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Schiff Base Complexes of Lanthanides and Actinides*

P. A. VIGATO**

Istituto di Chimica e Tecnologia dei Radioelementi, CNR, Padua, Italy

and D. E. FENTON

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

Abstract

The coordination chemistry of lanthanide and actinide cations with Schiff bases has been investigated and reviewed over the last few years. More recently, acyclic and macrocyclic ligands (including binucleating and/or compartmental ligands) have been synthesized and their interaction with f-ions studied.

The formation of metal complexes with binucleating ligands is of interest because the opportunity is provided to study the intramolecular binding and possible activation of small molecules between the metal centres, along with magnetic exchange interactions and multielectron redox reactions.

The facile generation of macrocyclic Schiff bases in the presence of alkaline earth metal cations has led to an interest in the use of lanthanide cations as templating agents in similar conditions. The comparable ion size suggests that such reactions should be successful. The actinides, with their high ionic radii and/or unusual coordination geometry can produce and stabilize expanded macrocyclic ligands. For these condensation reactions keto-precursors and facultative amines have been used. The condensation products, often obtained by template synthesis are thus of the type where the head and the lateral units can be varied, with the consequent formation of macrocycles with different donor atoms and/or different cavity size.

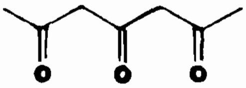
Introduction

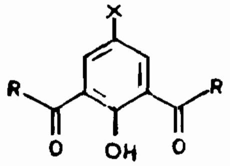
Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most of the metal ions of the Periodic Table. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes since it has been recognized that many of these complexes may serve as models for biologically important species.

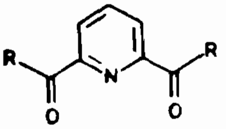
Simple di-, ter-, tetra- and penta-dentate ligands **I–VII** have been used for metal complexation and many lanthanide and actinide complexes have been characterized also by X-ray diffraction [1].

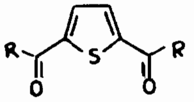
Recently, acyclic and macrocyclic ligands (including dinucleating and/or compartmental ligands) have been synthesized and their interaction with f-ions studied [2].

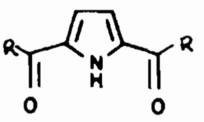
The formation of metal complexes with binucleating ligands is of interest because the opportunity is provided to study the intramolecular binding and possible activation of small molecules between the metal centres, along with magnetic exchange interactions and multielectron redox reactions. The facile generation of macrocyclic Schiff bases in the presence of alkaline earth metal cations has led to an interest in the use of lanthanide cations as templating agents under similar conditions. The comparable ion size suggests that such reaction should be successful. The actinides, with their high ionic radii and/or unusual coordination geometry can produce and stabilize expanded macrocyclic ligands. For these condensation reactions keto-precursors of the type:

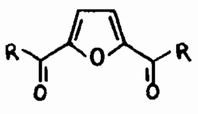












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**Author to whom correspondence should be addressed.

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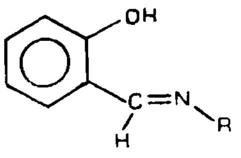
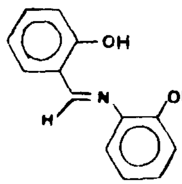


I



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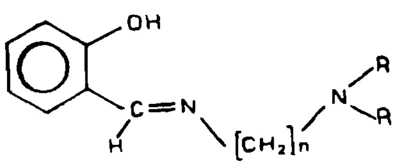

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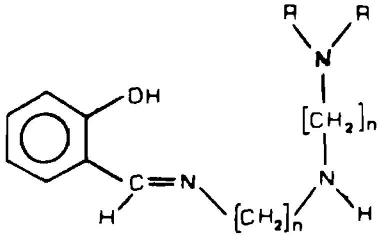

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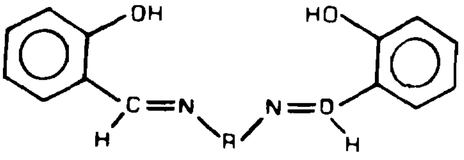

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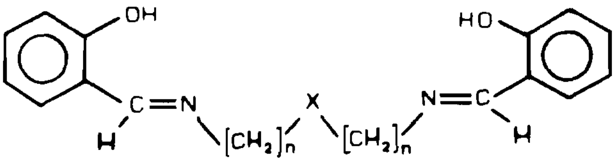

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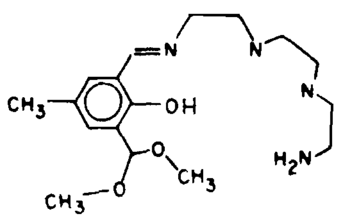


VII

and facultative amines have been used. The condensation products, often obtained by template synthesis, are thus of the type reported in Fig. 1, with the formation of (1 + 1) and (2 + 2) macrocycles, depending on the ion used.

With certain precursors (*i.e.*, 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane) (3 + 3) 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 size (Fig. 2). Furthermore, the steady ionic radius contraction in the lanthanide series could facilitate a fine-tuning effect in the synthetic pathway.

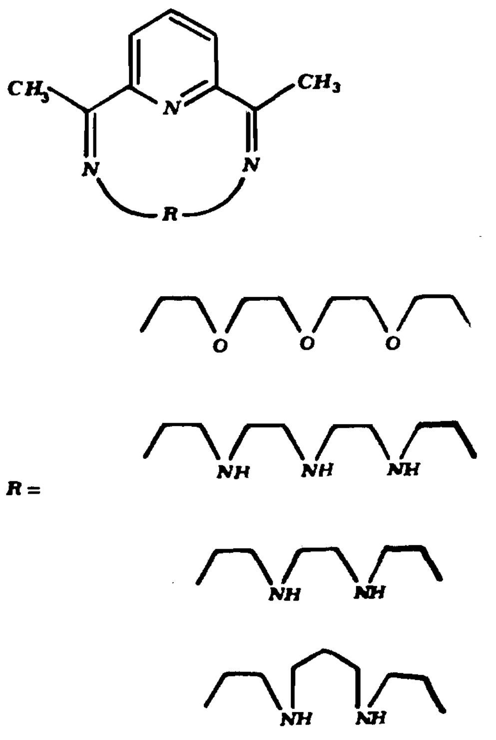
Lanthanide Complexes with Macrocyclic Ligands

(1 + 1) Macrocycles

Lanthanide (Ln) ions have been used as templates to prepare the Schiff base macrocycles **VIII**–**XI**. The complexes [La(**VIII**)]$(NO_3)_3 \cdot nH_2O$, [(La(**IX**)]$(NO_3)_3 \cdot nH_2O$, [La(**X**)$(NO_3)_2OH \cdot nH_2O$ and [Ln(**XI**)]$(NO_3)_2OH \cdot nH_2O$ have been obtained [3,4]; Ce and Sm complexes with **VIII** are also available [3].

When $La(SCN)_3$ is used as the template, the OH–SCN complexes [La(**VIII**)]$(SCN)_2(OH)$, [La(**IX**)]$(SCN)_2(OH)$, [La(**X**)]$(SCN)(OH)_2$ and [La(**XI**)]$(SCN)(OH)_2$ are obtained [4]. These complexes, on dissolution in water, precipitate the metal hydroxide.

The ^1H NMR of the complexes [Ln(**VIII**)]$(NO_3)_3$ (Ln = La, Ce) have been recovered from acetonitrile solution and indicate the integrity of the macrocycle in that medium [3].



VIII

IX

X

XI

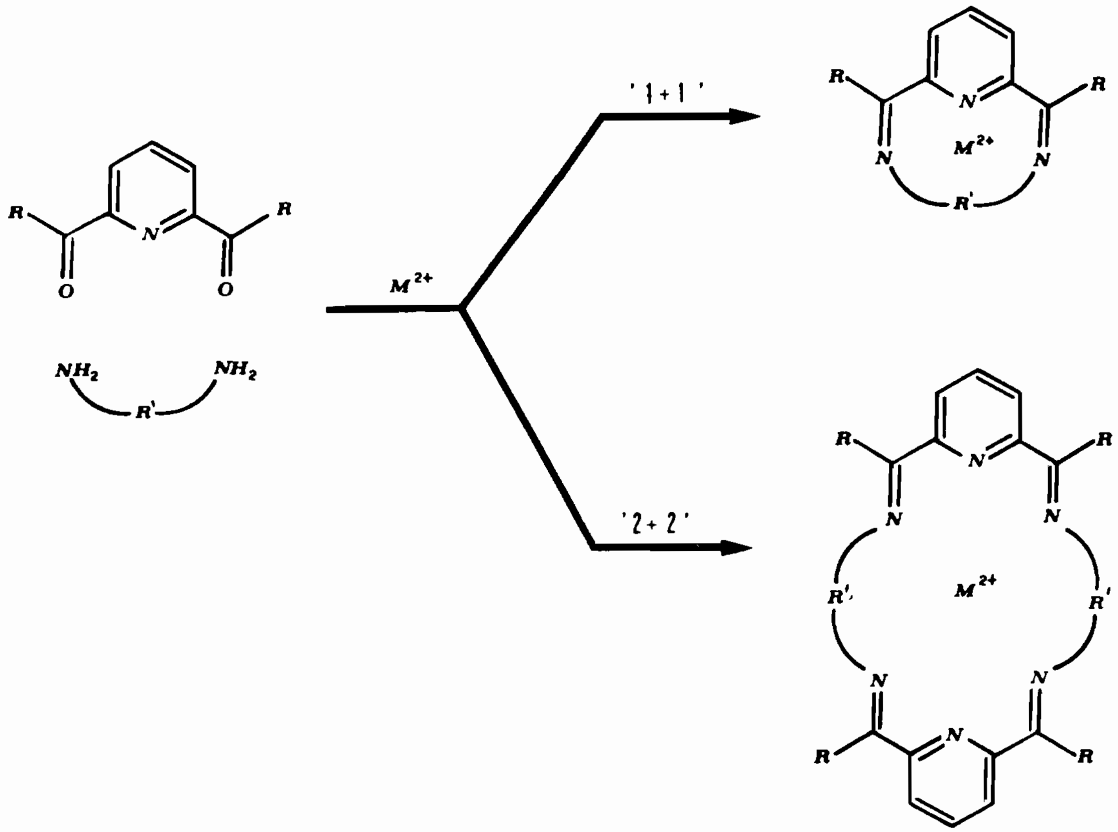


Fig. 1. Schematic pathways for the formation of (1 + 1) and (2 + 2) macrocyclic complexes.

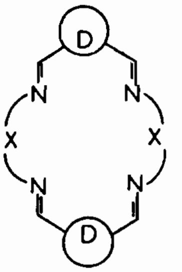
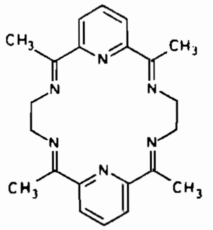
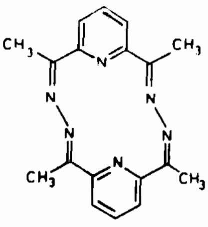


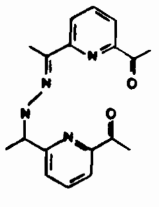
Fig. 2. Schematic representation of a tetraimine Schiff base macrocycle: head unit: D = pyridine, furan, thiophen, pyrrole or phenol; lateral unit: X = 1,*n*-diamine.



XII



XIII



XIV

(2 + 2) Macrocycles

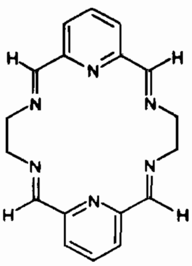
It was originally reported that the reaction of hydrated lanthanide nitrates, 1,2-diaminoethane and 2,6-diacetylpyridine in a 1:2:2 molar ratio in alcohol gave the macrocyclic complexes [Ln(XII)]$(NO_3)_3$ only for lanthanum and cerium [5]. The corresponding perchlorate complex [La(XII)$(H_2O)_2$] $[ClO_4]_3$ has also been reported [6].

The complexes exist in aqueous solution mainly as [Ln(XII)$(H_2O)]^{3+}$. The macrocycle is resistant to hydrolysis on treatment with KF or KOH in aqueous solution and the complex appears to be kinetically stable to dissociation.

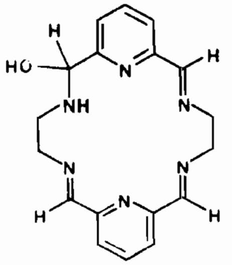
The heavier lanthanides were not found to be effective templating agents in the formation of the 18-membered ring [5,6] but were effective as templating agents in the synthesis of the smaller 14-membered ring (XIII) [7].

The complexes [Ln(XIII)$(H_2O)_2$]$(ClO_4)_3 \cdot 4H_2O$ were recovered with Ln = Tb, Dy, Ho, Er, Tm, Yb and Lu; use of the lighter lanthanides as templates gave complexes of the acyclic derivatives (XIV), and a small amount of the lanthanide complexes of 2,6-diacetylpyridine. On reaction with water the macrocyclic species ring-opened to give the complexes [Ln(XIV)$(H_2O)_2$]$(ClO_4)_3 \cdot 2H_2O$.

More recent comprehensive surveys of the template potential of the lanthanides have indicated a greater breadth to the above reactions. Using 2,6-diformylpyridine as the carbonyl precursor, complexes of the macrocycle (**XV**) were recorded for all of the lanthanides, except Pm [8]. For the heavier lanthanides (Nd → Lu, except Pm and Eu) the addition of water across the imine double bond leads to the formation of the carbinolamine species **XVI**.



XV



XVI

The structure of the samarium complex shows that the compound is $Sm(XV)(OH)(NO_3)_2 \cdot H_2O$ [9]. The samarium cation is enclosed in the cyclic ligand and is coordinated to the six nitrogen atoms as well as to a bidentate nitrate anion, a water molecule and a hydroxide anion. The coordination geometry is best described as an irregular antiprism capped on its square faces by the pyridinyl nitrogen atom.

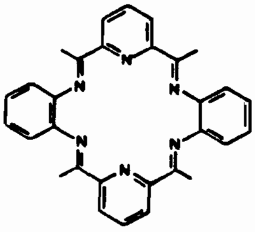
It is also likely that when heat is applied to effect dissolution in water prior to recrystallization, a higher temperature is reached than in the original reaction in ethanol; the reaction moves on to completion and the ligand results. The stabilization of the carbinolamine therefore represents the stabilization of a reaction intermediate via the facile coordination of the smaller lanthanide cations.

Tetraimine Schiff base macrocyclic complexes derived from 2,6-diformylpyridine and 1,2-diaminopropane, and from 2,6-diformylpyridine and 1,3-diaminopropane, have been isolated for the lanthanides, except Pm. With the latter complexes no evidence of carbinolamine species was found.

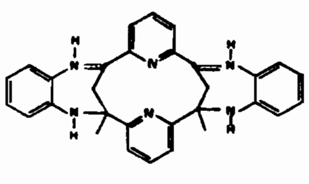
The metal template procedure has now been used to extend the range of complexes available from 2,6-diacetylpyridine [10]. Complexes of the general formulae $Ln(XII)(CH_3COO)_2Cl \cdot nH_2O$ ($n = 3$–6) and $Ln(XII)(ClO_4)_2OH \cdot nH_2O$ ($n = 0$–2) have been recovered for all of the lanthanides except prometheum. This contrasts with the earlier results and the ease and yield of the reaction depend upon the counter anion present. Good O-donor anionic ligands such as CH_3COO^- favour the reaction more than Cl^- or ClO_4^-.

In solution the macrocycle remains intact in the presence of H_2O and dimethylsulphoxide and this is evidenced by the NMR spectra recorded in these solvents. Typical precipitating agents such as F^-, OH^- or $C_2O_4^{2-}$ do not remove the lanthanide cation.

The condensation of 1,2-diaminobenzene with 2,6-diacetylpyridine in the presence of lanthanide nitrates (La, Ce, Pr, Nd) has been reported to give the complexes $[Ln(XVII)](NO_3)_3 \cdot 2H_2O$. During attempts to repeat and extend this work, only a yellow crystalline product having the tricyclic structure (**XVIII**) was obtained [11]: it is identical to the product recovered by direct reaction of 2,6-diacetylpyridine and 1,2-diaminobenzene in the absence of metal ions.



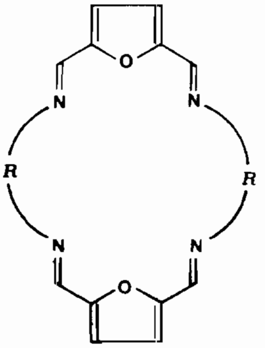
XVII



XVIII

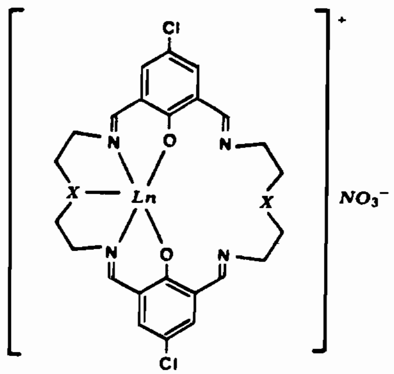
Very recently however, the X-ray structure of the praseodymium complex has demonstrated the possibility of the formation of complexes with **XVII** [11].

By metal template procedure, the complexes $[Ln(XIX)](NO_3)_3 \cdot nH_2O$ ($n = 0$–2), Ln = La–Eu except Pm; $[Ln(XX)](NO_3)_3 \cdot nH_2O$ ($n = 0$–2), Ln = La, Ce, Pr; and $[Ln(XXI)](NO_3)_3 \cdot nH_2O$ ($n = 0, 1$), Ln = La, Ce, Pr of the macrocycle (**XIX**–**XXI**) have been recovered [12].

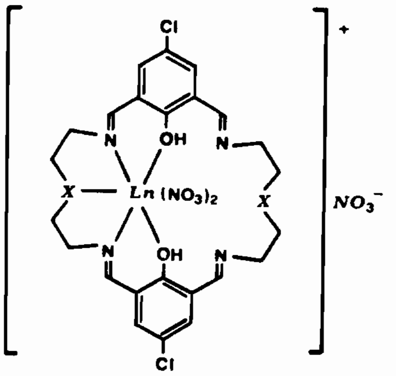


R	
$-CH_2-CH_2-$	**XIX**
$-CH_2-CH(CH_3)-$	**XX**
$-CH_2-CH_2-CH_2-$	**XXI**

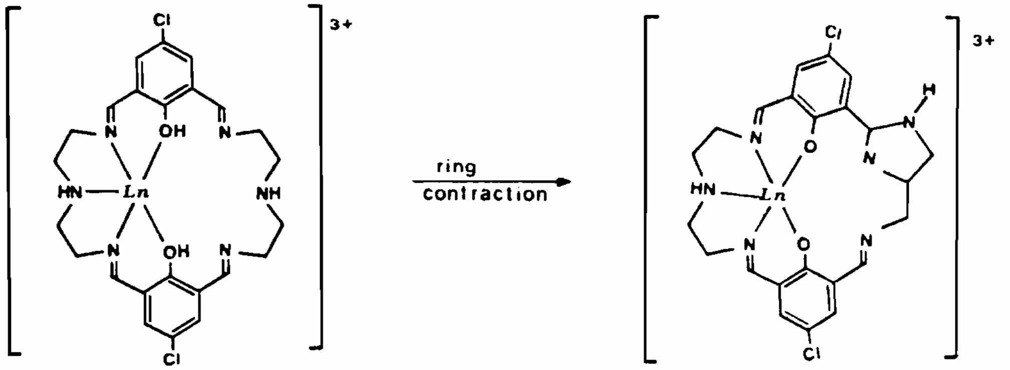
When the heavier lanthanides (Gd–Lu) were used with ethylenediamine as the lateral unit, analyses corresponding to the ratio three metal cations to two macrocyclic units were obtained, *i.e.*, $[Ln_3(XIX)_2](NO_3)_9 \cdot 4H_2O$. The observation of this unexpected stoichiometry may be related to decreased cation size. In contrast to the pyridine-based macrocycles, but in keeping with lanthanide complexes of cyclic polyethers [13], the complexes of (**XIX**–**XXI**) decompose in water.



X = NH **XXII**
X = S **XXIII**



X = NH **XXIV**
X = S **XXV**



XXII **XXVI**

The lability of the lanthanides has been explored in the transmetallation reaction [12]. The reaction of [La(**XXI**)]$(NO_3)_3$ with copper(II) perchlorate gave the homodinuclear complex [Cu_2(**XXI**)$(OH)_2$]-$(ClO_4)_2 \cdot 3H_2O$, which differs only in the hydration number from the analogous complex derived by transmetallation from [Ba(**XXI**)]$(ClO_4)_2$ [14]. 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-diaminoethane or 1,2-diaminopropane to transmetallate with copper(II) [4].

The reaction of 2,6-diformyl-4-chlorophenol, polyamines and the appropriate lanthanide nitrate gave the macrocyclic complexes **XXII**–**XXV** respectively in the absence and in the presence of base and by employing different solvents [15]. For the macrocyclic complexes with X = S the ligand does not suffer further reactions and it coordinates intact as pentadentate to the lanthanide ions.

In the complexes derived from X = NH, a ring contraction occurs; this allows a contraction of the central cavity and a reduction in ligand denticity with the formation of **XXVI**. The terbium complex (and the isostructural europium) **XXVI** (Ln = Eu, Tb) never incorporates solvent molecules as solvates; the metal ion is nona-coordinate, being bound to five donor atoms from the cyclic polydentate ligand and to four oxygen atoms of two bidentate nitrate groups, the third nitrate being ionic (Fig. 3). Very roughly the oxygen and nitrogen atoms of the macrocycle form a pentagon around the metal ion, while the two bonded nitrates are chelate on the opposite sides in bisphenoidal positions [15] (Fig. 4).

The coordination polyhedron around Tb can be best described as a distorted tricapped trigonal prism in which O(2), O(4) and N(4) are the caps, as schematized in Fig. 5.

The synthesis of the homodinuclear macrocyclic complexes [Ln_2(**XXVII**)]$(NO_2)_4 \cdot nH_2O$ or [Ln_2-(**XXVII**)]$(NO_3)_{4-x}OH_x$ ($x = 1$ or 2) has been achieved using the condensation of 2,6-diformyl-4-cresol and triethylentetramine in the presence of $Ln(NO_3)_3$, [16].

Recently, these studies have been extended by employing 1,8-diamine-3,6-dioxaoctane and 2,6-diformyl-4-chlorophenol as precursors [17]. The complexes obtained are of the type Ln_2(**XXVIII**)-$(NO_3)_4 \cdot nH_2O$. The magnetic moment of the terbium complex of 13.42 BM (9.5 BM per metal ion) shows

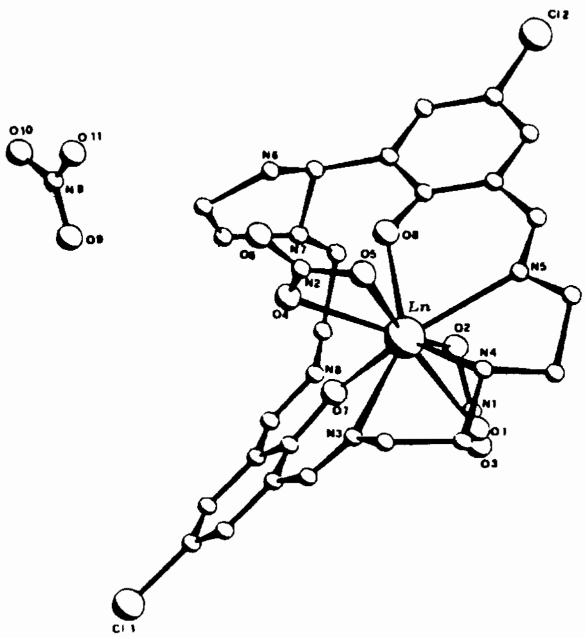


Fig. 3. Crystal structure of **XXVI** (Ln = Tb, Eu).

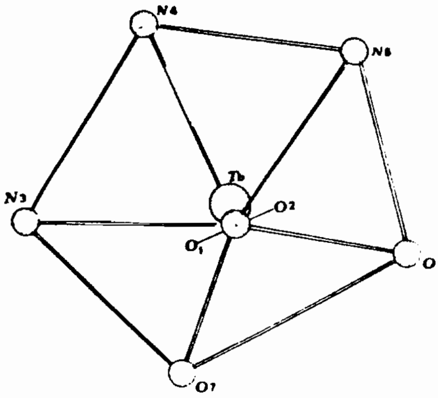


Fig. 4. Crystal structure of **XXVI**. Projection of the coordination polyhedron along the N(1)····N(2) direction. The five donor atoms from the macrocycle form a distorted pentagon around the lanthanide ion.

it is almost unaffected by metal–metal interaction, its value being due to the contribution of magnetically diluted terbium(III) ions. As an explanation, it is possible that in these complexes the ligand does not behave as a compartmental but as a binucleating macrocyclic ligand where the two ions are coordinated at a large distance from each other with no heteroatoms shared between the metal ions.

A different macrocyclic complexity with a different complex formation can be invoked, however, as suggested on the basis of X-ray and NMR data for the complex $Ln_3(XXIX)(NO_3)_6$ [18].

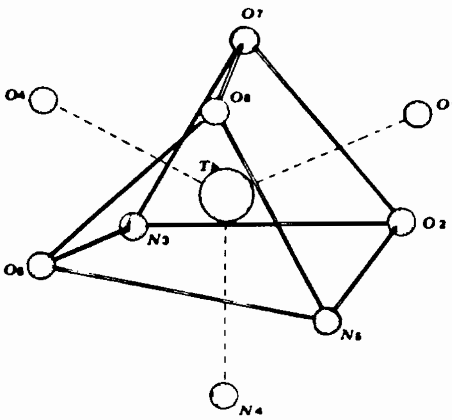
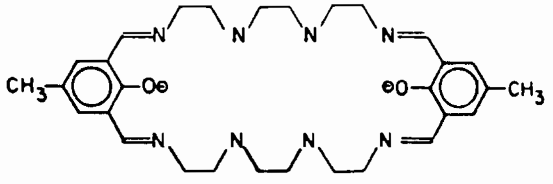
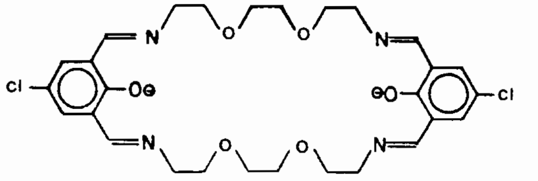


Fig. 5. Crystal structure of **XXVI**. The coordination polyhedron around Tb.



XXVII

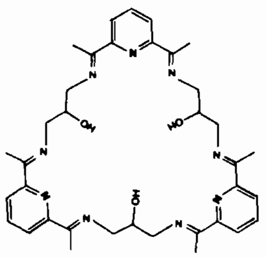


XXVIII

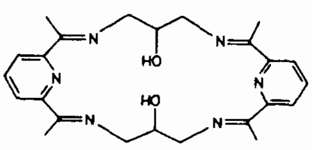
(3 + 3) Macrocycles

By template reaction of $La(NO_3)_3$ with diacetylpyridine and 1,3-diamine-2-hydroxypropane in alcohol, the trinuclear complex $Ln_3(XXIX)(NO_3)_6$ has been characterized. This adds to the series of polyimine Schiff base macrocycles and fills the gap between the known (2 + 2) (**XXX**) and (4 + 4) (**XXXI**) complexes [18].

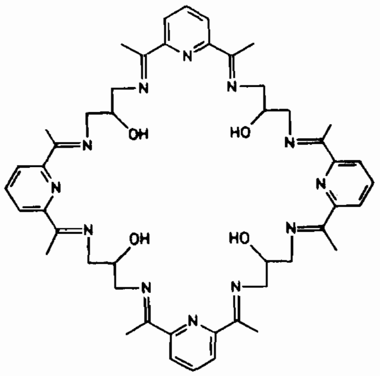
The trinuclear complex has been characterized also by FAB positive mass spectrometry and ^1H NMR spectra. NMR data were obtained with D_2O as solvent, since the macrocycle is insoluble in all non-oxidizing organic solvents. Even in D_2O a solution formed very slowly, but heating was avoided as this accelerated the breakdown of the complex. All the experiments were carried out on fresh samples. The complexity of the methyl region in the proton NMR spectrum precludes the assignment of the reaction product to a (2 + 2) macrocycle, and the integration of the four methyl signals eliminates possibilities of a (4 + 4) macrocycle. Oxazolidine formation can be ruled out on chemical shift arguments. The CH_3 signals in the spectrum are at too high a frequency



H_3-XXIX



XXX



XXXI

for protons of an sp^3 carbon also attached to O and N substituents.

The product is considered to be a (3 + 3) macrocycle containing three lanthanum ions, together with minor species. The major species is a (3 + 3) macrocycle with C_{2v} symmetry. The minor species is an $n \times n$ macrocycle and lack of evidence for other peaks in the mass spectrum supports the postulation that it too is (3 + 3); if so, it has C_{3v} symmetry. The complex slowly decomposes on standing in water solution [18].

Lanthanide and Actinide Complexes with Acyclic Ligands

Dinucleating Schiff bases have been extensively studied and used for the preparation of homo- and hetero-dinuclear complexes [2]. These ligands are generally planar and are especially designed to incorporate, in a planar fashion, two identical or different metal ions. The compartmental ligands represent a particular case of the above compounds and give rise to complexes with the metal sharing at least one donor atom of the ligand. They contain adjacent sites in which the central donor atoms behave as bridging groups between the two metal ions [2] (Fig. 6).

The 'side-off' ligands have been successfully used in the preparation of homo- and hetero-dinuclear complexes containing lanthanide and actinide ions [19–21]. On the contrary, the 'end-off' ligands seem to be not suitable for coordination of lanthanides and actinides owing to their coordination geometry and ionic radii which are considerably different from those of the d-metal ions used for the synthesis of dinuclear complexes. For instance, thorium(IV) is usually eight- or nine-coordinate in the square antiprismatic, dodecahedral, monocapped square antiprismatic, or trigonal tricapped prismatic coordination geometry.

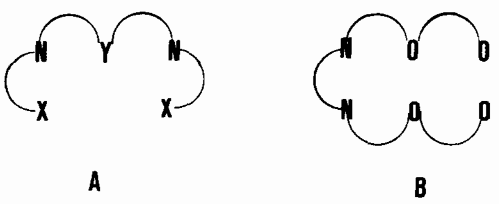
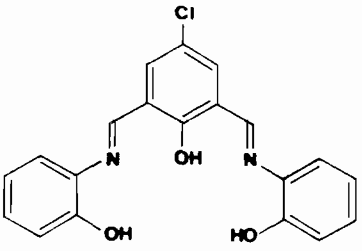


Fig. 6. Schematic representation of compartmental ligands: A, 'end-off' (N_2YX_2; X = N, O, S; Y = O, S); B, 'side-off' (N_2O_4).

The Schiff base **H_3-XXXII**, obtained by condensation of 2,6-diformyl-4-chlorophenol with *o*-aminophenol, can be seen as the 'half-unit' of the above macrocycles and was reacted with lanthanide(III) and actinide(IV) ions in order to ascertain its compartmental behaviour with large metal ions [17, 22].



H_3-XXXII

The reaction of **H_3-XXXII** with the appropriate lanthanide(III) nitrate (Ln = La → Yb) in the presence of the stoichiometric amount of base (LiOH) produces the complex Ln(**XXXII**)·H_2O (Ln = La, Sm, Pr, Eu, Gd, Tb, Dy, Yb) [17].

There is a difficulty, according also to models, for **XXXII** to behave as a pentadentate ligand towards one lanthanide ion and, although this should occur, there is a coordination unsaturation about the metal ion, also considering the solvent molecules present, and consequently an oligomerization of the complex could be suggested.

The binucleating behaviour of **XXXII** with f-ions was recently demonstrated for the complex Mg(Th_2(**XXXII**)$_3$)$_2$·$6H_2O$ [22], obtained by reaction of the preformed ligands or of the keto- and amino-precursor with $Th(NO_3)_4 \cdot 4H_2O$ in the presence of

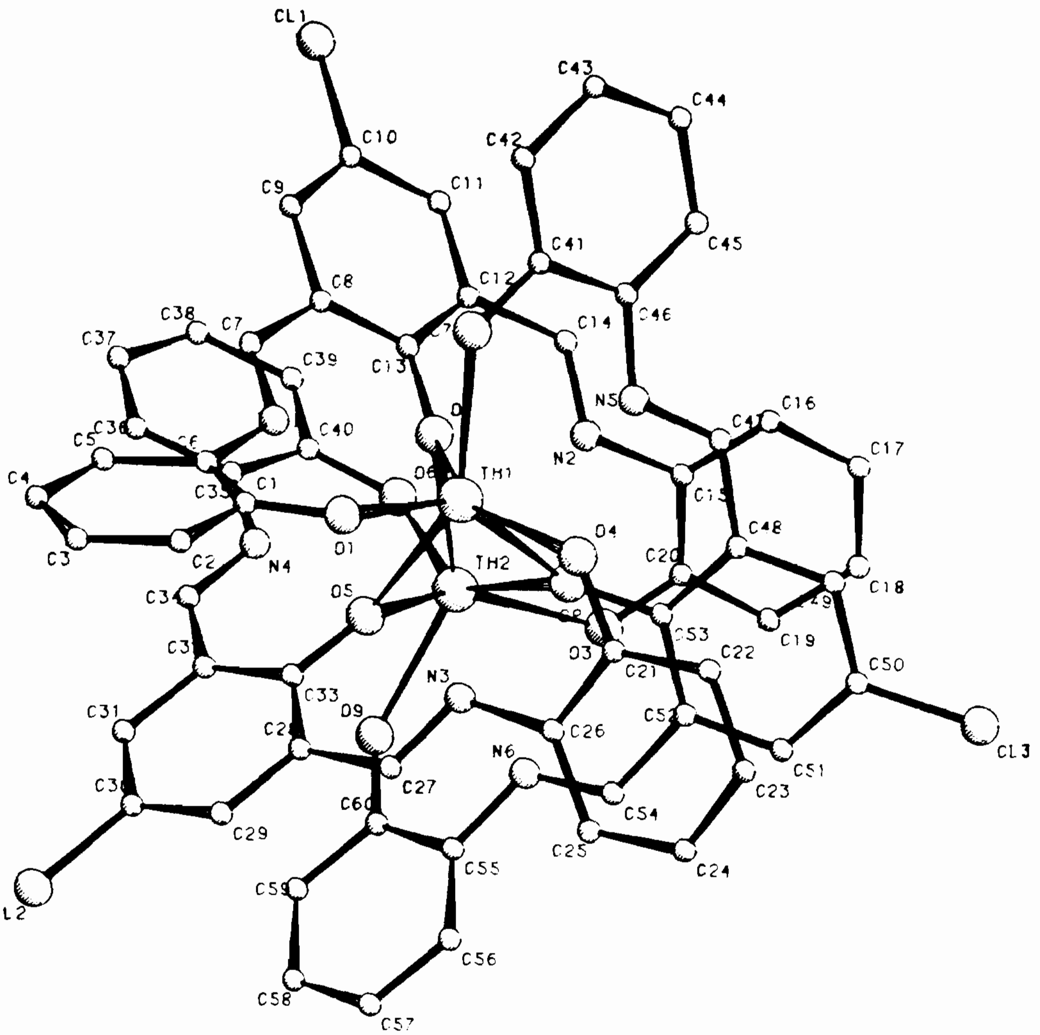


Fig. 7. Crystal structure of the anionic dinuclear unit $[Th_2(XXXII)_3]^-$.

LiOH and $Mg(CH_3COO)_2 \cdot 4H_2O$. Each anion is a dinuclear unit (Fig. 7) in which two Th atoms are bridged by three oxygen atoms from three different ligands. Each ligand, which is trianionic pentadentate, is coordinated with two atoms to the first Th atom, with two atoms to the second Th atom and with the central oxygen atom to both Th atoms. The two independent Th atoms are nona-coordinate in a slightly distorted tricapped trigonal prism (Fig. 8). The Mg^{2+} cations are octahedrally surrounded by six water molecules.

The magnetic moments of the lanthanide complexes Ln(**XXXII**)$\cdot H_2O$ are lower than those expected (this could be caused however by oligomerization only) and it was possible to prepare complexes of the type $Mg_3[Ln_2(XXXII)_3]_2 \cdot H_2O$ or $Li_3[Ln_2(XXXII)] \cdot H_2O$, where the anionic stoichiometry is the same as the thorium complex.

It was suggested that also in these complexes the ligand **XXXII** has a compartmental behaviour [17].

Actinide Complexes with Macrocyclic Ligands

The intermediate size (1.00 Å for eight coordination) and the preference for equatorially directed bonding suggest that the *trans*-dioxouranium(VI) ion should promote the formation of flat macrocyclic systems. In the presence of UO_2^{2+}, the condensation of 2,6-dicarbonylpyridines and 1,2-diaminoethane proceeds smoothly to yield the complexes $[UO_2(\mathbf{XII})]X_2$ and $[UO_2(\mathbf{XV})]X_2$ ($X = ClO_4^+$, NO_3^- and I^-) [23, 24] where all six aza-donors of the ring are reported to be coordinated to the U(VI). There is an exceptional inertness towards the release of UO_2^{2+} in solution, even towards acid or strongly competing ligands, which suggests that systems of this type may be of value when efficient sequestering of actinide ions is necessary.

The reaction of 2,6-diformyl-4-chlorophenol with diethylenetriamine give, on addition of dioxouranium(VI) salt, mononuclear macrocyclic com-

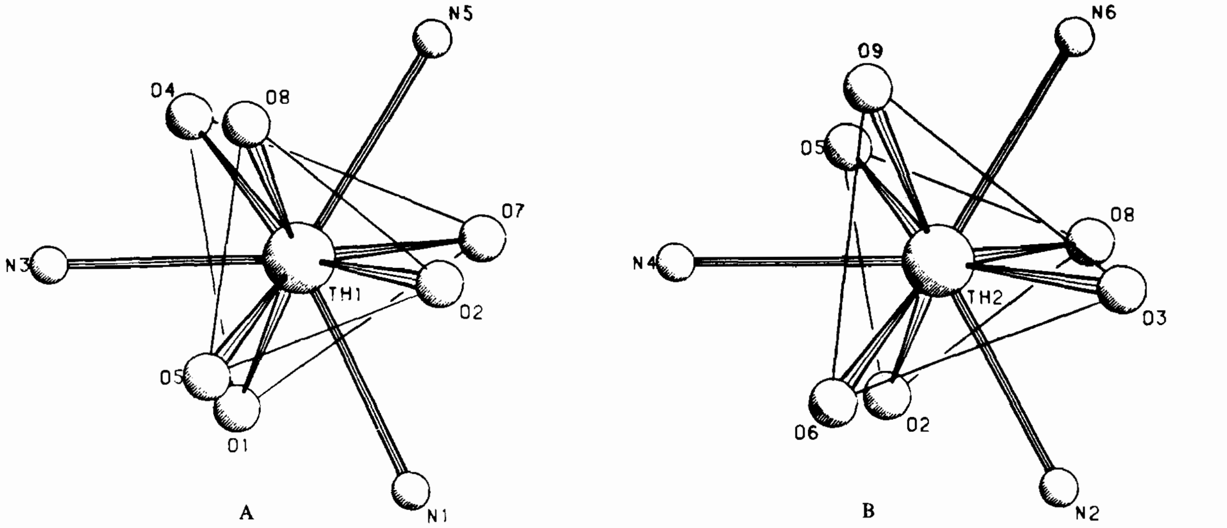
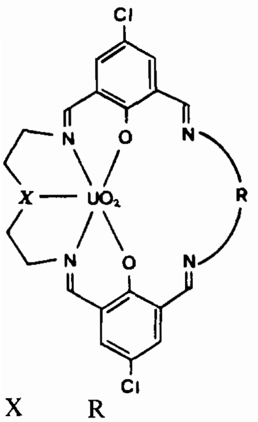


Fig. 8. The coordination polyhedron around Th(1) (A) and Th(2) (B) in the dinuclear anionic unit $[Th_2(XXXII)_3]^-$.



X	R	
NH	$-CH_2-CH_2-$	**XXXIII**
NH	$-CH_2-CH_2-CH_2-$	**XXXIV**
NH	$-CH_2-CH(CH_3)-$	**XXXV**
NH	$-CH_2-CH_2-NH-CH_2-CH_2-$	**XXXVI**
S	$-CH_2-CH_2-$	**XXXVII**
S	$-CH_2-CH_2-NH-CH_2-CH_2-$	**XXXVIII**
S	$-CH_2-CH_2-S-CH_2-CH_2-$	**XXXIX**

plexes; as an extension of this synthetic procedure, by using different polyamines, symmetric and non-symmetric macrocycles and the related uranyl(VI) mononuclear complexes (**XXXIII–XXXIX**) have been obtained [25–28].

The X-ray structure of **XXXIX** confirms that the UO_2^{2+} is equatorially coordinated by the N_2O_2S donor atoms from one of the two identical compartments, the second site remaining empty; a 'butterfly-fold' occurs in the ligand [27]. The metal ion is seven-coordinated in the usual distorted pentagonal bipyramidal coordination geometry (Fig. 9). The site occupancy in the non-symmetric macrocyclic complex **XXXVIII** is believed to be in the 'harder' $-N_3O_2$ compartment, although this has not yet been verified by X-ray crystallography.

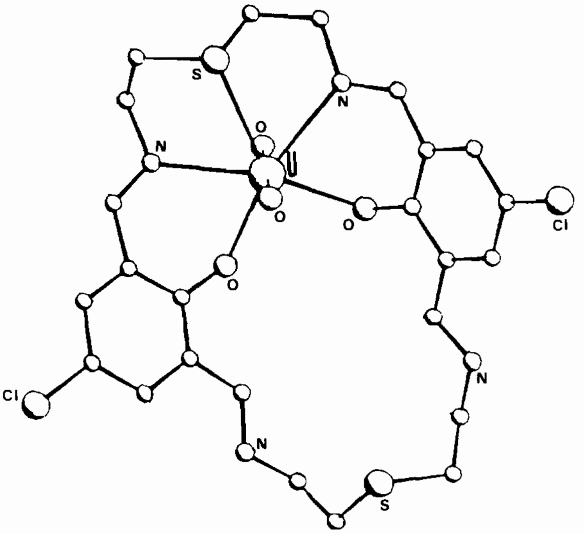


Fig. 9. Crystal structure of **XXXIX**.

It has not yet been possible to add a second UO_2^{2+} to these systems to give homodinuclear complexes, yet they can act as ligands towards transition metals to give heterobinuclear complexes.

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