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Heterodinuclear metal complexes of phenol-based compartmental macrocycles

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Contents

Abstract

This article concerns recent progress in the derivation of heterodinuclear metal complexes from phenol-based compartmental macrocycles. Focus is placed on the design of unsymmetrical macrocycles whose two metal-binding sites, sharing two phenolic oxygens, are dissimilar with respect to the cavity size, coordination number, or the nature of donor atom. The stereochemistry, physicochemical properties and reactivities of the heterodinuclear complexes derived from these compartmental macrocycles are reviewed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Heterodinuclear; macrocycle; compartmental ligands

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1. Introduction

The application of designer compartmental ligands to the study of dinuclear metal complexes first occurred in the early 1970s and the term *binucleating ligand* was introduced by Robson [1] for polydentate chelating ligands that are capable of

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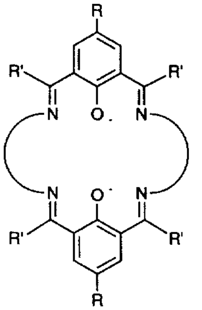
simultaneously binding two metal ions in close proximity. If the metal ions used are of the same type then the term *homodinuclear* is used and if the two metal ions are different then the complex is termed *heterodinuclear*.

One interest in such bimetallic complexes lies in the area of magnetochemistry. Studies on the magnetic properties of homo- and heterodinuclear complexes have significantly helped in advancing our understanding of spin-exchange mechanisms, relating them to the geometries and to the ground state electronic configurations of the constituting metal ions, and to the nature of the bridging group [2]. A second area of interest is bioinorganic chemistry where dinuclear complexes can serve as synthetic analogs for bimetallobiosites and so give insight into the significance of the bimetallic cores present therein [3]. This is very topical with the recent recognition of the heterodinuclear cores at the metallobiosites in purple acid phosphatase (FeZn) [4], human calcineurin (FeZn) [5] and human protein phosphatase 1 (MnFe) [6] stimulating a search for model complexes of unsymmetrical ligands which can bind two dissimilar metal ions in close proximity [7].

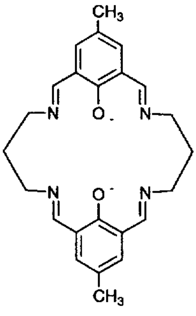
Various types of compartmental ligands including the end-off type, the side-off type and the macrocyclic type have been developed [8–11]. The macrocyclic Schiff bases (**1**), derived from the [2+2] condensation of a 2,6-diacyl-substituted phenol and a diamine, form a unique family of compartmental ligands. Many modifications can be made to the basic structure such as the provision of different lateral chains, the introduction of an additional donor atom on one lateral chain, and partial or full saturation at the azomethine linkages. For the macrocycles which have been reduced at the azomethine groups, a potentially donating auxiliary can be introduced at the aminic nitrogen as a pendant arm. Unsymmetrical modifications of the macrocycles are of importance for providing discrete heterodinuclear core complexes. The present review is concerned with heterodinuclear metal complexes derived from symmetrical and unsymmetrical phenol-based compartmental ligands of this family.



1

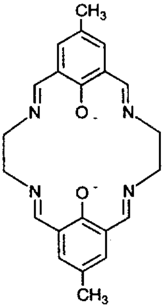
2. Heterodinuclear complexes of N(imine)$_4$O$_2$-type macrocycles

The symmetrical macrocycle $(L^1)^{2-}$ (**2**) was first obtained by Pilkington and Robson in 1970 as the dinuclear metal(II) complexes $M_2(L^1)X_2$, in a one pot reaction of 2,6-diformyl-4-methylphenol, 1,3-diaminopropane and a M(II) ion [12]. This "direct template reaction" has been used for providing homodinuclear complexes of $(L^1)^{2-}$ and related symmetrical macrocycles [13–17]. The N_2O_2 cavity of $(L^1)^{2-}$, formed by a trimethylene lateral chain, has an appropriate size to accommodate a wide range of metal ions within its cavity. The analogous macrocycle $(L^2)^{2-}$ (**3**), the smallest member in this family, can accommodate only the small Cu(II) and Ni(II) ions [18–21] because the cavity derived from the ethylene lateral chain is small and the "salen" (N,N′-ethylenedisalicylaldiminate)-like entity embedded in the macrocyclic framework has little flexibility compared with salen itself. The synthesis of the metal-free, protonated form of $(L^1)^{2-}$ and $(L^2)^{2-}$ (and their homologs) has been described by Schroder et al. [22].



$(L^1)^{2-}$

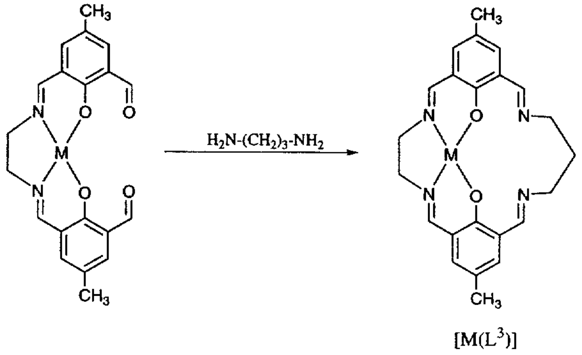
2



$(L^2)^{2-}$

3

In order to provide discrete heterodinuclear complexes of various combinations of metal ions, it was necessary to establish a general synthetic procedure for a wide range of macrocycles having similar and dissimilar lateral chains. The unsymmetrical macrocycle $(L^3)^{2-}$ was first reported by one of the present authors (H.Ō.) [18]. The copper(II) or nickel(II) complex of acyclic N,N′-ethylenedi(3-formyl-

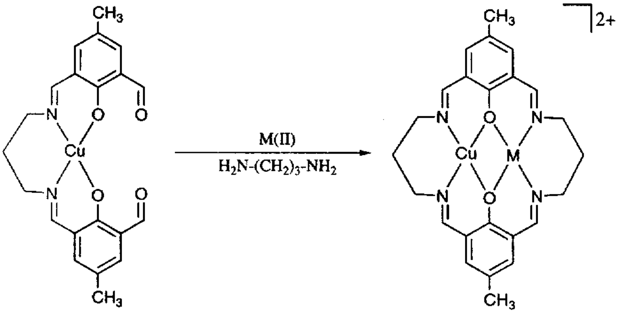


Scheme 1. Template synthesis of monometallic $[M(L^3)]$.

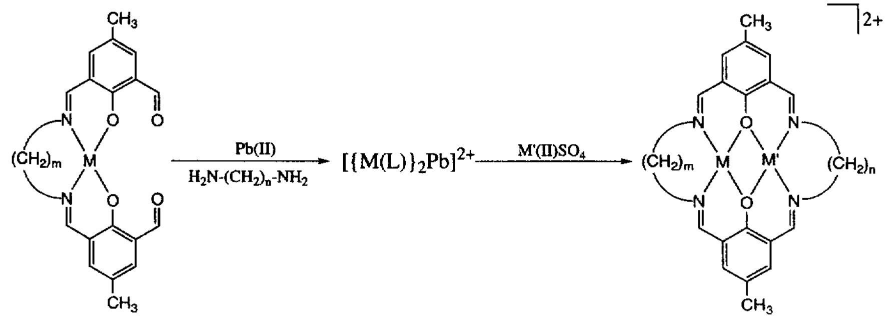
5-methylsalicylideneaminate) was prepared and subsequently reacted with an equimolar amount of 1,3-diaminopropane to obtain the mononuclear complex $[M(L^3)]$ (M = Cu(II), Ni(II)) (Scheme 1). The mononuclear complex can incorporate a second metal ion forming homodinuclear metal complexes $[M_2(L^3)]^{2+}$ [19]. This synthetic method was also applicable to symmetrical $(L^1)^{2-}$ and $(L^2)^{2-}$ but gave poor results for larger macrocyclic analogs.

A modification of this stepwise template reaction is to use a transition metal ion in the second step of the cyclization (Scheme 2) [23,24]. In this reaction the second metal ion is bound at the O_4 site to give efficient cyclization with a second diamine. This method was used by Gagne et al. for the preparation of heterodinuclear $Cu^{II}M^{II}$ (M = Mn, Fe, Co, Ni) complexes of $(L^1)^{2-}$ [25,26].

A more elegant modification of the template reaction has been made in our laboratory (Kyushu) that uses the Pb(II) ion in the second step of the cyclization (Scheme 3) [27]. In this reaction macrocycles with different combinations of lateral chains were obtained as trinuclear $M^{II}Pb^{II}M^{II}$ complexes and transmetallation of the Pb(II) with a transition metal, M′(II), to give dinuclear M(II)M′(II) complexes was successfully performed by using M′(II) sulfate salts. This method has a practical use for obtaining unsymmetrical macrocycles as described below.



Scheme 2. Synthesis of $[CuM(L^1)]^{2+}$ complexes.

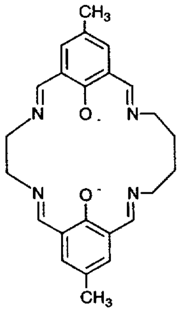


Scheme 3. Template synthesis of macroyclic heterodinuclear complexes via MPbM intermediates.

The electrochemical [25,28] and magnetic [29] properties of the Cu(II)M(II) (M = Mn, Fe, Co, Ni, Cu, Zn) complexes of $(L^1)^{2-}$ were studied. Significant antiferromagnetic interaction operates within a pair of metal ions (except for M = Zn) and good magnetic simulations have been obtained using the isotropic Heisenberg model except for the case of M = Co where zero-field splitting effect and spin–orbit coupling for the Co(II) ion are not negligible. A trend towards increasing antiferromagnetic interaction is observed in the series; $-J = 30$ (for CuMn) < 71 (CuFe) < 103 cm^{-1} (CuNi). For the corresponding CuCu complex a larger exchange integral of $-J = 294\ \mathrm{cm}^{-1}$ is obtained [15]. Electrochemical studies on the heterodinuclear complexes show that the magnetic interaction between the metal ions has little effect upon the Cu(II)/Cu(I) redox potential. The mixed-valence $\mathrm{Cu^ICu^{II}}$ complex is stabilized by 140 mV (3.2 ± 0.8 kcal mol^{-1}) relative to the heterobimetallic $\mathrm{Cu^IM^{II}}$ species and the stabilization is ascribed to electronic delocalization in the mixed-valence complex. No significant electronic delocalization is suggested for the $\mathrm{Cu^IM^{II}}$ complexes from their consistent $\mathrm{Cu^{II}M^{II}/Cu^IM^{II}}$ potentials.

The nature of the Cu(II)Ni(II) complex of $(L^4)^{2-}$ (4), $[\mathrm{CuNi}(L^4)(H_2O)(\mathrm{dmf})](\mathrm{ClO_4})_2 \cdot \mathrm{dmf}$, is shown in crystal structure (5) [30]. The Cu(II) resides in the N_2O_2 site with the ethylene lateral chain and assumes a planar geometry. The Ni(II), in the N_2O_2 site bonded by the tetramethylene chain, acquires a pseudo octahedral geometry by further interaction with dmf and water oxygen atoms at the axial sites. A very strong antiferromagnetic interaction operates between the metal ions ($J = -90\ \mathrm{cm}^{-1}$ based on $-2JS_{\mathrm{Cu}}S_{\mathrm{Ni}}$) to allow the thermal population only of the spin-doublet ($S_T = 1/2$) ground state at 80 K. The electronic structure of the spin-doublet ground state was studied by means of ESR spectroscopy at liquid nitrogen temperature. The recognition of a four-line hyperfine structure due to Cu ($I_{\mathrm{Cu}} = 3/2$) and the relationships, $g_\perp > g_\parallel$ and $A_\parallel = -(1/3)A_{\mathrm{Cu}}$ (A_{Cu}: the hyperfine coupling constant for analogous CuZn complex) [31,32], demonstrate that one unpaired electron of the spin-coupled complex exists in the molecular orbital of d_{z^2} character comprising d_{z^2}(Cu) and d_{z^2}(Ni) and is delocalized over the CuNi dinuclear core.

The dinuclear Ni(II)Mn(II) complexes, $[\mathrm{NiMn}(L^3)(\mathrm{dmf})_2](\mathrm{ClO_4})_2$ and $[\mathrm{NiMn}(L^4)(\mathrm{dmf})_2](\mathrm{ClO_4})_2$ [33], have the Ni(II) in the N_2O_2 site with the ethylene



$(L^4)^{2-}$

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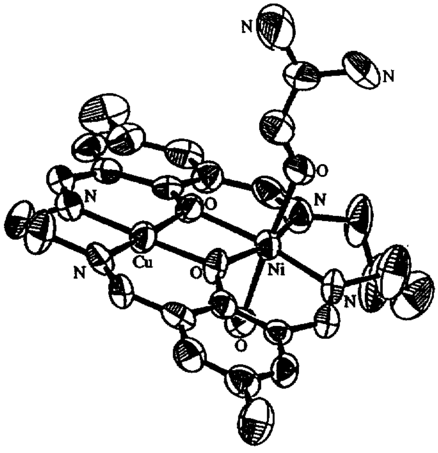
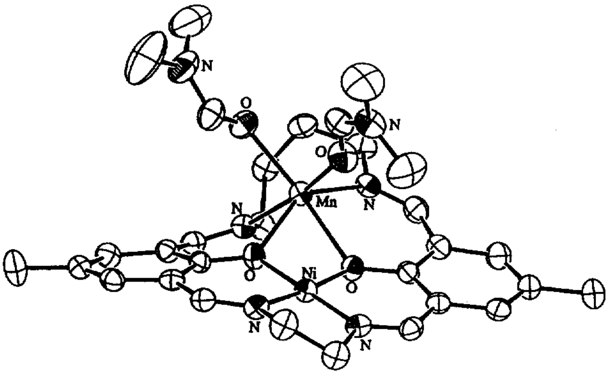


$[CuNi(L^4)(H_2O)(dmf)]^{2+}$

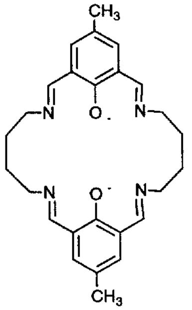
5

lateral chain and the Mn(II) in the N_2O_2 site derived from the trimethylene or tetramethylene lateral chain (**6**). The Ni(II) has a planar geometry and is diamagnetic. The Mn(II) cannot reside within the cavity because of the mismatch between the cavity size and the ionic radius of the Mn(II) ion and so assumes a distorted six-coordinate geometry with two DMF molecules in *cis* position. The deviation of the Mn from the N_2O_2 least-squares plane is 0.982 Å for the complex of $(L^3)^{2-}$ and 0.966 Å for that of $(L^4)^{2-}$. A similar deformed configuration about Mn has been found for $[Mn_2(L^1)(AcO)_2]$ where two neighboring positions of the six-coordinate Mn(II) are occupied by a chelating acetate group; the deviation of each metal from the basal N_2O_2 least-squares plane is smaller (0.75 Å) [34]. In the complex of the larger macrocycle $(L^5)^{2-}$ (**7**), $[Mn_2(L^5)(AcO)_2]$, two metal ions can reside within the cavity, bridged by two acetate groups at the axial sites (**8**) [35].



$[Mn_2(L^4)(dmf)_2]^{2+}$

6



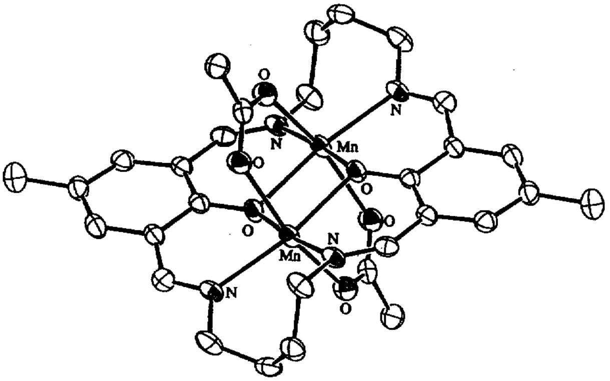
$(L^5)^{2-}$

7

Cyclic voltammetry indicates that the NiMn complexes are reversibly reduced to Ni(I)Mn(II) species (near −1.0 V vs SCE) and oxidized to Ni(II)Mn(III) species (near +1.5 V). The deeply green colored Ni(I)Mn(II) complex was generated in situ by controlled potential reduction and shows three visible bands of significant intensity at 570, 640 and 800 nm. These bands are attributable to d–d transitions of planar Ni(I) [36].

The Cu(II)Mn(II) complexes of $(L^1)^{2-}$, $(L^3)^{2-}$ and $(L^4)^{2-}$ probably have a similar core structure to that of the NiMn complexes, with a large deviation of the Mn(II) ion from the N_2O_2 cavity. A significantly strong antiferromagnetic interaction has been observed between the Cu(II) and Mn(II) ions ($-J=23$–$37\ cm^{-1}$) [33]. The complexes are stable at the electrode in DMF and DMSO and reversibly reduced to Cu(I)Mn(II) near −0.6 V and oxidized to Cu(II)Mn(III) near +1.0 V. The Cu(I)Mn(II) and Cu(II)Mn(III) complexes were also generated in situ by controlled potential electrolysis and characterized by visible spectroscopy.

In contrast to the difficult oxidation of Mn(II) in these NiMn and CuMn com-



$[Mn_2(L^5)(AcO)_2]$

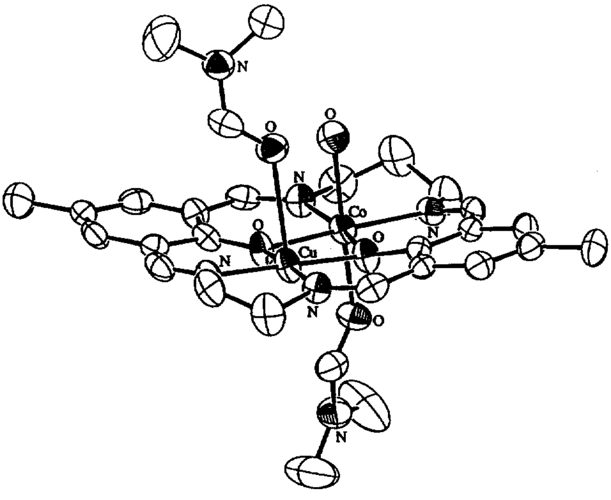
8

plexes (> +1.0 V), the corresponding dinuclear Mn(II) complexes are readily oxidized to Mn(II)Mn(III) species near +0.4 V [34,35]. In accord with the different electrochemical properties, the dinuclear Mn complexes catalyze the decomposition of hydrogen peroxide but the NiMn and CuMn complexes do not have such activity [34].

The Ni(II)Co(II) complexes of $(L^3)^{2-}$ and $(L^4)^{2-}$ and the Cu(II)Co(II) complexes of $(L^1)^{2-}$, $(L^3)^{2-}$ and $(L^4)^{2-}$ were obtained and the crystal structure of $[CuCo(L^3)(dmf)_2(H_2O)](ClO_4)_2$ was determined (**9**) [37]. The Cu in the N_2O_2 site with the ethylene lateral chain assumes a square-pyramidal geometry with a DMF oxygen at the apical site. The Co at the N_2O_2 site having the trimethylene lateral chain resides within the cavity and assumes a pseudo octahedral geometry together with DMF and water oxygens at the axial sites. The CuCo complexes have a subnormal magnetic moment at room temperature (4.26–4.42 μ_B per CuCo) due to antiferromagnetic interactions between the metal ions but magnetic simulations were unsuccessful owing to the significant contribution of a secondary effect like zero-field and/or spin–orbit interaction. The NiCo complexes are paramagnetic ($S_{Ni}=0$), and are reversibly reduced at the electrode to Ni(I)Co(II) and then to Ni(I)Co(I). The deeply green colored Ni(I)Co(II) complexes were prepared in situ and are characterized by three visible bands typical of planar Ni(I). Similarly, the CuCo complex of $(L^2)^{2-}$ is stepwise reduced to Cu(I)Co(II) and then to Cu(I)Co(I). On the other hand, the CuCo complexes of $(L^3)^{2-}$ and $(L^4)^{2-}$ showed unusual electrochemical behavior at the electrode suggesting a scrambling or site-exchange of the metal ions.

3. Heterodinuclear complexes of $N(imine)_4O_2X$-type macrocycles

The unsymmetrical macrocycle $(L^6)^{2-}$ (**10**) has an additional amine nitrogen on one lateral chain to provide a four-coordinate and a potential five-coordinate metal-



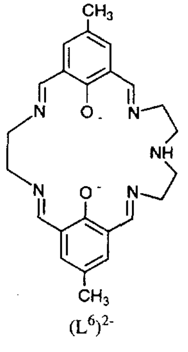
$[CuCo(L^3)(dmf)_2(H_2O)]^{2+}$

9

binding site sharing the phenolic oxygens. This ligand was obtained by a stepwise template reaction to give CuPb complexes with different counter anions [38]. The structure of $[CuPb(L^6)(AcO)]BPh_4$ indicates that the amine nitrogen is involved in the coordination to the Pb(II) ion. The CuPb complexes are good precursors for Cu(II)M(II) complexes (M = Mn, Fe, Co, Ni, Cu, Zn). The X-ray crystallography for $[CuMn(L^6)(AcO)]BPh_4$ has revealed a dinuclear core bridged by an acetate group (**11**). The Cu(II) is bonded to the original N_2O_2 four-coordination site and assumes a square-pyramidal geometry with an acetate oxygen at the apical site. The Mn(II) has a six-coordinate geometry derived from the N_3O_2 site and a bridging acetate oxygen. The geometry around the Mn is distorted from octahedral and has large Mn-to-ligand bond distances. Because of these steric reasons the Mn(II) is oxidized to Mn(III) with difficulty. This is also the case for the Co(II) in $[CuCo(L^6)]^{2+}$. On the other hand, the corresponding Cu(II)Fe(II) complex is readily oxidized to a $Cu^{II}Fe^{III}$ species at +0.64 V (SCE). The facile oxidation of the Fe(II) is due to the electronically preferred d^5 configuration of the Fe(III) ion. An antiferromagnetic interaction is observed for all the Cu(II)M(II) complexes.

A series of Ni(II)M(II) (M = Mn, Fe, Co, Ni, Cu, Zn) complexes of $(L^6)^{2-}$ has been obtained which contain planar Ni(II) [39]. Electrochemical properties have been reported for the complexes of M = Mn, Fe and Co.

The sulfur-containing macrocycle $(L^7)^{2-}$ (**12**) is prepared by a similar template reaction using 1,5-diamino-3-thiapentane, as a mononuclear Cu(II) complex containing a non-stoichiometric amount of perchloric acid, $Cu(L^7) \cdot nHClO_4$ $(0<n<2)$ [40]. Despite the lack of Pb(II) in this product, this ion is essential for cyclization since the non-template reaction between the acyclic ligand complex and 1,5-diamino-



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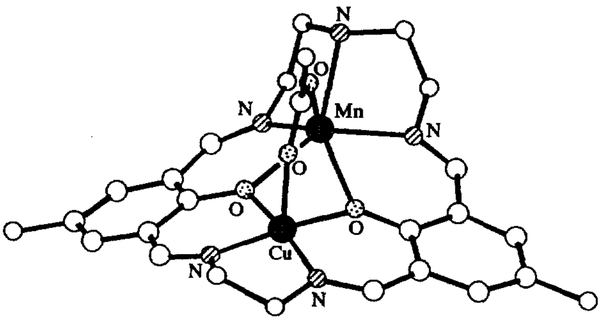
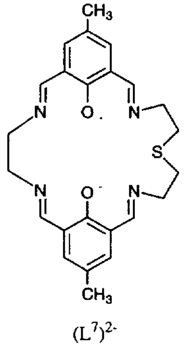


$[CuMn(L^6)(AcO)]^+$

11

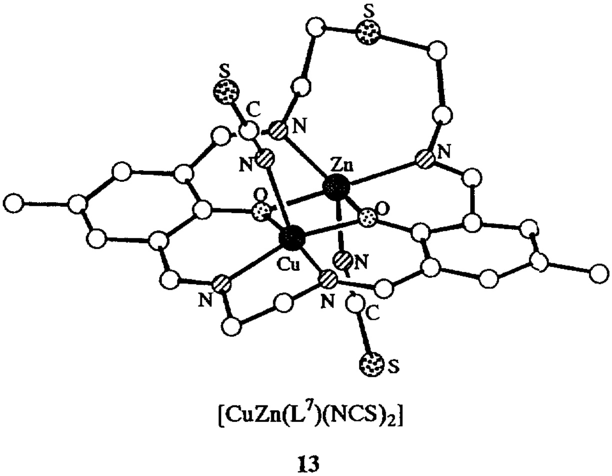
3-thiapentane gave a tarry mass. The non-stoichiometry of the perchloric acid indicates a mixture of two products $[Cu(L^7)]$ and $[Cu(H_2L^7)](ClO_4)_2$ and, in fact, acidification of the reaction mixture gave only the latter product. The two protons of $[Cu(H_2L^7)](ClO_4)_2$ are hydrogen-bonded in the five-coordination sites and characterized by ν(O–H) vibrations in the region of 3250–3100 cm^{-1}.

$[Cu(H_2L^7)](ClO_4)_2$ reacts with a second metal ion under alkaline conditions to form Cu(II)M(II) complexes $[CuM(L^7)(NCS)_2]\cdot H_2O$ (M=Co, Ni, Zn) and a Cu(II)Cu(I) complex $[Cu_2(L^7)]ClO_4$. In the dmf adduct of the CuZn complex $[CuZn(L^7)(NCS)_2]\cdot$dmf (**13**), the Cu resides in the four-coordination (N_2O_2) site and assumes a square-pyramidal geometry with an isothiocyanate nitrogen at the axial site; the axial Cu–N bond is 2.20(1) Å. The Zn in the S-containing N_2O_2S site also assumes a square-pyramidal geometry with two phenolic oxygens and two imine nitrogens in the basal plane and a thiocyanate nitrogen at the apex. The sulfur is disposed toward the Zn but the S–Zn separation (3.48 Å) is too large to be regarded as a coordination bond. However, the X-ray crystallographic result suggests that the sulfur could be involved in coordination when the exogenous thiocyanate is



12

replaced with a weakly coordinating anion. In the Cu(II)Cu(I) complex $[Cu^{II}Cu^{I}(L^{7})]ClO_4$ sulfur coordination to the Cu(I) ion certainly occurs; this complex shows the Cu(I)/Cu(II) process at positive potential (+0.07 V vs SCE). In the dinuclear copper(II) complex of $(L^6)^{2-}$, $[Cu_2(L^6)](ClO_4)_2$, the Cu(I)/Cu(II) process of the Cu in the N_3O_2 site occurs at −0.35 V (vs SCE) [38]. The sulfur coordination effect in electrochemistry giving rise to a positive shift of the Cu(II)/Cu(I) redox potential is well documented [41–43].

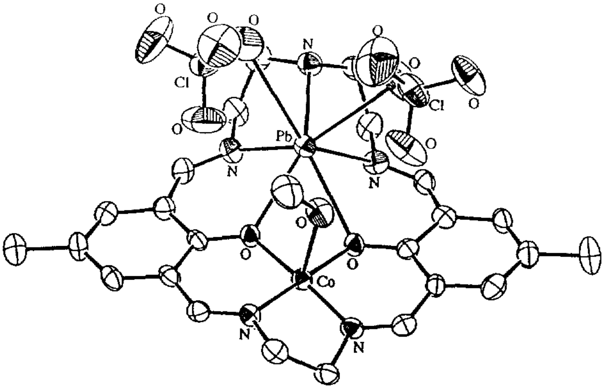


$[CuZn(L^7)(NCS)_2]$

13

Heterodinuclear complexes of $(L^6)^{2-}$, having the Co(II), Fe(II) or Mn(II) ion at the "salen"-like N_2O_2 site, are of particular interest because the salen complexes of these ions are reactive towards molecular dioxygen [44–46]. The $Co^{II}Pb^{II}$ complex $[CoPb(L^6)(MeOH)](ClO_4)_2$ has been obtained as orange prisms [47]. The Co(II) resides at the "salen"-like cavity to assume a square-pyramidal geometry together with a methanol ligand at the axial site (**14**). The Pb at the N_3O_2 site has a seven-coordinate geometry together with two perchlorate oxygens. The deviation of the

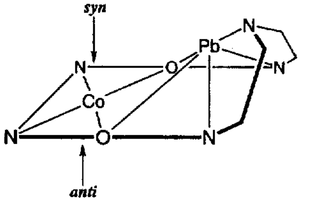
Pb from the least-squares plane defined by the two phenolic oxygens and two imine nitrogens and the coordination of two perchlorate groups to the Pb ion provide a large cavity above the planar Co(II), allowing the coordinative incorporation of one methanol in the cavity. The interatomic separation between the Pb and the methanol oxygen is 3.323 Å and suggests a bonding interaction between them. The axial methanol is readily released and replaced with dioxygen in the open air to give a superoxo-cobalt(III) complex $[CoPb(L^6)O_2](ClO_4)_2$, which was characterized by bulk magnetic susceptibility and EPR measurements. When heated at 80 °C in vacuo, the dioxygen adduct was deoxygenated into $[CoPb(L^6)](ClO_4)_2$. The reversible oxygenation–deoxygenation cycle of the CoPb complex has been confirmed by EPR and visible spectroscopies. Such an oxygenation does not occur in solution because of the collapse of the cave structure.



$[CoPb(L^6)(MeOH)(ClO_4)_2]$

14

At lower temperature in solution (<20 °C), the CoPb complex shows another oxygenation reaction to form a peroxo complex $[\{CoPb(L^6)\}_2O_2](ClO_4)_4$ [48]. 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*) (**15**). 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 $\{CoPb(L^6)\}$ entities with respect to the Co–O–O–Co linkage is prohibited. The formation of the *syn* structure of the peroxo complex is supported by recognizing that the $Co^{III}(OH)Pb$ complex, resulting from the hydrolytic substitution of the peroxo group ($Co^{III}\text{–O–O–}Co^{III} + 2H_2O = 2Co^{III}(OH) + H_2O_2$), has a *syn* core with a strong bonding interaction between the hydroxo oxygen and the neighboring Pb ion (Pb–O 3.04 Å). Based on this fact and together with the Pb–O(methanol) interaction in $[CoPb(L^6)(MeOH)](ClO_4)_2$, it is inferred that the oxygenation in the *syn* mode is facilitated by a $Pb\text{–}O_2^{2-}\text{–}Pb$ bonding interaction and this interaction prohibits the free rotation of the two CoPb entities with respect to the peroxo O–O bond (**16**).



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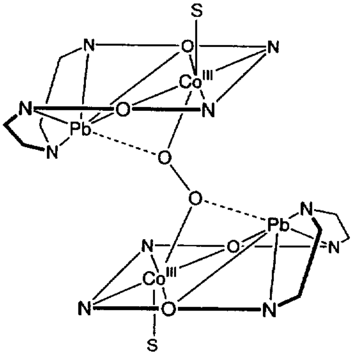
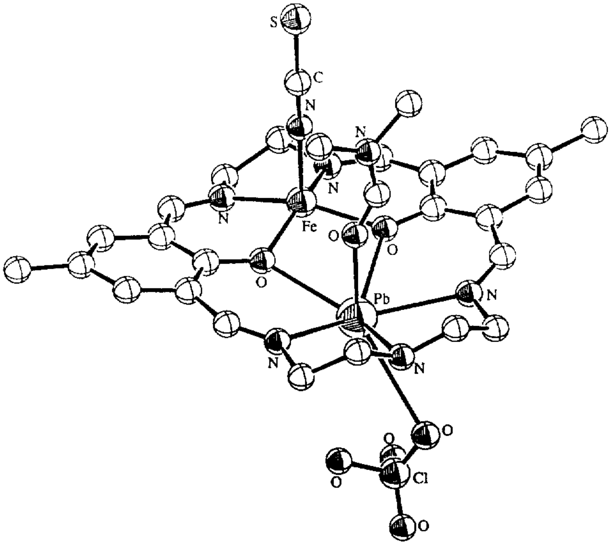


16

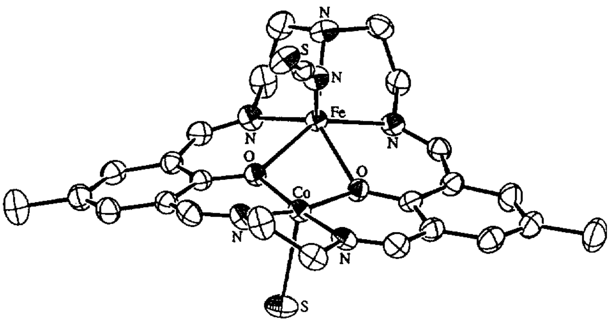
The *anti* and *syn* core structures of the dinuclear complexes of $(L^6)^{2-}$ were presumed not to interconvert readily. However, the Fe(II)Pb(II) complex $[FePb(L^6)(NCS)(dmf)]ClO_4$ is shown to have an intermediate core between *anti* and *sym* (**17**) [49]. The Pb in the five-coordination N_3O_2 site has a seven-coordinate geometry together with one DMF oxygen and one perchlorate oxygen. The geometry can be depicted as a distorted pentagonal-bipyramid with the N_3O_2 donor atoms of the cavity on the basal plane and the DMF and perchlorate oxygens at the axial sites. The sum of the in-plane bite angles O1–Pb–O2, O2–Pb–N3, N3–Pb–N4, N4–Pb–N5 and N5–Pb–O1 is 348.6°. The Pb–O3(DMF) distance is the shortest among the Pb-to-ligand bonds (2.394(1) Å), however the Pb–O4(perchlorate) distance is significantly elongated (3.15(2) Å). The structure of the FePb complex suggests that the *syn* and *anti* cores can be interconverted to each other.

A series of Co(II)M(II) (M = Mn, Fe, Co) complexes of $(L^6)^{2-}$ have been derived from the CoPb complex by transmetallation [50]. The acetate complexes $[CoM(L^6)(AcO)]ClO_4$ have a *syn* core bridged by the acetate group, very similar to that of $[CuMn(L^6)(AcO)]BPh_4$ (**11**). The thiocyanate complexes $[CoM(L^6)(NCS)]ClO_4$ have an *anti* core with the thiocyanate sulfur at the axial site of the Co(II) (**18**). The terminal thiocyanate nitrogen coordinates to the M(II) ion of another complex, providing a linear chain with Co(II)–SCN–M(II) linkage. The Co(II) is high-spin in the acetate complexes but low-spin in the thiocyanate complexes.



[FePb(L^6)(NCS)(dmf)(ClO_4)]

17



[CoFe(L^6)(NCS)]$^+$

18

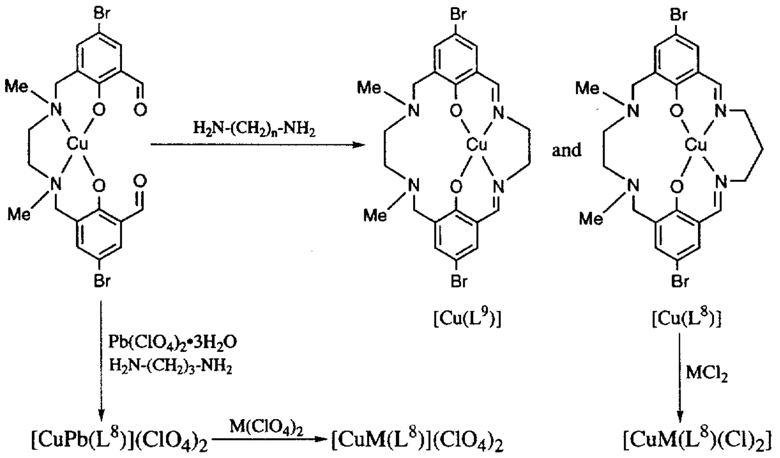
Unsymmetrical macrocycles with an alcoholic hydroxy group on one lateral chain have been obtained [24,51]. The hydroxy group is involved in coordination to the Pb in the Cu(II)Pb(II) complexes. However, the OH group is not coordinated in the transition metal dinuclear complexes, though it can play a role in association of dinucleating units in bulk.

4. Heterodinuclear complexes of N(amine)$_2$N(imine)$_2$O$_2$-type macrocycles and analogs having auxiliaries at amino nitrogens

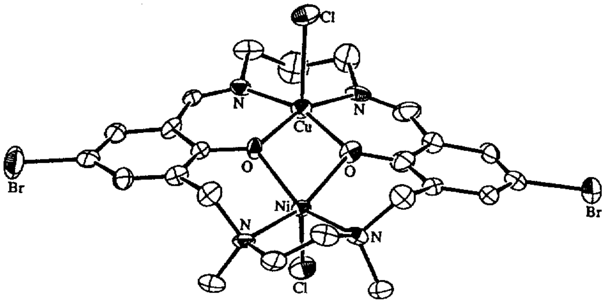
Unsymmetrical compartmental macrocycles having N(amine)$_2$O$_2$ and N(imine)$_2$O$_2$ metal-binding sites sharing two phenolic oxygens are still limited. In order to provide such unsymmetrical macrocycles it is recommended to use an appropriate acyclic precursor in the template cyclization. Acyclic N,N′-dimethyl-N,N′-ethylenedi(5-bromo-3-formyl-2-hydroxybenzylamine) was prepared by the Mannich reaction and used for the template synthesis of two macrocycles of this type, $(L^8)^{2-}$ and $(L^9)^{2-}$ (Scheme 4) [52]. Based on IR and visible spectra, the copper(II) complex of the acyclic ligand has the Cu ion in the N(amine)$_2$O$_2$ site. The reaction of the complex with ethylenediamine or 1,3-diaminopropane gave [Cu(L^8)] and [Cu(L^9)], respectively. The crystal structure for [Cu(L^8)]·2PrOH demonstrates that the Cu(II) ion migrates from the N(amine)$_2$O$_2$ site to the N(imine)$_2$O$_2$ in the cyclization process.

[Cu(L^8)] reacts with metal(II) chlorides to form dinuclear Cu(II)M(II) complexes [CuMCl$_2$(L^8)] (M = Mn, Co, Ni, Cu, Zn) [53]. The crystal structure of [CuNiCl$_2$(L^8)]·CH$_3$OH shows that the Cu is in the original iminic site and the Ni in the aminic site (**19**). Both of the metal ions have a square-pyramidal geometry with a chloro ligand at the axial site. The Ni–Cl bond distance is 2.295(5) Å, while the Cu–Cl bond distance is elongated (2.573(5) Å) owing to the Jahn–Teller effect.

The macrocycle $(L^8)^{2-}$ is more readily obtained by the modified stepwise template reaction using Pb^{II} as the second template ion (Scheme 4) [54]. The crystal structure of [CuPb(L^8)(BzO)(DMF)]ClO$_4$ indicates that the Cu resides in the iminic site and Pb in the aminic site. The transmetallation of the Pb using a transition metal(II) gave a series of Cu(II)M(II) complexes (M = Mn, Co, Ni, Cu, Zn). The X-ray crystallographic study for [CuZn(L^8)(AcO)]ClO$_4$ demonstrates the migration of the



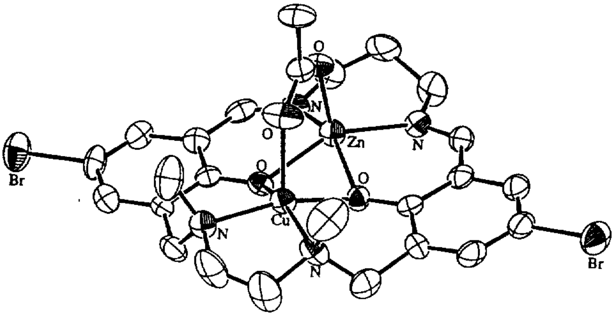
Scheme 4. Synthetic methods for Cu^{II}M^{II} complexes of L^8



$[CuNi(L^8)Cl_2]$

19

Cu(II) ion from the iminic site in the CuPb complex to the aminic site in the CuZn complex (**20**).

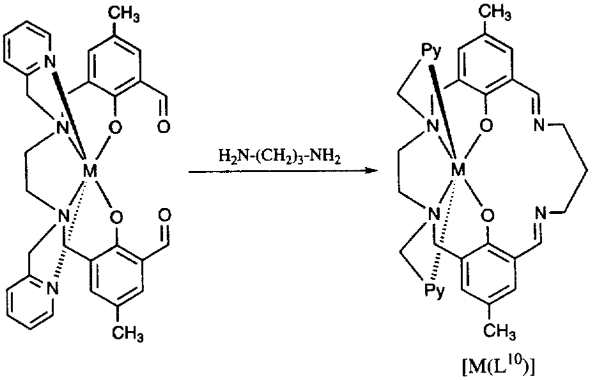


$[CuNi(L^8)(AcO)]^+$

20

The introduction of a donor auxiliary to each amino nitrogen provides new macrocycles having a potentially six-coordinate aminic N_4O_2 site and a four-coordinate iminic N_2O_2 site. Such a macrocycle $(L^{10})^{2-}$, having two pyridyl auxiliaries attached to the amino nitrogens, was prepared prior to the preparation of $(L^8)^{2-}$ [55]. The acyclic precursor dialdehyde was prepared and its Zn(II), Co(II) and Mn(II) complexes reacted with 1,3-diaminopropane to give mononuclear complexes of $(L^{10})^{2-}$, $[M(L^{10})]$ (Scheme 5). A similar reaction with ethylenediamine or *o*-phenylenediamine gave intractable products because these diamines cannot easily span the two aldehyde centers.

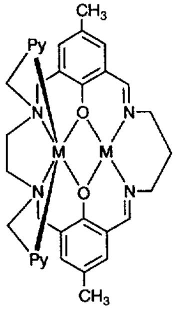
Homodinuclear complexes of $(L^{10})^{2-}$ are readily prepared by first adding two equivalents of a metal(II) acetate followed by cyclization with 1,3-diaminopropane. The site-specific heterodinuclear complexes $[Zn(L^{10})MCl]PF_6$ (M = Co(II), Mn(II)) and $[Mn(L^{10})ZnCl]PF_6$ were obtained by cyclizing the monometallic dial-



Scheme 5. Template synthesis of $[M(L^{10})]$.

dehyde complex with 1,3-diaminopropane under acid catalysis and then adding a metal(II) chloride salt.

Single-crystal X-ray diffraction structures were reported for homodinuclear $[Mn_2(L^{10})Cl]PF6$, $[Co_2(L^{10})Cl]PF6$ and $[Co_2(L^{10})](PF6)_2$ and mixed-valence $[Mn_2(L^{10})(\mu\text{-}Cl)Cl]PF_6$ [55]. In the first three complexes the metal in the N_4O_2 site has a deformed *cis* structure with the two pyridyl ligands on the same side of the mean molecular plane (**21**). Because of this distortion the Mn(II) and Co(II) ions in the six-coordination site are oxidized with difficulty. In the mixed-valence $Mn^{II}Mn^{III}$ complex, the oxidized Mn is that in the four-coordination site. The additional chloro ion bridges the pair of Mn ions, providing a nearly octahedral geometry about the Mn^{III}. The Mn^{II} in the six-coordination site has a trigonal-prismatic geometry where one of the phenolic oxygens is disconnected.

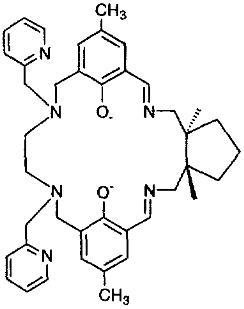


$[M_2(L^{10})]^{2+}$

21

The catalytic ability of the bimetallic complexes for epoxidation of styrene was studied using iodosobenzene. The $Mn^{II}Mn^{II}$ and $Mn^{II}Mn^{III}$ species are the most effective catalysts, but the MnZn and ZnMn species in coordination-position isomeric forms are effective too.

The analogous macrocycle $(L^{11})^{2-}$ (**22**) with the larger chiral diamine (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane is obtained as monometallic complexes $[M(L^{11})(H^+)_2]^{2+}$ (M(II)=Zn, Cu, Ni, Co, Mn) [56]. These complexes contain the M(II) ion in the aminic N_4O_2 site and two hydrogen-bonded protons in the iminic N_2O_2 site. The M(II), except for Cu(II), has a C2 symmetric six-coordinate geometry with a *trans* arrangement of the two pyridine ligands. The Cu(II) in the potentially six-coordinate site adopts a deformed five-coordinate geometry, and because of this reason the Cu(II) complex proved more difficult to prepare in the pure form.

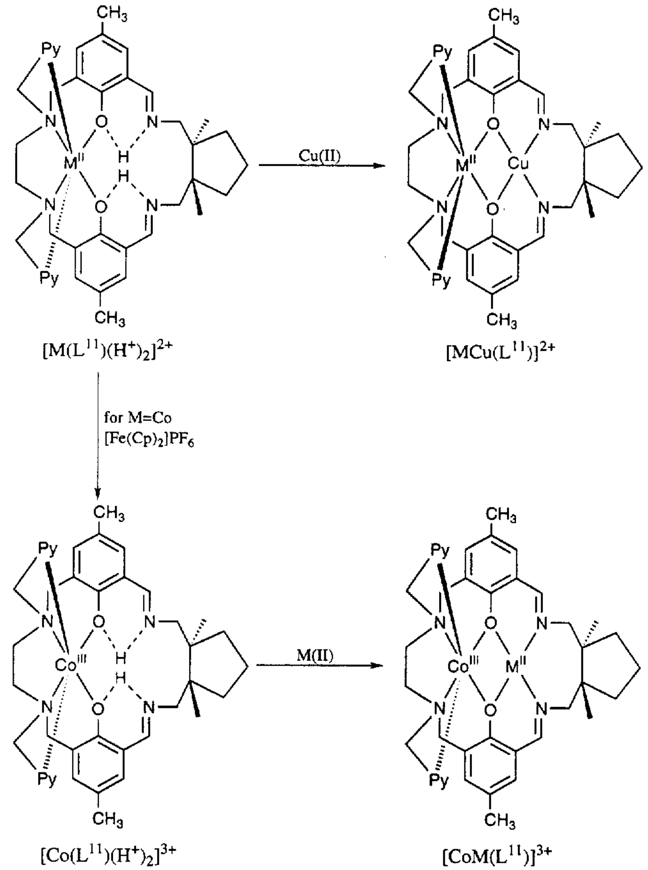


$(L^{11})^{2-}$

22

The oxidation of $[Co^{II}(L^{11})(H^+)_2]^{2+}$ with $[Fe(Cp)_2]PF_6$ gave the stable Co(III) complex $[Co^{III}(L^{11})(H^+)_2]^{3+}$ from which a series of heterodinuclear Co(III)M(II) complexes, $[Co(L^{11})MCl]^{2+}$ (M=Zn, Ni, Co, Mn) and $[Co(L^{11})Cu]^{3+}$, were prepared and isolated (Scheme 6) [56]. Another series of M(II)Cu(II) complexes $[M(L^{11})Cu]^{2+}$ (M=Zn, Cu, Ni, Co, Mn) were derived from $[M(L^{11})(H^+)_2]^{2+}$. In the former series the Co(III) in the aminic site has a C2 symmetric geometry with a *trans* arrangement of two pyridyl groups whereas in the latter series the M(II) (except for Cu(II)) has a deformed configuration with *cis* arrangement of the pyridyl groups.

The N–M–N bite angle is less than 90° when the M in the aminic N_4O_2 site is a divalent metal ion, and the angle becomes smaller as the radius of the metal ion increases: the bite angle is 78° and 83° for $[Mn(L^{11})(H^+)_2]^{2+}$ and $[Zn(L^{11})(H^+)_2]^{2+}$, respectively. A smaller N–M–N angle gives rise to a larger *trans* O–M–O phenoxide–metal angle and in a larger imine-site cavity in monometallic complexes: the O–M–O bite angle is 115° and 98° for $[Mn(L^{11})(H^+)_2]^{2+}$ and $[Zn(L^{11})(H^+)_2]^{2+}$, respectively. In bimetallic complexes containing two phenoxide bridges the O–M–O angle is about 80°. Thus, the metal binding in the iminic metal-binding site necessitates a considerable contraction in the O–M–O angle, which is constrained by the *trans* N–M–N angle of the ethylenediamine bridge. In order to accommodate the second metal, either a small radius metal ion such as Co(III) is required in the aminic N_4O_2 site or, when a larger metal ion is present, the ligand undergoes conformational and topological arrangement.

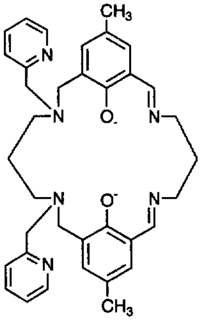


Scheme 6. Site-selective synthesis of $M^{II}Cu^{II}$ and $Co^{III}M^{II}$ complexes of L^{11}

Different M(II)–Cu(II) pairs may adapt in different ways to the binding sites of $(L^{11})^{2-}$, depending upon the preferred geometries of the M(II) in the aminic N_6O_2 site and the Cu(II) in the iminic site. The degree of the conformational changes in the M(II)Cu(II) complexes is thence reflected in their physicochemical properties. The Cu(II)/Cu(I) potential was monitored for the series of $[M(L^{11})Cu]^{2+}$ to show considerable variation with the M(II) ion; −0.54 V for Co(II), −0.72 V for Ni(II) and −0.92 V (vs Ag/AgCl) for Zn(II). The Co(III)/Co(II) potential was tracked as a function of the metals in the iminic site for the two series $[Co(L^{11})MCl]^{2+}$ (M(II)=Zn, Ni, Co, Mn) and $[Co(L^{11})M]^{3+}$ (M(II)=Zn, Cu, Ni, Co, Mn). The Co(III)/Co(II) couple range from −0.32 to −0.43 V for the former series and from −0.27 to −0.44 V for the latter series. The apparent differences in the Co(III)/Co(II) couple reflect the preferred structure of the M(II) in the iminic site; the preference of a M(II) for a geometry is communicated to the Co(III) ion at the aminic site.

The macrocycle $(L^{12})^{2-}$ (**23**) has been obtained as the monometallic complexes

$[M(L^{12})(H^+)_2]^{2+}$ (M(II) = Co, Zn) from which bimetallic complexes have been derived [57]. The introduction of a trimethylene lateral chain in both the aminic and iminic metal-binding sites allows the accommodation of two metal ions within the cavities [57,58]. The ^1H NMR spectra and X-ray crystallography for $[Zn(L^{12})(H^+)_2](PF_6)_2$ and $[Zn(L^{12})Zn(OAc)]PF_6$ demonstrate a six-coordinate structure about the Zn in the aminic site, with *trans* arrangement of the pyridine groups. Neither the $[Co(L^{12})(H^+)_2]^{2+}$ nor the $[Co(L^{12})ZnCl]^+$ complex could be oxidized by the ferrocenium ion to the Co(III) complex.



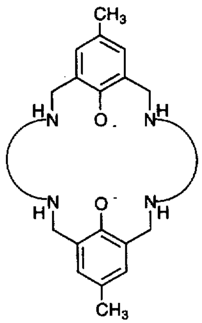
$(L^{12})^{2-}$

23

5. Heterodinuclear complexes of N(amine)$_4$O$_2$-type macrocycles and analogs having auxiliaries at amino nitrogens

Macrocyclic analogs fully saturated at azomethine linkages (**24**) have been obtained by the $NaBH_4$ reduction of the CuPbCu [59], PbPb [60] or MgMg [61–64] complexes of the tetra-imine macrocycles. This type of macrocycle shows a high flexibility for coordination and can adopt a non-planar, folded conformation depending upon the steric requirement of the metal ion and the nature of the counter anion [60,63–68].

The macrocycle $(L^{13})^{2-}$ (**25**), having two different cavities provided by ethylene and trimethylene bridges, respectively, reacts with $VO(acac)_2$ to produce a mixture of oxovanadium(IV) and -(V) complexes [66]. This mixture reacts with nickel(II) perchlorate to afford three complexes $[(V^{IV}O)(L^{13})Ni(H_2O)_2](ClO_4)_2$, $[Ni(L^{13})(V^{IV}O)](ClO_4)_2$ and $[\{(V^{IV}O)(L^{13})Ni(H_2O)\}\{(V^VO_2)(HL^{13})\}](ClO_4)_2 \cdot 3H_2O \cdot 2.5CH_3OH$. In the $\{(V^{IV}O)(L^{13})Ni(H_2O)\}^{2+}$ unit of the last complex, the V(IV) resides in the site of the trimethylene lateral chain and the Ni(II) in the site of the ethylene chain (see **26**). In the $\{(V^VO_2)(HL^{13})\}$ unit the V(V) occupies the smaller site of the ethylene chain, while the empty larger site assumes a folded configuration with one of its amine nitrogens protonated. The coordination geometry about the V(V) is *cis*-octahedral including the two oxo oxygens. The



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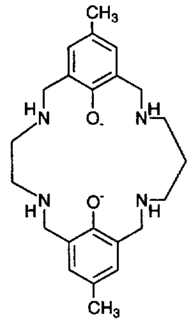
$\{(V^{IV}O)(L^{13})Ni(H_2O)\}^{2+}$ and $\{(V^{V}O_2)(HL^{13})\}$ units are anchored by the VO_2^+ oxygens, providing a six-coordinate environment for both V(IV) and Ni(II) in the dinuclear unit (**26**). A similar heterodinuclear core is supposed for $[(V^{IV}O)(L^{13})Ni(H_2O)_2](ClO_4)_2$ based on visible spectroscopic considerations. The Ni(II) in this unit is paramagnetic and a ferromagnetic spin-exchange is observed between the Ni(II) and V(IV) ions in the unit. $[Ni(L^{13})(V^{IV}O)](ClO_4)_2$ contains diamagnetic Ni(II), which is presumably bound to the smaller site of the macrocycle (**27**).

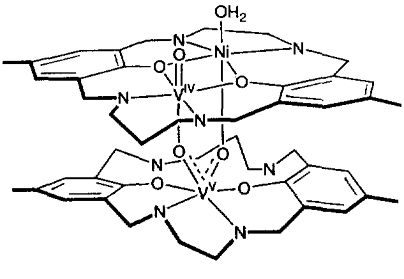


$(L^{13})^{2-}$

25

The monomeric oxovanadium(IV) complex, $[(V^{IV}O)(H_2L^{13})(SO_4)]\cdot 5H_2O$, was proven by X-ray crystallography to have the V(IV) ion in the larger site, in a six-coordinate mode together with an oxo and a unidentate sulfate oxygen. The reaction of this complex with $Ni(acac)_2\cdot 2H_2O$ gave $[Ni(L^{13})(V^{IV}O)(SO_4)]\cdot H_2O$ which contains diamagnetic Ni(II). The removal of the coordinated sulfate by $Ba(ClO_4)_2$ provides an alternative synthetic pathway for $[Ni(L^{13})(V^{IV}O)](ClO_4)_2$.

Two oxovanadium(IV)–nickel(II) complexes of the symmetrical macrocycle $(L^{14})^{2-}$, $[(VO)(L^{14})Ni(H_2O)_2(SO_4)]\cdot H_2O$ (purple) and $[(VO)(L^{14})Ni(\mu\text{-}SO_4)(H_2O)]\cdot 2H_2O$ (violet) [67], have been derived from the mononuclear precursor



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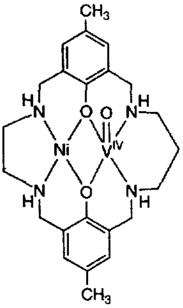

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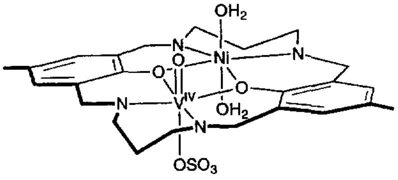
$[VO(H_2L^{14})SO_4] \cdot 3H_2O$ [64]. They are isomeric in composition but differ from each other in IR and electronic spectra and electrochemistry. In the former, the V(IV) and Ni(II) centers are reversibly oxidized at +0.436 and +0.756 V, respectively, while in the latter irreversible oxidation of both metal centers takes place at +1.05 and +1.25 V. Both show ferromagnetic interaction but the exchange integrals observed differ in magnitude ($J = +10$ and $+6\ cm^{-1}$, respectively). Based on IR spectroscopic considerations, monodentate sulfato-coordination is supposed for the former and the sulfato-bridging core for the latter (see **28** and **29**).



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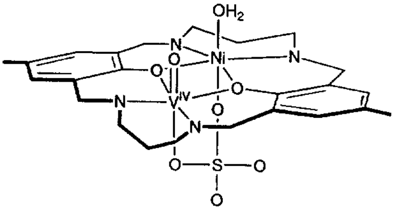
A series of FeM heteronuclear complexes of $(L^{14})^{2-}$, $[Fe^{III}M^{II}(L^{14})(\mu\text{-}OAc)(AcO)(H_2O)](ClO_4) \cdot nH_2O$ (M = Mn, Co, Ni, Zn) and $[\{Fe^{III}Co^{III}(L^{14})(\mu\text{-}OAc)(OAc)\}_2(\mu\text{-}O)](ClO_4)_2 \cdot 3H_2O$, have been reported [68]. The $Fe^{III}Ni^{II}$ complex has a μ-acetato-bis(μ-phenoxo) core where the geometry about



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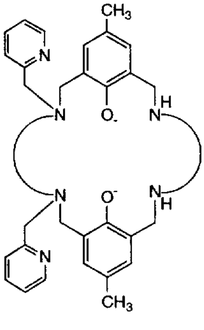
the Fe is six-coordinate together with an aqua oxygen and that about the Ni is also six-coordinate together with an acetate oxygen. $[\{Fe^{III}Co^{III}(L^{14})(\mu\text{-OAc})(OAc)\}_2(\mu\text{-O})](ClO_4)_2 \cdot 3H_2O$ has two μ-acetato-bis(μ-phenoxo)$Fe^{III}Co^{III}$ cores, similar to that of the $Fe^{III}Ni^{II}$ complex, and the two $Fe^{III}Co^{III}$ cores are combined by an oxo group at the axial site of the Fe^{III} ions.

The macrocycles with two pyridyl auxiliaries attached to the amino nitrogens of one metal-binding site (**30**) have been derived by $NaBH_4$ reduction of the corresponding diimino macrocyclic complexes comprised of lateral-chain combinations of tn/tn, tn/en, en/tn and en/en [69]. This type of saturated macrocycle has a high flexibility for coordination relative to the di-imine analogs and notable effects upon electronic properties and reactivities are reported for their mononuclear and homodinuclear metal complexes. Heterodinuclear meal complexes are not yet reported but these ligands will be of interest for their potential metal-selective complexation behavior.



30

Acknowledgements

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