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RARE EARTH COMPLEXES WITH NEUTRAL MACROCYCLIC LIGANDS

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A. SCOPE OF THE REVIEW

To help understand biological processes, chemists often design abiotic systems that reproduce one, or preferentially, some of the features of these processes. To achieve this goal, insight is needed into the structural recognition occurring through complexation, which explains the current interest for both macrocyclic, polycyclic and related open-chain ligands. Multiple site binding is indeed required to provide a high structural organization of the complex, which can be either a host/guest or a ligand/metal ion entity. Macrocyclic ligands are comprised of lipophilic (mainly alkyl chains) and hydrophilic elements (oxygen, nitrogen atoms or other functional groups). Their cavity can encapsulate a metal ion, a property that was recognized in the early sixties when complexation of potassium and sodium ions by naturally occurring macrocycles, e.g. valinomycin, was reported. Following this discovery, model ligands such as crown ethers and cryptands were soon synthesized and a new field of coordination chemistry was opened, giving rise to the publication of more than a thousand papers. A literature survey is presented in ref. [1] while analytical applications are described in refs. 2–4. A substantial part of this work is devoted to alkali and alkaline-earth ions.

Trivalent lanthanide ions have a $4f^n5s^25p^6$ electronic configuration resulting in weak crystal field and directional effects. In some respects, their chemical properties resemble those of the I_a and II_a cations, so that the investigation of their interaction with macrocyclic ligands is a logical extension of the work with alkali and alkaline-earth metals [5]. Moreover, such a study has additional specific motivations which include, among others, (i) the use of lanthanoid ions as spectroscopic probes [6], (ii) the stabilization of uncommon oxidation states and (iii) the systematic study of the lanthanoid ion coordination properties.

In this review the properties of the complexes between rare-earth ions and the following ligand classes: crown ethers, hetero-substituted crown ethers and cryptands are discussed. Complexes of polyethyleneglycol derivatives, the open-chain analogues of the crown ethers, are also partly included for comparison purposes. The publications referred to in this paper have been found by means of a computer search of Chemical Abstracts up to the end of 1983 (vol. 99).

B. NOMENCLATURE

According to IUPAC rules, the following nomenclature should be used for the metal ions: lanthanides for Ce to Lu, lanthanoids for La to Lu, and rare earths for Y, Sc, La to Lu. In this contribution, however, we shall loosely use

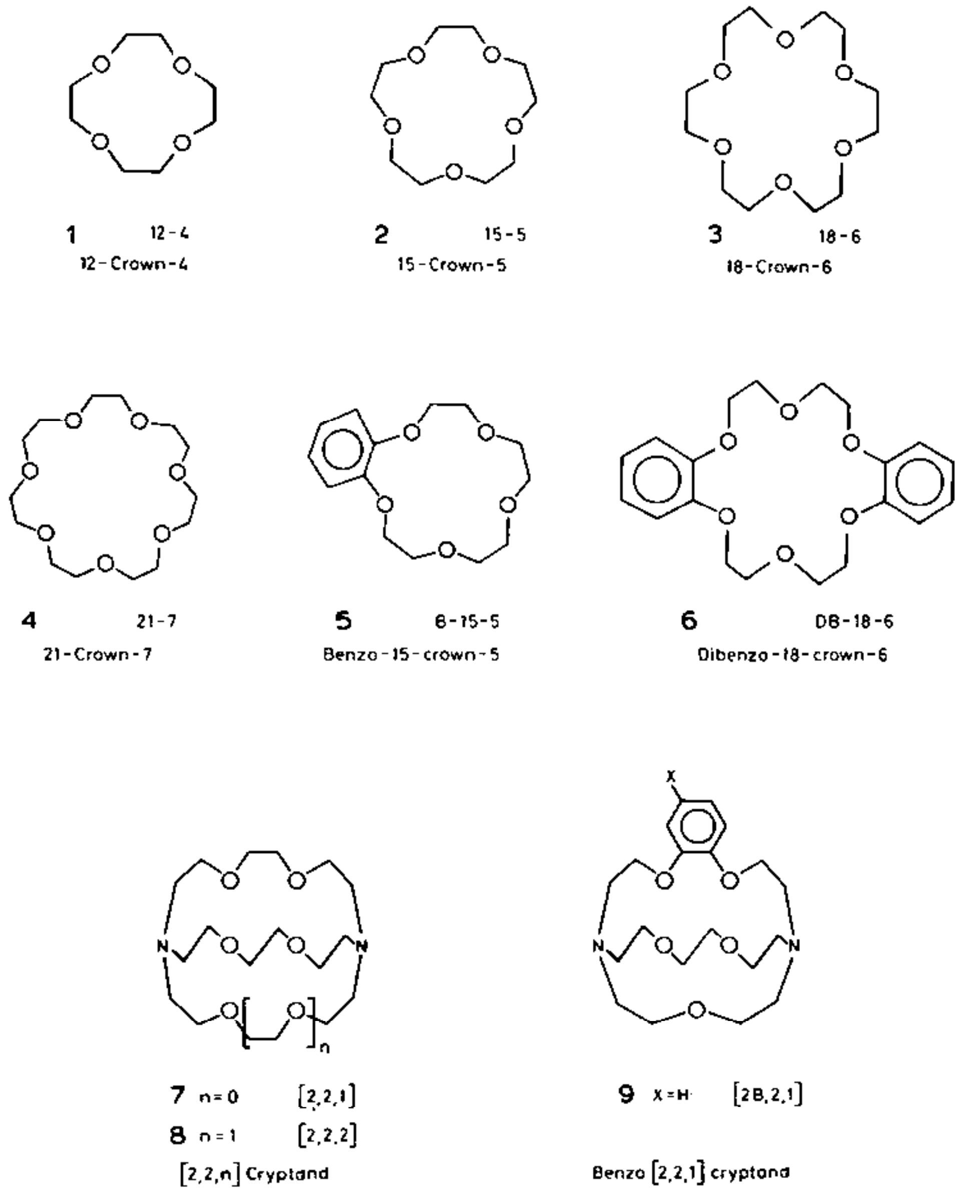


Fig. 1. Formulae and names of some crown ethers and cryptands.

these three terms as synonymous and represent them by the symbol Ln. Moreover, when the notation La–Lu is used, La–Lu except Pm is usually meant: promethium is indeed radioactive and very few chemists work with this element.

The ligands' nomenclature poses a more difficult problem: the IUPAC rules make the nomenclature of crown ethers and other macrocyclic ligands extremely involved. This explains why simplified systems have been proposed by the discoverers of these new ligand classes. These systems are, however, limited and cannot cope with the rapid expansion of the field. A new proposal for a systematic nomenclature of macrocyclic, polycyclic, and open-chain multidentate ligands was put forward in 1980 by Weber and Vögtle [1]; this nomenclature system allows an easier recognition of the ligand type and of other properties, such as its topology and the nature of its donor centres. The open-chain ligands are called podands, the monocyclic ligands are named coronands and the polycyclic spherical molecules keep their original cryptand designation. In order to differentiate the ligands from their metal complexes, the terms podates, coronates and cryptates are used. Table 1 illustrates the different nomenclature systems. To keep our text as comprehensible as possible, we shall adopt the simplified nomenclature system and notation (Fig. 1).

C. STOICHIOMETRY OF COMPLEXES WITH Ln(III) IONS

Rare earth ions form quite stable solvates with polar solvents so that their complexes with neutral ionophoric ligands must usually be isolated from non-aqueous solutions in solvents with low to moderate donor strength, e.g. acetone or acetonitrile. The metal : ligand ratio depends upon the nature of both the Ln(III) ion, the counterion X and the ligand L; in some instances too, different experimental conditions can lead to the isolation of complexes with different stoichiometries. Depending upon the relative size between the

TABLE 1

Nomenclature systems for multidentate open-chain and macrocyclic ligands

IUPAC designation	2,5,8,11,14,17-Hexaoxaoctadecane	1,4,7,10,13,16-Hexaoxacyclooctadecane	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[9.9.9]hexacosane
Short or trivial name	Pentaglyme	18-Crown-6	[2,2,2]Cryptand
Notation		[18]C-6, 18C6, 18-6	[2.2.2], [2,2,2], (2,2,2)
Weber and Vögtle nomenclature [1]	1,16-Dimethyl-$\langle O_6$-podand-6$\rangle$	18$\langle O_6$-coronand-6$\rangle$	$\langle N[O_2]_3N$-cryptand-8$\rangle$

ionic diameter of the metal ion and the cavity diameter of the ligand, the Ln(III) ion may either be located inside the cavity, i.e. encapsulated, or in the case of the coronands and cryptands, it can lie outside this cavity, being coordinated by a more or less folded ligand. In most cases, the cation remains exposed on the axial side(s) to further bonding by the counterions or by solvent molecules, which explains why some of the complexes are isolated as solvates. Alternatively, sandwich complexes are also found in which the metal ion is coordinated to two coronands. The reported metal to ligand ratios are 2 : 1, 3 : 2, 4 : 3, 1 : 1, and 1 : 2 and possibly 1 : 3 (in solution). In this section, the different stoichiometries obtained in the solid state are summarized and discussed according to the different ligand classes.

(i) Crown ether complexes

In his original work, Pedersen mentioned the formation, in solution, of 1 : 1 complexes between La(III) and/or Ce(III) and three coronands: dibenzo-18-crown-6, dicyclohexyl-18-crown-6, and dibenzo-24-crown-8 [7,8]. The first crystalline complexes between lanthanide ions and crown ethers were isolated simultaneously in Italy [9] and in the U.S.A. [10]. The Italian group reported 1 : 1 complexes, $Ln(NCS)_3 \cdot L$ and $Ln(NO_3)_3 \cdot L$ (Ln = La–Lu), with benzo-15-crown-5 (B-15-5) and dibenzo-18-crown-6 (DB-18-6) ethers; King and Heckley [11–13] found somewhat different results for the nitrate complexes: with B-15-5, unsolvated complexes form with La–Sm only, while stoichiometric compounds of DB-18-6 can only be obtained for La–Nd. This latter result was confirmed in our laboratories [14] and by Desreux [15]. In 1975, Olszanski and Melson isolated solvated scandium complexes with 1 : 2 and 3 : 2 metal : ligand ratios, $Sc(NCS)_3 \cdot (DB\text{-}18\text{-}6)_2 \cdot 3THF$ and $[ScCl_3]_3 \cdot (B\text{-}15\text{-}5)_2 \cdot H_2O$ [16,17]. Their crystal structures were not established; the authors suggested the first compound is probably not a sandwich complex, but rather contains an uncomplexed polyether in the lattice. The second compound is thought to have a complex formulation, $[ClSc(B\text{-}15\text{-}5)ClSc(B\text{-}15\text{-}5)Cl][ScCl_6] \cdot H_2O$, in which each Sc(III) in the cationic complex would lie in the plane of the polyether and have two axially coordinated chlorides; the resulting idealized coordination polyhedra, two pentagonal bipyramids, would then be linked together through an apical bridging chloride. Bünzli and Wessner later discovered that both a 1 : 1 and a 4 : 3 complex crystallize out of a solution containing neodymium nitrate and 18-crown-6 ether [18,19]; it turned out that the 4 : 3 compounds form a large class of complexes which are thermally more stable than the 1 : 1 complexes [18,30,42] and which contain a hexakis(nitrato) moiety, $[Ln(NO_3)_2 \cdot L]_3[Ln(NO_3)_6]$. Sandwich 1 : 2 complexes were found to form with small cyclic polyethers in the presence of weakly coordinating counteranions [20–23].

TABLE 2

Metal : ligand ratios found in isolated crown ether complexes

M : L	Counteranion (Ln(III) ions)
12-Crown-4 complexes	
1 : 2	ClO_4^- (La–Lu) [20,21,23]
1 : 1	NO_3^- (La–Lu) [24], Cl^- (Pr, Eu) [22,25,26], Br^- (Eu) [26], CF_3COO^- (La, Ce) [26], $CF_3SO_3^-$ (Pr) [26], X (La, Pr, Eu) [27] [a]
3 : 2	CF_3COO^- (Pr, Eu, Er) [26]
2 : 1	CF_3COO^- (Nd, Sm) [26]
O-Benzenediketone-14-crown-4 complex	
1 : 1	NO_3^- (Sc) [28]
15-Crown-5 complexes	
1 : 2 [b]	ClO_4^- (La–Eu) [23], PF_6^- (La–Gd) [26]
1 : 1	NO_3^- (La–Lu) [18,29,30], Cl^- (Pr, Eu) [21,26], Br^- (Eu) [26], NCS^- (Pr) [21], $CF_3SO_3^-$ (Pr) [22]
4 : 3	NO_3^- (Gd–Lu) [19,30,31]
2 : 1	CF_3COO^- (La–Eu) [22,26]
Benzo-15-crown-5 complexes	
1 : 1	NO_3^- (La–Lu) [10–12], Cl^- (Nd, Eu) [38], NCS^- (Sc, La–Lu) [9,16,17]
3 : 2	Cl^- (Sc) [9,16]
1,8-Naphtho-16-crown-5 complexes	
1 : 1	NO_3^- (La–Nd) [32,33], NCS^- (Y) [34]
O-Benzenediketone-17-crown-5 complex	
1 : 1	NO_3^- (Sc) [28]
Substituted-18-crown-5 complex	
1 : 1	NO_3^- (Sm) [35]
18-Crown-6 complexes	
1 : 1	ClO_4^- (Pr, Eu) [21,26], NO_3^- (La–Lu) [18,19,21,29,30] [36], Cl^- (Pr, Eu) [21,26], Br^- (Eu) [26], NCS^- (Pr) [21], $CF_3SO_3^-$ (Pr) [22], CF_3COO^- (La–Eu) [26]
4 : 3	NO_3^- (La–Lu) [18,19,30,31,36], Cl^- (Pr) [22], Br^- (Pr) [26]
2 : 1	CF_3COO^- (Y, Eu–Yb) [22,26]
Dicyclohexyl-18-crown-6 complexes	
1 : 1	NO_3^- (La–Eu, Ho) [37,38], Cl^- (La–Eu) [38], NCS^- (La–Eu) [38]
Dibenzo-18-crown-6 complexes	
1 : 2	NCS^- (Y) [17]
1 : 1	ClO_4^- (La–Eu, Dy–Er, Yb) [39,40], NO_3^- (La–Nd) [12,14], Cl^- (Sc) [17], NCS^- (Y) [41]
3 : 2	Cl^- (Eu) [26]

TABLE 2 (continued)

M : L	Counteranion (Ln(III) ions)
21-Crown-7 complexes	
1 : 1	NO_3^- (Er, Yb) [42]
4 : 3	NO_3^- (La–Nd, Eu, Tb–Lu) [42]
Dibenzo-30-crown-10 complexes	
1 : 1	ClO_4^- (La–Eu, Dy–Yb) [43]

[a] The anion is not given. [b] 1 : 1 : 1 complexes containing both 12-crown-4 and 15-crown-5 ethers have also been isolated (Ln = Pr–Gd, ClO_4^-) [21,23].

A list of all the complexes isolated in the solid state and for which either an elemental analysis or a structure is available, is given in Table 2; the solvation has been omitted for the sake of clarity. To rationalize the metal : ligand ratios, four main factors have to be considered: (i) the ionic diameter to cavity diameter ratio, D_i/D_e, (ii) the nature of the counteranion, (iii) the ligand flexibility, and (iv) the number of donor atoms of the ligand or, more correctly, the need for the lanthanide ions to achieve a high coordination number, usually between 8 and 12 [44]. The first criterion is difficult to define quantitatively since both diameters are difficult to estimate. The effective ionic diameters of the Ln(III) ions strongly depend on both the atomic number and the coordination number *CN*; a variation of approximately 0.4 Å is found between La(III) and Lu(III) and, for a given metal ion, between $CN = 8$ and $CN = 12$. The cavity diameter depends upon the conformation adopted by the ligand; it may be evaluated as follows [26] for unsubstituted crown ethers: 1.8–2.1 Å for 12-crown-4, 2.1–2.4 Å for 15-crown-5, 2.5–2.8 Å for 18-crown-6, and 3.4–4.2 Å for 21-crown-7 (Table 3). In the absence of an appreciable cation/anion interaction (ClO_4^-, PF_6^-), the following approximate rule may be proposed: if D_i/D_e is larger than one, sandwich complexes are isolated, whereas 1 : 1 complexes form if this ratio is smaller than one. On the other hand, with the strongly coordinating and bidentate nitrate ions, one observes the easy formation of 1 : 1 complexes when D_i/D_e is larger than one; if $D_i/D_e < 1$, the strong anion/cation interaction governs the metal : ligand ratio and 4 : 3 complexes are obtained with unsubstituted crown ethers, which contain a $[Ln(NO_3)_6]^{3-}$ moiety. These compounds can either be crystallized out of solutions (18-crown-6 and 21-crown-7 ethers) or be obtained by thermal decomposition of the corresponding 1 : 1 complexes (15-crown-5 and 18-crown-6 ethers). Halide and isothiocyanate complexes have been less systematically studied than nitrato and perchlorato compounds; from the data of Table 2, one sees, however, that these anions have more or less the same influence as the nitrate ion; in particular 4 : 3 complexes also form, which can be explained by the large stability of the hexakis(halogen) or hexakis(isothiocyanate) species. The trifluoromethanesulfonate ion (triflate) seems to induce the formation of 1 : 1 complexes only and, therefore, behaves differently from the other weakly coordinating anions; coordination of metal ions by triflate has been reported and induces only slight anion structural changes [45]. The stoichiometries of the complexes with the trifluoroacetates are not easy to explain, especially since the structures of the 3 : 2 and 2 : 1 complexes are not known; it seems there is no driving effect in the $Ln(CF_3COO)_3$/crown ether interaction so that the resulting metal : ligand ratio often depends upon the experimental conditions.

The influence of the ligand flexibility is illustrated in the case of the 18-crown-6 ether; 1 : 1 complexes between the dibenzo-substituted ligand and the lanthanide nitrates can only be prepared with the larger metal ions (La–Nd). Due to the stiffening of the polyether skeleton by benzo condensation, the ligand cannot adopt the folded conformation necessary to achieve the correct Ln–O distances. The non-isolation of 4 : 3 complexes with benzo-substituted polyethers is, however, somewhat surprising since in these complexes the ligand has an almost planar conformation.

(ii) Coronates

A few 1 : 1 complexes have been isolated with 14- and 15-membered nitrogen-containing ligands and with 18-membered nitrogen- or sulphur-containing macrocycles (Fig. 2). They are listed in Table 4. Lanthanide ions bind quite strongly to amine groups so that the replacement of two ether func-

TABLE 3

Selected ionic diameters D_i and ratios of D_i to the cavity diameters D_e of unsubstituted crown ethers versus the coordination number (*CN*) of the Ln(III) ions

Ln	D_i (Å)				D_i/D_e			
	$CN = 8$	$CN = 9$	$CN = 10$	$CN = 12$	$CN = 8$ [a]	$CN = 9$ [b]	$CN = 10$ [c]	$CN = 12$ [d]
La	2.32	2.43	2.54	2.72	1.1–1.3	1.0–1.2	1.0–1.1	0.8–0.9
Nd	2.22	2.33	2.45 [e]	2.59	1.1–1.2	1.0–1.1	0.9–1.1	0.8–0.9
Eu	2.13	2.24	2.36	2.50	1.0–1.2	0.9–1.1	0.9–1.0	0.8–0.9
Gd	2.11	2.21	2.33 [e]	2.48 [e]	1.0–1.2	0.9–1.1	0.9–1.0	0.8
Er	2.01	2.12	2.23	2.38 [e]	1.0–1.1	0.9–1.0	0.8–1.0	0.7–0.8
Lu	1.95	2.06	2.18 [e]	2.32 [e]	0.9–1.1	0.9–1.0	0.8–0.9	0.7–0.8

[a] $D_e = D_e$(12-crown-4). [b] D_e = mean value of D_e(12-crown-4) and D_e(15-crown-5). [c] $D_e = D_e$(15-crown-5). [d] $D_e = D_e$(18-crown-6). [e] Inter- or extrapolated from ionic radii vs. *CN* plots (R.D. Shannon, Acta Crystallogr. Sect. A, 32 (1976) 751) and/or from data for adjacent Ln(III) ions.

tions of the 18-crown-6 ligand by two NH groups results in the easy formation of unsolvated 1 : 1 complexes for the entire lanthanide series; no 4 : 3 compound forms. The larger Ln(III)/NH interaction, with respect to the Ln(III)/ether interaction, is exemplified by the isolation of a lanthanum complex with ligand **15** from an aqueous solution. On the other hand, thioether groups have a relatively low affinity for hard cations and complexes with ligands **16**, **17** and **18** are difficult to synthesize.

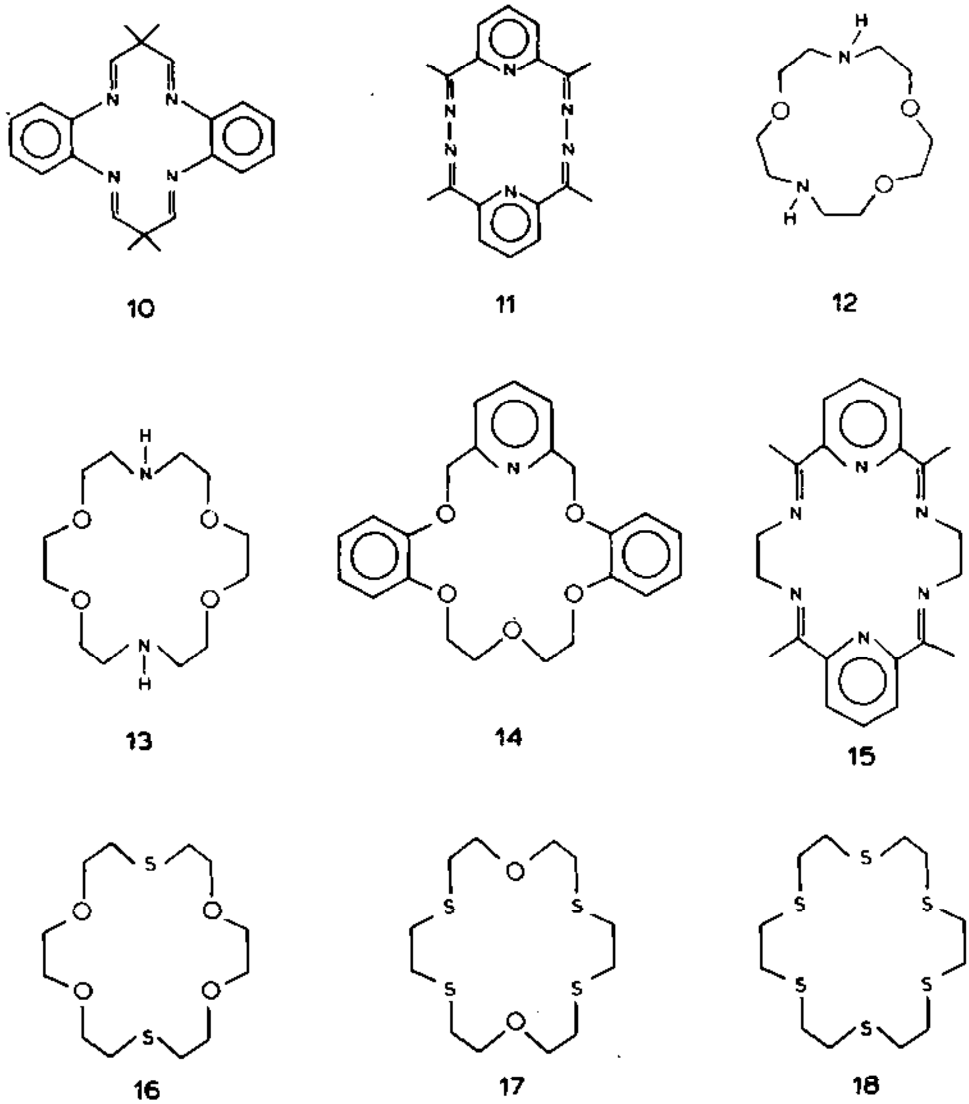


Fig. 2. Formulae of some coronands.

(iii) Cryptates

Complexes with macrobicyclic ligands are more stable than coronates. However, although lanthanide cryptates are highly kinetically inert towards dissociation in aqueous solutions and can therefore be studied in water, their formation constant is not large enough to allow their synthesis in such a polar solvent. On the contrary, the preparation of unsolvated 1 : 1 complexes requires strictly anhydrous conditions. Gansow and Triplett have developed such syntheses [55]; the hydrated lanthanide salt solutions in weakly coordinating organic solvents (e.g. acetonitrile) are treated by a dehydrating agent such as triethylorthoformate prior to complexation with equimolar quantities of cryptand. Crystallization of the complexes is induced by concentrating the solution and adding a non-polar solvent. The preparation of 1 : 1 cryptates is usually easier when a good coordinating counteranion is provided. Analytical determinations are only reported for $EuCl_3 \cdot (2,2,1)$ and $La(NO_3)_3 \cdot (2,2,2)$, but the synthetic procedures described by the authors are claimed to produce unsolvated 1 : 1 cryptates with all the lanthanide perchlorates, nitrates and chlorides. When the experimental conditions are not as well controlled, different compounds can form [56], including solvated 1 : 1 cryptates, 4 : 3, 3 : 2 and 2 : 1 complexes (Table 5). In particular, metal : ligand ratios larger than one tend to be obtained if a more polar solvent is used, methanol for instance. Until now, only (2,2,1), benzosubstituted-(2,2,1), and (2,2,2) cryptands have been found to form crystalline complexes with lanthanide ions. The cavities of these ligands indeed have radii that fit the Ln(III) ionic radii well: 0.8 and 1.15 Å for (2,2,1) and (2,2,2), respectively.

TABLE 4

Complexes isolated with coronands (refer to Fig. 2. for the numbering of the ligands; all the complexes have a 1 : 1 stoichiometry)

Ligand	Counteranion	
10	NCS^-	(Sc) [46]
11	ClO_4^-	(Sc, Tb–Lu) [47,48]
12	Cl^-	(La–Yb, except Ce) [49]
13	NO_3^-	(La–Lu) [15,50]
14	NO_3^-	(La, Ce, Pr) [51]
15	NO_3^-	(La, Ce) [52], ClO_4^- (La) [53a]
15a [a]	NO_3^-	(La) [53b]
16	ClO_4^-	(La–Eu, Ho, Yb) [54]
17	ClO_4^-	(Eu) [54]
18	ClO_4^-	(Sm, Eu, Yb) [54]

[a] Dibenzo-substituted ligand **15**.

(iv) Podates

Podates are usually less stable, and also more labile, than the corresponding coronates. For instance, the potassium complex with pentaglyme $CH_3O(CH_2CH_2O)_5CH_3$, the open-chain analogue of 18-crown-6 ether is 10^4 less stable than the coronate. Due to the larger cationic charge, this effect is much smaller for the trivalent lanthanides, and complexes with polyethylene glycols and polyethylene glycol dimethyl ethers are easily isolated (Table 6).

TABLE 5

Complexes isolated with cryptands (refer to Fig. 1. for formulae of the ligands)

Ligand	M : L ratio	Anion	Solvation	Ln(III) ions
(2,2,1)	1 : 1	Cl^-	None	La, Pr, Eu, Gd, Yb [57]; La–Gd [58]; La–Lu [55]; La, Eu [56]; La–Yb, except Ce [49]
		NO_3^-	None	La, Ce, Pr [59]; La–Sm [58], La–Lu [55]
		ClO_4^-	None	La [58]; La–Lu [55]
			$\cdot H_2O \cdot MeOH$	La, Pr, Nd, Sm [38]
	4 : 3	NO_3^-	None	Tb, Dy [58]
			$\cdot 2\ MeOH$	La [38,56]
	3 : 2	Cl^-	None	Dy [58]
		NO_3^-	None	Ho, Yb [58]
	2 : 1	NO_3^-	None	Eu [58]
			$\cdot H_2O \cdot 2\ MeOH$	Nd, Sm [38]
(2B,2,1) [a]	1 : 1	Cl^-	None	La–Lu [55]
		NO_3^-	None	La, Ce, Pr [59]; La–Lu [55]
		ClO_4^-	None	La–Lu [55]
(2B,2,1) [b]	1 : 1	NO_3^-	None	La, Pr, Eu [59,60]
(2B,2,1) [c]	1 : 1	NO_3^-	None	La, Ce, Eu [59]
(2,2,2)	1 : 1 [d]	Cl^-	None	La–Nd [58]; Sm, Eu [49]; La–Lu [55]
		NO_3^-	None	La–Pr [57–59]; La–Lu [55]
		ClO_4^-	None	La–Lu [55]
			$\cdot MeCN$	Pr, Nd, Eu [55]
			$\cdot MeCONH_2$	Er, Yb [61]
			$\cdot H_2O \cdot 0.5\ MeCN$	La, Ce, Sm, Eu, Dy [61]
	4 : 3	NO_3^-	None	La [56,62]
	3 : 2	Cl^-	None	Eu [56]
		NO_3^-	None	Sm, Eu, Gd [58]
	2 : 1	NO_3^-	None	Er, Yb, Lu [58]
			$\cdot H_2O$	Sm [63]
			$\cdot MeOH$	Pr [38]
			$\cdot H_2O \cdot MeOH$	Eu [38]

[a] $X = H$. [b] $X = NH_2$. [c] $X = NO_2$. [d] An organolanthanide cryptate complex with formula $LaCl_2(CPhe_3) \cdot (2,2,2)$ has also been reported [64].

The stoichiometry of the rare-earth nitrate complexes are similar to those observed for the coronates; in particular, 4 : 3 complexes are obtained with the 18-crown-6 and 21-crown-7 analogues. The podands are indeed known to adopt a conformation similar to that of the corresponding coronands [1].

Complexes have also been isolated with three other ionophores (Fig. 3): $[Ln(NO_3)_3]_3 \cdot (\mathbf{27})_2$ (Ln = Pr, Nd) [69], $Ln(ClO_4)_3 \cdot (\mathbf{28})_2 \cdot 2H_2O$ (Ln = La, Pr, Nd, Sm) [48], $Ln(ClO_4)_3 \cdot (\mathbf{28}) \cdot 4H_2O$ (Ln = Eu–Lu) [48] and $Eu(BF_4)_3 \cdot (\mathbf{29})_2$ [70].

D. STRUCTURAL PROPERTIES OF COMPLEXES WITH Ln(III) IONS

(i) *Crystal and molecular structure*

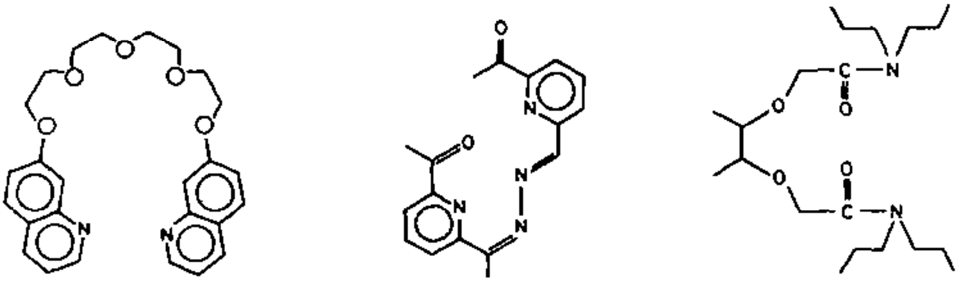
X-ray crystal structures have been determined for 18 coronates, 3 cryptates, and 5 podates of the lighter rare-earth elements. The ions most studied

TABLE 6

Lanthanide nitrate and chloride complexes isolated with various polyethylene glycols and polyethylene glycol dimethyl ethers

Ligand	M:L ratio	Ln(III) ions	
		NO_3^-	Cl^-
19 $HO(CH_2CH_2O)_2H$	1:2	Pr, Nd, Sm, Eu [65]	
20 $HO(CH_2CH_2O)_3H$	1:1	Y, La–Lu [65,66]	Y, La–Lu [67]
21 $HO(CH_2CH_2O)_4H$	1:1	Y, La–Lu [65,66]	Y, La–Lu [67]
22 $HO(CH_2CH_2O)_5H$	1:1	La–Lu [65,66]	Y, La–Lu [67]
23 $HO(CH_2CH_2O)_7H$	2:1	La, Ce [65,66]	
24 $H_3CO(CH_2CH_2O)_4CH_3$ [a]	1:1	La–Sm [65,66]	La–Ho [67]
25 $H_3CO(CH_2CH_2O)_5CH_3$ [b]	1:1	La [68]	La, Pr [67]
	4:3	La–Sm [65]; La–Eu [68]	
26 $H_3CO(CH_2CH_2O)_6CH_3$ [c]	4:3	La–Nd [65]	

[a] 15-Crown-5 analogue. [b] 18-Crown-6 analogue. [c] 21-Crown-7 analogue.



27 28 29

Fig. 3. Formulae of some podands.

are lanthanum (9 structures), neodymium (6), samarium (4), and europium (3); due to its strong coordinating properties which make the complexes less sensitive to moisture and easier to crystallize, nitrate was usually chosen as counterion. In many cases, the determinations were only carried out to unravel the coordination polyhedra of the metal ions and were therefore not refined completely, so that only 10 determinations are reported with a final R_F value lower than 5%. Partial disorders of the ligands and/or the counterions (perchlorates) sometimes prevented an accurate solution of the structure.

The results obtained for 1 : 1 complexes of lanthanide nitrates are displayed in Table 7. The 12-crown-4 and 15-crown-5 complexes have similar arrangements around the metal ion: the ligand is coordinated on one side while the three nitrate groups are bidentate and coordinated on the opposite side; the lanthanide ion is therefore not encapsulated into the polyether cavity, which is too small (Fig. 4). A similar structure is obtained with (1,8-naphtho)-16-crown-5 ether and, partially, with (2-methoxy-1,3-xylyl)-18-crown-5 ether; in the latter complex, however, unfavourable steric and/or conformational conditions result in the coordination of only three of the six ether functions of the ligand, including the prominent methoxyarylic oxygen atom. When the ligand cavity is larger, encapsulation is better achieved; in the case of 18-crown-6 and DC-18-crown-6 ethers, the ligands adopt a folded conformation in order to equalize the Ln–O distances; with the more rigid hexadentate nitrogen-donor macrocycle **15**, the lanthanum ion lies more or less at the centre of the cavity. In all the complexes with 18-membered coronands, the three nitrate groups are bidentate and two of them are coordinated on the less hindered side while the other is bonded on the opposite side. The two complexes $Ln(NO_3)_3 \cdot (18\text{-}6)$, Ln = La, Nd, constitute an isostructural pair, despite the significant difference in the ionic radii of the metal ions, 1.36 Å ($CN = 12$) for La(III), compared with 1.29 Å for Nd(III). In fact, the effects of steric crowding of the neodymium complex are absorbed by just two oxygen atoms in *trans* positions in the polyether [36]. The ligand flexibility is, however, limited, as illustrated by $Gd(NO_3)_3 \cdot (18\text{-}6) \cdot (H_2O)_3$, the crystal structure of which was also investigated [36]. In this compound, the ligand cannot absorb the steric crowding arising from the smaller ionic radius (1.25 Å, $CN = 12$) and it is not coordinated to the metal ion; the Gd(III) ions are bonded to three bidentate nitrates and three water molecules while the polyether is held in the lattice by weak hydrogen bonds from coordinated water molecules.

One noteworthy feature of these structures is the fact that the coordination number of the Ln(III) ions can easily be tuned by modifying the number of donor atoms of the coronand. In particular, few cases of undecacoordination were known before the publication of the structures of the

TABLE 7

Structural data for 1 : 1 complexes $Ln(NO_3)_3 \cdot L$ (L = coronand, podand)

Ligand	Ln	Space group [a]	Z [b]	CN [c]	Mean Ln–O distances (Å) [d]			R_F	Ref.
					Overall	O (ether)	O (NO_3^-)		
12-Crown-4	Eu	$M, P2_1/c$	4	10	2.49 (5)	2.52 (4)	2.47 (4)	0.079	25
15-Crown-5	La	$M, P2_1/c$	4	11	n.a.			0.051	71
	Ce	$M, P2_1/a$	4	11	2.65 (10)	2.57 (6)	2.72 (9)	0.073	72
	Pr	$M, P2_1/a$	4	11	2.62 (10)	2.55 (7)	2.69 (8)	0.080	73
	Nd	$M, P2_1/c$	4	11	n.a.			0.080	71
	Eu	$Tr, P3_2$	3	11	2.56 (9)	2.63 (6)	2.53 (8)	0.037	74
16-Crown-5 [f]	La	$M, P2_1/n$	4	11	2.63 (6)	2.67 (7)	2.60 (2)	0.108	32
18-Crown-5 [g]	Sm	$O, P2_1P2_1P2_1$	4	10	2.53 (9) [h]	2.61 (10)	2.51 (4)	0.102	35
18-Crown-6	La	$O, Pbca$	8	12	2.69 (5)	2.72 (6)	2.66 (1)	0.040	36
	Nd	$O, Pbca$	8	12	2.65 (7)	2.70 (10)	2.60 (2)	0.036	75
DC-18-6	La	M, Cc	4	12	n.a.	2.61–2.91	2.63–2.71	0.108	37
18-6(6N), **15**	La	$M, P2_1/c$	4	12		2.67–2.73 [i]	2.69–2.77	0.036	52
Podand **20**	Nd	$M, P2_1/n$	4	10	2.53 (3)	2.52 (3)	2.56 (2)	0.095	76
Podand **21**	La	$M, P2_1/n$	4	11	2.64 (7)	2.70 (4)	2.64 (8)	0.049	77
	Nd	$M, P2_1/n$	4	10	2.57 (6)	2.65 (4)	2.55 (2)	0.047	78
Podand **22**	Nd	$M, P2_1/n$	4	10	2.54 (5)	2.59 (3)	2.52 (3)	0.110	79

[a] The crystallographic system is also indicated: M = monoclinic, Tr = trigonal, O = orthorhombic. [b] Number of molecules in the unit cell. [c] Coordination number of the Ln(III) ion. [d] The estimated standard deviations are in parentheses; when mean distances are not available, minimum and maximum values are reported. [e] *In ref. 74 the 1 and 2 indices were inadvertently permuted; the correct space group is* $P3_2$. [f] 1,8-Naphtho-18-crown-5 ether. [g] 1-Methoxy-1,3-xylyl-18-crown-5 ether monohydrate. [h] Including the Sm–O(water) distance; only three O atoms from the ether are coordinated. *i* La–N distances.

complexes with 15-crown-5 polyether [71–74]; now, 11-coordination appears to be almost as common for Ln(III) ions as 10- or 12-coordination. The data of Table 7 also reveal that mean Ln–O bond distances are not much affected by the nature of the ligands; calculated ionic radii are in good agreement with values inter- or extrapolated from ionic radii versus coordination number plots [26]. Moreover, the coordination polyhedra around the metal ions tend to be as symmetrical as possible, taking into account the steric

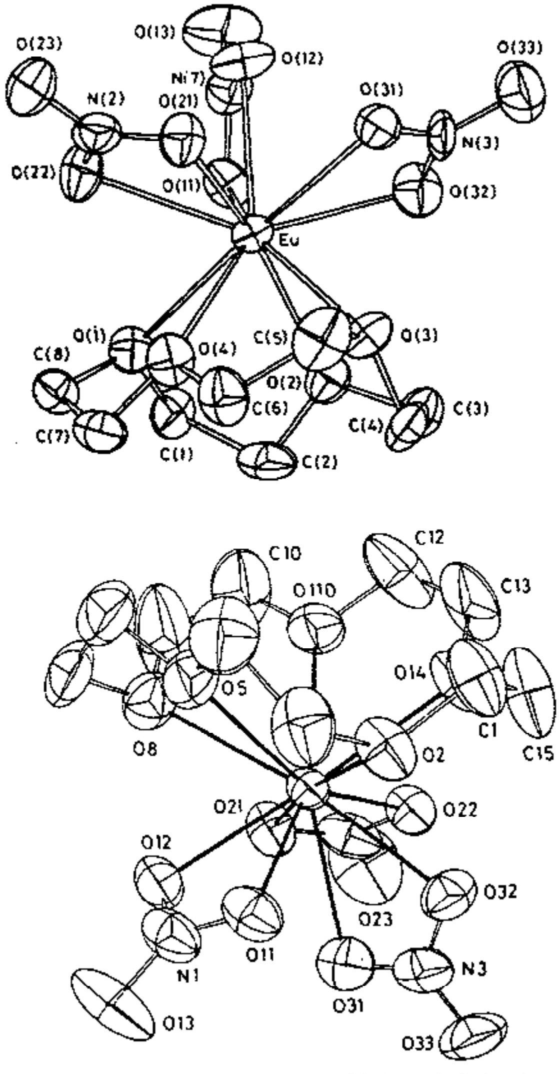


Fig. 4. Crystal structures of $Eu(NO_3)_3 \cdot (12\text{-}4)$ (top) and $Eu(NO_3)_3 \cdot (15\text{-}5)$ (bottom). Reprinted, with the permission of Elsevier-Sequoia SA (Lausanne) from ref. 25 and with the permission of the American Chemical Society from ref. 74, respectively.

constraint imposed by the macrocyclic ligand [80], despite a fairly large scatter of the Ln–O bond distances.

It is of considerable interest to compare the structures of the podates with those of the coronates even if the polyethylene glycols are not the exact analogues of the crown ethers. The podands adopt a ring-like configuration with all the oxygen atoms pointing towards the metal ion. The lanthanide ion and these oxygen atoms are more or less coplanar; two bidentate nitrates are coordinated axially above and below this plane while the third nitrate is either bonded to the Ln(III) ion through the open side of the ligand chain, or not bonded (ligand **22**). In the latter complex, the coordination number of the Nd(III) ion is lower by two units, compared with $Nd(NO_3)_3 \cdot$(18-6). A difference also appears between the lanthanum and the neodymium complexes of tetraethylene glycol: the nitrate group bonded through the open side of the ligand is bidentate in the former and monodentate in the latter complex; the Ln–O distances are: 2.60 and 2.79 Å for Ln = La [77], 2.53 and 2.91 Å for Ln = Nd [78]. This may again be explained by the larger steric crowding of the neodymium podate. The difference with the coronates arises from the podand which can wrap around the metal ion, contrary to the coronand.

Some of the structural data for perchlorato complexes are reported in Table 8. They all concern 1 : 1 complexes since in the pentahydrated samarium 1 : 2 complex one crown ether is not coordinated to the metal ion but held in the lattice through hydrogen bonding with three water molecules; a fourth water molecule is coordinated to Sm(III) and forms hydrogen bonds with one perchlorate ion and the fifth water molecule [81]. The coordination number of the Sm(III) ion is larger in the dibenzo-18-crown-6 complex and reaches 10 because of the perchlorate coordination: two ClO_4^- ions are monodentate and bonded on the less hindered side of the ligand while the third one is bidentate and lies on the opposite side; the samarium atom is 0.24 Å out of the mean plane defined by the oxygen atoms, which are not all strictly coplanar, two of them being displaced towards the bidentate ClO_4^- group [39]. Another crystal structure has been reported for a DB-18-crown-6 complex: $Y(NCS)_3 \cdot$(DB-18-6) [82]; the compound is orthorhombic (P_{nma}, $Z = 2$) and Y(III) is nonacoordinated, being bonded to the six oxygen atoms of the ligand and to the three nitrogen atoms of the NCS^- ions. In the lanthanum complex of the dithia-substituted 18-crown-6 ether, the four oxygen atoms of the ligand are coplanar and both the two sulphur atoms and the lanthanum ions are displaced out of this plane by 1.47, 1.57 and 0.5 Å, respectively [54]. Although encapsulation of the Eu(III) ion is realized in the (2,2,2) cryptate, the ligand is sufficiently flexible to allow the coordination of another moiety, namely a bidentate perchlorate group (Fig. 5). It is noteworthy that the mean Ln–O bondlength in this complex is equal to the

TABLE 8

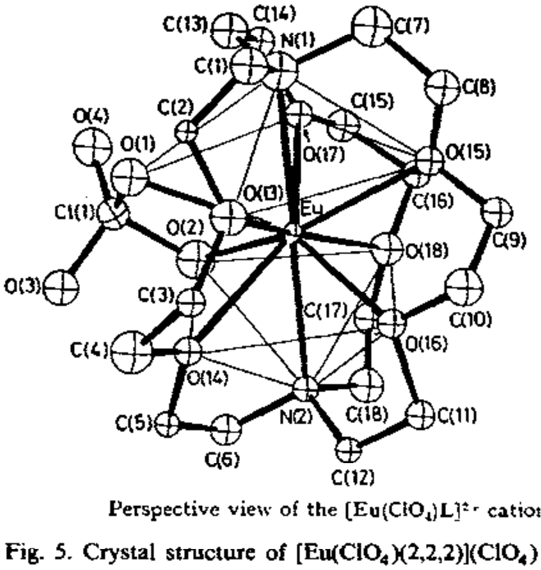
Structural data for perchlorato complexes $Ln(ClO_4)_3 \cdot (L)_n$ (L = coronand, cryptand)[a]

Complex formula	Space group	Z	CN	Complex species		R_F	Ref.
				Ln–O distance (Å) (mean)	Ln–O(ClO_4)[b] or Ln–X distance (Å)		
$Sm(ClO_4)_3 \cdot (15\text{-}5)_2 \cdot 5\,H_2O$	M, $P2_1/c$	4	9	$[Sm(15\text{-}5)(H_2O)_4]^{3+}$		0.067	81
				2.47 (5)	– –		
$Sm(ClO_4)_3 \cdot (DB\text{-}18\text{-}6)$	O, $Fdd2$	8	10	$[Sm(DB\text{-}18\text{-}6)(ClO_4)_3]$		0.047	39
				2.51 (8)	m, 2.36; b, 2.64		
$La(ClO_4)_3 \cdot (Dithia\text{-}18\text{-}6) \cdot H_2O$[c]	M, $P2_1/a$	4	10	$[La(L)(H_2O)(ClO_4)_2]^+$		0.038	54
				2.61 (8)	m, 2.49; b, 2.71 La–S: 3.04(1)		
$Eu(ClO_4)_3 \cdot (2,2,2) \cdot MeCN$	O, $P2_12_12_1$	4	10	$[Eu(L)(ClO_4)]^{3+}$		0.075	61
				2.54 (10)	b, 2.69 (3) Eu–N: 2.67 (4)		

[a] Key: see Table 7. [b] Monodentate, m; bidentate, b. [c] Ligand **16** (Fig. 2).

value found for $Eu(NO_3)_3 \cdot (15\text{-}5)$ (cf. Table 7).

More complicated structures have also been reported for 2 : 1 and 4 : 3 complexes, which contain very stable polynitrato moieties (Table 9). The structural similarity of the three 4 : 3 compounds is particularly striking. These complexes contain one $[Ln(NO_3)_6]^{3-}$ anion and three $[Ln(L)(NO_3)_2]^+$ cations with two different symmetries. In the neodymium cation with D_{2h} symmetry, the 10-coordinate metal ion lies in the centre of the polyether and is held into the cavity by one bidentate nitrate group on each side (Fig. 6). The crown ether is considerably flattened with respect to its usual conformation. The complex cation with a lower symmetry has a twofold multiplicity and it contains a disordered ligand oscillating between two positions. The replacement of the crown ether by the 18-podand-6 only results in somewhat lower symmetries. The essential features of the structure are retained, in particular the disorder of the ligand in the second dinitrato cation, which could not be resolved completely even with low temperature data [84]. The ligand wraps around the metal ion similarly to the pentaethylene glycol in $Nd(NO_3)_3 \cdot$ (**22**) but the presence of the two methyl group prevents the nitrate coordination through the open side of the ligand chain. In the lanthanum cryptate, the three dinitrato cations have the same general arrangement of ligands with two bidentate NO_3^- ions positioned in the gaps between two $CH_2CH_2(OCH_2CH_2)_2$ chains of the cryptand. Only one nitrate is coordinated in the samarium cryptate, probably because of the smaller ionic radius. The three structures reported for lanthanide cryptates demonstrate that the (2,2,2) ligand is flexible enough to include all the heteroatoms



Perspective view of the $[Eu(ClO_4)L]^{2+}$ cation

Fig. 5. Crystal structure of $[Eu(ClO_4)(2,2,2)](ClO_4)_2$. Reprinted, with permission from The Royal Society of Chemistry (London), from ref. 61.

TABLE 9

Structural data for 2:1 and 4:3 nitrato complexes [a]

Complex formula	Space group	Z	Complex species	Local symmetry	*CN*	Mean Ln–X dist. (Å)	R_F	Ref.
$[Nd(NO_3)_3]_4 \cdot (18\text{-}6)_3$	*M*, $C2/m$	2	$[Nd(NO_3)_6]^{3-}$	D_{2h}	12	Nd–O = 2.59(4)	0.061	83
			$[Nd(L)(NO_3)_2]^+$	D_{2h}	10	Nd–O = 2.52(8)		
			$[Nd(L)(NO_3)_2]^+$	C_S	10	Nd–O = 2.56(4) [b]		
$[La(NO_3)_3]_4 \cdot (\mathbf{25})_3$ [c]	*M*, $I2$	2	$[La(NO_3)_6]^{3-}$	C_2	12	La–O = 2.64(4)	0.061	84
			$[La(L)(NO_3)_2]^+$	C_2	10	La–O = 2.59(11)		
			$[La(L)(NO_3)_2]^+$	C_1	10	[d]		
$[La(NO_3)_3]_4 \cdot (2,2,2)_3 \cdot 2\,MeOH$	*M*, $C2/c$	4	$[La(NO_3)_6]^{3-}$	C_i	12	La–O = 2.61–2.71	0.037	62
			$[La(L)(NO_3)_2]^+$	C_2	12	La–O = 2.63–2.74		
			$[La(L)(NO_3)_2]^+$	C_1	12	La–O = 2.81–2.85		
$[Sm(NO_3)_3]_2 \cdot (2,2,2)$	*T*, $P\bar{1}$	2	$[Sm(NO_3)_5(H_2O)]^{2-}$	C_1	11	Sm–O = 2.55(6)	0.038	63
			$[Sm(L)(NO_3)]^{2+}$	C_1	10	Sm–O = 2.50(4)		
						Sm–N = 2.76(2)		

[a] Key: see Table 7. [b] For one position of the disordered crown ether. [c] Ligand **25** is the open-chain analogue of 18-crown-6 ether. [d] Not available because of disorder.

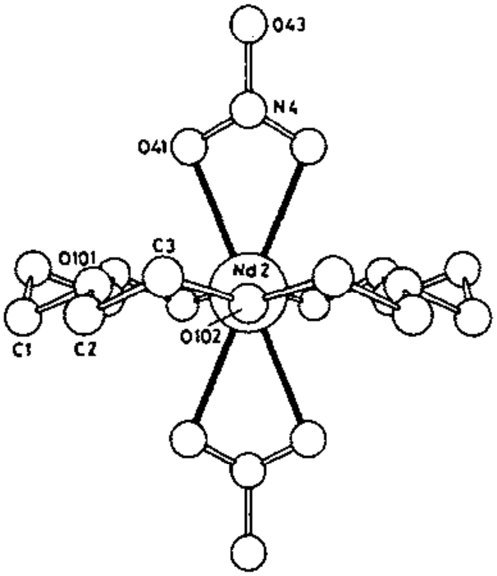


Fig. 6. Crystal structure of $[Nd(NO_3)_2(18\text{-}6)]^+$. Reprinted, with permission from Elsevier Sequoia SA (Lausanne), from ref. 83.

in the coordination polyhedron and to allow additional bonding of small ligands to fulfil the *CN* requirements of the metal ions (10–12).

(ii) Other structural information

No detailed structure determination has been published for a sandwich complex. However, preliminary X-ray crystal data indicate a tetragonal system with a I-centered unit cell for $Eu(ClO_4)_3 \cdot (15\text{-}5)_2$ and a detailed interpretation of the Eu(III) emission spectrum clearly points to the presence of an inversion centre at the metal site. The idealized coordination polyhedron would then be a pentagonal antiprism [26].

The structure of many other complexes may be related to the results discussed above by comparing both their X-ray powder diagrams and their vibrational spectra (Table 10). The $Ln(NO_3)_3 \cdot (12\text{-}4)$ complexes for Ln = Nd–Lu all have the same structure and, probably, the La–Pr complex too since the Eu-doped La complex presents an emission spectrum identical to that of the Eu complex [25]. Two isomorphous series were found for $Ln(NO_3)_3 \cdot (15\text{-}5)$ [19], a result which has since been confirmed by single-crystal X-ray structure determinations for La–Nd and Eu (cf. Table 7). A good test of the structure of 18-crown-6 complexes is the ring-breathing vibrational mode which occurs at ca. 880 cm^{-1}: this mode is IR-forbidden and Raman-allowed if the ligand has an inversion centre, which is the case in

TABLE 10

Isomorphous series in nitrato complexes with crown ethers and podands, as determined from X-ray powder patterns

Ligand	M:L	Isomorphous series
12-Crown-4	1:1	Nd–Lu [24]
15-Crown-5	1:1	La–Nd; Sm, Eu [19,30]
18-Crown-6	1:1	La–Nd [19,30]
	4:3	Ce–Eu, Ho [30]; Nd–Tb [36]; Dy–Lu [36]
21-Crown-7	1:1	Er, Yb [42]
	4:3	La–Eu; Tm–Lu; Gd, Tb, Ho [a] [42]
$HO(CH_2CH_2O)_3H$	1:1	La, Ce; Pr–Lu [65]
$HO(CH_2CH_2O)_4H$	1:1	La–Eu; Tb–Lu [65]
$HO(CH_2CH_2O)_5H$	1:1	La, Ce; Pr–Lu [65]
$H_3CO(CH_2CH_2O)_5CH_3$	4:3	Ce–Nd; Sm, Eu [68]

[a] From examination of IR spectra; these compounds do not give diffraction patterns.

4 : 3 complexes. These latter also present an IR-absorption band at 1275 cm^{-1} assigned to the hexanitrato moiety. A close examination of the vibrational spectra of the 1 : 1 complexes between the heavier lanthanide ions (Gd–Lu) and the 15-crown-5 or 18-crown-6 ethers reveals the presence of bands which may be assigned to both coordinated and uncomplexed ligand molecules [30]. That is, these compounds, which are often hydrated, may either be 4 : 3 complexes with an uncomplexed ligand molecule held in the lattice (cf. the structure of $Sm(ClO_4)_3 \cdot (15\text{-}5)_2 \cdot 5H_2O$) or have a structure similar to that of $Gd(NO_3)_3 \cdot (18\text{-}6) \cdot 3H_2O$.

The complexes with polyethylene glycols containing from four to six oxygen atoms usually form two isomorphous series. These are characterized by very similar IR spectra [65] so that structural differences are probably small, as exemplified by the data of Table 7 for the complexes between $HO(CH_2CH_2O)_4H$ and $Ln(NO_3)_3$, Ln = La, Nd.

E. THERMAL, MAGNETIC AND SPECTROSCOPIC PROPERTIES OF COMPLEXES WITH Ln(III) IONS

In this Section, only solid state data are reported and discussed.

(i) Thermoanalytical data

Thermoanalytical data (TG, DTG, DTA, DSC) have been reported for many crown ether complexes in order to study their thermal dissociation, decomposition and transformation.

Upon heating, the monohydrated isothiocyanate complexes with benzo-

15-crown-5 undergo the following changes [85]

$$\mathrm{Ln(NCS)_3 \cdot L \cdot H_2O \xrightarrow{I} Ln(NCS)_3 \cdot L + H_2O \xrightarrow{II} Ln(NCS)_3 + L \xrightarrow{III} decomp.}$$

Step I occurs between 110 and 150 °C and step II between 218 and 232 °C (under N_2 atmosphere) or between 170 and 224 °C (under reduced pressure). The ligand can be collected during step II and identified by its melting point and its IR spectrum. Appropriate treatment of the thermoanalytical curves allows the determination of both the "activation energy" E_a^* and the enthalpy change $\Delta_r H$ of the ligand dissociation; this latter ranges between 63 and 268 kJ $\mathrm{mol^{-1}}$ (71–184 kJ $\mathrm{mol^{-1}}$ under reduced pressure). Step III, which is exothermic contrary to steps I and II, is not well defined and sometimes starts before the ligand dissociation process is complete. The complexes with dibenzo-18-crown-6 ether $\mathrm{Ln(NCS)_3 \cdot L}$ (Ln = La–Lu) undergo a one-step ligand dissociation at 224–270 °C (N_2 atom) or 174–250 °C (reduced pressure) [86]; the corresponding yttrium compound dissociates at 285 °C [41]. For Ln = La–Lu, the $\Delta_r H$ ranges are 142–761 (N_2 atm) and 96–343 kJ $\mathrm{mol^{-1}}$ (reduced pressure) [86]. For both the 15- and the 18-membered ligands the E_a^* and $\Delta_r H$ plots vs. $1/r$, where r stands for the ionic radius, display a kind of periodicity between the lighter and the heavier cations.

Under the same experimental conditions, nitrato complexes with B-15-crown-5 and DB-18-crown-6 ethers undergo violent and rapid thermal decomposition [12,85–87], while $\mathrm{EuCl_3 \cdot (DB\text{-}18\text{-}6) \cdot H_2O}$ decomposes in two steps, at 220 and 450 °C, after loss of the water molecule [88].

As was briefly mentioned in Section C, some of the 4 : 3 complexes can be obtained by thermal decomposition of the 1 : 1 complexes. The following reactions are observed for the nitrato adducts

$$\mathrm{Ln(NO_3)_3 \cdot L \cdot }n\mathrm{H_2O \xrightarrow{I} Ln(NO_3)_3 \cdot L + }n\mathrm{H_2O}$$

$$\mathrm{4Ln(NO_3)_3 \cdot L \xrightarrow{II} Ln_4(NO_3)_{12} \cdot L_3 + L}$$

$$\mathrm{Ln_4(NO_3)_{12} \cdot L_3 \xrightarrow{III} dec.(LnONO_3, Ln_2O_3) + L}$$

$$\mathrm{Ln(NO_3)_3 \cdot L \xrightarrow{IV} dec.(LnONO_3, Ln_2O_3) + L}$$

The temperatures at which these various steps occur are reported in Table 11. They are not always reproducible and often depend upon the exact experimental conditions. The 12-crown-4 complexes are thermally stable up to ca. 300 °C and then decompose according to IV, in what seems to be a

TABLE 11

Temperatures at which the various thermolysis reactions of the $Ln(NO_3)_3 \cdot L \cdot nH_2O$ complexes start (°C) (refer to the scheme on p. 212 for reaction details)

Ligand	Ln	n	$T_{\rm I}$	$T_{\rm II}$	$T_{\rm III}$	$T_{\rm IV}$	Ref.
12-Crown-4	Nd	0				340	31
	Lu	0				280	31
15-Crown-5	La	0				260	30, 31
	Pr	0				240	30, 31
	Eu	0				170	30, 31
	Gd	4.2	100	160	250		30, 31
	Tb	2.0	100	110	260		30, 31
	Dy	4.6	90	90	260		30, 31
	Ho	5.1	90	90	270		30, 31
	Er	3.4	105	110	275		30, 31
	Yb	3.9	105	105	270		30, 31
16-Crown-5 [a]	La	0				235	33
	Ce	0				170	33
	Pr	0				220	33
	Nd	0				204	33
18-Crown-5	La	0		210	230	305	30, 31
				185	250	310	36
	Ce	0		180	230	250	36
	Pr	0		130	220	290	30, 31
				155	250	305	36
	Nd	0		110	180	270	30, 31
				160	250	310	36
	Sm	0				305	36
	Eu	0			300		36
		0.4	50	110	280		30, 31
	Gd	3	95	160	295		36
	Tb	3	100	160	395		36
		3.5	100	110	290		30, 31
	Dy	3	95	160	280		36
	Ho	3	100	150	270		36
	Er	3	105	155	260		36
		3.1	100	135	270		30, 31
	Tm	3	105	160	245		36
	Yb	3	110	170	240		36
		3.5	105	120	235		30, 31
	Lu	3	120	160	240		36
21-Crown-7	Er	0				150	42

[a] 1,8-Naphtho-16-crown-5 ether.

one-step exothermic reaction. The 15-crown-5 adducts of the lighter rare earths (Ln = La–Eu) exhibit the same thermal behaviour although their decomposition temperature is lower and strongly decreases with increasing atomic number. From Gd on, the thermolysis occurs according to reactions I, II and III; that is, intermediate compounds form with a metal : ligand ratio equal to 4 : 3, the stability range of which is approximately 55–100 °C. The 1 : 1 → 4 : 3 transformation is quantitative and the ligand can be recovered unchanged, as proven by its IR spectrum. Complexes with 1,8-naphtho-16-crown-5 ether (Ln = La–Nd) do not seem to transform into 4 : 3 compounds; their thermal decomposition starts at relatively low temperature and extends over a large temperature range [33]. All the 18-crown-6 complexes undergo the transformation into the thermally more stable 4 : 3 complexes; again, this reaction is quantitative and the ligand can be recovered unchanged. Generally speaking, DTA curves recorded simultaneously with TG curves reflect a quite small $\Delta_r H$ for reaction II, except in the case of $Ln(NO_3)_3 \cdot (18\text{-}6)$, Ln = La–Nd. For these complexes, $\Delta_r H$ was measured by a DSC technique which yielded the following, uncorrected endothermic values: +57.0 (Ln = La, temperature range: 207–233°C), 47.2 (Ce, 168–187 °C), 43.4 (Pr, 128–150 °C), and 37.6 kJ mol^{-1} (Nd, 101–129°C); no enthalpic effect could be measured for Ln = Eu [31]. This decrease may be partially explained by considering that the energetically unfavourable strain resulting from the ligand planar conformation (cf. Section D) will decrease if the metal ion radius becomes smaller. Other 1 : 1 → 4 : 3 transformations are observed for $PrCl_3 \cdot (18\text{-}6)$ at 210 °C ($\Delta_r H = +39.7$ kJ mol^{-1}, 204–219 °C) [31] and for $EuBr_3 \cdot (18\text{-}6)$ [26], but not for $PrCl_3 \cdot (12\text{-}4)$, $PrCl_3 \cdot (15\text{-}5)$, and $Pr(NCS)_3 \cdot (18\text{-}6)$ [26]. A study of the trifluoroacetate complexes reports that both the 1 : 1 and 3 : 2 complexes with 12-crown-4 ether are transformed into the more thermally stable 2 : 1 complexes [26].

The thermal properties of the crown ether complexes can be understood on the basis of their structure (Section D) and on consideration of their stoichiometry (Section C). In particular, the formation of 4 : 3 species, when $D_i/D_e < 1$, results in a less sterically crowded environment for the metal ion ($CN = 10$ and 12, vs. 12).

(ii) Magnetic moments

Magnetic susceptibilities have been measured for some crown ether complexes; the calculated paramagnetic moments, corrected for diamagnetic susceptibility contributions [19] are reported in Tables 12 and 13. The values for the nitrato complexes do not depend much upon the ligand nature; they are consistently lower than the free ion moments, by 6–9% for Ce–Nd, 2–3% for Sm, Eu, and less than 1% for Gd (as expected [90]). For Pr, these values are similar to the moment measured for the anhydrous trinitrate. A better evaluation of the ligand influence can be made from the data for complexes with various praseodymium salts (Table 13). In particular, the effect of the two ligands in the sandwich complex $Pr(ClO_4)_3 \cdot (15\text{-}5)_2$ results in a value similar to those found for the nitrato complexes. All these data point to a weak to moderately strong chemical bonding between the polyether and the Ln(III) ions.

(iii) Vibrational data

IR spectra are routinely presented and discussed for most of the isolated complexes; Raman spectra sometimes complement these data. Although quite informative, the vibrational spectra will not be reviewed in all details, since their interpretation is not always straightforward. Within an isomorphous series of complexes, these spectra are very similar, but for small systematic shifts, usually towards higher wavenumbers, when the atomic number increases. Therefore, they may be used along with X-ray powder

TABLE 12

Corrected magnetic moments in B.M. (1 B.M. $= 9.274 \times 10^{-24}$ Am^2) at 21 ± 1°C of the Ln(III) ions in various crown ether complexes with lanthanide nitrates [19]

Ln	μ_{calc} [89] [a]	(12-4)	(15-5)	(18-6)	(18-6)	(21-7)
		1:1	1:1	1:1	4:3	4:3
Ce	2.54	2.41	2.36	2.38	2.35	2.36
Pr [b]	3.62	3.42	3.33	3.33	3.35	3.36
Nd	3.68	3.37	3.34	3.37	3.32	3.35
Sm	1.65	1.66	1.58		1.59	
Eu	3.40	3.31	3.31		3.30	3.38
Gd	7.94	7.87	7.88		7.89	

[a] Calculated values for the free ions. [b] The value for anhydrous $Pr(NO_3)_3$ is 3.35 B.M.

TABLE 13

Corrected magnetic moments (B.M.) at 21 + 1° C of the Pr(III) ion in various anhydrous salts and crown ether complexes [19,21]

Complex	μ (B.M.)	Complex	μ (B.M.)
$PrCl_3$	3.57	$Pr(ClO_4)_3$	3.50
$PrCl_3 \cdot (15\text{-}5)$	3.49	$Pr(ClO_4)_3 \cdot (12\text{-}4)(15\text{-}5)$	3.46
$PrCl_3 \cdot (18\text{-}6)$	3.48	$Pr(ClO_4)_3 \cdot (15\text{-}5)_2$	3.37
$Pr(NCS)_3 \cdot 2\ EtOH$	3.64	$Pr(ClO_4)_3 \cdot (18\text{-}6)$	3.45
$Pr(NCS)_3 \cdot (15\text{-}5)$	3.48		
$Pr(NCS)_3 \cdot (18\text{-}6)$	3.41		

pattern diagrams to help determine such isomorphous series. The vibrational spectra also afford evidence for the complexation of both the counterion, the ligand and other (solvent) molecules.

The isothiocyanate group has been found either to be coordinated through the nitrogen atom or uncoordinated [9,16,19,21] as indicated by the positions of the $\nu(C\equiv N)$, $\nu(C–S)$, and $\delta(NCS)$ absorptions: 1990–2070, 780–820 and 475–490 cm^{-1}, respectively, for bonded NCS^- [19]. The perchlorate ion can be either ionic, with a T_d local symmetry, monodentate (C_{3v}), or bidentate (C_{2v}); these three forms have been observed by crystal structure determinations [39,54,61], which allow one to assign the observed vibrations. The main vibrational band of ClO_4^- occurs around 1100 cm^{-1} and is often obscured by interferences from the ligand vibrations, so that the best spectral region to distinguish between the various forms of the perchlorate ions is between 600 and 660 cm^{-1}. Ionic perchlorate presents one band at 620–630 cm^{-1}, monodentate ClO_4^- has two absorptions at 640–660 and 615–625 cm^{-1}, while the bidentate anion gives rise to three bands at 610–620, 625–635 and 640–660 cm^{-1} [91,92]. These frequencies are not perfectly unambiguous, but the observed data are in agreement with the structure determinations [39,54,61], especially if one takes into account that similarly coordinated anions may not be structurally exactly equivalent. The assignment of the nitrate vibrations is more difficult. In principle, ionic NO_3^-, with D_{3h} symmetry, possesses three IR-active vibrational modes at 1390 cm^{-1}, 830 cm^{-1} and 720 cm^{-1}. Upon coordination of the anion, the symmetry is lowered, the vibrations of higher and lower energies are split into two components and the fourth vibrational mode becomes IR-allowed, so that six IR absorptions should be observed, ν_5 and ν_3 at 710, 740 cm^{-1}, ν_6 at 820 cm^{-1}, ν_2 at 1030 cm^{-1}, ν_4 and ν_1 at 1300, 1500 cm^{-1}. The distinction between monodentate and bidentate nitrate groups is quite difficult and polarization measurements of the Raman emission bands only provide an unequivocal differentiation between the two types of nitrate [92]. In the absence of such data, which are difficult to determine for polycrystalline powders [93], two criteria have been proposed. One is the magnitude of the splittings $|\nu_1-\nu_4|$ and $|\nu_3-\nu_5|$ *; the former, which is easier to measure, despite possible interferences from $-CH_2-$ vibrational modes, amounts to ca. 120 cm^{-1} for monodentate nitrate ions and to ca. 180–200 cm^{-1} for bidentate NO_3^- [94]. The second criterion, proposed by many authors [94–96], is based on the number of components and on the splitting of the two nitrate combination bands in the 1700–1800 cm^{-1} region. The separation of these bands amounts to 5–25 cm^{-1} for monodentate nitrate groups and to 20–65

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* The assignments ν_1, ν_4 and ν_3, ν_5 are in the opposite order for mono- and bidentate nitrate groups [92].

cm^{-1} for bidentate anions. One should also realize that the analysis may be further complicated by the presence of non-equivalent nitrate groups and/or by bridging nitrato moieties. Most of the studies related to macrocyclic complexes of the lanthanide ions deduce the presence of bidentate nitrate groups with local C_{2v} symmetry [11,16,19]. Indeed, $|\nu_1-\nu_4|$ ranges between 180 and 220 cm^{-1} and the separation of the two combinations in the 1700–1800 cm^{-1} region usually ranges between 25 and 50 cm^{-1} [11,19], with a few exceptions for more complicated compounds (4:3 complexes for instance) having many non-equivalent nitrate groups. Both ionic and bidentate NO_3^- are found in cryptates [58,59]. An interesting test of the above-mentioned criteria is given by the podates with polyethylene glycols, since the crystal structure determinations revealed the presence of ionic, monodentate, and bidentate nitrate groups [76–79]. According to these determinations, two nitrate ions of $Nd(NO_3)_3 \cdot$ (**21**) are bidentate, with a C_{2v} local symmetry, and the third one is monodentate. The IR spectrum displays only two combination bands at 1745 and 1780 cm^{-1}, pointing to three equivalent and bidentate nitrate groups. In fact, a close inspection of the crystallographic data reveals that the third nitrate also possesses local C_{2v} symmetry and that the only difference with respect to the other nitrate ions lies in two quite different Nd–O distances (cf. Section D) [78]. Similarly, IR data do not provide evidence for the presence of one ionic nitrate in $Nd(NO_3)_3 \cdot$ (**22**); according to the crystal structure determination this ion is clearly uncoordinated, but its local symmetry is C_{2v}, one O–N–O angle being substantially smaller than the other two. In conclusion, care must be exercised when such criteria, based on IR data, are used to determine the nature of the nitrate ions in complexes. Regarding the complexes containing hexakis(nitrato) species, their IR spectrum usually displays a band at 1275 cm^{-1} which can be assigned to this species [30].

The ligand vibrations are also affected by the complexation and they may be used to assess whether coordination has occurred or not. The more characteristic vibrational modes are those involving the donor atoms, that is the ν(CCX) vibrations, with X = O, N, S. Ligands containing ether functions have two ν(CCO) modes, symmetrical and antisymmetrical; the latter is shifted towards lower wavenumbers upon complexation while $\nu(CCO)_s$, which is often masked by other interfering vibrations, is blue-shifted. Splitting of these vibrations often occurs so that an exact interpretation of the observed shifts is difficult. Generally speaking (Table 14), $\Delta\nu(CCO)_{as}$ ranges between -20 and -50 cm^{-1} for crown ether complexes; this shift is larger for cryptates, -40 to -60 cm^{-1}, but approximately the same for nitrogen-containing coronates (ligands **10** [46] and **13**) or for podates (ligand **27**). It is noteworthy that $\Delta\nu(CCO)_{as}$ is larger in $[Ln(NO_3)_2(18\text{-}6)]_3Ln(NO_3)_6$ than in $Ln(NO_3)_3 \cdot (18\text{-}6)$, e.g. -50 vs. -30 cm^{-1} for Ln = Pr [19], which reflects a larger Ln–O interaction in the cationic species. The splitting of the $\Delta\nu(CCO)_s$ vibration of $Ln(ClO_4)_3 \cdot (L)_2$ complexes has been interpreted as reflecting the presence of two non-equivalent polyethers in these sandwich complexes [23].

Finally, the vibrational spectra may give some information about the ligand conformational changes induced by complexation; these have been discussed for 12-crown-4 [24,27] and 18-crown-6 ethers [19,30] (cf. Section D).

(iv) Absorption and emission spectra

Electronic spectra are used to assess the strength of the Ln(III)–ligand interaction and to determine the geometry of the coordination polyhedron.

The forbidden *f–f* transitions are weak and difficult to measure by reflectance methods: they seem to be little affected when the Ln(III) ion is complexed by crown ethers [11,36]. Benzo-substituted crown ethers **5** and **6** exhibit two benzenoid absorptions at 227–228 and 275–276 nm, which are slightly shifted and modified upon complexation [38]. Similar effects are observed for complexes with N-containing coronands [47,48,53]. Ciampolini et al. [39,43,54,61] have studied the ligand-to-metal charge transfer bands for the complexes of Sm, Eu and Yb ions with various coronands and cryptands (Table 15) and have calculated the optical electronegativity [97] of these ligands.

Emission spectra are very sensitive to changes in the first coordination sphere and many studies of europium and terbium complexes are reported. An investigation of the photophysical properties of benzo-15-crown-5 com-

TABLE 14

Observed shifts (cm^{-1}) of the $\nu(CCO)$ vibrations upon complexation ($\nu_{compl.} - \nu_{uncompl.}$)

Ligand	$\Delta\nu(CCO)_{sym}$	$\Delta\nu(CCO)_{asym}$	Ref.
12-Crown-4	+9 to +16	−25 to −35 [a]	19, 21, 23
15-Crown-5	+15 to +25	−18 to −43	19, 30
B-15-Crown-5		−20 to −51 [b]	11, 12
18-Crown-6		−23 to −33 [c]	19, 30, 36
DB-18-Crown-6		−20 to −40	11, 12
Ligand **13**		−35	50
21-Crown-7	+10 to +22	−15 to −25	19, 42
(2,2,1), (2,2,2)		−40 to −60	58, 59, 64
Ligand **27**		−25 to −35	69

[a] The band comprises many components; the assignment is not unambiguous. [b] −1 to −20 cm^{-1} for Sc complexes [16,17]. [c] −40 cm^{-1} in 4:3 complexes [19,30].

plexes with various terbium salts reveals that the fluorescence of the ligand at 302 nm is quenched and accompanied by an emission from the Tb(III) $^5D_4$ excited level; this emission is only weakly observed when the metal ion is directly excited at 77 K through the $^5L_{10} \leftarrow {}^7F_6$ transition. The phosphorescence of the polyether occurs at 415 and 440 nm and it is not quenched in the complexes, which indicates that the energy transfer from the ligand to the metal ion originates in the singlet state. A similar situation is observed for europium complexes, but the fluorescence quenching is less effective [98]. The room-temperature emission spectra of $Eu(NCS)_3 \cdot (DB\text{-}15\text{-}5) \cdot H_2O$ and $Eu(NO_3)_3 \cdot (TMU)_3$, where TMU stands for *N,N,N′,N′*-tetramethylurea, are very similar and were interpreted as arising from a nine-coordinate species [87].

The transitions from the Eu(III) $^5D_0$ level to the ^7F_J manifold are particularly useful in determining the site symmetry of the metal ion: the splitting of the *J*-levels in a crystal field may easily be determined and the application of the selection rules allows a prediction of the number of symmetry-allowed transitions for a given symmetry and *J* value. Moreover, since both the $^5D_0$ and $^7F_0$ levels cannot be split by crystal-field effects, the number of components of the transition between them indicates the minimum number of differently coordinated Eu species present in the compound. However, care must be exercised when performing such analyses since the intensity of all, in principle forbidden, transitions may vary considerably upon small perturbations of the Eu(III) environment [99]. Moreover, vibronic transitions may further complicate the spectrum. To be conclusive these studies should be performed at low temperature (77 K or better, 4 K), with use of selective excitations by laser lines and the emission spectra should be recorded at high resolution (< 0.1 nm) since the crystal field splittings are sometimes quite small. Medium- to low-resolution spectra usually lead to the observation of too few transitions and to a wrong, too high site symmetry. Finally,

TABLE 15

Energies of the ligand-to-metal charge transfer transitions (E_{CT}, cm^{-1}, from reflectance spectra) for various 1:1 perchlorato complexes of Sm(III), Eu(III) and Yb(III)

Ligand	Optical electroneg. [a]	E_{CT}(Sm)	E_{CT}(Eu)	E_{CT}(Yb)	Ref.
18-Crown-6	3.2		39600		54
DB-18-Crown-6	2.7	32100	22500	27400	39
Ligand **16**	2.8	37200	28300	30700	54
DB-30-Crown-10	2.7	32800	24100	27000	43
(2,2,2)	3.0	41300 [b]	32100	38100 [b]	61

[a] Ligand values calculated from these data. [b] In CH_3CN solution.

whenever possible doped samples (1–2%) should be investigated in order to avoid complications arising from energy transfer from one metal ion to the other; this in turn requires that either the La, Gd or Lu complex be isostructural with the compound investigated. To illustrate this point, we shall review two studies, on $Eu(NO_3)_3 \cdot (15\text{-}5)$ [74] and $Eu(NO_3)_3 \cdot (12\text{-}4)$ [25], which reported both the X-ray crystal structure and the high resolution emission spectrum of these complexes.

In the 15-crown-5 complex, the Eu(III) ion is 11-coordinated; it lies on a site without symmetry and the coordination polyhedron is a 2:3:5:1 polytope. This latter may, however, be described as a distorted monocapped pentagonal antiprism (C_{5v} symmetry). At first sight this pentagonal symmetry seems to be reflected in the emission spectrum, which displays a moderately intense $^5D_0 \rightarrow {}^7F_0$ transition (symmetry-allowed in C_{nv} point groups [100]) and a two-line $^5D_0 \rightarrow {}^7F_1$ transition. Under high resolution, one of these components appears clearly as split into two lines. The splitting amounts to only 11 cm^{-1} and requires a 0.2 nm resolution to be observed. Henceforth, the $^7F_1$ level is split into three components, consistent with the low symmetry mentioned above. This unravels another feature of the Eu(III) ion emission spectra. Due to the high coordination numbers of this ion, and to weak directional effects in its chemical bonding, the actual coordination polyhedra often appear to arise from small distortions of more symmetrical, ideal polytopes and this "pseudo-symmetry" is then reflected in the crystal field splitting patterns [80,99]. This may lead to erroneous interpretations if the spectra are not recorded under high resolution. The second interesting feature in the emission spectrum of $Eu(NO_3)_3 \cdot (15\text{-}5)$ is the presence of six to seven components for the $^5D_0 \rightarrow {}^7F_2$ transition in addition to some weak vibronic transitions. This problem was solved by doping the lanthanum complex with 1.4% Eu *: the resulting spectrum displays five bands and is quite similar to the spectrum of the Eu complex, except for two bands which are no longer present. The authors interpreted these two components as arising from "luminescent traps" which come from crystal defects or from slight impurities in the crystal.

In the 12-crown-4 complex, the Eu(III) ion lies on a site without symmetry. This site is unique as indicated both by the crystallographic and the emission data (one sharp $^5D_0 \rightarrow {}^7F_0$ transition). However, the $^5D_0 \rightarrow {}^7F_2$ transition consists of 23 lines, 14 of which may be assigned to vibronic transitions. The spectrum of the isostructural lutetium complex doped with 1.5% Eu displays the same spectrum, so that the above explanation cannot be invoked. The authors propose that the extraneous splittings (2–5 cm^{-1}) may

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* The La and Eu complexes are not strictly isostructural (Table 10), but the Gd complex could not be crystallized [30].

arise from Fermi-type resonances between the electronic ^7F_J sublevels and vibrational states.

The structure of $[Eu(NO_3)_2(18\text{-}6)]_3Eu(NO_3)_6$ has been probed by high resolution, laser-excited emission and excitation spectroscopies at 77 and 4 K. Preliminary results include the assignment of the two main components of the $^5D_0 \rightarrow {}^7F_0$ transition, themselves split into four to five lines each [101]. It is concluded that this complex has a structure which resembles the structure of the neodymium complex, with additional distortions arising from different conformations of the crown ether. The corresponding complex with 21-crown-7 also displays an emission spectrum with two main $^5D_0 \rightarrow {}^7F_0$ components [42]. The site symmetry of the Eu(III) ion has also been probed in $EuCl_3 \cdot (DC\text{-}18\text{-}6) \cdot H_2O$, $EuCl_3 \cdot (B\text{-}15\text{-}5) \cdot 4H_2O$, $Eu(NCS)_3 \cdot (DC\text{-}18\text{-}6)$, $Eu(NO_3)_3 \cdot (DC\text{-}18\text{-}6)$, $Eu(ClO_4)_3 \cdot (2,2,2)$ [38].

Horrocks and Sudnik have developed an approach to estimate the number of water molecules coordinated onto the metal ion in Eu(III) complexes [102]. This number is equal to $q = 1.05\ [k(H_2O) - k(D_2O)]$, where the k terms are the rate constants for non-radiative deactivation via coupling with OH and OD oscillators. The k values are determined by lifetime measurements. This method yields $q = 1.7$ for solid $EuCl_3 \cdot (2,2,1) \cdot 2H_2O$ and $q = 2.2$ for frozen aqueous solutions (77 K) of this cryptate [103]. A similar study performed on $Eu(BF_4)_3 \cdot (\mathbf{29})_2$ indicates that only one water molecule can coordinate ($q = 0.9 \pm 0.4$). The detailed analysis of the laser-excited luminescence spectrum is consistent with a metal site symmetry lower than D_{2h}. The authors conclude that the Eu(III) ion is coordinated in a fashion similar to that of the analogous Ca(II) complex, $CaCl_2 \cdot (\mathbf{29})_2$ with Ca(II) in a site of D_2 symmetry [70].

(v) Other spectroscopic properties

A Mössbauer investigation has been reported for $Eu(NCS)_3 \cdot (DB\text{-}18\text{-}6)$ and $Eu(NCS)_3 \cdot (B\text{-}15\text{-}5) \cdot H_2O$ [87]. A small positive isomeric shift, with respect to EuF_3, is found for both complexes, meaning that the *s*-electron density at the Eu nucleus is larger in the complexes.

F. SOLUTION STUDIES OF COMPLEXES WITH Ln(III) IONS

(i) Complex formation as observed by electronic spectra

Evidence for an interaction in solution between Ln(III) ions and benzo-substituted crown ethers has been reported by many authors. The absorption of the benzene ring at ca. 275 nm is indeed modified upon complexation: two bands corresponding to both complexed and uncomplexed ligand are usually observed, indicating incomplete coordination. For instance, Pedersen

[8] mentions the appearance of an additional absorption at slightly longer wavelength for $La(OAc)_3$ solutions in methanol containing the DB-18-6 ether; no modification of the absorption spectrum is, however, observed for solutions containing the DB-24-8 polyether. A similar hypsochromic shift (< 5 nm) is found for $Ln(NCS)_3$ solutions in CH_3CN (Ln = Sc, Ce, Nd, Sm, Gd, Tb [9,16]) and $Ln(NO_3)_3$ solutions in acetone [11] containing the B-15-5 and DB-18-6 crown ethers. On the other hand, ethanolic solutions of $LnX_3 \cdot (\text{B-15-5})$, with Ln = Eu, Gd, Tb and $X = NO_3^-$, NCS^-, ClO_4^-, do not show a red shift of the benzenoid band, which has the same absorption coefficient as in the uncomplexed ligand solutions [98]. However, the ligand fluorescence is quenched in Tb(III) complexes: the quantum yield of this fluorescence decreases by 23%, 30% and 15%, for $X = NO_3^-$, NCS^- and ClO_4^-, respectively. Simultaneously, a metal-ion sensitized emission occurs, with a quantum yield equal to 0.4×10^{-3}, 0.3×10^{-3}, and 2.2×10^{-3} for $X = NO_3^-$, NCS^-, and ClO_4^-, respectively. Such an emission, which is caused by an energy transfer from the singlet state of the ligand to the metal ion only occurs weakly in Eu(III) complexes [98].

Ciampolini et al. have studied the ligand-to-metal charge transfer bands of $Ln(ClO_4)_3$ solutions in CH_3CN containing the DB-18-6 and the DB-30-10 ethers and found that they reflect partial formation of the complexes [39,43].

The *f–f* transitions are also affected by complexation; their energies are only slightly changed, but their oscillator strength may vary up to 30%, cf. $LnX_3 \cdot L$ in $CH_3CN/EtOH$ mixtures, with Ln = Nd, Ho, $X = NO_3^-$, NCS^-, Cl^-, and ClO_4^-, and L = B-15-5, DB-18-6, DC-18-6, (2,2,1), and (2,2,2) [38]. The luminescence spectra of $EuCl_3$ in alcohol or benzene are modified when DB-18-crown-6 is added, which points to the formation of a complex in these solutions [104].

The $^1D_2 \leftarrow {}^3H_4$ transition of the Pr(III) ion could be used to demonstrate the formation of a 1 : 1 complex between $Pr(NO_3)_3$ and 18-crown-6 in anhydrous acetonitrile [30]. When 4 : 3 complexes are dissolved, the resulting solution has a molar conductance larger than that of solutions with the corresponding 1 : 1 complexes. In view of the structure of these complexes, this can be explained by the presence of the following equilibria in solution [30,36]

$$3[LnX_2 \cdot (L)]^+ + LnX_6^{3-} \leftrightarrows LnX_3 \cdot (L) + LnX_5^{2-} \\ + 2[LnX_2 \cdot (L)]^+ \leftrightarrows 3LnX_3 \cdot (L) + LnX_3$$

For $X = NO_3^-$, it has been noticed that hexakis(nitrato) species dissociate completely in solution [105]. Moreover, the high resolution excitation spectra of solutions containing $Eu(NO_3)_3$ and various concentrations of 21-crown-7 in CH_3CN confirm this scheme: three $^5D_0 \rightarrow {}^7F_0$ transitions are observed at

579.4, 578.8 and 578.4 nm, which correspond to the presence of three different Eu-containing species. Since the intensity of the last decreases upon addition of ligand, it is assigned to $Eu(NO_3)_3$ [42].

Electronic spectra have also been reported for various coronates, with ligands **10** [46], **11** [47,48], **14** [51], **15** [53a] and **16** [54], for podates [104,106] as well as for cryptates [58,59,61,107]. In the case of oligooxaalkanes, both 1 : 1 and 1 : 2 complexes were reported for $LnCl_3$, $Ln(NO_3)_3$ (Ln = La, Nd, Eu, Er, Lu) and derivatives of mono- and diethyleneglycols [106]. A study of the photophysical properties of $EuCl_3 \cdot (2,2,1)$ in water shows that the Eu(III) ion is encapsulated into the ligand cavity and lies on a site of low symmetry (C_{2v}). The cryptand only partially shields the Eu(III) ion against further interaction with solvent molecules: the method described above (Section E) to estimate the number of coordinated water molecules yields $q = 3.2$, which means that three water molecules are bonded through the holes between the aliphatic chain of the (2,2,1) cryptand [103].

(ii) Stability constants

Key information is provided by the stability constants of the complexes and their associated thermodynamic parameters, which allow an understanding of the leading effects in the Ln–macrocycle interaction. The log β_n have been measured for many complexes by use of different techniques, potentiometry, calorimetry, electronic and NMR spectroscopies; we shall discuss them first and correlate these values with the observations made in Section C upon the stoichiometry of the isolated adducts.

Table 16 lists the results of a systematic study by Desreux et al. [108–110] on the complexes with various substituted and unsubstituted crown ethers. With small polyethers, 12-crown-4 and 15-crown-5, both 1 : 1 and 1 : 2 complexes form in propylene carbonate. The stability constants for the former are more or less constant over the lanthanide series. When Z increases, the cation charge density increases, bringing about stronger electrostatic interactions with both the ligand and the solvent. Since the complexation is accompanied by partial desolvation of the Ln(III) ion, it appears that the favourable larger interaction with the ligand is compensated by a more difficult desolvation, leading to almost no variation in log β_1. On the other hand, the stability of the 1 : 2 complexes is much larger than that of the 1 : 1 adducts and decreases with increasing Z for the two ligands, an effect which can be accounted for by structural considerations. The two polyethers are brought closer together when the ionic radius decreases and steric interactions are likely to become important at the end of the rare-earth series. It is noteworthy that both ligands show a complexation trend which is opposite to the one exhibited by non-cyclic ligands, but which is typical of

TABLE 16

Stability constants (log β_n) at 25 °C and $\mu = 0.1$ for complexes between $Ln(CF_3SO_3)_3$ and various crown ethers in anhydrous propylene carbonate, as determined by a competitive potentiometric method with respect to Pb(II) or Tl(I)

Ln	12-Crown-4 [a]		15-Crown-5 [a]		Subst.-15-5 [a,b]	Subst.-18-6 [c,d]	DB-30-Crown-10 [a]
	1:1	1:2	1:1	1:2	1:1	1:1	1:1
La	5.00±0.12	6.98±0.15	6.49±0.14	10.18±0.11	3.26±0.04 [e]	5.14±0.05	4.29±0.04
Ce					3.62±0.04	4.95±0.03	4.10±0.03
Pr	5.27±0.08	7.09±0.10	6.22 [f]		3.60±0.08	4.79±0.05	4.12±0.04
Nd	5.19±0.09	6.74±0.12	6.55±0.13	8.65±0.04	3.75±0.04	4.58±0.06	4.10±0.05
Sm	5.17±0.10	6.76±0.14	6.11 [f]		3.45±0.04	4.00±0.04	3.75±0.03
Tb	5.15±0.13	6.09±0.20	5.96±0.14	7.66±0.19	3.02±0.05	3.62±0.13	3.53±0.04
Gd					2.85±0.05	3.50±0.08	4.07±0.06
Dy			5.66 [f]		2.90±0.12	3.40±0.07	
Ho					2.80±0.08	3.29±0.15	
Er			5.53 [f]		2.82±0.07	3.16±0.05	4.48±0.05
Tm					2.81±0.05	2.94±0.09	
Yb	4.94±0.09	[g]	5.53 [f]		2.80±0.10	2.57±0.09	4.76±0.04
Lu	5.00±0.11	[g]	5.83±0.16	7.89±0.22	2.80±0.06	2.51±0.06	4.80±0.05

[a] Refs. 108, 109. [b] 4-tert-Butylbenzo-15-crown-5. [c] Ref. 110. [d] 4,4′(5′)-Di-tert-butylbenzo-18-crown-6. [e] Log $\beta_2 = 5.91 \pm 0.08$. [f] At $\mu = 0.2$, from [49], ±0.05 to ±0.10. [g] No significant concentration of 1:2 complexes.

larger macrocycles. Both 1 : 1 and 1 : 2 complexes with 15-crown-5 are one to four orders of magnitude more stable than the corresponding complexes with 12-crown-4. This difference is due to the greater number of donor atoms, which allows better fulfillment of the coordination number requirements of the Ln(III) ions. In addition, the better flexibility of 15-crown-5 could also partly account for the greater stability of its complexes. The log β_n values are consistent with the findings that (i) a 1 : 1 complex cannot be isolated with 15-crown-5, even in the presence of a large excess of $Pr(ClO_4)_3$ [21] and (ii) mixed complexes $Ln(ClO_4)_3 \cdot (12\text{-}4) \cdot (15\text{-}5)$ do not crystallize for Ln = La and Ce [23].

The presence of a phenyl substituent on the 15-membered cycle causes a large decrease of the stability constants, by approximately three orders of magnitude. Moreover, 1 : 2 complexes do not form, except with La(III). This lower stability may be associated with the electron-withdrawing effect of the phenyl ring, resulting in a lower basicity of the oxygen atoms. In addition, the substitution induces a larger rigidity and a small decrease in the cavity size. The log β_1 values exhibit a maximum for the Nd(III) ion, followed by a decrease; from Tb(III) on, they remain constant. This behaviour reflects the delicate balance prevailing between the favourable and unfavourable factors influencing the complexation process. The large stability difference between the Sm(III) and Eu(III) complexes may explain why King and Heckley could isolate $Ln(NO_3)_3 \cdot (B\text{-}15\text{-}5)$ complexes for Ln = La–Sm only. The log β_1 values for the substituted DB-18-crown-6 ligand decrease with increasing atomic number. The La(III)/Lu(III) selectivity, $\Delta \log \beta_1 = 2.6$, is comparable to the one achieved in water with, for instance, isobutyric acid, but is smaller than that exhibited by EDTA. Again, the data reveal a large decrease in stability between Nd(III), Sm(III) and Eu(III) complexes, which may be related to the failure to obtain crystalline $Ln(NO_3)_3 \cdot (DB\text{-}18\text{-}6)$ complexes [11–16]. The complexes with substituted DB-18-crown-6 are more stable than those with substituted B-15-crown-5 for Ln = La–Er. The log β_1 difference decreases with increasing Z and the reverse trend is observed at the end of the lanthanide series, probably because of the unfavourable D_i/D_c ratio. The DB-30-crown-10 ether is a highly flexible ligand and can wrap around the metal ions. Complexes of 1 : 1 stoichiometry can be isolated with the lanthanide perchlorates La–Eu and Dy–Yb [43]. This can be partly rationalized considering the log β_1 values for the complexes, which exhibit unusual behaviour: the plot log β_1 vs $1/r$ is a V-shaped curve with a sharp minimum at Ln = Gd. Desreux et al. [108–110] explain this feature by a structural change occurring after Gd. Calorimetric data support this hypothesis. The $\Delta_f S$ values are nearly constant for Ln = La–Gd while the $\Delta_f H$ values become less exothermic, reflecting a weaker interaction. From Gd to Yb, both $\Delta_f S$ and $\Delta_f H$ values become more negative. Complexes with

DB-30-crown-6 and substituted DB-18-crown-6 have approximately the same stability, despite the greater number of donor atoms of the former ligand. In the "wrap around" structure that may be assumed in the presence of the larger Ln(III) ions, the ligand conformation is highly strained, which leads to a reduction in stability. The decrease of the metal ionic radius causes the intraligand repulsions to become progressively stronger; further contraction is no longer possible for accommodating ions smaller than Gd(III), hence the structural change.

The influence of both the anion and the solvent upon the complexation of unsubstituted 18-crown-6 is displayed in Table 17. The stability of $Ln(CF_3SO_3)_3 \cdot (18\text{-}6)$ complexes in propylene carbonate decreases only slightly from La to Yb [49]. The log β_1 values are three to five orders of magnitude larger than for substituted dibenzo-18-crown-6 ether, for reasons similar to those discussed in the case of 15-membered ligands. The presence of a strongly coordinating anion reduces the charge density of the cation, resulting in a large drop in stability: a comparison of $La(CF_3SO_3)_3$ in propylene carbonate [49] with $La(NO_3)_3$ in acetonitrile [30] indicates $\Delta \log \beta_1 = 4.35$. The stability is also decreased in polar solvents. For instance, $LnCl_3$ complexes in methanol/water are 10 times less stable than $Ln(NO_3)_3$ complexes in acetonitrile and no complexation is observed after gadolinium

TABLE 17

Stability constants (log β_1) at 25 °C of 1 : 1 complexes between 18-crown-6 ether and LnX_3 salts, in various solvents

Ln	Cl^-; CH_3OH/H_2O [a]	Cl^-; CH_3OH [b]	NO_3^-; CH_3CN [c]	$CF_3SO_3^-$; PC [d]
La	3.29 ± 0.03 [e]	3.25	4.4	8.75
Ce	3.57 ± 0.20	2.81	4.5	
Pr	2.63 ± 0.28	2.47	3.7	8.60
Nd	2.44 ± 0.16	2.16	3.5	
Sm	2.03 ± 0.07	< 1.6	2.6	8.10
Eu	1.84 ± 0.14	< 1.5		
Gd	1.32 ± 0.12			
Dy	[f]	< 1.2		7.90
Er		< 1.4		7.67
Yb			2.3 [g]	7.50
Ref.	111	112	30	49

[a] Titration calorimetry, $\mu = 0.005$. [b] Potentiometric competitive method (Na(I) selective electrode), at 26 ± 0.5 °C, $\mu = 0.2$, ± 0.01. [c] NMR measurements, in anhydrous acetonitrile, variable μ: [Ln(III)] between 0.9 and 1.7×10^{-2} mol l^{-1}, ± 0.2. [d] Competitive potentiometric method using H^+ or Ag^+ as auxiliary cations, with Et_4NClO_4 as supporting electrolyte, $\mu = 0.2$, in anhydrous propylene carbonate, ± 0.1–0.2. [e] Another value was proposed, 4.08 ± 0.10, obtained by a fluorimetric method [113]. [f] No measurable heat of dilution from Tb(III) on. [g] In CD_3CN, 2.8 [36].

[111]. This may be rationalized by considering the strong competition from the solvent molecules.

Data pertaining to (2,1,1), (2,2,1) and (2,2,2) cryptates, as well as to a 15-membered, N-containing coronate are collected in Table 18. The lanthanide cryptates present very slow kinetics of formation so that measurements are difficult to perform. Using a titrimetric method, Anderegg [116] has found that one month is necessary to obtain equilibrium in MeOH/water for the La(III) ion; furthermore, solvolysis competes with the complex formation and no formation constant could be determined by this author for the heavier Ln(III) ions. As expected, the stability of the (2,2,1) cryptates is larger than the one exhibited by the crown ether complexes. In propylene carbonate, log β_1 is around 19 for the cryptates and around 8 for 18-crown-6 complexes [49]. With respect to the monocyclic ligand, the "macrocyclic effect" amounts to $\Delta\log\beta_1 = 4$ in this solvent, a value similar to that found for alkaline-earth ions, Ag(I), Pb(II) and Cd(II). The same authors [49] also report the following stability sequence: Eu(III) $\approx$ Ag(I) > Pb(II) > Ca(II) > Na(I). An interesting result is the relative insensitivity of the formation constants to ionic radius changes along the lanthanide series. One explanation traces this fact back to the influence of the two amine groups which have a great stabilizing effect: log β_1 increases by 8–10 units when two ether functions of the 15-crown-5 ether are replaced by –NH groups [49]. A somewhat smaller difference exists between the 18-crown-6 ether (log β_1 = 3.29 in MeOH/water [111]) and its diaza-substituted homologue (log β_1 = 6.18 [116]), but the 1:1 complex $[La \cdot L]^{3+}$, where L = 1,4,7,10,13,16-hexaazacyclooctadecane (hexaaza-18-crown-6) is quite stable in water: log $\beta_1 = 5.7 \pm 0.3$ [117]. According to one study [49], a certain specificity towards the metal ion radius seems to be present in methanol: $\Delta\log\beta_1(La/Yb) = 3.72$, the ytterbium complex with (2,2,1) being more stable. (The "macrobicyclic effect" is smaller in this solvent, $\Delta\log\beta_1 = 1.5$, probably because of the solvation effect.) This tends to be consistent with the metal ion specificity observed between the cryptates with (2,2,1) and (2,2,2) by electrochemical measurements [118], the former complex being more stable by more than two orders of magnitude. At variance with these results are the pH titration data of Burns and Baes [115], obtained after allowing 4–6 weeks for equilibrium to be reached: almost no difference is observed in aqueous solution either between (2,2,1) and (2,2,2) cryptates, or along the lanthanide series. Since this question of specificity is of considerable significance in cryptate chemistry, Pizer and Selzer [114] carried out the determination of the stability constants by a visible spectroscopic method using murexide as metal ion indicator; they used dimethyl sulfoxide as solvent to remove the difficulties associated with metal ion hydrolysis. The resulting data, displayed in Table 18, show a lack of metal ion specificity, which may

TABLE 18

Stability constants (log β_1) at 25 °C of Ln(III) complexes with various cryptands and with ligand (2,1) [a]

Ln	(2,1) [a]		(2,1,1)		(2,2,1)				(2,2,2)		
	MeOH	PC	DMSO [b]	H_2O [c]	MeOH [a]	PC [a]	DMSO [b]	H_2O [c]	DMSO [b]	H_2O [c]	MeOH [d]
La	7.08	14.4			8.28	18.6		6.59		6.45	9.4
Pr	7.94	14.5	3.86		9.31	18.7	3.47	6.58	3.22	6.37	8.4
Nd	7.86		3.97		9.86		3.01		3.26		
Sm	7.00	14.9		6.8	9.70	19.0		6.76		5.94	
Eu	8.59	14.6_5			10.57	19.0		6.8		5.90	
Gd	7.67		3.87		10.14		3.26	6.7	3.45		
Tb	8.29				10.26			6.6			
Dy	8.96	15.1_5			10.45	19.0					
Ho	8.81		3.80	6.21	10.86		3.11		3.47	6.2	
Er	8.70	14.8			10.78	19.2		6.6			
Tm	9.46			6.8	11.61			6.88			
Yb			4.43	6.51 [e]	12.00	19.1	4.00		4.11 [f]		

[a] From [49], (2,1) = 4,13-diaza-1,7,10-trioxacyclopentadecane, PC = propylene carbonate; see footnote d of Table 17 for the other details. [b] Visible absorption spectrometry, with murexide as metal indicator, lanthanide chlorides 10^{-4} to 10^{-5} M, ±0.06 to 0.13 [114]. [c] Titrimetric method, lanthanide chlorides, $\mu = 0.5$, ±0.1 to 0.2, except for $[\mathrm{Tm(2,2,1)}]^{3+}$: ±0.4 [115]. [d] Titrimetric method, MeOH : H_2O 95 : 5 V/V, $\mu = 0.1$ [116]. [e] 6.55 for Ln = Lu. [f] 3.00 in presence of 0.02 M Et_4NCl.

come from interactions with the solvent. Indeed, the structural and spectroscopic data discussed previously reveal that small molecules, e.g. water [103], or anions may coordinate onto the lanthanide ion through the holes between the aliphatic chains of the cryptand in order to increase the coordination number of the cation. When chloride is added to the Yb(III) solution, log β_1 (2,2,2) is reduced from 4.11 to 3.00, whereas no effect is observed on the formation constant of the Sr(II) cryptate [114], which confirms the above explanation. In fact, stability constants for the formation of $[Eu(2,2,1)X]^{2+}$, $[Eu(2,2,1)X_2]^+$ complexes with X = F, OH, as well as $[Eu(2,2,2)F]^{2+}$ and $[Eu(2,2,2)F_2]^+$ complexes are reported [58,118]: they range between 2×10^4 and 3×10^5 (log β_1) and between 3 and 7×10^6 (log β_2), respectively. The hydroxyl association is stronger than the fluoride interaction. With respect to the aquo-ion, the F^- association is approximately 10 times larger with the cryptate, whereas OH^- interaction is the same for both systems.

The thermodynamic parameters available for the complexation of 18-crown-6 are listed in Table 19. In a polar solvent such as methanol, the enthalpy of complexation is positive and the complexes are stabilized by entropic effects. In anhydrous acetonitrile, the nitrato complexes display exactly the reverse trend: they are stabilized by enthalpic effects and destabilized by entropic effects. These latter may include an unfavourable conformational change of the ligand upon complexation. The same trend was observed for DB-30-crown-10 complexes in propylene carbonate (vide supra) [108].

(iii) NMR and electrochemical studies: structural and kinetic data

Data pertaining to shift reagent studies, e.g. $Eu(fod)_3$ complexes, are

TABLE 19

Thermodynamic parameters $\Delta_f H$ (kJ mol^{-1}) and $\Delta_f S$ (J mol^{-1} K^{-1}) at 25 °C for the formation of 18-crown-6 complexes

Ln	Cl^-; $MeOH/H_2O$ [111] [a]		Cl^-; MeOH [112] [b]		NO_3^-; MeCN [119] [c]	
	$\Delta_f H$	$\Delta_f S$	$\Delta_f H$	$\Delta_f S$	$\Delta_f H$	$\Delta_f S$
La	11.8 ± 0.2	102.5	9.6	94.0	−36.2	−37.3
Ce	10.6 ± 0.5	104.0	16.1	108.1	−43.0	−55.6
Pr	18.7 ± 1.7	113.0	18.6	109.5	−44.0	−76.9
Nd	20.0 ± 1.1	113.7	25.7	127.7	−36.2	−54.3
Sm	15.4 ± 0.2	90.4				
Eu	12.8 ± 0.6	78.2			−12.8	+8.7
Gd	15.6 ± 0.6	77.6				
Yb						

[a] See footnote [a], Table 17. [b] See footnote [b], Table 17. [c] By a calorimetric method, in anhydrous acetonitrile, [Ln] ca. 0.05 M.

described in the next paragraph; moreover, the Ln(III)/Ln(II) reduction kinetics will be reviewed in Section G.

^{1}H NMR data are often used to probe complex formation in solution. The proton spectra of dibenzo-15-crown-5 complexes in acetone, $Ln(NO_3)_3 \cdot (DB\text{-}15\text{-}5) \cdot 3H_2O \cdot (CH_3)_2CO$ (Ln = Sm, Eu, Tm, Yb, Lu) exhibit small isotropic shifts with respect to the ligand alone, ±0.04 to 0.5 ppm, except for Ln = Tm (+0.24 to +1.33 ppm); these shifts are much less important than those arising from the tris(dipivaloylmethanato)Eu(III) shift reagent [11,12]. In addition, the spectra display signals from coordinated solvent molecules, H_2O and $(CH_3)_2CO$, in agreement with the formulae of the complexes. Similar shifts are observed for Tb complexes in the same solvent [98]. The spectra of $ScCl_3$ and $Sc(NCS)_3$ complexes with both B-15-crown-5 and DB-18-crown-6 also attest to the presence of solvent coordination (THF, CH_3CN, H_2O) [16,17]; they are typical of a weak Ln(III)–ligand interaction. The same authors have pioneered the use of ^{45}Sc NMR spectroscopy to unravel changes in the chemical environment of the Sc(III) ion [120]. No evidence for complex formation is found when DC-18-crown-6, B-15-crown-5 or DB-18-crown-6 are added to $Sc(ClO_4)_3$ solutions in water; the addition of (2,1,1) or (2,2,2) cryptands, however, modifies the spectrum: a small shift is observed (6–22 ppm with respect to the salt solution) and the lines are broadened. A detailed analysis of the ^{1}H and ^{13}C NMR spectra of $Ln(ClO_4)_3$ (Ln = La, Sm, Pr) solutions in $CD_3CN/CDCl_3$ containing the DC-18-crown-6 polyether is reported by Catton et al. [121]. Both upfield and downfield shifts are observed; moreover these experiments show that the ligand exchange reactions are slow since signals from both complexed and free ligand are present at room temperature. The experimental spectra for Pr are adequately fitted using a theory based on the assumption that the molecular species present in solution has the same structure as $La(NO_3)_3 \cdot (DC\text{-}18\text{-}6)$ [37], with C_2 symmetry. The non-axially symmetric susceptibility tensor used produced a good fit for both the spectra of the initial solution and those of solutions containing added water and tributylphosphate. It is suggested that the observed susceptibility anisotropy is caused by unequal ligand fields from the six oxygen atoms and from non-axially asymmetric coordination of the ligands situated above the polyether ring.

NMR data are also reported for 1 : 1 and 4 : 3 $Ln(NO_3)_3$ complexes with 18-crown-6, Ln = La–Nd, Eu, Yb [30]. Again, signals from both free and bonded ligand molecules are observed in acetonitrile at room temperature, allowing determination of the stability constants. Solutions of 1 : 1 and 4 : 3 complexes give essentially the same spectra, except for Nd; this reflects the presence of the above-mentioned equilibria in solutions containing the 4 : 3 complexes. The addition of water has a small effect up to a $[H_2O]:[Ln]$ ratio of 10–20. Low temperature spectra fall into two categories. For Ln = La, Eu, Yb, the resonance of the coordinated polyether is broadened and shifted. For Ln = Ce, Pr, Nd, this resonance is split into two components of approximately the same intensity. Inter- and intramolecular exchange reactions account for this behaviour [30], but they could not be completely elucidated. For Ln = Nd, heating the solution to 70 °C resulted in a broadening of the free ligand resonance corresponding to an intermolecular exchange rate of 12 s^{-1}. The spectrum of $Yb(NO_3)_3 \cdot (H_2O)_3 \cdot (18\text{-}6)$ was analyzed by Backer-Dirks et al. [36] between 292 and 343 K. Over this temperature range, the ligand dissociation is approximately constant so that $\Delta_{diss}H$ is close to zero.

The paramagnetic shifts of the lanthanide perchlorate 1 : 2 complexes with 12-crown-4 in acetonitrile are interpreted as arising essentially from a dipolar origin [20]. Using the known equation [122]

$$\frac{\Delta\nu}{\nu} = -D\left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle$$

Desreux and Duyckaerts deduced the average distance between the central metal ion and the oxygen donor atoms of the polyether under the assumption that the complexes investigated are axially symmetric. This distance is found to decrease from Pr to Yb, in agreement with the concept of lanthanide ionic radii contraction. The absolute Ln–O distances are, however, to be taken with care in view of the simplified treatment applied to the experimental data. Moreover, only the Pr, Ho, Er, Tm and Yb adducts yield spectra with sufficiently narrow lines to be interpreted. For the $La(ClO_4)_3/(12\text{-}4)/CD_3CN$ system, the analysis of the spectra as a function of the ligand to metal ratio and of the temperature (−30 °C to +40 °C) indicates a dissociative mechanism for the intermolecular ligand exchange, with $k = 4$ s^{-1} at 25 °C [23].

The NMR spectra of $Pr(NO_3)_3 \cdot$(**13**) in CD_3NO_2 point to a complex with an irregular conformation similar to the structure of NaSCN · (18-6) and to slow ligand exchange kinetics [50]. The coronates $Ln(NO_3)_3 \cdot$(**15**), Ln = La, Ce remain undissociated in water; the NMR spectra, which indicate that the cerium compound has a biaxial susceptibility tensor, remain unaltered after addition of Ce(III) to the La-complex or of La(III) to the Ce-complex [52]. The kinetic inertness of these complexes is further indicated by the fact that no precipitate is observed upon addition of KF or KOH to their aqueous solutions. The NMR spectra of other coronates are consistent with the proposed complex formulae [47,48,53].

Cryptates are highly inert complexes: treatment by a base at pH = 10 for several days does not induce the precipitation of lanthanide hydroxides [57]; their NMR spectra therefore easily provide evidence for the formation of complexes in solution [123] as, for instance, between $La(NO_3)_3$ and a macrotricyclic ligand [124] belonging to the {3}-cryptand class [1]. The lanthanide (2,2,1) cryptates have been studied in great detail in D_2O and CD_3CN [58,125]. The induced paramagnetic shifts obey the equation

$$\delta_i = A_i(S_z) + DG_i$$

where δ_i is the shift of the ith proton measured from the resonance position of the diamagnetic La complex, $A_i(S_z)$ is the Fermi contact term, D, Bleaney's constant [126] specific to a given Ln ion, and G_i a geometric factor dependent on the position of the proton relative to the ion. The relative linewidths depend on the radial distance H–Ln(III); X-ray structural data allow the calculation of these distances, so that the eight paramagnetically shifted resonances could be assigned. The plots of δ_i vs. D for Ce–Eu, Tb–Er all give straight lines passing through the origin, which means that contact interactions are negligible and that the geometry of the complexes is the same for the entire series. Moreover, the analysis of the coupling constants of $La(NO_3)_3 \cdot (2,2,1)$ in CD_3CN indicates that a single conformation of the ligand is highly favoured [125]. A limited number of (2,2,2) cryptates with $Ln(NO_3)_3$ were also studied (Ln = La, Ce, Pr, Nd, Sm) [58,123]. The paramagnetic shifts are smaller than for the (2,2,1) cryptates; the assignment of the $-N-CH_2$ resonances were done using a deuterated ligand. Only three resonances are observed, pointing to highly symmetrical inclusion complexes. Approximate half-lives for the aquation of $[Sm(2,2,2)]^{3+}$ and $[Nd(2,2,2)]^{3+}$ at 0 °C were found to be 45 and 65 min, respectively [58]. The spectra of (2B,2,1) cryptates are also reported [59,60]: the observed shifts are typical of true inclusion complexes.

Further kinetic data are provided by electrochemical studies: the differences in the voltammetric behaviour between aquated and encryptated Ln(III) ions can be used to follow the kinetics of dissociation [55]. Table 20 summarizes the rate constants and activation parameters for Eu- and Yb-cryptates. The reaction is found to be acid catalyzed and the pH dependence of the rate constant follows the rate law

$$k'_d = k_d + k_{H^+} \cdot [H^+]$$

The presence of significant concentrations of OH^- and F^- also has an accelerating effect upon the dissociation rates: $t_{1/2}$ for the aquation of $[Eu(2,2,1)]^{3+}$ is reduced from 27 days at 25 °C to 2.8 days and 22 min upon addition of 0.05 M F^- and OH^-, respectively [118].

(iv) Shift reagent studies

Lanthanide ions, especially Pr(III) and Eu(III), are used as structural probes in high resolution NMR spectroscopy. Earlier studies used tris(di-

TABLE 20

Rate constants, activation parameters and acid catalysis for the dissociation of Eu- and Yb-cryptates at 25 °C [118]

Cryptate	Medium	k_d [a] (s^{-1})	ΔH_d^* (kJ mol^{-1})	ΔS_d^* (J K^{-1} mol^{-1})	k_d [b] (s^{-1})	k_{H^+} [c] (l mol^{-1} s^{-1})
$[Eu(2,2,1)]^{3+}$	0.5 M $NaClO_4$, pH ~ 7	4.1×10^{-7}				
	0.5 M $NaClO_4$, pH = 2.5	3.0×10^{-7}	79.1	−106.7		
	1 M $LiClO_4/HClO_4$				3.0×10^{-7}	$\sim1.0\times10^{-6}$
$[Yb(2,2,1)]^{3+}$	0.5 M $NaClO_4$	1.3×10^{-6}	93.3	−43.9		
$[Eu(2,2,2)]^{3+}$	0.1 M Et_4NClO_4, pH ~ 7	1.1×10^{-3}	57.8	−108.8		
	0.1 M $LiClO_4/HClO_4$				1.0×10^{-3}	0.2

[a] First-order rate constant obtained at pH values where the acid-independent pathway dominates. [b] From intercept of plot k'_d vs. $[H^+]$. [c] From slope of plot k'_d vs. $[H^+]$.

pivaloylmethanato) complexes, Ln(dpm)$_3$, but it was soon realized that tris(heptafluorodimethyloctanedionate) complexes, Ln(fod)$_3$, were more suitable: they are stronger Lewis acids and more soluble in non-polar solvents. The complexing constants K(LSR) for the binding of organic molecules to the lanthanide shift reagents (LSR) can be calculated unambiguously from measurements of the induced chemical shift δ(LSR) as a function of the substrate concentration, at constant LSR concentration. Since adducts of different stoichiometries (2:1, 1:1, 1:2) may form and coexist in equilibrium in solution, it is essential to determine these constants from several resonances.

Eu(dpm)$_3$ was used to elucidate the NMR spectra of several polyalkylene glycols; it was found that when two isopropylene groups are present, some resonances are separated into two doublets, which may be explained by the presence of optical isomers [127]. Mono- and diaza derivatives of benzo-15-crown-5 ether were investigated with the use of Eu(fod)$_3$ [128]. A clear differentiation in behaviour for the various sets of H nuclei of B-15-5 and B-21-7 ethers was ascribed to differences in basicity of the individual O atoms and, therefore, to their selective coordination to the LSR [129]. Data for experimental formation constants of several adducts with coronands are

TABLE 21

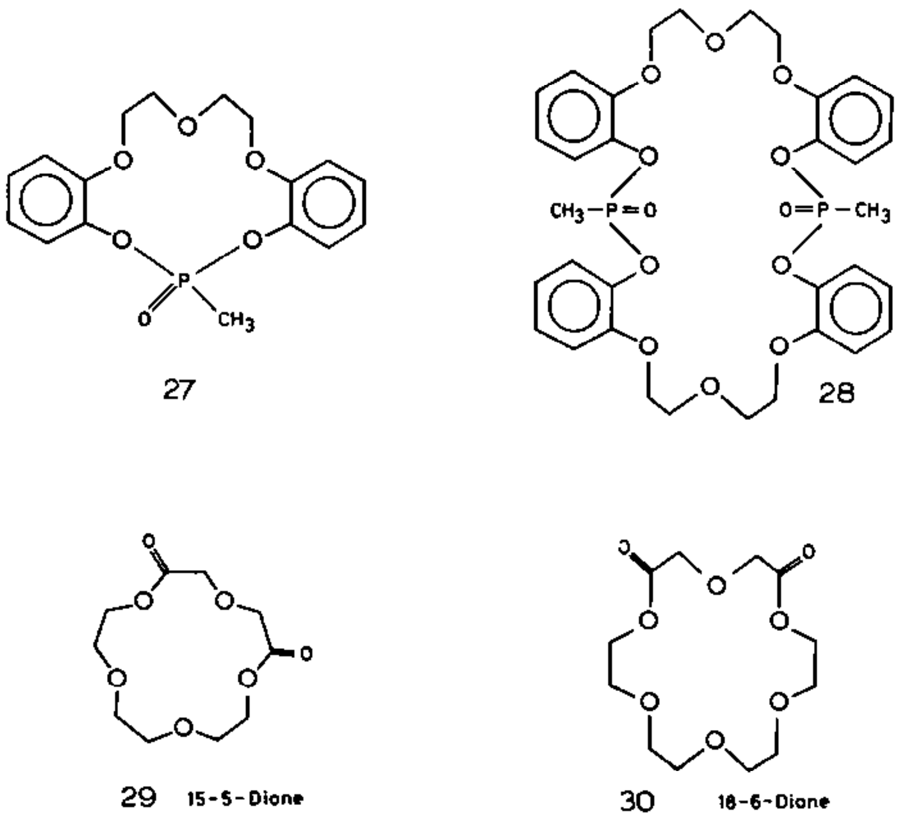
Formation constants of the Ln(fod)$_3$ 1:1 adducts with various crown ethers and coronands, from ^{1}H NMR spectra

Ligand	Ln	T (°C)	Solvent	K (LSR) (l mol^{-1})	Ref.
12-Crown-4	Eu	30	C_6D_6	108.8[a]	130
15-Crown-5	Eu	30	$CDCl_3$	181.3[a]	130
18-Crown-6	Eu	30	$CDCl_3$	85.7[a]	130
	Eu	28	$CDCl_3$	19 ± 1	131, 132
	Eu	28	$CDCl_3$	21 ± 2[b]	132, 133
	Pr	[c]	$CDCl_3$	22.4 ± 0.4	134
DB-18-Crown-6	Eu	27	CD_2Cl_2	21 ± 2	135
	Eu	[c]	$CDCl_3$	21 ± 1[d]	131, 135
	Eu	28	$CDCl_3$	25 ± 2[e]	132, 133
	Pr	[c]	CD_2Cl_2	11 ± 1	131
	Pr	27	$CDCl_3$	16 ± 2	131, 135
	Pr	27	$CDCl_3$	19 ± 3	133
Ligand **16**[f]	Eu	[c]	$CDCl_3$	5.35	136
21-Crown-7	Eu	30	$CDCl_3$	37.7[a]	130
Ligand **27**[g]	Eu	28	$CDCl_3$	46.3	137

[a] From ^{13}C NMR data. [b] K_2 for the 1:2 complex: 4.0 ± 0.5. [c] Not given. [d] $K_2 = 3.0 \pm 0.5$ [135] or 2.5 [132]. [e] $K_2 = 2.5 \pm 0.5$ [135]. [f] Dithia-substituted 18-crown-6 ether. [g] Refer to Fig. 7.

reported in Table 21. They are small, which points to unstable complexes. Moreover, values obtained with ^1H NMR experiments are very different from those calculated from ^{13}C NMR data. In the dithia-18-crown-6 (ligand **16**) adduct, the shift reagent is coordinated to the O atoms [136], while for ligands **27** and **28** (Fig. 7), the coordination proceeds preferentially over the phosphoryl groups [137]. Formation constants for the complexes with 2,6-diones (ligands **29** and **30**, Fig. 7) are also reported [130].

The ligand exchange kinetics of $Eu(fod)_3 \cdot (18\text{-}6)$ have been studied in $CDCl_3$. At 22 °C, $\log k = 4.8$ for 0.05 M solutions, and the activation energy, determined between −60 and +40 °C, amounts to $E_a = 37.7$ kJ mol^{-1}. A slightly positive entropy of activation is found leading to the conclusion that a dissociative mechanism is operative [138]. Similar results are found for $Pr(fod)_3 \cdot (18\text{-}6)$: $\log k = 5.4$ at 20 °C and $E_a = 39.8 \pm 0.8$ kJ mol^{-1} [134].



27

28

29 15-5-Dione

30 18-6-Dione

Fig. 7. Formulae of phosphoryl-containing coronands and of dione derivatives of 15-crown-5 and 18-crown-6 ethers.

Other studies involving macrocyclic polyamino polyacetate ligands are not reviewed here [139–144].

G. COMPLEXES WITH DIVALENT LANTHANIDE IONS

(i) Electrochemical reduction of Ln(III) ions in the presence of macrocyclic ligands

Gansow and co-workers [55,57,60,118] have pointed out that the encryptation of Ln(III) ions, especially Eu(III) and Yb(III), has a marked effect upon the electrochemical properties of the Ln(III)/Ln(II) redox couples. The cyclic voltammograms of the aquo ions are irreversible, while the encapsulated ions display a reversible oxidation–reduction process. The cyclic voltammograms serve therefore as evidence that the metal ions reside inside the ligand cavity. Moreover, the reduction potential of the cryptates is shifted towards less negative values, which means a stabilization of the Ln(II) oxidation state by the macrocyclic ligand. The difference in formal potential, ΔE_f, between the complexed and uncomplexed one-electron redox couples is directly related to the difference in free energy for these processes

$$\Delta E_f = \frac{2.303\,RT}{F}\log\frac{K_{II}}{K_{III}} = \frac{\Delta G^0_{III} - \Delta G^0_{II}}{F}$$

The results of various studies in water are reported in Table 22. The formal potentials E_f do not vary upon addition of an excess ligand or a change of electrolyte (e.g. 0.1 M $NaClO_4$ instead of 0.1 M Et_4NClO_4). Moreover, the logarithmic analysis of the reduction waves yields linear relationships with a slope close to the theoretical value of 59 mV. Therefore, one can conclude that the reduction of $[LnL]^{3+}$ leads to the formation of $[LnL]^{2+}$, via a one-electron exchange mechanism. The Ln(II) complexes are 10^3 to 10^7 times more stable than the Ln(III) complexes. The more stable Ln(II) cryptates are those with the (2,2,2) ligand, the cavity of which is too large for the Ln(III) ions. Yee et al. [118] have evaluated the enthalpic and entropic contributions to this stabilization and found that $\Delta(\Delta G^0) = \Delta S^0_{III} - \Delta S^0_{II}$ is positive so that the large positive values of $\Delta(\Delta G^0)$ are associated with quite large values of the enthalpic terms. A similar stabilization is obtained in methanol: log $(\beta_{II}/\beta_{III}) = 2.2$ and ≈ 2.4 for Sm and Eu cryptates with (2,2,1), respectively [49]. On the other hand, the same authors do not find any stabilization of the Sm(II) cryptates in propylene carbonate: the reduction waves of the latter occur between -1.85 and -2.00 V, whereas that of the solvate has an apparent potential of -1.23 V [49].

Both the trivalent and the divalent cryptates are substitutionally inert on the cyclic voltammetric time scale and the rate constant for electrochemical exchange, k_{el}, is large, between 0.8 and 1.1 cm s^{-1} [145]. Yee et al. have reported a polarographic study of the one electron reduction kinetics of the Eu(III) cryptates with (2,2,1) and (2,2,2) by the aquo ions $M(II)_{aq}$ (M = V, Eu), as well as the oxidation kinetics of $[Eu(2,2,1)]^{2+}$ by $[Co(NH_3)_6]^{3+}$ [146]. An estimate of the rate constants for the Eu(III/II) self-exchange, k_{ex}, could be made from the second-order rate constants for the acid-independent pathway. For the reactions involving the $V(II)_{aq}$ ion, they amount to 2×10^{-6}, 13 and 14×10^{-2} l mol^{-1} s^{-1} for $Eu(III/II)_{aq}$, [Eu(III/II) · (2,2,1)] and [Eu(III/II) · (2,2,2)], respectively. That is, the encapsulation of the europium ion by the cryptands (2,2,1) and (2,2,2) results in an increase of these constants by 6.5×10^6 and 2×10^4, respectively. This difference between the two cryptates is expected since the ligand conformational changes anticipated during the electron transfer are smaller for [Eu(III/II)(2,2,2)]: the smaller (2,2,1) ligand is less flexible than the (2,2,2) cryptand. The authors suggest that non-adiabaticity is not primarily responsible for the low reactivity of the aquo-ions [146].

The Ln(II) ions are also stabilized by crown ethers [15,110] (cf. Table 23). The effect for 1 : 1 complexes is similar to that observed for (2,2,1) cryptates

TABLE 22

Stabilization of Ln(II) vs. Ln(III) by cryptands in water: formal potential E_f (mV) vs. saturated calomel electrode and $\log(\beta_{II}/\beta_{III})$ for 1:1 complexes at 25 °C; supporting electrolyte, 0.1 M Et_4NClO_4

Ln	Ligand	$-E_f$ (mV)	$\log(\beta_{II}/\beta_{III})$	Ref.
Eu	H_2O	626 [a]		118
	(2,2,1)	425	3.4	118
	(2,2,2)	205	7.1	118
		208	7.1	145
	(2B,2,1) [b]	370 [c]	4.3	118
	$(2B_{NH_2},2,1)$ [d]	365 [c]	4.4	59
Sm [e]	H_2O	≈1780 [f]		49
	(2,2,1)	1640	≈ 2.4	49
	(2,2,2)	1410	≈ 6.3	49
Yb	H_2O	1423		118
	(2,2,1)	1105	5.4	118
		1094 [g]	5.5	145
	(2B,2,1) [b]	1100 [c]	5.4	55,57

[a] Electrolyte: 0.1 M sodium *p*-tosylate. [b] Ligand 9, Fig. 1, X = H. [c] Electrolyte: 0.5 M $NaClO_4$. [d] Ligand 9, Fig. 1, X = NH_2. [e] At 22 °C. [f] Not reversible. [g] Electrolyte: 0.1 M tributylammonium perchlorate at 22 °C.

in water. Because Yb(II) and Ca(II) on the one hand and Sm(II) and Sr(II) on the other, have quite similar ionic radii, it is expected they will form complexes with comparable stability. This is indeed the case for the latter pair of metal ions whereas the complexation constants of the Yb(II) crown adducts are always between those of Ca(II) and Sr(II) [147]. A determination of the Eu(II/III) stabilization in propylene carbonate could not be achieved by potentiometry or by polarography, either because of the reduction by the amalgams used or because the III → II polarographic wave of the complexed metal ion is displaced beyond the oxidation wave of mercury [109]. A slight stabilization of Sm(II) and Yb(II) by the unsubstituted 18-crown-6 ether has also been observed in propylene carbonate, but log (β_{II}/β_{III}) remains smaller than 1; no stabilization occurs with the diaza-substituted 15-crown-5 ether [49].

Finally, polarographic experiments show that 18-crown-6 stabilizes the Sm(II) and Yb(II) oxidation states in water [148].

(ii) Solution studies of Ln(II) complexes

In 1980, Donohue investigated the spectroscopic properties of Ln(III) ion solutions in methanol containing 18-crown-6 and found that complexation causes large changes in both charge-transfer and *f–f* transition bands [149]. Furthermore, he discovered that the quantum yield for the photoreduction of Eu(III) to Eu(II) is dramatically increased in the presence of the polyether. Upon photolysis of a 0.001 M solution of $EuCl_3$ by an argon laser (351–363 nm), the absorbance of the 320 nm band of the divalent species is increased by a factor of ca. 10 in the presence of 18-crown-6 ether. A similar

TABLE 23

Stabilization of Ln(II) ions by crown ethers in propylene carbonate at 25 °C; $Ln(CF_3SO_3)_3$, ionic strength adjusted to 0.1 (Et_4NClO_4); 1 : 1 and 1 : 2 complexes observed [109,110]

Ln	Ligand	Log (β_{II})		Log (β_{II}/β_{III})	
		1 : 1	1 : 2	1 : 1	1 : 2
Sm	12-4	[a]	8.4 ± 0.2		1.6 ± 0.3
	subst.-15-5 [b]	[a]	10.8 ± 0.1		
	subst.-18-6 [c]	7.60 ± 0.05	[a]	3.63 ± 0.03	
	DB-30-10	8.3 ± 0.1	[a]	4.55 ± 0.13	
Yb	12-4	[a]	8.3 ± 0.2		
	subst.-15-5 [b]	[a]	8.4 ± 0.1		
	subst.-18-6 [c]	7.32 ± 0.10	[a]	4.63 ± 0.05	
	DB-30-10	7.5 ± 0.1	[a]	2.74 ± 0.14	

[a] Complex not observed. [b] 4-tert-Butylbenzo-15-crown-5. [c] 4,4′(5′)-Di-tert-butylbenzo-18-crown-6.

enhancement is observed when Sm(III) solutions are irradiated by an excimer KrF laser (248 nm): photolysis of the trichloride solutions containing 18-crown-6 produces a transient blue colour with a lifetime of 3 h. Complexation with (2,2,2) cryptand causes a more pronounced effect: the photolytically produced species has a lifetime of 4 h. By comparison, the Sm(II) lifetime amounts to only a few seconds in the absence of complexing agents. Attempts to photoreduce Ln(III) ions using a mercury lamp have been unsuccessful, which points to a multiphoton process. No substantial increase of the Yb(II) lifetime is, however, observed upon addition of crown ether or cryptand [150].

The absorption and emission properties of $[Eu(2,2,2)]^{2+}$ in water have been studied by Sabbatini et al. [151] at both room temperature and 77 K. The encapsulation results in changes in the spectroscopic properties of Eu(II). In particular, whereas no emission spectrum is observed for $Eu(II)_{aq}$ at room temperature, the cryptate displays a measurable luminescence with a lifetime of 3 ns (550 ns at 77 K).

A systematic study of the luminescent properties of freshly prepared solutions of Eu(II) complexes with various crown ethers, cryptands and polyethylene glycols in anhydrous methanol has been undertaken by Adachi et al. [152,153]. The stoichiometry of the complexes formed in solution is determined by Job's plots in which the emission intensity is plotted vs. the metal mole ratio. Such plots have to be interpreted with care in the case where different complexes may form having similar emission spectra but different quantum yields. For instance, the observation of 3 : 2 and 4 : 3 complexes is surprising in dilute solutions ($[Eu(II)] = 4 \times 10^{-3}$ M) and one result, with 18-crown-6 ether, was not confirmed by NMR measurements. The luminescence quantum yields are markedly enhanced by complex formation with the (2,2,2) cryptand and with crown ethers, especially with 15-crown-5 (Table 24). This latter forms a 1 : 3 adduct probably shielding the metal ion from solvent interaction and preventing radiationless deexcitation; the luminescence of this complex is 700 times larger than that of $EuCl_3$ solutions. A low temperature NMR study reveals the presence of two differently coordinated ligands in the ratio 1 : 2 [153]. A possible application to the production of phosphors from methanolic solutions of Eu(II) complexes with crown ethers has been described [154].

Another report mentions that despite the published evidence for the stabilization of Eu(II) by 18-crown-6, the dissolution of $EuCl_2 \cdot (18\text{-}6)$ in degassed absolute methanol results in a rapid oxidation of the divalent ion. RPE measurements indeed indicate that the addition of the polyether to methanolic solution of europium dichloride catalyzes the oxidation process: the more polyether added, the faster the conversion [26]. An explanation is that the dissociation of the trivalent complex in methanol is more rapid than the one-electron exchange process (cf. Section G(i))

$$[\mathrm{Eu}\cdot\mathrm{L}]^{2+} \rightleftarrows [\mathrm{Eu}\cdot\mathrm{L}]^{3+} + \mathrm{e}^- \rightleftarrows \mathrm{Eu}^{3+}_{\mathrm{solv}} + \mathrm{L} + \mathrm{e}^-$$

Once uncomplexed, the Eu(III) ion cannot be reduced to the divalent form in this medium. One should recall here that the trivalent Eu complex has a small formation constant in methanol.

The use of 18-crown-6 to transport europium, after reduction to its divalent state, through H_2O–$CHCl_3$–H_2O liquid membranes has been proposed by Brown et al. [155]. The $Eu(NO_3)_2$ flux through the membrane is indeed comparable to that of $Sr(NO_3)_2$ and 600 times larger than the $Eu(NO_3)_3$ flux.

(iii) Isolation of Ln(II) complexes and solid state studies

The isolation of Ln(II) complexes with macrocyclic ligands turns out to be difficult since the compounds are often very sensitive to oxidation. Good

TABLE 24

Quantum yields Q and lifetime τ of methanolic solutions of Eu(II) complexes with crown ethers, coronands, cryptands and polyethylene glycols: $[\mathrm{Eu(II)}] = 4\cdot 10^{-3}$ M, room temperature [153]

Ligand	Eu:L ratio	Q (%)	τ (ns)
Methanol		0.04	20 [a]
12-Crown-4	[b]	3.6	300
15-Crown-5	1:3 (1:3) [c]	28	160
18-Crown-6	4:3 (1:1) [c]	9.4	160
DC-18-crown-6	4:3	6.7	100
DC-24-crown-8	1:1	2.9	290
B-15-crown-5	[b]	1.8	140
B-18-crown-6 [d]	1:1	0.2	35 [a]
Diaza-15-crown-5	[b]	7.1	42 [a]
Diaza-18-crown-6	3:2	4.6	16 [a]
(2,1,1)	[b]	0.05	[b]
(2,2,1)	3:1	1.4	24 [a]
(2,2,2)	1:1 (1:1) [c]	9.3	200
$HO(CH_2CH_2O)_3H$	[b]	0.06	[b]
$HO(CH_2CH_2O)_4H$	[b]	0.14	[b]
$HO(CH_2CH_2O)_5H$	1:1	0.10	[b]
$HO(CH_2CH_2O)_6H$	2:1	0.12	43 [a]
$HO(CH_2CH_2O)_7H$	2:1	0.18	59 [a]

[a] Unreliable value. [b] Not established or measured. [c] By NMR measurements.

[d] Monobenzo-substituted 18-crown-6 ether.

starting solutions for crystallizing complexes are either $EuCl_2 \cdot 2H_2O$ in methanol [26] or SmI_2 in tetrahydrofuran. This latter solution is prepared by reacting metallic Sm (Yb can also be used) with 1,2-diiodoethane [156,157]. It is essential to check the purity of the complexes by measuring their magnetic susceptibility. Indeed, some of the isolated complexes may contain only 30–60% Ln(II), the remainder already being oxidized [26].

A few Ln(II) complexes are described. $Eu(ClO_4)_2 \cdot$ (DB-18-6) is a colourless, microcrystalline complex which turns pale blue when irradiated with sunlight. The complex is obtained by mixing equimolar amounts of salt and ligand in N_2-degassed acetonitrile. It is thermally stable up to 320 °C and decomposes completely at 342 °C [158]. The complexes of $EuCl_2$ with B-15-crown-5, 18-crown-6, DB-18-crown-6, DC-18-crown-6 and of $YbCl_2$ with DC-18-crown-6 have been prepared from Ln(III)-containing solutions with Li/naphthalene as reductant. A 4 : 3 stoichiometry was found for all these complexes [88]. The 1 : 1 complex $EuCl_2 \cdot$ (18-6) was obtained at 0 °C from a methanolic solution containing an excess of ligand. Its IR spectrum affords evidence for the complexation by the polyether, the ν_{as}(CCO) vibration being shifted by 25 cm^{-1} towards lower wavenumbers [26]. The intense-blue samarium(II) complex $SmI_2 \cdot$ (18-6) has a corrected magnetic moment of 3.36 B.M. at 294 K; it is quite air- and water-sensitive and only sparingly soluble in organic solvents. At 77 K, its emission spectrum displays a broad and structured band (720 nm) assigned to a $4f^5 5d^1 \rightarrow 4f^6$ transition; *f–f* transitions appear on top of this band. The $^5D_0 \rightarrow {}^7F_1$ transition is comprised of two components only, indicating that the Sm(II) ion may lie on a site with relatively high symmetry [26].

H. COMPLEXES WITH CERIUM(IV) IONS

Little work is reported on Ce(IV) complexes with macrocyclic ligands. Reacting $Ce(NO_3)_4$ with dibenzo-18-crown-6 in acetonitrile leads to the isolation of a dark brown crystalline complex of formula $Ce(NO_3)_4 \cdot$ (DB-18-6) $\cdot$ CH_3CN [159]. This complex is almost insoluble in most organic solvents, except in DMF and DMSO; it is decomposed by water. Its thermal decomposition starts at 198 °C and is rather complicated, involving four different steps. The isolation of a diamagnetic adduct $(NH_4)_2Ce(NO_3)_6 \cdot (12\text{-}4)_4$ [26] and of a complex between $Ce(NO_3)_4$ and an 18-membered hexaaza macrocyclic ligand [160] is also reported.

The template reaction leading to the formation of a fluorinated Schiff base complex of Ce(IV), bis[1,1,1,2,2,2-hexafluoro-2,11-bis(trifluoromethyl)-4,9-dimethyl-2,11-diolato-5,8-diazadodeca-4,8-diene(2-)]cerium(IV), was investigated by Timmons et al. [161]. The initial reaction mixture contains Ce(III), ethylene diamine and 5,5,5-trifluoro-4-hydroxy-4-trifluoromethyl-2-

pentanone and both condensation and oxidation of the cerous ion occur. The crystal structure of the pale yellow adduct has been solved; the space group is $P2_1/c$ ($R_F = 0.036$). The Ce(IV) ion is eight-coordinate being bonded to four O atoms and to four N atoms; this is the first crystallographic evidence for Ce–N bonding. The mean Ce–O and Ce–N distances are 2.21(2) and 2.62(1) Å, respectively. The coordination polyhedron may be described as a distorted square antiprism [161].

Some studies have shown that a Ce(IV) complex is involved in the cerium(IV)-catalyzed graft copolymerization of acrylamide onto polyether urethane [162] and in the emulsion polymerization of styrene [163].

I. APPLICATIONS OF Ln(III) COMPLEXES

(i) Spectroscopic applications

The gadolinium cryptate with (2,2,1) was proposed as a relaxation agent for metal nuclide and ^{15}N magnetic resonance measurements in water [164]. The advantage of such a reagent is a shortening of the T_1 relaxation time without inducing contact shifts since the encapsulation of Gd(III) prevents it from close interaction with solute molecules. The efficiency of this cryptate has been demonstrated for ^{15}N, ^{89}Y, ^{111}Cd and ^{183}W NMR measurements [164,165].

Several lanthanide ions display an intense luminescence from long-lived excited states and may be used as spectroscopic probes [166]. Since the photons emitted by a luminescent sample can be detected with high sensitivity, for instance using photon counting [167], these luminescent ion probes are often useful in solving a variety of chemical and biochemical problems. Tundo and Fendler have investigated the chiral recognition in tryptophan derivatives of 18-crown-6 ether [168]. The addition of $TbCl_3$ to methanolic solutions of the polyether produces a quenching of the excited states by the metal ion. The formation constants of the Tb(III)/crown ether complexes, estimated from a treatment of the fluorescence data, are the same for both D-crown-L-tryptophan and L-crown-L-tryptophan: $K = 2.8 \times 10^4$ M^{-1} in CH_3OH. This means the terbium complexation is unaffected by the chirality of the host. However, substantial differences are observed in the energy transfer efficiency from the tryptophan side arms, which therefore provides a measure of the host conformational changes.

An extension of the spectroscopic use of macrocyclic complexes with Ln(III) ions is to attach them to a more complex support; for instance, the introduction of long alkyl chains to make the macrocycle ligand insoluble in water and soluble in nonpolar organic solvents. Polymer-linked systems may be used as efficient phase-transfer catalysts which can easily be recycled.

Systems containing hydroxymethyl derivatives of the 18-crown-6 ether and (2,2,2) cryptand bonded onto a polymer are suitable for extracting cations from dilute aqueous solutions, a property which has been used to extract the lanthanide shift reagents $Eu(fod)_3$ and $Pr(fod)_3$ in order to retain a normal NMR spectrum [169].

Kausar has proposed a diazo coupling of lanthanide benzo cryptates to proteins, which would then become amenable to spectroscopic and radiochemical analyses [59]. The diazotation of $[La(2B_{NH_2}, 2,1)]^{3+}$ can be carried out in water and be followed by a coupling to bovine serum albumin; the modified protein displays a different absorption spectrum. The coupling of a radioactive $[Pr(2B_{NH_2},2,1)]^{3+}$ cryptate to ribonuclease-A has also been achieved to prove that the metal ion remains encapsulated after the cryptate is attached to the biochemical molecule.

There is little doubt that such experiments will provide interesting opportunities in bioinorganic research, especially since syntheses for the derivatization of macrocyclic ligands are now becoming available [59,170].

(ii) Lanthanide separation, extraction and analysis

The similarities in the ionic radii and chemical properties of the various lanthanide ions make their separation difficult. It was therefore logical to take practical advantage of the size-selective cation-coordinating ability of the cyclic polyethers for this separation. King and Heckley [11,12] have chromatographed a mixture of hydrated praseodymium and erbium nitrates in acetone on a column made up of solid dibenzo-18-crown-6 ether. This ligand was preferred to benzo-15-crown-5 because it forms less stable complexes with the lanthanides, which renders the elution process by an acetone: hexane mixture more rapid. The visible-spectroscopic analysis of the eluates showed that Pr(III) could be obtained free from Er(III), this latter demonstrating a weaker retention. These first experiments were, however, not pursued. Analytical separation of La–Tb mixtures can be performed by paper chromatography. Such an experiment, with ethyleneglycol monoethers mixed with oxine as developing agent, was described as early as 1972 [171]. A more recent study used paper chromatography and static adsorption experiments to investigate the complexation between Ln(III) ions and several crown ethers [172]: B-15-crown-5, DB-18-crown-6 and their HCHO-copolymers.

Solvent extraction (and separation) of lanthanide ions based on either crown ether- (Table 25) or podand-containing systems has generated several studies. No synergetic effect was observed in the extraction of europium nitrate by cyclohexyl-15-crown-5 ether and trioctylphosphine oxide [173]. For several extraction systems investigated, 15-crown-5 or its derivatives

TABLE 25

Some systems used in the solvent extraction of lanthanide ions by crown ethers, and stoichiometries of the extracted complexes

Organic phase	Aqueous phase Ln	Ln : L ratio	Separation factors or comments	Ref.
Cyclohexyl-15-5/TOPO[a]	$Eu(NO_3)_3/HNO_3$ 1 M			173
4-Methyl-B-15-5/$CHCl_3$	Aqueous picric acid	1 : 2	K_{extr}:	174
	^{144}Ce, ^{147}Nd, $^{152+154}Eu$,		Nd > Eu > Ce > Tm > Yb	
	^{169}Yb, ^{170}Tm			
4-tert-Butyl-B-15-5/$C_6H_5NO_2$	Ln picrates	1 : 2	$S(Ce:Sm) = 1.14$	175
	^{144}Ce, ^{147}Nd, $^{152+154}Eu$,		$S(Sm:Lu) = 0.76$	
4-Bromo-B-15-5/$C_6H_5NO_2$	^{169}Yb, ^{170}Tm, ^{177}Lu	1 : 2		
B-15-5/CH_2Cl_2	Ln picrates	1 : 2	$S(Pr:Nd)_{max} = 3.66$	176
B-18-6/CH_2Cl_2	La–Lu	1 : 2		
DC-18-6/CH_2Cl_2		3 : 4 (Nd-Lu), 1 : 1 (La-Pr)		
12-4/$C_6H_5NO_2$	$Ln(NO_3)_3$/picric acid	1 : 2	Best ligand: 15-5	177
15-5/$C_6H_5NO_2$	La–Lu	1 : 1	Best extracted Ln's: Tb,Yb	
DB-18-6/$C_6H_5NO_2$		1 : 1		

[a] Trioctylphosphine oxide.

proved, however, to be the best extraction agents; the extracted complexes usually have a 1 : 2 stoichiometry. The distribution ratios of several lanthanide ions have been determined by tracer methods using the γ-radioactive isotopes ^{144}Ce, ^{147}Nd, $^{152+154}Eu$, ^{169}Yb, ^{170}Tm and ^{177}Lu [174,175]. With 4-methyl-benzo-15-crown-5 in $CHCl_3$, the extracted species are $Ln(picrate)_3 \cdot L_2$ and the extraction equilibrium constants vary in the order Nd > Eu > Ce > Tm > Yb; the extraction is improved if the organic phase is rendered more polar either by addition of isopropyl or butyl alcohol or by using nitrobenzene instead of chloroform [174]. With t-butylbenzo-15-crown-5 in nitrobenzene, similar complexes are extracted, but the extractability shows a maximum for Sm(III): Ce < Nd < Sm > Eu > Tm > Yb > Lu; the distribution ratios obtained with this ligand are twice those with 4-bromobenzo-15-crown-5 ether [175]. The influence of the polyether substituents has been investigated [176]: unsubstituted crown ethers in CH_2Cl_2 (12-crown-4, 15-crown-5, 18-crown-6) have a better extraction ability than their cyclohexyl- or benzo-derivatives. The different isomers of DC-18-crown-6 also display different extraction behaviour. The distribution ratios exhibit a maximum at Sm for both B-15-crown-5 and DB-18-crown-6. A systematic study of the extraction ability of 12-crown-4, 15-crown-5 and DB-18-crown-6 in nitrobenzene has recently been published [177]. Europium nitrate in picric acid solutions was found to be extracted better by the 15-membered crown ether. In these systems, only 12-crown-4 gives rise to sandwich 1 : 2 complexes, whereas the extracted adducts have a 1 : 1 stoichiometry with both 15-crown-5 and DB-18-crown-6 ethers. The picric acid concentration also affects the extraction; mixed species $[Ln(picrate)_2(NO_3) \cdot L]$ may form. Other organic acids, e.g. acetic, citric, oxalic, etc., have a negative influence upon the distribution coefficient *D*. The graph of *D* versus the atomic number of the extracted Ln ions is reproduced in Fig. 8: Nd, Eu, Gd, Tb and Yb are the most easily extracted ions. The presence of other metal ions may also influence the extraction process: it is found that Hg(II) and Pb(II) indeed interfere, contrary to other transition metal ions, such as Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and UO_2^{2+}.

Liquid membranes can also be used for cation extraction. For instance, a water-oil emulsion containing sorbitan trioleate, DB-18-crown-6 and chloroform can separate praseodymium nitrate from europium nitrate, this latter remaining in the aqueous phase [178]. As seen above, polymer-bonded crown ethers are suitable for extracting cations from dilute aqueous solutions [169].

Crown ethers and their derivatives are, however, expensive ligands so that attempts have been made to replace them by their much cheaper open-chain analogues. For instance, Zolin et al. have shown that oligooxaalkanes in chloroform extract neodymium europium and erbium salts from aqueous solutions [106]. Hirashima et al. [179,180] have attempted to separate hydrated lanthanoid nitrates by fractional crystallization in the presence of $HO(CH_2CH_2O)_nH$ ligands ($n = 2$–5,7). The stoichiometry of the crystalline complexes is reported in Table 6. The crystallization time in ethylacetate: water mixtures varies from a few seconds ($n = 4$; Ln = La, Pr) to several days (e.g. $n = 5$; Ln = Sm, Eu) or weeks (e.g. $n = 2$; Ln = Dy, Er). Tetraethylene glycol ($n = 4$) seems to be the best ligand and crystallization is best achieved when the water content of the solution is low. The separation factors for several lanthanide pairs are as follows: 1.7 (La–Ce), 1.4 (Ce–Pr), 2.0 (Pr–Nd), 5.5 (Sm–Nd), 2.9 (Sm–Eu) and 2.0 (Eu–Gd). They are more or less comparable to those obtained with ethylenediaminetetraacetic acid or with bis(2-ethylhexyl)hydrogenophosphate [179]. The introduction of polyethylene glycol in ammonium phosphotungstate sorbents results in a synergetic factor of about 100 for Ce(III) [181].

Podands have also proved useful in the preparation of cation-selective electrodes [182] and a system working for 5*f* cations has recently been proposed [183]. There is, however, only one report mentioning an eventual application to 4*f* elements [184].

(iii) *Miscellaneous*

Polymeric thermoplastic materials possessing useful electrical properties

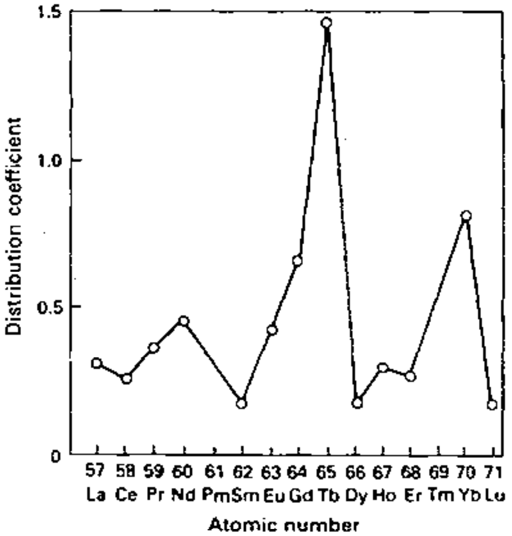


Fig. 8. Distribution coefficients *D* versus atomic numbers of Ln(III) ions (40 μg ml^{-1}) extracted by 15-crown-5 (0.1 g in 10 ml nitrobenzene) from aqueous solutions of picric acid (10 mg ml^{-1}). Reprinted, with the permission of the Royal Society of Chemistry (London), from ref. 177.

have been designed [185], comprising a metal salt (including lanthanide salts) and a polymer backbone incorporating ether, thioether or methane linkages.

J. CONCLUSIONS

Macrocyclic ligands have added a new dimension to the coordination chemistry of lanthanide ions. In particular, they allowed the study of highly coordinated compounds; for instance, the $Ln(NO_3)_3 \cdot (15\text{-}5)$ adducts are the first series of complexes in which the Ln(III) ions are 11-coordinate. Basic thermodynamic data are still needed to fully understand the effects influencing the Ln/macrocyclic ligand interaction. Indeed, as was demonstrated for monovalent cations [186], the observed facts cannot be simplistically rationalized in terms of ion diameter to cavity diameter relationships. Moreover, kinetic data on ligand exchange are very scarce and further studies in this field are certainly desirable.

Regarding the application of the complexes with both macrocyclic ligands and their open-chain analogues, a wealth of properties could be used, especially in the extraction and analysis (ion-selective electrodes) of the rare earths. The use of these complexes to attach spectroscopic probes to complex materials will probably undergo interesting developments.

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REFERENCES

1 E. Weber and F. Vögtle, Top. Curr. Chem., 98 (1981) 1.
2 I.M. Kolthoff, Anal. Chem., 51 (1979) 1R.
3 E. Blasius and K.-P. Janzen, Top. Curr. Chem., 98 (1981) 165.
4 M. Yoshio and H. Noguchi, Anal. Lett., A15 (1982) 1197.
5 E.R. Birnbaum, in T. Moeller and E. Schleitzer-Rust (Eds.), Gmelin Handbook of Inorganic Chemistry, Sc, Y, La–Lu, Part D3, Springer Verlag, Berlin, 1980, p. 275.
6 J. Reuben in K.A. Gschneidner Jr. and Le Roy Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 3, North Holland Publishing Co., Amsterdam, 1979, chap. 39.
7 C.J. Pedersen, J. Am. Chem. Soc., 89 (1967) 2495.
8 C.J. Pedersen, J. Am. Chem. Soc., 89 (1967) 7017.
9 A. Cassol, A. Seminara and G. de Paoli, Inorg. Nucl. Chem. Lett., 9 (1973) 1163.
10 P.R. Heckley and R.B. King, in C.J. Kerane and T. Moeller (Eds.), Proc. 10th, Rare Earth Res. Conf., Carefree, AZ, Vol. 1, 1973, p. 311.
11 P.R. Heckley, Dissertation, Univ. Microfilms, Order No. 75-8152, 1974.

12 R.B. King and P.R. Heckley, J. Am. Chem. Soc., 96 (1974) 3118.
13 R.B. King, U.S. NTIS Rep., AD-A013817 (1975).
14 J.-C.G. Bünzli and H.T.T. Oanh, unpublished results.
15 J.F. Desreux, Bull. Cl. Sci., Acad. R. Belg., 64 (1978) 814.
16 D.J. Olszanski, Dissertation, Univ. Microfilms, Order No. 76-5618, 1975.
17 D.J. Olszanski and G.A. Melson, Inorg. Chim. Acta, 26 (1978) 263.
18 J.-C.G. Bünzli and D. Wessner, Helv. Chim. Acta, 61 (1978) 1454.
19 D. Wessner, Ph.D. Thesis, University of Lausanne, Switzerland, 1980.
20 J.F. Desreux and G. Duyckaerts, Inorg. Chim. Acta, 35 (1979) L313.
21 J.-C.G. Bünzli, D. Wessner and H.T.T. Oahn, Inorg. Chim. Acta, 32 (1979) L33.
22 J.-C.G. Bünzli, D. Wessner, A. Giorgetti and Y. Frésard, in G.J. McCarthy, H.B. Silber and J.J. Rhyne, (Eds.), The Rare Earths in Modern Science and Technology, Vol. 3, Plenum Press, New York, 1982, p. 85.
23 J.-C.G. Bünzli, H.T.T. Oanh and B. Gillet, Inorg. Chim. Acta, 53 (1981) L219.
24 J.-C.G. Bünzli and D. Wessner, Inorg. Chim. Acta, 44 (1980) L55.
25 J.-C.G. Bünzli, B. Klein, D. Wessner and N.W. Alcock, Inorg. Chim. Acta, 59 (1982) 269.
26 J.-C.G. Bünzli and D. Wessner, Isr. J. Chem., 24 (1984) fasciculus 4.
27 C. Erk, Chim. Acta Turcica, 7 (1979) 255.
28 Tan Minyu, Wang Liufang, Ma Tairu, Shu Cisheng, Yu Lanping and Quian Limin, Gaodeng Xuexiao Huaxue Xuebao (Chem. J. Chinese Univ.), 4 (1983) 271.
29 J.-C.G. Bünzli, D. Wessner and B. Klein, in G.J. McCarthy, H.B. Silber and J.J. Rhyne (Eds.), The Rare Earths in Modern Science and Technology, Vol. 2, Plenum Press, New York, 1980, p. 99.
30 J.-C.G. Bünzli and D. Wessner, Helv. Chim. Acta, 64 (1981) 582.
31 J.-C.G. Bünzli, D. Wessner and P. Tissot, Experientia Suppl., 37 (1979) 44.
32 Wan Zhu-Li, Rao Zi-He, Liang Dong-Cai, Yao Xin-Kan, Yan Shi-Ping and Wang Geng-Lin, Huaxue Xuebao (Acta Chim. Sin.), 40 (1982) 1087.
33 Wang Genglin, Yan Shiping, Li Xueyao, Yao Xinkan, Wan Zhuli, Rao Ziha and Liang Dongcai, Sci. Sin., B25 (1982) 916.
34 Wang Genglin and Yan Shiping, Huaxue Shiji, 6 (1981) 343, 336; Chem. Abstr., 97 (1982) 65387d.
35 G. Tomat, G. Valle, A. Cassol and P. Di Bernardo, Inorg. Chim. Acta, 76 (1983) L13.
36 J.D.J. Backer-Dirks, J.E. Cooke, A.M.R. Galas, J.S. Ghotra, C.J. Gray, F.A. Hart and M.B. Hursthouse, J. Chem. Soc. Dalton Trans., (1980) 2191.
37 M.E. Harman, F.A. Hart, M.B. Hursthouse, G.P. Moss and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1976) 396.
38 A. Seminara and A. Musumeci, Inorg. Chim. Acta, 39 (1980) 9.
39 M. Ciampolini, N. Nardi, R. Cini, S. Mangani and P. Orioli, J. Chem. Soc. Dalton Trans., (1979) 1983.
40 Xiao Wen Jin, Wang Jing Qiu, Wan Jie, Yang Zhi Kuan and Lou Run Huo, Wuhan Ta Hsueh Pao, Tzu Jan Ko Hsueh Pan, (1981) 66.
41 Wang Genglin, Zhang Yunshi, Yao Xinkan, Yan Shiping and Wang Lianyuan, Kao Teng Hueh Hsiao Hua Hsueh Hsueh Pao (Chem. J. Chin. Univ.), 1 (1980) 23.
42 D. Wessner, A. Giorgetti and J.-C.G. Bünzli, Inorg. Chim. Acta, 65 (1982) L25.
43 M. Ciampolini and N. Nardi, Inorg. Chim. Acta, 32 (1979) L9.
44 L.C. Thompson in K.A. Gschneidner Jr. and Le Roy Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 3, North Holland Publishing Co., Amsterdam, 1979, chap. 25.
45 M.B. Humphrey, W.M. Lamanna, M. Brookhart and G.R. Husk, Inorg. Chem., 22 (1983) 3355.

46 D.J. Olszanski and G.A. Melson, Inorg. Chim. Acta, 23 (1977) L4.

47 W. Radecka-Paryzek, Inorg. Chim. Acta, 35 (1979) L349.

48 W. Radecka-Paryzek, Inorg. Chim. Acta, 52 (1981) 261.

49 A.C. Almasio, F. Arnaud-Neu and M.J. Schwing-Weill, Helv. Chim. Acta, 66 (1983) 1296.

50 J.F. Desreux, A. Renard and G. Duyckaerts, J. Inorg. Nucl. Chem. 39 (1977) 1587.

51 E. Weber and F. Vögtle, Chem. Ber., 109 (1976) 1803.

52 J.D.J. Backer-Dirks, C.J. Gray, F.A. Hart, M.B. Hursthouse and B.C. Schoop, J. Chem. Soc. Chem. Commun., (1979) 774.

53 (a) W. Radecka-Paryzek, Inorg. Chim. Acta, 45 (1980) L147. (b) W. Radecka-Paryzek, Inorg. Chim. Acta, 54 (1981) L251.

54 M. Ciampolini, C. Mealli and N. Nardi, J. Chem. Soc. Dalton Trans., (1980) 376.

55 O.A. Gansow and K.B. Triplett, U.S. Pat. 4257955 (1981).

56 J.-C.G. Bünzli and A. Strawczynski, unpublished results.

57 O.A. Gansow, A.R. Kausar, K.M. Triplett, M.J. Weaver and E.L. Yee, J. Am. Chem. Soc., 99 (1977) 7087.

58 D.J. Pruett, Dissertation, Univ. Microfilms, Order No. 80-10779, 1978.

59 A.R. Kausar, Dissertation, Univ. Microfilms, Order No. 80-10778, 1978.

60 O.A. Gansow and A.R. Kausar, Inorg. Chim. Acta, 72 (1983) 39.

61 M. Ciampolini, P. Dapporto and N. Nardi, J. Chem. Soc. Chem. Commun., (1978) 788; J. Chem. Soc. Dalton Trans., (1979) 974.

62 F.A. Hart, M.B. Hursthouse, K.M.A. Malik and S. Moorhouse, J. Chem. Soc. Chem. Commun., (1978) 549.

63 J.H. Burns, Inorg. Chem., 18 (1979) 3044.

64 G. Campari and F.A. Hart, Inorg. Chim. Acta, 65 (1982) L217.

65 Y. Hirashima, K. Kanetsuki, I. Yonezu, K. Kamakura and J. Shiokawa, Bull. Chem. Soc. Jpn., 56 (1983) 738.

66 Y. Hirashima and J. Shiokawa, Chem. Lett., (1979) 463.

67 Y. Hirashima, K. Ito and J. Shiokawa, Chem. Lett., (1983) 9.

68 B. Ammann and J.-C.G. Bünzli, unpublished results.

69 B. Tümmler, G. Maass, E. Weber, W. Wehner and F. Vögtle, J. Am. Chem. Soc., 99 (1977) 4683; F. Vögtle, Chimia, 33 (1979) 239.

70 M. Albin, A.C. Goldstone, A. Sommerville Withers and W. DeW. Horrocks Jr., Inorg. Chem., 22 (1983) 3182.

71 Lu Pinzhe, Shen Cheng, Fan Yuguo, Jin Songchun, Zhang Shugong, Yu Fenglan, Fenzi Kexue Yu Huaxue Yanjiu, 3 (1983) 77; Chem. Abstr., 99 (1983) 46322d.

72 Lin Yong-Hua and Xing Yan, Huaxue Xuebao (Acta Chim. Sin.), 41 (1983) 97.

73 Lin Yong-Hua, Xing Yan, Hin Song-Chun, Wuli Xuebao, 31 (1982) 685.

74 J.-C.G. Bünzli, B. Klein, G. Chapuis and K.J. Schenk, Inorg. Chem., 21 (1982) 808.

75 J.-C.G. Bünzli, B. Klein and D. Wessner, Inorg. Chim. Acta, 44 (1980) L147; G. Bombieri, G. de Paoli, F. Benetello and A. Cassol, J. Inorg. Nucl. Chem., 42 (1980) 1417.

76 Y. Hirashima, T. Tsutsui and J. Shiokawa, Chem. Lett., (1982) 1405.

77 U. Casellato, G. Tomat, P. di Bernardo and R. Graziani, Inorg. Chim. Acta, 61 (1982) 181.

78 Y. Hirashima, T. Tsutsui and J. Shiokawa, Chem. Lett., (1981) 1501.

79 Y. Hirashima, K. Kanetsuki, J. Shiokawa and N. Tanaka, Bull. Chem. Soc. Jpn., 54 (1981) 1567.

80 J.-C.G. Bünzli and B. Klein, in G.J. McCarthy, H.B. Silber and J.J. Rhyne (Eds.), The Rare Earths in Modern Science and Technology, Vol. 3, Plenum Press, New York, 1982, p. 97.

81 T.J. Lee, H.-R. Sheu, T.T. Chiu and C.T. Chang, Acta Crystallogr. Sect. C, 39 (1983) 1357.

82 Xu Zhangbao, Gu Yuanxin, Zheng Qitai, Shen Fulin, Yao Cingkai, Yan Sipin and Wang Genglin, Wuli Xuebao, 31 (1982) 956; Chem. Abstr., 97 (1982) 172793e.

83 J.-C.G. Bünzli, B. Klein, D. Wessner, K.J. Schenk, G. Chapuis, G. Bombieri and G. de Paoli, Inorg. Chim. Acta, 54 (1981) L43.

84 J.-C.G. Bünzli, B. Ammann, J.-M. Pfefferlé, G. Chapuis, K.J. Schenk and F. Zuniga, Helv. Chim. Acta, 67 (1984) 1121.

85 A. Seminara, S. Gurrieri, G. Siracusa and A. Cassol, Thermochim. Acta, 12 (1975) 173.

86 S. Gurrieri, A. Seminara, G. Siracusa and A. Cassol, Thermochim. Acta, 11 (1975) 433.

87 S. Calogero, A. Seminara and U. Russo, Gazz. Chim. Ital., 109 (1979) 45.

88 Zou Jinping and Tan Minyu, J. Chin. Rare Earth Soc., 1 (1983) 34.

89 N.E. Topp, The Chemistry of the Rare Earth Elements, Elsevier, Amsterdam, 1965.

90 E.A. Boudreaux and L.N. Mulay, Theory and Applications of Molecular Paramagnetism, John Wiley, New York, 1976.

91 B.J. Hathaway and A.E. Underhill, J. Chem. Soc., (1961) 3091.

92 C. Mabillard, Ph.D. Thesis No. 505, Ecole Polytechnique Fédérale, Lausanne, 1983.

93 D.P. Strommen and K. Nakamoto, Appl. Spectrosc., 37 (1983) 436.

94 N.P. Curtis and Y.P. Curtis, Inorg. Chem., 4 (1965) 804.

95 A.B.P. Lever, E. Mantovani and B.S. Ramaswamy, Can. J. Chem., 49 (1971) 1957.

96 D.G. Hendricker and R.J. Foster, Inorg. Chim. Acta, 6 (1972) 371.

97 R. Reisfeld and C.K. Jørgensen, Lasers and Excited States of Rare Earths, Springer Verlag, Berlin, 1977.

98 S.M. De B. Costa, M.M. Queimado and J.J.R.F. Da Silva, J. Photochem., 12 (1980) 31.

99 J.-C.G. Bünzli, B. Klein, G.-O. Pradervand and P. Porcher, Inorg. Chem., 22 (1983) 3763.

100 P. Porcher and P. Caro, J. Lumin., 21 (1980) 207.

101 J.-C.G. Bünzli, B. Klein, G.-O. Pradervand and J.-R. Yersin, Proc. first meeting of Luminescence group, Electrochemical Society European section, Bellevue (France), July 1981, pp. 181–187; J.-C.G. Bünzli, B. Klein and G.-O. Pradervand, J. Less-Common Met., 94 (1983) 407.

102 W. DeW. Horrocks, Jr. and D.R. Sudnik, J. Am. Chem. Soc., 101 (1979) 334.

103 M. Sabbatini, S. Dellonte, M. Ciano, A. Bonazzi and V. Balzani, Chem. Phys. Lett., 107 (1984) 212.

104 L.G. Koreneva, V.A. Barabanova, V.F. Zolin and S.L. Davydova, Sov. J. Coord. Chem. (Engl. transl.), 4 (1978) 143.

105 I.M. Walker and D.H. Weeden, Inorg. Chem., 12 (1973) 772.

106 V.F. Zolin, L.G. Koreneva, V.M. Dziomko, I.S. Markovich, L.I. Blokhina, N.I. Kruglova and Y.S. Ryabokobylko, Sov. J. Coord. Chem. (Engl. transl.), 7 (1981) 224.

107 J.R. Peterson, Report ORO-4447-085, Avail. NTIS, 1979.

108 J.F. Desreux and J. Massaux, in G.J. McCarthy, H.B. Silber and J.J. Rhyne (Eds.), The Rare Earths in Modern Science and Technology, Vol. 3, Plenum Press, New York, 1982, p. 87.

109 J. Massaux and J.F. Desreux, J. Am. Chem. Soc., 104 (1982) 2967.

110 J. Massaux, J.F. Desreux, C. Delchambre and G. Duyckaerts, Inorg. Chem., 19 (1980) 1893.

111 R.M. Izatt, J.D. Lamb, J.J. Christensen and B.L. Haymore, J. Am. Chem. Soc., 99 (1977) 8344.

112 Zhou Jinzhong and Wang Dexi, He Huaxue Yu Fangshe Huaxue, 4 (1982) 1714; Zhou Jinzhong, Wu Xi and Wang Dexi, Abstr., First Int. Conf. Chemistry and Technology of Lanthanides and Actinides, ICLA, Venice, 1983, p. 41.

113 Wang Genglin and Jiang Zonghui, Gaodeng Xuexiao Huaxue Xuebao (Chem. J. Chin. Univ.), 1 (1980) 117.
114 R. Pizer and R. Selzer, Inorg. Chem., 22 (1983) 1359.
115 J.H. Burns and C.F. Baes, Inorg. Chem., 20 (1981) 616.
116 G. Anderegg, Helv. Chim. Acta, 64 (1981) 1790.
117 M. Kodama, E. Kimura and S. Yamaguchi, J. Chem. Soc. Dalton Trans., (1980) 2536.
118 E.L. Yee, O.A. Gansow and M.J. Weaver, J. Am. Chem. Soc., 102 (1980) 2278.
119 B. Ammann and J.-C.G. Bünzli, Experientia Suppl., 37 (1979) 50; B. Ammann and J.-C.G. Bünzli, Calorimétrie et Analyse Thermique, Journées de Genève, Vol. 13, 1982, p. III-6.36.
120 G.A. Melson, D.J. Olszanski and A.K. Rahimi, Spectrochim. Acta, Part A, 33 (1977) 301.
121 G.A. Catton, M.E. Harman, F.A. Hart, G.E. Hawkes and G.P. Moss, J. Chem. Soc. Dalton Trans. (1978) 181.
122 W. DeW. Horrocks, Jr., in G.H. La Mar, W. DeW. Horrocks, Jr. and R. Holm (Eds.), NMR of Paramagnetic Molecules, Academic Press, New York, 1973, p. 479.
123 A.R. Kausar, J. Chem. Soc., Pakistan, 4 (1982) 151.
124 J. Cheney, J.M. Lehn, J.P. Sauvage and M.E. Stubbs, J. Chem. Soc. Chem. Commun., (1972) 1101.
125 O.A. Gansow, D.J. Pruett and K.B. Triplett, J. Am. Chem. Soc., 101 (1979) 4408.
126 B. Bleaney, J. Magn. Reson., 8 (1972) 91.
127 B.S. Perrett, I.A. Stenhouse, United Kingdom Atomic Energy Authority Research Group, Rep. AERE-R 7042, 1972.
128 J.C. Lockhart, A.C. Robson-Lindsell, M.E. Thompson, S.D. Furtado, C.K. Kaura and A.R. Allan, J. Chem. Soc. Perkin Trans., 1 (1973) 577.
129 J.C. Lockhart, B. Atkinson, G. Marshall and B. Davies, J. Chem. Res. (S), (1979) 32.
130 C. Erk, Fresenius Z. Anal. Chem., 316 (1983) 477.
131 K.B. Yatsimirskii, N.K. Davidenko, V.A. Bidzilya and L.P. Golovkova, Stroenie, Svoistva I Primen. Beta-Diketonatov Met., 3rd Mater. Uses. Semin., 1977, p. 19. (publ. 1978); Chem. Abstr. 91 (1979) 113210r.
132 N.K. Davidenko, V.A. Bidzilya and L.P. Golovkova, Sov. J. Coord. Chem. (Engl. Transl.), 6 (1980) 757.
133 K.B. Yatsimirskii and L.I. Budarin, Zh. Neorg. Khim., 7 (1962) 1090.
134 V.A. Bidzilya and L.P. Golovkova, Teor. Eksp. Khim., 16 (1980) 218. (Engl. transl.).
135 N.K. Davidenko, V.A. Bidzilya, L.P. Golovkova, S.L. Davydova and K.B. Yatsimirskii, Teor. Eksp. Khim., 13 (1977) 404. (Engl. transl.).
136 V.A. Bidzilya and L.P. Golovkova, Teor. Eksp. Khim., 16 (1980) 214 (Engl. transl.).
137 K.B. Yatsimirskii, V.A. Bidzilya, L.P. Golovkova and A.S. Shtepanek, Dokl. Akad. Nauk. SSSR, 244 (1979) 78 (Engl. transl.).
138 V.A. Bidzilya, Teor. Eksp. Khim., 14 (1978) 708 (Engl. transl.); 15 (1979) 553.
139 J.F. Desreux, Inorg. Chem., 19 (1980) 1319.
140 C.C. Bryden, C.N. Reilley and J.F. Desreux, Anal. Chem., 53 (1981) 1418.
141 C.C. Bryden and C.N. Reilley, Anal. Chem., 54 (1982) 610.
142 C.C. Bryden, C.N. Reilley and J.F. Desreux, in G.J. McCarthy, H.B. Silber and J.J. Rhyne (Eds.), The Rare Earths in Modern Science and Technology, Vol. 3, Plenum Press, New York, 1982, p. 53.
143 M. Albin, W. deW. Horrocks, Jr. and F.J. Liotta, Chem. Phys. Lett., 85 (1982) 61.
144 C.A. Chang and M.E. Rowland, Inorg. Chem., 22 (1983) 3866.
145 N. Koizumi and S. Aoyagui, J. Electroanal. Chem., 124 (1981) 345.
146 E.L. Yee, J.T. Hupp and M.J. Weaver, Inorg. Chem., 22 (1983) 3465.

147 J. Massaux, G. Roland and J.F. Desreux, Inorg. Chim. Acta, 60 (1982) 129.
148 H. Yamana, T. Mitsugashira, Y. Shiokawa and S. Suzuki, Bull. Chem. Soc. Jpn., 55 (1982) 2615.
149 T. Donohue, in G.J. McCarthy, H.B. Silber and J.J. Rhyne (Eds.), The Rare Earths in Modern Science and Technology, Vol. 2 Plenum Press, New York, 1980, p. 105.
150 T. Donohue, in G.J. McCarthy, H.B. Silber and J.J. Rhyne (Eds.), The Rare Earths in Modern Science and Technology, Vol. 3, Plenum Press, New York, 1982, p. 223.
151 N. Sabbatini, M. Ciano, S. Dellonte, A. Bonazzi and V. Balzani, Chem. Phys. Lett., 90 (1982) 265.
152 G.-Y. Adachi, K. Tomokiyo, K. Sorita and J. Shiokawa, J. Chem. Soc. Chem. Commun., (1980) 914.
153 G.-Y. Adachi, K. Sorita, K. Kawata, K. Tomokiyo and J. Shiokawa, J. Less-Common Met., 93 (1983) 81.
154 Jpn. Kokai Tokkyo Koho 81, 104, 986 (1981), Mitsubishi Chem. Ind. Co. Ltd.
155 P.R. Brown, R.M. Izatt, J.J. Christensen and J.D. Lamb, J. Membr. Sci., 13 (1983) 85.
156 J.L. Namy, P. Girard and H.B. Kagan, Nouv. J. Chim., 1 (1977) 5; P. Girard, J.L. Namy and H.B. Kagan, J. Am. Chem. Soc., 102 (1980) 2693.
157 J.L. Namy, P. Girard, H.B. Kagan and P. Caro, Nouv. J. Chim., 5 (1981) 479.
158 Wang Genglin, Yan Shiping and Li Xueyao, Gaodeng Xuexiao Huaxue Xuebao (Chem. J. Chin. Univ.), 4 (1983) 13.
159 Tan Minyu and Gao Yici, Lan-Chou Ta Hsueh Hsueh Pao, Tzu Jan K'o Hsueh Pao, (1978) 143; Ko Hsueh T'ung Pao (Kexue Tongbao), 25 (1980) 170; Kexue Tongbao, 25 (1980) 482 (Eng.).
160 G. Wang, R. Zhang, and Z. Jiang, Gaodeng Xuexiao Huaxue Xuebao, 4 (1983) 535.
161 J.H. Timmons, J.W.L. Martin, A.E. Martell, P. Rudolf, A. Clearfield, J.H. Arner, S.J. Loeb and C.J. Willis, Inorg. Chem., 19 (1980) 3553.
162 Quin Kunyuan, Feng Xiaojun and Feng Xinde, Kexue Tongbao, 26 (1981) 990, 1176 (Eng.).
163 Y. Ohisuka and H. Kawaguchi, Kobunshi Robunshu, Engl. Edn., 3 (1974) 1553.
164 O.A. Gansow, K.M. Triplett, T.T. Peterson, R.E. Botto and J.D. Roberts, Org. Magn. Reson., 13 (1980) 77.
165 O.A. Gansow, R.K.C. Ho and W. Klemperer, J. Organomet. Chem., 187 (1980) C27.
166 W. DeW. Horrocks Jr. and M. Albin, Progr. Inorg. Chem., 31 (1984) 1.
167 J.-C.G. Bünzli, in R. Bock, W. Fresenius, H. Günzler and W. Huber (Eds.), Analytiker Taschenbuch, Band 3, Springer Verlag, Berlin, 1983, chap. 1.
168 P. Tundo and J.H. Fendler, J. Am. Chem. Soc., 102 (1980) 1760.
169 F. Montanari and P. Tundo, J. Org. Chem., 47 (1982) 1298.
170 C. Detellier and D.H. Stover, Synthesis, (1983) 990.
171 H. Nagai, T. Deguchi and K. Nakai, Bunseki Kagaku, 21 (1972) 788.
172 Yang Yansheng and Zhu Jiaqin, Gaodeng Xuexiao Huaxue Xuebao, 31 (1982) 6; Chem. Abstr. 96 (1982) 206305u.
173 W.F. Kinard, W.J. McDowell and R.R. Shoun, Sep. Sci. Technol., 15 (1980) 1013.
174 Wang Wenji, Chen Bozhong, Hin Zhonggao and Wangl Ailing, Gaodeng Xuexiao Huaxue Xuebao, 2 (1981) 431; Chem. Abstr., 97 (1982) 46213c.
175 Yang Yusheng, Ding Yuzhen, Wang Qiuyin, Yao Zhongqi and Pan Guangming, He Huaxue Yu Fangshe Huaxue, 4 (1982) 21; Chem. Abstr., 96 (1982) 137986y.
176 Kao Yuan and Ni Jiazan, He Huaxue Yu Fangshe Huaxue, 5 (1983) 146.
177 Lin-Mei Tsay, Jeng-Shang Shih and Shaw-Chii Wu, Analyst, 108 (1983) 1108.
178 T. Kudo and Y. Oba, Jpn. Pat. JP Kokai Tokkyo Koho 78137080 (1978); Chem. Abstr., 93 (1979) 22424i

179 Y. Hirashima, Y. Moriwaki and J. Shiokawa, Chem. Lett., (1980) 1181.
180 T. Arakawa, Y. Hirashima and J. Shiokawa, Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai, 36 (1980) 277.
181 J. Rais, P. Selucky, V. Jirasek and F. Sebesta, J. Radioanal. Chem., 35 (1977) 351.
182 W.E. Morf, D. Ammann, R. Bissig, E. Pretsch and W. Simon, in R.M. Izatt and J.J. Christensen (Eds.), Progress in Macrocyclic Chemistry, Vol. 1, John Wiley, New York, 1979, chap. 1.
183 P.A. Bertrand, G.R. Choppin, Lin Geng Rao and J.-C.G. Bünzli, Anal. Chem., 55 (1983) 364.
184 T. Shono and K. Kimura, Kagaku (Kyoto), 32 (1977) 314.
185 R.E. Wetton and D.B. James, U.S. Pat. 4200701 (1980).
186 C.W. Gokel, D.M. Goli, C. Minganti and L. Echegoyen, J. Am. Chem. Soc., 105 (1983) 6786.