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Review

Metal complexes of polyaza and polyoxaaza Schiff base macrocycles

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Contents

Abstract

This review describes the development on the coordination chemistry of multidentate Schiff base macrocycles with an emphasis on the author's contribution to the field. Particular attention is paid to effectiveness of metal ions – especially lanthanides – in supramolecular self-assembly of the components leading to organized structures. The article is focused on the design, template synthesis and characterization of the Schiff base mono- and homo- or heterodinuclear polyaza and polyoxaaza macrocyclic complexes. The factors which prove to be of much importance in directing the synthetic pathway in these systems are discussed.

Keywords: Lanthanides; Macrocycles; Schiff base complexes; Self-assembly; Template synthesis

1. Introduction

Interest in exploring metal ion complexes with macrocyclic ligands has been continually increasing owing to the recognition of their role played by these structures in metalloproteines. Schiff base macrocycles have been of great importance in macrocyclic chemistry. They were among the first artificial metal macrocyclic complexes to be synthesized. The metal complexes containing synthetic macrocyclic ligands have attracted a great deal of attention because they can be used as models for more intricate biological macrocyclic systems: metalloporphyrins (hemoglobin, myoglobin, cytochromes, chlorophylls), corrins (vitamin B_{12}) and antibiotics (valinomycin, nonactin). These discoveries have created supramolecular chemistry and its enormous diversity [1–5].

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Our research effort for the last 25 years has been focused on the design, template synthesis and characterization of the new supramolecular polyaza and polyoxaaza Schiff base mono- and homo- or heterodinuclear macrocyclic complexes of metal ions of varying radii and electron configuration – in particular rare earth elements – and the factors which prove to be of importance in directing the synthetic pathway in these systems.

Selective recognition and incorporation of rare earth elements into organized architectures has been the subject of growing importance in supramolecular chemistry. The peculiar chemical, structural, spectroscopic and magnetic properties of the trivalent lanthanide ions associated with their $4f^n$ configuration make them suitable for development of novel fascinating supramolecular photonic light-converting devices and sensors [6–21], contrast agents in magnetic resonance imaging [22–36], potential radiopharmaceuticals [24,37–40], sensitizers for photodynamic therapy and biomedical diagnostics [41–48], and artificial nucleases for hydrolytic cleavage or transesterification of the DNA and RNA phosphate diester backbone [49–64]. Because ionic radii, coordination chemistry and binding behavior of lanthanide(III) cations and alkaline earth metal cations are similar, the lanthanides with their remarkable multitude of spectroscopic and magnetic properties, have been broadly used as presumed isomorphous replacement for calcium and, to a lesser degree, other biometals, and serve as informative spectroscopic probes of metal binding sites in biologically important macromolecules [65–70]. The latest suggestion that lanthanides can be applied as therapeutic agents in the treatment of inflammation, arthritis and atherosclerosis is based on the ability of lanthanide ions to antagonize calcium-dependent processes [6,43,44,65,68,71]. Conjugation of macrocyclic complexes of yttrium and lanthanide radioisotopes to proteins in monoclonal antibody technology yields agents for radioimmunotherapy and other medical applications [10,72–74]. In all these cases the metal complex must be sufficiently stable in vivo and inert to metal release under physiological conditions in order to prevent damaging of nontarget cells. The Schiff base macrocyclic complexes, which form neutral or cationic complexes with the metal of interest, fulfill these requirements, because they are extremely rigid and display kinetic inertness towards metal release, whereas exocyclic ligands are labile and easy to change.

Macrocyclic Schiff bases have been widely studied because they can selectively chelate certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of the metal center, and coordinating properties of counterions. The chemistry of macrocyclic Schiff base complexes has been reviewed in excellent papers [75–81]. In this review we would like to illustrate the versatility of the macrocylic systems obtained through the condensation of diamines with dicarbonyl compounds, with the focus on our own research. Particular attention is paid to the lanthanide(III) macrocyclic Schiff base complexes. Selected results of others in the field are included.

2. Template synthesis of Schiff base macrocyclic complexes

Recognition of the importance of complexes containing macrocyclic ligands for supramolecular science, bioinorganic chemistry, biomedical applications, separation and encapsulation processes as well as formation of compounds with unusual properties and structures has led to considerable effort to develop methods for the synthesis of these compounds. Ideally the macrocyclic complex is formed by adding the required metal ion to a preformed macrocycle. However, the direct synthesis of macrocycles often results in very low yield of the desired product with the domination of competing linear polymerization or other side reactions.

Many synthetic routes to macrocyclic ligands involve the use of the metal ion template to orient the reacting groups of linear substrates in the desired conformation for the ring to close. The favorable enthalpy for the formation of metal–ligand bonds overcomes the unfavorable entropy of the ordering of the multidentate ligand around the metal ion and hence it promotes the cyclization reaction [1,81,82]. The effective method for the synthesis of Schiff base macrocyclic complexes which involves the condensation reaction between suitable dicarbonyl compounds and primary diamines carried out in the presence of appropriate metal ions which serve as templates in directing the steric course of the reaction. In this metal template effect the metal ion – through coordination – organizes the linear substrates to facilitate the condensation process which may lead toward either [1 + 1] or [2 + 2] macrocyclic products (Fig. 1).

Whether the cyclization proceeds through an intramolecular condensation to give a [1 + 1] macrocycle or through the bimolecular steps leading to a [2 + 2] macrocycle depends on

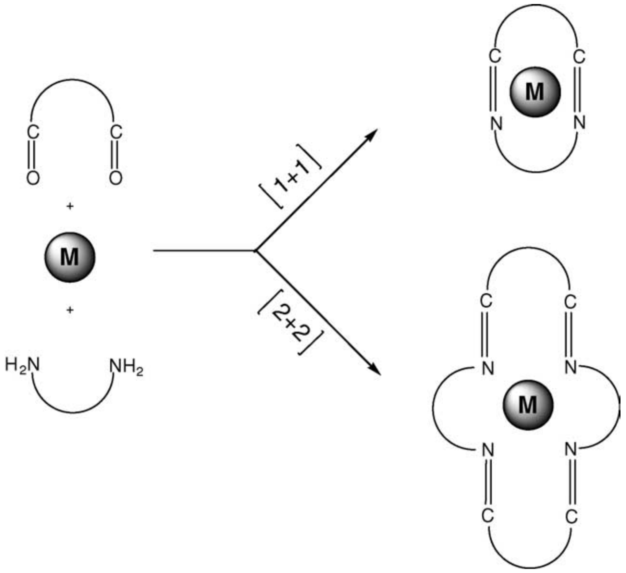


Fig. 1. Metal templated synthesis of [1 + 1] and [2 + 2] Schiff base macrocyclic complexes.

the relative proportions of linear substrates, the nature of the cation and reactants (chain length, number and location of potential donor atoms), the ratio of the template ionic radius to the cavity size, conformation of acyclic intermediates and coordination properties of counterions.

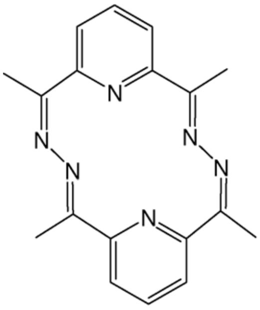
Rare earth metal ions have found to be very efficient metal templates in the synthesis of the complexes of this type. The first example of such an action of these ions in the synthesis of polyaza Schiff base macrocyclic compounds was reported for scandium(III) ion [83]. Rare earth elements are known to have little or no stereochemical requirements and can be accommodated by the stereochemical constraints enforced by the template process.

In some cases the mononuclear or dinuclear open-chain chelates with two terminal carbonyl groups or one terminal carbonyl group and one terminal amine group – considered as potential intermediates in the template process [1,81,82] – can be the final products of the Schiff base condensation [84–89]. The formation of these compounds instead of the expected macrocycles may be attributed to the unfavorable positioning of the terminal groups which decreases the probability of intermolecular linkage with next diamine molecule or a possibility of the nucleophilic attack of the amine nitrogen on the carbon atom of the carbonyl group and stabilizes the open-chain product once formed. The investigation of the mechanism of the formation of Schiff base complexes demonstrates that the structure and coordination mode of potential intermediates is one of the key factors that determine the preferred pathway of the metal-ion-templated condensation in the Schiff base systems and must be taken into account in the design and synthesis of desired products.

3. Tetradentate Schiff base macrocyclic complexes

The first example of the effectiveness of rare earth elements in the synthesis of Schiff base macrocycles is the template condensation reaction of 2,6-diacetylpyridine with hydrazine performed in the presence of scandium perchlorate [83]. The scandium ion has proved to be suitable template agent for the synthesis of the planar tetradentate nitrogen-donor macrocycle (L1) yielding the complex of formula $[ScL1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$. Zinc(II) and magnesium(II) ions may also act as templates for this macrocycle construction [90]. The investigation of the coordination template effect in generation of Schiff base macrocycles was then extended to the lanthanides. The heavier lanthanide cations (Ln = Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}) were found to be effective templating agents in the synthesis of L1 [91]. The complexes $[LnL1(H_2O)_2](ClO_4)_3 \cdot 4H_2O$ were isolated using nonstoichiometric amounts of reactants in order to prevent the formation of 2,6-diacetylpyridinedihydrazone. In contrast, an analogous reaction involving lighter lanthanides gave acyclic complexes $[Ln(L2)_2](ClO_4)_3 \cdot 2H_2O$ (Ln = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}) and $[LnL2(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ (Ln = Eu^{3+}, Gd^{3+}). A noticeable cation-cavity control is seen in the formation of L1 macrocycle, where the larger-radius lanthanides are ineffective as templates. The acyclic azine L2 is expected to be more flexible than the L1 macrocycle and thus able to form complexes with different geometries and adjust itself to the specific features of the coordinated metal ion. Yttrium(III) and dioxouranium(VI) ions, which are similar in size to scandium(III), dysprosium(III) and holmium(III) ions, can also promote the formation of the L1 macrocycle and give complexes of formula $[YL1(NO_3)_3] \cdot 2H_2O$ [92] and $[UO_2L1](NO_3)_2 \cdot 2H_2O$ [93]. In all these cases small quantities of metal chelates with 2,6-diacetylpyridine were isolated together with the above major products. When treating the latter compounds with hydrazine, L1 complexes of Tb^{3+} to Lu^{3+}, Y^{3+}, $UO_2{}^{2+}$ and L2 complexes of La^{3+} to Gd^{3+} were obtained. Thus the complexes of 2,6-diacetylpyridine are regarded as possible intermediates in the formation of macrocyclic L1 and acyclic L2 Schiff base complexes. The presence of a pyridine between the two carbonyl groups in 2,6-diacetylpyridine ensures initial chelation of the metal ion through the pyridine nitrogen and two oxygen atoms. Such coordination makes the carbonyl more susceptible to a hydrazine nitrogen donor attack. The synthesis of the free L1 macrocycle has also been achieved under high dilution conditions by treating L2 with an excess of hydrazine without the coordination template effect, albeit with low yield [90]. The importance of the metal ion in promoting the cyclic condensation is thus clear.

The scandium(III) ion has been shown to be effective template for the synthesis of a 14-membered Schiff base [1 + 1] cyclocondensation compound derived from 2,6-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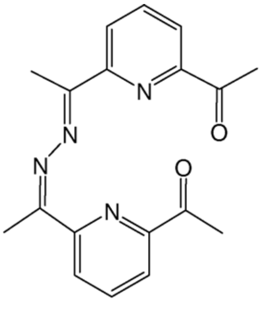
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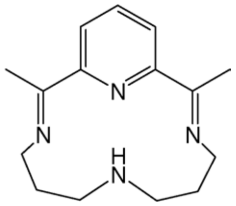
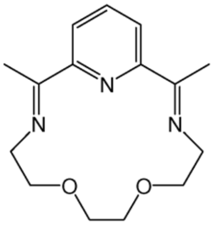

L3

diacetylpyridine and 3,3′-diaminodipropylamine [94]. The coordination number of five can be assigned to the scandium complex formulated as $[ScL3(H_2O)]Cl_3 \cdot 5H_2O$ assuming that the coordination sphere is filled by four nitrogen donor atoms of the ligand and oxygen atom of one water molecule. These findings appear to be of interest in view of applications of the stable Schiff base macrocyclic complexes of the radioactive ions conjugated to proteins in monoclonal antibody technology. ^{47}Sc, ^{90}Y, ^{153}Sm, ^{169}Yb, ^{177}Lu have sufficient energy to cause cell death following DNA cleavage. Consequently, they are clinically used in radioimmunodiagnosis and radioimmunotherapy [10,37,74].

Recently it was found that a nickel(II) complex of L3 represents one of the most reactive and selective catalysts for the site-specific DNA oxidation and it is convenient as a probe for DNA and RNA structures. An appropriately designed macrocyclic ligand for the metal ion can thus fine tune the activity of the complex toward the selective molecular recognition of nucleotides in DNA and RNA [95].

4. Pentadentate Schiff base macrocyclic complexes

The template reaction of 2,6-diacetylpyridine with 1,8-diamine-3,6-dioxaoctane in the presence of yttrium(III), dysprosium(III), erbium(III), thulium(III) and lutetium(III) chlorides and perchlorates (MX_3) produces the complexes of general formula $ML4(H_2O)_{3-6}X_3$ containing a pentadentate 15-membered L4 macrocycle with an N_3O_2 set of donors atoms as a result of [1 + 1] Schiff base cyclocondensation [96,97]. Attempts to obtain these macrocyclic compounds in the presence of metal(III) nitrates were unsuccessful. Nitrate anions are relatively good complexing agents for rare earth elements. The involvement of nitrate groups in the coordination with these cations may result in increasing the ionic radii to the values, for which the metal ions do not perfectly fit in the cavity of this macrocycle. Thus, when planning the template synthesis of macrocyclic compounds, the complexing properties of counterions should be also taken into account. Under the same reaction conditions the lighter lanthanides were found to be ineffective as templates in the synthesis of this 15-membered macrocycle. In the reactions in which 2,6-diacetylpyridine reacts with 1,8-diamine-3,6-dioxaoctane in the presence of lanthanum(III), samarium(III) and europium(III) chlorides and perchlorates (LnX_3), the ring closure does not occur. Instead, the $LnL5(H_2O)_6X_3$ complexes with ligand L5 as acyclic product of partial Schiff base condensation of two diketone molecules with one diamine molecule are formed [97]. However, rare earth elements act as suitable templates in the synthesis of related macrocycle L6 with greater ring size yielding the complexes of general formula $ML6X_3 \cdot nH_2O$, where $X = NO_3{}^-$ or Cl^-, $n = 1–6$ [98]. The 19-membered macrocycle L6 is product of the yttrium(III) and lanthanide(III)-promoted Schiff base condensation reaction between one molecule of 2,6-diacetylpyridine and one molecule of 1,12-diamine-4,9-dioxadodecane. L6, contrary to the 15-membered coronand L5 with a similar set of donor atoms, appears to be large enough to encapsulate all the lanthanides, irrespective of the ionic radii size of central atoms. As the lanthanides may be employed as informative spectroscopic probes for binding sites of biometals and in biomedical applications [6,41–48,65,68,71] it seemed to be of interest to relate the template action of rare earth metal ions and biologically important magnesium(II), zinc(II) and cadmium(II) ions in the synthesis of this system. The magnesium complex $MgL6(ClO_4)_2 \cdot 6H_2O$ and zinc complex $ZnL6(ClO_4)_2 \cdot H_2O$ were found to be less stable in comparison with the complex of cadmium $CdL6(ClO_4)_2 \cdot H_2O$ as well as with yttrium and lanthanide L6 complexes [98,99]. The difference in the stability of these complexes may be explained on the basis of the idea of size-match selectivity in the design and synthesis of Schiff base macrocyclic systems. Cadmium and lanthanide ions have similar ionic radii and may coordinate with 19-membered macrocycle in a planar conformation. Magnesium and zinc ions are evidently smaller and the formation of macrocyclic complexes in metal-promoted synthesis requires the adoption of an appreciably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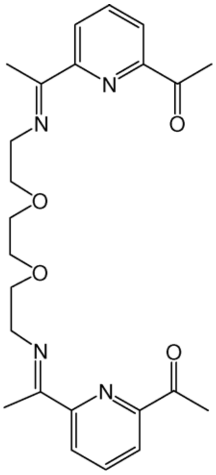
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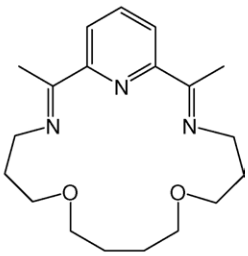
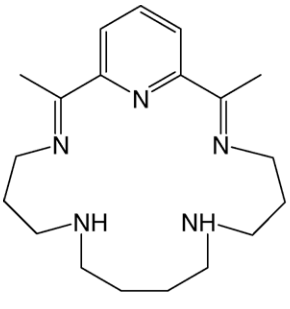

L6

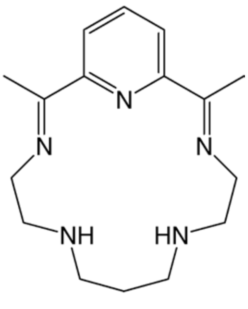
folded conformation of the macrocycle in order to maintain the pentadentate coordinating behavior of the ligand. This may cause steric crowding on one side of the macrocycle. The readjustment of the macrocycle conformation from the preferred one could explain the observed lower stability of the macrocyclic complexes with smaller metal ions in contrast to the behavior of the corresponding cadmium and rare earth element complexes.

Much effort has been devoted in recent years to the preparation and characterization of uranyl-specific complexing agents – “uranophiles” – with the objective of possible application as carriers for the transport of uranyl ion and neutral molecules through supported liquid membranes [100–103] and artificial receptors for anion recognition [104], as specific chelators for extraction purposes [105,106] and mimicry of active sites in metalloenzymes [107]. The effective sequestering of the radioactive species [7,108] and the antimicrobial activity of uranyl Schiff base complexes continues to be also a topic of vital interest [109]. The dioxouranium(VI) ion, which is normally surrounded equatorially by 4–6 donor atoms, was found to act as an effective templating agent for the synthesis of 19-membered macrocyclic compound L6 derived from 1,12-diamine-4,9-dioxadodecane and 2,6-diacetylpyridine [89]. The axial O═U═O unit in $[UO_2L6](NO_3)_2{\cdot}6H_2O$ complex is surrounded by N_3O_2 set of donor atoms of the polyoxaaza macrocycle in or close to the equatorial plane, so as to provide seven-coordinate pentagonal bipyramidal geometry. The U–O bond distance of 1.72 Å for this complex is typical for this structure. The ready formation of di-, tri-, tetra-, penta-, hexa- and hepta-uranyl-oxygen cluster ions in fast atom bombardment mass spectrometry experiments appears to be the general behavior of uranyl complexes irrespective of the ligand type [88,110].

The replacement of oxygen atoms by two nitrogen atoms using biogenic amine spermine (1,12-diamine-4,9-diazadodecane) instead of 1,12-diamine-4,9-dioxadodecane in metal-directed Schiff base [1 + 1] cyclocondensation reaction with 2,6-diacetylpyridine in the presence of yttrium(III) and lanthanide(III) (M) perchlorates yields 19-membered pentadentate macrocyclic complexes of formula $ML7(ClO_4)_2{\cdot}nH_2O$, where $n = 3–4$ [111].



L7



L8

Macrocyclic compounds containing biogenic amines are of particular interest as synthetic models of natural macrocyclic spermine alkaloids with high affinity toward nucleic acids [112,113].

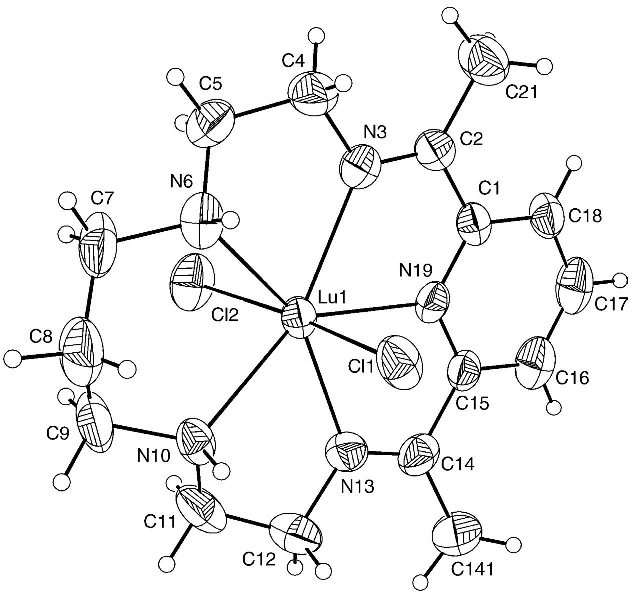


Fig. 2. Anisotropic-ellipsoid representation of the $[LuL8Cl_2]^+$ complex cation with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are depicted as spheres of arbitrary radii [114].

Template reactions of 2,6-diacetylpyridine with 3,7-diazanonane-1,9-diamine in the presence of trivalent yttrium and lanthanide salts (MX_3) produce 16-membered macrocyclic complexes of general formula $ML8X_3{\cdot}nH_2O$, where $X = NO_3^-$, ClO_4^-, Cl^-, $CF_3SO_3^-$, $n = 0–5$ with an N_5 set of donor atoms as a result of a [1 + 1] Schiff base cyclocondensation [114–116]. After numerous unsuccessful attempts the preparation of single crystals suitable for X-ray analysis was finally achieved for the lutetium(III) and ytterbium(III) L8 complexes isolated from the template reaction of 2,6-diacetylpyridine with 3,7-diazanonane-1,9-diamine carried out in the presence of mixed lutetium or ytterbium chloride and perchlorate salts in argon with the argon atmosphere maintained during the crystallization process. The X-ray structure of $[LuL8Cl_2]ClO_4$ [114], isostructural with that of the ytterbium complex [115,116], is shown in Fig. 2.

The central metal ion is in the seven-coordinate environment with the N3, N6, N10, N13 and N19 donor atoms of the macrocycle occupying the equatorial plane and the axial position being filled with chlorine atoms. An uncoordinated perchlorate anion balances the ionic charge of the complex cation. The coordination polyhedron is best described as a pentagonal bipyramid. The five nitrogen atoms of the macrocycle are almost coplanar (maximum deviation from the least squares plane is 0.030(3) Å for the Lu ion and 0.033(2) Å for Yb) and the metal ion is only slightly (0.104(2) Å for Lu and 0.114(2) Å for Yb) tilted out of this plane. To our knowledge, just one example of a structurally characterized pentaaza macrocyclic lutetium(III) complex has been reported previously [117]. By comparison, in this pentadentate texaphyrin lutetium(III) complex – regarded as an example of near-to-complete in plane metal coordination – the eight-coordinate metal center is found to be 0.269 Å above the mean plane of the macrocycle and the maximum deviation from planarity is 0.072 Å.

UV–vis, NIR, ^{1}H NMR and ESI spectral data reveal that the integrity of the complexes is maintained in solution. The properties of this ytterbium complex were found to be very important and promising in the area of ytterbium physical chemistry. For the first time the spectrum of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition has been obtained for a molecular complex of ytterbium with organic ligands in which all ligand-field components of the ground and excited state are well displayed at room temperature [116].

Unlike the majority of the polyaza macrocyclic complexes of lanthanides, these L8 complexes show no tendency to include solvent molecules in either the metal coordination sphere or the crystal lattice. The electronic and steric requirements of central metal atoms appear to be fully satisfied by coordination to the five nitrogen donors of the macrocycle and two chlorine donors. The stabilization of seven-coordination and pentagonal bipyramidal geometry in this complexes, relatively uncommon in the lanthanide series, seems to be a consequence of the “best fit” between the size of cations and the cavity of the macrocycle generated during the template process. To the best of our knowledge these results constitute the only structurally documented instances of such a geometry among lutetium and ytterbium macrocyclic compounds. These pentaaza macrocyclic complexes exhibit the structural similarity to the lutetium texaphyrins, which are tested as photosensitizers for use in the photodynamic treatment of recurrent breast cancer (LUTRIN^{TM}), photoangioplastic reduction of atherosclerosis (ANTRIN^{TM}) and light-based treatment of age-related macular degeneration (OPTRIM^{TM}) [46]. Moreover, Yb^{3+} complexes are now of increasing interest due to their potential application in various areas of biomedical sciences and technology as promising probes for fluoroimmunoassays [118], as effective therapeutic and diagnostic agents [65], in optical amplification [119–123] and in laser systems [124].

Slow diffusion of dioxane into a solution of these complexes in acetonitrile upon exposure to air leads to – unprecedented so far – facile conversion of oxygen into a peroxo bridge of symmetrical side-on bonding type by the polyaza macrocyclic lanthanide complexes. This fact is exemplified by the isolation, characterization and X-ray structure determination of isomorphous centrosymmetric dinuclear lutetium(III) and ytterbium(III) macrocyclic complexes of formula $[Ln_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)(L8)_2Cl_2](ClO_4)_2$, where Ln = Lu [125] or Yb [114,115], in which the peroxo ligand acts as a planar doubly bidentate bridge (Fig. 3).

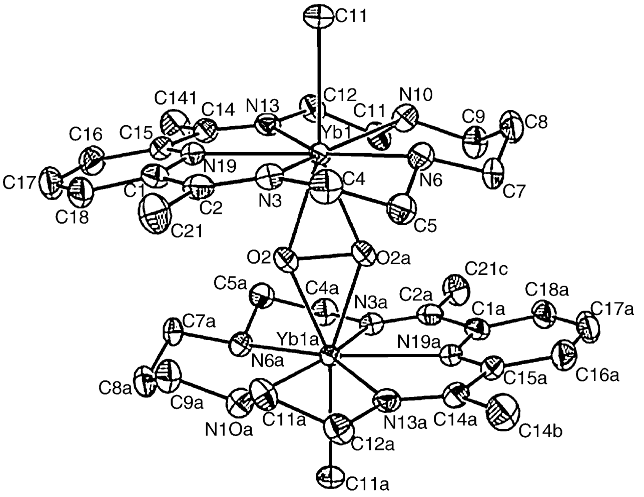


Fig. 3. Anisotropic-ellipsoid representation of the $[Yb_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)(L8)_2Cl_2]^{2+}$ peroxo complex cation (from the dioxane solvate structure) with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are depicted as spheres of arbitrary radii [115,116].

These results expand the unique series of compounds containing this particular coordination mode of the peroxide which is considered biologically significant because it is known to occur in some oxyhemocyanins and it is postulated as a new mode of binding or activation of dioxygen in other biological systems. The first solid evidence for the formation of an entirely novel planar μ-η^2:η^2-peroxide geometry was found in peroxo bis(trimethylsilyl)-amido dinuclear lanthanum species [126] and till now remained the only known and structurally characterized example of such a coordination mode of $O_2{}^{2-}$ in lanthanide chemistry. The peroxo-group showed previously unreported behavior, acting as a symmetrical doubly bidentate bridge between the two metal atoms. The use of appropriately positioned, highly hindered tris(pyrazolyl)borate ligands made it possible to structurally establish this novel coordination mode of the peroxide in d-block element complexes [127]. These μ-η^2:η^2-peroxo dinuclear copper(II) complexes were found to have physicochemical properties strikingly similar to those of oxyhemocyanin. Subsequently, the crystal structure of oxyhemocyanin from the horseshoe crab (*Limulus polyphemus*) was solved, revealing the presence of precisely this type of the μ-η^2:η^2-peroxide moiety [128]. In this case the accurate structural model compounds preceded the determination of the protein structure. Based on reports involving binuclear Cu(II) peroxo species, the formation of a μ-η^2:η^2-peroxo intermediate was proposed as an attractive novel possibility for the mechanism of water oxidation and O_2 evolution during photosynthesis catalyzed by tetranuclear manganese clusters, although no such Mn complex has been synthesized yet [129]. It seems worthy to note that the synthesis of the μ-η^2:η^2-peroxo dinuclear copper(II) complexes, regarded as models for oxyhemocyanin and oxytyrosinase, required severe conditions: treatment with H_2O_2 under anaerobic conditions or low-temperature (ca. −70 °C) direct dioxygen addition. The formation of Schiff base macrocyclic lanthanide μ-η^2:η^2-peroxo complexes appear to be a result of a one-step template synthesis followed by slow crystallization on the air.

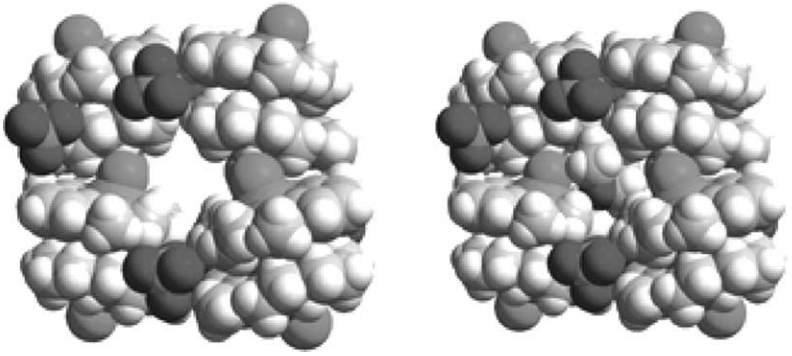


Fig. 4. Van der Waals radii representation of the building block of the $[Yb_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L8)_2Cl_2]^{2+}$ peroxo complex cation structure without (left) and with (right) the solvent dioxane molecule [115,116].

Inclusion of an appropriate solvents molecule into the crystal structure of $[Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L8)_2Cl_2](ClO_4)_2$ peroxo dinuclear complexes generates a supramolecular architecture in which the solvent-controlled self-assembly is observed [115,116]. Solvent molecules play a very important role in the formation of the three-dimensional structure of the crystal. To some extent at least, the shape, symmetry and hydrogen-bonding (or more general: weak interactions) properties of the solvent molecule influence the resulting crystal structure.

The building block of the crystal structure of the dioxane solvate of $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo dimers is created by a centrosymmetric hydrogen-bonded tetramer of complexes and perchlorate anions (Fig. 4, left). The solvent (dioxane molecule) fits perfectly into the voids of this structure. The shape, symmetry and hydrogen-bond accepting properties of dioxane are compatible with the shape and properties of the void (Fig. 4, right) [115,116].

The two three-dimensional structures of crystals of $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo ytterbium(III) complexes obtained from simple aromatic solvents: benzene [115] and toluene [116], are almost identical and contain chains of molecules connected by hydrogen bonds with water molecules; these chains are interconnected via perchlorate anions and this network leaves voids (Fig. 5, left) that can accommodate small flat molecules of the solvent. Because there are no specific interactions with only very weak π-stacking (Fig. 5, right), solvent molecules are highly disordered. This disorder is more severe in the benzene solvate, probably due to the higher symmetry and smaller steric hindrance of benzene compared with toluene.

Crystals of the methanol solvate of ytterbium(III) complex are a very special case [116]. The unit cell contains two different dimeric complex molecules, four chloride and four perchlorate anions and one partially occupied methanol molecule: in one of them, formulated as $[Yb_2O_2(L8)_2(H_2O)_2]^{4+}$ there is a $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo bridge between the two Yb^{3+} centers (Fig. 6), while the other, formulated as $[Yb_2(OH)_2(L8)_2(H_2O)_2]^{4+}$ has two hydroxyl bridges (di-μ-OH) between the ytterbium ions (Fig. 7).

The molecule with a $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo bridge is similar to the previous ones except for the molecules occupying the axial positions (water molecules instead of chlorides). The molecule with two hydroxyl bridges is more folded. In both molecules, due to symmetry requirements, the central Yb–O–Yb–O fragments are exactly planar, but because of the difference in the nature of the bridging oxygen atoms, the distances between the Yb atoms are significantly different: 4.0662(4) and 3.6920(4) Å, respectively. Crystal packing is determined by the complicated hydrogen bond system involving coordinated water molecules and N–H groups as hydrogen-bond donors, and chloride anions and oxygen atoms from the perchlorate groups as acceptors.

These results provide an interesting example of inorganic self-organization involving templating as the first step of

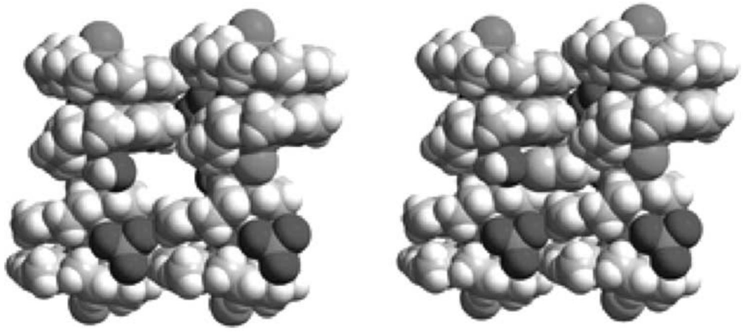


Fig. 5. Van der Waals radii representation of the building block of the $[Yb_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L8)_2Cl_2]^{2+}$ peroxo complex cation structure without (left) and with (right) the solvent toluene molecule [116].

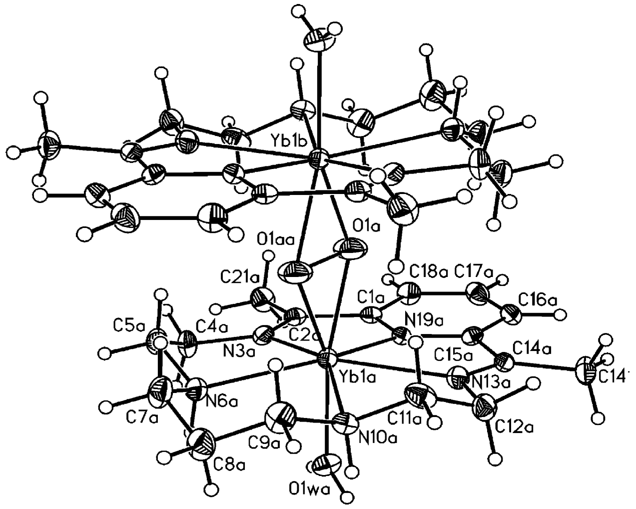


Fig. 6. Anisotropic-ellipsoid representation of the μ-η^2:η^2-peroxo-bridged $[Yb_2O_2(L8)_2(H_2O)_2]^{4+}$ cation with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are depicted as spheres of arbitrary radii [116].

the assembly of well-defined supramolecular architectures of higher complexity. They confirm the efficiency of specially designed macrocycles with rigidity sufficient enough to present a donor set with a defined geometry to impose unusual coordination arrangement around the metal ion. The lutetium(III) and ytterbium(III) ions serve as templates to orient the reacting groups of linear precursors in the desired conformation for the condensation process, which ultimately ends with the pentaaza macrocyclic Schiff base complex. These complexes are able to form the unique dimeric species linked through the biologically significant μ-η^2:η^2-peroxo bridge. The driving force underlying this unusual behavior may be attributed to the stabilizing effect provided by the specific steric arrangement of the two macrocycles. In the crystal structure, the next level of self-assembly is observed. Complementarity in the supramolecular network, created by the molecules of the peroxo complex acting as a host for the solvent guest, is evident. These results point to the role of solvent molecules in the assembly of supramolecular architectures. These findings reveal that the new macrocyclic ytterbium(III) structures with very peculiar characteristics [116] hold the potential to provide a unique opportunity for the physicooptical and NMR spectral investigation. This system will likely become a powerful tool used for defining interesting features relating both to spectroscopy and lanthanide macrocyclic chemistry.

5. Hexadentate Schiff base macrocyclic complexes

5.1. Hexadentate macrocyclic complexes derived from 2,6-diacetylpyridine

The failure of the system involving 2,6-diacetylpyridine and hydrazine to undergo complete condensation and cyclization in the presence of lighter lanthanides [91] prompted us to investigate the template action of lanthanum(III) using ethylenediamine or *o*-phenylenediamine. The lanthanum(III) ion was found to be an effective template in the synthesis of 18-membered macrocycle L9 – product of the [2 + 2] Schiff base condensation of 2,6-diacetylpyridine with ethylenediamine [130]. The set of lanthanides usable as substrates for this macrocycle was subsequently extended to the whole lanthanide series [76,131,132]. Lanthanide contraction is clearly reflected by the coordination number reduction through the series from 12 for La to 9 for Lu. Employment of an appropriate combination of anions favors the isolation of the complexes in the crystalline form. Structural data suggest that the conformational differences existing among various lanthanide complexes of the L9 macrocycle, which result from the changes in metal sizes and from the steric requirements of the exocyclic ligands, are also influenced by the interaction of the ligand with the external water molecules interacting in these compounds with hydrogen bonds to the L9 ligand [133]. Treatment of the complexes with a variety of counterions and with strong acids resulted in the anion metathesis without any change in the macrocyclic cations. For example, the anion metathesis between aqueous K_2CrO_4 and $[LnL9(CH_3COOO)_2]Cl$ complexes, where Ln is an appropriate lanthanide(III) ion, gave the yellow $[(CrO_4)L9Ln(\mu\text{-}CrO_4)LnL9(CrO_4)]\cdot nH_2O$ (Ln = Sm–Ho, $n = 10$ or 11), containing chelating as well as bridging chromate, and the photochromic $[LnL9(CrO_4)(H_2O)]_2(Cr_2O_7)\cdot 2H_2O$ (Ln = Sm–Gd), containing chelating chromate and ionic dichromate. These results are the first structures reported for metal chromate/dichromate complexes containing organic ligands [134].

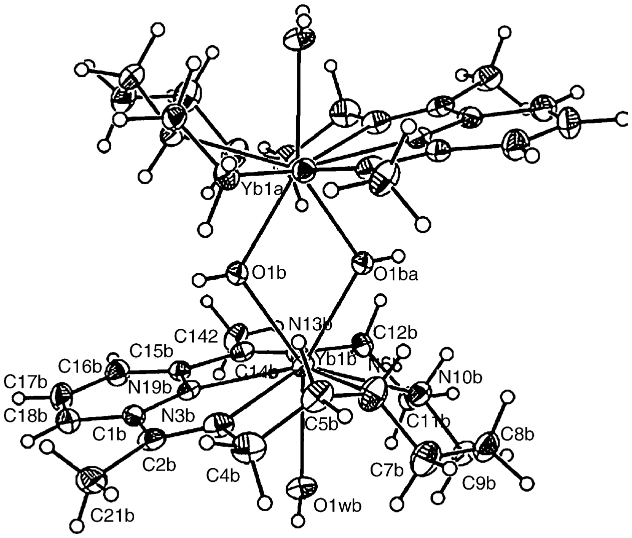
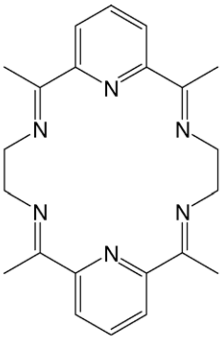
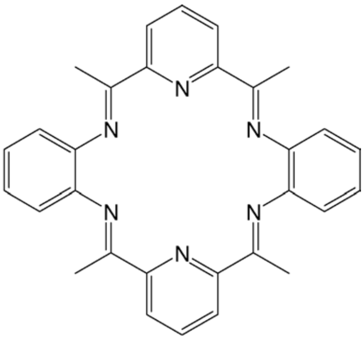


Fig. 7. Anisotropic-ellipsoid representation of di-μ-hydroxo-bridged $[Yb_2(OH)_2(L8)_2(H_2O)_2]^{4+}$ cation with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are depicted as spheres of arbitrary radii [116].



L9



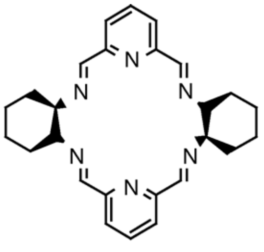
L10

Lanthanum(III), cerium(III), praseodymium(III) and neodymium(III) ions may promote the synthesis of a closely related 18-membered hexaaza macrocycle L10. Complexes $LnL10(NO_3)_3{\cdot}2H_2O$ (Ln = La–Nd) were isolated from the reaction of these lanthanide nitrates with 2,6-diacetylpyridine and *o*-phenylenediamine [135]. The structure of the praseodymium complex was then definitively established by X-ray crystallography [136]. The metal ion is coordinated to the six nitrogen donor atoms of the highly symmetrical macrocycle L10, to a bidentate chelating nitrate and to a methanol molecule on the one side of the macrocycle and to another bidentate chelating nitrate on the opposite side. The macrocycle is double bent into a saddle shape. The saddle distortion, although less severe, is observed in Sr^{2+}, Pb^{2+} and Cd^{2+} complexes of the analogue of L10 without the methyl substituents [137]. The crystal structures indicate that the 18-membered hexaaza macrocycles provide cavities that, if planar, would be too large for these cations and distort by tilting the pyridine and benzene rings to opposite sides of the tetraimine plane. The coordination ability of the polyoxaaza Schiff base macrocycles containing pyridine head and phenyl lateral units toward yttrium(III), lanthanide(III), calcium(II), zinc(II) and cadmium(II) ions has recently been reported [138].

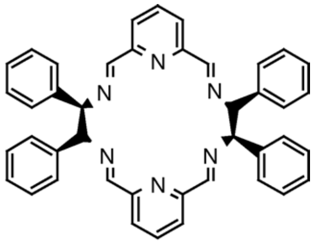
The L9 and L10 lanthanide complexes were found to be very effective catalysts with high site selectivity for RNA transesterification and are considered as promising synthetic nucleases [50,51,139]. Unlike the lanthanide chelates of linear ligands, these macrocyclic complexes are extremely rigid and display kinetic inertness toward metal release and decomposition in the presence of competing ligand which makes them useful for biologically relevant applications. The europium complex of L9 was found to satisfy the major requirements for a luminescent bio-marker [140]. The lanthanide complexes with this macrocycle having functionalized peripheral substituents suitable for attachment to biosubstrates may thus serve as markers for histochemical techniques and immunoassays [140,141]. The symmetrically substituted complexes of L9 were synthesized by the lanthanide-templated Schiff base [2 + 2] cyclocondensation of 2,6-diacetylpyridine with carbon-substituted ethylenediamine: $=N{-}CH_2{-}CH(R){-}N{=}$, where $R = {-}CH_3$, $-CH_2{-}OH$, $-CH_2{-}C_6H_5$, $-H_2{-}C_6H_4{-}OH$, $-CH_2{-}C_6H_4{-}NH_2$. The hydroxo-benzyl group forms esters by the reaction with acid anhydrides, and the primary amino-benzyl group reacts with thiophosgene to produce the corresponding isothiocyanate, which in turn combines with primary amines through a thiourea linkage. The lanthanide(III) L9 macrocycles with peripheral isothiocyanate groups can be easily coupled to proteins. Due to the inertness of the lanthanide-macrocycle entity the resulting conjugates are stable and exhibit characteristic lanthanide properties, such as luminescence and paramagnetism as well as the specific affinity to the protein. The lanthanide complexes of the L9 macrocycle with benzyl-type substituents carrying hydroxo, amino and isothiocyanato functionalities are therefore suitable for coupling a variety of substrates such as biomolecules, polymers and glass surfaces.

5.2. *Chiral Schiff base macrocycles*

The introduction of chiral diamines in the synthesis of hexaazamacrocycles leads to chiral macrocyclic lanthanide(III) complexes. These compounds are interesting from the perspective of a recent application of lanthanide(III) complexes of chiral crown ethers as enantioselective catalysts [142,143]. The first Schiff base complexes of this type were obtained for the ligand L11, both as racemates [144] and in the enantiopure form [145]. The latter complexes have been shown to exhibit circularly polarized luminescence and their photophysical properties have been studied in detail [145].



L11



L12

Both RRRR and SSSS enantiomers of these $[LnL11](NO_3)_3$ complexes can be easily obtained in a template condensation of R,R- or S,S-1,2-diaminocyclohexane and 2,6-diformylpyridine. The chirality of the diamine fragments dictates the direction of the helical twist of the macrocycle in each enantiomer. The metal complexes of the hexaaza macrocylces containing two 2,6-substituted pyridine rings usually exhibit a helical twist of the macrocycle (often accompanied by a substantial fold). The twist is measured as the angle determined by two pyridine rings or, better, by the *cis* torsion angle determined by C–N bonds of two pyridine rings. Its values are moderate for lanthanide complexes (0.44–30.66°) and much larger for transition metal ions [146–148]. The molecular structures of $[NdL11](NO_3)_3$ and $[TmL11](NO_3)_3$ complexes have been determined [149]. The lanthanide(III) ions in both complexes are coordinated by a helically twisted hexadentate macrocycle and two bidentate nitrate anions (Fig. 8). The angles between the pyridine rings are 23.8° and 28.0° for the Nd(III) and Tm(III) compounds, respectively. This dif-

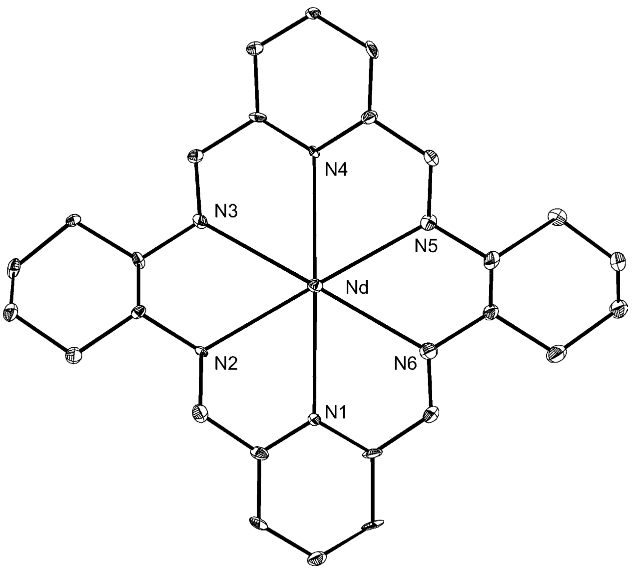


Fig. 8. View of the complex cation $[NdL11]^{3+}$. The nitrate anions have been omitted for clarity [149].

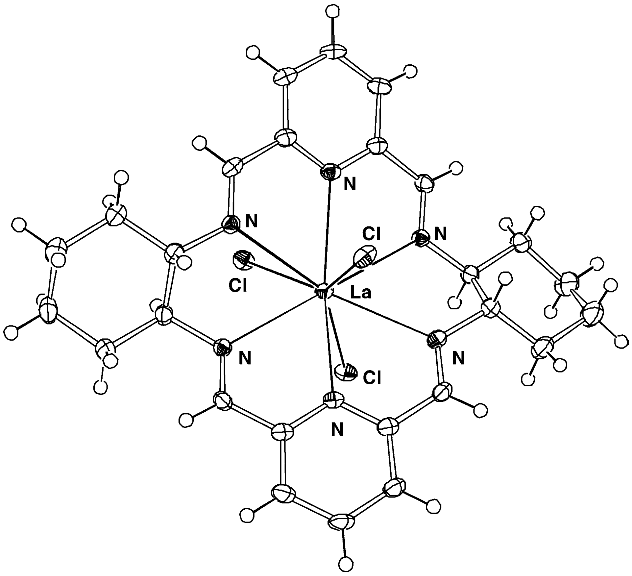


Fig. 9. View of the $[LaL11]Cl_3$ complex [150].

ference reflects tighter wrapping of the macrocycle around the Ln(III) ion with decreasing ion radii. The conformation of the macrocycle in both complexes is essentially of D_2 symmetry. These compounds give rise to eight signals in their ^1H NMR spectra and seven signals in ^{13}C NMR spectra, which is consistent with the presence of diastereotopic cyclohexane protons and indicates the effective D_2 symmetry of the $[LnL11](NO_3)_3$ complexes in the investigated solutions.

In contrast, the solid state X-ray crystal structure of the chloride derivative $[LaL11]Cl_3$ shows lower symmetry of the complex with the twist-bent conformation of the ligand (Fig. 9) and unsymmetrical coordination of three chloride anions [150]. Similar structure is observed for a related racemic $[GdL11(H_2O)_3]Cl_3{\cdot}3H_2O$ complex [144], where coordination of three axial water molecules is observed. This structure, with approximate C_2 symmetry, should give rise to 15 ^1H NMR signals and 13 ^{13}C NMR signals.

On the other hand, NMR spectra of the chloride derivatives in methanol/chloroform and deuterated water solution show 8 ^1H NMR and 7 ^{13}C NMR lines and indicate effective D_2-symmetry. The discrepancy between the number of expected and observed signals can be explained by the dynamic exchange of chloride anions, e.g. through a dissociative process depicted in Fig. 10 that results from the fast dynamic exchange of chloride anions.

The 15 ^1H NMR signals consistent with C_2 symmetry are observed for the hydroxide derivatives of lanthanide(III) complexes with L11 [151]. These derivatives can be directly synthesized in a template synthesis [63] or obtained from mononuclear complexes [151]. Their crystal structures show the formation of a di-μ-hydroxo-bridged species (Fig. 11). NMR studies show that the dimeric structure is preserved in solution, as indicated by the formation of heterodinuclear dimers containing two different lanthanide ions and observation of close contacts between protons of two macrocycles indicated by NOESY spectra. The NMR study also shows that only homochiral hydroxo-bridged dinuclear (both homo- and heterodinuclear) lanthanide(III) complexes of ligand L11 are formed. In other words, after the coordination of the hydroxide anion to the lanthanide(III) ion the enantiomeric self-recognition of the chiral mononuclear units takes place [152]. Interestingly, these dimeric complexes are one of only a few examples of artificial catalysts for hydrolytic DNA cleavage [63]. The development of lanthanide(III)-based synthetic nucleases stimulates the investigation of dinuclear and polynuclear hydroxo-bridged lanthanide complexes [153,154]. In particular, the hydroxo-bridged dinuclear lanthanide complexes have proved to be very active catalysts [155,156] that are more efficient than the corresponding mononuclear species. While most of these complexes are characterized in the solid state, dinuclear hydroxo-bridged lanthanide(III)

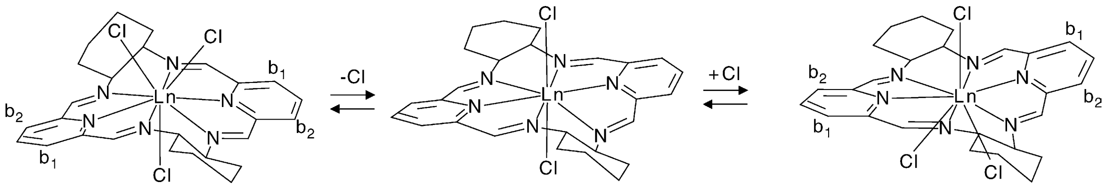


Fig. 10. The dynamic axial ligand exchange in $[LnL11]Cl_3$ complexes [150].

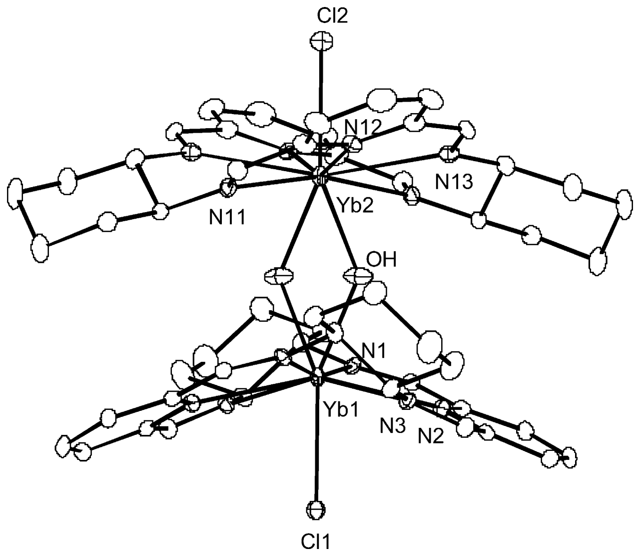


Fig. 11. Side view of the complex dimer of $[Yb_2(OH)_2Cl_2(L11)_2]Cl_2$ [151].

complexes that are well-defined in solution are relatively rare.

Similar difference between the solid state structure and effective symmetry in solution indicated by NMR described above for chloride complexes of L11 is observed for $[LnL12]Cl_3 \cdot nH_2O$ ($Ln = La^{3+}$, Ce^{3+} and Eu^{3+}) complexes [157]. The crystal structure of the Ce(III) derivative shows a relatively flat macrocycle with slight bend and moderate helical twist of the L12 macrocycle. The Eu(III) complex, however, exhibits large bending of the macrocycle reflecting its flexibility to adjust to the lanthanide(III) ion size and axial ligands [157] (Fig. 12).

Crystal structures of the chiral complexes with the derivatives of L9 macrocycle formed from 2,6-diacetylpyridine and carbon-substituted ethylenediamine with chiral substituents show twist-bend conformation of the ligands similar to those described above with a moderate helical twist [140,141].

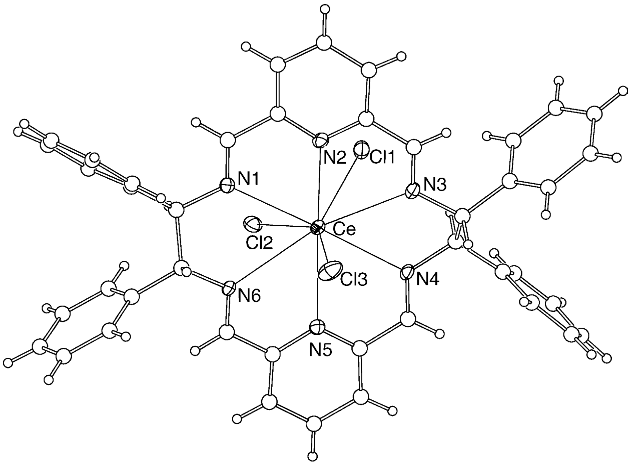


Fig. 12. View of the $[CeL12]Cl_3$ complex [157].

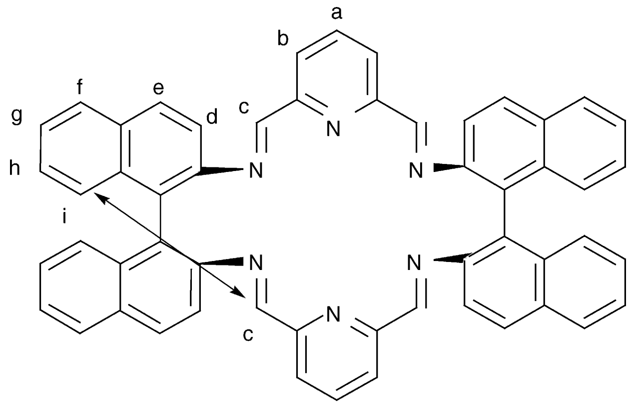
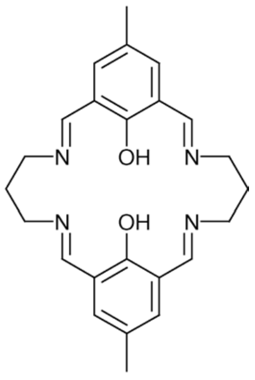


Fig. 13. Structure and labeling scheme of ligand L13. Arrows indicate “long-range” NOESY correlation observed for $[LnL13](NO_3)_3$ complexes [158].

Introduction of 1,1′-binaphthyl fragments into the macrocycle skeleton leads to the formation of lanthanide(III) complexes of ligand L13 [158]. NOESY spectra of the La(III) and Eu(III) complexes of L13 show a close contact between protons **i** and **c** (Fig. 13) that points to sizable wrapping of the macrocycle around the Ln(III) ion. Indeed, both the MM+ modeled structure and the preliminary X-ray crystal structure show that the value of the dihedral CNNC angle exceeds 60°, which corresponds to the largest helical twist for this class of complexes. Interestingly, a closely related N_2O_4 crown ether possessing the identical carbon skeleton of the macrocycle adopts a bent structure and does not coordinate lanthanide(III) ions [158].

5.3. Hexadentate macrocycles derived from 2,6-diformylphenols

The incorporation of a phenol fragment into the macrocyclic core leads to the formation of ligands that are particularly suitable for coordination of two metal ions. The bridging hydroxyl groups protrude toward the center of the macrocycle, dividing it into two compartments that can accommodate metal ions. The first and most often studied macrocycle of this type is L14 derived from propylenediamine, called the Robson ligand [159,160]. This ligand is able to form a variety of homodinuclear complexes with first row transition metal ions including Cu(II), Cu(I), Ni(II), Zn(II), Fe(II), Fe(III) [161–169], as well as second row transition metal ions Pd(II) and Ru(III) [170,171]. Recently, the Robson ligand with a *tert*-butyl substituent has been prepared for the first time in its free form and used as a selective extractant for copper(II) ions [172]. Modification of one of the lateral propylene chains, e.g. by an ethylene bridge leads to formation of two compartments of different diameters preferring two different transition metal ions. The stepwise formation of such unsymmetrical N_4O_2 macrocycles can be exploited in the synthesis of heterodinuclear complexes [75,173–177]. The heterodinuclear complexes are interesting as models for metalloenzymes possessing two different metal ions in their active site, such as cytochrome *c* oxidase, nitrogenase, nickel containing hydrogenase, superoxide dismutase, alkaline phosphatase or purple acid phosphatase.



L14

The X-ray crystal structures of the dinuclear complexes of ligand L14 usually exhibit almost flat conformation of the macrocycle core [161–163,165,167,169–171], with two propylene chains pointing to opposite directions. Typically, the metal ion is five-coordinate and is positioned somewhat out of the N_2O_4 plane of the coordinating compartment. In the case of six-coordinate ions, the metal ion is located within the N_2O_4 plane. In contrast, the free ligand L14 in its protonated form adopts highly bent conformation [170,171]. In the mononuclear complex of L14, $[NiH_2L14](ClO_4)_2\cdot 2CH_3OH$, macrocycle L14 is also bent [178], although the angle between the two phenol rings is smaller than that in the free ligand (Fig. 14). Similar conformation of the L14 macrocycle is observed in the related Pb(II) complex [179].

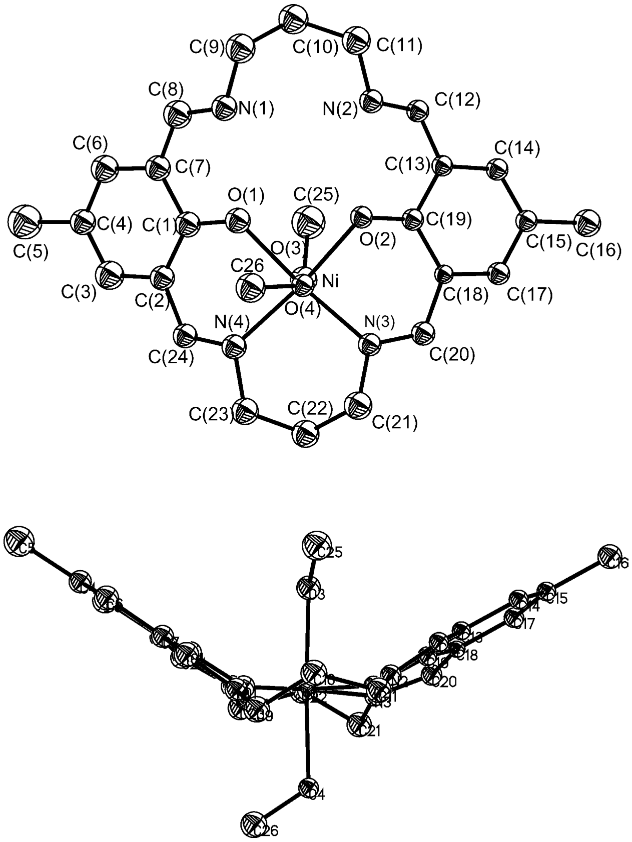


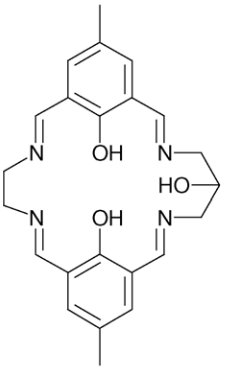
Fig. 14. Top and side view of the $[NiH_2L14(CH_3OH)_2]^{2+}$ complex cation [178].

The $[NiH_2L14](ClO_4)_2\cdot 2CH_3OH$ complex is a convenient precursor for heterodinuclear complexes. Unlike the complexes of heterodinuclear complexes with unsymmetrical macrocycles mentioned above, heterodinuclear nickel(II) complexes $[NiML14](ClO_4)_2\cdot 2H_2O$, where $M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Cu^{2+}, can be easily prepared from metal acetates and $[NiH_2L14](ClO_4)_2\cdot 2CH_3OH$ in one step [180]. Similarly, the mixed cobalt(II)–zinc(II) complex can be generated from the analogous mononuclear Co(II) complex of L14. The purity and heterodinuclear nature of the complexes has been verified by mass spectrometry and NMR spectroscopy. The first heterodinuclear macrocyclic Schiff base complex containing both first and second row transition metal ions, $[NiPdL14](ClO_4)_2\cdot 3CH_3CN$ has also been synthesized in this way [178]. Its structure, typical for the complexes of L14, is shown in Fig. 15.

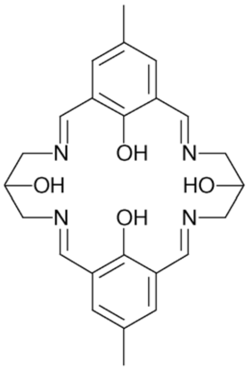
6. Extended macrocyclic systems derived from 2,6-diformylphenols

In general, macrocyclic Schiff bases are synthetically flexible ligands. If their core diameters are properly adjusted, selective coordination of metal ions of different sizes may occur. By selecting appropriate diamines in the synthesis of Schiff base macrocycles, lateral chains of various lengths as well as additional coordinating groups such as amine, alcohol or ether functionality can be incorporated into the macrocycle. This modification of phenol-based macrocycles leads to the formation of larger N_2O_3, N_3O_2, etc. coordinating compartments. Such compartments are suitable for coordination of larger ions, e.g. Pb(II) [181,182] or Ba(II) [183]. Asymmetrical macrocycles of this type as well as macrocycles possessing additional pendant arms with coordinating groups, such as pyridine, are suitable for the formation of heterodinuclear complexes [75,184–192]. Furthermore, macrocycles containing Schiff base chamber and adjacent crown-ether-like chamber can recognize two different metal ions forming stable s–f and d–f heterodinuclear species [193,194].

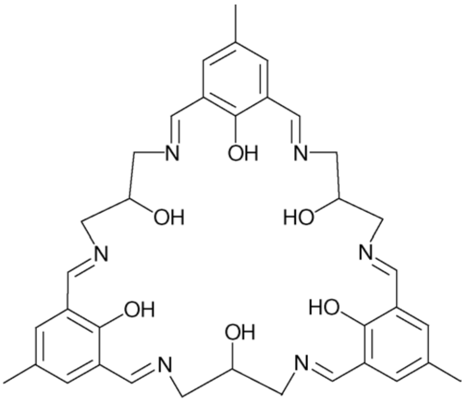
The heterodinuclear and heteropolynuclear complexes containing both f- and d-block elements are relatively rare [194,195]. Studies of the complexes focus on the interesting magnetic properties of the Gd(III)–Cu(II) couple. Since the chemistry of lanthanides and d-block transition metal ions remarkably differs, the combination of the different reactivities of these ions may lead to unique catalytic systems. Some of the macrocyclic ligands based on 2,6-diformylphenols seem to be particularly suited for this purpose, since they can stabilize both types of ions by macrocyclic effect [194,196,197].



L15



L16



L17

The first structurally characterized complex of this type is $[LaNiL15]Cl_3$ [198] (Fig. 16). The NMR data of $[LnNiL15]Cl_3$ complexes, where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Eu(III), show that the solution structures of these complexes are consistent with the solid state X-ray crystal structure of the Ni(II)–La(III) complex. The macrocyclic Schiff base L15 has also been shown to form heterodinuclear complexes containing the large Pb(II) ion [181].

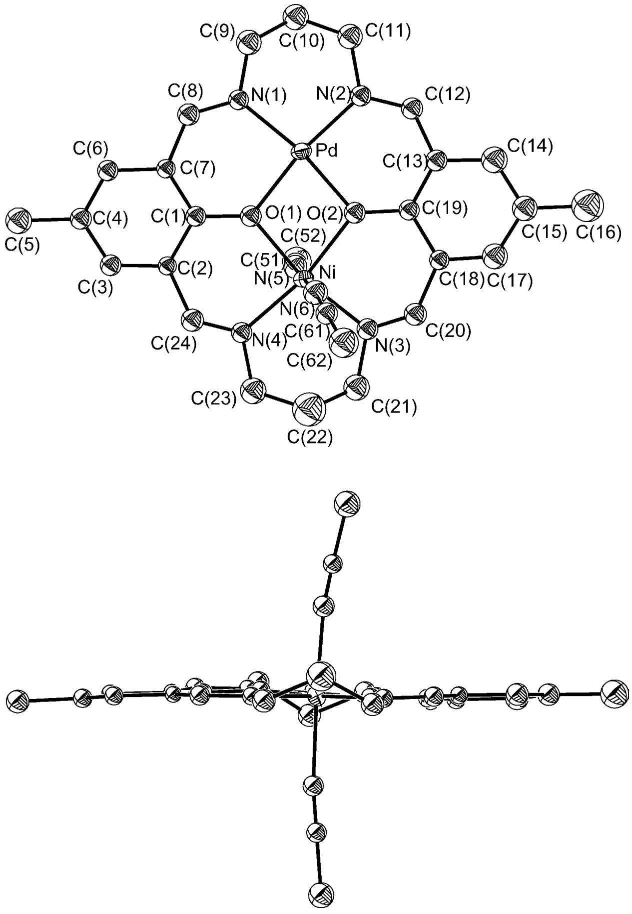


Fig. 15. Top and side view of the $[NiPdL14(CH_3CN)_2]^{2+}$ complex cation [178].

The introduction of two alcohol groups into the lateral chains in ligand L16 should create two lanthanide binding sites analogous to the Ln(III) binding site of ligand L15. In fact, homodinuclear Pb(II) complexes of L16 are known [182], however attempts to incorporate two lanthanide ions into macrocycle L16 failed and mononuclear lanthanide(III) complexes have been obtained [199]. These complexes of the formula $Ln(H_4L16)Cl_3{\cdot}nH_2O$ have been synthesized in the template condensation of 1,3-diamino-2-hydroxypropane and 2,6-diformyl-4-methylphenol in the presence of La(III), Ce(III) and Eu(III) ions [199,200].

The isotropic shifts of the paramagnetic Ce(III) and Eu(III) derivatives indicate the unsymmetrical coordination of the lanthanide(III) ions within the macrocyclic ligand H_4L16, as confirmed by X-ray crystal structure of the Eu(III) complex [199] (Fig. 17). While the insertion of the second lanthanide(III) ion into $Ln(H_4L16)Cl_3{\cdot}nH_2O$ complexes to form heterodinuclear f–f Ln(III) complexes failed, heterodinuclear d–f complexes can be obtained [152]. The lanthanide(III) complexes of L16 react with excess of transition metal

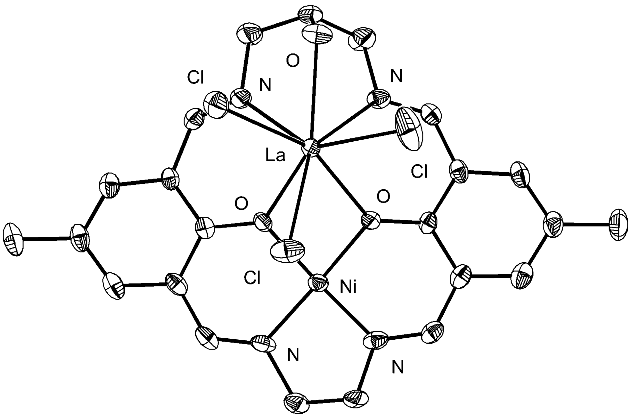


Fig. 16. View of the $[LaNiL15]Cl_3$ complex [198].

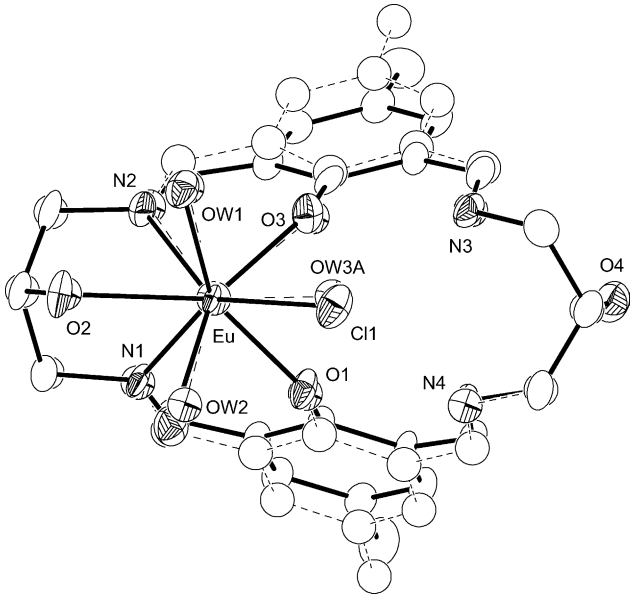
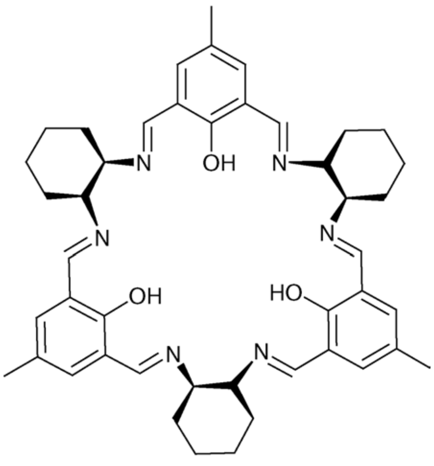


Fig. 17. View of two superimposed complex cations of the Eu(III) complex of L16 [199].

ion to give dinuclear complexes of L16 analogous to complexes of L14. However, direct condensation of 2,6-diformyl-4-methylphenol with 1,3-diamino-2-hydroxypropane, templated by transition metal ions, results in dodecanuclear complexes that are dimers of hexanuclear complexes of the [3 + 3] macrocycle L17 [201].

Appropriate extension of diamine fragments made it possible to construct macrocyclic Schiff bases that form complexes of higher nuclearity such as the trinuclear mixed-valence manganese complex of N_8O_4 macrocycle [202] or tetranuclear complexes of N_4O_4 and $N_4O_2S_2$ macrocycles [203,204]. Tetranuclear complexes of transition metals are formed also by interesting extended macrocycles that contain four phenol and four diamine fragments. Such systems can be obtained directly in the [4 + 4] condensation of 2,6-diformylphenolate and diamine [205,206] or in a stepwise fashion from partially saturated precursors [207,208]. The condensation of 2,6-diformylphenols with tris(2-aminoethyl)amine leads to interesting Schiff base [2 + 3] macrobicycles [209–218]. These versatile ligands can form mononuclear lanthanide(III) cryptates, homodinuclear transition metal d-d and lanthanide(III) f–f cryptates (Fig. 18) and heterodinuclear d–f cryptates.

N_4O_2 macrocyclic Schiff bases, analogous to ligands L11 and L12, can be obtained in the [2 + 2] condensation of 2,6-diformylphenols with 1,2-diaminocyclohexane or 1,2-diphenylethylenediamine. The Mn(III) complexes of these enantiopure macrocycles were applied in the asymmetric epoxidation of olefins and Co(II) complexes in the borohydride reduction of ketones [219]. The condensation of 1,2-diaminocyclohexane and 2,6-diformyl-4-methylphenol affords also an enantiopure macrocycle L18 that is a [3 + 3] condensation product [220].



L18

The reaction of this macrocycle with transition metal ions results in the rearrangement of the system, and dinuclear complexes of the related [2 + 2] macrocycle [221] are obtained instead of trinuclear complexes of L18. The successful formation of a trinuclear complex was observed in the reaction of the Zn(II) ions with the reduced form of the macrocycle L18 [222]. The formation of an enlarged [3 + 3] chiral macrocycle was also observed in the condensation of 2,6-diformylpyridine with 1,2-diaminocyclohexane without the metal template [223]. The condensation of 1,2-diaminocyclohexane with diamines built from two salicylaldehyde fragments leads to another enantiopure chiral macrocyclic Schiff bases called “calixsalenes” (Fig. 19) capable of binding metal ions [224,225].

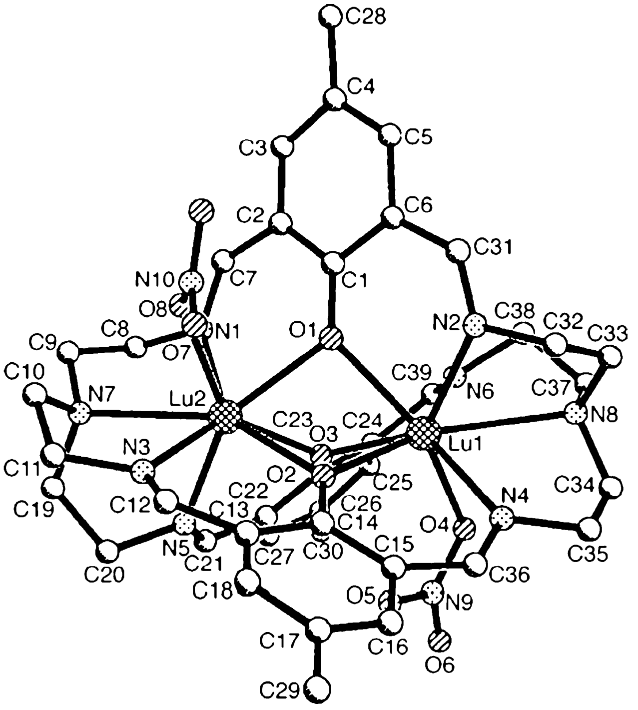


Fig. 18. Structure of dinuclear Lu(III) cryptate (reproduced by permission of The Royal Society of Chemistry from Ref. [210]).

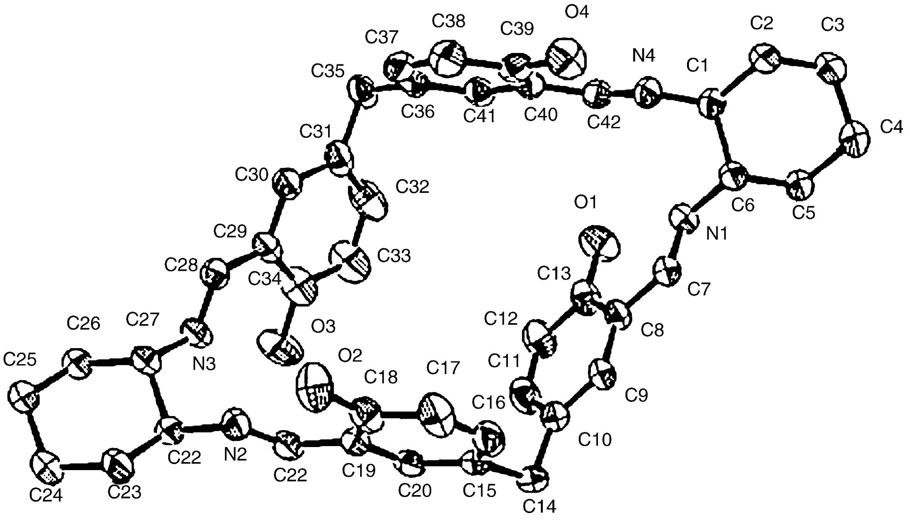


Fig. 19. Structure of calixsalene Schiff base macrocycle (reproduced by permission of The Royal Society of Chemistry from Ref. [224]).

7. Axial ligand exchange in macrocyclic lanthanide complexes

The coordination sphere of the lanthanide(III) ion in macrocylic complexes is usually completed by additional axial ligands such as counterions or solvent molecules. While the macrocycle itself is often very strongly bound to the metal ion due to macrocyclic effect, the axial ligands are bound weakly and can be easily exchanged. The axial reactivity is crucial in the catalytic activity of these complexes (in reactions such as hydrolytic cleavage of phosphate esters or aldol condensation) and in biomedical applications (interactions of contrast agents with biomolecules and anions occurring in biological fluids).

The exchange of axial ligands is usually not accompanied by major changes of the structure of macrocyclic unit containing the bound lanthanide(III) ion, hence not all spectroscopic techniques are sensitive to this kind of changes. For instance, when the axial ligands under study do not produce NMR signals, NMR spectra of diamagnetic La(III) and Lu(III) complexes, with different axial ligands, are very similar. In the case of paramagnetic lanthanide complexes, however, the change of axial ligands brings about dramatic differences in dipolar shifts and, consequently, of the NMR spectra. This effect was discovered for the first time in the lanthanide(III) complexes of texaphyrins [226]. It was observed that after the exchange of the axial nitrate anions for phosphate-type anions, the ^{1}H NMR signals can move as much as 250 ppm. Texaphyrin ligands are related both to Schiff base macrocycles, such as L8 and porphyrins and are unique among macrocycles in their rigidity. The X-ray crystal structures of lanthanide texaphyrins [226,227] differing in bound axial ligands show similar, almost flat conformation of the macrocycle. Thus the observed spectral changes cannot be explained by a substantial change of the macrocycle structure.

In paramagnetic metal complexes, the observed nucleus experiences additional paramagnetic shift, called the isotropic shift, δ_{iso}, that arises from the interaction of nuclear and electronic spins [228–230]. The isotropic shift can be separated into through-space, dipolar contribution δ_{dip} and through-bonds, contact contribution δ_{con}. The dipolar shift is given by Eq. (1):

$$\delta_{\text{dip}} = D_1G_1 + D_2G_2 = \frac{\bar{\chi} - \chi_{zz}}{2N}\left\langle\frac{1-3\cos^2\theta}{r^3}\right\rangle + \frac{\chi_{xx} - \chi_{yy}}{2N}\left\langle\frac{\sin^2\theta\cos 2\varphi}{r^3}\right\rangle \quad (1)$$

where χ_{xx}, χ_{yy} and χ_{zz} are the principal components of the magnetic susceptibility tensor and r, θ and φ are polar coordinates of the given nucleus.

Computer simulations [226] of NMR shifts of lanthanide(III) texaphyrins enabled an explanation of observed changes in the NMR spectra by the variation of the parameters of Eq. (1). The χ_{xx}, χ_{yy} and χ_{zz} values as well as orientation of magnetic axes that determine dipolar shifts were calculated. They significantly differ for various sets of axial ligands. These calculations showed that the exchange of axial ligands leads to substantial changes of crystal field parameters and, in consequence, changes of parameters of magnetic anisotropy, which in turn leads to very strong variations of paramagnetic shifts. The binding of phosphate-type ligands to lanthanide(III) texaphyrins was studied also by ^{31}P NMR spectroscopy [231].

The NMR spectroscopy was used to study mononuclear and dinuclear μ-η^2:η^2-peroxo-bridged Yb(III) complexes of ligand L8 [116]. The ^{1}H NMR spectrum of the peroxo complex is remarkably different from the spectrum of mononuclear complex, as a result of different axial ligation. The proton signals of the latter complex are shifted downfield,

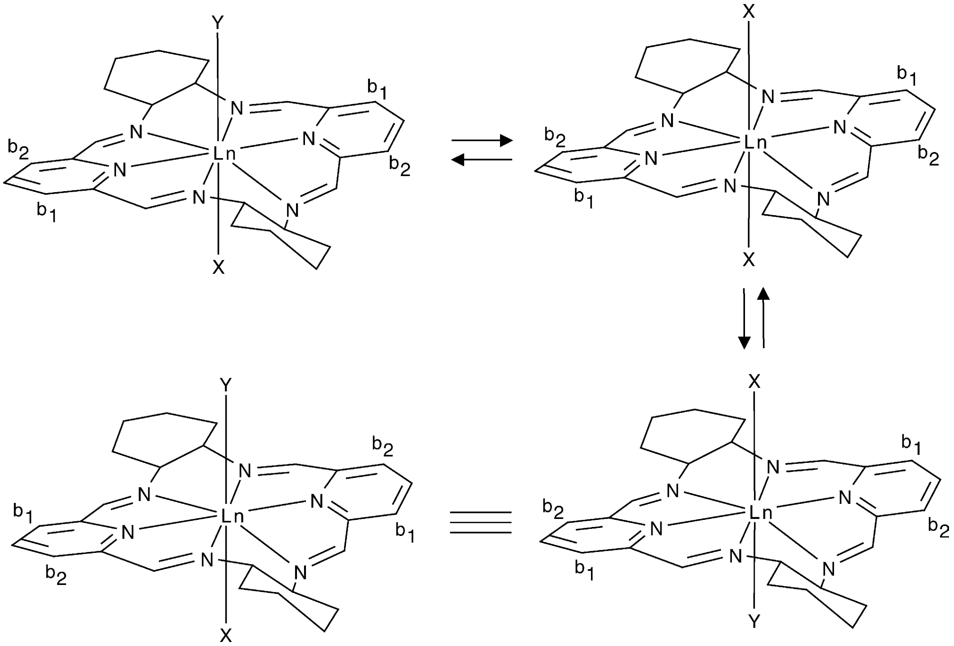


Fig. 20. Exchange dynamics in solution of $[LnL11XY)]^+$ complexes [232].

while the signals of the corresponding mononuclear complex are shifted upfield; the differences of chemical shifts between two complexes exceed 114 ppm for some positions.

Similar profound changes of the NMR spectra, accompanying the axial ligand exchange, were observed for the Yb(III) complexes of the ligand L11 [232] including di-μ-hydroxodimers [151]. Here the chirality of the ligand leads to additional effects related to changes of symmetry of the complexes. When the axial ligands at the two sides of the macrocycle plane are identical, the complex is of D_2 symmetry and 8 ^1H NMR signals are observed. In the case of derivatives with a mixed axial ligand set, the two sides of the macrocycle are different, and 15 ^1H NMR signals are observed that correspond to a complex of C_2 symmetry. Thus the signals in the latter complexes are doubled, e.g. one of the signals of the azomethine protons in the complex $[YbL11Cl(AcO)]^+$ is shifted downfield, the other is shifted upfield and their chemical shifts differ by more than 80 ppm [232]. This large difference in chemical shifts corresponding to the signals of protons of the same type can be explained again by the computer simulation of dipolar shifts. The fits of isotropic shifts to Eq. (1) showed that the axial ligand exchange leading to formation of C_2-symmetric complexes is accompanied by the rotation of the magnetic axes within the plane of the macrocycle. The analysis of the 2D NMR EXSY spectra of mixtures of C_2 and D_2 symmetric complexes allowed us to establish the presence of dynamic equilibria depicted in Fig. 20. The axial ligand exchange in YbL11 complexes affected also f–f transitions as detected by near-IR circular dichroism. This method was used to investigate the solution equilibria involving the competing axial ligands and to derive a spectroscopic series for Yb.

When the axial ligand is chiral, it can form diastereomeric complexes with enantiopure LnL11 complexes. The sensitivity of chemical shifts to axial ligation can be used in the application of these complexes as chiral shift reagents. The reaction of $[EuL11](NO_3)_3$ complex with D,L-histidine and L-histidine monoanions indeed shows that the diastereomers can be detected by NMR. The differences of chemical shifts of the azomethine proton of the macrocycle exceed 1.5 ppm for the two histidine enantiomers [233]. Similar effects were observed for the Eu(III) and Yb(III) complexes of pendant arm macrocycles based on cyclen, for which the axially coordinated solvent ligands strongly influence NMR shifts [234]. NMR spectroscopy was also used to follow axial coordination of chiral carboxylates and amino acids in the related chiral lanthanide macrocyclic complexes based on cyclen ring [235]. Large chemical shift differences were also observed for enantiomers of chiral carboxylates including deprotonated forms of important drugs ibuprofen and naproxen.

8. Conclusion

Macrocyclic Schiff bases are versatile ligands that can coordinate virtually any metal ion. The synthesis based on the condensation of diamines with dicarbonyl compounds is very flexible and allows easy modification of the macrocycle. The varied denticities and sets of coordinating atoms can be achieved by controlled changing of the number of imine nitrogen atoms, by the incorporation of pyridine, pyridazine, bipyridine, phenol, thiophenol, etc. into macrocycle rings and by introducing additional coordinating functionalities in lateral chains such as alcohol, ether or amine. In the above condensation reactions extended macrocyclic systems can be created that are suitable for the inclusion of relatively large metal ions or simultaneous coordination of two or more metal ions. The Schiff base macrocycles can be easily reduced to analogous amine macrocycles that are more stable toward hydrolytic decomposition. These amine macrocycles can be further modified at nitrogen atoms by the introduction of pendant arms with a wide range of coordination possibilities. The condensation of chiral diamines leads to enantiopure chiral macrocyclic complexes.

The chemistry of macrocyclic Schiff base complexes and related macrocycles is rapidly expanding. With peculiar characteristics these structures are found to be powerful tools used to defining interesting features relating to general chemistry and application. Increasingly sophisticated systems are synthesized both as a result of ingenious design and serendipity. Even though the enormous number of Schiff base macrocycles and their complexes have already been described, many more interesting systems of this type surely await discovery.

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