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New Trends in the Structural Chemistry of Actinide and Lanthanide Coordination Compounds*

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Abstract

The structural chemistry of the actinide and lanthanide elements has recently undergone considerable development and a wide variety of coordination numbers and geometries have been observed. This structural versatility arises from the lack of strong crystal field effects for the 4f and 5f electronic configurations, as well as from the large ionic radii of these metal ions which change markedly with either oxidation number or atomic number for both the lanthanides and the actinides. Accordingly, the coordination numbers and geometries of actinide and lanthanide complexes are determined primarily by the denticity, geometry and steric bulk of the ligands. Examples are the monodentate, sterically hindered substituted ureas and amides and, more importantly, the wide variety of polydentate sequestering ligands such as the coronates, cryptates and podates. A critical survey of the various structures observed for these complexes is presented and the relevant structural trends are related to steric and electronic effects.

Introduction

The structural chemistry of the actinide and lanthanide elements has recently undergone considerable development and a wide variety of coordination numbers and geometries have been observed. This structural versatility arises from the lack of strong crystal field effects for the 4f and 5f electronic configurations as well as from the large ionic radii of these metal ions which change markedly with either oxidation number or atomic number for both the lanthanides and the actinides.

The major differences in electronic structure which establish the chemical differences between actinides and lanthanides are: for the lighter actinides the 5f orbitals are not completely shielded from the influence of the 6s and 6p electrons, allowing radial expansion of the 5f orbitals sufficient for overlapping with the ligand orbitals and, as a consequence, they are rather versatile in their oxidation numbers. On going to the right in the actinide series the increase in nuclear charge causes a contraction of the 5f orbitals with decreasing metal–ligand overlap and the trivalent oxidation state dominates with an even more highly ionic character in the bonding. However, the only structural evidence for covalent bonding in actinide chemistry is related to the actinyl ions MO_2^+ and MO_2^{2+}, where there is clear evidence that both f and d orbitals participate in the actinyl bond. In the lanthanides the 4f orbitals are more shielded with respect to the external influence of 5s and 5p electrons because they are greatly contracted along the series, with a resulting highly ionic character in the trivalent oxidation state, and their ionic radii decrease monotonically with increasing atomic number because of the regular increase in the nuclear charge.

The predominant ionic character in the bonding in their complexes has in consequence a variety of coordination numbers and ligand arrangements as steric and electrostatic factors become dominant. High coordination numbers, usually in the range of six to ten are observed and, under particular conditions, they can be either as high as twelve or as low as three or four.

Results and Discussion

Recently we have investigated a series of thorium(IV) and uranium(IV) halide and pseudohalide derivatives which form complexes of variable stoichiometry with differently substituted amide and urea ligands.

The substituted amide ligands considered were: $EtCONMe_2$ (*N,N*-dimethylpropionamide, DMPA); $Me_2CHCONMe_2$ (*N,N*-2-trimethylpropionamide, DMIBA); $EtCONEt_2$ (*N,N*-diethylpropionamide, DEPA); $MeCON(CHMe_2)_2$ (*N,N*-diisopropylacetamide, DIPPA); $EtCON(CHMe_2)_2$ (*N,N*-diisopropylpropionamide, DIPPA); $Me_2CHCON(CHMe_2)_2$ (*N,N*-diisopropyl-1-methylpropionamide, DIPIBA). The

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substituted urea ligands were: $(Me_2N)_2CO$ (tetramethylurea, TMU); $(PhMeN)_2CO$ (*N,N'*-dimethyl-*N,N'*-diphenylurea, DMDPU); $(Et_2N)_2CO$ (tetraethylurea, TEU).

We have found a variety of coordination numbers and geometries depending partially on the large ionic radii of uranium(IV) (0.93 Å) and thorium(IV) (0.99 Å) but principally on the bulk of the neutral ligand involved and the bulk of the anions. The lower coordination number six with a *trans*-octahedral coordination geometry is shown by three Th complexes with one of the amide ligands and two of the urea ligands: $ThBr_4(DIPA)_2$ [1], $ThBr_4(TEU)_2$ [1] and $Th(NO_3)_4(TMU)_2$ [2]. In this last example the coordination number (CN) is formally 10 as the nitrate groups are bidentate on the Th ion, but the coordination polyhedron could be better described as an octahedron since each nitrate may be considered as occupying one coordination position because of its small bite (about 2 Å) (see Fig. 1). (The alternative description considering all the coordinate atoms is a distorted bicapped square-antiprism.) In these examples the bulk of the anionic ligand determines the low coordination number (6) and in the case of the nitrate derivative, the crowding of the nitrate groups around thorium is also responsible for the bending of the O(1)–Th–O(2) angle to the value of 151.3(2)°, while in the other two complexes it is 180° (the molecules lie on crystallographic inversion centres). In general we have observed that the bis complexes MBr_4L_2 (L = DMIBA, M = Th [3]; L = DIPDMU or DIPDPU, M = Th or U) [4]) are characteristic of the tetrabromides owing to the great steric demand of the large bromine ion.

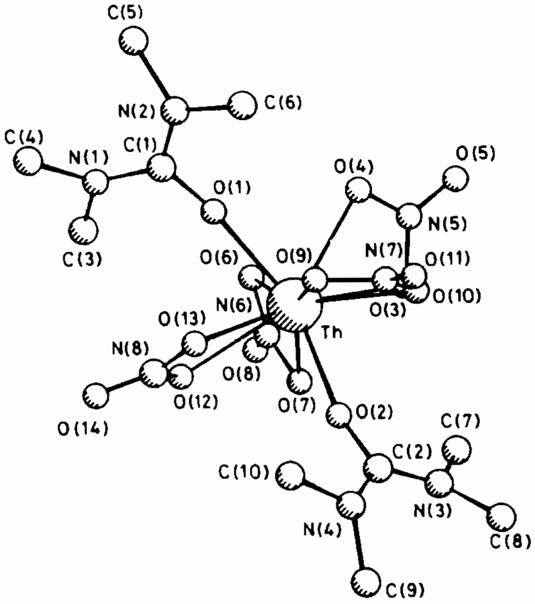


Fig. 1. View of the $Th(NO_3)_4(TMU)_2$ complex.

Seven-coordination with pentagonal bipyramidal coordination geometry is often found in this class of compound with the less-hindered sites of the bipyramid (the two axial positions) being occupied, with the shortest bonds, by two unidentate anionic ligands. This geometry is the most common for the actinyl 7-coordinated complexes and is also the one most widely represented (the axial sites are occupied by the two actinyl oxygens and the five additional donor atoms are in the equatorial plane), but was first found in a neutral actinide(IV) complex in $U(NCS)_4(DMIBA)_3$ [5] (see Fig. 2). (The other possible geometries would be the capped octahedron and capped trigonal prism, which in principle are more favourable in a hard sphere model.)

The compounds examined were three isothiocyanate derivatives $U(NCS)_4(DIPPA)_3$ [1], $U(NCS)_4(DMIBA)_3$ [5], $Th(NCS)_4(DIPIBA)_3$ [6] and two tetrachloro derivatives $ThCl_4(DEPA)_3$ [7] and $ThCl_4(DMDPU)_3$ [8]. All these compounds have in the axial positions two anionic ligands either NCS or Cl, and in the equatorial plane the other two anionic ligands, together with the three neutral ligands. Among the possible geometrical isomers (see Fig. 3) characteristic of compounds of the class MX_4L_3, the most stable ones are those with one of the three neutral ligands between two anionic ligands in the equatorial plane (see Fig. 4). In Table I are reported some significant bond distances and angles found in these compounds. It should be noted that the axial bonds are shorter with respect to the equatorial ones; with the exception of $ThCl_4(DMDPU)_3$ where the axial angle Cl–Th–Cl is bent to 172(1)°, in the other examples this angle is quite close to linearity.

Among the factors which seem to influence the observed differences between axial and equatorial

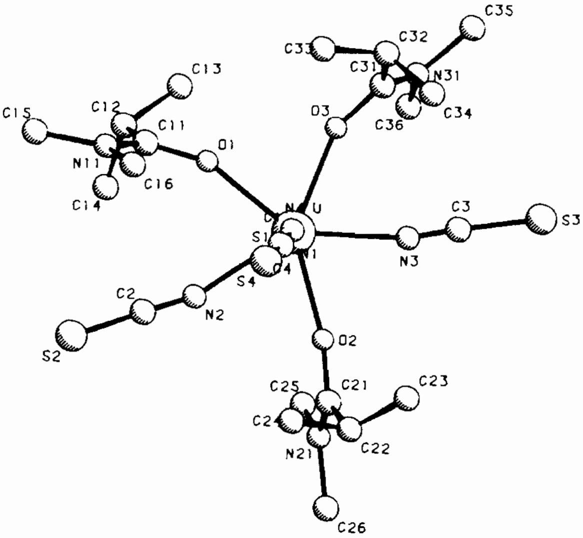


Fig. 2. Perspective view of the $U(NCS)_4(DMIBA)_3$ molecule.

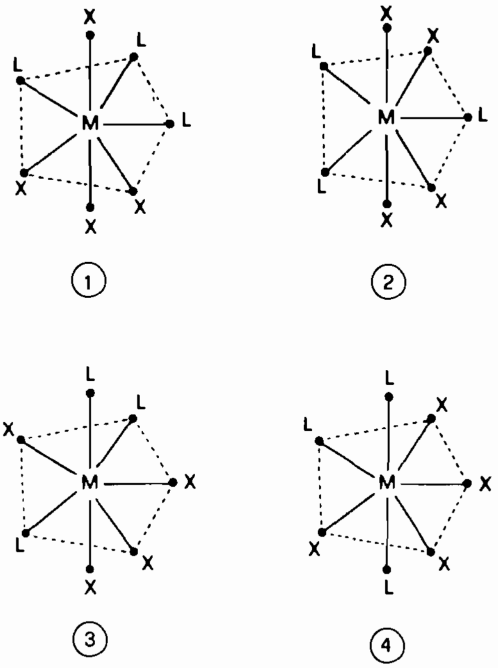


Fig. 3. Possible geometrical isomers for pentagonal bipyramidal coordination geometry.

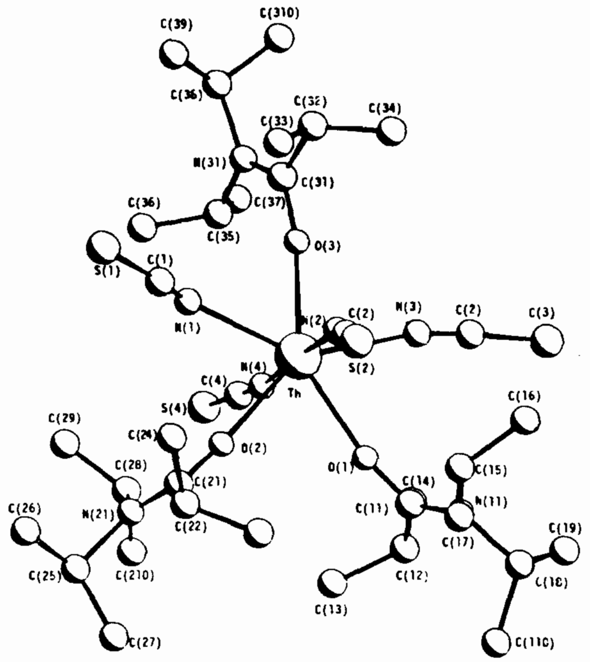


Fig. 4. Perspective view of $Th(NCS)_4(DIPIBA)_3$.

TABLE I. Comparison Between Significant Structural Parameters in U(IV) and Th(IV) Complexes with Pentagonal Bipyramidal Coordination Geometry

	Bond distances (Å)			Bond angle X–M–X (°)
	M–X_{ax} [a]	M–X_{eq}	M–O	
$U(NCS)_4[EtCON(Pr^i)_2]_3$ (DIPPA)	2.42(2) 2.34(2)	2.54(3) 2.50(3)	2.15(2) 2.17(2) 2.45(2)	176.8(7)
$U(NCS)_4(Me_2CHCONMe_2)_3$ (DMIBA)	2.36(2) 2.32(2)	2.43(3) 2.34(3)	2.30(2) 2.29(2) 2.30(2)	177.4(9)
$Th(NCS)_4[Me_2CHCON(Pr^i)_2]_3$ (DIPIBA)	2.42(1) 2.42(1)	2.46(2) 2.46(2)	2.344(8) 2.336(9) 2.335(9)	177.8(4)
$ThCl_4(EtCONEt_2)_3$ (DEPA)	2.696(3) 2.687(3)	2.751(1) 2.757(3)	2.333(8) 2.352(9) 2.336(9)	175.5(1)
$ThCl_4(PhMeNCONMePh)_3$ (DMDPU)	2.695(3) 2.696(3)	2.729(2) 2.758(3)	2.370(5) 2.413(5) 2.375(5)	171.8(1)

[a] X = anionic ligand.

bond distances within the anionic ligands, an important role seems to be played by the neutral ligands: shorter M–O bond distances cause a lengthening of the axial M–X bonds and also of the M–X_{eq} bonds. In particular, noticeable irregularities in the bond distances and angles in the uranium coordination sphere of $(U(NCS)_4(DIPPA)_3)$ [1] are present.

The U–N_{ax} bond distances are rather asymmetric [U–N(1) = 2.34(2) Å and U–N(2) = 2.42(2) Å] and on average are somewhat longer [2.38(3) Å *versus* 2.34(3) Å in DMIBA] with respect to that of the DMIBA derivative; this is also the case with the U–N_{eq} bond distances [2.52(3) Å *versus* 2.39(3) Å). The U–O_{eq} distances are of two types: U–O(1) =

2.15(2) Å and U–O(3) = 2.17(2) Å for the two adjacent neutral ligands, whereas U–O(2) is 2.45(2) Å. This is related to the different steric hindrance of the two neutral ligands: $EtCON(Pr^i)_2$ (DIPPA) and $(Pr^i)_2CONMe$ (DMIBA). In fact in $U(NCS)_4(DMIBA)_3$ [5] in the equatorial plane the O–U–N and O–U–O angles are all close to 72°, due to the quasi symmetrical shape of the ligand (two methyls bonded to the nitrogen and two others to the carbon adjacent to the C=O moiety), which is reflected in a higher degree of regularity in the U–L bond distances. In $U(NCS)_4(DIPPA)_3$ [1] the O(1)–U–O(3) equatorial angle is 81(1)°, while the two N(4)–U–O(2) and N(3)–U–O(2) angles are 70(1)°. The two bulky isopropyl substituents on the nitrogen in the propionamide derivative, together with the flexibility of the ligand allow shorter U–O distances (2.15(2) Å and 2.17(2) Å), however, their higher steric hindrance is responsible for the irregularities in bond distances and angles in the U coordination sphere (see Fig. 5).

In the thorium derivatives, the Th–O neutral ligands are comparable, independent of the anionic ligands with which they are associated and of the bulk of the neutral ligands. In particular, in the two $ThCl_4$ derivatives, the $Th–Cl_{ax}$ distances [$Th–Cl_{av}$ = 2.692(3) Å in $ThCl_4(DEPA)_3$ and 2.696(3) Å in $ThCl_4(DMDPU)_3$] are equal to each other, as are the $Th–Cl_{eq}$ distances of 2.743(3) Å in the first and 2.754(3) Å in the second. This would cause a higher covalency in the $Th–Cl_{ax}$ bonds as the different hindrance of the neutral ligands in the equatorial plane does not seem to affect the Th–Cl equatorial bonds. The different bulk of the DMDPU and DEPA ligands seems to influence only the Th–O bond distances and, in particular, the bulk of the DMDPU ligand affects the bending of the Cl–Th–Cl axial angle. (The other Cl–Th–Cl angles are less than 90°, except for one case.)

To summarize, the presence of anionic ligands (excluding bromine) which occupy the axial positions and the steric requirements of the neutral ligands seem to be the main factors responsible for this pentagonal bipyramidal coordination geometry.

Octa-coordination is fairly common for actinide compounds and the most frequently observed polyhedra are square-antiprism and dodecahedron. The compounds studied belonging to this category were: $U(NCS)_4(DIPA)_4$ [9], $Th(NCS)_4(DIPA)_4$ [1], $Th(NCS)_4(DMPA)_4$ [10] and $Th(NCS)_4(TMU)_4$ [11].

With DIPA as the ligand we have already reported the hexa-coordinate *trans*-octahedral $ThBr_4(DIPA)_2$ structure [1]. By replacing the bromine with the thiocyanate ligand the number of neutral ligands increases to four, as in the isostructural uranium derivative $U(NCS)_4(DIPA)_4$ [9]. (In these cases it is the bulk of the anion which determines the molecular complexity and not that of the neutral ligand.) The coordination polyhedron is a dodecahedron, with the N atoms of the NCS groups in the dodecahedral B sites and the O atoms of the neutral ligands in the A sites. The M–N (M = Th or U) are longer than the M–O bond distances and should prefer in principle the more crowded positions of the polyhedron, *i.e.*, the A sites. The central M atom lies on the $\bar{4}$ crystallographic axis and the molecular symmetry is forced to be $\bar{4}$ as expected for a regular dodecahedral polyhedron [Th–O = 2.413(4) Å, U–O = 2.363(8) Å and Th–N = 2.504(6) Å, U–N = 2.444(1) Å, in agreement with the differences in the U and Th ionic radii] (see Fig. 6). It should be noted that with the same anion (NCS) the less bulky DIPA ligand allows coordination of four neutral ligands around the M atom, while with the DIPPA ligand (which differs by

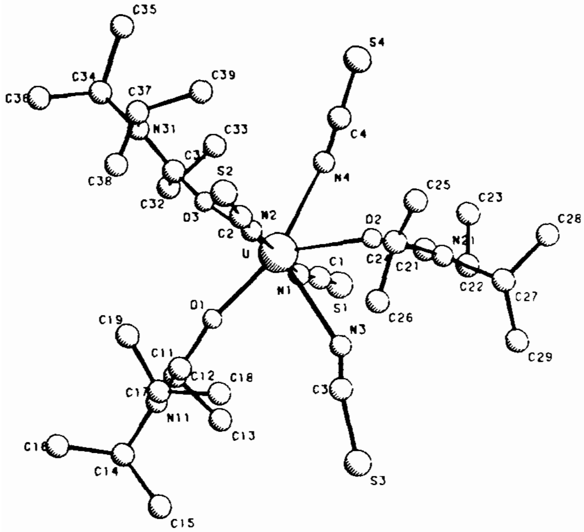


Fig. 5. Perspective view of $U(NCS)_4(DIPPA)_3$.

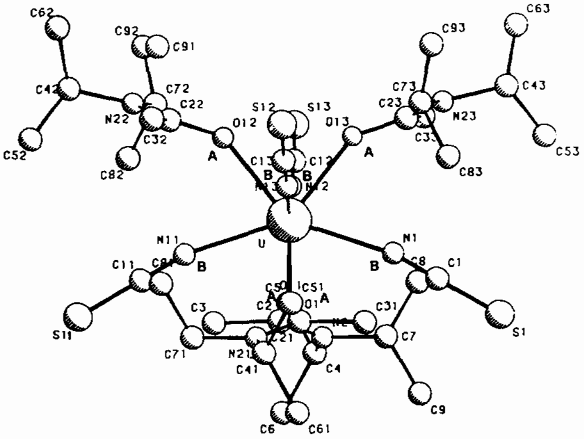


Fig. 6. View of the $U(NCS)_4(DIPA)_4$ molecule showing the A and B sites of the dodecahedral coordination.

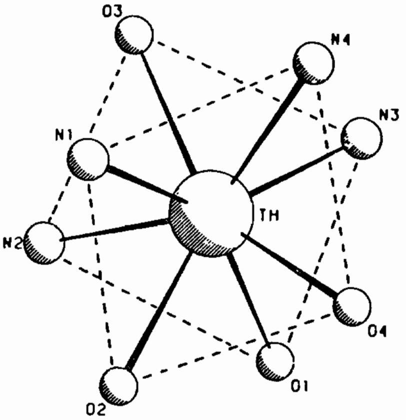


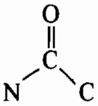
Fig. 7. Square-antiprismatic coordination geometry in $Th(NCS)_4(DMPA)_4$.

one methyl group) only three neutral ligands are coordinated to the metal, at least in the uranium derivative $U(NCS)_4(DIPPA)_3$.

Four molecules of the less sterically hindered ligand DMPA can be bound to the Th in the complex $Th(NCS)_4(DMPA)_4$ [10] with a square-antiprismatic coordination geometry around the metal atom. In one 'square', atoms of the same type are in adjacent positions (see Fig. 7) and in the second square nitrogens and oxygens are *trans* to each other, the deviations from planarity being ±0.20 Å lower when compared with ±0.27 Å in the first square.

The average Th–O distance is 2.37(1) Å, while Th–N is 2.49(2) Å, in agreement with the values reported for $Th(NCS)_4(TMU)_4$ [$Th{-}O_{av} = 2.37(1)$, $Th{-}N_{av} = 2.52(1)$ Å]. This last compound has a distorted dodecahedral coordination geometry with oxygens and nitrogens equally distributed between A and B sites and the neutral ligand hindrance is comparable to that of DMPA. (On energetic grounds, square-antiprismatic and dodecahedral geometries have roughly the same stability.) As before, the *trans*-octahedral $Th(NO_3)_4(TMU)_2$ derivative with only two TMU ligands exists due to the greater hindrance of NO_3 with respect to NCS.

A general survey on the reported structures indicates, in the first instance, that the bulk of the halide or pseudohalide ligand determines the number of the coordinated neutral ligands; in the second instance, with an equal number of anionic ligands the number of neutral ligands which can be coordinated strongly depends on the bulk of the substituent attached to N or C in the amide derivatives considering the planar fragment **I** or to both N atoms in the urea derivatives (planar fragment **II**) and it does not matter if the bulkier substituents are on one side or on the other. The bonds are essentially of an electrostatic and ionic nature, but some degree of covalency seems to exist along the axial bonds in the hepta-coordinated complexes.



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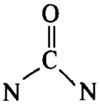


II

Table II shows the significant structural parameters for all the compounds considered.

Another interesting class of structures deals with complexes of the 'host–guest' type as, for example, the complexes between an actinide (An) or lanthanide (Ln) metal ion and ionophores, where the guest moiety is encapsulated in the host molecule which is generally a cyclic or open-chain molecule.

The ionophores considered here belong to the class of cyclic polyethers or polyamines. In these complexes the metal-to-ligand ratio depends on the nature of the metal ion, the anion and the ligand. The ratio ionic diameter/cavity diameter, the macrocycle flexibility and the nature of the counter anion are the most important factors which determine the type of complex obtainable. Preformed cyclic ligands containing four or five donor atoms in the cycle have a cavity diameter too small to encapsulate the metal ion. Generally in these cases the ligand is coordinated on one side while the remaining non-cyclic ligands lie on the opposite side. There is only one example of insertion of a uranyl group into a five donor atom macrocycle, *i.e.*, dioxocyclopentakis(2-iminoisoindoline)uranium(VI), where the macrocycle is obtained by a template synthesis [12].

With the crown ether 18-crown-6, which contains six donor atoms, we have achieved insertion of the Ln and An in the macrocycle; U(IV) has been inserted into the complex $2[UCl_3\text{-}18\text{-crown-}6][UO_2Cl_3(OH)\text{-}H_2O]$ [13] (see Fig. 8). Four oxygens of the crown ether are displaced towards the unique chlorine atom and two towards the two chlorines opposite to the unique chlorine. The crown ether 18-crown-6 adopts this folded conformation in order to equalize the U–O distances. With UO_2^{2+} we have only crown ether systems with hydrogen bond interactions between coordinated water molecules and etheric oxygen atoms [14]. $Ln(NO_3)_3(18\text{-crown-}6)$ (where Ln = La [15], Nd [16]) are isostructural despite the difference in the ionic radii and the structure is comparable with that of $[UCl_3\text{-}18\text{-crown-}6]^+$ with the three nitrates substituted by the chlorine atoms. $Gd(NO_3)_3(H_2O)_3(18\text{-crown-}6)$ [15] forms only adducts with the crown ether, while in $[GdCl_2(18\text{-crown-}6)(EtOH)]^+$, Gd is inserted into the macrocycle and the conformation adopted is that usually expected [17].

In $(Nd(NO_3)_3)_4(18\text{-crown-}6)_3$ [18] there are three species: $[Nd(NO_3)_6]^{3-}$, one ordered cation $[Nd(NO_3)_2(18\text{-crown-}6)]^+$ and two disordered cations $[Nd(NO_3)_2(18\text{-crown-}6)]^+$ (see Fig. 9). The conformation of the ligand is more symmetrical

TABLE II. Significant Bond Distances (Å) and Angles (°) in Th(IV) and U(IV) Tetrahalide or Pseudohalide Derivatives with Differently Substituted Ureas and Amides

Complex	Coordination number	Bond distances		Bond angle M–O–C (°)
		M–halogen or pseudo	M–O neutral ligand	
$ThBr_4(DIPA)_2$	6	2.827(3)	2.272(5)	155.7(5)
		2.830(2)		
$ThBr_4(TEU)_2$		2.831(4)	2.266(9)	171.6(8)
		2.836(4)		
$Th(NO_3)_4(TMU)_2$		2.511(7)	2.304(6)	168.6(6)
		2.513(6)	2.301(5)	164.9(5)
		2.556(6)		
		2.507(6)		
$U(NCS)_4(DIPPA)_3$	7	2.42(2)	2.15(2)	158(2)
		2.34(2)	2.17(2)	152(2)
		2.50(3)	2.45(2)	160(2)
		2.54(3)		
$U(NCS)_4(DMIBA)_3$		2.36(3)	2.30(2)	156(2)
		2.43(3)	2.29(2)	
		2.34(3)	2.32(2)	
		2.32(3)		
$Th(NCS)_4(DIPIBA)_3$		2.46(1)	2.34(1)	162(1)
		2.46(1)	2.34(1)	168(1)
		2.42(1)	2.34(1)	164(1)
		2.42(1)		
$ThCl_4(DEPA)_3$		2.696(3)	2.352(9)	152(1)
		2.687(3)		
		2.751(3)	2.336(9)	164(1)
		2.757(3)		
$ThCl_4(DMDPU)_3$		2.695(3)	2.370(5)	160.3(8)
		2.696(3)	2.413(5)	154.8(5)
		2.729(2)	2.375(5)	155.8(6)
		2.758(3)		
$U(NCS)_4(DIPA)_4$	8	2.444(11)	2.363(8)	144(1)
$Th(NCS)_4(DIPA)_4$		2.504(6)	2.413(4)	143.6(6)
$Th(NCS)_4(DMPA)_4$		2.46(2)	2.40(1)	150(1)
		2.48(2)	2.39(1)	147(1)
		2.50(2)	2.35(1)	149(2)
		2.50(1)	2.35(1)	152(1)

(more flattened crown) with respect to that of $Nd(NO_3)_3L$ due to the presence of one NO_3 group on each side.

Dicyclobenzyl-18-crown-6 forms with Sm the complex $SmClO_4(Bz_2\text{-}18\text{-crown-}6)$ [19] with the coordination of monodentate and bidentate perchlorate groups. The shape of the crown resembles that of $Ln(NO_3)_3(18\text{-crown-}6)$ with four oxygens in the direction of the unique ClO_4 and two in the opposite direction.

Dicyclohexyl-18-crown-6 (= L) forms both 1:1 and 3:2 complexes with $La(NO_3)_3$ [20]. In the former, the coronate has the configuration *cis-syn-cis* (isomer A), while the *cis-anti-cis* isomer B is found in the 3:2 complex $[Ln(NO_3)_5ONO_2Ln(NO_3)Cy_2\text{-}18\text{-crown-}6]^-$ $[Ln(NO_3)_2Cy\text{-}18\text{-crown-}6]^+$ (Ln = La, Pr).

The complex anion $[Ln(NO_3)_2L\cdot Ln(NO_3)_5]^-$ has one bridging tridentate nitrato ion [bidentate on $LnL(NO_3)$ and monodentate on $Ln(NO_3)_5$]. The O bridging distance is significantly larger with respect to the other Ln–O(nitrate). The nitrates are in axial positions *trans* to each other, as in $[Nd(NO_3)_2(18\text{-crown-}6)]^+$ [18].

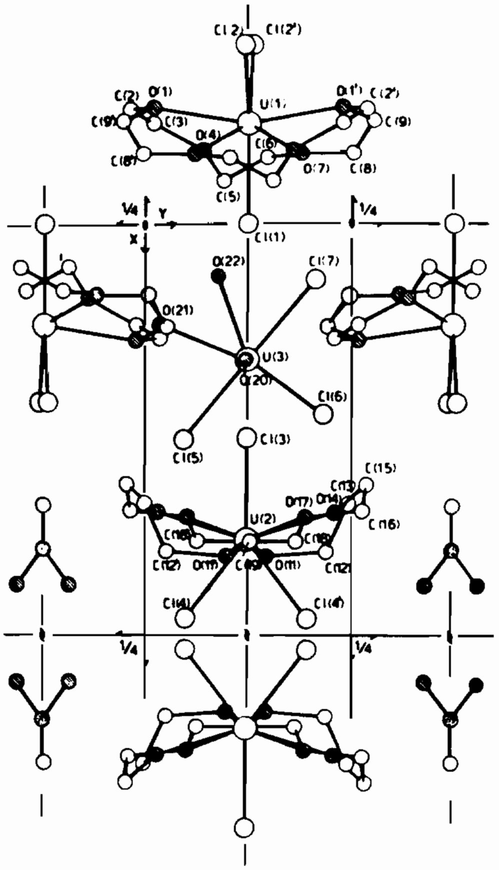
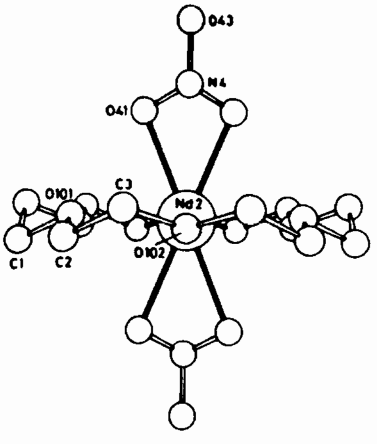


Fig. 8. Molecular packing in the $[UCl_3\text{-}18\text{-crown-}6]_2\text{-}[UO_2Cl_3(OH)H_2O]$ complex.

Trivalent lanthanides can act as templating agents in the formation of polyaza macrocyclic systems of appropriate cavity size. In particular, complexes containing the hexaaza hexadentate macrocycles L_A, L_B and L_C are formed in the presence of O-donor counterions (see Fig. 10).

The structures presented are closely related to that of the crown ether analogues and the main difference is that the nitrogen ligands have stability constants greater (at least 1 order) than the corresponding crown ethers, and are kinetically stable in aqueous solution. With L_A as ligand the structures are known of the complexes with La, $[La(NO_3)_3L_A]$ [21]; Lu, $(LuL_A(CH_3COO)(OH)(ClO_4)(CH_3OH)(H_2O)_{0.5})$ [22]; Y, $(YL_A(CH_3COO)_2(H_2O)(ClO_4)(CH_3OH)_{0.5})$ [23] and $YL_A(NCS)_3$ [24]; Eu, $(EuL_A(NCS)_3$ [25]. With the ligands L_B and L_C the structures are known of the complexes $SmL_B(NO_3)_2(OH)(H_2O)MeOH$ [26] and $(PrL_C(NO_3)_2(CH_3OH))(ClO_4)$ [27].

Some selected structural parameters for lanthanide complexes with hexaaza and hexaoxa hexadentate macrocycle ligands are reported in Table III. In the crown ether series, the competition between strongly



$[Nd(NO_3)_2\ (18\text{-Crown-}6)]^+$

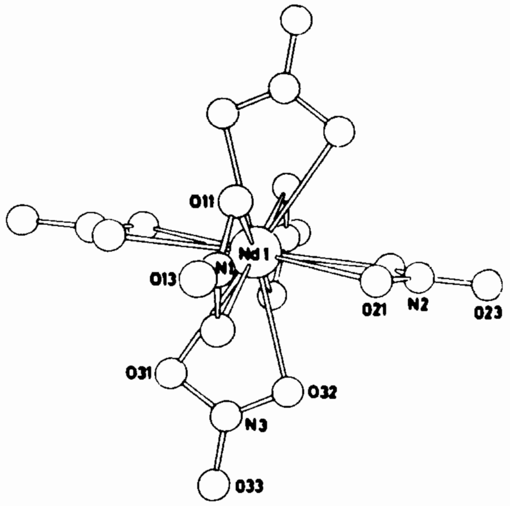


Fig. 9. View of the $[Nd(NO_3)_2(18\text{-crown-}6)]^+$ cation and $[Nd(NO_3)_6]^{3-}$ anion.

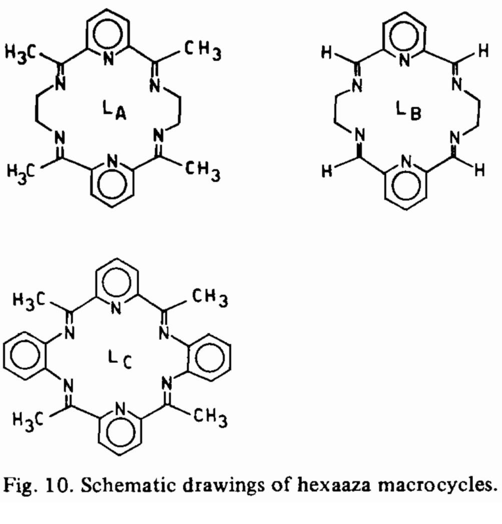


Fig. 10. Schematic drawings of hexaaza macrocycles.

TABLE III. Selected Structural Parameters for Lanthanide Complexes with Hexaazadentate and Hexaoxadentate Macrocycle Ligands

Complexes with hexaazadentate macrocycles	C.N.	Ln–N(pyridine)	Ln–N(imine)	Ln–O(anionic)	Ionic radii	'Wings' angle (°)
$[LaL_A(NO_3)_3]$	12	2.746 2.764	2.672–2.729	2.689–2.767	1.061	
$[SmL_B(NO_3)(OH)H_2O]^+(NO_3^-)(CH_3OH)$	10	2.65(1) 2.66(1)	2.60(1)–2.64(1)	2.51(1) 2.52(1)	0.964	
$[LuL_A(CH_3COO)(H_2O)]^{2+}(CH_3OH)(OH^-)(ClO_4^-)$	9	2.556(7) 2.556(9)	2.471(7)–2.620(9)	2.326(6) 2.365(7)	0.848	114(1)
$[LuL_A(CH_3COO)(CH_3OH)]^{2+}(OH^-)(ClO_4^-)$				2.232(6)		
$[YL_A(CH_3COO)_2]^+(ClO_4^-)(CH_3OH)$	9	2.578(7) 2.590(6)	2.495(9)–2.625(11)	2.356(7)–2.416(7)	0.88	115.6(6)
$[YL_A(CH_3COO)(H_2O)]^{2+}(CH_3COO^-)(ClO_4^-)\cdot 0.5H_2O$				2.273(8)		
$[YL_A(NCS)_3]$	9	2.55(3) 2.56(3)	2.49(3)–2.64(3)	2.36–2.46(2) (NCS)	0.88	111(1)
$[EuL_A(NCS)_3]$	9	2.61(1) 2.66(1)	2.51(1)–2.68(1)	2.45–2.50(1) (NCS)	0.95	111(1)
$[PrL_C(NO_3)_2(CH_3OH)]^+(ClO_4^-)\cdot 0.5CH_3OH$	11	2.65(1) 2.66(1)	2.65(1)–2.68(1)	2.56–2.71(1)	1.013	113(1)

Complexes with hexaoxadentate macrocycles	C.N.	Ln–O(ether)	Ln–O(anionic)	Ionic radii
$La(NO_3)_3$(18-crown-6)	12	2.627–2.772(6)	2.644–2.675(6)	1.061
$La(NO_3)_3$(dicyclohexyl-18-crown-6)	12	2.61–2.92	2.63–2.71	
$Nd(NO_3)_3$(18-crown-6)	12	2.598(5)–2.778(4) 2.576(6)–2.770(6)	2.580(4)–2.615(4) 2.566(6)–2.598(7)	0.995
$[Nd(NO_3)_2$(18-crown-6)$]_3[Nd(NO_3)_6]$ (cation)	10	2.54(2)–2.71(2)	2.42(2)–2.57(2)	0.995
(anion)	12		2.67(1)–2.66(2)	
$[Gd(Cl_2(EtOH)$(18-crown-6)$]^+(Cl^-)$	9	2.497(6)–2.608(5) 2.414(6)		0.938
$[Gd(NO_3)_3(OH_2)_3]$(18-crown-6)	9	2.422(4)–2.454(6)[a]	2.411(11)–2.533(13)	
$[UCl_3$(18-crown-6)$]_2[UO_2Cl_3(OH)(H_2O)]$[c]	9	2.48(5)–2.61(5)		0.93

[a] The distances are Gd–O(H_2O). [b] e.s.d.s were not given in the reference. [c] The distances given are with U.

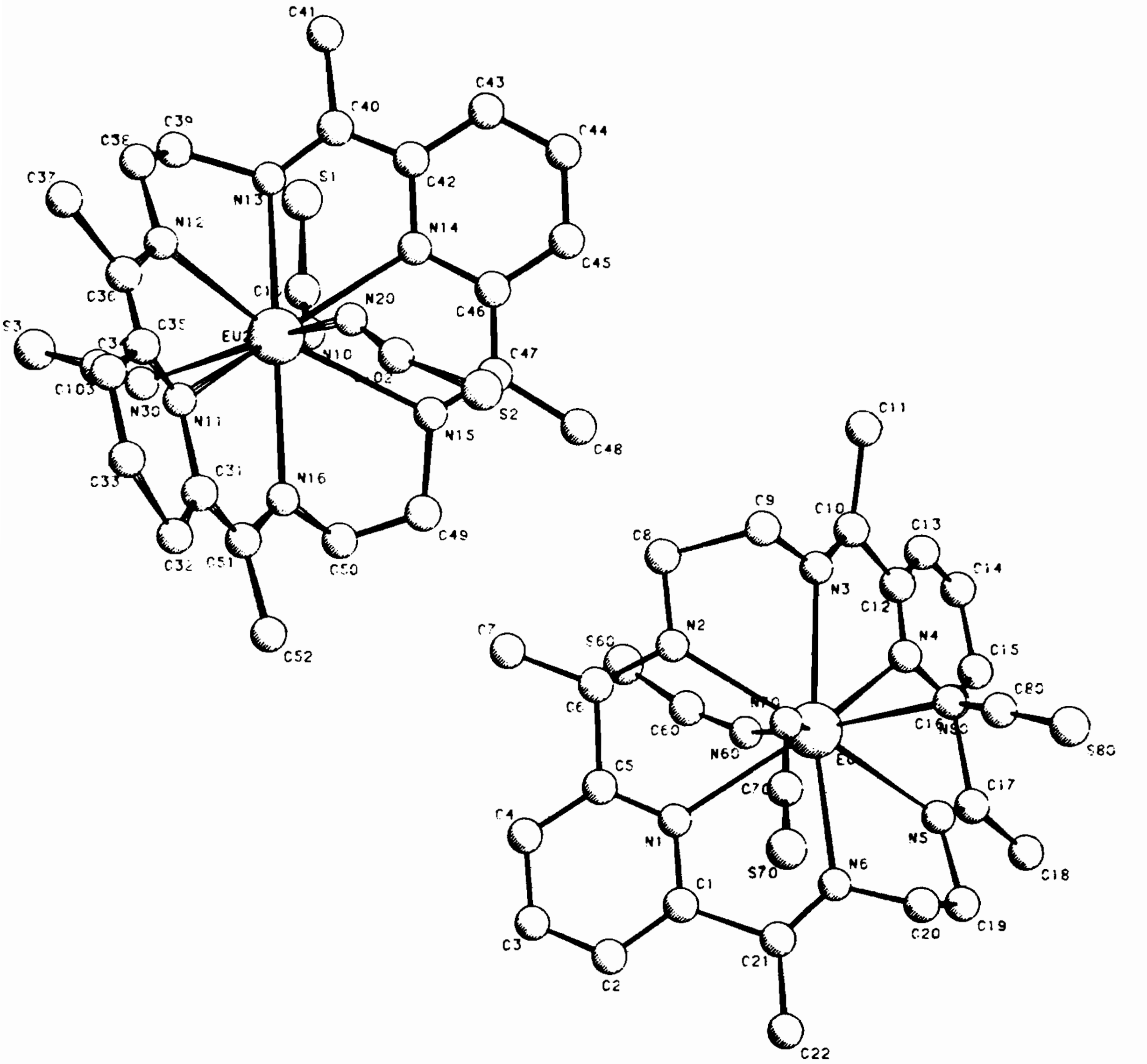


Fig. 11. Perspective view of the two asymmetric units in $Eu(NCS)_3L_A$.

ligating NO_3 and O donor organic ligands is actually reflected in the stoichiometry of the complexes. Species with a Ln-to-crown ether ratio higher than 1 are stabilized by the $Ln(NO_3)_6^{3-}$ moiety, as in $[Nd(NO_3)_6][Nd(18\text{-crown-}6)(NO_3)_2]_3$ [18]. Coordination of the crown ether does not take place with gadolinium(III) nitrate [15], even though it occurs with the chloride [17].

The general feature of these complexes is the hingeing of the macrocycle at the two flexible $-CH_2-CH_2-$ side chains (for L_A and L_B macrocycles) in order to relieve steric strains within the macrocycle and also to minimize repulsion among the hetero ligands, thus allowing the central metal to attain its highest possible coordination number. With large lanthanide ions, three NO_3 groups can be bidentate on the metal ion (two on one side, the third on the opposite side) with wrapping of the macrocycle on the less hindered side of the macrocycle (*i.e.*, in the direction of the unique nitrate). On decreasing the ionic radii, as with Pr, one nitrato position is replaced by the less hindering methanol, while with Sm the positions of two nitrato ligands are replaced by a hydroxide group and a water molecule. Eu and Y give, with the less hindering NCS anion and the L_A ligand, two isostructural neutral compounds $M(NCS)_3L_A$ (see Fig. 11). With the smallest ion, Lu, a C.N. of 9 seems to be the maximum attainable, due to the presence of uncoordinated potential O-donor ligands such as hydroxide or methanol in the complex cation $[LuL_A(CH_3COO)(CH_3OH)]^{2+}$ [22].

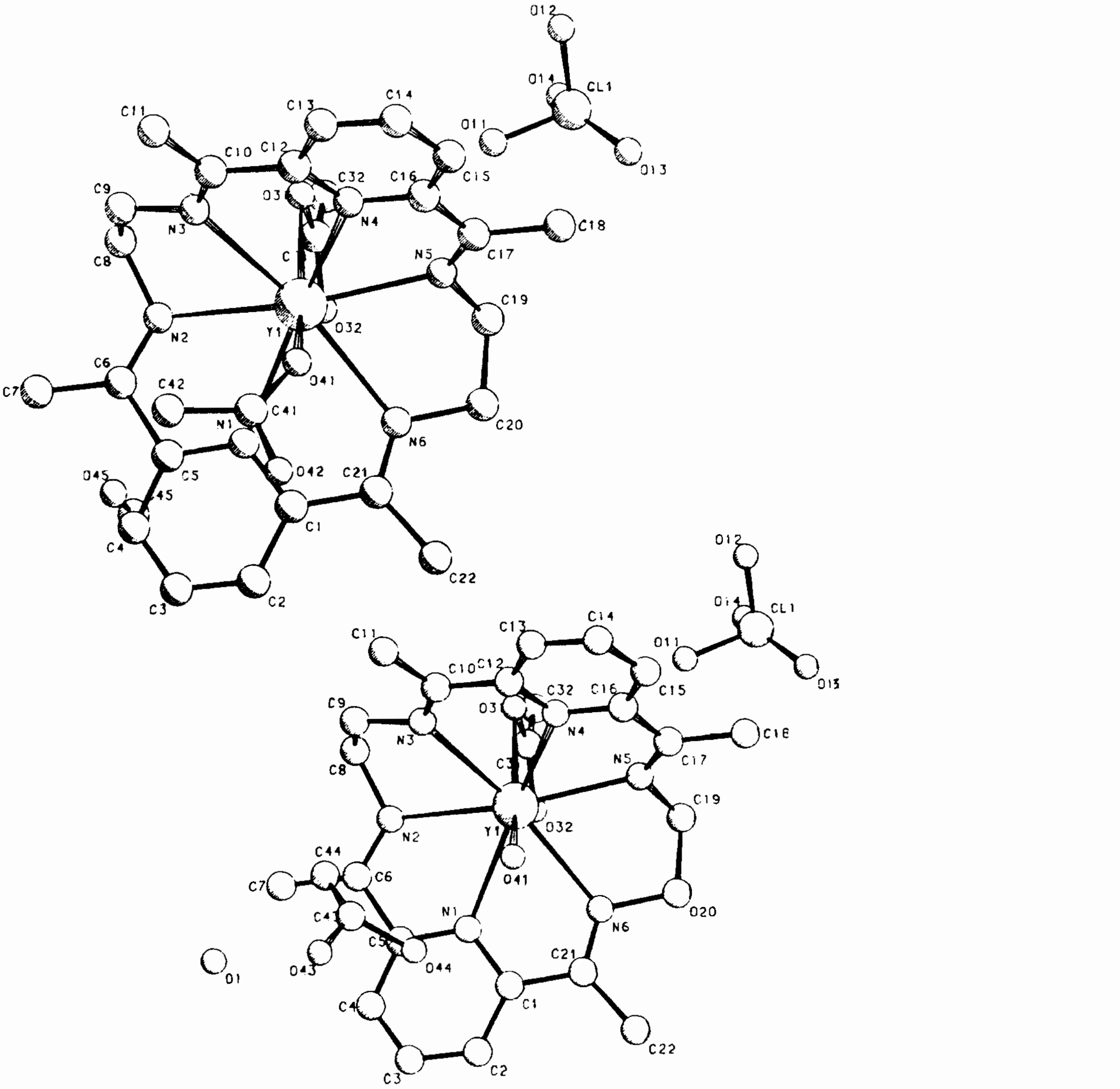


Fig. 12. The $[YL_A(CH_3COO)_2]^+$ and $[YL_A(CH_3COO)(H_2O)]^{2+}$ cations. (The free anions ClO_4^- and CH_3COO^- are also reported.)

With nitrate or acetate as counter anion, cationic species with +1 or +2 charges are frequently formed, and in the particular case of YL_A acetate and perchlorate [23] we have achieved the presence in the same crystal of the singly and doubly charged complex species $[YL_A(CH_3COO)_2]^+$ and $[YL(CH_3COO)(H_2O)]^{2+}$ (see Fig. 12).

The $[PrL_C(NO_3)_2(CH_3OH)]^+$ cation (see Fig. 13) is worthy of particular comment. The L_C ligand in principle should be fairly planar when compared with L_A and L_B ligands because of the presence of the two fused phenyl rings. On the contrary, no electron delocalization is present along the ring, and also in this case there is the bending of the cyclic ligand which allows the metal ion to coordinate to three extra ligands. The bending in this case is along the C–N bonds adjacent to the phenyl rings, as shown in Fig. 14.

Considering the chelated nitrate or acetate as single coordinating groups, it appears that the most common coordination geometries, either for hexaoxa or hexaaza complexes, are with two ligands co-linear and roughly perpendicular to the plane of the macrocycle donor atoms, or with three ligands in a V shape with the macrocycle wrapped towards the unique ligand.

In this way the folding of the macrocycle in lanthanide or actinide complexes seems to be determined more by the ionic size of the metal than by the steric requirements of the hetero ligands.

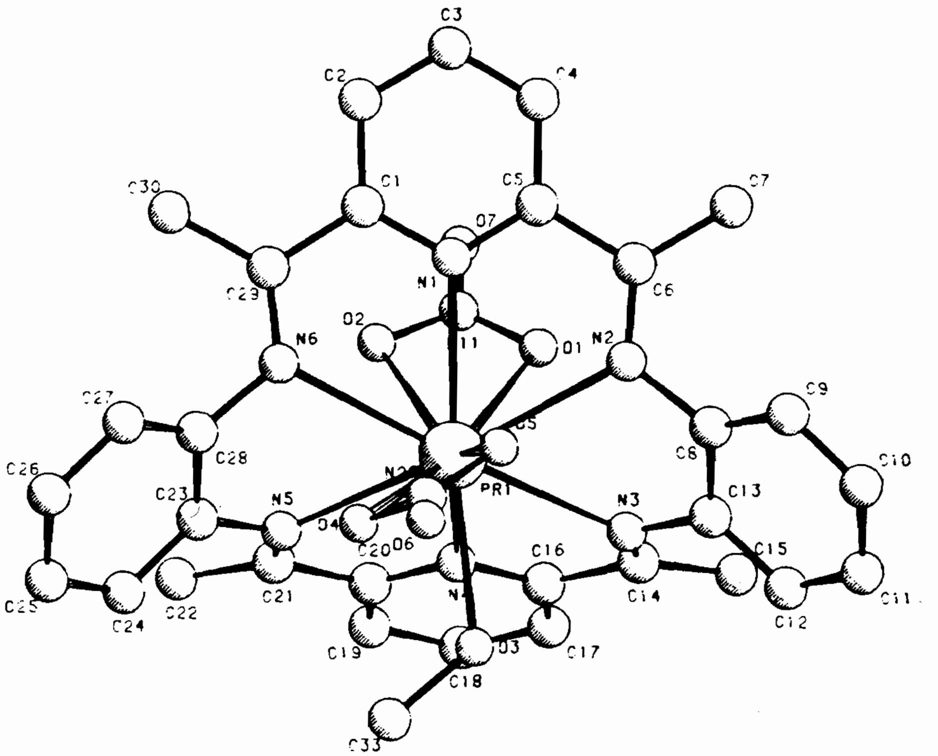


Fig. 13. The $[PrL_C(NO_3)_2CH_3OH]^+$ cation.

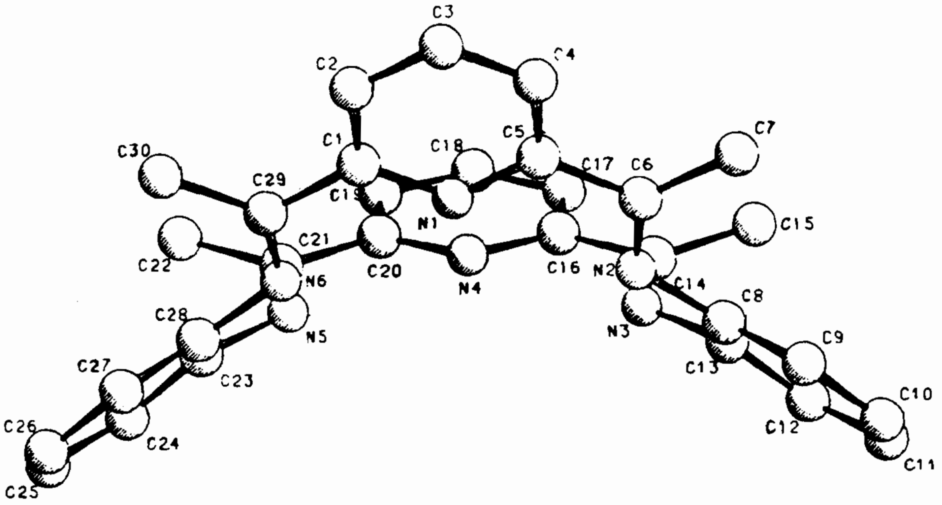


Fig. 14. L_C ligand conformation in the cation $[PrL_C(NO_3)_2CH_3OH]^+$.

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