

Synthesis and Application of Macrocyclic and Macroacyclic Schiff Bases

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The challenge presented by the design and synthesis of ligands capable of organising more than two metal centres into a predetermined arrangement in order to develop new materials is discussed.

The design and synthesis of macropolycyclic and/or macropolyacyclic Schiff bases, which have the potential to act as metal-specific ligands, or can allow the simultaneous incorporation of two or more metals in well defined homo- or heterodinuclear arrays, is presented together with the role of metal ions as templating devices and the opportunities to utilise transmetallation reactions. Formation of Schiff bases followed by reductive demetallation leads to a variety of more stable, and flexible, ligands useful in metal transfer studies. C- and N-functionalisation of macrocyclic Schiff bases produces pendant-armed ligands which permit a more dynamic complexation of the metal ion than is found in bicyclic ligands.

Much effort has been devoted, in recent years, to the preparation and characterization of metal complexes with macrocyclic and/or macroacyclic ligands.^{1–9} As a consequence, these systems have reached a very high level of sophistication: starting from quite simple linear or cyclic compounds, well defined classes of synthetic systems such as macro-di- or macro-tricycles, catenands, compartmental ligands and calixarenes, have been synthesized and classified,^{1,10,17} with the aim of enhancing their ability to form molecular complexes with metal ions or neutral organic molecules. Bioinorganic chemistry, materials science, catalysis, separation and encapsulation processes, hydrometallurgy, formation of compounds with unusual properties, metal–metal interactions, transport and activation of small molecules have received considerable stimulus from the employment of such ligands.^{1–26} The development of these studies presented the opportunity to design and synthesize larger polydentate systems capable of securing into their coordination environment more than one metal ion, and combines the opportunity offered by a series of new coordinating systems with the properties arising from the simultaneous presence of identical or different metal centres.

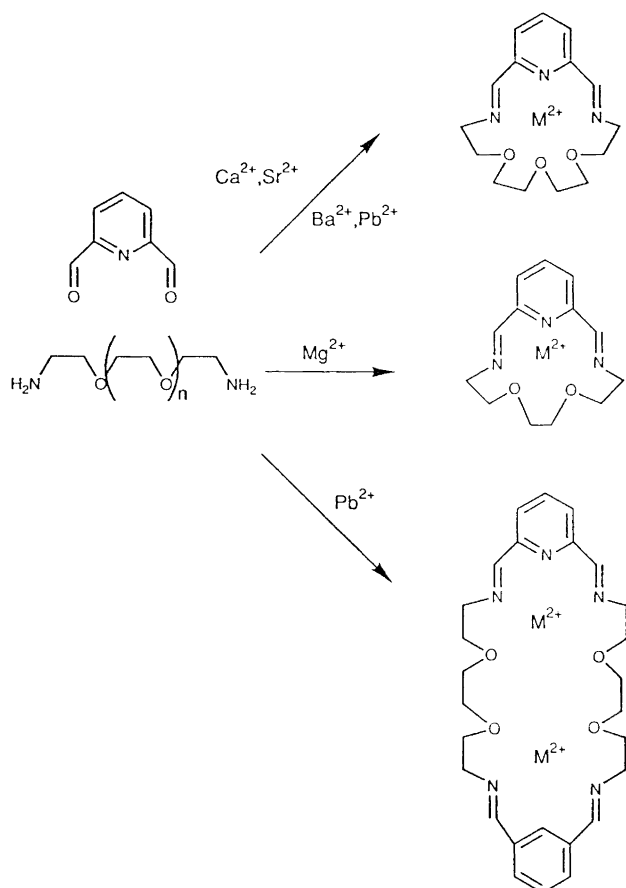
Many excellent papers have been published during the last two decades on the preparation and properties of dinuclear complexes. In particular, attention was devoted to their correlation with the active site of metalloenzymes and metalloproteins containing dinuclear metal centres, in or-

der to elucidate the factors that determine the reversible binding and activation of O₂ in various natural oxygen transport systems and mono- and dioxygenases and to mimic their activity.^{1–12,27,28} In particular, the preparation of complexes which contain two transition metal ions separated by distances of 3.5–6 Å is of considerable interest. At these distances no direct interaction between the metal ions is expected, yet a substrate could interact simultaneously with both ions, and it has been shown that pairs of metal ions at a suitable distance and/or with an appropriate structure can mediate certain chemical reactions better than, or in a manner different to, isolated metal centres.¹¹

Macrocyclic and macroacyclic ligands have also been used for the generation of compounds with specific spectroscopic and magnetic properties. Using compartmental ligands, dinuclear complexes can be synthesized in which the two metal centres, if paramagnetic, can interact with each other through the bridging donor atoms of the ligands in a ferromagnetic or antiferromagnetic way. By changing the type of ligand, the distance between the two chambers and/or the paramagnetic centres, it is possible to vary the magnetic interaction considerably, and for particular complexes ferromagnetic interactions have been observed. Thus these complexes may be good building blocks for the fabrication of a molecular ferromagnet.

Complexes in which a single ligand organizes more than two metal centres into some predetermined arrangement may show unique behaviour, and recently attention has been devoted to the synthesis and characterization of poly-

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Scheme 1. Schiff base macrocycle synthesis in the presence of non-transition metal templates.

nuclear species, closely related to the dinuclear analogues, which can extend, magnify, and in some case considerably modify, the unusual properties of dinuclear complexes.

Pendant-arm macrocycles and their metal complexes have also attracted attention.²⁹⁻³² Arms bearing additional potential ligating groups have been introduced at both carbon and nitrogen atoms of macrocycles which have generally been based on polyaza- or polyoxa-donor sets. One potential in this area derives from the concept that the presence of two pendant arms, bearing ligating groups, attached at appropriate positions on a macrocyclic framework, would result in an 'opened' cryptand, thus leading to

modified complexation properties relative to the corresponding clathrochelates or simple macrocyclic precursors.^{33,34}

This review presents a personalized account of the progress made in the development of synthetic procedures for the preparation of mono-, di- and polynuclear Schiff base systems, with particular reference to lanthanide and actinide complexes.

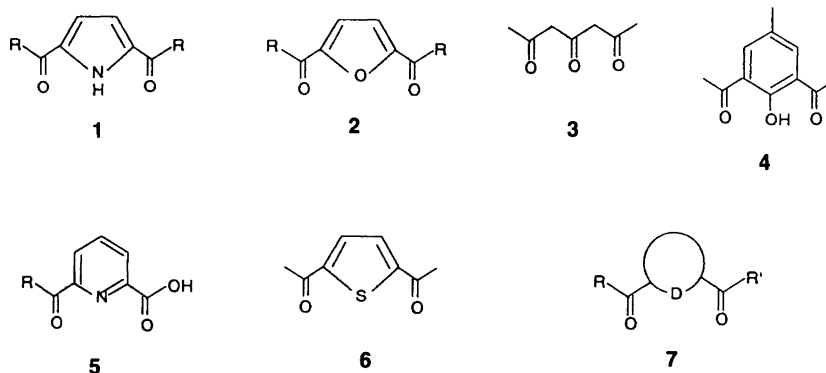
Macrocyclic Schiff bases

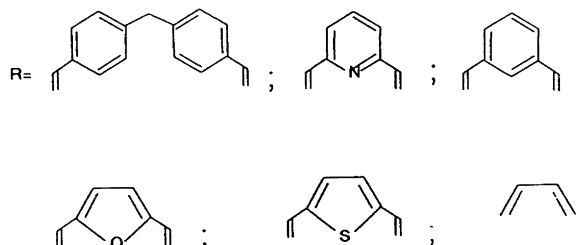
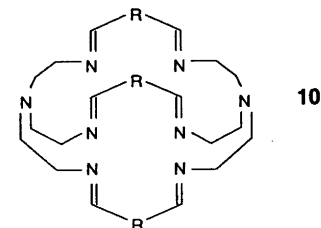
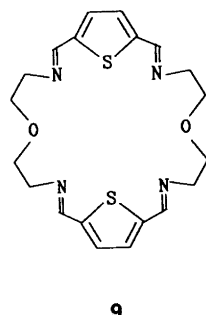
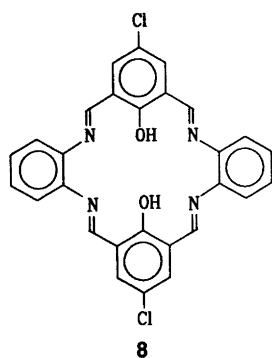
The template effect. Ideally a macrocyclic complex is formed by adding the required metal ion to a preformed ligand. However, the synthesis of the required macrocycle often results in a low yield of desired product, with side reactions, such as polymerization, predominating. In order to bypass this problem the ring-closure step in the synthesis may be carried out under conditions of 'high dilution', or 'rigid groups' may be introduced to restrict rotation and internal entropy losses in the open-chain precursor and so facilitate cyclization. One effective method for the synthesis of macrocyclic complexes involves an *in situ* approach wherein the presence of a metal ion in the cyclization reaction markedly increases the yield of the cyclic product. The metal ion plays an important role in directing the steric course of the reaction, and this effect has been termed the metal-template effect.³⁵

The size of the cation used as a template has proved to be of importance in directing the synthetic pathway in Schiff base systems (Scheme 1). Of the alkaline earth cations only magnesium generates the pentadentate [1+1] macrocycle, but it is ineffective in generating the hexadentate [1+1] macrocycle, which is readily synthesized in the presence of the larger cations calcium, strontium, barium and lead(II). These cations, however, generate the [2+2] macrocycle derived from the components giving the [1+1] macrocycle with magnesium.³⁶

The similarity in ionic radii between the alkaline earth metal cations and the lanthanide(III) cations suggested that the latter should also be efficient templating devices, and this has proved to be the case.¹²

The actinides, with their high ionic radii and/or unusual coordination geometry, can produce and stabilize ex-



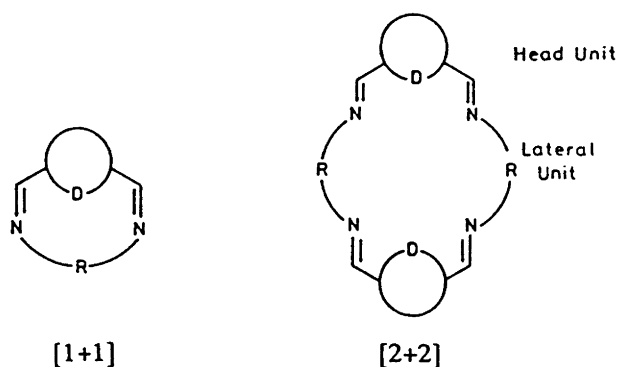


panded macrocyclic ligands, as in the preparation of 'superphthalocyanines'.³⁷

With certain precursors (i.e. 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane) [3+3] and [4+4] macrocyclic complexes have been synthesized. For the [2+2] ligands the head and the lateral units can be varied, with the consequent formation of macrocycles with different donor atoms and/or different cavity sizes.¹²

Metal-free condensation reaction. Whilst simple di-, ter-, tetra- and pentadentate Schiff bases are readily synthesized by non-template procedures, there is sparse reference to macrocyclic Schiff base ligands being synthesized by this method.^{12,38}

For the synthesis of macrocycles, dicarbonyl precursors of the type 1-6 (7 is a schematic representation of these compounds) and a wide range of diamines have been used.



Scheme 2. Schematic representation of the [1+1] and [2+2] Schiff base macrocycles.

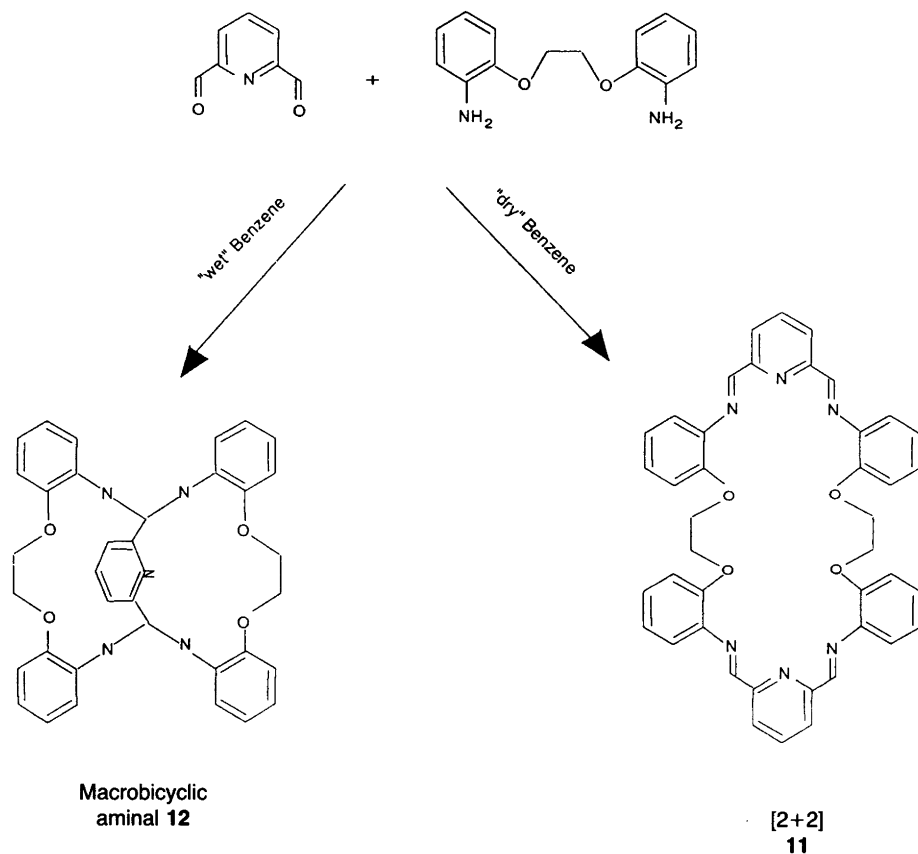
The condensation products, more usually obtained by template cyclocondensation, are thus of the type reported in Scheme 2, with the formation of [1+1] and [2+2] macrocycles. The X-ray structure of the macrocycles **8** and **9**, obtained by condensation of 2,6-diformyl-4-chlorophenol and *o*-phenylenediamine³⁹ or of 2,5-diformylthiophen and 1,5-diamino-3-oxapentane,⁴⁰ respectively, are examples of self-assembled [2+2] macrocycles with an appropriate cavity for dinuclear complexation.

A natural evolution from these complexes is the recent generation of macrobicyclic cages **10**, produced in one-step condensation reactions, capable of acting as dinuclear ligands.⁴¹⁻⁴⁵

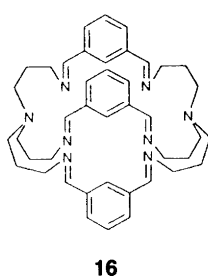
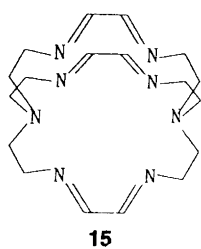
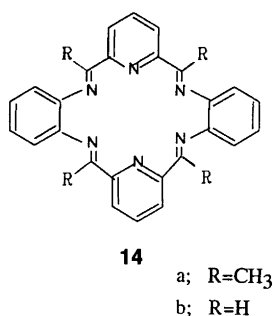
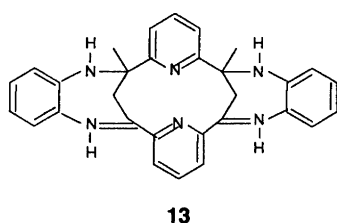
The solvent employed in the condensation reaction, and its purity, is of primary importance and can considerably influence Schiff base formation. A representative example is the condensation reaction of 2,6-diformylpyridine with 1,2-bis(1-aminophenoxy)ethane, which produces, in 'dry' or 'wet' benzene, the expected [2+2] macrocyclic product **11** or the macrobicyclic amina **12**, according to Scheme 3.⁴⁶

The condensation of 1,2-diaminobenzene with 2,6-diacetylpyridine forms the tricyclic compound **13** instead of the macrocyclic Schiff base **14**, as confirmed by X-ray diffraction studies.⁴⁷ Its facile recovery during attempts to obtain metal complexes of **14a** by template procedures led to the conclusion that steric crowding inhibited the formation of **14a**. This could arise *via* interaction of the methyl groups with proximal aromatic hydrogen atoms. In contrast, the related condensation of 1,2-diaminobenzene with 2,6-diformylpyridine in the presence of Ca(II), Sr(II), Ba(II) and Pb(II) templates readily gives complexes of the hexaazamacrocyclic **14b**,⁴⁸ bearing out the predictions made for this [18]-annulene analogue via theoretical calculations.⁴⁹ In a recent communication the structure of [Pr(**14a**)(NO₃)₂·MeOH]ClO₄·0.5MeOH has been reported, revealing the reality of the formation of macrocyclic complexes of **14a**.⁵⁰

Although a pattern appears to be emerging for non-template formation of macrocycles (high dilution reactions



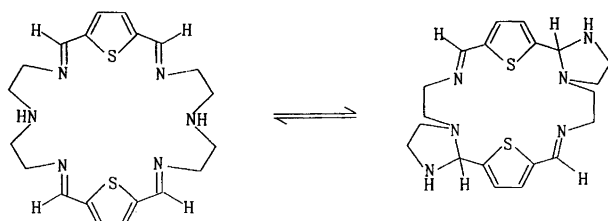
Scheme 3. Preparation of the polyamine 26 and related complexes Cu(26)(ClO₄)₂ and [Ba(27)(SCN)₂].



in non-protic solvents, access to ring-contracted forms), it is too early to state that any general behavioural principle has been established.

Transmetalation reaction. It has been generally found that for the larger Schiff base macrocycles, transition metal cations are ineffective as templates. Consequently the kinetic lability of the metals present in the generation of macrocyclic complexes derived from the use of alkaline earth, lanthanides and main group templating agents had enabled the generation of the corresponding transition metal complexes through the transmetalation reaction.^{36,51-53} This approach has been particularly successful when applied to the generation of dinuclear copper complexes of tetraimine Schiff base macrocycles. A pertinent example concerns a series of related bibrachial [2+2] macrocyclic Schiff base complexes derived from functionalised triamines. Thus diacetylpyridine and [NH₂-(CH₂)₂]₂-N-(CH₂)₂OCH₃, in the presence of barium perchlorate, produce the mononuclear macrocyclic [2+2] ten-coordinate barium(II) complex [Ba(m/c)](ClO₄)₂ (where m/c is the macrocycle obtained by condensation of diacetylpyridine with [NH₂-(CH₂)₂]₂-N-(CH₂)₂OCH₃). This barium(II) complex, by reaction with copper(II) perchlorate, then forms the dinuclear [2+2] copper(II) tetra-perchlorate complex [Cu₂(m/c)](ClO₄)₄.⁵⁴

The lability of lanthanides has been explored in the transmetalation reaction with copper(II) perchlorate to



Scheme 4.

give the corresponding homodinuclear copper(II) complex. The general applicability of the reaction is indicated by the ability of the lanthanum complexes of the [2+2] macrocycles, derived from 2,6-diformylpyridine and 1,2-diaminopropane, to transmetallate with copper(II).³⁸

Similar procedures have been employed for obtaining mono and/or dinuclear complexes with the macrobicyclic [2+3] polyazacryptand **15**, obtained by condensation of tris-(2-ethylamino)amine with glyoxal⁵⁵ or with the octaaza-hexa Schiff base macrocyclic ligand **16**, derived from the reaction of tris(3-aminopropyl)amine with benzene-1,3-dicarbaldehyde.⁵⁶

Ring contraction and ring expansion. A ring contraction of the macrocyclic cavity of Schiff bases, often leading to the stabilization of metal-free ligands, has been observed when there is a group such as =NH or -OH available for addition to the imine bond and/or there is a metal ion too small for the macrocyclic cavity. In this second case the ring contraction causes a smaller, more accommodating cavity for the available metal.

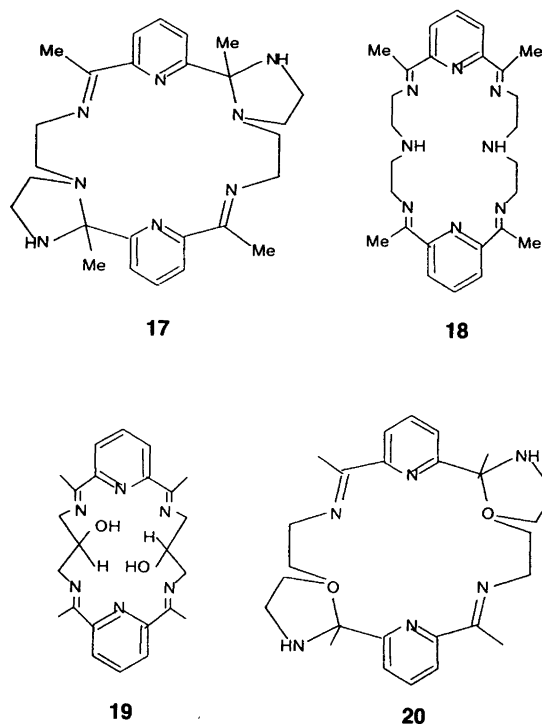
For example, the [2+2] cyclization reaction of 2,5-diformylthiophen with the facultative polyamines H₂N-R-NH₂ [R = -(CH₂)_n with n = 3,4,5,6; -(CH₂)₂-X-(CH₂)₂- with X = S, NH, O; -(CH₂)₃-NH-(CH₂)₃-; -(CH₂)₂-O-(CH₂)₂-; -(CH₂)₂-O-(CH₂)₂-O-(CH₂)₂-O-(CH₂)₂-] readily occurs when equimolecular amounts of the precursors are reacted in methanol.³⁷ The NMR spectra of the macrocycles with R = -(CH₂)₂-NH-(CH₂)₂- and -(CH₂)₃-NH-(CH₂)₃- which contain, in addition to the signals due to the tetraamine macrocycles, a further set corresponding to macrocycles in which a ring contraction has occurred, indicate the presence of more than one solution species (Scheme 4). Analogously the direct [2+2] condensation of isophthalaldehyde with diethylenetriamine produces a {24} → {18} ring closure; in the solid state the macrocycle contains an 18-membered inner ring, two imine bands and two five-membered imidazoline outer rings, while in solution a series of isomers was observed.²⁸

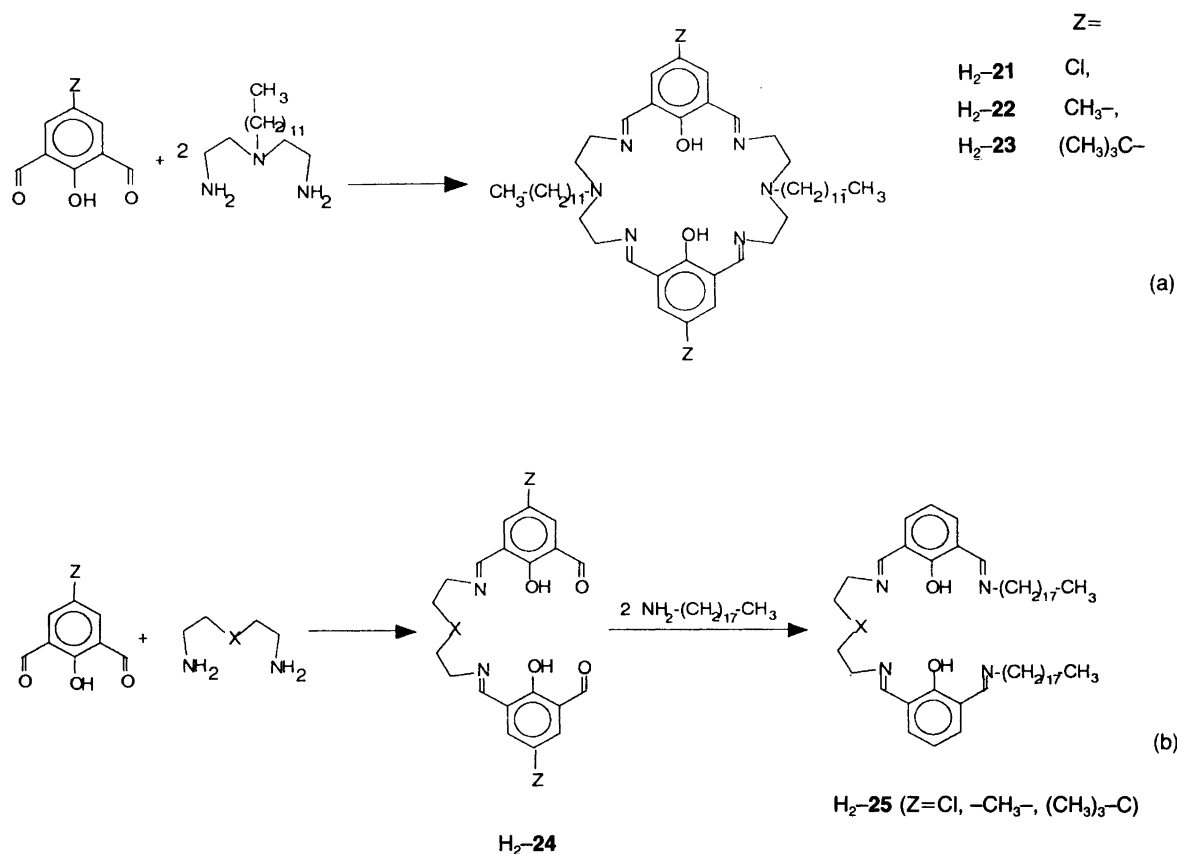
Reaction of 2,6-diacetylpyridine with diethylenetriamine in the presence of Ba²⁺, Sr²⁺ or Ca²⁺, in refluxing methanol, forms complexes of the macrocyclic ligand **17**.^{56,57} On treatment of [Sr(**17**)](ClO₄)₂ with AgClO₄ the dinuclear complex [Ag₂(**18**)](ClO₄)₂ is obtained, in which a ring expansion of the coordinated macrocycle occurs. This **17** → **18** ring expansion on exchange of the coordinated alkaline-earth metal ion by two silver(I) ions was found to be

reversible: treatment of [Ag₂(**18**)](ClO₄)₂ with BaCl₂ in methanol gave AgCl along with the complex [Ba(**17**)](ClO₄)₂, identical in properties to an authentic sample prepared via the template method.⁵⁷

The same behaviour was also found for the [2+2] condensation reaction of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-azapentane.⁵⁸ This reaction, carried out in the presence of lanthanide(III) salts [i.e. Eu(NO₃)₃ or Tb(NO₃)₃], revealed that the metal ion coordinates only two oxygen and three nitrogen atoms of one chamber of the macrocycle, which is in the Schiff base form. The other chamber, not engaged in coordination, suffers a ring closure with the formation of one five-membered imidazoline outer ring.^{59,60} The metal ion is non-coordinated, being directly bonded also to four oxygen atoms of two bidentate nitrate ions, while the third nitrate is ionic.^{59,60}

The reaction of 2,6-diacetylpyridine with 1,3-diamino-2-hydroxypropane in methanol, in the presence of Ba(NCS)₂ or Ba(ClO₄)₂, leads readily to the corresponding mononuclear barium complex of [2+2] {20}-membered ring macrocycle **19**. Transmetalation reactions in the presence of Pb(NCS)₂ or Pb(ClO₄)₂, resulted in isolation of the corresponding lead complex of the ring-contracted macrocycle {18}-membered ring **20**,⁶¹ as found in the X-ray structure of [Pb(**20**)](NCS)·MeOH.⁶¹ No evidence was obtained from ¹H NMR for the existence of an equilibrium in solution between the open and contracted isomers. Again the ring contraction, from an octadentate, {20}-membered ring unit to a hexadentate, {18}-membered ring unit, is believed to be facilitated by the use of the smaller Pb²⁺ cation and its requirement for the smaller ring cavity.⁶¹





Scheme 5.

Functionalized ligands. The development of specific macrocyclic and macroacyclic ligands soluble in organic solvents has opened new possibilities of practical applications in the field of selective metal ion recognition, transport and separation.

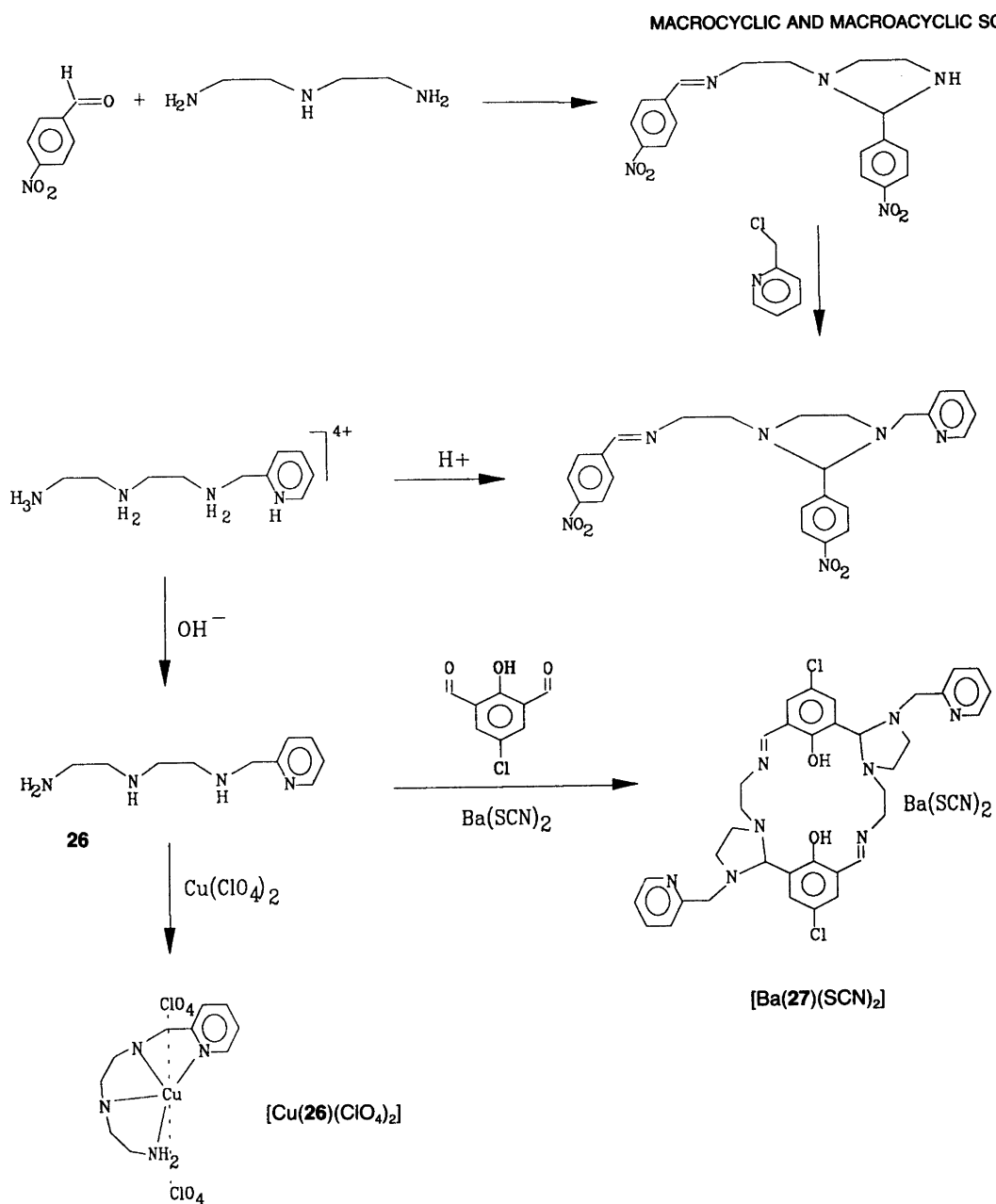
The addition of lateral chains to the Schiff bases considerably enhances the solubility of the related complexes in aromatic or aliphatic solvents^{62,63} (Scheme 5). The ketoprecursors 2,6-diformyl-4-Z-phenols [Z=Cl, CH₃-; (CH₃)₃C-], by reaction with 4-N-dodecyldiethylenetriamine in chloroform or in methanol in a 1:1 molar ratio, produce yellow oils or sticky solids formulated, according to the physicochemical data, as the macrocycles H₂-21...H₂-23 reported in Scheme 5a. Electron impact mass spectrometry and/or FAB-MS revealed for all the three macrocycles well detectable molecular peaks at the appropriate *m/z* values.^{62,63}

The same 2,6-diformyl-4-Z-phenols give with the facultative diamines 1,5-diamino-3-azapentane or 1,5-diaminothiopentane the acyclic potentially pentadentate ligands, H₂-24, which contain C=O groups that can be involved in further condensation reactions with primary amines. Using NH₂-(CH₂)₁₇-CH₃, the macroacyclic ligand H₂-25 of Scheme 5b has been obtained. Both macrocyclic and macroacyclic ligands are capable of forming complexes that are soluble in hydrocarbons.^{62,63}

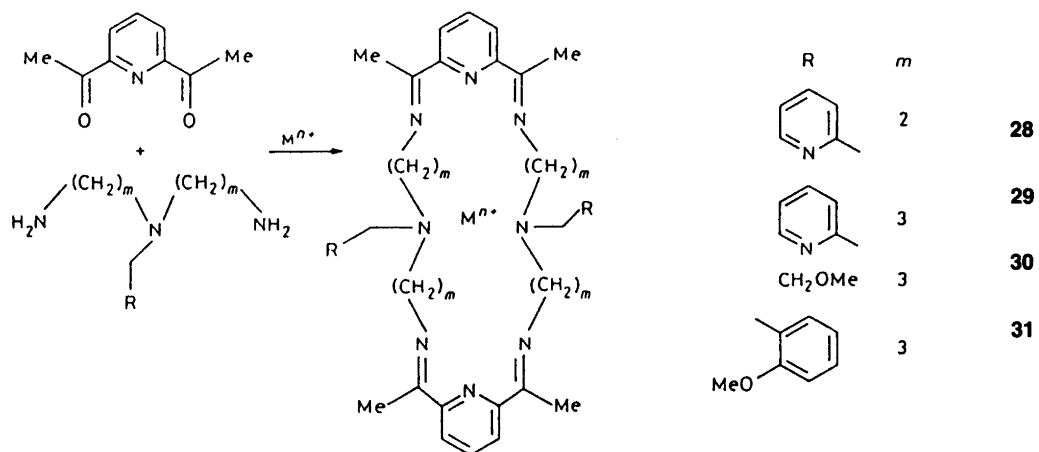
In addition, a series of functionalized polyamines and related open cryptands have been prepared. The polyamine 7-(2'-pyridyl)-3,6-diazaheptylamine (**26**) was obtained according to Scheme 6, and its reactivity toward 2,6-diformylphenol and/or metal ions was studied.^{64,65}

In the complexes [Cu(**26**)(ClO₄)₂], the quadridentate ligand **26** is equatorially coordinated to the metal ion through the nitrogen donor atoms. The metal ion makes two relatively long axial Cu...O contacts with oxygen atoms from the two ClO₄⁻ anions.⁶⁴ In the complex [Ba(**27**)-(SCN)₂], synthesized by template condensation of 2,6-diformyl-4-chlorophenol and **26** in the presence of barium(II) dithiocyanate, the macrocycle ligand behaves as a neutral hexadentate ligand; two SCN⁻ ions, N-bonded to Ba²⁺, complete the coordinate polyhedron around the metal, which can approximately be described as a distorted square antiprism.⁶⁴

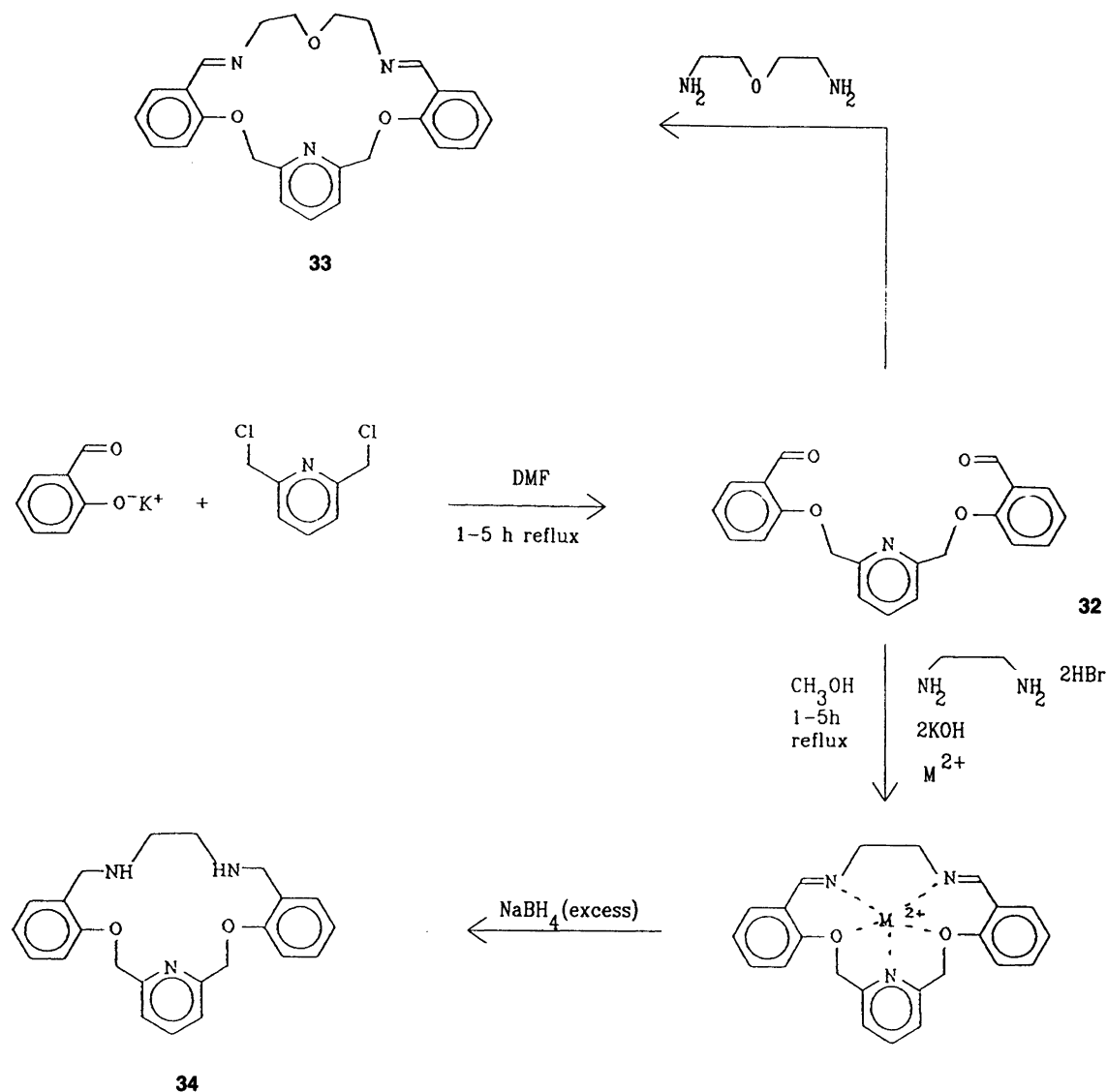
[2+2] Tetraimine Schiff-base macrocycles are readily prepared by the template cyclocondensation of heterocyclic dicarbonyl derivatives and 1,*n*-diaminoalkanes. Extension of this approach to include functionalised triamines bearing 2-pyridylmethyl, 2-methoxyethyl and 2-methoxybenzyl substituents leads to the synthesis of *N,N'*-bibracchial macrocyclic (**28**–**31**) complexes of the templating cation. Mono- and dinuclear complexes are recovered in the presence of barium and silver(I) templates, respectively. The crystal



Scheme 6.



Scheme 7.



Scheme 8.

structures of a mononuclear barium complex of **28** and of four homodinuclear silver(I) complexes, one from each macrocyclic ligand **28–31**, have been reported (Scheme 7).⁶⁶

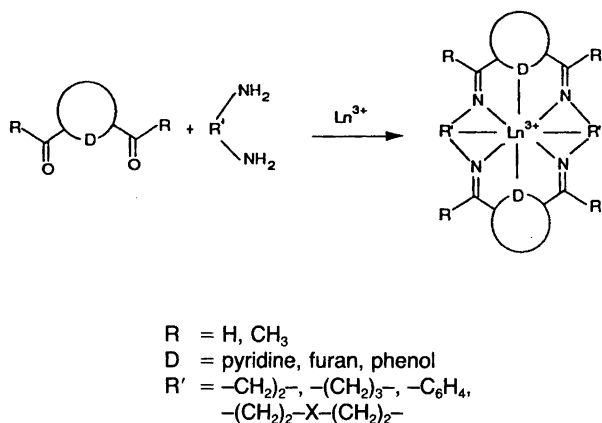
The macrocycle in $[\text{Ba}(\mathbf{28})](\text{ClO}_4)_2$ is folded back upon itself to provide a 'molecular cleft' in which the pyridyl fragments at opposite ends lie approximately parallel, with the barium sandwiched, but displaced towards the more open part of the macrocycle. All ten nitrogen atoms from the ligand are close enough to interact with the central barium ion.⁶⁶

In the complex $[\text{Ag}_2(\mathbf{28})](\text{ClO}_4)_2$ the macrocycle retains its cleft-like appearance and is coordinated to two silver atoms which are closely spaced [$\text{Ag}\cdots\text{Ag}$ 3.068 Å]. The coordination geometries of the silver atoms are not closely related to regular polyhedra. In the structure of the dication $[\text{Ag}_2(\mathbf{29})]^{2+}$, in which the macrocyclic ring size has been expanded from {24}- to {28}-membered, the macro-

cycle again coordinates to two silver atoms which are in very similar and separated environments ($\text{Ag}\cdots\text{Ag}$ 6.824 Å).⁶⁶

In the structure of the $[\text{Ag}_2(\mathbf{30})]^{2+}$ dication, the macrocycle coordinates to two silver atoms which are unsymmetrically bridged by a pair of imino groups and a silver–silver distance of 2.907 Å, which may be compared with that of 2.89 Å in silver metal.⁶⁶ The macrocycle adopts a conformation which closely resembles that of $[\text{Ag}(\mathbf{28})]^{2+}$, where the smaller {24}-membered macrocycle carries pendant pyridyl substituents of a greater donor capacity, rather than that of $[\text{Ag}_2(\mathbf{29})]^{2+}$, where the {28}-membered macrocycle also carries pendant pyridyl groups.⁶⁶

In the cation $[\text{Ag}_2(\mathbf{31})]^{2+}$ the macrocycle coordinates to two silver atoms which are in very similar and well separated environments ($\text{Ag}\cdots\text{Ag}$ 5.828 Å). The cleft in the molecule between the planes of the pyridyl rings has opened such that the angle between their planes is 44°. This



Scheme 9.

may be compared with the complex dications $[\text{Ag}_2(\mathbf{29})]^{2+}$ and $[\text{Ag}_2(\mathbf{30})]^{2+}$ where, for the same macrocyclic framework, the pyridyl groups are approximately parallel. In the latter they give a narrow cleft with a short silver–silver distance, whereas in the former the macrocycles had suffered a ‘concertina’ expansion. Presumably this is attributable to the greater donor capacity of the methyl aryl ether as compared with its alkyl counterpart.

It is notable that on forming the dinuclear silver(I) complexes the cleft-like appearance of the macrocyclic ligand is retained by the $\text{Ag} \cdots \text{Ag}$ separation (2.91–6.82 Å) and the configuration of the ligand changes with both ring expansion and the introduction of pendant groups of varying donor strength.⁶⁶

The use of two imino residues as bridging or semi-bridging groups, and the consequent silver–silver distances that ensue, seems likely to be related to the donor capacity of the pendant groups, and the need to achieve adequate coordination of the silver ions.

New polydentate macrocycles via Schiff base formation and reduction

As reported above, it is possible to obtain cyclic Schiff bases by reaction of the appropriate precursors if the condensation product is stable to hydrolysis. Thus the reaction of the diformyl derivative (**32**) with 1,5-diamino-3-oxapentane produces a potentially hexadentate macrocycle (**33**).⁶⁷ Generally a template cyclocondensation is carried out; the Schiff base complexes can undergo a subsequent reductive demetallation by NaBH_4 . The X-ray structures of the Schiff base **33** and of the reduced macrocycle **34** confirm the reaction sequence reported in Scheme 8.^{67,68} Template cyclocondensation followed by a reductive demetallation is therefore generally a pathway for the easy formation of a wide variety of new macrocyclic ligands.

These macrocycles show intermediate rigidity that is sufficient to present a donor set with a defined geometry to a metal ion but flexible enough to encourage favourable kinetics of metal ion incorporation and release which may facilitate the selective complexation and transport of metal

ions. However, when metal ions are discriminated against by a poor fit for the cavity the possibility exists that the favoured mode of interaction will involve exomacrocyclic complexation using only part of the macrocyclic donor set.

The dioxatriazamacrocycle **34** has been successfully employed for the complexation of different metal ions, and a comparison of the species obtained in the solid state and in solution has been made.⁶⁹ Complexes with a 1:1 and 1:2 metal:ligand ratio have been found. The metal ion is generally retained in the macrocyclic moiety, but variation of the anion can induce the metal ion to be coordinated exocyclically to the macrocycle via the two secondary amine nitrogen atoms. Thus the coordination of iodide favours for zinc(II) and mercury(II) a tetrahedral geometry at the metal.

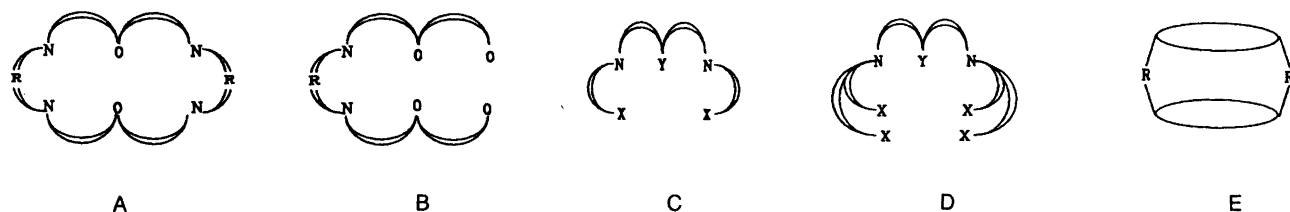
The structure of the 1:2 nickel(II) nitrate complex shows the metal ion is six-coordinated, with the coordination environment being provided by the aliphatic nitrogen atoms from the macrocycle, one chelating pair from each ring, and a bidentate nitrate anion. The nickel(II) is therefore complexed in an exomacrocyclic manner. Transfer and extraction studies involving (**34**) show that Cu(II) is favoured over Ni(II); and stability constant studies show that there is a stronger complexation to cadmium than to zinc.^{66–69}

Mononuclear complexes

Although formation of mononuclear macrocyclic complexes, via template procedures, has been achieved with transition or alkaline earth metal cations, the early work concerning the use of lanthanide templates in the synthesis of [2+2] tetraimine Schiff base macrocycles suggested that the potential application was limited.⁷⁰ Nevertheless the formation of mononuclear macrocyclic complexes in the presence of lanthanide(III) ion has been widely studied, and the progress made reviewed.¹² [2+2] Macrocylic complexes have been prepared through the reaction procedure of Scheme 9, and the X-ray structure of several lanthanide(III) complexes with different counter-anions confirms the nature of the reaction products.¹² When 2,6-diacetylpyridine and facultative polyamines, containing additional donor atoms into the R' chain [$R' = -(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}-\text{CH}_2-$; $-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-$; $-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-$; $-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_2-$], are reacted in the presence of lanthanide(III) ions, [1+1] macrocycles are obtained.^{12,71}

Lanthanide(III), $\text{Ln}(\text{H}_2\text{-L})(\text{X})_3$, and uranyl(VI), $\text{UO}_2(\text{L})$, complexes [where Ln represents almost any lanthanide (III) ion, $\text{H}_2\text{-L}$ are the functionalized macrocyclic $\text{H}_2\text{-21} \cdots \text{H}_2\text{-23}$ and macroacyclic $\text{H}_2\text{-25}$ ligands of Scheme 5 and X is NO_3^- or Cl^-] have been obtained by reaction of the preformed ligands with an appropriate metal ion or by the template procedure.^{62,63,72}

The Schiff bases behave as neutral pentadentate ligands in the lanthanide complexes but as pentadentate dianionic ligands in the dioxouranium(VI) analogues. Both ligands



Scheme 10.

and complexes are soluble enough in organic solvents to be used for the separation of f-ions; their solubility depends on the substituent Z and follows the order $-\text{Cl} < -\text{CH}_3 < -\text{C}(\text{CH}_3)_3$.

The ligands $\text{H}_2\text{-21} \cdots \text{H}_2\text{-23}$ offer the advantages of a single-step preparation and, owing to their cyclic nature, a better selectivity towards lanthanides; they are good extractants for some trivalent lanthanides (Dy-La) from a nitrate medium. Competitive extractions were conducted to determine whether selectivity could be achieved from aqueous solutions containing equimolar amounts of two lanthanides nitrate or chloride salts: Dy/La; Dy/Eu; La/Eu. Such extraction experiments have been carried out with the two ligands $\text{H}_2\text{-22}$ and $\text{H}_2\text{-23}$ and several aqueous phases which differ from one another in the pH, in the nature of the counter anion (Cl^- or NO_3^-) and in the presence (or absence) of an excess of a monovalent cation as Li^+ or NH_4^+ (ionic radius, $r/\text{\AA}$: $\text{Li}^+ = 0.68$; $\text{NH}_4^+ = 1.43$; $r_{\text{Li}^+} < r_{\text{Ln}^{3+}}$; $r_{\text{NH}_4^+} > r_{\text{Ln}^{3+}}$).

Loading the aqueous phase with an 'inert' salt is an approach to decrease the tendency for macrocycles to diffuse into the aqueous phase. On the other hand the excess of anion may promote the recovery of trace lanthanides from a solution loaded with other metals. The difficulty is to find a sufficiently 'inert' cation, because at the concentration required to produce the desired salting effect the cation may compete with the macrocycle, and the lanthanide distribution will be lowered.

For Dy/La mixtures, the best results have been obtained in nitrate media and in the presence of an excess of ammonium nitrate (which might act as a salting-out agent decreasing the water activity and facilitating cleavage of the bond between the central metal ion and the coordinated water molecule); moreover, this shows that the ammonium ion is not extracted with the ligand. For example D_{Dy} increases from 8.6 to 24 and D_{La} from 0.24 to 0.55 (contact time 30 min) with an excess of NH_4NO_3 in the feed (D is the distribution coefficient, defined as $M_{\text{org}}/M_{\text{aq}}$).⁷²

The presence of Li^+ decreases both Dy and La extraction; this is related to a competitive extraction of Li^+ with $\text{H}_2\text{-22}$ and $\text{H}_2\text{-23}$.⁷² Under the same experimental conditions (excess of NH_4^+), Dy and La were extracted to a lower extent from chloride medium.⁷²

The selectivity of the macrocycles for Dy and Eu over La is very high and it is possible to extract preferentially either Dy or Eu over La from mixtures of these ions. Separation factors $S_{\text{Dy/La}} = 44$ and $S_{\text{Eu/La}} = 37$ have been evaluated.⁷²

Both extractants exhibit a slightly higher selectivity for Dy than for Eu: in the same conditions as reported above, the value of the separation factor $S_{\text{Dy/Eu}}$ equals only 2.

From these competitive extraction experiments, the macrocyclic ligands exhibit the following order of affinity for the three rare-earths tested: $\text{Dy} > \text{Eu} \gg \text{La}$.⁷²

The distribution ratio D_{Ln} versus the corresponding ionic radius shows that the larger the ionic radius is, the lower the D value will be: $D_{\text{Ln}} > 3$ for $r \leq 0.95 \text{ \AA}$ (in nitrate medium with an excess of NH_4^+). Several problems arise from the acid transportation through the membrane. The important advantage found in using these compounds is that the ligands are efficient in the extraction of lanthanides in the trivalent state without addition of a synergic agent as required with the neutral crown ethers.⁷²

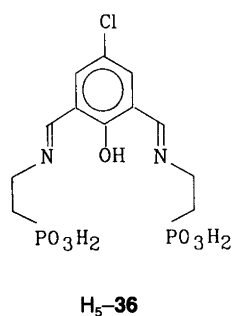
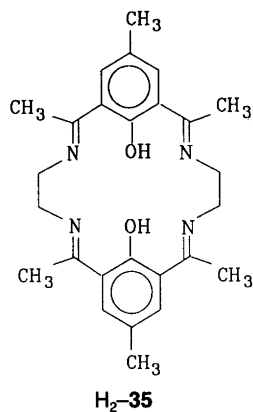
It was also found that it is possible to use a mixture containing aliphatic and aromatic hydrocarbons as organic phase. The results obtained in this case are in line with those obtained with xylene, or of industrial diluents (solvesso 150 or isopar G).⁷²

Dinuclear complexes

Studies on the activation of small molecules (especially oxygen) have received considerable impetus through the use of bimetallic complexes as activators. The simultaneous presence of two metal ions at a suitable distance from each other is a prerequisite for the formation of an activation space necessary for the coordination of dioxygen and/or organic substrates and for their subsequent oxidation. It was found that pairs or clusters of metal ions are sometimes capable of mediating certain chemical reactions more efficiently or in a different way than do isolated centres.¹¹

In order to synthesise such complexes, series of ligands belonging to the five types depicted in Scheme 10 have been synthesised and characterized.^{1,10}

Ligands of type A are macrocycles, derived from [2+2] condensations; type B are side-off acyclic ligands in which a [1+2] condensation occurs; type C are end-off acyclic ligands in which a [2+1] condensation occurs (in the related metal complexes, Y provides an endogeneous bridge and a further exogeneous bridge may be provided by a mono- or bi-dentate anion). Type D are polyodal ligands and type E contain remote chambers with the two macrocycles constrained in a stacked configuration. The chains R and R' (Scheme 10) can contain additional donor atoms (NH, S, O, PPh, etc.) producing a multiplicity of different compartments. Many dinuclear complexes belonging to the differ-



ent types of ligands shown in Scheme 10 have now been fully characterized and the area has recently been reviewed.^{10,11}

The dicopper complex $[\text{Cu}_2(\mathbf{35})(\text{H}_2\text{O})_2](\text{BF}_4)_2$ (**H₂-35** is the macrocycle derived by condensation of ethylenediamine and 2,6-diacetyl-4-methylphenol) is an example of a macrocyclic [2+2] compound.⁷³ The entire binuclear cation, apart from the apical water molecule, is roughly planar; the copper atoms are five-coordinated in a square pyramidal configuration.

The complex $\text{Na}_2[\text{Cu}_2(\mathbf{36})(\text{OH})] \cdot 11\text{H}_2\text{O}$ [where **H₅-36** is the Schiff base obtained by condensation of 2,6-diformyl-4-chlorophenol and (±)-1-aminoethane phosphonic acid in the presence of NaOH] is an example of [1+2] end-off acyclic complexes. The copper ions are five-coordinated square pyramidal. A phenolato oxygen provides the endogenous bridge, while an OH^- group provides the exogenous bridge; two water molecules occupy apical positions.⁷⁴

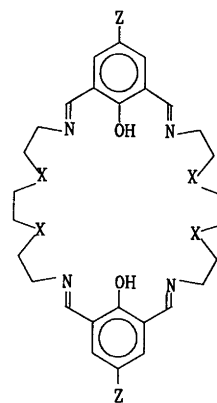
Several polydodal ligands (type D) have been prepared and used for dinuclear complexation. These complexes, owing to their flexibility, appear to be very promising agents in oxygen activation and in oxidation reactions. The ligands contain ionizable (i.e. COOH) or neutral (i.e. pyridine) groups in the pendant arms X, while the central bridging group Y is a phenolic or an alcoholic OH.

General synthetic methods for the construction of cylindrical macrocycles (type E) which contain similar or different macrocyclic subunits have been reported.¹¹ These ligands can complex two different cations or stabilize differ-

ent oxidation states. In these macropolycycles each macrocyclic subunit may serve as a receptor site for a metal cation. Because of the difference in ring size and number of binding sites, macrotricycles may present different complexation properties. Based on crystal structure data, the intercationic distances may be grossly estimated to be 5–7 Å for dinuclear macrotricyclic cryptates.¹¹ Thus there is space for inclusion between the cations of a substrate of compatible size and suitable binding properties, and insertion of a substrate molecule (O_2 , N_2 etc.) between the two metal cations of dinuclear complexes leads to cascade complexes which may have interesting properties for fixation and dinuclear catalysis (such as the reduction of the included molecules).

The asymmetric side-off acyclic ligands (type B) formed by complexation can give rise to mono- or heterodinuclear positional isomers.

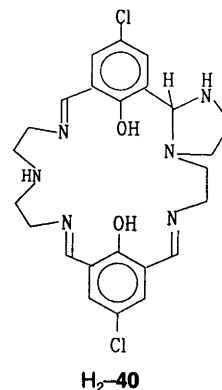
The ligands have often been designed and prepared with coordination sites that are sufficiently different (in the shape, in the number and/or in the type of donor atoms) to allow easy formation of pure heterodinuclear complexes.⁷⁵ Sometimes the chemical behaviour of different metal ions favours heteronuclear complexation, as obtained for $[\text{UO}_2\text{Ni}(\text{aapen})(\text{dmsO})_2]$ and $[\text{UO}_2\text{Cu}(\text{aapen})\text{dmsO}]$. (**H₂aapen** is the potentially hexadentate Schiff base derived by

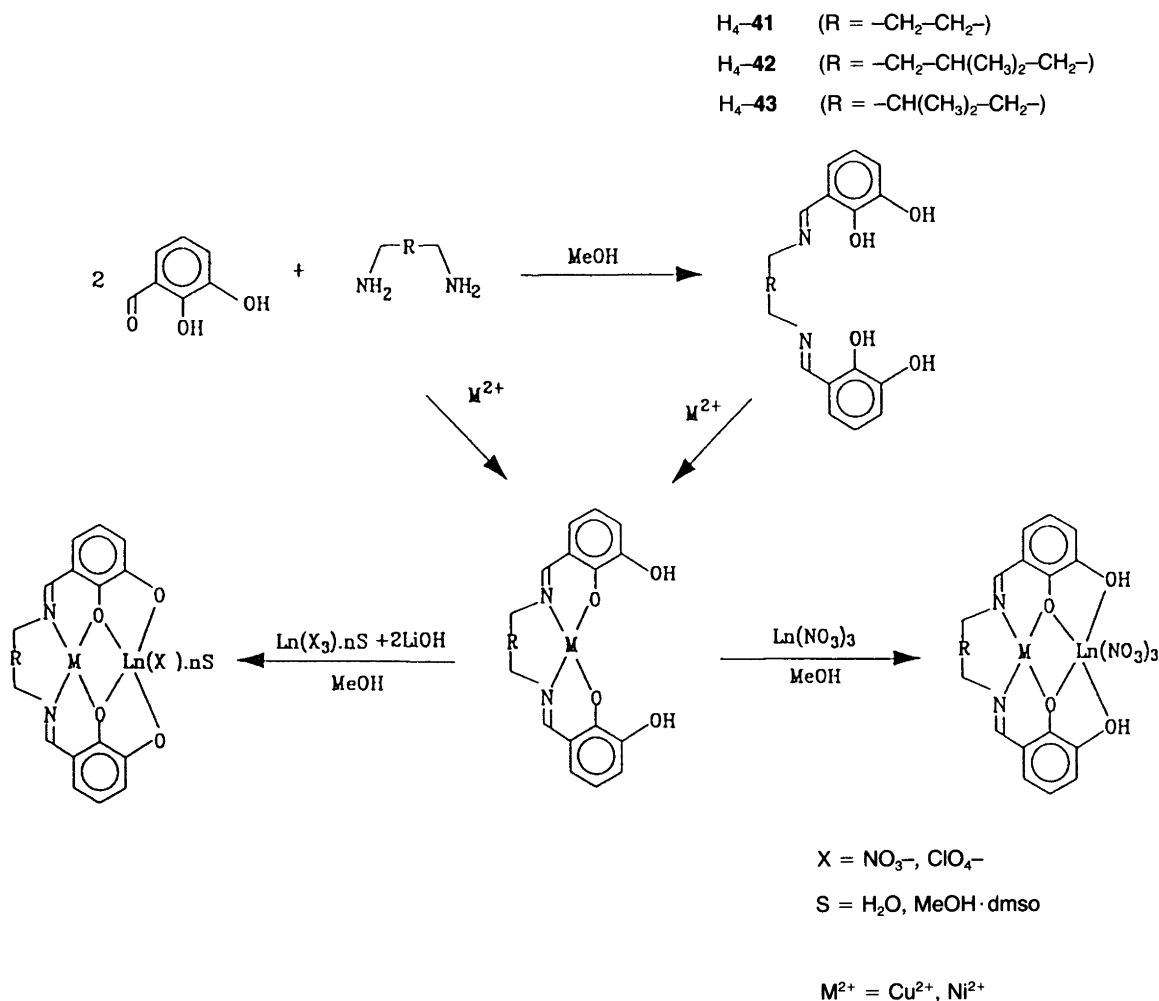


H₂-37 (Z=CH₃, X=NH)

H₂-38 (Z=CH₃, X=O)

H₂-39 (Z=Cl, X=O)

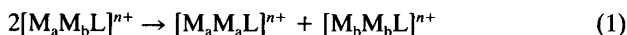




Scheme 11.

condensation of *o*-acetoacetylphenol and ethylenediamine in a 2:1 ratio, and contains an inner N₂O₂ chamber and an outer O₂O₂ chamber.) The uranium ion in the external O₂O₂ compartment achieves its preferred seven-coordination by adding an equatorial dimethylsulfoxide molecule, while the nickel(II) or the copper(II) occupies the inner N₂O₂ chamber. The same heteronuclear complexation to ligands with different chambers also occurs with transition metal ions as confirmed by X-ray structures.^{76,77}

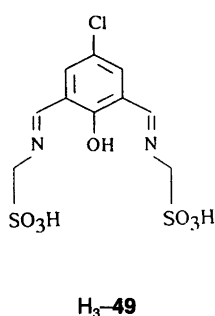
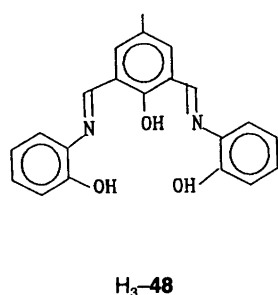
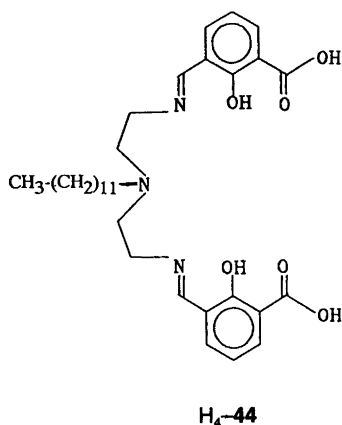
On the contrary, when symmetric ligands or similar metal ions are used, particular experimental procedures must be used in order to avoid reactions of the type (1).



Homodinuclear complexes have been found to catalyze *o*-quinone formation from the corresponding *o*-diphenol, and the epoxidation of olefins better than the analogous mononuclear complexes. Heterodinuclear metal centres seem to be necessary for the asymmetric activation of CO₂.¹¹

The specific spectroscopic and magnetic properties of lanthanide(III) ions have made them essential components in the preparation of new materials and ideal as probes in studies of biological systems. These investigations have often been carried out with the help of macrocyclic ligands.

It has recently been shown that it is possible to introduce two lanthanide ions into a macrocyclic cavity; for instance the Schiff bases H₂-37...H₂-39, obtained by condensation of 2,6-diformyl-4-substituted phenols with the facultative diamines [NH₂-(CH₂)₂-X-(CH₂)₂-X-(CH₂)₂-NH₂; (X=NH,O)], provide a coordination moiety large enough to allow the preparation of homo- and heterodinuclear complexes.⁷⁸⁻⁸¹ In particular, homo- and heterodinuclear lanthanide(III) complexes of the type Ln₂(39)(NO₃)₄·nH₂O (Ln=La, Pr, Sm, Eu, Gd, Tb, Dy; n = 1,2) and Ln¹_xLn²_(2-x)(39)(NO₃)₄·H₂O (Ln¹Ln² = LaSm, LaGd, LaDy, LaEu, DyGd, DyEu, GdEu, GdTb, EuTb, LaTb; x = 1,2), have been synthesized, and their possible structure and the interaction between the metal ions have been inferred from spectroscopic, mass spectrometric and magnetic data, together with scanning electron microprobe analyses.



With these heterodinuclear complexes it is feasible to study the energy transfer from the ligand to the two different lanthanide ions inside the macrocycle and from one lanthanide ion to the other. Such energy transfer has been well defined, especially for the complex $\text{EuTb(39)(NO}_3)_4$.⁸⁰

Similar processes have also been studied for the simpler complex $[\text{Eu(H}_2\text{-40)(NO}_3)_2]\text{NO}_3$.⁶⁰ Spectroscopic investigations on heterodinuclear species have quantified the ligand $\rightarrow \text{Ln(III)}$ and $\text{Tb(III)} \rightarrow \text{Eu(III)}$ energy transfers also for an evaluation of the intermetallic distance.⁸⁰ The reported Gd-Gd distance (3.97 Å) for the complexes $[\text{Gd}_2(\mathbf{38})(\text{NO}_3)_4] \cdot 2\text{H}_2\text{O}$ is considerably shorter than that estimated for the similar complexes with $\text{H}_2\text{-39}$. Moreover, in the Eu-Eu complex with $\text{H}_2\text{-38}$, the lifetime is much shorter than the lifetime reported for the complex with $\text{H}_2\text{-39}$. It was suggested that the different R-substituent

may induce a different conformation of the ligand and hence different Ln...Ln distances.^{80,81}

These homo- and heterodinuclear complexes have been used as useful precursors in the formation of crystallographically pure oxides (Ln_2O_3 or $\text{Ln}^1\text{Ln}^2\text{O}_3$) by their thermal decomposition.⁸² Thus in the decomposition of $[\text{DyEu(39)(NO}_3)_4] \cdot \text{H}_2\text{O}$ the water molecule is lost at 80–100°C. At about 600°C there is a range of stability of the intermediate, which has been determined to be $\text{DyEuO}_2\text{CO}_3$. At about 1200°C DyEuO_3 , in a cubic symmetry, was formed, while at about 1600°C DyEuO_3 with a monoclinic symmetry is obtained.⁸²

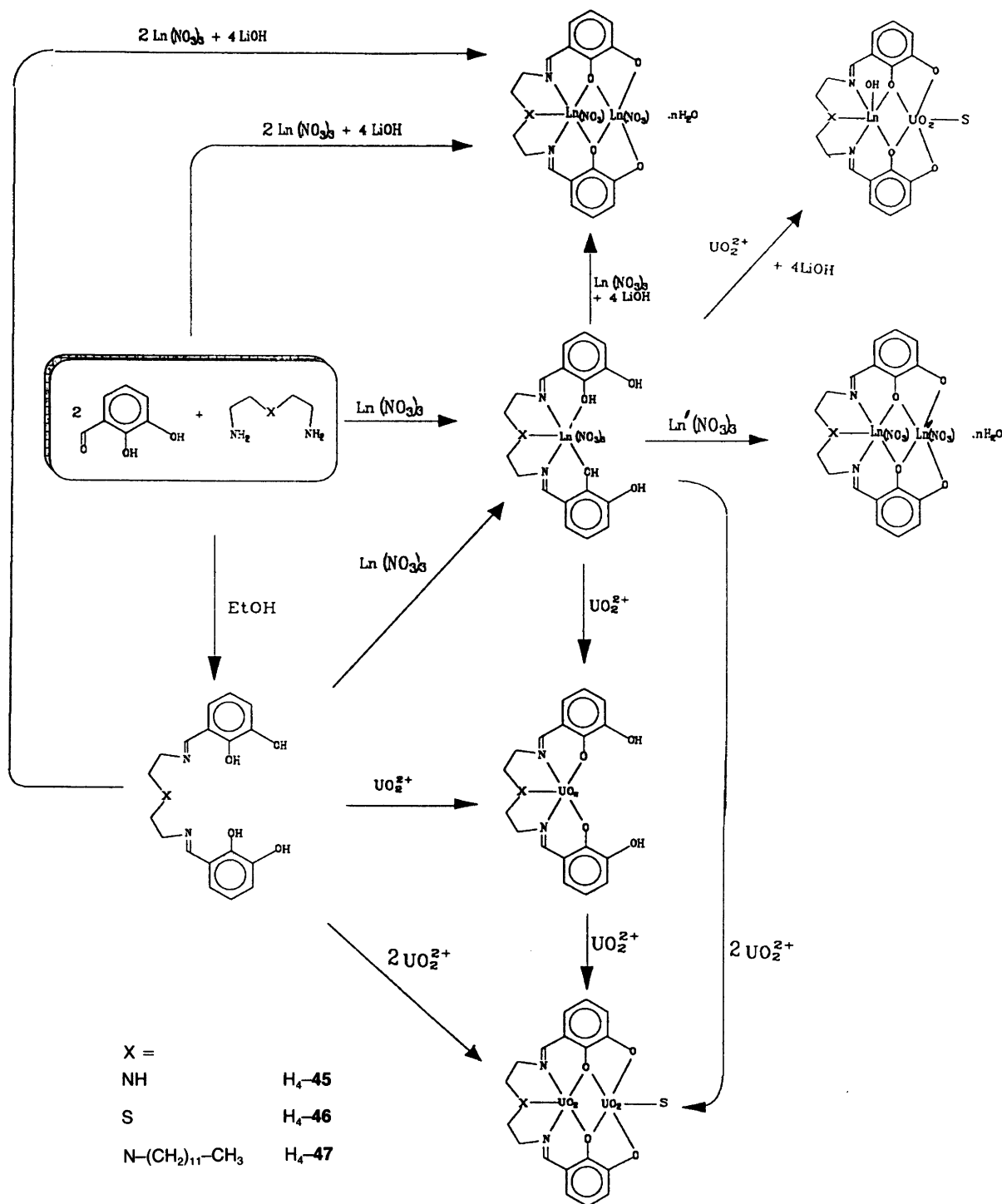
The acyclic compartmental ligands $\text{H}_4\text{-41} \cdots \text{H}_4\text{-43}$ (Scheme 11) have been obtained by condensation of 2,3-dihydroxybenzaldehyde with the appropriate diamine in alcoholic solution; they contain an inner N_2O_2 chamber particularly designed for a d-transition metal ion and an outer O_2O_2 site too large for such an ion but suitable for a f-ion, as confirmed by the X-ray structure of $\text{H}_4\text{-42}$.⁸³ Consequently it is possible to produce well defined compounds without positional isomers or undesired species. The preparation of mono- and hetero-dinuclear complexes follows the reaction sequence reported in Scheme 11.⁸³ By reaction of the mononuclear complex with uranyl(VI) or barium(II) salts the corresponding heterodinuclear complex is obtained; in these complexes no anions are present, and the coordination sphere about the outer metal ion is completed by solvent molecules.

The enhanced selectivity of these ligands towards the different metal ions is evidenced by their capability to form pure heterodinuclear complexes when a transition metal ion [i.e. copper(II) or nickel(II) and an f-metal ion [lanthanide(III) or uranyl(VI)] are added, one after the other, to the ligands without the previous separation and purification of the mononuclear species. The transition metal ion always occupies the inner and the f-ion the outer chamber. X-Ray data reveal that, in the mononuclear complexes, copper(II) and nickel(II) are square planar N_2O_2 isomers and are evidence of the correct size of the outer O_2O_2 chamber for the coordination of large metal ions (as f-ions or barium).

An X-ray investigation on crystals of $\text{CuY(41)(NO}_3)_3(\text{dmsO})$,⁸³ grown from a dimethylsulfoxide/methanol solution, shows that the copper(II) is tetracoordinated in the inner N_2O_2 chamber while the yttrium(III) is eight-coordinated in the outer O_2O_2 site. The complex is a tetranuclear asymmetric unit, two yttrium ions being held together by phenolate oxygen bridges. The coordination of each yttrium(III) ion is completed by the oxygens of a bidentate nitrate ion and of a dimethylsulfoxide molecule.

This oligomerization, via the phenolic oxygen of the outer chamber, can be prevented by the addition of anions, which fill the coordination sphere about the lanthanide(III) ion with the consequent formation of monomeric species, as observed in $\text{CuLn(H}_2\text{-41)(NO}_3)_3$.⁸³⁻⁸⁵

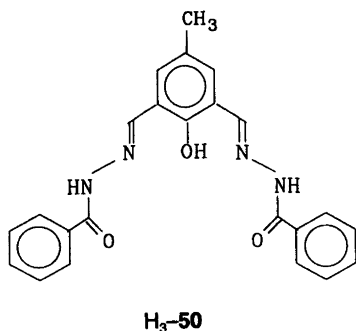
X-Ray powder diffraction studies on copper(II)-yttrium(III) and copper(II)-gadolinium(III) complexes $[\text{CuLn(41)-}$



Scheme 12.

(NO₃)(S)] show that they are isostructural.^{84,85} Hence both can be assumed to be tetranuclear, with a structure quite similar to that found for [CuY(41)(NO₃)(dmsO)]₂. Preliminary X-ray structural data confirm that the complexes MLn(H₂-41)(NO₃)₃ are dinuclear; the copper(II)⋯lanthanide(III) distance is comparable in both tetranuclear and dinuclear structures.^{84,85}

Magnetic experiments on the copper(II)–gadolinium(III) [CuGd(41)(NO₃)(H₂O)]₂ and CuGd(H₂-41)(NO₃)₃ complexes show the presence of a similar Cu–Gd ferromagnetic interaction in both compounds, while in the tetrameric unit a Gd–Gd antiferromagnetic coupling also seems to be operative. The presence of a ferromagnetic 4f–3d coupling, in full agreement with previous findings in completely different ligand systems, helps confirm the model of spin polar-



ization proposed for the interactions involving rare earths.^{84,85}

These heterodinuclear and heterotetranuclear complexes have been used as precursors in the synthesis, by thermal decomposition, of mixed oxides; for example $\text{CuLn(41)(NO}_3\text{)}$ produces CuLn_2O_4 with an orthorhombic or a tetragonal symmetry, this depending on the lanthanide used.⁸³

When the inner coordination chamber is enlarged and contains an additional donor atom (i.e. N_2XO_2), it is possible to accommodate a large f-ion in this coordination site. Thus mono- and homodinuclear uranyl(VI) complexes have been prepared by reaction of uranyl(VI) salts with the ligands, obtained by condensation of 1,5-diamino-3-azapentane or 1,5-diamino-3-thiapentane with 2-formylsalicylic acid.^{86,87} It was also verified that Schiff bases with a donor set N_3O_2 coordinate the lanthanide ions, roughly in their equatorial plane.^{59,60} Thus the two coordination chambers N_3O_2 and O_2O_2 of the ligand $\text{H}_4\text{-44}$, prepared by condensation of 2-formylsalicylic acid with *N*-dodecyl-diethylenetriamine, are suitable for an easy coordination of 4f-ions, and homodinuclear complexes have been obtained by reaction of the preformed ligand with the appropriate lanthanide(III) salt or by a template procedure.⁸⁴

The effective magnetic moment of $[\text{Gd}_2\text{(44)(NO}_3\text{)}_2] \cdot 4\text{H}_2\text{O}$ decreases on decreasing the temperature, passing from $10.97 \mu_{\text{B}}$ at room temperature to $7.96 \mu_{\text{B}}$ at 4.2 K. The room-temperature value is slightly lower than that expected for a couple of non-interacting $S = 7/2$ ions ($11.17 \mu_{\text{B}}$). The significant decrease in the χ^{T} values as the temperature is lowered indicates that an antiferromagnetic interaction, with a coupling constant $J = 0.211(4) \text{ cm}^{-1}$ between the gadolinium(III) ions, occurs; a superexchange mechanism through the bridging atoms is operative in this compound.⁸⁴

Attempts to prepare mono- and heterodinuclear lanthanide(III) complexes with these ligands failed, whereas a successful procedure was followed with the ligands $\text{H}_4\text{-45} \cdots \text{H}_4\text{-47}$ (Scheme 12).⁸⁶⁻⁸⁸ The mononuclear lanthanide(III) complexes, in which the Schiff base behaves as a neutral pentadentate, undergo a transmetalation reaction when treated with uranyl(VI) salts, giving rise to the mononuclear and homodinuclear uranyl(VI) complexes.

In the mononuclear complex $\text{UO}_2(\text{H}_2\text{-45}) \cdot \text{dmf}$ the ligand, using the inner coordination chamber, binds equatorially to UO_2^{2+} , leading to seven-coordinated uranium in

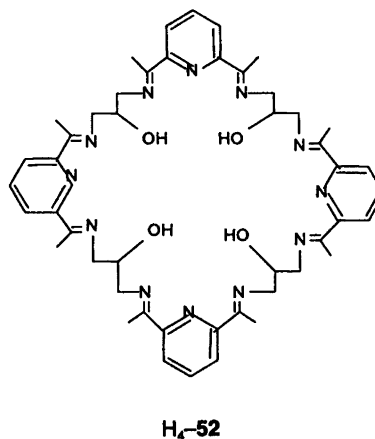
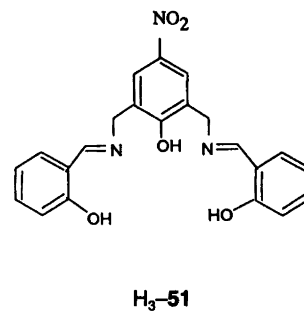
a distorted bipyramidal coordination geometry. The dmf molecule is hydrogen-bonded to the phenolic oxygens of the ligand. The ability of $\text{H}_4\text{-45} \cdots \text{H}_4\text{-47}$ to act as compartmental dinucleating agents toward f-ions has also been verified on the complexes $(\text{UO}_2)_2(\text{45})(\text{dmsO})$ and $(\text{UO}_2)_2(\text{45})(\text{dmf})$. The chelating ligand coordinates the inner UO_2^{2+} , as in $\text{UO}_2(\text{H}_2\text{-45}) \cdot \text{dmf}$, while the outer UO_2^{2+} is coordinated by four oxygen atoms of the dinucleating ligand and by the oxygen atom of the solvent molecule.⁸⁸

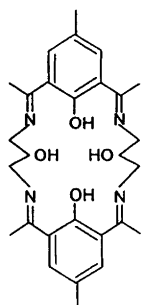
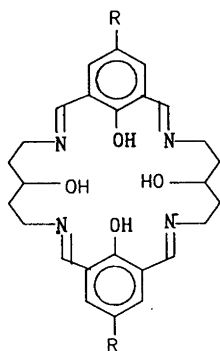
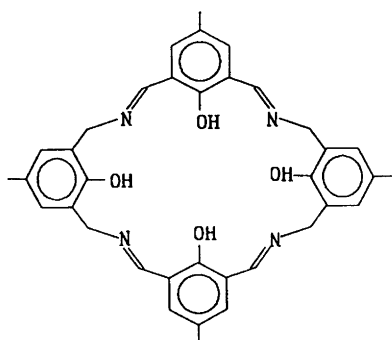
In contrast to the outer linear UO_2^{2+} group in the dinuclear $(\text{UO}_2)_2(\text{45})(\text{S})$ complexes, which reaches its equatorial pentacoordination through the coordination of a solvent molecule (dmsO, dmf, H_2O , etc.), the outer lanthanide(III) can achieve coordination saturation through oligomerization. Thus in the lanthanide(III) complexes with $\text{H}_4\text{-44} \cdots \text{H}_4\text{-47}$ a dimerization through the phenolic oxygens, in order to fill the coordination sphere about the rare earth metal ion, has been suggested. This also causes low solubility for the complexes derived from $\text{H}_4\text{-44}$ or $\text{H}_4\text{-47}$, in spite of the introduction of a long aliphatic chain.⁸⁴

Dinucleating ligands, containing quite different coordination sites, which allow the easy formation of heterodinuclear complexes, have also been synthesized, by combining porphyrins with bipyridine, Schiff bases or crown-ether systems.⁸⁹⁻⁹²

From dinuclear to polynuclear systems

The presence of hydroxo groups has been found to favour



H₄-53H₄-54 R = -C(CH₃)₃H₄-55 R = -CH₃H₄-56

the formation of polynuclear assemblies. The X-ray structure of the copper–yttrium complex $[\text{CuY}(\mathbf{41})(\text{NO}_3)(\text{dmsO})]_2$ shows the ability of the phenolato oxygen atoms to act as bridges, giving rise to tetranuclear species via dimerization.⁸³

Analogously the hydroxo oxygen atoms can behave as a bridge leading to the formation of $\mu_3\text{-OH}$ polynuclear complexes from dinuclear coordination entities.^{93–98}

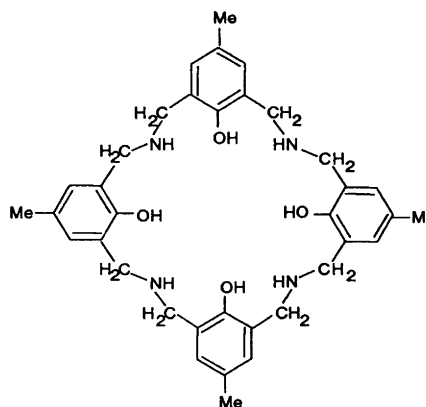
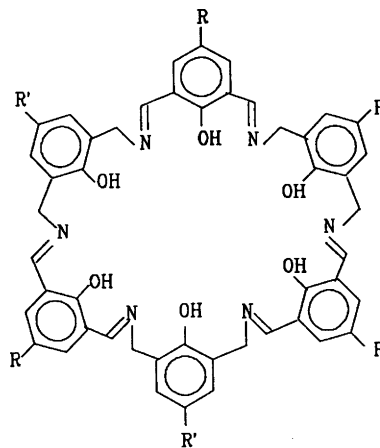
One of the species obtained by reaction of the ligand H₃-48 with cobalt(II) acetate is the tetranuclear compound $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mathbf{48})(\text{OH})(\text{CH}_3\text{COO})]_2$, where two $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\mathbf{48})(\text{OH})(\text{CH}_3\text{COO})]$ moieties are bridged by two μ_3 -hydroxo oxygen atoms.⁹³ In the dinuclear unit, the Co(II) and Co(III) ions are bridged through the central phenolato oxygen of 48, the acetato group and one hydroxo group. The analogous nickel(II) complexes were assumed to involve similar neutral tetranuclear species as a consequence of molecular weight and conductivity measurements.⁹³

Upon reacting H₃-48 with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in a nitrogen atmosphere and in MeOH, the dodecanuclear manganese(II) complex $[(\text{Mn})_{12}(\mathbf{48})_6(\text{CH}_3\text{COO})_2]$ was obtained and characterized by X-ray diffractometry.⁹⁴

By using the compartmental ligand H₃-49, the tetranuclear complex $[\text{Cu}_2(\mathbf{49})(\text{OH})(\text{dmsO})(\text{H}_2\text{O})]_2$ was obtained from dimethylsulfoxide.⁹⁵ The molecule, formed by two dinuclear parallel units held together by two $\mu_3\text{-OH}$

bridges, adopts a chair conformation. One copper of the dinuclear unit is five-coordinated in a square pyramidal arrangement, while the second copper is square planar. A similar tetranuclear structure has been obtained for the copper(II) complex $[\text{Cu}_2(\mathbf{50})(\text{OH})]_2\text{dmf}$ with the ligand 2,6-diformyl-4-methylphenol-di-(benzoylhydrazone) (H₃-50).⁹⁶ 4-Nitro-2,6-bis[salicylideneamino)methyl] phenol, H₃-51, forms the hexanuclear copper(II) complex aggregate $[\text{Cu}_3(\mathbf{51})(\text{OH})(\text{dmf})]_2(\mu\text{-Cl})(\mu\text{-51}) \cdot 2\text{dmf}$, which consists of two $\mu_3\text{-Cu}_3(\text{OH})$ cores held by three peripheral bridging ligands and a μ -chloro bridge.^{97,98}

Structural studies in solution show that when lanthanum nitrate is used as a template in the reaction of 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane a [3+3] macrocycle containing three lanthanum ions is the predominant species formed. ¹H NMR decoupling and NOE difference spectroscopy confirm the presence of a two-fold axis of symmetry where two sides of the macrocycle are identical and different from the third.⁹⁹ This triangular array has recently been confirmed by X-ray structure analysis.¹⁰⁰ This condensation reaction, in the presence of $\text{Ba}(\text{SCN})_2$, yields

H₄-57H₆-58

the mononuclear $\text{Ba}(\text{SCN})_2$ complex of the [2+2] macrocycle **19**, which undergoes a transmetallation reaction with $\text{Cu}(\text{ClO}_4)_2$ to produce a dimetallic copper complex in which a proton is lost from one OH group and the alkoxide bridges both copper ions. In the crystal, the intact OH group hydrogen bonds to a molecule stacked below.¹⁰¹

It has been shown that when $\text{Mn}(\text{ClO}_4)_2$ is used in a transmetallation reaction with barium complexes of the [2+2] macrocycle **19**, the [4+4] macrocycle **52** with four Mn^{2+} ions is formed in low yield.¹⁰² The four manganese(II) centres, together with the four deprotonated alkoxy groups of the ligand, form a novel cubane-type cluster. There is no evidence for any metal-metal bonding; the shortest manganese-manganese distance is 3.32 Å.¹⁰²

The templated cyclocondensation of 1,3-diamino-2-hydroxypropane with 2,6-diformyl-4-methylphenol leads to a mononuclear barium(II) complex,¹⁰³ but lead(II) gives both mono- and dinuclear complexes of H_4 -**53**.¹⁰⁴

Dinuclear complexes have also been obtained by condensation of one equivalent each of 2,6-diformyl-4-methylphenol and 1,3-diamino-2-hydroxypropane, in the presence of manganese(II) or nickel(II) ions. The phenolic groups of the macrocycle are deprotonated and bridge the two metal ions. The alcohol groups retain their protons and are not involved in coordination to the metal ions.¹⁰³

The higher homologue 1,5-diamino-3-hydroxypentane, on condensation with 2,6-diformyl-4-*t*-butylphenol in the presence of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, forms the tetranuclear [2+2] macrocyclic complex $[\text{Cu}_4(\text{54})(\text{OH})] \cdot 3\text{H}_2\text{O}$.¹⁰⁵ The same polyamine reacts with 2,6-diformyl-4-methylphenol, in the presence of $\text{Mn}(\text{CH}_3\text{COO})_2$ and KCl, to form the tetranuclear complex $[\text{Mn}_2^{\text{II}}\text{Mn}_2^{\text{III}}(\text{55})(\text{O})(\text{CH}_3\text{COO})_3(\text{Cl})(\text{CH}_3\text{OH})] \cdot \text{CH}_3\text{OH}$.¹⁰⁵

The tetranickel complex, $\text{Ni}_4(\text{56})(\text{CH}_3\text{COO})_2(\text{CH}_3\text{O} \cdot \text{H} \cdot \text{OCH}_3)$, was obtained by template condensation in methanol of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride in the presence of an excess of nickel(II) acetate and acetic acid-sodium acetate buffer. The results from an X-ray crystallographic study of green monoclinic crystals of the tetramethanolate, grown by vapour diffusion of water into a methanolic solution in the presence of additional nickel acetate, reveal four nickels at the corners of the rectangle.¹⁰⁶ A similar ligand arrangement is present in $\text{Zn}_4(\text{56})(\text{CH}_3\text{COO})_3(\text{OH}) \cdot 2.64\text{CH}_3\text{OH} \cdot 2.5\text{H}_2\text{O}$.¹⁰⁶ Reduction of the dihydrochloride of the macrocyclic Schiff base H_4 -**56**, using an excess of NaBH_4 in ethanol at 0°C, produces the corresponding, more flexible, tetraminomacrocyclic H_4 -**57**,¹⁰⁷ which, by reaction with zinc acetate in the presence of lithium acetate and tetraethylammonium hydroxide, forms the complex $\text{Zn}_4(\text{57})(\text{OH})(\text{CH}_3\text{COO})_3$.¹⁰⁷

The reaction of 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride, 2,6-diformyl-4-methylphenol, copper(II) acetate monohydrate in boiling methanol, in the presence of an excess of tetrabutylammonium tetrafluoroborate, gave, after concentration and standing, a green crystalline product of formula $[\text{Cu}_6(\text{58})(\text{CH}_3(\text{COO})_2)_2(\text{OH})_2(\text{MeOH})_2$ -

$(\text{H}_2\text{O})](\text{BF}_4)_2 \cdot 4.4\text{MeOH}$, where H_6 -**58** is the [3+3] macrocyclic hexa-Schiff base hexaphenolate ligand derived by condensation of three diamine and three diformyl precursors.¹⁰⁸

When 2,6-diformyl-4-methylphenol, 1,5-diamino-3-hydroxypentane and copper(II) perchlorate hexahydrate were refluxed in ethanol for ca. 24 h, a green product, probably the tetranuclear $[\text{Cu}_4(\text{55})(\text{OH})](\text{ClO}_4)_3$, was obtained. Recrystallization of this compound from 1:1 dimethylformamide-methanol by diffusion of diethyl ether produces the octamer $[\text{Cu}_4(\text{55})(\text{O})(\text{ClO}_4)]_2(\text{ClO}_4)_2$.¹⁰⁹ The octacopper structure is maintained in dmf solution, while the unrecrystallized tetramer, in the same solvent, changes slowly with time and, after approximately 3 days, is identical with that of the octamer. The same spectral change is accomplished within a few seconds in the presence of a base such as triethylamine. Addition of small amounts of acid will reverse the reaction, but excess acid leads to other, as yet unidentified, products. Very similar behaviour is observed for the tetracopper complex $[\text{Cu}_4(\text{54})(\text{OH})](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, which by recrystallization from dmf, yields an octacopper complex with a structure very similar to that of $[\text{Cu}_4(\text{55})(\text{O})(\text{ClO}_4)]_2(\text{ClO}_4)_2$.¹⁰⁹

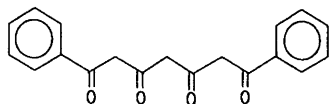
The spectroscopic data imply that both tetrameric complexes undergo slow dimerization in dmf to yield octacopper complexes and that the reaction is promoted by base and reversed by acid. In protic solutions such as ethanol the tetracopper monomer with hydroxide at the centre is favoured, while in less protic solution (i.e. dmf) the octacopper species is preferred but the rate of the interconversion is slow; addition of base increases the rate by promoting dissociation of the hydroxo proton.¹⁰⁷

The β -polydiketones form a planar homologous series of ligands of which the well known 1,3-diketones are the simplest members. These ligands are readily enolizable and form polyanionic species in the presence of a base. By use of a homologous series of ligands, a similar series of chelates may be prepared in which the major structural features are constant.

1,3,5-Triketonate chelates and their properties (magnetic, optical, redox, catalytic, etc.), together with those of the related Schiff base complexes, have been studied in detail and also reviewed.¹¹⁰⁻¹¹³

Homotrinnuclear or homodinuclear copper(II), nickel(II) and cobalt(II) complexes have been prepared by reaction of 1,3,5,7-heptanetrione and the appropriate metal salt in methanol/water or acetone/water solution and in the presence of a base. Isolation of complexes with two or three metal ions appears to depend upon preparative details, such as the solvent, temperature and base used.

Magnetic data indicate that trinuclear copper(II) complex exhibits a reduced magnetic moment owing to strong antiferromagnetic interactions, while the binuclear complex shows a normal magnetic behaviour typical of isolated copper(II) ions. The lack of free carbonyl absorptions in the infrared spectra of the binuclear complexes supports the conclusion that in these compounds the metal ions



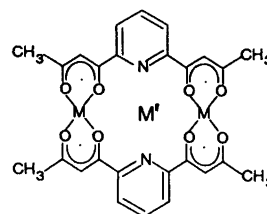
H₄-59

occupy the external chambers and are separated rather than adjacent to one another in the inner coordination sites.¹¹³

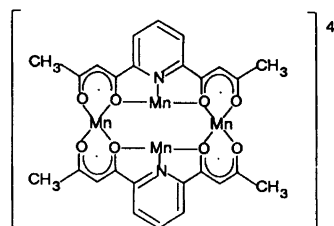
Several isomorphous heterotrinnuclear bis[1,7-diphenyl-1,3,5,7-heptanetetronato(3)] bisdioxouranium(VI)-metal(II)-4-tetrapyridine complexes UO₂M(59)₂(py)₄ [metal(II) = Zn, Cu, Ni, Co, Fe, Mn] have been prepared and characterized.^{114,115}

It was suggested that a reasonable precursor to the observed product is the dinuclear uranyl(VI) complex, (UO₂)₂(H₂-59)₂(S)₂, where the two uranyl(VI) ions occupy the two external O₂O₂ chambers; again a solvent molecule fills the fifth equatorial site about the metal ion. This could explain the ease and specificity with which these heterotrinnuclear complexes form in the preparative solutions containing 2:2:1 ratios of ligand: UO₂²⁺:M²⁺. Indeed attempts were made to prepare 1:1 UO₂²⁺:M²⁺ and 1:2 UO₂²⁺:M²⁺ di- and trinnuclear complexes by changing the reaction stoichiometries; however, the only products isolated were the (UO₂)₂M(59)₂(py)₄ complexes.

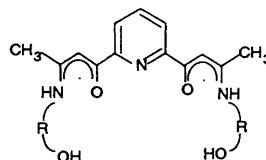
The tetraketones 1,1-(1,3-phenylene)bis-1,3-butanedione, 1,1-(1,4-phenylene)bis-1,3-butanedione, 1,4-bis-(acetoacetyl)piperazine, *N*-(*o*-tolyl)diacetoacetamide and 1,1'-(2,6-pyridyl)bis-1,3-butanedione and related Schiff bases have been synthesized and used in the preparation of



60 M=Cu²⁺, Ni²⁺, Zn²⁺
M'=Ba²⁺, Zn²⁺

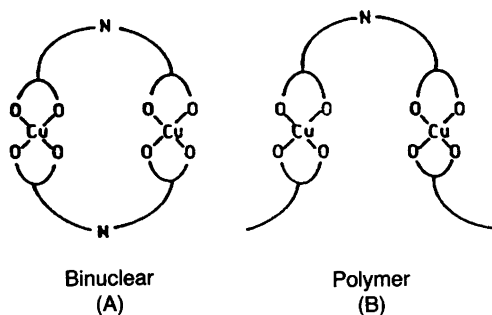


61



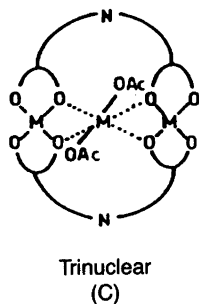
62 R=C₆H₄

63 (CH₂)_n (n=2-5)

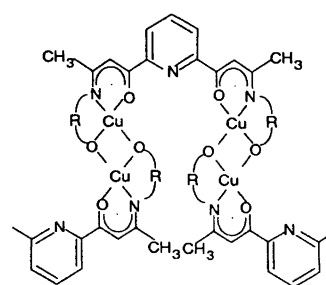


Binuclear (A)

Polymer (B)



Trinnuclear (C)

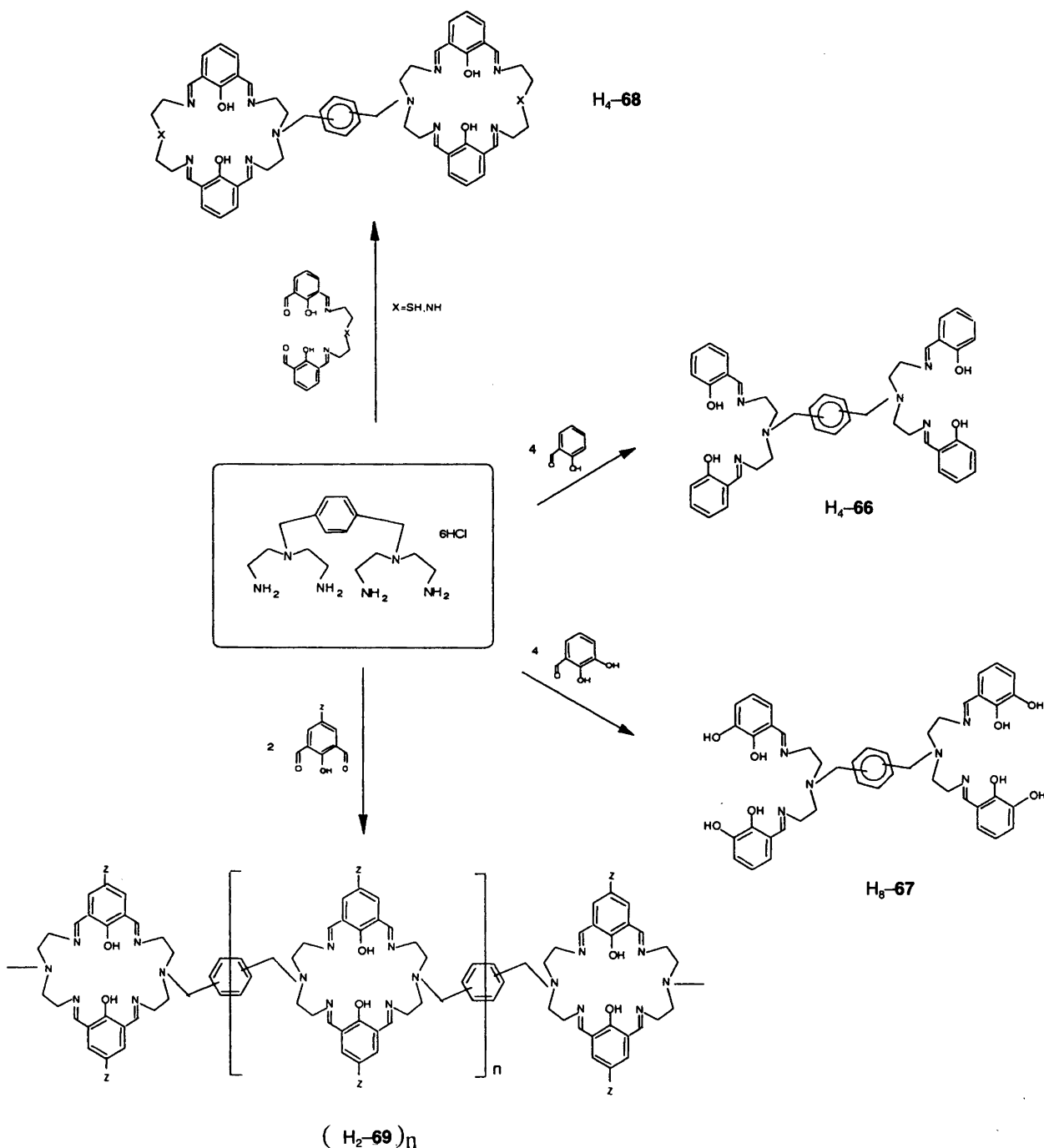


64

polynuclear coordination systems.^{116,117} The first two ligands offer two isolated β-diketonate moieties and thus the complexes obtained resemble the β-diketonate ones.

In *N*-(*o*-tolyl)diacetoacetamide and 1,1-(2,6-pyridyl)bis-1,3-butanedione, the four ketonic moieties are at the appropriate positions to form homo- or heterotrinnuclear complexes (C) in addition to homodinuclear ones, for which the two alternative structures A and B reported in Scheme 13 have been proposed.¹¹⁷

Scheme 13.



Scheme 14.

The dinuclear complexes can easily be converted into the trinuclear ones by common synthetic procedures. The dinuclear complexes show physicochemical properties typical of isolated β -diketonato compounds, while in the trinuclear species [e.g. trinuclear copper(II) complexes] significant antiferromagnetic interactions take place, indicating that the metal ions are held together in adjacent coordination chambers.

With 1,1-(2,6-pyridyl)bis-1,3-butanedione, the discrete trinuclear complexes **60** have been suggested for $M=\text{Zn}^{2+}$,

Cu^{2+} or Ni^{2+} and $M'=\text{Zn}^{2+}$ or Ba^{2+} , while manganese(II) forms a tetranuclear compound **61**. This indicates that the central cavity could contain two metal ions, as observed for related hexadentate Schiff base macrocycles.¹¹⁷

1,1-(2,6-Pyridyl)bis-1,3-butanedione reacts with a series of hydroxyalkyl- or hydroxyarylamines in ethanol to give the Schiff bases **62** and **63**.¹¹⁷

The Schiff bases produce, by reaction with copper(II) salts, complexes formulated, on the basis of their reduced magnetic moments, as polymers of the type **64**. In some

complexes (containing bromide as anion), the ligand behaves as a neutral entity: the copper atoms are also coordinated by bromide ions.¹¹⁷

As an extension, the hexaketone 1,3-bis(2-methyl-4,6,8-octanetrione-8-yl)benzene (H_4 -65) and the homo- and heterotetranuclear complexes $[Cu_4(65)_2(py)_4]_2py$ and $[(UO_2)_2(Zn)_2(65)_2(py)_6]$ have been prepared.¹¹⁸ Strong magnetic superexchange between the copper(II) ions in the binuclear units renders the molecule diamagnetic at room temperature. Cyclic voltammetry in pyridine in the range 0–1.2 V yields one quasireversible wave with $E_{1/2} = 0.8$ V. Chronoamperometric results show that this wave is due to a four-electron-transfer process. Owing to the structural similarity of this complex with bis(1,3,5-triketonato)dicopper(II) complexes, which are known to undergo sequential two-electron transfer, this process can be viewed as two-electron transfer in non-interacting binuclear centres.¹¹⁸

Minor modification of procedures used to generate dinuclear compartmental ligands can be used to generate polynuclear complexes of the lanthanides or actinides. The acyclic and macrocyclic Schiff bases of Scheme 14 have been obtained either by self-condensation of the precursors or as metal complexes, by template procedures.^{119,120} The acyclic ligands H_4 -66 and H_8 -67 have been obtained by condensation of polyamine 1,4- or 1,3-bis[bis(2-aminoethyl)aminomethyl]benzene, respectively, with salicylaldehyde or 2,3-dihydroxybenzaldehyde in a molar ratio of 1:4 and in methanol.

A FAB mass spectrometry investigation has revealed the presence of the parent peak at the appropriate m/z value for both ligands, while 1H and ^{13}C NMR spectroscopies confirm the structure proposed in Scheme 14. The reaction of H_4 -66 and H_8 -67 with $UO_2(CH_3COO)_2 \cdot 2H_2O$ in the appropriate molar ratio in boiling methanol produces the dinuclear $(UO_2)_2(66) \cdot 2H_2O$ or $(UO_2)_2(H_2-68) \cdot 2H_2O \cdot 2dmf$ and the tetranuclear $(UO_2)_4(68) \cdot 2H_2O \cdot 2dmf$ complexes. An X-ray investigation of $(UO_2)_2(66) \cdot dmsO \cdot C_6H_6$ shows that the quasilinear uranyl(VI) ion is equatorially coordinated to give, by the O_2N_3 donor set of the Schiff base ligand, the usual, slightly distorted, bipyramidal pentagonal configuration.¹¹⁹ Dinuclear $Ln_2(H_2-67)(NO_3)_2$, homo- and heterotetranuclear lanthanide(III) complexes, $Ln_4(67)(NO_3)_2$ or $Ln^I_2Ln^{II}_2(NO_3)_2(OH)_2$, have been prepared with a procedure similar to that employed for tetrauranyl(VI) analogues.

A template synthesis was also employed for the preparation of uranyl(VI) and lanthanide(III) complexed with the ligand H_4 -68. These complexes, $(UO_2)_2(68)$ and $(La)_2(68)(NO_3)_2$, have been synthesized by reaction of the acyclic mononuclear complexes with hexamine in alcoholic solution.^{120,121}

By reaction of the same polyamines with 2,6-diformylphenols, the 'face-to-face' H_4 -68 or polynuclear $(H_2-69)_n$ compounds have been obtained¹²⁰ (Scheme 14). The organic polymer is quite insoluble, and hence difficult to characterize fully; the complexes have been obtained only by a template procedure.¹²⁰

Very recently we have begun the synthesis and characterization of compartmental acyclic and macrocyclic polynucleating ligands obtained by condensation of 1,2,4,6-tetraaminobenzene and 2,3-dihydroxybenzaldehyde or 2,6-diformyl-4-Z-phenols [$Z = Cl-, CH_3-, (CH_3)_3C-$].¹²¹ In the past we have prepared homo- and heterodinuclear complexes containing transition metal ions with similar macrocyclic or macroacyclic dinucleating Schiff bases.¹²² It should therefore be possible to prepare homo- and heteropolynuclear complexes by procedures similar to those employed to obtain the dinuclear analogues, and we are now trying to achieve this objective.

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