(\text{361c})(\text{Cl})]^+$ or $[\text{Fe}_2(\text{363c})(\text{Cl})]^+$ in CH_3CN causes the formation of the iron(III)-phenolate complexes. The addition of another equivalent of ferrocenium ion to these solutions does not cause further oxidation, indicating that after the oxidation of the first iron ion, the other is deactivated to oxidation.

The redox potentials of the iron(II) complexes relative to the ferrocenium/ferrocene couple are consistent with the chemical oxidations. For the three monometallic complexes, the two with $\text{CH}_2\text{CH}_2\text{CH}_2$ links in the N_4O_2 site have more positive potentials than those when CH_2CH_2 link is present in the same site. Reduction of the imine to the related amine groups leads to monometallic complexes which have redox potentials considerably more negative, by about 0.4 V. This observation provides strong evidence that conformational flexibility of the ligand has a strong influence on the redox potential. $[\text{Fe}_2(\text{361c})(\text{Cl})]^+$ shows two reversible waves which are separated by 0.85 V. Because the -0.16 V wave is essentially the same as the potential of $[\text{Fe}(\text{H}_2\text{-361c})]^+$, this couple is associated with the N_4O_2 site iron ion. Similarly, the ferrocenium oxidation of the $[\text{Fe}_2(\text{361c})(\text{Cl})]^+$ complex involves oxidation of the N_4O_2 site iron ion. This is probably also the case when the $[\text{Fe}_2(\text{363c})(\text{Cl})]^+$ complex is oxidized by ferrocenium ion. The N_2O_2 ligand environment about the iron(II) ion would be expected to allow for ready oxidation to the iron(III) state in a monometallic complex. The fact that the N_2O_2 site iron(II) in the bimetallic complex $[\text{Fe}_2(\text{361c})(\text{Cl})]^+$ has a large positive potential suggests that special forms of deactivation exist in bimetallic complexes.

For the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ complexes, the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ potentials are much more positive than the corresponding potentials found for $[\text{Fe}(\text{H}_2\text{-361c})]^{2+}$ and $[\text{Fe}_2(\text{361c})(\text{Cl})]^+$, this probably reflecting structural differences [427].

A number of heterodinucleating ligands ($\text{H}_2\text{-254}$) have been synthesized by barium(II) templated 1:1 macrocyclization of the appropriate dialdehydes with the suitable diamines followed by demetallation of the resulting complexes with guanidinium sulfate or by self-condensation procedure. The ligands have a Schiff base cavity suitable for complexation of transition metal cations and a crown-ether like cavity suitable for complexation of alkali-, alkaline-earth or lanthanide(III) cations. Thus the mononuclear barium, alkali, alkaline-earth or lanthanide(III) complexes could be converted into the hetero-dinuclear complexes upon reaction with nickel(II), copper(II), zinc(II), cobalt(II), manganese(III) salts, etc. [428].



Scheme 52.

The mononuclear complexes have been obtained by reaction of the preformed ligand with the metal salt or by template synthesis. The d-metal ion invariably coordinates the Schiff base site while the s- or 4f-metal ion always fills the crown-ether like chamber. Thus this specific coordination preference allows the formation of pure hetero-dinuclear complexes (Scheme 52). The properties of several of these complexes, including the X-ray structures (i.e. NiBa, NiNa, ZnBa, etc.) have been already reported in previous reviews [5,42].

The reaction of $\text{H}_2\text{-254e}$, derived from the condensation in an inert atmosphere of 1,2-diaminobenzene with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, forms $[\text{Mn}(\text{254e})] \cdot \text{CH}_3\text{OH}$ whose oxygenation in CH_3OH followed by the addition of NH_4PF_6 produced the manganese(III) monomer $[\text{Mn}(\text{254e})](\text{PF}_6)$. The same reaction in the presence of O_2 in CH_3CN produced $[\text{Mn}(\text{254e})(\text{CH}_3\text{COO})]$ as a red-brown precipitate. The low solubility of $[\text{Mn}(\text{254e})(\text{CH}_3\text{COO})]$ in CH_3CN may be due to formation of a polymeric material in which acetate groups bridge the manganese(III) centers [429].

The addition of sodium, potassium, calcium or barium triflates to $[\text{Mn}(\text{254e})(\text{CH}_3\text{COO})]$ in CH_3CN , followed by a slow diffusion of diethylether into the resulting solution affords $[\text{MnM}(\text{254e})(\text{CH}_3\text{COO})(\text{CF}_3\text{SO}_3)_x] \cdot n\text{H}_2\text{O}$ [429] (Fig. 256). In $[\text{MnBa}(\text{254e})(\text{CH}_3\text{COO})(\text{CF}_3\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$

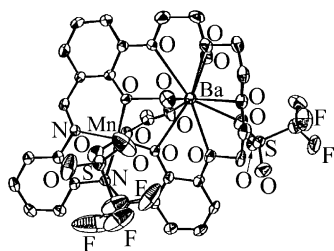


Fig. 256. Structure of $[\text{MnBa}(\mathbf{254e})(\text{CH}_3\text{COO})(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})]$ (adapted from Ref. [429]).

the manganese(III) ion adopts a pseudo-octahedral geometry with the equatorial plane consisting of two imine nitrogens and two phenolate oxygens of the Schiff-base ligand. An oxygen from one triflate group and an oxygen from the acetate are the axial ligands. The barium ion is coordinated by ten oxygens: four from the crown ether, two from the H_2O molecules, two from the Schiff base phenolate groups, one from the triflate group not bound to manganese and one from the acetate group [429].

It was reported above that the macrocyclic ligands of Scheme 52 coordinate lanthanide(III) ions into the crown-ether chamber rather than into the N_3O_2 Schiff base. On the other hand the same crown-ether chambers are involved in the coordination of alkali ions. Thus, although both ions prefer coordination at the O_2O_3 chamber, it was surmised that the use of the Na^+ containing complex may force the coordination of the lanthanide(III) ion into the Schiff base chamber. This synthetic strategy was successful as shown by the spectroscopic properties and X-ray structure of $[\text{YbNa}(\mathbf{156})(\text{Cl})_2(\text{CH}_3\text{OH})]$ (Fig. 257) [430]. The ytterbium(III) ion is coordinated by two chlorine atoms in *trans* positions and by three nitrogen and two negatively charged phenyl oxygen atoms of the ligand, reaching heptacoordination with a pentagonal bipyramidal geometry. The sodium ion is coordinated by the three ether oxygen atoms and the two phenolic oxygens that act as a bridge. A methanol molecule is also coordinated in the apical position of the resulting pentagonal pyramidal polyhedron.

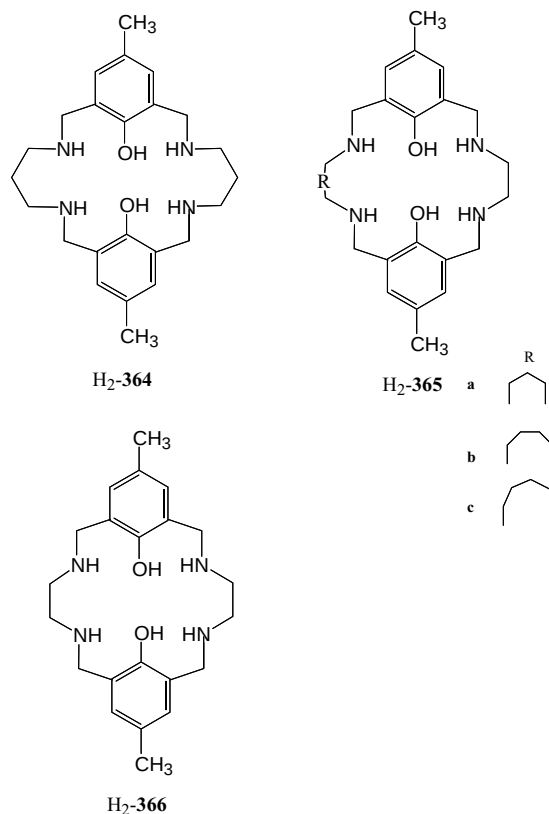
The high temperature ^1H NMR spectrum (65°C , CD_3OD) of $[\text{YbNa}(\mathbf{156})(\text{Cl})_2(\text{CH}_3\text{OH})]$ is consistent with the occurrence of a motion in the macrocyclic ring which reduces to half of the number (12) of the observed resonances. Although the spectrum covers a range of ca. 70 ppm, the resonances associated with the two N_3O_2 and O_2O_3 chambers can be unambiguously assigned. In fact, the paramagnetic ytterbium(III) ion causes a large spread of the five protons (and of the methyl group) associated with the Schiff base compartment (-15 to -57 ppm) whereas the protons associated with the crown ether and aromatic moieties fall in the region $+7$ to -8 ppm, i.e. they only feel in part the paramagnetism of the lanthanide ion [430]. The ^{23}Na NMR spectrum at ambient temperature consists of the broad absorption of the bound sodium ion (Na^b) at ca. 40 ppm up field from that of the free sodium ion (Na^f). Upon increasing the temperature the exchange between Na^f and

Na^b becomes fast on the NMR timescale and, at 65°C , a relatively narrow absorption at ca. -16 ppm is observed. It seems reasonable to suggest that the release of the sodium ion from the crown-ether chamber induces an overall flexibility of the macrocycle as the ^1H NMR spectrum recorded at ambient temperature is more complex than that obtained at 65°C . The high and negative paramagnetic ^{23}Na NMR shift observed for Na^b strongly suggests that the principal axis of the magnetic susceptibility tensor associated with the ytterbium(III) ion lies along the Yb–Na direction rather than along an axis perpendicular to the macrocyclic plane. This finding may be highly relevant to development of a novel class of ^{23}Na -shift reagents which could be very useful in separating the ^{23}Na NMR resonances from intra- and extra-cellular components [430].

8.4. Dinuclear complexes with macrocyclic polyaza ligands

Great attention has been paid, especially to the [2+2] tetraamine macrocycles obtained by reduction of the corresponding tetraimine Schiff bases. Analogously to the related Schiff bases systems, these reduced ligands can give rise to a large variety of mononuclear, homo- or hetero-dinuclear complexes.

The addition of 1 equiv. of $\text{H}_2\text{-364}$ to an ethanol solution of $[\text{VO}(\text{OEt})_3]$ yields an orange yellow compound of composition $[\text{VO}(\mathbf{364})]\cdot\text{H}_2\text{O}$. The formation of a vanadyl(IV) complex from a vanadium(V) precursor indicates that the ligand anion stabilizes the neutral $[\text{VO}(\mathbf{364})]$ species [431].



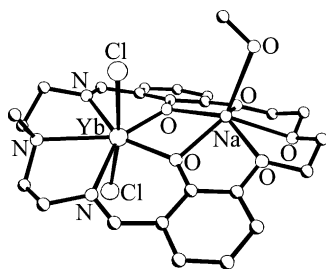


Fig. 257. Structure of $[\text{YbNa}(\mathbf{156})(\text{Cl})_2(\text{CH}_3\text{OH})]$ (adapted from Ref. [430]).

The reaction between $\text{H}_2\text{-364}$ and vanadyl sulfate (1:1) in methanol affords $[\text{VO}(\text{H}_2\mathbf{364})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ [139]. When 1 equiv. of $\text{H}_2\text{-364}$ is treated with 2 equiv. of vanadyl sulfate in the presence of 2 equiv. of triethylamine, $[(\text{VO})_2(\mathbf{364})(\mu\text{-SO}_4)] \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$ is obtained along with $[\text{VO}(\text{H}_2\mathbf{364})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ [431,432].

$[\text{VOZn}(\mathbf{364})(\text{SO}_4)] \cdot 4\text{H}_2\text{O}$ was obtained by treating $[\text{VO}(\text{H}_2\mathbf{364})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ with zinc perchlorate and triethylamine [431,432].

The EPR and IR spectra of $[\text{VO}(\mathbf{364})] \cdot \text{H}_2\text{O}$ indicated stacking of the molecules due to $\text{V}=\text{O} \cdots \text{V}=\text{O}$ interactions. In $[\text{VO}(\text{H}_2\mathbf{364})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ and $[\text{VOZn}(\mathbf{364})(\text{SO}_4)] \cdot 4\text{H}_2\text{O}$ the unidentate sulfate is bound to the octahedral vanadium and two of the secondary amino groups in $[\text{VO}(\text{H}_2\mathbf{364})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ are protonated. Both of these complexes undergo oxidation to produce oxovanadium(V) species with $E_{1/2} = 0.40$ V for $[\text{VO}(\text{H}_2\mathbf{364})(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$, 0.455 V for $[\text{VOZn}(\mathbf{364})(\text{SO}_4)] \cdot 4\text{H}_2\text{O}$ versus saturated calomel electrode (SCE). A fairly strong antiferromagnetic exchange interaction ($J = -128 \text{ cm}^{-1}$) has been found in $[(\text{VO})_2(\mathbf{364})(\mu\text{-SO}_4)] \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$.

In $[(\text{VO})_2(\mathbf{364})(\mu\text{-SO}_4)] \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$ the two octahedral vanadium centers, separated by 3.077 Å, are bridged by sulfate and have a *syn-oxo* configuration (Fig. 258a) [431,432].

Analogously homo-dinuclear copper(II) and nickel(II) complexes have been prepared and fully characterized also by X-ray diffractometry [431,432]. $[\text{Cu}_2(\mathbf{364})(\text{ClO}_4)_2]$ (Fig. 258b) consists of two copper(II) centers bridged by two phenoxide oxygen atoms with two secondary amine nitrogen donors completing the distorted CuN_2O_2 plane. The copper coordination is a severely distorted, axially elongated octahedron. The equatorial CuN_2O_2 chromophore is twisted and the copper center lies in the mean plane of the N_2O_2 donor set, separated by 2.993 Å [431,432].

The related complex $[\text{Cu}_2(\mathbf{364})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$, prepared in dry methanol [431,432], consists of two square pyramidal copper(II) centers bridged by two phenoxide oxygen atoms with two secondary amine nitrogen donors completing the distorted CuN_2O_2 plane. The copper center is displaced from the mean plane of the N_2O_2 atoms toward the coordinated methanol and the two copper centers are separated by 3.088 Å. The methanol molecules are bound in a

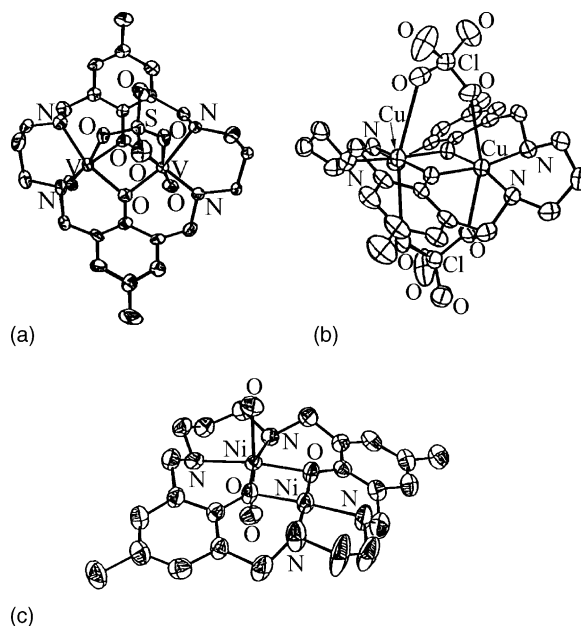


Fig. 258. Structure of $[(\text{VO})_2(\mathbf{364})(\mu\text{-SO}_4)]$ (a), $[\text{Cu}_2(\mathbf{364})(\text{ClO}_4)_2]$ (b), and $[\text{Ni}_2(\mathbf{365a})(\text{H}_2\text{O})_2]^{2+}$ (c) (adapted from Refs. [431,432]).

trans fashion, above and below the dinuclear center and the methanol–copper interaction is relatively weak [431].

Similarly the structure of $[\text{Cu}_2(\mathbf{364})(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$ involves a *trans* arrangement of two axially bound chlorine atoms about the binuclear center [431,432].

A noticeable feature of these dicopper(II) compounds is that they undergo four one-electron transfers to generate dicopper species with oxidation states varying between 1+ and 3+.

$[\text{Ni}_2(\mathbf{364})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$ consists of two nickel(II) centers bridged by two phenoxide oxygen atoms with two secondary amine nitrogen donors completing the NiN_2O_2 plane. The metal centers reach pseudo-octahedral environments by interacting with *trans* axially disposed methanol molecules and perchlorate ions. The two metal centers are separated by 3.135 Å [431].

In $[\text{Ni}_2(\mathbf{364})(\text{py})_2](\text{ClO}_4)_2$ the two nickel(II) centers are in a square pyramidal configuration with N_2O_2 in planar donor sets, involving two phenoxide bridges and two *trans*-axially disposed pyridines. The distance between the two nickel(II) centers is 3.206 Å [431,432].

The asymmetric macrocycle $\text{H}_2\text{-365a}$ was synthesized by the sequential addition of 1 equiv. each of 1,2-diaminoethane and 1,3-diaminopropane to a boiling methanol solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ and 2,6-diformyl-4-methylphenol in a 1:1:2 molar ratio over a period of several hours. After a reduction of the dimagnesium Schiff base macrocyclic complex thus formed with NaBH_4 , the metal-free $\text{H}_2\text{-365a}$ was separated by sequestering magnesium with disodium ethylenediaminetetracetate. Noticeably, if the order of the addition of the diamines is reversed, instead of $\text{H}_2\text{-365a}$, solely $\text{H}_2\text{-364}$ is obtained [431,432].

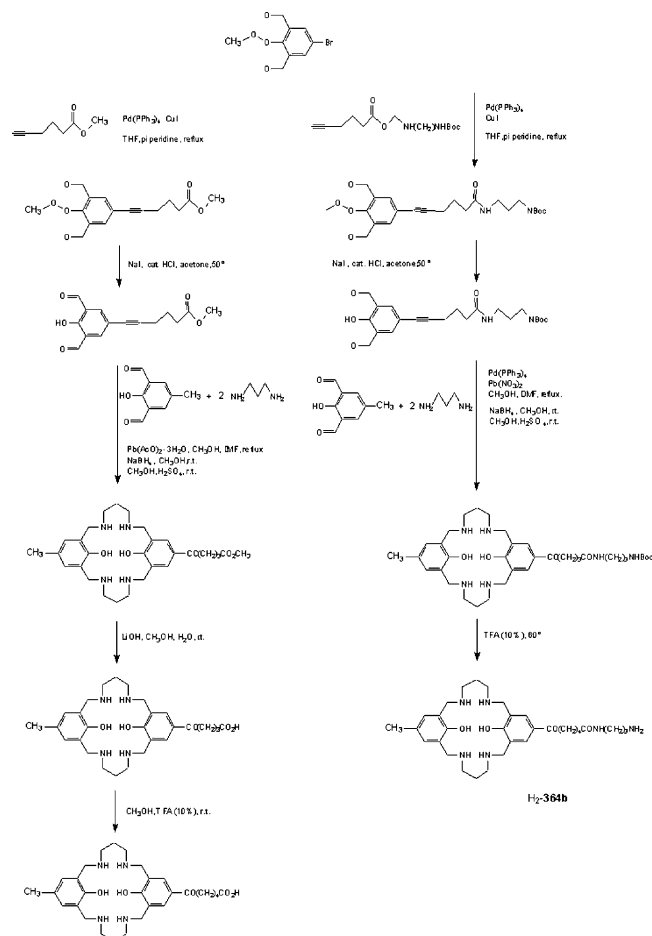
Although treatment of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with $\text{H}_2\text{-365a}$ in the presence of triethylamine gave a deep red solution of $[\text{Ni}_2(\text{365a})(\text{H}_2\text{O})_2]^{2+}$, the perchlorate salt was not amenable to crystallization. Several counter anions were tried but only the iodide salt turned out to afford single crystals of $[\text{Ni}_2(\text{365a})(\text{H}_2\text{O})_2](\text{I})_2$, which is a mixed spin-state complex where one nickel(II) is square planar in the smaller N_2O_2 chamber and the other nickel(II) is octahedral in the larger N_2O_2 chamber (Fig. 258c). By the reaction with pyridine, $[\text{Ni}(\text{365a})(\text{H}_2\text{O})_2](\text{I})_2$ produces $[\text{Ni}_2(\text{365a})(\text{py})](\text{I})_2$ where one nickel(II) ion is square planar while the other nickel(II) ion is square pyramidal [431,432].

For $[\text{Ni}_2(\text{364})(\text{CH}_3\text{OH})_2(\text{ClO}_4)_2]$ in DMSO with a glassy-carbon electrode, the two one-electron reduction steps ($E_{1/2} = -1.32, -1.65$ V versus SCE) occur quasi reversibly. The $\text{Ni}^{\text{II}}\text{Ni}^{\text{I}}$ species were not stable in the coulometric time scale. The cyclic voltammogram of $[\text{Ni}(\text{364})(\text{CH}_3\text{OH})_2(\text{ClO}_4)_2]$ in CH_3CN with a Pt electrode at positive potential range exhibits two reversible one-electron oxidation steps ($E_{1/2} = 0.94, 1.08$ V versus SCE). The occurrence of these two waves at the indicated potentials was also observed in differential-pulse voltammetric measurements. Controlled-potential electrolysis at 1.3 V consumed 2 equiv. of charge implicating the two-electron oxidation of $[\text{Ni}(\text{364})(\text{CH}_3\text{OH})_2(\text{ClO}_4)_2]$ to a dinickel(III) species. The ligand itself and $[\text{Zn}_2(\text{364})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ do not show any electrochemical response in the entire potential range -2.0 to $+1.7$ V. The stability of the mixed-valence $\text{Ni}^{\text{II}}\text{Ni}^{\text{I}}$ and $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ species can be related to their comproportionation constants, K_{com} ; although $K_{\text{com}} = 3.8 \times 10^5$ for the reduction process implies considerable stability of the $\text{Ni}^{\text{II}}\text{Ni}^{\text{I}}$ species, a much lower value of K_{com} (2.3×10^2) for the oxidation process suggest easier access to the dinickel(III) species [431].

The reaction of $\text{H}_2\text{-364}$ with CuCl_2 forms green brown crystals of the trinuclear complex $[\text{Cu}_3(\text{364})(\text{Cl})_4]$ [431]. Conductance measurements in DMSO indicate that this trinuclear compound is a 1:1 electrolyte. The dissociation of this complex is perhaps most likely to occur with the formation of the cation $[\text{Cu}_2(\text{364})]^{2+}$ and a solvated chloro-occupate anion.

$[\text{Ni}_2(\text{364})(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 4\text{NH}_2\text{CONH}_2$, $[\text{Ni}_2(\text{364})(\text{CH}_3\text{OH})_2(\text{ClO}_4)_2] \cdot 2\text{NH}_4\text{ClO}_4$, $[\text{Ni}_2(\text{364})(\text{py})_2](\text{ClO}_4)_2$, $[\text{Ni}_2(\text{364})(\mu\text{-OOCCH}_2\text{NH}_3)(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}_2(\text{364})(\text{NCS})_2(\text{H}_2\text{O})_2] \cdot 2\text{Me}_2\text{NCHO}$ have been prepared and characterized also by X-ray diffractometry [431,432,435]. In the inclusion complex $[\text{Ni}_2(\text{364})(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 4\text{NH}_2\text{CONH}_2$ each nickel(II) ion in the cation $[\text{Ni}_2(\text{364})(\text{H}_2\text{O})_4]^{2+}$ is coordinated to two secondary amine nitrogen donors, a two bridging phenolate groups from the macrocycle and the tetragonally distorted octahedral geometry is obtained by axial coordination of two water molecules. The Ni_2O_2 (phenolate) group from an exact plane and there is a center of inversion at the middle of this plane [432].

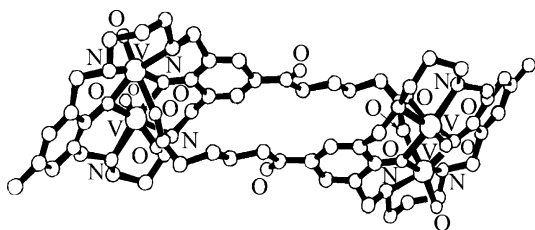
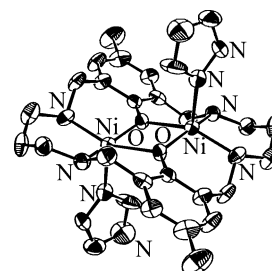
Functionalized 2,6-diformylphenols, the related [2+2] asymmetric Schiff bases and the reduced macrocyclic poly-



Scheme 53.

amines $\text{H}_3\text{-364a}$ and $\text{H}_2\text{-364b}$ have been obtained according to Scheme 53 [432]. An addition of 2 equiv. of $\text{VO}(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ in CH_3OH in the presence of Et_3N to either hexadentate ligands $\text{H}_3\text{-364a}$ and $\text{H}_2\text{-364b}$ affords the vanadyl(IV) complexes $[(\text{VO})_2(\text{H-364a})](\text{CF}_3\text{COO})_2$ and $[(\text{VO})_2(\text{364b})](\text{CF}_3\text{COO})_2$. In the X-ray structure of $[(\text{VO})_2(\text{H-364a})](\text{CF}_3\text{COO})_2$, both vanadyl groups occupy eclipsed axial positions with a weakly bound bridging carboxylate in the *trans*-position. Although solution studies suggest that various carboxylates can occupy the bridging site *trans* to both vanadyls, the solid state structure reveals that the bridging carboxylate is provided intramolecularly to form a tetranuclear entity (Fig. 259) [432].

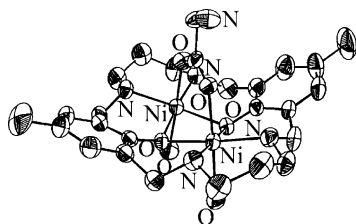
The dinucleating macrocycles $\text{H}_2\text{-L}$ ($\text{H}_2\text{-L} = \text{H}_2\text{-364}$, $\text{H}_2\text{-365a-c}$, $\text{H}_2\text{-366}$), containing similar or dissimilar coordination sites, have been prepared by reduction of the corresponding lead Schiff base complexes with NaBH_4 [433]. The reaction of these macrocycles with $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in a methanol/water mixture formed the dinuclear nickel(II) complexes $[\text{Ni}_2(\text{L})(\text{CH}_3\text{COO})_2](\text{solv})_x$ ($\text{solv} = \text{H}_2\text{O}$, CH_3OH) as blue crystals. $[\text{Ni}_2(\text{365a})(\text{CH}_3\text{COO})(\text{NCS})(\text{CH}_3\text{OH})]$ was obtained as green microcrystals when $\text{H}_2\text{-365a}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and NH_4SCN were

Fig. 259. Structure of $[(VO)_2(H\text{-}364a)]_2^{4+}$ (adapted from Ref. [432]).Fig. 261. Structure of $[Ni_2(364)(H\text{-}Im)_2]^{2+}$ (adapted from Ref. [434]).

reacted in a 1:2:1 molar ratio in methanol. These dinuclear nickel(II) complexes show a ferromagnetic interaction ($J = 10.1\text{--}2.1\text{ cm}^{-1}$) [433].

In $[Ni(366)(CH_3COO)_2] \cdot 10H_2O$ the six coordination about each nickel(II) ion is reached by two phenolic oxygens and two amino nitrogens of the macrocycle and two carboxylate oxygens of the chelating acetate group. The macrocycle assumes a folded conformation and each N_2O_2 donor set coordinates in a non-planar manner affording a *cis*- β -octahedral geometry about each nickel(II) ion. The $Ni \cdots Ni$ distance is $3.004\text{ \AA}$. $[Ni_2(364)(CH_3OH)_2(ClO_4)_2] \cdot 2NEt_3 \cdot HClO_4$ on reaction with glycine, β -alanine and glycylglycine affords the μ -carboxylato complexes $[Ni_2(364)(\mu\text{-OOC-R-NH}_3)(H_2O)_2](ClO_4)_2 \cdot nH_2O$. The complex where $R = CH_2$ consists of two nickel(II) centers bridged by two phenolic oxygens and two carboxylate oxygens of the zwitterionic form of glycine. The coordination environment NiN_2O_4 of each nickel center is completed by two secondary amine nitrogen donors of the macrocyclic ligand and a water molecule *trans* axially disposed to the carboxylate oxygen. The NiO_2Ni group forms a distorted square plane in which the two metal centers are separated by $3.066\text{ \AA}$ [432,433] (Fig. 260). Again a ferromagnetic interaction between the two nickel(II) ions occurs as a consequence of the small $Ni\text{--}O\text{--}Ni$ angles. Similar dinickel(II) complexes with larger $Ni\text{--}O\text{--}Ni$ angles show an antiferromagnetic behaviour.

Electrochemical studies prove that the coordination of acetate in $Ni_2(L)(CH_3COO)_2 \cdot nH_2O$ ($H_2\text{-}L = H_2\text{-}364$, $H_2\text{-}365a\text{--}c$, $H_2\text{-}366$) destabilizes the nickel(I) state; the stability of the mixed $Ni^I Ni^{II}$ species derived from $[Ni_2(364)(CH_3COO)_2]$ is lower than that of $[Ni_2(364)(CH_3OH)(ClO_4)_2]$. On the contrary the stability of the $Ni^I Ni^{III}$ species derived

Fig. 260. Structure of $[Ni_2(364)(\mu\text{-OOCCH}_2\text{NH}_3)(H_2O)_2]^{2+}$ (adapted from Refs. [432,433]).

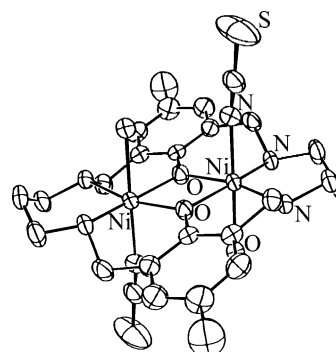
from $[Ni_2(364)(CH_3COO)_2]$ appears to be larger than that of $[Ni_2(364)(CH_3OH)_2](ClO_4)_2$ [431,433].

$[Ni_2(364)(H\text{-}Im)_2]^{2+}$ shows that two square pyramidal nickel(II) centers are bridged by two phenoxide oxygens and the distorted Ni_2O_2 plane is completed by two secondary amine nitrogens. The imidazole ligands are bound in a *trans* fashion above and below the dinuclear centers. The center of inversion is at the middle of Ni_2O_2 plane. The apical displacement of the nickel(II) center towards the imidazole is $0.307\text{ \AA}$ [434] (Fig. 261).

In $[Ni_2(364)(NCS)_2(H_2O)_2]$ (Fig. 262) the two nickel centers are bridged by two phenoxide oxygen atoms with two secondary amine nitrogen donors completing the NiN_2O_2 basal plane. Each of the metal centers achieves a pseudo-octahedral configuration through the axial coordination of thiocyanate ions and water molecules, which are *trans* to each other. The macrocyclic donor atoms, N_2O_2 , form an exact plane, from which the nickel ion is displaced by $0.127\text{ \AA}$. The two nickel(II) ions are separated by $3.113\text{ \AA}$. A NH group of the macrocycle is involved in hydrogen bonding with the oxygen atom of a water molecule. Surprisingly, the nitrogen atom of the thiocyanate ion is also involved in a hydrogen bonding with a water molecule [431,432,435].

$[Ni_2(364)(NCS)_2(H_2O)_2]$ undergoes two reversible one-electron oxidation steps ($E_{1/2} = 0.90, 1.05\text{ V}$ versus SCE, Pt/ CH_3CN) with the formation of $Ni^II Ni^{III}$ and $Ni^{III} Ni^{III}$ species [431,432,435].

Variable-temperature ($5\text{--}300\text{ K}$) susceptibility measurements carried out for the binuclear nickel(II) complexes

Fig. 262. Structure of $[Ni_2(364)(NCS)_2(H_2O)_2]$ (adapted from Ref. [435]).

$[\text{Ni}_2(\mathbf{364})(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 4\text{NH}_2\text{CONH}_2$, $[\text{Ni}_2(\mathbf{364})(\text{NCS})_2(\text{H}_2\text{O})_2] \cdot 2\text{Me}_2\text{NCHO}$, $[\text{Ni}_2(\mathbf{364})(\text{CH}_3\text{OH})_2(\text{ClO}_4)_2] \cdot 2\text{NHEt}_3\text{ClO}_4$, $[\text{Ni}_2(\mathbf{364})(\text{H-Im})_2](\text{ClO}_4)_2$, $[\text{Ni}_2(\mathbf{364})-(\text{py})_2](\text{ClO}_4)_2$ and $[\text{Ni}_2(\mathbf{364})(\mu\text{-OOCCH}_2\text{NH}_3)(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ show they behave antiferromagnetically with the exchange parameter, J , respectively of -17 , -21 , -29 , -50 , -67 and -1 cm^{-1} . The decrease in the value of J from the first to the third complex is attributed to the increase in tetragonal distortion around the metal centers. The change in stereochemistry of nickel(II) to the square pyramidal configuration leads to the significant decrease in the value of J for the fourth and the fifth complexes. The net effective exchange coupling constant of the sixth complex, in which two orthogonal superexchange pathways are involved, is very small [431,432,434].

The reaction of equimolar amounts of $\text{H}_2\text{-364}$ and $\text{Fe}(\text{ClO}_4)_3$ in methanol in the presence of triethylamine (2 equiv.) forms $[\text{Fe}_2(\text{H-364})_2(\mu\text{-OH})_2](\text{ClO}_4)_2$. This complex, when treated with NaOH , produces $[\text{Fe}_2(\mathbf{364})_2(\mu\text{-OH})_2] \cdot 2\text{H}_2\text{O}$ and, when treated with HClO_4 , $[\text{Fe}(\text{H}_2\text{-364})(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$. The hydroxide bridged diiron(III) complexes $[\text{Fe}_2(\text{H}_2\text{-365a})_2(\mu\text{-OH})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ and $[\text{Fe}_2(\mathbf{365a})_2(\mu\text{-OH})_2] \cdot 2\text{H}_2\text{O}$ were prepared in the same way [434].

In these complexes only N_2O_2 donation to the metal centers occurs, while the two uncoordinated amino nitrogens either remain singly protonated or one or both of these is doubly protonated. The structure of $[\text{Fe}_2(\text{H-364})_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ (Fig. 263) consists of two macrocyclic FeO_3N_2 coordination cores linked by two hydroxyl groups which lead to edge sharing between two FeO_4N_2 octahedra. Of the six N_4O_2 donor atoms of the macrocyclic ligand only two nitrogen and two oxygen atoms are involved in coordination and one of the two non coordinated amine nitrogens is protonated. Thus, although both phenols are deprotonated the macrocycle behaves as monoanionic. The macrocyclic ligand is folded in such a way that the two phenolate oxygens are in a *cis* position. A distorted octahedral geometry occurs about the iron centers which are separated by $3.085 \text{ \AA}$.

Variable-temperature magnetic susceptibility data for $[\text{Fe}_2(\text{H-364})_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ and $[\text{Fe}_2(\text{H}_2\text{-365a})(\mu\text{-OH})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ indicate weak antiferromagnetic interactions in each case with a $J = -5.5$ and -7.3 cm^{-1} , respectively.

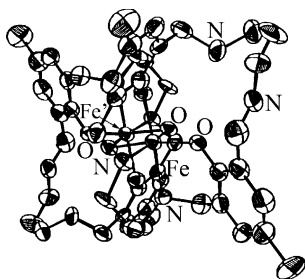


Fig. 263. Structure of $[\text{Fe}_2(\text{H-364})_2(\mu\text{-OH})_2]^{2+}$ (adapted from Refs. [434,436]).

Electronic and Mössbauer spectra indicate that $[\text{Fe}_2(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$, prepared by reaction of $[\text{Fe}_2(\text{H-364})_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ with $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ under nitrogen in the presence of CH_3COONa is a valence trapped complex while $[\text{Fe}_2(\mathbf{43})(\mu\text{-CH}_3\text{COO})_2](\text{ClO}_4)$ is a valence delocalized complex showing a fast electron delocalization rate [436]. No magnetic interaction has been detected for $[\text{Fe}_2(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$ [436].

The hetero-dinuclear complexes $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Zn}^{2+}$, Co^{2+} , Ni^{2+} , Mn^{2+}), obtained by transmetallation reaction of $[\text{Fe}_2(\text{H-364})_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ with the appropriate metal perchlorate in the presence of an excess of sodium acetate and in an acetonitrile/methanol solution, have closely related structures. In the cation $[\text{FeNi}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})]^+$ the two metal high-spin six coordinated centers are bridged by the two phenolate oxygens and one an acetate oxygens. They show an irregular octahedral geometry and have N_2O_2 equatorial donors provided by the macrocyclic ligand. The remaining apical position of the iron(III) center is occupied by a water molecule, while that of the nickel(II) ion by an acetate oxygen. The $\text{Fe} \cdots \text{Ni}$ distance is $3.03 \text{ \AA}$ [437] (Fig. 264).

$[\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)$ shows a weak antiferromagnetic behaviour ($J = -1.8 \text{ cm}^{-1}$) while the $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Co}^{\text{II}}$ complexes exhibit a weak ferromagnetic behaviour ($J = 1.7$ and 4.2 cm^{-1} , respectively).

The iron(III) center in $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)$ exhibits quasi-reversible redox behaviour between -0.44 and -0.48 V versus Ag/AgCl associated with reduction to iron(II). The oxidation of cobalt(II) in the $\text{Fe}^{\text{III}}\text{Co}^{\text{II}}$ complex occurs quasi-reversibly at 0.74 V , while both nickel(II) and manganese(II) in the $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}$ complexes undergo irreversible oxidation at 0.85 V [437].

$\text{H}_2\text{-365a}$ reacts with $\text{VO}(\text{acetylacetonate})_2$ to produce a mixture of two monomeric oxovanadium(IV) and one oxovanadium(V) complexes: the two monomeric vanadium(IV) complexes are the positional isomers of composition $[\text{VO}(\mathbf{365a})]$, which differ with respect to the ligand

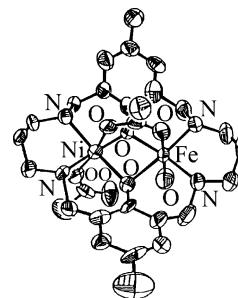


Fig. 264. Structure of $[\text{FeNi}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]^+$ (adapted from Ref. [437]).

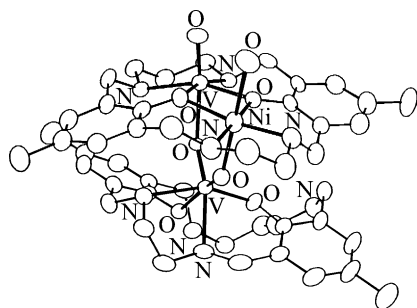


Fig. 265. Structure of $[\{VONi(365a)(H_2O)\}\{VO_2(H-365a)\}]^{2+}$ (adapted from Ref. [438]).

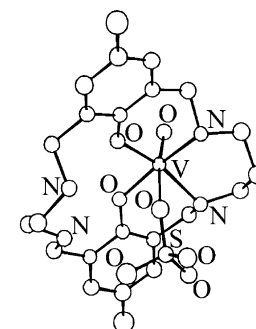
compartment occupancy, while the vanadium(V) complex has been formulated as $[VO(365a)(OH)]$. Oligomeric $V=O \cdots V=O \cdots$ interactions in these species can be held responsible for their poor solubility behaviour [438].

This mixture of complexes reacts with nickel(II) perchlorate affording three compounds of composition $[VONi(365a)(H_2O)_2](ClO_4)_2$, $[\{VONi(365a)(H_2O)\}\{VO_2(H-365a)\}](ClO_4)_2 \cdot 3H_2O \cdot 2.5CH_3OH$ and $[NiVO(365a)](ClO_4)_2$. $[VONi(365a)(H_2O)](ClO_4)_2$ reacts with pyridine to produce $[VONi(365a)(py)](ClO_4)_2 \cdot H_2O$. The coordination geometry of nickel is octahedral in the first two complexes, square planar in the third complex, and square pyramidal in the fourth one [438].

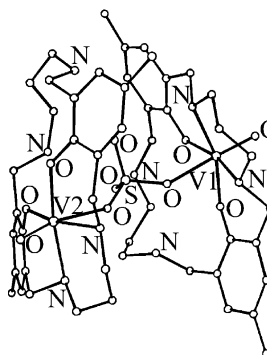
The formation of the mixed-valence heterotrimeric complex, $[\{VONi(365a)(H_2O)\}\{VO_2(H-365a)\}](ClO_4)_2$, solvent, has been structurally verified (Fig. 265). In the cation $[\{VONi(365a)(H_2O)\}\{VO_2(H-365a)\}]^{2+}$, the two metal centers in the $\{VONi(365a)(H_2O)\}^{2+}$ unit are bridged by the two phenolate oxygens of the macrocyclic ligand and each of the metal ions have N_2O_2 equatorial planes, of which the larger ligand compartment is occupied by the vanadium. Both the metal centers have a distorted octahedral geometry. The $\{VONi(365a)(H_2O)\}$ unit is of convex shape when viewed down the $V=O$ and $Ni-O$ (water) bonds. This may be realized by considering the displacements of the metal centers and phenolate oxygens, all in the same direction, from an exact plane formed by the four amine nitrogens. In this context it may be noted that while the nickel ion is only slightly displaced (0.02 Å) from its N_2O_2 basal plane, the vanadium ion is pushed toward the oxygen atom by about 0.32 Å from its N_2O_2 equatorial plane. Furthermore, the two metal centers are separated by 3.006 Å.

In the mononuclear $\{VO_2(H-365a)\}$ unit the vanadium ion occupies the smaller ligand compartment, while the empty larger ligand compartment adopts a folded configuration with one of its amine nitrogens protonated. The coordination environment of this vanadium(V) ion is *cis*-dioxo octahedral, the metal ion being displaced from its basal N_2O_2 plane towards one of the oxo groups by 0.18 Å.

When H_2-365a is reacted with vanadyl(IV) sulfate, $[VO(H_2-365a)(SO_4)] \cdot 5H_2O$ is obtained exclusively. Two secondary amines are protonated and the vanadium(IV) ion



(a)



(b)

Fig. 266. Structure of $[VO(H-365a)(SO_4)]$ (a) and $[\{VO(H_2-364)\}(\mu-SO_4)]^{2+}$ (b) (adapted from Refs. [438,439]).

occupies the N_2O_2 equatorial plane provided by the larger compartment of the ligand and is axially coordinated by one the oxygen atom of a sulfate group [438] (Fig. 266a).

$[VO(H_2-365a)(SO_4)] \cdot 5H_2O$ quantitatively transforms into $[VO(H_2-365a)](NO_3)_2$ on treatment with lead nitrate. In CH_3CN this complex behaves as a 1:2 electrolyte and in the solid state the infrared spectrum shows bands due to the ionic nitrate group [438].

The insertion of a nickel(II) ion into the vacant ligand compartment of $[VO(H_2-365a)(SO_4)] \cdot 5H_2O$ cannot be carried out straightforwardly. However, when it is reacted with 1 equiv. of $[Ni(acac)_2]$, the nickel ion smoothly gets introduced producing $[NiVO(365a)(SO_4)]$ which is a nonelectrolyte with a square planar geometry for the nickel(II) ion. The removal of the coordinated sulfate in $[NiVO(365a)(SO_4)]$ by $Ba(ClO_4)_2$ provides an alternative pathway for generating $[NiVO(365a)](ClO_4)_2$ [438].

The cyclic voltammograms for $[VO(H_2-365a)(SO_4)] \cdot 5H_2O$, $[VONi(365a)](ClO_4)_2$, $[(VO)(H_2-365a)](NO_3)_2 \cdot 2H_2O$ and $[VONi(365a)(SO_4)]$ exhibit a redox couple due to $V^{IV}O \rightleftharpoons V^VO$ oxidation in all the cases. The six coordinated oxovanadium complexes $[VO(H_2-365a)(SO_4)] \cdot 5H_2O$ and $[VONi(365a)(SO_4)]$ undergo more facile oxidation ($E_{1/2} = 0.57$ V versus $Ag/AgCl$) relative to the five coordinated species $[VONi(365a)](ClO_4)_2$ and $[(VO)(H_2-365a)](NO_3)_2 \cdot 2H_2O$ ($E_{1/2} = 0.80$ V).

$[VONi(365a)(H_2O)_2](ClO_4)_2$, $[\{VONi(365a)(H_2O)\}\{VO_2(H-365a)\}](ClO_4)_2 \cdot 3H_2O \cdot 2.5CH_3OH$ and $[VONi(365a)(py)](ClO_4)_2 \cdot H_2O$ behave ferromagnetically with an

exchange coupling constant respectively of $J = 12$, 2 and 5 cm^{-1} [438].

$\text{H}_2\text{-364}$ reacts almost quantitatively with $[\text{VO}(\text{acac})_2]$ to produce $[\text{VO}(\text{364})]\cdot\text{H}_2\text{O}$. The protonated mononuclear oxovanadium(IV) complex $[\text{VO}(\text{H}_2\text{-364})(\text{SO}_4)]\cdot 3\text{H}_2\text{O}$, whose structure seems to be similar to that determined for $[\text{VO}(\text{H}_2\text{-365a})(\text{SO}_4)]\cdot\text{H}_2\text{O}$, reacts with lead(II) nitrate in a 2:1 molar ratio to produce the violet complex $[\{\text{VO}(\text{H}_2\text{-364})\}_2(\mu\text{-SO}_4)](\text{NO}_3)_2$, where the sulfate group bridges two different monomeric units [439].

Moreover when $[\text{VO}(\text{H}_2\text{-364})(\text{SO}_4)]\cdot 3\text{H}_2\text{O}$ is treated with 1 equiv. of $[\text{Ni}(\text{acac})_2]$, $[\text{VONi}(\text{364})(\text{H}_2\text{O})_2(\text{SO}_4)]\cdot\text{H}_2\text{O}$ is obtained. On the other hand, the reaction between $[\text{VO}(\text{364})]\cdot\text{H}_2\text{O}$ and nickel(II) sulfate affords $[\text{VONi}(\text{364})\text{-(SO}_4)(\text{H}_2\text{O})]$. IR spectra suggest that in the first violet complex the sulfate group coordinates as unidentate while in the second one as bridging [439].

In $[\{\text{VO}(\text{H}_2\text{-364})\}_2(\mu\text{-SO}_4)](\text{NO}_3)_2$ the $\{\text{VO}(\text{H}_2\text{-364})\}$ units joined through the sulfate moiety. Each vanadium(IV) ion is coordinated to the secondary amine nitrogens and two phenolate oxygens, which provide the equatorial plane, and a distorted octahedral configuration is obtained through the axial coordination of an oxo oxygen and bridging sulfate oxygen. The two vanadium(IV) ions are very similar but not identical. The molecular structure also reveals the presence of at least ten fairly strong hydrogen bonds, of which seven are intramolecular. They are mainly between the protonated amines and the oxygen atoms of the sulfate or nitrates [439] (Fig. 266b).

$[\{\text{VO}(\text{H}_2\text{-364})\}_2(\mu\text{-SO}_4)](\text{NO}_3)_2$ undergoes stepwise oxidation to produce $\text{VO}^{\text{IV}}\text{VO}^{\text{V}}$ and $\text{VO}^{\text{V}}\text{VO}^{\text{V}}$ species respectively with $E_{1/2} = 0.445 \text{ V}$ and $E_{1/2} = 0.60 \text{ V}$ versus Ag–AgCl electrode; the comproportionation constant is $K_{\text{com}} = 4.2 \times 10^2$. $[\text{VONi}(\text{364})((\text{SO}_4)(\text{H}_2\text{O})_2)]\cdot\text{H}_2\text{O}$ and $[\text{VONi}(\text{364})(\mu\text{-SO}_4)(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ have different electrochemistry. In the first complex the oxovanadium(IV) and nickel(II) centers are reversibly oxidized at 0.436 and 0.756 V, respectively, while in the second one irreversible oxidation of both metal centers takes place at 1.05 and 1.25 V.

The magnetic moment of $[\{\text{VO}(\text{H}_2\text{-364})\}_2(\mu\text{-SO}_4)]\text{-(NO}_3)_2$ decreases with the lowering of the temperature from 299 to 5 K, indicating very weak intra-/or inter-molecular exchange interactions. Its EPR spectra in fluid solution and glass, however, showed the absence of $\text{VO}\cdots\text{VO}$ electron-spin interaction, while the hetero-dinuclear VONi complexes behave ferromagnetically and their exchange coupling constants J are 10 and 6 cm^{-1} , respectively. This magnetic behaviour is expected since both the magnetic orbitals of nickel ($d_{x^2-y^2}$ and d_z^2) one orthogonal to that of vanadium (d_{xy}) [439].

When $[\text{VO}(\text{364})]\cdot\text{H}_2\text{O}$ is reacted with an equimolar amount of $\text{M}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+}) in the presence of CH_3COONa , $[\text{VOCu}(\text{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{OH})](\text{ClO}_4)$ and $[\text{VOM}(\text{364})(\mu\text{-CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)\cdot\text{H}_2\text{O}$ are obtained.

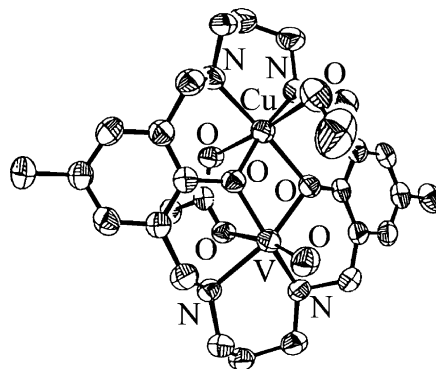


Fig. 267. Structure of $[\text{VOCu}(\text{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{OH})]^+$ (adapted from Ref. [440]).

The mixture of the two forms of $[\text{VO}(\text{365a})]$ along with a small fraction of $[\text{VO}(\text{365a})(\text{OH})]$, resulting from the reaction between $[\text{VO}(\text{acac})_2]$ and $\text{H}_2\text{-365a}$, on treatment with $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ and CH_3COONa leads to the formation of $[\text{VOCu}(\text{365a})(\mu\text{-CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)\cdot\text{H}_2\text{O}$ [440].

In $[\text{VOCu}(\text{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{OH})](\text{ClO}_4)$ (Fig. 267) the two metal centers are triply bridged by the two phenolate oxygens and the acetate ion. Both the metal centers are six coordinated with distorted octahedral geometry and have N_2O_2 equatorial donors provided by the macrocyclic ligand. The remaining position of vanadium is occupied by the oxo oxygen and that of copper by distant contact with the methanol oxygen. Although, the copper center is only slightly displaced from its N_2O_2 basal plane, the vanadium center is pushed toward the oxo oxygen by $0.258 \text{ \AA}$ from the N_2O_2 equatorial plane. As a result of the acetate bridging, the complex is distorted [440].

$[\text{VOCu}(\text{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{OH})](\text{ClO}_4)$ undergoes quasi reversible reduction in CH_3CN while is not electroactive in the positive potential range 0–1.5 V. In this range both VONi and VOCu complexes undergo two successive irreversible electron-transfer reactions at ca. 1.0 and 1.2 V. For the VOMn complex, a quasi-reversible couple due to $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ occurring at 0.62 V ($\text{DEp} = 100 \text{ mV}$ at $V = 100 \text{ mV s}^{-1}$), while the oxidation of $\text{V}^{\text{IV}}\text{O}$ to $\text{V}^{\text{V}}\text{O}$ takes place irreversibly at ca. 1.0 V. Again in the case of the VOFe complex, facile oxidation of the iron(II) center takes place nearly reversibly at 0.21 V ($\text{DEp} = 80 \text{ mV}$ at $V = 100 \text{ mV s}^{-1}$) [440].

Variable-temperature (4–300 K) magnetic susceptibility measurements of $[\text{VOCu}(\text{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{OH})](\text{ClO}_4)$, $[\text{VOM}(\text{364})(\mu\text{-CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Ni}^{2+}$, Co^{2+} , Fe^{2+}) and of $[\text{VOCu}(\text{365a})(\mu\text{-CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)$ indicate that all the complexes, except the VOMn one, exhibit ferromagnetic exchange interaction with the following values of J (cm^{-1}): 42.5 for VOCu , 12.0 for VONi , 4.4 for VOCu , 4.4 for VOFe , and 46.0 cm^{-1} for VOCu derived from $\text{H}_2\text{-365a}$; the VOMn complex behaves antiferromagnetically ($J = -14.2 \text{ cm}^{-1}$) [440].

$\text{H}_2\text{-314a}$ and $\text{H}_2\text{-314b}$ have been synthesized by reduction with NaBH_4 of the related diled Schiff base complex

derived by the condensation [2+2] of 2,6-diformyl-4-methylphenol and 1,5-diamino-3-azapentane or 1,7-diamino-4-azaheptane in the presence of $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$. $\text{H}_2\text{-314a}$ reacts with $\text{Ni}(\text{ClO}_4)_2$ to form $[\text{Ni}_2(\text{314a})](\text{ClO}_4)_2$ which consists of two nickel(II) centers, 3.092 Å apart, bridged by two phenoxide oxygen atoms completing the Ni_2O_2 plane. Each metal center obtains a five coordinated environment by interacting with three secondary amine nitrogen donors. The complex molecule contains a crystallographic center of symmetry, thereby making the two nickel(II) ions chemically and crystallographically equivalent in the solid state. The perchlorate ion is not coordinated to the nickel(II) ion. The macrocycle adopts a twisted configuration and each N_3O_2 donor set coordinates in a non-planar manner affording a square pyramidal geometry about each nickel(II) ion (Fig. 268a) [440].

The cyclic voltammogram of the complex shows two reversible one electron oxidation steps ($E_{1/2} = 0.835$, 1.05 V, versus SCE, $\text{Pt}/\text{CH}_3\text{CN}$) with the formation of $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ and $\text{Ni}^{\text{III}}\text{Ni}^{\text{III}}$ species. Based on this equation the K_{com} value is evaluated at 4.3×10^3 . This value is larger than that (2.3×10^2) reported for $[\text{Ni}_2(\text{364})(\text{ClO}_4)_2(\text{CH}_3\text{OH})_2]$. It appears that the fully saturated macrocycle $\text{H}_2\text{-314a}$ destabilizes the nickel(III) state more than the macrocycle $\text{H}_2\text{-364}$.

$[\text{Cu}_2(\text{314b})(\text{Br})_2] \cdot \text{CH}_3\text{OH}$ was obtained from a $[\text{H}_8\text{-314b}](\text{Br})_6\text{:Cu(II)}$ (2:1) methanol solution at $\text{pH} > 8$, by diffusing ethylacetate into the system over 2 weeks. Each of the two copper(II) ions is bridged by one of the macrocyclic

moieties of the ligand, and is coordinated with a distorted square pyramid conformation by one phenolate group, and three nitrogen donors on one side of the macrocycle and one bromide ion. The phenolate group and three amino nitrogens form the basal plane, while the bromide ion occupies the axial site. The two moieties of the ligand behave as two separate ligands. There is a large room in the cavity of the macrocycle. This reveals that the two moieties of the ligand react with copper(II) ions separately, and function like two independent binding groups [440] (Fig. 268b).

Also in $[\text{Zn}_2(\text{314b})](\text{Br})_2\text{-dioxane}$, obtained by slow evaporation of a $[\text{H}_8\text{-314b}](\text{Br})_6/\text{Zn(II)}$ (1:2) methanol/dioxane (5:1) solution at $\text{pH} > 8$, the zinc(II) ions have a distorted square pyramidal conformation, but bridged very differently by two phenolate groups, and three nitrogen donors on one side of the macrocycle. Two phenolate groups and two amino nitrogens form the basal plane with another amino nitrogen from the ligand occupying the apical position. The zinc(II) ions are out of plane [440] (Fig. 268c).

Condensation of equimolar 2,6-di-formyl-4-methylphenol and *N*-(2-aminoethyl)-1,3-propanediamine in the presence of $\text{Pb}(\text{SCN})_2$ as the template agent leads to the corresponding [2+2] hexamine Schiff base, which by hydrogenation with sodium tetrahydroborate gives the corresponding saturated [26]-membered hexaazamacrocyle $\text{H}_2\text{-314c}$. Due to this reaction, two kinds of hexaamines could be obtained, respectively $\text{H}_2\text{-314c}$ and $\text{H}_2\text{-314'c}$. But only $\text{H}_2\text{-314c}$ was obtained as confirmed by the X-ray structure of the

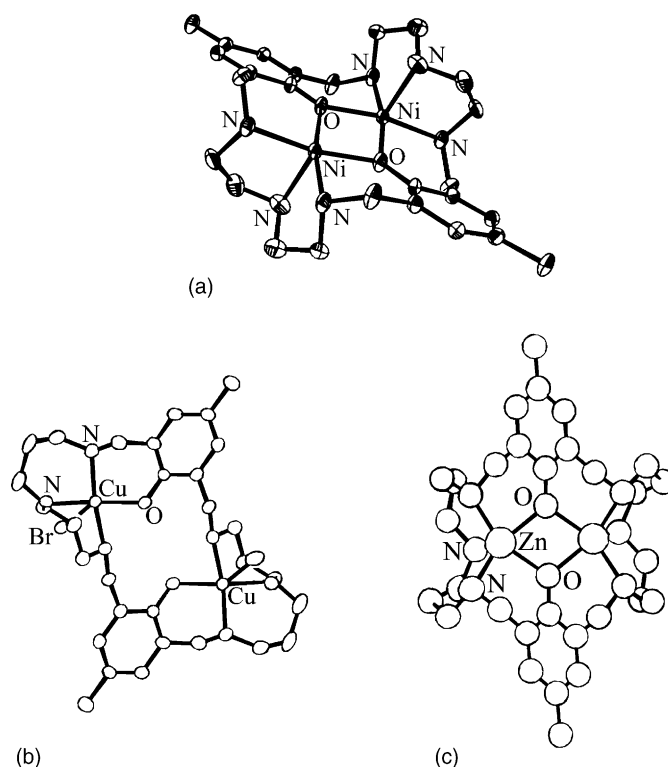


Fig. 268. Structure of $[\text{Ni}_2(\text{314a})]^{2+}$ (a), $[\text{Cu}_2(\text{314b})(\text{Br})_2]$ (b) and $[\text{Zn}(\text{314a})]^{2+}$ (c) (adapted from Ref. [440]).

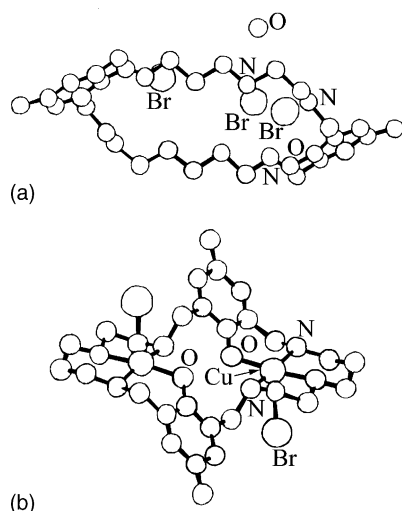


Fig. 269. Structure of $[H_8\text{-}314c](Br)_6 \cdot 2H_2O$ (a) and $[Cu_2(314c)(Br)_2]$ (b) (adapted from Ref. [440]).

hexabromide salt [440]. The six protonated nitrogen atoms of the macrocycle are coplanar while the six bromide ions and two water molecules are located symmetrically outside the macrocyclic cavity [440] (Fig. 269a).

The ligand maintains dinuclear integrity for copper(II) complexes, while facilitating the formation of non-bridged dicopper centers. Potentiometric equilibrium studies indicate that a variety of protonated, mononuclear and dinuclear copper(II) complexes are formed from pH 2 to 12 in aqueous solution. The stability constants and species distribution, as a function of the pH of the 1:1 and 1:2 ($H_2\text{-}314c:Cu^{2+}$) complexes, were determined in KCl supporting electrolyte ($\mu = 0.100$ M) at 25 °C [440]. No hydroxo copper(II) complex species are found in the whole titration range investigated. The stability constants of the copper(II) complexes with fully deprotonated ligands $[Cu(314c)]$ and $[Cu_2(314c)]^{2-}$, are higher than those of the corresponding zinc(II), cobalt(II) and cadmium(II) complexes [440].

$[H_8\text{-}314c](Br)_6 \cdot 2H_2O$, when neutralized with KOH and treated with $Cu(ClO_4)_2 \cdot 6H_2O$ in $CH_3OH/CHCl_3$, forms $[Cu_2(314c)(Br)_2] \cdot CHCl_3$. Two copper(II) ions are located in separate compartments and each of them is five coordinated, being bonded to three nitrogen donors from an *N*-(2-aminoethyl)-1,3-propanediamine unit of the macrocycle, one phenolic oxygen and one bromide. The geometries around the two copper ions are the same, both being square pyramidal coordination polyhedrons with three nitrogen atoms and one oxygen atom forming the basal plane and the bromide ion at the apical position. The macrocyclic ligand serves as the N_3O donor to each copper(II) ion. The intramolecular $Cu \cdots Cu$ distance is 5.814 Å. The macrocyclic skeleton adopts a chair conformation [440] (Fig. 269b).

$H_2\text{-}314a$ and $H_2\text{-}314b$ form the hetero-dinuclear complexes $[MM'(L)]^{2+}$ ($M = Cu^{2+}$, $M' = Zn^{2+}$, Mn^{2+} , $L = 314a^{2-}$; $M = Cu^{2+}$, $M' = Zn^{2+}$, Cd^{2+} , Ni^{2+} ,

$L = 314b^{2-}$ and $M = Co^{2+}$, $M' = Ni^{2+}$, Pb^{2+} $L = 314a^{2-}$) [440].

Titration experiments show that the hetero-dinuclear species $[CuM(314a)(OH)]$ and $[CuM(314a)(OH)_2]$ coexists in water solution at a pH range 7–12 [440].

It was verified that if the two metal ions have similar stability constants, they will easily scramble and will not be distinguished in the investigation of hetero-dinuclear complexation in solution. However, when two metal ions possess larger differences of stability constants, they will give stable complexes and a clear reaction order or route. These studies suggested that the copper(II) complexes of these macrocyclic ligands can form the basis for discrete and stable hetero-dinuclear complexes and can be used to investigate the complexation behaviour in solution by taking copper(II) as one fixed moiety of the center of the hetero-dinuclear complex [440].

Catalytic experiments reveal that $[CuM(314a)](OH)_n]^{2-n}$ ($M = Zn^{2+}$, Mn^{2+}) can dismutate H_2O_2 to O_2 effectively in basic water solution. Mechanism studies by means of electronic and EPR spectra and show that the active center of these catalysts is a dimer structure. The substrate H_2O_2 molecules are dismutated through a homo-cleaving pathway. The catalytic activity of copper(II) can be greatly enhanced by the other phenol bridged metal ions in the same complex molecule. An inter- and intra-molecular cooperation mechanism was proposed to illustrate the efficient catalytic process [440].

In the case of copper(II)-zinc(II) catalyst it was proposed that in the first step, H_2O_2 coordinates in the center of the dimer. A transitional state was formed. In the second step H_2O_2 reacts with the OH^- ligand of the zinc(II) ion while the copper(II) ion was reduced to the copper(I) ion with the release of O_2 . In the third step, another molecule of H_2O_2 coordinated between the two copper(I) ions. After the rapid process of O–O homolysis, the initial catalyst was recovered in the final step [440].

For the $[CuM(314a)](OH)_n]^{2-n}$ catalyst both copper(II) and manganese(II) ions are involved in the redox processes by intramolecular and intermolecular mechanisms [440].

$[H_6\text{-}314](Cl)_4$, obtained by treating the crude sample with a methanol solution containing 5% HCl, adopts a parallelogram arrangement with two phenolic atoms and two pyridyl nitrogen atoms oriented toward the center of the macrocycle and the aromatic groups at the farther corners. The four amino nitrogens lie on a perfect plane while the two pyridines and the two aromatic phenolic rings are inclined to this N_4 plane. The macrocycle is shaped by internal hydrogen bonding [441].

The potentiometric titrations of 1:1 molar ratio of $Fe^{3+}:[H_6\text{-}314]^{4+}$ in H_2O at 25 °C and 0.1 M indicate that the initial species formed is a diprotonated chelate $[Fe(H_2\text{-}314)]^{3+}$ as a major component from pH 3 to 6. With increase of pH hydrolysis of $[Fe(H_2\text{-}314)]^{3+}$ occurs to produce $[Fe(H_2\text{-}314)(OH)]^{2+}$ [441]. Subsequently, the uncoordinated ammoniums of the ligand undergo deprotonation

reaction to produce $[\text{Fe}(\text{H-314})(\text{OH})]^+$ and $[\text{Fe}(\text{314})(\text{OH})]$.

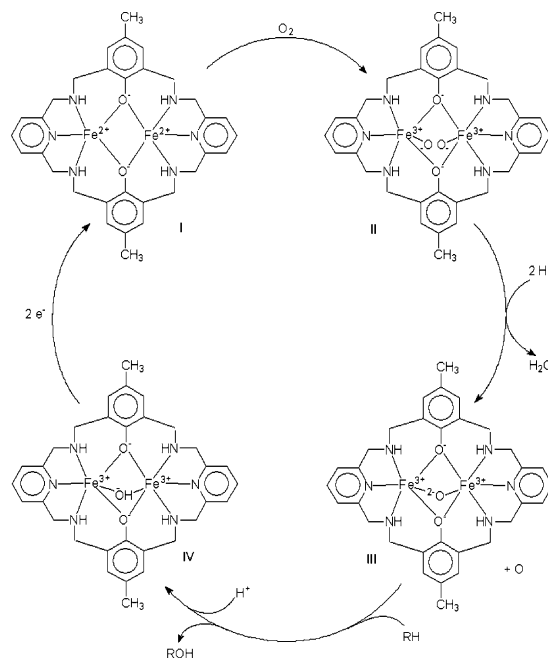
These protonated and hydroxo mononuclear complexes are characterized by high stability thus they can undergo hetero-dinuclear complexation. In the 1:1:1 systems $\text{H}_2\text{-314}:\text{Fe}^{3+}:\text{M}^{2+}$ ($\text{M}^{2+} = \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Cu}^{2+}$) no formation of species like $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\text{314})]^{3+}$ was observed. The hydroxo dinuclear complex $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\text{314})(\text{OH})]^{2+}$ is present after $[\text{Fe}(\text{H}_2\text{-314})(\text{OH})]^{2+}$ has been formed. With increase of pH bis(hydroxo) species or μ -oxo species, even tris(hydroxo) species are produced for the FeZn system [441].

In the $\text{H}_2\text{-314}:\text{Fe}^{3+}:\text{Cu}^{2+}$ system, due to the fact that both iron(III) and copper(II) ions have strong affinity to $\text{H}_2\text{-314}$, the dinuclear complex $[\text{FeCu}(\text{314})]^{3+}$ is present from pH 3 to 7, and reaches its maximum concentration at pH 5.1. Above pH 6 $[\text{FeCu}(\text{314})]^{3+}$ converts first into $[\text{FeCu}(\text{314})(\text{OH})]^{2+}$ and then into $[\text{FeCu}(\text{314})(\text{OH})_2]^+$ or $[\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}(\text{314})(\mu\text{-O})]^+$. The case of the $\text{H}_2\text{-314}:\text{Fe}^{3+}:\text{Cd}^{2+}$ system is similar to that of $\text{H}_2\text{-314}:\text{Fe}^{3+}:\text{Mn}^{2+}$ except that a small amount of $[\text{FeCd}(\text{314})]^{3+}$ forms between pH 6 and 7 [441].

The potentiometric titrations of 2:1 $\text{Fe}^{3+}:[\text{H}_6\text{-314}](\text{Cl})_4$ system indicate that $[\text{Fe}(\text{H}_2\text{-314})]^{3+}$ predominates from pH 2 to 3. Then another ferric ion coordinates to the macrocycle to form $[\text{Fe}_2(\text{314})]^{4+}$ and reaches a maximum concentration (27%) at pH 3.1. Between pH 3.5 and 7, $[\text{Fe}^{\text{III}}_2(\text{314})(\mu\text{-OH})]^{3+}$ dominates while above pH > 7, $[\text{Fe}^{\text{III}}_2(\text{314})(\mu\text{-O})]^{2+}$ and its further hydrolytic species become the main components in aqueous solution [441].

$[\text{H}_6\text{-314}](\text{Cl})_4$ in the presence of iron(II) and iron(III) ions in a 1:1:1 molar ratio initially forms $[\text{Fe}^{\text{III}}(\text{H}_2\text{-314})]^{3+}$ by the coordination of the ferric ion to one of the subunits. When the pH raises, the amino groups deprotonate and the iron(II) ion coordinates the donor groups on the other side of the macrocycle to form the mixed valence $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{314})]^{3+}$ complex. Subsequently the μ -hydroxo species and further hydrolytic mixed-valence species are formed in more alkaline solution [441].

The dinuclear iron(II) complexes $[\text{Fe}_2(\text{312})]^{2+}$ and $[\text{Fe}_2(\text{314})]^{2+}$ prepared in situ, by reaction of the appropriate macrocycles with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in CH_3CN /pyridine solution, catalyze the hydroxylation of the hydrocarbons cyclohexane and adamantane respectively to adamantol (3C-OH and C2-OH isomers) and cyclohexanol and cyclohexane in the presence of a two-electron reductant (H_2S) and O_2 ; thus they may serve as functional models of methane monooxygenase [441]. These dinuclear iron(II) complexes are believed to react with oxygen to form a diiron-peroxide intermediate. The active species may decay to a dinuclear iron(III) complex with an oxo bridge, releasing an oxygen atom for hydroxylation of a hydrocarbon. In the presence of a two-electron reductant the dinuclear iron(III) species may revert back to the dinuclear iron(II) complex to complete the catalytic cycle [441]. H_2S serves as both an electron and a proton donor. The diiron(II) complex can be regenerated



Scheme 54.

from the oxidized diiron(III) complex with H_2S as a two electron reductant to produce a sulfur precipitate.

For these catalytic processes the proposed mechanism (Scheme 54) involves a reaction of the dinuclear Fe(II) complex **I** with molecular oxygen to form a dioxo complex, possibly the peroxo-bridged dinuclear iron(III) complex **II**. This complex **II** rearranges with the elimination of H_2O to apparently give the macrocycle **III**, which is suggested to involve a high valent form of iron bridged by a μ -oxo group. This complex may then be pictured as generating the reaction product, ROH, plus a hydroxo-bridged dinuclear iron(III) macrocyclic complex. A two-electron reductant, such as H_2S (ascorbic acid or other reductant would also suffice) converts the dinuclear iron(III) macrocyclic complex, **IV**, back to the dinuclear iron(II) complex, **I**, which then undergoes the cyclic process in the presence of dioxygen and a two-electron reductant [441].

In the control experiments for the oxidation of cyclohexane, the turnover is 1.1 in 8 h with Fe^{2+} as a catalyst and is 1.7 in 8 h with pyridine as a ligand. Significantly, the turnover is 28.4 in 8 h with the use of the macrocyclic ligand. Auto-oxidation is clearly ruled out by comparison with these turnover numbers.

It is interesting that the oxidation of adamantane produces only hydroxylation products. The ratio of tertiary adamantanol to secondary adamantol is around 1.2 for both catalysts. No ketonization product is observed even when the turnover is 45.1 after 20 h. The turnover numbers show that the iron complex of the [24]-membered macrocycle is a better catalyst for these oxidation reactions than that of the [30]-membered macrocycle. The turnovers (i.e. the sum of mmols of products/mmol of catalyst) show that these

macrocyclic iron complexes are several times more effective as hydroxylating catalysts for cyclohexane in respect to adamantol. Thus the dinuclear macrocyclic iron(II) complexes are among the most effective functional models of methane monooxygenase reported so far.

The oxidation of cyclohexane gives cyclohexanol and cyclohexanone. The turnovers are 24.4 after 6 h for the [24]-membered macrocyclic diiron complex as a catalyst, or 21.4 after 6 h with the [30]-membered macrocyclic complex. The ratios of cyclohexanol to cyclohexanone are 1.9 and 1.1 for $[\text{Fe}_2(\mathbf{314})]^{4+}$ and $[\text{Fe}_2(\mathbf{312})]^{4+}$, respectively, during the whole period of time of the oxidation reactions.

$\text{H}_2\text{-}\mathbf{314}$ forms a number of protonated, neutral and/or hydroxo mononuclear, homo-dinuclear and hetero-dinuclear copper(II), cadmium(II), manganese(II) and zinc(II) complexes controlled by the stoichiometry of the metal ion and ligand as well as the pH values of the solution [441].

Solution studies prove that interactions of $\text{H}_2\text{-}\mathbf{314}$ with these metal ions in 1:1 ratios led mainly to mononuclear chelates where two kinds of complexation were observed with the zinc(II) and copper(II) ions [441].

The titration curves of the $\text{M}^{2+}:\text{[H}_6\text{-}\mathbf{314}]^{4+}$ systems ($\text{M}^{2+} = \text{Zn}^{2+}, \text{Mn}^{2+}$), reveal that the complex initially formed is $[\text{M}(\text{H}_2\text{-}\mathbf{314})]^{2+}$, where two protons are probably not attached to phenolic groups but to amino groups located on one side of the macrocycle. In $[\text{Zn}(\text{H}_2\text{-}\mathbf{314})](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, obtained from a 1:1 $\text{Zn}^{2+}:\text{[H}_6\text{-}\mathbf{314}]^{4+}$ aqueous solution at $a = 4$ with excess KNO_3 , the zinc(II) ion is coordinated with a distorted trigonal bipyramidal conformation by two phenolate groups and three nitrogen donors on one side of the macrocycle. Two phenolate oxygens and a pyridyl nitrogen form the basal plane, while two amino nitrogens occupy the axial sites (Fig. 270a). For the 1:1 $\text{Cu}^{2+}:\text{[H}_6\text{-}\mathbf{314}]^{4+}$ system, the inflection starting at $a = 3$ suggests that the species initially formed is $[\text{Cu}(\text{H}_3\text{-}\mathbf{314})]^{3+}$, where the copper(II) ion is complexed by half the coordination sites of the macrocycle. For the cadmium(II) system, the inflection at $a = 4$ is quite similar to those for the zinc(II) and manganese(II) systems, but mathematical analysis of the titration points reveals that, in addition to $[\text{Cd}(\text{H}_2\text{-}\mathbf{314})]^{2+}$, $[\text{Cd}(\text{H}_3\text{-}\mathbf{314})]^{3+}$ in appreciable amounts (maximum of 21% at pH 5.7) is formed concomitantly and is found to be converted sequentially into $[\text{Cd}_2(\mathbf{314})]^{2+}$ by combination with another cadmium(II) ion. The protonated mononuclear complexes initially formed undergo simple deprotonation reactions at higher p[H]. The stability constants of the mononuclear complexes show that the affinity of the ligand for metal ions increases in the order $\text{Mn}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ [441].

Titration of the metal ions with $[\text{H}_6\text{-}\mathbf{314}]^{4+}$ in 2:1 molar ratio indicates that the mononuclear species $[\text{M}(\text{H}_3\text{-}\mathbf{314})]^{3+}$ or $[\text{M}(\text{H}_2\text{-}\mathbf{314})]^{2+}$ are intermediate in the formation of the dinuclear complexes. At $a = 6$ the dinuclear complexes $[\text{M}_2(\mathbf{314})]^{2+}$ form. They hydrolyze at basic conditions to form $[\text{M}_2(\mathbf{314})(\text{OH})]^+$ and/or $[\text{M}_2(\mathbf{314})(\text{OH})_2]$ [441]. At

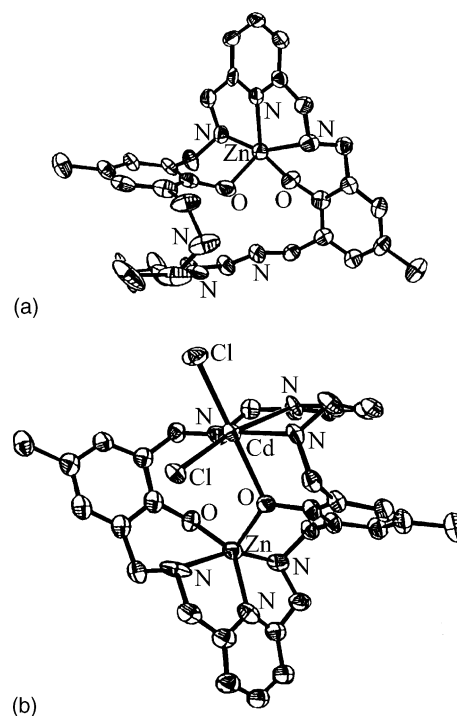


Fig. 270. Structure of $[\text{Zn}(\text{H}_2\text{-}\mathbf{314})]^{2+}$ (a) and $[\text{ZnCd}(\mathbf{314})(\text{Cl})_2]$ (b) (adapted from Ref. [441]).

$a = 6$ solutions containing $\text{Cu/Cd/H}_2\text{-}\mathbf{314}$ or $\text{Zn/Mn/H}_2\text{-}\mathbf{314}$ solution in 1:1:1 ratio form the hetero-dinuclear complexes $[\text{MM}'(\mathbf{314})]^{2+}$ [441]. The hetero-dinuclear species $[\text{MM}'(\mathbf{314})]^{2+}$ are formed with high yields in broad p[H] regions (6.8–10.2 for ZnCd , 7.0–10.3 for CuCd , and 8.6–9.2 for ZnMn with 80% content). The monohydroxo species $[\text{MM}'(\mathbf{314})(\text{OH})]^+$ are detected in all mixed systems, including the CdCd case, as the content of $[\text{MM}'(\mathbf{314})]^{2+}$ decreases.

The comproportionation constants calculated from the formation constants of the homo-dinuclear and hetero-dinuclear complexes ($\log K_{\text{com}} = 3.20$ for ZnCd , 2.08 for ZnMn , and 0.07 for CuCd), indicate that the hetero-dinuclear complexes are more stable than the mixture of two homo-dinuclear complexes.

In the crystals of $[\text{ZnCd}(\mathbf{314})(\text{Cl})_2] \cdot 6\text{H}_2\text{O}$, obtained directly from the titration solution with KCl at $a = 6\text{--}7$ upon evaporation at room temperature, the zinc(II) ion has almost same coordination conformation, bond lengths, and bond angles as those in $[\text{Zn}(\text{H}_2\text{-}\mathbf{314})](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$. Only one oxygen atom of the phenolates bridges the zinc and cadmium ions. The cadmium(II) ion is hexacoordinated: three nitrogen donors on one side of the macrocycle and one chloride form the basal plane while another chloride and the bridging oxygen of the phenolate in the *trans* position complete the distorted octahedral coordination geometry (Fig. 270b).

It was verified that the dihydroxo dilanthanum(III) complex with the ligand $\text{H}_2\text{-}\mathbf{314}$, which is formed in aqueous

solution at pH 10, is capable of hydrolyzing bis(*p*-nitrophenyl)hydrogenphosphate with a remarkably high rate constant [442]. The catalysis occurs at such an unprecedented rate that it takes only 6 min for one turnover at pH 10. The rate constant versus pH profile clearly shows the most efficient catalyst is the dinuclear dihydroxo complex $[\text{La}_2(\mathbf{314})(\text{OH})_2]^{2+}$. A mechanism was proposed where two dinuclear lanthanum(III) complexes coordinate the partially negatively charged phosphate oxygens. A third dinuclear lanthanum(III) complex coordinates both ester groups and attacks the phosphorus center with one of its bridging hydroxide nucleophiles. The *p*-nitrophenolate group is displaced and the monophosphate ester is generated. The products are displaced and the $[\text{La}_2(\mathbf{314})]^{4+}$ complex molecules coordinate another incoming substrate. The active catalyst $[\text{La}_2(\mathbf{314})(\text{OH})_2]^{2+}$ is regenerated by the loss of protons from the coordinated waters. Hydrolysis is fast because there are three dinuclear lanthanum(III) complexes withdrawing electron density from the phosphorus center. This makes that phosphorus center extremely susceptible to nucleophilic attack from the coordinated hydroxide nucleophile [442].

The macrocycle **174** forms both mononuclear and dinuclear copper(II) complexes; the mononuclear complex $[\text{Cu}(\mathbf{174})]^{2+}$ forms two protonated complexes $[\text{Cu}(\text{H}-\mathbf{174})]^{3+}$ and $[\text{Cu}(\text{H}_2-\mathbf{174})]^{4+}$, indicating that the metal ion is coordinated to one diethylenetriamine moiety, leaving the other free for protonation. The dinuclear complex $[\text{Cu}_2(\mathbf{174})]^{4+}$ is characterized by strong hydrolytic tendencies to form mono- and dihydroxo complexes. It was suggested that the hydroxide ions are bridging groups coordinated simultaneously to both metal ions [443].

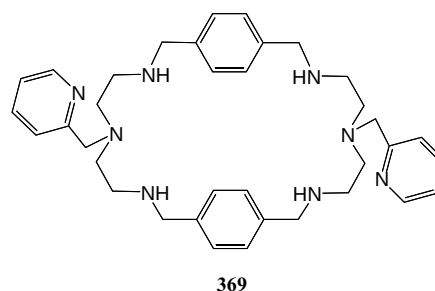
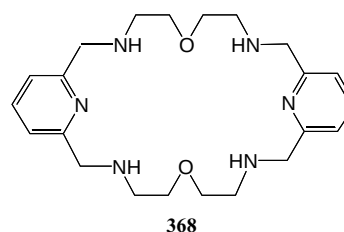
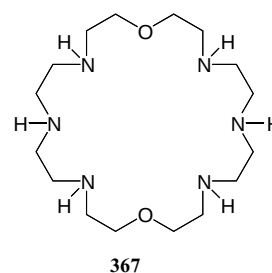
$[\text{Cu}_2(\mathbf{174})(\text{SO}_4)_2]$ was obtained by the slow diffusion of acetone into an aqueous solution of $[\text{H}_6-\mathbf{174}](\text{Br})_6$, derived by the reduction of the corresponding Schiff base in EtOH with NaBH_4 followed by the subsequent extraction of the product with CH_2Cl_2 and by the final crystallization of the obtained oil from a $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ mixture containing HBr, and $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ in 1:2 molar ratio that had been adjusted to pH 6.3 with dilute KOH [443]. The macrocycle binds two copper(II) ions by way of its diethylenetriamine moieties which provide three nitrogen donors to each metal ion. The coordination set around the copper ion is completed by one sulfate oxygen atom in an equatorial position and another sulfate oxygen atom, from a different sulfate anion, in an apical position, thus resulting in a distorted square pyramidal geometry. Because the sulfate anions bridge the two copper centers in neighbouring molecules, the crystal has an extended polymeric structure [443].

Even though the solid state structure of $[\text{Cu}_2(\mathbf{174})(\text{SO}_4)_2]$ shows that the macrocycle adopts a chair type conformation, with one coordinating diethylene triamine moiety flipped down and the other flipped up, this is not necessarily the structure adopted in solution. It is expected that the cation would be able to attain a configuration where both diethylenetriamine moieties were flipped to the same side in order

to accommodate larger bridging anions such as pyrophosphate. The interatomic distance between the copper(II) ions within the same macrocycle is 5.31 Å [443].

The host–guest interaction between ortho-, pyro- and tripoly-phosphate anions and the dinuclear copper(II) complex with **174**, investigated by potentiometric methods, shows that ternary complexes are formed in aqueous solution as a result of coordinate bonding, hydrogen bond formation, and coulombic attraction between the host and guest [443]. The dinuclear copper(II) complexes of **174** show strong selectivity for pyrophosphate ions in the presence of orthophosphate ions over the whole pH range while the pyrophosphate/tripolyphosphate selectivity is pH-dependent [443].

1,4,7,13,16,19-Hexaza-10,22-dioxacyclotetracosane (**367**), a macrocyclic ligands containing a pair of diethylenetriamine moieties connected by means of two five-atom diethylether bridges, is capable of up to hexaprotonation, homo- or binuclear metal ion coordination and anion recognition. The X-ray structure of $[\text{H}_6-\mathbf{367}](\text{Cl})_6$ (Fig. 271) shows a capped nature of the ring. The central amines are pointed down so that they are almost in line with the two neighbouring ammonium moieties. The two ether oxygens lie at the vertices of the long axis of the ellipse, which results in a geometry in which the amines are almost lined up along the curve of the long axis. One chloride seems to be more intimately associated unsymmetrically with two pair of opposite N^+-H groups [444].



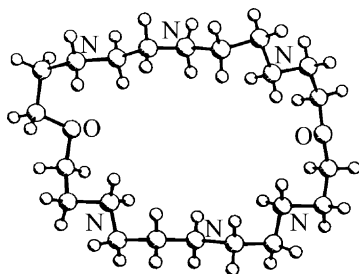


Fig. 271. Structure of $[H_6\text{-}367]^{6+}$ (adapted from Ref. [444]).

Potentiometric studies of the stability constants of **367** with Cu^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} show the ligand is flexible enough to form stable mononuclear macrocyclic complexes in which from four to six of the basic nitrogen donors seem to be coordinated to the metal ion [445]. The dinuclear copper(II) chelate is sufficiently stable to form extensively in solution and is further stabilized by a bridging hydroxide ion in neutral- and high-pH solution.

In addition, the dinuclear cobalt(II) and copper(II) complexes are stabilized by secondary ligands that provide two- or three-atom bridges between the metal ions. Thus neutral imidazole and the imidazolate anion form stable, cascade type, bridged dinuclear copper(II) complexes of **367** [446].

The reaction in methanol of **367** with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in the presence of sodium imidazolate and NaClO_4 and with $\text{Cu}(\text{ClO}_4)_2$ produces $[\text{Cu}_2(\text{367})(\text{H-Im})(\text{Im})](\text{ClO}_4)_3$ and $[\text{Cu}_2(\text{367})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)_2 \cdot \text{CHCl}_3$ [446].

In $[\text{Cu}_2(\text{367})(\mu\text{-Im})(\text{H-Im})_2](\text{ClO}_4)_3$ (Fig. 272) the $[\text{Cu}_2(\mu\text{-Im})]^{3+}$ ionic entity is incorporated into the cryptate macrocycle, using the two diethylenetriamine units at the poles of the cavity. Each copper(II) ion is further coordinated to a neutral imidazole ligand, achieving overall pentacoordination. The copper geometry has been described as distorted trigonal bipyramidal. The two ether oxygen atoms of macrocycle do not coordinate to the metal ions [446].

In $[\text{Cu}_2(\text{367})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)_2 \cdot \text{CHCl}_3$ the two copper(II) ions are coordinated to the two diethylenetriamine poles of the macrocycle. A single hydroxide ion bridges the two metals centers; a disordered perchlorate group also bridges the resulting μ -hydroxo-dicopper(II) unit through axial bonds [447] (Fig. 273a). The two copper(II) ions are strongly antiferromagnetic coupled ($-J \sim 500 \text{ cm}^{-1}$).

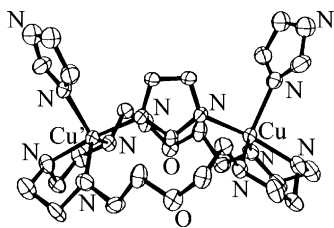
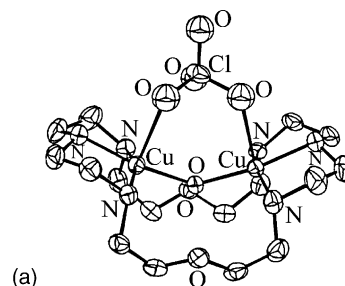
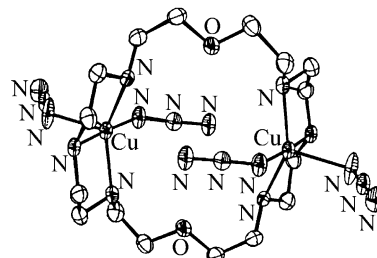


Fig. 272. Structure of $[\text{Cu}_2(\text{367})(\mu\text{-Im})(\text{H-Im})_2]^{3+}$ (adapted from Ref. [446]).



(a)



(b)

Fig. 273. Structure of $[\text{Cu}_2(\text{367})(\text{OH})(\text{ClO}_4)]^{2+}$ (a) and $[\text{Cu}_2(\text{367})(\text{N}_3)_4]$ (b) (adapted from Refs. [445,447]).

$[\text{Cu}_2(\text{367})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)_2$ reacts with NaN_3 to give $[\text{Cu}_2(\text{367})(\text{N}_3)_4]$ which results from the binding of two $\text{Cu}(\text{N}_3)_2$ units into the macrocyclic ligand [447]. The two copper(II) ions, the four azide anions and two nitrogen atoms of the macrocyclic ligand are situated in the symmetry plane; the two oxygen atoms are located on the two-fold axis. The macrocyclic ligand adopts a chair-type conformation (Fig. 273b), which is apparently unstrained. The two copper(II) ions are located inside the macrocyclic ligand linked each to a N_3 ligand donor set of the two diethylenetriamine chelating sequences at the two poles of the macrocyclic cavity and to two nitrogen atoms of two end-on-bound azide ions. The two copper cations are pentacoordinate CuN_5 centers, with square-base pyramidal geometry, involving three ring nitrogens and two terminally bound azide ions; one azide ion is directed outside the cavity of the macrocyclic ligand and the other one inside the cavity parallel to the intramolecular $\text{Cu} \cdots \text{Cu}$ axis. The $\text{Cu} \cdots \text{Cu}$ distance (5.973 Å) explains why the two copper(II) ion are magnetically uncoupled [445,447].

The coordination behaviour of the related macrocyclic ligand **368** towards copper(II), cobalt(II) and zinc(II) ions has been studied [448]. **368**, owing to the presence of the pyridine rings, shows a lower basicity than that of **367**. **368** contains six nitrogens able to act as donor atoms in coordination complexes; they are arranged in two separate subunits and it is expected that mononuclear complexes $[\text{M}(\text{368})]^{2+}$ will be formed by coordination of the metal ion to one of the tridentate subunits [448].

The titration curve of 1:1 $\text{M}^{2+}:\text{368}$ system ($\text{M}^{2+} = \text{Cu}^{2+}$, Co^{2+} , Zn^{2+}) reveals that $[\text{M}(\text{H}_2\text{-}368)]^{4+}$ is formed at a very low pH and it deprotonates to form other mononuclear species at higher pH. The 2:1 curve shows the formation

of $[M_2(\mathbf{368})]^{4+}$ that hydrolyzes to give the hydroxo complex $[M_2(\mathbf{368})(OH)]^{3+}$.

The cobalt(II) and zinc(II) complexes with **368** are less stable than those of copper(II) complexes [448]. The complexes $[M(\mathbf{368})]^{2+}$ in all cases are less stable than the analogous compounds with **367** probably because of the lower basicity of **368**. Protonation of $[M(\mathbf{368})]^{2+}$ to form $[M(H\text{-}\mathbf{368})]^{3+}$ occurs for all the metal complexes. However, the formation of $[M(H_2\text{-}\mathbf{368})]^{2+}$ species is observed only for nickel(II) and cobalt(II) probably because mononuclear complexes of copper(II) and zinc(II) are less stable and they begin to form at higher pH.

The hydrolysis of $[M(\mathbf{368})]^{2+}$ to form $[M(\mathbf{368})(OH)]^+$ occurs in all the cases but the formation of $[M(\mathbf{368})(OH)_2]$ has been observed only for zinc(II). An addition of the second metal ion to $[M(\mathbf{368})]^{2+}$ to form $[M_2(\mathbf{368})]^{4+}$, is characterized by a lower stability constant than the formation of $[M(\mathbf{368})]^{2+}$ [448].

The distribution of complex species in solutions containing 1:1 and 2:1 molar ratios of Cu(II) to **368** shows that the formation of mononuclear complexes begins at a very low pH in the 1:1 solution, and they are the predominant species at pH values higher than 3.2. A significant amount of $[M_2(\mathbf{368})]^{4+}$ is formed between pH 3 and 6. For the case of the 2:1 solution, dinuclear complexes are predominant at pH higher than 3.8, $[M(H_2\text{-}\mathbf{368})]^{2+}$ being the major species under more acidic conditions. The mononuclear complexes represent only a small percentage of the total amount of ligand at pH values higher than 5. $[M_2(\mathbf{368})]^{4+}$, $[M_2(\mathbf{368})(OH)]^{3+}$ and $[M_2(\mathbf{368})(OH)_2]^{2+}$ are then the predominant species depending on the pH of the solutions. As a consequence of the lower stabilities of these species, complex formation begins at higher pH and mononuclear complexes become the predominant species in 1:1 solution only at pH higher than 5. No significant formation of dinuclear complexes occurs in the 1:1 solution, with $[M_2(\mathbf{368})(OH)]^{3+}$ representing only a maximum of 3.3% of the total amount of ligand. For the case of the 2:1 solution, binuclear complexes begin to form at pH 5, but whereas the concentration of $[M_2(\mathbf{368})(OH)]^{3+}$ increases continuously as the pH is raised, $[M_2(\mathbf{368})]^{2+}$ is only a minor species in solution, illustrating again the strong tendency to form the hydroxo-bridged binuclear complex [448].

The pH profile obtained for a solution containing the cobalt(II) ion and **368** in 2:1 molar ratio under an oxygen atmosphere indicates that dioxygen complexes are not very stable, but sufficiently so to prevent the precipitation of cobalt(II) hydroxide. Dioxygen complexes are not formed in acidic solutions. However, under basic conditions a dioxygen complex is formed and it hydrolyzes to give soluble hydroxo species. Dioxygen complexes begin to form at pH close to 7 but they are the predominant species only at pH 8.5 and higher. The dibridged $[M_2(\mathbf{368})(OH)(O_2)]^{3+}$ complex is only a minor species because, when it is formed in a significant amount, the basic conditions favour its conver-

sion to the di- and trihydroxo complexes $[Co_2(\mathbf{368})(OH)_2(O_2)]^{2+}$ and $[Co_2(\mathbf{368})(OH)_3(O_2)]^+$ [448].

The functionalized octadentate macrocycle **369**, a receptor for imidazole and for any molecule bearing an imidazole residue, was synthesized by treatment of the related [2+2] tetraimino macrocycle, derived by condensation of 1,4-diformylbenzene and 1,5-diamino-3-azapentane, with 2 equiv. of 2-picoly chloride in toluene (90 °C) in the presence of $CsCO_3$, followed by reduction of the crude product with $NaBH_4$ in methanol. The macrocycle **369** was purified as its hexaammonium salt [449].

The coordinating behaviour of **369** toward copper(II) was investigated through pH titration experiments. In an aqueous solution containing 1 equiv. of **369** and 2 equiv. of Cu^{2+} , the dimetallic species begins to form at pH 6.5. At pH 9, 100% of the copper(II) is present as the dinuclear complexes $[Cu_2(\mathbf{369})]^{4+}$, (15%), $[Cu_2(\mathbf{369})(OH)]^{3+}$, (65%) and $[Cu_2(\mathbf{369})(OH)_2]^{2+}$ (20%). Thus, an aqueous solution containing 1 equiv. of the octadentate ligand **369** and 2 equiv. of Cu^{2+} , adjusted to pH 9 with morpholine- HNO_3 buffer and titrated with a standard solution of imidazole, proves the formation of the 1:1 receptor-imidazolate adduct $[Cu_2(\mathbf{369})(\mu\text{-Im})]^{3+}$. An addition of even a large excess of the titrating solution does not cause any increase of the absorbance or alteration of the spectrum, indicating that further imidazole molecules are not able to remove the 2-picoly pendant arms from their coordination sites and to modify the 1:1 stoichiometry [449].

The specificity derives from the unique ability of the imidazole fragment to bridge a prepositioned pair of copper(II) cations, with the simultaneous release of a proton. Histidine binding can be visually perceived even at a 10^{-4} mol dm^{-3} level through the appearance of the blue colour and can be quantitatively determined through a simple spectrophotometric titration experiment [449].

The dicopper(II) complexes with the **367** display an even stronger affinity than $[Cu_2(\mathbf{369})]^{4+}$ towards imidazole. However, the incorporation of the imidazolate fragment within the cage is remarkably slow, probably due to steric effects, an undesirable feature for sensing purposes. For instance, equilibration of 1 equiv. of $[Cu_2(\mathbf{367})]^{4+}$ with 1 equiv. of imidazole at pH 8 takes several hours while $[Cu_2(\mathbf{369})]^{4+}$, in view of its open and flexible nature, guarantees instantaneous binding of the imidazole residue [449].

The reduced macrobicyclic $[H_8\text{-}\mathbf{173}](Cl)_8$ reacts in distilled water with $CuBr_2$ in the presence of KOH forming a complex, formulable as $Cu_2(\mathbf{173})(\mu\text{-OH})(Br)_3$, which, when redissolved in water containing HNO_3 , slowly separates $[Cu_2(\mathbf{173})(\mu\text{-CO}_3)(H_2O)](Br)_3 \cdot 3H_2O$; the bridging carbonate originates from atmosphere CO_2 [450].

In $[Cu_2(\mathbf{173})(\mu\text{-CO}_3)(H_2O)](Br)_3 \cdot 3H_2O$ (Fig. 274) the cation consists of two five-coordinate copper(II) ions, separated by 5.850 Å. The copper ions are simultaneously bridged by the binucleating ligand **173** and the oxygen atoms of the exogenous carbonate ligand. The coordination geometry about each copper(II) ion has been described as

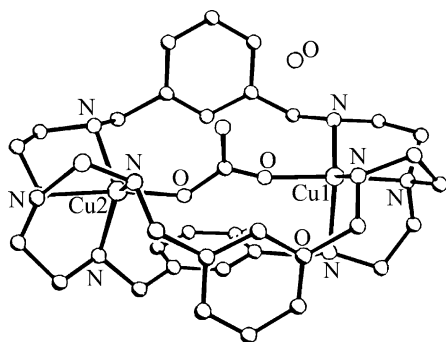


Fig. 274. Structure of $[\text{Cu}_2(\mathbf{173})(\mu\text{-CO}_3)(\text{H}_2\text{O})]^{3+}$ (adapted from Ref. [450]).

trigonal bipyramidal with the carbonate oxygen atoms and tertiary nitrogen and the secondary nitrogen atoms occupying respectively the axial of the macrobicycle and the equatorial sites. The cation resembles the free ligand in the overall Y shape with the uncoordinated oxygen atom of the carbonate ligand directed between two of the macrobicyclic legs. The cation is hydrogen bonded to adjacent bromine and water molecules, which in turn form a three-dimensional network of cation, bromine, and water molecules. A strong hydrogen bond takes place between the hydronium ion and one oxygen atom of the CO_3^{2-} group [450].

$[\text{Cu}_2(\mathbf{173})]^{2+}$ was used as receptor for polyatomic anions [450]. One of the convenient features offered by such a dimetallic cryptate is that anion coordination can be visually detected through a sharp colour change. As an example, the blue solution of the $[\text{Cu}_2(\mathbf{173})]^{4+}$ cryptate, adjusted to pH 8, on progressive addition of a standard solution of NaN_3 turns bright green owing to the formation of $[\text{Cu}_2(\mathbf{173})(\text{N}_3)]^{3+}$. Titration studies on the $\text{Cu}^{2+}:\mathbf{173}$ system (2:1 molar ratio) have shown that the dominating species (>99%) at pH 8 is $[\text{Cu}_2(\mathbf{173})(\text{OH})]^{3+}$. Thus, the anion coordination equilibrium, involves a replacement of OH^- by the N_3^- ion.

The structure of $[\text{Cu}_2(\mathbf{173})(\text{N}_3)](\text{CF}_3\text{SO}_3)_2(\text{ClO}_4)$ shows that N_3^- is collinearly bound to the two metal centers as observed also in the corresponding dicobalt(II) cryptate [451].

Spectrophotometric titration experiments, carried out with a series of inorganic and organic anions show that in all cases anion addition caused a sharp spectral change and the formation of 1:1 complexes. The obtained data indicate that the dimetallic cryptate $[\text{Cu}_2(\mathbf{173})]^{4+}$ is a very appropriate receptor for the linear anions N_3^- and NCO^- , however, it forms a much less stable complex with the other linear anion NCS^- . HCO_3^- ion, which typically displays poor coordinating tendencies towards transition metal centers, forming a very stable inclusion complex with this dicopper(II) cryptate. Noticeably, a neutral or slightly basic solution of $[\text{Cu}_2(\mathbf{173})]^{4+}$, when exposed to air, takes in a few minutes to form a green colour, due to carbon dioxide uptake and HCO_3^- incorporation. The X-ray structure of the corresponding crystalline complex has

shown that two oxygen atoms of HCO_3^- bridge the two copper(II) ions, lying on the line that joins the two metal centers.

The above observations suggest that the stability of the inclusion complex is not related to the intrinsic donating tendencies of the anion, but rather to its capability to place two of its donor atoms in the fifth coordination site of each copper(II) center. The linear N_3^- and NCO^- ions and the triangular HCO_3^- anion show the highest affinity as their bite fits well with the distance between the two copper(II) fifth coordination sites' within the cryptate. On the other hand, the linear NCS^- ion has a too long bite and its inclusion should induce an endothermic rearrangement of the cryptate and of its organic backbone. In a similar way, the triangular NO_3^- has a too short bite and should make the macropolycyclic cavity contract, which involves an endothermic steric rearrangement again and makes log K to decrease. Thus, it is the colinear fitting that determines selectivity. This steric effect is dominating and overcomes effects related to coordinative tendencies and charge. In particular, the usually strongly coordinating anion SCN^- gives a less stable adduct than other linear triatomic anions, due to its poor fitting. Moreover, the too large SO_4^{2-} anion is bound weakly, in spite of the double negative charge. In conclusion, the receptor does not recognize the donor tendencies or shape, but simply recognizes the bite length of the anion [450].

$[\text{Cu}_2(\mathbf{173})(\text{N}_3)](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN} \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ and $[\text{Cu}_2(\mathbf{173})(\text{NCO})](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN} \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ are isostructural and show a collinear M–NXY–M geometry (Fig. 275). The copper ions in $[\text{Cu}_2(\mathbf{173})(\text{NCO})]^{3+}$ are each coordinated to four amine nitrogen atoms and to the bridging cyanate ion. The geometry at one copper(II) ion approximates to a trigonal bipyramid but the other copper(II) ion has a less regular environment. The cyanate is approximately linear [451]. The asymmetric unit also contains three perchlorate anions, one acetonitrile solvate molecule and 1.5 molecules of ethanol. One of the perchlorate ions is severely disordered, and the full-occupancy ethanol molecule is disordered between two orientations [451].

Variable temperature magnetic susceptibility studies indicate only slight interaction which appears to be in opposite senses for the two complexes, i.e. ferromagnetic for $[\text{Cu}_2(\mathbf{173})(\text{N}_3)](\text{ClO}_4)_3$ ($2J = 15 \text{ cm}^{-1}$) and antiferromag-

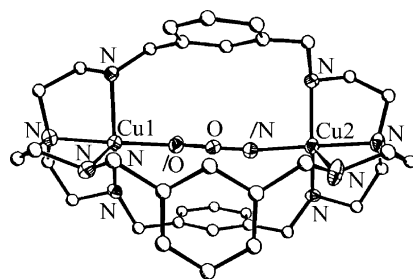


Fig. 275. Structure of $[\text{Cu}_2(\mathbf{173})(\text{NCO})]^{3+}$ (adapted from Ref. [451]).

netic for $[\text{Cu}_2(\mathbf{173})(\text{NCO})](\text{ClO}_4)_3$ ($-2J = 7 \text{ cm}^{-1}$). Likewise weak ferromagnetic exchange is also evident in $[\text{Cu}_2(\mathbf{173})(\text{N}_3)](\text{CF}_3\text{SO}_3)_3$ ($2J = 10 \text{ cm}^{-1}$). Whereas the CF_3SO_3^- salt shows no evidence of interdimer interaction, the decrease in magnetic moment below 10 K for the ClO_4^- salt suggests an antiferromagnetic interdimer exchange term; presumably this interaction operates via the stacking arrangement of adjacent cryptate ions. Epr spectral and magnetic susceptibility data for complex $[\text{Cu}_2(\mathbf{173})(\text{N}_3)](\text{ClO}_4)_3$ indicate a small stabilisation of the triplet relative to the singlet state. Despite the isoelectronic nature of the ligands and isostructural nature of the complexes, a triplet ground state does not seem to be the consequence of collinear geometry in the m-cyanato-dicopper(II) assembly in $[\text{Cu}_2(\mathbf{173})(\text{NCO})](\text{ClO}_4)_3$ [451].

As above reported **173** reacts in CH_3CN with $\text{Zn}(\text{ClO}_4)_2$ to form $[\text{Zn}(\mathbf{173})](\text{ClO}_4)_2$. Upon addition of 1 equiv. of copper perchlorate in the same solvent to this monozinc complex, the hetero-dinuclear complex $[\text{ZnCu}(\mathbf{173})](\text{ClO}_4)_4$ was obtained. The subsequent addition of imidazole (Him) in acetonitrile gives rise to $[\text{ZnCu}(\mathbf{173})(\text{Im})](\text{ClO}_4)_3$ [227,452].

The octaamine cryptand **106**, derived from **104** by tetrahydroborate reduction is expected to stabilize copper(II) in relation to copper(I). **106** reacts with copper(I) salts under anaerobic conditions to generate the dicopper(I) cryptate $[\text{Cu}_2(\mathbf{106})](\text{ClO}_4)_2$ as a microcrystalline white solid which quickly oxidizes to copper(II) in the solid state and solution. The dicopper(I) complexes with **106** are also more susceptible to attack by carbon monoxide. On bubbling CO through a $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ solution containing **106** and $[\text{Cu}(\text{CH}_3\text{CH}_2)_4](\text{BF}_4)$, $[\text{Cu}_2(\mathbf{106})(\text{CO})_2](\text{BF}_4)_2$ was obtained as white precipitate which can be stored in air for months while $[\text{Cu}_2(\mathbf{106})](\text{ClO}_4)_2$ turning green within days. This product shows a slightly greater redox stability than the parent dicopper(I) complex, retaining its pale yellow colour in solution for around an hour in air while $[\text{Cu}_2(\mathbf{106})](\text{ClO}_4)_2$ acquired a green colour within seconds [453].

Treatment of **106** with copper(II) salts in the presence of base gave $[\text{Cu}_2(\mathbf{106})(\mu\text{-OH})]^{3+}$ in good yield as bright green needles. Moreover, bridges other than $\mu\text{-OH}^-$ could be accommodated between the copper(II) cations held within. Thus, treatment with a stoichiometric amount of imidazole and azide generated the blue $\mu\text{-imidazolate}$ complex $[\text{Cu}_2(\mathbf{106})(\mu\text{-Im})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ and the golden-brown $\mu\text{-azido}$ complex $[\text{Cu}_2(\mathbf{106})(\text{N}_3)](\text{CF}_3\text{SO}_3)_3$, respectively [453].

In $[\text{Cu}_2(\mathbf{106})(\text{OH})](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ [453] each copper(II) ion coordinates to three amine nitrogens, a bridgehead amine, and a bridging hydroxide. The furan oxygen atoms are not coordinated to copper but there is a hydrogen bond between one ring and the central hydroxide. There are no significant interactions between the cation and the triflate anions or solvate water molecules. The copper ions have reasonably good trigonal bipyramidal geometry, although the copper ions lie slightly out of the plane of the three imine

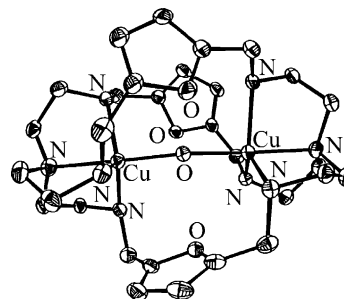


Fig. 276. Structure of $[\text{Cu}_2(\mathbf{106})(\text{OH})]^{3+}$ (adapted from Ref. [453]).

nitrogens, in the direction of the hydroxo-bridge. The $\text{Cu}-\text{O}-\text{Cu}$ angle is 174° . So the prediction of linearity based on magnetic silence is accurate. The $\text{Cu} \cdots \text{Cu}$ distance is $3.90 \text{ \AA}$. The slight deviation of OH^- from the line of the $\text{Cu}-\text{Cu}$ direction in fact derives from a small movement of the OH^- toward the furan oxygen with which is hydrogen bonded [453] (Fig. 276).

In this complex a very strong antiferromagnetic interaction ($-2J = 880 \text{ cm}^{-1}$) is operating; in agreement with these results, the EPR spectrum in frozen solution shows only ill-defined absorption associated with the small proportion of paramagnetic impurity [453]. For $[\text{Cu}_2(\mathbf{106})(\mu\text{-Im})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, moderate antiferromagnetic interaction was mediated via the heterocyclic bridge ($-2J = 92 \text{ cm}^{-1}$).

For the $\mu\text{-azido}$ complex $[\text{Cu}_2(\mathbf{106})(\text{N}_3)](\text{CF}_3\text{SO}_3)_3$, electronic and vibrational spectra suggest a linearly bridged 1,3-azido mode. Accordingly, the complex exhibits a magnetic behaviour similar to that reported for other $\mu\text{-azido}$ complexes believed to contain the linear $\text{Cu}-\text{NNN}-\text{Cu}$ entity. The magnetic exchange coupling constant ($2J = 4 \text{ cm}^{-1}$) agrees with a weak ferromagnetic interaction and the EPR spectrum likewise suggests a triplet ground state.

Cyclic voltammetry of $[\text{Cu}_2(\mathbf{106})](\text{ClO}_4)_2$ show irreversible behaviour in the redox processes. The presence of the $\mu\text{-azido}$ link in $[\text{Cu}_2(\mathbf{106})(\text{N}_3)](\text{CF}_3\text{SO}_3)_3$ affects the electrochemistry. As well as stabilising the +2 state, which shifts redox potentials to more negative values, the system now shows some reversibility. A pair of quasi-reversible overlapped waves centered around -870 and -700 mV is seen, suggesting that two sequential one-electron redox processes are in operation, following the scheme $\text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{II}} \text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{I}} \text{Cu}^{\text{I}}$, which involves a mixed valence species.

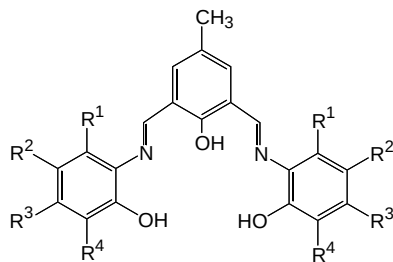
Thus, the hexamine cryptand **104** can accommodate a pair of copper(I) cations with $4.2 \text{ \AA}$ separation, or a $\mu\text{-hydroxo}$ dicopper(II) assembly, but no other dicopper(II) complexes of this ligand were characterised. With the octaamine cryptand **106**, on the other hand, air-sensitive copper(I) complexes are obtained, but a wide range of stable dicopper(II) complexes are also found. Bridging the links studied include the single atom hydroxide and the bent three-atom imidazolate as well as the linear three-atom azido. Magnetic interactions range from weak ferromagnetism in the $\mu\text{-azido}$ complex with **106** to virtual magnetic silence in the $\mu\text{-hydroxo}$ complexes of both ligands **104** and **106**.

9. Dinuclear complexes with acyclic ligands

9.1. Complexes with end-off symmetric ligands

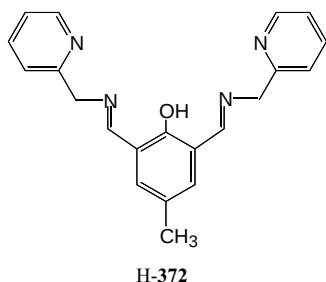
The complex $\text{Na}_2[\text{Cu}_2(\mathbf{230})(\text{OH})]\cdot 11\text{H}_2\text{O}$ (Fig. 277) ($\text{H}_5\text{-230a}$ is the Schiff base obtained by condensation of 2,6-diformyl-4-chlorophenol and 1-aminoethane phosphonic acid in the presence of NaOH) is an example of [1+2] end-off acyclic complexes. The copper ions are five coordinated square pyramidal. A phenolate oxygen provides the endogenous bridge while an OH^- group provides the exogenous one. Two water molecule are in the apical positions [5,42,272].

2,6-Bis{[(2-hydroxyphenyl)imino]methyl}-4-methylphenol ($\text{H}_3\text{-370}$) and its alkylated derivatives ($\text{H}_3\text{-371a-c}$) react with ferric nitrate in the presence of sodium acetate, propionate, or benzoate to yield $[\text{Fe}_2(\text{L})(\text{RCOO})_3]$ ($\text{L} = [\mathbf{370}]^{3-}$, $[\mathbf{371a-c}]^{3-}$) [454]. Identical products were obtained by reaction of the presynthesized ligands with the appropriate iron salt. The complexes were routinely prepared using $\text{Fe}(\text{NO}_3)_3$ as the iron source; however, reaction with FeCl_2 also gave diferric products via oxidation of both metal centers. The solubilities of the complexes were limited in most common organic solvents and solution studies were primarily carried out in pyridine or dimethylformamide.



$\text{H}_3\text{-370}$ $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$

$\text{H}_3\text{-371}$ a $\text{R}^2 = \text{CH}_3$, $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}$
 b $\text{R}^3 = \text{CH}_3$, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$
 c $\text{R}^2 = \text{R}^4 = \text{CH}_3$, $\text{R}^1 = \text{R}^3 = \text{H}$



H-372

Charged complexes of the type $[\text{Fe}_2(\mathbf{370})](\text{X})_3$ or $[\text{Fe}_2(\mathbf{371a-c})](\text{X})_3$ were obtained with various counterions, which were methanol soluble for $\text{X}^- = \text{NO}_3^-$, PF_6^- , BF_4^- and ClO_4^- and insoluble for $\text{X} = \text{BPh}_4^-$ [454].

Infrared and ^{13}C NMR proof indicates the benzoates are coordinated in the solid state and each bridges two metal centers. Two of the carboxylates probably bridge between

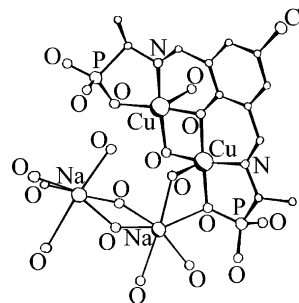


Fig. 277. Structure of $\text{Na}_2[\text{Cu}_2(\mathbf{230a})(\text{OH})]\cdot 11\text{H}_2\text{O}$ (adapted from Ref. [272]).

the diiron centers. The third carboxylate may bridge between iron centers in different complexes, leading to a polymeric structure. In pyridine solution one free benzoate iron is observed, possibly displaced by the solvent. Varying the carboxylate ligands did not significantly affect the electronic nature of the complex; however, additional alkyl substituents on the acyclic compartmental ligand further stabilized the iron(III) metal centers [454].

The condensation of 2,6-diformyl-4-methylphenol and 2-(2-aminoethyl)pyridine in the presence of manganese(II) acetate and sodium perchlorate or ammonium thiocyanate in the 1:2:2:2 molar ratio, forms $[\text{Mn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{ClO}_4)$ or $[\text{Mn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2(\text{NCS})]$ [455].

$[\text{Mn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{ClO}_4)$ (Fig. 278a) has a μ -phenoxo-di- μ -acetato-bridged dinuclear core. The two manganese(II) ions, 3.366 Å apart, are bridged by the central phenoxo oxygen atom of the pentadentate Schiff base ligand and the two bidentate acetate ions. The two manganese environments are different: the coordination geometry of

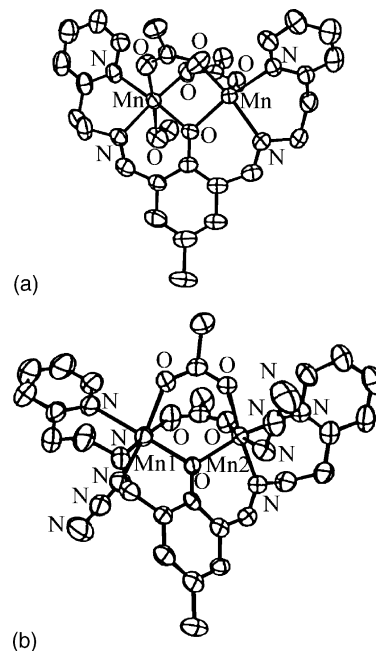


Fig. 278. Structures of $[\text{Mn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]^+$ (a) and $[\text{Mn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2(\text{N}_3)_2]$ (b) (adapted from Ref. [455]).

one manganese(II) ion is a distorted octahedron formed by the two nitrogen and one oxygen atom of $[372]^-$, the oxygen atoms of the two acetate ions and the oxygen atoms of the methanol molecule. The other manganese(II) ion is in a distorted square pyramid where the basal plane is formed by the nitrogen and the oxygen atoms from $[372]^-$ and the oxygen atom of the acetate ion and the fifth coordination site is occupied by the oxygen atom of the other acetate ion.

The structure of $[\text{Mn}_2(372)(\text{CH}_3\text{COO})_2(\text{NCS})]$ is similar to that of $[\text{Mn}_2(372)(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{ClO}_4)$. The two manganese ions are bridged by a phenoxo oxygen of the Schiff base ligand $[372]^-$ and two acetate. Two nitrogen donor atoms from either side arm of the pentadentate ligand coordinate and complete N_2O_3 coordination about each manganese atom. The sixth coordination site of one manganese(II) ion is occupied by the nitrogen atom of the thiocyanate ion [455].

The two high-spin manganese(II) ions are antiferromagnetically coupled ($J = -3.4 \text{ cm}^{-1}$). The antiferromagnetic interactions in these complexes are comparable to those of similar dinuclear manganese(II) complexes with 2,6-bis-[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol ($J = -4.9$ to 5.5 cm^{-1}) [455].

Both complexes are 1:1 electrolytes in DMF; therefore, the thiocyanate ion may be dissociated and replaced by a solvent molecule. Also the similarity between the EPR spectra of the complexes in frozen DMF solution is possibly due to the replacement of the coordinated methanol molecule by DMF in $[\text{Mn}_2(372)(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{ClO}_4)$.

In $[\text{Mn}(\text{H-}372)(\text{NCS})_2(\text{H}_2\text{O})]$, obtained from the 1:2:2:10 reaction methanol mixture of 2,6-diformyl-4-methylphenol, 2-(2-aminoethyl)pyridine, manganese(II) acetate tetrahydrate, and ammonium thiocyanate, the octahedral coordination around the manganese(II) ion is formed by a phenolate oxygen, an imino nitrogen, and a pyridyl nitrogen of the Schiff base ligand H-372, two nitrogens of the thiocyanate groups, and the oxygen of the water molecule. One of the side-arm pyridyl nitrogens of the dinucleating ligand is not coordinated [455].

When a mixture of manganese(II) acetate tetrahydrate and manganese(III) acetate dihydrate, is reacted in methanol with the Schiff base ligand H-372 in the presence respectively of ClO_4^- , SCN^- , N_3^- , the mixed-valence dinuclear complexes $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(372)(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$, $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(372)(\text{CH}_3\text{COO})_2(\text{NCS})_2]$ or $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(372)(\text{CH}_3\text{COO})_2(\text{N}_3)_2] \cdot 2\text{C}_3\text{OH}$ were isolated [455]. Moreover, H-372 reacts with manganese(III) acetate in the presence of sodium azide to yield the mononuclear species $[\text{Mn}^{\text{III}}(\text{H-}372)(\text{N}_3)_3]$, where the manganese(III) ion is coordinated by a phenolate oxygen, an imino nitrogen, and a pyridyl nitrogen of the dinucleating ligand H-372 and three nitrogens of the azide ions [455].

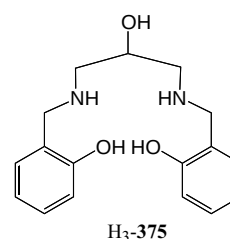
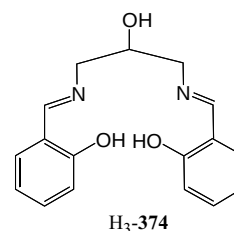
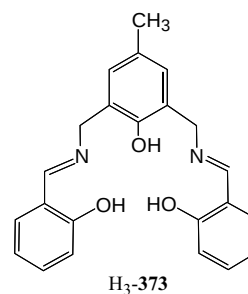
In $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(372)(\text{CH}_3\text{COO})_2(\text{N}_3)_2] \cdot 2\text{C}_3\text{OH}$ the two manganese ions are bridged by the central phenoxo oxygen atom of the Schiff base ligand and by two bidentate acetate

groups. Both manganese ions are in a distorted octahedral coordination with a phenoxo oxygen, an imino nitrogen and a pyridyl nitrogen atom of the dinucleating ligand $[372]^-$, two oxygen atoms of the acetate groups and a nitrogen atom of the azide ion. However, the structural parameters of the two manganese ions are significantly different and consistent with the presence of a manganese(II) ion in a distorted octahedral coordination geometry and a manganese(III) ion in an elongated octahedral coordination geometry [455] (Fig. 278b).

$[\text{Mn}_2(372)(\text{CH}_3\text{COO})_2(\text{N}_3)_2] \cdot 2\text{C}_3\text{OH}$ does not show an IT band in the near infrared region owing to the valence-trapped $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ structure. A similar behaviour was obtained for $[\text{Mn}_2(372)(\text{CH}_3\text{COO})_2(\text{NCS})_2]$ [455].

The mixed-valent complexes $[\text{Mn}_2(372)(\text{CH}_3\text{COO})_2(\text{NCS})_2]$ and $[\text{Mn}_2(372)(\text{CH}_3\text{COO})_2(\text{N}_3)_2]$ are antiferromagnetically coupled ($J = -3.6$ and -4 cm^{-1} , respectively) [455].

2,6-Bis[(salicylidene)-aminomethyl]-4-methylphenol (H_3 -373) reacts with nickel(II) salts to form dinuclear and tetranuclear complexes [456]. When the ligand, nickel(II) perchlorate, pyrazole and triethylamine were mixed in a ratio of 1:3:3:5 in methanol, the tetranuclear complex $[\text{Ni}_4(373)_2(\text{pz})_2(\text{CH}_3\text{OH})]$ was obtained. However, a similar reaction with a greater excess of pyrazole afforded the dinuclear complex $[\text{Ni}_2(373)(\text{pz})(\text{H-pz})(\text{CH}_3\text{OH})]\text{CH}_3\text{OH}$ which hinders the association of two dinuclear units. These results show that the amount of pyrazole may be an important factor governing the formation of the tetranuclear complex [456].



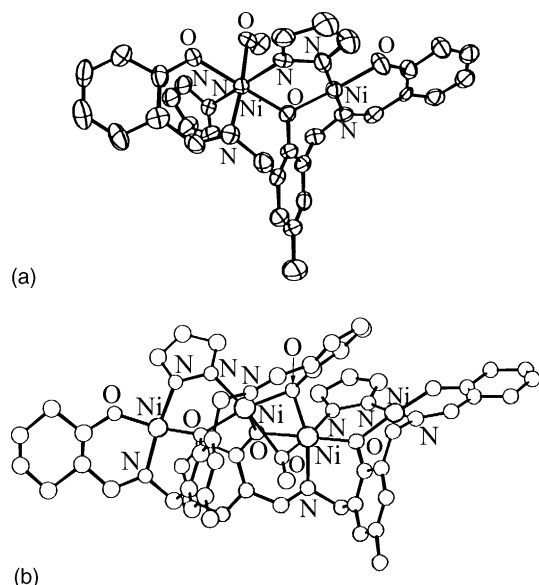


Fig. 279. Structure of $[\text{Ni}_2(\mathbf{373})(\text{pz})(\text{H-pz})(\text{CH}_3\text{OH})]$ (a) and $[\text{Ni}_4(\mathbf{373})_2(\text{pz})_2(\text{CH}_3\text{OH})]$ (b) (adapted from Ref. [456]).

In the dinuclear complex (Fig. 279a) the two nickel ions are bridged by a phenoxo-oxygen atom, and two pyrazolate nitrogen atoms. The $\text{Ni} \cdots \text{Ni}$ separation is 3.387 Å. One nickel(II) ion is coordinated by an imine nitrogen, two pyrazolate nitrogens, a bridging phenoxo oxygen, a terminal phenoxo oxygen and a methanol oxygen, forming a distorted octahedron, while the second nickel(II) ion takes a square planar arrangement with an imine nitrogen, a pyrazolate nitrogen, a bridging phenoxo oxygen, and a terminal phenoxo oxygen [456].

$[\text{Ni}_4(\mathbf{373})_2(\text{pz})_2(\text{CH}_3\text{OH})]$ has a tetranuclear structure consisting of two dinuclear units (Fig. 279b); in one dinuclear half two nickel ions are bridged by a central phenoxo oxygen atom of $[\mathbf{373}]^{3-}$ and the nitrogen atoms of pyrazolate ion. Similarly, the other two nickel(II) ions are bridged by a phenoxo oxygen atom and the nitrogen atoms of a pyrazolate ion in the other dinuclear unit. These two dinuclear halves are associated to a zigzag-shaped tetranuclear molecule by two terminal phenoxo-oxygen atoms of $[\mathbf{373}]^{3-}$ and a methanol oxygen atom. The two central nickel(II) ions consequently take distorted octahedral geometries, forming a face-shared bioctahedron while the other two lateral nickel ions, assume square planar geometries [456].

The magnetic data of $[\text{Ni}_2(\mathbf{373})(\text{pz})(\text{H-pz})(\text{CH}_3\text{OH})] \cdot \text{CH}_3\text{OH}$ prove the existence of one paramagnetic high-spin and one diamagnetic low-spin nickel(II) ion per dinuclear molecule. The mixed-spin state is maintained in DMF [456]. The effective magnetic moment of the tetranickel(II) complex, 2.25 BM/Ni at room temperature, lower than the spin-only value (2.83 BM) for the high-spin nickel(II) ion and the temperature dependence of the magnetic susceptibilities, in the temperature range 80–300 K, shows that there is an antiferromagnetic interaction between the two central nickel(II) ions ($J = -4.71 \text{ cm}^{-1}$) [456].

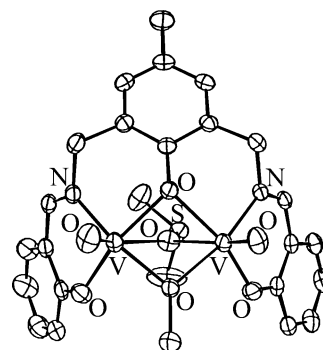


Fig. 280. Structure of $[(\text{VO})_2(\mathbf{373})(\mu\text{-CH}_3\text{O})(\text{DMSO})]$ (adapted from Ref. [457]).

In $[(\text{VO})_2(\mathbf{373})(\mu\text{-CH}_3\text{O})(\text{DMSO})]$, synthesized by reaction of $\text{H}_3\text{-}\mathbf{373}$ with $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ in the presence of $\text{N}(\text{Et})_3$ [457], the two vanadium(IV) ions with terminal oxo groups are bridged by a phenoxo-oxygen, a methoxo-oxygen and an oxygen atom of dimethyl sulfoxide, forming a distorted octahedral environment for each metal center. The $\text{V} \cdots \text{V}$ separation is 3.026 Å. The terminal oxo groups are in *syn*-positions with respect to each other. The two vanadium(IV) ions are further bridged by an oxygen atom of dimethyl sulfoxide. The dinucleating ligand takes a roof-shaped structure [457] (Fig. 280). There is a significant antiferromagnetic interaction between the two vanadium(IV) ions [457].

The dinuclear di(μ -alkoxo)-bridged $[\text{Fe}_2(\mathbf{374})_2]$, $[\text{Fe}_2(\mathbf{375})_2]$ and di(μ -phenoxo)-bridged $[\text{Fe}_2(\mathbf{373})_2]$ and $[\text{Fe}_2(\mathbf{376})_2]$ complexes have been synthesized by reaction of iron(III) chloride with the appropriate ligand in methanol or tetrahydrofuran/methanol. In order to obtain the similar complexes with the reduced ligands triethylamine was used in addition.

The asymmetric unit of $[\text{Fe}_2(\mathbf{374})_2] \cdot \text{CH}_2\text{Cl}_2$ consists of two crystallographically independent molecules with small variations in bond distances and angles. Both the molecules have two *trans*- FeN_2O_2 coordination cores bridged by two alkoxo oxygen atoms. The Fe_2O_2 portion of the bridge units is perfectly planar in both the molecules (Fig. 281a). The two alkoxo bridges in molecule B are asymmetric while in A one alkoxo bridge is significantly asymmetric but the other alkoxo bridge is relatively symmetric [458].

$[\text{Fe}_2(\mathbf{375})_2] \cdot \text{H}_2\text{O}$ has a centrosymmetric structure where the two crystallographically equivalent iron(III) centers are bridged by the two alkoxo oxygen atoms. Unlike the Schiff base ligand $\text{H}_3\text{-}\mathbf{374}$, the highly flexible $\text{H}_3\text{-}\mathbf{375}$ winds itself around the five coordination sites of the metal ion in such a way that the two amine nitrogen atoms and two phenolate oxygen atoms are in the *cis* positions. The coordination sphere is completed by the alkoxo oxygen atom of the second ligand resulting in the formation of a unique dialkoxo bridged dimeric complex with two FeN_2O_4 coordination cores. The dialkoxo bridge is highly asymmetric [458] (Fig. 281b).

In $[\text{Fe}_2(\mathbf{373})_2] \cdot \text{CH}_2\text{Cl}_2$ the asymmetric center consists of two iron(III) ions bridged by two phenoxo oxygen atoms. Two phenolate oxygen atoms and two azomethine nitrogen atoms coordinate each metal ion in addition to the two bridging phenoxo oxygen atoms to give two *trans*- FeN_2O_4 coordination cores. One of the bridging phenolate rings is perpendicular. The severe distortion from the octahedral geometry in the complex appears to result from the bonding constraints of the ligand (Fig. 281c) [458].

Cyclic voltammetric studies of $[\text{Fe}_2(\mathbf{373})_2]$, $[\text{Fe}_2(\mathbf{374})_2]$ and $[\text{Fe}_2(\mathbf{376})_2]$ in dichloromethane reveal stepwise reduction of the $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$ to the mixed-valence $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ and the reduced $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ species while $[\text{Fe}_2(\mathbf{375})_2]$ exhibits a single quasi reversible reduction peak corresponding to the mixed-valence form [458].

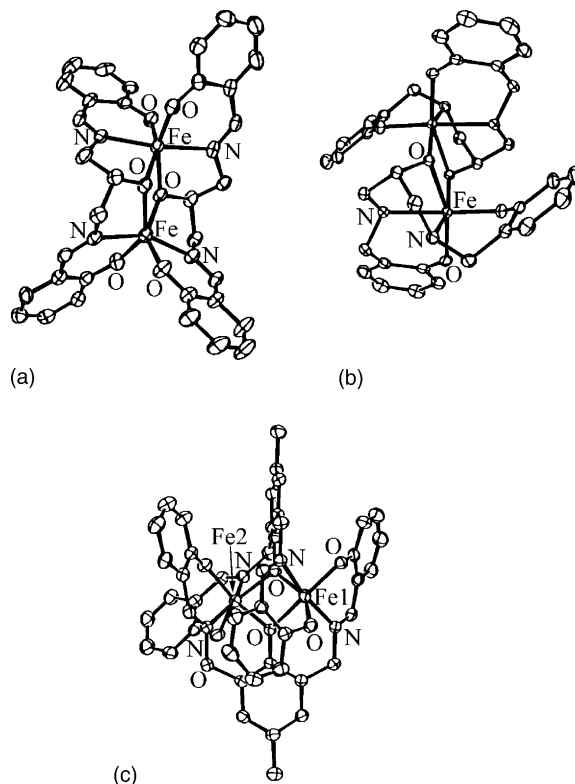
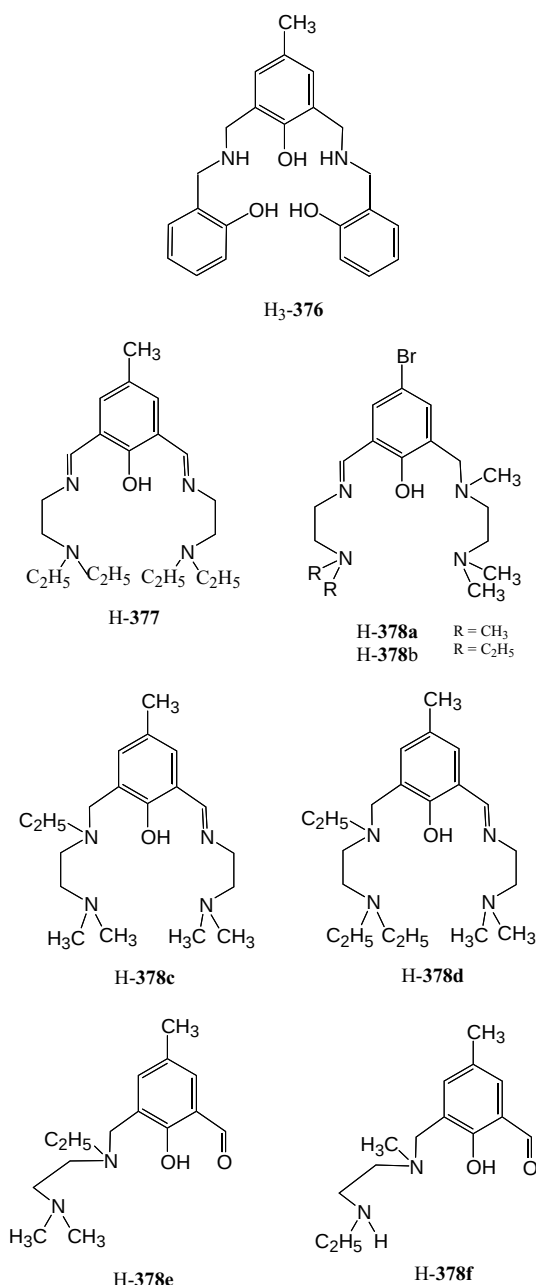


Fig. 281. Structures of $[\text{Fe}_2(\mathbf{374})_2]$ (a), $[\text{Fe}_2(\mathbf{375})_2]$ (b) and $[\text{Fe}_2(\mathbf{373})_2]$ (c) (adapted from Ref. [458]).

H-310 and **H-377** form the dinuclear manganese(II) complexes $[\text{Mn}_2(\text{L})(\text{RCO}_2)_2(\text{NCS})]$ and $[\text{Mn}_2(\text{L})(\text{Cl})_3]$ [430]. The carboxylate thiocyanate complexes are air stable in both the solid state and also in solution and are 1:1 electrolytes in dimethylformamide, suggesting that the thiocyanate ion is dissociated. On the other hand, the chloride complexes are essentially non-electrolytes in DMF. It was suggested that one chloride ion acts as a bridge between a pair of manganese(II) ions and the remaining two chloride ions each coordinates singly to each manganese.

In $[\text{Mn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2(\text{NCS})] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (Fig. 282a) the two manganese(II) ions are bridged by the phe-

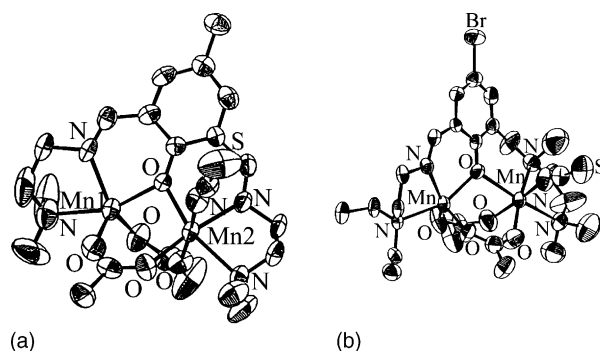


Fig. 282. Structure of $[\text{Mn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2(\text{NCS})]$ (a) and $[\text{Mn}_2(\mathbf{378b})(\text{CH}_3\text{COO})_2(\text{NCS})]$ (b) (adapted from Ref. [460]).

nolic oxygen of **[310]**[−] and two acetate groups, affording a μ -phenoxo-bis(μ -carboxylato)dimanganese(II) core structure. The thiocyanate group coordinates to one manganese ion in order to afford a pseudo-octahedral environment with the oxygen and the nitrogen atoms of **[310]**[−], one oxygen atom of the bridging acetate groups, and the nitrogen atom of the thiocyanate group. The environment around the other manganese ion is regarded as trigonal bipyramidal with the imino nitrogen and the two acetate oxygens in the basal plane and the phenolic oxygen and the amino nitrogen at the apices. A similar asymmetry in the dimanganese(II) structure has been found for the related complex **[Mn₂(372)(CH₃COO)₂(NCS)]** where the geometry of the five coordinated manganese is regarded as square pyramidal [460].

Magnetic data of **[Mn₂(310)(RCOO)₂(NCS)]** suggest that the manganese(II) ion is high-spin in all the complexes and there is an antiferromagnetic interaction within a pair of manganese(II) ions. The exchange integrals J fall in the range -2 to -5 cm^{−1} and in line with values ($J = -2$ to 5 cm^{−1}) found for the μ -phenoxo-bis(μ -carboxylato)dimanganese(II) complex derived from H-372 [459,460].

When H₂O₂ is added to a DMF solution of **[Mn₂(310)(C₆H₅COO)₂(NCS)]** catalytic decomposition of H₂O₂ occurred with more than 1000 turnovers based on volumetric measurements of evolved dioxygen. The initial rate was slow, but after a lag period the rate significantly increased and the colour of the solution changed from yellow to purple.

Electronic spectral and mass spectrometric results of this purple solution prove the formation of species containing the groups Mn^{II}Mn^{IV}(=O) and {Mn^{IV}(=O)}₂, which retain the original μ -phenoxo-bis(μ -carboxylato)dimanganese core structure. It was also observed that **[Mn^{II}Mn^{IV}(310)(C₆H₅COO)₂(NCS)]** is formed at an early stage of the H₂O₂ disproportionation reaction whereas **[(Mn^{IV}O)₂(310)(C₆H₅COO)₂(NCS)]** appears after the lag period. The initial complex between **[Mn₂(310)(C₆H₅COO)₂(NCS)]** and H₂O₂ must be {Mn₂(310)(C₆H₅COO)₂(OOH)}, which is converted into the {Mn^{II}Mn^{III}(OH)} species through the peroxo-bridged dimeric intermediate {Mn₂(310)(CH₃COO)₂}₂(O₂^{2−}) or to the {Mn^{III}(OH)}₂ species through the μ -peroxo-intermediate {Mn₂(310)(CH₃COO)₂}. Further oxidation of the {Mn^{II}Mn^{III}(OH)} and {Mn^{III}(OH)}₂ species with H₂O₂ forms **[Mn^{II}MnO(310)(C₆H₅COO)₂(NCS)]** and **[(Mn^{IV}O)₂(310)(C₆H₅COO)₂(NCS)]**, respectively. The lag period before the formation of **[(Mn^{IV}O)₂(310)(C₆H₅COO)₂(NCS)]** has been explained by the fact that the μ -peroxo intermediate is hardly formed owing to the steric requirement of **310** rendering five-coordinate geometry about one metal ion.

A mechanism for the H₂O₂ disproportionation reaction by **[Mn₂(310)(C₆H₅COO)₂(NCS)]** was proposed where **[(Mn^{IV}O)₂(310)(C₆H₅COO)₂(NCS)]** oxidizes H₂O₂ to O₂ producing the {Mn^{III}(OH)}₂ species which in turn reduces H₂O₂ to water reproducing the {Mn^{IV}(=O)}₂ species. Both

{Mn^{IV}(=O)}₂ and {Mn^{III}(OH)}₂ inevitably have *cis* configuration with respect to the two oxo or hydroxo groups so that the cycle between the two species is easily performed by the chelating interaction with H₂O₂, in agreement with a high catalytic activity of **[(Mn^{IV}O)₂(310)(C₆H₅COO)₂(NCS)]**. On the other hand, the cycle between {Mn^{II}Mn^{IV}(=O)} and {Mn^{II}Mn^{III}(OH)} must be slower since this involves intermolecular bridging interaction with H₂O₂. This leads to a low catalytic activity of **[Mn^{II}(Mn^{IV}O)(310)(C₆H₅COO)₂(NCS)]** [461].

The time course of O₂ evolution by **[Mn₂(310)(C₆H₅COO)₂(SCN)]** is sigmoid, where the initial slow reaction and the faster reaction after an induction period are concerned with the disproportionation of H₂O₂. In DMF, **[Mn₂(310)(C₆H₅COO)₂(NCS)]** exists as **[Mn₂(310)(C₆H₅COO)₂]⁺** whose molecular symmetry can be approximated as pseudo-C_s with the two vacant sites in *cis* positions. The vacant site of one manganese ion is significantly buried so that hydrogen peroxide preferentially interacts with the other manganese(II) ion to form {Mn^{II}Mn^{IV}(=O)} as the final oxidation product. The H₂O₂ disproportionation catalysed by {Mn^{II}Mn^{IV}(=O)} corresponds to the slow reaction. When the complex cation **[Mn₂(310)(C₆H₅COO)₂]⁺** is slightly deformed, both vacant sites are available for the co-ordination of H₂O₂ to form *cis*-{Mn^{IV}(=O)}₂ as the final oxidation product. This faster reaction occurs after an induction period due to the necessary deformation of the precursor cation, but the *cis*-{Mn^{IV}(=O)}₂ species is more efficient in disproportionating H₂O₂ [461].

[Mn₂(372)(CH₃COO)₂(NCS)] also exists as **[Mn₂(372)(CH₃COO)₂]⁺** in DMF, and the time course of O₂ evolution is essentially sigmoid. The initial rate by **[Mn₂(372)(CH₃COO)₂(NCS)]** is however slower than that by **[Mn₂(310)(CH₃COO)₂(NCS)]**. Furthermore, the second faster reaction by **[Mn₂(372)(CH₃COO)₂(NCS)]** occurs after a longer induction period and its rate is significantly slower when compared with that of **[Mn₂(310)(CH₃COO)₂(NCS)]** under the same conditions. The crystal structure analysis for **[Mn₂(372)(CH₃COO)₂(NCS)]** has revealed the pseudo-C₂ symmetry of the cation **[Mn₂(372)(CH₃COO)₂]⁺** where the sixth vacant sites of the two manganese ions are *trans* to each other. Deformation of this *trans* structure (C₂ symmetry) to a *cis* structure (C_s symmetry) is essential for this complex to form *cis*-{Mn^{IV}(=O)}₂ and this seems to be difficult as gauged by the long induction period [461].

The dinuclear manganese(II) complexes **[Mn₂(L)(CH₃COO)₂(NCS)]**, formed when H-378a and H-378b are reacted with Mn(CH₃COO)₂·*n*H₂O and NaSCN in methanol [462], are air stable in the solid state and in DMF solution. IR data suggest they have a μ -phenoxo-bis(μ -carboxylato)-dimanganese(II) core structure as observed in the structure of **[Mn₂(378b)(CH₃COO)₂(NCS)]** (Fig. 282b), where the two manganese ions are bridged by the phenolic oxygen of **[378b]**[−] and two acetate groups. The Mn···Mn distance is 3.376 Å. The geometrical environments around the two manganese ions are different: one

manganese(II) ion shows a distorted trigonal bipyramidal with the imino nitrogen and the two acetate oxygens in the basal plane and the phenolic oxygen and the amino nitrogen at the apices while the geometry of the other manganese(II) ion is distorted octahedral being bond to the phenolic oxygen and the amino nitrogens of **[378b]**[−], the oxygen atoms of the bridging acetate groups, and the nitrogen of the isothiocyanato group [462].

These complexes are 1:1 electrolytes in DMF where dissociation of the NCS[−] group occurs. Magnetic susceptibility measurements over the temperature range 4.2–300 K indicated weak antiferromagnetic interaction ($J = -3$ to -5 cm^{-1}) [462].

Cyclic voltammetry for $[\text{Mn}_2(\mathbf{378a})(\text{CH}_3\text{COO})_2(\text{NCS})]$ in CH_2Cl_2 revealed three quasi-reversible redox couples ($E_{1/2} = 0.63, 1.07$ and 1.24 V versus saturated calomel electrode) due to the stepwise oxidations $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}} \rightarrow \text{Mn}^{\text{II}}\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{III}}\text{Mn}^{\text{II}} \rightarrow \text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$.

All the complexes show a catalase-like activity, disproportionating H_2O_2 into O_2 and H_2O [462].

H-310, **H-378a** and **H-372** form $[\text{Zn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2](\text{PF}_6)$, $[\text{Zn}_2(\mathbf{310})(\text{NCS})_3]$, $[\text{Zn}_2(\mathbf{378a})(\text{CH}_3\text{COO})_2](\text{PF}_6)$, $[\text{Zn}_2(\mathbf{378a})(\text{NCS})_3]$, $[\text{Zn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2](\text{PF}_6)$ and $[\text{Zn}_2(\mathbf{372})(\text{NCS})_3]$ when reacted with zinc(II) acetate tetrahydrate in the presence of PF_6^- or ClO_4^- ion or $\text{Zn}(\text{NCS})_2$ [462]. The diacetato complexes are stable in DMF. ^1H NMR spectra indicate that $[\text{Zn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2](\text{PF}_6)$ retains the di-(μ -acetato- μ -phenolato)-dizinc core in DMF, if one assumes D_2 symmetric in solution. For $[\text{Zn}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2](\text{ClO}_4) \cdot \text{CHCl}_3$ NMR spectral features suggest a slow molecular inversion with respect to the mean molecular plane. The tri(thiocyanato) complexes $[\text{Zn}_2(\text{L})(\text{NCS})_3]$ act as 1:1 electrolytes in DMF, indicating that one NCS[−] group is dissociated.

$[\text{Zn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2](\text{PF}_6)$ has a di-(μ -acetato- μ -phenolato)-dizinc(II) core with a $\text{Zn} \cdots \text{Zn}$ interatomic separation of $3.237 \text{ \AA}$. The geometry about the two zinc ions, similar but not equivalent, can be regarded as trigonal bipyramid with the phenolic oxygen and the terminal nitrogen at the axial sites and with the imino nitrogen and the two acetate oxygens on the trigonal plane (Fig. 283a).

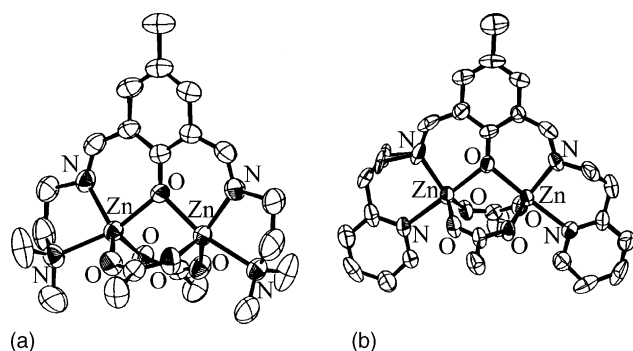


Fig. 283. Structure of $[\text{Zn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2]^+$ (a) and $[\text{Zn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2]^+$ (b) (adapted from Ref. [462]).

The dinuclear core of $[\text{Zn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2](\text{PF}_6)(\text{DMF})_{0.5}(\text{CH}_3\text{CHOHCH}_3)_{0.5}$ is essentially the same as that of $[\text{Zn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2](\text{PF}_6)$. The two zinc ions, $3.297 \text{ \AA}$ apart, are bridged by the phenolic oxygen of $[\mathbf{372}]^-$ and two acetate groups in the *syn-syn* mode. The two zinc(II) ions have a similar trigonal bipyramidal geometry with the phenolic oxygen and the terminal nitrogen at the axial sites and with the imino nitrogen and the two acetate oxygens on the trigonal base [462] (Fig. 283b).

$[\text{Zn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2](\text{PF}_6)$, $[\text{Zn}_2(\mathbf{378a})(\text{CH}_3\text{COO})_2](\text{PF}_6)$ and $[\text{Zn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2](\text{PF}_6)$, with C_2 symmetry and a μ -acetato- μ -phenolato dizinc(II) core, hydrolyze tris(*p*-nitrophenyl)phosphate (TNP) into bis(*p*-nitrophenyl) hydrogenphosphate (HBNP) in aqueous dimethylformamide [462]. A mechanism of the TNP hydrolysis by these three acetato complexes was prepared where the addition of water or TNP to one zinc center of $[\text{Zn}_2(\text{L})(\text{CH}_3\text{COO})_2]^+$ affords $[\text{Zn}_2(\text{L})(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]^+$ or $[\text{Zn}(\text{L})(\text{CH}_3\text{COO})_2(\text{TNP})]^+$. The further addition of TNP to $[\text{Zn}(\text{L})(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})(\text{TNP})]^+$ or the addition of water to $[\text{Zn}(\text{L})(\text{CH}_3\text{COO})(\text{TNP})]^+$ leads to the intermediate $[\text{Zn}(\text{L})(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})(\text{TNP})]^+$ that allows a nucleophilic attack of the water (or hydroxide) to the phosphorus nucleus of the adjacent TNP. The low hydrolytic activity of $[\text{Zn}_2(\mathbf{310})(\text{CH}_3\text{COO})_2](\text{PF}_6)$, $[\text{Zn}_2(\mathbf{378a})(\text{CH}_3\text{COO})_2](\text{PF}_6)$ and $[\text{Zn}_2(\mathbf{372})(\text{CH}_3\text{COO})_2](\text{PF}_6)$ may relate to their D_2 symmetric core that is distorted with difficulty into the C_s symmetric core [462].

H-310 and **H-378a** have been used to form $[\text{Ni}_2(\mathbf{310})(\text{CH}_3\text{COO})_2(\text{NCS})_2(\text{CH}_3\text{OH})]$, $[\text{Ni}_2(\mathbf{310})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{BPh}_4)$, $[\text{Ni}_2(\mathbf{378a})(\text{CH}_3\text{COO})_2(\text{NCS})_2(\text{CH}_3\text{OH})]$, $[\text{Ni}_2(\mathbf{378a})(\text{CH}_3\text{COO})_2](\text{BPh}_4)$ and $[\text{Ni}_2(\mathbf{378a})(\text{NCS})_3(\text{CH}_3\text{OH})]$ [463]. In particular the addition of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ to **H-310** followed by the addition of $\text{Na}(\text{BPh}_4)$ affords $[\text{Ni}_2(\mathbf{310})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{BPh}_4)$ (Fig. 284). One bridged phenolic oxygen of $[\mathbf{310}]^-$ and two acetate groups in the *syn-syn* mode, provide a (μ -phenoxo)-bis(μ -carboxylato) dinickel(II) core in the $\text{Ni} \cdots \text{Ni}$ separation of $3.311 \text{ \AA}$. A methanol molecule coordinates to one nickel(II) ion, forming an asymmetric core about the two

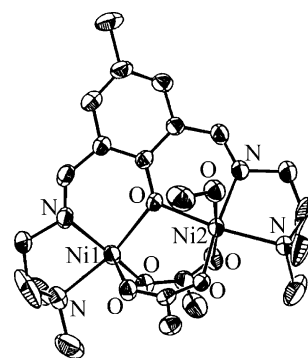


Fig. 284. Structure of $[\text{Ni}_2(\mathbf{310})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]^+$ (adapted from Ref. [463]).

nickel(II) ions. The geometry around the five coordinated nickel(II) ion is depicted as a square pyramid with two nitrogens and oxygen atoms and one oxygen of acetate bridge on the basal plane and the oxygen of another acetate bridge at the apex. The geometry around the six coordinate nickel(II) ion is a distorted octahedron [463].

The reaction of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with $\text{H}_2\text{-378a}$, followed by the addition respectively of NaSCN or $\text{Na}(\text{BPh}_4)$, affords $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})(\text{NCS})_2(\text{CH}_3\text{OH})]$ or $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2](\text{BPh}_4)$; when nickel(II) thiocyanate is used instead of nickel(II) acetate, $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{CH}_3\text{OH})]$ is obtained.

In $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})(\text{NCS})_2(\text{CH}_3\text{OH})]$ a pair of six coordinated nickel(II) ions are bridged by the phenolic oxygen of $[\text{378a}]^-$, an isothiocyanate nitrogen, and an acetate group in the *syn-syn* mode. The $\text{Ni} \cdots \text{Ni}$ separation is 2.993 Å. The sixth position of one nickel(II) ion is occupied by a methanol oxygen and the sixth position of the other nickel(II) ion is occupied by an isothiocyanate nitrogen, the methanol molecule on one nickel and the thiocyanate group on the other nickel being situated *cis* relative to each other with respect to the mean molecular plane (Fig. 285a). The acetate group bridges the two nickel ions at their axial sites [463].

In $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2](\text{BPh}_4)$ (Fig. 285b) a pair of nickel ions, 3.25 Å apart, are bridged by the phenolic oxygen

of $[\text{378a}]^-$ and an acetate group in the *syn-syn* mode. The nickel(II) ion bound to the iminic pendant arm has a square planar geometry with a slight distortion to a tetrahedron. The other nickel(II) ion bound to the aminic pendant arm has a six coordinate geometry with further coordination of an acetate group in the chelating mode [463].

In $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{CH}_3\text{OH})]$ (Fig. 285c) the aminic pendant arm adopts an out-of-plane chelating mode. The two nickel(II) ions are bridged by the phenolic oxygen of $[\text{378a}]^-$ and an isothiocyanate nitrogen; the $\text{Ni} \cdots \text{Ni}$ separation is 3.142 Å. The nickel(II) ion bound to the iminic pendant arm has a five coordinated square pyramidal structure with the oxygen and the nitrogen atoms of $[\text{378a}]^-$; the nitrogen of a monodentate isothiocyanate group and the nitrogen of the bridging isothiocyanate group. The other nickel(II) ion bound to the aminic pendant arm, has a pseudo octahedral geometry with further coordination of a methanol molecule, its equatorial coordination plane being formed by the oxygen and the nitrogen atoms of $[\text{378a}]^-$, the nitrogen atom of the bridging isothiocyanate group and the nitrogen atom of the monodentate isothiocyanate group. The axial sites are occupied by the terminal nitrogen of the pendant arm and a methanol oxygen [463].

For $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})(\text{NCS})_2(\text{CH}_3\text{OH})]$, $[\text{Ni}_2(\text{377a})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{BPh}_4)$ and $[\text{Ni}_2(\text{377a})(\text{CH}_3\text{COO})(\text{NCS})_2(\text{CH}_3\text{OH})]$, the magnetic moments gradually decrease with decreasing temperature, suggesting the presence of an antiferromagnetic interaction between the pair of nickel(II) ions ($J = -0.8, 1.0$ and -1.7 cm^{-1} , respectively). The magnetic moment of $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{CH}_3\text{OH})]$ is $3.25 \mu_{\text{B}}$ at room temperature, and gradually increases with decreasing temperature up to a maximum of $3.56 \mu_{\text{B}}$ near 20 K; a ferromagnetic interaction operates between the pair of nickel ions ($J = +10 \text{ cm}^{-1}$). The magnetic moment of $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2](\text{BPh}_4)$ ($3.31 \mu_{\text{B}}$ per molecule at room temperature) is almost independent from temperature down to 10 K. This, together with X-ray crystallographic and visible spectral data, shows that it is a mixed-spin complex having one low-spin and one high-spin nickel(II) ion [463].

$[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2](\text{BPh}_4)$ and $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{CH}_3\text{OH})]$ form the urea adducts $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2(\text{urea})](\text{BPh}_4)$ and $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{urea})]$, respectively. Urea binding, through its oxygen, occurs at the four coordinate nickel center for $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2(\text{urea})](\text{BPh}_4)$. Its room temperature magnetic moment is $3.29 \mu_{\text{B}}$ per one nickel, clearly indicating that both nickel ions are paramagnetic.

$[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{urea})]$ (Fig. 286) retains the dinuclear core of $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{CH}_3\text{OH})]$, the main difference being the replacement of methanol by urea in the sixth exogenous ligand of the octahedral nickel(II). The $\text{Ni} \cdots \text{Ni}$ separation is 3.155 Å. In $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2(\text{urea})](\text{BPh}_4)$ and $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{urea})]$ a ferromagnetic interaction between the two metal ions occurs ($J = 10.0 \text{ cm}^{-1}$) [463].

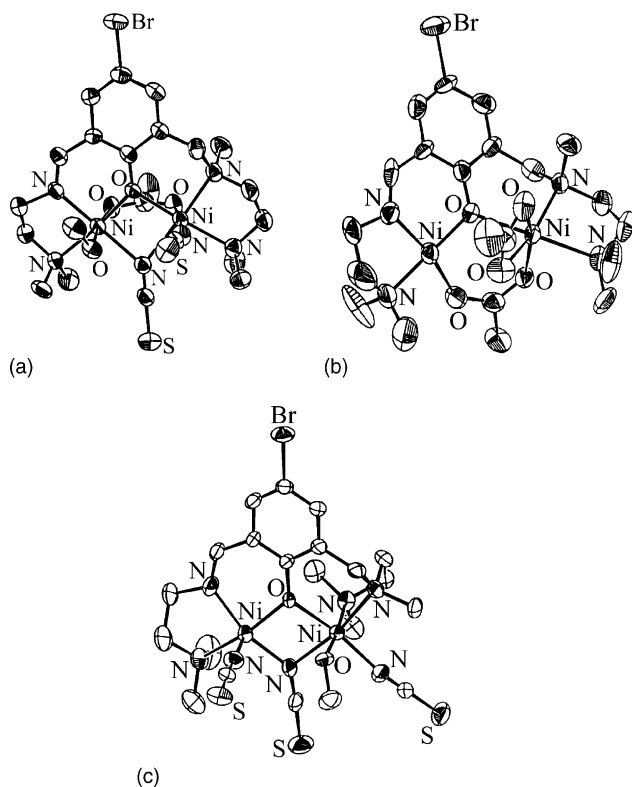


Fig. 285. Structures of $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2(\text{NCS})_2(\text{CH}_3\text{OH})]$ (a), $[\text{Ni}_2(\text{378a})(\text{CH}_3\text{COO})_2]^+$ (b) and $[\text{Ni}_2(\text{378a})(\text{NCS})_3(\text{CH}_3\text{OH})]$ (c) (adapted from Ref. [463]).

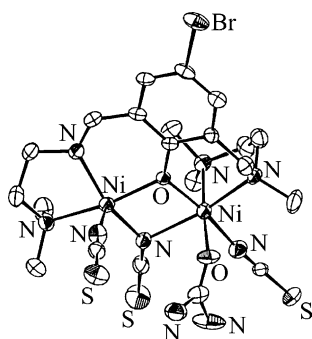


Fig. 286. Structure of $[\text{Ni}_2(\mathbf{378a})(\mu\text{-NCS})(\text{NCS})_2(\text{urea})]$ (adapted from Ref. [463]).

The reaction of $\text{H}_2\text{-378c}$ with CuBr_2 and the subsequent recrystallization of the product from methanol forms $[\text{Cu}_2(\mathbf{378c})(\text{Br}_3)]$. The coordination environment at each copper(II) ion is a $\text{N}_2\text{Br}_2\text{O}$ square pyramidal arrangement derived from donor atoms from the ligands and the bromides. At one copper(II) ion the base of the pyramid stems from the N_2O compartment derived from the aminic side arm of the ligand and a counter anionic non-bridging bromide, with the bridging bromide providing the apex. At the other copper(II) ion the base is derived from the N_2O compartment provided by the iminic side-arm of the ligand, with the fourth corner of the base occupied by the bridging bromide, the apical coordination is supplied by a non-bridging bromide. The $\text{Cu}\cdots\text{Cu}$ separation is 3.221 Å [463] (Fig. 287a).

The reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with $\text{H}_2\text{-378d}$ produces $[\text{Cu}_2(\mathbf{378d})(\text{ClO}_4)](\text{ClO}_4)$ where a $\text{Cu}\cdots\text{Cu}$ separation of 2.96 Å occurs [463]. Each copper ion has a square pyramidal arrangement of N_2O_3 donor atoms. The two nitrogens at one copper ion are supplied by the iminic side-arm and at the other copper the two nitrogens are from the aminic pendant arm. The coordination environment at each metal ion is completed by the oxygens atoms from an endogenous μ -phenoxy bridge derived from the compartmental ligand itself, an exogenous μ -hydroxy bridge and an oxygen atom from a bridging bidentate perchlorate anion (Fig. 287b).

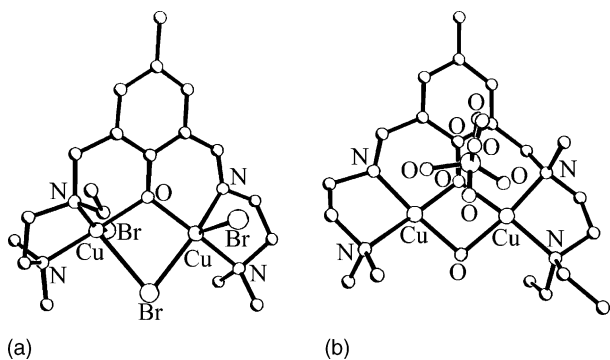


Fig. 287. Structure of $[\text{Cu}_2(\mathbf{378c})(\text{Br}_3)]$ (a) and $[\text{Cu}_2(\mathbf{378d})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ (b) (adapted from Ref. [463]).

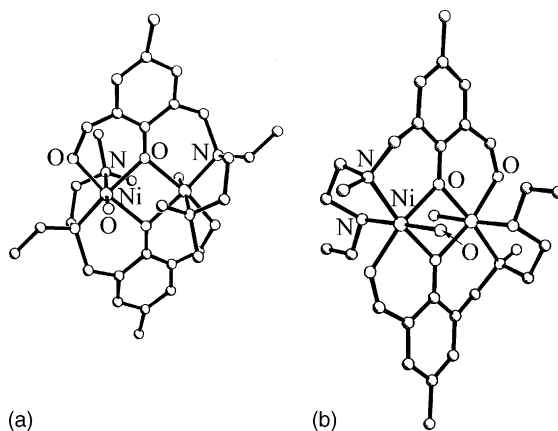


Fig. 288. Structure of $[\text{Ni}_2(\mathbf{378e})(\text{H}_2\text{O})_2]^{2+}$ (a) and $[\text{Ni}_2(\mathbf{378f})_2(\text{H}_2\text{O})_2]^{2+}$ (b) (adapted from Ref. [463]).

In contrast to the reaction with copper(II) salts, the reaction of H-378a and H-378b with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol followed by recrystallization gave complexes where hydrolysis of the Schiff base arm has occurred. The structure of $[\text{Ni}_2(\mathbf{378e})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ shows that a dinuclear nickel(II) complex has been formed and that the imine bond of the unsymmetrical unsaturated proligand has undergone hydrolysis to give the corresponding aldehyde H-378e . The two molecules of the hydrolysed ligand then assumed an octahedral arrangement around each nickel(II) ion. The $\text{Ni}\cdots\text{Ni}$ distance is 3.088 Å (Fig. 288a). Each nickel(II) ion is coordinated by the two nitrogen atoms from the saturated pendant arm moiety and the octahedral coordination at each metal ion is completed by interaction with the bridging phenolic oxygen atom, the carbonyl oxygen atom and an oxygen atom from a water molecule. The water molecules lie on either side of the ligand plane and so are *trans* to each other. The phenolic oxygen atoms serve as non-symmetric di(μ -phenoxy) bridges between the two nickel ions; the perchlorate anions are not coordinated [463].

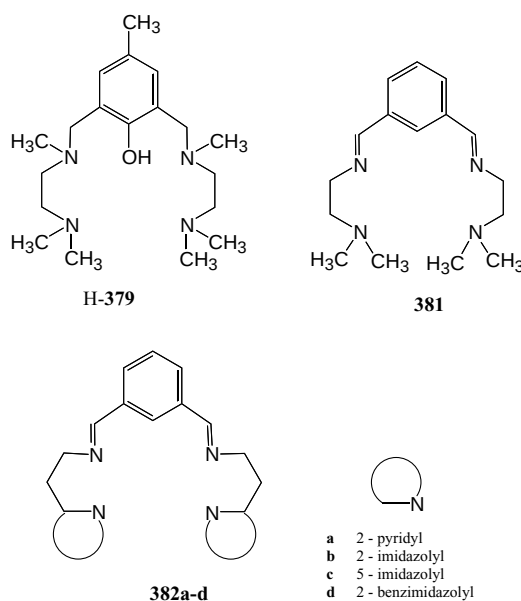
The reaction of H-378d with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol followed by recrystallization gave $[\text{Ni}(\mathbf{378f})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{CH}_3\text{OH}$. Analogously $[\text{Ni}(\mathbf{378f})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ CH_3CN was obtained from the reaction of H-378d with $\text{Ni}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$ in methanol followed by recrystallization from acetonitrile [463]. There is again an octahedral arrangement of N_2O_4 donors around each nickel(II) ion, supplied by two molecules of hydrolysed ligand and a water or an acetonitrile molecule. The $\text{Ni}\cdots\text{Ni}$ distances are 3.017 and 3.107 Å, respectively. Each metal ion is doubly bridged by a non-symmetric di(μ -phenoxy) bridge from the hydrolysed ligand. The coordination is completed by two nitrogen donors from the aminic pendant arm, an oxygen from the carbonyl group and an oxygen from a water molecule or a nitrogen from an acetonitrile molecule (Fig. 288b) [463].

The magnetic moment ($1.85\mu_{\text{B}}$) of $[\text{Cu}_2(\mathbf{378c})(\text{Br}_3)]$ at room temperature is almost independent of temperature down to liquid nitrogen showing that no appreciable

magnetic spin exchange operates between the pair of copper(II) ions. On the contrary in $[\text{Cu}_2(\mathbf{378d})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ an antiferromagnetic interaction between the two ions occurs ($J = -215 \text{ cm}^{-1}$). Also for the nickel(II) complexes with **H-378e** and **H-378f** an antiferromagnetic coupling was observed ($J = -31$ and -17 cm^{-1} , respectively) [463].

Cyclic voltammetric studies on $[\text{Cu}_2(\mathbf{378c})(\text{Br})_3]$ (using a glassy carbon electrode in DMF and a Ag/AgCl reference electrode) show a quasi-reversible couple at -0.03 V and a reversible couple at -0.85 V , attributed to the stepwise reductions at the metal center, $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$, respectively. $[\text{Cu}_2(\mathbf{378d})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ shows a weak couple at -0.30 V , ascribed to the monomeric copper impurity and an irreversible couple near -0.9 V . The facile reduction of $[\text{Cu}_2(\mathbf{378c})(\text{Br})_3]$ relative to $[\text{Cu}_2(\mathbf{378d})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ certainly relates to the square pyramidal geometry about the copper ion in $[\text{Cu}_2(\mathbf{378c})(\text{Br})_3]$ and the involvement of the soft donor Br^- anion. The reduction of the copper ion of $[\text{Cu}_2(\mathbf{378d})(\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ is more difficult because the square planar environment about the metal ions is an unfavourable geometric environment for the copper(I) ion [463].

2,6-Bis{[*N*-(2-dimethylaminoethyl)-*N*-methyl]aminomethyl}-4-methylphenol (**H-379**), prepared by a Mannich reaction between 4-methylphenol and *N,N,N'*-trimethylethane-1,2-diamine in the presence of paraformaldehyde, reacts with $\text{Mn}(p\text{-XC}_6\text{H}_4\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{H}, \text{Cl}, \text{CH}_3, \text{NO}_2$) and NaSCN to form $[\text{Mn}_2(\mathbf{379})(p\text{-XC}_6\text{H}_4\text{COO})_2(\text{NCS})(\text{CH}_3\text{OH})]$ [464].



$\text{Mn}_2(\mathbf{379})(\text{C}_6\text{H}_5\text{COO})_2(\text{NCS})(\text{CH}_3\text{OH})$ (Fig. 289) shows two manganese ions, 3.548 Å apart, bridged by the phenolic oxygen and two benzoate groups, forming a μ -phenoxo-bis(μ -benzoato)dimanganese(II) core structure. One manga-

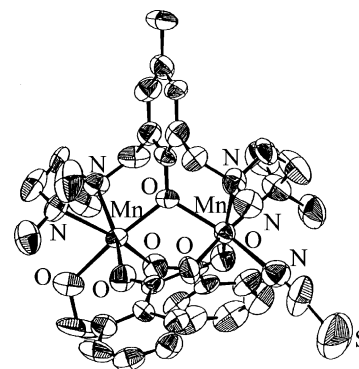


Fig. 289. Structure of $[\text{Mn}_2(\mathbf{379})(\text{C}_6\text{H}_5\text{COO})_2(\text{NCS})]$ (adapted from Ref. [464]).

nese(II) ion is six coordinated to one oxygen and two nitrogen atoms of $[\mathbf{379}]^-$, the oxygen atoms of two benzoate groups and the oxygen atom of the methanol molecule; the other manganese(II) ion is also six coordinated with an isothiocyanate nitrogen as the sixth donor atom. It appears that $[\mathbf{379}]^-$ is more flexible for coordination, relative to $[\mathbf{310}]^-$ and $[\mathbf{378a}]^-$, and allows a six coordinate geometry for both manganese ions [455,459,462,464].

These compounds are stable in the solid state but gradually oxidized in DMF changing from yellow to brown. They are 1:1 electrolytes in DMF. Magnetic susceptibility measurements, carried out in the range 4.2–300 K, prove an antiferromagnetic interaction within a pair of manganese(II) ions (J ranging from -2.9 to -4.1 cm^{-1}) [464].

The complexes show a catalase-like activity in disproportionating H_2O_2 into O_2 and H_2O ; the rate constants decrease increasing bulkiness of the para-substituent of the bridging benzoate group. The catalytic disproportionation of H_2O_2 by complexes $[\text{Mn}_2(\mathbf{379})(p\text{-XC}_6\text{H}_4\text{COO})_2(\text{NCS})(\text{CH}_3\text{OH})]$ may proceed by the intramolecular two-electron transfer mechanism through *cis*- $\{\text{Mn}^{\text{III}}(\text{OH})\}_2$, and *cis*- $\{\text{Mn}^{\text{IV}}(\text{=O})\}_2$ above reported for similar dimanganese(II) complexes [464].

The binuclear copper(II) complexes, $[\text{Cu}_2(\mathbf{380})(\mu\text{-N}_3)](\text{ClO}_4) \cdot 1.5\text{C}_2\text{H}_5\text{OH}$, $[\text{Cu}_2(\mathbf{380})(\mu\text{-CH}_3\text{O})(\text{ClO}_4)](\text{ClO}_4) \cdot \text{C}_2\text{H}_5\text{OH}$ and $[\text{Cu}_2(\mathbf{380})(\mu\text{-C}_3\text{H}_3\text{N}_2)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, where **H-380** is the pentadentate ligand 5-(*tert*-butyl)-2-hydroxybenzene-1,3-dicarbaldehyde bis (benzoylhydrazone), were synthesized by template procedure in the presence of the appropriate NaX salt [465].

The structure of $[\text{Cu}_2(\mathbf{380})(\mu\text{-CH}_3\text{O})(\text{ClO}_4)](\text{ClO}_4) \cdot \text{C}_2\text{H}_5\text{OH}$ (Fig. 290) shows that both copper ions of the binuclear unit are connected by an endogenous phenolato oxygen atom and an exogenous methoxy oxygen atom. One copper ion is five coordinated with a square-pyramidal coordination geometry, the axial coordination site being occupied by a perchlorate group, whilst the other copper is four coordinate with a square planar geometry. This core structure is very similar to the ethanolate-cinanolato-bridged binuclear copper(II) complex $[\text{Cu}_2(\mathbf{380})(\mu\text{-C}_2\text{H}_5\text{O})(\text{CH}_3\text{OH})](\text{ClO}_4)_2$ [465].

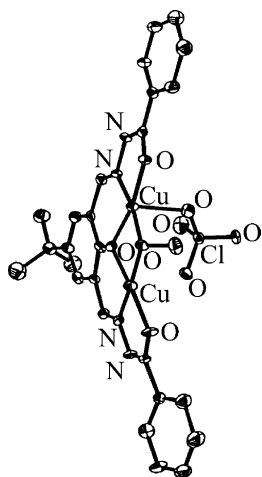


Fig. 290. Structure of $[\text{Cu}_2(\mathbf{380})(\mu\text{-CH}_3\text{O})(\text{ClO}_4)]^+$ (adapted from Ref. [465]).

Variable temperature magnetic susceptibility data (4–300 K) indicate that there is an antiferromagnetic interaction between the copper(II) ions in these complexes with an exchange parameter $2J$ of -119.1 cm^{-1} for $[\text{Cu}_2(\mathbf{380})(\mu\text{-N}_3)](\text{ClO}_4) \cdot 1.5\text{-C}_2\text{H}_5\text{OH}$ and -361.8 cm^{-1} for $[\text{Cu}_2(\mathbf{380})(\mu\text{-Im})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.

1,3-Bis[(2-dimethylaminoethyl)iminomethyl]benzene, (**381**), reacts with the appropriate metal(II) salt in a nitrogen atmosphere to form $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3](\text{BPh}_4) \cdot \text{CH}_3\text{CN}$, $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3(\text{NCS})]$, $[\text{Co}_2(\mathbf{381})(\text{CH}_3\text{COO})_3](\text{BPh}_4)$, $[\text{Co}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3](\text{BPh}_4)$ and $[\text{Zn}_2(\mathbf{381})(\text{CH}_3\text{COO})_3](\text{BPh}_4)$ [466].

In $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3(\text{NCS})] \cdot \text{DMF}$ (Fig. 291a) the two manganese ions are bridged by two benzoate groups in the symmetric $\eta^1\eta^1$ mode and one benzoate group in unsymmetrical $\eta^1\eta^2$ mode. One manganese(II) ion is six coordinated with the nitrogen atoms of one pendant arm of **381**, the oxygen atoms of the chelating benzoate group the oxygen atoms of the two symmetrically bridging benzoate groups. The surroundings are largely distorted from a reg-

ular octahedron. The other manganese(II) is also six coordinated with the two nitrogens of the pendant arm of **381**, three oxygens of the bridging benzoate groups and the nitrogen of the isothiocyanate group. The $\text{Mn} \cdots \text{Mn}$ intermetallic separation is 3.501 Å .

In $[\text{Co}_2(\mathbf{381})(\text{CH}_3\text{COO})_3](\text{BPh}_4)$ (Fig. 291b) the two cobalt(II) ions are bridged by three acetate groups in the $\eta^1\eta^1$ mode and the $\text{Co} \cdots \text{Co}$ intermetallic separation is 3.449 Å . The geometry about the cobalt(II) ions has been depicted as a trigonal bipyramid with the particular nitrogen of one pendant arm and one acetate oxygen at the axial sites and the terminal nitrogen of the pendant arm and two acetate oxygens in the equatorial plane [466].

$[\text{Co}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3](\text{BPh}_4) \cdot \text{CH}_3\text{CN}$ and $[\text{Zn}_2(\mathbf{381})(\text{CH}_3\text{COO})_3](\text{BPh}_4)$ have a tri(μ -carboxylato)dicobalt(II) or dizinc(II) core very similar to that found for $[\text{Co}_2(\mathbf{381})(\text{CH}_3\text{COO})_3](\text{BPh}_4)$. Each zinc ion assumes a trigonal bipyramidal geometry and the $\text{Zn} \cdots \text{Zn}$ separation is 3.465 Å [466].

For $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3](\text{BPh}_4) \cdot \text{CH}_3\text{CN}$ and $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3(\text{NCS})]$ the magnetic data suggest the operation of an antiferromagnetic spin exchange within each manganese(II) core ($J = 2.10\text{ cm}^{-1}$ for the first and $J = -1.73\text{ cm}^{-1}$ for the second complex). Also in the dinuclear cobalt(II) complexes an antiferromagnetic interaction between the two cobalt(II) ions seems to take place [466].

The dimanganese and dicobalt complexes are able to disproportionate H_2O_2 into H_2O and O_2 in DMF at 0°C , while the zinc complex showed no CAT-like activity. For $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3](\text{BPh}_4) \cdot \text{CH}_3\text{CN}$ the oxygen evolution suggests the involvement of the above mentioned slow catalytic process, occurring at the initial stage and faster catalytic process appearing after a lag time. $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_2(\text{NCS})]$ also showed a similar evolution profile where the fast catalytic process appeared after a longer lag time of ca. 150 min.

When thiocyanate ion was added to the catalysis by $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3](\text{BPh}_4)$ (complex: $\text{NCS}^- = 1:1$), the evolution profile was exactly the same as that for the catalysis by $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3(\text{NCS})]$, the thiocyanate ion acting as an inhibitor to the fast catalytic process. Using $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3(\text{NCS})]$ both catalytic processes are small and the lag time is large relative to the catalysis by (μ -phenoxo)di(μ -carboxylato)dimanganese(II) complexes above reported [466].

Both complexes act as 1:1 electrolytes in DMF, showing that the $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3]^+$ core persists in solution. The core has a five coordinate manganese(II) ion and its sixth vacant site is available for binding hydrogen peroxide. The bridge of hydrogen peroxide between two $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3]^+$ cores may lead to $\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{OH})\}$ species which can be involved in the slow catalytic process through the interconversion of $\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{OH})\}/\{\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}(=\text{O})\}$. The involvement of a $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ mixed-valence species in the slow catalytic process has

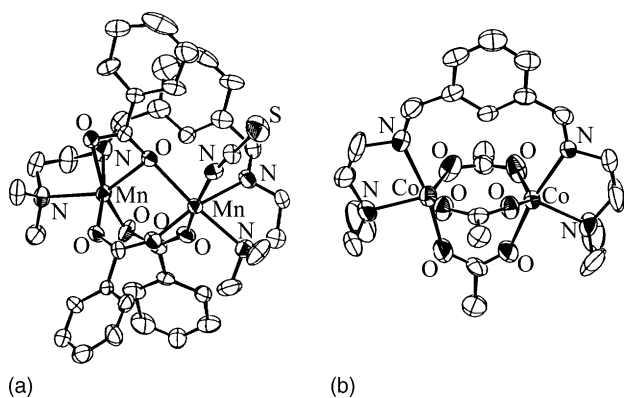


Fig. 291. Structures of $[\text{Mn}_2(\mathbf{381})(\text{C}_6\text{H}_5\text{COO})_3(\text{NCS})]$ (a), and $[\text{Co}_2(\mathbf{381})(\text{CH}_3\text{COO})_3]^+$ (b) (adapted from Ref. [466]).

been demonstrated by EPR spectroscopy for macrocyclic dinuclear manganese complexes [467].

The fast catalytic process is believed to employ a C_s , symmetric dinuclear manganese core with an appropriate $Mn \cdots Mn$ separation to allow chelate bonding of H_2O_2 to the core. To achieve such binding of H_2O_2 the $[Mn_2(381)(C_6H_5COO)_3]^+$ core must release one of the acetate bridges to give $[Mn_2(381)(C_6H_5COO)_2]^{2+}$ and this is related to the delayed appearance of the fast catalytic process relative to the slow process. Added thiocyanate ion may coordinate to one of the manganese ions of $[Mn_2(381)(C_6H_5COO)_2]^{2+}$, forming $[Mn_2(381)(C_6H_5COO)_2(NCS)]^+$ and this explains the inhibiting function of the ion in the fast catalytic process.

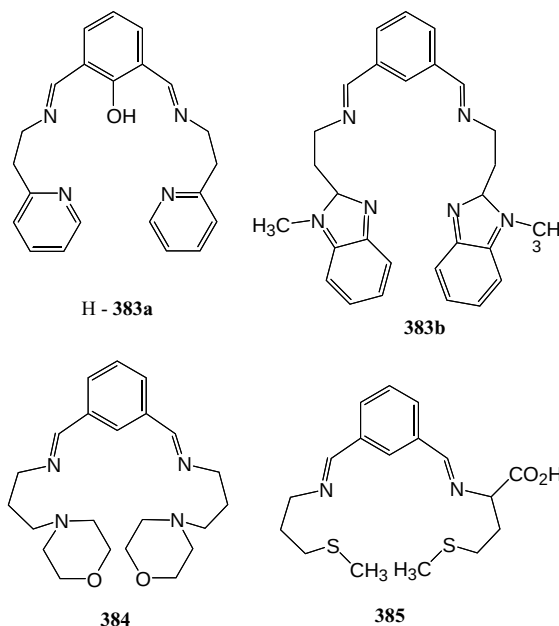
It was suggested that fast catalytic process proceeds through the interconversion of $cis\text{-}\{Mn^{III}(OH)\}_2$ and $cis\text{-}\{Mn^{IV}(=O)\}_2$. It must be mentioned that the oxygen evolution profile with $[Mn_2(381)(C_6H_5COO)_3](BPh_4)$ at 20 °C showed no lag period for the fast process and the absorption spectrum showed no characteristic band. This is because the catalytic cycle between $cis\text{-}\{Mn^{III}(OH)\}_2$ and $cis\text{-}\{Mn^{IV}(=O)\}_2$ becomes fast at elevated temperatures so that the $cis\text{-}\{Mn^{IV}(=O)\}_2$ species has a short lifetime and cannot be detected by visible spectroscopy.

The cobalt complexes $[Co_2(381)(CH_3COO)_3](BPh_4)$ and $[Co_2(381)(C_6H_5COO)_3](BPh_4)$ show a comparable CAT-like activity, with an involvement of cobalt(III) in the catalysis.

The similar dinuclear complexes $[Cu_2(382a\text{--}d)](X)_2$ have been prepared by the condensation the appropriate amine with isophthalaldehyde in the presence of tetrakis(acetonitrile)copper(I) tetrafluoroborate or hexafluorophosphate under an inert atmosphere. Treatment of $[Cu_2(382a\text{--}d)](X)_2$ with dioxygen in methanol in the presence of acid led to formation of 2-hydroxy-1,3-benzenedicarbaldehyde after hydrolysis of the ligand [468].

$[Cu_2(382a)(CH_3CN)_2](BF_4)_2$ and the 5-nitro derivative $[Cu_2(NO_2\text{-}382a)(CH_3CN)_2](BF_4)_2$ react with O_2 to form the phenolate-bridged copper(II) complexes $[Cu_2(383a)(OH)(H_2O)](BF_4)_2$ and $[Cu_2(NO_2\text{-}383a)(OH)(H_2O)](BF_4)_2$ [468,469]. The structure of these complexes confirms incorporation of two oxygen atoms, one being inserted into an aryl-hydrogen bond (arene hydroxylation) and the second being incorporated into the hydroxo bridge. The structure of $[Cu_2(383a)(OH)(H_2O)](BF_4)_2$ has a water molecule coordinated to one of the copper ions and is different from $[Cu_2(383a)(OH)](BF_4)_2$ where each copper(II) ion is in a slightly distorted square planar N_2O_2 coordination environment provided by the ligand and exogenous hydroxo bridge [470]. In $[Cu_2(383a)(OH)(H_2O)](BF_4)_2$ one copper ion is five coordinate and the other copper ion is four coordinate while in $[Cu_2(NO_2\text{-}383a)(OH)(H_2O)_3](BF_4)_2$ one copper is five coordinate and the other copper is six coordinate. The bridges in the Cu_2O_2 units are essentially symmetric, and the Cu_2O_2 units are less deviated from planarity than in the nonsolvated complex. The $Cu \cdots Cu$ separations are 3.029

and 3.031 Å, respectively. Several species exist in the solutions used. A detailed kinetic study for $[Cu_2(382a)(CH_3CN)](BF_4)_2$ and $[Cu_2(NO_2\text{-}382a)(CH_3CN)_2](BF_4)_2$ indicates that the oxidation takes place with the occurrence of an intermediate peroxo complex that cannot be observed spectroscopically [469].

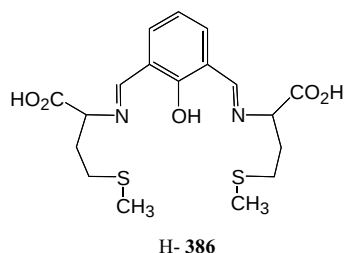


$[Cu_2(383b)]^{2+}$, $[Cu_2(384)]^{2+}$ and $[Cu_2(385)]^{2+}$ were prepared by metal template condensation of the appropriate amines $H_2NC_2H_4X$ (methionine, 4-(2-aminoethyl)morpholine and 1-methyl-2-(2-aminoethyl)-benzimidazole) with benzene-1,3-dicarbaldehyde in the presence of $[Cu(CH_3CN)_4](ClO_4)$ under an inert atmosphere [471].

When dilute solutions of these copper(I) complexes in methanol are exposed to dioxygen, a rapid colour change from yellow to green takes place. The reactions are complete in a few minutes and give rise to the phenoxo-bridged binuclear copper(II) complexes, as confirmed by the recovery of 2-hydroxybenzene-1,3-dicarbaldehyde, upon treatment of the product residues, after evaporation of the solvent, with mineral acids and extraction with dichloromethane.

It was found that the growth rate of the 360 nm band of $[Cu_2(L)(OH)]^{2+}$ ($L = 383b, 384, 385$) is inversely correlated with the basicity of the nitrogen donor group. The slower reactivity of the methionine complex $[Cu_2(385)]^{2+}$ is probably due to the stabilization of the copper(I) state by the thioether ligand. When carefully dried acetonitrile is used as solvent the oxygenation is largely or completely depressed in favour of simple copper(I) oxidation. It was suggested that an electrophilic copper-peroxo or copper-hydroperoxo complex may represent the active species in the hydroxylation process [471].

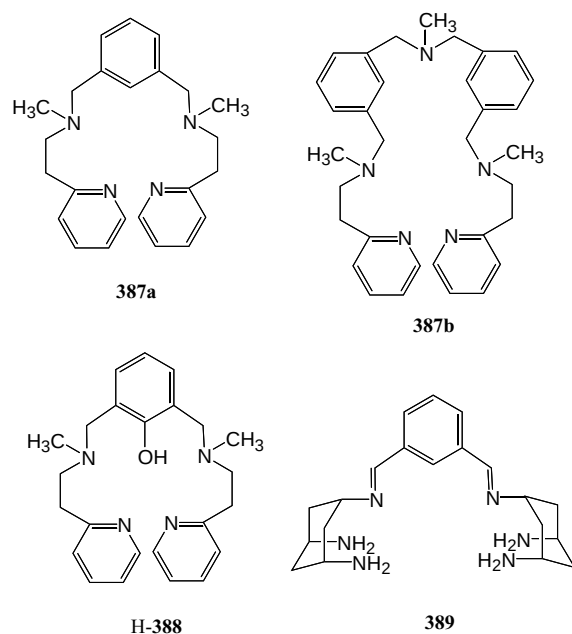
$[\text{Cu}_2(\mathbf{385})](\text{ClO}_4)_2$, prepared by the condensation between benzene-1,3-dicarbaldehyde and two molecules of L-methionine in the presence of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$, when reacted with dioxygen suffers a partial aromatic hydroxylation of the ligand, giving rise to the dinuclear (μ -phenoxo- μ -hydroxo)-dicopper(II) complex $[\text{Cu}_2(\mathbf{386})-(\text{OH})](\text{ClO}_4)_2$, together with other copper oxidation products [472].



Solutions of $[\text{Cu}_2(\mathbf{386})(\text{OH})](\text{ClO}_4)_2$ are unstable to hydrolysis of the imine bonds by trace of water: upon standing methanolic solutions of $[\text{Cu}_2(\mathbf{386})(\text{OH})](\text{ClO}_4)_2$ deposit blue crystals of the dinuclear copper(II) complex of the anion of 2-hydroxybenzene-1,3-dicarbaldehyde. In this complex two deprotonated 1,3-diformylphenoxide ligands bind two copper(II) ions, with di- μ -phenoxo bridges. Each copper is essentially square pyramidal, with a basal O_4 donor set, including two phenoxide and two carbonyl oxygen atoms from two 2-hydroxybenzene-1,3-dicarbaldehyde ligands. Two perchlorate oxygen atoms are bound in axial positions on opposite sides of the Cu_2O_6 plane.

In order to check the possible involvement of H_2O_2 in the sulfur oxygenation, the reaction between $[\text{Cu}_2(\mathbf{386})(\text{OH})](\text{ClO}_4)_2$ and H_2O_2 was studied. When $[\text{Cu}_2(\mathbf{386})(\text{OH})](\text{ClO}_4)_2$ was treated with hydrogen peroxide, a rapid oxidation of the methionine ligand to methionine sulfoxide occurred through the probable intermediacy of the hydroperoxide complex $[\text{Cu}_2(\mathbf{386})(\text{OOH})]^{2+}$. The increase in the content of methionine sulfoxide in the amino acid mixture, after decomposition of the product complex, corresponds to the amount of hydrogen peroxide used in the reaction. Blank experiments using copper(II) salt and methionine showed that no sulfoxide is formed by hydrogen peroxide through non-specific reactions under the same conditions [472].

α, α' -Bis[(*N*-methyl-2-pyridil)ethylamino]-*m*-xylene, (**387a**), prepared by condensation of α, α' -*m*-dibromoxylene and 2-(2-methylaminoethyl)pyridine in the presence of Na_2CO_3 in refluxing acetonitrile for 4 days, reacts with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ in dichloromethane under nitrogen to give a yellow suspension of an extremely air-sensitive copper(I) complex which when exposed to O_2 (1 atm; room temperature) for 12 h, turns into a blue grey precipitate. Slow evaporation of an acetonitrile solution of this solid affords at first only a few light blue crystals of $[\text{Cu}_2(\mathbf{387b})(\text{OH})_2](\text{ClO}_4)_2$ and a bulk of the green compound $[\text{Cu}_2(\mathbf{388})(\text{OH})](\text{ClO}_4)_2$ [473].



$[\text{Cu}_2(\mathbf{388})(\text{OH})](\text{ClO}_4)_2$ revealed incorporation of two oxygen atoms into the complex (Fig. 292a). The two copper(II) ions are in almost identical square planar coordination environments. The coordination about each copper is completed with one pyridyl donor and one tertiary aliphatic amine donor from the terminal arms of the binucleating ligand $[\mathbf{388}]^-$ and the bridging phenolate and hydroxide donors.

The phenol ligand H-388 could be separated from $[\text{Cu}_2(\mathbf{388})(\text{OH})](\text{ClO}_4)_2$ upon treatment with ammonia.

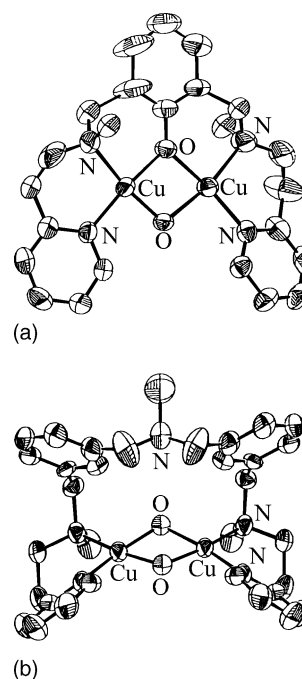


Fig. 292. Structures of $[\text{Cu}_2(\mathbf{388})(\text{OH})]^{2+}$ (a) and $[\text{Cu}_2(\mathbf{387b})(\text{OH})_2]^{2+}$ (b) (adapted from Ref. [473]).

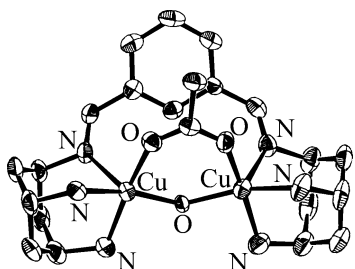


Fig. 293. Structure of $[\text{Cu}_2(\mathbf{389})(\mu\text{-CH}_3\text{COO})(\mu\text{-OH})]^{2+}$ (adapted from Ref. [474]).

The ^1H NMR spectrum of the product was similar to that of the ligand prepared separately by the reaction between 2,6-bis(chloromethyl)-4-methylphenol and 2-[(2-methylamino)ethyl]pyridine.

The light blue complex $[\text{Cu}_2(\mathbf{387b})(\text{OH})_2](\text{ClO}_4)_2$ (Fig. 292b) has a dicationic $\{\text{Cu}_2(\text{OH})_2\}$ bridging unit while **387b** is a by-product formed during the synthesis of **387a**. The terminal coordination at each copper ion is the same as that of $[\text{Cu}_2(\mathbf{388})(\text{OH})](\text{ClO}_4)_2$ and the stereochemistry at each copper(II) center is square planar formed by the two oxygen atoms of the hydroxy groups and by the nitrogen atoms of the pyridine and NCH_3 groups.

The proper placement of the $\mu\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}$ group seems to be a prerequisite for aromatic ring hydroxylation and this is the reason why **387b** has a dihydroxy bridged structure with no ring hydroxylation being observed [473]. Isophthalaldehyde, *cis,cis*-1,3,5-triaminocyclohexane and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ refluxed in methanol for 48 h, form $[\text{Cu}_2(\mathbf{389})(\text{CH}_3\text{COO})(\text{OH})](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ [474] whose structure (Fig. 293) shows two copper(II) ions are bridged by an hydroxo and an acetato group. Each copper(II) ion has a square pyramidal coordination geometry with the basal plane described by the two amino nitrogen atoms and the oxygen atoms of the acetato and hydroxo groups. The third imino nitrogen atom occupies the axial position. The $\text{Cu} \cdots \text{Cu}$ separation is 3.491 Å. Two non-coordinated tetrafluoroborate anions and a single water molecule, hydrogen bonded to one of the amino groups of **389**, complete the structure.

$[\text{Cu}_2(\mathbf{389})(\text{CH}_3\text{COO})(\text{OH})](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ is EPR silent as a solid at both room temperature and 100 K. Magnetic susceptibility studies gave a $2J$ value of -152.1 cm^{-1} [474].

The complexation versatility of 1,3-bis(salicylideneimino)-2-propanol, (**H₃-374**), has been demonstrated by the obtainment of the dimanganese(II) complex $\text{Na}_2[\text{Mn}(\text{H-374})]_2 \cdot 2\text{CH}_3\text{OH}$, prepared by the reaction of **H₃-374** with 3 equiv. of NaOCH_3 and 1 equiv. of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol. This complex can be oxidized by O_2 in acetonitrile to give the corresponding symmetric dimanganese(III) dimer $[\text{Mn}(\mathbf{374})]_2$ [475].

The structure of the corresponding 5-nitro derivative $[\text{Mn}(\mathbf{5-NO}_2\text{-374})]_2$ shows a symmetric geometry with two μ_2 -alkoxo core with symmetric manganese ion environments (Fig. 294).

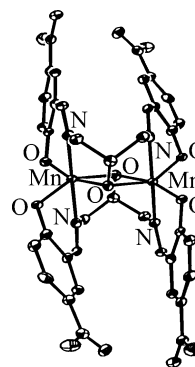
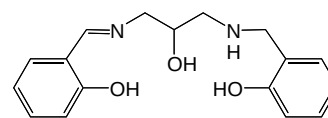


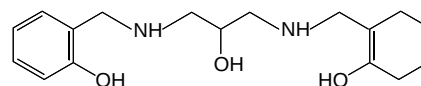
Fig. 294. Structure of $[\text{Mn}(\mathbf{5-NO}_2\text{-374})]_2$ (adapted from Ref. [475]).

$[\text{Mn}(\mathbf{374})]_2$, when reacted with H_2O_2 in acetonitrile, cycles between the $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$ and $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ oxidation levels, maintaining its dinuclear integrity throughout the process. It shows respectable turnover rates, exhibits saturation kinetics with H_2O_2 , is reasonably stable (showing greater than 1000 turnovers), has the same $^{18}\text{O}_2$ labelling as the enzyme, is azide insensitive under conditions that the manganese catalase is not inhibited by azide, and forms a catalytically inactive $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ species (with an almost identical EPR spectrum to that of the enzyme) that can be reduced to a catalytically active state by NH_2OH [475].

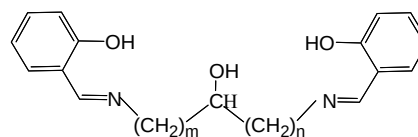
1,3-Bis(salicylideneamino)-2-propanol (**H₃-374**) can be partially or totally hydrogenated in CH_3CN by NaBH_4 to form the **H₃-390** and **H₃-390a**. The unsymmetrical ligand **H₃-390** forms with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in the presence of triethylamine and in methanol $[\text{M}_2(\mathbf{390})_2] \cdot 2\text{CH}_3\text{CN}$ [476].



H₃-390



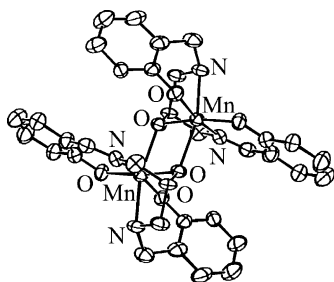
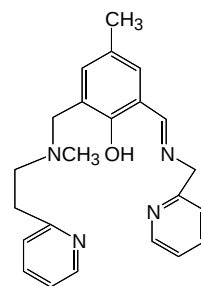
H₃-390a



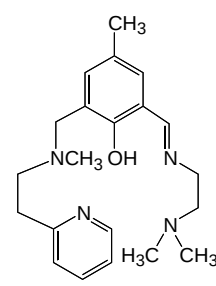
H₃-391

a $m = 2, n = 1$

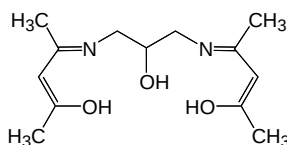
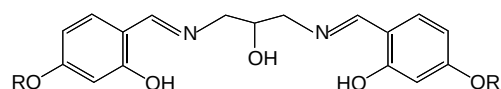
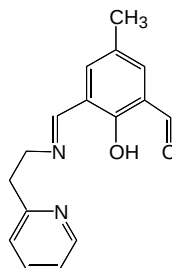
b $m = 2, n = 2$

Fig. 295. Structure of $[\text{Mn}_2(\mathbf{390})_2]$ (adapted from Ref. [476]).

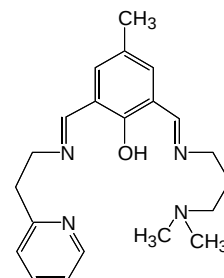
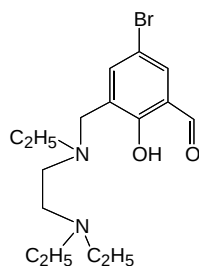
H - 392f



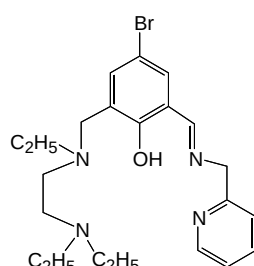
H - 392g

H₃-391cH₃-391d R = $(\text{CH}_2)_n\text{H}$ 

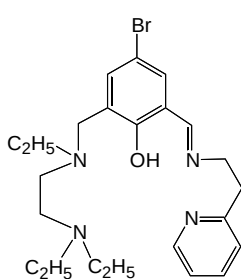
H - 393a

H₂ - 393b

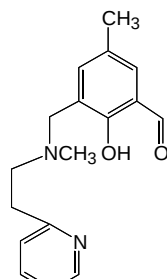
H - 392a



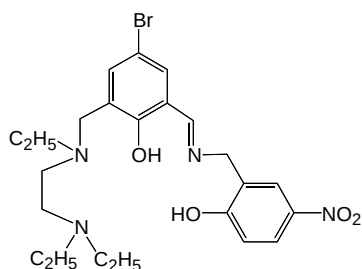
H - 392b



H - 392c



H - 392e



H - 392d

$[\text{Mn}_2(\mathbf{390})_2] \cdot 2\text{C}_3\text{CN}$ (Fig. 295) shows a dimeric unit where the two manganese(II) ions are bridged by the alcoholic oxygen atoms of the two ligands, $[\mathbf{390}]^{3-}$, forming an Mn_2O_2 core. The center of symmetry lies in the center of this core. The $\text{Mn} \cdots \text{Mn}$ separation is 3.243 Å. Each manganese(III) ion has an N_2O_4 donor set in an elongated octahedral geometry [476]. $[\text{Fe}_2(\mathbf{390})_2] \cdot 2\text{C}_3\text{CN}$ has a very similar structure. In both complexes CH_3CN is present as crystal solvent [476].

For the dimanganese(III) complex the effective magnetic moment per manganese(III) ion increases gradually from 5.08 BM at 280 K to 5.56 BM at 81 K, a behaviour characteristic of an intramolecular ferromagnetic coupling ($J = +4.5 \text{ cm}^{-1}$). On the other hand, the magnetic susceptibility data of the diiron(III) complex have been interpreted in terms of an intramolecular antiferromagnetic coupling ($J = -2.8 \text{ cm}^{-1}$) [476].

In the presence of Et_3N , $\text{H}_3\text{-390a}$ reacts in methanol with iron(II) perchlorate in a 1:1 stoichiometry to form $[\text{Fe}_2(\mathbf{390a})_2] \cdot 2\text{H}_2\text{O}$ [476], whose structure resembles that of the dimanganese(III) complex [476]. Magnetic susceptibility measurements in the range 4.5–300 K indicate very weak antiferromagnetic coupling between the iron ions ($J = -2.2 \text{ cm}^{-1}$), consistent with the long Fe–O distance and the small Fe–O–Fe angle within the bis(μ -alkoxo)diiron(III) entity. The complex shows a quasi-reversible redox couple at -0.93 versus NHE corresponding to the $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ couple. While the $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ form is electrochemically readily accessible the $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ form is more difficult to obtain. The $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ species is stable under argon [476].

The μ -alkoxo- μ -pyrazolato dinuclear nickel(II) complexes $[\text{Ni}_2(\mathbf{374})(\text{pz})]$, $[\text{Ni}_2(\mathbf{391a})(\text{pz})]$ and $[\text{Ni}_2(\mathbf{391b})(\text{pz})]$ have been prepared by reaction of the appropriate ligand and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of pyrazole and KOH [477].

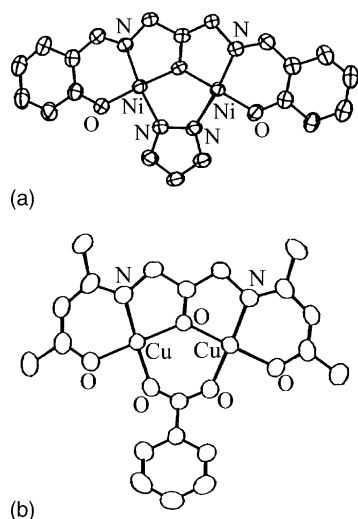


Fig. 296. Structures of [Ni₂(**374**)(pz)] (a) and [Cu₂(**391c**)(C₆H₅COO)] (b) (adapted from Refs. [477,478]).

The structures of [Ni₂(**374**)(pz)] (Fig. 296a), [Ni₂(**391a**)(pz)] and [Ni₂(**391b**)(pz)] show two nickel ions are bridged by two alkoxo oxygen atoms and two pyrazolate nitrogen atoms in a square plane environment. The Ni...Ni separation is respectively 3.245, 3.277, and 3.193 Å. For [Ni₂(**391b**)(pz)] the molecule has a bent structure, caused by the twisting of the Schiff base backbone; this leads to a smaller Ni...Ni separation and a smaller Ni–O–Ni angle [Ni₂(**374**)(pz)], [Ni₂(**391a**)(pz)] and [Ni₂(**391b**)(pz)] are essentially diamagnetic.

The binuclear copper(II) complexes [Cu₂(**391c**)(X)]·*n*S (X = C₆H₅COO[−], *n*S=O; X = 2-(CH₃)C₆H₄COO[−], *n*S = 1/2CH₃OH; X = 2,6-(CH₃)₂C₆H₃COO[−], *n*S=O; X = 2,6-(Cl)₂C₆H₃COO[−], *n*S = 0.7DMF; X = (C₆H₅)₂-(CH₃)SiCOO[−], *n*S=O) have a mixed double-bridge consisting of alkoxo and carboxylato ligands [478]. The coordination environment around the copper(II) ions is approximately square planar. As an explanatory example the structure of [Cu₂(**391c**)(C₆H₅COO)] is reported (Fig. 296b). These complexes are antiferromagnetic and their $-2J$ values are 183, 188, 133, 207, and 95 cm^{−1}, respectively [478].

Dicopper(II) complexes of *N,N'*(propan-2-ol)-bis(4-alkoxysalicylaldimines) (H₃-**391d**), containing a μ -3,4,5-trialkoxybenzoate- or acetate- exogenous-bridge have been prepared by the condensation of 2-hydroxy-4-alkoxybenzaldehydes with 1,3-diaminopropan-2-ol in the presence of the appropriate copper(II) salt [478]. The structure of [Cu₂(**391d**)(CH₃COO)] (*n* = 10) at 150 K shows the Schiff

base derivative is dinucleating and the two copper(II) ions are bridged by the secondary alkoxo and the acetate moiety. There are no significant intermolecular interactions between neighbouring dinuclear entities. The overall molecular shape is rod-like and nearly flat and the intramolecular Cu...Cu distance is 3.498 Å. Both copper(II) centers have essentially planar coordination of the N₂O₂ donor sets [478] (Fig. 297).

The formation of mesomorphic phases was found to be dependant upon the bridging groups used: acetate-bridged compounds form a smectic phase and benzoate-bridged compounds form a hexagonal columnar phase [478].

9.2. Complexes with asymmetric end-off ligands

The introduction of different pendant arms into the 2- and 6-positions of 4-substitued phenol leads to the formation of asymmetrical Schiff bases [479]. In Section 9.1 we have already reported some examples of these asymmetric systems in order to discuss their relationship with the related symmetric systems. One synthetic approach starts from 4-bromosalicylaldehyde and introduces first a methyleneamine group on the unsubstituted 2-position through the Mannich reaction to form H-**392a** and then an imine function on the 6-position by reaction of a primary amine with the free carbonyl group [479] to give rise to the Schiff bases H-**392b**, H-**392c**, and H-**392d**. The molecular structures of the dinuclear copper(II) cation in [Cu₂(**392b**)(μ -Br)(μ -HCOO)]₂[Cu₂Br₄] (Fig. 298a) shows the constitution of the deprotonated Schiff base ligand with the phenolate group acting as an endogenous bridge. In addition, there are two exogenous bridges: a formate and a bromide. Each copper ion is five coordinated and the donor sets are completed by two nitrogen atoms from the side arms of the ligand. Although, both side arms contain a N₂O donor set, the chemical environments they provide are different. The geometry of one copper(II) ion is distorted square pyramidal with the bridging bromide as the apical ligand. The geometry of the second copper(II) ion is significantly distorted from both square-based pyramidal and trigonal bipyramidal. The dinuclear copper(I) anion [Cu₂Br₄]^{2−} is a planar species in which the metal geometry is trigonal planar with two of the bromides acting as asymmetric bridges. The magnetic behaviour of this complex is characteristic of a pair of copper(II) ions interacting antiferromagnetically ($2J$ = −42 cm^{−1}) [479].

Moreover, the formyl precursor H-**392e**, derived from the reaction in tetrahydrofuran of 2-formyl-4-methyl-6-chloromethylphenol and 2-(*N*-methyl aminoethyl) pyridine, is

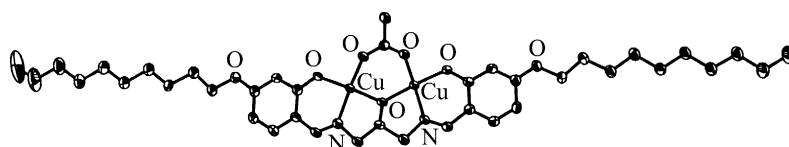


Fig. 297. Structure of [Cu₂(**391d**)(CH₃COO)] (adapted from Ref. [478]).

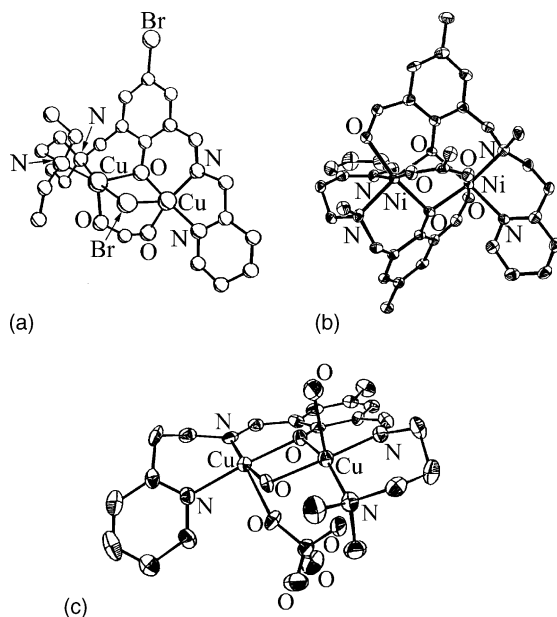


Fig. 298. Structures of $[\text{Cu}_2(\mathbf{392b})(\mu\text{-Br})(\mu\text{-HCOO})]^+$ (a), $[\text{Ni}_2(\mathbf{392e})_2(\text{CH}_3\text{COO})]^+$ (b) and $[\text{Cu}_2(\mathbf{393b})(\mu\text{-OH})(\text{ClO}_4)]^+$ (c) (adapted from Refs. [479,480]).

converted into the Schiff bases **H-392f** and **H-392g** by condensation respectively with 2-aminomethylpyridine or *N,N*-dimethylethylenediamine. **H-392f** reacts with $\text{Cu}(\text{ClO}_4)_2$ or CuBr_2 to form $[\text{Cu}_2(\mathbf{392f})(\text{OH})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\mathbf{392f})(\text{Br})_3 \cdot 3\text{H}_2\text{O}]$ [480]. $[\text{Cu}_2(\mathbf{392f})(\text{OH})](\text{ClO}_4)_2$, when recrystallized from methanol, affords $[\text{Cu}(\text{H}_2\mathbf{392f})(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$. In the cation $[\text{Cu}(\text{H}_2\mathbf{392f})(\text{H}_2\text{O})]^{3+}$ the copper ion sits in the N_2O compartment derived from the iminic side-arm and is coordinated to the deprotonated phenolic oxygen atom, the iminic nitrogen and the pyridine nitrogen of $[\mathbf{392f}]^-$ and the oxygen of water molecule. The geometry at the copper ion is not perfectly square planar. The amino and pyridinyl nitrogen atoms of the aminic side-arm not involved in coordination are protonated [480].

The reaction of **H-392g** with nickel(II) ethanoate and sodium perchlorate affords $[\text{Ni}_2(\mathbf{392e})_2(\text{CH}_3\text{COO})](\text{ClO}_4)$ where hydrolysis of the ligand had occurred and a bidentate bridging ethanoate bound to the dinuclear center. The constraints imposed by the ethanoate bridge place the ethanoate oxygen atoms in *cis* apical positions, with the nitrogen atoms from the pendant pyridines occupying an equatorial position at one nickel(II) ion and an apical position at the other nickel(II) ion. Also the carbonyl oxygen atoms of the ligands occupy an apical position at one nickel(II) ion and an equatorial position at the other nickel(II) ion. The distorted octahedral arrangement of N_3O_3 donors around each nickel(II) ion is completed by two sp^3 nitrogen donors from the aminic pendant arm and two oxygen atoms from the non-symmetric (μ -phenoxy) (μ -phenoxy) bridges. The $\text{Ni} \cdots \text{Ni}$ distance is 3.112 Å [480] (Fig. 298b).

Another approach is based on the partial condensation of one of the two aldehyde functions of 2,6-diformyl-4-methylphenol to form the [1+1] Schiff base **H-393a** which by further condensation with *N,N*-dimethylethylenediamine give rise to the asymmetric Schiff base **H-393bb**. This asymmetric Schiff base **H-393b** reacts with copper(II) salts to form the dicopper(II) complex $[\text{Cu}_2(\mathbf{393b})(\text{OH})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Fig. 298c) where both copper ions are in square pyramidal surroundings. The apical position of one copper is occupied by the oxygen atom of a perchlorate group; this copper ion is slightly pulled out from the basal plane in the direction of the perchlorate group. The apical position of the second copper is occupied by a water molecule [479].

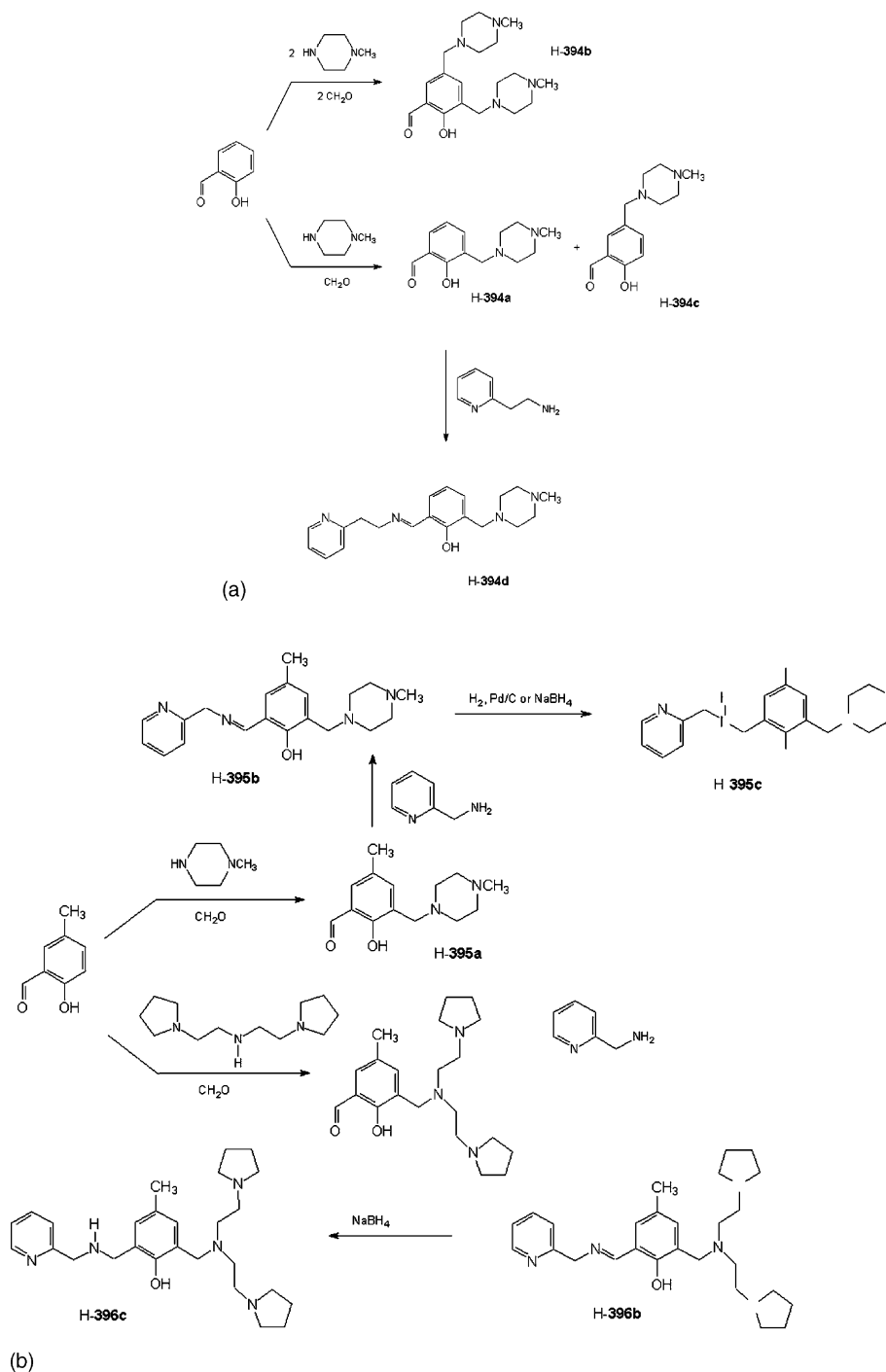
Similar Mannich reaction on salicylaldehydes forms the formyl precursors **H-394a**, **H-394b** and **H-394c** [481]. In particular aminomethylation of salicylaldehyde with 2 equiv. of 1-methylpiperazine affords the 3,5-diaminomethylated salicylaldehyde **H-394b** (Scheme 55a). When 1 equiv. of 1-methylpiperazine was used, mixtures of 3- and 5-aminomethylated salicylaldehyde were obtained. The desired 3-aminomethylated salicylaldehyde **H-394a** can be separated from the 5-aminomethylated salicylaldehyde **H-394c** by column [452]. **H-394a**, when engaged in condensation reaction with 2-aminoethane pyridine, affords the asymmetric Schiff base complex **H-394d** or $[\text{Cu}_2(\mathbf{394d})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$ when the same condensation reaction is carried out on the presence of $\text{Cu}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ and NaClO_4 .

To prevent the undesired aminomethylation at the 5-position, an obvious choice is the use of 5-methylsalicylaldehyde, which by aminomethylation with diamines and triamines affords 3-aminomethylated 5-methylsalicylaldehydes. The aminomethylation of 5-methylsalicylaldehyde with 1-methylpiperazine or with bis[2-(pyrrolidin-1-yl)ethyl]amine gives rise to the functionalized salicylaldehydes **H-395a** and **H-396a**. These formyl precursors (**H-395a** and **H-396a**) by condensation reaction with 2-aminomethylpyridine form the corresponding Schiff bases **H-395b** and **H-396b** which can be reduced the related amine derivatives respectively **H-395c** and **H-396c** (Scheme 55b) [481,482].

H-394d forms $[\text{Cu}(\mathbf{394d})(\text{CH}_3\text{COO})]$ and $[\text{Cu}_2(\mathbf{394d})(\text{CH}_3\text{COO})_2](\text{CH}_3\text{COO})$ when reacted with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\mathbf{394d})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$ when NaClO_4 is added to the solution [481,482].

In the structure of $[\text{Cu}_2(\mathbf{394d})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$ (Fig. 299) the geometries around the copper ions have been described as square pyramidal with the apical positions being occupied by the oxygen atoms of two different acetate groups. The two copper ions, 3.029 Å apart, are bridged by a phenoxy oxygen and by two acetate groups. One acetate group is *syn-syn* bidentate bridging; the other acetate group is monodentate μ -oxo bridging [482]. The copper centers in $[\text{Cu}_2(\mathbf{394d})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$ are weakly antiferromagnetically coupled ($2J = -15 \text{ cm}^{-1}$).

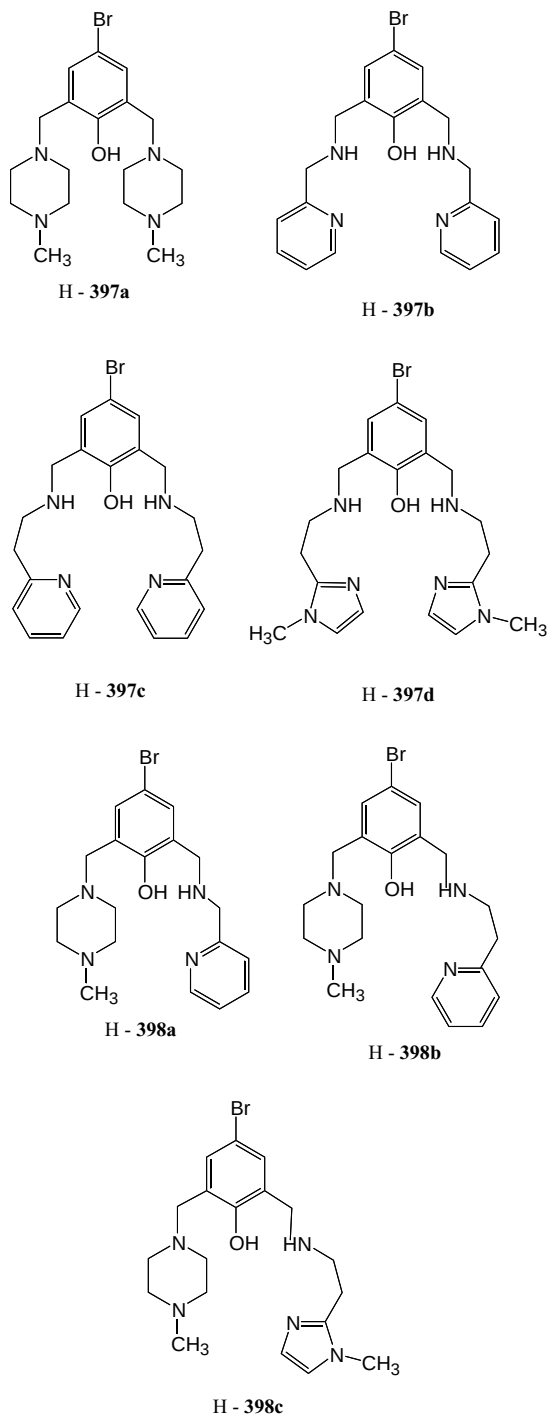
Microcalorimetric and UV-Vis spectroscopic measurements establish the stepwise complexation behaviour of



Scheme 55.

the ligand; the dinuclear complex $[\text{Cu}_2(\mathbf{394d})(\text{CH}_3\text{COO})_2]^+$ is formed via the initial formation of a mononuclear copper complex. Although these measurements unambiguously show a stepwise complexation of $\text{Cu}(\text{CH}_3\text{COO})_2$ by the nonsymmetric dinucleating ligand **H-394d**, it is not possible at this stage to differentiate between initial complexation at the pyridylimine or at the *N*-methylpiperazine moiety [482].

$[\text{Cu}_2(\mathbf{397a})(\text{OH})(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\text{Cu}_2(\mathbf{397b})(\text{OH})](\text{NO}_3)_2$, $[\text{Cu}_2(\mathbf{397c})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$, $[\text{Cu}_2(\mathbf{397d})(\text{OH})(\text{CH}_3\text{OH})_2](\text{BF}_4)_2$, $[\text{Cu}_2(\mathbf{398a})(\text{CH}_3\text{O})](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$, $[\text{Cu}_2(\mathbf{398b})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})](\text{ClO}_4)(\text{ClO}_4)$ and $[\text{Cu}_2(\mathbf{398c})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ as models of the type 3 copper protein catechol oxidase were synthesized by reaction of the symmetric or asymmetric ligands with the appropriate copper(II) salt [483].



$[\text{Cu}_2(\mathbf{397a})(\text{OH})(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})](\text{ClO}_4) \cdot \text{H}_2\text{O}$, $[\text{Cu}_2(\mathbf{397c})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$, $[\text{Cu}_2(\mathbf{397d})(\text{OH})(\text{CH}_3\text{OH})_2](\text{BF}_4)_2$, $[\text{Cu}_2(\mathbf{398b})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ and $[\text{Cu}_2(\mathbf{398c})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ consist of dinuclear cations in which the copper centers are bridged by the phenolate oxygen of the respective deprotonated pentadentate ligand and an exogenous hydroxide or methanolate anion. The $\text{Cu} \cdots \text{Cu}$ distances vary between 2.87 and 3.00 Å. Each of the copper ions has two nitrogen donors of the ligand as terminal equatorial ligands. The axial positions are occupied by one or two solvent molecules or

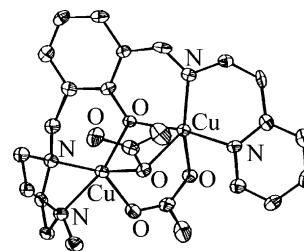


Fig. 299. Structure of $[\text{Cu}_2(\mathbf{394d})(\text{CH}_3\text{COO})_2]^+$ (adapted from Ref. [482]).

counter anions with elongated distances typical for Jahn–Teller distortion. Within the common structural motif, each of the complexes shows its own substantial characteristic features (Fig. 300).

$[\text{Cu}_2(\mathbf{397a})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$ was obtained by reaction of 2,6-bis $[(N\text{-methyl piperazin-1-yl})\text{methyl}]\text{-4-bromophenol}$ (**H-397a**), prepared by Mannich reaction of 4-bromophenol, formaldehyde and *N*-methylpiperazine, with $\text{Cu}(\text{CH}_3\text{COO})_2$ in a 2:1 molar ratio followed by the addition of NaClO_4 . In this complex, the ligand is pentadentate donating two nitrogens as well as a bridging oxygen to each copper. Two acetates bridge the copper ions through basal and apical positions to yield square pyramidal coppers with a distorted square base. The variable temperature magnetic studies reveal an antiferromagnetic interaction between the two metal centers ($2J = -93 \text{ cm}^{-1}$) while electrochemical data show that the complex undergoes a chemical change after reduction, possibly a structural reorganization of the copper coordination sphere [484].

Only the symmetric complex $[\text{Cu}_2(\mathbf{397a})(\text{OH})(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$ and the asymmetric complexes $[\text{Cu}_2(\mathbf{398a})(\text{CH}_3\text{O})](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$, $[\text{Cu}_2(\mathbf{398b})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ and $[\text{Cu}_2(\mathbf{398c})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})(\text{ClO}_4)](\text{ClO}_4)$ have significant catalytic activity with respect to the aerial oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to its corresponding o-quinone. The decisive thermodynamic property determining an electron-transfer reaction is the redox potential of each reactant. The electrochemical behaviour of the complexes was investigated in acetonitrile solution revealing only irreversible and ill defined reduction steps. The potentials for the oxidation of 3,5-DTBC to its corresponding semiquinone and quinone are very sensitive to the degree of protonation and/or the number

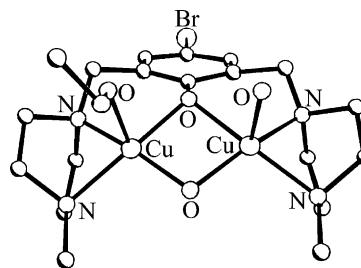


Fig. 300. Structure of $[\text{Cu}_2(\mathbf{397a})(\text{OH})(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})]^{2+}$ (adapted from Ref. [483]).

of transferred electrons. No clear relationship between the electrochemical properties of the complexes and the reported data for the oxidation of 3,5-DTBC exists, possibly owing to the poorly defined redox chemistry of this class of complexes.

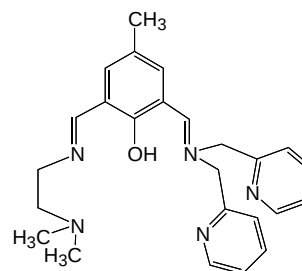
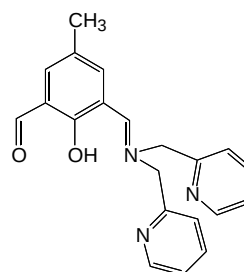
The common characteristic of the active complexes is the coordinating piperazine group within their ligand framework. This distinguishes the active complexes from the inactive ones. Obviously, this structural unit is essential for catecholase activity of the studied series of complexes. The crystal structures have revealed that the square-pyramidal coordination geometries of the copper ions in the active complexes are strongly distorted and that for the dinuclear cations on the whole a strained structure results. The symmetric non active complexes on the contrary are present in a relaxed, energetically favoured conformation. This leads to the assumption that the differences in reactivity are primarily based on geometric factors [484].

[Cu(**397a**)(OH)(C₂H₅OH)(H₂O)](ClO₄)₂ is definitely the most strained system. This strain is caused by the exogenous μ -hydroxo bridge forcing the rigid ligand framework to assume an unfavoured conformation. In the presence of alternative bridging coordination partners with a larger bite distance, the complex will adopt a relaxed conformation. Therefore, [Cu₂(**397a**)(OH)(C₂H₅OH)(H₂O)](ClO₄)₂ is willing to give up the μ -hydroxo bridged structural motif in favour of a bridging catechol coordination. This is also valid for [Cu₂(**398a**)(CH₃O)](ClO₄)₂·2CH₃OH, [Cu₂(**398b**)-(CH₃O)(CH₃OH)(ClO₄)](ClO₄) and [Cu₂(**398c**)(CH₃O)-(CH₃OH)(ClO₄)](ClO₄) although in a weakened sense. Binding of catechol was proven by spectroscopic titrations. In contrast to this, [Cu₂(**397b**)(OH)](NO₃)₂, [Cu₂(**397c**)-(CH₃O)(CH₃OH)(ClO₄)](ClO₄) and [Cu₂(**397d**)(OH)-(CH₃OH)](BF₄)₂ are completely indifferent towards catechol. Even in the presence of a large excess of 3,5-DTBC no binding is observed. The structural motif of a μ -hydroxo and μ -alkoxo bridged dicopper(II) center, respectively, is significantly more stable than a bridging catechol coordination. However, coordination of catechol is a necessary condition for electron transfer to the copper centers.

The oxidation rates of the active compounds is in accord with the strain within the complexes. For the most strained complex [Cu₂(**397a**)(OH)(C₂H₅OH)(H₂O)](ClO₄)₂ a turnover number of 214 h⁻¹ was determined, for the less strained systems [Cu₂(**398a**)(CH₃O)](ClO₄)₂·2CH₃CH, [Cu₂(**398b**)-(CH₃O)(CH₃OH)(ClO₄)](ClO₄) and [Cu₂(**398c**)(CH₃O)-(CH₃OH)(ClO₄)](ClO₄), binding of catechol was proven; turnover values between 33 and 48 h⁻¹ were obtained [484].

2-[*N,N*-Di(2-pyridylmethyl)aminomethyl]-6-[*N*-[2-(dimethylamino-ethyl)iminomethyl]-4-ethylphenol] (H-**399a**) was prepared in situ by refluxing equimolar methanolic solutions of *N,N*-dimethylethylenediamine and the formyl precursor 3-[*N,N*-di(2-pyridylmethyl)amino methyl]-5-methylsalicylaldehyde (H-**399b**), obtained by the reaction of 3-chloromethyl-5-methylsalicylaldehyde and di(2-pyridylmethyl)amine in tetrahydrofuran. H-**399a**, when reacted with copper(II) acetate monohydrate at reflux followed by

the addition of NaClO₄, gives rise to [Cu₂(**399a**)(OH)]-(ClO₄)₂ [485] (Fig. 301a). The two copper ions are bridged by the endogenous phenolic oxygen and the exogenous hydroxide oxygen; the Cu···Cu separation is 2.93 Å. The copper ion bound to the bidentate arm has a near square pyramidal geometry with the two nitrogen atoms of the arm and the two bridging oxygens on the equatorial base and acetic acid oxygen at the apex. The other copper ion, bound to the tridentate arm, has a five coordinated trigonal bipyramidal geometry with the hydroxo oxygen and the aminic nitrogen at the axial sites and the phenolic oxygen and two pyridine nitrogens on the trigonal base.

H - **399a**H - **399b**

The magnetic moment, 1.56 μ_B per Cu at room temperature, decreases with decreasing temperature to 0.78 μ_B at liquid nitrogen temperature indicating an antiferromagnetic spin-exchange interaction ($J = -85$ cm⁻¹).

In the cyclic voltammogram (glassy carbon electrode, in DMF) two quasi-reversible couples are observed at -0.49 and -0.98 V (versus Ag/Ag⁺). The former couple appearing at a considerably high potential is attributed to the reduction of the copper(II) center in the trigonal bipyramidal environment [485].

The reaction of H-**399a** with nickel(II) acetate tetrahydrate in methanol followed by the addition of NaNCS or NH₄PF₆ formed respectively [Ni₂(**399a**)(CH₃COO)(NCS)₂] and [Ni₂(**399a**)(CH₃COO)₂(CH₃OH)](PF₆) [485]. Attempts to obtain a dinickel perchlorate complex by the reaction of H-**398a** and nickel(II) perchlorate hexahydrate in methanol failed, and addition of a methanolic suspension of KPF₆ to the reaction mixture resulted in the precipitation of [{Ni₂(**399a**)(OH)(CH₃OH)}₂(CO₃)](PF₆)₂ after 1 week. The involved carbonate ion certainly originates from interaction of the dinuclear species with atmospheric carbon dioxide. In fact, [{Ni₂(**399a**)(OH)(CH₃OH)}₂(CO₃)](PF₆)₂

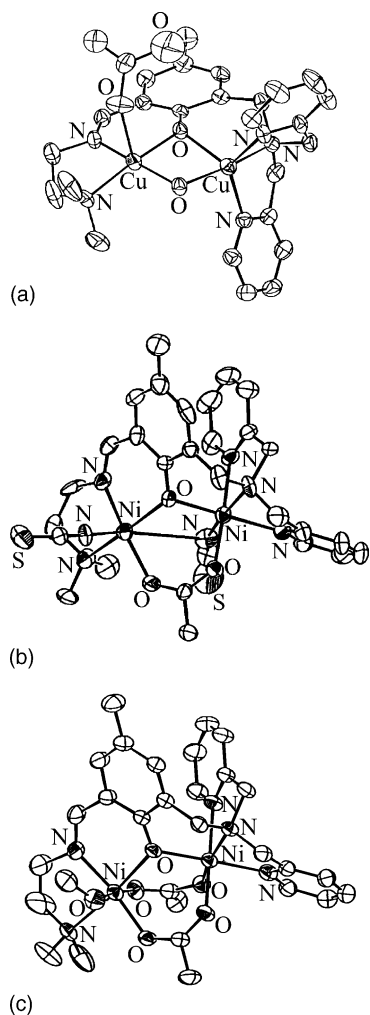


Fig. 301. Structure of $[\text{Cu}_2(\mathbf{399a})(\text{OH})]^{2+}$ (a), $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})_2]$ (b) and $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})]^+$ (c) (adapted from Ref. [485]).

was not obtained when the synthetic operations were carried out under nitrogen [485].

In $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})_2]$ (Fig. 301b) a pair of nickel(II) ions, 3.37 Å apart, are bridged by the phenolic oxygen of $[\mathbf{399a}]^-$ and an acetate group in *syn-syn* mode. An isothiocyanate nitrogen atom binds to each nickel ion and, consequently, the complex has an asymmetric core. The geometry about the nickel ion, bound to the iminic bidentate arm, has been described as square pyramidal with the oxygen and two nitrogens of the ligand and the oxygen of the bridging acetate group on the base and the nitrogen of isocyanate at the apex. The geometry about the other nickel ion bound to the aminic tridentate arm is pseudo octahedral. The bridging acetate group coordinates to an equatorial site of the pentacoordinated nickel(II) ion through one oxygen atom but to an axial site of the octahedral nickel(II) ion through the other oxygen atom with respect to the mean molecular plane [485].

$[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{PF}_6)$ (Fig. 301c) has a dinuclear core bridged by the phenolic oxygen of $[\mathbf{399a}]^-$

and two acetate groups in *syn-syn* mode, providing a μ -phenoxo, bis(μ -carboxylato)dinickel(II) core with a $\text{Ni} \cdots \text{Ni}$ separation of 3.396 Å. A methanol molecule coordinates to the nickel(II) ion bound to the iminic bidentate arm [485].

$[\{\text{Ni}_2(\mathbf{399a})(\text{OH})(\text{CH}_3\text{OH})\}_2(\text{CO}_3)](\text{PF}_6)_2$ has a carbonate bridged dimer structure derived from an asymmetric dinuclear unit. In each dinuclear unit a pair of nickel(II) ions are bridged by the phenolic oxygen and a hydroxo oxygen with a $\text{Ni} \cdots \text{Ni}$ separation of 3.087 Å. The nickel(II) ion, bound to the iminic bidentate arm, has a six coordinated geometry composed of the nitrogen donor atoms, the bridging oxygen atoms and the carbonate oxygens. The observed significant distortion from regular octahedron is due to the presence of the four-membered chelate ring involving the carbonate ion. The nickel(II) ion, bound to the aminic tridentate arm, also assumes a six coordinated geometry comprised of the nitrogen atoms, the bridging phenoxo oxygen the bridging hydroxo oxygen and the methanol oxygen. The dimeric structure of this complex is due to bridging by the carbonate group. The $\text{Ni} \cdots \text{Ni}$ separation between two $\{\text{Ni}_2(\mathbf{399a})(\text{OH})(\text{CH}_3\text{OH})\}$ units is 4.308 Å [485] (Fig. 302a).

The magnetic data of $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})_2]$ and $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{OH})](\text{PF}_6)$ suggests an antiferromagnetic behaviour with a spin exchange within each dinuclear core $J = -5.0$ and -7 cm^{-1} , respectively. In contrast, in $[\{\text{Ni}_2(\mathbf{399a})(\text{OH})(\text{CH}_3\text{OH})\}_2(\text{CO}_3)](\text{PF}_6)_2$ no or a very weak magnetic interaction occurs.

These complexes in ethanol with urea or with potassium cyanate gives rise to $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})(\text{NCO})]$, $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCO})(\text{C}_2\text{H}_5\text{OH})](\text{PF}_6)$ and $[\{\text{Ni}_2(\mathbf{399a})(\text{NCO})(\text{C}_2\text{H}_5\text{OH})\}_2(\text{CO}_3)](\text{PF}_6)_2$ [485].

A very slow dissociation of urea into ammonium and cyanate under acidic conditions is known ($\text{NH}_2\text{-CONH}_2 = \text{NH}_4^+ \text{NCO}^-$). The fast formation of the isocyanate complexes under moderate pH clearly indicates that the dinuclear core plays an essential role in the conversion of urea into NCO^- . The conversion proceeds in absolute ethanol or acetonitrile at a comparable rate. This fact means that a hydrolytic process by a trace of water is not important in the present case. The isocyanate complex $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})(\text{NCO})]$ is also formed in the reaction with *N*-methylurea or *N,N*-dimethylurea but the starting complex $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})_2]$ was recovered in the reaction with *N,N*-dimethylurea or *N,N,N',N'*-tetramethylurea. Evidently, the presence of one NH_2 group is essential for the conversion of ureas into cyanate by $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})_2]$. This observation suggests that bridging of urea over the dinuclear core, through one amino nitrogen to one nickel and the carbonyl oxygen to another nickel, is a key step for the conversion [485].

The structure of $[\{\text{Ni}_2(\mathbf{399a})(\text{NCO})(\text{C}_2\text{H}_5\text{OH})\}_2(\text{CO}_3)](\text{PF}_6)_2$ is similar to that of $[\{\text{Ni}_2(\mathbf{399a})(\text{OH})(\text{C}_2\text{H}_5\text{OH})\}_2(\text{CO}_3)](\text{PF}_6)_2$ (Fig. 302b), except for the replacement of OH^- and methanol with the isocyanate ion and

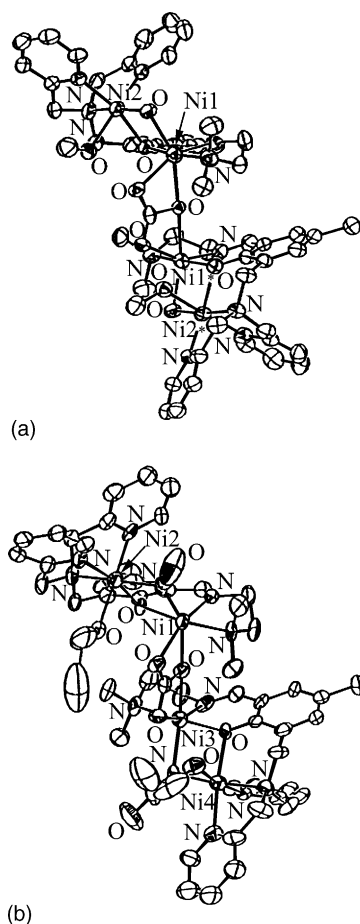


Fig. 302. Structure of $[\{\text{Ni}_2(\mathbf{399a})(\text{OH})(\text{CH}_3\text{OH})\}_2(\text{CO}_3)]^{2+}$ (a) and $[\{\text{Ni}_2(\mathbf{399a})(\text{NCO})(\text{C}_2\text{H}_5\text{OH})\}_2(\text{CO}_3)]^{2+}$ (b) (adapted from Ref. [485]).

ethanol, respectively. In each dinuclear unit a pair of nickel(II) ions are bridged by the phenolic oxygen and the isocyanate nitrogen in the average $\text{Ni} \cdots \text{Ni}$ intermetallic separation of 3.14 Å. The carbonate bridge in the dimer remains intact. A dinuclear core, bridged by the phenolic oxygen of $[\mathbf{399a}]^-$ and an exogenous isocyanate nitrogen atom, has been proposed for $[\text{Ni}_2(\mathbf{399})(\text{CH}_3\text{COO})(\text{NCS})(\text{NCO})]$ and $[\text{Ni}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCO})(\text{C}_2\text{H}_5\text{OH})]$. In these complexes the remaining acetate group may function as an additional bridge between a pair of nickel ions [485].

H-**399a** forms $[\text{Zn}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$, $[\text{Zn}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2(\text{NCS})_2]$ and $\text{Zn}_2(\mathbf{399a})(\text{NCS})_3$ when reacted with $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in the presence of PF_6^- or ClO_4^- and $\text{Zn}(\text{NCS})_2$ [462].

In $[\text{Zn}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2](\text{ClO}_4) \cdot \text{CHCl}_3$ the two zinc ions are bridged by the phenolic oxygen and two acetate groups in the *syn-syn* mode. The $\text{Zn} \cdots \text{Zn}$ interatomic separation is 3.29 Å. The geometry about the zinc ion bound to the bidentate arm can be regarded as a distorted square pyramid with the phenolic oxygen, the nitrogens of the bidentate arm and one acetate oxygen on the equatorial base and another acetate oxygen at the apex. The zinc ion bound to the tridentate arm has a six coordinated geometry.

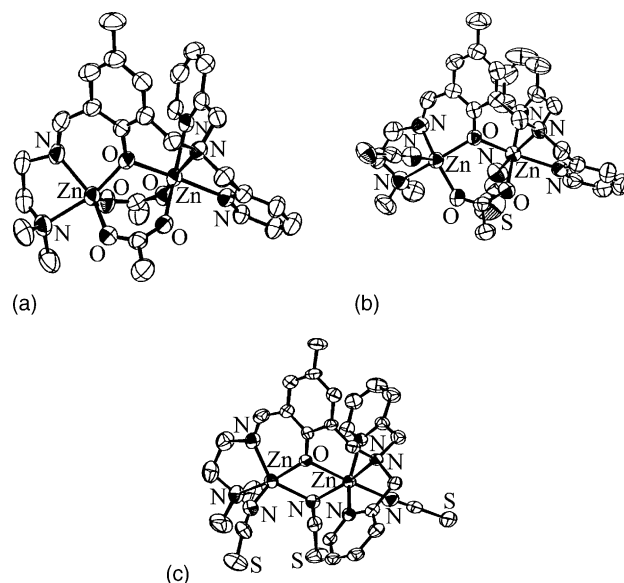


Fig. 303. Structure of $[\text{Zn}_2(\mathbf{399a})(\text{CH}_3\text{COO})_2]^+$ (a), $[\text{Zn}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})_2]$ (b) and one of the two crystallographically independent molecules in $[\text{Zn}_2(\mathbf{399a})(\text{NCS})_3]$ (c) (molecule A) (adapted from Ref. [462]).

One of the pyridyl nitrogens is situated *trans* to the phenolic oxygen, and the other pyridyl nitrogen is *cis* to the phenolic oxygen [462] (Fig. 303a).

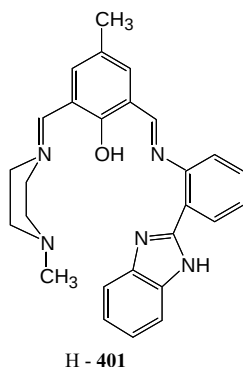
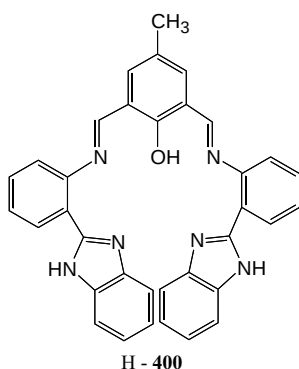
$[\text{Zn}_2(\mathbf{399a})(\text{CH}_3\text{COO})(\text{NCS})_2] \cdot \text{CH}_3\text{CHOHCH}_3$ has a μ -acetato- μ -phenolato-dizinc(II) dinuclear core in a $\text{Zn} \cdots \text{Zn}$ interatomic separation of 3.524 Å. The zinc ion bound to the bidentate arm has a square pyramidal geometry with the oxygen and the two nitrogens of $[\mathbf{399a}]^-$ and the oxygen of the bridging acetate group on the base and an isothiocyanate nitrogen at the apex. The zinc ion bound to the tridentate arm has a six coordinated geometry together with the oxygen of the bridging acetate group and a thiocyanate nitrogen. One of the pyridyl nitrogens is situated *trans* to the bridging phenolic oxygen, and the other pyridyl nitrogen is situated *cis* to the phenolic oxygen. The terminal thiocyanate group on one zinc and that on the other zinc are situated *trans* to each other with respect to the mean molecular plane formed by the two zinc ions, the phenolic oxygen and the acetate bridge (Fig. 303b) [462].

For $[\text{Zn}_2(\mathbf{399a})(\text{NCS})_3] \cdot 3\text{CHCl}_3$ there are two crystallographically independent molecules (A and B) in the crystal. In molecule A, the two zinc ions are doubly bridged by the endogenous phenolic oxygen and an exogenous thiocyanate nitrogen, in the $\text{Zn} \cdots \text{Zn}$ separation of 3.245 Å. The zinc ion bound to the bidentate arm has a square pyramidal geometry with the oxygen and the nitrogens of $[\mathbf{399a}]^-$ and the bridging thiocyanate nitrogen on the base and a terminal thiocyanate nitrogen at the axial site. The zinc ion bound to the tridentate arm has a six coordinated environment with further coordination of a terminal thiocyanate nitrogen. This nitrogen atom is situated *trans* to the bridging phenolic oxygen and the two pyridyl nitrogens are situated *cis* to the phenolic oxygen.

In molecule B, the two zinc ions are singly bridged by the endogenous phenolic oxygen in a $\text{Zn} \cdots \text{Zn}$ intermetallic separation of 3.543 Å. The zinc ion bound to the bidentate arm has a five coordinated environment together with two terminal thiocyanate nitrogens. The geometry about this metal ion is regarded as a square pyramid with the oxygen and the nitrogens of [399a][−] and a thiocyanate nitrogen on the base and another thiocyanate nitrogen at the apex. The zinc ion bound to the tridentate arm has a distorted five coordinated environment with further coordination of a thiocyanate nitrogen. The geometry about this metal ion is regarded as a trigonal bipyramid, with the amine nitrogen and a thiocyanate nitrogen at the axial sites and with the phenolic oxygen and the pyridyl nitrogens on the trigonal base [462] (Fig. 303c).

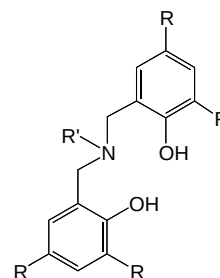
$[\text{Zn}_2(\text{399a})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$ has no hydrolytic activity towards tris-(*p*-nitrophenyl)phosphate [462].

H-400 and H-401, obtained as a yellow solids respectively by the reaction in ethanol of 2,6-diformyl-4-methyl-phenol with 2-aminophenylbenzimidazole (1:2) and 2-formyl-6-(4-methyl-piperazin-1-yl) methyl-4-methylphenol with 2-aminophenyl-benzimidazole (1:1), react with copper(II) perchlorate and NaX ($\text{X} = \text{Cl}^-$, OH^- , CH_3COO^-) affording $[\text{Cu}_2(\text{400})(\text{X})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{401})(\text{X})](\text{ClO}_4)_2$ [486]. These complexes are 2:1 electrolytes in DMF. Electrochemical data show two distinctive reduction peaks at negative potentials due to the reactions $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$. The complexes of H-401 undergo reduction at less negative potential ($E^1 = -0.15$ to -0.25 V, $E_{\text{pc}}^2 = -0.45$ to -0.65 V) when compared to the complexes of H-400 ($E_{\text{pc}}^1 = -0.45$ to -0.58 V, $E_{\text{pc}}^2 = -1.07$ to -1.103 V).

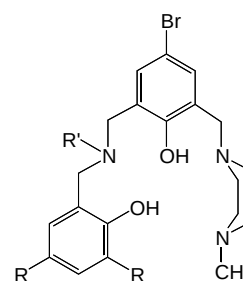


A variable temperature magnetic study on the complexes with the ligand H-400 showed strong antiferromagnetic coupling between the copper ions ($-2J = 285$ – 295 cm^{-1}), while the complexes with the ligand H-401 showed weaker antiferromagnetic interaction ($-2J = 60$ – 85 cm^{-1}) [486].

Bis-(3,5-disubstituted-2-hydroxybenzyl)-*N*-alkylamines (H₂-402a–d), prepared by the reaction of 2,4-disubstituted phenols, formaldehyde and various primary amines in a 2:2:1 molar ratio, react with copper(II) perchlorate in ethanol to give $[\text{Cu}_2(\text{402a–d})_2]$. Their dimeric nature has been confirmed by FAB mass spectrometry. Also EPR spectral studies in DMF indicate that the complexes are dimeric and undergo dissociation on addition of pyridine. The complexes undergo quasi reversible two step single electron transfers at negative potentials ($E_{\text{pc}}^1 = -0.34$ to -0.48 V, $E_{\text{pc}}^2 = -0.59$ to -0.72 V). Variable temperature magnetic studies indicate that the complexes are antiferromagnetically coupled ($-2J = 290$ – 400 cm^{-1}) [487].



- H₂ - 402
- a R = R' = CH₃
 - b R = R' = C₂H₅
 - c R = Cl, R' = CH₃
 - d R = Cl, R' = C₂H₅
 - e R = Cl, R' = C₆H₁₁



- H₂ - 403a R = R' = CH₃
H₂ - 403b R = Cl, R' = C₆H₁₁

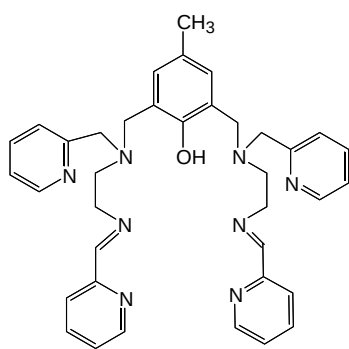
4-Bromo-2-[(4-methylpiperazin-1-yl)methyl]-6-[*N*-(3,5-dimethyl-2-hydroxybenzyl)-methylaminomethyl]phenol (H₂-403a) and 4-bromo-2-[(4-methyl-piperazin-1-yl)methyl]-6-[*N*-(3,5-dichloro-2-hydroxybenzyl)-*N*-cyclohexylaminomethyl]phenol (H₂-403b) have been obtained by reaction of H₂-402a or H₂-402e with *N*-methylpiperazine and formaldehyde in a 1:1 molar ratio. H₂-403a and H₂-403b, when reacted with copper(II) salts in the presence

of NaX, gives rise to $[\text{Cu}_2(\mathbf{403a})(\text{X})]\text{ClO}_4$, and $[\text{Cu}_2(\mathbf{403b})(\text{X})](\text{ClO}_4)$ ($\text{X} = \text{OH}^-$, Br^- , CH_3COO^-) [488].

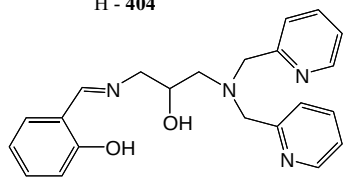
The complexes undergo two quasi reversible redox peak ($E_{\text{pc}}^1 = -0.35$ to -0.70 V, $E_{\text{pc}}^2 = -0.75$ to 0.97 V). Complexes of the ligand $\text{H}_2\text{-}\mathbf{403b}$ undergo reduction at less negative potential ($E_{\text{pc}}^1 = -0.35$ to -0.42 V and $E_{\text{pc}}^2 = -0.75$ to -0.85 V) when compared to the complexes of the ligand $\text{H}_2\text{-}\mathbf{403a}$ ($E^1 = -0.55$ to -0.70 V and $E^2 = -0.85$ to -0.97 V) [488]. Electrochemical study of the complexes indicates that the reduction potentials are strongly dependant on the nature of the exogenous bridging donor atoms X and peripheral substituents.

Variable temperature magnetic susceptibility studies of these complexes show the presence of antiferromagnetic interaction between the copper ions ($-2J = 69\text{--}124\text{ cm}^{-1}$). Relatively larger spin exchange coupling values are observed for the complexes of the ligand $\text{H}_2\text{-}\mathbf{403a}$, when compared to the complexes of the ligand of $\text{H}_2\text{-}\mathbf{403b}$ [488].

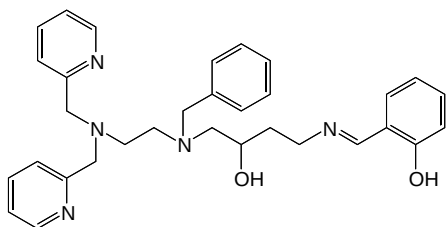
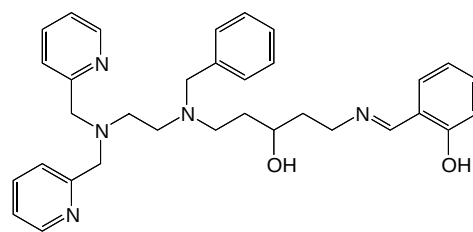
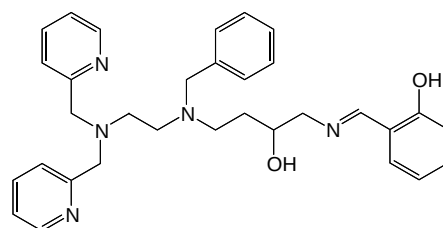
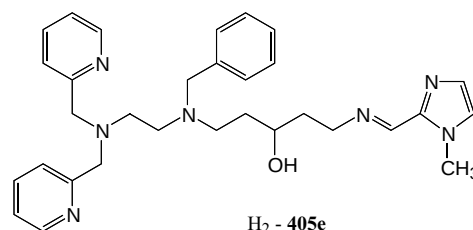
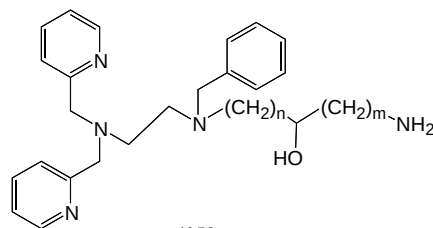
$[\text{Fe}_2(\mathbf{404})(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})(\text{PF}_6)_2$ was obtained by reacting in methanol under anaerobic conditions 4-methyl-2,6-bis[*N*-(2-pyridylmethyl)-*N*-(2-pyridylmethyleneaminoethyl) aminomethyl]phenol ($\text{H-}\mathbf{404}$), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, acetic acid and triethylamine in the presence of NaPF_6 and FeCl_3 . $[\text{Fe}_2(\mathbf{404})(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})(\text{BPh}_4)_2$ was prepared in a similar manner using NaBPh_4 instead of NaPF_6 [489].



H - 404

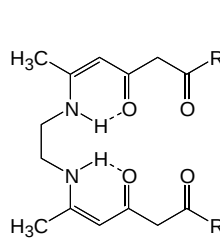


H - 405a

 H_2 - 405b H_2 - 405c H_2 - 405d H_2 - 405e

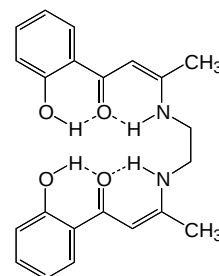
405f

$n = 1, m = 2$
 $n = 2, m = 1$
 $n = 2, m = 2$



H4 - 406

R
 CH_3
 C_2H_5
 $\text{C}(\text{CH}_3)_3$



H4 - 407

The formation of a diiron mixed-valence complexes was confirmed by Mössbauer spectroscopy. The spectra consist of a quadruple doublet, due to an high-spin iron(II) ion and another doublet due to a low spin iron(III) ion. The cryomagnetic properties of these two complexes parallel the Mössbauer data and give $-2J$ values of -19.9 and 20 cm^{-1} , respectively [489].

No optical transitions have been detected in the visible or near-infrared region due to intramolecular electron transition between different oxidation states. The mixed-valence complexes $[\text{Fe}_2(\mathbf{404})(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})(\text{X})_2$ ($\text{X} = \text{PF}_6^-$, BPh_4^-) have been classified as firmly trapped electron compounds [489]. Two pathways are considered for such magnetic interaction: an s-orbital pathway leading to ferromagnetic interaction and a p-orbital pathway leading to antiferromagnetic interaction. The J values observed show that the latter pathway predominates. The EPR spectra are indicative of no apparent interaction (within the EPR time-scale) between two metal orbitals of the complexes in the ground state.

The cyclic voltammograms of the complexes in CH_3CN show two redox processes. For $[\text{Fe}_2(\mathbf{404})(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})(\text{PF}_6)_2$ the quasi-reversible redox couple at $E_1 = -0$ to 0.7 V ($\Delta E_p = 0.11$ V) versus SCE is assigned to the couple $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ and an irreversible redox couple $E_2 = 0.58$ V ($\Delta E_p = 0.10$ V) versus SCE to $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$. The values observed for $[\text{Fe}_2(\mathbf{404})(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})(\text{BPh}_4)_2$ were -0.05 ($\Delta E_p = 0.10$ V) and 0.60 V ($\Delta E_p = 0.11$ V) versus SCE. These redox couples correspond to one-electron electrochemical processes at both of the redox sites. The comproportionation constants K_{com} at 293 K were ca. 1.0×10^{12} and 0.9×10^{12} , respectively [489].

$[\text{Cu}_2(\mathbf{405a})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{H}_2\text{O} \cdot 0.5\text{NaClO}_4$, prepared by condensation of *N,N*-2-(pyridylmethyl)-1,3-diaminopropan-2-ol with salicylaldehyde in the presence of copper(II) acetate, triethylamine and sodium chloride, consists of two crystallographically independent dinuclear complex cations, sodium cations, perchlorate anions, and lattice waters. The two complex cations are geometrical isomers with a differ-

ent configuration of an asymmetric carbon atom of $[\mathbf{405a}]^{2+}$ linked by sodium cation which is located in a distorted octahedron formed by the oxygen atoms of phenolates, bridging carboxylates, and perchlorates. Both complex cations consist of a square planar and a distorted square pyramidal site, in which two copper ions are doubly bridged by endogenous alkoxide and exogenous acetate oxygens. The $\text{Cu} \cdots \text{Cu}$ separations of the two complex cations are 3.426 and 3.428 Å, respectively (Fig. 304a). Distortion from a square pyramidal structure in one complex cation is more pronounced than that in the other. EPR spectra of frozen solution in CH_3CN and of powders are similar and show that, although there are two structurally distinct species in solid state, only one species is present in solution [490].

The cyclic voltammograms show only one reduction wave at -0.67 V versus SCE indicating the square planar sites have no significant influence on the redox chemistry of five coordinate sites, while the five coordinate sites affect the redox chemistry of square planar sites [490].

The magnetic susceptibility of a powdered sample of $[\text{Cu}_2(\mathbf{405a})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{H}_2\text{O} \cdot 0.5\text{NaClO}_4$, measured in the temperature range 300–5 K, indicates the presence of antiferromagnetic interaction between copper ions. Taking into account that there are two different species in the solid state and EPR data give only one g value ($g = 2.12$) a good fit to the experiments data was obtained with $J_1 = -0.18 \text{ cm}^{-1}$ and $J_2 = -9.05 \text{ cm}^{-1}$ [490].

The Schiff bases $\text{H}_2\text{-}\mathbf{405b}$ and $\text{H}_2\text{-}\mathbf{405e}$, obtained by condensation of the appropriate formyl derivative with the functionalized amines $\mathbf{405f}$, have been designed as potentially dinucleating ligands. However, they have a strong tendency to form oligomeric complexes [490].

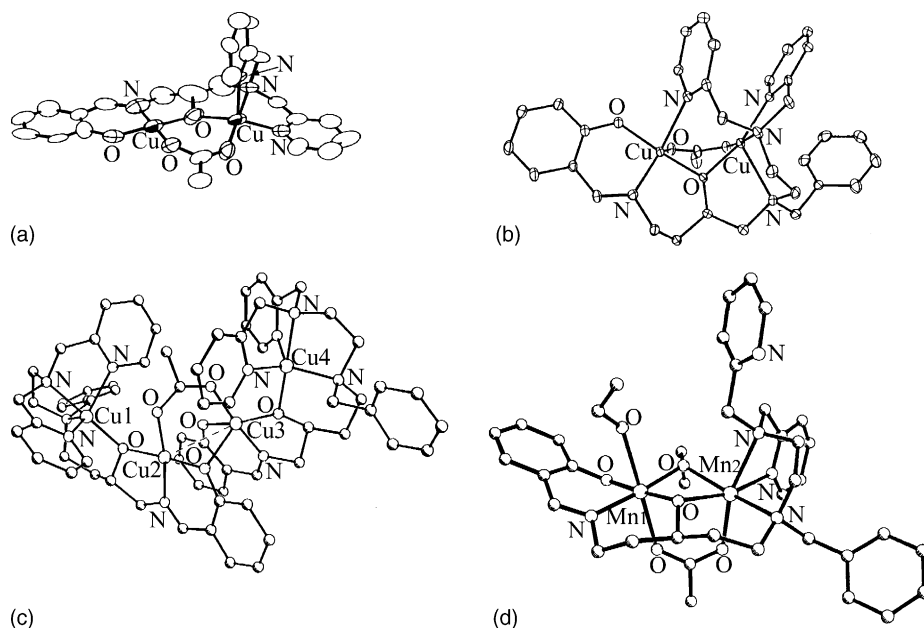


Fig. 304. Structure of $[\text{Cu}_2(\mathbf{405a})(\text{CH}_3\text{OH})]^+$ (a), $[\text{Cu}_2(\mathbf{405b})(\mu\text{-CH}_3\text{COO})]^+$ (b), $[\text{Cu}_4(\mathbf{405d})_2(\mu\text{-CH}_3\text{COO})]^{3+}$ (c) and $[\text{Mn}_2(\mathbf{405c})_2(\text{C}_2\text{H}_5\text{O})(\mu\text{-CH}_3\text{COO})(\mu\text{-C}_2\text{H}_5\text{O})]^+$ (d) (adapted from Ref. [490]).

Only **H₂-405b** gives rise to the dinuclear copper(II) complexes $[\text{Cu}_2(\mathbf{405b})(\mu\text{-CH}_3\text{COO})](\text{PF}_6)$ when reacted with copper(II) acetate monohydrate in methanol [490]. The copper(II) ions are bridged by the alkoxide oxygen atom and by an acetate group. The copper(II) ions are five coordinate, one in a distorted trigonal bipyramidal geometry and the other in a distorted square pyramidal geometry [490] (Fig. 304b).

Under similar conditions **H₂-405d** forms $[\text{Cu}_4(\mathbf{405d})_2(\mu\text{-CH}_3\text{COO})](\text{PF}_6)_3 \cdot \text{H}_2\text{O}$ whose structure consists of two different dicopper(II) units bridged by an acetate group and a phenolate oxygen atom. The pairs of copper(II) ions of each unit are bridged by alkoxide oxygen atoms. The two copper(II) ions, Cu(1) and Cu(4) are in a distorted trigonal bipyramidal geometry, whereas Cu(2) is square planar and Cu(3) is square pyramidal (Fig. 304c).

A tetranuclear structure was found for $[\text{Cu}_4(\mathbf{405e})_2(\mu\text{-CH}_3\text{COO})_2](\text{PF}_6)_4$ and $[\text{Cu}_4(\mathbf{405c})_2(\mu\text{-CH}_3\text{COO})_2](\text{PF}_6)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$. The first complex lies on a center of inversion. The two central copper(II) ions are bridged by the alkoxide groups of the two ligands and the terminal copper(II) ions are bridged to the two central ions by acetate groups. All copper(II) ions are five coordinated; the two central copper(II) ions are in distorted square pyramidal geometries whereas the terminal copper(II) ions are in distorted trigonal bipyramidal geometries [490].

Also the second complex $[\text{Cu}_4(\mathbf{405c})_2(\mu\text{-CH}_3\text{COO})_2](\text{PF}_6)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$, has a center of inversion and generally resembles the tetramer formed by $[\text{Cu}_4(\mathbf{405e})(\mu\text{-CH}_3\text{COO})_2](\text{PF}_6)_4$. The major difference is associated with the acetate ligands which, in this case, are terminally bonded to the outer copper(II) ions. As a consequence, the inner two copper(II) ions are square planar and are bridged to each other by the alkoxide groups of the two ligands. The terminal copper(II) ions are in a distorted trigonal bipyramidal geometry [490].

H₂-405c, when reacted with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in ethanol under an inert atmosphere gives a yellow-orange solution which turns orange upon the addition of 1 equiv. of triethylamine. The addition of $[\text{NH}_4](\text{PF}_6)$ to the heated solution leads to the formation of a brown suspension. After filtration, the filtrate, exposed to air forms the orange-brown crystals of $[\text{Mn}_2(\mathbf{405c})(\mu\text{-CH}_3\text{COO})(\mu\text{-C}_2\text{H}_5\text{O})](\text{PF}_6)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$. The structure of this complex suggests that it is a mixed-valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}$ compound [490]. In the structure, the two manganese ions are bridged by the alkoxide group of the ligand, by an exogenous ethoxide ion and by an acetate ligand. Both manganese ions are six coordinate with Mn(1) bonded to a terminal ethoxide ligand. The asymmetry and the average bond lengths of the two metal ions suggest that Mn(1) is in the manganese(IV) oxidation state and that Mn(2) is in the manganese(II) oxidation state. Consistent with this mixed-valence assignment is the presence of four negative oxygen ligands coordinated to the manganese(IV) ion. The ability of O_2 to oxidize manganese(II) to manganese(IV) probably depends on the presence of these oxygen

donors. One pyridine nitrogen of the binucleating ligand is not coordinated (Fig. 304d) [490].

9.3. Complexes with side-off ligands

The potentially hexadentate compartmental side-off Schiff bases **H₄-406** and **H₄-407** react with metal acetates to give complexes which clearly show the coordination selectivity patterns available. In the case of the uranyl(IV) cation, the metal ion lies in the O_2O_2 compartment with a solvent molecule occupying the fifth equatorial site of a pentagonal bipyramid. This is confirmed by X-ray structural analyses of $[\text{UO}_2(\text{H}_2\text{-406})(\text{CH}_3\text{OH})]$ and of $[\text{UO}_2(\text{H}_2\text{-407})(\text{DMF})]$ [491].

The crystal structure of $[\text{UO}_2(\text{H}_2\text{-406})(\text{CH}_3\text{OH})]$ ($\text{R} = \text{CH}_3$) [491] consists of discrete units which are involved in hydrogen bonding. Surprisingly, the chemical composition of the ligand is not the same in the two molecules of the asymmetric unit; whereas in one molecule the ligand has the expected formula with the nitrogen atoms bonded through a $-\text{CH}_2\text{-CH}_2-$ aliphatic chain, in the other molecule there is a $-\text{CH}=\text{CH}-$ chain. The two resulting complexes are consequently similar but chemically different and this explains the presence of eight molecules in a cell which has only 4 equiv. positions. Apart from this, the main structural features are the same in both molecules, with the uranium atoms seven-coordinated in a slightly distorted pentagonal bipyramid geometry.

In $[\text{UO}_2(\text{H}_2\text{-407})(\text{DMF})]$ [491] the uranyl(VI) ion again occupies the outer O_2O_2 compartment; the oxygen of a dimethylformamide molecule completes the equatorial pentacoordination about the O-U-O group.

Positional isomers of the mononuclear complex of copper(II) with **H₄-407** have been prepared [5,42]. When $\text{CHCl}_3/\text{C}_2\text{H}_5\text{OH}$ was used, the green O_2O_2 isomer was obtained, while in refluxing methanol the light brown N_2O_2 isomer was isolated.

For $[\text{Ni}(\text{H}_2\text{-407})]$ the magnetic measurements can easily distinguish between the two positional mononuclear isomers, the nickel(II) being diamagnetic in the N_2O_2 set and paramagnetic in the O_2O_2 set. The complex is diamagnetic, showing that the nickel(II) ion is coordinated to two nitrogen

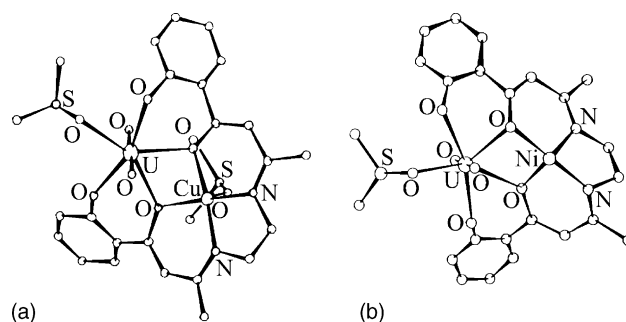
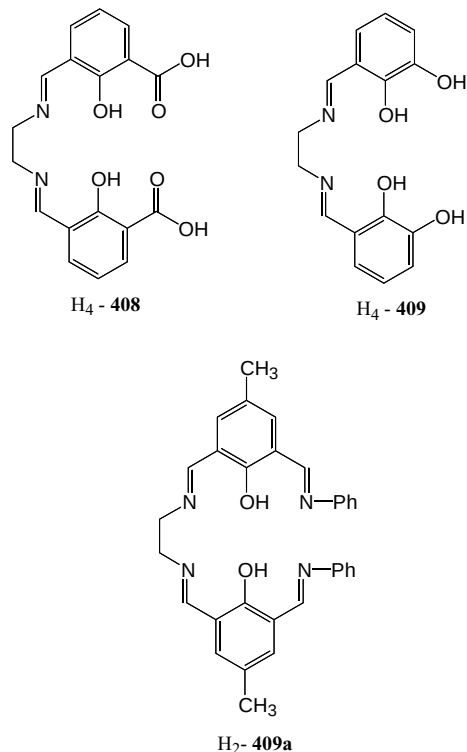


Fig. 305. Structures of $[\text{CuUO}_2(\mathbf{407})(\text{DMSO})_2]$ (a) and $[\text{NiUO}_2(\mathbf{407})(\text{DM-SO})]$ (b) (adapted from Ref. [492]).

and two oxygen atoms in a square planar configuration as confirmed by an X-ray investigation [5,42].

In a similar way, mononuclear dioxouranium(VI), nickel(II) and copper(II) complexes with the ligand H₄-408 or H₄-409 have been prepared.



By using the side-off compartmental ligands, it was possible to prepare hetero-dinuclear complexes as the site occupancy of the metal ion can be guaranteed and scramble reactions are avoided or depressed considerably [492]. Using the appropriate pure mononuclear isomers, the second metal ion was easily introduced in the desired chamber.

In [CuUO₂(407)(DMSO)₂] (Fig. 305a) and [NiUO₂-(407)(DMSO)] (Fig. 305b) [492] the dioxouranium(VI) moiety lies in the O₂O₂ set and is further bonded to a molecule of DMSO. In the two complexes, the polyhedron around the uranium ion is a slightly distorted pentagonal bipyramid. The copper(II) and the nickel(II) ions are retained in the inner N₂O₂ chamber; the copper(II) ion is five coordinated, being also bonded to a DMSO molecule. The nickel(II) ion is four coordinated but not square planar as expected. It shows an unusual *cis*-divacant structure.

It was also found that both copper(II) and nickel(II) homo-dinuclear complexes with the side-off ligands can undergo a transmetallation reaction with uranyl salts leading to the formation of hetero-dinuclear products. These hetero-dinuclear complexes are identical to those prepared by the stepwise procedure. Moreover, the site selectivity of palladium(II) for the N₂O₂ site and of UO₂²⁺ for the O₂O₂ site makes the formation of hetero-dinuclear complexes with only one positional isomer straightforward.

H₄-408, H₄-409 and H₄-37, especially designed for the simultaneous coordination of a d and a f metal ion, have been synthesized by condensation of 2,3-dihydroxybenzaldehyde with the appropriate diamine in alcoholic solution; they contain an inner N₂O₂ chamber, particularly suitable for a d-transition metal ion and an outer O₂O₂ site too large for such an ion but suitable for a f-ion, as confirmed by the X-ray structure of H₄-37. Consequently, it is possible to produce well defined compounds without positional isomers or undesired species [493]. X-ray data reveal that, in the mononuclear complexes, copper(II) and nickel(II) are square planar N₂O₂ isomers and indicate the correct size of the outer O₂O₂ chamber for the coordination of large metal ions such as f-ions or barium.

The condensation reaction of 2,3-dihydroxybenzaldehyde and ethylenediamine, using uranyl(VI) or lanthanide(III) ions as templating agents, leads to the formation of [UO₂(H₂-409)(CH₃OH)] and [Ln(H₄-409)(NO₃)₃]; the Schiff base coordinates as neutral in the lanthanide(III) complex and as dinegative in the uranyl(VI) one. In these complexes, the metal ion is suggested to be in the outer O₂O₂ compartment with a solvent molecule occupying the fifth equatorial site of a pentagonal bipyramid for the uranyl(VI) compounds and with nitrate anions filling the coordination sphere for the lanthanide(III) ones [491].

Hetero-dinuclear d,s- or d,f-complexes have been obtained by reaction of the mononuclear d-complexes with uranyl(VI) salts in coordinating solvents and with lanthanide(III) or barium(II) ions in methanol and in presence of a base. The enhanced selectivity of the two chambers of these ligands towards the different metal ions is indicated by their capability to form pure hetero-dinuclear complexes also when a transition metal ion (i.e. copper(II) or nickel(II)) and an f-metal ion (i.e. lanthanum(III) or uranyl(VI)) are added in sequence to the ligands without previous separation and purification of the mononuclear species. The transition metal ion invariantly occupies the inner chamber and the f-ion the outer chamber [493].

These hetero-dinuclear complexes have been used as precursor in the synthesis, by thermal decomposition, of mixed oxides; for example [CuLa(409)(NO₃)] produces CuLa₂O₄ with an orthorhombic symmetry [493].

An X-ray investigation of [CuY(409)(NO₃)(DMSO)]₂ shows the copper(II) ion is tetracoordinated in the inner N₂O₂ chamber while the yttrium(III) is eight coordinated in the outer O₂O₂ site. The complex is a tetranuclear asymmetric unit, two yttrium(III) ions being held together by phenolate oxygen bridges. The coordination of each yttrium(III) ion is completed by the oxygens of a bidentate nitrate group and of a dimethylsulfoxide molecule.

This oligomerization, via the phenolic oxygens of the outer chamber, can be prevented by the addition of anions which fill the coordination sphere about the lanthanide(III) ion with the consequent formation of monomeric species, as found for [CuLn(H₂-409)(NO₃)₃].

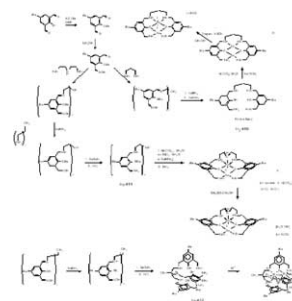
The temperature dependence of the magnetic susceptibility of $[\text{NiGd}(\text{H}_2\text{-409})(\text{NO}_3)_3]$, measured in the 2.5–200 K range, is indicative that the nickel(II) ion is in a square planar environment and, therefore, in a low spin configuration. The magnetic data measured in the same temperature range, for $[\text{CuGd}(\text{H}_2\text{-409})(\text{NO}_3)_3]$ indicate a coupling constant $J_{\text{CuGd}} = 1.59 \text{ cm}^{-1}$. The magnetic behaviour of the tetranuclear complex $[\text{CuGd}(\text{409})(\text{NO}_3)(\text{H}_2\text{O})_2]$, similar to that of the dinuclear complex $[\text{CuGd}(\text{H}_2\text{-409})(\text{NO}_3)_3]$, has been interpreted as due to the magnetic coupling in a tetrameric linear unit where one GdGd and 2 equiv. GdCu interactions are operative: ($J_{\text{CuGd}} = 3.76 \text{ cm}^{-1}$, $J_{\text{GdGd}} = 0.16 \text{ cm}^{-1}$). Thus a ferromagnetic interaction is, even in this system, operative within the $\text{Gd}^{\text{III}}\text{Cu}^{\text{II}}$ pairs with a mechanism which does not depend on the geometry and nature of the bridging atoms. This result seems to confirm the presence of a spin polarization mechanism in 3d–4f pairs. The observed anti-ferromagnetic $\text{Gd}^{\text{III}}\text{Gd}^{\text{III}}$ coupling is weak, but in any case the observed coupling constant is indicative that some exchange mechanism is operative together with the pure dipolar one.

Copper(II)–lanthanide(III) complexes with *N,N'*-bis(3-carboxysalicylidene)-1,2-ethane diamine or with the similar 2-propanediamine and 1,5-diethylenetriamine have been prepared by reaction in methanol of the mononuclear copper(II) complex with $\text{Ln}(\text{NO}_3)_3$ in the presence of the LiOH. The copper(II) ion is bound at the inside N_2O_2 site while the lanthanide ion occupies the outer O_2O_2 chamber [493].

The reaction in air of *N,N'*-ethylene-bis(3-formyl-5-methylsallylaldimine) with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in refluxing ethanol forms the corresponding mononuclear manganese(III) complex $[\text{Mn}(\text{42})(\text{Cl})]$ ($\text{Z} = \text{CH}_3$, $\text{R} = \text{CH}_2\text{CH}_2$) but not the corresponding dinuclear homologue. Also $[\text{Mn}(\text{42})(\text{Cl})]$ failed to produce hetero-dinuclear complexes. This difficulty was overcome by condensing the formyl groups with aniline. This Schiff base complex is able to form the corresponding hetero-dinuclear complexes $[\text{MnM}(\text{409a})(\text{Cl})_3] \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+} , Co^{2+} ; $n = 1\text{--}3$) and $[\text{MnM}(\text{409a})(\text{Cl})_4] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Fe}^{3+}$, Mn^{3+}). The presence of the second metal ion does not alter the high-spin state of the manganese(III) ion in the dimetallic complexes [494].

In $[\text{Mn}(\text{42})(\text{Cl})]$ the manganese(III) ion is pentacoordinated and the geometry square pyramidal. The two phenolic oxygen atoms and two imine nitrogen atoms of the Schiff base occupy the basal plane of the square pyramid. This clearly indicates that the formyl groups in this ligand do not coordinate to the manganese(III) ion.

The catalytic properties of these complexes for epoxidation of alkenes have been investigated using PhIO as a terminal oxidant. The binuclear manganese(III) complexes are less efficient epoxidation catalysts than the mononuclear manganese(III) complex. The reduced activities of the bimetallic complexes may be due to both the low rates of formation of a $\text{Mn}(\text{V})=\text{O}$ intermediate and the transfer of oxygen from this intermediate to the alkene. Furthermore, the bimetallic complexes also transformed into a catalyti-



Scheme 56.

cally inactive species in the presence of PhIO indicated by UV-Vis spectroscopy studies [494].

N,N'-Bis[2-thio-3-aminomethyl-5-*tert*-butylbenzyl]-1,3-diamine, ($\text{H}_2\text{-410}$) prepared according to Scheme 56, reacts with $\text{Ni}(\text{ClO}_4)_2$ in methanol in the presence of sodium methanolate and in a 2:1:6 molar ratio to give $[\text{Ni}_2(\text{410})](\text{ClO}_4)_2$ [495] which by recrystallization from methanol, affords $[\text{Ni}_2(\text{410})](\text{ClO}_4)_2 \cdot 3\text{CH}_3\text{OH}$ (Fig. 306a) [494]. The dication $[\text{Ni}_2(\text{410})]^{2+}$ is formed by two approximately planar *cis*- $\text{N}_2\text{S}_2\text{Ni}$ coordination units joined by the thiolate sulfur atoms, with a similar bowl-shaped molecular structure. The chelate ring adopts the typical chair conformation with enantiomeric configurations (*R*) and (*S*) for asymmetric nitrogen atoms. While this isomer seems to be the thermodynamically most stable form (or the least soluble form), it is likely that the other possible isomers coexist with (*R,S*)- $[\text{Ni}_2(\text{410})](\text{ClO}_4)_2$ in solution.

$[\text{Ni}_2(\text{410})](\text{ClO}_4)_2$ reacts with a variety of substrates such as NaCN, NH_4SCN , NaN_3 or NaHS [494]. For instance, when $[\text{Ni}_2(\text{410})](\text{ClO}_4)_2 \cdot 3\text{CH}_3\text{OH}$ was allowed to react with KSCN in methanol, $[\text{Ni}_2(\text{410})(\text{NCS})_2] \cdot \text{CH}_3\text{OH}$ was obtained. In this complex both thiocyanate anions are nitrogen bonded to one nickel ion of the dinuclear isothiocyanate complex. Thus one nickel ion is octahedral and the other is

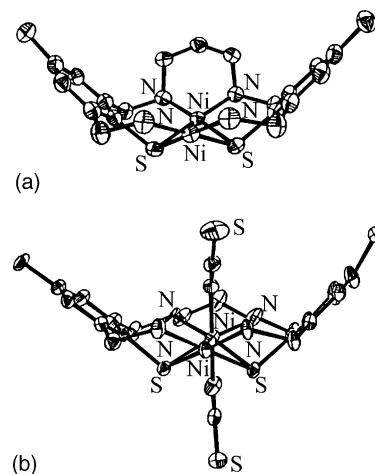


Fig. 306. Structures of $[\text{Ni}_2(\text{410})]^{2+}$ (a) and $[\text{Ni}_2(\text{410})(\text{NCS})_2]$ (b) (adapted from Ref. [494]).

four coordinated. The linear isothiocyanate ions occupy *trans*-positions in N_4S_2Ni octahedron. The remaining coordination sites at this nickel(II) ion are occupied by two bridging thiolate sulfur atoms and by two secondary amine nitrogen atoms. The neutral complexes stack in pairs. The intramolecular $Ni \cdots Ni$ separation is 3.124 Å (Fig. 306b). The 1,3-diazacyclohexane chelate ring adopts a conformation with (*S*)-N and (*R*)-N nitrogen configurations, thus the (*R*)-N and (*S*)-N nitrogen configurations in $[Ni_2(410)](ClO_4)_2 \cdot 3CH_3OH$ change to (*S*)-N and (*R*)-N ones in $[Ni_2(410)(NCS)_2] \cdot CH_3OH$.

In dimethylformamide $[Ni_2(410)](ClO_4)_2 \cdot 3CH_3OH$ and $[Ni_2(410)(NCS)_2] \cdot CH_3OH$ undergo two successive reductions at potentials of -0.95 and -1.53 V versus SCE, assigned to the formation of mixed-valent $[Ni^I Ni^{II}(410)]^+$ and $[Ni_2(410)]$ species, respectively. The similar electrochemical properties of these complexes suggest that the *trans*-axially bound isothiocyanate ions in $[Ni_2(410)(NCS)_2] \cdot CH_3OH$ are replaced by solvent molecules in DMF solution. Upon reduction, these solvent molecules decoordinate to produce an unsolvated $[Ni^I Ni^{II}(410)]^+$ species with two planar N_2S_2Ni units [495].

Using $H_2N(CH_2)_2NH(CH_2)_2NH_2$ instead of $H_2N(CH_2)_nNH_2$ ($n = 1, 2$) the potentially heptadentate N_5S_2 ligand **411** and related nickel(II) complexes have been prepared (Scheme 56) [495]. $[Ni_2(411)(CH_3OH)](ClO_4)_2$, $[Ni_2(411)(Cl)](Cl)$, $[Ni_2(411)(CH_3OH)](BPh_4)$ and $[Ni_2(411)(NCS)](OH) \cdot H_2O$ are all paramagnetic ($\mu_{eff} = 3.0\text{--}3.1\mu_B$) in the solid state at 295 K, implying that the complexes are all composed of a planar, diamagnetic $Ni^{II}N_2S_2$ unit and an octahedral, paramagnetic $Ni^{II}N_3S_2$ center per molecule of complex as confirmed for $[Ni_2(411)(CH_3OH)](ClO_4)_2$ and $[Ni_2(411)(CH_3OH)](BPh_4)$ by X-ray determinations and for $[Ni_2(411)(Cl)](Cl)$ and $[Ni_2(411)(NCS)](OH) \cdot H_2O$ by electronic absorption spectroscopy.

In $[Ni_2(411)(Cl)](Cl)$ one nickel(II) ion is planar in a N_2S_2 environment while the other nickel(II) ion is octahedral in a N_3S_3Cl environment (Fig. 307a).

$[Ni_2(411)(NCS)](OH) \cdot H_2O$ (Fig. 307b) is composed of the dinuclear complex $[Ni_2(411)(NCS)]^+$, a water molecule of crystallization and a hydroxide ion. The hydroxide ion forms a strong $H_2O \cdots H-O$ hydrogen bonding contact to the water solvent molecule. Once again, one nickel(II) ion is square planar in a N_2S_2 environment while the other nickel(II) ion is octahedral in a N_4S_2 environment.

$[Ni_2(411)(Cl)](Cl)$ undergoes two successive one-electron oxidations at $+0.88$ and $+0.41$ V versus SCE; the oxidized species are not thermally stable, but electronic absorption spectra and EPR spectra are indicative of the presence of nickel(III) species.

The nonadentate N_6S_3 ligand $H_3\text{-}412 \cdot 6H_2O$, (Scheme 56), was isolated as the hexahydrochloride salt $H_3\text{-}412 \cdot 6HCl$, a pale-yellow solid that can be handled in air for short periods of time without any sign of oxidative decomposition. For long-term usage the compound must be stored under an atmosphere of dry nitrogen [496].

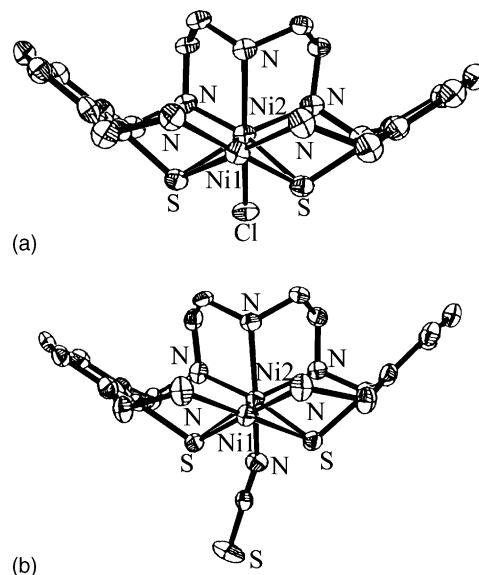


Fig. 307. Structures of $[Ni_2(411)(Cl)]^+$ (a) and $[Ni_2(411)(NCS)]^+$ (b) (adapted from Ref. [495]).

Reaction of $H_3\text{-}412 \cdot 6HCl$, $CoCl_2 \cdot 6H_2O$ and $N(Et)_3$ initially produces a pale red solution containing $[Co^{II}_2(412)]^+$ which rapidly oxidizes in the presence of air to give $[Co^{III}_2(412)]^{3+}$. Similarly $[Ni^{II}_2(412)]^+$ and $[Fe^{II}_2(412)]^+$ are obtained by reaction of $NiCl_2 \cdot 6H_2O$ or $FeCl_2$, $H_3\text{-}412 \cdot 6HCl$, and $NaOCH_3$ in a 2:1:9 stoichiometric ratio in methanol. These reactions demand a strict exclusion of air, otherwise the $[M^{II}_2(412)]^+$ complexes oxidize to give the mixed-valent complexes $[M^{III}M^{II}(412)]^{2+}$. Oxidation may also be achieved with 0.5 equiv. of iodine or by controlled potential electrolysis; the former reaction has been used in the preparation of $[Ni^{III}Ni^{II}(412)](BPh_4)_2 \cdot CH_3OH$ [496].

The mixed-valent species can be further oxidized to give the fully oxidized $[M^{III}_2(412)]^{3+}$ species. Hetero-dinuclear complexes of nickel and cobalt were prepared by successive metalations of $H_3\text{-}412 \cdot 6HCl$. The not isolated mononuclear cobalt(II) complex $[Co^{II}(412)]^-$ was oxidized to inert $[Co^{III}(412)]$ prior to the addition of $Ni(ClO_4)_2 \cdot 6H_2O$ to give the dark-green species $[Co^{III}Ni^{II}(412)](BPh_4)_2$ [496]. When the metal salts were added in the reverse order, it was also possible to obtain the positional isomer, $[Ni^{II}Co^{III}(412)]^{2+}$ [496].

The formulation of the positional isomers $[Co^{III}Ni^{II}(412)]^{2+}$ and $[Ni^{II}Co^{III}(412)]^{2+}$ is based on their characteristic UV-Vis spectral and electrochemical properties, which are quite different from those of the homo-dinuclear complexes $[Ni_2(412)]^{n+}$ and $[Co_2(412)]^{n+}$. Also, the properties of $[Co^{III}Ni^{II}(412)](BPh_4)_2$ and $[Ni^{II}Co^{III}(412)](BPh_4)_2$ are similar but not identical. Since the electronic absorption spectra and electrochemical properties of solutions of these two complexes remain unchanged over periods of weeks, inter- or intra-molecular metal scrambling reactions can be excluded. Since all homo- and hetero-dinuclear complexes were prepared by methods essentially identical with those

used to prepare $[\text{Co}^{\text{III}}_2(\mathbf{412})]^{3+}$, all are assumed to be discrete, dinuclear species [496].

All complexes underwent two electrochemically and chemically reversible one-electron-transfer reactions which convert the respective $[\text{M}_2(\mathbf{412})]^{n+}$ species. For $\text{M}^{\text{III}}\text{M}^{\text{III}}/\text{M}^{\text{III}}\text{M}^{\text{II}}$ $E_{1/2}^1$ and for $\text{M}^{\text{III}}\text{M}^{\text{II}}/\text{M}^{\text{II}}\text{M}^{\text{II}}$ $E_{1/2}^2$, respectively, -0.40 and -0.84 V ($\text{M} = \text{Co}$), $+0.49$ and $+0.05$ V ($\text{M} = \text{Ni}$), $+0.21$ and -0.33 V ($\text{M} = \text{Fe}$) versus SCE were obtained. Electrochemically generated solutions of $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{412})]^{2+}$ and $[\text{Co}^{\text{II}}_2(\mathbf{412})]^+$ exhibit characteristic electronic absorption spectra, which remain unchanged for days under anaerobic conditions. These species could also be prepared by sodium borohydride reduction of $[\text{Co}^{\text{III}}_2(\mathbf{412})]^{3+}$. The $\text{Co}^{\text{II}}\text{Co}^{\text{II}}$ and $\text{Co}^{\text{III}}\text{Co}^{\text{II}}$ complexes, when exposed to air, readily underwent reoxidation to the red-brown $\text{Co}^{\text{III}}\text{Co}^{\text{III}}$ complex. The respective electron-transfer processes are thus also chemically reversible. All mixed-valent complexes are very stable to disproportionation. $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{412})](\text{BPh}_4)_2$ and $[\text{Ni}^{\text{II}}\text{Co}^{\text{III}}(\mathbf{412})](\text{BPh}_4)_2$ also give rise to two consecutive one-electron-transfer processes at $E_{1/2}^1$ ($\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$) and $E_{1/2}^2$ ($\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$): $+0.55$, -0.71 V for the first complex and $+0.60$, -0.86 V for the second one respectively. Comparison of the electrochemical properties of $[\text{Co}^{\text{III}}\text{Ni}^{\text{II}}(\mathbf{412})]^{2+}$ and $[\text{Ni}^{\text{III}}\text{Ni}^{\text{II}}(\mathbf{412})]^{2+}$ reveals the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ redox potential in the dinuclear complexes to be influenced by the oxidation state of the adjacent metal ion. At 77 K the mixed-valent $\text{Ni}^{\text{III}}\text{Ni}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ complexes exhibit localized and delocalized valences, respectively, as indicated by UV-Vis, EPR and ^{57}Fe Mössbauer spectroscopy [496].

Analogously, $[\text{Ni}^{\text{II}}\text{Fe}^{\text{II}}(\mathbf{412})]^+$ was obtained by reaction of $[\text{Ni}^{\text{II}}(\mathbf{412})]^-$, prepared in situ from $\text{H}_3\text{-}\mathbf{412}\cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and NEt_3 , with 1 equiv. of anhydrous FeCl_2 in methanol. It was isolated as the one-electron-oxidized complex $\{[\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}(\mathbf{412})]_2(\text{Cl})\}(\text{BPh}_4)_3$ by exposing the reaction mixture to air and adding excess NaBPh_4 [496]. $\{[\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}(\mathbf{412})]_2(\text{Cl})\}(\text{BPh}_4)_3$ consists of a face-sharing bioctahedral NiFe complex, $[\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}(\mathbf{412})]^{2+}$ with a $\{\text{N}_3\text{Ni}^{\text{III}}(\mu\text{-SR})_3\text{Fe}^{\text{III}}\text{N}_3\}$ core structure [496] (Fig. 308).

Mössbauer spectra show the presence of a low-spin iron(III) ion. Room temperature magnetic data ($\mu_{\text{eff}} = 2.3\mu_{\text{B}}$) suggest an intramolecular antiferromagnetic

exchange interaction between the Ni^{II} ($S_1 = 1$) and low-spin Fe^{III} ($S_2 = 1/2$) ions.

A cyclic voltammogram of $\{[\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}(\mathbf{412})]_2(\text{Cl})\}(\text{BPh}_4)_3$ in DMF displays two electrochemically reversible one-electron steps at $E_{1/2}^1 = +0.45$ V ($\text{Ni}^{\text{III}}\text{Fe}^{\text{III}}/\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}$) and at $E_{1/2}^2 = -0.43$ V ($\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}/\text{Ni}^{\text{II}}\text{Fe}^{\text{II}}$) versus SCE. There is a clearly discernible mutual influence of the constituent iron(III) and nickel(II) ions on the respective $\text{M}^{\text{III}}/\text{M}^{\text{II}}$ potentials. Comparison with the electrochemical properties of homo-dinuclear complexes $[\text{Ni}_2(\mathbf{412})]^{n+}$ and $[\text{Fe}_2(\mathbf{412})]^{n+}$ reveals that the ferric ion raises the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ couple by ca. $+400$ mV to more anodic potentials, whereas the divalent Ni ion shifts the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ potential to more cathodic potentials [496].

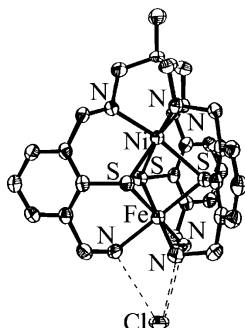
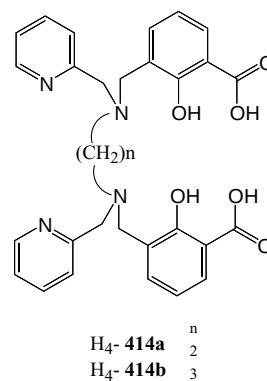
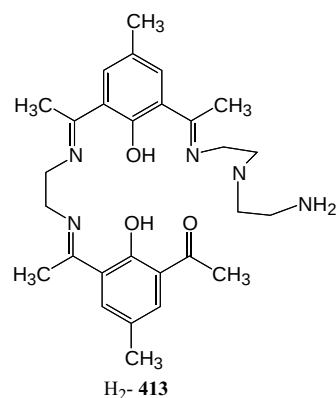


Fig. 308. Structure of $\{[\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}(\mathbf{412})]_2(\text{Cl})\}^{3+}$ (adapted from Ref. [496]).

$[\text{Ni}_2(\mathbf{413})](\text{ClO}_4)_2$, derived from the asymmetrical acyclic ligand $\text{H}_2\text{-}\mathbf{413}$, was prepared by the reaction of 1,5-diamino-3-azamethylpentane and $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 6\text{H}_2\text{O}$ with the [2+1] acyclic nickel(II) complex, synthesized by the 2:1 condensation of 2,6-diacetyl-4-methylphenol and ethylenediamine in the presence of 1 equiv. of $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 6\text{H}_2\text{O}$. This last [2+1] acyclic complex has been also obtained by reaction of the preformed acyclic Schiff base with $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 6\text{H}_2\text{O}$. $[\text{Ni}_2(\mathbf{413})](\text{ClO}_4)_2$ is a mixed spin-state nickel(II) complex where one nickel center is square planar, accommodated into the smaller N_2O_2 cavity provided by the phenolic oxygens and the iminic nitrogens while the other nickel center is octahedral, accommodated into the larger cavity N_3O_3 provided by the phenolic oxygens, the iminic

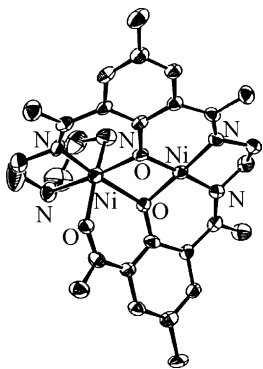
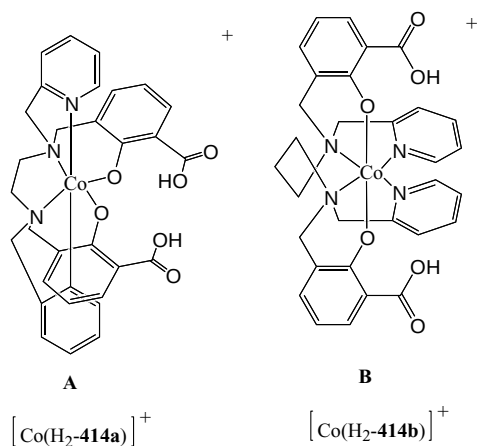


Fig. 309. Structure of $[\text{Ni}_2(\mathbf{413})]^{2+}$ (adapted from Ref. [497]).

and the aminic nitrogens. Diethylenetriamine takes the skew configuration, which inhibits the full cyclization. This leads to one primary amino nitrogen and one acetyl oxygen on both sides of the octahedral nickel completing the fifth and sixth coordination sites (Fig. 309) [497].

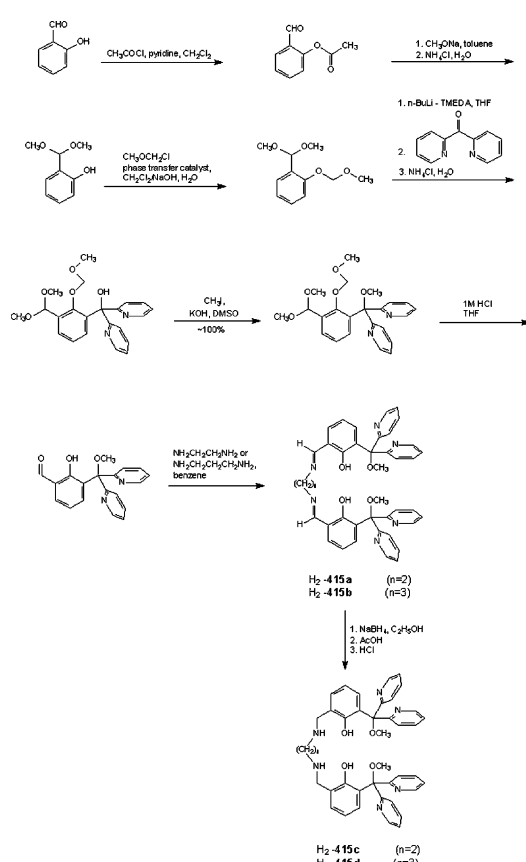
The dinucleating functionalized macroacyclic ligands, $\text{H}_4\text{-414a}$ and $\text{H}_4\text{-414b}$, containing one N_4O_2 and O_2O_2 coordination chamber, forms with the divalent first-row transition metal salts the mononuclear complexes $[\text{M}(\text{H}_2\text{-414a})]$ and $[\text{M}(\text{H}_2\text{-414b})]$ where the metal ion is probably in the N_4O_2 site. The insolubility of these complexes precluded attempts to synthesise bimetallic species [498].



Both of the insoluble pink complexes $[\text{Co}(\text{H}_2\text{-414a})]$ and $[\text{Co}(\text{H}_2\text{-414b})]$ were prepared in DMSO solutions by mixing $\text{Co}(\text{CH}_3\text{COO})_2$ with the respective ligands. They can be oxidized in acetonitrile with ferrocenium hexafluorophosphate to the maroon $[\text{Co}(\text{H}_2\text{-414a})](\text{PF}_6)$ and the dark green $[\text{Co}(\text{H}_2\text{-414b})](\text{PF}_6)$ complexes, which are soluble in common polar organic solvents. The ^1H NMR spectra of these two complexes indicate that both are C_2 symmetric and that the product obtained from oxidation consisted of a single topological isomer in both cases. Also ^1H NMR and absorption spectra indicate that the complexes $[\text{Co}(\text{H}_2\text{-414a})]^+$ and $[\text{Co}(\text{H}_2\text{-414b})]^+$ have the structures **A** and **B**, respectively, where the axial positions are occupied by the pyridine nitrogens and the oxygens of the phenolate groups respectively.

Owing to its **B** structure $[\text{Co}(\text{H}_2\text{-414b})]^+$ cannot form bimetallic complexes and indeed attempts to make them failed. The structure **A** of $[\text{Co}(\text{H}_2\text{-414a})]^+$ appears ideal for forming bimetallic species; however the reaction of $[\text{Co}(\text{H}_2\text{-414a})]^+$ with $\text{M}(\text{CH}_3\text{COO})_2$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+} , Co^{2+} , Mn^{2+}) in the presence of triethylamine and in a variety of solvents, gave evidence for the formation of the expected heterobimetallic species, but attempts to isolate the pure compounds failed. In all cases the material isolated contained varying amounts of the second labile metal. The qualitative evidence suggests that the equilibrium related to the formation of $[\text{CoM}(\mathbf{414})]$ from the reaction of $[\text{Co}(\text{H}_2\text{-414})]$ and $\text{M}(\text{CH}_3\text{COO})_2$ cannot be driven completely in favour of the bimetallic complexes even in the presence of added base [498].

The macroacyclic Schiff bases $\text{H}_2\text{-415a}$ and $\text{H}_2\text{-415b}$ and the related reduced analogues $\text{H}_2\text{-415c}$ and $\text{H}_2\text{-415d}$, prepared according to Scheme 57, react with the appropriate metal acetate or chloride and in the presence of triethylamine to form, after the addition of PF_6^- , the dinuclear complexes $[\text{M}_2(\text{L})](\text{PF}_6)_2$ ($\text{H}_2\text{-L} = \text{H}_2\text{-415a} \cdots \text{H}_2\text{-415d}$) poorly soluble in protic solvent and soluble in acetonitrile or dimethylformamide [499]. In all of these preparations presumably oligomeric complexes were formed first and only after an unusual time of heating did the complexes assemble to the desired products. Fortunately the bimetallic



Scheme 57.

complexes crystallized from the solvent mixtures. In the cases of the manganese(II), iron(II) and iron(III) and cobalt(II) only oligomeric complexes were isolated. In attempting to prepare the diamanganese(II) complex of **H₂-415a**, $[\text{Mn}(\text{H}_2\text{-415a})](\text{PF}_6)_2 \cdot \text{CH}_2\text{CN}$ was isolated [499].

In $[\text{Cu}_2(\text{415a})](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$ the copper(II) ion in the N_2O_2 site is four coordinated square planar while the second copper(II) ion in the outer N_4O_2 site is in a six coordinated environment (Fig. 310a). In $[\text{Cu}_2(\text{415b})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ the copper ion in the inner N_2O_2 site is in a distorted trigonal bipyramidal geometry with the acetonitrile ligand occupying the equatorial plane, whereas the other copper(II) ion in the outer N_4O_2 site is six coordinated, in an octahedral, highly distorted geometry [499] (Fig. 310b).

$[\text{Mn}(\text{H}_2\text{-415c})](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$, obtained in attempting to prepare the dimanganese(II) complex, is stable to aerial oxidation in the solid state but, when dissolved in CH_3CN and exposed to dioxygen, the solution slowly turns brown. If 2 equiv. of LiCl in methanol are added initially to such solutions, they are very rapidly oxidized by O_2 and deep red-brown needles of $[\text{Mn}(\text{415c})(\text{Cl})_2] \cdot \text{H}_2\text{O}$ are deposited. The X-ray structure shows the manganese(IV) ion is octahedrally coordinated in the four coordinated N_2O_2 site of the ligand. The other potentially six coordinating site supports a water molecule (Fig. 310c).

In CH_3CN solutions this manganese(IV) compound is stable and the orange solution is a nonelectrolyte. In methanol the material dissolves to give a purple-blue solution and in dimethylformamide a green solution is observed. In these solutions the compound is a 1:1 electrolyte, indicating the colour changes are the result of Cl^- ion dissociation. Over

time, both the methanol and DMF solutions slowly change colour, suggesting that reduction of the metal ion may occur. In CH_3CN or CH_2Cl_2 solutions, the compound appears to be indefinitely stable. In CH_3CN solution cyclic voltammetry reveals a quasi-reversible wave at +0.07 V and an irreversible wave at +0.87 V versus Ag/AgCl [499].

The dinucleating properties of the Schiff base **H₂-416** arise from the presence of a N_2O_2 Schiff base cavity as the inner binding site and a O_2N_2 donor set derived from the pyridyl groups as the outer binding site. Dropwise introduction of a hot ethanolic solution of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ to **H₂-416** in ethanol in a 1:1 molar ratio gives rise to $[\text{Ni}(\text{416})]$, which reacts with $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in refluxing $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{CN}$ followed by anion exchange with ammonium hexafluorophosphate to afford the isomorphous complexes $[\text{Ni}_2(\text{416})(\text{C}_2\text{H}_5\text{OH})_2](\text{PF}_6)_2$ and $[\text{NiCu}(\text{416})(\text{C}_2\text{H}_5\text{OH})_2](\text{PF}_6)_2$ [500] (Fig. 311) where the nickel(II) ion is located in the inner Schiff base N_2O_2 cavity and exhibits a square planar coordination geometry, while the second metal ion (nickel(II) or copper(II)) occupies the outer O_2N_2 binding site with two ethanol molecules as the axial ligands in an octahedral coordination environment. The two metal ions are bridged by two phenolic oxygen atoms to show a planar $\text{Ni}-\text{O}_2-\text{M}$ four-membered ring. The $\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}$ complex exhibits structural discrepancy in the coordination sphere around the copper(II) center and an elongation of the axial M-O bonds attributed to the Jahn–Teller distortion which is characteristic of octahedral copper(II) complexes. The $\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}$ complex exhibits a smaller metal–metal separation in comparison to the dinickel(II) complex ($\text{Ni} \cdots \text{Cu}$ 2.898 Å cf. $\text{Ni} \cdots \text{Ni}$ 2.950 Å) [500].

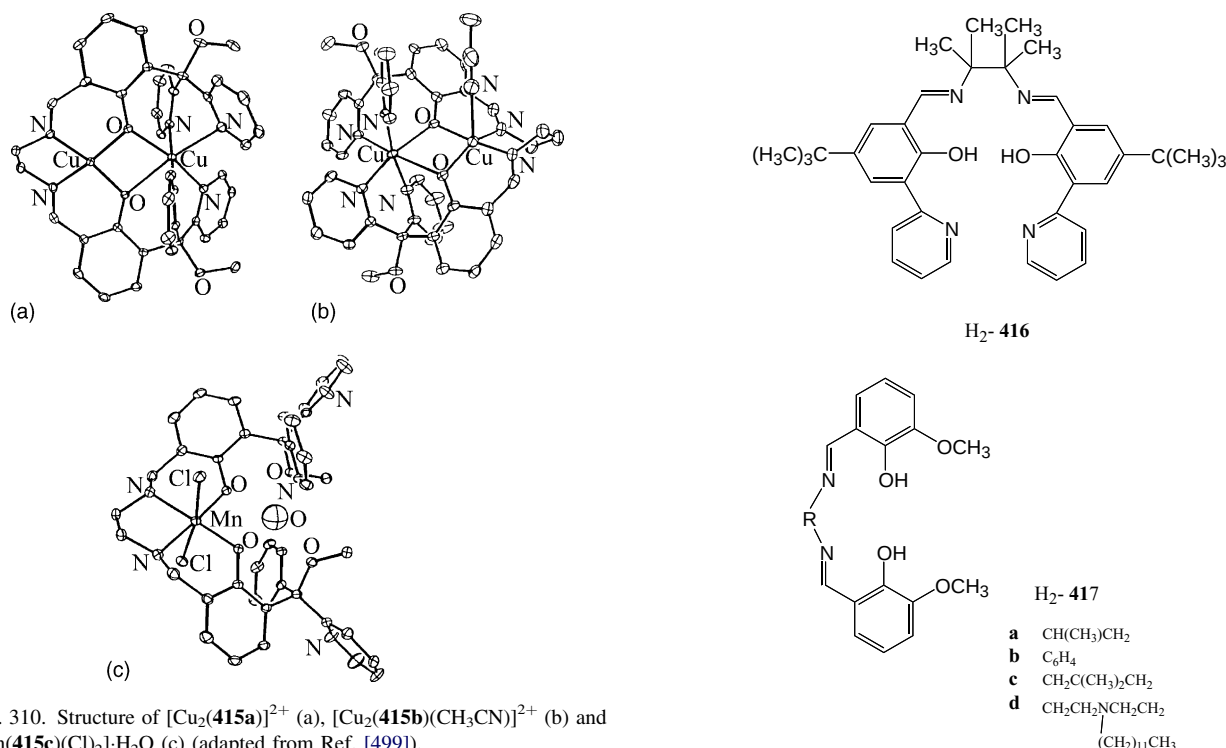


Fig. 310. Structure of $[\text{Cu}_2(\text{415a})]^{2+}$ (a), $[\text{Cu}_2(\text{415b})(\text{CH}_3\text{CN})]^{2+}$ (b) and $[\text{Mn}(\text{415c})(\text{Cl})_2] \cdot \text{H}_2\text{O}$ (c) (adapted from Ref. [499]).

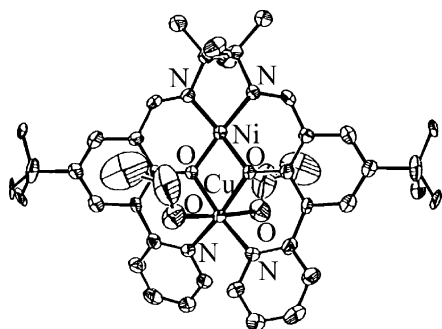


Fig. 311. Structure of $[\text{NiCu}(\mathbf{416})(\text{C}_2\text{H}_5\text{OH})_2]^{2+}$ (adapted from Ref. [500]).

The copper(II), nickel(II), iron(III), tin(II), uranyl(VI) and lanthanide(III) complexes with the Schiff bases $\text{H}_2\text{-207d-e}$ and $\text{H}_2\text{-417a-d}$ have been used for a study of the recognition properties of the external O_2O_2 chamber and for the preparation of heteropolynuclear complexes [5,42,501]. In particular the 1:1 addition complexes between the mononuclear nickel(II) compounds of $\text{H}_2\text{-207d}$ and $\text{H}_2\text{-417a-b}$ with $\text{Sn}(\text{R})_2(\text{Cl})_2$ ($\text{R} = \text{CH}_3$, C_6H_5), $\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-CH}_3)(\text{Cl})_3$ or SnCl_4 have been found to be generally mono-aqua adducts of the tin Lewis acids with the water engaged in hydrogen bonding with the methoxy and phenolic oxygen atoms of the Schiff base ligand. Crystal structure determinations revealed that the mono-aqua adducts of dimethyltin dichloride, which exist in the structures $\{[\text{Ni}(\mathbf{207d})][\text{Sn}(\text{CH}_3)_2(\text{Cl})_2(\text{H}_2\text{O})]\}$ and $\{[\text{Ni}(\mathbf{417a})][\text{Sn}(\text{CH}_3)_2(\text{Cl})_2(\text{H}_2\text{O})]_2\}$, differ in that, in the former the tin(IV) ion is in a trigonal bipyramidal environment, whereas in the latter it is in an octahedral environment as a result of an inter-

molecular $\text{Sn} \cdots \text{Cl}$ contact of 3.615 Å (Fig. 312a and b) [502].

SnCl_2 , SnBr_2 and $\text{Sn}(\text{NCS})_2$ react with $[\text{Ni}(\mathbf{207e})]$ in CH_3CN to form $[\text{NiSn}(\mathbf{207e})(\text{Br})(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{Br})$ (Fig. 312c). The tin(II) ion is coordinated in the outer O_2O_2 coordination chamber to two phenolic and two methoxy oxygen atoms; a bromine ion completes the coordination sphere about the tin(II) ion. The second bromine is ionic [502]. The coordination about tin has been described as skew trapezoidal pyramidal with the bromine atom occupying the apical position [474]. The nickel(II) ion occupies the inner N_2O_2 coordination chamber; one molecule of CH_3CN and one of H_2O complete the octahedral geometry about nickel(II). Each bromide is within hydrogen bonding distance from oxygen of a water molecule coordinated to the nickel in within the asymmetric unit, while it is also within hydrogen bonding distance to a similar type of oxygen in a neighbouring asymmetric unit. In this way, zigzag chains of alternating oxygen atoms and bromide ions, linked by hydrogen bonds, are generated [502].

When the inner coordination chamber is enlarged and contains an additional donor atom, it is possible to accommodate an f-ion in this coordination site. Mononuclear and homo-dinuclear uranyl(VI) complexes have been prepared by reaction of uranyl(VI) salts with the ligands $\text{H}_4\text{-417a-d}$ and $\text{H}_4\text{-418a-b}$; these last ligands were obtained by condensation of 1,5-diamino-3-azapentane or 1,5-diamino-3-aza(dodecyl)pentane with 2-formylsalicylic acid [503]. It was also verified that the Schiff bases, with a donor set N_3O_2 , coordinate the lanthanide ions roughly in their equatorial plane [503]; thus the two coordination chambers N_3O_2 and O_2O_2 of $\text{H}_4\text{-418a}$ and $\text{H}_4\text{-418b}$ seem to be suitable for an easy coordination of 4f-ions.

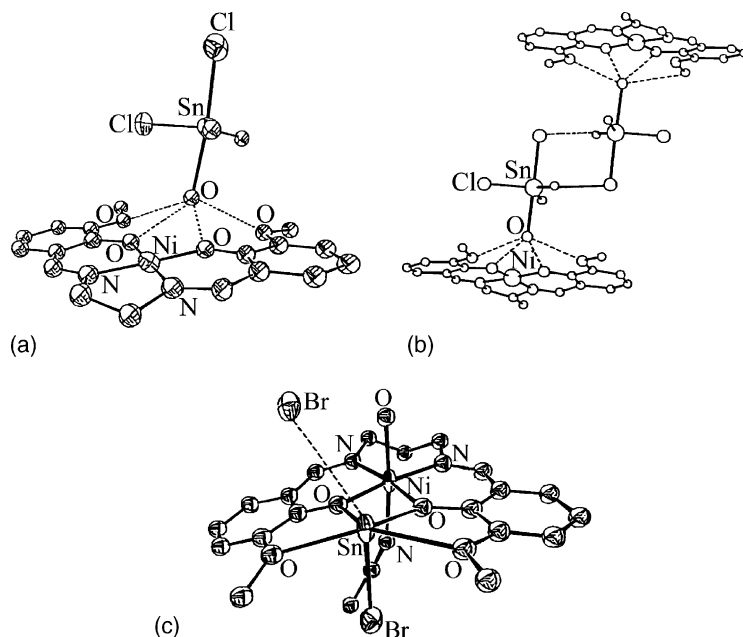
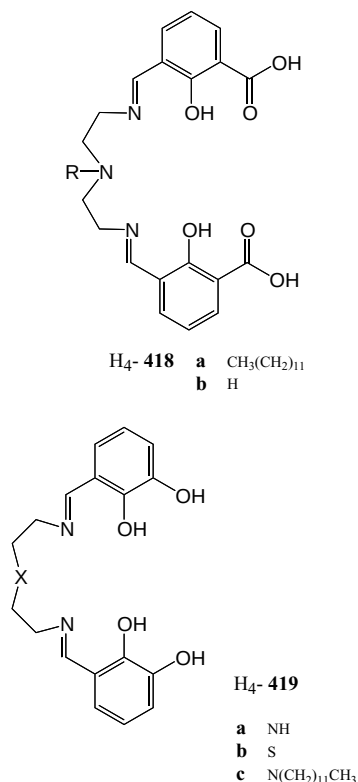


Fig. 312. Structures of $\{[\text{Ni}(\mathbf{207})][\text{Sn}(\text{CH}_3)_2(\text{Cl})_2(\text{H}_2\text{O})]\}$ (a), $\{[\text{Ni}(\mathbf{417})][\text{Sn}(\text{CH}_3)_2(\text{Cl})_2(\text{H}_2\text{O})]_2\}$ (b) and $[\text{NiSn}(\mathbf{207e})(\text{Br})(\text{H}_2\text{O})](\text{Br})$ (c) (adapted from Ref. [502]).



The homo-dinuclear lanthanide(III) complexes $[\text{Ln}_2\text{-(418)}(\text{X})_2]$ have been obtained by reaction of $\text{H}_4\text{-418}$ with the appropriate lanthanide(III) salt or by template procedure [493]. In $[\text{Gd}_2(\text{418a})(\text{NO}_3)_2] \cdot 4\text{H}_2\text{O}$ an antiferromagnetic interaction ($J = -0.211 \text{ cm}^{-1}$) occurs, possibly due to a superexchange mechanism through the bridging atoms [493,503].

Attempts to prepare mononuclear and hetero-dinuclear lanthanide(III) complexes with $\text{H}_4\text{-418}$ failed, whereas a

successful procedure was followed with the ligands $\text{H}_4\text{-419a-c}$ [493,503].

The mononuclear lanthanide(III) complexes, where the Schiff base behaves as neutral pentadentate, undergo transmetallation reaction when treated with uranyl(VI) salts, giving rise to the mononuclear and homo-dinuclear uranyl(VI) complexes.

In the mononuclear complex $[\text{UO}_2(\text{H}_2\text{-419a})] \cdot \text{DMF}$, (Fig. 313a) the compartmental ligand binds equatorially to the uranyl(VI) group using the inner coordination chamber leading to seven coordinated uranium(VI) ion in a distorted bipyramidal coordination geometry. The DMF molecule is hydrogen bonded to the phenolic oxygens of the ligand. The ability of $\text{H}_4\text{-419a-c}$ to act as compartmental dinucleating agents toward f-ions has also been verified on the complexes $[\text{UO}_2)_2(\text{419a})(\text{DMSO})]$ (Fig. 313b) and $[(\text{UO}_2)_2(\text{419a})(\text{DMF})]$ (Fig. 313c). The chelating ligand coordinates the inner uranyl(VI) ion as in the mononuclear complex $[\text{UO}_2(\text{H}_2\text{-419a})](\text{DMF})$, while the outer uranyl(VI) ion is coordinated by four oxygen atoms of the dinucleating ligand and by the oxygen atom of the solvent molecule [503].

Differently from the outer linear uranyl(VI) group in the dinuclear $[\text{UO}_2)_2(\text{419a})(\text{S})]$ complexes, which reaches its equatorial pentacoordination through the coordination of a solvent molecule (DMSO, DMF, H_2O , etc.), the outer lanthanide(III) ion can reach its coordination saturation through oligomerization. Thus in the lanthanide(III) complexes with $\text{H}_4\text{-419a-c}$ a dimerization through the phenolic oxygens, which fills the coordination sphere about the rare earth metal ion, has been suggested. This causes low solubility also for the complexes derived from $\text{H}_2\text{-207d}$ or

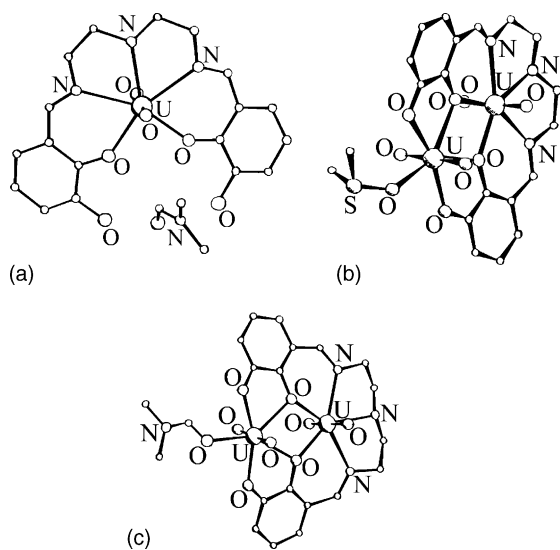


Fig. 313. Structures of $[\text{UO}_2(\text{H}_2\text{-419a})] \cdot \text{DMF}$ (a), $[(\text{UO}_2)_2(\text{419a})(\text{DMSO})]$ (b) and $[(\text{UO}_2)_2(\text{419a})(\text{DMF})]$ (c) (adapted from Ref. [503]).

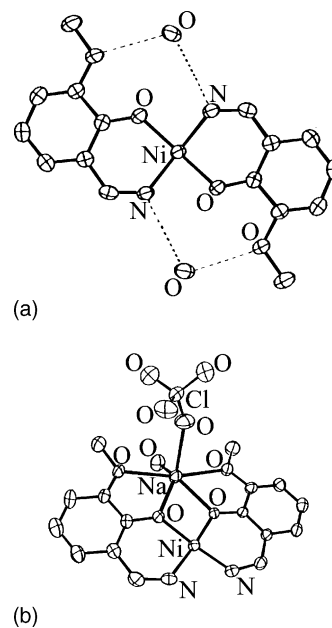
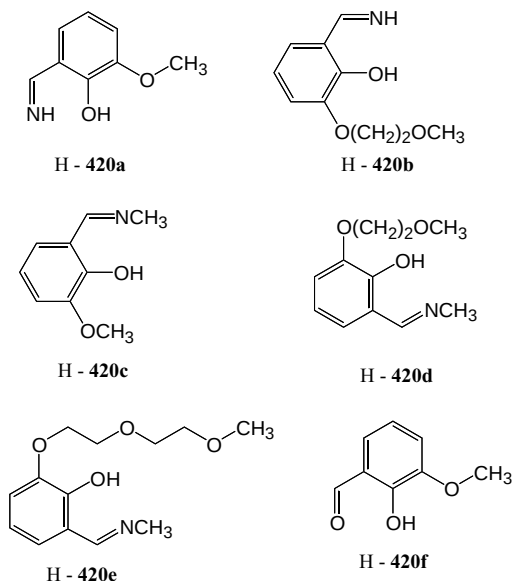


Fig. 314. Structures of $[\text{Ni}(\text{420a})_2] \cdot 2\text{H}_2\text{O}$ (a) and $[\text{NiNa}(\text{420a})_2](\text{ClO}_4) \cdot (\text{H}_2\text{O})$ (b) (adapted from Ref. [504]).

H₄-**419c** in spite of the introduction of a long aliphatic chain [493,503].

The direct condensation of *o*-vanillin with ammonia fails to yield the expected Schiff base H-**420a**, but the related mononuclear complexes [M(**420a**)₂] (M = Ni²⁺, Cu²⁺) are easily prepared [504]. Reaction of these mononuclear complexes with sodium or lithium perchlorate in acetone affords the complexes [NiM(**420a**)₂](ClO₄) which precipitate from the reaction mixture as orange powders. Due to the insolubility of KClO₄ in acetone, the related potassium complex was obtained in the [NiK(**420a**)₂(I)] form.



In [Ni(**420a**)₂] $\cdot$ 2H₂O (Fig. 314a) the two ligands coordinate the nickel ion in a *trans* configuration. The chromophore NiN₂O₂ adopts a perfectly planar geometry. Two water molecules are involved in pattern of hydrogen bonds which stabilize the *trans* configuration around each nickel ion and connect indirectly different [Ni(**420a**)₂] units [504].

In [NiNa(**420a**)₂](ClO₄)(H₂O)] (Fig. 314b) the NiN₂O₂ chromophore adopts a *cis* configuration so that the two ligands are organized around the nickel ion to create an external binding site via four oxygen atoms from the side arms and the phenolate groups. The sodium cation affixes itself to this site and achieves its environment with two oxygen atoms coming from a water molecule and the perchlorate anion. Its coordination polyhedron is the rather unusual pentagonal pyramidal which is probably imposed by the rigidity of the [Ni(**420a**)₂] backbone. The coordination around the nickel ion is approximately square planar [504].

The key points of the hetero-dinuclear formation of [NiM(**420a**)₂](X) (X = ClO₄[−] or I[−]) are the assembly of two imine molecules around the nickel ion to form a *trans*-NiN₂O₂ chromophore and then, in the presence of Li⁺, Na⁺, or K⁺ cations, the alteration of the *trans*-form to *cis*-form with the concomitant creation of an external O₄ binding site. It may be emphasized that the assembling process does not cause any dimerization and/or modification of the coordina-

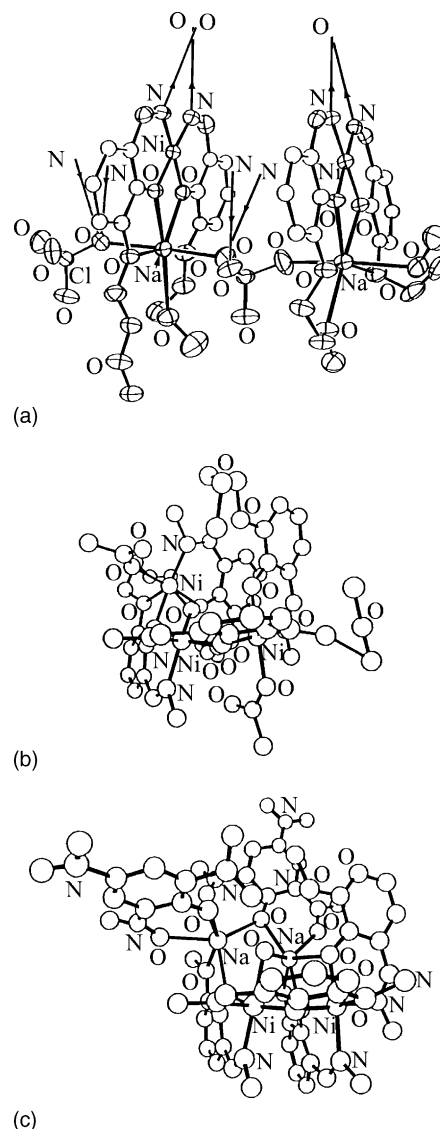


Fig. 315. Structures of [Ni₂Na₂(**420b**)₄(μ-ClO₄)(ClO₄)] (a), [Ni₃(**420d**)₄(CH₃COO)₂(H₂O)₂] (b) and Ni₂Na₂(**420c**)₄(picrate)(H₂O)] (c) (adapted from Refs. [505,506]).

tion sphere of the ions. Evaluation of the stability constants via the line width of the ²³Na NMR signal shows Na⁺ is significantly favoured over Li⁺ and K⁺ in acetone solution.

By using a synthetic procedure identical to that employed for [Ni(**420a**)₂] $\cdot$ 2H₂O, [Ni(**420b**)₂] was obtained which reacts with NaClO₄ to yield [NiNa(**420b**)₂](ClO₄) [505]. The most important and unexpected features of the structure (Fig. 315a) originate in the contribution afforded by the perchlorate anions to the organization of the system. First, two independent monomeric subunits are bridged to form the dimeric entity [NiNa(**420b**)₂](ClO₄)₂ while the second ClO₄[−] anion acts as a terminal ligand. Then a network of hydrogen bonds from the imino NH groups to the oxygen atoms of the bridging and terminal ClO₄[−] anions links two symmetrically related dimers to yield a dimer of dimers [505].

Within each of the monomeric species $\{\text{NiNa}(\mathbf{420b})_2(\text{ClO}_4)\}$ two deprotonated Schiff base ligands are assembled around the nickel ion so that the resulting chromophore NiN_2O_2 adopts a *cis* (or *syn*) configuration while a *trans* (or *anti*) configuration most likely exists in the monometallic precursor $[\text{Ni}(\mathbf{420b})_2]$. The *syn* configuration leads to the formation of an outer pseudo-crown unit comprising six potentially donor sites. Surprisingly, the way in which the oxygenated side arms are involved in Na binding differs in the two $\{\text{NiNa}(\mathbf{420b})_2(\text{ClO}_4)\}$ units. Indeed, one sodium ion is bonded to the six oxygen atoms of its related ligands $[\mathbf{420b}]^-$ and completes its environment with an oxygen coming from the bridging ClO_4^- . The other sodium ion is surrounded by five oxygen atoms from its ligands $[\mathbf{420b}]^-$ and two oxygens from the two ClO_4^- anions which are bridging and terminal, respectively. Finally, it appears that the four constituents of the system are intimately involved in the assembling process to give a highly ordered solid state structure. The monometallic precursor $[\text{Ni}(\mathbf{420b})_2]$ likely reacts with NaClO_4 in its *trans* configuration to yield a mixed-metal NiNa species which has an inner *cis*- $\text{N}_2\text{O}_2\text{Ni}$ chromophore and can accommodate the sodium ion in the outer pseudocavity. The ClO_4^- anions not only are integral parts of the structure but also participate in the organizing process. Indeed, formation of a dimeric entity is achieved by a bridging ClO_4^- while hydrogen bonds from the imino groups to terminal and bridging ClO_4^- link two dimers to yield a dimer of dimers [505].

3-Methoxy-*N*-methylsalicylaldimine (H-**420c**) and 3-(2-methoxyethoxy)-*N*-methylsalicylaldimine (H-**420d**) react with NiSO_4 or $\text{Ni}(\text{CH}_3\text{COO})_2$ in a 1:0.5 or 1:0.8 ratio to form respectively $[\text{Ni}(\mathbf{420c})_2]$ and $[\text{Ni}_3(\mathbf{420d})_4(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ [506].

In the trinuclear complex (Fig. 315b), the stereochemistry of each nickel(II) ion is octahedral. The oxygenated side arms are involved in metal cation binding; two of these oxygenated side arms are involved in nickel(II) coordination, while the other two are simply hovering about the structure. Ni(2) and Ni(3) are approximately within the same plane, while Ni(1) is located above and to the left. Two water molecules are present in the coordination spheres of these atoms. Ni(2) and Ni(3) share one water molecule, while Ni(1) and Ni(2) share a second. Two acetate residues complete the octahedral array: one coordinates to Ni(1) and the other coordinates to Ni(3).

$[\text{Ni}(\mathbf{420c})_2]$, which is a dimer, reacts with sodium picrate in a 1:1 ratio and in $\text{CHCl}_3/\text{acetone}$ solution under reflux to form $[\text{Ni}_2\text{Na}_2(\mathbf{420c})_4(\text{picrate})_2(\text{H}_2\text{O})]$. The structure of this tetranuclear complex (Fig. 315c) shows the picrate counter anion is an integral part of the complex. The nickel cluster also contains a water molecule that is directly involved in the formation (and organization) of the complex. The methoxy side arms, designed to participate in binding by forming a pseudo-crown subunit that binds the sodium ion, coordinate very differently. Two of the methoxy groups bind sodium, and one binds nickel, but the fourth is too far away from

sodium to be directly involved in binding. Each nickel ion is six coordinated [506].

The nickel(II) complexes are able to transfer alkali picrate from H_2O into CHCl_3 solution [506]. The nickel(II) ion can act as a template to allow the assembly of the dimeric, cation-selective inclusion complexes from the imines H-**420c**, H-**420d** and H-**420e**, which can be prepared by monoalkylation of 2,3-dihydroxybenzaldehyde with appropriate bromide derivative and condensation with methylamine [507]. The resulting complexes are able to extract alkali metal ions efficiently from aqueous solution forming $[\text{NiM}(\mathbf{420c})_2]^+$, $[\text{NiM}(\mathbf{420d})_2]^+$ and $[\text{NiM}(\mathbf{420e})_2]^+$ with selectivities that are dependant on both the structure of the polyether chain and on the structure of the nickel(II) chelate. $[\text{Ni}(\mathbf{420d})_2]$ extracts metal ions effectively even when generated in situ [507]. The ability of $[\text{Ni}(\mathbf{420d})_2]$ to transport alkali metal ions selectively into chloroform solution was tested with the picrate extraction technique. H-**420d** is unable to transport any alkali metal ion examined into chloroform solution, however the complex $[\text{Ni}(\mathbf{420d})_2]$ functions as an ionophore and is able to transport almost 50% of the sodium ion present into chloroform [507].

$[\text{Ni}(\mathbf{420d})_2]$ displays substantial cation selectivity; its ability to extract Na^+ (44%) may be compared with its ability to extract Li^+ (30%), K^+ (14%), Rb^+ (13%), or Cs^+ (15%). Therefore, the rigid geometry of the transition-metal chelate has partially preorganized the flexible iminic ligand H-**420d** and has generated a cation-selective ionophore.

$[\text{Ni}(\mathbf{420c})_2]$, with four oxygens available to bind an alkali metal ion, preferentially extracts Li^+ (63%), in comparison to Na^+ (40%), K^+ (16%), Rb^+ (15%), or Cs^+ (16%). It is interesting that this selectivity does not parallel the selectivity of the crown-ether 12-crown-4, which prefers Na^+ in organic solvents. This result is presumably a reflection of the geometric constraints imposed by the tetrahedral nickel(II) ion [507].

The increasing length of the polyether chain causes a decrease in selectivity, toward larger cations caused by the increased flexibility of the ligand. Although $[\text{Ni}(\mathbf{420e})_2]$ does show some preference for Na^+ , extraction of K^+ by this complex is almost as efficient [507].

$[\text{Ni}(\mathbf{420d})_2]$ is square planar, with a *trans*- N_2O_2 configuration. It can be electrochemically oxidized and reduced irreversibly. Addition of an excess of NaClO_4 to an acetone solution of $[\text{Ni}(\mathbf{420d})_2]$ leads to a substantial loss of the visible absorption and a blue shift of the charge-transfer band to 366 nm, which also increases substantially in intensity. These solutions exhibit paramagnetically shifted proton NMR spectra, and the Evans method gives a solution magnetic moment of $2.8\mu_B$, based on the $[\text{Ni}(\mathbf{420d})_2]$ monomer. The complex with bound sodium ion appears to contain octahedral nickel(II) ions and to be dinuclear. Thus, the presence of the sodium ion induces a transition in the ionophore complex, suggesting that the binding affinity is large enough to force the metal center out of its lowest energy mononuclear conformation. The complex is hardly

oxidized and reduced in the presence of the sodium ion. Vapour-pressure osmometry studies performed in 0.1 M NaClO₄ acetone solution give a molecular weight, consistent with a dinuclear entity containing the {Ni₂(**420d**)₄} unit. This is evidence that the complex with bound sodium ion is dinuclear in a solvent in which the complex is monomeric and square-planar in the absence of the alkali-metal cation. Thus, addition of dry NaClO₄ to an acetone solution of [Ni(**420d**)₂] causes a shift from a mononuclear square planar complex to a dinuclear complex with bound sodium ion [508].

3-Methoxysalicylaldehyde (H-**420f**) reacts with Gd(NO₃)₃·5H₂O in the presence of CsOH to form the homotrimeric complex [Gd₃(**420f**)₃(OH)₂(NO₃)₂(H₂O)₄](NO₃)₂·(H₂O)₄ [509]. The cation [Gd₃(**420f**)₃(OH)₂(NO₃)₂·(H₂O)₄]²⁺ contains a Gd₃O₅ core where the three gadolinium ions are held together by a multiple bridging network supported by five oxygen atoms. Each of the two hydroxo ions is simultaneously bound to the three gadolinium ions, which otherwise are linked two by two by monatomic and tetratomic bridges afforded by the [**420f**][−] ligands. The monatomic bridges are formed by the phenolato oxygens while the polyatomic pathways go through the phenolato and methoxo groups. The aldehyde oxygen atoms bind terminally to the metal ions. To achieve their environment two lanthanide ions make use of a water molecule and a bidentate nitrato ion while the third metal ion resorts to two water molecules. The two first ions are nine coordinated and the third one eight coordinated. The intramolecular Gd···Gd distances range from 3.559 to 3.573 Å while the intermolecular distances vary from 8.188 to 9.734 Å. The hydroxo ions, the coordinated and the uncoordinated water molecules, and the uncoordinated nitrato ions participate in an extended network of hydrogen bonds [509] (Fig. 316).

Starting from bis(3-methoxysalicylaldehydato)copper(II), [Cu(**420f**)₂], which contains a CuO₄ chromophore, different routes to obtain discrete dinuclear Cu^{II}Ln^{III} complexes (Ln = Pr³⁺, Eu³⁺, Gd³⁺, Yb³⁺) have been developed [510]. The pairs of chromophores occurring in the resulting complexes are either Cu(O₂O₂)/Ln(O₂O₂) or Cu(N₂O₂)/Ln(O₂O₂), the coordination sphere of the lanthanide(III) ions being completed, in both cases, with six oxygen atoms afforded by three nitrato groups (Scheme 58).

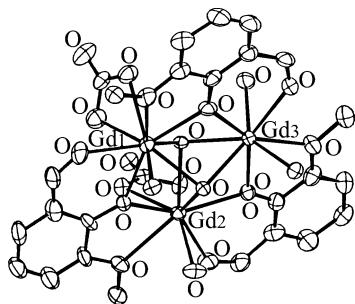
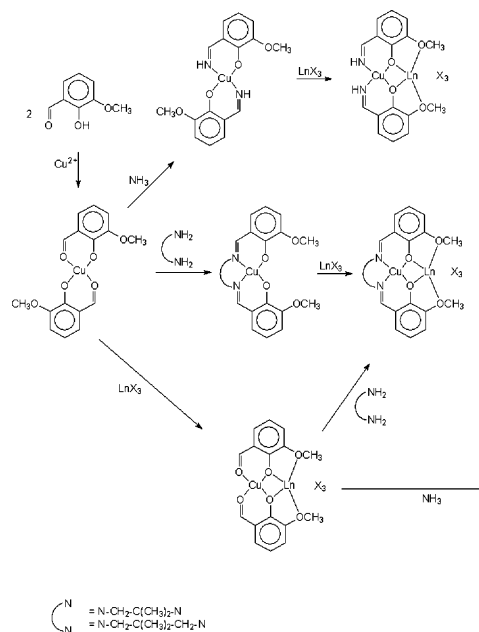


Fig. 316. Structure of [Gd₃(**420f**)₃(OH)₂(NO₃)₂(H₂O)₄]²⁺ (adapted from Ref. [509]).



Scheme 58.

[Cu(**420f**)₂] reacts with NH₃ to afford [Cu(**420a**)₂], which, upon addition of alkali-metal ions, yields [CuM(**420a**)₂](X) (M⁺ = Na⁺, Li⁺ or K⁺ and X[−] = ClO₄[−] or NO₃[−]). Again an alteration of configuration of the imine molecules from *trans* to *cis* with the concomitant creation of an external O₄ binding site occurs on going from [Cu(**420a**)₂] to [CuM(**420a**)₂](X), [510]. This process has been used also to prepare dimetallic CaBa and CuCa complexes.

Substituting H₂N–R–NH₂ for NH₃ has led to the isolation of structurally characterized examples of discrete binuclear complexes. This process of self-assembly and organization is not restricted to the complexes of the imino ligand H-**420a** but may be applied to the complexes of the precursor 3-methoxy salicylaldehyde H-**420f**. Then the resulting dinuclear species [MLn(**420f**)₂(NO₃)₃] may be reacted with ammonia or a suitable diamine to obtain the complexes [MLn(**420a**)₂(NO₃)₃], and [MLn(**417**)(NO₃)₃]. Using these different processes the complexes [CuGd(**420f**)₂(NO₃)₃], [CuGd(**420a**)₂(NO₃)₃], [CuYb(**420a**)₂(NO₃)₃], [CuEu(**420a**)₂(NO₃)₃], [CuPr(**420a**)₂(NO₃)₃], [CuGd(**417a**)₂(NO₃)₃], and [CuGd(**417c**)(NO₃)₃] have been prepared [510].

The reaction of [Cu(**417c**)] or [Ni(**417c**)] with Ln(NO₃)₃·6H₂O (Ln = La³⁺...Lu³⁺ except promethium) in acetone leads to the formation of [CuLn(**417c**)(NO₃)₃(CH₃COCH₃)] and [NiLn(**417c**)(NO₃)₃(CH₃COCH₃)] [509–511]. The spin state of the nickel(II) ion depends on the nature of the diimino chain present in the Schiff base ligand. Shortening the chain from N–C–C–C–N to N–C–C–N prevents the axial coordination of solvent molecules and stabilizes the low-spin state of the nickel(II) ion.

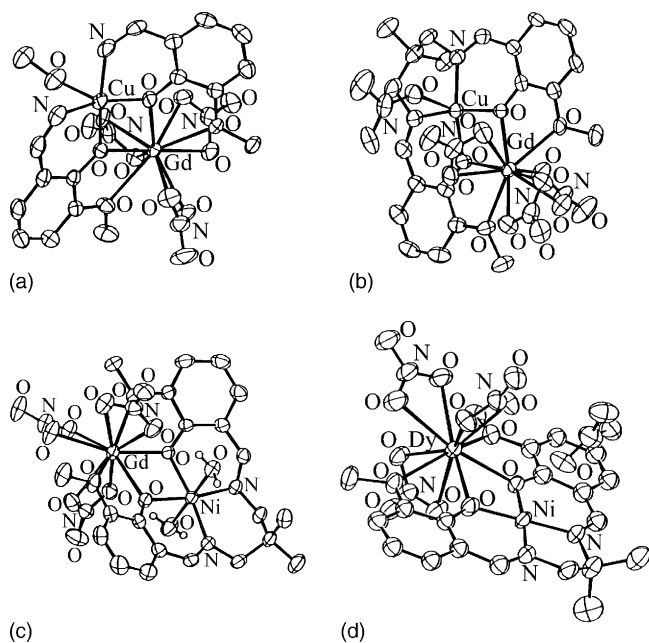


Fig. 317. Structures of $[\text{CuGd}(\mathbf{420a})_2(\text{NO}_3)_3(\text{CH}_3\text{OH})]$ (a), $[\text{CuGd}(\mathbf{417c})-(\text{NO}_3)_3](\text{CH}_3\text{COCH}_3)]$ (b), $[\text{NiGd}(\mathbf{417c})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$ (c) and $[\text{NiDy}(\mathbf{417c})(\text{NO}_3)_3]$ (d) (adapted from Ref. [510]).

At first sight, the structures of $[\text{CuGd}(\mathbf{420a})_2(\text{NO}_3)_3(\text{CH}_3\text{OH})]$ and $[\text{CuGd}(\mathbf{417c})(\text{NO}_3)_3(\text{CH}_3\text{COCH}_3)]$ (Fig. 317a and b) [510] offer great similitudes. Indeed, in each unit the central region is occupied by copper(II) and gadolinium(III) ions which are bridged one to the other by two phenolato oxygen atoms from two $[\mathbf{420a}]^-$ or one $[\mathbf{417c}]^{2-}$ and with $\text{Cu} \cdots \text{Gd}$ separations of 3.484 and 3.523 Å, respectively. The copper(II) ion adopts a square pyramidal coordination mode, the equatorial N_2O_2 donors being afforded by two $[\mathbf{420a}]^-$ or one $[\mathbf{417c}]^{2-}$ while the axial position is occupied by an oxygen atom from a solvent molecule. The gadolinium(III) ion is 10 coordinated. In addition to the two phenolate oxygens, the rare earth ion completes its environment with two oxygens from the methoxy side arms and six oxygens coming from the three bidentate nitrato ions. The separations between metal ions belonging to neighbouring molecules are large: the $\text{Cu} \cdots \text{Cu}$ separations are 8.346 Å for $[\text{CuGd}(\mathbf{420a})_2(\text{NO}_3)_3]$ and 7.952 Å for $[\text{CuGd}(\mathbf{417c})(\text{NO}_3)_3]$ while values of 8.351 and 8.906 Å are observed for $\text{Gd} \cdots \text{Gd}$ and values of 6.271 and 7.848 Å for $\text{Cu} \cdots \text{Gd}$. They preclude any significant intermolecular magnetic interaction [509]. A quantitative analysis of the magnetic properties of the CuGd complexes shows that the interaction is ferromagnetic with a J constant varying from 4.8 to 7.0 cm^{-1} .

Also $[\text{CuGd}(\mathbf{417a})(\text{NO}_3)_3] \cdot \text{CH}_3\text{COCH}_3$ has been structurally characterized as a genuine example of a strictly dinuclear complex. Its magnetic behaviour demonstrates undoubtedly the ferromagnetic nature of the copper(II)–gadolinium(III) interaction [510]. The unit cell contains four discrete entities $[\text{CuGd}(\mathbf{417a})(\text{NO}_3)_3]$ and intervening

acetone molecules. The central region of the structure is occupied by the copper(II) and gadolinium(III) ions which are bridged one to the other via the two phenolic oxygen atoms of the ligand $[\mathbf{417a}]^{2-}$. The four atoms of the GdO_2Cu network roughly form a plane. The copper···gadolinium separation is 3.428 Å. The copper(II) ion completes its coordination sphere with two imine, nitrogen atoms from $[\mathbf{417a}]^{2-}$. The four atoms of the N_2O_2 chromophore are almost coplanar. The copper(II) ion is pulled out the equatorial plane by 0.107 Å in spite of the absence of any apical ligand. The gadolinium ion is 10 coordinated. In addition to the two phenolic oxygens, the rare earth achieves its environment with two methoxy oxygen atoms from $[\mathbf{417a}]^{2-}$ and six oxygen atoms coming from three bidentate nitrato groups. Again the separations between metal ions belonging to neighbouring molecules are large ($\text{Gd} \cdots \text{Cu} = 7.730 \text{ Å}$, $\text{Gd} \cdots \text{Gd} = 9.084 \text{ Å}$, and $\text{Cu} \cdots \text{Cu} = 8.010 \text{ Å}$) and preclude any significant intermolecular interaction [510].

$[\text{NiGd}(\mathbf{417c})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$, prepared following the same procedure used for $[\text{CuGd}(\mathbf{417c})(\text{NO}_3)_3]$, [510] (Fig. 317c) is a dinuclear entity where the gadolinium(III) and nickel(II) ions are doubly bridged by the phenoxo oxygen atoms of ligand $[\mathbf{417c}]^{2-}$. The four atoms of the GdO_2Ni network are almost coplanar. The nickel ion occupies the inner coordination site and has a distorted octahedral environment. The equatorial plane consists of two oxygen and two nitrogen atoms from the ligand $[\mathbf{417c}]^{2-}$. The four N_2O_2 atoms are almost coplanar. The apical positions are occupied by the oxygen atoms of two water molecules. The gadolinium ion is 10 coordinated, four oxygen donors being afforded by $[\mathbf{417c}]^{2-}$ and six by three bidentate nitrato ions. This environment is similar to those of the related GdCu complexes. The separations between metal ions belonging to neighbouring molecules are large ($\text{Gd} \cdots \text{Ni} = 6.711 \text{ Å}$, $\text{Gd} \cdots \text{Gd} = 8.894 \text{ Å}$, and $\text{Ni} \cdots \text{Ni} = 8.306 \text{ Å}$) and preclude any significant intermolecular magnetic interaction. This conclusion is not weakened by the presence of two intermolecular hydrogen bonds. Indeed, they link the oxygens of the water molecules with the oxygen atoms of two nitrato ions belonging to symmetry-related units. They are unable to support any interaction between the two metal ions [510]. The temperature dependence of the magnetic susceptibility in the range 4–300 K indicates that the gadolinium(III)–nickel(II) interactions is ferromagnetic ($J = 3.6 \text{ cm}^{-1}$) [511,512].

In the isomorphous complexes $[\text{CuCe}(\mathbf{417c})(\text{NO}_3)_3]$, $[\text{CuYb}(\mathbf{417c})(\text{NO}_3)_3]$ and $[\text{NiDy}(\mathbf{417c})(\text{NO}_3)_3]$ the central region of the structure is occupied by the copper(II) or nickel(II) and the lanthanide(III) ions which are bridged one to the other by two phenolato oxygen atoms from the ligand. The four atoms of the bridging entity are not exactly coplanar which leads to a roof-shaped MO_2Ln core. The acetone molecule is axial with respect to the metal(II) ion, but not coordinated to it in the case of the NiDy complex and at best, semi coordinated for the CuCe and CuYb complexes. The copper ion adopts a square-based pentagonal coordina-

tion mode, the equatorial N_2O_2 donors are from $[\mathbf{417c}]^{2-}$. The copper ion protrudes out of the mean N_2O_2 plane by 0.11–0.12 Å. The geometry around the nickel ion is square planar. The lanthanide(III) ion is 10 coordinated. In addition to the two phenolate oxygen atoms, the coordination sphere contains two oxygen atoms from the OCH_3 side arms of $[\mathbf{417c}]^{2-}$ and six oxygen from the three bidentate nitrate ions. The separations between metal ions belonging to neighbouring dinuclear units, much larger than the related intramolecular $\text{M} \cdots \text{Ln}$ separations, preclude any significant intermolecular interaction (Fig. 317d).

A structural study of the copper(II)–europium(III) and nickel(II)–europium(III) complexes show that these complexes are also isomorphous. The isomorphism of NiLn and CuLn complexes and the diamagnetism of the nickel(II) ion allowed an empirical evaluation of the effect of the crystal field on the magnetic properties as well as an approach towards the nature of the coupling between the copper(II) and the lanthanide(III) ions in the $[\text{CuLn}(\mathbf{417c})(\text{NO}_3)_3(\text{CH}_3\text{COCH}_3)]$ complexes [511]. The Cu–Ln interaction was proposed to be antiferromagnetic for $\text{Ln} = \text{Ce}^{3+}$, Nd^{3+} , Sm^{3+} , Tm^{3+} , and Yb^{3+} , and ferromagnetic for $\text{Ln} = \text{Gd}^{3+}$, Tb^{3+} , Dy^{3+} , Ho^{3+} and Er^{3+} ; however, the CuPr and the CuEu pairs are devoid of any significant interaction along with the CuLa and CuLu pairs in accordance with the nonmagnetic nature of the ground state for these lanthanide ions [511,512].

The reaction of $[\text{Cu}(\mathbf{417c})] \cdot 2\text{H}_2\text{O}$ with $\text{Gd}_2(\text{thd})_6$ ($\text{H-thd} = 2,2,6,6$ -tetramethyl-heptane-3,5-dione) in methanol forms $[\text{CuGd}(\mathbf{417c})(\text{CH}_3\text{OCOO})(\text{thd})_2]$. The same complex has been obtained in a better yield by mixing $\text{Cu}(\mathbf{417c}) \cdot 2\text{H}_2\text{O}$ with a methanolic solution of H-thd and the equivalent amount of $\text{CsOH} \cdot \text{H}_2\text{O}$ and then adding GdCl_3 [513]. Bases favour the formation of monomethyl carbonate. CO_2 is taken up spontaneously from air at room temperature, under very mild conditions.

In $[\text{CuGd}(\mathbf{417c})(\text{CH}_3\text{OCOO})(\text{thd})_2]$ the central region is occupied by copper(II) and gadolinium(III) ions that are triply bridged one to the other by two phenolato oxygen atoms from the ligand $[\mathbf{417c}]^{2-}$ and the oxygen atoms from the monomethyl carbonate anion. The four atoms of the bridging entity are not exactly coplanar, leading to a roof-shaped CuO_2Gd core. The $\text{Cu} \cdots \text{Gd}$ separation is 3.472 Å. The copper ion adopts a square-based pentagonal coordination mode; the equatorial N_2O_2 donors are provided by $[\mathbf{417c}]^{2-}$ while the axial position is occupied by a CO_2 group from the monomethyl carbonate anion. The copper center is displaced from the mean equatorial N_2O_2 coordination plane by 0.2185 Å. The gadolinium ion is nine coordinated. In addition to the two phenolate oxygens, the rare earth ion completes its environment with two oxygen atoms from the OCH_3 side arms, four oxygens coming from the two bidentate tetramethylheptanedionato units and one oxygen from the monomethyl carbonate anion. The separations between metal ions belonging to neighbouring molecules are large: the $\text{Cu} \cdots \text{Cu}$ separation is equal to

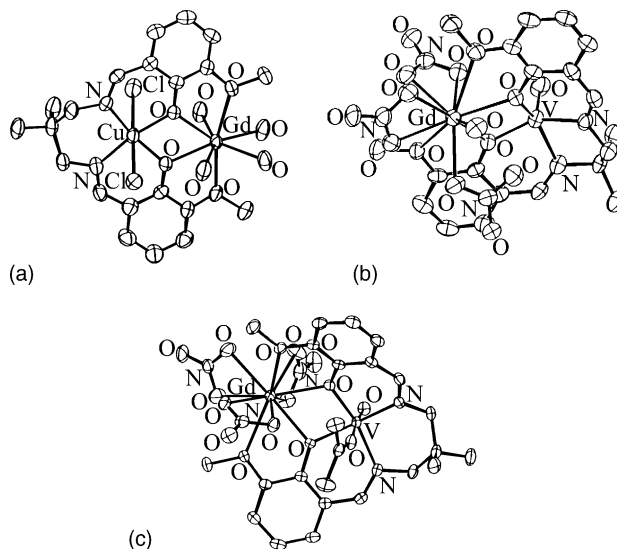


Fig. 318. Structure of $[\text{CuGd}(\mathbf{417c})(\text{Cl})_2(\text{H}_2\text{O})_4]^+$ (a), $[\text{VOGd}(\mathbf{417c})(\text{NO}_3)_3(\text{H}_2\text{O})]$ (b) and $[\text{VOGd}(\mathbf{417c})(\text{NO}_3)_3(\text{CH}_3\text{COCH}_3)]$ (c) (adapted from Refs. [513,514]).

6.655 Å while values of 10.179 and 8.412 Å are respectively observed for $\text{Gd} \cdots \text{Gd}$ and for $\text{Cu} \cdots \text{Gd}$, precluding any significant intermolecular magnetic. A ferromagnetic interaction ($J = 4.2 \text{ cm}^{-1}$) takes place between the two metal ions [513].

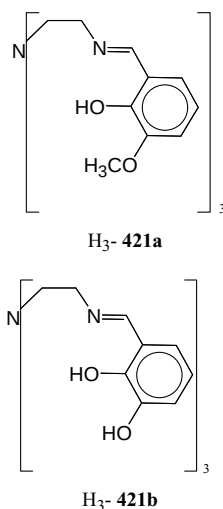
$[\text{Cu}(\mathbf{417c})]$ reacts with $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ to form $[\text{CuGd}(\mathbf{417c})(\text{Cl})_2(\text{H}_2\text{O})_4](\text{Cl}) \cdot 2\text{H}_2\text{O}$ [513] where copper(II) and gadolinium(III) ions, bridged by two phenolato oxygen atoms offered by $[\mathbf{417c}]^{2-}$, are 3.512 Å apart. The gadolinium ion is eight coordinated. In addition to all two anionic oxygens from the phenolate groups of $[\mathbf{417c}]^{2-}$, the gadolinium(III) ion completes its coordination sphere with six neutral oxygen donors, two from the OCH_3 side arms and four from water molecules. The copper ion is surrounded by six donor atoms. The equatorial N_2O_2 donors afforded by $[\mathbf{417c}]^{2-}$ are nearly coplanar. The two uncoordinated water molecules are involved in a hydrogen bond network which also includes the three chloride ions and the four water molecules coordinated to the gadolinium(III) ion (Fig. 318a). The complex displays a ferromagnetic interaction ($J = 10.1 \text{ cm}^{-1}$) [513].

The vanadyl(VI) precursors $\text{VO}(\mathbf{417a}) \cdot \text{H}_2\text{O}$ and $\text{VO}(\mathbf{417c}) \cdot \text{H}_2\text{O}$ react with $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to yield $[\text{VOGd}(\mathbf{417c})(\text{NO}_3)_3(\text{H}_2\text{O})]$ and $[\text{VOGd}(\mathbf{417c})(\text{NO}_3)_3(\text{CH}_3\text{COCH}_3)]$ [514] where the two metal ions are doubly bridged by two phenolato oxygen atoms of $[\mathbf{417a}]^{2-}$ or $[\mathbf{417c}]^{2-}$. The most pertinent difference between the two complexes concerns the GdO_2V bridging core, which is almost planar in the first complex but not in the second one. The $\text{Gd} \cdots \text{V}$ separations are 3.319 and 3.504 Å, respectively. In both compounds, gadolinium(III) is decacoordinated, although in $[\text{VO}(\text{Gd}(\mathbf{417c})(\text{NO}_3)_3(\text{CH}_3\text{COCH}_3))]$ the coordination sphere comprises four oxygens from $[\mathbf{417c}]^{2-}$ and six from three chelating NO_3^- , while in the other VOGd complex one

chelating NO_3^- group is replaced by one monodentate NO_3^- group and a water molecule involved in a hydrogen bonding network through an uncoordinated H_2O and a bound NO_3 . Nevertheless, the intermolecular $\text{Gd} \cdots \text{Gd}$ distance is large (7.751 Å) and slightly shorter than in $[\text{VO}(\text{Gd}(\mathbf{417c})(\text{NO}_3)_3(\text{CH}_3\text{COCH}_3)]$ (8.381 Å). The vanadium(IV) ion is pentacoordinated in the former and hexacoordinated in the latter complex, due to the presence of an additional acetone molecule which is loosely bound in an axial position [514] (Fig. 318b and c).

$[\text{VOGd}(\mathbf{417c})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ has a ferromagnetic ground state with a coupling constant J of 1.5 cm^{-1} , while for $[\text{VOGd}(\mathbf{417c})(\text{NO}_3)_3(\text{CH}_3\text{COCH}_3)]$ an antiferromagnetic ground state occurs ($J = -2.6 \text{ cm}^{-1}$) [514].

$[\text{Fe}(\mathbf{421a})]$, obtained by reaction of the tripodal Schiff base $\text{H}_3\text{-421a}$ with FeCl_3 and triethylamine, affords $[\text{FeGd}(\mathbf{421a})(\text{NO}_3)_3]$ when reacted with $\text{Gd}(\text{NO}_3)_3$ in acetone [515]. The complex shows a ferromagnetic behaviour ($J = 0.50 \text{ cm}^{-1}$).



The reaction $\text{H}_3\text{-421a}$ with PbCl_2 in the presence of $\text{N}(\text{Et})_3$ generates exclusively $[\text{Pb}_2(\mathbf{421a})(\text{Cl})]$. This contrasts with the corresponding reaction using the unsubstituted tripodal ligand $\text{H}_3\text{-421b}$ which gives exclusively $[\text{Pb}(\text{H-421b})]$. Anion metathesis of $[\text{Pb}_2(\mathbf{421a})(\text{Cl})]$ using AgClO_4 or $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in methanol gives $[\text{Pb}_2(\mathbf{421a})](\text{ClO}_4)$ [516] where the two lead(II) ions exist in dissimilar environments. The inner lead(II) ion is bound by all of the nitrogen atoms and phenolate oxygens of $[\mathbf{421a}]^{3-}$ and is seven coordinated. The $[\text{Pb}(\mathbf{421a})]^-$ unit acts as a tridentate ligand to the other lead(II) ion binding through the three phenolate oxygen atoms to give the dinuclear cation $[\text{Pb}_2(\mathbf{421a})]^+$, which possesses pseudo- C_{3v} symmetry (Fig. 319a). The central Pb_2O_3 core of this complex can be considered as a trigonal bipyramid, with the two metal ions providing the apical vertices. The outer lead(II) ion has close contacts with an oxygen atom from the perchlorate counter ion. The coordination geometry about the inner lead(II) ion has been described as a distorted monocapped

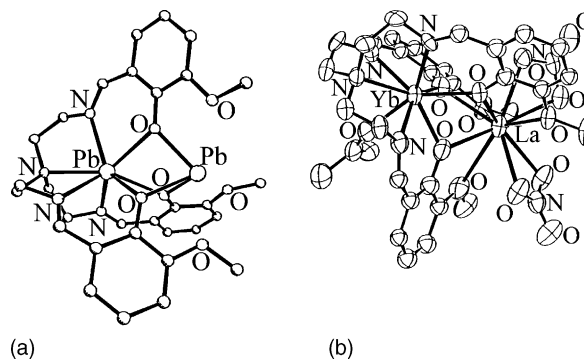


Fig. 319. Structure of $[\text{Pb}_2(\mathbf{421a})]^+$ (a) and $[\text{YbLa}(\mathbf{421a})(\text{NO}_3)_2]^+$ (b) (adapted from Refs. [516,517]).

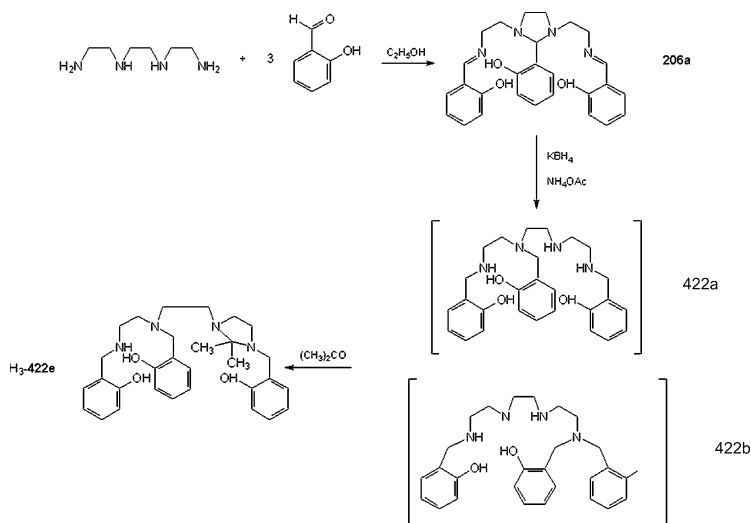
octahedron, with the triangular faces defined by the three imine nitrogens and the three phenolate oxygens atoms, respectively, with the apical nitrogen atom capping the imine face. The *o*-methoxy substituents of $[\mathbf{421a}]^{3-}$ increase the electron density at the phenolate oxygen atoms sufficiently to allow binding of a second lead(II) center; thus the outer lead(II) ion closes the ligand pocket around the inner lead, the mismatch in size leading to distortions in the overall geometry of the encapsulated metal atom. The outer lead ion can be described as having a distorted tetrahedral geometry.

$[\text{Yb}(\mathbf{421a})] \cdot 0.5\text{H}_2\text{O}$ was obtained by the reaction in warm methanol of $\text{H}_3\text{-421a}$, $\text{CsOH} \cdot \text{H}_2\text{O}$ and $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Using the same procedure, $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ forms $[\text{GdCs}(\mathbf{421a})(\text{NO}_3)_3] \cdot 3\text{H}_2\text{O}$ [517].

$[\text{Yb}(\mathbf{421a})] \cdot 0.5\text{H}_2\text{O}$, when reacted with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in a 1:1 molar ratio, forms $[\text{YbLa}(\mathbf{421a})(\text{NO}_3)_3]$; similarly $[\text{GdCs}(\mathbf{421a})(\text{NO}_3)_3] \cdot 3\text{H}_2\text{O}$ reacts with $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to form $[\text{Gd}_2(\mathbf{421a})(\text{NO}_3)_3]$ [517].

Slow diffusion of diethyl ether into a filtered acetone solution of $[\text{Yb}(\mathbf{421a})] \cdot 0.5\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in excess yielded crystals of $\{[\text{YbLa}(\mathbf{421a})(\text{NO}_3)_2]_2 [\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})]\}$. In the cationic unit (Fig. 319b) the ytterbium(III) and lanthanum(III) ions are encapsulated by the ligand, triply bridged one to the other via the three phenolate oxygens from $[\mathbf{421a}]^{3-}$. The YbO_3La core is asymmetric and the resulting $\text{Yb} \cdots \text{La}$ separation is 3.633 Å. The ytterbium(III) ion is eight coordinated, bonding to the three bridging oxygen and the four nitrogen atoms of $[\mathbf{421a}]^{3-}$, the coordination sphere being completed by an oxygen from a solvent acetone molecule. The tertiary nitrogen, which caps the structure, is tucked in with its lone pair of electrons directed at the ytterbium(III) ion. In the cationic unit, the lanthanum(III) ion is 10 coordinated, being bonded to the three bridging oxygens, the three methoxy oxygens of the side arms, and four oxygens from two bidentate nitrate ions. In the anionic unit, the 10 coordination sites of lanthanum(III) ion are filled by 10 oxygen atoms from five bidentate NO_3^- groups [517].

$[\text{Gd}_2(\mathbf{421a})(\text{NO}_3)_3]$ shows of an antiferromagnetic behaviour ($J = -0.104 \text{ cm}^{-1}$) [517].



Scheme 59.

The potentially heptadentate Schiff bases **H₃-206a-c** were prepared by the condensation of $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ with 3 equiv. of salicylaldehyde or 5-substituted salicylaldehyde. A mixture of the isomeric amine phenols **H₃-422a** and **H₃-422b** was obtained by the KBH_4 reduction of **H₃-206a**. Pure **H₃-422a** was obtained by the decomposition of its ytterbium(III) complex [518].

^1H NMR and FAB mass spectra suggest that the borohydride reduction of **H₃-206a** gives **H₃-422c** which is the acetone adduct of **H₃-422a** [518]. The five-membered imidazolidine ring formed in the Schiff base condensation opened during the reduction which likely resulted in the middle arm migration (Scheme 59). The identified by-product was the ligand **H₃-422b**. It was suggested that the $\text{C}=\text{N}$ linkages on the terminal arms may be reduced first, then the lone pairs on the secondary nitrogens begin to attack the carbon to form an intermediate. This intermediate can either give the product **H₃-422a** through reduction or form another intermediate, which leads to the minor by-product **H₃-422b**. After acetone addition, another five-membered imidazolidine ring was formed at the backbone. The five-membered ring formed in the reduction will reopen, and **H₃-422c** will appear as $[\mathbf{422a}]^{3-}$ after complexing [518].

The X-ray structures of **H₃-206a** and **H₃-206c** show the formation of a five-membered imidazolidine ring and the presence of strong intramolecular and weak intermolecular hydrogen bonding interactions [518].

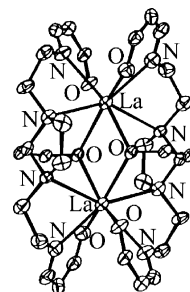
Reaction of **H₂-206a-c** with 1 equiv. of a lanthanide nitrate in a small volume of solvent in the absence of a weak base produces $[\text{Ln}(\text{H}_3\text{-206a-c})(\text{NO}_3)_3]$ in which the ligand is tridentate and capped. The sequence of the addition of the starting materials is very important for the lanthanum complexes. When a solution of ligand was added to a solution of lanthanum nitrate, mixtures always resulted despite extensive washing with chloroform to remove possible impurities. When the sequence was reversed, the

analyses of the lanthanum(III) complexes fitted the formulation.

The complexes $\text{Ln}(\text{H}_3\text{-206a-c})(\text{NO}_3)_3$ are air stable but very unstable in solution and spontaneously convert to the sandwich dimers $[\text{Ln}(\mathbf{206a-c})_2]$. This auto conversion of the mononuclear Schiff base complexes wherein the ligand is tridentate to the sandwich dinuclear complexes indicates that the complexes $[\text{Ln}(\mathbf{206a-c})_2]$ are quite stable and extremely rigid.

$[\text{Ln}(\mathbf{206a-c})_2]$ were prepared also from the reactions of the appropriate lanthanide(III) salt with **H₃-206a-c** in the presence of excess weak base (acetate). These sandwich complexes could also be prepared from the reaction of lanthanide nitrate with 1 equiv. of the Schiff base because of the instability of the capped Schiff base complexes $\text{Ln}(\text{H}_3\text{-206a-c})(\text{NO}_3)_3$ and their auto conversion to sandwich dimer complexes.

The structure of $[\text{La}(\mathbf{206c})_2]$ (Fig. 320) reveals that the two ligands bridge the two metal ions forming a sandwich structure. $[\text{La}(\mathbf{206c})_2]$ has a square antiprismatic geometry around each lanthanum ion which is eight coordinated by an N_4O_4 donor set, N_2O from each ligand and two bridging phenolate oxygen atoms, one from each heptadentate ligand with a $\text{La} \cdots \text{La}$ separation of 4.023 Å [518].

Fig. 320. Structure of $[\text{La}(\mathbf{206c})_2]$ (adapted from Ref. [518]).

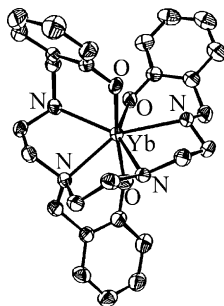


Fig. 321. Structure of [Yb(422a)] (adapted from Ref. [518]).

The reaction of the amine phenol **H₃-422a** with 1 equiv. of the appropriate lanthanide nitrate in the presence of diethyl ether produced the capped tridentate ligand complex [Ln(**H₃-422a**(NO₃)₃)] or, in the presence of excess of strong base, [Ln(**422a**)] [518].

The structure of [Yb(**422a**)] (Fig. 321) shows this to be an encapsulated ligand complex with pentagonal bipyramidal coordination. Two independent molecules (with very slight differences in bond lengths and angles) comprise the asymmetric unit. The ligand is triply deprotonated and all seven donor atoms (N₄O₃) are coordinated to the metal ion. After complexation, the imidazolidine ring in the ligand opened, which made the backbone and the three arms more flexible. Four nitrogens and one oxygen of a terminal arm easily wrapped around the metal ion, while the remaining two arms stretched out to occupy the axial positions [518].

H₃-206a affords [CuZn(**206a**)(CH₃COO)]·2H₂O when treated with Cu(CH₃COO)₂·2H₂O and Zn(CH₃COO)₂·2H₂O in a sequential fashion [519]. The complex includes a bridging endogenous imidazolidine ligand linking copper(II) and zinc(II) ions at a 3.259 Å distance (Fig. 322). The copper(II) and zinc(II) ions are in slightly different square pyramidal coordination environments. The coordination about the copper(II) ion is very distorted owing to the presence of the zinc(II) ion as indicated also by EPR spectra. Outside the bridging groups the coordination around the copper and zinc ions is completed with one imine nitrogen donor and one phenolate oxygen donor from the terminal arms of the binucleating ligand [**206a**]^{3−}. Two water molecules are present in the unit cell [519].

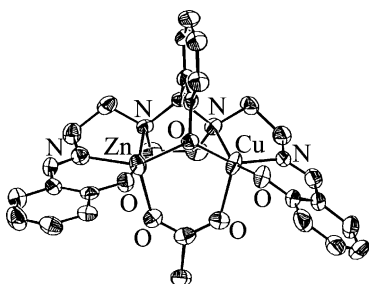


Fig. 322. Structure of [CuZn(**206c**)(CH₃COO)] (adapted from Ref. [519]).

10. Polynuclear complexes with symmetric macrocyclic ligands

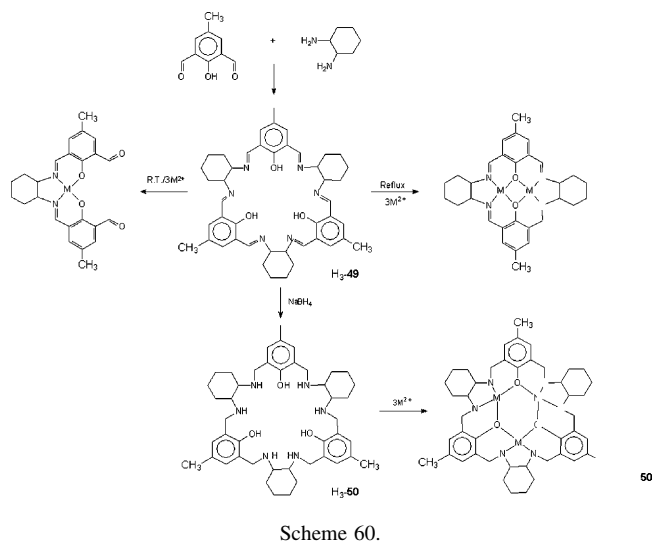
The complexes containing three or more metal centers in some predetermined arrangement can exhibit quite peculiar chemical and/or physical behaviour. Multielectron reduction or oxidation of substrates may be possible. The relatively accessible arrangement of the four metal centers provided by the organizing ligand may enable substrates to be brought under the influence of two or three or even all four metals simultaneously; only a modest 2e[−] change per metal is then required for the transfer of up to 8e[−] either to or from the substrate. Thus for example, the interaction of appropriate complexes with substrates such as O₂ and N₂, which are of considerable chemical, biological and industrial importance, could prove interesting and useful. Tetramanganese derivatives may provide realistic and useful models for the dioxygen generating component of the photosynthetic system, which appears to involve four manganese centers in close proximity [520].

A preordered arrangement of several metal ions can be dominated by the use of different synthetic strategies: (i) a single ligand, which can secure into its coordination moiety the desired metal ions; (ii) macrocyclic or macroacyclic ligands (especially dinucleating) which contain bridging groups capable of binding several metal ions as well as mediating magnetic and/or electronic interaction among them; (iii) suitable simpler complexes which can act as building blocks for the preparation of more sophisticated systems; (iv) suitable bridging ligands (Cl[−], ClO₄[−], N₃[−], NCS[−], etc.).

The reaction of 2,6-diformyl-4-methylphenol and *trans*-(1*R*,2*R*)-cyclohexyldiamine in methanol at room temperature results in the facile formation of the [3+3] condensed optically active, chiral macrocyclic Schiff base **H₃-49**. Its [3+3] entity has been inferred especially by FAB mass spectrometry.

The reduction of **H₃-49** by NaBH₄ resulted in the formation of the related [3+3] hexamacrocyclic derivative **H₃-50** as indicated by FAB mass spectrometry and ascertained by the X-ray structural determination, reported in a previous section. **H₃-50** reacts with transition metal salts in dry methanol under nitrogen atmosphere and in a 1:3 molar ratio to form the trinuclear complexes [M₃(**50**)(CH₃COO)](ClO₄)(PF₆)·H₂O or [M₃(**50**)](X)₃·nH₂O (X = ClO₄[−], Cl[−], n = 1, 3) [132] (Scheme 60).

[Zn₃(**50**)(μ-CH₃COO)](ClO₄)(PF₆) (Fig. 323) [521] has an internal hydrophilic core and an outer hydrophobic surface. The centrally located three zinc ions and three bridging phenoxo oxygens constitute a cyclic six-membered chair form. The structure reveals that the two zinc(II) ions have geometrically different environments from the third one despite the fact that the macrocycle is potentially capable of providing identical binding sites. Two zinc(II) ions are coordinated by N₂O₃ donor sets from two bridged phenoxo oxygens, two amine nitrogens of the cyclohexyl rings and



are bridged by an axially coordinated acetato group. The geometry around these two zinc ions has been described as distorted trigonal bipyramidal. The 1,2-cyclohexyldiamine nitrogens are not coordinated in the equatorial plane of the metal ion. The rigidity ensured by the *trans*-geometry of cyclohexyldiamine moiety and the flexibility offered by the $-\text{CH}_2-\text{NH}-$ linkage together with the large size of the macrocyclic ring influence the ligand to twist, forcing one nitrogen to coordinate axially and the other equatorially. The distance between these two zinc ions is 3.37 Å. The three aromatic rings are inclined diagonally to the cyclohexyl rings and form a three bladed propeller like conformation. The third zinc ion, separated from the dinuclear pair of zinc ions by 3.21 and 3.50 Å respectively, is coordinated by two amine nitrogens and two bridging phenoxide oxygens and has distorted tetragonal geometry. Alternatively a distorted trigonal bipyramidal geometry, with a missing fifth coordinating donor was proposed for this zinc ion.

The reaction of the preformed [3+3] Schiff base $\text{H}_3\text{-49}$, with metal(II) salts (1:3 ratio) in hot methanol gives rise to a macrocyclic ring contraction with the consequent formation of the [2+2] macrocyclic complexes $[\text{M}_2(\text{49a})(\text{X})_2]$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+} , Fe^{2+} , Co^{2+} , Mn^{2+}) (Scheme 60).

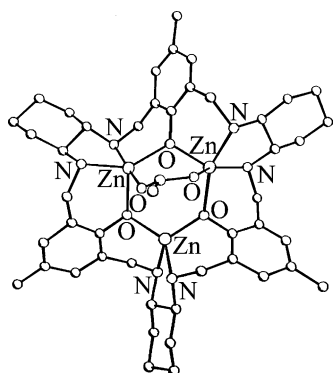


Fig. 323. Structure of $[\text{Zn}_3(\text{50})(\mu\text{-CH}_3\text{COO})]^{2+}$ (adapted from Ref. [132]).

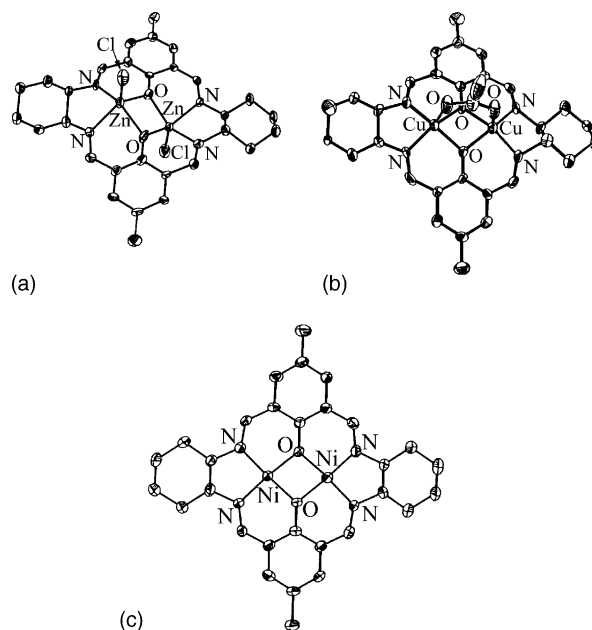


Fig. 324. Structure of $[\text{Zn}_2(\text{49a})(\text{Cl})_2]$ (a), $[\text{Cu}_2(\text{49a})(\mu\text{-CH}_3\text{COO})]^+$ (b) and $[\text{Ni}_2(\text{49a})]^{2+}$ (c) (adapted from Ref. [521]).

Crystals of $[\text{Zn}_2(\text{49a})(\text{Cl})_2]$ (Fig. 324a), obtained from a slow evaporation of a $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1) solution, show the phenoxo groups serve as bridges between the metal centers. Each metal ion has square pyramidal geometry bridged by two oxo groups and coordinated by two imine nitrogens. The fifth coordination is occupied by chloride anion in axial position. The $\text{Zn} \cdots \text{Zn}$ distance is 3.19 Å. The macrocycle is planar and the metal ions are located above and below the plane formed by the N_2O_2 donors [521].

Analogously in $[\text{Cu}_2(\text{49a})(\mu\text{-CH}_3\text{COO})](\text{ClO}_4) \cdot \text{CH}_3\text{CN}$, (Fig. 324b) the two copper centers, strongly antiferromagnetic interacting each other, are bridged by two phenolic oxygens and are coordinated by two imine nitrogens. An acetate group forms a bridge between the two copper ions. The geometry around the copper ion is square pyramidal with the ligand N_2O_2 donor atoms forming the basal plane with acetate oxygen at the apical position. The two copper ions are above the N_2O_2 plane towards the acetate groups. The $\text{Cu} \cdots \text{Cu}$ distance is 2.872 Å [521].

$[\text{Cu}_2(\text{49a})(\mu\text{-CH}_3\text{COO})](\text{ClO}_4) \cdot \text{CH}_3\text{CN}$, shows two step-wise one-electron reduction peaks in negative potential at -0.63 and -1.25 V in acetonitrile corresponding to $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$; and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$.

In the diamagnetic complex $[\text{Ni}_2(\text{49a})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$, (Fig. 324c) the nickel environments are square planar generated by two imine nitrogens and two bridging oxygen atoms from the ligand. The nickel ions are in the plane of N_2O_2 compartment at a $\text{Ni} \cdots \text{Ni}$ distance of 2.80 Å [521]. The complex has two uncoordinated perchlorate anions and a methanol and an acetonitrile molecule in the crystal lattice.

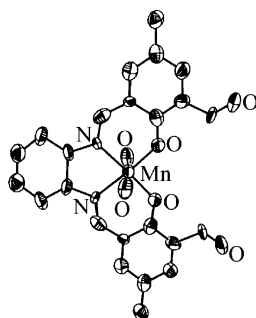


Fig. 325. Structure of $[\text{Mn}(\mathbf{42})(\text{H}_2\text{O})_2]$ ($Z = \text{CH}_3$, $R = \text{C}_6\text{H}_{10}$) (adapted from Ref. [521]).

This nickel complex shows two stepwise one-electron reduction peaks in negative potential at -0.72 and -1.32 V in acetonitrile corresponding to $\text{Ni}^{\text{II}}\text{Ni}^{\text{II}} \rightleftharpoons \text{Ni}^{\text{II}}\text{Ni}^{\text{I}}$, and $\text{Ni}^{\text{II}}\text{Ni}^{\text{I}} \rightleftharpoons \text{Ni}^{\text{I}}\text{Ni}^{\text{I}}$. In the positive potential it shows two quasi-reversible one-electron oxidation peaks at $+0.67$ and $+1.37$ V, respectively to the corresponding $\text{Ni}^{\text{II}}\text{Ni}^{\text{II}} \rightleftharpoons \text{Ni}^{\text{II}}\text{Ni}^{\text{III}}$ and $\text{Ni}^{\text{II}}\text{Ni}^{\text{III}} \rightleftharpoons \text{Ni}^{\text{III}}\text{Ni}^{\text{III}}$.

The [3+3] Schiff base $\text{H}_3\text{-49}$, when treated at room temperature for 2 h with metal acetate and metal perchlorate in a ratio 1:1.5:1.5 and in the presence of NH_4PF_6 , affords the [2+1] mononuclear acyclic Schiff base complexes $\text{M}(\mathbf{42})(\text{PF}_6) \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{3+}$, Fe^{3+}) and $\text{M}(\mathbf{42}) \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+}) as confirmed by the X-ray structure of $[\text{Mn}(\mathbf{42})(\text{H}_2\text{O})_2](\text{PF}_6)$ ($Z = \text{CH}_3$, $R = \text{C}_6\text{H}_{10}$) (Fig. 325). In this complex the manganese(III) ion has a distorted octahedral geometry. The two phenoxide oxygens and azomethine nitrogen atoms are coordinated in the equatorial plane and two water molecules are coordinated in the axial positions [521].

In a previous section it was reported that [2+2] compartmental macrocyclic ligands of the type $\text{H}_2\text{-43} \cdot \text{H}_2\text{-46}$ or $\text{H}_2\text{-324}$ have been primarily designed to give rise to homonuclear complexes.

$[\text{H}_4\text{-43}](\text{PF}_6)_2$, obtained by condensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol in the presence of HBr followed by metathesis of the resulting compound $[\text{H}_4\text{-43}](\text{Br})_4$ with NH_4PF_6 in methanol, reacts with 2 equiv. of $\text{Ni}(\text{CH}_3\text{COO})_2$ in the presence of an excess of triethylamine in CH_3CN to give $[\text{Ni}_4(\mathbf{43})_2(\text{CH}_3\text{COO})_2](\text{PF}_6)_2$ where $[\text{Ni}_2(\mathbf{43})(\text{CH}_3\text{COO})]^+$ units have dimerized to give an Ni_4O_4 cubane-type structure (Fig. 326a). The central core is composed by a $\text{Ni}_4\text{N}_8\text{O}_4$ unit. Each nickel(II) center is in a distorted octahedral environment, being equatorially bound to the N_2O_2 donor set of one $[\mathbf{43}]^{2-}$ macrocycle and with axial interactions to a carboxylic oxygen donor of a bridging CH_3COO^- group and a phenoxy oxygen donor from a $[\mathbf{43}]^{2-}$ macrocycle from the other half of the dimer. The $\text{Ni} \cdots \text{Ni}$ distance within the macrocycle $[\mathbf{43}]^{2-}$ is $3.024 \text{ \AA}$. The four Ni-Ni vectors describe a distorted tetrahedron with the superimposed O_4 tetrahedron of the phenoxy oxygen donors. The macrocycle in $[\text{Ni}_4(\mathbf{43})_2(\text{CH}_3\text{COO})_2]^{2+}$ is non planar. The two CH_3COO^- and $[\mathbf{43}]^{2-}$ groups in

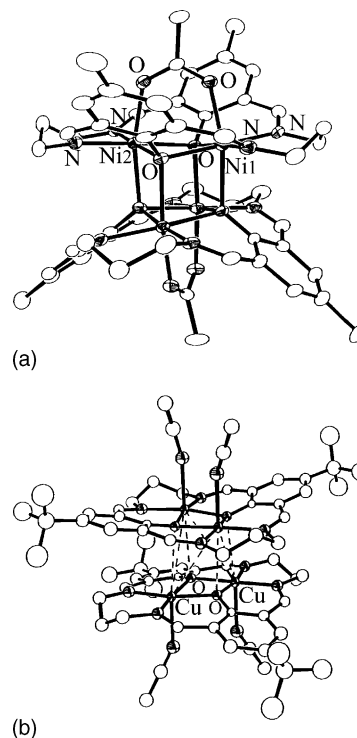


Fig. 326. Structure of $[\text{Ni}_4(\mathbf{43})_2(\text{CH}_3\text{COO})_2]^{2+}$ (a) and $[\text{Cu}_4(\mathbf{44})_2(\text{CH}_3\text{CN})_4]^{4+}$ (b) (adapted from Ref. [522]).

$[\text{Ni}_4(\mathbf{43})_2(\text{CH}_3\text{COO})_2]^{2+}$ are orthogonal to each other, so there is no possibility for intramolecular $\pi\text{-}\pi$ interactions between neighbouring macrocycles within the same molecule [522].

Possibly the cubane structure is maintained in solution since no colour change is observed on dissolution of $[\text{Ni}_4(\mathbf{43})_2(\text{CH}_3\text{COO})_2]^{2+}$ in coordinating solvents. The driving force for the dimerization is probably the requirement of the nickel(II) centers for octahedral coordination, since the ligand field strength of $[\mathbf{43}]^{2-}$ is insufficient to give diamagnetic, square planar nickel(II) complexes [522].

Also the reaction of $[\text{H}_4\text{-44}](\text{PF}_6)_2$ with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in $\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{OH}$ in the presence of an excess of triethylamine leads to the formation of $[\text{Cu}_4(\mathbf{44})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_4$ where the $[\text{Cu}_4(\mathbf{44})_2(\text{CH}_3\text{CN})_4]^{4+}$ units have a distorted Cu_4O_4 cubane-type structure. The $\text{Cu} \cdots \text{Cu}$ separation is $3.119 \text{ \AA}$ within each Cu_2O_2 unit. Each copper(II) ion is in a tetragonally distorted octahedral coordination environment [522] (Fig. 326b).

The more elongated nature of the $[\text{Cu}_4(\mathbf{44})_2(\text{CH}_3\text{CN})_4]^{4+}$ cube compared to that of $[\text{Ni}_4(\mathbf{43})_2(\text{CH}_3\text{COO})_2]^{2+}$ reflects the expected Jahn–Teller distortion at the copper(II) ions and the greater degree of electrostatic repulsion between the two halves of the Cu_4O_4 system. Whilst these long-range interactions between neighbouring Cu_2O_2 units are too long to be regarded as genuine bonds, the interaction causes each macrocycle to deviate noticeably from planarity. The CH_3CN ligands in $[\text{Cu}_4(\mathbf{44})_2(\text{CH}_3\text{CN})_4]^{4+}$ do not coordinate in a linear fashion. Interestingly, the complex $[\text{Cu}_2(\mathbf{43})\text{-}$

$(\text{CH}_3\text{COO})^+$ does not form a tetranuclear species but consists of discrete dinuclear units [523].

The reaction of equivalent amounts $\text{Zn}(\text{ClO}_4)_2$, 2,6-diformyl-4-methylthiophenol and 1,3- $\mu\text{-CH}_3\text{CN}/\text{Et}_2\text{O}$, afforded the tetranuclear complex $[\text{Zn}_4(\mathbf{320})_2(\mu\text{-OH})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 327) [523]. In the complex two $[\text{Zn}_2(\mathbf{320})]^{2+}$ units bridged via two $\mu\text{-OH}$ bridges. The B subunit contains 2 equiv. zinc(II) centers in square pyramidal geometries, each equatorially bound to the N_2S_2 donor set of one macrocycle and axially bound to one $\mu\text{-hydroxy}$ moiety which bridges to form the dimeric links to subunit A. The macrocycle in subunit B adopts a folded conformation. This folding creates the necessary space required by the bulky bridging thiolates. However, the macrocycle in subunit A cannot fold in the same manner as in subunit B owing to the bent nature of the $\mu\text{-OH}$ bridges. Thus, the macrocycle adopts an alternative orientation involving flipping of one thiophenolate head unit towards the B subunit. The coordination geometries at the zinc(II) ions in subunit A may be described as intermediate between square pyramidal and trigonal bipyramidal. The $\text{Zn} \cdots \text{Zn}$ distances are in the range 3.540–3.497 Å.

The template reaction of 2,6-diformyl-4-methylphenol, 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = CH_3 for $\text{H}_2\text{-423a}$ or CH_2CH_3 for $\text{H}_2\text{-423b}$) and manganese(II) benzoate tetrahydrate in 1:1:2 molar ratio leads to the formation of the macrocyclic tetranuclear manganese(II) complexes $[\text{Mn}_4(\mathbf{423a-b})(\text{C}_6\text{H}_5\text{COO})_6]$ [524].

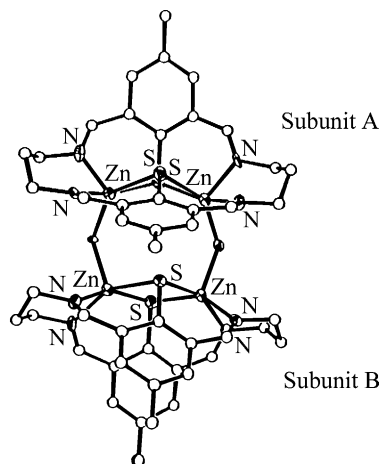
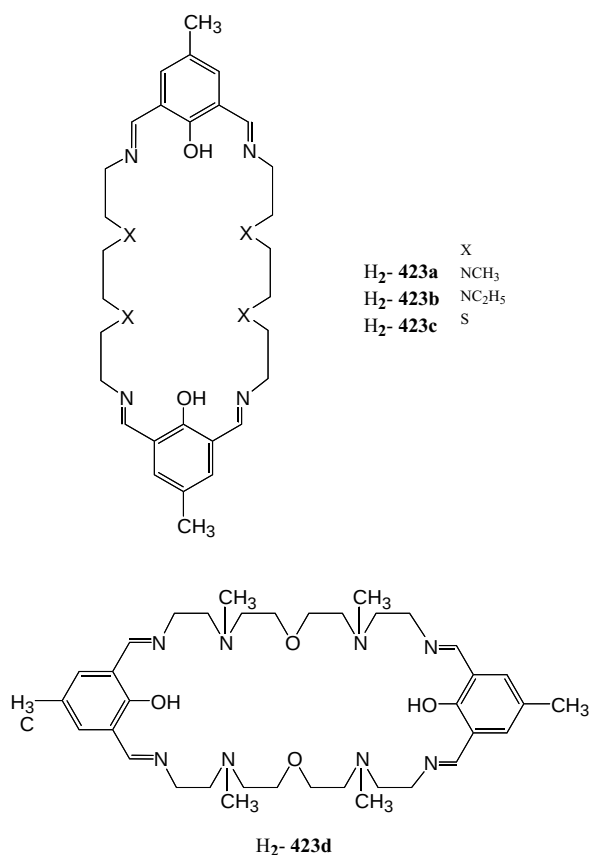


Fig. 327. Structure of $[\text{Zn}_2(\mathbf{320})(\mu\text{-OH})_2]^{2+}$ (adapted from Ref. [523]).

The success in the template synthesis of these complexes depends upon the operating conditions employed. When 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = CH_3 , $\text{CH}_2\text{-CH}_3$) and manganese(II) benzoate dihydrate were mixed first in methanol and 2,6-diformyl-4-methylphenol, then added to the resulting reddish brown solution, no crystalline complex was obtained. A similar reaction under anaerobic conditions led to formation of orange solutions from which, however, the desired macrocyclic complexes could not be obtained. When manganese(II) benzoate dihydrate and 2,6-diformyl-4-methylphenol were mixed first in methanol and then the tetraamine was added to this mixture under aerobic conditions, the reaction mixture assumed an orange colour and formed the macrocyclic complexes in good yields. A synthetic mechanism for the formation of the macrocyclic complexes is proposed where manganese(II) benzoate reacts with 2,6-diformyl-4-methylphenol to form an air-stable $\mu\text{-phenoxo-bis}(\mu\text{-benzoato})\text{dimanganese(II)}$ core structure. Upon treatment with the tetraamine, this complex forms the 1:1 Schiff base complex ($\text{R} = \text{CH}_3$ or C_2H_5), in which one of the formyl groups and one of the primary amino groups of the tetraamine remain intact. Dimerization of this complex affords the macrocyclic tetranuclear manganese(II) structure [524].

$[\text{Mn}_4(\mathbf{423a})(\text{C}_6\text{H}_5\text{COO})_6(\text{CH}_3\text{CHOHCH}_3)_2] \cdot 2\text{CH}_2\text{Cl}_2$, obtained by the diffusion of propan-2-ol into a dichloromethane solution of $[\text{Mn}_4(\mathbf{423a})(\text{C}_6\text{H}_5\text{COO})_6]$, (Fig. 328) is centrosymmetric and contains two pairs of disordered octahedral manganese ions bridged by a phenolic oxygen of the Schiff base and two benzoate groups affording a $\mu\text{-phenoxo-bis}(\mu\text{-carboxylato})\text{dimanganese(II)}$ core. The manganese ions in each pair are inequivalent: one is bound to one phenolic oxygen, one imino nitrogen, two amino nitrogens and two benzoate oxygens while the other is bound to one phenolic oxygen and one imino nitrogen of the Schiff base, two bridging benzoate oxygens, one monodentate benzoate oxygen and one propan-2-ol oxygen.

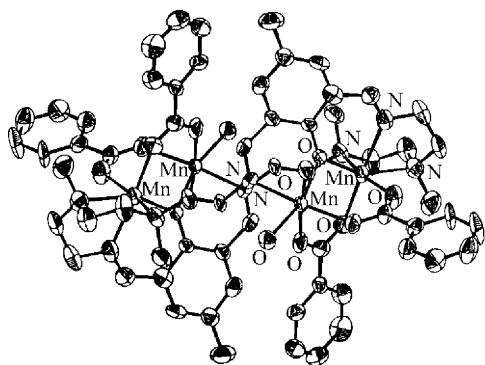


Fig. 328. Structure of $[\text{Mn}_4(\mathbf{423a})(\text{C}_6\text{H}_5\text{COO})_6(\text{CH}_3\text{CHOHCH}_3)_2]$ (adapted from Ref. [524]).

Magnetic susceptibility measurements over the temperature range of 4.2–300 K indicate a weak antiferromagnetic interaction between the manganese(II) ions in each pair ($J \cong -4 \text{ cm}^{-1}$) and no magnetic interaction between the two pairs [524].

Macrocyclic tetranuclear copper(II) complexes of the general formula $[\text{Cu}_4(\mathbf{L})(\text{OH})_2(\text{X})_2(\text{Y})_2]$ ($\text{H}_2\text{-L} = \text{H}_2\text{-315}$, $\text{X} = \text{Y} = \text{ClO}_4^-$ or $\text{X} = \text{CH}_3\text{COO}^-$, $\text{Y} = \text{PF}_6^-$; $\text{H}_2\text{-L} = \text{H}_2\text{-423c}$, $\text{X} = \text{Y} = \text{ClO}_4^-$ or $\text{X} = \text{Y} = \text{PF}_6^-$) have been obtained by the [2+2] condensation of 2,6-diformyl-4-methylphenol with 3,6-diazaoctane-1,8-diamine ($\text{H}_2\text{-315}$) or 3,6-dithiaoctane-1,8-diamine ($\text{H}_2\text{-423c}$) in the presence of copper(II) acetate as templating agent and NH_4PF_6 . The tetranuclear nature of these complexes has been established by X-ray structural determinations of $[\text{Cu}_4(\mathbf{315})(\text{OH})_2(\text{CH}_3\text{CHOHCH}_3)_2(\text{CH}_3\text{CN})_2](\text{CH}_3\text{COO})_2(\text{PF}_6)_2$ and $[\text{Cu}_4(\mathbf{423c})(\text{OH})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_4 \cdot 4\text{H}_2\text{O}$ [525].

The centrosymmetric tetranuclear complex cation $[\text{Cu}_4(\mathbf{315})(\text{OH})_2(\text{CH}_3\text{CHOHCH}_3)_2(\text{CH}_3\text{CN})_2]^{4+}$ (Fig. 329a) contains two dinuclear copper(II) units in a dimer-of-dimers arrangement. In each dinuclear unit two copper(II) ions are bridged by an endogenous phenolic oxygen of $[\mathbf{315}]^{2-}$ and an exogenous hydroxide oxygen with a $\text{Cu} \cdots \text{Cu}$ separation

of 2.95 Å. The two copper ions in each dimer are not equivalent. The geometry about one copper(II) ion is square pyramidal with the phenolic oxygen, the imine nitrogen, the amine nitrogen and the bridging hydroxide oxygen at the basal plane and a propan-2-ol oxygen at the axial site. The geometry about the other copper(II) ion is also square pyramidal but the axial site is occupied by an acetonitrile nitrogen. The tetranuclear skeleton $\{\text{Cu}_4(\mathbf{315})(\text{OH})_2\}$, except for the axial ligands, forms a near coplane with small deviations of the atoms from the least-squares plane. The two dinuclear units are in close proximity with two bridging hydroxide ions in a face-to-face mode. The $\text{Cu} \cdots \text{Cu}$, interatomic separations range from 5.426 to 6.510 Å. The two acetate ions are free from coordination [525].

$[\text{Cu}_4(\mathbf{423c})(\text{OH})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_4 \cdot 4\text{H}_2\text{O}$, (Fig. 329b) has a dimer-dimers structure similar to that of $[\text{Cu}_4(\mathbf{315})(\text{OH})_2(\text{CH}_3\text{CHOHCH}_3)_2(\text{CH}_3\text{CN})_2]^{4+}$. Each copper(II) ion assumes a square pyramidal geometry with an acetonitrile nitrogen at the axial site. The intradimer $\text{Cu} \cdots \text{Cu}$ separation is 2.976 Å while the interdimer $\text{Cu} \cdots \text{Cu}$ separations range from 6.212 to 7.084 Å.

$[\text{Cu}_4(\mathbf{315})(\text{OH})_2](\text{ClO}_4)_4$, shows four redox couples attributable to the stepwise reductions $\text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{I}}$. $[\text{Cu}_4(\mathbf{423c})(\text{OH})_2](\text{PF}_6)_4 \cdot \text{CH}_3\text{OH}$ shows two irreversible couples near -0.45 V versus, SCE ($E_{\text{pc}} -0.52$, $E_{\text{pa}} -0.38 \text{ V}$) and at -0.86 V versus SCE ($E_{\text{pc}} -0.93$, $E_{\text{pa}} -0.79 \text{ V}$), which have been tentatively assigned to the two-electron processes $\text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}}$ and $\text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{II}} \text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{I}} \text{Cu}^{\text{I}}$, respectively.

In these tetranuclear complexes the two dinuclear units are magnetically isolated from each other and a significant antiferromagnetic interaction operates within each dicopper(II) unit ($-J = 229\text{--}357 \text{ cm}^{-1}$) [525].

The Schiff base condensation of 2,6-diformyl-4-methylphenol and 1,11-diamino-3,9-dimethyl-3,9-diazo-6-oxaundecane in methanol and in air using $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as the template core in the presence of triethylamine with a mole ratio of 2:2:4:2 gave $[\text{Mn}_3(\mathbf{423d})(\mu\text{-OCH}_3)_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ where three manganese ions are encapsulated into the macrocycle in a bent-chain form. Each of the two facing phenoxide moieties bridges a pair of adjacent manganese ions which are further bridged by an exogenous methoxide ion. The two terminal manganese centers have essentially the same significantly distorted octahedral coordination geometry. The central manganese has an elongated octahedral geometry where its axial positions are occupied by the two phenoxide oxygen atoms. The three metal ions in the macrocycle are in the mixed-valence state $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}$ [525] (Fig. 330). Weak ferromagnetic interactions ($J = 1.83 \text{ cm}^{-1}$) operate between the adjacent $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ pairs while interactions between the terminal ions are negligible.

The same metal-template reaction in argon atmosphere yielded a yellow powder formulated as $[\text{Mn}_3(\mathbf{423d})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}]$ [525].

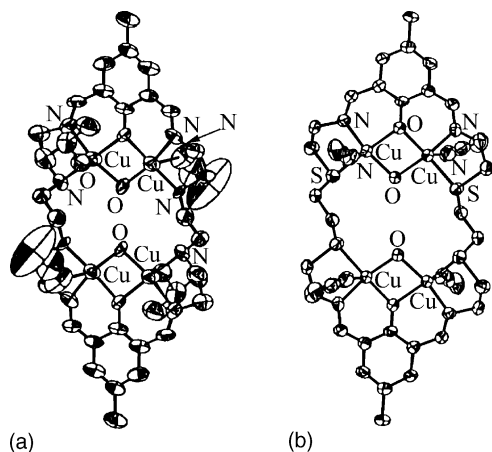


Fig. 329. Structure of $[\text{Cu}_4(\mathbf{315})(\text{OH})_2(\text{CH}_3\text{CHOHCH}_3)_2(\text{CH}_3\text{CN})_2]^{4+}$ (a) and $[\text{Cu}_4(\mathbf{423c})(\text{OH})_2(\text{CH}_3\text{CN})_4]^{4+}$ (adapted from Ref. [525]).

The ligands with a small cavity form mononuclear lanthanide(III) or dinuclear copper(II) or nickel(II) complexes, while the macrocycles H_2 -**74** and H_2 -**424a**, containing a further enlargement of the coordination cavity, obtained by the reaction of 2,6-diformyl-4-chlorophenol and 1,8-diamino-3,6-dioxaoctane or 1,11-diamino-3,6,9-trioxaundecane, form the tetranuclear complexes $M_4(\mathbf{74})(X)_{6-x}(\text{OH})_x \cdot n\text{H}_2\text{O}$ ($M = \text{Cu}^{2+}$, Ni^{2+} ; $X = \text{CH}_3\text{COO}^-$, NO_3^- , Cl^- , ClO_4^-) and $\text{Cu}_4(\mathbf{424a})(\text{CH}_3\text{COO})_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. With lanthanide(III) salts only dinuclear complexes were obtained [154].

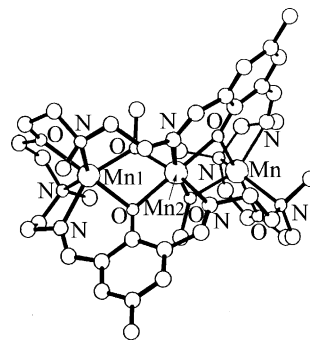
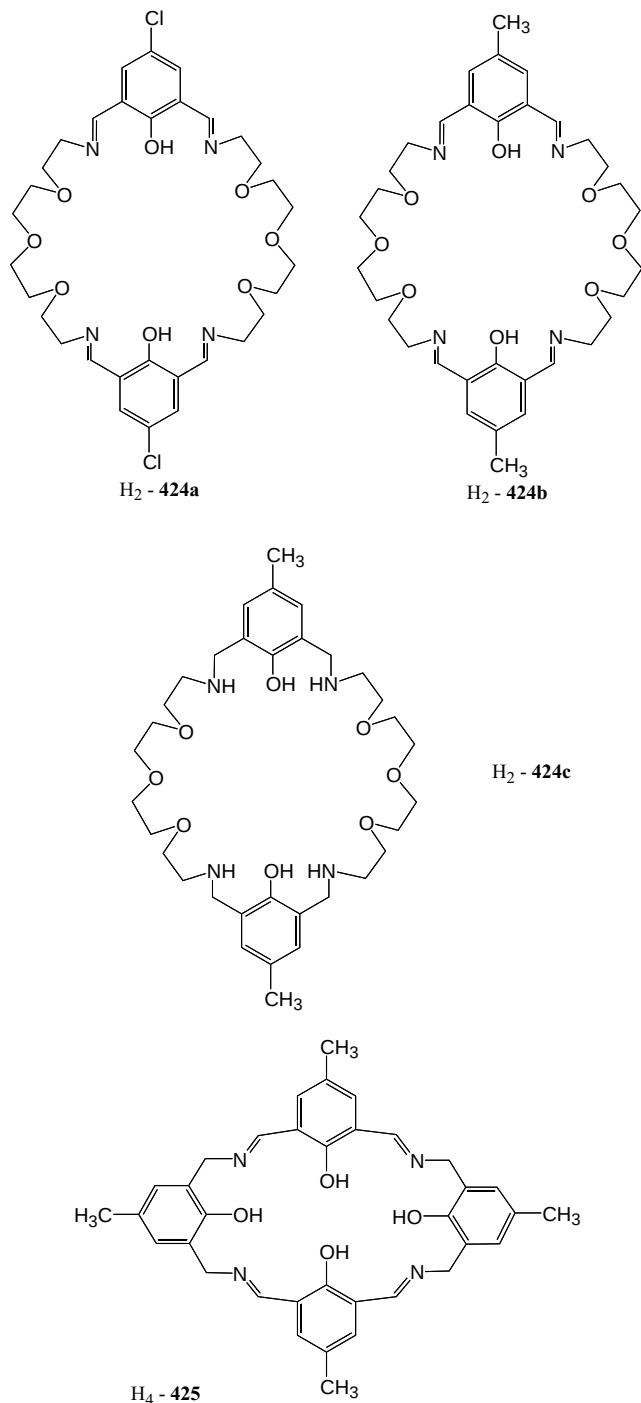


Fig. 330. Structure of $[\text{Mn}_3(\mathbf{423d})(\mu\text{-OCH}_3)_2]^{3+}$ (adapted from Ref. [525]).

The template condensation of 2,6-diformyl-4-methylphenol with 1,11-diamino-3,6,9-trioxaundecane using zinc(II) acetate as the metal source, followed by addition of an excess of NaClO_4 gave the tetranuclear zinc(II) complexes $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4](\text{ClO}_4)_2$ and $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. This last complex by reduction with sodium tetrahydroborate gave $[\text{Zn}_2(\mathbf{424c})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. From this dinuclear complex the reduced macrocycle H_2 -**424c** was isolated using H_4edta to remove the zinc ions in alkaline solution [526].

In $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4](\text{ClO}_4)_2$ (Fig. 331a) the macrocycle has a planar form and linear conformation with respect to its polyether chains, producing a large cavity in the center of the ring, into which four zinc ions are encapsulated as a pair of μ -phenoxo-bis(μ -carboxylato)dizinc species. The two zinc ions in each dinuclear core are at a distance of 3.158 Å and are crystallographically inequivalent. However, the metal ions have essentially the same

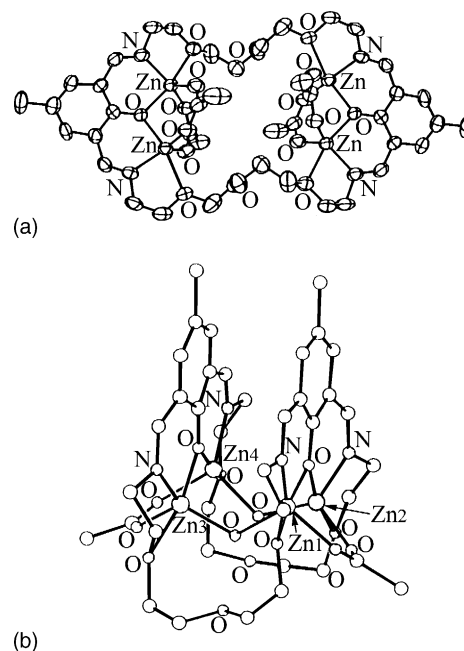


Fig. 331. Structure of $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$ (a) and $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$ (b) (adapted from Ref. [526]).

distorted trigonal bipyramidal coordination geometry, each possessing an NO_4 donor set, i.e. a bridging phenoxo oxygen, an imine nitrogen, and an acetato oxygen, with the phenoxo and ether oxygen atoms occupying the axial sites.

In $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ there is only one bridging acetate each dinuclear zinc core (Fig. 331b). One of the bridging acetate groups at each dinuclear zinc core of $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$ has been replaced by two hydroxo ions in $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2]$, which further coordinate to the other zinc pair thereby linking the two dimer units, yielding a Zn_4O_4 cluster-like ring core. Unlike the planar form of $[\mathbf{424b}]^{2-}$ in $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$, the two polyether chains of the ligand in $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$ are folded and the two dimeric units formed by the phenoxo bridges are paired parallel to each other by π - π stacking of two phenolate rings at a distance of ca. 3.4 Å, which may contribute to the close proximity of the two dimeric units, finally yielding the bis- μ -hydroxo dimer pair. In this compound the four zinc ions are crystallographically inequivalent, while their coordination geometry is trigonal bipyramidal consisting of NO_4 donor sets with the phenoxo and ether oxygens being in axial positions, as is also the case in $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$.

Both compounds have very high symmetry in their solution structures, probably D_{2h} for $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$ and C_{2v} for $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$ on the NMR time-scale. Thus in solution, they retain their respective planar and vent stacking forms seen in the solid state.

$[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$ and $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$ could be selectively isolated by the subtle difference in the solvent used, i.e. the use of dry methanol preferentially gave the first and hydrous methanol gave the second complex. This result suggests that these complexes are interchangeable in solution, depending upon conditions, e.g. water content in the solvent used. In fact, addition of one drop of D_2O to a saturated solution of $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$ in CD_3CN changed its ^1H NMR spectrum to that of $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$. Furthermore, a similar titration experiment using acetic acid with $[\text{Zn}_4(\mathbf{424b})(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})_2]^{2+}$ showed reversion to $[\text{Zn}_4(\mathbf{424b})(\mu\text{-CH}_3\text{COO})_4]^{2+}$, which was also confirmed by ^1H NMR spectroscopy. Thus interconversion between the two tetramine complexes occurs readily in solution, depending on the presence of water or acetic acid.

The dizinc complex derived from $\text{H}_2\text{-424c}$ has been formulated as $[\text{Zn}_2(\mathbf{424c})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]$ or $[\text{Zn}_2(\text{H-424c})(\text{OH})(\text{ClO}_4)_2]$ with different plausible structures for the first formulation: one where the two zinc(II) ions are connected by two phenolate bridges and the other with the two unbridged zinc(II) ion far each other. In the second formulation the two zinc(II) ions are doubly bridged by a phenolate and an hydroxide oxygen. NMR spectroscopy provides evidence that in solution the dimeric complex has

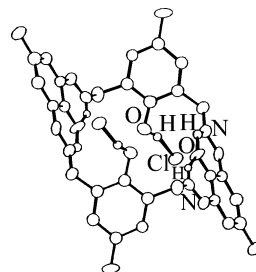


Fig. 332. Structure of $\text{H}_4\text{-425} \cdot 2\text{HCl}$ (adapted from Ref. [527]).

the structure $[\text{Zn}_2(\mathbf{424c})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]$ with the two zinc(II) ions connected by two phenolate bridged [526].

The X-ray structure of the Schiff base obtained by metal free condensation of 2,6-diformyl-4-methylphenol and 2,6-bis(aminoethyl)-4-methylphenol confirms that the product is indeed the [2+2] Schiff base macrocycle $\text{H}_4\text{-425}$. The crystals contain $[\text{H}_6\text{-425}]^{2+}$ cations hydrogen bonded to chloride ions (Fig. 332). The molecule is located around a crystallographic center of inversion [527]. The macrocycle consists of four separate, essentially internally planar blocks hinged together at the four methylene carbon centers, where pronounced twisting of one block relative to its attached neighbour occurs. The most outstanding feature of the molecule is that, despite the overall dipositive charge resulting from protonation, the dialdehyde-derived oxygens are present as deprotonated phenoxide anions. Hydrogen atoms are discernible, attached to all four imine nitrogen centers and to the two oxygen centers which are hydrogen bonded to the chloride ions. The bond lengths within the dialdehyde-derived residue are consistent with the deprotonation of the phenolic group which then acquires some quinonoid character [527].

The reaction of manganese(II) acetate with 2,6-bis(aminoethyl)-4-methylphenol and 2,6-diformyl-4-methylphenol in the presence of lithium acetate and sodium perchlorate in boiling methanol followed by saturation of the solution with dioxygen after it had cooled to room temperature, gave brown crystals which, after being reexposed to the atmosphere, form $[\text{Mn}_2(\text{H}_2\text{-425})(\mu\text{-CH}_3\text{COO})(\mu\text{-OH})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ [527]. The cation $[\text{Mn}_2(\text{H}_2\text{-425})(\mu\text{-CH}_3\text{COO})(\mu\text{-OH})(\text{CH}_3\text{OH})_2]^{2+}$ is situated around a crystallographic two-fold axis of symmetry passing through the bridging hydroxide and through the carbon-carbon bond of a bridging acetate. Each manganese ion has a tetragonally distorted six coordinated environment, indicative of a manganese(III) ion with a high-spin d^4 configuration (Fig. 333).

Magnetic properties confirm the manganese(III) oxidation state. The magnetic moment per Mn is $4.61\mu_B$ at room temperature falling to $1.8\mu_B$ at 10 K, indicative of weak antiferromagnetic coupling ($J = -40 \text{ cm}^{-1}$) [527].

As an extension, the pyridine-modified macrocycle $\text{H}_2\text{-426}$ was prepared by N-alkylation in methanol of $\text{H}_2\text{-319}$ with 2-(chloromethyl)pyridine monohydrochloride in the presence of NaHCO_3 . It can encapsulate four divalent metal

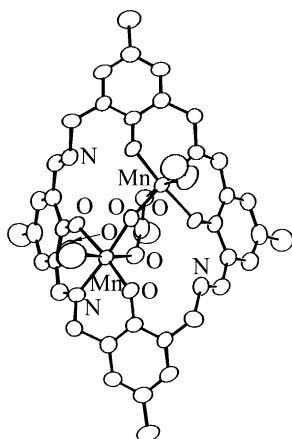


Fig. 333. Structure of $[\text{Mn}_2(\text{H}_2\text{-425})(\mu\text{-OH})(\text{CH}_3\text{COO})_4]^{2+}$ (adapted from Ref. [527]).

ions (Mn^{2+} , Ni^{2+} , Zn^{2+}) when reacted with the appropriate metal acetate hydrate in a 1:4 molar ratio and in the presence of NaClO_4 , giving rise to $[\text{M}_4(\text{426})(\text{CH}_3\text{COO})_4](\text{ClO}_4)_2$ [528]. In the structure of $[\text{Ni}_4(\text{426})(\text{CH}_3\text{COO})_4](\text{ClO}_4)_2$ (Fig. 334) the macrocycle has a planar form and linear conformation with respect to its polyether chains, producing a large cavity in the center of the ring, into which four nickel(II) ions are encapsulated as a pair of μ -phenoxo-bis(μ -carboxylato)dinuclear species. The two nickel ions in each dinuclear core are at a distance of 3.338 Å and are crystallographically inequivalent although they have essentially the same distorted octahedral coordination geometry with N_2O_4 donor sets [528].

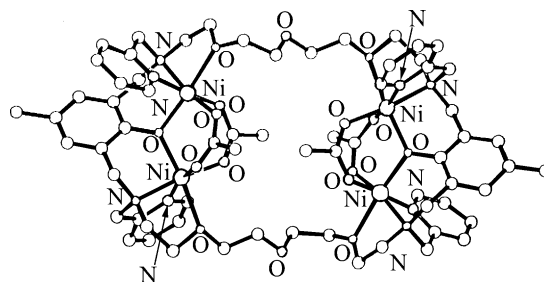
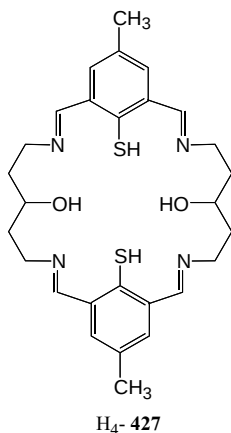
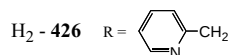
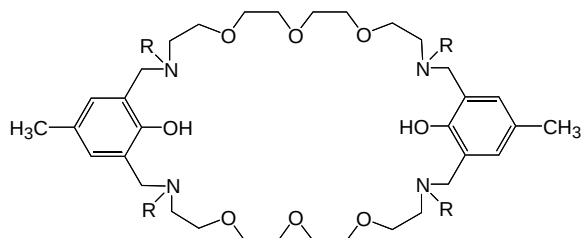


Fig. 334. Structure of $[\text{Ni}_4(\text{426})(\text{CH}_3\text{COO})_4]^{2+}$ (adapted from Ref. [528]).

The μ_{eff} values, 3.07 and 5.46 BM, respectively, for the nickel(II) and manganese(II) complexes at room temperature, indicate that the two metal ions are in the high-spin state. Slight increase of μ_{eff} in $[\text{Ni}_4(\text{426})(\text{CH}_3\text{COO})_4](\text{ClO}_4)_2$ with decreasing temperature with the maximum at ca. 15 K suggests a weak ferromagnetic coupling between the nickel(II) ions. On the other hand, continuous decrease of μ_{eff} in $[\text{Mn}_4(\text{426})(\text{CH}_3\text{COO})_4](\text{ClO}_4)_2$ with decreasing temperature indicates antiferromagnetic coupling between the manganese(II) ions ($J = -4.6 \text{ cm}^{-1}$) [528].

$[\text{Ni}_4(\text{427})(\text{OH})(\text{CH}_3\text{COO})_3(\text{CH}_3\text{COOH})]$, where $\text{H}_4\text{-427}$ is a macrocyclic ligand incorporating thiophenolate, alkoxy and imine donors, was prepared, by the template condensation using solid $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 2,6-diformyl-4-methylthiophenol and 1,5-diamino-3-hydroxypentane under an inert atmosphere in methanol/isopropyl alcohol [529]. In the methanol solvate, $[\text{Ni}_4(\text{427})(\text{OH})(\text{CH}_3\text{COO})_3(\text{CH}_3\text{COOH})] \cdot \text{CH}_3\text{OH}$, (Fig. 335) the four coplanar nickel(II) ions are each coordinated to one thiophenolate sulfur, one alkoxy oxygen and one imine from the macrocycle and to a central μ_4 -hydroxo group. Six coordination is completed by three bridging acetate ligands and one acetic acid group. The macrocyclic donors are *fac* for Ni(1) and Ni(3) but *mer* for Ni(2) and Ni(3). The coordinated acetic acid molecule forms a one atom bridge between Ni(2) and Ni(3) and is also quite strongly hydrogen-bonded to a macrocyclic alkoxy donor. The three acetate ligands act as conventional *syn-syn* three-atom bridges between pairs of nickel ions on the same side of the macrocyclic ring; one of the acetate ions is hydrogen-bonded to the solvent methanol. The oxygen atom of the

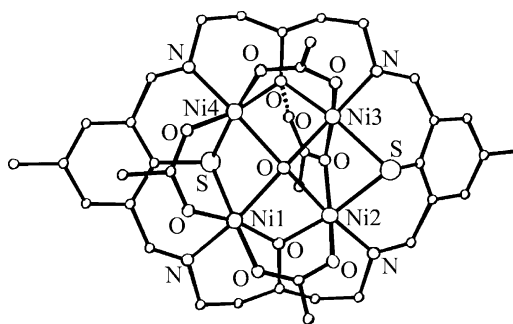
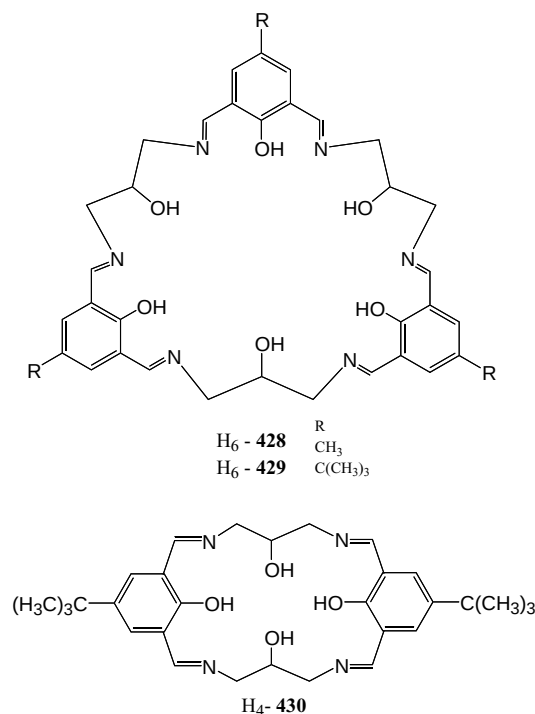


Fig. 335. Structure of $[\text{Ni}_4(\text{427})(\text{OH})(\text{CH}_3\text{COO})_3(\text{CH}_3\text{COOH})]$ (adapted from Ref. [529]).

central μ_4 -hydroxo group projects 0.581 Å from the plane of the four nickel ions into the cavity bounded by the three acetate ligands and is prevented from interacting with any other species. Each nickel ion is linked to the next via three bridging groups. For Ni(1)···Ni(2) and Ni(3)···Ni(4) these are one alkoxo, one hydroxo, one 1,3-acetato group; for Ni(1)···Ni(4), thiophenolato, hydroxo and 1,3-acetato, while Ni(2) and Ni(3) are linked by three single-atom bridges, so that they share one octahedral face [529]. The same structure seems to be maintained in solution. The nickel ions are high-spin and the complex shows net anti-ferromagnetic coupling.

The template condensation of 2,6-diformyl-4-(R)phenol (R = CH₃, C(CH₃)₃) with 1,3-diamino-2-hydroxypropane in the presence of copper(II) or nickel(II) salts and base results in the formation of hexacopper(II) and hexanickel(II) complexes of the [30]-membered, [3+3] macrocyclic ligands H₆-**428**, and H₆-**429**. The macrocyclic rings contain pseudo-hexagonal benzene-like arrangements of metal centers, which are linked by alternating double (μ_2 -phenoxide, μ_2 -hydroxide) and single (μ_2 -alkoxide) bridges within each ring: [Cu₆(L)(μ_2 -OH)₃]₂(X)₆·yH₂O (L = [**428**]⁶⁻, X = NO₃⁻, y = 10; X = ClO₄⁻, y = 6; X = BF₄⁻, y = 8; L = [**429**]⁶⁻, X = ClO₄⁻, y = 8; X = BF₄⁻, y = 14) and [Ni₆(**428**)(μ_2 -OH)₃(H₂O)₆]₂(X)₆·yH₂O (X = ClO₄⁻, y = 4; X = NO₃⁻, y = 16) [530].



The addition of thiocyanate to the mother liquor of [Cu₆(**429**)(μ_2 -OH)₃]₂(ClO₄)₆·8H₂O produced a dinuclear thiocyanate complex with the ligand in the contracted [2+2] macrocyclic form, indicating the formation of an oligomeric mixture in the template reaction [530].

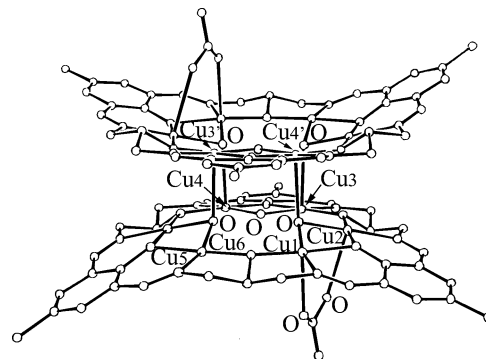


Fig. 336. Structure of [Cu₆(**428**)(μ_2 -OH)₃(NO₃)₂]⁴⁺ (adapted from Ref. [530]).

In the structure of [Cu₆(**428**)(μ_2 -OH)₃(NO₃)₂](NO₃)₄·10H₂O (Fig. 336), the hexanuclear fragment shows a hexagonal arrangement of the six pseudo-square planar copper(II) centers, which are bridged alternately by the μ_2 -hydroxide and μ_2 -phenoxide pair and the μ_2 -alkoxide. The copper ions themselves are consequently linked by alternate short (Cu···Cu = 2.927–2.960 Å; double) and long (Cu···Cu = 3.547–3.571 Å; single) contacts. The chelate rings at the phenolic groups are six-membered, while the alkoxide bridges generate five-membered chelate rings. The net effect of the alternating 6,6,5,5 chelate ring arrangement is to establish a fairly flat hexagonal ring of copper centers, with equatorial copper-oxygen and copper-nitrogen bonds that are all quite short. The essentially planar hexacopper array is unique. The central cavity of each macrocyclic ring is occupied by the three hydroxides, with an asymmetric triangular arrangement of oxygen atoms. The hexanuclear macrocyclic rings are dished slightly and coupled together via their convex faces by two of the hydroxide oxygens, which act as μ_3 linkages connecting Cu(1) and Cu(2) on one ring with Cu(4') on the other and Cu(5) and Cu(6) on one ring with Cu(3') respectively, on the other. The molecular symmetry dictates that this intermacrocyclic bridging also involves symmetry-related atoms, and so the two rings are held together by four axial hydroxide bridges in the dodecanuclear structural arrangement. The inter-ring contacts are relatively short indicating a significant axial interaction at the hydroxide oxygens. A pair of symmetry-related, bidentate nitrate groups, bonded to Cu(1) and to Cu(2), are located on the outer face of the complex. A second pair of oxygen atoms are bonded axially on the outer face to Cu(5) and Cu(6) at a distance of 2.42 Å and are assumed to be part of a second bidentate nitrate. A methanol molecule is coordinated weakly in an axial, external fashion to Cu(4) and a water molecule is bound similarly to Cu(3). A structure determination of [Cu₆(**428**)(μ_2 -OH)₃]₂(ClO₄)₆·8H₂O, shows a similar dodecanuclear arrangement with four relatively short hydroxide contacts linking the hexanuclear halves [530].

The structure of the dicopper(II) complex [Cu₂(**430**)-(NCS)₂]_n, obtained from the mother liquor of [Cu₆(**429**)-

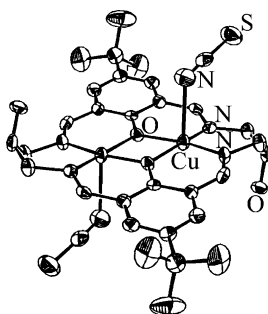


Fig. 337. Structure of $[\text{Cu}_2(\mathbf{430})(\text{NCS})_2]_n$ (adapted from Ref. [530]).

$(\mu_2\text{-OH})_3]_2(\text{ClO}_4)_6 \cdot 8\text{H}_2\text{O}$, (Fig. 337) involves the coordination of two copper(II) centers to the [2+2] macrocycle $[\mathbf{430}]^{2-}$ with the two phenoxide groups bridging the two metals. The secondary alcohol group is not coordinated. The $\text{Cu} \cdots \text{Cu}$ separation is 3.094 Å. The copper centers are bound by four in-plane ligand atoms. A weak bond axial isothiocyanate completes a nominal square pyramidal coordination. The copper ion is displaced by 0.093 Å from the mean plane of the equatorial N_2O_2 donor set. However an additional longer axial contact from one of the secondary disordered alcoholic oxygens effectively completes a distorted six coordinated structure at each copper center and generates a rather complex 2D extended structural arrangement [530].

This dicopper complex although formally polymeric, has a magnetic behaviour typical of the dinuclear copper(II) complexes with a strong antiferromagnetic coupling ($-2J = 675 \text{ cm}^{-1}$).

The variable-temperature magnetic properties of the dodecanuclear copper(II) and nickel(II) complexes have been interpreted using both 6- and 12-spin cluster models and successful data have been obtained with three antiferromagnetic exchange interactions, two occurring within the rings and one between the metallacyclic rings. Thus attempts to fit the magnetic susceptibility to a model with 12 copper(II) centers, arranged in 2 equiv. rings, with alternating coupling constants ($-2J_1$, and $-2J_2$) and with the two rings coupled through 4 equiv. magnetic interactions ($-2J_3$) show that for $[\text{Cu}_6(\mathbf{428})(\mu_2\text{-OH})_3]_2\text{X}_6 \cdot y\text{H}_2\text{O}$ ($\text{X} = \text{NO}_3^-$, $y = 10$, $\text{X} = \text{ClO}_4^-$, $y = 6$) the best fit parameters are $-2J_1 = 303.8 \text{ cm}^{-1}$, $-2J_2 = 262.8 \text{ cm}^{-1}$, and $-2J_3 = 20.0 \text{ cm}^{-1}$ for the first complex and $-2J_1 = 484.5 \text{ cm}^{-1}$, $-2J_2 = 479.0 \text{ cm}^{-1}$, and $-2J_3 = 16.4 \text{ cm}^{-1}$ for the second one. When a six-copper(II) ion model obtained by the intramolecular magnetic interaction within the ring containing the six metal ion, is used, the following data were obtained and $-2J_1 = -2J_2 = 318.4 \text{ cm}^{-1}$ for $[\text{Cu}_6(\mathbf{429})(\mu_2\text{-OH})_3]_2(\text{NO}_3)_6 \cdot 10\text{H}_2\text{O}$, $-2J_1 = -2J_2 = 485.2 \text{ cm}^{-1}$ for $[\text{Cu}_6(\mathbf{428})(\mu\text{-OH})_3](\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$ and $-2J_1 = -2J_2 = 598.8 \text{ cm}^{-1}$ for $[\text{Cu}_6(\mathbf{429})(\mu_2\text{-OH})_3]_2(\text{ClO}_4)_6 \cdot 8\text{H}_2\text{O}$.

On the assumption that the nickel derivatives have a structure similar to those of the copper analogues, using the strategy employed for the copper(II) derivatives, the

complexes $[\text{Ni}_6(\mathbf{428})(\mu_2\text{-OH})_3(\text{H}_2\text{O})_6]_2(\text{X})_6 \cdot y\text{H}_2\text{O}$, ($\text{X} = \text{ClO}_4^-$, $y = 4$ and $\text{X} = \text{NO}_3^-$, $y = 16$) show the exchange couplings $2J_1 = 31.4 \text{ cm}^{-1}$, $2J_2 = -3.0 \text{ cm}^{-1}$ and $2J_3 = 0.34 \text{ cm}^{-1}$, $2J_2 = -4.0 \text{ cm}^{-1}$, respectively. For both complexes, the data indicate that both ferromagnetic and antiferromagnetic exchange mechanisms are operative; for the first complex it is apparent that the ferromagnetic term dominates, while for the second one the net exchange is antiferromagnetic [530].

The transmetallation of $[\text{Ba}(\text{H}_2\text{-}\mathbf{118})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, where $\text{H}_2\text{-}\mathbf{118}$ is the macrocyclic ligand formed by a [2+2] condensation of 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol, with manganese(II) acetate tetrahydrate in methanol can yield either the pentamanganese(II) complex $[\text{Mn}_5(\mathbf{118})_2(\text{CH}_3\text{COO})_2(\text{ClO}_4)_2](\text{ClO}_4)_2$ or the tetramanganese(II) complex $[\text{Mn}_4(\mathbf{118})_2(\text{CH}_3\text{COO})_2](\text{ClO}_4)_2$ [531]. Transmetallation reactions in which the Ba/Mn ratio was 1:2 or less always resulted in formation of the tetramanganese complex. Similarly, ratios greater than 1:3 yielded only the pentamanganese product. Only in one case, where Ba/Mn was 1:3 and the solution was refluxed, was a mixture of both complexes isolated. When the Ba/Mn ratio is 1:2.5, however, the nature of the product is controlled by the treatment of the manganese(II) acetate solution before addition to the refluxing solution of the barium complex. Freshly prepared, cold solutions yielded only the tetramanganese complex whereas briefly heating the solution to reflux resulted in isolation of the pentamanganese complex. Further, investigations using ethanol as solvent in place of methanol have yielded only the pentamanganese complex. Addition of sodium methoxide to a fresh cold solution of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in methanol, followed by transmetalation yields the tetramanganese species [531].

$[\text{Mn}_5(\mathbf{118})_2(\text{CH}_3\text{COO})_2(\text{ClO}_4)_2]^{2+}$ (Fig. 338a), consists of two folded binuclear macrocyclic units, bridged by an octahedrally coordinated manganese ion and two supporting acetate groups. The structure is centrosymmetric; Mn(3) is located on an inversion center, bonded to the two deprotonated alkoxide groups of each macrocycle and to both acetate groups. Each acetate ion bridges three manganese ions, one from each macrocyclic sub-unit plus Mn(3) and exhibit both single and three-atom bridging modes. Mn(2) and Mn(3) are linked by a three-atom acetate bridge but Mn(3) and Mn(1) are bridged by a single oxygen atom from the acetate group. The geometry of the acetate bridge can be described as *syn-syn, anti* coplanar. Mn(1) and Mn(2) are both seven coordinated with approximate pentagonal bipyramidal geometry. The pentagonal plane contains the macrocyclic donor atoms (three nitrogen atoms and two alkoxide groups) and the axial ligands are acetate and an oxygen atom from a perchlorate ion. The cavity created by the folding of the macrocycle is occupied by a coordinated perchlorate anion and the perchlorate oxygen acts as an asymmetric single atom bridge linking the two manganese ions. In the pentanuclear cation the fold in the macrocycle creates a preorganized cleft incorporating the vacant coordination

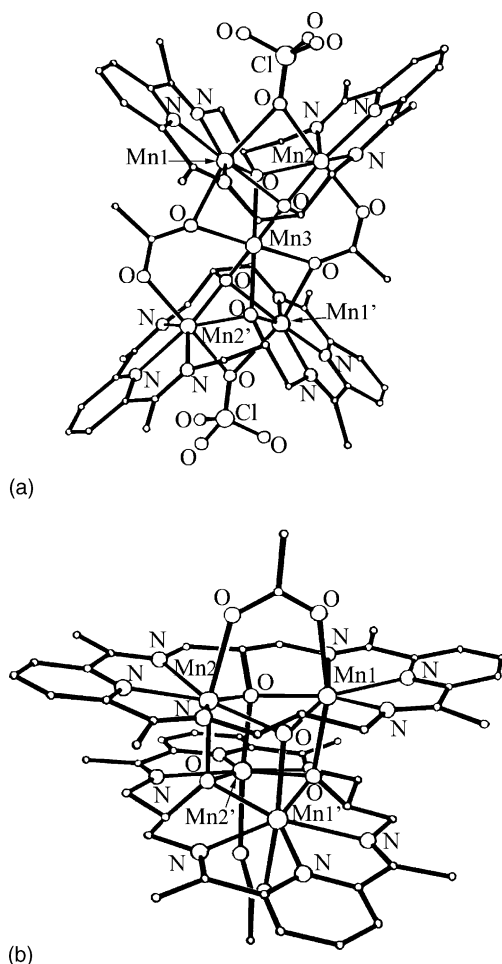


Fig. 338. Structures of $[\text{Mn}_5(\mathbf{118})_2(\text{CH}_3\text{COO})_2(\text{ClO}_4)_2]^{2+}$ (a) and $[\text{Mn}_4(\mathbf{118})_2(\text{CH}_3\text{COO})_2]^{2+}$ (b) (adapted from Ref. [531]).

sites on two manganese ions, this constitutes an attractive binding site for any available donor. It is possible to replace the bridging perchlorate by bridging water or DMF without significant change to the rest of the structure [531].

The cations $[\text{Mn}_4(\mathbf{118})_2(\text{CH}_3\text{COO})_2]^{2+}$ (Fig. 338b), and $[\text{Mn}_4(\mathbf{118})_2(\text{HCOO})_2]^{2+}$ are very similar; both are dimeric, each half containing one binuclear macrocycle and an acetate (or formate) group bridging the two manganese(II) ions in *syn-syn* coplanar geometry. The dimers are held together by four manganese-alkoxide bonds, resulting in formation of a $\{\text{Mn}_4(\text{alkoxide})_4\}$ cubane core. The manganese ions have approximate pentagonal bipyramidal geometry, the donors in the pentagonal plane come from one macrocyclic ligand, one axial donor is an alkoxide from the second macrocycle and the second is from the bridging carboxylate group. Formation of the central cubane requires that the two macrocycles be staggered with respect to each other, rather than eclipsed as in $[\text{Mn}_5(\mathbf{118})_2(\text{CH}_3\text{COO})_2(\text{ClO}_4)_2]^{2+}$. A further difference is that in the two tetramanganese complexes the macrocyclic ligands are approximately planar, whereas in the pentamanganese complex there is marked folding of the ligand [531]. The manganese

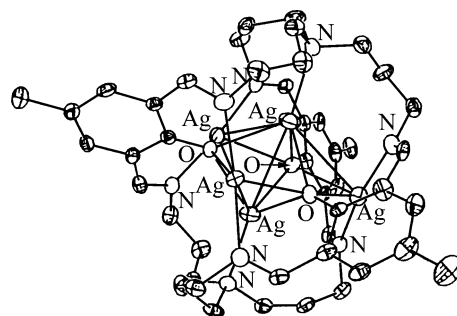


Fig. 339. Structure of $[\text{Ag}_5(\mathbf{334})]^{2+}$ (adapted from Ref. [532]).

ions in both tetramanganese complexes are in essentially the same pentagonal bipyramidal geometry.

All the complexes are stable in solution and there is no indication of aerobic oxidation. Cyclic voltammetry on $[\text{Mn}_4(\mathbf{118})(\text{HCOO})_2]^{2+}$ showed no signals attributable to metal redox within the accessible range (−2.0 to 1.0 V). $[\text{Mn}_5(\mathbf{118})(\text{CH}_3\text{COO})_2(\text{ClO}_4)_2]^{2+}$ however shows an irreversible oxidation peak at 0.78 V (relative to Ag/AgClO_4 (0.01 M)) and an associated reduction process close to 0.0 V [531]. Bulk controlled potential electrolysis confirmed that the 0.78 V peak corresponds to a one-electron oxidation process, consistent with the suggestion that only the central, six coordinated manganese is being oxidized. Cyclic voltammetry of the solution following the electrolysis confirmed the irreversible nature of the process.

$[\text{Mn}_5(\mathbf{118})_2(\text{CH}_3\text{COO})_2(\text{ClO}_4)_2](\text{ClO}_4)_2$ and $[\text{Mn}_4(\mathbf{118})_2(\text{CH}_3\text{COO})_2](\text{ClO}_4)_2$ show net weak antiferromagnetic coupling.

The pentanuclear silver(I) compounds $[\text{Ag}_5(\mathbf{334})](\text{ClO}_4)_2 \cdot 4\text{CH}_3\text{OH}$ and $[\text{Ag}_5(\mathbf{334})](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ were obtained by [3+2] condensation of 2,6-diformyl-4-methylphenol and tris(2-aminopropyl)amine in the presence of AgNO_3 as template in methanol, followed by the addition respectively of NaClO_4 or NaBF_4 [532]. In $[\text{Ag}_5(\mathbf{334})]^{2+}$ (Fig. 339), the five silver(I) centers are enclosed within the polyaza cryptand and are coordinated by phenoxide oxygens and imine nitrogens. The central Ag_5O_3 core exhibits a hexagonal bipyramidal geometry with distorted D_{3h} symmetry. Three silver ions and three phenolic oxygens form the hexagonal base while the other two silver ions are located symmetrically on the axis. The $\text{Ag} \cdots \text{Ag}$ distances range between 3.083 Å and 3.389 Å. The coordination mode of the polyazacryptate to the silver(I) cluster is quite unusual, the macrocyclic phenolic groups are all deprotonated and participate in coordination together with all the nitrogen atoms of the ligand which exerts a profound stabilizing effect to the cluster. The bridgehead nitrogens coordinate with the axial silver ions thus the two bridgehead nitrogens can be considered to be located approximately on the principal axis. The two imine nitrogens of each bridge chain originating from the ridge head nitrogens bind to two in-plane silver ions from opposite directions.

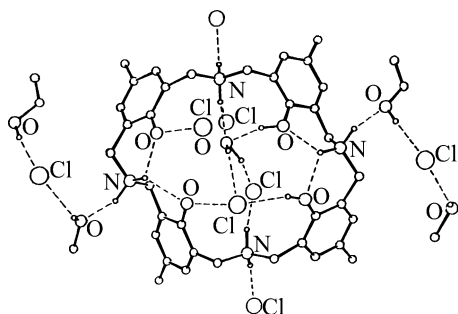


Fig. 340. Structure of $[(H_8-431)](Cl)_4 \cdot H_2O \cdot CH_3OH \cdot C_2H_5OH$ (adapted from Ref. [533]).

The coordination of six nitrogen atoms of the imine groups makes the three bridge chains *cis*-spiral up along the principal axis from the outside of the silver(I) cluster. The three bridge chains are located symmetrically in accord with the ^1H NMR spectra. The coordination of oxygen atoms of phenolic hydroxy, the large cavity of cryptand and the spiral binding of the three highly flexible bridge chains make the assembly of this silver(I) cluster within the cryptand possible, and lead to the high stability of this structure [532].

The reduction with $NaBH_4$ of the macrocyclic Schiff base H_4-427 affords the corresponding tetraaminotetraphenolic macrocyclic ligand H_4-431 . The structure of $[H_8-431](Cl)_4 \cdot H_2O \cdot CH_3OH \cdot C_2H_5OH$, reveals the $[H_8-431]^{4+}$ cation adopts a dome-shaped arrangement with all four phenolic oxygen atoms oriented toward the top of the dome and the aromatic methyl groups along its lower rim. The four nitrogen atoms are close to planar. The four aromatic rings are inclined almost equally to this average N_4 plane (Fig. 340). The macrocycle is deformed by internal hydrogen bonding. Two of the chlorides and both the methanol and ethanol are located outside the $[H_8-431]^{4+}$ dome whereas the water and the other two chlorides are inside. The water molecule is approximately centrally located within the macrocyclic cavity [533].

The reaction of $[H_8-431](Cl)_4$ with zinc acetate in methanol containing tetraethylammonium hydroxide affords $[Zn_4(431)(OH)(CH_3COO)_3(CH_3OH)] \cdot 1.5CH_3OH$ (Fig. 341a).

The complex is bowl-shaped but totally lacking in symmetry, being present in the crystal in enantiomeric pairs. The four zinc arrangement resembles an unsymmetrical kite with Zn(1) at the moist acute vertex, which has been bent from planarity around its short diagonal, $Zn(2) \cdots Zn(4)$. Each zinc(II) ion is bound to $[431]^{4-}$ by two phenolate oxygens and one nitrogen. An approximately centrally located hydroxide is strongly coordinated to Zn(2) and Zn(4) less strongly to Zn(3) and weakly if at all to Zn(1). An acetate on the concave surface of the bowl bridges Zn(2) and Zn(4). A monodentate acetate completes the coordination sphere of Zn(1) which has an irregular four-coordinate geometry if the weak interaction with the central hydroxo ligand is ignored. Zn(2) is of pseudo-octahedral geometry

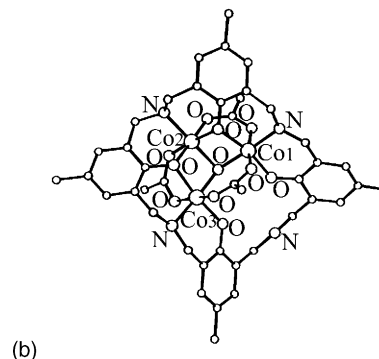
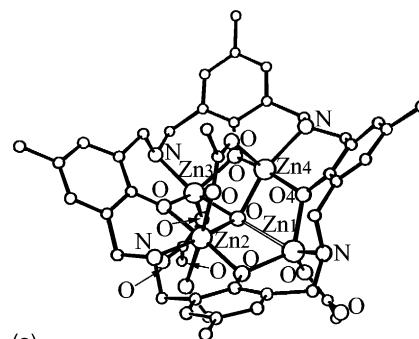


Fig. 341. Structures of $[Zn_4(431)(OH)(CH_3COO)_3(CH_3OH)]$ (a) and $[Co_3(431)(OH)(CH_3COO)_3]^+$ (b) (adapted from Ref. [533]).

with a coordinated methanol *trans* to the bridging acetate oxygen. Zn(3) with a monodentate acetate has an irregular five coordinated geometry, intermediate between square pyramidal and trigonal bipyramidal. Zn(4) is five coordinated, being bonded to two phenolates and one nitrogen of $[431]^{4-}$, to the central hydroxide, and to an oxygen of the bridging acetate; its geometry approximates to square pyramidal with the acetato oxygen occupying the apical position [533].

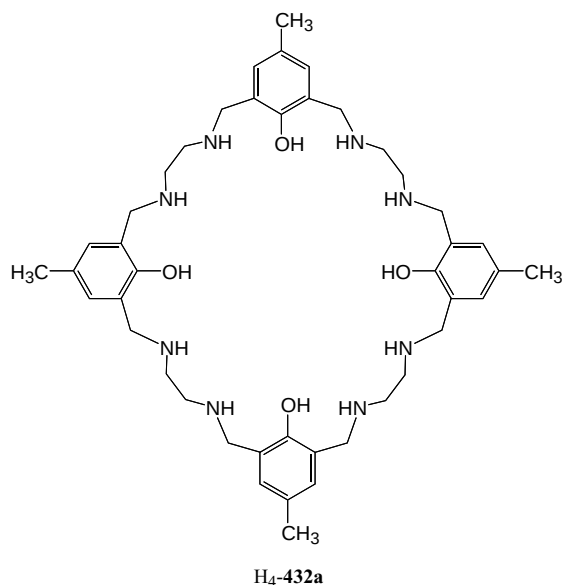
^{13}C and ^1H NMR spectra of a freshly dried sample of the tetrazinc complex in $CDCl_3$ are consistent with the presence of solution species undergoing rapid interconversion so as to produce an averaged arrangement with C_{2v} symmetry [533].

The reaction in air of $[H_8-431](Cl)_4$ with cobalt(II) acetate in the presence of OH^- and BF_4^- yields $[Co^{III}_3(431)(OH)(CH_3COO)_3](BF_4) \cdot 3.83H_2O$ (Fig. 341b). The cation $[Co_3^{III}(431)(OH)(CH_3COO)_3]^+$ adopts a saddle-shaped conformation with three cobalt(III) ions in a triangular arrangement $[Co(1) \cdots Co(2) = 2.851 \text{ \AA}; Co(1) \cdots Co(3) = 3.369 \text{ \AA}; Co(2) \cdots Co(3) = 2.804 \text{ \AA}]$. The fourth nucleation site provided by the macrocycle is vacant. Each of the three metal ions is essentially octahedral, the macrocyclic ligand providing two phenolate oxygen donors and one amine nitrogen donor to each, meridional at Co(1) and Co(3) and facial at Co(2). A pyramidal μ_3 -hydroxide is almost equidistant from the three cobalt ions and is $0.667 \text{ \AA}$ below the Co(3) plane. Two acetate coligands on the same side of the Co(3) plane as the hydroxide bridge from Co(1) to Co(2)

and from Co(3) to Co(2) such that they are *cis* at Co(2). A third μ_2 -acetate on the opposite side of the Co(3) plane bridges from Co(1) to Co(3) so the two acetates bound to each of these centers are *trans* to each other. The hydrogens of the three coordinating amines are mutually *syn* on the same side of the Co(3) plane as the hydroxide. The two bridging phenoxide oxygen centers are markedly pyramidal [533].

^1H and ^{13}C NMR spectra in CD_3OD are consistent with the presence in solution of the two enantiomeric conformers seen in the crystal structure undergoing rapid inter-conversion by ligand flexing so as to generate an averaged conformation with C_s symmetry [533].

The facile synthesis of the [38]-membered highly flexible macrocyclic ligand, **H₄-432a**, provides an entry to polynuclear complexes where metal–ligand self assembly is controlled by the steric requirement of the metal ions [534]. **H₄-117** was synthesized by reacting in methanol 2,6-diformyl-4-methylphenol, 1,2-diaminoethane, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a 2:2:1:1 molar ratio. The subsequent reduction of the magnesium Schiff base by NaBH_4 , followed by acidification of the resulting product with HCl , affords **H₄-432a**·8HCl.



An aqueous solution of **H₄-432a**·8HCl, on treatment with NH_3 , followed by extraction with CHCl_3 and recrystallization from $\text{CHCl}_3/\text{CH}_3\text{OH}$, gave **H₄-432a**. The uncomplicated NMR spectra of **H₄-432a** indicate that in solution conformational changes are very rapid. The self-assembly of metal ions with this macrocycle is governed primarily by the steric requirements of the metal ions. When a metal ion prefers six coordination the presence of other auxiliary bridging and/or coordinating molecules or anions are essential. On the other hand, a square planar orienting metal ion will force the ligand to adopt a helically twisted configuration.

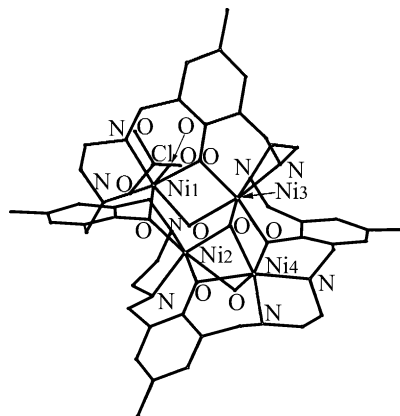


Fig. 342. Structure of $[\text{Ni}_4(\mathbf{432a})(\text{OH})(\text{H}_2\text{O})_2(\text{ClO}_4)]^{2+}$ (adapted from Ref. [534]).

$[\text{Ni}_4(\mathbf{432a})(\mu_3\text{-OH})(\mu\text{-H}_2\text{O})_2(\text{ClO}_4)](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{COCH}_3 \cdot \text{H}_2\text{O}$ has been synthesized by refluxing equimolar methanolic solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and **H₄-432a** in the presence of triethylamine, followed by recrystallization of the crude product from acetone. The cation $[\text{Ni}_2(\mathbf{432a})(\mu_3\text{-OH})(\mu\text{-H}_2\text{O})_2(\text{ClO}_4)]^{2+}$ (Fig. 342) completely lacks symmetry. Within the macrocycle, the four non coplanar nickel ions are in a distorted octahedral environment, and each metal ion is coordinated to two amine nitrogens and two bridging phenoxide oxygens. Three of these metal centers, Ni(2), Ni(3), and Ni(4), are anchored by the tricoordinated hydroxyl oxygen, while each pair of metal ions is bridged by the water molecules. The sixth coordination site of Ni(1) is occupied by the perchlorate oxygen. The intramolecular distances between the nickel ions lie in the range 2.93–5.13 Å [534].

The reaction of copper(II) acetylacetonate and **H₄-432a** in a 2:1 molar ratio produces $[\text{Cu}_2(\mathbf{432a})] \cdot \text{H}_2\text{O}$ which readily reacts with zinc and magnesium perchlorate or nitrate to give the heterotrimeric complexes $[\text{Cu}_2\text{Zn}(\text{H-}\mathbf{432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, $[\text{Cu}_2\text{Mg}(\text{H-}\mathbf{432a})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{Mg}(\text{H-}\mathbf{432a})](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$. In these complexes the ligand is mono-protonated at an uncoordinated secondary amine nitrogen. When $[\text{Cu}_2(\mathbf{432a})] \cdot \text{H}_2\text{O}$ is treated with copper(II) perchlorate, the tetranuclear complex $[\text{Cu}_4(\mathbf{432a})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ is obtained instead of the expected tricopper species. $[\text{Cu}_4(\mathbf{432a})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ can be directly synthesized from 4 equiv. of copper(II) perchlorate, 1 equiv. of **H₄-432a** and 4 equiv. of triethylamine. This compound on treatment with 1 equiv. of sodium hydroxide affords the hydroxide-bridged complex $[\text{Cu}_4(\mathbf{432a})(\mu_3\text{-OH})](\text{ClO}_4)_3 \cdot \text{CH}_3\text{OH}$ [535].

The structure of $[\text{Cu}_2\text{Zn}(\text{H-}\mathbf{432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ (Fig. 343) consists of a hetero-dinuclear CuZn core and an isolated copper site. In the hetero-dinuclear unit the two metal centers are bridged by the phenolate oxygens; the copper ion lies in a distorted N_2O_2 square plane, while the zinc ion has a N_3O_2 trigonal bipyramidal geometry. The isolated copper ion also obtains a square planar geometry by

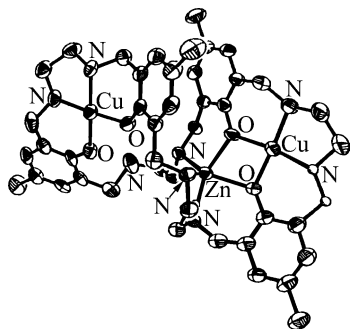


Fig. 343. Structure of $[\text{Cu}_2\text{Zn}(\text{H-432a})]^{3+}$ (adapted from Ref. [535]).

coordinating with the amine nitrogen atoms and the phenolate oxygen atoms. The composition of $[\text{Cu}_2\text{Zn}(\text{H-432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ suggests that the remaining uncoordinated amine nitrogen atom is protonated. The two amine nitrogen atoms and one phenolic oxygen atom provide the N_2O basal plane of the trigonal bipyramidal coordination sphere of zinc, the axial donors being one phenolic oxygen and one nitrogen aminic atom. Further, compared to the distance of 3.08 Å between copper and zinc ions within the dinuclear unit, the isolated copper ion is separated from the other copper and zinc ions by 8.13 and 5.61 Å, respectively. In the coordinating process with the metal ions the macrocycle is extensively twisted and has attained an incomplete helical structure. Clearly, in the metal–ligand self assembly the helical twist occurs as a result of the steric requirement of the square plane orienting the copper(II) centers, and the role of the zinc ion in $[\text{Cu}_2\text{Zn}(\text{H-432a})]^{3+}$ (or of the magnesium ion in $[\text{Cu}_2\text{Mg}(\text{H-432a})]^{3+}$) is to stabilize this configuration by anchoring the available donor sites [535].

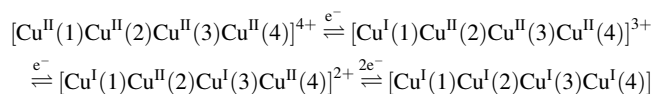
The electronic spectra of $[\text{Cu}_2\text{Zn}(\text{H-432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, $[\text{Cu}_2\text{Mg}(\text{H-432a})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{Mg}(\text{H-432a})](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ show that the two non-interacting copper(II) centers have approximately square planar geometry with some displacement from the respective basal planes. By contrast, the adjacent metal centers in $[\text{Cu}_4(\text{432a})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ are linked by phenolate bridges and each of the copper(II) ions is presumably bound to a water molecule and therefore they probably have a square pyramidal geometry. In $[\text{Cu}_4(\text{432a})(\mu_3\text{-OH})](\text{ClO}_4)_3 \cdot \text{CH}_3\text{OH}$ the three copper(II) centers anchored to the hydroxide ion are likely to be more displaced from the square plane and have a different stereochemistry from that of the remaining copper(II) center which, in turn, probably is bound to the methanol molecule [535].

In the structure of $[\text{Cu}_2\text{Zn}(\text{H-432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, both the copper(II) centers have an N_2O_2 coordination environment, but one is linked to the zinc ion by two phenolate bridges. Thus, the two copper(II) centers are magnetically non-equivalent because the localized electron densities are not the same as indicated by the ESR spectra which show also that $[\text{Cu}_2\text{Mg}(\text{H-432})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ is isostructural with

$[\text{Cu}_2\text{Zn}(\text{H-432})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$. In the 90–300 K temperature range the magnetic moment of $[\text{Cu}_2\text{Zn}(\text{H-432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ remains essentially unchanged showing the two copper(II) centers are magnetically not interacting [535].

The redox behaviour of $[\text{Cu}_2\text{Zn}(\text{H-432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ and $[\text{Cu}_4(\text{432a})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ have been studied by cyclic voltammetry and differential pulse voltammetry using $(\text{CH}_3)_2\text{SO}$ solutions and a glassy carbon working electrode for scanning in the negative potential ranges while CH_3CN solutions and a platinum electrode were employed at positive potentials. $[\text{Cu}_2\text{Zn}(\text{H-432a})](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ reduction of both the copper(II) centers takes place irreversibly, however the copper bridged with zinc is reduced more easily relative to the other. The cyclic voltammetry of $[\text{Cu}_2\text{Zn}(\text{H-432a})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ shows that in the cathodic sweep two closely spaced waves with peaks at -0.58 and -0.70 V are followed by a third wave at -1.32 V. In the reverse scan, however, instead of three, only two peaks are observed at -1.08 and -0.46 V.

Apparently in $[\text{Cu}_4(\text{432a})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ the anodic peak at -0.46 V indicates that two one-electron charge-transfer processes are succeeded by a single-step two-electron transfer. The addition of the first electron to one of the copper(II) centers, for example $\text{Cu}^{\text{II}}(1)$, is closely followed by the addition of the second electron to the diagonally opposite metal center $\text{Cu}(3)$. Further addition of electrons is more difficult because the positive charge of the complex cation is now depleted. Since the probabilities of electron transfer to $\text{Cu}^{\text{II}}(2)$ and $\text{Cu}^{\text{II}}(4)$ are equal, sequential addition of two electrons to these two metal centers occurs either at the same or nearly same potentials.



The electrochemical behaviour of complexes $[\text{Cu}_2\text{Zn}(\text{H-432a})]^{3+}$ and $[\text{Cu}_4(\text{432a})]^{4+}$ with regard to oxidation at the metal centers is characterized by slow rates of heterogeneous electron-transfer processes. Consequently, up to $+1.5$ V a single irreversible wave occurs with a peak at 0.95 V for $[\text{Cu}_2\text{Zn}(\text{H-432a})]^{3+}$ and 1.2 V for $[\text{Cu}_4(\text{432a})]^{4+}$ [535].

The hydroxo bridge in $[\text{Ni}_4(\text{432a})(\mu_3\text{-OH})(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{COCH}_3 \cdot 2\text{H}_2\text{O}$ can be replaced by other bridging anions (NCS^- , N_3^- , CH_3COO^- , Cl^-) to generate $[\text{Ni}_4(\text{432a})(\mu_2\text{-NCS})_2(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$, $[\text{Ni}_4(\text{432a})(\mu_2\text{-N}_3)_2(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$, $[\text{Ni}_4(\text{432a})(\mu_2\text{-CH}_3\text{COO})_2(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, and $[\text{Ni}_4(\text{432a})(\mu_2\text{-Cl})_2(\mu_2\text{-H}_2\text{O})_2](\text{Cl})_2 \cdot 4\text{H}_2\text{O}$ [536].

When $\text{Ni}(\text{acac})_2$ is reacted with $\text{H}_4\text{-432a}$, irrespective of the ratio of the reactants, $[\text{Ni}_3(\text{432a})(\text{acac})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ is obtained. This compound on further reaction with nickel(II) perchlorate forms the tetranuclear complex $[\text{Ni}_4(\text{432a})(\text{acac})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ [536].

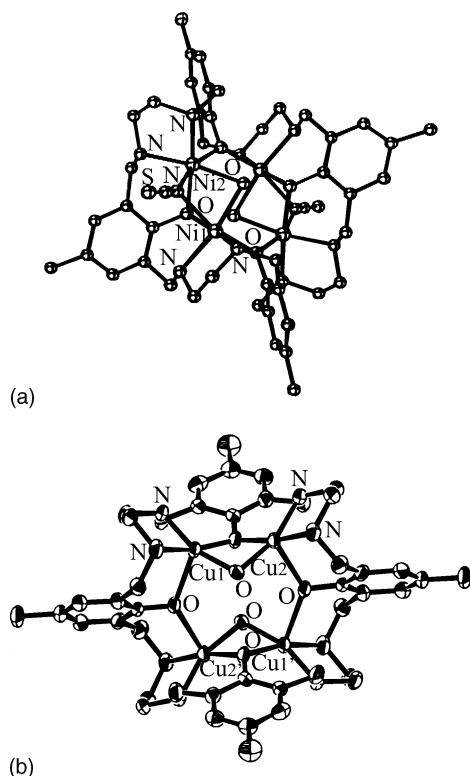


Fig. 344. Structure of $[\text{Ni}_4(\mathbf{432a})(\text{NCS})_2(\mu\text{-H}_2\text{O})_2]^{2+}$ (a) and $[\text{Cu}_4(\mathbf{432a})(\mu\text{-OH})_2]^{2+}$ (b) (adapted from Ref. [536]).

The structure of $[\text{Ni}_4(\mathbf{432a})(\mu_2\text{-NCS})_2(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ shows the nickel ions are triply-bridged by a phenoxide oxygen, an aqua oxygen and a thiocyanate nitrogen; an additional bridge is provided to each of the metal centers by other phenoxide oxygens. The coordination sphere NiN_3O_3 is completed by two secondary amine nitrogens of the macrocyclic ligand. A significant distortion of the octahedral geometry of nickel(II) has been observed. The distances between the metal centers are: $\text{Ni}(1) \cdots \text{Ni}(2) = 2.845 \text{ \AA}$ and $\text{Ni}(1) \cdots \text{Ni}(2') = 3.808 \text{ \AA}$ (Fig. 344a).

Under similar experimental conditions $\text{H}_4\text{-432a}$ reacts with NaOH and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in a 1:4:4 molar ratio to form a greenish powder which, after recrystallization from a methanol solution containing few drops of $\text{N}(\text{Et})_3$, affords $[\text{Cu}_4(\mathbf{432a})(\text{OH})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$. The hydroxo bridge is considered to be formed in the basic solution of methanol with triethylamine on recrystallization when taking into account that the recrystallization without triethylamine gave the water bridged complex $[\text{Cu}_4(\mathbf{432a})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_4$. The tetranuclear structure, confirmed by X-ray analysis on $[\text{Cu}_4(\mathbf{432a})(\text{OH})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$, shows the coordination sites of copper(II) ions are occupied with two secondary amine nitrogens, two μ -phenoxo oxygens, and μ -hydroxo oxygen. The copper(II) ions are alternately singly- and doubly-bridged with phenoxo oxygen and hydroxo and phenoxo

oxygens in a square pyramidal configuration (Fig. 344b) [536].

The description of the magnetic properties of $[\text{Ni}_4(\mathbf{432a})(\mu_3\text{-OH})(\mu_2\text{-H}_2\text{O})_2(\text{ClO}_4)](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{COCH}_3 \cdot \text{H}_2\text{O}$, owing to its non symmetrical structure has been modelled by considering two J values while the exchange interaction in $[\text{Cu}_4(\mathbf{432a})(\text{H}_2\text{O})_4](\text{ClO}_4)_4$ has been modelled by considering a single J because each of the metal centers are bridged by a pair of phenoxides only. Accordingly variable-temperature (4–300 K) magnetic susceptibility measurements indicate that the best-fit spin exchange parameters obtained are respectively: $J = -288 \text{ cm}^{-1}$ for $[\text{Cu}_4(\mathbf{432a})(\text{H}_2\text{O})_4](\text{ClO}_4)_4$; $J_1 = -8.1 \text{ cm}^{-1}$, $J_2 = -10.2 \text{ cm}^{-1}$ for $[\text{Ni}_4(\mathbf{432a})(\mu_3\text{-OH})(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{COCH}_3 \cdot \text{H}_2\text{O}$; $J_1 = -34.5 \text{ cm}^{-1}$, $J_2 = -9.5 \text{ cm}^{-1}$ for $[\text{Ni}_4(\mathbf{432a})(\mu_2\text{-NCS})_2(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$; $J_1 = -34 \text{ cm}^{-1}$, $J_2 = 11 \text{ cm}^{-1}$ for $[\text{Ni}_4(\mathbf{432a})(\mu_2\text{-N}_3)_2(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$; $J_1 = -30 \text{ cm}^{-1}$, $J_2 = -7.0 \text{ cm}^{-1}$ for $[\text{Ni}_4(\mathbf{432a})(\mu_2\text{-CH}_3\text{COO})_2(\mu_2\text{-H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$; $J_1 = -32 \text{ cm}^{-1}$, $J_2 = -4 \text{ cm}^{-1}$ for $[\text{Ni}_4(\mathbf{432a})(\mu_2\text{-Cl})_2(\mu_2\text{-H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ [536]. $[\text{Cu}_2(\mathbf{432a})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ shows an antiferromagnetic behaviour with a selectively small coupling constant value ($J = -35 \text{ cm}^{-1}$) while for $[\text{Cu}_2(\mathbf{432a})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_4$ a J value of -323 cm^{-1} was calculated [536].

The formation of the hetero-dinuclear complexes $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\mathbf{364})(\mu_2\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot n\text{H}_2\text{O}$ ideally requires a mononuclear iron(III) precursor complex which, however, is not accessible. On the other hand, the dimeric complex $[\text{Fe}_2^{\text{III}}(\text{H-364})_2(\mu_2\text{-OH})_2](\text{ClO}_4)_2$, readily obtained by reacting iron(III) perchlorate with $\text{H}_2\text{-364}$ in the presence of either sodium acetate or triethylamine [537], reacts with 2 equiv. of the divalent metal perchlorate in the presence of an excess of sodium acetate to form the hetero-dinuclear complexes $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\text{H-364})(\mu_2\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot n\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Zn}^{2+}$, Ni^{2+} , Co^{2+} , Mn^{2+}). The cobalt(III) center in the $\text{Fe}^{\text{III}}\text{Co}^{\text{III}}$ complex can be oxidized with alkaline hydrogen peroxide to produce the heterotetranuclear complex $[\{\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})\}_2(\mu\text{-O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, in a rather poor yield because substantial decomposition the precursor complex occurs due to undesirable side reaction of hydrogen peroxide. The IR and UV-Vis spectra of the $\text{Fe}^{\text{III}}\text{M}^{\text{II}}$ complexes indicate that in all the cases the metal ions have similar coordination environments. A disordered crystal structure determined for $[\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot n\text{H}_2\text{O}$ reveals that the two metal centers are bridged by the two phenolate oxygens as well as by an acetate. Both the metal centers are six coordinated with irregular octahedral geometry and have N_2O_2 equatorial donors provided by the macrocyclic ligand. The remaining apical position of the iron(III) center is occupied by a water molecule, while that of the nickel(II) by an acetate oxygen (Fig. 345a).

$[\{\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})\}_2(\mu\text{-O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Fig. 345b) comprises two identical hetero-dinuclear

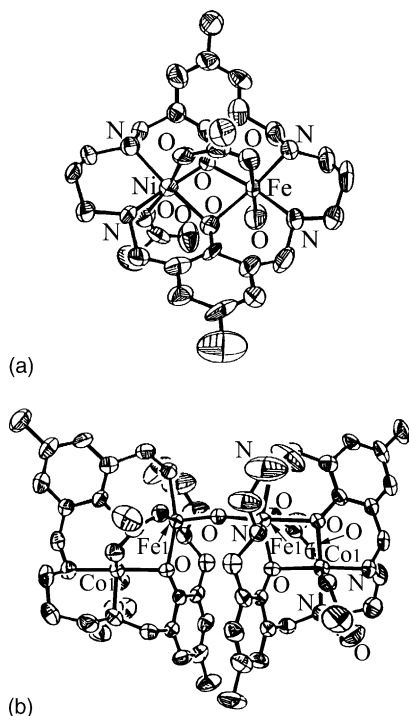


Fig. 345. Structures of $[\text{FeNi}(\mathbf{364})(\mu\text{-CH}_3\text{COO})_2(\text{H}_2\text{O})]^+$ and $[\{\text{CoFe}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})\}_2(\mu\text{-O})]^{2+}$ (b) (adapted from Ref. [537]).

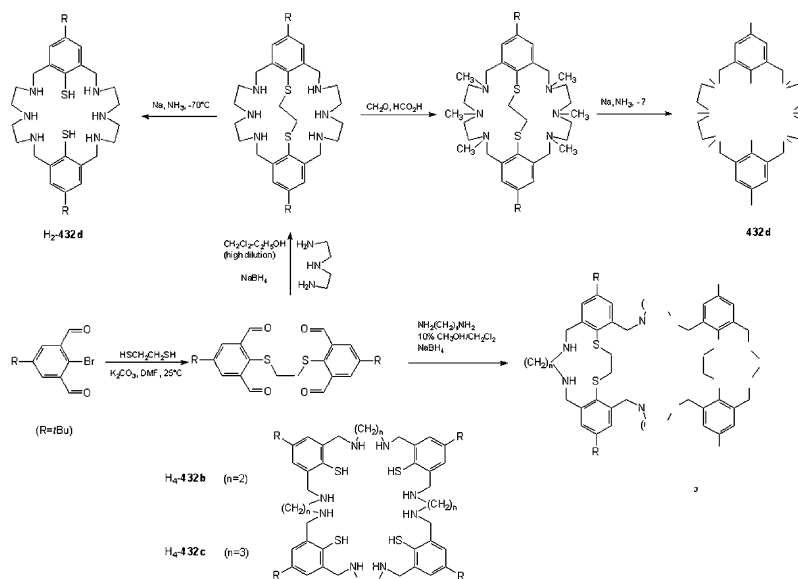
$\text{Co}^{\text{III}}\text{Fe}^{\text{III}}$ cores joined by a Fe–O–Fe linkage. The iron and cobalt centers in the asymmetric unit are triply bridged by two phenoxides and an acetate ion. The coordination sphere CoO_4N_2 is completed by two equatorial amine nitrogen donors of the ligand and an axial acetate anion. The iron(III) center is also six coordinated and its remaining coordination sites are occupied by the other two nitrogen atoms of the macrocycle. The structural features of the cobalt(III) center

indicate a regular octahedral geometry. By contrast, the iron(III) center has a highly distorted octahedral geometry. In the hetero-dinuclear unit the nonbonding Fe···Co distance (3.029 Å) is very similar to the Fe···Ni distance (3.03 Å) in $[\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$ [537]. The structure of $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})]_2(\mu\text{-O})(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, in retrospect, verifies that its precursor $[\text{FeCo}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)$ is isostructural with $[\text{FeNi}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)$.

The iron(III) center in $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4) \cdot n\text{H}_2\text{O}$ exhibits quasi-reversible redox behaviour between -0.44 and -0.48 V versus Ag/AgCl associated with reduction to iron(II). The oxidation of cobalt(II) in the $\text{Fe}^{\text{III}}\text{Co}^{\text{II}}$ complex occurs quasi-reversibly at 0.74 V, while both nickel(II) and manganese(II) in the $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}$ complexes undergo irreversible oxidation at 0.85 V. The electrochemical reduction of $[\{\text{FeCo}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})\}_2(\mu\text{-O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ leads to the generation of the corresponding dinuclear $\text{Fe}^{\text{III}}\text{Co}^{\text{II}}$ complex $[\text{FeCo}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{H}_2\text{O})_2]^+$.

The two iron(III) centers in $[\text{FeCo}(\mathbf{364})(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})_2(\mu\text{-O})](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ are strongly antiferromagnetically coupled ($J = -100 \text{ cm}^{-1}$) whereas $[\text{Fe}_2(\text{H}-\mathbf{364})_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ and $[\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}(\mu_2\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)$, exhibit a weak antiferromagnetic exchange coupling with $J = -4.5$ and -1.8 cm^{-1} , respectively. The dinuclear $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Co}^{\text{II}}$ complexes, however, exhibit weak ferromagnetic behaviour with $J = 1.7$ and 4.2 cm^{-1} , respectively [537].

The [4+4] octaminetetraethiophenol macrocycles $\text{H}_4\text{-432b}$ and $\text{H}_4\text{-432c}$ and related dinuclear and tetranuclear nickel(II) complexes were prepared according to Scheme 61 [538].



Scheme 61.

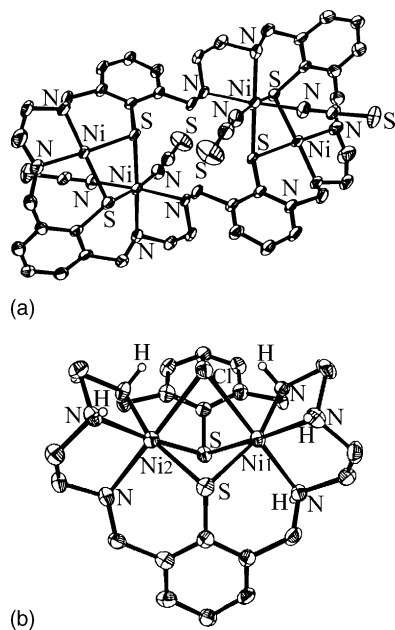


Fig. 346. Structure of $[\text{Ni}_4(\mathbf{432b})(\text{NCS})_4]$ (a) and $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})]^+$ (b) (adapted from Ref. [538]).

In $[\text{Ni}_4(\mathbf{432b})(\text{NCS})_4] \cdot 10\text{CH}_3\text{CN}$ all donor atoms of the [36]-membered macrocycle are involved in coordination to the four nickel(II) ions to give two four coordinate $\text{N}_2\text{S}_2\text{Ni}$ and two six coordinate $\text{N}_4\text{S}_2\text{Ni}$ coordination units. Each nickel(II) ion forms a five-membered chelate ring with one of the four ethane diamine moieties of the ligand. These N_2Ni units are bridged by two thiophenolate sulfur atoms to give two symmetry-related binuclear $\{\text{N}_2\text{Ni}(\mu\text{-SR})_2\text{NiN}_2(\text{NCS})_2\}$ units. The intramolecular distance between the two distorted *cis*-octahedral and the two distorted planar nickel ions, at 6.144 and 9.005 Å, respectively, may be used to describe the distance between the two binuclear subunits. Noticeably the isothiocyanate groups within each binuclear unit occupy *cis* positions at the six coordinated nickel ion [538] (Fig. 346a).

The [2+2] macrocycles $\text{H}_2\text{-}\mathbf{432d}$ and $\text{H}_2\text{-}\mathbf{432e}$ were also prepared according to Scheme 61 [538]. The reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with $\text{H}_2\text{-}\mathbf{432d} \cdot 6\text{HCl}$ in methanol using $\text{N}(\text{Et})_3$ as base (2:1:8 molar ratio) produces $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})](\text{ClO}_4)$ in high yield [538] which consists of a cofacial bioctahedral species (Fig. 346b). The coligand is found in a bridging position. All attempts to replace the halide substituent in $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})](\text{ClO}_4)$ have failed so far; using similar reaction conditions $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})](\text{ClO}_4)$ was prepared. This complex shows two bands at 920 and 1002 nm in the UV-Vis spectrum; these bands are shifted to lower energies with respect to $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})](\text{ClO}_4)$, where they lie at 894 and 941 nm, indicative of a significantly weaker ligand field strength of $\text{H}_2\text{-}\mathbf{432e}$. The structure of $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})](\text{BPh}_4)$ may be simply derived from that of $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})](\text{ClO}_4)$ by replacing the six NH hydrogen atoms by methyl groups. Binding studies demonstrate

that utilization of the permethylated ligand $\text{H}_2\text{-}\mathbf{432e}$ in place of $\text{H}_2\text{-}\mathbf{432d}$ drastically alters the ease of substitution of the bridging halide substituent, presumably because of the more hydrophobic microenvironment about the $\mu\text{-Cl}$, function in $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})](\text{BPh}_4)$. Thus, while the latter reacts with $[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4](\text{OH})$ in acetonitrile to produce the $\mu\text{-OH}$ complex $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})](\text{BPh}_4)$, $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})](\text{ClO}_4)$ was found to be unreactive. Even the addition of a halide scavenger such as $\text{Pb}(\text{ClO}_4)_2$ did not lead to substitution of the Cl^- ion. $[\text{Ni}_2(\mathbf{432e})(\mu\text{-OH})](\text{BPh}_4)$ is isostructural with $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})](\text{BPh}_4)$. The OH group replaces the $\mu\text{-Cl}$ ligand, demonstrating that the substitution reaction takes place without gross structural changes of the parent complex. The separation of the nickel ions has decreased to 3.037 Å. It is also worth mentioning that the OH unit is not involved in hydrogen bonding interactions [538].

Cyclic voltammetry experiments have shown that $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})](\text{ClO}_4)$ undergoes two one-electron oxidations at $E_{1/2}^1 = 0.27$ V ($\text{Ni}^{\text{III}}\text{Ni}^{\text{II}}/\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}$) and at $E_{1/2}^2 = 1.05$ V ($\text{Ni}^{\text{III}}\text{Ni}^{\text{III}}/\text{Ni}^{\text{III}}\text{Ni}^{\text{II}}$), irreversible versus SCE. The cyclic voltammogram of $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})](\text{ClO}_4)$ is very similar, but this complex is oxidized at more positive potentials [$E_{1/2}^1 = +0.43$ and at +1.37 V, irreversible versus SCE]. The first oxidation of $[\text{Ni}_2(\mathbf{432e})(\mu\text{-OH})](\text{BPh}_4)$, on the other hand, occurs at less positive potentials ($E_{1/2}^1 = +0.26$ V; the value for $E_{1/2}^2$ could not be determined due to oxidation of the BPh_4^- anion; $[\text{Ni}_2(\mathbf{432e})(\mu\text{-OH})](\text{ClO}_4)$ could not be obtained in a pure form. The shift of the redox potential can be explained by the different coordination environment about nickel ions. Tertiary amine donors exert weaker ligand field than secondary amine function; $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})]^+$ is thus more difficult to oxidize than $[\text{Ni}_2(\mathbf{432d})(\mu\text{-Cl})]^+$. The OH ligand in $[\text{Ni}_2(\mathbf{432e})(\mu\text{-OH})]^+$ on the other hand, exerts a stronger ligand field than the halide ion in $[\text{Ni}_2(\mathbf{432e})(\mu\text{-Cl})]^+$ and the former complexes is thus more easily oxidized. Remarkably, all $\text{Ni}^{\text{III}}\text{Ni}^{\text{III}}$ species are not stable on the time-scale of a cyclic voltammetry experiment. This is in marked contrast to the behaviour of coordinatively saturated nickel amine-thiolate complexes, which can be reversibly oxidized to $\text{Ni}^{\text{III}}\text{Ni}^{\text{III}}$ species. It is assumed that the different electrochemical properties are due to redox transformations of the bridging coligand or decomposition reactions of the nickel(III) species [538].

11. Polynuclear complexes with asymmetric macrocyclic ligands

In a previous section we have reported that the macrocyclic ligand $\text{H}_2\text{-}\mathbf{358}$, containing two dinuclear N_2O_2 and N_3O_2 adjacent sites, gives rise to homo- and hetero-dinuclear complexes. It was also reported that, when reacted with cobalt(II) acetate in the presence of ClO_4^- , it gives rise to $[\text{Co}_2(\mathbf{358})(\text{CH}_3\text{COO})](\text{ClO}_4)$ which in DMF bounds O_2 at

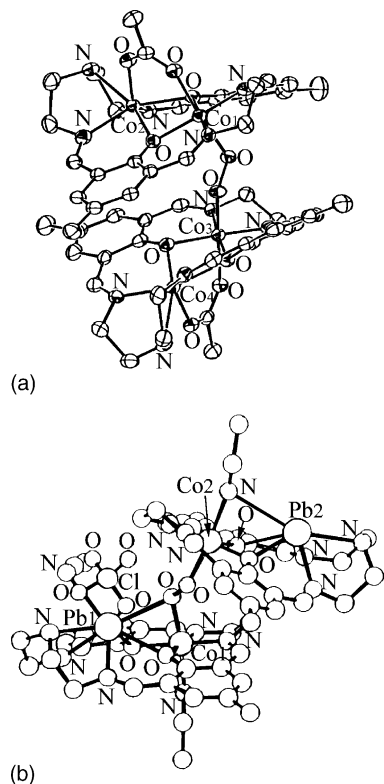


Fig. 347. Structure of $[\{Co_2(358)(CH_3COO)\}_2(O_2)]^{2+}$ (a) and $[\{CoPb(358)(CH_3CN)\}_2(O_2)(ClO_4)]^{3+}$ (b) (adapted from Ref. [415]).

room temperature with an instantaneous colour change from red to dark red, but the resulting dioxygen complex was gradually oxidized to form a yellow solution.

The dioxygen complex $[\{Co_2(358)(CH_3COO)\}_2(O_2)](ClO_4)_2 \cdot 4CH_3CN$ was isolated in a good crystalline form, when an acetonitrile solution of the oxygenated complex was diffused with diethyl ether at $-30^\circ C$ [415] (Fig. 347a). The $\{Co_2(358)(CH_3COO)\}$ part has a μ -acetato-di(μ -phenoxo)dicobalt core and the oxygenation occurs at the cobalt ion in the N_2O_2 site to form a trans- μ - η' - η' -peroxo complex with the Co–O–O–Co linkage. The Co...Co intermetallic separation is 4.352 Å. In each $\{Co_2(358)(CH_3COO)\}$ unit the cobalt ions in the N_2O_2 site assumes a pseudo-octahedral geometry together with the acetate oxygens and the peroxo oxygens at the axial sites. The cobalt ions in the N_3O_2 site is not concerned with the oxygenation. It assumes a distorted trigonal prismatic geometry together with the acetate oxygens. The local configuration about the cobalt ion resembles that of $[Co_2(358)(CH_3COO)](ClO_4)$ but some noticeable geometrical changes occur on the oxygenation [415].

$[Co_2(358)(CH_3COO)](ClO_4)$ is more sensitive toward dioxygen than $[Co(207a)]$ that slowly forms a peroxo complex in DMF at room temperature. Its high sensitivity to O_2 is ascribed to the strong axial coordination of the acetate oxygen, by the support of the cobalt(II) ion in the N_3O_2 site.

$[Co_2(358)(NCS)](ClO_4)$ is much more sensitive to O_2 so as to be irreversibly oxidized even at $-30^\circ C$. These findings

indicate that the oxygenation on the $Co^{II}Co^{II}$ core can be drastically changed when the core structure is modulated by the choice of the counter ion [415].

$[CoPb(359)(CH_3OH)](ClO_4)_2$ reacts with O_2 in CH_3CN at $0^\circ C$ forming the peroxo complex $[\{CoPb(359)(CH_3CN)\}_2(O_2)](BPh_4)_2(ClO_4)_2 \cdot 4CH_3CN \cdot 5H_2O$ upon addition of an excess of $NaBPh_4$. Upon warming at $25^\circ C$ the original $Co^{II}Pb$ complex was regenerated, showing that a reversible oxygenation/deoxygenation cycle takes place [415]. The complex cation consists of one $\{CoPb(358)(CH_3CN)_2(ClO_4)\}$ entity (unit A), one $\{CoPb(358)(CH_3CN)\}$ entity (unit B) and a peroxo group. The cobalt and lead ions in unit A are triply bridged by the two phenolic oxygens of $[359]^{2-}$ and one terminal oxygen of the peroxo group, and the cobalt and lead ions in unit B are triply bridged by the two phenolic oxygens and an acetonitrile nitrogen. The two intermetallic Co...Pb separations are 3.460 and 3.452 Å [415].

The peroxo group adopts a rare bridging mode, where one peroxo oxygen bridges the cobalt and the lead ions at the *syn* site in unit A and another oxygen unidentantly coordinates to the *anti* site of the cobalt ion in unit B. In unit A the cobalt ion in the N_2O_2 site has a pseudo octahedral geometry together with the peroxo oxygen at the *syn* axial site and an acetonitrile nitrogen at the *anti* axial site. The lead ion in the N_3O_2 site is eight coordinated including the peroxo oxygen, an acetonitrile nitrogen and a perchlorate oxygen. The geometry about the cobalt ion in unit B is also pseudo-octahedral with the peroxo oxygen at the *anti* axial site and an acetonitrile nitrogen at the *syn* axial site. The acetonitrile nitrogen makes a bridge to the adjacent lead completing six coordination [415] (Fig. 347b).

Similar $Co^{II}Pb^{II}$ and $Co^{II}Co^{II}$ complexes, where the CH_2CH_2 chain of the N_2O_2 chamber has been substituted by the $C(CH_3)_2C(CH_3)_2$ chain, are inert toward dioxygen [415].

$[Ni(420c)]_2$ and $[Ni(420b)]_2$ react with $Ba(ClO_4)_2$ to form $[Ni_2Ba(420c)_4](ClO_4)_2 \cdot 2H_2O$ and $[Ni_2Ba(420b)_4](ClO_4)_2 \cdot 2H_2O$, respectively [539]. In $[Ni_2Ba(420b)_4](ClO_4)_2 \cdot 2H_2O$ (Fig. 348) the barium(II) ion is encapsulated between two $\{Ni(420b)_2\}$ units; there is no short contact between the barium(II) ion and the perchlorate anions. Within each

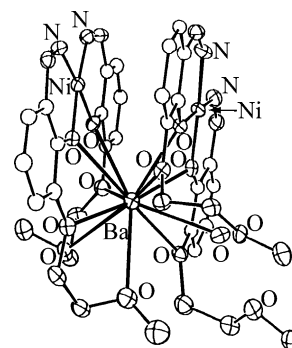
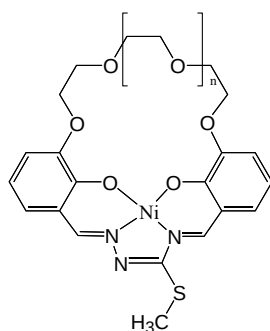


Fig. 348. Structure of $[Ni_2Ba(420b)_4]^{2+}$ (adapted from Ref. [539]).

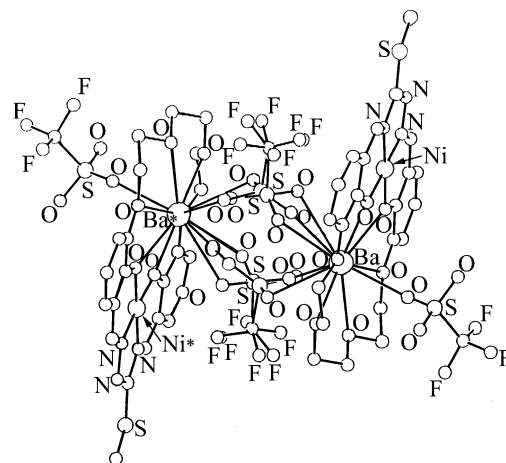
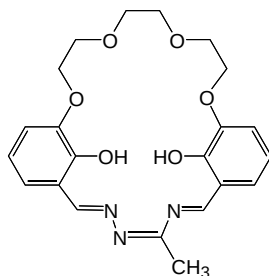
{Ni(**420b**)₂} unit, two deprotonated Schiff base ligands are assembled around the nickel ion in such a way that the resulting NiN₂O₂ chromophore adopts a *cis* (or *syn*) configuration which leads to the formation of an outer site comprising six oxygen atoms. In one {Ni(**420b**)₂} unit the six oxygen atoms are linked to the barium(II) ion, while only four oxygen atoms of the second {Ni(**420b**)₂} participate in the barium coordination sphere. Two methoxy groups of the second {Ni(**420b**)₂} unit remain free except that they are hydrogen bonded to the water molecule, which completes the coordination sphere of the barium(II) ion. Coordination of the oxygen atoms to the barium(II) ion leads to the formation of 6 five-membered chelating rings. The coordination around the nickel ions of the {Ni(**420b**)₂} units is square planar [539].

[Ni₂Ba(**420c**)₄](ClO₄)₂·2H₂O in acetone and DMSO, behaves as extensively ionized but the cation [Ni₂Ba(**420c**)₄]²⁺ remains undissociated. On contrary [Ni₂Ba(**420b**)₄](ClO₄)₂ in acetone suffers dissociation processes, the final products being [Ni(**420b**)₂] and Ba²⁺. Moreover [Ni₂Ba(**420b**)₄](ClO₄)₂ is dissociated to a very large extent for (CD₃)₂SO while the dissociation is vanishingly small for CD₂Cl₂. This behaviour contrasts with that of complexes [Ni₂Ba(**420c**)₄](ClO₄)₂·2H₂O which remains almost unaffected in CD₂Cl₂, (CD₃)₂CO, and (CD₃)₂SO [539].

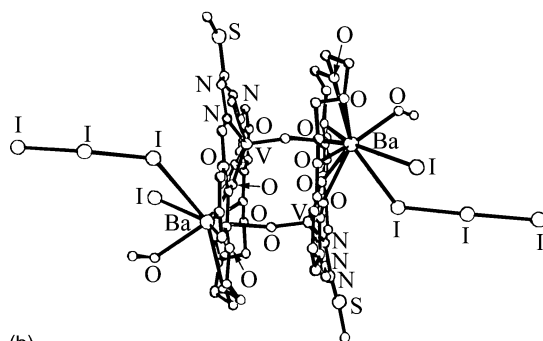
The diformyl derivatives H₂-**253**, when treated with S-methylisothiosemicarbazide-hydroiodide in the presence of Ba(CF₃SO₃)₂ in refluxing methanol/tetrahydrofuran followed by addition of nickel(II) acetate, give [BaNi(**433a**)(CF₃SO₃)₂]₂ and [BaNi(**433b**)(CH₃OH)₃](I₃)(I) which have been recrystallized from a methanol/tetrahydrofuran solution saturated with pentane [539].



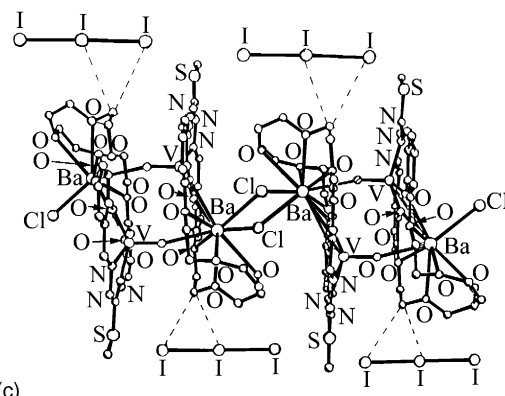
	<i>n</i>
H ₂ - 433a	1
H ₂ - 433b	2



(a)



(b)



(c)

Fig. 349. Structure of [NiBa(**433c**)(CF₃SO₃)₂]₂ (a) [VOBa(**433b**)(I)(I₃)-(CH₃OH)₂] (b) and {[VOBa(**433b**)(Cl)(I₃)]_n (c) (adapted from Ref. [539]).

[BaNi(**433a**)(CF₃SO₃)₂]₂ is a centrosymmetric dimeric complex, bridged by two CF₃SO₃[−] ligands (Fig. 349a). Each barium(II) ion carries an additional terminal CF₃SO₃[−] ligand. The CF₃SO₃[−] ligands bridge by bonding with one oxygen atom to one barium(II) ion and two oxygen atoms to the other. The terminal CF₃SO₃[−] groups are bonded by a single oxygen atom to the barium ion, the remaining oxygen atoms being much further away. The barium(II) cation is coordinated by all six oxygen atoms of the macrocycle, giving a total coordination number to the barium(II) cation of ten. The six oxygen atoms of the [17]-membered

metallomacrocyclic are disposed at the vertices of an almost regular hexagon. The size of the macrocycle permits the barium(II) cation to take up a position close to the center of the polyether cycle. The cation is, however, displaced from the mean plane of the polyether oxygen atoms by 0.60 Å towards the bridging ligands. Its displacement out of the mean plane is probably due to the inability of the barium(II) cation to fit exactly into the cavity of the cyclic polyether. The nickel(II) ion has a square planar coordination and the Ni···Ba distance is 3.664 Å [539].

The treatment of [BaNi(**433a**)(CF₃SO₃)₂]₂ with an aqueous solution of guanidinium sulfate results in removal of the barium(II) cation and liberation of [Ni(**433a**)·H₂O], where the incapsulation of a water molecule into the polyether part of the macrocyclic ligand occurs.

The structure of [BaNi(**433b**)(CH₃COO)₃](I₃) (I) shows the barium cation bonded to all the oxygen atoms of the macrocyclic ligand as in [BaNi(**433a**)(CF₃SO₃)₂]₂ and, in addition, to the oxygen atoms of three methanol ligands. The coordination geometry of the nickel(II) ion is strictly planar. The coordination number of the barium(II) cation is 10 and the polyether chain adopts a locally non planar conformation in order to ensure that all its oxygen atoms are bonded to the cation. As a consequence of the ring conformation the two metal ions are able to approach one another. The resulting Ba···Ni distance is 3.723 Å [539].

The condensation of the dialdehydes H₂-**253** with *S*-methylisothiosemicarbazide-hydroiodide proceeds smoothly in the presence of Ba²⁺ as template [539]. The reaction of the appropriate dialdehyde H₂-**253** with *S*-methylisothiosemicarbazide-hydroiodide, in the presence of Ba(CF₃SO₃)₂ in methanol/tetrahydrofuran at 60 °C followed by addition of zinc(II) acetate, yields orange crystals of [ZnBa(**433a**)(I)(CF₃SO₃)(CH₃OH)]₂·0.5H₂O. The same reaction, without the subsequent addition of Zn(CH₃COO)₂·2H₂O, forms [Ba(H₂-**433a**)(CF₃SO₃)₂] [539].

Treatment of [ZnBa(**433a**)(I)(CF₃SO₃)(CH₃OH)]₂·0.5H₂O with Ag(CF₃SO₃) in methanol yields the orange complex [ZnBa(**433a**)(CF₃SO₃)₂(H₂O)]₂. Removal of the barium(II) ion from this complex with an aqueous solution of guanidinium sulfate results in the liberation of [Zn(**433a**)·2H₂O], a yellow-orange powder which is insoluble in most common organic solvents. [CuBa(**433a**)(CF₃SO₃)₂]₂ and [CuBa(**433b**)(CF₃SO₃)₂]₂, were obtained analogously to the ZnBa complex, by using *S*-methylisothiosemicarbazide-hydrochloride instead of the hydroiodide. Again the barium(II) ion can easily be removed from [CuBa(**433a**)(CF₃SO₃)₂]₂ and [CuBa(**433b**)(CF₃SO₃)₂]₂ with guanidinium sulfate and the brown copper(II) complexes [Cu(**433a**)·2H₂O] and [Cu(**433b**)·2H₂O] can be recovered [539].

The structure of [ZnBa(**433a**)(I)(CF₃SO₃)(CH₃OH)]₂·0.5H₂O shows the barium(II) ion is coordinated to 10 oxygen atoms: three from the bridging triflate groups, six from the macrocyclic ligand and one from a methanol

molecule. The CF₃SO₃[−] ligands bridge one oxygen atom to one barium atom and two oxygen atoms to the other barium atom. The six oxygen atoms of the [17]-membered metallomacrocyclic are disposed at the vertices of an almost regular hexagon, with the six coordinating oxygen atoms lying within 0.14 Å of their mean plane. The barium(II) cation is displaced from the mean plane of the polyether oxygen atoms by 0.7 Å towards the bridging CF₃SO₃[−] ligands, owing to the probable inability of the barium(II) cation to fit exactly in the cavity of the cyclic polyether. The phenolate oxygen atoms simultaneously act as bridging atoms to the zinc(II) ion. Although the N₂O₂ donor set of macrocycle coordinated to the zinc(II) ion is coplanar, the metal ion deviates from the mean plane by 0.6 Å towards I[−]. The coordination sphere of the zinc(II) ion is thus distorted square pyramidal, with the two salicylideneiminato groups of the macrocycle occupying the basal plane and I[−] in the apical position. The Zn···Ba distance is 3.736 Å [539].

Spectroscopic data show each zinc(II) ion in [ZnBa(**433a**)(CF₃SO₃)₂(H₂O)]₂ is coordinated to a water molecule, and that the triflate ligands take up bridging positions. The ¹³C NMR spectrum of this compound in DMSO shows that both triflate ligands are attached to the same barium(II) ion. The EI mass spectrum exhibits a peak with *m/z* 951 corresponding to [ZnBa(**433a**)(CF₃SO₃)₂]⁺, indicating that the triflate ligands are strongly bound, and presumably these remain attached to the metal in solution. Recrystallization of [ZnBa(**433a**)(CF₃SO₃)₂(H₂O)]₂ from dry ethanol results in the NMR signals for a bound water molecule being replaced by those of C₂H₅OH [539].

Cyclic voltammetric data for the copper(II) and copper(II)-barium(II) complexes show two irreversible reductions due to Cu^{II} → Cu^I → Cu⁰. The hard barium cation, complexed in the polyether cavity causes a reduction in the electron density at the phenolic oxygen atoms. This in turn reduces the electron donating ability of the ligand towards the transition metal ion and results in a reduction of the electron density on the copper ion thus making reduction easier [539].

The reaction of H₂-**253** (*n* = 1) with acetamidrazone hydrochloride in the presence of barium triflate, followed by addition of nickel(II), copper(II) or zinc(II) acetate, yields respectively [NiBa(**433c**)(CF₃SO₃)₂]₂, [CuBa(**433c**)(CF₃SO₃)₂]₂ and [ZnBa(**433c**)(CF₃SO₃)₂(CH₃OH)]₂. Removal of Ba²⁺ from these complexes, by using an aqueous solution of guanidinium sulfate, affords [Ni(**433c**)·2H₂O], [Cu(**433c**)·1.5H₂O] and [Zn(**433c**)·2H₂O].

[NiBa(**43c**)(CF₃SO₃)₂]₂ is a centrosymmetric dimeric complex, which is bridged by two CF₃SO₃[−] ligands. Each barium(II) ion carries an additional terminal triflate ligand. The CF₃SO₃[−] ligands bridge the macrocyclic units by bonding with one oxygen atom to one barium(II) ion and two oxygen atoms to the other barium. The terminal CF₃SO₃[−] ligands are linked by a single oxygen atom

to the barium remaining oxygen atoms being much further away. The 10 coordinated barium cation is also bound to the six oxygen atoms of the macrocycle; the nickel(II) ion has a square planar coordination [539] (Fig. 349a).

The reaction of H₂-**253** ($n = 1$) with *S*-methylisothiosemicarbazide hydroiodide, in the presence of Ba(CF₃SO₃)₂ in hot methanol, followed by addition of oxovanadium(IV) chloride yields a ~1:0.3 mixture of [VOBa(**433a**)(I)(I₃)(CH₃OH)]₂ and [VOBa(**433a**)(CF₃SO₃)₂(CH₃OH)_{0.5}(H₂O)_{0.5}]₂ whereas the same reaction starting from H₂-**253** ($n = 2$) leads to the formation of {[VOBa(**433b**)(Cl)](I₃)}_{*n*}. Attempts to separate [VOBa(**433b**)(I)(I₃)(CH₃OH)]₂ and [VOBa(**433a**)(CF₃SO₃)₂(CH₃OH)_{0.5}(H₂O)_{0.5}]₂ by crystallization from different solvents failed but removal of the barium(II) ion from [VOBa(**433b**)(I)(I₃)(CH₃OH)]₂, [VOBa(**433a**)(CF₃SO₃)₂(CH₃OH)_{0.5}(H₂O)_{0.5}]₂ and {[VOBa(**433b**)(Cl)](I₃)}_{*n*} with an aqueous solution of guanidinium sulfate results in the liberation respectively of [VO(**433a**)] and [VO(**433b**)].

The reaction of [VO(**433a**)] with Ba(CF₃SO₃)₂ in methanol gives [VOBa(**433a**)(CF₃SO₃)₂(CH₃OH)_{0.5}(H₂O)_{0.5}]₂ in high yield [539]. [VOBa(**433a**)(I)(I₃)(CH₃OH)]₂ and [VOBa(**433a**)(CF₃SO₃)₂(CH₃OH)_{0.5}(H₂O)_{0.5}]₂ crystallise in the form of centrosymmetric dimers, held together by V=O···Ba bridges. The major difference between these structures is around the barium(II) ions. In [VOBa(**433b**)(I)(I₃)(CH₃OH)]₂ the barium cation carries an additional methanol molecule, as well as I[−] and a I₃[−] anions needed to neutralise the cation. All these three ligands appear to be coordinated to the metal ion (Fig. 349b). In [VOBa(**433a**)(CF₃SO₃)₂(CH₃OH)_{0.5}(H₂O)_{0.5}]₂ the barium(II) cation is attached to two triflate ions, one bidentate and the other monodentate, together with a further ligand (a water and a methanol molecule) occupying statistically approximately the same site. In both compounds the barium(II) ion lies the same distance above the macrocyclic ligand in spite of the difference in the coordination numbers of the barium(II) cations in the two complexes: 10 for [VOBa(**433b**)(I)(I₃)(CH₃OH)]₂ and 11 for [VOBa(**433a**)(CF₃SO₃)₂(CH₃OH)_{0.5}(H₂O)_{0.5}]₂. The conformation of the macrocycle also appears to be little influenced by this difference and the polyether shows little sign of strain. The coordination polyhedron of the vanadium(IV) ion in both complexes approximates to a square pyramid, with the two salicylideneiminato groups of the macrocycle occupying the basal plane [539].

Also {[VOBa(**433b**)(Cl)](I₃)}_{*n*} shares many of the features observed in the crystal structures of the above two VOBa complexes. Again the barium(II) and vanadium(IV) ions sit on opposite sides of the macrocyclic ligand. The intramolecular Ba···V distance of 3.914 Å. The coordination polyhedron of the vanadium(IV) ion is square pyramidal. The larger macrocyclic ring in [**333b**]^{2−} adopts a strongly non planar conformation in order that all its seven oxygen atoms can coordinate to the barium cation which is

not attached to the I₃[−] anions but it is bonded to a neighbouring cation via two chloride bridges. Indeed, the I₃[−] anions are pushed to the extremities of the complexes and occupy channels between the infinite parallel chains [539] (Fig. 349c).

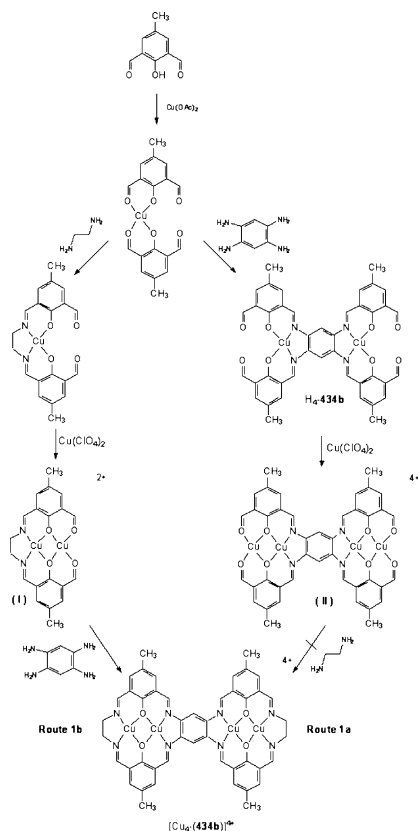
[Mn(**254f**)](PF₆), obtained by transmetallation of [Ba(H₂-**254f**)](CF₃SO₃)₂ with Mn(CH₃COO)₂·4H₂O in the presence of O₂ and an excess of NH₄PF₆, has been reduced by [Co(C₅H₅)₂] to [Mn(**254f**)] which, by reaction with O₂ in CH₃CN formed the dinuclear manganese(IV) complex [Mn(**254f**)(μ-O)]₂ [540]. The free crown-like compartments of this last complex may be engaged in further complexation with Na⁺, K⁺, Ca²⁺ and Ba²⁺ forming the corresponding complexes [Mn^{IV}M^I(**254f**)(μ-O)]₂(PF₆)₂ (M' = K⁺, Na⁺) and [Mn^{IV}M^{II}(**254f**)(μ-O)]₂(SO₃CF₃)₄ (M^{II} = Ca²⁺, Ba²⁺) [540].

The EPR spectrum (6 K, frozen CH₃CN solution) of the mixed-valent dimer [Mn(**254f**)(μ-O)]₂[−], prepared by chemical reduction of [Mn(**254f**)(μ-O)]₂ with 1 equiv. of [Co(C₅H₅)₂] or electrochemical reduction by one electron, is consistent with the assignment of this species as an antiferromagnetically coupled, valence-trapped Mn^{III}Mn^{IV} dimer. As the spectra of the reduced hetero-dinuclear complexes closely resemble the spectrum of [Mn(**254f**)(μ-O)]₂[−] these compounds are also considered as antiferromagnetically coupled, valence-trapped Mn^{III}Mn^{IV} dimers.

The heteropolynuclear complexes analyzed by electrospray ionization mass spectrometry (ESI) using CH₂Cl₂ and CH₃OH as solvents, evidence the replacement of one or more of the cations (K⁺, Ca²⁺ and Ba⁺) in the starting complex with Na⁺. Not unexpectedly, the deliberate addition of Na⁺ or K⁺ through the use of NaBPh₄ or KPF₆ resulted in substantial replacement of the original cation (Ca²⁺, Ba²⁺). For all but [Mn₂Na₂(**254f**)₂(μ-O)₂](PF₆)₂, the incorporation of H⁺ was also observed. The protons probably derive from trace water in the CH₂Cl₂. The use of acetonitrile as the electrospray solvent causes a significant change in the ion distribution for all four of the complexes where it is shown that even more extensive Na⁺ substitution for K⁺, Ca²⁺, and Ba²⁺ occurs in CH₃CN as compared to CH₂Cl₂ [540].

The exchange of divalent cations for monovalent ones in the ESI mass spectra is interesting because solution electrochemical results indicate the reverse behaviour. Cyclic voltammograms show the conversion of [Mn₂Na₂(**254f**)₂(μ-O)₂](PF₆)₂ to the barium(II) derivative as sequential additions of Ba(CF₃SO₃)₂ are made to a CH₃CN solution of [Mn₂Na₂(**254f**)₂(μ-O)₂](PF₆)₂. After four molar equivalents of Ba(CF₃SO₃)₂ have been added, the complex in solution is [Mn₂Ba(**254f**)₂(μ-O)₂]⁴⁺ consistent with the higher binding constants determined for the association of alkaline earth cations [540].

Minor modification of procedures used to generate the dinuclear compartmental ligands can afford polynucleating ligands, and additional types of reactivities or physicochemical properties stemming from the flexibility may be



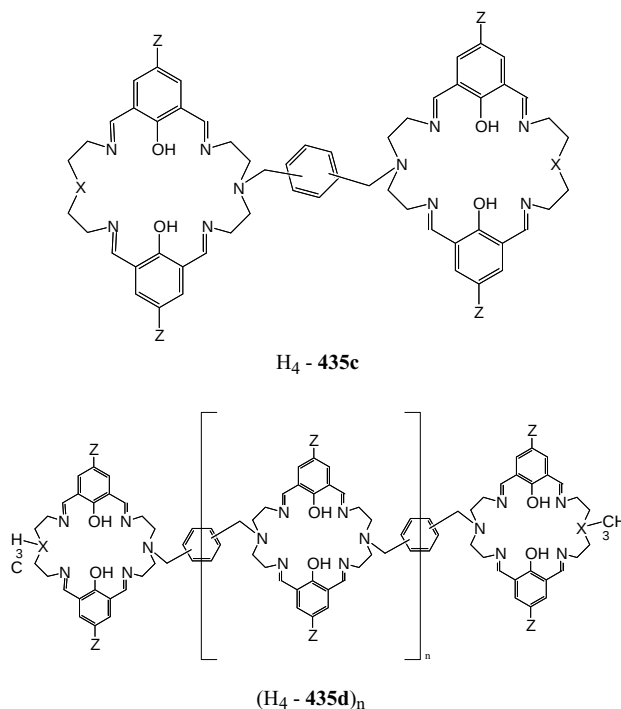
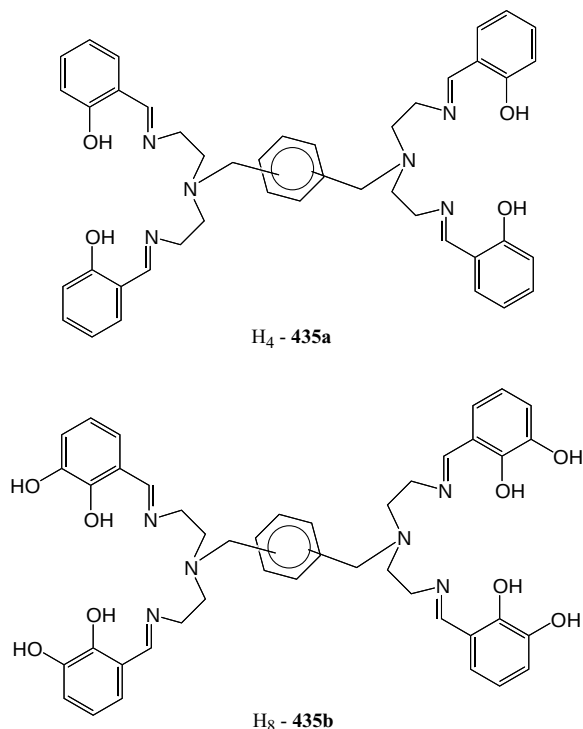
Scheme 62.

observed. Thus, acyclic and cyclic dinuclear or tetranuclear complexes have been prepared from the macrocyclic ligand derived by the condensation of 2,6-diformyl-4-methylphenol, 1,2-diaminoethane and 1,2,4,5-phenylenetetramine according to Scheme 62 [521].

The subnormal room temperature magnetic moment value per copper(II) ion in $[\text{Cu}_4(\mathbf{434b})](\text{X})_4$ (1.06 BM), comparable to the value of 1.15 BM per copper atom reported for the dinuclear copper(II) perchlorate complex $[\text{Cu}_2(\mathbf{46})](\text{ClO}_4)_2$, indicates an antiferromagnetic interaction in the dinuclear fragments. Moreover the cyclic voltammetric profile of $[\text{Cu}_4(\mathbf{434b})](\text{X})_4$ in DMF shows one quasi-reversible redox couple at -0.54 V with ΔE value of 108 mV and an irreversible peak at -1.25 V. Again these data are comparable with those found for $[\text{Cu}_2(\mathbf{46})](\text{ClO}_4)_2$ which shows two reduction potentials at -0.52 and -1.01 V assigned to successive reduction of the two copper(II) centers to two copper(I) centers (i.e. $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$). From the cyclic voltammetric and magnetic moment data, the two dinuclear fragments of $[\text{Cu}_2(\mathbf{434b})](\text{X})_4$ appear to behave as two independent units as expected from the proposed structure. Absence of any significant interactions between the two dinuclear units may be the result of their separation by the phenyl ring [521].

Moreover the acyclic and macrocyclic Schiff bases $\text{H}_4\text{-}\mathbf{435a} \cdots \text{H}_2\text{-}\mathbf{435d}$ have been obtained either by self condensation of the precursors or as metal complexes by template

procedures [541,542]. The acyclic ligands $\text{H}_4\text{-}\mathbf{435a}$ and $\text{H}_8\text{-}\mathbf{435b}$ have been synthesized by condensation in methanol of 1,4- or 1,3-bis[bis(2-aminoethyl)aminomethyl]benzene respectively with salicylaldehyde or 2,3-dihydroxybenzaldehyde in a 1:4 molar ratio.



A fast atom bombardment mass spectrometry investigation has revealed the presence of the parent peak at the

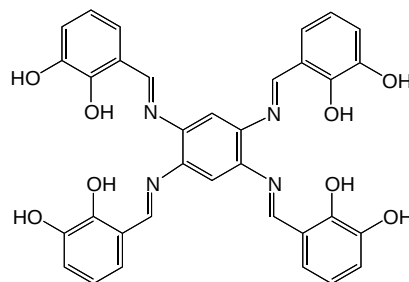
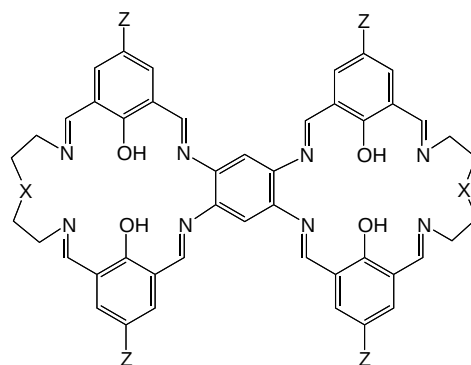
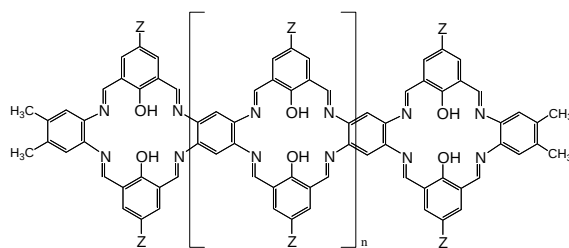
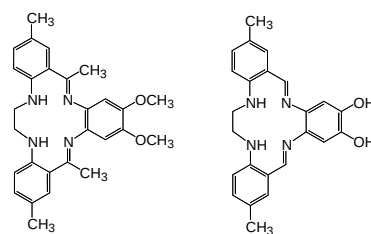
appropriate m/z value for both ligands while ^1H and ^{13}C NMR data confirm the proposed structure for $\text{H}_4\text{-435a} \cdot \text{H}_2\text{-435d}$ [541,542].

The reaction of $\text{H}_4\text{-435a}$ and $\text{H}_8\text{-435b}$ with $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in the appropriate molar ratio and in boiling methanol produces the dinuclear complexes $[\text{UO}_2]_2(\text{435a}) \cdot 2\text{H}_2\text{O}$ or $[(\text{UO}_2)_2(\text{H}_2\text{-435b})] \cdot 2\text{H}_2\text{O} \cdot 2\text{DMF}$ and the tetranuclear complex $[(\text{UO}_2)_4(\text{435b})] \cdot 2\text{H}_2\text{O} \cdot 2\text{DMF}$. An X-ray investigation on $[(\text{UO}_2)_2(\text{435a})] \cdot \text{DMSO} \cdot \text{C}_6\text{H}_6$ shows [541,542] the quasi-linear uranyl(VI) ion is equatorially coordinated in the usual, slightly distorted, bipyramidal pentagonal configuration by the O_2N_3 donor set of the Schiff base ligand which forms an irregular equatorial puckered pentagon.

The dinuclear and tetranuclear lanthanide(III) complexes, $\text{Ln}_2(\text{435a})(\text{X})_2$ ($\text{X} = \text{NO}_3^-$, OH^-) and $\text{Ln}_4(\text{435b})(\text{NO}_3)_2(\text{OH})_2$, have been prepared with a procedure similar to that employed for the uranyl(VI) analogues.

By the condensation of 1,4- or 1,3-bis[bis(2-aminoethyl)aminomethyl benzene], respectively with the [2+1] acyclic Schiff base derived by the reaction of 2,6-diformyl-4-substituted phenol ($\text{Z} = \text{Cl}$, CH_3) and $\text{H}_2\text{N}(\text{CH}_2)_2\text{-X}(\text{CH}_2)_2\text{NH}_2$ ($\text{X} = \text{NCH}_3$, S , O) the face-to-face $\text{H}_4\text{-435c}$ or polynuclear $[\text{H}_2\text{-435d}]_n$ compounds have been obtained [541,542]. The organic polymer is quite insoluble and hence difficult to characterise fully; the complexes have been obtained only by a template procedure. $[(\text{UO}_2)_2(\text{435c})]$ and $[\text{La}_2(\text{435c})(\text{NO}_3)_2]$ have been synthesized by reaction of the acyclic mononuclear complexes with the hexamine in alcoholic solution.

Finally, by the condensation of 1,2,4,5,-tetraaminobenzene with 2,3-dihydroxybenzaldehyde, N,N' -bis[-3-formyl-5-methyl(or 5-chloro)-]salicylidene-3-aza (or 3-thia or 3-oxa)1,5-diaminopentane, 2,6-diformyl-4-methylphenol or 2,6-diformyl-4-chlorophenol, the ligands $\text{H}_8\text{-436a}$, $\text{H}_4\text{-436b}$ and $[\text{H}_2\text{-436c}]_n$ have been obtained [541,542]. With these multicompartmental systems (especially those derived from 2,3-dihydroxybenzaldehyde), it seems also possible to prepare pure heteropolynuclear species of the type $[\text{M}_2\text{-Ln}_2(\text{H}_4\text{-436a})(\text{NO}_3)_6]$ or $[\text{M}_2\text{Ln}_2(\text{H}_4\text{-436b})(\text{NO}_3)_6]$ and $[\text{M}_2\text{Ln}_2(\text{436a})(\text{NO}_3)_2]_n$ or $[\text{M}_2\text{Ln}_2(\text{436b})(\text{NO}_3)_2]_n$ without prior isolation of the monomeric complexes, this being due to the capability of the Schiff base N_3O_2 and N_2O_2 and crown ether like O_2O_2 sites to coordinate preferentially d and f metal ion, respectively. These heteropolynuclear complexes have been synthesized also by template procedure: $[\text{M}_2(\text{H}_4\text{-436a})]$ or $[\text{M}_2(\text{H}_4\text{-436b})]$, derived from the reaction of $\text{H}_8\text{-436a}$ or $\text{H}_8\text{-436b}$ with the appropriate metal salt ($\text{M} = \text{Cu}^{2+}$, Na^{2+}) react with $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in alcoholic solution to form $[\text{M}_2\text{Ln}_2(\text{H}_4\text{-436a})(\text{NO}_3)_6]$ or $[\text{M}_2\text{Ln}_2(\text{H}_4\text{-436b})(\text{NO}_3)_6]$ which in the presence of 4 equiv. of LiOH give rise to the designed polynuclear complexes $[\text{M}_2\text{Ln}(\text{436a})(\text{NO}_3)_2]_n$ or $[\text{M}_2\text{Ln}(\text{436b})(\text{NO}_3)_2]_n$ [541,542]. $[\text{H}_2\text{-436c}]_n$ forms almost exclusively the homopolynuclear complexes $\{[\text{M}_2(\text{436c})](\text{X}_2)\}_n$ containing d-metal ions.

H₈ - 436aH₄ - 436b
Z = Cl, CH₃
X = S, NH, OH₂ - 436c Z = Cl, CH₃H₂ - 437aH₄ - 437b

Mononuclear and heterotrimeric complexes with the ligands $\text{H}_2\text{-437a}$ and $\text{H}_4\text{-437b}$ have been prepared. The macrocyclic complexes $[\text{M}(\text{437a})]$, obtained by reaction in DMF of the preformed ligand $\text{H}_2\text{-437a}$ with the appropriate metal acetate or by template procedure, can be demethylation by KSC_2H_5 to give rise to the catechol complexes $[\text{M}(\text{H}_2\text{-437b})]$ which become very soluble in most organic solvents. The catechol function of these complexes has been used as ligand for further metal ions

complexation and the trinuclear complex $[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4]_2[\text{Ni}_2\text{Cu}(\mathbf{437b})_2]$ has been synthesized [543].

$[\text{Ni}(\text{H}_2\text{-}\mathbf{437b})]\cdot 2\text{THF}$ is very close to being planar. In the lattice, the catechol functional groups interact with two molecules of tetrahydrofuran via hydrogen bonding [543].

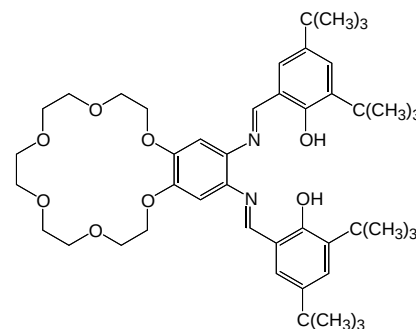
$[\text{Co}(\text{H}_2\text{-}\mathbf{437b})]\cdot 2\text{THF}$ crystallizes in dimeric form as a result of strong hydrogen bonding and contains two tetrahydrofuran molecules per dimer. The two catechols are hydrogen-bonded in an intramolecular fashion using two of the four catechol protons for mutual hydrogen bonding. In addition, each catechol utilizes the other available proton to hydrogen bond to a solvent molecule. Also $[\text{Co}(\text{H}_2\text{-}\mathbf{437b})]$ has been crystallized with DMF rather than THF in the lattice. The hydrogen bonded dimeric structure persists in this form of the complex. The structural features of this molecule are similar to those of the $[\text{Co}(\text{H}_2\text{-}\mathbf{437b})]\cdot 2\text{THF}$. The dimers do not interact with each other in the solid state. The closest interdimer $\text{Co}\cdots\text{Co}$ distance is 7.481 Å and the intradimer $\text{Co}\cdots\text{Co}$ distance is 11.692 Å [543].

In addition to the monomeric complex $[\text{Ni}(\text{H}_2\text{-}\mathbf{437b})]\cdot 2\text{THF}$, a dimeric form of $[\text{Ni}(\text{H}_2\text{-}\mathbf{437b})]\cdot 2\text{THF}$, isomorphous to the corresponding $[\text{Co}(\text{H}_2\text{-}\mathbf{437b})]\cdot 2\text{THF}$ was obtained. The crystallization of a monomeric rather than dimeric complex is affected by the concentration of the complex in tetrahydrofuran/diethyl solutions and dilute solutions give the monomeric form.

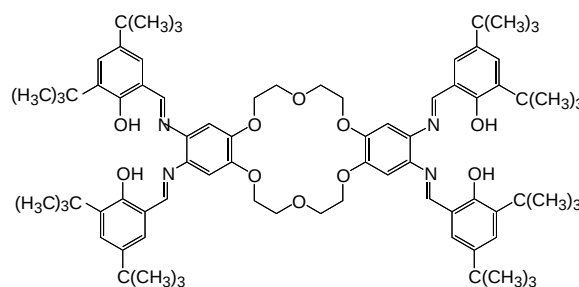
In $[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4]_2[\text{Ni}_2\text{Cu}(\mathbf{437b})_2]\cdot 4\text{DMF}$ (Fig. 350) the nickel(II) ion, coordinated to the N_4 macrocyclic ligand, retains its planar geometry upon coordination to the copper(II) ion. Also the copper ion atom is in a square planar geometry. The $\text{Ni}\cdots\text{Cu}$ distance is 7.676 Å; the $\text{Ni}\cdots\text{Ni}$ distance is 15.352 Å and the $\text{Ni}\cdots\text{Ni}$ intermolecular distance is 8.055 Å. The shortest $\text{Cu}\cdots\text{Cu}$ intermolecular distance is 10.260 Å [543].

4,5-Bis(3,5-di-*tert*-butylsalicylideneimino)benzo-18-crown-6 ($\text{H}_2\text{-}\mathbf{438}$) was obtained by a Schiff base condensation reaction between 4,5-diaminobenzo-18-crown-6 and 3,5-di-*tert*-butylsalicylaldehyde [544]. 4,5-Diaminobenzo-18-crown-6 has been prepared by hydrogenation of 4,5-dinitrobenzo-18-crown-6 over palladium/activated carbon catalyst in methanol while the starting 4,5-dinitrobenzo-18-crown-6 reagent has been synthesized by nitration (con-

centrated HNO_3) of commercially available benzo-18-crown-6 [544,545].



$\text{H}_2\text{-}\mathbf{438}$



$\text{H}_4\text{-}\mathbf{439}$

$\text{H}_2\text{-}\mathbf{438}$ affords with nickel acetate in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, after evaporation of the solvents, $[\text{Ni}(\mathbf{438})]$ which reacts with KI and CsI to give $[\text{NiK}(\mathbf{438})](\text{Cl})\cdot\text{H}_2\text{O}$ and $[\text{NiCs}(\mathbf{438})](\text{I})$, respectively. The reaction of $[\text{Ni}(\mathbf{438})]$ with CsI in a 2:1 molar ratio gave $[\text{Ni}_2\text{Cs}_2(\mathbf{438})_2](\text{I})_2$ [544,545].

In $[\text{NiK}(\mathbf{438})](\text{Cl})$ the seven coordinate potassium(I) ion is bound to a water molecule in addition to the six crown-ether oxygen donors (Fig. 351a). The basic structural features of the cesium(I) derivatives are determined by the coordination requirements of the large cesium(I) ions that are coordinatively unsaturated when bound only by the oxygen donors of a single 18-crown-6 unit. This is the case with $[\text{Ni}_2\text{Cs}_2(\mathbf{438})_2](\text{I})_2$ where the presence of one cesium(I) ion per $\{\text{Ni}(\mathbf{438})\}$ results in dimer formation (Fig. 351b). The cesium(I) ions in each of the two $\{\text{NiCs}(\mathbf{438})\}$ units, in addition to being coordinated by the 18-crown-6 moiety are also coordinated by two oxygen atoms of the Schiff base. The Cl^- or I^- are ionic.

An examination of the ^1H NMR spectra of $[\text{NiCs}(\mathbf{438})]^+$ shows that the dimer persists in CH_2Cl_2 but dissociates in $(\text{CH}_3)_2\text{SO}$ [544].

Similarly $[\text{Cu}(\mathbf{438})]$, $[\text{Mn}(\mathbf{438})(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})](\text{X})$, $[\text{Mn}_2(\mathbf{439})(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})](\text{Cl})_2$ and $[\text{MnM}'(\mathbf{438})(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})](\text{X})_2$ or $[\text{Mn}_2\text{Cs}(\mathbf{438})_2(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{X})_3$ ($\text{M}' = \text{K}^+, \text{Cs}^+$; $\text{X} = \text{Cl}^-, \text{I}^-$) have been prepared and their structure determined [543]. In the manganese complexes the manganese(III) ion is octahedral into the N_2O_2 Schiff base, the two axial position being filled by the oxygen atoms of one water and ethanol molecule [544] (Fig. 352a and b).

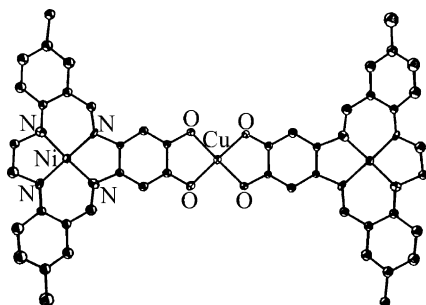


Fig. 350. Structure of $[\text{Ni}_2\text{Cu}(\mathbf{437b})_2]^{2-}$ (adapted from Ref. [543]).

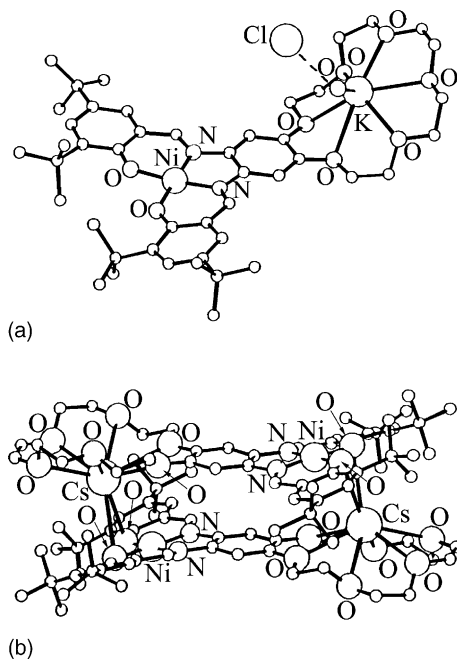


Fig. 351. Structures of $[\text{NiK}(\mathbf{438})](\text{Cl})$ (a) and $[\text{Ni}_2\text{Cs}_2(\mathbf{438})_2]^{2+}$ (b) (adapted from Ref. [544]).

These complexes, totally insoluble in water but very soluble in nonpolar solvents, have been found to be effective in the facilitated transport of hydrophobic amino acids and serotonin across CHCl_3 bulk liquid membranes. The metal ion within the N_2O_2 coordination site, and its affinity for axial ligands, determines transport efficiency. The neutral nickel(II) derivatives of the ditopic receptors, with little affinity for axial ligands, are poor carriers and their efficiency in the transport of tryptophan is roughly equal to the unmetallated ligands or benzo-18-crown-6 ether. In contrast, the monocationic manganese(III) derivatives are very efficient carriers in the facilitated transport of tryptophan and serotonin. In these carriers the counter ions that can also coordinate to the manganese(III) ion inhibit transport and

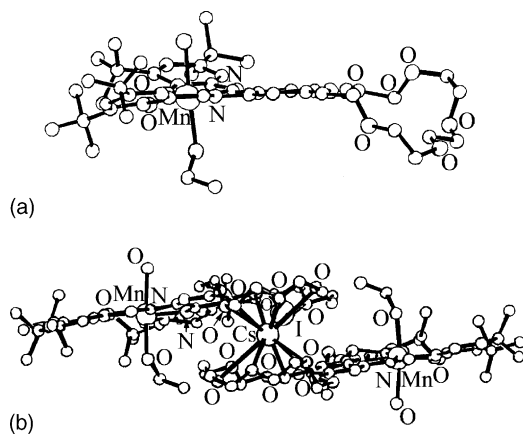


Fig. 352. Structure of $[\text{Mn}(\mathbf{438})(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})]^{2+}$ (a) and $[\text{Mn}_2\text{Cs}(\mathbf{438})_2(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})_2]^{3+}$ (b) (adapted from Ref. [544]).

the inhibition is roughly correlated to the magnitude of interaction [543].

12. Polynuclear complexes with acyclic ligands

12.1. Complexes with Schiff bases derived from substituted salicylaldehydes

Cobalt(II) complexes with simple Schiff bases, derived from the condensation of substituted salicylaldehyde respectively with 1,2-diminoethane or 1,2-diaminobenzene, react with sodium metal giving rise to compounds with different complexity and metal ion assembly. Depending on the ligand used, a redox reaction, involving also the coordinated ligands, occurs.

The reduction of $[\text{Co}(\mathbf{207e})]$ with sodium metal in THF allows the formation of the dinuclear complex $[\text{CoNa}(\mathbf{207e})(\text{THF})_2]$ and the tetranuclear complex $[\text{CoNa}(\mathbf{207e})(\text{THF})]_2$ [546]. Both complexes are present in the asymmetric unit. In both molecules, the $[\text{Cu}(\mathbf{207e})]^-$ anion provides a planar cavity of four oxygen atoms which accommodates a sodium cation. In the dinuclear complex, the coordination around the sodium ion is completed by the oxygen atoms of the tetrahydrofuran molecules, while in the tetranuclear complex it is completed by the oxygen atom from one tetrahydrofuran molecule and the methoxy oxygen atom of a second, centrosymmetric molecule which gives rise to a dimer. The cobalt ions lie nearly in the plane defined by the N_2O_2 core of the donor atoms. The Schiff base ligand assumes a flattened umbrella configuration. In $[\text{CoNa}(\mathbf{207e})(\text{THF})_2]$ (Fig. 353a) the coordination around the sodium ion is mainly imposed by the conformation of the Schiff base behaving as a tetradentate ligand. The four oxygen atoms define a coordination plane containing the sodium cation. The oxygen atoms from the THF molecules are symmetrically arranged on opposite sides with respect to that plane. In $[\text{CoNa}(\mathbf{207e})(\text{THF})]_2$ (Fig. 353b), the coordination polyhedron of the sodium cation has been described as a distorted pentagonal pyramid where the basal plane is defined by the four oxygen atoms of the Schiff base and by the oxygen atoms of a THF molecule and the apex is occupied by a methoxy oxygen atom of the adjacent molecule. This metal ion is significantly displaced from the oxygen basal plane [546].

Changing the Schiff base around the cobalt ion led to completely different results in the reduction of $[\text{Co}(\mathbf{204})]$ and $[\text{Co}(\mathbf{417b})]$ with sodium: respectively $[\text{Co}_2\text{Na}_2(\mathbf{224})(\text{THF})_6]$ and $[\text{Co}_2\text{Na}_2(\mathbf{440})(\text{THF})_4]$. Both reactions give rise to reductive coupling of the two imino groups, which in turn leads to C–C bond bridging of the two Schiff base units. The major difference between these two tetranuclear complexes, $[\text{Co}_2\text{Na}_2(\mathbf{224})(\text{THF})_6]$ and $[\text{Co}_2\text{Na}_2(\mathbf{440})(\text{THF})_4]$, concerns the coordination sphere of the sodium cation. In the latter case, the resulting Schiff base $[\mathbf{440}]^{6-}$ behaves as a compartmental ligand having two

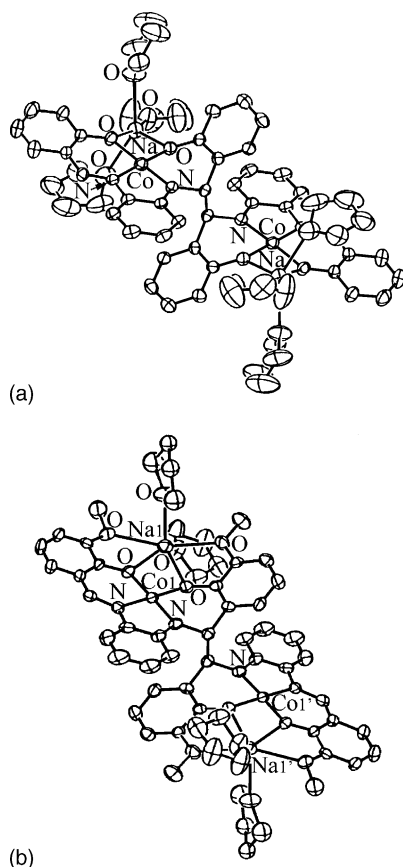


Fig. 353. Structures of [CoNa(**207e**)(THF)₂] (a) and [CoNa(**207e**)(THF)]₂ (b) (adapted from Ref. [546]).

N₂O₂ donor sets for the cobalt(II) and two sets O₄ for the sodium cation, both in a nearly square planar geometry. In both complexes reduction does not affect the oxidation state of the metal (remaining cobalt(II)) but, rather, the ligand. The cobalt(II) is paramagnetic ($\mu_{\text{eff}} = 2.21$ and $2.23\mu_{\text{B}}$ at 293 K for [Co₂Na₂(**224**)(THF)₆], and [Co₂Na₂(**440**)(THF)₄], respectively); these values are very close to those of the starting complexes [Co(**204**)] and [Co(**417b**)] (2.30 and $2.35\mu_{\text{B}}$ at 293 K, respectively).

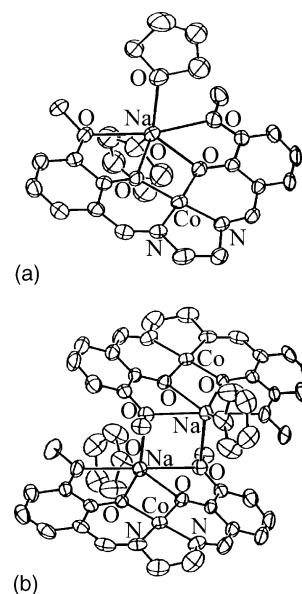
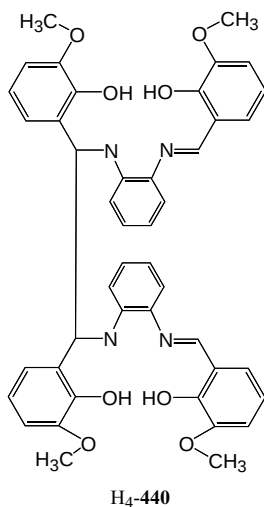


Fig. 354. Structures of [Co₂Na₂(**224**)(THF)₆] (a) and [{Co₂Na₂(**440**)(THF)₄}] (b) (adapted from Ref. [546]).

The formation of a C–C bond converts two dianionic [**204**]²⁻ into the Schiff base ligand, [**224**]⁶⁻, where two of the nitrogen atoms becomes amido donor atoms. The structure of [Co₂Na₂(**224**)(THF)₆] (Fig. 354a) consists of {Co(**204**)} units linked in centrosymmetric dimers through a C–C bond between the imine carbon atoms of the original [**204**]²⁻ molecules. The compound is isostructural with the analogous nickel derivative. One sodium cation for each {Co(**204**)} unit interacts with the oxygen atoms of the Schiff base and three THF molecules, resulting in a distorted square pyramidal coordination about the sodium ion with a phenolic oxygen at the apex. Coordination around the cobalt(III) ion is almost planar, with the metal ion lying in the mean plane through the N₂O₂ core.

The structure of [Co₂Na₂(**440**)(THF)₄] (Fig. 354b) consists of {Co(**417b**)} units linked in centrosymmetric dimers through a C–C bond provided by a reduced imino carbon of the Schiff base. One sodium cation for each {Co(**417b**)} unit coordinates to the four oxygen atoms of THF molecules. The cobalt(II) ion exhibits the usual square planar coordination, lying in the mean plane through the N₂O₂ core. The sodium(I) cation is accommodated in the cavity provided by the four oxygen atoms of the Schiff base completing the coordination through the oxygen atoms from two THF molecules [546].

Sodium, potassium and cesium nitrate react with [M(**207e**)] to form exclusively adducts of 1:1 stoichiometry [547]. The geometry about sodium is extremely similar in [MNa(**207e**)(NO₃)(CH₃OH)] (M = Cu²⁺, Ni²⁺) (Fig. 355). The sodium sits in the plane of the Schiff base oxygen atoms and is involved in electrostatic interactions with all four. Further significant interactions with two nitrate oxygen atoms and a methanol oxygen, trans to the nitrate, complete

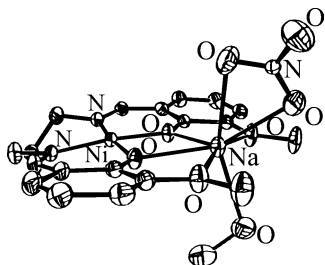


Fig. 355. Structure of $[\text{NiNa}(\mathbf{207c})(\text{NO}_3)(\text{CH}_3\text{OH})]$ (adapted from Ref. [547]).

the coordination sphere, thus resulting in an unusual seven coordination geometry about the sodium ion [547].

The asymmetric unit of the cesium adduct corresponding to the formula $[\text{CsNi}(\mathbf{207e})(\text{NO}_3)]_3 \cdot \text{CH}_3\text{OH}$ is part of an infinite sandwich structure (Fig. 356). The three crystallographically independent cesium ions are in similar locations insofar as they are each sandwiched between two sets of five oxygen atoms. Four of the five oxygens in each set belong to a nickel salicylaldimine molecule while the fifth belongs to a nitrate group. The oxygens of each set are approximately coplanar and lie at the corners of an elongated pentagon, the elongation in each case originating from the displacement of the nitrate oxygen from the more ideal pentagonal geometry location. As a result of the sandwich arrangement so described, each cesium ion has a pentagonal antiprismatic coordination geometry. There are, however, additional Cs–O contacts resulting from nitrate and methanol such that the overall coordination geometries of Cs(1) and Cs(3) has been described as monocapped pentagonal antiprisms. Apart from forming close contacts with cesium ions, the three nitrate oxygens also form bonds to nickel ions. The former two oxygens complete the octahedral geometry about Ni(1), while the latter oxygen, along with a methanol oxygen complete the octahedral geometry about Ni(3). There are no bonds to Ni(2) other than those provided

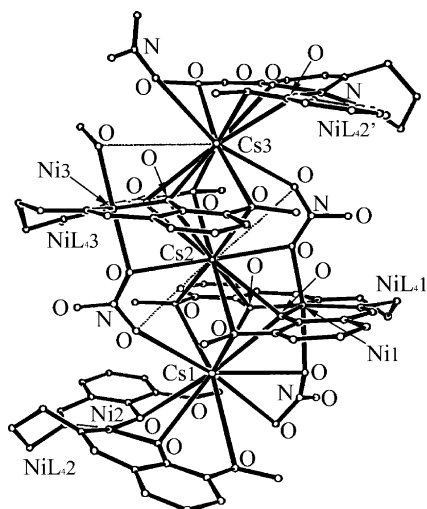


Fig. 356. Structure of $[\text{NiCs}(\mathbf{207c})(\text{NO}_3)]_3$ (adapted from Ref. [547]).

by the Schiff base ligand. Thus, the infinite sandwich structure consists of pairs of nickel salicylaldimines with octahedral nickel separated by single square planar nickel salicylaldimines [547].

A similar structure was also proposed for the analogous potassium adduct $[\text{NiK}(\mathbf{207e})(\text{NO}_3)]$ [547].

Both potassium and cesium iodides, like their nitrate analogues, react with the appropriate metal salicylaldimines (i.e. those derived from $\text{H}_2\text{-207a}$, $\text{H}_2\text{-417a}$ and $\text{H}_2\text{-417b}$) to yield the 1/1 adducts with notable exceptions. Thus both potassium and cesium iodides form 1:2 adducts with $[\text{Ni}(\mathbf{417b})]$; also potassium iodide and cesium iodide form respectively 1:2 and a 2:3 adducts with $[\text{Cu}(\mathbf{417b})]$.

The sodium adducts with the nickel salicylaldimines are of 1:2 stoichiometry, whereas those with the copper salicylaldimines are of 1:1 stoichiometry except for the adduct with $[\text{Cu}(\mathbf{417b})]$, which appears to be of 2:3 stoichiometry. As had been the case with sodium nitrate, sodium iodide does not form adducts with $[\text{Zn}(\mathbf{207e})]$.

In $[\text{Ni}_2\text{Na}(\mathbf{207e})_2](\text{I}) \cdot \text{C}_2\text{H}_5\text{OH}$ two nickel salicylaldimines approach the sodium ion which achieves fairly regular dodecahedral geometry (Fig. 357a). The iodide ion has no meaningful contacts with either sodium or nickel but is involved in weak hydrogen-bonding interactions with water and ethanol molecules of crystallization.

Although the adduct that immediately precipitates from solution following reaction of cesium iodide with $[\text{Ni}(\mathbf{417a})]$ is of 1:1 stoichiometry, the compound obtained from slow crystallization is the 1:2 adduct $[\text{Ni}_2\text{Cs}(\mathbf{417a})_2](\text{I}) \cdot \text{H}_2\text{O}$. The structure of this adduct is strikingly different from that of the

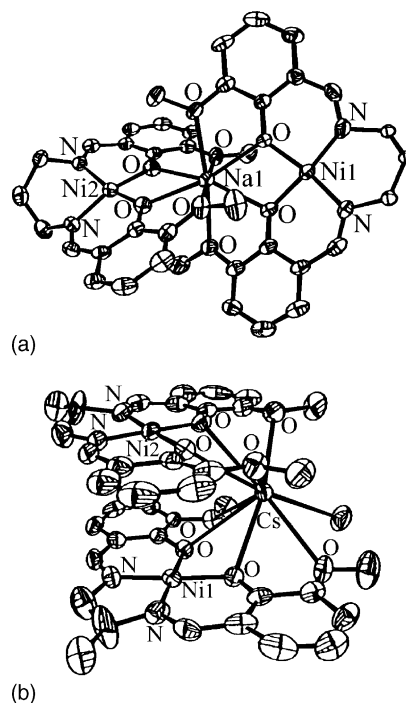


Fig. 357. Structure of $[\text{Ni}_2\text{Na}(\mathbf{207c})_2]^+$ (a) and $[\text{Ni}_2\text{Cs}(\mathbf{417a})_2](\text{I})$ (b) (adapted from Ref. [547]).

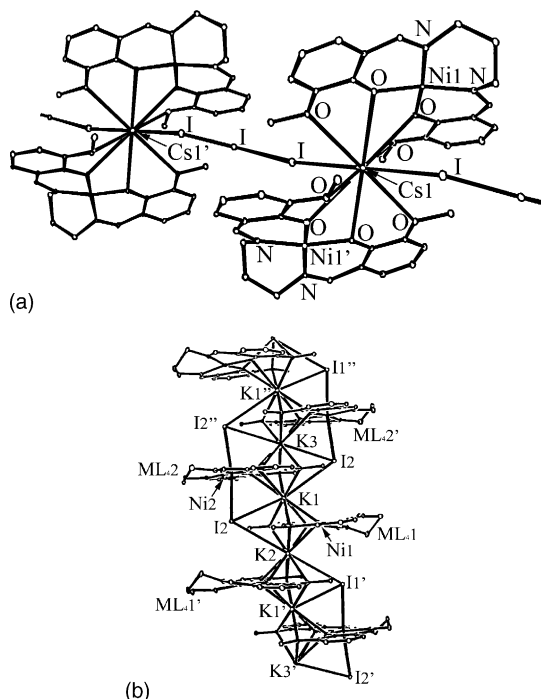


Fig. 358. Structure of $[\text{Ni}_2\text{Cs}(\mathbf{207e})(\text{I}_3)]_n$ (a) and $[\text{NiK}(\mathbf{207e})(\text{I})]_n$ (b) (adapted from Ref. [547]).

sodium iodide adduct structure described above, the difference being dictated by the much larger size of cesium relative to that of sodium. In this case (Fig. 357b) the cesium ion is sandwiched between two sets of Schiff base oxygen atoms. Each set of Schiff base oxygens is essentially coplanar, and these planes are essentially parallel. The cesium ion is also bound to an iodide ion which brings the overall cesium coordination number to nine [547].

Addition of I_2 to a methanol solution of $[\text{Ni}_2\text{Cs}(\mathbf{207e})_2(\text{I})]$ gives rise to $[\text{Ni}_2\text{Cs}(\mathbf{207e})_2(\text{I}_3)]$ which has a polymeric structure as a result of bridging triiodide groups. The cesium ions, sandwiched between two sets of Schiff base oxygens, are 10 coordinated in a distorted pentagonal antiprismatic arrangement (Fig. 358a).

Also $[\text{NiK}(\mathbf{207e})(\text{I})_n]$, the 1:1 adduct of potassium iodide with $[\text{Ni}(\mathbf{207e})]$, shows an infinite sandwich structure (Fig. 358b) where the potassium ions achieve 10 coordination while nickel(II) alternates a six octahedral with two trans nickel–iodine bonds and a square planar coordination [547].

Potassium thiocyanate and acetate react with $[\text{M}(\mathbf{207e})]$ to give exclusively 1:1 adducts. NaBPh_4 reacts with all of the complexes $[\text{M}(\mathbf{207e})]$ to give 1:2 adducts, whereas cesium and potassium tetraphenylborates react with $[\text{M}(\mathbf{207e})]$ ($\text{M} = \text{Cu}^{2+}$, Co^{2+} , Ni^{2+}) to give adducts of 2:3 stoichiometry. Sodium tetraphenylborate yields an adduct with $[\text{Zn}(\mathbf{207e})]$, whereas sodium nitrate and iodide salts failed to do so. The reverse situation was observed in the case of the potassium and cesium adducts. Potassium and cesium tetraphenylborates failed to give adducts with this zinc

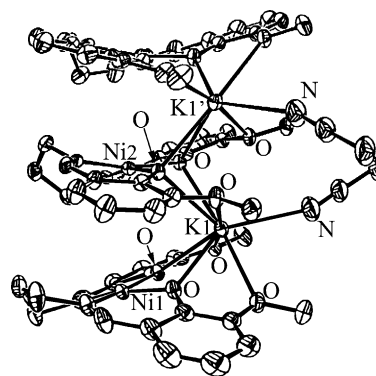


Fig. 359. Structure of $[\text{Ni}_3\text{K}_2(\mathbf{207e})_3(\text{CH}_3\text{CN})_2]^{2+}$ (adapted from Ref. [547]).

salicylaldehyde, whereas the nitrate and iodide salts readily yield 1:1 adducts.

When CH_3CN is used as solvent $[\text{Ni}_3\text{K}_2(\mathbf{207e})_3(\text{CH}_3\text{CN})_2](\text{BPh}_4)_2$ was obtained. The asymmetric unit of this adduct consists of a full nickel salicylaldehyde molecule, a potassium ion with an acetonitrile molecule coordinated to it, and half of a second nickel salicylaldehyde molecule two-fold axis passing through nickel. This two-fold axis generates the full cation (Fig. 359) consisting of three nickel salicylaldehyde molecules and two potassium ions (with associated acetonitrile molecules) in a club sandwich type structure, thus accounting for the 2:3 stoichiometry. Each potassium ion is eight coordinated being involved in interactions with all four Schiff base oxygens of a terminal nickel salicylaldehyde molecule, three oxygens of the central nickel salicylaldehyde and the nitrogen of an acetonitrile molecule [547].

All of the potassium and cesium tetraphenylborate adducts isolated from acetonitrile, being of the same stoichiometry and containing acetonitrile, presumably have the same structure [547].

12.2. End-off complexes derived from 2,6-diformyl-4-methylphenol and related derivatives

The condensation of 2,6-diformyl-4-methylphenol and primary amines, bearing additional donor groups, gives rise to [1+2] end-off compartmental ligands which, in addition to will defined dinuclear complexes, can form polynuclear entities.

Dark-brown crystals of the pentanuclear iron(III) complex $[\text{Fe}_5(\mathbf{383c})_2(\text{O})_4(\text{CH}_3\text{COO})_3](\text{ClO}_4)_2 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ were prepared by condensation of 2,6-diformyl-4-methylphenol and histamine in the presence of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}(\text{CH}_3\text{COO})$ and $\text{Na}(\text{ClO}_4)$, filtering the solution and adding $\text{N}(\text{Et})_3$ to the filtrate [548]. The five iron ions are located at the corners of a defective double cubane. The shorter $\text{Fe} \cdots \text{Fe}$ distances within the cubanes range from 2.888 to 3.002 Å. In one dinuclear unit, the Fe(1) and Fe(2) ions are bridged by a phenoxo oxygen atom of the dinucleating ligand, an oxo ion and one acetate group. Similarly, in the other dinuclear unit

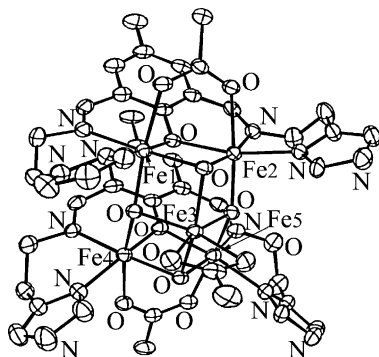


Fig. 360. Structure of $[\text{Fe}_5(\mathbf{383c})_2(\text{O})_4(\text{CH}_3\text{COO})_3]^{2+}$ (adapted from Ref. [548]).

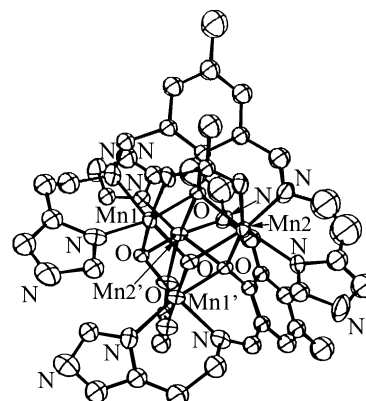
the Fe(4) and Fe(5) ions are bridged by a phenoxo oxygen atom of the dinucleating ligand, an oxo ion and one acetate group. These dinuclear units are stacked upon each other by oxo bridges which are connected to the Fe(3) ion. The coordination environments of the five iron(III) ions are not equivalent. The Fe(1), Fe(2), Fe(4) and Fe(5) ions have an N_2O_4 donor set in a distorted octahedron, while the Fe(3) atom is coordinated to the four $\mu_3\text{-O}$ ions and bidentate acetate group forming a distorted octahedron (Fig. 360).

Mössbauer spectra, measured for a polycrystalline sample of this pentanuclear iron(III) complex at 300 and 80 K, are characteristic of high-spin iron(III) complexes. These spectra are slightly broadened, which might indicate the existence of two differing sites; one for the Fe(1), Fe(2), Fe(4) and Fe(5) ions which have $\text{Fe}^{\text{III}}\text{N}_2\text{O}_4$ environments and the other for the Fe(3) ion which has a $\text{Fe}^{\text{III}}\text{O}_6$ environment [549].

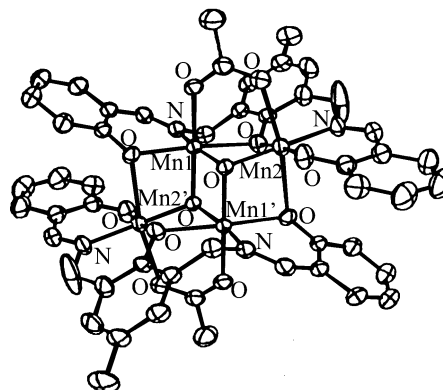
The effective magnetic moment of the pentairon(III) species, $7.75\mu_{\text{B}}$ at 297 K, smaller than the expected value for five uncoupled iron(III) ions, steadily decreases on lowering the temperature, reaching $6.22\mu_{\text{B}}$ at 80 K, indicative of antiferromagnetic coupling between the five high-spin iron(III) centers [549].

The same reaction in the presence of $\text{Mn}(\text{CH}_3\text{COO})\cdot 4\text{H}_2\text{O}$, NaClO_4 and triethylamine gives rise to the tetranuclear manganese(II)–manganese(III) complex $[\text{Mn}_4(\mathbf{383c})_2(\text{O})_2(\text{CH}_3\text{COO})_2](\text{ClO}_4)_2\cdot 2\text{C}_2\text{H}_5\text{OH}\cdot 2\text{H}_2\text{O}$ with a cubane structure [549] (Fig. 361a). In one dinuclear unit, the two manganese ions are bridged by a phenoxo oxygen of $[\mathbf{383c}]^-$, the oxo ion and the oxygens of an acetate group. The coordination environment about each manganese ion is completed by two nitrogen donors of $[\mathbf{383c}]^-$. The bond distances are indicative of one high-spin Mn(III) ion and one high-spin manganese(II) ion. The other dinuclear unit is related to this dinuclear unit by a two-fold axis.

The effective magnetic moment of $[\text{Mn}_4(\mathbf{383c})_2(\text{O})_2(\text{CH}_3\text{COO})_2](\text{ClO}_4)_2\cdot 2\text{C}_2\text{H}_5\text{OH}\cdot 2\text{H}_2\text{O}$ is 8.58 BM at 297 K, smaller than the expected one for four $\text{Mn}_2^{\text{II}}\text{Mn}_2^{\text{III}}$ uncoupled ions, steadily decreases on decreasing temperature, reaching 7.56 BM at 80 K indicating a significant antiferromagnetic coupling between the metal ions.



(a)



(b)

Fig. 361. Structure of $[\text{Mn}_4(\mathbf{383c})_2(\text{O})_2(\text{CH}_3\text{COO})_2]^{2+}$ (a) and $[\text{Mn}_4(\mathbf{373c})_2(\text{O})_2(\text{CH}_3\text{COO})_2]$ (b) (adapted from Refs. [549,551]).

The frozen solution EPR spectrum of $[\text{Mn}_4(\mathbf{383c})-(\text{O})_2(\text{CH}_3\text{COO})_2](\text{ClO}_4)_2$ indicates that possibly this tetranuclear complex may break into two dinuclear units in dimethylformamide/toluene, giving rise to the multiline EPR signal [549].

2,6-Bis(salicylideneaminomethyl)-4-methylphenol [550, 551] reacts with manganese(II) acetate or benzoate in acetonitrile and in the presence of triethylamine to form the tetranuclear complex $[\text{Mn}_4(\mathbf{373})_2(\text{O})_2(\text{RCOO})_2]\cdot 2\text{CH}_3\text{CN}$ ($\text{R} = \text{CH}_3$; C_6H_5) [551]. $[\text{Mn}_4(\mathbf{373})_2(\text{O})_2(\text{CH}_3\text{COO})_2]\cdot 2\text{CH}_3\text{CN}$ is non electrolyte in DMF and is very stable at the manganese(III) oxidation state. Thus in the absence of any further addition of aqueous solution, which can be a source of oxo ions, the two dinuclear units associate to the tetranuclear complex by virtue of the phenoxo oxygens of the Schiff bases and the oxo ions which might be generated from traces of water in the solvent. In the dinuclear half, the two manganese ions are bridged by the central phenoxo oxygen atom of $[\mathbf{373}]^{3-}$, the oxo ion, and the acetate group. These two dinuclear halves are associated to form the tetranuclear molecule by the oxo ions and the terminal phenoxo oxygen atoms of $[\mathbf{373}]^{3-}$. Both manganese ions take elongated octahedral geometries. The square plane around the one manganese ion is formed by the imine

nitrogen atom of $[\mathbf{373}]^{3-}$ the two oxo ions and the oxygen atom of the acetate ion, whereas the plane for the other manganese ion consists of the two phenoxy oxygen and the imine nitrogen atoms of $[\mathbf{373}]^{3-}$ and the oxo ion. The $\text{Mn}\cdots\text{Mn}$ separations range from 2.831 to 3.051 Å (Fig. 361b).

The magnetic susceptibility data show on overall anti-ferromagnetic interaction ($J = -2.51 \text{ cm}^{-1}$, $J' = -2.12 \text{ cm}^{-1}$ for $[\text{Mn}_4(\mathbf{373})_2(\text{O})_2(\text{CH}_3\text{COO})_2]$; $J = -1.90 \text{ cm}^{-1}$, $J' = -1.75 \text{ cm}^{-1}$ for $[\text{Mn}_4(\mathbf{373})_2(\text{O})_2(\text{C}_6\text{H}_5\text{COO})_2]$) [550, 551].

The pentanuclear iron(III) complex $[\text{Fe}_5(\mathbf{373})_2(\text{O})(\text{OH})_2(\text{CH}_3\text{COO})_5(\text{DMF})]$, synthesized by addition of a methanol solution of sodium hydroxide to a benzene/dimethylformamide solution of $\text{H}_3\text{-}\mathbf{373}$ and basic iron(III) acetate, is formed by association of the two dinuclear units by virtue of linking to the fifth iron moiety $\{\text{FeO}(\text{OH})_2(\text{CH}_3\text{COO})_3\}$ (Fig. 362a). The five iron ions in the cluster are arranged as a rectangular based pyramid with the central metal ion at the apex of the pyramid. The distances between the central metal ion and the four peripheral metal ions vary from 3.370 to 3.657 Å. The distances between the peripheral metal ions range from 2.960 to 5.367 Å. The four peripheral iron ions form roughly a planar structure and the central iron ion is 1.55 Å above this plane. In one dinuclear unit, the two iron ions are bridged by a phenoxo-oxygen atom of the dinucleating ligand and one acetate ion. Similarly, in the other dinuclear unit, the other two iron ions are bridged by a phenoxo oxygen atom of the dinucleating ligand and one acetate ion. These dinuclear units are connected to the central metal atom by oxo, hydroxo and acetate ions. The coordination geometries of all the iron ions are distorted octahedra. The sixth coordination site of one iron ion is occupied by the oxygen atom of the dimethylformamide [552].

$[\text{Fe}_6\text{Na}_3(\mathbf{373})_3(\text{CH}_3\text{COO})_{12}]$ has been synthesized when the above reaction was performed in acetonitrile. The molecule contains six iron(III) and three sodium ions in an alternating cyclic arrangement of $[\text{Fe}_2(\mathbf{373})(\text{CH}_3\text{COO})_2]^-$ and sodium ions. Each pair of iron ions is bridged by the central phenoxo oxygen atom of $[\mathbf{373}]^{3-}$ (Fig. 362b). The $\text{Fe}\cdots\text{Fe}$ distances range from 3.533 to 3.539 Å. Two acetate groups are incorporated in each dinuclear iron unit as exogenous *syn-syn* bridges. Each iron ion adopts a distorted octahedral coordination geometry. The two terminal phenoxo oxygens of each $[\mathbf{373}]^{3-}$ ligand, coordinated to one iron(III) ion, also act as bridging groups between iron(III) and sodium ions. The sodium ion is further coordinated by two monoatomic bridging acetate groups, resulting in η^3 -bridges of the acetate groups. The iron and sodium ions are further bridged by an acetate group in a *syn-syn* mode. Each sodium ion takes a distorted octahedral geometry. The $\text{Fe}\cdots\text{Na}$ distances are in the range 3.376–3.443 Å. Thus, the adjacent metal–metal separations alternate between two short ($\text{Fe}\cdots\text{Na}$) and one long ($\text{Fe}\cdots\text{Fe}$) contacts in the distorted nonagon [552].

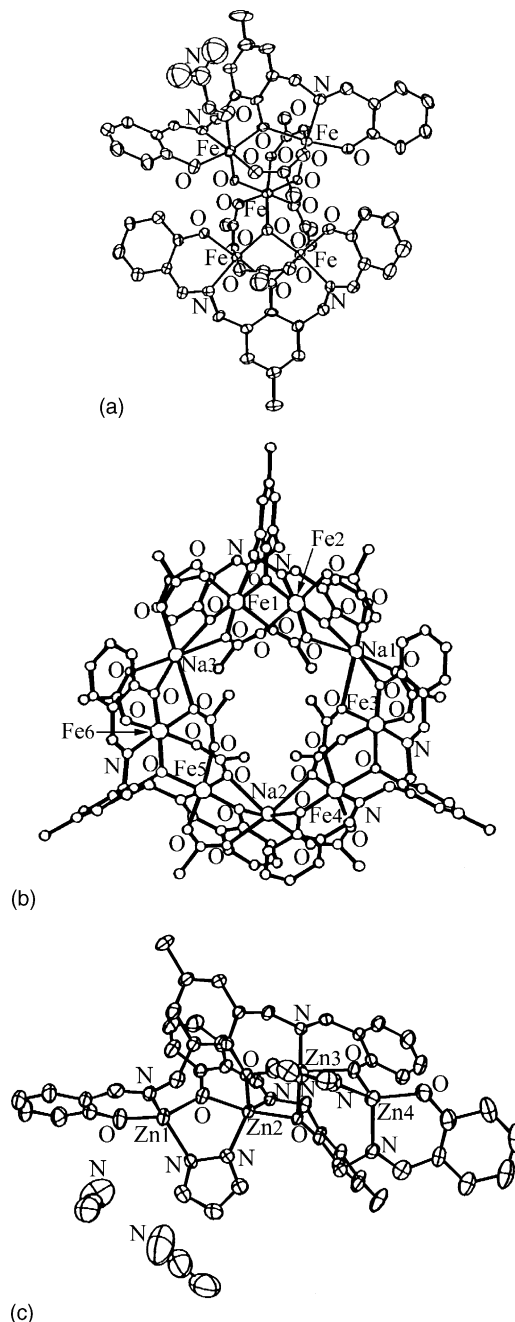


Fig. 362. Structure of $[\text{Fe}_5(\mathbf{373})_2(\text{O})(\text{OH})_2(\text{CH}_3\text{COO})_5(\text{DMF})]$ (a), $[\text{Fe}_6\text{Na}_3(\mathbf{373})_3(\text{CH}_3\text{COO})_{12}]$ (b), and $[\text{Zn}_4(\mathbf{372})_2(\text{pyrazolate})_2]\cdot 2\text{CH}_3\text{CN}$ (c) (adapted from Ref. [552]).

The effective magnetic moment of $[\text{Fe}_5(\mathbf{373})_2(\text{O})(\text{OH})_2(\text{CH}_3\text{COO})_5]\cdot\text{DMF}$ (9.40 BM at 300 K), smaller than the expected one for five uncoupled iron(III) ions, steadily increases on decreasing temperature, reaching a maximum of 16.37 BM at ca. 7 K. Below 7 K the magnetic moment decreases with decreasing temperature. The increase in effective magnetic moment with decreasing temperature indicates an increase in the average unpaired spin density at low temperatures relative to that found at room temperature. The magnetic moments of $[\text{Fe}_6\text{Na}_3\text{-}$

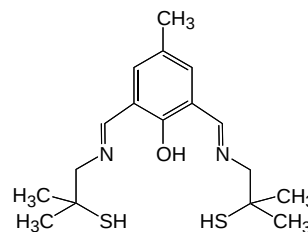
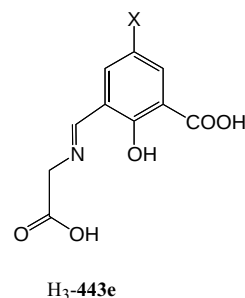
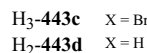
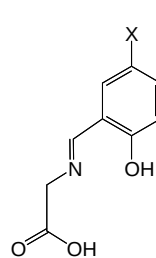
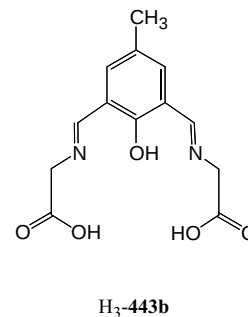
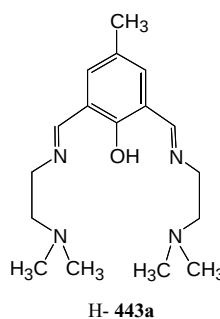
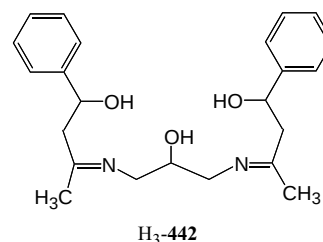
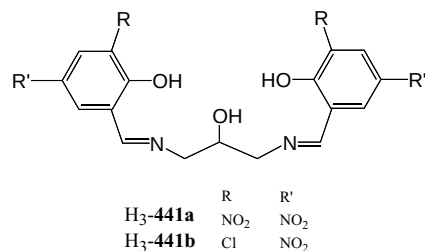
(**373**)(CH₃COO)₁₂] lower than expected at room temperature (12.59 BM), decreases upon cooling, indicating an antiferromagnetic interaction ($J = -9.3 \text{ cm}^{-1}$) [552].

The treatment of H₃-**373** with Zn(ClO₄)₂·6H₂O in acetonitrile containing pyrazole and triethylamine afforded [Zn₄(**373**)(pyrazolate)₂]·2CH₃CN where the four zinc ions are arranged in a Z shape at a Zn(1)···Zn(2) = 3.042 Å and, Zn(3)···Zn(4) = 3.248 Å distances (Fig. 362c) [552]. The outside zinc ions (Zn(1) and Zn(4)) take a similar tetrahedral coordination geometry with two phenoxo oxygen atoms and an imino nitrogen atom of two [**373**]^{3−} ligands and pyrazolato nitrogen atom while the geometries of the inside zinc ions (Zn(2) and Zn(3)) are trigonal bipyramidal with a phenoxo oxygen atom of [**373**]^{3−}, an imino nitrogen atom of another [**373**]^{3−} and a pyrazolato nitrogen atom in the equatorial plane and two phenoxo oxygen atoms [**373**]^{3−} at the axial positions. Each Schiff base ligand is bound to the four metal ions. One Schiff base ligand binds Zn(1), Zn(2), Zn(3) and Zn(4) ions in different ways: it acts as a bidentate ligand for tetrahedral Zn(1) with the terminal phenoxo oxygen and imino nitrogen, as monodentate ligand for trigonal-bipyramidal Zn(2) with the central phenoxo oxygen, as tridentate ligand for trigonal bipyramidal Zn(3) with a central phenoxo oxygen, an imino nitrogen and a terminal phenoxo oxygen, and as monodentate ligand for tetrahedral Zn(4) with a terminal phenoxo oxygen. The other Schiff base ligand is bound to Zn(1), Zn(2), Zn(3), and Zn(4) ions in a similar fashion (monodentate for Zn(1), tridentate for Zn(2), monodentate for Zn(3), and bidentate for Zn(4)) [552].

All signals in the ¹H NMR spectrum in CDCl₃ have been reasonably assigned based on the 1:1 molar ratio of [**373**]^{3−} and pyrazolate ions. This is in harmony with the solid state structure, although the symmetric dinuclear species [Zn₂(**373**)(pz)] is more realistic in solution [552].

Under strictly anaerobic conditions, reaction of twice the molar amount of Mn(CH₃COO)₂·2H₂O with 1,5-bis(3,5-dinitrosalicylideneamino)pentan-3-ol, (H₃-**441a**) in a methanolic sodium hydroxide solution leads to the very air sensitive orange compound [Mn₂(**441a**)(OH)(THF)₂·2THF [553]. The structure of this tetranuclear complex (Fig. 363) shows that the trianionic pentadentate ligand [**441a**]^{3−} bridges two manganese(II) ions through its alkoxo oxygen atom. Each manganese(II) ion is additionally bonded to one azomethine nitrogen and one phenolate oxygen atom of [**441a**]^{3−}. A hydroxo bridge further stabilizes the two manganese(II) centers of each dinuclear unit. The structure of [Mn₂(**441a**)(OH)(THF)₂·2THF is best viewed as two layers of dinuclear subunits linked by two bridging phenolate oxygen atoms of [**441a**]^{3−} and two μ₃-OH[−] ions. The bis-dinuclear molecule is located at a crystallographic inversion center. Different coordination sphere for the two manganese ions in the same subunit results from the weak binding of a THF molecule at the remaining apex of the one manganese coordination octahedron. This manganese ion has a donor set formed by one nitrogen and five

oxygen atoms, consequently the other manganese ion is in a square pyramidal environment of one nitrogen and four oxygen atoms. The Mn···Mn distance ranges from 3.166 to 3.281 Å while one Mn···Mn distance is 5.547 Å [553].



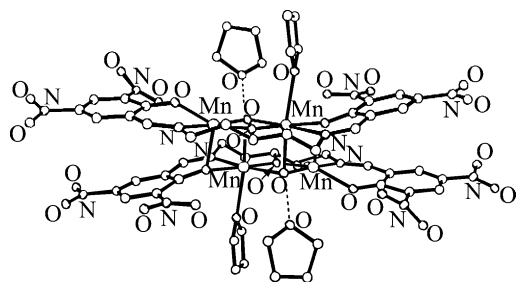


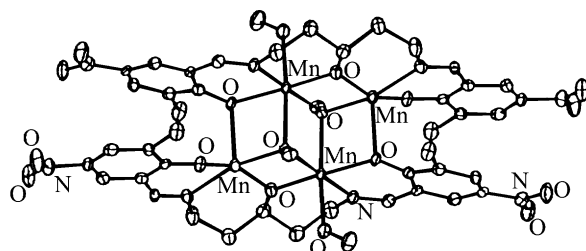
Fig. 363. Structure of $[\text{Mn}_2(\mathbf{441a})\text{OH}(\text{THF})_2]_2$ (adapted from Ref. [553]).

The X-band EPR powder spectra of $[\text{Mn}_2(\mathbf{441a})\text{OH}(\text{THF})_2]_2 \cdot 2\text{THF}$ are consistent with the presence of magnetically interacting manganese(II) ions in the solid state while X-band EPR spectra of the compound in DMF/toluene glasses at 100 K indicate that the tetranuclear structure is retained in solution. The magnetic susceptibility measured between 300 and 2 K shows the μ_{eff} value per Mn center is lower than the spin only value at 300 K and decreases from 5.56 to $2.31\mu_{\text{B}}$ at 2 K, indicating an overall antiferromagnetic coupling between the manganese(II) ions [553].

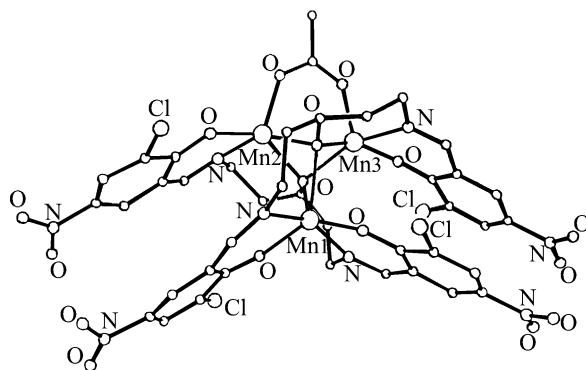
The reaction of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with 1,5-bis(3-Cl-5- NO_2 -salicylideneimino)pentan-3-ol ($\mathbf{H}_3\text{-441b}$) and NaOH (2:1:3 molar ratio) in methanol yields the very air sensitive orange complex $[\text{Mn}_2(\mathbf{441b})(\mu_3\text{-OCH}_3)(\text{CH}_3\text{OH})_2]$. Treatment of the initial mother liquor with water induces precipitation of a second compound which, by crystallisation from tetrahydrofuran/pentane, gives $\text{Na}[\text{Mn}_3(\mathbf{441b})_2(\mu_2\text{-CH}_3\text{COO})] \cdot \text{H}_2\text{O} \cdot 0.25\text{THF}$ [553].

$[\text{Mn}_2(\mathbf{441b})(\mu_2\text{-OCH}_3)(\text{CH}_3\text{OH})_2]$ has a bisdinuclear structure: two layered $\{\text{Mn}_2(\mathbf{441b})\}$ dinuclear units, bridged by two methoxo anions from $[\mathbf{441b}]^{3-}$ and two phenolato oxygen atoms from $[\mathbf{441b}]^{3-}$, are related by a crystallographic inversion center (Fig. 364a). The two manganese(II) ions within the $\{\text{Mn}_2(\mathbf{441b})\}$ unit have different coordination spheres: one manganese ion is in a square pyramidal NO_4 ligand environment while the NO_5 environment of the other manganese ion is distorted octahedral [553].

$\text{Na}[\text{Mn}_3(\mathbf{441b})_2(\mu_2\text{-CH}_3\text{COO})] \cdot \text{H}_2\text{O} \cdot 0.25\text{THF}$ (Fig. 364b) has an array of trinuclear $[\text{Mn}_3(\mathbf{441b})_2(\mu_2\text{-CH}_3\text{COO})]^-$ anions bonded to sodium cations. The core of the complex anion is a triangle of manganese(II) cations bridged by the alkoxo $\mu_3\text{-O}$ atoms of both $[\mathbf{441b}]^{3-}$ ligands. The presence of manganese(II) ions is deduced from stoichiometric and structural considerations, further confirmed by the EPR and magnetic studies. In addition to the two alkoxo $\mu_3\text{-O}$ oxygens, the trigonal prismatic Mn(1) coordination sphere includes one imine nitrogen and one phenolate oxygen from each $[\mathbf{441b}]^{3-}$ ligand. The basal plane of the square pyramidal ligand environment of Mn(2) and Mn(3) includes one imine nitrogen, one phenolate oxygen and the alkoxo $\mu_3\text{-O}$ oxygen atoms from one $[\mathbf{441b}]^{3-}$ ligand, in addition to the alkoxo $\mu_3\text{-O}$ oxygen atom from the second $[\mathbf{441b}]^{3-}$ ligand. The apical position of each square pyramid is occupied by one oxygen atom of the bridging acetate. As



(a)



(b)

Fig. 364. Structures of $[\text{Mn}_2(\mathbf{441b})(\mu_3\text{-OCH}_3)(\text{CH}_3\text{OH})_2]$ (a) and $[\text{Mn}_3(\mathbf{441b})_2(\mu_2\text{-CH}_3\text{COO})]^-$ (b) (adapted from Ref. [553]).

a result, Mn(1) is doubly bridged to Mn(2) and Mn(3) while Mn(2) and Mn(3) are triply bridged, which is reflected in the Mn(2) $\cdots$ Mn(3) distance ($3.067\text{ \AA}$) compared to the Mn(1) $\cdots$ Mn(2) ($3.174\text{ \AA}$) and Mn(1) $\cdots$ Mn(3) ($3.121\text{ \AA}$) separations. Both $[\mathbf{441b}]^{3-}$ ligands are helically arranged around the trinuclear metal core, and show π -stacking interactions between their aromatic rings [553]. Additional aromatic ring interactions operate between adjacent trinuclear units through out the crystal lattice, resulting in a 1D supramolecular array of alternating pairs of $[\text{Mn}_3(\mathbf{441b})_2(\mu_2\text{-CH}_3\text{COO})]^-$ anions and Na^+ cations. Sodium cations interact with terminal 5-nitro and central alkoxo functions of $[\mathbf{441}]^{3-}$ and bridging acetate anions of the anionic trinuclear units. In addition each sodium cation also interacts with one water molecule [553].

The 300–80 K X-band EPR powder spectra of $[\text{Mn}_2(\mathbf{441b})_2(\mu_2\text{-OCH}_3)(\text{CH}_3\text{OH})_2]$ indicate a typical tetranuclear manganese(II) complex and the presence of weak extended interactions in the solid state. Its 100 K DMF/toluene X-band glass spectrum indicates that the tetranuclear structure is retained in solution and that the weak extended interactions are not operating in solution, where the 1D chains of hydrogen-bonded tetranuclear molecules are broken [553]. The 300–80 K X-band EPR powder spectra of $\text{Na}[\text{Mn}_3(\mathbf{441b})_2(\mu_2\text{-CH}_3\text{COO})] \cdot \text{H}_2\text{O} \cdot 0.25\text{THF}$ are typical of magnetically interacting manganese(II) ions. On the other hand, its 100 K DMF/toluene glass X-band EPR spectrum indicates dissociation, not only of its supramolecular architecture, but also of the trinuclear complex

anion. Two resulting manganese(II) species are clearly identified: a mononuclear one and a dinuclear one [553].

The magnetic moment of $[\text{Mn}_2(\mathbf{441b})(\mu_3\text{-OCH}_3)(\text{CH}_3\text{-OH})_2]$ and $\text{Na}[\text{Mn}_3(\mathbf{441b})_2(\mu_2\text{-CH}_3\text{COO})]\cdot\text{H}_2\text{O}\cdot 0.25\text{THF}$ at 300 K, lower than the spin-only value for non-interacting spin systems, decreases from 10.50 to $4.89\mu_B$ for the first and from 9.00 to $4.91\mu_B$ for the second complex at 2 K, indicating overall antiferromagnetic coupling of the manganese(II) ions in both complexes [553].

Bis(benzoylacetone)-1,3-diimino-propan-2-ol ($\text{H}_3\text{-}\mathbf{442a}$) reacts with manganese(II) acetate in the presence of sodium perchlorate and triethylamine to form black crystals of the trinuclear manganese(III) complex $[\text{Mn}_3(\mathbf{442a})_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})(\text{C}_2\text{H}_5\text{OH})](\text{ClO}_4)\cdot\text{CH}_3\text{OH}$ [542,554] where the three manganese(III) ions occupy the corners of an isosceles triangle and are bridged by the alkoxo oxygen atom of a dinucleating ligand. Two manganese(III) ions are also bridged by two methoxo oxygens and show an elongated octahedral geometry. Each square plane is formed by the NO_2 donor atoms of $[\mathbf{442a}]^{3-}$ and the bridging methoxo oxygen atom occupies one site of the apical position. The elongated octahedral coordination is achieved by the weak coordination of a methanol molecule (for one manganese) or an ethanol molecule (for the other manganese). For the third manganese(III) ion each dinucleating ligand is tridentate and acts as a meridional bis chelate with one keto oxygen, one in-line nitrogen, and one alkoxo oxygen atom in a distorted octahedron.

The room temperature magnetic moment (7.31 BM) for this trinuclear manganese(III) complex is smaller than the spin-only value expected for a three high-spin d^4 system. The magnetic susceptibility data measured over a temperature range 80–300 K give a significant antiferromagnetic coupling between the two methoxo bridged manganese ions [542,554].

$\text{H}_3\text{-}\mathbf{442a}$ reacts with $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ to form the tetranuclear cobalt(II)–cobalt(III) complex $[\text{Co}_4(\mathbf{442a})_2(\text{C}_2\text{H}_5\text{O})_4]\cdot\text{CH}_3\text{CN}$ [554] (Fig. 365a). Each of the two Schiff base ligands is coordinated to three cobalt ions by the central alkoxo oxygen atom; an ethoxo oxygen atom is further bonded to each pair of cobalt ions. The result is a core with a di- μ -alkoxo- μ -ethoxo bridge, two μ -alkoxo- μ -ethoxo bridges, and a μ -ethoxo bridge. The Co(1) and Co(2) ions take a distorted octahedral six coordination with a keto-oxygen, an imino nitrogen and two alkoxo oxygen atoms of $[\mathbf{442a}]^{3-}$ and two ethoxo oxygen atoms. On the other hand, the coordination geometry of the Co(3) and Co(4) ions is five coordinated trigonal bipyramid with an imino nitrogen atom of $[\mathbf{443a}]^{3-}$ and two ethoxo oxygen atoms in the equatorial plane, and a keto oxygen and an alkoxo oxygen atoms of $[\mathbf{443a}]^{3-}$ at the axial positions. The oxidation state of these cobalt ions are different: Co(1) and Co(2) are low spin cobalt(III) ions while Co(3) and Co(4) are high-spin cobalt(II) ions. The $\text{Co}\cdots\text{Co}$ distances are, respectively, 2.595 and 3.414 Å. The other $\text{Co}\cdots\text{Co}$ distances range from 3.042 to 3.117 Å.

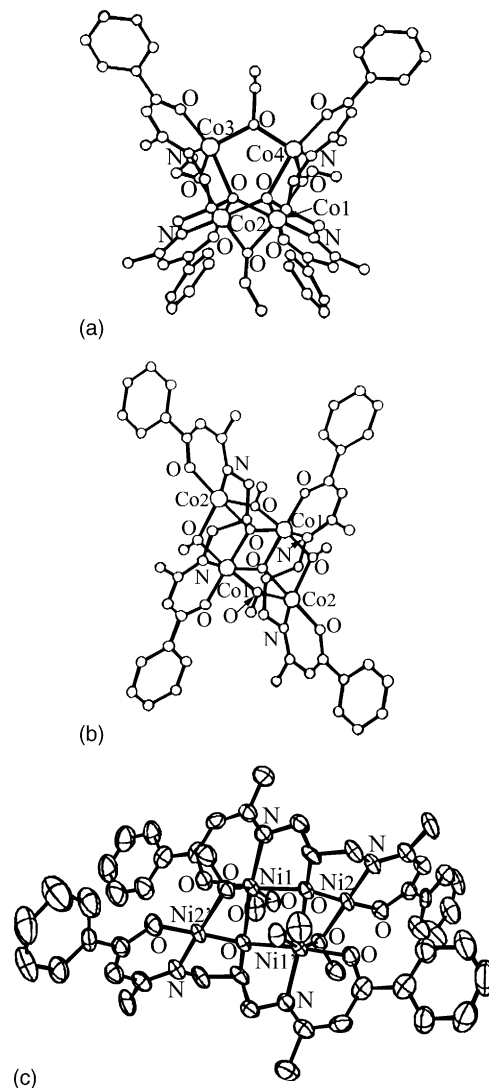


Fig. 365. Structures of $[\text{Co}_4(\mathbf{442})(\text{C}_2\text{H}_5\text{O})_4]$ (a) $[\text{Co}_4(\mathbf{442})_4(\text{CH}_3\text{O})_4]$ (b) and $[\text{Ni}_4(\mathbf{442})_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ (c) (adapted from Ref. [554]).

In contrast, treatment of $\text{H}_3\text{-}\mathbf{442a}$ with cobalt(II) chloride hexahydrate in $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ led to the mixed-valent tetranuclear complex with a stepped cubane-like core $[\text{Co}_4(\mathbf{442a})_2(\text{CH}_3\text{O})_4]\cdot 2\text{CH}_2\text{Cl}_2$ (Fig. 365b). The molecule has a crystallographic inversion center at the midpoint between the Co(1) and Co(1') ions. In the asymmetric unit, the Co(1) and Co(2) ions are bridged by the alkoxo oxygen atom of $[\mathbf{442}]^{3-}$ and a methoxo oxygen atom and further bound to the Co(2') and Co(1') ions of the other asymmetric unit by a methoxo oxygen atom, respectively. The Co(1) ion adopts a distorted octahedral geometry with a keto oxygen, an imino nitrogen, and alkoxo oxygen atoms of $[\mathbf{442a}]^{3-}$, an alkoxo oxygen atom of another $[\mathbf{442a}]^{3-}$ ligand, and two methoxo oxygen atoms, while the Co(2) ion has a trigonal bipyramidal arrangement with an imino nitrogen of $[\mathbf{443a}]^{3-}$ and two methoxo oxygen atoms in the equatorial plane and a keto oxygen and an alkoxo oxygen of $[\mathbf{442}]^{3-}$ at the axial positions.

The reaction of $\text{H}_3\text{-442}$ with nickel(II) nitrate hexahydrate in $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ containing triethylamine at room temperature gives $[\text{Ni}_4(\text{442})_4(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ [554]. In the asymmetric unit the Schiff base ligand $[\text{442}]^{3-}$ binds two nickel ions with one alkoxo oxygen, one imino nitrogen and one keto oxygen atom. The two dinuclear units are held together through the methoxo oxygen atoms and alkoxo oxygen atoms of $[\text{442}]^{3-}$ to form a tetranuclear Ni_4 core with a twisted chair form consisting of μ -alkoxo- μ -methoxo di- μ -alkoxo and μ -alkoxo- μ -methoxo-bridges. The metal...metal separations are the range 2.847–3.604 Å. The Ni(1) ion adopts a distorted octahedral coordination geometry with one alkoxo oxygen atom, one imino nitrogen atom and one keto-oxygen atom of $[\text{442}]^{3-}$ and an alkoxo oxygen atom of the other $[\text{442}]^{3-}$, a methoxo oxygen atom and methanol oxygen atom. On the other hand, the Ni(2) ion assumes a square planar coordination with one alkoxo oxygen atom, one imino nitrogen atom, and one keto oxygen atom of $[\text{442}]^{3-}$ and a methoxo oxygen atom. Thus the Ni(1) and Ni(1') ions were assigned to high-spin paramagnetic nickel(II) ions and the Ni(2) and Ni(2') ions to low spin diamagnetic nickel(II) ions, respectively [554].

The mixed-spin state of $[\text{Ni}_4(\text{442})_4(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ has been confirmed by magnetic susceptibility measurements. The effective magnetic moment of $[\text{Ni}_4(\text{442})_4(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ 4.59 BM per molecule at room temperature, significantly larger than the spin-only value for non-interacting two paramagnetic ($S = 1$) ions, increases with lowering of temperature, reaching a maximum at 6 K, and then slightly decreasing down to 4.5 K. This magnetic behaviour indicates that a ferromagnetic interaction is operating between the two octahedral nickel(II) ions ($J = 2.51 \text{ cm}^{-1}$). The bridge angle close to 90° may be a major factor for the observed ferromagnetic behaviour of $[\text{Ni}_4(\text{442})_4(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$. A very weak antiferromagnetic coupling has been noted in the related complex $[\text{Ni}_2\text{Zn}_2(\text{442})_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ ($J = -0.05 \text{ cm}^{-1}$) containing an analogous tetranuclear structure owing to the Ni–O–Ni bridge angle (99.4°) larger than that of the nickel(II) complex [554].

For $[\text{Co}_4(\text{442})(\text{C}_2\text{H}_5\text{O})_4]$ an antiferromagnetic interaction ($J = -8.5 \text{ cm}^{-1}$) through the ethoxo bridge is operating between the two cobalt(II) ions while $[\text{Co}_4(\text{442})_4(\text{CH}_3\text{O})_4]$ shows a ferromagnetic interaction ($J = 2.2 \text{ cm}^{-1}$) between the two cobalt(II) ions mediated by the $\text{Co}^{\text{III}}_2\text{O}_2$ moiety [554].

The reaction of zinc(II) chloride, $\text{H}_3\text{-442}$ and triethylamine in acetonitrile at room temperature gave $[\text{Zn}_4(\text{H-442})_4] \cdot 4\text{CH}_3\text{CN}$ [554]. Each Schiff base is double deprotonated and acts as a meridional chelate with one keto oxygen, one imino nitrogen, and one alkoxo oxygen atom; each zinc ion adopts a distorted trigonal bipyramid coordination geometry with two alkoxo oxygen atoms, and one imino nitrogen atom in the equatorial plane and one keto oxygen atom and one alkoxo oxygen atom at the axial positions. The other keto oxygen and imino nitrogen atoms are not coordinated to any metal ions (Fig. 366a) [554].

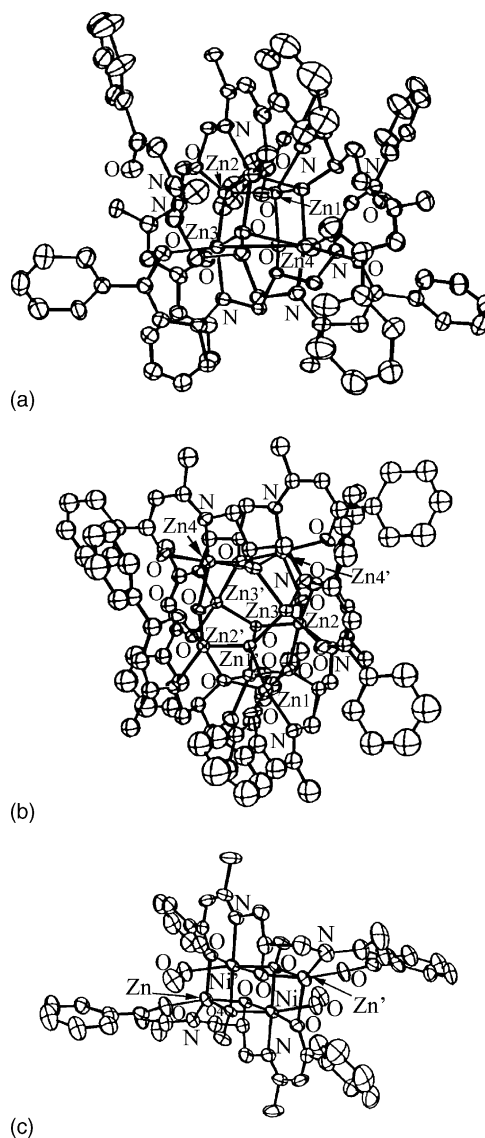


Fig. 366. Structures of $[\text{Zn}_4(\text{H-442})_4]$ (a), $[\text{Zn}_8(\text{442})_4(\text{OH}_4)_2]$ (b) and $[\text{Zn}_2\text{Ni}_2(\text{442})_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ (c) (adapted from Ref. [554]).

Under a more basic condition with zinc(II) perchlorate hexahydrate as the metal source, a combination of pale yellow crystals of $[\text{Zn}_4(\text{H-442})_4] \cdot 4\text{CH}_3\text{CN}$ and colourless crystals of $[\text{Zn}_8(\text{442})_4(\text{OH}_4)_2] \cdot 2\text{CH}_3\text{CN}$ was obtained. The X-ray structure of the octanuclear complex consists of two severely distorted hexahedra connected by hydroxo ions (Fig. 366b). Each Schiff base ligand is triply deprotonated and bound to each of eight zinc ions with three O_2N donor atoms in a meridional fashion. The coordination geometry around each zinc ion is a distorted trigonal bipyramid with a hydroxo oxygen atom and an alkoxo oxygen atom and an imino nitrogen atom of two $[\text{442}]^{3-}$ ligands in the equatorial plane and an alkoxo oxygen atom and a keto oxygen atom of $[\text{442}]^{3-}$ at the axial positions [554].

When a methanol solution of nickel(II) acetate tetrahydrate and triethylamine were successively added to a

dichloromethane solution of $[\text{Zn}_4(\text{H-442})_4] \cdot 4\text{CH}_3\text{CN}$, $[\text{Zn}_2\text{Ni}_2(\text{442})_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ was formed as yellowish green plates whose structure consists of discrete tetranuclear units (Fig. 366c). In the asymmetric dinuclear unit, the zinc and nickel ions are bridged by the central alkoxo oxygen atom of one Schiff base ligand $[\text{442}]^{3-}$ and a methoxo oxygen atom. Furthermore dinuclear units are held together through the methoxo and the keto oxygen atoms of $[\text{442a}]^{3-}$ to form a defective double cubane $\text{Zn}_2\text{Ni}_2\text{O}_6$ core. The nickel ions take a distorted octahedral six coordination, while the geometries of the zinc ions are trigonal bipyramidal five coordinate. Two methanol molecules are also coordinated [554].

The magnetic moment of $[\text{Zn}_2\text{Ni}_2(\text{442a})_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ at room temperature (4.66 BM) is close to that expected for non-interacting four metal ions. The temperature dependence (80–300 K) of the magnetic susceptibility of $[\text{Zn}_2\text{Ni}_2(\text{442a})_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ shows a very weak antiferromagnetic interaction operating between the two nickel(II) ions ($J = -0.05 \text{ cm}^{-1}$) [554].

As reported above in a previous section, the presence of appropriate bridging systems can favour the formation of dinuclear species instead of polynuclear ones. Thus in $[(\text{VO})_2(\text{442})(\mu\text{-piz})]$, derived by treatment of $\text{H}_3\text{-442}$ with $[\text{VO}(\text{acetylacetonate})_2]$ in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ containing pyrazole, the two vanadium ions with terminal oxo groups, 3.446 Å apart, are bridged by an alkoxo oxygen of $[\text{442}]^{3-}$ and pyrazolato group, forming a distorted square pyramidal environment for each metal center. A weak antiferromagnetic interaction ($J = -2.3 \text{ cm}^{-1}$) is operating between the two vanadium(IV) ions [554].

In $[\text{Zn}_2(\text{443a})(\text{CH}_3\text{COO})_2](\text{X})$ ($\text{X} = \text{ClO}_4^-$, PF_6^-) ($\text{H-443a} = 2,6\text{-bis}\{N\text{-}[2\text{-dimethylaminoethyl}]\text{iminomethyl}\}\text{-4-methylphenol}$), prepared by template procedure [555], the two zinc ions, 3.234 Å apart, are bridged by the deprotonated phenolic oxygen of $[\text{443a}]^-$ and two acetate groups. Each metal center is five coordinated through the imine nitrogen, the amine nitrogen and the phenolate and acetate oxygens. The coordination geometry of the zinc ions is a distorted trigonal bipyramid with the phenolic oxygen and amine nitrogen occupying the apical positions (Fig. 367a).

$[\text{Zn}_2(\text{443a})(\text{CH}_3\text{COO})_2](\text{ClO}_4)$ reacts with glycine ethyl ester in D_2O at pD 7.4 and room temperature to form $[\{\text{Zn}_2(\text{443b})(\text{CH}_3\text{COO})_2\}_2\text{Zn}(\text{H}_2\text{O})_4] \cdot 4.5\text{H}_2\text{O}$ where $\text{H}_3\text{-443b}$ derives from the condensation of glycine and 2,6-diformyl-4-methylphenol both formed by the hydrolysis of glycine ethyl ester and the Schiff base $\text{H}_2\text{-443a}$ [553]. The same complex was prepared by template reaction. Slow evaporation of the filtrate gave a second product of composition $[\text{Zn}(\text{H-443b})] \cdot 3\text{H}_2\text{O}$.

$[\{\text{Zn}_2(\text{443b})(\text{CH}_3\text{COO})_2\}_2\text{Zn}(\text{H}_2\text{O})_4] \cdot 4.5\text{H}_2\text{O}$ is built up of two $\{\text{Zn}_2(\text{443b})(\text{CH}_3\text{COO})_2\}$ moieties linked through bridging carboxylate functions of the ligand side arm to the fifth zinc ion that is located on a crystallographic inversion center. The zinc ions of the dinuclear unit are five coordinated through imine nitrogen, carboxylate, phenolate

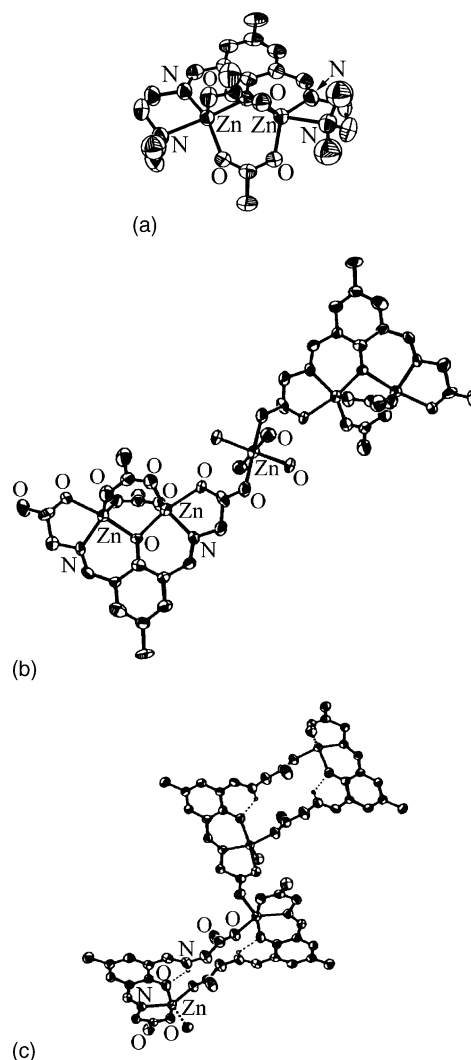


Fig. 367. Structures of $[\text{Zn}_2(\text{443a})(\text{CH}_3\text{COO})_2]^+$ (a), $[\{\text{Zn}_2(\text{443b})(\text{CH}_3\text{COO})_2\}_2\text{Zn}(\text{H}_2\text{O})_4]$ (b) $[\text{Zn}(\text{H-443b})]_n$ (c) (adapted from Ref. [555]).

and two acetate oxygens. The intermetallic distance is 3.175 Å. The coordination geometry of these zinc ions is trigonal bipyramidal. The carboxylate and bridging phenolic oxygens occupy the apical positions; the equatorial planes are formed by the acetate oxygens and the imine nitrogens. The central zinc ion is six coordinated through two carboxylate functions trans to each other and four water ligands. The coordination geometry deviates only slightly from an ideal octahedron (Fig. 367b) [555].

$[\text{Zn}(\text{H-443b})] \cdot 3\text{H}_2\text{O}$ is a polymeric, three-dimensional network, built up of dimeric subunits $\{\text{Zn}(\text{H-443b})\}_2$ interconnected through carboxylate bridges. Each ligand coordinates one zinc ion through the deprotonated phenolic oxygen and one chelating side arm. The other side arm binds via a carboxylate oxygen to the second zinc ion of the dimer, while its imine nitrogen is protonated with the proton forming a hydrogen bond to the phenolate oxygens. The five coordination sphere of the zinc ions is completed by the carboxylate oxygen of the adjacent dimer. The coordination

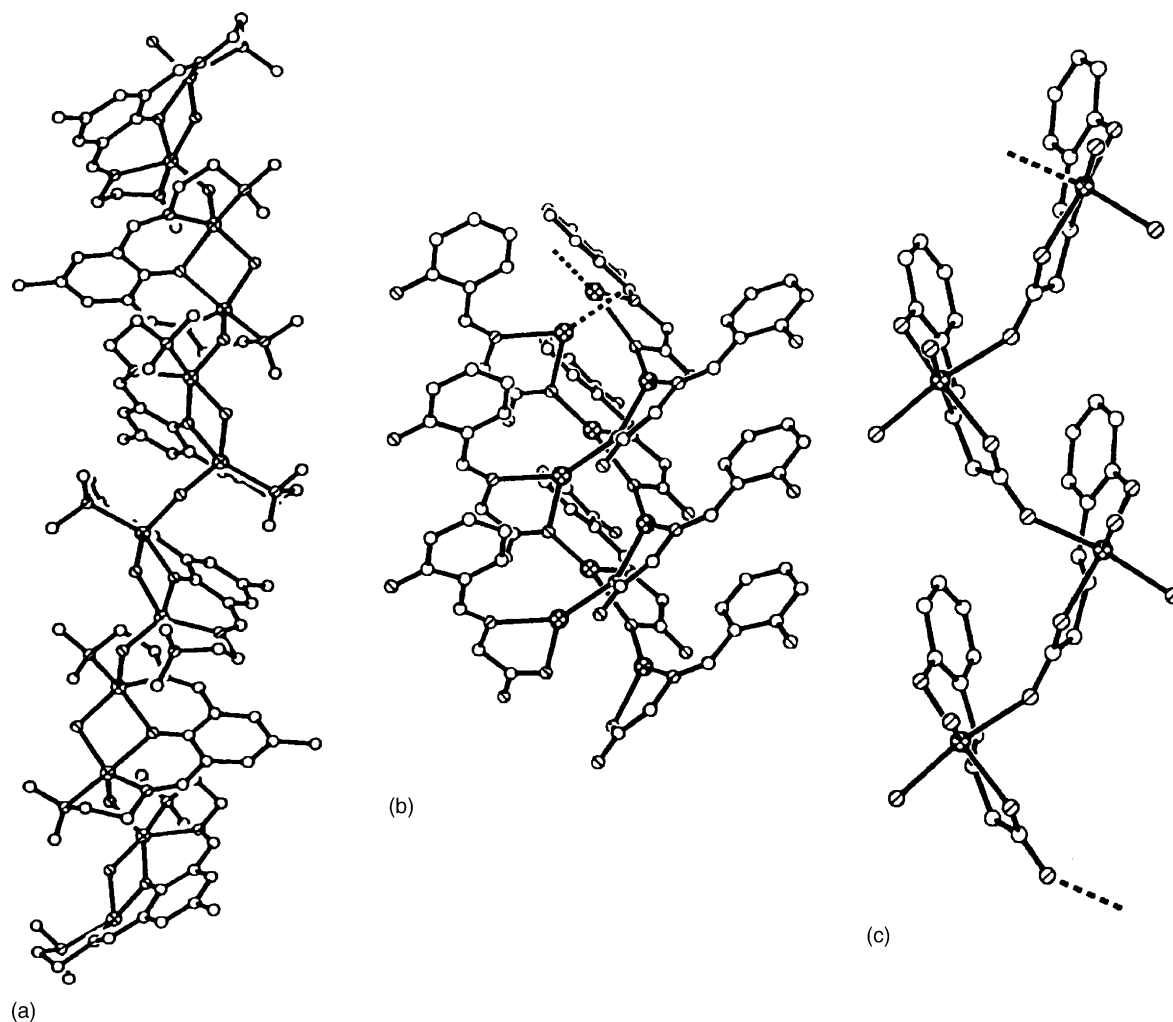


Fig. 368. The helical polymer structure of $\{Zn(\mathbf{443a})(\mu\text{-OH})\} \text{NO}_3 \cdot 2\text{H}_2\text{O}$ ((a), $[Ag(\text{H-}\mathbf{443c})]_n$ (b) and $[Mg(\mathbf{443c})(\text{H}_2\text{O})_2]_n$ (c) (adapted from Ref. [555]).

geometry around the zinc ions is distorted trigonal bipyramidal with the phenolic and carboxylate oxygens occupying the apical positions. In the three-dimensional structure the dimeric subunits are connected in such a way that long channels are produced along the crystallographic y axis that are stabilised by water of crystallisation. The disordered water molecules form hydrogen bonds among each other and to the carboxylate oxygens. The phenolic rings are stacked along the y -axis so that neighbouring rings overlap partly (Fig. 367c) [555].

However, the condensation of 2,6-diformyl-4-methylphenol with 2 equiv. of N,N -dimethylenediamine in the presence of $Zn(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in aqueous solution followed by addition of base, gave the helical complex $\{[Zn_2(\mathbf{443a})(\mu\text{-OH})(\text{OH})](\text{NO}_3) \cdot 2\text{H}_2\text{O}\}_\infty$. The structure is built up of dinuclear $\{[Zn_2(\mathbf{443a})(\mu\text{-OH})]\}^{2+}$ entities (Fig. 368a) that are connected through single hydroxo bridges. Within the subunits, the five coordinated zinc ions are bridged by the deprotonated phenolic oxygen of the ligand and a hydroxo group at a distance of 3.161 Å. Further donor atoms are the

imine and amine nitrogens of the ligand side arms [555]. The coordination geometry of the zinc ions is a distorted square pyramidal, the axial positions being occupied by the hydroxo group that links the subunits to each other resulting in an infinite $Zn_2(\mu\text{-OH})$ strand. The mono- μ -hydroxo-bridged zinc ions are 3.673 Å apart. Twelve zinc ions span one helical turn so that the helix is considerably stretched. Since the ligand itself is achiral, equal amounts of P- and M-helices are formed. The diameter of the helix is approximately 8 Å. The distance between the axes of neighbouring helices extending along the c -axes of the unit cells in the crystal lattice is 11.340 Å. The channels with diameters of about 3 Å between the helices are filled with nitrate anions and water molecules of crystallization that are connected through hydrogen-bonding interactions [555].

The one dimensional double helical coordination polymer of composition $\{[Ag(\text{H-}\mathbf{443c})] \cdot 0.33\text{H}_2\text{O}\}_n$ was obtained by reacting $Ag\text{NO}_3$ with glycine and salicylaldehyde in methanol/water followed by recrystallization from methanol [555]. The silver(I) ion coordinates to the imine nitrogen

and carboxylate oxygen of the side arm of the tridentate ligand while the phenolic oxygen does not participate in the coordination. The carboxylate oxygen forms a monatomic bridge to the next silver ion so that each metal ion has an NO_2 coordination sphere. Owing to the narrow bite of the chelating ligand side arm, the silver(I) ion assumes a distorted Y-shaped coordination geometry. The formation of monatomic carboxylate bridges results in an infinite chain of alternating silver and oxygen atoms extending along a three-fold screw axis. Two unconnected helical chains then wind around each other to form a double helix as shown in Fig. 368b. The helix has a pitch height of 9.298 Å and a diameter of about 13 Å. In the crystal lattice three double helices are connected through hydrogen-bonding interactions involving the phenolic OH groups and the uncoordinated carboxylate oxygens so that long channels along the crystallographic z -direction are produced. These channels having diameters of about 5 Å are filled with water molecules of crystallization [555].

$[\text{Mg}(\mathbf{443c})(\text{H}_2\text{O})_2]_n$, $[\text{Mg}(\text{H-}\mathbf{443d})(\text{H}_2\text{O})_2]$ and $[\text{Mg}(\text{H-}\mathbf{443d})(\text{H}_2\text{O})_3]$ have been prepared by reaction of the appropriate ligand with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of base; the same complexes can be prepared by reaction of the analogous zinc(II) complexes with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in dimethylsulphoxide [555].

$[\text{Mg}(\text{H-}\mathbf{443e})(\text{H}_2\text{O})_3]$ has a monomeric structure while $[\text{Mg}(\mathbf{443c})(\text{H}_2\text{O})_2]_n$ a polymeric one; in both compounds the magnesium(II) ion has an octahedral geometry with the Schiff base bonded to the central ion via the three NO_2 donor site. In $[\text{Mg}(\mathbf{443d})(\text{H}_2\text{O})_3]$ three water oxygens complete the coordination environment while in $[\text{Mg}(\mathbf{443c})(\text{H}_2\text{O})_2]_n$ only two water molecules are coordinated to the central metal ion. Adjacent $[\text{Mg}(\mathbf{443c})(\text{H}_2\text{O})_2]$ entities are linked through carboxylate groups, bonded in a *syn-anti* fashion, forming infinite chains which extend in the z -direction [555] (Fig. 368c).

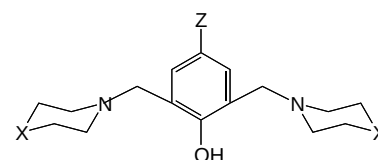
The treatment of $\text{H}_3\text{-}\mathbf{443f}$, derived by condensation of 2,6-diformyl-4-methylphenol and $\text{H}_2\text{NCH}_2\text{C}(\text{CH}_3)_2\text{SH}$ in a 1:2 molar ratio, with zinc salts yielded impure compounds; however, the same condensation reaction using diethylzinc both as the base and as the source of zinc yielded crystalline products in good yields. When alcohols were present either as a solvent or as a coreagent (methanol, ethanol or 4-trifluoromethylbenzyl alcohol) the complexes $[\text{Zn}_2(\mathbf{443f})(\text{OR})]_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CF}_3\text{CH}_2\text{C}_6\text{H}_4$) have been obtained; these compounds are soluble in polar aprotic organic solvents and crystallize as yellow solvates from chloroform or dichloromethane [556].

The structure of $[\text{Zn}_2(\mathbf{443f})(\text{OC}_6\text{H}_4\text{CH}_2\text{CF}_3)]_2$ confirms this complex is a tetranuclear aggregate assembled from two pentadentate ligands. In each of the two dinuclear units, the compartmental ligand exerts its expected ligation pattern by giving both zinc ions a square environment. The dimerization of the two dinuclear units is brought about by placing them face to face across a center of symmetry and linking them through the unshared electron pairs of oxygens from

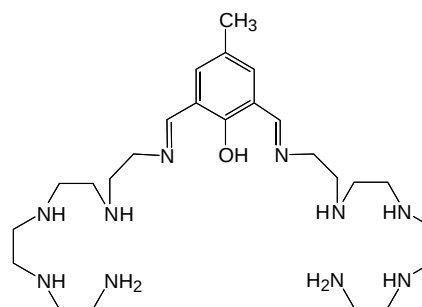
the 4-trifluoromethylbenzyl alcoholate and thiolate sulfur of the compartmental ligand $[\mathbf{443f}]^{3-}$. Thereby the linkage is represented by four rungs of a ladder, and the resulting $\text{Zn}_4\text{O}_4\text{S}_2$ core has the shape of two open cubes sharing a common face. The coordination of all four zinc ions is square pyramidal. Both zinc ions inside each dinuclear entity have a basal ZnO_2NS coordination, but the apical donor is oxygen for one zinc ion and sulfur for the other zinc ion. Accordingly, the compartmental ligand uses one of its thiolate functions as a terminal and the other as a bridging ligand [556] (Fig. 369).

Reaction in methanol of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with 1,3-bis-(salicylideneamino)-propan-2-ol, ($\text{H}_3\text{-}\mathbf{374}$), in the presence of sodium benzoate yields $[\text{Zn}_3(\mathbf{374})_2(\text{C}_6\text{H}_5\text{COO})_2] \cdot 2\text{CH}_3\text{OH}$ which consists of one central octahedrally coordinated zinc ion and two terminal zinc ions surrounded by five donor atoms in the form of a square pyramid. The left and right zinc ions are connected to the central metal ion via two phenolate oxygens of the dinucleating ligand and the oxygens of the benzoate ion [556] (Fig. 369).

The similar ligands $\text{H-}\mathbf{444a-c}$ have been obtained by a Mannich reaction between *p*-cresol or *p*-nitrophenol, formaldehyde and morpholine or piperidine [556,557]. In $\text{H-}\mathbf{444b}$ and $\text{H-}\mathbf{444c}$, the piperidine and morpholine rings assume a chair conformation. The molecules are stabilized by van der Waals interactions apart from an intermolecular $\text{N-H} \cdots \text{O}$ hydrogen bonding [557].



	Z	X
H-444a	CH_3	O
H-444b	NO_2	CH_2
H-444c	NO_2	O



H-445

$\text{H-}\mathbf{444a}$, when reacted in methanol with $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of sodium benzoate, forms $[\text{Zn}_6(\mathbf{444a})_3(\text{OH})_6](\text{ClO}_4)_3$ with the zinc ions arranged in form of a regular trigonal prism. Three dinuclear subunits are connected to each other by hydroxide groups [556] (Fig. 370a).

The reaction of 2,6-bis(morpholinemethyl)-4-methylphenol, ($\text{H-}\mathbf{444a}$), with CuBr_2 or $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and sodium

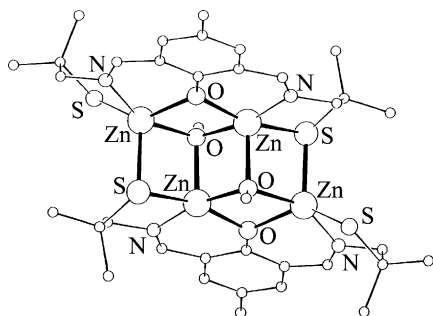


Fig. 369. Structure of $[\text{Zn}_4(\mathbf{443f})_2(\text{OC}_6\text{H}_4\text{CH}_2\text{CF}_3)_2]$ (adapted from Ref. [556]).

benzoate in methanol yields $[\text{Cu}_4(\mathbf{444a})_2(\text{O})(\text{Br})_4] \cdot 2\text{CH}_3\text{OH}$ and $[\text{Cu}_4(\mathbf{444a})(\text{O})(\text{C}_6\text{H}_5\text{COO})_4] \cdot \text{H}_2\text{O}$ [558].

$[\text{Cu}_4(\mathbf{444a})_2(\text{O})(\text{Br})_4] \cdot 2\text{CH}_3\text{OH}$ (Fig. 370b) consists of a tetrahedron of copper(II) ions centered by a μ_4 -bridging oxygen atom and with μ -bromine atoms bridging four of the six edges of the Cu_4 tetrahedron. The remaining two edges are occupied by μ -phenoxo bridges from the deprotonated $[\mathbf{444a}]^-$ ligands. The structure is completed by four terminal nitrogen bonded morpholine groups, one of them per each copper ion. The tetrahedron around the central oxygen shows unusual high distortion. The coordination of the four

copper ions is approximately trigonal bipyramidal. A nitrogen atom and the central μ_4 -oxide occupy the axial positions, and two bromine and one phenolate ligands coordinate the equatorial sites. The copper ions are displaced out of the planes of the equatorial ligand atoms by 0.285 Å in the direction of the nitrogen atoms of the morpholine groups. The $\text{Cu} \cdots \text{Cu}$ distances range from 2.998 to 3.216 Å [558].

The structural details of $[\text{Cu}_4(\mathbf{444a})_2(\text{O})(\text{C}_6\text{H}_5\text{COO})_4] \cdot \text{H}_2\text{O}$ (Fig. 370c) are completely different from the tetrabromo complex although the main $\{\text{Cu}_4\text{O}\}$ framework is conserved. The kernel of $[\text{Cu}_4(\mathbf{444a})_2(\text{O})(\text{C}_6\text{H}_5\text{COO})_4] \cdot \text{H}_2\text{O}$ is an oxygen atom surrounded tetrahedrally by four copper ions. Two of these copper centers have a coordination geometry which approximates to square pyramidal; the third is square planar and the fourth is octahedrally coordinated. This very unsymmetrical coordination of the metal centers is due to the nature of the $\mu_{1,3}$ -benzoate bridge bonding. The copper tetrahedron around the μ_4 -oxygen is even more distorted than in the tetrabromo complex. The arrangement of the ligands around the copper centers has been described as square basal planes with two further coordinating oxygen atoms in axial positions at Cu(1) and one additional benzoate oxygen in the coordination spheres of Cu(3) and Cu(4). The copper ions lie outside the plane defined by the four equatorial ligands. Each of the

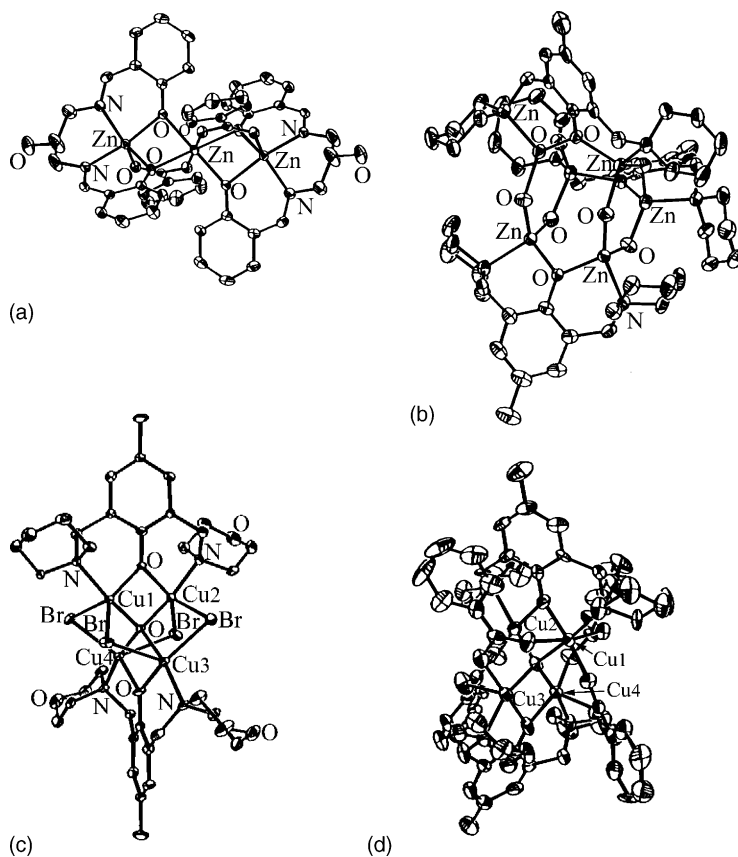


Fig. 370. Structure of $[\text{Zn}_4(\mathbf{374})_2(\text{C}_6\text{H}_5\text{COO})_2]$ (a), $[\text{Zn}_6(\mathbf{444a})_3(\text{OH})_6]^{3+}$ (b), $[\text{Cu}_4(\mathbf{444a})(\text{O})(\text{Br})_4]$ (c) and $[\text{Cu}_4(\mathbf{444a})(\text{O})(\text{C}_6\text{H}_5\text{COO})_4]$ (d) (adapted from Refs. [557,558]).

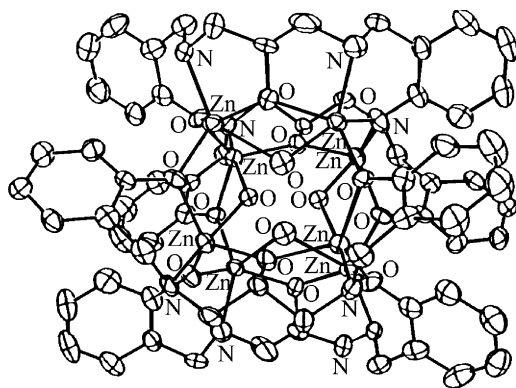


Fig. 371. Structure of $[\text{Zn}_8(\mathbf{375})_4(\text{OH})_2]^{2+}$ (adapted from Ref. [559]).

$[\mathbf{444a}]^-$ ligand molecules in $[\text{Cu}_4(\text{O})(\text{C}_6\text{H}_5\text{COO})_4] \cdot \text{H}_2\text{O}$ link two copper ions (Cu(1), Cu(2) and Cu(3), Cu(4)) by a μ -phenoxo bridge. All morpholine nitrogen and phenoxo donors are equatorially bonded, whereas the benzoate oxygens are coordinated alternately in axial and equatorial positions. The $\text{Cu} \cdots \text{Cu}$ distances range from 2.988 to 3.293 Å [558].

Both tetracopper complexes show a significant antiferromagnetic coupling between the copper(II) centers [558].

$[\text{Zn}_8(\mathbf{375})_4(\text{OH})_2](\text{ClO}_4)_2 \cdot 8\text{CH}_3\text{OH}$ has been isolated by the reaction of $\text{H}_3\text{-375}$, derived by the reduction of the related Schiff base $\text{H}_3\text{-374}$, with 2 equiv. of zinc(II) perchlorate [559]. The structure of $[\text{Zn}_8(\mathbf{375})_4(\text{OH})_2](\text{ClO}_4)_2 \cdot 8\text{CH}_3\text{OH}$ (Fig. 371) reveals an octanuclear zinc(II) complex cation arranged at vertices of a severely distorted rectangular parallelepiped with $\text{Zn} \cdots \text{Zn}$ distances ranging from 3.313 to 3.754 Å. These zinc ions are linked through four $[\mathbf{375}]^{3-}$ ligands. The N_2O_3 donor atoms of $[\mathbf{375}]^{3-}$ occupies eight coordination sites of four zinc ions and the central alkoxo oxygen acts as the bridging atom binding two zinc ions. Hydroxide ions are incorporated as exogenous bridging groups. The two terminal phenoxo oxygens of each $[\mathbf{375}]^{3-}$ ligand act as bridging groups for two zinc ions. The coordination geometry around each zinc ion can be regarded as a severely distorted trigonal bipyramid with an alkoxo oxygen and two phenoxo oxygen atoms of two $[\mathbf{375}]^{3-}$ ligands in the equatorial plane, and an amino nitrogen atom of $[\mathbf{375}]^{3-}$ and hydroxide ion at the axial positions. If the hydroxide ions are neglected, the coordination environment can be described as a distorted tetrahedral geometry [559].

When a similar hydrogenation reaction of $\text{H}_3\text{-374}$ in the presence of manganese(III) or iron(III) ions was tried, dinuclear species with an unsymmetrical ligand, 1-salicylideneamino-3-salicylamino-2-propanol instead of metal complexes of $\text{H}_3\text{-390}$ have been isolated. In this case, hydrogenation reaction occurs in only one of the two imino groups of $\text{H}_3\text{-374}$, resulting in the formation of species containing manganese(III) or iron(III) centers [559].

The reaction of anhydrous NdCl_3 , $\text{H}_3\text{-374}$, sodium amide and sodium carbonate in THF at room temperature results in

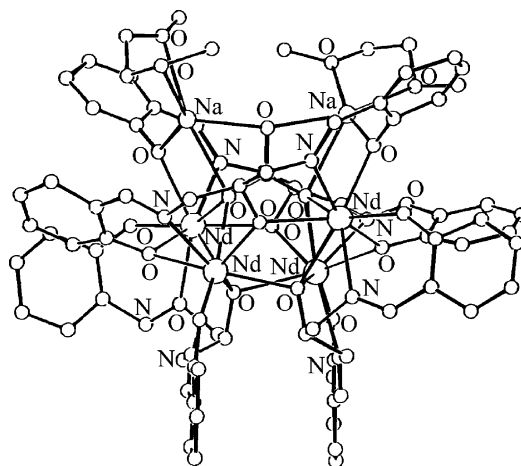


Fig. 372. Structure of $[\text{Nd}_4\text{Na}_2(\mathbf{374})_4(\text{CO}_3)(\text{dme})_2]$ (adapted from Ref. [560]).

the formation of the air- and moisture-sensitive pink complex $[\text{Na}_2\text{Nd}_4(\mathbf{374})(\text{CO}_3)(\text{THF})_4]$ which, by recrystallization from 1,2-dimethoxyethane (dme) yields the air- and moisture-sensitive pink complex $[\text{Na}_2\text{Nd}_4(\mathbf{374})(\text{CO}_3)(\text{dme})_2] \cdot 1.5\text{dme}$. The same synthesis in the absence of sodium carbonate gives a product with analytical composition $[\text{Nd}(\mathbf{374})(\text{THF})_2]$ which could not be crystallized in a form suitable for X-ray studies nor were the solubility properties suitable for characterization in solution [560].

The structures of both complexes $[\text{Nd}_4\text{Na}_2(\mathbf{374})_4(\text{CO}_3)(\text{THF})_4]$ and $[\text{Nd}_4\text{Na}_2(\mathbf{374})_4(\text{CO}_3)(\text{dme})_2]$ (Fig. 372) feature a tetranuclear, bowl-shaped cage $\{\text{Nd}_4(\mathbf{374})_4\}$ with quasi-two-fold symmetry. Within the cavity of the cage the multiply anchored, solvated sodium carbonate molecule, $\{\text{Na}_2(\text{CO}_3)(\text{THF})_4\}$ or $\{\text{Na}_2(\text{CO}_3)(\text{dme})_2\}$ resides. One carbonate oxygen bridges two sodium ions, whilst each of the others bridges one sodium and two neodymium ions. The carbonate coordination appears unique in combining bridging with chelation to two of the bridged atoms. Each sodium ion is five coordinated, being bound not only by the chelating carbonate and THF or dme, but also by a bridging aryloxy oxygen of the cage. Thus sodium carbonate is securely bonded to the cage.

The $\{\text{Nd}_4(\mathbf{374})_4\}$ cage contains square antiprismatic eight coordinated neodymium ions with two neodymium ions of $[\text{Nd}_4\text{Na}_2(\mathbf{374})_4(\text{CO}_3)(\text{dme})_2] \cdot 1.5\text{dme}$ different from the other two neodymium ions. The former are coordinated by two imide nitrogens, one η^1 - and two μ -aryloxy (NdONd and NdONa) oxygens, one μ_3 - and one μ -aryloxy oxygen, and a μ_3 -carbonate oxygen (NdO_2Na). By contrast, the latter pair are coordinated by two nitrogens, one η^1 - and one μ -(NdONd)aryloxy oxygen, one μ - and two μ_3 -alkoxy oxygens and a μ_3 -carbonate oxygen.

The deprotonated ligands are bridging pentadentate and bind to each of two neodymium(III) ions with three donor atoms, and to a further neodymium(III) ion by one donor atom. However, two ligands have μ_3 -alkoxy donors and

two η^1 -aryloxide oxygens whereas the other two contain μ -alkoxo donors and two μ -aryloxide oxygens. The $\text{Nd} \cdots \text{Nd}$ separations are in the range 3.803–3.844 Å [560].

Other complexes have been prepared and crystallographically characterized which incorporate the $\{\text{Nd}_4(\mathbf{374})_4\}$ group. These include $[\text{Nd}_4\text{Na}_5(\mathbf{374})_4(\text{OH})(\text{OCH}_3)_4(\text{CH}_3\text{OH})(\text{dme})_3]$, which contains the $\{\text{Nd}_4(\mathbf{374})_4\}$ cage in a different arrangement and encapsulates NaOH and NaOCH_3 molecules. This indicates the cage can be prepared independently of Na_2CO_3 and will accommodate other species [560].

12.3. Complexes derived from Schiff bases containing additional donor auxiliaries

2,6-Diformyl-4-methylphenol or 3-formylsalicylic acids have been conveniently used as formyl-precursors for the preparation, via condensation with suitable amines, of polynucleating ligands bearing additional cyclic or acyclic donor auxiliaries.

The tetranuclear complex $[\text{Cu}_4(\mathbf{445})(\mu\text{-OH})(\text{Cl})_2](\text{PF}_6)_4$, possessing a dinuclear Cu_2 core and two mononuclear Cu auxiliaries, was prepared as green microcrystals by the reaction of μ -chloro- μ -(2,6-diformyl-4-methylphenolato)dichlorodicopper(II) and 1,4,7,10,13-pentaaza tridecanecopper(II) hexafluorophosphate (in a 1:2 molar ratio) in acetonitrile at reflux temperature [561].

The cyclic voltammogram of $[\text{Cu}_4(\mathbf{445})(\mu\text{-OH})(\text{Cl})_2](\text{PF}_6)_2$ in acetonitrile showed pseudo-reversible couples at +0.47 and –0.65 (V versus SCE), assigned to the oxidation of the dinuclear core $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}/\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}$ and the reduction of the two mononuclear auxiliaries $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ respectively. Coulometry was done at –0.60 V with the aim to provide the $\{[\text{Cu}^{\text{I}}\text{–Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{–Cu}^{\text{I}}]\}$ complex, but electrolyzed solution showed EPR and UV-Vis spectra that suggest an intramolecular electron transfer: $\{\text{Cu}^{\text{I}}\text{–Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{–Cu}^{\text{I}}\} \rightarrow \{\text{Cu}^{\text{II}}\text{–Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{–Cu}^{\text{II}}\}$.

An isomerization of linear 1,4,7,10,13-pentaazatridecane to branched 4-(2-aminoethyl)-1,4,7,10-tetraazadecane occurs during the slow reoxidation (approximately 2 days) of the electrolyzed $\{\text{Cu}^{\text{I}}\text{–Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{–Cu}^{\text{I}}\}$ complex. From the reoxidized solution, after prolonged standing in air, the dinuclear copper(II) complex $[\text{Cu}_2(\text{H}_2\text{-}\mathbf{315})](\text{Cl})_4 \cdot 2\text{H}_2\text{O}$ was obtained. The dinuclear copper(II) cation contains a macrocycle in the neutral form ($\text{H}_2\text{-}\mathbf{315}$) which may be derived by the [2+2] condensation of 2,6-diformyl-4-methylphenol and branched 4-(2-aminoethyl)-1,4,7,10-tetraazadecane instead of assembly complex. The geometry around each copper(II) ion is a distorted trigonal bipyramid with the imino nitrogens the primary amino nitrogen and the secondary amino nitrogen at the basal plane and with the phenolic oxygen and the tertiary amino nitrogen at the apical sites. One of the imine nitrogens is free from coordination and is hydrogen-bonded to the phenolic oxygen. The two copper ions in the macrocycle are separated by 8.15 Å from each other [561] (Fig. 373).

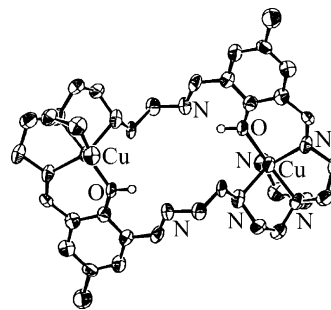
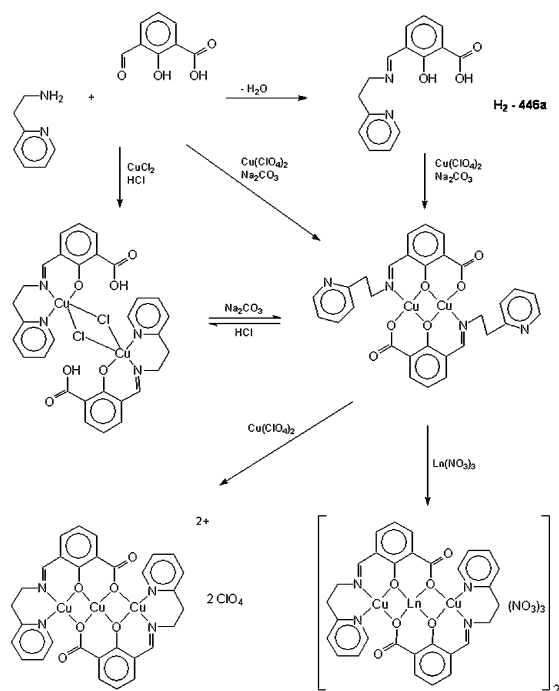


Fig. 373. Structure of $[\text{Cu}_2(\text{H}_2\text{-}\mathbf{315})]^{4+}$ (adapted from Ref. [561]).

The octanuclear copper(II) complex $[\text{Cu}_8(\mathbf{442b})_4(\text{OH})_3](\text{ClO}_4) \cdot 3\text{H}_2\text{O} \cdot \text{C}_7\text{H}_{12}$ has been prepared by the reaction of copper(II) perchlorate hexahydrate with 2-hydroxy-1,3-propanediylbis(acetylacetoneimine) $\text{H}_3\text{-}\mathbf{391c}$, in the presence of KOH in methanol [562]. The complex consists of four alkoxo bridged dinuclear copper units, $[\text{Cu}_2(\mathbf{391c})]^{+}$, that are covalently linked by one $\mu_2\text{-OH}$ and two $\mu_3\text{-OH}$ ligands to form the octacopper(II) core. Each copper ion in this octanuclear entity is in an axially elongated square pyramidal NO_4 coordination environment with the axial positions being occupied by the oxygen atom of the pentadentate ligand. Two copper ions display an additional weak axial ligation by water molecules. The $\text{Cu} \cdots \text{Cu}$ distances lie in the range 2.93–3.65 Å. The assembly of four $[\text{Cu}_2(\mathbf{442b})]^{+}$ units gives an unusual lateral-type metallamacrobicyclic core with a small inner cavity that consists the three hydroxo oxygen atoms [562].

The unsymmetrical tetradentate ligand of 3-[N-2-(pyridylethyl)formido]salicylic acid, $\text{H}_2\text{-}\mathbf{446a}$, prepared by treating 3-formylsalicylic acid and 2-(2-aminoethyl)pyridine in ethanol, should generate either the binuclear $[\text{M}_2(\mathbf{446a})_2]$ or the trinuclear $[\text{M}_3(\mathbf{446a})_2]^{2+}$ complexes. The dinuclear complexes may be engaged in further hetero-complexation reaction to form $[\text{M}_2\text{Ln}(\mathbf{446a})_2]^{3+}$ when treated with the appropriate lanthanide(III) salt. The metal-to-ligand molar ratio as well as the presence of a base (Na_2CO_3 or LiOH) or, alternatively, of an acid (HCl) influence the nature of the polynuclear complexes which are formed [563].

In a basic medium, with metal-to-ligand molar ratios of 1:1 and 3:2, respectively, $\text{H}_2\text{-}\mathbf{446a}$ can form either the binuclear $[\text{Cu}_2(\mathbf{446a})_2]$ or the trinuclear $[\text{Cu}_3(\mathbf{446a})_2](\text{ClO}_4)_2$ species. Conversely, in HCl solution the chloro-bridged dimer $[\text{Cu}_2(\text{H-}\mathbf{446a})_2(\text{Cl})_2]$ is obtained. It is interesting that the formation of two chelate rings with the copper(II) ion favours most probably the deprotonation of the phenolic group instead of the carboxyl one. The chloro-bridged dimer $[\text{Cu}_2(\text{H-}\mathbf{446a})_2(\text{Cl})_2]$ can be converted into $[\text{Cu}_2(\mathbf{446a})_2]$ by treating it with a Na_2CO_3 or LiOH aqueous solution. The reaction of $[\text{Cu}_2(\mathbf{446a})_2]$ with copper(II) perchlorate yields the trinuclear complex $[\text{Cu}_3(\mathbf{446a})_2](\text{ClO}_4)_2$ which may be used as precursor for the formation of the hexanuclear cluster $[\text{Cu}_2\text{Ln}(\mathbf{446a})_2(\text{NO}_3)_3]_2$ [563] (Scheme 63).



Scheme 63.

The structure of [Cu(H-446a)(Cl)]₂ (Fig. 374a) consists of dimeric neutral entities related by an inversion center. Each copper ion is bonded unsymmetrically by two chloride anions, thus forming a double bridge. The Cu...Cu distance in the dimeric entity is 3.825 Å. Almost orthogonal to the plane occur two ligands centered around the copper ion, the ligating atom set being, nearly planar. The copper ions are coordinated by two chloride atoms, two nitrogen atoms and one oxygen atom. The coordination polyhedron of the copper ions is a distorted square pyramid with two nitrogen a phenolic oxygen and a chloride atom forming the equatorial bonds and the other chloride forming the axial one [563].

The structure of [Cu₂(446a)₂(H₂O)₂] (Fig. 374b) consists of neutral centrosymmetric binuclear entities. The copper(II) ions are bridged by phenolic oxygen atoms. The pyridyl groups are not coordinated. The coordination geometry around the copper ions is square pyramidal. The basal positions are occupied by one nitrogen atom arising from the azomethine group and by three oxygen atoms, two bridging phenolic oxygens and one from the carboxylato group, while the apical position is occupied by the aqua ligand [563].

The structure of the praseodymium(III)–copper(II) complex [Cu₄Pr₂(446a)₄(NO₃)₆] shows that the six metal ions form a chair-shaped hexagon (Fig. 374c). The two praseodymium ions are located of both sides of a double layer containing the four copper ions. This hexanuclear entity may be viewed as a pair of heterotrinnuclear units. The copper ions belonging to two PrCu₂ units are bridged two-by-two by carboxylato groups. Within a trinuclear unit, each praseo-

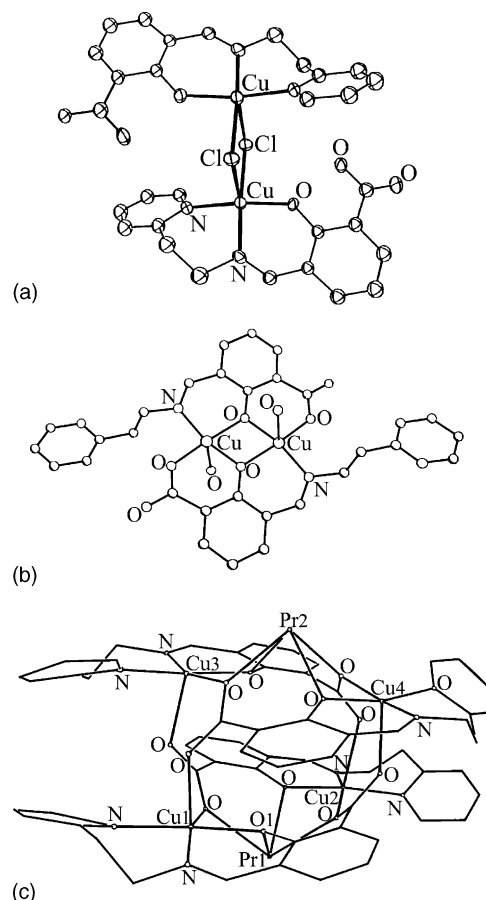


Fig. 374. Structure of [Cu(H-446a)(Cl)]₂ (a), [Cu₂(446a)₂(H₂O)₂] (b) and of [Cu₄Pr₂(446a)₄(NO₃)₆] where the nitrate groups are omitted for clarity (c) (adapted from Ref. [563]).

dymium ion is bridged to two copper ions through one carboxylic and one phenolic oxygen atom. The Pr...Cu distances range from 3.400 to 3.428 Å. The copper environments may be considered as elongated distorted octahedra. The equatorial positions are occupied by two nitrogen and two oxygen atoms, one of the apical positions is occupied by the oxygen atom carboxylic group involved in the bridges between the layers. The other apical position is occupied by an oxygen atom belonging to a nitrate ion already linked to a rare earth atom. In addition to the oxygen atoms belonging to the [446a]²⁻ ligands, the rare earth ions achieve their environment with six oxygen atoms coming from three bidentate nitrate ions. The coordination polyhedron around the praseodymium ions has been described as a bicapped square antiprism [563].

Variable temperature magnetic susceptibility measurements indicated a very weak ferromagnetic coupling of the copper(II) ions in [Cu₂(H-446)₂(Cl)]₂ ($J = 0.15 \text{ cm}^{-1}$) and an antiferromagnetic coupling in [Cu₂(446)₂] and [Cu₃(446)₂](ClO₄)₂ ($J = -617$ and -228 cm^{-1} , respectively) [563].

As far as the magnetic properties are concerned, the hexanuclear clusters {Cu₄Ln₂} may be viewed as two

independent $\{\text{Cu}^{\text{II}}\text{Ln}^{\text{III}}\text{Cu}^{\text{II}}\}$ triads. The magnetic susceptibility data for the Cu_4La_2 complex have revealed a weak antiferromagnetic copper(II)–copper(II) interaction through the closed-shell rare earth ion ($J_{\text{CuCu}} = -3.13 \text{ cm}^{-1}$). The magnetic susceptibility data for Cu_4Gd_2 have shown that the ground-state spin for the $\{\text{Cu}^{\text{II}}\text{Gd}^{\text{III}}\text{Cu}^{\text{II}}\}$ triad is $S = 9/2$; the gadolinium(III)–copper(II) interaction is ferromagnetic ($J_{\text{GdCu}} = 6.0 \text{ cm}^{-1}$). The field dependence of the magnetization measured at both 2 and 30 K confirms the nature of the ground state and of the gadolinium(III)–copper(II) interaction. The ferromagnetic nature of this gadolinium(III)–copper(II) interaction is attributed to the coupling between the $\text{Gd}^{\text{III}}\text{Cu}^{\text{II}}$ ground configuration and the $\text{Gd}^{\text{II}}\text{Cu}^{\text{III}}$ charge-transfer excited configuration in which an electron is transferred from the singly-occupied 3d-type copper orbital toward an empty 5d-type gadolinium orbital. A semiquantitative estimate of J_{GdCu} , agrees fairly well with the value deduced from the magnetic data. It is emphasized that the gadolinium(III)–copper(II) interaction is quite peculiar in the sense that owing to the contraction of the 4f orbitals the usual mechanisms involving 4f–3d overlap densities are inoperative [563].

$[\text{Zn}_2(\mathbf{446b})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Zn}_2(\mathbf{446a})_2(\text{CH}_3\text{COO})_2] \cdot 6\text{H}_2\text{O}$ have been obtained by reaction of ZnX_2 ($\text{X} = \text{NO}_3^-$, CH_3COO^-) with 3-formylsalicylic acid and *N,N*-dimethylethylenediamine at neutral or slightly acidic pH [563]. In $[\text{Zn}_2(\mathbf{446b})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ the centrosymmetric cation is built up of two Schiff base ligands that bridge a pair of zinc ions at a distance of $3.126 \text{ \AA}$ through the deprotonated phenolic oxygens. Further coordination sites of the ligands are the imine nitrogens and carboxylate oxygens, while the amino groups of the ligand sidearms are protonated. The donor atoms of the ligands span the basal plane of a square pyramidal, the apical position of which is occupied by a water molecule (Fig. 375a).

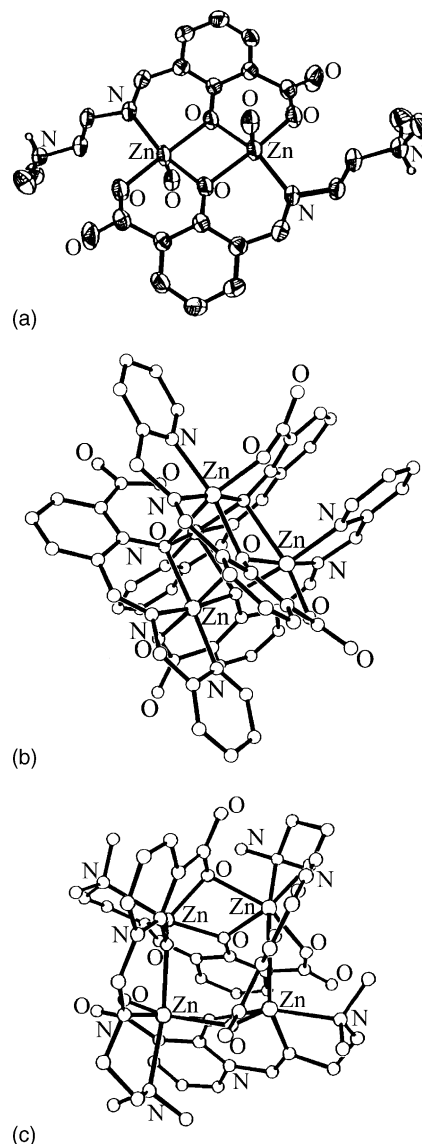
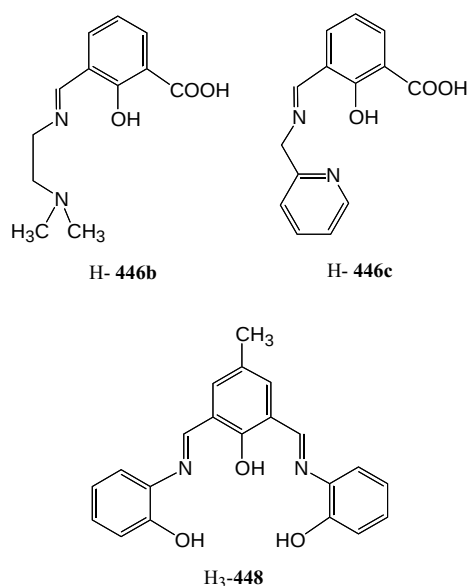


Fig. 375. Structure of $[\text{Zn}_2(\mathbf{446b})(\text{H}_2\text{O})_2]^{2+}$ (a), $[\text{Zn}_4(\mathbf{446b})_4]$ (b) and $[\text{Zn}_4(\mathbf{446c})_4]$ (c) (adapted from Ref. [563]).

The basic structure of $[\text{Zn}_2(\mathbf{446b})_2(\text{CH}_3\text{COO})_2] \cdot 6\text{H}_2\text{O}$ is identical to that of $[\text{Zn}_2(\mathbf{446b})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Again, the metal centers are five coordinated, with the water ligands being replaced by acetate groups. Compared with $[\text{Zn}_2(\mathbf{446b})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ the zinc(II) ions assume a more distorted square pyramidal coordination geometry in the acetate complex [563].

On dissolution in DMSO or DMF these dizinc complexes are converted into the mononuclear species $[\text{Zn}(\text{H-446b})]^+$. Cleavage of the dinuclear complexes is accompanied by migration of the ammonium proton to the carboxylate group and coordination of the amino nitrogen to zinc [563].

From the alkaline solution of $[\text{Zn}_2(\mathbf{446b})_2(\text{CH}_2\text{COO})_2] \cdot 6\text{H}_2\text{O}$ yellow cubes of $[\text{Zn}_4(\mathbf{446b})_4]$ were obtained whose structure shows that the four zinc ions are located at the corners of a nearly planar rectangle. Each ligand binds one

zinc ion through the phenolate oxygen, the imine nitrogen, and the amine nitrogen. Neighbouring zinc ions are connected through phenolate bridges. The carboxylate group of the ligand bound to Zn(2) forms an asymmetric, single-atom bridge between Zn(3) and Zn(4). Likewise, Zn(1) and Zn(2) are linked through a carboxylate oxygen of the ligand of Zn(4) in addition to a phenolate bridge. By contrast, the carboxylate groups of the remaining ligands coordinate only terminally to Zn(2) and Zn(4). Owing to the different coordination modes of the carboxylate groups, distorted octahedral N_2O_4 coordination spheres are observed for Zn(2) and Zn(4), with the ligands being mer, while Zn(1) and Zn(3) are five coordinate. The N_2O_3 coordination polyhedra of Zn(1) and Zn(3) are distorted square pyramids with bridging carboxylate oxygens occupying the apical positions. The zinc ions and phenolate oxygens form an eight-membered ring in which the phenolate oxygens lie alternating below and above the plane defined by the four zinc ions (Fig. 375b) [563].

In contrast to 3- $\{N-[(\text{dimethylamino})\text{ethyl}]\text{imino-methyl}\}$ salicylic acid 3- $\{N-(2\text{-pyridylmethyl})\text{iminomethyl}\}$ salicylic acid, ($H_2\text{-446c}$) forms the mononuclear complex $[\text{Zn}(\text{H-446c})_2(\text{H}_2\text{O})(\text{NO}_3)]$ in acidic solution, with the ligand binding the zinc ion through the deprotonated phenolic oxygen, the imine nitrogen, and the pyridine nitrogen, while the carboxyl group is protonated. The coordination sphere of the zinc ion is completed by a water molecule and a bidentate nitrate. The oxygen atoms of a nitrate are symmetrically bound [563].

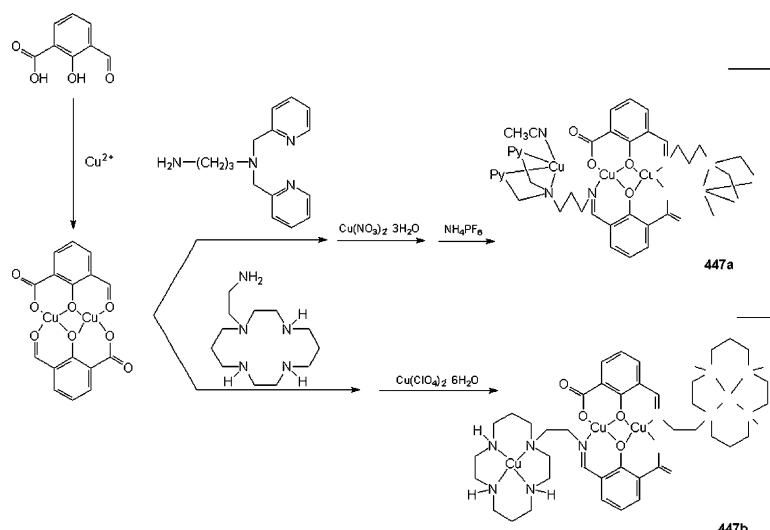
When a solution of $[\text{Zn}(\text{H-446c})(\text{H}_2\text{O})(\text{NO}_3)]$ is brought to pH 9, deprotonation of the carboxyl group results in crystallization of the tetranuclear compound $[\text{Zn}_4(\text{446c})_4 \cdot 4.5\text{H}_2\text{O}]$. Four $[\text{Zn}(\text{446c})]$ entities with $[\text{446c}]^{2-}$ coordinating via the phenolate oxygen and the chelating sidearm assemble to a tetramer containing a cubane-like $\{\text{Zn}_4\text{O}(\text{phenolate})_4\}$ core situated around a crystallographic two-

fold axis of symmetry. The subunits are linked through the carboxylate oxygens that bind in a monodentate mode to the respective neighbouring zinc ion and bridging phenolate oxygens that are attached to three zinc ions each resulting in octahedral N_2O_4 coordination polyhedra. Within the Zn_4O_4 cube the phenolate bridges are asymmetric [563] (Fig. 375c).

$[\text{Cu}_4(\text{447a})](\text{PF}_6)_4 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$ and $[\text{Cu}_4(\text{447b})](\text{ClO}_4)_4 \cdot \text{CH}_3\text{OH}$, comprised of one dimetallic di(3-imino-methylsalicylato)dicopper(II) core and two monometallic copper(II) auxiliaries attached to the imino nitrogens of the dinuclear core through an alkane chain, have been prepared by the synthetic procedure of Scheme 64. $[\text{Cu}_4(\text{447a})](\text{PF}_6)_4 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$ has di-(2-pyridylmethyl)aminocopper(II) as the monometallic auxiliary, and $[\text{Cu}_4(\text{447b})](\text{ClO}_4)_4 \cdot \text{CH}_3\text{OH}$ has 1,4,8,11-tetraazacyclotetradecanecopper(II) as the monometallic auxiliary [564].

The cryomagnetic property suggests that the dimetallic core and the monometallic auxiliaries are magnetically independent of each other and a strong antiferromagnetic interaction operates within the dimetallic core to achieve a perfect coupling above 100 K [564].

$[\text{Cu}_4(\text{447a})](\text{PF}_6)_4 \cdot 2\text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$ in acetonitrile shows a two-electron reduction at -0.08 V (versus SCE) followed by a one-electron reduction at -0.42 V. Together with EPR studies for electrolyzed solutions, it is shown that the two monometallic auxiliaries are reduced at -0.08 V, followed by an intramolecular electron transfer from one of the reduced auxiliaries to the dimetallic core and by the second reduction at the resulting monometallic copper(II) center at -0.42 V: $\{\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\} \rightarrow \{\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\} \rightarrow \{\text{Cu}^{\text{I}}\text{-Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\} \rightarrow \{\text{Cu}^{\text{I}}\text{-Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{-Cu}^{\text{I}}\}$. The CV of $[\text{Cu}_4(\text{447b})](\text{ClO}_4)_4$ in DMSO shows two couples at -0.68 and -0.99 V attributable to the stepwise reductions: $\{\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\} \rightarrow \{\text{Cu}^{\text{II}}\text{-Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\} \rightarrow \{\text{Cu}^{\text{I}}\text{-Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}\}$. $[\text{Cu}_4(\text{447a})](\text{PF}_6)_4$ is reduced with ascorbic acid

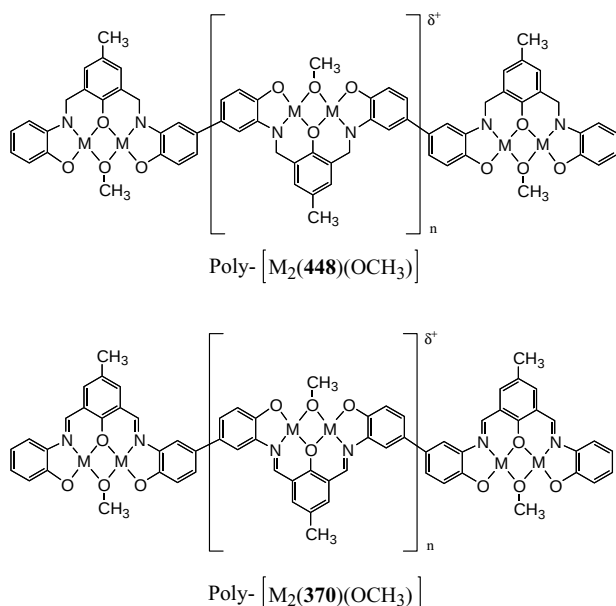


Scheme 64.

to the $\{\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}\}$ species, whereas $[\text{Cu}_4(\mathbf{447b})](\text{ClO}_4)_4$ is not reduced with ascorbic acid [564].

Modified electrodes have been prepared on the basis of electroactive polymers containing bimetallic cores formed by complexes with $\text{H}_3\text{-370}$, $\text{H}_3\text{-374}$ or $\text{H}_3\text{-448}$ [565].

Upon electrochemical oxidation at a potential in the 1.1–1.4 V range, of $[\text{M}_2(\mathbf{370})(\text{OCH}_3)]$, $[\text{M}_2(\mathbf{448})(\text{OCH}_3)]$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+}) and $[\text{Cu}_2(\mathbf{374})(\text{CH}_3\text{COO})]$, an irreversible two-electron oxidation occurs that leads to polymer formation on the electrodes; the coupling between two entities occurs probably via a cation-radical–cation-radical (CR–CR) coupling mechanism at the para position of the phenolate. The synthesis of the polymer films may occur either at a controlled potential, or upon repetitive cycling in the solution. However, although the oxidation begins slightly before 1.0 V, a potential between 1.3 and 1.6 V is required to obtain clean films [565]. Usually, optimum polymerization is obtained at potential values quite above that required for the formation of classical polysalens. The potential range where efficient polymerization takes place is also wider than in the case of the polymerization of simple Schiff bases or functionalized conducting polymers in general (e.g. polypyrrole) [565].

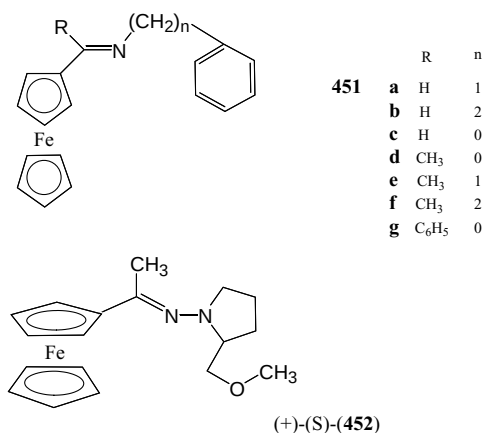
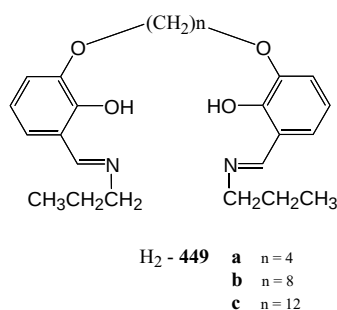


The dinuclear complexes $[\text{M}_2(\mathbf{375})(\text{CH}_3\text{COO})]$ ($\text{M} = \text{Cu}^{2+}$, Ni^{2+}) cannot be transformed into electroactive polymers under the same experimental conditions as their unsaturated Schiff base analogous complexes.

The peculiar behaviour of the series derived from $\text{H}_3\text{-448}$ in particular should be outlined since the binuclear amine complexes $[\text{M}_2(\mathbf{448})(\text{OCH}_3)]$ readily polymerize, like their Schiff-base analogues $[\text{M}_2(\mathbf{370})(\text{OCH}_3)]$. $\text{Poly-}[\text{M}_2(\mathbf{448})(\text{OCH}_3)]$ exhibit very different electrochemical properties compared with their $\text{poly-}[\text{M}_2(\mathbf{370})(\text{OCH}_3)]$ analogues, suggesting that the monomer structure

(imine or amine bonds) is indeed retained in the subsequent final polymer [565].

The ligands $\text{H}_2\text{-449a-c}$ were prepared in good yields by reaction of the dianion of 2,3-dihydroxybenzaldehyde with the appropriate alkyl α,ω -dibromide in dimethyl sulfoxide followed by the treatment of the resulting dialdehydes with *n*-propylamine. Reaction of these ligands with $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in a 1:1 molar ratio in ethanol afforded the diamagnetic square planar complexes $[\text{Ni}(\mathbf{449a-c})]$ as light-green solids. $[\text{Ni}(\mathbf{449a})]$ when dissolved in pyridine, on addition of Et_2O , forms the paramagnetic non planar complex $[\text{Ni}(\mathbf{449a})(\text{py})_2]$ [566].



$[\text{Ni}(\mathbf{449a})(\text{py})_2]$ is a cyclic trimer, where each nickel(II) ion is octahedrally coordinated by two pairs of O_2N coordination sites of two different ligands and two pyridine nitrogens. The molecule has a pseudo-three-fold axis. As the ligands turn around as a helix fragment, the molecule is chiral, but forms racemic crystals because helices of opposite chirality regularly alternate in the centrosymmetric $P2_1/c$ space group (Fig. 376a) [566].

Crystals of $[\text{Ni}_2(\mathbf{449b})_2] \cdot \text{THF}$, obtained by slow evaporation of a solution of $[\text{Ni}(\mathbf{449b})]$ (Fig. 376b), show that dinuclear molecules result from the coordination of two ligands to two nickel centers. Each metal ion is linked in a *trans*-square planar geometry by two NO coordination sites of different ligands. The nickel ions and chelating groups lie approximately on parallel planes spaced by 3.46 Å. The planes are bonded by two octyl chains which are twisted forming a double helix. On going from one nickel(II) ion to

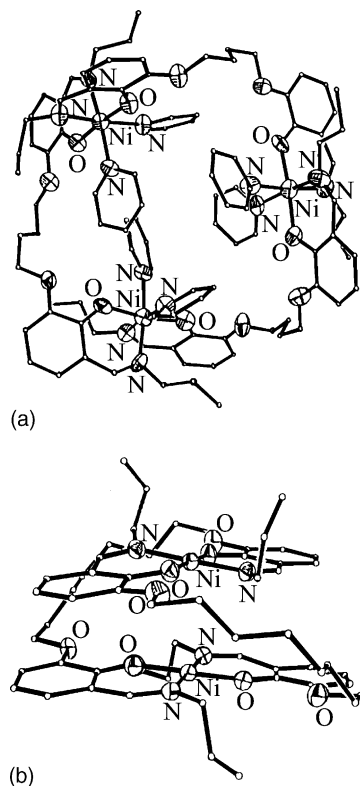


Fig. 376. Structure of $[\text{Ni}_3(\mathbf{449a})_3(\text{py})_6]$ (a) and $[\text{Ni}_2(\mathbf{449b})_2]$ (b) (adapted from Ref. [565]).

the other nickel(II) ion the chains twist by a quarter of a turn. The whole molecule possesses a pseudo D_2 symmetry, one of the two-fold axes passing through the nickel ions [565].

While in the solid state the ligand $[\mathbf{449b}]^{2-}$ is able to coordinate each chelating arm to a different metal center to give a bridged dinuclear species, in solution it prefers to act as a tetradentate chelate to a single nickel(II) ion, presumably in a *cis*-square planar geometry [566].

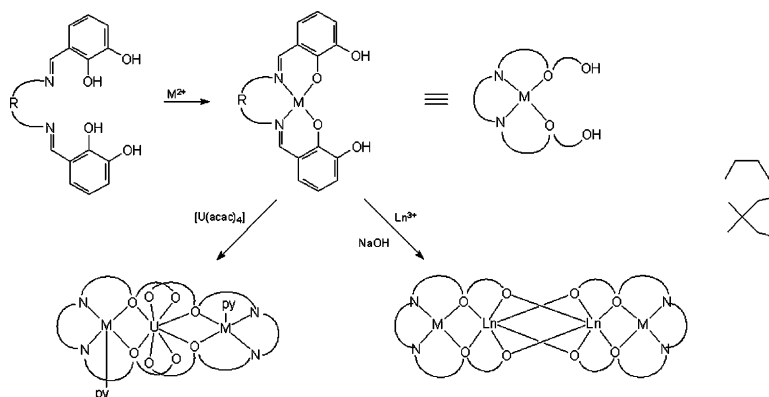
It was already reported above that the tetranuclear complex $[\text{CuY}(\mathbf{409})(\text{NO}_3)(\text{DMSO})]_2$ has been obtained and structurally characterized [493]. Similarly linear $\text{M}_2^{\text{II}}\text{U}^{\text{IV}}$ complexes ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$) have been pre-

pared by reaction under argon of the mononuclear transition metal complexes $[\text{M}(\text{H}_2\text{-}\mathbf{37})]$ with $[\text{U}(\text{acetylacetonate})_4]$ (Scheme 65) [567].

$[\text{Co}_2\text{U}(\mathbf{37})_2(\text{py})_2]$ is built by two $\{\text{Co}(\mathbf{37})\}$ units which are linked to the central uranium(IV) ion, through two Co–O–U bridges, by two pairs of oxygen atoms of the salicylidene fragments and also by two bonds between the uranium and the phenolate oxygen atoms at the 3-position of the $[\mathbf{37}]^{4-}$ ligand. The uranium(IV) ion is therefore surrounded by eight oxygen atoms in a dodecahedral arrangement. The equivalent sites A and B of the dodecahedron are occupied by the bridging and terminal oxygen atoms. The pseudo D_{2d} symmetry of the complex is broken by the presence of a single pyridine molecule attached to each cobalt ion. The cobalt(II) ion thus adopts a square pyramidal coordination mode, being displaced from the N_2O_2 base by 0.38 Å towards the axial pyridine ligand. The three metal centers are almost linear with intramolecular $\text{U} \cdots \text{Co}$ separations of 3.68 Å (Fig. 377).

The Zn_2U complex is isostructural with $[\text{Co}_2\text{U}(\mathbf{37})_2(\text{py})_2]$. Also $[\text{Cu}_2\text{Zr}(\mathbf{37})_2(\text{py})_2]$, was prepared by a similar procedure. The magnetic susceptibility of the Cu_2U and Zn_2U complexes decreases with the temperature, and in the latter compound the deviation from the Curie law results entirely from the crystal field of the U^{IV} ion [567].

A comparison of the magnetic behaviour of Cu_2Zr and Cu_2U complexes suggest a ferromagnetic interaction in the Cu_2U complex while in Cu_2Zr one the two ions are not coupled [567]. These data strongly suggest that the U^{IV} center is able to mediate the ferromagnetic interaction between the two Cu^{II} ions ($J = 13.6 \text{ cm}^{-1}$). This coupling exchange would involve the *f* orbitals of the U^{IV} ion that have the appropriate energy and symmetry to overlap with the $d_{x^2-y^2}$ type magnetic orbitals centered on each Cu^{II} ion; these are the $f_{x(y^2-z^2)}$ and $f_{y(x^2-z^2)}$ orbitals, which belong to the irreducible representation in the symmetry group D_{2d} . The ferromagnetism in the Cu_2U complex could then be explained either by the presence of two degenerate molecular orbitals of type *e* which would accommodate the two unpaired electrons from the copper(II) ions, leading to a



Scheme 65.

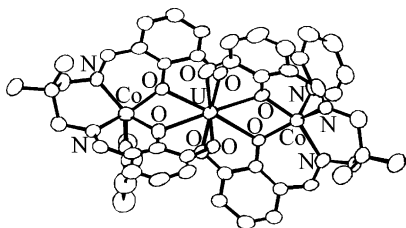


Fig. 377. Structure of $[\text{Co}_2\text{U}(\mathbf{37})_2(\text{py})_2]$ (adapted from Ref. [567]).

triplet state, or within a more localized picture and in line with the proposed mechanism of the $\text{Ln}^{\text{III}}\text{--Cu}^{\text{II}}$ interaction, the transfer of the unpaired electron of copper(II) towards an empty 5f orbital of U^{IV} . This process would force the d and f electrons to align parallel and in the case of a Cu–U–Cu triad, leading to the parallel alignment of the copper(II) electrons [567].

13. Polynuclear complexes with ligands containing ferrocene derivatives

Schiff bases and related reduced analogues bearing redox-active systems have been widely investigated and their properties and possible application reviewed [568].

Ferrocene containing compounds have been conveniently proposed owing to their potential in catalysis, material science, molecular devices, hydrometallurgy, etc. These systems can electrochemically recognize the binding of any charged or neutral inorganic or organic guest molecule, by either interaction or communication via various bond linkages between the receptor site and the redox center. Systems bearing such reactive groups, based on Schiff bases, exhibit appropriate physico-chemical properties and can offer a valid chance to their use as redox catalysts or as binding blocks for the preparation of molecular devices or as switching agents in the selective cation transport [541,568].

As mentioned in a previous section, formylferrocene and 1,1'-diformylferrocene are excellent precursors in the preparation of acyclic and cyclic Schiff bases containing redox active groups in close proximity to the coordinating moieties. [1+1], [2+1] and [3+1] acyclic Schiff bases bearing a progressively increasing number of ferrocene-groups have been prepared by condensation in acetonitrile or methanol of formylferrocene and the desired amine, using the appropriate molar ratio, according to Scheme 66. By a similar synthetic procedure the [1+2] macroacyclic or the [2+2] macrocyclic Schiff bases of Scheme 67 have been obtained by condensation of 1,1-diformylferrocene and the appropriate amine in a 1:2 and 1:1 molar ratio, respectively. Moreover the condensation of 1,1-diformylferrocene with particular polyamines as 1,5-diamino-3-azapentane or 1,4-bis(3-aminopropyl)piperazine affords the [1+1] macrocyclic compounds [568]. Also suitable polyamines precursors, as 1,4-diamino methylbenzene reacts with formylferrocene and 1,1'-diformylferrocene to yield respectively the [2+1]

condensation product and the $[2+2]_n$ oligomeric or polymeric species of Schemes 66 and 67 [568].

FAB mass spectrometry, a particularly valid analytical tool for the characterization of these systems, indicates the parent peak $[M + \text{H}]^+$ at the appropriate m/z value in almost all the prepared compounds; moreover, the fragmentation patterns are consistent with the proposed structure.

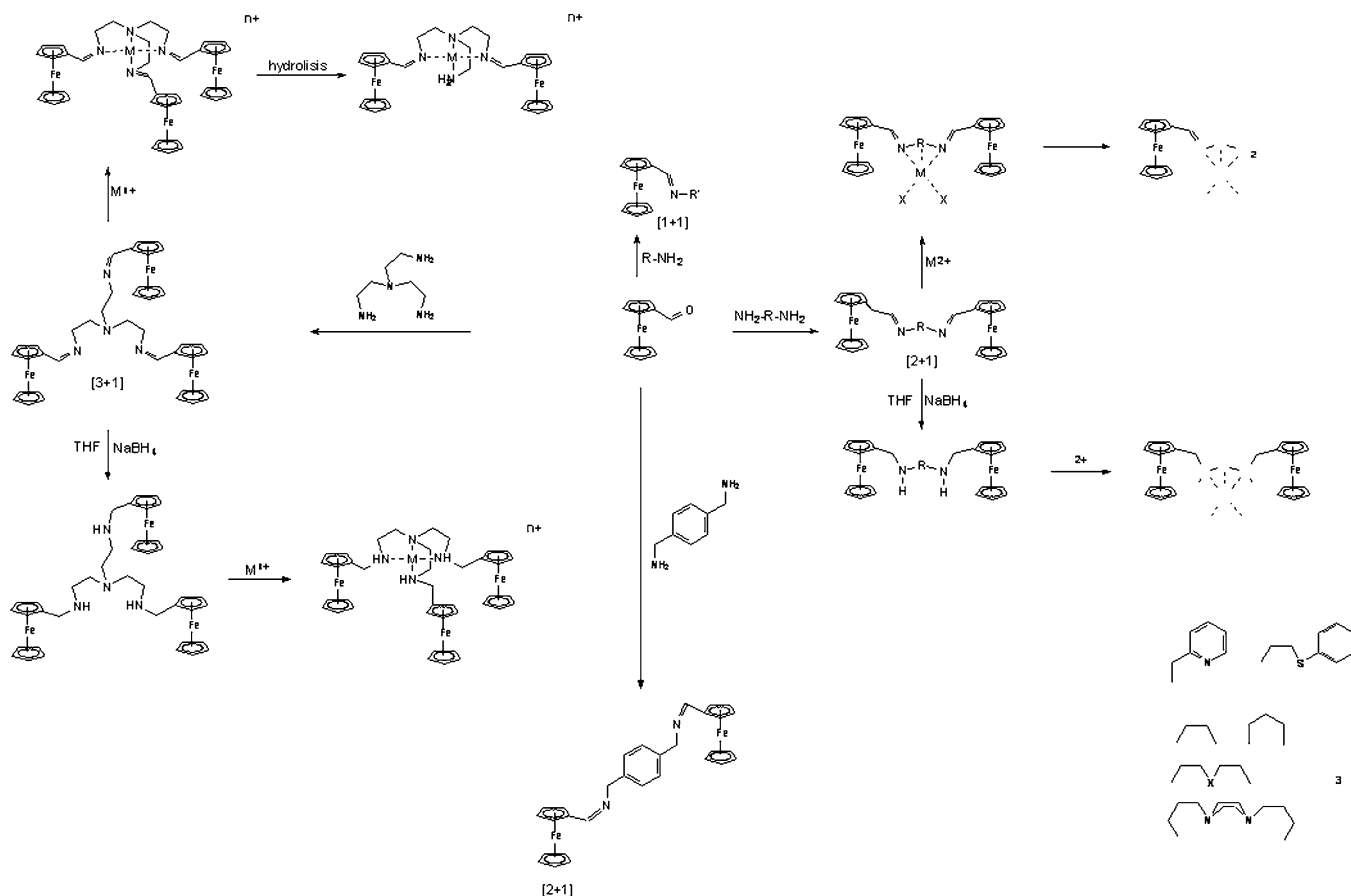
The coordination properties of these ferrocene Schiff bases (**L**) have also been studied; when reacted with transition metal salts they form complexes formulated as $\text{M}(\text{L})(\text{X})_2$ ($\text{M} = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Pd}^{2+}$; $\text{X} = \text{Cl}^-, \text{ClO}_4^-$). When dissolved for crystallization, these complexes quite often suffer additional reactions; thus these complexes are not very stable in solution and easily give rise to hydrolytic products. Also these hydrolytic processes can occur before the isolation of the Schiff base complex. Similarly the Schiff bases derived by condensation of ferrocenylamine can be hydrolyzed in solution [568].

In all these Schiff bases the close proximity the ferrocene groups to the coordinating site can cause hydrolysis when reacted with metal ions. In order to avoid this behaviour, maintaining the coordinating ability of the Schiff base, aminomethylferrocene was prepared [568] and reacted in the appropriate molar ratio with suitable formyl- or diformyl-precursors (i.e. 2,6-diformylpyridine, 2,6-diformyl-4-chlorophenol, salicylaldehyde, 3-methoxy-2-hydroxybenzaldehyde, etc.), to produce the [2+1] or [1+1] acyclic compounds of Scheme 68 [568].

The Schiff bases of Schemes 66–68 have been reduced to the corresponding acyclic or cyclic polyamines by reaction with NaBH_4 in tetrahydrofuran; the same reactions have also been successfully carried out in methanol and water. The obtained compounds are stable both in air and solution. IR and NMR spectra clearly indicate marked differences between the Schiff bases and their reduced analogues. FAB mass spectra give further useful information on their structure; in these spectra the parent peaks at the appropriate m/z value accompanied by the $[M + \text{Na}]^+$ cations are clearly detectable. FAB mass spectroscopy in particular offers an essential support the [2+2] and the [1+1] nature of the cyclic compounds.

These reduced ferrocene-amines do not suffer hydrolysis as a consequence of the reaction with the appropriate metal salts, (i.e. Cu^+ , Cu^{2+} , Ni^{2+} , Pd^{2+} , Rh^{3+}) and easily form the related stable, well-defined complexes in which the metal:ligand ratio depends on the shape of the ligand and also on the experimental conditions (Scheme 66) [568].

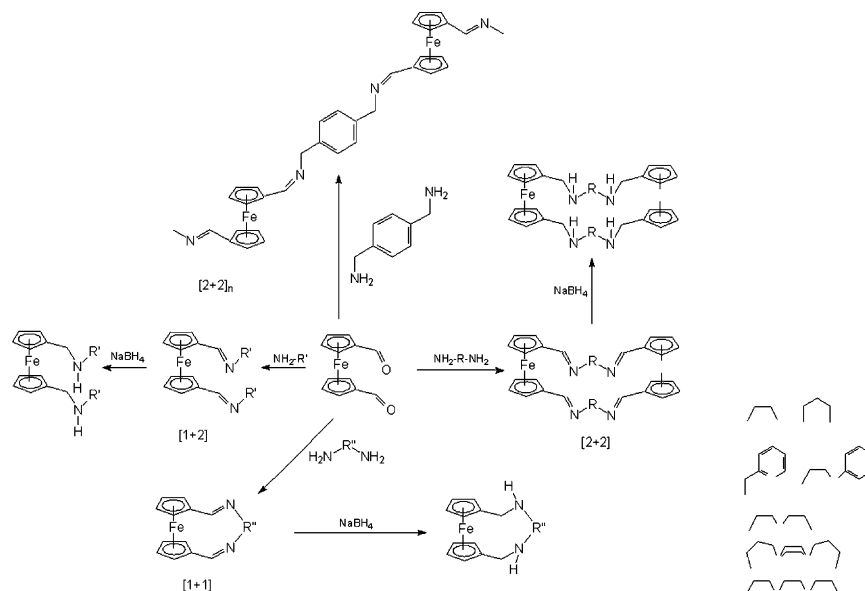
The Mössbauer spectra of the ligands and complexes of Schemes 66–68 show the presence of a single iron site deriving from the electronic and structural identity of the two or three ferrocene groups (Fc) in the same compound and may be diagnostic of the presence of Fc-CH=NR , $\text{Fc-CH}_2\text{-N=CHR}$ or $\text{Fc-CH}_2\text{-NHR}$ groups. Moreover, the complexation of different metal salts to the aminic groups induces only minor effects on the Mössbauer parameters. These results indicate that the presence of a CH_2 spacer



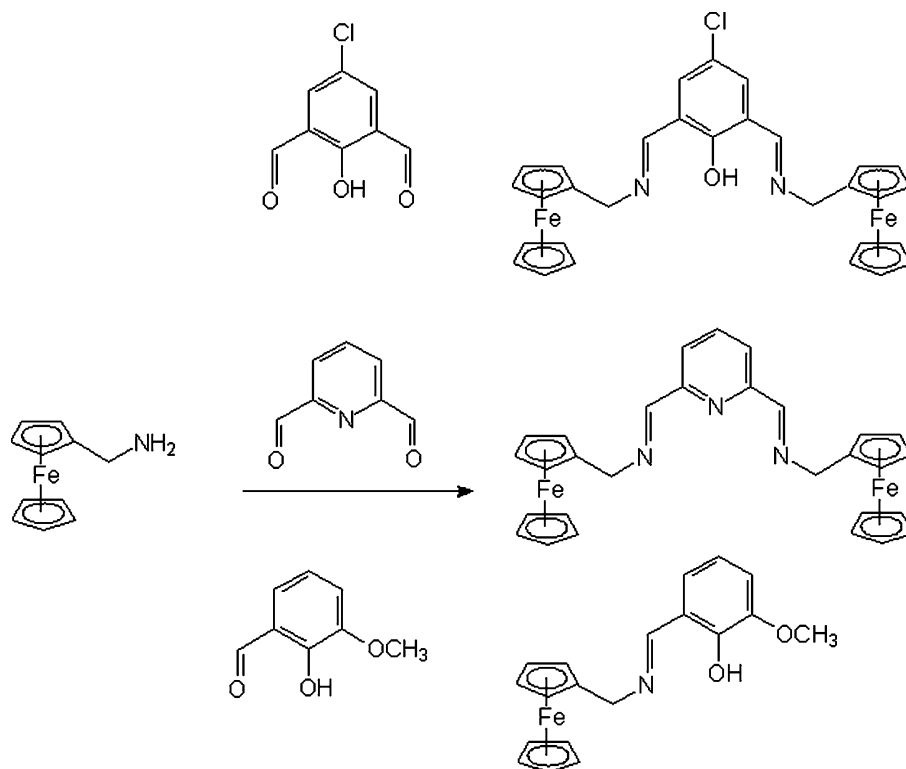
Scheme 66.

between ferrocene and iminic or aminic moieties seems to be the crucial reason of the significant variation of the Mössbauer parameters with respect to the imine derivatives containing $\text{Fc}-\text{CH}=\text{N}-\text{R}$ groups [568].

Parallel studies show that these systems can facilitate the transfer of Cu^{2+} , Cd^{2+} , Ni^{2+} and Zn^{2+} across the water/1,2-DCE interface when the aqueous phase is at appropriate pH [568].



Scheme 67.



Scheme 68.

13.1. Complexes derived from [1+1] acyclic ferrocene derivatives

Aminoferrocene, formylferrocene, acetylferrocene and benzoylferrocene react with a series of primary amines to form the corresponding [1+1] Schiff bases which can be easily reduced to the related amine derivatives.

The nature of these ferrocene derivatives and/or their complexes compounds has been unequivocally confirmed by X-ray diffractometric investigations. The Schiff base **H-450**, formed by condensation of ferrocenylamine with salicylaldehyde is stable in the solid state and easily hydrolyzed in solution. Its structure (Fig. 378a) indicates almost coplanarity between the chelating moiety and the adjacent cyclopentadienyl ring of ferrocene, with the hydrogen atom of the hydroxyl group bridging between the nitrogen and oxygen atoms [569].

The complexes $[M(\mathbf{450})_2]$ ($M = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+}), prepared by reaction in methanol of **H-450** with the appropriate metal salt in the presence of KOH, on the basis of their X-ray, visible spectral and magnetic susceptibility data, show a tetrahedral or pseudo-tetrahedral structure. $[\text{Cu}(\mathbf{450})_2]$ consists of discrete molecules with the oxygen and nitrogen donor atoms of two ligand anions bonded to the copper(II) ion in a distorted tetrahedral coordination [569] (Fig. 378b).

Cyclic voltammetric experiments on **H-450**, $[M(\mathbf{450})_2]$ and the reference species ferrocene and ferrocenylamine in DMF at room temperature and in the presence of

$[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4](\text{ClO}_4)$ show one-electron oxidation which changes the ferrocenyl group into the ferrocenium cation. The more easily oxidized species is ferrocenylamine which has a value of -0.40 V versus ferrocene and 0.05 V versus SCE. The potentials indicate that oxidation depends appreciably on the nature of the central metal ion. Whilst **H-450** is as easily oxidizable as $[M(\mathbf{450})_2]$, the oxidation

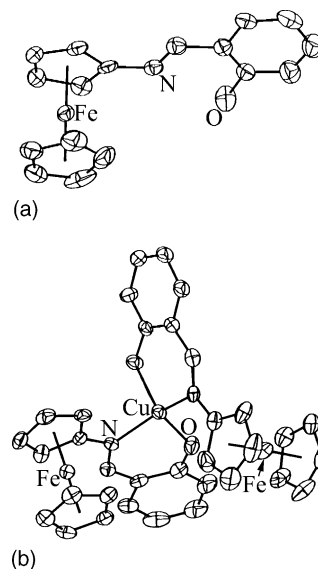


Fig. 378. Structure of **H-450** (a) and $[\text{Cu}(\mathbf{450})_2]$ (b) (adapted from Ref. [569]).

process for the $[M(450)_2]$ species is facilitated in the order $Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+}$.

Single crystal X-ray work on $[Cu(450)_2]$ seems to indicate that π -electron conjugation between the peripheral ferrocenyl groups and the central Schiff-base chelating system is not significant. Electrochemical data, on the other hand, show a dependence of the first oxidation potential ($Fe^{II} \rightarrow Fe^{III}$) on the nature of the central metal ion, which might mean that electronic contact is possible via the π -bonding system. The two ferrocenyl groups within $[Zn(450)_2]$ are electrochemically indistinguishable and are simultaneously oxidized [569].

The condensation of acetylferrocene or benzyl ferrocene with a series of substituted amines to form the corresponding ferrocenyl imines **451d**–**451g** occurs only in dry benzene and in the presence of molecular sieves (5 Å) and a large excess of amines to force the displacement of the equilibria [570]. The Schiff bases derived from formylferrocene **451a**–**451c** are more stable than those derived from acetylferrocene, which undergo slow decomposition even at 20 °C, yielding the corresponding amine and acetylferrocene precursors [570].

The structure of **451a**, **451c** and **451d** consists of discrete molecules held together by van der Waals forces. The replacement of a hydrogen by a methyl group at the imine carbon atom is reflected in a variation of several bond lengths and angles, due to the steric repulsion between the C_5H_4 ring and methyl groups. A similar structure has been found for **451g** [569] (Fig. 379a–d).

The ligands **451a**–**g** react in methanol with $Na_2[Pd(Cl)_4]$ in the presence of sodium acetate to form the dinuclear cyclopalladate complexes $[Pd_2(451a-g-H)_2(\mu-Cl)_2]$ [570]. Addition of an excess of phosphine ligands (PPh_3 , PEt_3) to acetone or benzene suspensions of these dimeric complexes

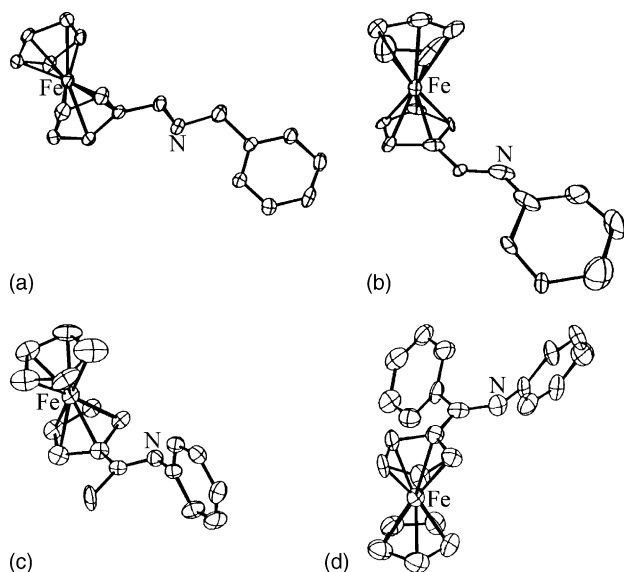


Fig. 379. Structure of **451a** (a), **451c** (b), **451d** (c) and **451g** (d) (adapted from Ref. [569]).

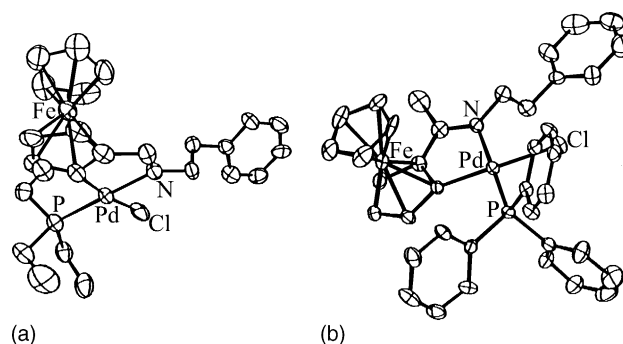


Fig. 380. Structures of $[Pd(451b-H)(PEt_3)(Cl)]$ (a) and $[Pd(451e-H)(PPh_3)(Cl)]$ (b) (adapted from Ref. [570]).

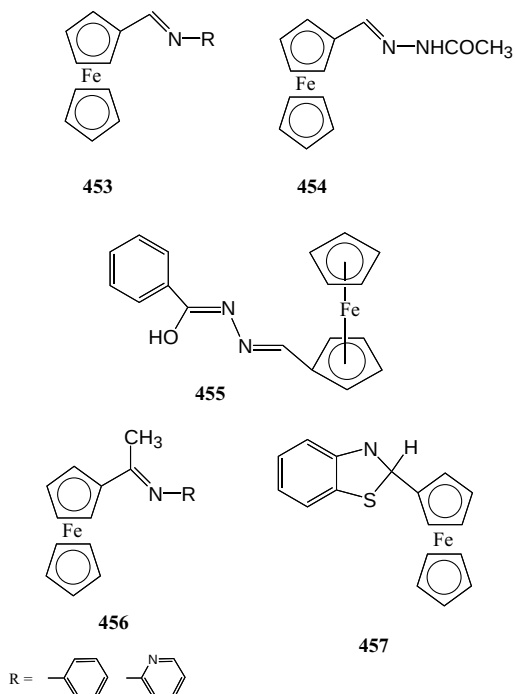
produced cleavage of the $\mu-Cl$ bridges and formation of the monomeric derivatives $[Pd(451a-g-H)(Cl)(PR_3)]$. The most outstanding feature of the dinuclear cyclopalladated complexes is the high stability of the Pd–N bond. The formation of bis(phosphine) derivatives was not observed even when the PR_3 :Pd molar ratio was 6:1. On the other hand, addition of 1,2-bis(diphenylphosphino)ethane (dppe) to an acetone suspension of the dimeric complexes produced the cationic cyclometallated compounds $[Pd(451a-g-H)(dppe)]^+$ in which the phosphine-donor ligand acts as a chelate [570].

^1H , ^{13}C and ^{31}P NMR studies on these complexes suggest that cyclopalladation occurs on the ferrocenyl moiety, thus producing five-membered metallacycles containing the C=N bond (*endo*-type structures) [570] as confirmed in the structure of $[Pd(451b-H)(PEt_3)(Cl)]$ (Fig. 380a) and in $[Pd(451e-H)(PPh_3)(Cl)]$ (Fig. 380b), where the palladium(II) ion is in a slightly distorted square planar environment coordinated to a chlorine, the phosphorus of the PPh_3 ligand, the imine nitrogen and the carbon atom of the ferrocenyl group. Also the structure confirms the formation of *endo* five-membered metallacycles containing σ Pd–C (ferrocene) bonds. The palladocycle is planar.

The reaction of acetylferrocene with (–)-(*S*)-1-amino-2-(methoxymethyl)pyrrolidine in dry benzene gave the chiral ferrocenylimine (+)-(*S*)-(**452**). Asymmetric cyclopalladation of this Schiff base with sodium tetrachloropalladate(II) and sodium acetate trihydrate in methanol at room temperature gave a mixture of diastereomeric cyclopalladated products $[Pd(452-H)(\mu-Cl)]_2$, respectively the *syn*-(+)-(R_p, S, S, R_p)- $[Pd(452-H)(\mu-Cl)]_2$, the anti-(–)-(R_p, S, S, S_p)- $[Pd(452-H)(\mu-Cl)]_2$ and *syn*-(–)-(S_p, S, S, S_p)- $[Pd(452-H)(\mu-Cl)]_2$. The three enantiopure compounds (product ratio 8:1:1) were isolated from the mixture through column-layer chromatography and their structural relationship was elucidated by single-crystal X-ray analysis [571] (Fig. 381a–c).

Various substituted ferrocene, containing systems of the type **453**, have been investigated to verify if they can serve as non-linear optical materials where the ferrocenyl moiety acts as the donor of a donor- π -acceptor system, (D- π -A), as molecular sensors, where the ferrocene properties are used to sense the presence of metal ions in another part of the

molecule [572]. It was verified that, for substituted ferrocenes, electron-donating substituents cause an increase in the quadrupole splittings (Δ) relative to ferrocene ($\Delta \approx 2.37 \text{ mm s}^{-1}$), whereas electron-withdrawing substituents cause a decrease in Δ [572].



The ferrocene entities are used as sensitive probes to understand the electron distribution throughout the molecules in consequence of conjugation interactions and the presence or absence of coplanarity in the substituents on the ferrocene molecules [572].

A number of the ferrocenyl Schiff base derivatives **453** [$R = \text{NHCH}_2(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)$, $\text{NH}(\text{C}_6\text{H}_4\text{-}p\text{-CN})$, $\text{NH}(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)$, $\text{NH}(\text{C}_6\text{H}_4\text{-}p\text{-F})$, $\text{NH}(\text{C}_6\text{H}_4\text{-}p\text{-Cl})$, $\text{NH}(\text{C}_6\text{H}_4\text{-}p\text{-Br})$, $\text{NH}(\text{C}_6\text{H}_4\text{-}\mu\text{-NO}_2)$, $\text{NH}(\text{C}_6\text{H}_4\text{-}o\text{-NO}_2)$, $\text{NH}(\text{C}_6\text{F}_5)$], prepared from ferrocenecarbaldehyde and a slight excess of the appropriate hydrazine in ethanol and in the presence of molecular sieve [572], contains the donor- π -acceptor-(D- π -A) structural motif desired for non-linear optical materials.

The behaviour of the ferrocenyl moiety as a donor is compared to that of the 4-dimethylaminophenyl group. The UV-Vis spectra of the compound where $R = \text{NHCH}_2(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)$ showed considerable solvatochromism. As a result of this and its extended donor- π -acceptor nature, this compound was tested for non-linear optical properties, specifically, second harmonic generation. The results, however, were negative because crystallization of the compound occurred in a centrosymmetric space group. Attempts to circumvent this, through the incorporation of the ferrocene derivative in cyclodextrins, failed [572].

The structure of this compound shows the unsubstituted C_5H_5 ring is disordered between the staggered and eclipsed positions with respect to the substituted ring. The most striking feature of the structure is the almost complete

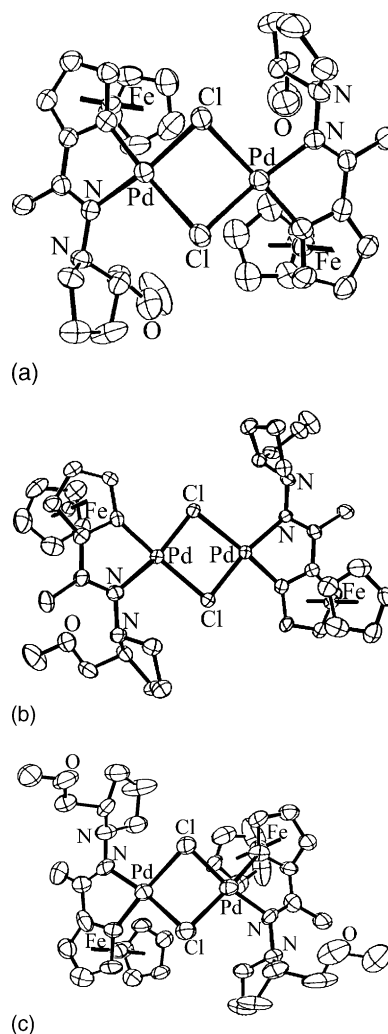


Fig. 381. Structures of *syn*-(+)-(R_p,S,S,R_p)-[Pd(**452-H**)(μ -Cl)]₂ (a) *syn*-(-)-(S_p,S,S,S_p)-[Pd(**452-H**)(μ -Cl)]₂ (b) and *anti*-(-)-(R_p,S,S,S_p)-[Pd(**452-H**)(μ -Cl)]₂ (c) (adapted from Ref. [571]).

planarity of the $\text{C}_5\text{H}_4\text{CHNNHCH}_2\text{C}_6\text{H}_4\text{-}p\text{-NO}_2$ fragment. From the planarity of the conjugation pathway between the donor and the acceptor groups, and the noted solvatochromic behaviour, hyperpolarizability would be expected for this type of molecule. The solid-state arrangement of this compound is best considered as centrosymmetrically related pairs of molecules. Stacking of these related pairs occurs with continuous staggering (along the *a* axis). The staggering leaves a ferrocenyl moiety almost perfectly above the nitrophenyl group of the neighbouring centrosymmetrically related pair. Perfectly aligned stacking sequences of this type extend throughout the lattice with their *a* axes parallel. The overall stacking sequence generates an infinite two dimensional ribbon which repeats at units of translation of *b*, but the immediately adjacent ribbon forms a herring-bone pattern to the first.

The staggering of the molecules generates the discrete DAAD structural motif rather than a DADA type stack. The ring-ring distances within the stack are in the range 3.529–

3.478 Å. These distances are within the range associated with π – π interactions.

While ferrocene readily sublimates, it is difficult to produce good-quality films, as large single crystals grow preferentially on the substrate. It was found [572] that the introduction of substituent groups onto the ferrocenyl moiety allows the facile preparation of good-quality thin films via sublimation. Thin films of compounds **453** where $R = \text{NHCH}_2\text{-(C}_6\text{H}_4\text{-}p\text{-NO}_2\text{)}$, $\text{NH(C}_6\text{H}_4\text{-}p\text{-NO}_2\text{)}$ and $\text{NH(C}_6\text{H}_4\text{-}o\text{-NO}_2\text{)}$ were prepared on optically transparent electrodes and the visible and reflectance IR spectra recorded. The essential features of the visible solution spectra are retained although the bands are broader and shifted to longer wavelength. In the case of the compound where $R = \text{NHCH}_2\text{(C}_6\text{H}_4\text{-}p\text{-NO}_2\text{)}$ this shift is considerable (≈ 60 nm). The film appears purple (like the crystals) in contrast to the red colour of this compound in solution. This is undoubtedly due to the solid-state interactions described above.

The acetylhydrazone **454** forms dinuclear and mononuclear palladium(II) complexes where a palladium–carbon bond is formed with the *ortho*-position of the ferrocenyl ring. The dinuclear μ_2 -dichloro complex $[\text{Pd}_2(\text{454-H})_2(\mu\text{-Cl})_2]$ reacts with pyridine to form the mononuclear complex $[\text{Pd}(\text{454-H})(\text{Cl})(\text{py})]$ with a *trans*-*N,N* and *trans*-C, Cl arrangement [573].

The lanthanide(III) complexes with formylferrocene benzoylhydrazone (**455**), $\text{Ln}(\text{455-H})_3 \cdot n\text{H}_2\text{O}$, ($\text{Ln} = \text{La}^{3+} \cdots \text{Lu}^{3+}$ except Pm^{3+} and Y^{3+} , $n = 1\text{--}3$), have been prepared by the reaction of **455** with the appropriate metal(III) chlorides in acetonitrile. The elemental analyses, IR and UV spectra, molar conductance and thermal analyses show that the ligand coordinates to the metal ions in the enolic form with a 3:1 molar ratio [574]. $\text{La}(\text{455-H})_3 \cdot 3\text{H}_2\text{O}$, $\text{Sm}(\text{455-H})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Lu}(\text{455-H})_3 \cdot \text{H}_2\text{O}$ lose their water molecules at about 60 °C showing that the water molecules are not coordinated to the metal ions. For these complexes a structure was proposed, where three molecules of $[\text{455-H}]^-$ coordinate to the lanthanide(III) ion through their nitrogen atom in azomethine and oxygen atom (in enolic form) in acetonitrile, accompanied by the release of three chloride ions. It is however possible, especially for the heavier lanthanide ions a coordination of CH_3CN in this solution and/or an oligomerization, especially in the solid state [574].

The reaction of 1,1-diacetylferrocene and phenyl- or 2-pyridyl-hydrazine in ethanol forms the corresponding 1,1'-bis(pyridyl)hydrazone **456**; glacial acetic acid is required for reaction to occur. The X-ray structure of **456** as its diacetate salt reveals that the carboxylate anions are hydrogen bonded to a protonated pyridine nitrogen and to a NH group. Attempts to synthesize metal complexes from these ferrocene derivatives failed to yield well characterized compounds, possibly owing to their low stability [575].

2-(Ferrocenyl)benzothiazoline (**457**), derived from the condensation of formylferrocene and *o*-amminothiophenol, reacts in toluene with an equimolar amount of $[\text{Pt}(\text{hfacac})_2]$ ($\text{H-hfacac} = \text{hexafluoroacetylacetone}$) to form a black solid

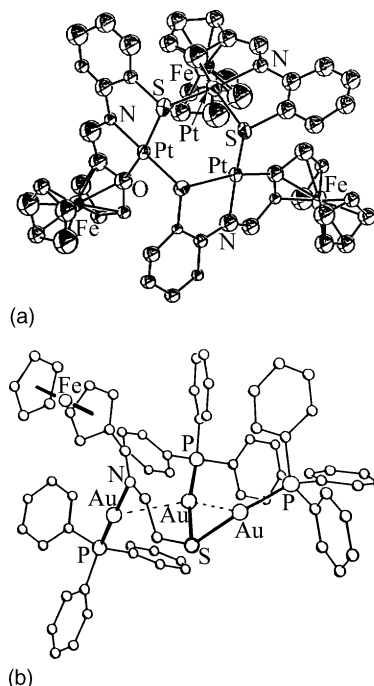


Fig. 382. Structure of $[\text{Pt}_3(\text{457-2H})_3]$ (a) and $[\text{Au}_3(\text{458})(\text{PPh}_3)_3]^{2+}$ (b) (adapted from Refs. [576,577]).

which, washed with diethylether, dissolved in dichloromethane and then purified on a silica gel column using dichloromethane as the eluant, gives rise to $[\text{Pt}_3(\text{457-2H})_3]$ [576]. The coordination geometry around each of platinum ions is square planar with a CNS_2 donor set where the two sulfur atoms are located in *cis*-position. The platinum ions are bridged by sulfur atoms. The framework of this complex consists of six-membered Pt_3S_3 ring in chair form. The $\text{Pt} \cdots \text{Fe}$ distances range from 3.49 to 3.69 Å (Fig. 382a). In CDCl_3 , ^1H NMR $[\text{Pt}_3(\text{457-2H})_3]$ indicates that its low symmetry without C_3 axis is maintained also in solution.

The reaction under nitrogen of formylferrocene with $\text{NH}_2(\text{CH}_2)_2\text{SH}$ in refluxing tetrahydrofuran resulted, after column chromatographic purification using $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) as eluant, in the formation of $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)\text{-CH=N(CH}_2)_2\text{SH}$ (**H-458**). If the same reaction is carried out in damp tetrahydrofuran and in air, the product is the air- and moisture-stable orange disulfide compound $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)\text{CH=N(CH}_2)_2\text{S}_2(\text{CH}_2)_2\text{N=CH(C}_5\text{H}_4)\text{Fe(C}_5\text{H}_5)$ that behaves as a nonconductor in acetone. The reaction of **H-458** with $[\text{Au}(\text{Cl})(\text{PPh}_3)]$ in the presence of Na_2CO_3 leads to the orange air- and moisture-stable thiolate gold derivative $[\text{Au}(\text{458})(\text{PPh}_3)]$. This complex reacts further with $[\text{Au}(\text{CF}_3\text{SO}_3)(\text{PPh}_3)]$ in various stoichiometries to furnish the di-, tri- or tetra-nuclear orange air- and moisture-stable gold species $[\text{Au}_2(\text{458})(\text{PPh}_3)_2](\text{CF}_3\text{SO}_3)$, $[\text{Au}_3(\text{458})(\text{PPh}_3)_3](\text{CF}_3\text{SO}_3)_2$ or $[(\text{Au}_4(\text{458})\text{PPh}_3)_4](\text{CF}_3\text{SO}_3)_3$ which behave as 1:1, 1:2 and 1:3 electrolytes, respectively. NMR spectra indicate $\text{Au} \cdots \text{Au}$ interactions. The reaction of the dinuclear gold complex $[\text{Au}_2(\text{CF}_3\text{SO}_3)_2(\mu\text{-dppf})]$ ($\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene) with **H-458** in the presence of

Na_2CO_3 leads to $[\text{Au}_2(\mathbf{458})(\mu\text{-dppf})](\text{CF}_3\text{SO}_3)$, as a yellow air- and moisture-stable solid. It behaves as 1:1 electrolyte in acetone solution. NMR and FAB mass spectra show a structure where the two gold centers bridged by the diphosphine are bonded to the sulfur atom. The same reaction, carried out in the molar ratio 1:2 gives the air- and moisture-stable red tetranuclear gold derivative $[\text{Au}_4(\mathbf{458})(\mu\text{-dppf})_2](\text{CF}_3\text{SO}_3)_3$ that has a conductivity value in accordance with a 1:3 electrolyte. NMR spectra indicate a structure similar to that of $[\text{Au}_4(\mathbf{458})(\text{PPh}_3)_4](\text{CF}_3\text{SO}_3)_3$, where gold-gold interactions may play an important role in the stability of the molecule [577].

In the structure of $[\text{Au}_3(\mathbf{458})(\text{PPh}_3)_3](\text{CF}_3\text{SO}_3)_2$ (Fig. 382b) two of the gold(phosphine) fragments are bonded to the sulfur atom and one is bonded to the nitrogen atom. They are located in such a manner that there are two short gold-gold interactions of 3.061 and 3.086 Å; Au(2) and Au(3) exhibit a linear coordination while the coordination around Au(1) deviates more appreciably from linearity as a consequence of the gold-gold interactions and Au(1) has been regarded as having a strongly distorted tetrahedral geometry. The cyclopentadienyl rings are staggered [577].

The electrochemical behaviour of these compounds has been studied by cyclic voltammetry at a platinum electrode in CH_2Cl_2 . The cyclic voltammograms of compounds H-**458** and the related disulfide derivative, at a scan rate of 100 mV s^{-1} , show a quasi-reversible redox couple assigned to ferrocene/ferrocenium species at potential values similar to those found in ferrocene itself [577].

The coordination of one or two gold(phosphine) fragments to the thiolate unit does not greatly affect the values of the potentials; thus $[\text{Au}(\mathbf{458})(\text{PPh}_3)]$ and $[\text{Au}_2(\mathbf{458})(\text{PPh}_3)_2](\text{CF}_3\text{SO}_3)$ show a pattern similar to that of the related thiophenol ligand H-**458**, with only a slight anodic shift in the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple ($\Delta = 0.08$ or 0.1 V , respectively). The coordination of three $\{\text{Au}(\text{PPh}_3)\}^+$ units in $[\text{Au}_3(\mathbf{458})(\text{PPh}_3)_3](\text{CF}_3\text{SO}_3)_2$ two of them to the bridging sulfur donor and one to the nitrogen donor of $[\mathbf{458}]^-$, has a more marked effect on the potentials. The potential for the ferrocene/ferrocenium wave increases considerably (0.73 V) whereas no amine oxidation wave is observed. The cyclic voltammogram of $[\text{Au}_4(\mathbf{458})(\text{PPh}_3)_4](\text{CF}_3\text{SO}_3)_3$ is similar, showing that the coordination of gold to the nitrogen atom produces an anodic shift in the ferrocene-based oxidation wave and a stabilization of the main toward oxidation. In $[\text{Au}_2(\mathbf{458})(\mu\text{-dppf})](\text{CF}_3\text{SO}_3)$ and $[\text{Au}_4(\mathbf{458})(\mu\text{-dppf})_2](\text{CF}_3\text{SO}_3)_3$ there are two or three ferrocene units, the peak potentials are very close, and thus the waves are not well defined [577].

13.2. Complexes with [1+2] and [2+1] acyclic ferrocene derivatives

[1+2] and [2+1] Acyclic ligands, bearing respectively one and two ferrocene moieties, have been obtained by condensation respectively of 1,1'-diformyl- or 1,1'-diace-

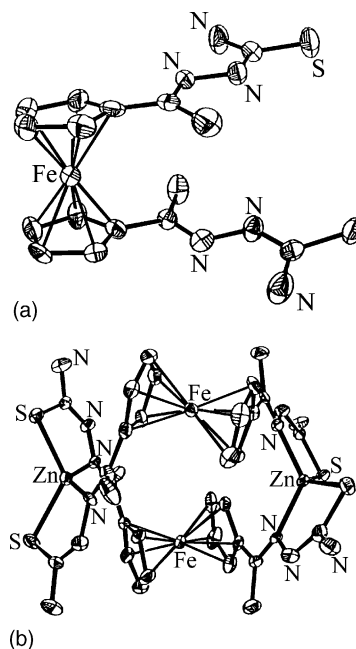


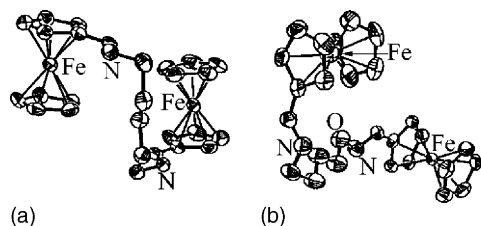
Fig. 383. Structure of $\text{H}_2\text{-459}$ (a) and $[\text{Zn}_2(\mathbf{459})_2]$ (b) (adapted from Ref. [578]).

tyl-ferrocene with the mono-amines one $\text{H}_2\text{N-R}$ or of formylferrocene with the diamines $\text{H}_2\text{N-R}'\text{-NH}_2$.

1,1'-Diacylferrocene reacts with thiosemicarbazide in the presence of acetic acid to form the bisbidentate ligand $\text{H}_2\text{-459}$ which shows a *cis* configuration with two thiosemicarbazone moieties positioned at the same side (Fig. 383a) [578], thus enabling $\text{H}_2\text{-459}$ to function as a double anionic N_2S_2 ligand.

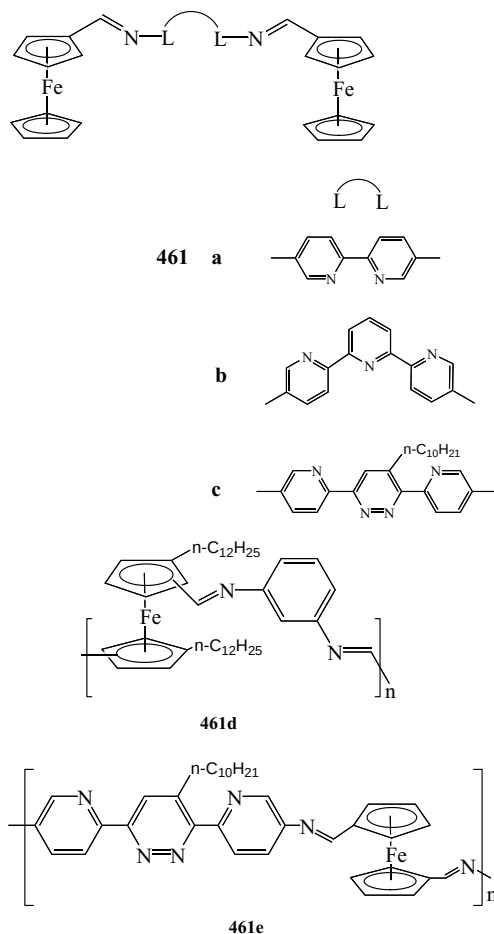
The reaction of $\text{H}_2\text{-459}$ with $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol at reflux gives $[\text{Zn}_2(\mathbf{459})_2]$. The structure of one of the two enantiomers confirms the formation of a double-helix composed of two anionic ligands $[\mathbf{459}]^{2-}$ wrapped around two zinc(II) ions which are separated by 7.74 Å . Each zinc center occupies a four coordinated pseudo-tetrahedral environment bound to the sulfur and nitrogen from one $[\mathbf{459}]^{2-}$ ligand, and to the sulfur and nitrogen atoms from a second ligand (Fig. 383b) [578]. X-ray diffraction analysis of the complex reveals that helices of each enantiomer interact with each other through hydrogen bonds forming an infinite tube. The imino nitrogen atoms of the thiosemicarbazone moieties act as H-bond acceptors while the amino nitrogen atoms act as donors, these pair up with the corresponding imino and amino nitrogen atoms of a parallel helix forming hydrogen bonds.

The [2+1] acyclic Schiff base, **460**, derived from the condensation of formylferrocene and 1,5-diamino-3-azapentane, contains two molecules in the cell unit, chemically equivalent but differently disposed in the crystal. In one molecule (a) the $(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$ chain is more elongated than in the other (b); consequently the $\text{Fe} \cdots \text{Fe}$ distance in this molecule is 6.592 Å while it is 10.008 Å in the other [568] (Fig. 384). The ferrocenyl groups are in the eclipsed

Fig. 384. Structure of **460** (adapted from Ref. [568]).

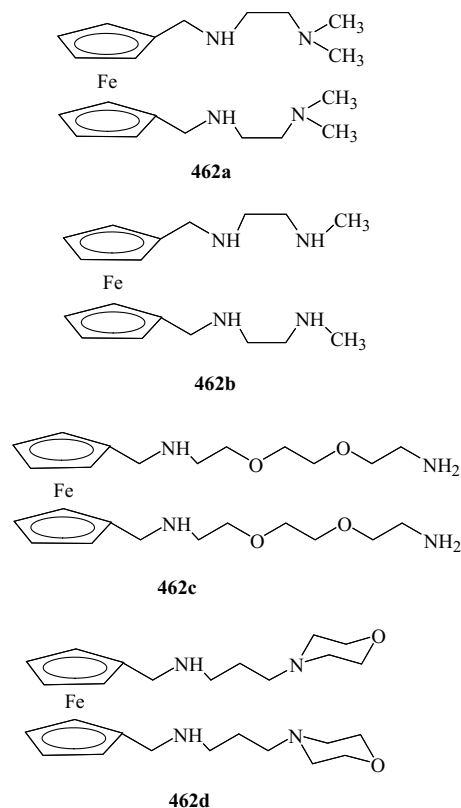
form and no relevant intra- or intermolecular interactions are present. The crystal packing shows a columnar arrangement of the molecules along the *a*-direction.

The reaction of formylferrocene with the appropriate polyamine in a 2:1 molar ratio gives rise to **461a–c** [579]. The condensation of a regioisomeric mixture of 1,1'-didodecylferrocenedicarbaldehyde, derived from the reaction of a regioisomeric mixture of 1,1'-didodecylidithioferrocenes and dimethylformamide, with 1,3-diaminobenzene in either uncatalysed or acid catalysed forms the corresponding Schiff bases **461d**. Moreover the condensation of 3,6-bis(5-amino-2-pyridyl)-4-*n*-decylpyridazine with 1,1'-difor-
mylferrocene in acidic dimethylformamide led to the polymer **461e**, an oil of low molar mass ($M_w = 4650$), soluble in common organic solvents such as chloroform and tetrahydrofuran, while **461e** is insoluble in common solvents [579].



The tetracarbonylmolybdenum complex [Mo(**461a**)-(CO)₄] was prepared by treating the appropriate diamine with molybdenum hexacarbonyl followed by the reaction of the resulting complexes [Mo(diam)(CO)₄] with ferrocene-carbaldehyde. The same heteropolynuclear complexes can be obtained by reacting the preformed Schiff base **461a** with Mo(CO)₆ [579].

1,1'-Bis(5-methyl-2,5-diazaheptyl)ferrocene, **462a**, and 1,1'-bis(2,5-diazaheptyl)ferrocene, **462b** have been prepared by condensation of 1,1'-difor-
mylferrocene and *N,N*-dimethyl- or *N*-methylethane-1,2-diamine in refluxing methanol and reducing the corresponding Schiff base by LiAlH₄. They have been purified by chromatography on alumina by using dichloromethane-methanol (10:1) as eluant. **462a** and **462b** are oils and have always been obtained impure with small amounts of starting materials; all attempts to isolate them as solids were unsuccessful [580]. They are soluble in organic solvents but are also water soluble, due to the presence of amino groups; **462a** is more soluble than **462b** in water. Aqueous saturated solutions of **462a** and **462b** can be prepared by boiling them in distilled water overnight to produce bright yellow solutions. **462a** forms both mono and dinuclear complexes with nickel(II), copper(II), zinc(II) and cadmium(II) ions, whereas only mononuclear species were found with the lead(II) ion. It was suggested that for 1:1 nickel(II), copper(II), zinc(II) and cadmium(II) complexes coordination takes only at one NH(CH₂)₂N(CH₃)₂ chain while for the lead(II) species a coordination where both NH(CH₂)₂N(CH₃)₂ chains are engaged in coordination is more favourable [580].



The electrochemical behaviour of **462a** has been studied in CH_2Cl_2 and water; $E_{1/2}$ is pH-dependent and from the $E_{1/2}$ versus pH curve the protonation constants of the oxidized compound $[\mathbf{462a}]^+$ containing the iron(III) ion, were determined. Similar electrochemical experiments were carried out for the $\mathbf{462a}/\text{H}^+/\text{M}^{2+}$ systems. The good agreement between the E versus pH and z versus pH curves (z is the average charge calculated from potentiometric data) appears to suggest that the ferrocene-substrate interaction is mainly electrostatic [580].

1,1'-Bis(1-amino-5,8-dioxa-2-azadecyl)ferrocene (**462c**) has been prepared by the reaction of 1,1'-diformylferrocene with 2,2'-ethylenedioxybis(ethylamine) that was previously blocked in one amine position with a butoxycarbonyl (BOC) group followed by further reduction of the imine formed and elimination of the BOC group with trifluoroacetic acid [580]. Analogously 1,1'-bis(5-morpholino-2-azapentyl)ferrocene (**462d**) was synthesized by reaction of 1,1'-diformylferrocene with amino-propylmorpholine to produce the related bis-imine ferrocene derivative that was reduced with NaBH_4 [580].

462a and **462d** have been used as receptors for anions. Their electrochemical response found against ATP and phosphate in water and of phosphate and sulfate in 1,4-dioxane water is quite poor with maximum cathodic shift of ca. 30–40 mV. The electrochemical response induced by HSO_4^- and H_2PO_4^- has also been studied in CH_3CN where a large cathodic shift for H_2PO_4^- up to ca. 200 mV was found [580].

13.3. Complexes with [2+2] or [1+1] macrocyclic ferrocene derivatives

Macrocyclic compounds have been synthesized by reaction of 1,1'-diformylferrocene with polyamine bearing two NH_2 -groups; their [2+2] or [1+1] cyclic nature of these ligands, strongly influenced by the polyamine used in these macrocondensation, has been inferred by mass spectrometry and confirmed by single crystal X-ray diffractometry.

1,1'-Diformylferrocene reacts with 1,2-diaminoethane in a 1:1 molar ratio to produce the [2+2] cyclic bis(ferrocene) Schiff base **463**. This reaction contrasts with the reactivity found for the reaction of 1,1'-diformylferrocene with 1,5-diamino-3-azapentane: under the same experimental condi-

tions the cyclic [1+1] ferrocene derivative **465** was found as unique product. A similar behaviour has been reported when other polyamines which react with 1,1'-diformylferrocene to produce the 1,1'-ferrocene derivatives **467** and **468** [581].

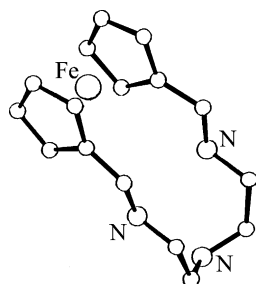
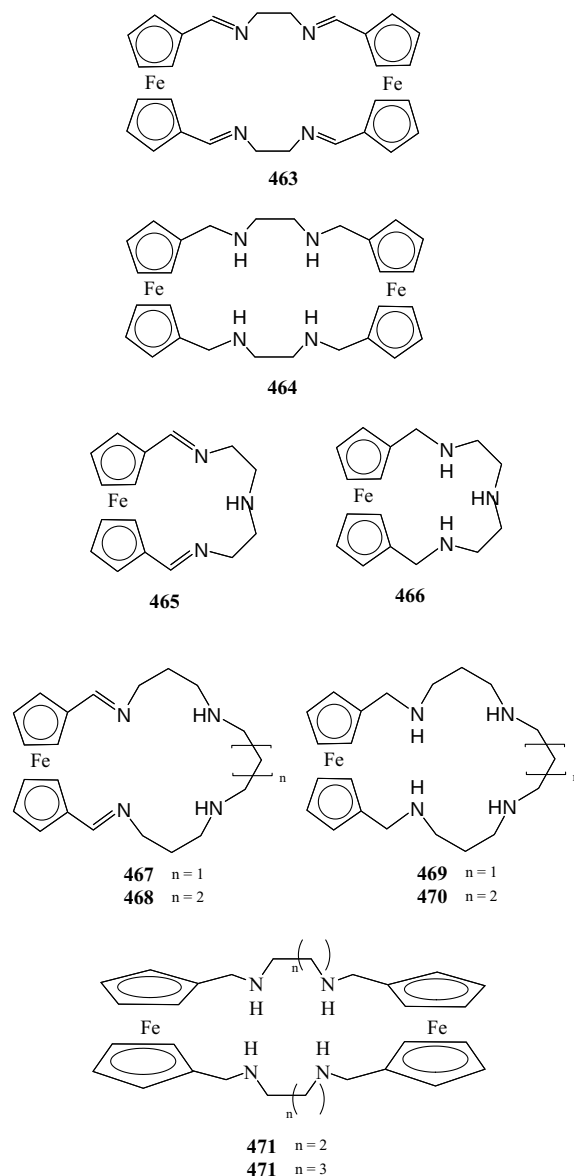


Fig. 385. Structure of **466** (adapted from Ref. [581]).

The different condensation behaviour between 1,2-diaminoethane and 1,5-diamino-3-azapentane (or the homologous superior linear tetraamines) seems to be related with the fact that the former is not long enough to produce monoferrocene derivatives without producing considerable strains in the molecule.

These cyclic Schiff bases have been reduced to the corresponding cyclic ferrocene polyamines **464**, **466**, **469** and **470**, by reaction with NaBH_4 or LiAlH_4 . In these reduction reactions the [1+1] or [2+2] cyclic nature of the original Schiff bases is maintained as confirmed by the X-ray structure of **466** (Fig. 385), **463** (Fig. 386a) and **464** (Fig. 386b).

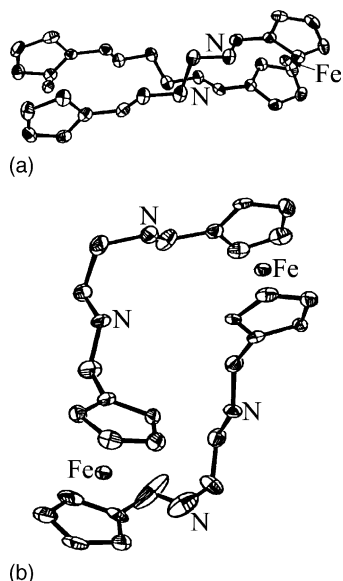


Fig. 386. Structure of **463** (a) and **464** (b) (adapted from Ref. [581]).

The structure of **463**, carried out on crystals obtained by slow diffusion of hexane into a solution of the compound in dichloromethane, confirms the [2+2] cyclic nature of this Schiff base. It consists of a ring built with two ferrocenyl units bridged by two 2,5-diazahexa-1,5-diene groups, which are covalently attached to the cyclopentadienyl rings. Half of the molecule is symmetrically related with the other half in the crystal by an inversion center located in the center of the molecule. The cyclopentadienyl rings were found to be planar [581].

Thus the reaction of the **463** with LiAlH_4 in freshly distilled tetrahydrofuran gave the related [2+2] reduced macrocycle **464** [581]. Crystals, grown by slow diffusion of hexane into a CHCl_3 solution of **464**, show two ferrocenyl units bridged by two 2,5-diazahexane moieties. Two molecules were found in the asymmetric unit. Although the two molecules are related by a mirror plane they appear not to be enantiomers because it seems that they can be converted into each other by a twist of the cyclopentadienyl rings [581].

The reaction of $\text{Ni}(\text{ClO}_4)_2$, $\text{Ni}(\text{CH}_3\text{COO})_2$, $\text{Cu}(\text{BF}_4)_2$ or $\text{Zn}(\text{ClO}_4)_2$ with **466**, **469** or **470** led to the successful isolation of the corresponding complexes, with a 1:1 ligand metal stoichiometry [581].

When an equimolar mixture of $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ ions was added to aqueous solutions of **469** and **470** the ferrocene/ferrocenium redox couple shifted anodically by an amount approximately the same as that induced by the copper(II) cation alone. According to this result **469** and **470** were suggested to be the first generation prototype copper-selective amperometric sensors, capable of detecting the copper(II) cation in the presence of nickel(II) and zinc(II) ions [581].

Cyclic voltammetric and ^{31}P NMR experiments reveal the electrochemical recognition of adenosine triphosphate

(ATP) and hydrogen-phosphate (HPO_4^{2-}) anion guests in water. At pH 6.5 cathodic shifts of 60–80 mV of the respective ferrocene redox couple of **466**, **469** and **470** are observed in the presence of ATP and HPO_4^{2-} anions [581].

The protonation of **464** was investigated by potentiometric titrations with KOH of previously acidified solutions of **464**. Although **464** is soluble in aqueous acid, it precipitates at neutral pH. Therefore tetrahydrofuran–water (70:30, v/v) was employed as solvent. Other solvent mixtures as dimethyl sulfoxide–water or dioxane–water could not be used because of the insolubility of **464**. At pH > 10.5 only the non-protonated species **464** is present. When the pH decreases, successive protonation processes are observed; at neutral pH mono- and di-protonated species coexist [581].

The complex formation of **464** with copper(II), nickel(II) and zinc(II) ions, studied potentiometrically, shows $[\text{Cu}(\text{464})]^{2+}$ is predominant over a wide pH range (5.2–10.8). From pH 3–6 this complex coexists with $[\text{Cu}(\text{H-464})]^{3+}$ and uncoordinated copper(II) ions. At pH > 9 $[\text{Cu}(\text{464})]^{2+}$ and the hydroxo species $[\text{Cu}(\text{464})(\text{OH})]^+$ coexist. For copper(II) only experimental data belonging to the range pH 2–10.5 were computed because of the precipitation of a brown solid at pH > 10.5. The distribution diagram of the $\text{Ni}^{2+}/\text{464}/\text{H}^+$ system shows in that at pH ≥ 4 the complexes $[\text{Ni}(\text{H-464})]^{3+}$, $[\text{Ni}(\text{464})]^{2+}$ and $[\text{Ni}(\text{464})(\text{OH})]^+$ coexist over a wide pH range. The stability constant of $[\text{Ni}(\text{464})]^{2+}$ is two orders of magnitude smaller than that of the corresponding copper(II) complex. The dihydroxo complex $[\text{Ni}(\text{464})(\text{OH})_2]$ exists at pH > 7. Data at pH > 8.5 were not computed due to the precipitation of a yellow-brown solid.

The distribution diagram of the $\text{Zn}^{2+}/\text{464}/\text{H}^+$ system is similar to that of nickel(II) with the coexistence of the species $[\text{Zn}(\text{H-464})]^{3+}$, $[\text{Zn}(\text{464})]^{2+}$, $[\text{Zn}(\text{464})(\text{OH})]^+$ and $[\text{Zn}(\text{464})(\text{OH})_2]$. Only data in the pH range 2–8.2 were computed because of the precipitation of a yellow solid. For nickel(II) and zinc(II) this solid is probably related to the neutral complexes $[\text{M}(\text{464})(\text{OH})_2]$, however all attempts to characterise them unequivocally have been unsuccessful [581].

464 can be considered as a selective electrochemical sensor for copper over a wide pH range; for example at pH 4.4 an $\Delta E_{1/2}$ of about –80 mV is found when copper(II) is added to the solution even in the presence of nickel(II) or zinc(II) ions [581].

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ reacts with **464** in methanol to form $[\text{Cd}(\text{464})(\text{NO}_3)_2]$; the metal ion is in a distorted octahedral surrounding with **464** acting as tetradentate in the equatorial plane while the apical positions are occupied by two oxygen atoms of two nitrate anions. Intramolecular $\text{Fe} \cdots \text{Cd}$ distances range from 4.114 to 5.303 Å (Fig. 387) [582].

Solution studies directed to the determination of the stability constants for the formation of complexes of **464** with Pb^{2+} , Hg^{2+} , and Cd^{2+} in THF/ H_2O 70:30 (v/v; containing 0.1 mol dm^{-3} of $[\text{N}(\text{Bu})_4](\text{ClO}_4)$) show the metal ions form stable $[\text{M}(\text{464})]^{2+}$ complexes. From pH 5 to 8 the

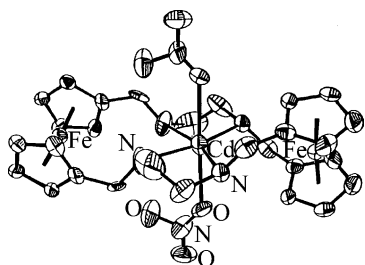


Fig. 387. Structure of $[\text{Cd}(\mathbf{464})(\text{NO}_3)_2]$ (adapted from Ref. [582]).

species $[\text{Hg}(\text{H}_2\text{-}\mathbf{464})]^{4+}$, $[\text{Hg}(\text{H-}\mathbf{464})]^{3+}$ and $[\text{Hg}(\mathbf{464})]^{2+}$ exist whereas at $\text{pH} > 9$ $[\text{Hg}(\mathbf{464})]^{2+}$ and the hydroxo species $[\text{Hg}(\mathbf{464})(\text{OH})]^+$ coexist. The stability constants of the $[\text{Cd}(\mathbf{464})]^{2+}$, $[\text{Pb}(\mathbf{464})]^{2+}$ and $[\text{Hg}(\mathbf{464})]^{2+}$ complexes are close to those observed for Zn^{2+} but are about two order of magnitude smaller than that of the corresponding $[\text{Cu}(\mathbf{464})]^{2+}$ complex. The stability constant for the $[\text{Cu}(\mathbf{464})]^{2+}$ complex is ca. 10^9 times smaller than that of the $[\text{Cu}(\mathbf{480})]^{2+}$ complex in the same medium, indicating that coordination of the nitrogen atoms to the central metal ion is less effective in $\mathbf{464}$ than in $\mathbf{480}$ [582].

Electrochemical studies on the shift of $E_{1/2}$ versus pH for the $\mathbf{464}/\text{H}^+/\text{M}^{2+}$ systems ($\text{M} = \text{Pb}^{2+}$, Hg^{2+} , or Cd^{2+} ; $\text{M}^{2+}/\mathbf{464}$ molar ratio 1:1) show the $\mathbf{464}/\text{H}^+/\text{Pb}^{2+}$ and $\mathbf{464}/\text{H}^+/\text{Cd}^{2+}$ curves are quite similar to that of the free ligand. However, Hg^{2+} is able to shift the oxidation potential of the ferrocenyl groups into the pH range 6–10. This suggests that there is a selective electrochemical response towards Hg^{2+} over Cd^{2+} and Pb^{2+} . In fact if the three metal ions are added to a solution of $\mathbf{464}$ at pH 8.5, the $\Delta E_{1/2}$ ($\Delta E_{1/2} = E_{1/2}(\mathbf{464}/\text{M}^{2+}) - E_{1/2}(\mathbf{464})$) observed is close to that found when only Hg^{2+} was present [582].

Water soluble pH dependent polyazaferrocene macrocyclic ligands have been used for the electrochemical recognition of a variety of transition metal cations and anions [583]. The condensation of 1,1'-diformylferrocene with *N,N'*-bis(3-aminopropyl)-1,3-propanediamine or spermine, initially gave the [1+1] Schiff bases which, reduced in situ using NaBH_4 , form the corresponding polyazaferrocene macrocyclic ligands $\mathbf{469}$ and $\mathbf{470}$. Analogous condensation reactions of 1,1'-diformylferrocene with 1,2-diaminoethane, 1,3-diaminopropane or 1,4-diaminobutane, followed by NaBH_4 reduction, gave the [2+2] macrocyclic products $\mathbf{464}$, $\mathbf{471}$ and $\mathbf{472}$ as supported by FAB mass spectrometry and ^1H and ^{13}C NMR spectroscopy and confirmed, at least for $\mathbf{472}$ ($n = 3$), by an X-ray structural determination on crystals grown from acetonitrile [583] (Fig. 388).

The paramagnetic light green nickel(II) acetate complex of $\mathbf{469}$ has an octahedral environment, whereas the diamagnetic dark red orange nickel(II) perchlorate complex has a square planar coordination [583].

Electronic spectra show that the addition of silver(I) to $\mathbf{472}$ causes the formation of the dinuclear silver(I) complex $[\text{Ag}_2(\mathbf{472})]^{2+}$ with the silver cations coordinating to the secondary amine nitrogen donor atoms nearby to the ferro-

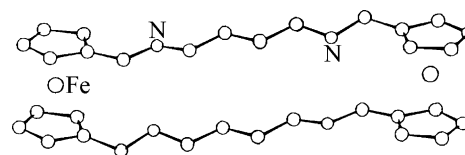


Fig. 388. Structure of $\mathbf{472}$ ($n = 3$) (adapted from Ref. [583]).

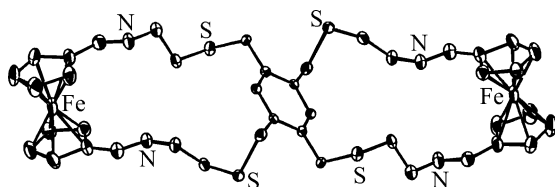
cene redox-center. It is noteworthy that when these solutions were left standing for 12 h or more metallic silver gradually precipitated leaving a dark green-blue solution indicative of ferrocenium cation. In contrast analogous silver cation titration experiments with $\mathbf{464}$ instantly produced the metallic silver precipitate suggesting, in agreement with electrochemical measurements, that ligand $\mathbf{464}$ is the relatively stronger reducing reagent. Thus the size of the polyazamacrocyclic cycle can tune the redox potential of the respective ferrocene moiety and consequently dictate the competition between silver cation–ligand complexation and silver cation–ligand redox reaction [583].

Cyclic voltammetry in acetonitrile or methanol shows the ligands $\mathbf{469}$ and $\mathbf{470}$ exhibit a one-electron oxidation wave whereas $\mathbf{464}$ and $\mathbf{472}$ display a single two-electron oxidation process.

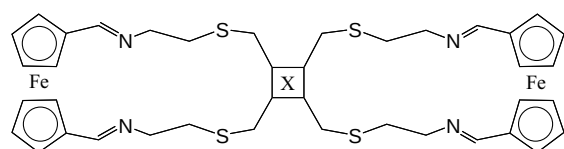
The addition of stoichiometric amounts of nickel(II), copper(II) and zinc(II) ions to acetonitrile electrochemical solutions of $\mathbf{469}$ and $\mathbf{470}$ led to large anodic shifts of the respective ferrocene/ferrocenium redox couple of up to 190 mV in the case of $\mathbf{469}$ and the copper(II) ion. $\mathbf{672}$ electrochemically recognises the silver(I) ion through a 45 mV anodic perturbation of its redox couple however instant oxidation precludes $\mathbf{464}$ from sensing this transition metal guest. The latter ligand does electrochemically sense copper(II) and nickel(II) cations.

Electrochemical investigations reveal these redox-active ligands can electrochemically sense various transition metal cations in polar organic solvents and in water at high pH values with $\mathbf{469}$ and $\mathbf{470}$. Aqueous electrochemical competition experiments with nickel(II), copper(II) and zinc(II) ions suggest that $\mathbf{469}$ and $\mathbf{470}$ exhibit a selectivity preference for the copper(II) cation. At lower pH values (6–8) the respective protonated polyammonium forms of $\mathbf{469}$, $\mathbf{470}$ and $\mathbf{472}$ bind and electrochemically detect the biologically important phosphate anions, ATP and hydrogen phosphate in the aqueous environment [583].

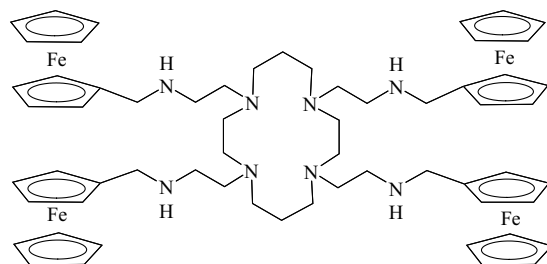
The bis macrocyclic ligands containing two ferrocenyl groups, *exolendo*-1,1':1'',1'''-[1,2,4,5-tetrakis(5-aza-2-thiahexa-5-enyl)benzene]bisferrocene ($\mathbf{473}$), 1,1,1':1'',1'''-[1,2:1',2'-tetrakis(5-aza-2-thiahexa-5-enyl)ethene]bisferrocene ($\mathbf{474}$), 1,1':1'',1'''-[1,1':2,2'-tetrakis(5-aza-2-thiahexa-5-enyl)ethene]bisferrocene ($\mathbf{475}$) and 1,1':1'',1'''-[tetrakis(5-aza-2-thiahexa-5-enyl)methane]bisferrocene ($\mathbf{476}$) have been synthesized by self-condensation of the appropriate polyamine with 1,1-diformylferrocene in a 1:1 molar ratio [584]. The ^1H NMR spectrum of $\mathbf{473}$ reveals that the *exolendo* isomers occur in a 10:3 ratio. The isomer ratio of $\mathbf{475}$ is

Fig. 389. Structure of *endo*-**473** (adapted from Ref. [584]).

approximately 2.5:10, based on the ^{13}C NMR data. The assignment of the NMR data to the two isomers of **473** was confirmed by an X-ray crystal structure analysis of *endo*-**473** (Fig. 389). The structure is centrosymmetric. The two ferrocenyl groups are parallel to each other. The $\text{Fe} \cdots \text{Fe}$ distance is 18.03 Å [584].



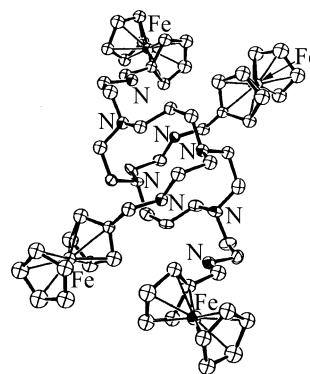
473 benzene
474 ethene
475 spiro C



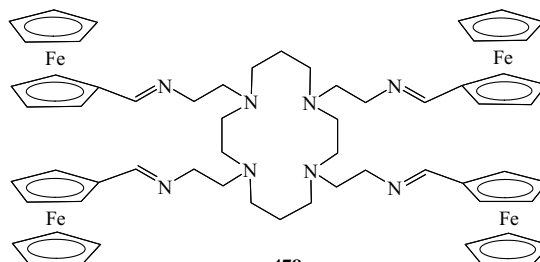
477

Reaction of a mixture of isomers of **473** or **475** with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ affords only $[\text{Cu}_2(\text{exo-473})](\text{ClO}_4)_2$ or $[\text{Cu}_2(\text{exo-475})](\text{ClO}_4)_2$. The *endo*-isomer with the two duryl protons directed toward the copper(I) centers is considerably less stable. The copper–iron distances are around 4 Å and electrochemistry, IR and Mössbauer spectroscopy indicate that there is a small but significant iron–copper interaction in these tetranuclear compounds [584].

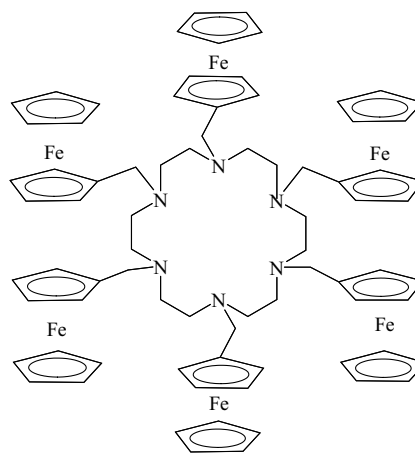
The highly branched ferrocene-functionalized polyazaalkane *N,N',N'',N'''*-tetrakis(4-ferrocenyl-3-azabutyl)-1,4,8,11-tetraazacyclotetradecane (**477**) was prepared by reduction of the corresponding Schiff base **478** [585]. In particular the reaction of *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane with ferrocenecarbaldehyde results in a red oil. Although not fully characterized, this compound should be the Schiff base derivative **478** as suggested by the fact that its reduction with lithium aluminium hydride results in the octaaza derivative **477** which can be isolated as a yellow solid [585]. **477** consists of a 1,4,8,11-tetradecane framework containing four 4-ferrocenyl-3-azabutyl groups covalently attached to the four nitrogen atoms of the cyclam ring. The ferrocenyl moieties show the typical sandwich

Fig. 390. Structure of **477** (adapted from Ref. [585]).

conformation [585]. There is a crystallographically imposed center of inversion in the middle of the tetraaza cyclic ring; **477** shows a conformation with two 4-ferrocenyl-3-azabutyl groups above the N_4 plane and two below the N_4 plane (Fig. 390) [585].



478



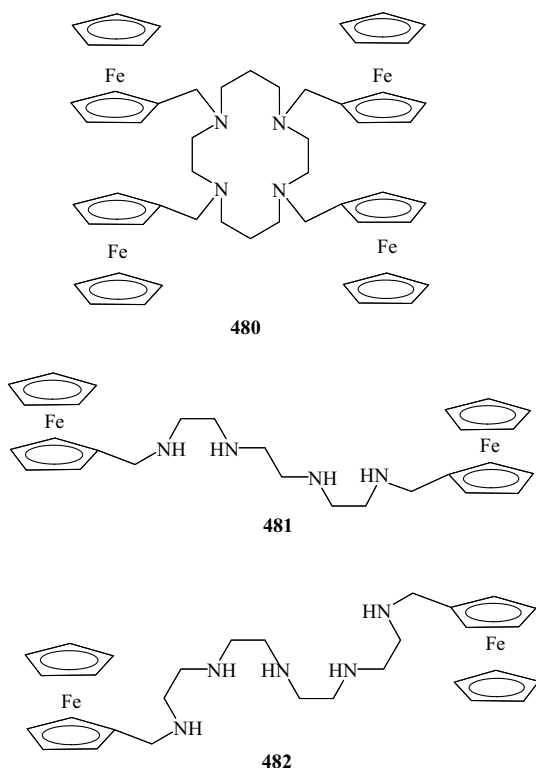
479

Potentiometric and electrochemical studies carried out in tetrahydrofuran/water (70:30, v/v), show that Cu^{2+} , Zn^{2+} and Cd^{2+} form 1:1 and 2:1 metal:**477** complexes. The number of protonated species displayed by the mononuclear species in conjunction with the high constants associated with the first and second protonations of these metal complexes $\{[\text{M}(\text{477})]^{2+} + \text{H}^+ \leftrightarrow [\text{M}(\text{H-477})]^{3+}$ and $[\text{M}(\text{H-477})]^{3+} + \text{H}^+ \leftrightarrow [\text{M}(\text{H}_2\text{-477})]^{4+}\}$ strongly suggest that not all the nitrogen atoms are involved in the coordination.

The presence of free donor atoms in **477** favours the formation of polynuclear complexes [585].

The stabilities of the copper(II) complexes are significantly higher than those of the zinc(II) and cadmium(II) complexes. The stability of the cadmium(II) complexes are, on the other hand, slightly higher than those of the zinc(II) ones [585].

Also the related macrocycles 1,4,7,10,13,16-hexa(ferrocenylmethyl)-1,4,7,10,13,16-hexaazacyclooctadecane (**479**) and 1,4,8,11-tetra(ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane (**480**) have been prepared by the reaction of the corresponding hexaaza or tetraaza macrocycles with trimethylammonium methyl ferrocene-iodide in CH₃CN and in the presence of Na₂CO₃ [586]. The structure of **480** consists of the polyazacycloalkane 1,4,8,11-tetraazacyclotetradecane containing ferrocenylmethyl groups covalently attached to the four nitrogen atoms. The ferrocenyl moieties show the typical sandwich configuration with parallel and planar cyclopentadienyl rings. **480** shows a conformation with two ferrocenylmethyl groups above the N₄ plane and the remaining two below the N₄ plane. The conformation of the cyclic ring of **480** is similar to that found in **477** [585,586].



The reaction of **480** with Cu(CH₃COO)₂·H₂O in methanol allowed the isolation of [Cu(**480**)](ClO₄)₂, where the copper(II) ion is coordinated by four coplanar nitrogen atoms from the ligand. **480** shows the more thermodynamically favourable isomer with the two ferrocenylmethyl groups above the N₄ plane and the remaining two below the N₄ plane [586].

The reaction of **480** with Ni(CH₃COO)₂·4H₂O in refluxing methanol and the further addition of [NH₄](PF₆), followed by crystallization of the resulting compound from a diethyl ether/acetonitrile solution, affords [Ni(**480**)(CH₃CN)](PF₆)₂·2CH₃CN [586]. Its low temperature single crystal structure shows the four nitrogen atoms from the macrocycle are not planar. The coordination geometry about the nickel(II) ion is between square pyramidal and trigonal bipyramidal. In contrast with the copper(II) complex, the ligand shows a conformation with the four ferrocenylmethyl groups pointing above the N₄ plane [586].

[Cd(**479**)](PF₆)₂, obtained by reaction **479** with cadmium nitrate in dichloromethane–ethanol and further addition of [NH₄](PF₆) and water, consists of an inner binding domain of six nitrogen atoms coordinating the central metal ion giving it a distorted octahedral geometry. The six nitrogen atoms are also covalently attached to six ferrocenylmethyl groups making up an outer redox-active sphere. The hexaazacyclooctadecane moiety adopts the *fac* configuration [586].

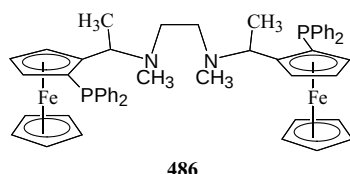
The extraction efficiency of Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ from water into CH₂Cl₂ solution containing **479** follows the order Cu²⁺ > Pb²⁺ > Cd²⁺ > Ni²⁺ > Zn²⁺; Cu²⁺ is quantitatively extracted with an extraction efficiency up to 99% followed by Pb²⁺ which shows an efficiency of 85%. Additionally it was observed that the presence of PF₆[−] anions in the organic phase enhances the distribution coefficient. For instance extraction efficiencies without PF₆[−] in the organic phase for Cu²⁺ and Pb²⁺ were 85 and 47%, respectively. Extraction appears to be due to the presence of the lipophilic ferrocenyl sphere which encapsulates a hydrophilic inner binding domain as suggested by the lower extraction efficiencies observed when the similar ferrocene-containing tetraazacycloalkane **480** is used as extractant under similar conditions (for example the efficiency values for **480** with Cu²⁺ and Pb²⁺ were 34 and 22%, respectively). However the smaller number of the nitrogen donor sites and the smaller size of the macrocyclic cavity can also be factors which could explain the different extraction efficiency of **480** when compared with **479** [586].

Oxidation of dichloromethane solutions containing the lead(II) complex of **479** in contact with an aqueous phase were tested. Thus extraction of Pb²⁺ from H₂O into the CH₂Cl₂ phase containing **479** (~90–95% after 0.5 h) was carried out in order to investigate the release of Pb²⁺ from CH₂Cl₂ into H₂O as a function of oxidation of the ferrocenyl groups. One-electron oxidation of the ferrocenyl groups causes an increase of the lead(II) concentration in water and hence a partial back extraction of this metal ion. However, further complete oxidation of all the ferrocenyl groups (six electrons) causes [Pb²⁺] in water to decrease again. This behaviour has been explained by supposing that some decomposition is coupled to the electrochemical process as the iron concentration in the aqueous phase, increases, as the oxidation in the organic phase progresses. This is in line with the chemical instability observed for the

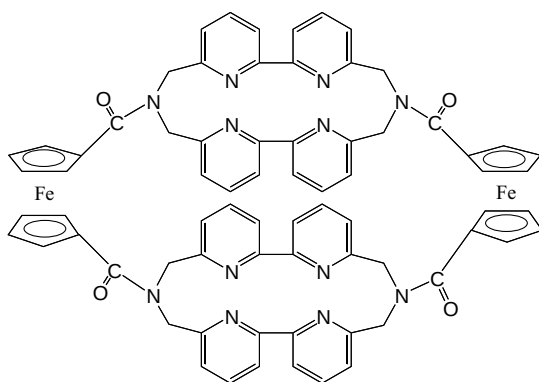
two-electron oxidation of the ferrocene fragment to shift anodically by 120 and 130 mV, respectively.

Electrolyses of sodium(I), copper(I) and silver(I) complexes with **484**, carried out at different oxidation potentials, produce unstable green mixtures containing diprotonated species. Protonation or complexation reactions have no effect on the Mössbauer parameters observed for $[\text{Na}(\text{484})](\text{PF}_6)$ and that no direct interaction occurs between the complexed cation and the iron center. In each molecule, both iron sides are in the same local environment [588].

The chiral bis-ferrocenyldiamine **485** was synthesized from the reaction of (*R*)-*N,N*-(dimethylamino)-1-ferrocenylethylamine with CH_3I followed by nucleophilic substitution with *N,N'*-dimethylethylenediamine, while the chiral diamine **486** was obtained from ortho-lithiation of **485** followed by electrophilic substitution with chlorodiphenylphosphine [589].



486



487

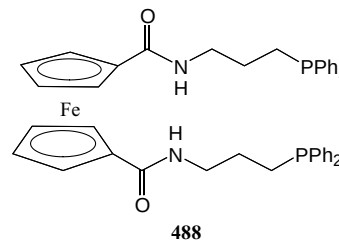
The reaction of **486** with $[\text{Ru}(\text{DMSO})_4(\text{Cl}_2)]$ yields $[\text{Ru}(\text{486})(\text{Cl})_2]$. The geometry about the metal ion is a distorted octahedron, where **486** occupies the square plane in a tetradentate manner with two chloride ligands being *trans* to each other. This complex exhibits catalytic activity toward asymmetric cyclopropanation of some olefins and alkyl diazoacetates, giving enantioselectivity up to 95% [589].

In the [2+2] cryptand **487**, synthesized from 1,1'-bis(chlorocarbonyl)ferrocene and the appropriate diamine, the carbonyl groups located on the periphery of the cryptand are mutually *trans* to each other with two of the bipyridyl units on the outside of the cryptand virtually orthogonal to the two corresponding bipyridyl units filling the cavity [590].

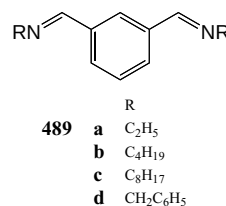
It reacts with Na^+ , Ca^{2+} and Eu^{3+} giving soluble (Na^+) and insoluble complexes (Ca^{2+} , Eu^{3+}). The dinuclear sodium perchlorate complex of **487**, crystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$, contains four molecules of acetonitrile per molecule of the complex. The two sodium cations are

bound by the four bipyridyl nitrogen atoms of one macrocyclic ring and one carbonyl oxygen of the other macrocyclic system in an approximate square pyramidal configuration. Each uncomplexed amide function remained *trans* to its partner but was not involved in binding the cation. The distance of 5.57 Å between the complexed sodium cations, enables a suitable anion (e.g. cyanate) or dianion (e.g. oxalate) to be accommodated within the cleft of the cryptate. The perchlorate counter ions are at a considerable distance from the sodium cations [590].

The ferrocene appended phosphine amide ligand **488** was prepared via the condensation of 1,1'-bis(chlorocarbonyl)ferrocene with 2 equiv. of 3-aminopropyl diphenylphosphine in toluene in the presence of triethylamine. The pure product was obtained after column chromatography and recrystallization from dichloromethane as orange microcrystals [591].



488



489

The high-dilution reaction of 1 equiv. amount of $[\text{M}(\text{CO})_4(\text{norbornadiene})]$ ($\text{M} = \text{Mo}, \text{Cr}$) and **488** in dichloromethane produces, after recrystallization from dichloromethane, the metallo-macrocyclic compounds $[\text{M}(\text{488})(\text{CO})_4]$ [591]. $[\text{Mo}(\text{488})(\text{CO})_4]$ and $[\text{Cr}(\text{488})(\text{CO})_4]$ are isomorphous. The metal ions are octahedral, being bonded to four carbonyls and two mutually *cis* phosphorus atoms. The two phosphorus atoms form a chelate ring containing 10 atoms and additionally a ferrocene moiety. The two amide groups in the molecule have a different orientation. The ferrocene groups are in the eclipsed conformation.

The rhodium(I) complex $[\text{Rh}(\text{488})(\text{CO})(\text{Cl})]$ was obtained by the high-dilution reaction of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ with 0.5 equiv. of **488** in dichloromethane while the reaction of $[\text{Ru}(\text{bipy})_2(\text{Cl})_2] \cdot 2\text{H}_2\text{O}$ and **488** in refluxing aqueous ethanol gave on addition of an excess of $[\text{NH}_4][\text{PF}_6]$ the bis(ruthenium) compound $[\text{Ru}_2(\text{488})(\text{bipy})_4(\text{Cl})_2](\text{PF}_6)_2$.

In $[\text{M}(\text{488})(\text{CO})_4]$ ($\text{M} = \text{Mo}, \text{Cr}$) the strength of anion binding decreases in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, which reflects the decrease in charge density of the anionic guest species. In contrast $[\text{Ru}_2(\text{488})(\text{bipy})_4(\text{Cl})_2](\text{PF}_6)_2$ displays a similar

strength of binding for chloride and iodide whilst bromide forms the strongest complex. The binding of dihydrogenphosphate is generally weak for all receptors. In the case of [Mo(**488**)(CO)₄] this may be a consequence of their macrocyclic cavities being too small to accommodate this relatively large anionic guest. Similarly the small macrocyclic cavity size of the rhodium(I) complex [Rh(**488**)(CO)(Cl)] may account for this receptor inability to complex the largest bromide, iodide and dihydrogenphosphate guest anions [591].

All these complexes can electrochemically sense halide, dihydrogen phosphate and hydrogensulfate anions via significant cathodic perturbations of the respective ferrocene and transition metal oxidation wave [591].

14. Polynuclear complexes with special acyclic or cyclic ligands

The reactions of *N,N'*-dialkylbenzene-1,3-dicarbaldiiimines (**L** = **489a**, **489b**, **489c**) and *N,N'*-dibenzylbenzene-1,3-dicarbaldiiimine (**489d**) with Pd(CH₃COO)₂ form the tetra-μ-acetato cyclopalladated compounds [Pd₄(**L**-2H)₂(CH₃COO)₄] in which metallation occurs at the 4,6 positions of the benzene ring as confirmed by NMR and mass spectrometry [592].

The acetato complexes can be converted smoothly to their chloro analogues by reaction with LiCl in CH₃OH. The chloro complexes can also be obtained directly by the reaction of Li₂[Pd(Cl)₄] with the desired Schiff base. The tetranuclear composition of these compounds was again verified by determining the relative molecular mass.

Bridge splitting reactions with consequent formation of dinuclear compounds occur when the tetranuclear [Pd₄(**489**-2H)₂(Cl)₄] complexes are treated with pyridine, 4-methylpyridine, *n*-butylamine, dimethylbenzylamine, pyrazole, 3,5-dimethylpyrazole and a number of monoprotic bidentate chelating ligands (H-L') as acetylacetone, dibenzoylmethane and its monothio analogue, ethylacetoacetate, salicylaldehyde, *N*-methyisalicylideneimine and sodium *N,N'*-dipropyldithiocarbamate [592]. With pyridine and amines (am) the complexes [Pd₂(**489**-2H)(am)₂(Cl)₂] have been isolated. Pyrazole (H-pz) and dimethylpyrazole (H-dmpz) react differently with chloro-bridged cyclopalladates: while H-pz affords the insoluble complex [Pd₂(**489a**)(H-pz)₂(Cl)₂], a soluble complex of composition [Pd₂(**489b**-2H)(H-dmpz)₂(μ-dmpz)](Cl)·CH₂Cl₂ was obtained with H-dmpz. The neutral, soluble dipalladium derivatives [Pd₂(**489**)(L')₂] have been obtained with monoprotic bidentate chelating ligands (H-L'). In all cases one single isomer was obtained.

[Pd₄(**489a**-2H)₂(Cl)₄], on treatment with pyridine in the presence of AgClO₄, produces [Pd₂(**489a**-2H)(py)₄](ClO₄)₂, where the palladium ions are in distorted square planar environments (Fig. 391) [592].

Analogously [Pd₄(**489a**-2H)(Cl)₄], which is almost insoluble in organic solvents, can be readily converted into the

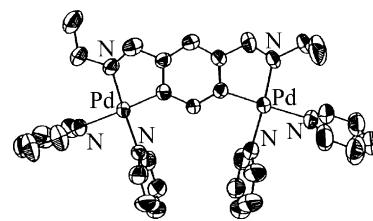
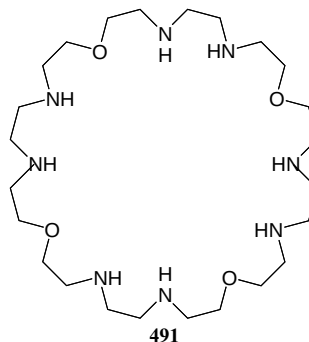
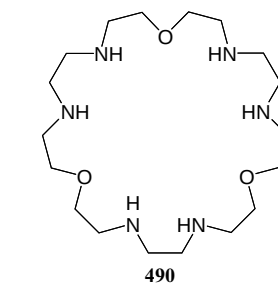


Fig. 391. Structure of [Pd₂(**489a**-2H)(py)₄]²⁺ (adapted from Ref. [592]).

colourless, soluble complex [Pd₂(**489a**-2H)(CH₃CN)₂(ClO₄)₂] by treating it with 4 equiv. of AgClO₄ in CH₃CN. [Pd₂(**489a**-2H)(CH₃CN)₂(ClO₄)₂] reverts to [Pd₄(**489a**-2H)(Cl)₄] on treatment with chloride ion. [Pd₄(**489a**-2H)₂(Br)₄] and [Pd₄(**489a**-2H)(N₃)₄] can be obtained by the same manner [593].

The chemistry of polyazamacrocycles has been the subject of many recent studies because of interest in the organization of polynuclear metal structures as models of non-heme polymetallic proteins, molecular recognition, and super complex formation. Complexation of saturated polyazamacrocycles with 7–12 nitrogen donor atoms separated by ethylene bridges was studied and the macrocycles with eight or more nitrogen atoms were shown to afford dinuclear copper(II), nickel(II) and zinc(II) complexes [594].

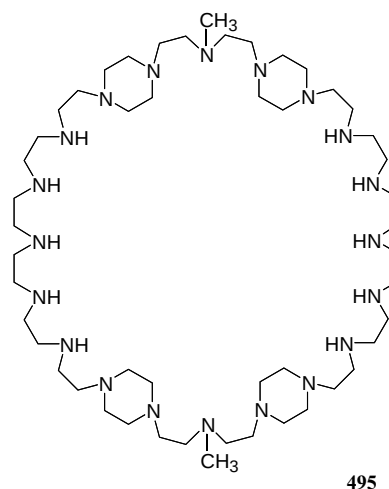
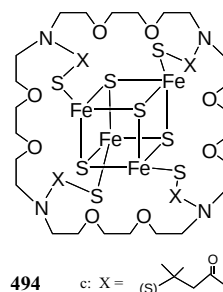
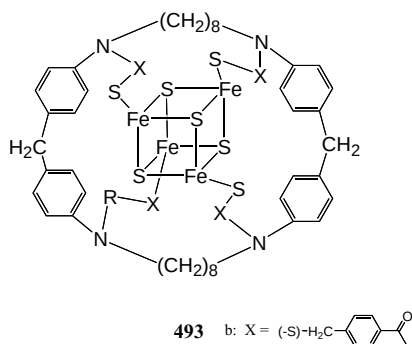
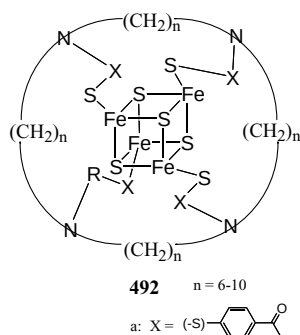
Dinuclear copper and cobalt complexes of macrocycles with two N₃ coordination sites separated by (CH₂)₂O(CH₂)₂ bridges and macrobicycles with two N₄ sites separated by similar bridges were reported [595]. Larger macrocycles, 1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane and 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexa-triacontane [596], are suggested to form trinuclear copper(II) complexes in solution. The first well characterized trinuclear copper(II) was obtained using the macrocycle **490** containing three ethylenediamine entities as donor sites separated by (CH₂)₂O(CH₂)₂ bridges [597].



The trinuclear complex $[\text{Cu}_3(\mathbf{490})(\text{OH})_2](\text{ClO}_4)_4(\text{H}_2\text{O})$ was isolated as blue crystals by treating **490** with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol. The cation $[\text{Cu}_3(\mathbf{490})(\text{OH})_2]^{4+}$ contains a central core formed by the assembly of three copper(II) ions and two hydroxo ions by the tritopic macrocycle **490** into a trigonal bipyramidal cluster $\{\text{Cu}_3(\text{OH})_2\}^{4+}$. This cluster is composed of 3 equiv. copper(II) ions bridged by two triply bound μ_3 -hydroxo ions; each copper(II) ion is coordinated to an ethylenediamine subunit and is held inside the cavity of the macrocycle in a cryptate fashion. The $\text{Cu} \cdots \text{Cu}$ separation is only 2.803 Å. The two μ_3 -hydroxo ions are located on a C_{6v} axis. The coordination polyhedron about each copper ion is a very elongated octahedron. The macrocycle has a three bladed propeller-like conformation of three-fold axial symmetry and encircles entirely the cationic core (Fig. 392) [597].

The tetratopic polyazamacrocyclic 1,10,19,28-tetraoxa-4,7,13,16,22,25,31,34-octaaza-cyclohexa-tricontane, **491**, incorporates four copper(II) ions by reaction with copper(II) perchlorate in the range pH 6–9 [598]. The resulting tetranuclear complex $[\text{Cu}_4(\mathbf{491})(\text{OH})_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ has a cubane-type $\{\text{Cu}_4(\text{OH})_4\}$ core surrounded by the macrocycle. IR, visible, FAB and EPR spectra, cyclic voltammetry, and cryomagnetic susceptibility agree with this suggestion.

Similarly a series of Fe_4S_4 clusters with large methylene **492**, cyclophane **493** and crown-ether rings **494**, which can serve as models for high potential iron–sulfur proteins, have been prepared [599]. The redox properties and the role of the macrocyclic moiety to provide a hydrophobic environment around the core in order to stabilize it toward molecular oxygen have been studied [599].



Finally the giant-size azamacrocyclic **495** has been synthesized by the reaction of the appropriate precursors in the absence of any cation templating agent. The surprising result in the preparation is the formation of the [60]-membered ring **495** rather than the expected [30]-membered ring [600]. The structure of **495** has been confirmed by X-ray analysis of a crystal of its dinuclear cadmium(II) complex, obtained by slow evaporation of an aqueous solution containing $\text{Cd}(\text{ClO}_4)_2$ and the hydrochloride salt of **495**, partially neutralised by addition of sodium hydroxide [600].

The structure of $[\text{Cd}_2(\text{H}_2\mathbf{495})](\text{ClO}_4)_6 \cdot 5\text{H}_2\text{O}$ (Fig. 393a) consists of discrete dinuclear $[\text{Cd}_2(\text{H}_2\mathbf{495})]^{6+}$ cations, perchlorate anions and lattice water molecules. The dinuclear complex cation is disposed around a crystallographic inversion center with the two cadmium(II) ions in an identical environment. The symmetry-related metal ions are separated by 10.233 Å. Each cadmium ion is coordinated in a

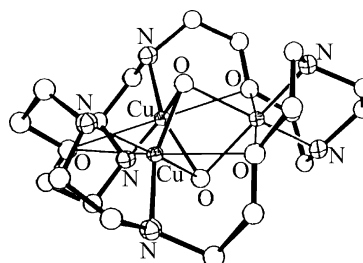


Fig. 392. Structure of $[\text{Cu}_3(\mathbf{490})(\text{OH})_2]^{4+}$ (adapted from Ref. [597]).

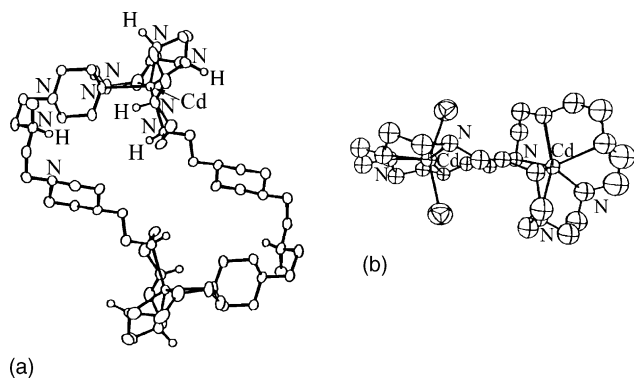


Fig. 393. Structure of $[\text{Cd}_2(\text{H}_2\text{-495})]^{6+}$ (a) and $[\text{Cd}_2(\text{496})(\text{Cl})_2]^{2+}$ (b) (adapted from Ref. [600]).

distorted trigonal prismatic environment by five secondary nitrogen atoms and by one nitrogen atom belonging to a piperazine ring. In the $[\text{Cd}_2(\text{H}_2\text{-495})]^{6+}$ cation, the two metal ions engage in coordination with the most flexible parts of the macrocycle which assumes an overall Z-conformation. The rigid piperazine rings produce an elongated macrocyclic cavity of approximate dimensions $4\text{ \AA} \times 16\text{ \AA}$ [600].

This structure can be compared with that of the dinuclear cadmium(II) complex of the [30]-membered macrocycle 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane, **496**, in which the smaller and less hindered macrocycle gives rise to a dinuclear complex where the two metal ions are in different coordination environments and are separated by $5.75\text{ \AA}$. In this structure, one of the two cadmium ions is octahedrally surrounded by two chloride ions and four adjacent nitrogen atoms of the ligand while the other is coordinated by the remaining six secondary nitrogen atoms connected by ethylenic chains and adopts a distorted trigonal prismatic coordination, very similar to that found in $[\text{Cd}_2(\text{H}_2\text{-495})]^{6+}$ [600] (Fig. 393b).

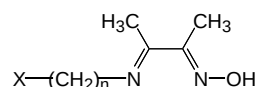
15. Polynuclear systems containing oxime ligands

15.1. Complexes with asymmetric end-off or side-off mono-oxime ligands

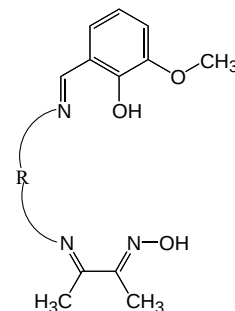
The design and synthesis of ligands containing oximes have been received attention, owing to their ability to form well defined homo- and hetero-polymetallic systems, where a relevant magnetic interaction can occur between paramagnetic centers, mediated by N–O bridges.

The coordinating ability of the imine–oxime ligands **H-497a–c** and the physico-chemical properties of the resulting complexes have been studied. The reaction in methanol of 2-[2-(2-pyridyl)ethyl]-imino-3-butanone oxime (**H-497a**), prepared in situ by condensation of diacetyl monoxime and 2-aminoethylpyridine, with $\text{Cu}(\text{ClO}_4)_2$ and the subsequent recrystallization of the crude product from CH_3CN afforded $[\text{Cu}_2(\text{497a})_2(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ [601]. The ligand

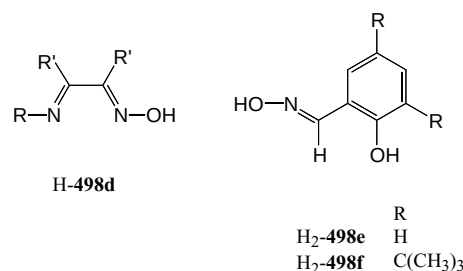
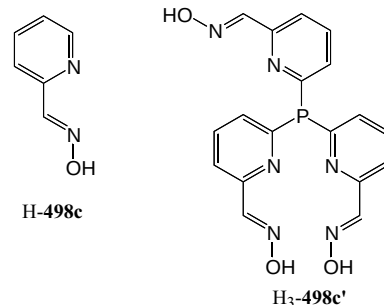
is coordinated to the copper ion to form a five-membered chelate ring involving the oxime nitrogen and the imine nitrogen and a six-membered chelate ring involving the imine nitrogen and the pyridine nitrogen. The fourth position in the coordination plane of each copper(II) ion is occupied by the oxygen of the second ligand of the dimer, resulting in bridging oxime groups. The fifth coordination position of the square pyramid about the copper ion is occupied by the weakly bound acetonitrile nitrogen. The copper(II) ion is $0.31\text{ \AA}$ above the least-squares plane of the basal coordinating atoms toward the axial ligand. The copper–copper distance is $3.693\text{ \AA}$ (Fig. 394a).



	X	n
H-497a	$\text{C}_6\text{H}_4\text{N}$	2
H-497b	$\text{C}_6\text{H}_4\text{N}$	1
H-497c	NH_2	2



H2-498a	$\text{R} = \text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$
H2-498b	$\text{R} = \text{C}(\text{CH}_3)_2\text{CH}_2$



The same reaction using ethylenediamine instead of 2-aminoethylpyridine gives rise to the tetranuclear complex

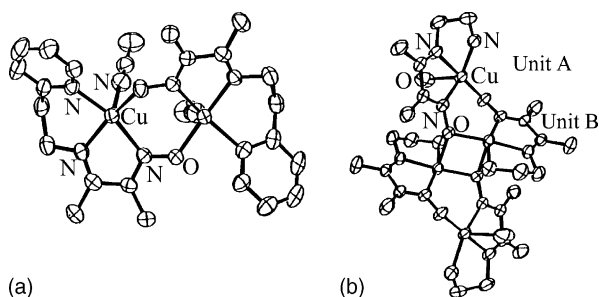


Fig. 394. Structure of $[\text{Cu}_2(\mathbf{497a})_2(\text{CH}_3\text{CN})_2]^{2+}$ (a) and of $[\text{Cu}_4(\mathbf{479c})_4(\text{ClO}_4)_2]^{2+}$ (b) (adapted from Ref. [601]).

$[\text{Cu}_4(\mathbf{497c})_4(\text{ClO}_4)_2](\text{ClO}_4)_2$ [601]. The asymmetric unit contains two copper(II) ions bridged by oxime groups to form a six-membered ring similar to that in $[\text{Cu}_2(\mathbf{497a})_2(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$. The square pyramidal coordination of the copper ions is also similar to that in $[\text{Cu}_2(\mathbf{497a})_2(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ except for the axial position; for one copper(II) ion the axial position is occupied by a perchlorate oxygen and for the remaining copper(II) ion this position is occupied by the oxime oxygen of a symmetry-related unit to form a four-membered Cu_2O_2 ring. The intradimer and interdimer $\text{Cu} \cdots \text{Cu}$ distances are respectively, 3.550 and 3.268 Å (Fig. 394b). Both dinuclear and tetranuclear copper(II) complexes show strong antiferromagnetic coupling.

$[\text{Cu}_2(\mathbf{497a})_2](\text{ClO}_4)_2$, $[\text{Cu}_2(\mathbf{497a})_2](\text{NO}_3)_2 \cdot \text{CH}_3\text{OH}$, $[\text{Cu}_2(\mathbf{497b})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ and $[\text{Cu}_2(\mathbf{497b})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, prepared by the reaction of the preformed oxime with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ [601], have a common cationic structure in which the two copper ions are bridged through two N–O groups of the oximate ligand to afford a dinuclear structure. In $[\text{Cu}_2(\mathbf{497a})_2](\text{NO}_3)_2 \cdot \text{CH}_3\text{OH}$ each copper(II) ion is coordinated to three nitrogen and to an oxygen atoms of the organic ligand and to an oxygen atom of a nitrate group providing a square pyramidal coordination. The $\text{Cu} \cdots \text{Cu}$ separation is 3.660 Å. In $[\text{Cu}_2(\mathbf{497b})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ the ClO_4^- anions are not coordinated. Each copper(II) ion has a square planar geometry. The cation moiety affords a twisted boat configuration. The $\text{Cu} \cdots \text{Cu}$ separation is 3.579 Å. In $[\text{Cu}_2(\mathbf{497b})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, derived from the crystallization of $[\text{Cu}_2(\mathbf{497b})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ in distilled water, each copper(II) ion provides a square pyramidal geometry through a weak coordination of a water molecule from the apical position, in addition to the coordination of three nitrogen and one oxygen atom in the equatorial plane [601]. ^1H NMR data show that the dinuclear structure is kept in solution.

The $-2J$ values, 835, 825, 550 and 510 cm^{-1} , respectively, indicate a strong antiferromagnetic interaction for these dicopper(II) complexes in the solid state. The $-2J$ values reflect the degree of distortion from the planarity of the dicopper(II) framework. The $-2J$ values roughly correlate with the ^1H NMR parameters; the larger the $-2J$ value, the smaller the chemical shifts and linewidths.

These complexes were found to undergo an autoreduction reaction in DMSO, DMF, and *N,N*-dimethylacetamide with the formation of mononuclear copper(I) complexes [601].

$[\text{CuGd}(\mathbf{498a})(\text{NO}_3)_3]$ and $[\text{CuGd}(\mathbf{498b})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$, deriving from the polydentate nonsymmetrical Schiff base ligands $\text{H}_2\mathbf{498a}$ and $\text{H}_2\mathbf{498b}$, have been prepared by reacting $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with the mononuclear copper(II) complexes $[\text{Cu}(\mathbf{498a})]$ or $[\text{Cu}(\mathbf{498b})]$. These mononuclear complexes have been obtained by condensation of bis-(3-methoxysalicylaldehydato)copper(II) respectively with 1-(2,5,5-trimethylhexahydro-2-pyrimidinyl)-1-ethanone oxime and 1-(2,4,4-trimethylhexahydro-2-imidazolidinyl)-1-ethanone oxime [602].

In $[\text{CuGd}(\mathbf{498a})(\text{NO}_3)_3]$ and $[\text{CuGd}(\mathbf{498b})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$ the copper(II) and gadolinium(III) ions are connected by a double bridge involving, on one hand, a phenolato oxygen and, on the other hand, nitrogen and oxygen atoms of a deprotonated oxime function. The bridging networks $\text{Cu}(\text{O}, \text{N}-\text{O})\text{Gd}$ are not planar. In $[\text{CuGd}(\mathbf{498a})(\text{NO}_3)_3]$ the copper(II) center and its four N_2O_2 neighbours are nearly coplanar while in $[\text{CuGd}(\mathbf{498b})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$ the copper(II) ion has a square pyramidal environment with an axial water molecule. The gadolinium(III) ion is 10 coordinated in both complexes, surrounded by three oxygens from $[\mathbf{498a}]^{2-}$ and seven oxygens from auxiliary ligands, from the nitrate groups and water. In $[\text{CuGd}(\mathbf{498a})(\text{NO}_3)_3]$ two nitrate ions chelate the gadolinium(III) ion while the third one chelates the gadolinium(III) ion through two oxygens and, via the third oxygen, acts as a monodentate ligand toward another symmetry-related gadolinium ion. The net result is the formation of a chain of dinuclear units $\{\text{Gd}(\text{Cu})-\text{ONO}_2=\text{Gd}(\text{Cu})-\text{ONO}_2\}$. Due to the respective orientations of neighbouring dinuclear units, the shortest contact is not a $\text{Gd} \cdots \text{Gd}$ one (6.615 Å) but a $\text{Gd} \cdots \text{Cu}$ one (5.473 Å). The related $\text{Cu} \cdots \text{Cu}$ separation is equal to 7.580 Å (Fig. 395a).

In $[\text{CuGd}(\mathbf{498b})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$ the gadolinium(III) coordination sphere is completed by seven oxygens from three chelating nitrate anions and a water molecule. The other ones are associated with oximate or nitrate groups to connect metal ions of different units. The shortest interunit metal contacts are $\text{Cu} \cdots \text{Gd} = 6.470$ Å, $\text{Gd} \cdots \text{Gd} = 6.2910$ Å, $\text{Cu} \cdots \text{Cu} = 7.986$ Å.

$[\text{CuGd}(\mathbf{498a})(\text{NO}_3)_3]$ presents an antiferromagnetic interaction, ($J \cong -0.49 \text{ cm}^{-1}$) while in $[\text{CuGd}(\mathbf{498b})(\text{NO}_3)_3]$ the interaction is ferromagnetic ($J \cong 3.5 \text{ cm}^{-1}$) [602].

A triangular $\{\text{Cu}_3\text{X}\}$ ($\text{X} = \text{OH}, \text{O}$) core is present in three related groups of copper(II) complexes. Structural feature common to all the groups is the presence three oximate functions spanning peripheral bridging positions and of three nitrogen atoms binding terminally. The three groups differ in having different types of terminal nitrogen. All complexes are strongly antiferromagnetic [602]. The trinuclear triangular copper(II) complexes of pyridine-2-carbaldoxime ($\text{H}\mathbf{498c}$) and isonitrosoketimine ligands of type

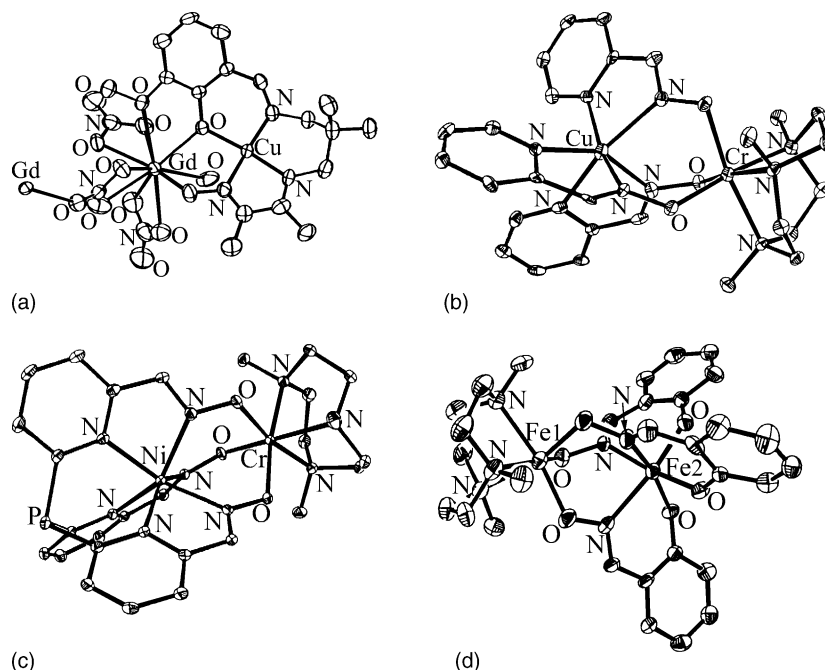


Fig. 395. Structure of $[\text{CuGd}(\mathbf{498a})(\text{NO}_3)_3]$ (a), $[\text{CrCu}(\mathbf{498c})_3(\text{Me}_3\text{-9-N}_3)]^{2+}$ (b) $[\text{CrNi}(\mathbf{498c}')(\text{Me}_3\text{-9-N}_3)]^{2+}$ (c) and $[\text{Fe}_2(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$ (d) (adapted from Refs. [602,603]).

RNC(R')C(R')NOH (**H-498d** $\text{R} = \text{CH}_2\text{CH}_3$, $(\text{CH}_2)_2\text{CH}_3$, $(\text{CH}_2)_3\text{CH}_3$, C_6H_5 ; $\text{R}' = \text{CH}_3$, C_6H_5) are strongly antiferromagnetic coupled complexes of the types $[\text{Cu}_3(\text{ligand})_3(\text{O})]^+$ and $[\text{Cu}_3(\text{ligand})_3(\text{OH})]^{2+}$, having $\{\text{Cu}_3\text{O}\}$ and $\{\text{Cu}_3\text{OH}\}$ cores, respectively [602].

Cyclic voltammetry and constant-potential electrolysis (platinum working electrode) show that complexes with a $\{\text{Cu}_3(\text{O})\}$ core uniformly display a one-electron-transfer process characterized by the oxidation-state description $\text{Cu}^{\text{III}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} + e^- \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ with E_{298}° in the range 0.3–0.6 V versus SCE in acetonitrile and dimethylformamide. The species with a $\{\text{Cu}_3(\text{OH})\}$ core do not have this electrochemical response. On the other hand, such species show a one-electron-transfer process of the type $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} + e^- \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ with E_{298}° in the range –0.3 to –0.45 V versus SCE at a hanging-mercury-drop electrode in acetonitrile. The $\{\text{Cu}_3(\text{O})\}$ core does not display this process. In effect the electrochemical behaviours of the two cores are complementary: the $\{\text{Cu}_3(\text{O})\}$ core undergoes oxidation while the $\{\text{Cu}_3(\text{OH})\}$ core undergoes reduction. Thus the core proton acts in a valve like fashion in controlling the direction of electron transfer. Addition of an acid (HClO_4) converts the $\{\text{Cu}_3(\text{O})\}$ species to the $\{\text{Cu}_3(\text{OH})\}$ species. Conversely, addition of a base (NEt_3) converts $\{\text{Cu}_3(\text{OH})\}$ to $\{\text{Cu}_3(\text{O})\}$. The electrochemical responses change accordingly with addition of acid or base. The interconversion reactions are also useful at preparative levels [602].

Pyridine-2-carbaldehyde oxime (**H-498c**) reacts with copper(II) ions to form a series of trinuclear complexes of composition $\text{Cu}_3(\mathbf{498c})_3(\text{OH})(\text{X})_n \cdot y\text{H}_2\text{O}$ ($\text{X} = \text{NO}_3^-$,

ClO_4^- , OH^- $n = 2$; $\text{X} = \text{SO}_4^{2-}$ $n = 1$) where the copper(II) ions are antiferromagnetically coupled [498]. The structure of $[\text{Cu}_3(\mathbf{498c})_3(\text{OH})(\text{SO}_4)] \cdot 16 \cdot 3\text{H}_2\text{O}$, based on a triangular Cu_3 core, confirms a prediction based on the observed magnetic moment of 1.0 BM per copper ion [603]. It is composed of trinuclear units of copper ions centered around three-fold crystallographic axes so that the three copper ions fall at the corners of an exact equilateral triangle of side 3.220 Å. In each trimeric unit the copper(II) ions are held together by the oxygen atom of the hydroxyl group, situated on the three-fold axis about which the trinuclear unit is centered, the sulfate-group, also lying on the three-fold axis but below the plane containing the copper ions, and acting as a tripod bridge bonding to all three copper ions through three of its oxygen atoms, and the three symmetry related pyridine-2-carbaldehyde oximato-groups, each of which functions as a bidentate chelate to one of the copper ions, through its two nitrogen atoms, and as a copper-copper bridging group through the nitrogen and oxygen atoms of the oximato moiety. Each copper ion is bonded to five atoms which are situated at the corners of an approximate tetragonal pyramid. The four atoms constituting the basal plane are the two nitrogen atoms one pyridine-2-carbaldehyde oximato-group, the oxygen atom from the oximato-moiety of the adjacent ligand and the oxygen atom of the central hydroxy-group. These four atoms are almost coplanar. The pyridine-2-carbaldehyde oximato-ligand is planar and the copper ion is also contained in the plane [603].

$[\text{Cr}^{\text{III}}\text{M}^{\text{II}}(\mathbf{498c})_3(\text{Me}_3\text{-9-N}_3)](\text{ClO}_4)_2$ ($\text{M} = \text{Cr}^{2+}$, Fe^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) were prepared by reaction of *syn*-pyridine-2-aldoxime in methanol with the appropriate metal(II)

salt in a 3:1 molar ratio and in the presence of triethylamine followed by the addition of $[\text{Cr}(\text{Me}_3\text{-}9\text{-N}_3)(\text{ClO}_4)_3(\text{Me}_3\text{-}9\text{-N}_3 = 1,4,7\text{-triazamethyl-}1,4,7\text{-triazacyclononane})]$ in methanol [603].

$[\text{Cr}^{\text{III}}\text{Co}^{\text{III}}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)](\text{ClO}_4)_3$ was prepared using $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and air as oxidizing agent. Although the presence of the $\text{Cr}^{\text{III}}\text{Co}^{\text{II}}$ species was observed unequivocally in the mass spectra, all attempts to isolate the species even under strict anaerobic conditions were in vain, presumably because of its strong reducing property, as is indicated by the electrochemical measurements [603].

Analogously $[\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}(\mathbf{498c}')(\text{Me}_3\text{-}9\text{-N}_3)](\text{ClO}_4)_2$ was obtained by adding $[\text{Cr}(\text{Me}_3\text{-}9\text{-N}_3)](\text{ClO}_4)_3$ to a methanolic solution containing tris-(2-aldoximate-6-pyridyl)phosphine, ($\text{H}^3\text{-}\mathbf{498c}^1$), $\text{N}(\text{Et})_3$ and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a 1:3:1 ratio [603].

In these syntheses no scrambling occurs probably because the reaction temperature is too low to surmount the activation barrier to dissociate; thus is not necessary to isolate the intermediates. The light to deep red-brown colour of these complexes is dominated by the $\{\text{Cr}^{\text{III}}\text{N}_3\text{O}_3\}$ chromophore. They are completely air-stable in the solid state and also in solution at least for a few days.

The structures of $[\text{Cr}^{\text{III}}\text{M}^{\text{II}}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)](\text{ClO}_4)_2$ ($\text{M} = \text{Mn}^{2+}$, Fe^{2+} , Ni^{2+} , Cu^{2+}), $[\text{Cr}^{\text{III}}\text{Co}^{\text{II}}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)](\text{ClO}_4)_3$ and $[\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}(\mathbf{498c}')(\text{Me}_3\text{-}9\text{-N}_3)](\text{ClO}_4)_2$ confirm that mixed-metal $\text{Cr}^{\text{III}}\text{M}^{\text{II}}$ and $\text{Cr}^{\text{III}}\text{Co}^{\text{II}}$ complexes have indeed been formed with a geometry in which two pseudo-octahedral polyhedra are joined by three oximate N–O groups. The chromium coordination geometry is distorted octahedral with three nitrogen atoms, from the facially coordinated tridentate macrocyclic amine $\text{Me}_3\text{-}9\text{-N}_3$ and three oxygen atoms, from the bridging oximate group. The second metal ion, separated from the chromium center at a distance of 3.4–3.7 Å, does not affect the geometry of the chromium center in these complexes. This second metal center is also six-fold coordinated yielding an MN_6 core. Coordination occurs facially through pyridine nitrogen atoms and three azomethine nitrogen atoms from the pyridinealdoxime ligand. The average bond lengths fall within the ranges that are considered as normal covalent bonds for manganese(II), iron(II), nickel(II) or cobalt(III) centers with high-spin configuration for the manganese(II) ion (d^5) in $[\text{CrMn}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)]^{2+}$, the nickel(II) ion (d^8) in $[\text{CrNi}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)]^{2+}$ and $[\text{CrNi}(\mathbf{498c}')(\text{Me}_3\text{-}9\text{-N}_3)]^{2+}$ and a d^6 low-spin electronic configuration for the iron(II) ion in $[\text{CrFe}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)]^{2+}$ and the cobalt(III) ion in $[\text{CrCo}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)]^{3+}$. The resultant coordination sphere around the copper center in $[\text{CrCu}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)]^{2+}$ is strongly distorted. The geometry of the copper center may be envisaged as pseudo-trigonal pyramidal with a non bonded pyridine. All of the structural data are consistent with the geometrical distortions from octahedron of the manganese(II), iron(II), cobalt(III), nickel(II) and copper(II) ions [603] (Fig. 395b and c).

The $\text{Cr}^{\text{III}}\text{Fe}^{\text{II}}$, $\text{Cr}^{\text{III}}\text{Zn}^{\text{II}}$ and $\text{Cr}^{\text{III}}\text{Co}^{\text{II}}$ complexes may be considered magnetically as mononuclear complexes. Above 20 K they exhibit essentially temperature-independent μ_{eff} values, of 3.87, 3.76 and 3.81 μ_{B} , respectively in line with three unpaired electrons localized on the chromium(III) center and thus with genuine $\text{Cr}^{\text{III}}\text{Fe}^{\text{II}}(1s)$, $\text{Cr}^{\text{III}}\text{Zn}^{\text{II}}$, and $\text{Cr}^{\text{III}}\text{Co}^{\text{II}}(1s)$ species with a low-spin diamagnetic iron(II) or cobalt(III) ions and a diamagnetic zinc(II) ion. In line with these data, the Mössbauer spectrum of $[\text{Cr}^{\text{III}}\text{Fe}^{\text{II}}(\mathbf{498c})_3](\text{ClO}_4)_2$ indicates the low spin nature of the iron(II) ion.

The magnetic moment μ_{eff} /molecule for the $\text{Cr}^{\text{III}}\text{Cr}^{\text{II}}$ complex (6.17 μ_{B} at 290 K) decreases monotonically with decreasing temperature until it reaches a value of 0.98 μ_{B} at 2 K, indicating an antiferromagnetic exchange coupling between the two paramagnetic centers ($J = -7.9 \text{ cm}^{-1}$).

The magnetic behaviour of the $\text{Cr}^{\text{III}}\text{Mn}^{\text{II}}$ complex is characteristic of a ferromagnetically coupled dinuclear complex. At 290 K the μ_{eff} value of 6.96 μ_{B} increases monotonically with decreasing temperature until it reaches a maximum at 10 K with $\mu_{\text{eff}} = 8.13 \mu_{\text{B}}$. Below 10 K there is a decrease in μ_{eff} reaching a value of 6.96 μ_{B} at 2 K.

The magnetic moment of the $\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}$ complex decreases as the temperature is lowered reaching a value of 1.71 μ_{B} at 7.4 K, resulting from the antiferromagnetic interaction between chromium(III) and nickel(II) ions ($J = -9.20 \text{ cm}^{-1}$). Below 7 K there is a decrease in μ_{eff} reaching a value of 1.46 μ_{B} .

The magnetic moment, μ_{eff} , for $\text{Cr}^{\text{III}}\text{Cu}^{\text{II}}$ complex, 4.25 μ_{B} at 290 K, on lowering of the temperature, increases monotonically until a plateau is reached in the temperature range 10–5 K with a μ_{eff} value of 4.53 μ_{B} , indicating a ferromagnetically coupled $\text{Cr}^{\text{III}}\text{Cu}^{\text{II}}$ compound ($J = +1.8 \text{ cm}^{-1}$).

$[\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}(\mathbf{498c}')(\text{Me}_3\text{-}9\text{-N}_3)](\text{ClO}_4)_2$ exhibits an essentially temperature-independent magnetic behaviour in the range 290–30 K ($\mu_{\text{eff}} = 4.85 \mu_{\text{B}}$). Below 30 K the magnetic moment decreases reaching a value of $\mu_{\text{eff}} = 3.82 \mu_{\text{B}}$ at 2 K. This is a clear indication that the antiferromagnetic exchange interaction between the chromium(III) and nickel(II) centers is negligibly small, if present at all.

The cyclic voltammograms of complexes $[\text{CrM}(\mathbf{498c})_3(\text{Me}_3\text{-}9\text{-N}_3)]^{n+}$ and $[\text{CrNi}(\mathbf{498c}')(\text{Me}_3\text{-}9\text{-N}_3)]^{2+}$, measured at room temperature in CH_3CN containing 0.1 M $[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4](\text{PF}_6)$ as supporting electrolyte at a glassy carbon working electrode, (all redox potentials are referenced in volts versus the ferrocenium/ferrocene couple used as an internal standard to be 0.09 V versus Ag/AgNO_3) show two irreversible electron-transfer waves, $E_{\text{p}}^{\text{ox}} \sim +1.30 \text{ V}$ and $E_{\text{p}}^{\text{red}} \sim -1.8 \text{ V}$ in the potential range +1.8 to –2.0 V, assigned to the redox processes of the ligand, rather than to the Cr^{III} - or M-centered electron-transfer. This ligand-centered reduction is not observed for the $\text{Cr}^{\text{III}}\text{Co}^{\text{III}}$ and $\text{Cr}^{\text{III}}\text{Cu}^{\text{II}}$ complexes where two reversible one-electron-transfer waves are detectable at $E_{1/2} = -0.52$ and -1.36 V , respectively for the $\text{Cr}^{\text{III}}\text{Co}^{\text{III}}/\text{Cr}^{\text{III}}\text{Co}^{\text{II}}$ and $\text{Cr}^{\text{III}}\text{Co}^{\text{II}}/\text{Cr}^{\text{III}}\text{Co}^{\text{I}}$ processes and one reversible

reduction is detectable at $E_{1/2} = -0.73$ V for the $\text{Cr}^{\text{III}}\text{Cu}^{\text{II}}/\text{Cr}^{\text{III}}\text{Cu}^{\text{I}}$ process.

The cyclic voltammetric behaviour of $[\text{CrM}(\mathbf{498c})_3(\text{Me}_3\text{-9-N}_3)]^{2+}$ ($\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}$), and $[\text{CrNi}(\mathbf{498c}')(\text{Me}_3\text{-9-N}_3)]^{2+}$ shows in each case one reversible one-electron oxidation at +0.71, +0.61, and +0.90 V, assigned to the M-centered oxidations resulting in the couples $\text{M}^{\text{III}}/\text{M}^{\text{II}}$ for CrMn complex, $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ for the CrFe complex and $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ for the $[\text{CrNi}(\mathbf{498c})_3(\text{Me}_3\text{-9-N}_3)](\text{ClO}_4)_2$ and $[\text{CrNi}(\mathbf{498c}')(\text{Me}_3\text{-9-N}_3)](\text{ClO}_4)_2$ complexes. No stabilization of the nickel(IV) state has been observed in the oxidation of these two last complexes [603].

$[\text{Mn}_2(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]^+$, $[\text{Fe}_2(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$, $[\text{Fe}_2(\mathbf{498f})_3(\text{Me}_3\text{-9-N}_3)]$ and $[\text{FeMn}(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$ were obtained by reaction of an appropriate metal salt with the desired salicyldioxime ligand in oxygen-free methanol, in the presence of triethylamine, followed either by the solid $[\text{Fe}(\text{Me}_3\text{-9-N}_3)(\text{Cl})_3]$ or $[\text{Mn}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{-9-N}_3)]^{2+}$ produced in situ, in stoichiometric equivalents. Attempts to characterize the species produced by the reaction of salicyldioxime with either iron(III) chloride or manganese(III) acetate are yet to be successful. However, these species are able to yield the appropriate dinuclear complexes in the presence of a base (i.e. triethylamine) and the $[\text{M}(\text{Me}_3\text{-9-N}_3)]^{3+}$ unit [$\text{M} = \text{Fe}^{3+}, \text{Mn}^{3+}$]. The function of the added base is to provide a medium needed for deprotonation of the $-\text{HC}=\text{N}-\text{OH}$ groups present [603]. $[\text{Fe}_2(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$ and $[\text{Fe}_2(\mathbf{498f})_3(\text{Me}_3\text{-9-N}_3)]$ are identical with respect to the coordination geometry of the iron(III) centers. In $[\text{Fe}_2(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$ the coordination geometry of one iron(III) ion is distorted octahedral with three nitrogen atoms, from the facially coordinated tridentate macrocyclic amine, and three oxygen atoms from the bridging oximate groups. The other iron(III) ion center is also six-fold coordinated. Coordination occurs facially through three phenolate oxygen atoms, and three azomethine nitrogen atoms from the three $[\mathbf{498e}]^{2-}$ ligands. The binuclear skeleton is not coplanar, but is bent with a $\text{Fe}\cdots\text{Fe}$ separation of 3.470 Å (Fig. 395d). The structure determination for these two diiron complexes unambiguously show that, in both structures, the presence of iron(III) ions with d^5 high-spin electron configuration [603].

Analysis of the susceptibility data yields antiferromagnetic interactions between the metal centers for the $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{III}}\text{Mn}^{\text{III}}$ complexes ($J = 4.8 \text{ cm}^{-1}$ for $[\text{FeMn}(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$, -11.8 cm^{-1} for $[\text{Fe}_2(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$ and -12.2 cm^{-1} $[\text{Fe}_2(\mathbf{498f})_3(\text{Me}_3\text{-9-N}_3)]$) but a ferromagnetic interaction for $[\text{Mn}_2(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$ ($J = 6.5 \text{ cm}^{-1}$).

Mössbauer spectra confirm the presence of the iron(III) ion in these complexes but also that in $[\text{FeMn}(\mathbf{498e})_3(\text{Me}_3\text{-9-N}_3)]$ the manganese(III) ion is coordinated to the $\text{Me}_3\text{-9-N}_3$ macrocyclic ligand. Thus Mössbauer spectra show that the metal ions have remained associated with their different ligands originating from their respective starting materials and practically no scrambling of the ligands has occurred [603].

The $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ complexes undergo two reversible oxidation processes at 0.30 and -0.28 V due to $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}\text{Mn}^{\text{IV}}$ metal centered electron transfer steps. Also it suffers two subsequent reduction processes at -0.40 and -2 V due to the reactions $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$. In both oxidation and reduction processes the first manganese ion involved is that bound to $\text{Me}_3\text{-9-N}_3$ macrocycle. The same occurs for the FeMn complex where the electrochemical oxidation $\text{Fe}^{\text{III}}\text{Mn}^{\text{III}}/\text{Fe}^{\text{III}}\text{Mn}^{\text{IV}}$ and the reductions $\text{Fe}^{\text{III}}\text{Mn}^{\text{III}}/\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}/\text{Fe}^{\text{II}}\text{Mn}^{\text{II}}$ were observed.

For the $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$ complexes the subsequent reductions $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ were observed; again the iron ion bound to $\text{Me}_3\text{-9-N}_3$ is the reduced first. The electrochemical processes with the formation of $[\text{Fe}_2]^{1+,2+,3+}$ are attributed to the generation of **498**-based phenoxyl radicals [603]. Thus for the two diiron complexes the electrochemical data suggest the generation of three ligand-centered oxidation processes, attributable to phenoxyl-radicals, rather than the formation of unusually high oxidation states at the central iron centers. On the contrary, in case of manganese, facile oxidation of metal centers rather than the ligands occurs. In contrast to the general notion that azomethine nitrogen-donor sets stabilize the 2+ oxidation state of iron centers, salicyldioxime as a ligand with coordinated phenolato and azomethine groups enormously stabilizes 3+ oxidation state in such metal centers. This is a general feature of the phenolato iron complexes [603].

The unsymmetrical Schiff base 3-((2-((1-methyl-3-oxobut-1-enyl)amino)ethyl)imino) butan-2-one oxime, ($\text{H}_2\text{-498g}$), readily obtained by reacting equimolar amounts of 4-((2-aminoethyl)amino)pent-3-en-2-one and butanedione monoxime in ethanol or in diisopropyl ether, reacts with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to give $[\text{Ni}(\text{H-498g})](\text{ClO}_4)$ that contains a protonated oxime function. The further addition of triethylamine to an acetone solution of $[\text{Ni}(\text{H-498g})](\text{ClO}_4)$ yields $[\text{Ni}(\mathbf{498g})]$ [603].

Although the same synthetic procedures allow the isolation of the related copper complexes, better yields are obtained through the use of $[\text{NH}_4\text{Et}_3][\text{Cu}(\mathbf{498g})](\text{Cl})$ or $[\text{Hpip}][\text{Cu}(\mathbf{498g})](\text{Cl})$ which are easily obtained by addition of a base (triethylamine or piperidine) to a mixture of equimolar amounts of $\text{H}_2\text{-498g}$ and CuCl_2 in acetone [603].

Precise information concerning the nature of the copper complexes is afforded by EPR spectroscopy which indicates that the environment of the copper ion comprises three nitrogen atoms, this implying that the oxygen atom of the oxime group is not involved in the coordination sphere [603].

This conclusion is supported for $[\text{Ni}(\text{H-498g})](\text{ClO}_4)$ by a structural determination. The nickel(II) ion has a slightly distorted square planar coordination and is surrounded by three nitrogen and one oxygen atoms from the ligand $[\mathbf{498g}]^{2-}$ so that the oxygen atom of the oxime function remains uncomplexed [603].

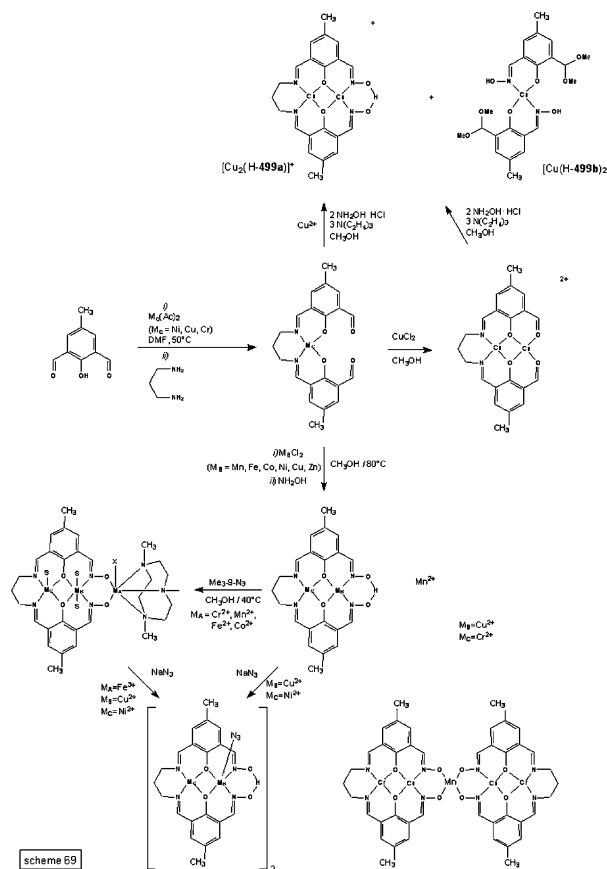
As expected the mononuclear precursors [Ni(**498g**)] and [Cu(**498g**)] effectively function as ligands to yield dinuclear or trinuclear complexes. The deprotonated oxime oxygen atom can react with auxiliary complexes to give the homo- and hetero-dinuclear and trinuclear entities [M₂(**498g**)(L)](ClO₄) (M = Cu²⁺, Ni²⁺), [MM^I(**498g**)(L)](ClO₄) (M = Cu²⁺, M^I = Ni²⁺; M = Ni²⁺, M^I = Cu²⁺), [CuCr(**498g**)(**207a**)](NO₃)·H₂O, [Cu₂M(**498g**)₂](ClO₄)₂·2H₂O (M = Cu²⁺, Zn²⁺), and [Cu₂Mn(**498g**)₂(bipy)](ClO₄)₂·3H₂O, where H-L is the Schiff base derived from the [1+1] condensation of hydroxyacetophenone and 1,2-diaminopropane. In [Cu₂(**498g**)(L)](ClO₄) a double bridge occurs between the copper ions via the oximate group and, more surprisingly, the ketonic oxygen of [**498g**]^{2−}. The former bridge links two equatorial positions while the latter is from an equatorial position at one copper(II) ion to an axial position at the copper(II) ion. One copper(II) ion is surrounded by [**498g**]^{2−} and displays a square planar N₃O geometry while the other copper(II) ion is in a square pyramidal environment, resulting in a CuN₂O₃ chromophore with an intramolecular copper···copper separation of 3.507 Å [603].

A moderate antiferromagnetic interaction is present in the dinuclear and trinuclear copper(II) complexes. A similar interaction is also observed in the Cu₂^{II}Ni^{II} and Cu₂^{II}Mn^{II} heterotrinuclear complexes and, more surprisingly, in the hetero-dinuclear Cu^{II}Cr^{III} entity (*J* = −39 cm^{−1}). In [Ni₂(**498g**)(L)](ClO₄) or [NiCu(**498g**)(L)](ClO₄) the diamagnetic nickel(II) ion is coordinated to [**498g**]^{2−}; consequently the related homo- or hetero-dinuclear complexes are paramagnetic [603]. In the trinuclear complexes [Cu₃(**498g**)₂](ClO₄)₂ and [M₂Zn(**498g**)₂](ClO₄)₂ the exchange integral between terminal copper(II) ion is *J* = −1.5 cm^{−1} while that between adjacent copper(II) ions is *J* = −108 cm^{−1} which is of the same order of magnitude as those obtained for the homo-dinuclear copper(II) complexes [603].

15.2. Complexes with symmetric side-off or end-off di-oxime ligands

Three dicopper(II) complexes with the symmetric side-off compartmental ligand H₄-**499a**, containing bridging phenolic oxygen atoms, were synthesized by stepwise condensation in the presence of copper(II) ions of 2,6-diformyl-4-methylphenol and diaminopropane, followed by hydroxylamine (Scheme 69) [602]. The complexes contain the same cation [Cu₂(H-**499a**)]⁺ and different anions, chloride, perchlorate and [Cu₂Cl₄]^{2−} [604]. The main product of the reaction precipitates in the form of [Cu₂(**499a**)](Cl). It is accompanied by a small amount of [Cu₂(H-**499a**)₂][Cu₂Cl₄], the copper(I) anion being probably formed by the reduction of copper(II) by hydroxylamine. The perchlorate salt was also obtained by the addition of NaClO₄ to a solution of the chloride derivative [604].

The main reaction (i.e. the formation of [Cu₂(H-**499a**)]⁺) is accompanied by a parallel reaction in which the azo-



Scheme 69.

methine bonds of the preformed Schiff base are cleaved, apparently with the replacement of diaminopropane by hydroxylamine. As a result, the copper(II) complex [Cu(H-**499b**)₂] was isolated as by product; the dimethyl acetal groups in [Cu(H-**499b**)₂] were formed under mild reaction conditions, by reaction of the aldehyde and/or azomethane groups with the solvent methanol [604].

In [Cu₂(H-**499a**)₂][Cu₂Cl₄] the dicopper complex cation is planar, with the copper(II) ions slightly displaced to opposite sides of the plane of the donor atoms. The Cu···Cu separation is 3.07 Å. The geometry of both copper(II) ions is square pyramidal, each forming an elongated fifth bond, either to an oxime oxygen of a different ligand or a chloride (Fig. 396a). The coordinated chloride is part of the complex [Cu₂Cl₄]^{2−} anion. The [Cu₂Cl₄]^{2−} anion is flat, with both copper(I) ions in trigonal planar environments and two chlorides bridging the two copper(I) centers. The [Cu₂Cl₄]^{2−} anion bridges two [Cu₂(H-**499a**)₂]⁺ cations, and the oxime–copper link to the other copper produces a chain structure [604].

In [Cu₄(H-**499a**)₂(CH₃OH)₃](ClO₄), two dinuclear cations, similar to those observed for [Cu₂(H-**499a**)₂][CuCl₄], are linked in a centrosymmetrical tetramer by axial coordination of oxime oxygens to copper(II) ions (Fig. 396b). The geometry of all copper(II) centers is square

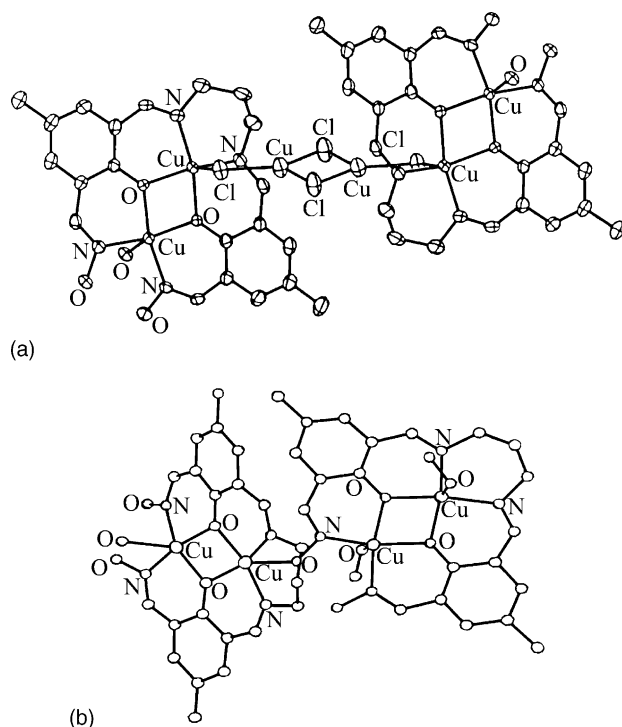


Fig. 396. Structure of $[\text{Cu}_2(\text{H-499a})]_2[\text{Cu}_2\text{Cl}_4]$ (a) and $[\text{Cu}_4(\text{H-499a})_2(\text{CH}_3\text{OH})_3]^+$ (b) (adapted from Ref. [604]).

pyramidal, with the elongated fifth bonds to axially coordinated methanol molecules or oxime oxygens. The terminal axially coordinated methanol molecules prevent the formation of a polymeric chain. The Cu–Cu separation in both terminal and central cations is 3.08 Å [604].

In $[\text{Cu}(\text{H-499b})_2]$ the copper(II) ion is located in a square planar environment, with two phenolate oxygens and two oxime nitrogens coordinated in a *trans*-geometry. The two functional groups of the ligand that are not bound to the metal ion have been converted into dimethylacetal groups and there is no oxime oxygen bridging.

The copper(II) ions in $[\text{Cu}_2(\text{H-499a})](\text{Cl})$ and $[\text{Cu}_2(\text{H-499a})]_2[\text{Cu}_2\text{Cl}_4]$ are antiferromagnetic coupled ($-2J = -698$ and -690 cm^{-1}) [604]. Moreover no significant magnetic interaction between dimers have been seen in $[\text{Cu}_2(\text{H-499a})]_2[\text{Cu}_2\text{Cl}_4]$. The asymmetrical Schiff base-oxime ligand provides an efficient pathway for magnetic interaction between two copper(II) ions. The antiferromagnetic coupling within this binuclear cation is almost the same as that in analogous symmetrical Schiff base ligands [604].

Cyclic voltammograms for $[\text{Cu}_2(\text{H-499a})](\text{Cl})$ in dimethylformamide show two separate reduction waves at -1.47 and -1.04 V , as well as an oxidation wave at $+0.04 \text{ V}$ (versus ferrocenium/ferrocene). The mixed-valent $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ complex is thermodynamically stable toward disproportionation [604].

Linear trinuclear complexes containing three different metal ions have been obtained through Scheme 69 [605]. In the structure of the complex dication $[\text{NiCu-}$

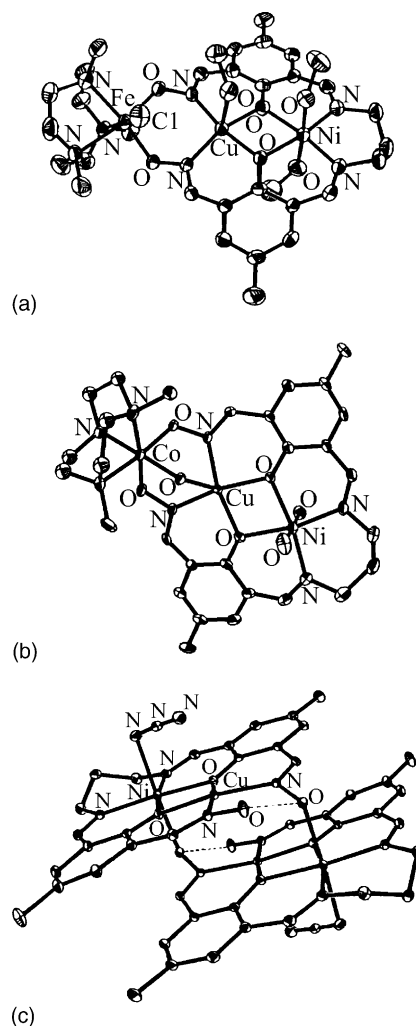


Fig. 397. Structure of $[\text{NiCuFe}(\text{499a})(\text{Me}_3\text{-9-N}_3)(\text{CH}_3\text{OH})_3]^{2+}$ (a), $[\text{NiCu-Co}(\text{499a})(\text{Me}_3\text{-9-N}_3)(\mu\text{-OH})(\text{H}_2\text{O})_2]^{2+}$ (b) and $[\text{NiCu}(\text{H-499a})(\text{N}_3)_2]$ (c) (adapted from Ref. [605]).

$\text{Fe}(\text{499a})(\text{Me}_3\text{-9-N}_3)(\text{Cl})(\text{CH}_3\text{OH})_3]^{2+}$ (Fig. 397a) containing the trinuclear $\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}$ core, the coordination geometry of the d^5 high-spin terminal iron(III) ion, is distorted octahedral with three nitrogen atoms from the facially coordinated macrocyclic amine, two oxygen atoms from the oxime ligands and a chloride ion resulting in the *fac*- $\text{FeN}_3\text{O}_2\text{Cl}$ core. The geometry of the central copper(II) ion is square pyramidal, with the elongated fifth bond to axially coordinated oxygen atom of a methanol molecule. The terminal nickel(II) ion is coordinated to two azomethine nitrogens and two bridging phenolate groups from the Schiff base oxime ligand. The nickel ion adopts a six coordinated environment by interacting with two *trans* axially disposed methanol molecules. The nickel N_2O_2 center is displaced by 0.014 Å from the mean basal plane atoms toward the oxygen atom of a methanol ligand. The Fe–Cu–Ni skeleton is almost planar, the intramolecular separations between the metal centers being $\text{Fe}\cdots\text{Cu}$ 3.695 Å , $\text{Fe}\cdots\text{Ni}$ 6.772 Å and $\text{Cu}\cdots\text{Ni}$ 3.087 Å [605].

Magnetic data on a polycrystalline sample of this trinuclear NiCuFe complex over the range 4–290 K indicate an antiferromagnetic behaviour where the magnetic exchange integrals are: $J_{\text{FeCu}} = -19.8 \text{ cm}^{-1}$, $J_{\text{CuNi}} = -118.6 \text{ cm}^{-1}$, $J_{\text{FeNi}} = 0$ (fixed) [605].

$[\text{NiCuCo}(\mathbf{499a})(\text{Me}_3\text{-9-N}_3)(\mu\text{-OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{-CN}$, also obtained according to Scheme 69, contains the trinuclear $\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}\text{Co}^{\text{III}}$ core. The coordination geometry of the terminal low spin cobalt(III) ion is distorted octahedral with three nitrogen atoms from the facially coordinated macrocycle $\text{Me}_3\text{-9-N}_3$, two oxygen atoms from the oxime ligands and a bridging hydroxide ion resulting in the fac CoN_3O_3 core. The Co–Cu–Ni skeleton is not linear; the intramolecular separations between the metal centers are $\text{Co} \cdots \text{Cu}$ 3.299 Å, $\text{Cu} \cdots \text{Ni}$ 3.081 Å and $\text{Co} \cdots \text{Ni}$ 6.236 Å. The geometry of the low spin cobalt(III) is octahedral in a CoN_3O_3 environment formed by the three nitrogen atoms of the macrocycle $\text{Me}_3\text{-9-N}_3$, the oxygen atom of a bridging $\mu\text{-OH}$ group and two oxygen atoms of the oximate ligand. The terminal nickel(II) ion is coordinated equatorially to the azomethine nitrogen atoms, and two bridging phenolate groups, from the Schiff base oxime ligand and adopts a six coordinated environment by interacting with two *trans* axially disposed water molecules. The nickel center is displaced by 0.022 Å from the mean N_2O_2 basal plane (Fig. 397b) [605].

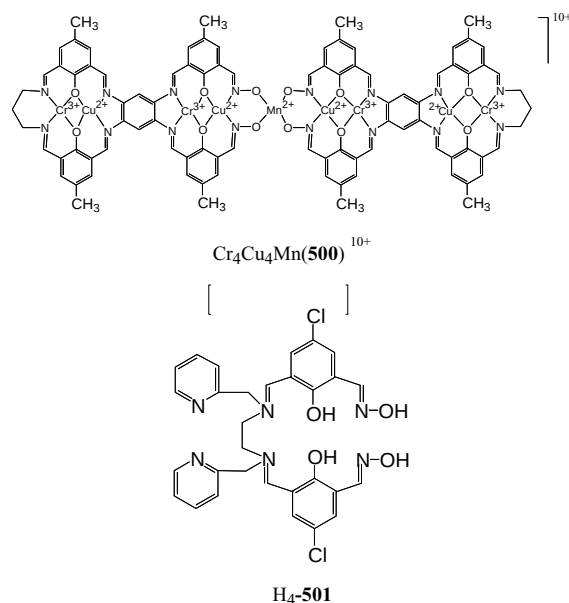
$[\text{NiCu}(\text{H-}\mathbf{499a})(\text{N}_3)]_2$, obtained by the reaction of the hetero-dinuclear complex $[\text{NiCu}(\text{H-}\mathbf{499a})](\text{Cl})_2\text{H}_2\text{O}$ or the heterotrinuclear complex $[\text{NiCuFe}(\mathbf{499a})(\text{Me}_3\text{-9-N}_3)(\text{Cl})(\text{CH}_3\text{OH})_3]^{2+}$ with NaN_3 [605], shows a centrosymmetric $[\text{CuNi}]_2$ tetranuclear structure with both nickel(II) centers having six coordinated NiN_3O_3 geometries, whereas both copper(II) are in square planar CuN_2O_2 stereochemistries. A crystallographic center of inversion lies at the midpoint of the $\text{Ni} \cdots \text{Ni}$ vector. The neighbouring nickel and copper ions in the ligand plane are bridged together through the phenolate oxygen atoms. Each copper ion is bound to two nitrogens of the oxime groups, one of which is protonated and the other deprotonated oxygen occupies the axial position of the crystallographically related second nickel by an inversion center. The azide ions are bound only to nickel ions. The $[\text{CuNi}]_2$ complex is built up of two hetero-dinuclear $\{\text{NiCu}(\text{H-}\mathbf{499a})(\text{N}_3)\}$ units, which are held together by two deprotonated oxime oxygens. Each of the oxygens is bound respectively to an axial position of nickel ions. The bridging network NiO_2Cu is nearly planar. The nickel center is coordinated to two azomethine nitrogen atoms, and two phenolate oxygen atoms in the equatorial plane. The copper center adopts a square planar geometry by coordination to two oxime nitrogen atoms, and to bridging phenolate oxygens. The copper ion is displaced by 0.115 Å from the mean N_2O_2 basal plane. The $\text{Cu} \cdots \text{Ni}$ distance is 3.085 Å in the ligand plane, while the same between the ligand planes is 4.039 Å [605] (Fig. 397c).

In DMF solution at 10 K the EPR spectra of the $[\text{CuNi}]_2$ and NiCuCo complexes exhibit a spin-doublet ground state

with inverted *g* values which demonstrate the delocalization of the unpaired electron over the CuNi core. Magnetic susceptibility measurements over the range 2–290 K confirm that the nickel(II) and copper(II) centers are antiferromagnetically coupled, ($J = -115 \text{ cm}^{-1}$ for the $[\text{CuNi}]_2$ complex and -130 cm^{-1} for the NiCuCo complex). Considering the dimer $[\text{CuNi}]_2$ as a single tetranuclear unit, the coupling constant *J'* through the path Cu–N–O–Ni is very small ($\approx 1 \text{ cm}^{-1}$) but positive (ferromagnetic coupling) [605].

A synthetic strategy for the preparation of the heteropentanuclear complex $[\text{Cr}_2\text{Cu}_2\text{Mn}(\mathbf{499a})_2]^{4+}$, containing chromium(III), copper(II) and manganese(II) ions has been developed starting from the acyclic compartmental ligand, obtained by condensation of 2,6-diformyl-4-chlorophenol and 1,3-diaminepentane (Scheme 69) [606]. The location of the chromium(III) ion was achieved by working with a partially synthesized ligand having only one desirable coordination site and a reactive form of chromium. Once that site is occupied by the chromium(III) ion, the intermediate in hand is substitution inert and is an ideal reagent for later stages of selective synthesis. The free formyl groups of the ligand are then altered to make the second compartment a strongly binding site and the complex is then formed with copper(II) ion. Since the tetradentate chelation site is strongly preferable to the external didentate site, the location of the copper ion is assured. Then it remains but to precipitate with the third metal ion, manganese, which does not compete effectively with copper(II) for the more strongly binding compartmental site. This pentanuclear complex has a high effective spin due to very strong magnetic coupling [606].

As an extension of this synthetic strategy, the complex $[\text{Cr}_8\text{Cu}_8\text{Mn}(\mathbf{500})_2]^{10+}$ has been prepared by the reaction the complex precursor $[\text{Cr}_4\text{Cu}_4(\mathbf{500})]^{8+}$ with manganese(II) salts [606].



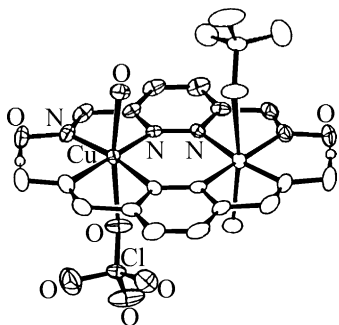


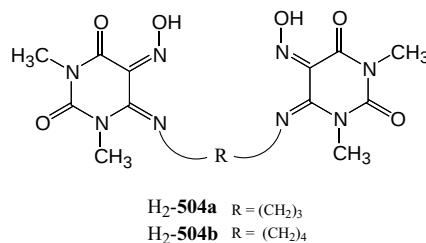
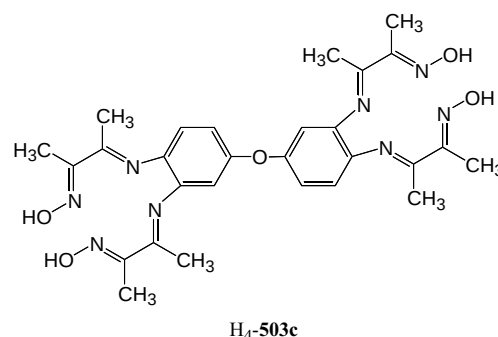
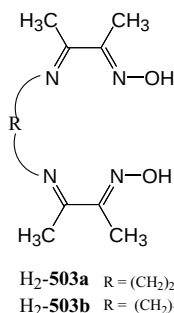
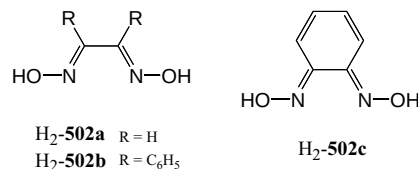
Fig. 398. Structure of $[\text{Cu}_2(\text{H-12c})_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$ (adapted from Ref. [607]).

The mononuclear nickel(II) complex $[\text{Ni}(\mathbf{360})]$, derived from the functionalized acyclic diformyl ligand $\text{H}_2\text{-360}$ ($\text{X} = \text{Cl}$), reacts with hydroxylamine hydrochloride in the presence of triethylamine to form the mononuclear complex $[\text{Ni}(\text{H}_2\text{-501})]$. The related dinuclear nickel(II) complex $[\text{Ni}_2(\text{H-501})](\text{Cl})$ has been obtained by either incorporation of the second metal ion in the preformed mononuclear complex $[\text{Ni}(\text{H}_2\text{-501})]$ or by the interaction of $[\text{Ni}(\mathbf{360})]$ with 1 equiv. of nickel(II) salt, followed by the addition of hydroxylamine hydrochloride and triethylamine [423].

In $[(\text{Cu}_2(\text{H-12c})_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2)]$, prepared by reaction in warm water or methanol of $\text{H}_2\text{-12c}$ with $\text{Cu}(\text{ClO}_4)_2$, the $\{\text{Cu}_2(\text{H-12c})_2\}^{2+}$ moiety is nearly planar (Fig. 398) and the two copper(II) ions, 3.760 Å apart, are linked by two diazine fragments in an essentially planar dimeric arrangement of two tetradentate ligands with oxime nitrogen atoms completing the equatorial coordination. The intra-complex hydrogen bridges link the terminal oximate moieties of the two H-12c anions to give a binucleating macrocycle type molecule. The hydrogen bridge is asymmetric with the hydrogen atom bonded to one oxygen atom of a ligand and hydrogen bonded to the other one. The copper(II) ion has an octahedral surrounding. Each basal plane includes two nitrogen atoms of the oximate groups and two nitrogen atoms of the pyridazine rings. The apical positions are occupied by oxygen atoms of a water molecule and a perchlorate anion. The crystal structure is further stabilized by intermolecular hydrogen bonds. The hydrogen atoms of coordinated water bridge one oxygen atom of one perchlorate anion and one oxygen atom of an oximate group [607]. In this complex a strong antiferromagnetic interaction ($J = -536 \text{ cm}^{-1}$) is operating [607].

The oximes $\text{H}_2\text{-502}$ and $\text{H}_2\text{-503}$, when reacted with transition metal ions, form the mononuclear complexes $[\text{M}(\text{H-502})_2]$ and $[\text{M}(\text{H-503})(\text{X})]$, which, under basic conditions, become excellent ligands for the subsequent synthesis of homo- or hetero-polynuclear complexes containing copper(II), nickel(II), chromium(III) ions, etc [608]. Thus the homotrimeric copper(II) complexes $[\text{Cu}_3(\text{L})_2(\text{bipy})_2(\text{CH}_3\text{OH})_2(\text{NO}_3)_2]$ and $[\text{Cu}_3(\text{L})_2(\text{phen})_2(\text{CH}_3\text{OH})_2(\text{NO}_3)_2]$ ($\text{H}_2\text{-L} = \text{H}_2\text{-502a}$, $\text{H}_2\text{-502b}$ or $\text{H}_2\text{-502c}$; $\text{bipy} = 2,2'$ -bipyridyl; $\text{phen} = 1,10$ -phenanthroline) were synthesized either

by the reaction of methanolic solution of $[\text{Cu}(\text{H-L})_2]$ and $[\text{Cu}(\text{bipy})_2](\text{NO}_3)_2$ or $[\text{Cu}(\text{phen})_2](\text{NO}_3)_2$ in the 1: 2 molar ratio or by the reaction of $[\text{Cu}(\text{H-L})_2]$, copper(II) nitrate trihydrate and an end-cap ligand (bipy or phen) in the 1:2:2 mol ratio. The nitrate complexes were obtained as the adducts of two methanol molecules while the similar perchlorate complexes were obtained as the solvent-free forms [608].



$[\text{Cu}_3(\mathbf{502a})_2(\text{NO}_3)_2(\text{bipy})_2(\text{CH}_3\text{OH})_2]$ and $[\text{Cu}_3(\mathbf{502b})_2(\text{NO}_3)_2(\text{bipy})_2(\text{CH}_3\text{OH})_2]$ have an essentially similar trinuclear structure where $[\text{Cu}(\mathbf{502a})]^{2+}$ or $[\text{Cu}(\mathbf{502b})]^{2+}$ functions as a bridge between two copper(II) ions through its deprotonated oximate oxygens. The configuration around the central copper (with two $[\mathbf{502a}]^{2+}$ and $[\mathbf{502b}]^{2+}$ ions) is an elongated octahedron with two NO_3^- ions above and below $[\text{Cu}(\mathbf{502a})_2]^{2-}$ or $[\text{Cu}(\mathbf{502b})_2]^{2-}$. The configuration around the terminal copper ion is a square pyramid with two

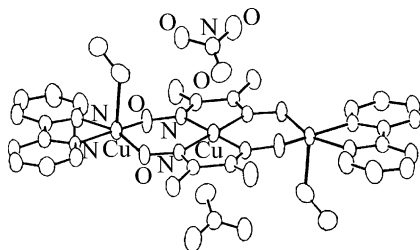


Fig. 399. Structure of $[\text{Cu}_3(\mathbf{502a})(\text{NO}_3)_2(\text{bipy})_2(\text{CH}_3\text{OH})_2]$ (adapted from Ref. [608]).

nitrogens of bipy and two oxygens of oximate groups in the basal plane and the methanol oxygen at the apical site [608] (Fig. 399).

Cryomagnetic investigations (80–300 K) reveal the operation of a very strong antiferromagnetic spin exchange ($-J > 300 \text{ cm}^{-1}$) through the oximate bridges, causing complete or nearly complete spin coupling even at room temperature. Based on EPR spectra in methanol, it was suggested that the unpaired electron is localized on the terminal copper ion. The complexes dimerizes in dimethylformamide, especially at a low temperature, their frozen solutions show an EPR spectrum typical of the spin-triplet state [608].

The mononuclear copper complex $[\text{Cu}(\text{H-}\mathbf{503a})(\text{H}_2\text{O})](\text{ClO}_4)$ was prepared by refluxing in methanol $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, CH_3COONa , 1,3-diaminopropane and 2,3-butanedione monooxime for 17 h, followed by precipitation with NaClO_4 . The crystals, obtained by recrystallization of the crude product from H_2O , show the coordination geometry about the copper(II) ion is square pyramidal. The basal plane of this square pyramid contains the four coplanar nitrogen atoms of the quadridentate ligand. The copper(II) ion is displaced only 0.40 Å above the plane of the four coordinating nitrogen atoms, in the direction of the water molecule which occupies the apical position in the coordination sphere about the metal ion [609].

The reaction in methanol of 1,3-diaminopropane, diacetylmonooxime and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ forms $[\text{Cu}(\text{H-}\mathbf{503a})(\text{ClO}_4) \cdot 1/2 \cdot \text{CH}_3\text{OH}]$ [609,610] where each copper ion is coordinated to a tetradentate ligand through four coplanar nitrogen atoms and each copper ion is also coordinated to an oxime oxygen of the adjacent unit to form singly bridged, zigzag chains. The methanol molecules are also weakly coordinated in axial positions of half of the copper ions [610]. Room temperature and their frozen solutions each showed an EPR spectrum typical of the spin-triplet state [610].

Under appropriate experimental conditions $[\text{Cu}(\text{H-}\mathbf{503a})]^+$ reacts with copper(II) perchlorate to form the trinuclear complex $[\text{Cu}_3(\mathbf{503a})_2](\text{ClO}_4)_2$. In this complex the central copper ion is located on the two-fold axis and coordinated by oximate oxygens of two $\{\text{Cu}(\mathbf{503})\}$ entities. The coordination geometry around the central copper ion is a flattened tetrahedron. The whole trinuclear cation is not

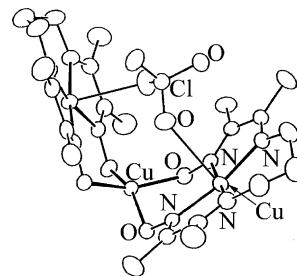


Fig. 400. Structure of $[\text{Cu}_3(\mathbf{503a})_2](\text{ClO}_4)_2$ (adapted from Ref. [611]).

coplanar and bent at the bridging oximate oxygens so that it assumes a butterfly shape. The interatomic distance between the central and the peripheric copper(II) ions is 3.551 Å. One of the perchlorate ions is located inside the cavity of the cation and weakly bonding to two copper ions. Another perchlorate ion is free from the coordination to copper and disordered. In the crystal the trinuclear cations interact with each other at the terminal copper ions. The peripheral copper ions are weakly coordinated by the oxime oxygen of the centrosymmetrically related adjacent molecule translated by one unit cell along the *c* axis. Thus, the interactions between adjacent cations form a doubly bridged infinite chain [611] (Fig. 400). Cryomagnetic investigations in the range 80–300 K reveal a strong antiferromagnetic spin-exchange interaction within the molecule ($J = -290.8 \text{ cm}^{-1}$).

$[\text{Cu}(\text{H-}\mathbf{503a})(\text{H}_2\text{O})](\text{ClO}_4)$ dissolves in methanol or water in the presence of a base with the concomitant formation of the neutral species $[\text{Cu}(\mathbf{503a})(\text{H}_2\text{O})]$ which can function as a ligand for the formation of the homo- and hetero-dinuclear complexes $[\text{Cu}_2(\mathbf{503a})(\text{Me}_3\text{-9-N}_3)]^{2+}$ and $[\text{CuM}(\mathbf{503a})(\text{X})(\text{Me}_3\text{-9-N}_3)]^{n+}$ ($n = 1, 2$; $\text{M} = \text{Cr}^{3+}, \text{Mn}^{2+}, \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Co}^{3+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$; $\text{X} = \text{Cl}^-, \text{CH}_3\text{COO}^-, \text{CH}_3\text{O}^-$), when reacted with the appropriate metal ion and $\text{Me}_3\text{-9-N}_3$ as end-up ligand. In the presence of a counter anion, e.g. ClO_4^- or PF_6^- dark crystals of the hetero-dinuclear complexes are assembled in this manner in good yields. The same type of reaction in the presence of acetate ions affords complexes containing a μ_2 -bridging acetate ion [612].

These dinuclear complexes are quasi-isostructural, with the copper(II) ion in a distorted square pyramidal CuN_4O environment and the M^{n+} ion, except for that in the dicopper(II) complex, six coordinated with a MN_3O_3 or $\text{MN}_3\text{O}_2\text{Cl}$ coordination sphere. For $\text{M} = \text{Cu}^{2+}$, the coordination geometry of the second copper(II) ion is square pyramidal with a CuN_3O_2 chromophore [612].

In $[\text{Cu}^{\text{II}}\text{Cr}^{\text{III}}(\mathbf{503})(\text{CH}_3\text{O})(\text{Me}_3\text{-9-N}_3)(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ the copper ion is in a distorted square pyramidal environment with four nitrogens in the basal plane and the fifth, apical position occupied by a water molecule. The chromium coordination geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine and three oxygen atoms from the

bridging oximate group and the third from a monodentate methoxy group. The binuclear skeleton is not coplanar but is slightly bent with a Cu...Cr separation of 3.86 Å. The coordinated water at the copper(II) center is situated at an antiposition with respect to the methoxy group of the chromium(III) center (Fig. 401a) [612].

The X-ray structure of $[\text{Cu}^{\text{II}}\text{Mn}^{\text{III}}(\mathbf{503a})(\mu\text{-CH}_3\text{COO})\text{-(Me}_3\text{-9-N}_3\text{)}]\text{ClO}_4\cdot 2\text{H}_2\text{O}$ confirms that a hetero-dinuclear complex with a Cu...Mn distance of 3.539 Å has indeed been formed as a result of the sharing of a face between a square pyramid and an octahedron. The coordination environment around the copper ion is distorted square pyramidal with four nitrogens at the equatorial planes and the carboxylate oxygen of the bridging acetate group at the axial position. One of the oxygen atoms of a perchlorate anion is situated at the other axial position of the copper(II) ion at a nonbonding distance. The manganese coordination geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine and three oxygen atoms, two from the bridging oximate group and one from the bridging acetate group. The ring conformation of the macrocyclic mine ligand ($\text{Me}_3\text{-9-N}_3$) in is $\delta\delta\delta$ (Fig. 401b) [612].

Also $[\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}(\mathbf{503a})(\text{Cl})(\text{Me}_3\text{-9-N}_3)(\text{H}_2\text{O})](\text{ClO}_4)_2$ (Fig. 401c) has an hetero-dinuclear structure. The d^5 high-spin iron(III) center is six coordinated, the nitrogen atoms of the cyclic amine and two oxygen atoms of the oxime oxygens

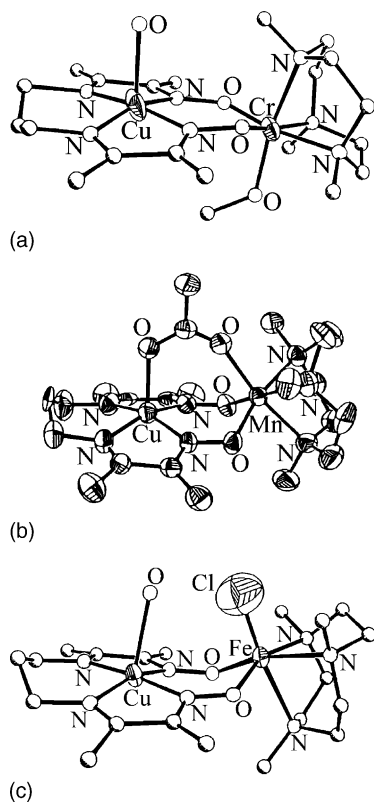


Fig. 401. Structure of $[\text{CrCu}(\mathbf{503a})(\text{CH}_3\text{O})(\text{M}_3\text{-9-N}_3)(\text{H}_2\text{O})]^{2+}$ (a) $[\text{CuMn}(\mathbf{503a})(\mu\text{-CH}_3\text{COO})(\text{Me}_3\text{-9-N}_3)]^{2+}$ (b) and of $[\text{CuFe}(\mathbf{503a})(\text{Cl})(\text{Me}_3\text{-9-N}_3)(\text{H}_2\text{O})]^{2+}$ (c) (adapted from Ref. [612]).

forming the equatorial plane of an octahedron, the apexes of which are occupied by the third nitrogen of the cyclic ligand $\text{Me}_3\text{-9-N}_3$ and a chlorine atom. The coordination geometry of the copper(II) center is square pyramidal. The coordinated water molecule at the copper center and the chloride ion at the iron(III) center are in the *cis* positions. The dinuclear cation is bent. The Cu...Fe separation is 3.66 Å. The iron ion is situated 0.29 Å above the basal plane toward the apical chlorine atom [612].

Analysis of the susceptibility data yields a strong anti-ferromagnetic interaction ($2J = -596 \text{ cm}^{-1}$) between adjacent copper(II) ions in the dicopper(II) complex. This is in complete accord with the lack of EPR signals up to 50 K. The strength of the effective antiferromagnetic interaction decreases with increasing number of unpaired electrons in this series, $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ ($J = -298 \text{ cm}^{-1}$) > $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ ($J = -99.2 \text{ cm}^{-1}$) > $\text{Cu}^{\text{II}}\text{Co}^{\text{II}}$ ($J = -53.8 \text{ cm}^{-1}$) > $\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}$ ($J = -41.4 \text{ cm}^{-1}$) $\sim$ $\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}$ ($J = -44.9 \text{ cm}^{-1}$ for CH_3COO^- and -38.8 cm^{-1} for $\text{X} = \text{Cl}$). Moderately strong ferromagnetic interactions have been observed for $\text{Cu}^{\text{II}}\text{Mn}^{\text{III}}$ ($2J = +109 \text{ cm}^{-1}$) and $\text{Cu}^{\text{II}}\text{Cr}^{\text{III}}$ complexes ($2J = +37 \text{ cm}^{-1}$) [612].

$[\text{Cu}(\text{H-}\mathbf{503a})(\text{H}_2\text{O})]^+$ forms with copper(II) or nickel(II) perchlorate in the presence of 2,2'-bipyridine (bipy), 2,2':6',2'' terpyridine (terpy) or 1,4,8,11-tetraazacyclotetradecane (cyclam) the complexes $[\text{Cu}_2(\mathbf{503})(\text{bipy})(\text{H}_2\text{O})_2](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$, $[\text{Cu}_2(\mathbf{503})(\text{terpy})](\text{ClO}_4)_2$ and $[\text{CuNi}(\mathbf{503a})(\text{cyclam})](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ [613].

In $[\text{Cu}_2(\mathbf{503a})(\text{bipy})(\text{H}_2\text{O})_2]^{2+}$ the $\{\text{Cu}(\mathbf{503a})\}$ fragment coordinates to the second copper(II) ion through the deprotonated oximate oxygens to afford a dinuclear entity doubly bridged by oximate groups in the *cis* arrangement (Fig. 402). $[\mathbf{503a}]^{2-}$ acts simultaneously as a tetradentate toward one copper ion and as a bidentate ligand toward the second copper ion through its nitrogen and oxygen atoms, respectively. The coordination geometry around both copper(II) ions is distorted square pyramidal. The four nitrogen atoms of $[\mathbf{503a}]^{2-}$ at one copper ion and two oximate oxygen atoms and the two bipyridyl nitrogen atoms at the other copper ion build the corresponding basal planes; the fifth coordination position of the square pyramids about the metal ions is occupied by weakly bound water molecules. The four nitrogen atoms from $[\mathbf{503a}]^{2-}$ are coplanar whereas the copper ion inside the N_4 site is slightly displaced from this mean plane by 0.170 Å towards the axial water oxygen. The intramolecular Cu...Cu separation (3.691 Å) is almost

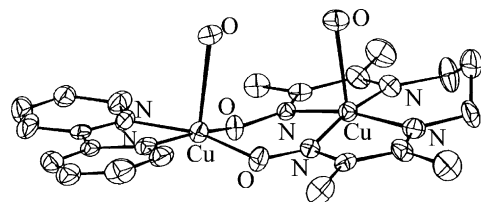


Fig. 402. Structure of $[\text{Cu}_2(\mathbf{503a})(\text{bipy})(\text{H}_2\text{O})_2]^{2+}$ (adapted from Ref. [612]).

identical to the shortest intermolecular metal–metal distance (3.697 Å) [612].

The magnetic behaviour of $[\text{Cu}_2(\mathbf{503a})(\text{bipy})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\text{Cu}_2(\mathbf{503a})(\text{terpy})](\text{ClO}_4)_2$ and $[\text{CuNi}(\mathbf{503a})(\text{cyclam})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, investigated in the temperature range 50–300 K, gives an exchange coupling constant value of -674 , -174 and -204 cm^{-1} , respectively [613].

Moreover the homo- and hetero-dinuclear complexes, $[\text{Cu}_2(\mathbf{503a})(\text{phen})(\text{CH}_3\text{OH})_2](\text{X})_2$ ($\text{X} = \text{NO}_3^-$, ClO_4^-), $[\text{NiCu}(\mathbf{503a})(\text{bipy})(\text{H}_2\text{O})](\text{ClO}_4)_2$, and $[\text{Ni}_2(\mathbf{503a})(\text{bipy})_2](\text{ClO}_4)_2$ together with the related complexes with 3,3'-ethylenedinitrilobis(2-butanoneoxime ($\text{H}_2\mathbf{503b}$)) have been prepared and characterized. In $[\text{Cu}_2(\mathbf{503a})(\text{phen})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$ the mononuclear entity $\{\text{Cu}(\mathbf{503})\}$ coordinates to the second copper(II) ion through the deprotonated oximate oxygens to afford a dinuclear skeleton doubly bridged by oximate groups in a *cis*-arrangement. The copper(II) ion is planarly surrounded by four nitrogen atoms of the oximate ligand $[\mathbf{503}]^{2-}$ [614]. One of the methanol molecules weakly coordinates to one copper ion. Further, one of the perchlorate ions is more weakly bonded to this copper ion. The configuration around one copper ion is a distorted octahedron with the metal ion slightly displaced from the N_4 plane towards the methanol oxygen. The other perchlorate ion is free from coordination and disordered. The coordination geometry around the other copper ion is a distorted square pyramid with two oximate oxygens and two nitrogens of the phenanthroline ligand on the basal plane and a methanol oxygen at the apical position [614].

The homo-dinuclear copper(II) complexes show a strong intramolecular antiferromagnetic spin-exchange interaction ($-J = 413.3\text{--}433.0 \text{ cm}^{-1}$). The magnetic moment (per molecule) of the nickel(II)–copper(II) complex is $1.80\mu_{\text{B}}$ at room temperature and the moment of the dinuclear nickel(II) complex is $2.94\mu_{\text{B}}$, demonstrating that the $\{\text{Ni}(\mathbf{503})\}$ entity of these complexes is diamagnetic [614].

The reactions of $[\text{Cr}(\mathbf{207a})(\text{H}_2\text{O})_2](\text{NO}_3)_3$ with $[\text{Cu}(\text{H}\mathbf{503a})](\text{ClO}_4)$ (1:1 mole ratio) or with $[\text{Cu}(\text{H}\mathbf{502a})](\text{ClO}_4)$ (2:1 mole ratio) readily form $[\text{CrCu}(\mathbf{503a})(\mathbf{207a})](\text{ClO}_4)$ and $[\text{Cr}_2\text{Cu}(\mathbf{502a})_2(\mathbf{207a})_2]$, respectively. Magnetic susceptibility measurements in the temperature range 4.2–300 K demonstrates the operation of a ferromagnetic interaction between the adjacent chromium(III) and copper(II) ions through oximate bridges in both complexes. The exchange integrals were evaluated as $+12.6$ and $+13.0 \text{ cm}^{-1}$ for $[\text{CrCu}(\mathbf{503a})(\mathbf{207a})](\text{ClO}_4)$ and $[\text{Cr}_2\text{Cu}(\mathbf{502a})_2(\mathbf{207a})_2]$, respectively [615].

The tetraoxime $\text{H}_4\mathbf{503c}$, accomplished by reacting 3,3'-4,4'-tetraminodiphenylether with 2,3-butanedione dioxime in aqueous CH_3OH at 50°C for 48 h and recrystallizing the resulting product from a mixture of H_2O and $\text{C}_2\text{H}_5\text{OH}$, reacts with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetone to afford $[\text{Cu}_2(\text{H}_2\mathbf{503c})](\text{ClO}_4)_2$ [615]. By reacting this dinuclear copper(II) complex in CH_3OH with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and a bipy the an end-cap ligand, $[\text{Cu}_4(\mathbf{503c})(\text{bipy})_2](\text{ClO}_4)_4$ was synthesized [615]. $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ reacts with $\text{H}_4\mathbf{503c}$ in

anhydrous acetone to form $\text{Co}_2(\text{H}_2\mathbf{503c})(\text{Br})_4$ which by metathesis with MX , i.e. KNCS , NaCN or NaN_3 , gives rise to $\text{Co}_2(\text{H}_2\mathbf{503c})(\text{Br})_2(\text{X})_2$. These dinuclear complexes, when treated with pyridine, produce $[\text{Co}_2(\text{H}_2\mathbf{503c})(\text{Br})_2(\text{py})_2](\text{X})_2$ or $[\text{Co}_2(\text{H}_2\mathbf{503c})(\text{CN})_2(\text{py})_2](\text{Br})_2$ [615].

N,N' -Bis(1,3-dimethyl-5-nitrosopyrimidine-2,4(1H,3H)-dion-6-yl)propylenediamine, $\text{H}_2\mathbf{504a}$, contains two ionisable protons that are involved in the amino–nitroso–ketone (**I**) $\leftrightarrow$ imino–oxime–ketone (**II**) $\leftrightarrow$ imino–nitroso–enol (**III**) tautomeric equilibrium. IR and ^1H NMR results seem to indicate that form **II** is dominant in both the solid state and solution. Even though form **II** is dominant in solution, just prior to complexation the tautomeric equilibrium may be modified by several factors, such as the nature of the solvent, the presence of base, or the nature of the metal cation, and therefore, a potentially rich coordination chemistry is available. Nevertheless, the tetradentate coordination modes of the ligand, in which the metal ion occupies the inside site, are expected to be favoured over the outside bidentate ones [616].

When $\text{H}_2\mathbf{504a}$ is allowed to react in hydroethanolic basic medium with a copper(II) salt, $[\text{Cu}(\mathbf{504a})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ is obtained in good yield while when $\text{H}_2\mathbf{504a}$ is reacted with an excess of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ethanol $[\text{Cu}_2(\text{H}\mathbf{504a})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})](\text{ClO}_4)_3$ is formed, where the ligand behaves as monodeprotonate bridging group. This dinuclear compound reacts with NaCl in ethanol/water (5:1) to afford $[\{\text{Cu}_3(\text{H}\mathbf{504a})(\mathbf{504a})(\text{H}_2\text{O})\}(\mu\text{-Cl})](\text{ClO}_4)_2 \cdot 4.88\text{H}_2\text{O}$ [616]. $\text{H}_2\mathbf{504a}$ reacts with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in absolute ethanol to form $[\text{Cu}(\text{H}\mathbf{504a})](\text{ClO}_4)$ which, by reaction with water, produces $[\text{Cu}(\mathbf{504a})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$. The same mononuclear complex was obtained also when $[\text{Cu}_2(\text{H}\mathbf{504a})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})](\text{ClO}_4)_3$ is dissolved in water. It seems that, depending on the water/ethanol ratio, complexes with deprotonated or partly deprotonated NOH groups can be obtained. This may explain the presence of both types of these groups in $[\{\text{Cu}_3(\text{H}\mathbf{504a})(\mathbf{504a})(\text{H}_2\text{O})\}(\mu\text{-Cl})](\text{ClO}_4)_2 \cdot 4.88\text{H}_2\text{O}$, which was prepared in water/ethanol [616].

$[\text{Cu}(\mathbf{504a})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ contains three lattice water molecules, involved in an extended network of hydrogen bonds. The CuN_4O coordination polyhedron exhibits a distorted square pyramidal geometry, in which two amino and two oximate nitrogen atoms form the basal plane whereas the oxygen atom from a water molecule occupies the apical position [616] (Fig. 403a).

A nearly coplanar dinuclear structure was assumed for $[\text{Cu}_2(\text{H}\mathbf{504a})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})](\text{ClO}_4)_3$ on the basis of the structure found for $[\text{Cu}_2(\mu\mathbf{504a})(\text{bipy})](\text{ClO}_4)_2$, obtained by $[\text{Cu}_2(\text{H}\mathbf{504a})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})](\text{ClO}_4)_3$ [616].

In $[\text{Cu}_3(\text{H}\mathbf{504a})(\mathbf{504a})(\mu\text{-Cl})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 4.88\text{H}_2\text{O}$ (Fig. 403b) the three copper ions are arranged at the corners of an isosceles triangle. Each terminal copper(II) ion and the central copper(II) ion are bridged by *syn*–*syn* oximate groups with a $\text{Cu} \cdots \text{Cu}$ distance of 3.373 Å , whereas a chloride anion bridges the two terminal copper ions with a

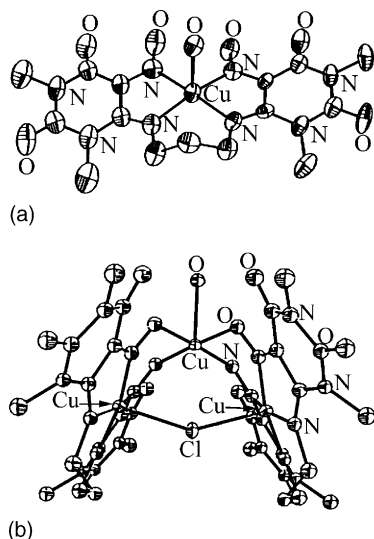


Fig. 403. Structure of $[\text{Cu}(\mathbf{504a})(\text{H}_2\text{O})]$ (a) and $[\{\text{Cu}_3(\text{H-}\mathbf{504a})(\mathbf{504a})-(\text{H}_2\text{O})\} (\mu\text{-Cl})]^{2+}$ (b) (adapted from Ref. [616]).

$\text{Cu} \cdots \text{Cu}$ distance of 4.770 Å. The central copper(II) ion exhibits a square pyramidal CuO_5 coordination environment with four oxygen atoms of oximate groups in the basal plane and the water oxygen at the apical site. The terminal copper ions occupy the N_4 inner site of the ligand with the chloride bridging anion occupying the axial position of the square pyramidal CuN_4Cl coordination environment [616].

Magnetic studies on $[\text{Cu}_2(\text{H-}\mathbf{504a})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})](\text{ClO}_4)_3$, and $[\text{Cu}_2(\mu\text{-}\mathbf{504a})(\text{bipy})](\text{ClO}_4)_2$ reveal that the very strong antiferromagnetic exchange interaction mediated by the oximate groups causes a complete spin coupling at room temperature: the complexes were found to be diamagnetic at room temperature [616]. Moreover $[\{\text{Cu}_3(\text{H-}\mathbf{504a})(\mathbf{504a})(\mu\text{-Cl})(\text{H}_2\text{O})\}(\text{ClO}_4)_2 \cdot 4.88\text{H}_2\text{O}]$ exhibits a very strong antiferromagnetic exchange interaction through the oximate bridges ($J = -189 \text{ cm}^{-1}$), leading to complete spin coupling at 120 K [616].

$[\text{Cu}(\mathbf{504a})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ reacts with $[\text{Ni}(\text{Me}_6\text{-14-N}_4)](\text{ClO}_4)_2$ in water or with a neutral aqueous solution of $[\text{Ni}(\text{OH})(\text{Me}_3\text{-12-N}_3)]_2(\text{ClO}_4)_2$ giving rise to $[\text{CuNi}(\mathbf{504a})(\text{Me}_6\text{-14-N}_4)(\text{ClO}_4)](\text{ClO}_4) \cdot \text{H}_2\text{O}$ and $[\text{CuNi}(\mathbf{504a})\text{Ni}(\text{Me}_3\text{-12-N}_3)(\text{ClO}_4)](\text{ClO}_4) \cdot \text{H}_2\text{O}$ respectively ($\text{Me}_6\text{-14-N}_4 = \text{D,L-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane}$ and $\text{Me}_3\text{-12-N}_3 = 2,4,4\text{-trimethyl-1,5,9-triazacyclododec-1-ene}$) [616].

In the cation $[\text{CuNi}(\mathbf{504a})(\text{Me}_6\text{-14-N}_4)(\text{ClO}_4)]^+$ the coordination of $[\text{Cu}(\mathbf{504a})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ to the $[\text{Ni}(\text{Me}_6\text{-14-N}_4)]^{2+}$ moiety takes place through an exocyclic oxygen atom of the uracil ring and a *syn-anti* nitroso-oximate group disordered on two sets of crystallographic positions, one with a 78% occupancy and the other with a 22% occupancy. The intramolecular $\text{Cu} \cdots \text{Ni}$ distance is 4.972 Å. The copper(II) ion, occupying the inside site of the ligand $[\mathbf{504a}]^{2-}$, exhibits a distorted square pyramidal

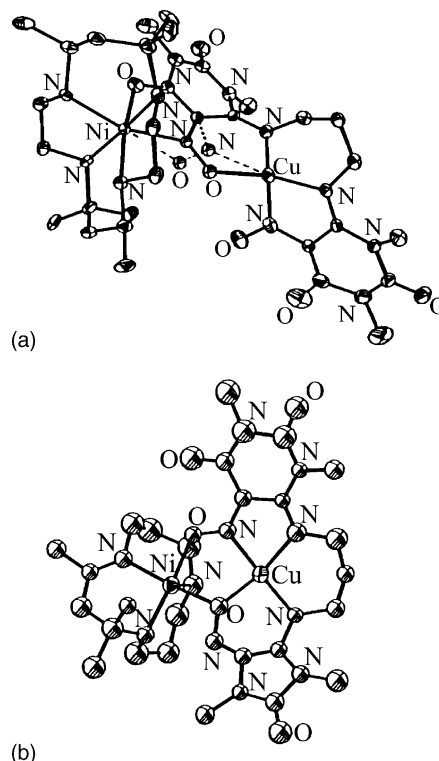


Fig. 404. Structure of $[\text{CuNi}(\mathbf{504a})(\text{Me}_6\text{-14-N}_4)(\text{ClO}_4)]^+$ (a) and $[\text{CuNi}(\mathbf{504a})(\text{Me}_3\text{-12-N}_3)(\text{ClO}_4)]^+$ (b) (the ClO_4^- groups are omitted for clarity) (adapted from Ref. [616]).

coordination environment. The basal plane comprises of two amino and one oximate nitrogen atoms and either an oxygen (occupancy 0.78) or a nitrogen atom (occupancy 0.22) from the other oximate group. The fifth position is occupied by a disordered oxygen atom, from a perchlorate anion. The nickel(II) ion is in a distorted octahedral geometry (Fig. 404a).

Within each hetero-dinuclear cation $[\text{CuNi}(\mathbf{504a})(\text{Me}_3\text{-12-N}_3)(\text{ClO}_4)]^+$, the copper(II) and nickel(II) ions are bridged by one oxygen diatomic *syn-syn* and one oxygen monatomic nitroso-oximate group from the pyrimidine and imidazole rings, respectively. The intramolecular $\text{Cu} \cdots \text{Ni}$ distances are 3.440 and 3.452 Å. The coordination geometry around each copper(II) ion is distorted square pyramidal CuN_3O_2 . The basal plane comprises of two amino and one oximate nitrogens and one oximate oxygen, whereas an oxygen atom of a disordered perchlorate anion occupies the apical position. The nickel(II) ion is in a distorted square pyramidal NiN_3O_2 environment. The basal plane is defined by two oximate oxygens and two nitrogens from the $\text{Me}_3\text{-12-N}_3$ ligand, the remaining nitrogen atom occupying the apical position (Fig. 404b) [616].

Magnetic susceptibility measurements in the temperature range 4.2–298 K revealed the occurrence of a weak intermolecular magnetic exchange interaction between copper(II) ions in $[\text{Cu}(\mathbf{504a})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ ($J = -2.3 \text{ cm}^{-1}$), whereas $[\text{CuNi}(\mu\text{-}\mathbf{504a})(\text{Me}_6\text{-14-N}_4)(\text{ClO}_4)](\text{ClO}_4) \cdot \text{H}_2\text{O}$ and $[\text{CuNi}(\mu\text{-}\mathbf{504a})(\text{Me}_3\text{-12-N}_3)(\text{ClO}_4)](\text{ClO}_4) \cdot \text{H}_2\text{O}$ were

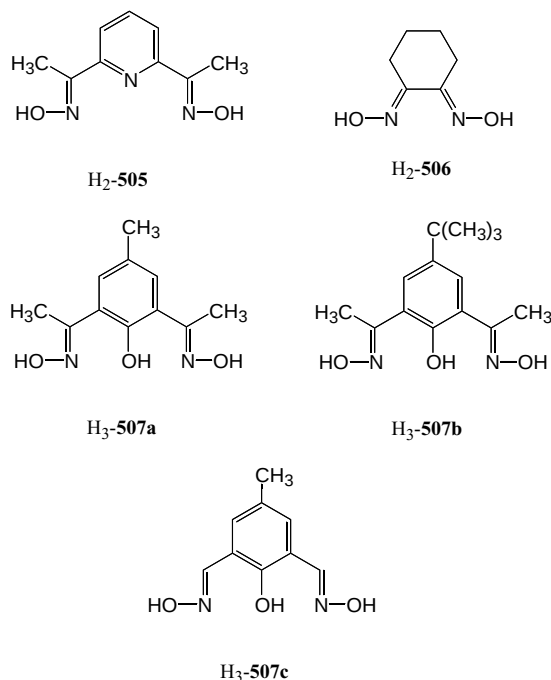
found to exhibit a strong antiferromagnetic interaction between copper(II) and nickel(II) ions with J values of -123.6 cm^{-1} and larger than -500 cm^{-1} , respectively. For $[\text{CuNi}(\mu\text{-504a})(\text{Me}_3\text{-14-N}_4)(\text{ClO}_4)](\text{ClO}_4)\cdot\text{H}_2\text{O}$, below 50 K, only the $S = 1/2$ state is thermally populated, whereas for the second one, the spin exchange interaction causes a complete or nearly complete spin coupling even at room temperature. The room temperature powder EPR spectrum of this complex exhibits a very large and intense signal independent of the temperature at approximately $g = 2.2$ and a broad signal at approximate $g = 4.0$, which vanishes when the temperature decreases. This is interpreted as being due to an axial ZFS in the excited quartet state. The powder EPR spectrum of $[\text{CuNi}(\mu\text{-504a})(\text{Me}_3\text{-12-N}_3)(\text{ClO}_4)](\text{ClO}_4)\cdot\text{H}_2\text{O}$ does not exhibit any signal at about $g = 4$, which may indicate that only the $S = 1/2$ state is thermally populated at room temperature, in agreement with the magnetic data. The difference between the exchange coupling observed for these hetero dinuclear copper(II)–nickel(II) complexes has been attributed to the structural differences in the bridging network [616].

The reaction of $[\text{Cu}_2(\text{H-504a})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})](\text{ClO}_4)_3$ with $[\text{Ni}(\text{Me}_6\text{-14-N}_4)](\text{ClO}_4)_2$ in water affords also a second hetero-dinuclear complex with the same formula $[\text{CuNi}(\text{504a})(\text{Me}_6\text{-14-N}_4)(\text{ClO}_4)](\text{ClO}_4)\cdot\text{H}_2\text{O}$ (complex CuNa b) but with relevant structural differences [617]. These structural differences however do not affect significantly the magnetic properties of the two forms of $[\text{CuNi}(\text{504a})(\text{Me}_6\text{-14-N}_4)(\text{ClO}_4)](\text{ClO}_4)\cdot\text{H}_2\text{O}$; in fact the J values for the two complexes (123.6 cm^{-1} and 136.4 cm^{-1}) are of the same order, thus the main structural difference relevant to the magnetism in both compounds, (i.e. the different NO *anti* bridging conformations) do not significantly affect the magnetic properties. Both Cu–N–O–Ni and Cu–O–N–Ni pathways mediate a similar antiferromagnetic exchange interaction [617].

The reaction of *N,N'*-bis(1,3-dimethyl-5-nitroso-2,4-dioxypyrimidin-6-yl)butane-1,4-diamine ($\text{H}_2\text{-504b}$) with copper(II) salts in ethanol yields $[\text{Cu}(\text{H-504b})(\text{X})]$ (X is the anion of the corresponding copper salt). These mononuclear precursors react with either copper(II) and 2,2-bipyridine (bipy) or $[\text{Ni}(\text{Me}_6\text{-14-N}_4)](\text{ClO}_4)_2$ to afford the homo-dinuclear complexes $[\text{Cu}_2(\text{504b})(\mu\text{-Cl})(\text{bipy})](\text{ClO}_4)$ and $[\text{Ni}_2(\text{H}_2\text{-504b})(\text{Me}_6\text{-14-N}_4)_2](\text{ClO}_4)_4$, respectively. Within $[\text{Cu}_2(\text{504b})(\mu\text{-Cl})(\text{bipy})](\text{ClO}_4)$ the copper(II) ions exhibit a pentacoordination environment. The dioxime ligand bridges the basal planes of the metal ions through the oximate groups in a symmetrical *syn-syn* fashion, the Cu...Cu distance being 3.364 Å , whereas their apical positions are occupied by a bridging chloride anion (Fig. 405a). In this complex the very strong antiferromagnetic exchange causes complete spin pairing at room temperature. In $[\text{Ni}_2(\text{H}_2\text{-504b})(\text{Me}_6\text{-14-N}_4)_2](\text{ClO}_4)_4$, $\text{H}_2\text{-504b}$ adopts an unusual bis(bidentate) open-chain coordination mode by elimination of the copper ion occupying the inner site of the pseudo-macrocyclic ligand in the mononuclear

precursor. This results in a Ni...Ni distance of 13.370 Å . The nickel(II) ions are octahedrally coordinated by four nitrogen atoms belonging to $\text{Me}_6\text{-14-N}_4$ and the nitrogen and the oxygen atoms from the nitroso and the carbonyl groups of $\text{H}_2\text{-504b}$ (Fig. 405b) [617].

$[\text{Cu}(\text{H}_2\text{-505})(\text{Cl})_2]$, formed readily from 2,6-diacetylpyridine dioxime ($\text{H}_2\text{-505}$) and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, is remarkably acidic, the pK for proton dissociation being 2.8 ± 0.1 in water at 25.1 °C while the second proton is not removed by aqueous base. Deprotonation of $[\text{Cu}(\text{H}_2\text{-505})(\text{X})_2]$ in alcoholic solution leads to the dimeric dication $[\text{Cu}_2(\text{H-505})_2]^{2+}$, which has been isolated as the chloride or tetrafluoroborate [618].



The structure of $[\text{Cu}_2(\text{H-505})_2](\text{BF}_4)_2\cdot 2\text{H}_2\text{O}$ (Fig. 406) shows that the nearly planar $[\text{H-505}]^-$ group behaves as a bridging tetradentate ligand. The distorted square pyramidal coordination about each copper(II) ion includes the three nitrogen donors from one oxime and one oxygen donor from the other oxime located basally in a distorted square planar arrangement with a loosely coordinated water molecule occupying the apical position. The copper ions are displaced ca. 0.2 Å above the respective plane of the four basal donor atoms. The structure allows a parallel alignment of dication pairs with an interdimer spacing of ca. 3.5 Å in the crystal lattice. However, since the shortest intermolecular Cu...Cu separation of 4.495 Å is substantially longer than the intramolecular Cu...Cu distance of 3.545 Å , intermolecular contributions to the electron-exchange interaction are not expected to contribute appreciably to the compounds solid-state magnetic behaviour [618].

The copper(II) centers are highly antiferromagnetically coupled, as indicated by the observed magnetic moment

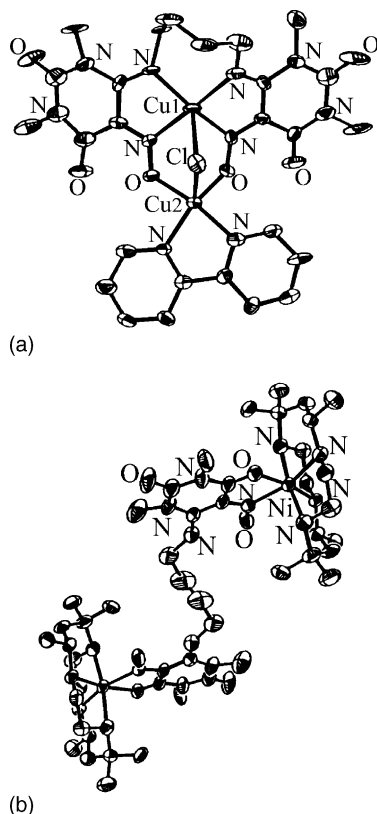


Fig. 405. Structure of $[\text{Cu}_2(\mathbf{504b})(\mu\text{-Cl})(\text{bipy})]^+$ (a) and $[\text{Ni}_2(\text{H}_2\text{-}\mathbf{504b})(\text{Me}_6\text{-14-N}_4)_2]^{4+}$ (b) (adapted from Ref. [617]).

($0.6\mu_{\text{B}}/\text{Cu}^{2+}$) and by the EPR spectrum. The dimeric structure is readily broken by coordinating solvents [618].

Homo- and hetero-trinuclear complexes of the type $[\text{Cu}_2\text{M}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ have been prepared by reaction of $\text{Me}_3\text{-9-N}_3$ with $\text{Cu}(\text{ClO}_4)_2$ in methanol with a subsequent charging with a sample of $[\text{M}(\text{H-}\mathbf{502a})_2]$ ($\text{M} = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Pd}^{2+}$) and triethylamine [619]. The yields of the reactions using $[\text{Ni}(\mathbf{502a})_2]^{2-}$ or $[\text{Pd}(\mathbf{502a})_2]^{2-}$ anions as bridging ligands are lower since the deprotonation reaction in methanol does not proceed readily; hence, an excess of triethylamine is used in the synthesis of the hetero-trinuclear complexes $[\text{Cu}_2\text{Ni}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu}_2\text{Pd}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2]^{2+}$ with nickel(II) or palladium(II) as the central ion to avoid the coprecipitation of the red $[\text{Ni}(\text{H-}\mathbf{502a})_2]$ or yellow-orange $[\text{Pd}(\text{H-}\mathbf{502a})_2]$ with the desired products [619]. $[\text{Cu}_2\text{Pd}(\mathbf{502a})_2(\text{Me}_4\text{-N}_2)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ was obtained by a similar procedure using N,N' -

tetramethyl ethylenediamine ($\text{Me}_4\text{-N}_2$) instead of the cyclic amine ($\text{Me}_3\text{-9-N}_3$) [619].

The same type of reaction using copper bromide, the cyclic amine $\text{Me}_3\text{-9-N}_3$ and $[\text{Cu}(\text{H-}\mathbf{502a})_2]$ as starting materials, affords $[\text{Cu}_3(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{Br})](\text{ClO}_4) \cdot \text{CH}_3\text{OH}$. In this homotrimeric complex each copper ion is in a distorted square pyramidal environment; the central copper ion is displaced by 0.4 Å from the mean basal plane of four nitrogen atoms of the dimethylglyoxime ligand toward the apical bromide ion. The $[\text{Cu}(\mathbf{502a})_2]^{2-}$ dianion bridges two terminal copper ions through its deprotonated oxime oxygen with a $\text{Cu}(\text{central}) \cdots \text{Cu}(\text{terminal})$ separation of 3.381 Å. The terminal copper ion is coordinated to two nitrogen atoms of the cyclic amine, two oxygen atoms of a $[\mathbf{502a}]^{2-}$ in the basal plane, and the third nitrogen atom of the cyclic amine in the apical position. The terminal copper ions lie nearly on the best basal plane comprising the N_2O_2 donor set. The trinuclear skeleton is not coplanar, but is slightly butterfly shaped (Fig. 407).

A complete X-ray structure determination of $[\text{Cu}_2\text{Ni}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was not possible because of crystal disorder, but a qualitative investigation showed that two water molecules are directly attached to the nickel center in a *cis*-planar fashion yielding a six coordinated nickel(II) ion. The three metal centers do not lie in a plane, but a bent structure is attained [619].

For $[\text{Cu}_2\text{Pd}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ each copper ion is located in distorted square pyramidal surrounding with two nitrogen atoms of the cyclic amine and two oxygen atoms of the dimethylglyoximate dianion in the basal plane and the third nitrogen atom of the 1,4,7-trimethyl-1,4,7-triazacyclononane in the apical position. The square planar $[\text{Pd}(\mathbf{502a})_2]^{2-}$ ion bridges two copper ions through its deprotonated oxime oxygens, and the trinuclear skeleton is nearly coplanar. The water molecules are not coordinated to the central palladium(II) ion, resulting in a square planar diamagnetic palladium(II) center [619].

A strong antiferromagnetic interaction ($J = -448 \text{ cm}^{-1}$) between adjacent copper(II) ions has been found for $[\text{Cu}_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2(\text{Br})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$. A similar magnetic interaction was observed for $[\text{Cu}_3(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ and $[\text{Cu}_3(\mathbf{502a})_2(\text{Me}_4\text{-N}_2)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$ ($J = -376$ and -345 cm^{-1} , respectively). The powder EPR spectra indicate a square pyramidal geometry for the copper(II) ions with a $d_{x^2-y^2}$ ground state in the homotrimeric complexes.

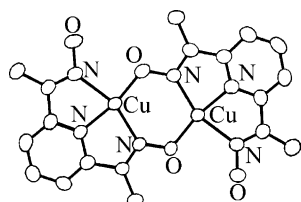


Fig. 406. Structure of $[\text{Cu}(\text{H-}\mathbf{505})]^{2+}$ (adapted from Ref. [618]).

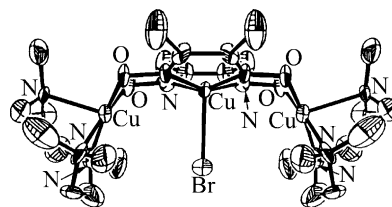


Fig. 407. Structure of $[\text{Cu}_3(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{Br})]^+$ (adapted from Ref. [619]).

The $\mu_{\text{eff}}/\text{Cu}$ values vary from $1.80\mu_{\text{B}}$ at 284 K to $1.31\mu_{\text{B}}$ at 4.2 K for $[\text{Cu}_2\text{Ni}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ and from $1.91\mu_{\text{B}}$ at 284 K to $1.47\mu_{\text{B}}$ at 4.2 K for $[\text{Cu}_2\text{Ni}(\mathbf{502a})_2(\text{Br})(\text{Me}_3\text{-9-N}_3)(\text{H}_2\text{O})_2](\text{PF}_6)$. These data, fitted by assuming that $[\text{Ni}(\mathbf{502a})_2(\text{H}_2\text{O})]^{2+}$ is diamagnetic, shows two not-interacting copper(II) ions ($J = -2.6 \text{ cm}^{-1}$ for the first complex and $J = -1.3 \text{ cm}^{-1}$ for the second one). The magnetic susceptibility data for $[\text{Cu}_2\text{Pd}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ shows a moderate antiferromagnetic interaction ($J = -36 \text{ cm}^{-1}$) between the two copper(II) ions, while no interaction was observed for $[\text{Cu}_2\text{Pd}(\mathbf{502a})_2(\text{Me}_4\text{-N}_2)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ($J = -0.8 \text{ cm}^{-1}$). The trinuclear Cu–Pd–Cu skeleton in $[\text{Cu}_2\text{Pd}(\mathbf{502a})_2(\text{Me}_4\text{-N}_2)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was supposed to be less coplanar than that in $[\text{Cu}_2\text{Pd}(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, and the resulting poor effective overlap between the magnetic orbitals results in practically no coupling ($J = -0.8 \text{ cm}^{-1}$) between spins of two copper centers through the multiple atom bridging ligands [619].

The cyclic voltammograms of the homotrimeric copper(II) complexes reveal, besides other features, a quasi-reversible one-electron oxidation corresponding to the reversible formation of the mixed-valence $\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}\text{Cu}^{\text{II}}$ species. This mixed-valence species seems to be stable on the voltammetric time scale and, hence, the chemical preparation of the oxidation products should be feasible.

$[\text{Cu}_3(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{Br})](\text{ClO}_4) \cdot \text{CH}_3\text{OH}$ shows an irreversible two electron reduction with the formation of a $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ species while $[\text{Cu}_3(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ and $[\text{Cu}_3(\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ undergo the one-electron irreversible reduction with the formation of a $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$ species [619].

$[\text{Cu}_2(\text{H-}\mathbf{502a})_2(\text{H}_2\text{-}\mathbf{502a})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\text{Cu}_2(\mathbf{502a})(\text{H-}\mathbf{502a})(\text{H}_2\text{-}\mathbf{502a})](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ and $[\text{Cu}_3(\mathbf{502a})_2(\text{H}_2\text{-}\mathbf{502a})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ were obtained by reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ respectively with $\text{H}_2\text{-}\mathbf{502a}$ in a 5:1 molar ratio, with $[\text{Cu}(\text{H-}\mathbf{502a})_2]$ in a 1:3 molar ratio and with $[\text{Cu}(\text{H-}\mathbf{502a})_2]$ in a 1:2 molar ratio [620].

The $\{\text{Cu}(\text{H}_2\text{-}\mathbf{502a})\}^{2+}$ fragment of $[\text{Cu}_2(\text{H-}\mathbf{502a})_2(\text{H}_2\text{-}\mathbf{502a})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ coordinates to the second copper(II) ion through the deprotonated oximate oxygens of $[\text{Cu}(\text{H-}\mathbf{502a})_2]$ to afford a dinuclear structure doubly bridged by the oximate groups in a *cis* arrangement. The intramolecular Cu...Cu separation is $3.526\text{\AA}$. The configuration about the copper ions is a distorted square pyramid: the basal plane for one copper ion comprises two nitrogens of $\text{H}_2\text{-}\mathbf{502a}$ and two oximate oxygens whereas that of the other copper ion is formed by four nitrogens of two $[\text{H-}\mathbf{502a}]^-$ groups; a water molecule occupies the apical position in both cases (Fig. 408).

Variable temperature magnetic susceptibility measurements (50–300 K) on these dinuclear or trinuclear copper(II) complexes revealed the occurrence of a very strong intramolecular antiferromagnetic interaction through the oximate bridges. The magnitude of the antiferromagnetic interaction in $[\text{Cu}_3(\mathbf{502a})_2(\text{H}_2\text{-}\mathbf{502a})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($-2J$

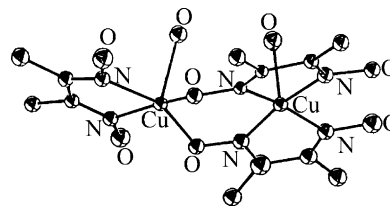


Fig. 408. Structure of $[\text{Cu}_2(\text{H-}\mathbf{502a})_2(\text{H}_2\text{-}\mathbf{502a})(\text{H}_2\text{O})_2]^{2+}$ (adapted from Ref. [620]).

$\cong 70 \text{ cm}^{-1}$) is smaller than that of $[\text{Cu}_2(\text{H-}\mathbf{502a})_2(\text{H}_2\text{-}\mathbf{502a})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Cu}_2(\text{H-}\mathbf{502a})(\text{H-}\mathbf{502a})_2(\text{H}_2\text{-}\mathbf{502a})](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ ($-2J \cong 850 \text{ cm}^{-1}$). This reduction of the exchange coupling, common to other trinuclear oximate-bridged copper(II) complexes, could be due to greater structural distortions in the trinuclear complexes with respect to the related dinuclears ones [620].

These systems are ideally suited for the study of intramolecular magnetic exchange interaction; also they have been used for the synthesis of ferrimagnetic molecular materials. Thus using $[\text{Cu}(\mathbf{502a})_2]^{2-}$ as a precursor, heteropolynuclear copper(II)–manganese(III) metamagnetic oximate-bridged complexes have been obtained [621]. In particular $[\text{Cu}(\text{H-}\mathbf{502a})_2]$ reacts in alcoholic solution and in the presence of oxygen with $\text{Mn}(\text{RCOO})_2$ ($\text{R} = \text{CH}_3$, C_2H_5 , C_6H_5) to form $[\text{MnCu}(\mathbf{502a})_2(\text{RCOO})(\text{H}_2\text{O})_2]_n$ [621]. These syntheses are highly reproducible even in other solvents such as CH_3CN or CH_2Cl_2 . Indeed, it is possible to obtain the same compounds in a high yield by reaction of $[\text{Mn}^{\text{III}}_3(\text{RCOO})_6(\text{py})_3]\text{ClO}_4$ with $[\text{Cu}(\text{H-}\mathbf{502a})_2]$ in CH_3CN . Thermogravimetric analysis of these complexes shows a loss of two water molecules per CuMn unit at 65°C [621]. IR data for $[\text{MnCu}(\mathbf{502a})_2(\text{RCOO})(\text{H}_2\text{O})_2]_n$ strongly support the presence of $[\text{Cu}(\mathbf{502a})_2]^{2-}$ and its coordination to the manganese(III) ion through oxygen oxime atoms, as well as the coordination of the carboxylate oxygen atoms in an equivalent fashion [621].

An X-ray adsorption study indicates a distorted octahedral environment for both metal ions and divalent and trivalent oxidation states for copper and manganese, respectively. The EXAFS data, indicate four nitrogen atoms and two oxygen atoms around the copper(II) ion and six oxygen atoms around manganese(III) ion [621].

The magnetic behaviour of these complexes, studied in the 1.8–300 K temperature range under different external fields ($J = -35000 \text{ G}$), is indicative of a relatively strong ferromagnetic coupling between copper(II) and manganese(III) ions. Also an antiferromagnetic interchain coupling, possibly due to carboxylate bridging between manganese(III) ions is operating. Thus these compounds have been considered to be two-dimensional, with a large ferromagnetic coupling within the chain and a weak antiferromagnetic coupling between the chains. By treating these systems as chains of chains, a very weak coupling between chains was observed; for $[\text{MnCu}(\mathbf{502a})_2(\text{CH}_3\text{COO})] \cdot 2\text{H}_2\text{O}$ a $J_{\text{inter}} = -0.078 \text{ cm}^{-1}$ was estimated [621].

At low temperature the $[\text{MnCu}(\mathbf{502a})_2(\text{RCOO})] \cdot 2\text{H}_2\text{O}$ complexes show magnetic properties consistent with a metamagnetic behaviour. Thus for $[\text{MnCu}(\mathbf{502a})_2(\text{CH}_3\text{COO})] \cdot 2\text{H}_2\text{O}$ χ_{MT} reaches a maximum a 12 K for low applied fields, which broadens as H_{A} is increased, and finally disappears for $H_{\text{A}} > 4000$ G, demonstrating that a field-induced transition from an antiferromagnetic to a ferromagnetic ground state occurs.

A similar behaviour was found for $[\text{MnCu}(\mathbf{502a})_2(\text{C}_2\text{H}_5\text{COO})] \cdot 2\text{H}_2\text{O}$ and $[\text{MnCu}(\mathbf{502a})_2(\text{C}_6\text{H}_5\text{COO})] \cdot 2\text{H}_2\text{O}$ whose H_{c} and T_{c} values are 4000 G and 11.5 K and 2500 G and 9 K, respectively. The structures of the complexes $[\text{MnCu}(\mathbf{502a})_2(\text{RCOO})] \cdot 2\text{H}_2\text{O}$ are likely to be very close as revealed by the similarity of their X-ray powder patterns. So, the most likely role of the R groups would be to separate the chains (or planes) from each other. Taking into account that $T_{\text{c}} \propto (J_{\text{intra}}J_{\text{inter}})^{1/2}$, where J_{intra} is the intrachain copper(II)–manganese(III) interaction and J_{inter} is the effective interchain interaction energy, an increase in the size of R would lead to a decrease of J_{inter} , in agreement with the observed trend $T_{\text{c}}(\text{R} = \text{CH}_3) > T_{\text{c}}(\text{R} = \text{C}_2\text{H}_5) > T_{\text{c}}(\text{C}_6\text{H}_5)$ and $H_{\text{c}}(\text{CH}_3) > H_{\text{c}}(\text{C}_2\text{H}_5) > H_{\text{c}}(\text{C}_6\text{H}_5)$ [621].

In the absence of single crystals suitable for X-ray diffraction, X-ray absorption studies on $[\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{502a})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ and $[\text{Mn}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{506})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ synthesized by air oxidation of methanolic solutions of iron(II) or manganese(II) acetate in the presence of $[\text{Cu}(\mathbf{502a})_2]^{2-}$ or $[\text{Cu}(\mathbf{506})_2]^{2-}$, respectively ($\text{H}_2\text{-506} = 1,2$ -cyclohexanedione oxime), reveal the metal ions exhibit elongated octahedral surroundings, N_4O_2 for copper(II) and O_6 for the manganese(III) or iron(III) ions. Manganese(III) exhibits a more pronounced axial distortion than iron(III), as expected from the Jahn–Teller effect in the former. Two manganese or two iron ions were found at ca. 3.3 Å from each copper atom in all these complexes, in agreement with the formation of oximate bridged bimetallic chains. The carboxylato groups which are bound to either manganese(III) or iron(III) should act as bridges between manganese(III) or iron(III) ions from different chains. Moreover, the structures according to X-ray powder diffraction, are likely to have a close resemblance [622].

Magnetic susceptibility data for $[\text{Mn}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{506})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ indicate that ferromagnetic interactions dominate while the magnetic behaviour of $[\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{502a})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ is characteristic of a ferrimagnetic chain with an antiferromagnetic coupling between copper(II) and iron(III) ions. AC susceptibility measurements in the temperature range 4–20 K show no out-of-phase signal.

According to the magnetic susceptibility data down to ca. 30 K for $[\text{Mn}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{506})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ and $[\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{502a})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$, respectively, a $J_{\text{intra}} = +51$ and -48 cm^{-1} was estimated. Below 30 K the experimental values of χ_{MT} indicate that ferromagnetic for MnCu and antiferromagnetic for FeCu interchain coupling occurs. Possibly in $[\text{MnCu}(\mathbf{506})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$, this magnetic interchain coupling is due to the acetate bridging between

the manganese(III) ions. According to such a structural arrangement, the MnCu and FeCu compounds would be two-dimensional, with a large intrachain magnetic interaction and a weak interchain one as in $[\text{MnCu}(\mathbf{502a})_2(\text{CH}_3\text{COO})]$. Consequently, these two-dimensional compounds, treated as a chain of chain (in the case of MnCu only for $T > T_{\text{c}}$), gave $J_{\text{inter}} = +0.07$ and -0.06 cm^{-1} , respectively. These values agree with a very weak interchain coupling.

The observed $J_{\text{intra}} = +51$ cm^{-1} for $[\text{MnCu}(\mathbf{506})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ is very close to that of $[\text{MnCu}(\mathbf{502a})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ (52 cm^{-1}). This ferromagnetic interaction between d^4 -manganese(III) and d^9 -copper(II) ions can be understood as follows: owing to the Jahn–Teller effect, which is operative in both metal ions, it is possible to achieve strict orthogonality between the magnetic orbitals d_{xy}^2 , d_{xz} and d_{z^2} of manganese(III) ($d_{x^2-y^2}$ orbital is empty) and the one of copper(II), $d_{x^2-y^2}$, if both metal ions are located in the xy-plane. The occurrence of an electron in the $d_{x^2-y^2}$ orbital of d^5 -iron(III) provides an antiferromagnetic pathway between iron(III) and copper(II) ions, responsible for the ferrimagnetism observed in the relative FeCu complex. The value of $J_{\text{intra}} = -48$ cm^{-1} for this complex is very similar to that reported for $[\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}(\mathbf{502a})(\text{phen})_2](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ ($J_{\text{Mn-Cu}} = -50$ cm^{-1}) [222].

Thus the study of the magnetic properties of the compounds $[\text{M}^{\text{III}}\text{Cu}^{\text{II}}(\text{L})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$, ($\text{M} = \text{Mn}$ and $\text{L} = \mathbf{502a}$ or $\mathbf{506}$ and $\text{M} = \text{Fe}$ and $\text{L} = \mathbf{502a}$, shows that $[\text{MnCu}(\mathbf{502a})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$, is a metamagnetic compound, $[\text{MnCu}(\mathbf{506})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$, is a bulk ferromagnet with $T_{\text{c}} = 9$ K and $[\text{FeCu}(\mathbf{502a})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$, orders antiferromagnetically at 7.5 K [622].

The linear heterotrimeric complexes $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}(\mathbf{502})_3(\text{Me}_3\text{-9-N}_3)](\text{ClO}_4)_2$ ($\text{M}^{\text{II}} = \text{Zn}^{2+}$, Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+}), with a $[\text{M}^{\text{II}}(\mathbf{502a})_3]^{4-}$ entity as bridging ligand, have been synthesized in an argon atmosphere by treating a methanolic solution of the cyclic triamine $\text{Me}_3\text{-9-N}_3$ with sequential additions of $\text{Fe}(\text{CH}_3\text{COO})_2$, $\text{M}(\text{CH}_3\text{COO})_2$ and $\text{H}_2\text{-502a}$ in a 1:05 1.5 molar ratio and in the presence of triethylamine. The complexes were precipitated as the perchlorate salt in the presence of air [623].

The X-ray structure of $[\text{Fe}_2\text{Cu}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2 \cdot 0.5\text{CH}_3\text{OH}$ (Fig. 409) shows the $[\text{Cu}(\mathbf{502a})_3]^{4-}$ anion bridges the two iron ions through its deprotonated oxime oxygens with a $\text{Cu} \cdots \text{Fe}$ separation of 3.58 Å. Two

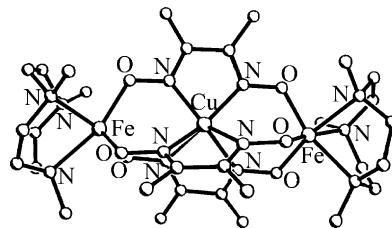


Fig. 409. Structure of $[\text{Fe}_2\text{Cu}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{2+}$, $[\text{Fe}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{2+}$, $[\text{Mn}_2\text{Zn}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{2+}$, $[\text{Mn}_3(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{2+}$ and $[\text{Mn}_2\text{Cu}(\mathbf{503a})_3(\text{Me}_3\text{-9-N}_3)_2]^{2+}$ show a similar structure (adapted from Ref. [623]).

facially coordinated tridentate amine ligands complete the trigonally distorted octahedral coordination sphere of the two d^5 high-spin iron(III) centers.

In the $\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}$ complex the magnetic interaction between the high-spin iron(III) and the copper(II) ions is antiferromagnetic. For the $\text{Fe}^{\text{III}}\text{Zn}^{\text{II}}\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(1s)\text{-Fe}^{\text{III}}$ complexes the magnetic behaviour is typical of antiferromagnetically coupled binuclear paramagnetic centers with a diamagnetic ground state. It is noteworthy that magnetic exchange coupling is observed in these compounds in which the iron(III) centers are separated by a large distance of ca. 7.0 Å [623].

These systems can be used in the study of long-range magnetic interactions and effectiveness of polyatomic bridging ligands in propagating exchange interaction, using diamagnetic metal complexes as spacer for the paramagnetic centers and thus changing the distances between interacting centers [623].

The complexes $[\text{Fe}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{X}_2)$ ($\text{X} = \text{ClO}_4^-$, PF_6^-) have been synthesized also by the reaction of $[\text{Fe}(\text{Me}_3\text{-9-N}_3)(\text{Cl})_3]$ with the $[\text{Ni}(\mathbf{502a})_3]^{4-}$, assembled in situ, but in comparatively low yield. The low yield is the result of presumably low concentration of the $[\text{Ni}(\mathbf{502a})_3]^{4-}$ ion in the solution, as indicated by the precipitation of a major part of the nickel(II) ions as $[\text{Ni}(\text{H-}\mathbf{502a})_2]$. These Fe_2Ni complexes are sparingly soluble in water with decomposition (precipitation of the insoluble red solid, $[\text{Ni}(\text{H-}\mathbf{502a})_2]$) but reasonably soluble in organic solvents such as acetone, alcohols and acetonitrile [624].

The structure of $[\text{Fe}_2\text{Ni}(\mathbf{502a})_3((\text{Me}_3\text{-9-N}_3)_2)(\text{PF}_6)_2 \cdot 0.5\text{CH}_3\text{OH}]$ confirms that a linear trinuclear complex has indeed been formed with a trioctahedral geometry containing one nickel(II) and two iron(III) ions. The central tris-(dimethylglyoximate)nickelate(II) ion, $[\text{Ni}(\mathbf{502a})_3]^{4-}$, bridges the two terminal iron(III) centers through the deprotonated oxime oxygens. The iron coordination geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate amine and three oxygen atoms from three bridging oximate groups. The central nickel ion is coordinated to six imine nitrogens, and the coordination geometry is strongly trigonally distorted. An intramolecular $\text{Fe}\cdots\text{Fe}$ separation of 6.982 Å has been found, the nearest intermolecular $\text{Fe}\cdots\text{Fe}$ separation is 7.37 Å. The nearest neighbour $\text{Fe}\cdots\text{Ni}$ distance within the trinuclear cation is 3.491 Å [624]. The bond lengths are consistent with a d^5 high-spin electron configuration of the iron(III) centers. The terminal iron ion is displaced by 0.176 Å from the mean basal N_2O_2 plane toward the apical nitrogen atom of the macrocyclic amine. The nickel(II) ion lies strictly on the mean N_4 plane [624].

Analysis of the susceptibility data yields an antiferromagnetic interaction between adjacent iron(III) and nickel(II) centers and a weak antiferromagnetic interaction between the terminal iron(III) centers ($J_{\text{FeNi}} = -32 \text{ cm}^{-1}$, $J_{\text{FeFe}} = -5 \text{ cm}^{-1}$ for the perchlorate salt; $J_{\text{FeNi}} = -29 \text{ cm}^{-1}$, $J_{\text{FeFe}} = -5 \text{ cm}^{-1}$ for the hexafluorophosphate salt) [624].

The cyclic voltammograms of the $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}$ complexes reveal two quasi-reversible one-electron oxidation due to the subsequent formation of $\text{Fe}^{\text{III}}\text{Ni}^{\text{III}}\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{III}}\text{Ni}^{\text{IV}}\text{Fe}^{\text{III}}$ and two reversible one-electron reduction processes assigned to the formation of $\text{Fe}^{\text{II}}\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{II}}\text{Ni}^{\text{II}}\text{Fe}^{\text{II}}$ species, respectively.

The red brown solution obtained from manganese(III) acetate and the cyclic amine $\text{Me}_3\text{-9-N}_3$ in methanol, reacts with $[\text{M}(\mathbf{502a})_3]^{4-}$ prepared in situ to afford in the presence of a counterion, e.g. ClO_4^- , dark brown crystals of $[\text{Mn}^{\text{III}}_2\text{-M}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ ($\text{M} = \text{Mn}^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+}) [623,625,626].

These $\text{Mn}^{\text{III}}\text{M}^{\text{II}}\text{Mn}^{\text{III}}$ trinuclear complexes are amenable to oxidation and give rise to $\text{Mn}^{\text{IV}}\text{M}^{\text{II}}\text{Mn}^{\text{IV}}$ species when oxidized in acetonitrile with NO^+ or $\text{S}_2\text{O}_8^{2-}$ as an oxidant. The same species can also be obtained by electrochemical oxidation. $[\text{Mn}_2^{\text{III}}\text{M}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ are sparingly soluble in water with decomposition but reasonably soluble in organic solvents such as acetone, alcohols, and acetonitrile. The related complexes $\text{Mn}^{\text{IV}}\text{M}^{\text{III}}\text{Mn}^{\text{IV}}$ are hardly soluble in common organic solvents but are readily soluble in water [623,625,626].

The structure of $\text{Mn}^{\text{III}}\text{Zn}^{\text{II}}\text{Mn}^{\text{III}}$ complex indicates that the $[\text{Zn}(\mathbf{502a})_3]^{4-}$ anion bridges two manganese(III) ions through its deprotonated oxime oxygens with a $\text{Mn}\cdots\text{Zn}$ separation of 3.565 Å. The high-spin d^4 manganese coordination geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate amine and three oxygen atoms from three oximate groups. The central ZnN_6 core is nearly trigonal prismatic [625].

The structure of the $\text{Mn}^{\text{IV}}\text{Zn}^{\text{II}}\text{Mn}^{\text{IV}}$ complex was not determined because of the unavailability of good quality crystals; it was reasonably assumed that the same structural unit is prevailing in $\text{Mn}^{\text{IV}}\text{ZnMn}^{\text{IV}}$ as in $\text{Mn}^{\text{III}}\text{ZnMn}^{\text{III}}$ complexes [625].

Cyclic voltammetry of the $\text{Mn}^{\text{III}}\text{Zn}^{\text{II}}\text{Mn}^{\text{III}}$ complex shows two reversible oxidation steps at $E_1^\circ = 0.81$ and $E_2^\circ = 0.57$ V versus Ag/AgCl corresponding to the $\text{Mn}^{\text{IV}}\text{Zn}^{\text{II}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{IV}}\text{Zn}^{\text{II}}\text{Mn}^{\text{IV}}$ species; two additional quasi-reversible waves at more negative potentials, $E_3^\circ = -0.17$ V and $E_4^\circ = -0.45$ V versus Ag/AgCl , have been attributed to the $\text{Mn}^{\text{III}}\text{Zn}^{\text{II}}\text{Mn}^{\text{II}}$ and $\text{Mn}^{\text{II}}\text{Zn}^{\text{II}}\text{Mn}^{\text{II}}$ species, respectively. The reversible character of E_1° and E_2° preclude any significant structural rearrangement during the redox processes; i.e. all three species have the same structure in solution and apparently can be described by the solid state structure as determined by X-ray diffraction. Identical cyclic voltammetric behaviour has been observed for the $\text{Mn}^{\text{IV}}\text{Zn}^{\text{II}}\text{Mn}^{\text{IV}}$ complex.

In $[\text{Mn}_2^{\text{III}}\text{Zn}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ the magnetic moments over the temperature range from room temperature to 4.1 K indicate that no- or a very negligible interaction occurs between the two manganese(III) ions. For the $\text{Mn}^{\text{IV}}\text{Zn}^{\text{II}}\text{Mn}^{\text{IV}}$ complex the magnetic moment decreases steadily with decreasing temperature and approaches the value of $0.64\mu_B$ at 4.1 K. This magnetic behaviour is typical

of antiferromagnetically coupled binuclear paramagnetic centers ($2J = -35.4 \text{ cm}^{-1}$) with a diamagnetic ground state.

The linear trinuclear complex $[\text{Mn}_2^{\text{III}}\text{Mn}^{\text{II}}(\mu\text{-}\mathbf{502a})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](\text{ClO}_4)_2$ has been formed in such a way that a trioctahedral geometry containing a manganese(II) and two manganese(III) ions is present. The central tris-(dimethylglyoximate)manganate(II) ion, $[\text{Mn}(\mathbf{502a})_3]^{4-}$, bridges the two terminal manganese(III) centers through the deprotonated oxime oxygens. The terminal d^4 -high-spin manganese(III) coordination geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine and three oxygen atoms from three bridging oximate groups. The central MnN_6 core is nearly trigonal prismatic. A $\text{Mn}\cdots\text{Mn}$ separation between adjacent molecules of $7.141 \text{ \AA}$ has been found while the nearest neighbour $\text{Mn}\cdots\text{Mn}$ distance within the trinuclear cation is $3.571 \text{ \AA}$ [623,626].

The cyclic voltammograms $[\text{Mn}_2^{\text{III}}\text{M}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-}9\text{-N}_3)_2]^{2+}$ and $[\text{Mn}_2^{\text{IV}}\text{M}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-}9\text{-N}_3)_2]^{4+}$ show two reversible and two quasi-reversible one-electron redox processes due respectively to $\text{Mn}^{\text{IV}}\text{M}^{\text{II}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{IV}}\text{M}^{\text{II}}\text{Mn}^{\text{IV}}$ and to $\text{Mn}^{\text{II}}\text{M}^{\text{II}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{II}}\text{M}^{\text{II}}\text{Mn}^{\text{II}}$ complexes. The central divalent metal ion in these complexes is redox-inactive. All attempts to isolate the mixed-valence complexes of either form $\text{Mn}^{\text{IV}}\text{M}^{\text{II}}\text{Mn}^{\text{III}}$ or the $\text{Mn}^{\text{III}}\text{M}^{\text{II}}\text{Mn}^{\text{II}}$ proved to be unsuccessful.

Magnetic susceptibility data indicate the presence of weak to moderate exchange interactions, both ferro- and antiferromagnetic, between the paramagnetic centers. The result is that some complexes show an antiferromagnetic, other a ferromagnetic behaviour [623,626].

Also in $[\text{Mn}_2^{\text{III}}\text{Cu}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](\text{ClO}_4)_2$, $[\text{Cu}(\mathbf{502a})_3]^{4-}$ bridges two terminal manganese(III) ions through its deprotonated oxime oxygens with a $\text{Mn}\cdots\text{Cu}$ separation of $3.578 \text{ \AA}$ and a $\text{Mn}\cdots\text{Mn}$ separation of $7.11 \text{ \AA}$. The nearest intermolecular $\text{Mn}\cdots\text{Mn}$ separation is $8.451 \text{ \AA}$. The trinuclear $\text{Mn}\text{--Cu}\text{--Mn}$ unit is not linear; it forms an angle of 167.3° . Two facially coordinated tridentate amine ligands complete the trigonally distorted octahedral coordination sphere of the two d^4 high-spin manganese(III) centers [626]. The geometry of the copper center may be envisaged as pseudo-square pyramidal, with an $\eta^2\text{-}[\mathbf{502a}]^{2-}$ ligand at the apical position, and is very similar to that found in the corresponding $\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}$ compound [626]. The coupling between manganese(III) and copper(II) ions in the $\text{Mn}^{\text{III}}\text{Cu}^{\text{II}}\text{Mn}^{\text{III}}$ complex is antiferromagnetic in nature.

$[\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_7]\cdot 3\text{H}_2\text{O}$ [627] and the cyclic amine $\text{Me}_3\text{-}9\text{-N}_3$ in methanol afford $[\text{Mn}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{-}9\text{-N}_3)_2]^{2+}$ [628] which reacts under nitrogen atmosphere and in the presence of $\text{N}(\text{Et})_3$ with the appropriate metal acetate and cyclohexane-1,2-dimethyldioxime, ($\text{H}_2\text{-}\mathbf{506}$) to form the trinuclear complexes $[\text{Mn}_2^{\text{III}}\text{M}^{\text{II}}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](\text{X})_2$ ($\text{X} = \text{ClO}_4$, toluene-*p*-sulfonate; $\text{M}^{\text{II}} = \text{Zn}^{2+}$, Cu^{2+} , Mn^{2+}) upon addition of ClO_4^- or toluene-*p*-sulfonate as counter anion [629]. The oxidation

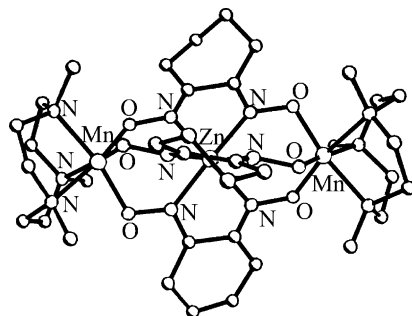


Fig. 410. Structure of $[\text{Mn}_2\text{Zn}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2]^{4+}$ ($[\text{Mn}_2\text{Cu}(\mathbf{506a})_3(\text{Me}_3\text{-}9\text{-N}_3)_2]^{4+}$ has a similar structure) (adapted from Ref. [629]).

of these complexes under argon gives rise to the complexes $[\text{Mn}^{\text{IV}}\text{M}^{\text{II}}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](\text{X})_4$.

$[\text{Mn}^{\text{IV}}_2\text{Zn}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](\text{ClO}_4)_4$ and $[\text{Mn}^{\text{IV}}_2\text{Cu}^{\text{II}}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](\text{ClO}_4)_4$ (Fig. 410) consist of a discrete tetracationic trinuclear unit and four non coordinatively bound perchlorate anions. In the first complex, $[\text{Zn}(\mathbf{506})_3]^{4-}$ bridges the two terminal manganese(IV) centers through the deprotonated oxime oxygens. The terminal manganese coordination geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine and three oxygen atoms from three bridging oximate groups. The central ZnN_6 core is nearly trigonal prismatic [629].

In the structure of the $\text{Mn}^{\text{IV}}\text{Cu}^{\text{II}}\text{Mn}^{\text{IV}}$ complex the central copper ion is six coordinated by the azomethine nitrogen atoms of the three nioxime ligands. The $[\text{Cu}(\mathbf{506})_3]^{4-}$ anion bridges two terminal manganese(IV) ions through its deprotonated oxime oxygens with a $\text{Mn}\cdots\text{Cu}$ separation of $3.54 \text{ \AA}$. The trinuclear $\text{Mn}\text{--Cu}\text{--Mn}$ unit is not perfectly linear with an angle of 171° and the $\text{Mn}\cdots\text{Mn}$ separation is $7.06 \text{ \AA}$. The coordination geometry of the terminal manganese ions is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine $\text{Me}_3\text{-}9\text{-N}_3$ and three oxygen atoms from the deprotonated $[\mathbf{506}]^{2-}$ ligands, resulting in *fac*- MnN_3O_3 chromophores [629]. The geometry of the copper center has been envisaged as a pseudo-square pyramid with an $\eta^2\text{-}[\mathbf{506}]^{2-}$ ligand at the apical position [629].

In $[\text{Mn}_2^{\text{III}}\text{Zn}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](p\text{-toluenesulfonate})_2$ a very weak antiferromagnetic coupling ($J = -2.4 \text{ cm}^{-1}$) was found between the two terminal manganese(III) ions, while in the oxidized compound $[\text{Mn}_2^{\text{IV}}\text{Zn}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](\text{ClO}_4)_4$ a moderately strong antiferromagnetic coupling ($J = -20.6 \text{ cm}^{-1}$) is operating. This $\text{Mn}^{\text{IV}}\text{ZnMn}^{\text{IV}}$ complex demonstrates the presence of intramolecular antiferromagnetic exchange coupling of considerable magnitude over distances of $\approx 7 \text{ \AA}$, indicating that the effective magnetic orbitals are favourably aligned.

The magnetism of $[\text{Mn}_2^{\text{III}}\text{Cu}(\mathbf{506})_3(\text{Me}_3\text{-}9\text{-N}_3)_2](p\text{-toluenesulfonate})_2$ has been interpreted in terms of an antiferromagnetic coupling between the neighbouring high-spin manganese(III) and copper(II) ion ($J_a = -70.0 \text{ cm}^{-1}$) and

between the terminal manganese(III) ions ($J_t = -3.9 \text{ cm}^{-1}$). Remarkably, contrary to this complex, the coupling between manganese(III) and copper(II) ions in other oxime bridged compounds is ferromagnetic in nature.

The exchange interaction between manganese(IV) and copper(II) ions, J_a , is ferromagnetic in nature, but the spin interaction between the terminal manganese(IV) ions is antiferromagnetic with $J_t \approx -18 \text{ cm}^{-1}$. This strong coupling, considering the long distance of $7.06 \text{ \AA}$ between the terminal manganese centers, has a profound influence on the structure of the spin ladder yielding a ground state with $S_t = 3/2$ for the $\text{Mn}_2^{\text{IV}}\text{Cu}^{\text{II}}$ complex. The magnetic behaviour of this complex is very similar to the analogous $\text{Mn}^{\text{IV}}\text{Cu}^{\text{II}}\text{Mn}^{\text{III}}$ complex with $[\mathbf{502a}]^{2-}$ as the bridging ligand [629].

For $[\text{Mn}_2^{\text{IV}}\text{Mn}^{\text{II}}(\mathbf{506})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_4$ a $J_a = +50.1 \text{ cm}^{-1}$ and $J_t = -17.7 \text{ cm}^{-1}$ was determined while $[\text{Mn}_2^{\text{III}}\text{Mn}^{\text{II}}(\mathbf{506})_3(\text{Me}_3\text{-9-N}_3)_2](p\text{-toluenesulfonate})_2$ shows a magnetic behaviour quite characteristic of a ferromagnetic coupling ($J_a = 4.7 \text{ cm}^{-1}$ and $J_t = -3.4 \text{ cm}^{-1}$). The analogous compound with dimethylglyoxime shows a $J_a = +4.7$ and $J_t = -2.95 \text{ cm}^{-1}$ while a dinuclear $\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}$ complex exhibits a weak ferromagnetic coupling ($J = +0.86$) [629].

For $[\text{Mn}_2^{\text{IV}}\text{Mn}^{\text{II}}(\mathbf{506})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_4$ a $J_a = +25.2 \text{ cm}^{-1}$ and a $J_t = -25.7 \text{ cm}^{-1}$ was evaluated. The quotient J_t/J_a of -1.02 results in the stabilization of the $S_t = 9/2$ ground state, which is 23.3 cm^{-1} below the first excited state of $7/2$. In the case of the corresponding $[\text{Mn}_2^{\text{IV}}\text{Mn}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{4+}$ complex the ground state of $S_t = 9/2$ is also well separated ($\Delta E = 17.2 \text{ cm}^{-1}$) from the $S_t = 7/2$ state.

The dinuclear chromium(III) complex $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ was synthesized by refluxing a suspension of $[\text{Cr}(\text{Me}_3\text{-9-N}_3)(\text{Br})_3]$, $\text{H}_2\text{-}\mathbf{502a}$ and triethylamine in methanol and in a 2:3:6 molar ratio until a deep red solution was obtained, by filtering the hot solution and by adding triethylammonium perchlorate to the filtrate [630]. The structure of this complex at 193 K clearly illustrates (Fig. 411) the metallamacrobicyclic nature of the [14]-membered heterocyclic ring. The coordination geometry of the chromium ions is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine ($\text{Me}_3\text{-9-N}_3$) and three oxygen atoms

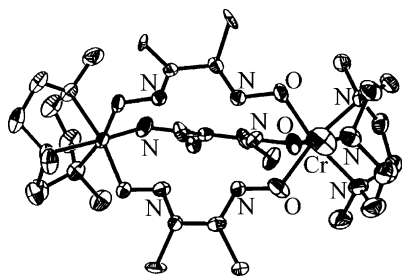


Fig. 411. Structure of $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2]^{2+}$ (adapted from Ref. [630]).

from three bridging dimethylglyoximate ligands, resulting in $\text{fac-Cr}_2\text{N}_3\text{O}_3$ cores. The chromium centers are nearly coplanar with the nitrogen atoms of a dimethylglyoxime ligand, with a $\text{Cr} \cdots \text{Cr}$ separation of $7.265 \text{ \AA}$ [630].

Again an exchange coupling is observed in this dichromium(III) complex ($J = -4.7 \text{ cm}^{-1}$), in which the chromium(III) centers are separated by a large distance of $7.27 \text{ \AA}$.

By slow addition of a concentrated aqueous solution of a strong base like tetrabutylammonium hydroxide to the doubly protonated complex $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$, the neutral species $[\text{Cr}_2(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]$ could be isolated as a red microcrystalline solid. Addition of concentrated HClO_4 to an acetone solution of $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ yielded the complex $[\text{Cr}_2(\text{H}_2\text{-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2]^{4+}$ containing tetraprotonated oxime nitrogens. At a very high concentration of protons, i.e. from an aqueous perchloric acid solution of $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$, $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\text{Me}_3\text{-9-N}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4$ was obtained [631].

$[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ has been proved to be an important precursor for generating the heterotrinuclear complexes $[\text{Cr}_2\text{M}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{n+}$ ($\text{M} = \text{Li}^+$, Mg^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{3+} , Fe^{2+} , Mn^{2+}) containing chromium(III) as the terminal ions by replacing the incorporated protons with different metal ions. Interestingly, the incorporation of a labile divalent metal ion, e.g. iron(II), into $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ is kinetically a very slow process [630,631].

In general, two different strategies were followed for synthesizing these trinuclear complexes. $[\text{Cr}_2\text{Cu}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ was directly prepared by refluxing a suspension of $[\text{Cr}(\text{Me}_3\text{-9-N}_3)(\text{Br})_3]$ and $\text{H}_2\text{-}\mathbf{502a}$ with the right stoichiometry in the presence of triethylamine to which metal(II) perchlorate was added. The other strategy involves the substitution of protons from the preformed macrobicyclic $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$, by the metal centers, like Li^+ , Mg^{2+} , Ni^{2+} , Co^{3+} , Fe^{2+} and Mn^{2+} in the presence of base.

$[\text{Cr}_2\text{Li}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ was obtained by neutralizing the protons in $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$, with a half-saturated solution of LiOH in ethanol. In the absence of a large excess of LiOH , $[\text{Cr}_2\text{Li}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ is unstable in protic solvents and $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ is reformed. Aqueous solution of $[\text{Cr}_2\text{Li}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ is strongly basic.

From an acetonitrile solution of $[\text{Cr}_2(\text{H-}\mathbf{502a})_2(\mathbf{502a})(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$ to which $\text{N}(\text{Et})_3$ was added, a microcrystalline red-brown precipitate of $[\text{Cr}_2\text{Mg}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ is obtained.

The trinuclear complex $[\text{Cr}_2^{\text{III}}\text{Fe}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$, where the iron(II) is low spin, is amenable to oxidation and gives rise to $[\text{Cr}_2\text{Fe}^{\text{III}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{3+}$, where the iron(III) is low spin, when oxidized in acetone with NO^+ . $[\text{Cr}_2^{\text{III}}\text{Fe}^{\text{III}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{3+}$ is very susceptible to reduction in solution and decomposes

slowly to the reduced form $[\text{Cr}_2\text{Fe}^{\text{II}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$.

Although the $\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}$ $[\text{Cr}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ and $\text{Cr}^{\text{III}}\text{Ni}^{\text{IV}}\text{Cr}^{\text{III}}$ $[\text{Cr}_2\text{Ni}^{\text{IV}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{4+}$ complexes could be synthesized in reasonably good yield, all attempts to isolate the $\text{Cr}^{\text{III}}\text{Ni}^{\text{III}}\text{Cr}^{\text{III}}$ species were in vain, presumably because of the small potential difference prevailing between the two higher oxidation states of nickel. That this is indeed the case is demonstrated by isolation of a mixture of $[\text{Cr}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ and $[\text{Cr}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{4+}$ in 1:1 ratio for all attempts to prepare $\text{Cr}^{\text{III}}\text{Ni}^{\text{III}}\text{Cr}^{\text{III}}$ species, which can be ascribed to a disproportionation reaction suffered by $[\text{Cr}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)]^{3+}$ [631]. $[\text{Cr}_2\text{Ni}^{\text{IV}}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{4+}$ as a black microcrystalline solid is formed by oxidation of $[\text{Cr}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ in acetonitrile with $\text{NO}(\text{ClO}_4)$ in the presence of a small amount of perchloric acid.

In $[\text{Cr}_2\text{Cu}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ the X-ray structure confirms the trinuclear nature of the cation (Fig. 412). The $[\text{Cu}(\mathbf{502a})_3]^{4-}$ anion bridges two terminal chromium(III) ions through its deprotonated oxime oxygens with a $\text{Cr} \cdots \text{Cu}$ separation of 3.583 Å. The trinuclear Cr-Cu-Cr unit is not perfectly linear. Two facially coordinated tridentate amine ligands complete the trigonally distorted octahedral coordination of the two chromium(III) centers. The coordination sphere about the copper ion is also strongly distorted. The copper(II) ion is thus displaced from the center of the complex and closer to two of the bridging dimethylglyoximate ligands; the distance to the third oxime ligand is remarkably long. The geometry of the copper(II) center has been envisaged as pseudo-square pyramidal with an $\eta^2\text{-}[\mathbf{502a}]^{2-}$ ligand at the apical position and is very similar to that found in the corresponding $\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}$ compound [631].

The structures of the dications in $[\text{Cr}_2\text{Ni}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ and $[\text{Cr}_2\text{Fe}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ are very similar to that of the dication in $[\text{Cr}_2\text{Cu}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$. The principal difference involves the systematic decrease of M–N bond lengths within the MN_6 coordination sphere in the order $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} \gg \text{Fe}^{2+}$.

The cyclic voltammograms of the complexes reveals both oxidation and reduction processes and indicates the forma-

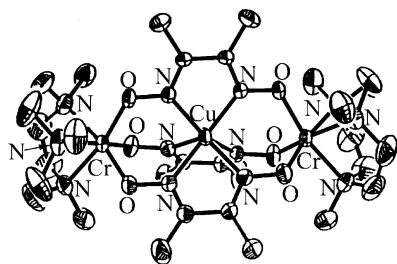


Fig. 412. Structure of $[\text{Cr}_2\text{Cu}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2]^{2+}$ (adapted from Ref. [631]).

tion of the uncommon species containing copper(III), nickel(III), nickel(IV) and low spin iron(III) ions.

Susceptibility data indicate the presence of weak to moderate exchange interactions, both ferro- and antiferromagnetic, between the paramagnetic centers. There are indeed two different coupling constants, J ($=J_{12}=J_{23}$) and J_{13} , operative in these clathrochelates. J_{13} represents the exchange interaction between the two terminal chromium(III) centers separated by a large distance of ~ 7.1 Å. The complexes containing only two paramagnetic centers, i.e. two chromium(III) centers, may be considered magnetically as dinuclear complexes. The evaluated exchange coupling constants for the chromium(III) complexes $[\text{Cr}_2^{\text{III}}(\text{H-}\mathbf{502a})_2(\mathbf{502})(\text{Me}_3\text{-9-N}_3)](\text{X})_2$ ($\text{X} = \text{Br}^-, \text{ClO}_4^-$) ($J_{13} = -5.1$ and -4.7 cm^{-1}), $[\text{Cr}_2^{\text{III}}(\text{H}_2\text{-}\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_4$ ($J_{13} = -3.1 \text{ cm}^{-1}$), $[\text{Cr}_2\text{Li}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)$ ($J_{13} = -5.8 \text{ cm}^{-1}$), $[\text{Cr}_2\text{Co}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ ($J_{13} = -0.3 \text{ cm}^{-1}$) and $[\text{Cr}_2\text{Fe}(\mathbf{502a})_3(\text{Me}_3\text{-9-N}_3)_2](\text{ClO}_4)_2$ ($J_{13} = 0 \text{ cm}^{-1}$) show that an intramolecular exchange coupling is observed in Cr_2 , and Cr_2Li complexes. The substitution of the protons in the dinuclear chromium(III) complexes by incorporating the low-spin d^6 Co(III) and Fe(II) ions, inhibits the exchange interaction ($J \approx 0$), demonstrating the different roles of the central diamagnetic ions on the magnitude of the magnetic interactions between the terminal chromium(III) centers separated by a distance of ~ 7.2 Å. The $\text{Cr}^{\text{III}}\text{Cu}^{\text{II}}\text{Cr}^{\text{III}}$ complex shows a ferromagnetic behaviour ($J_{12} = 18.5 \text{ cm}^{-1}$; $J_{13} = -7 \text{ cm}^{-1}$) while the other complexes show an antiferromagnetic behaviour: for $\text{Cr}^{\text{III}}\text{Fe}^{\text{III}}(1\text{s})\text{Cr}^{\text{III}}$ a $J_{12} = -15.7 \text{ cm}^{-1}$ and a $J_{13} = -3 \text{ cm}^{-1}$ and for $\text{Cr}^{\text{III}}\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}$ a $J_{12} = +4.5 \text{ cm}^{-1}$ and $J_{13} = -11.5 \text{ cm}^{-1}$ were found [631].

$[\text{Cu}_2\text{Zn}(\text{H-}\mathbf{502a})_2(\mathbf{502a})_2(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{-}\mathbf{502a} \cdot \text{H}_2\text{O}$ (Fig. 413), synthesized by reaction of $[\text{Cu}(\text{H-}\mathbf{502a})_2]$ with $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in alcoholic solution [632], consists of a chain of neutral $[\text{Cu}_2\text{Zn}(\text{H-}\mathbf{502a})_2(\mathbf{502a})_2(\text{H}_2\text{O})]$ units, together with noncoordinated $\text{H}_2\text{-}\mathbf{502a}$ and water molecules. The configuration around the zinc ion is distorted trigonal bipyramidal with four oximate oxygens from two $\{\text{Cu}(\text{H-}\mathbf{502a})(\mathbf{502a})\}$ fragments (each one acting as a bidentate ligand through its deprotonated oximate oxygens in *cis*

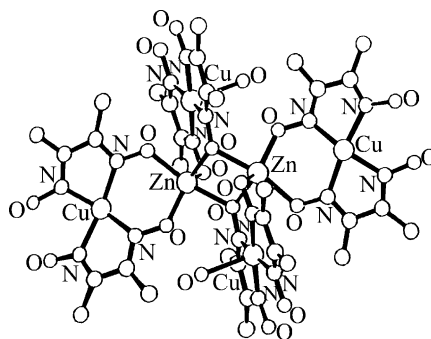


Fig. 413. Structure of $[\text{Cu}_2\text{Zn}(\text{H-}\mathbf{502a})_2(\mathbf{502a})_2(\text{H}_2\text{O})]_2$ (adapted from Ref. [413]).

positions) occupying one axial and the three equatorial positions and an additional oximate oxygen from a symmetry-related $\{\text{Cu}(\text{H-502a})(\text{502a})\}$ fragment filling the remaining axial position. The environment around the two copper(II) ions is distorted square pyramidal with four oximate nitrogen atoms building the equatorial plane. An oxygen atom from a water molecule and an oximate oxygen from a symmetry-related $\{\text{Cu}(\text{H-502a})(\text{502a})\}$ fragment occupy the apical position of the square pyramids around these copper ions. The trinuclear units are repeated through inversion centers. The intramolecular $\text{Cu}\cdots\text{Cu}$, and the intermolecular $\text{Zn}\cdots\text{Zn}$, and $\text{Cu}\cdots\text{Cu}$ separations are 5.506, 3.390, and 3.930 Å, respectively [632].

The magnetic behaviour of this complex from room temperature to liquid helium shows an overall ferromagnetic exchange interaction between the copper(II) ions. The exchange pathway and the magnetic interactions between the copper(II) centers occur intramolecularly (J) and intermolecularly (J') with an exchange coupling constant of 3.9 and 5.1 cm^{-1} , respectively. The results of the fit reveal the occurrence of ferromagnetic coupling in both exchange pathways within the Cu_4Zn_2 hexameric unit, that is through the diamagnetic zinc(II) ion and through the out-of-plane oximate bridge, the former being slightly less efficient than the latter. Variable-field magnetization data of $[\text{Cu}_2\text{Zn}(\text{H-502a})_2(\text{502a})_2(\text{H}_2\text{O})]$ at 2.0 K provide a further confirmation of the occurrence of ferromagnetic interactions within the Cu_4Zn_2 hexanuclear unit under consideration. The experimental data are very close to the theoretical curve corresponding to a quintet spin state and far above those arising from two non-interacting triplets and four isolated doublets. So the magnetic pathway within the Cu_4Zn_2 hexameric unit accounts quite well for the observed magnetic behaviour of $[\text{Cu}_2\text{Zn}(\text{H-502a})_2(\text{502a})_2(\text{H}_2\text{O})]$ [632].

15.3. Complexes with compartmental di acyclic and cyclic ligands derived from 2,6-diformyl-4-substituted phenols or 3-formylsalicylic acid

2,6-Diformyl-4-substituted phenols contain two formyl groups, capable to react with $\text{H}_2\text{N}-\text{OH}$ with the consequent formation of [1+2] compartmental end-off dioximine acyclic ligands. Macrocyclization of these systems occurs by treating them with trifluoro-ethyletherate. 3-Formylsalicylic acid can also react with $\text{H}_2\text{N}-\text{OH}$ to form the related [1+1] acyclic end-off compartmental monooxime derivatives.

These systems are excellent di- or poly-nucleating systems; the resulting complexes show peculiar magnetic properties: their antiferromagnetic or ferromagnetic behaviour, mediated by the N–O bridges, can be tuned by changing the metal ion assembly.

Reaction of 2,6-diacetyl-4-methylphenol, 2,6-diacetyl-4-*tert*-butylphenol or 2,6-diformyl-4-methylphenol with a large excess of both $\text{NH}_2\text{OH}\cdot\text{HCl}$ and CH_3COOK in ethanol affords, after aqueous work-up, the corresponding dioximes

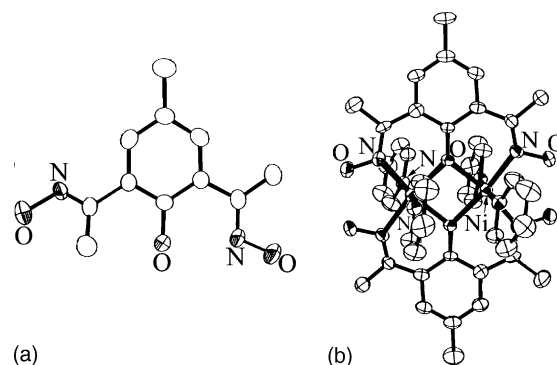


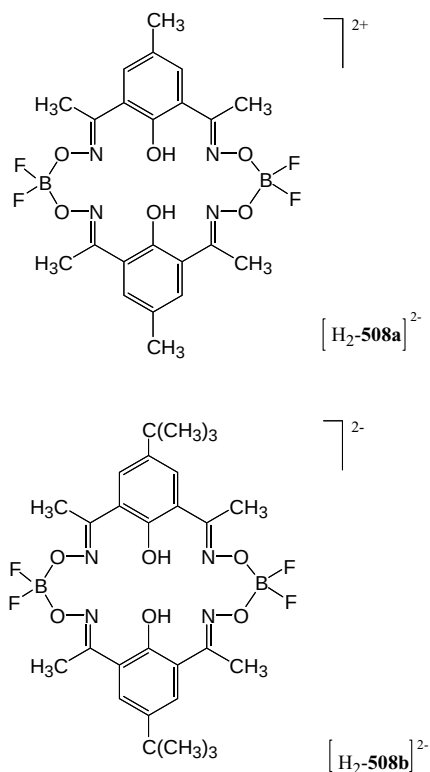
Fig. 414. Structure of $\text{H}_3\text{-507a}$ (a) and $[\text{Ni}_2(\text{H-507a})_2(\text{py})_4]$ (b) (adapted from Ref. [633]).

$\text{H}_3\text{-507a}$, $\text{H}_3\text{-507b}$ and $\text{H}_3\text{-507c}$ [633,634]. The structure of $\text{H}_3\text{-507a}$, obtained by slow evaporation from a $(\text{CD}_3)_2\text{CO}$ solution of the compound, (Fig. 414a), confirms that each $\text{C}=\text{N}$ double bond has a *E* configuration with the oxime hydroxyl groups and the aromatic ring on opposite sides of the double bond. An intramolecular hydrogen bond is observed within each dioxime molecule between the phenolic oxygen atom and a nitrogen donor of the oxime group. The dioxime molecules are associated through extensive intermolecular hydrogen bonding to produce extended molecular chains. This contrasts with the structure of salicylaldoxime in which only hydrogen-bonded dimers are formed. Association between adjacent chains occurs via long-range π -stacking interactions, the separation between adjacent ring centroids being ca. 3.7 Å.

$[\text{Cu}_2(\text{H-507a})_2]$ is stable enough to be prepared in glacial acetic acid using equivalent amounts of $\text{H}_3\text{-507a}$ and $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$. This compound is insoluble in common organic solvents, but can be obtained as pure microcrystals by diluting the reaction mixture with $\text{C}_2\text{H}_5\text{OH}$. All the other dicopper(II) and dinickel(II) complexes of the oximes $\text{H}_3\text{-507a}\cdots\text{H}_3\text{-507c}$ were obtained from the reaction of the corresponding oxime and metal(II) acetate in CH_3OH . Pyridine solutions of $[\text{Ni}_2(\text{H-507a})_2(\text{CH}_3\text{OH})_2]\cdot\text{CH}_3\text{OH}$ afford pink crystals of $[\text{Ni}_2(\text{H-507a})_2(\text{py})_4]\cdot 2\text{py}$ [633] whose structure (Fig. 414b) contains two nickel(II) centers bridged by two phenoxide oxygen atoms with two imine nitrogen donors completing the NiN_2O_2 equatorial plane. The center of inversion is between the two nickel ions. Each of the metal centers achieves a pseudo-octahedral configuration through the axial coordination of pyridine nitrogens. The two nickel atoms are separated by 3.058 Å. The pyridine rings on the same side of the equatorial plane are almost parallel and are separated by approximately 3.5 Å. This π -interaction is probably responsible for the stability of the octahedral tetrapyridine adduct in pyridine solution and in the solid state under a sensible pyridine vapour pressure. The apparent equivalence of the two nickel ions in $[\text{Ni}_2(\text{H-507a})_2(\text{py})_4]\cdot 2\text{py}$ indicates that the hexapyridine adduct loses two coordinated pyridine molecules and a pyridine of solvation in the absence of pyridine vapour and forms square

pyramidal $[\text{Ni}_2(\text{H-507a})_2(\text{py})_2]\cdot\text{py}$. Strong H-bonding between the oxime oxygens of one ligand and the oximate-oxygen of the other ligand renders the structure pseudo-macrocyclic [633].

Macrocyclization of these dioximato complexes was effected by treating them with boron trifluoride ethyl etherate; by this procedure $[\text{Cu}_2(\text{508a})]$, $[\text{Cu}_2(\text{508b})]$ and $[\text{Ni}_2(\text{508b})]$ have been obtained [633]. $[\text{Ni}_2(\text{508b})]$ consists of a neutral binuclear nickel(II) complex with no close intermolecular contacts and with a marked saddle-shaped bending of the macrocyclic ligand. This dramatic curvature puts the boron atoms 1.45 Å above the NiN_2O_2 center. The coordination sphere about the nickel(II) ions is planar (Fig. 415).



The copper(II) centers in $[\text{Cu}_2(\text{H-507a})_2]$, $[\text{Cu}_2(\text{508a})]$ and $[\text{Cu}_2(\text{508b})]$ are strongly antiferromagnetically coupled with $-2J$ values in the range 550–800 cm^{-1} . The nickel(II) centers in $[\text{Ni}_2(\text{H-507a})_2(\text{CH}_3\text{OH})_2]\cdot\text{CH}_3\text{OH}$ and $[\text{Ni}_2(\text{H-507a})_2(\text{py})_2]\cdot\text{py}$ are respectively weakly ($-2J = 3.2 \text{ cm}^{-1}$) or moderately ($-2J = 19.5 \text{ cm}^{-1}$) antiferromagnetically coupled, whereas $[\text{Ni}_2(\text{H-507b})(\text{H}_2\text{O})_2]$ shows a moderate ferromagnetic interaction ($2J = 5.1 \text{ cm}^{-1}$). All the complexes are electrochemically reducible in two one-electron steps [633].

Treatment of $\text{H}_3\text{-507c}$ with 1 equiv. of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ in CH_3OH affords $[\text{Co}_2(\text{H}_2\text{-507c})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_2](\text{Cl})_2\cdot 2\text{CH}_3\text{OH}$ (Fig. 416a) where each octahedral cobalt(II) center is bound to an N_2O_4 donor set from two dioxime ligands, one axial H_2O molecule and one axial CH_3OH molecule. The $\text{Co}\cdots\text{Co}$ distance is 3.092 Å. The two cobalt(II) ions lie in

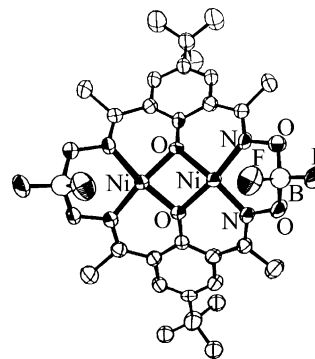


Fig. 415. Structure of $[\text{Ni}_2(\text{508b})]$ (adapted from Ref. [638]).

the plane defined by the four nitrogen and two oxygen donor atoms of the dioxime ligands. The complex has a pseudo-macrocyclic structure which results from hydrogen bonding between the two dioxime ligands. Opposite pairs of oxime hydroxyl groups lie marginally above and below this plane as a result of accommodating this hydrogen bond [634].

The reaction of $\text{H}_3\text{-507c}$ with a slight excess of $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ in tetrahydrofuran/methanol affords $[\text{Ni}_2(\text{H}_2\text{-507c})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ whose structure shows a centrosymmetric binuclear structure with both nickel(II) centers having octahedral stereochemistries. Each nickel(II) ion is bound to a N_2O_4 donor set from two dioxime ligands and to two axially coordinated water molecules (Fig. 416b). As in $[\text{Co}_2(\text{H}_2\text{-507c})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_2](\text{Cl})_2\cdot 2\text{CH}_3\text{OH}$, the nickel(II) ions in $[\text{Ni}_2(\text{H}_2\text{-507c})_2(\text{H}_2\text{O})_4]^{2+}$ lie almost in the plane defined by the four nitrogen and two oxygen donor atoms of the two dioxime ligands, at a $\text{Ni}\cdots\text{Ni}$ distance of 3.049 Å. The opposing pairs of oxime hydroxyl groups lie slightly above and below this plane as a result of accommodating a hydrogen bond between them. Again, this association results in the complex having a pseudo-macrocyclic structure. In addition, there is a hydrogen bond between the two water molecules above each face of the complex [634].

Reaction between $\text{H}_3\text{-507c}$ and other nickel(II) salts such as $\text{NiCl}_2\cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ affords extremely insoluble pale green solids in all cases [634]. The FAB mass spectral data indicate the presence of $[\text{Ni}_2(\text{H}_2\text{-507c})_2]^{2+}$ units within these products [634].

Reaction between $\text{H}_3\text{-507c}$ and a range of copper(II) salts affords similarly insoluble solids. The FAB mass spectral data indicate the presence of binuclear $[\text{Cu}_2(\text{H}_2\text{-507c})_2]^{2+}$ units within these materials although the precise nature of these products is unknown.

A solution of $\text{H}_3\text{-507c}$, frozen and then allowed to thaw by gradual warming to room temperature, reacts with 2 equiv. of $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ in CH_3OH to form $[\text{Cu}_2(\text{H}_2\text{-507c})_2(\text{ClO}_4)_2]$ where both copper(II) centers, 2.994 Å apart, display octahedral coordination geometries (Fig. 416c). The two dioxime ligands and the two copper(II) ions form an approximately planar array. Two symmetry-related bidentate ClO_4^- anions bridge in an asymmetric

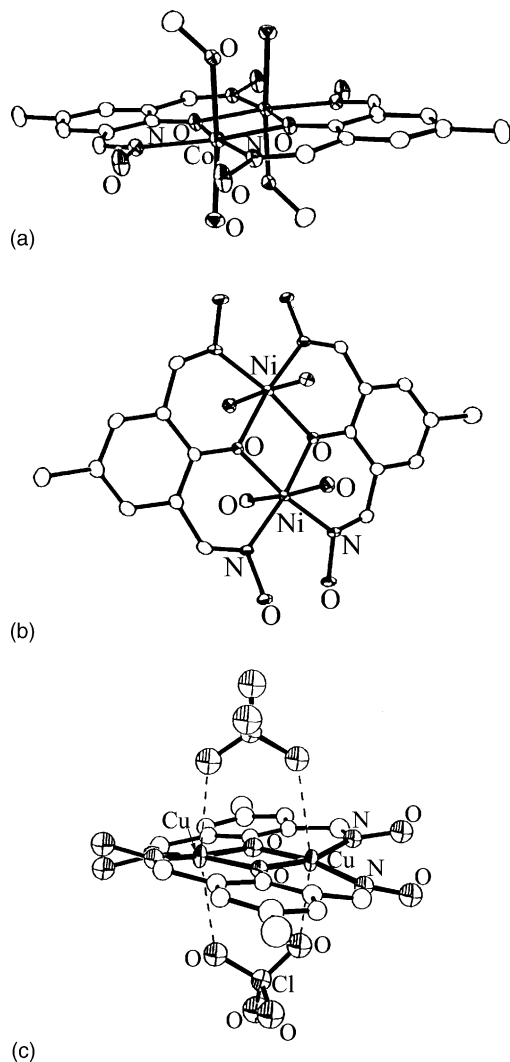


Fig. 416. Structure of $[\text{Co}_2(\text{H}_2\text{-507c})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_2]^{2+}$ (a) $[\text{Ni}_2(\text{H}_2\text{-507c})_2(\text{H}_2\text{O})_4]^{2+}$ (b) and $[\text{Cu}_2(\text{H}_2\text{-507c})_2(\text{ClO}_4)_2]$ (c) (adapted from Ref. [634]).

manner between the two copper(II) ions, one above and one below the plane of the hydroxydioxime ligands [634].

Magnetic susceptibility measurements over the range 2.5–340 K confirm that the complexes are antiferromagnetically coupled ($J = -6.9$, -16.0 and -452 cm^{-1} for $[\text{Co}_2(\text{H}_2\text{-507c})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2](\text{Cl})_2$, $[\text{Ni}_2(\text{H}_2\text{-507c})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{H}_2\text{-507c})_2(\text{ClO}_4)_2]$, respectively) [634].

The linear tetranuclear $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}$ complex $[\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_2(\text{507c})_2(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{-9-N}_3)_2(\text{CH}_3\text{OH})_2](\text{BF}_4)_2$ was synthesized by refluxing a suspension of $[\text{Fe}(\text{Me}_3\text{-9-N}_3)(\text{Cl})_3]$, $\text{H}_3\text{-507c}$, $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ and triethylamine in methanol and in a 1:1, 5:1:4 molar ratio for 1 h followed by filtration of the hot dark coloured solution of and by addition to the resulting solution of tetrabutylammonium tetrafluoroborate [635]. Each nickel(II) ion is coordinated to two azomethine nitrogens and two bridging phenolate groups from the oxime ligands. The nickel centers adopt distorted octahedral environments by interacting with *trans*

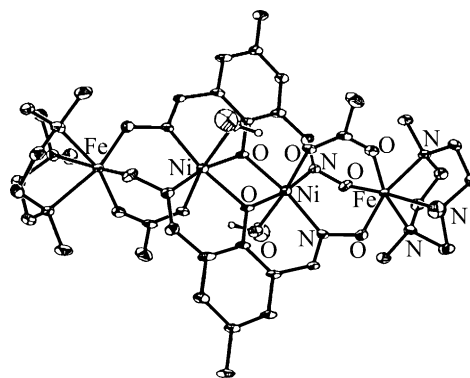
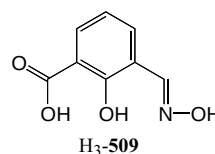


Fig. 417. Structure of $[\text{Fe}_2\text{Ni}_2(\text{507c})_2(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{-9-N}_3)_2(\text{CH}_3\text{OH})_2]^{2+}$ (adapted from Ref. [635]).

axially disposed methanol molecules and acetate ions that act as bridging ligands between the iron and nickel centers. The nickel centers deviates toward the methanol molecules from the mean plane of the N_2O_2 (phenoxide) donor set (Fig. 417). The two nickel(II) centers are separated by $3.086 \text{ \AA}$. The coordination geometry of the d^5 high-spin terminal iron(III) ions is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine $\text{Me}_3\text{-9-N}_3$, two oxygen atoms from the oxime ligands and one oxygen atom from the bridging acetate resulting in *fac*- FeN_3O_3 cores. The terminal iron(III) ions are displaced by $0.074 \text{ \AA}$ from the mean basal plane comprising atoms toward the apical nitrogen atom of the macrocyclic amine. The Fe-Ni-Ni-Fe skeleton is not perfectly linear. An intramolecular separation between the terminal iron ions of $9.996 \text{ \AA}$ is found while the $\text{Fe} \cdots \text{Ni}$ distance is $3.505 \text{ \AA}$ [635].

The magnetic interaction prevailing in $[\text{Fe}^{\text{III}}_2\text{Ni}_2(\text{507c})_2(\text{Me}_3\text{-9-N}_3)_2(\mu\text{-CH}_3\text{COO})(\text{CH}_3\text{OH})](\text{BF}_4)_2$ is antiferromagnetic in nature ($J_{12} = J_{34} = -6.8$, $J_{13} = J_{24} = -3.2$, $J_{23} = -7.7$, $J_{14} = -1.8 \text{ cm}^{-1}$) [635].

3-Formylsalicyclic acid oxime ($\text{H}_3\text{-509}$), derived from the condensation of 3-formylsalicyclic acid and hydroxylamine in aqueous solution, forms $[\text{Cu}_2(\text{H-509})_2] \cdot 0.5\text{H}_2\text{O}$ or $[\text{Ni}_2(\text{H-509})_2(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$, when allowed to stand for several days with copper(II) perchlorate in DMF/ H_2O or with nickel(II) acetate in water [636]. $\text{H}_3\text{-509}$ reacts with copper(II) acetate and NaOH in a 1:1:3 molar ratio in H_2O to afford $\text{Na}[\text{Cu}_2(\text{H-509})(\text{509})] \cdot 3\text{H}_2\text{O}$ which gives rise to $[\text{MnCu}_4(\text{H-509})(\text{509})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O} \cdot 2\text{DMF}$ with manganese(II) perchlorate in DMF/ H_2O [636].



$[\text{Ni}_2(\text{H-509})_2(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ has a dinuclear core with a *trans* arrangement of the two $[\text{H-509}]^{2-}$ ligands. There exists an inversion center at the center of the four-membered

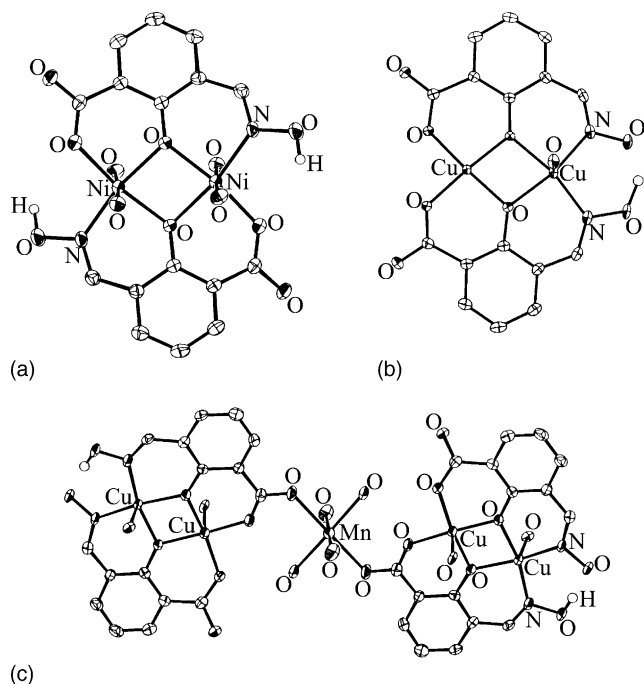


Fig. 418. Structure of $[\text{Ni}_2(\text{H-509})_2(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ (a), $[\text{Cu}_2(\text{H-509})(\text{509})(\text{H}_2\text{O})]^-$ (b) and $[\text{MnCu}_4(\text{H-509})_2(\text{509})_2(\text{H}_2\text{O})_4]$ (c) (adapted from Ref. [636]).

ring formed by the two nickel(II) ions and the two phenolic oxygen atoms. Four of the 12 water molecules are involved in axial donation to the nickel(II) ions, providing a pseudo-octahedral environment about each nickel(II) ion. The two basal NiNO_3 planes are coplanar but the two $[\text{H-509}]^{2-}$ ligands are bent [636]. Six water molecules in the lattice are hydrogen-bonded to the complex molecule. The remaining water molecules are captured in the crystal lattice [636] (Fig. 418a).

In $\text{Na}[\text{Cu}_2(\text{H-509})(\text{509})(\text{H}_2\text{O})]$ the *cis*-arrangement of the two ligands ($[\text{H-509}]^{2-}$ and $[\text{509}]^{3-}$) provides nonequivalent CuN_2O_2 and CuO_4 chromophores, sharing the two phenolic oxygen atoms. The $\text{Cu} \cdots \text{Cu}$ separation is 2.961 Å. The N_2O_2 cavity has a hydrogen-bonded $\text{N} \cdots \text{O} \cdots \text{H} \cdots \text{O} \cdots \text{N}$ linkage formed by the dioximate groups. The copper(II) ion in the N_2O_2 site has a square pyramidal geometry with a water molecule at the apical site while the other copper(II) ion in the O_4 site has a planar configuration [636] (Fig. 418b).

$[\text{Cu}_2(\text{H-509})_2]$, was proposed to have a *trans* configuration, which converts into *cis*- $[\text{Cu}_2(\text{H-509})(\text{509})]^-$ when reacted with an equimolar amount of NaOH ; this last complex, in turn, transforms into *trans*- $[\text{Cu}_2(\text{H-509})_2]$ by treatment with acid. This *cis*-*trans* interaction does not occur with the similar $[\text{Ni}_2(\text{H-509})_2(\text{H}_2\text{O})_4]$ species.

$[\text{MnCu}_4(\text{H-509})_2(\text{509})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O} \cdot 2\text{DMF}$ has a linear pentanuclear structure formed by the coordination of two $\{\text{Cu}_2(\text{H-509})(\text{509})\}^-$ units to the manganese(II) ion through one outer carboxylate oxygen. The copper(II) ions have a

square pyramidal geometry while the manganese(II) ion is pseudo octahedral [636] (Fig. 418c).

$[\text{Cu}_2(\text{H-509})_2]$ and $[\text{Cu}_2(\text{H-509})(\text{509})(\text{H}_2\text{O})]$ shows an antiferromagnetic interaction ($J = -225$ and 355 cm^{-1} , respectively). Similarly the magnetic behaviour of $[\text{Ni}_2(\text{H-509})_2]$ is antiferromagnetic ($J = -10 \text{ cm}^{-1}$). In the pentanuclear MnCu_4 complex an antiferromagnetic interaction operates between the adjacent copper(II) and manganese(II) ions through the carboxylate group and between the adjacent pentanuclear units, probably through the Cu-O-N-Cu pathway [636].

16. Conclusion

The very large number of papers published recently reveal the critical role played by Schiff bases in the preparation of polynucleating systems capable of binding two or more metal ions at preordered distances or in well defined arrays.

In these studies particular attention was devoted to asymmetric compartmental ligands, especially designed for different selective recognition processes at the adjacent sites. Interesting molecular devices or probes based on these recognition phenomena have been proposed.

These systems allow a more detailed comprehension of the magnetic, optical electronic and electric properties arising from the mutual interaction between the different metal ions. An appropriate asymmetry in the coordinating moiety of these compartmental systems assures a well defined coordination into the different adjacent coordination chambers; consequently the physico-chemical properties of these systems strongly depend on the features of the two chambers. It was shown that positional isomers quite often show remarkably different chemical and physical properties. Thus isomers with an antiferromagnetic or ferromagnetic behaviour, and with completely different fluorescent or luminescent behaviour were obtained.

The redox processes of the different metal ions at the two adjacent sites were extensively studied and attempts to isolate and characterize the intermediate compounds were often successful.

The possibility to address the well known reaction between suitable diformyl- or keto- and amine-precursors towards $[1+1]$, $[2+2]$, $[3+3]$, or $[4+4]$, macrocyclic and the $[1+1]$, $[1+2]$, $[2+1]$, or $[3+1]$ acyclic Schiff bases was further demonstrated, and the experimental conditions for a self-condensation of the precursors or a template procedure, in the presence of suitable metal ion, better established.

Appropriate preparative procedures were identified to reduce iminic groups to the corresponding amine analogues maintaining the designed macrocyclic or macroacyclic nature of the systems with a heterogeneous catalytic or stoichiometric procedure have been successfully studied.

These macrocyclic and macroacyclic Schiff bases and their reduced analogues have become quite sophisticated;

thanks to the possibility to insert branches, bridges and connections. Suitable structures have been developed to selectively encapsulate cations and/or anions or neutral molecules, facilitating their transport and separation or specific activation and reactivity. Thus very efficient, new separation or catalytic methodologies and technologies were proposed on the basis of knowledge of the parameters influencing the recognition and/or inclusion phenomena and the dynamic complexation and decomplexation of specific ionic or neutral species at specific carriers.

The use of host–guest, multiple recognition, replication processes, etc. offers the possibility to obtain highly reproducible molecular systems in appreciable yield with a well defined architecture. For instance the easy synthesis of oligo- or polymeric helicates was proven.

Moreover the formation of ceramic materials by hetero-dinuclear or -polynuclear systems, modified surfaces by coordination compounds was studied and a growing literature is currently available. In this field, special effort was devoted to the development of uni- and poly-dimensional molecular systems.

The availability of appropriate Schiff bases or their reduced analogues and the insertion of suitable functionalities at the periphery of their coordination moiety offers the possibility for them to be used as valuable, inexpensive bricks in the preparation of new molecular devices, probes, and materials, and facilitates a molecular approach to the description of the phenomena associated with these very complex systems.

All this acquired knowledge allows us to be more confident in directing exclusively or preferentially the chemical synthesis toward a mononuclear, dinuclear or polynuclear molecular system using quite simple Schiff base ligands and appropriate metal ions. Several examples have been reported in this review.

Thus knowledge of the coordination properties of the different metal ions quite often assures the synthesis of mono- or polydimensional systems by starting from quite simple and well known coordinating Schiff bases. On the contrary quite sophisticated compounds, cyclic and tridimensional in nature, are very promising in selective activation, reactivity and catalysis and also in unconventional transport and separation technology.

These data together with the large variety of results, published in recent years, and partially reported in the present review, assure a brilliant future for Schiff base ligands and related derivatives, perhaps completely unexpected when the first condensation reactions were carried out a long time ago.

This is strongly supported by the large number of very reputable papers published in 2002, not included in this review, dealing with synthesis, characterization and possible applications of new formyl- [637–644] and amine precursors [645–647], acyclic [648–653] and macrocyclic systems [654–659], compartmental symmetric [660–670] or asymmetric acyclic [671–674], macrocyclic [675–686] and

macropolycyclic ligands [687–691] and related homo- and hetero-dinuclear or -polynuclear complexes.

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