Lanthanide Complexes with Mono- and Bicyclic Macromolecules. Synthesis and Spectroscopic Studies

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Complexes of lanthanide(III) chlorides, thiocyanates, nitrates and perchlorates with three cyclic polyethers containing five or six oxygen atoms in the cycle and two bicyclic macromolecules containing five or six oxygen and two nitrogen atoms in the cycles have been prepared and characterized. Possible arrangements around the cation are proposed on the ground of conductivity measurements, vibrational and electronic spectra.

Introduction

Several complexes of the alkali and alkaline earth and d-transition metals with cyclic polyethers have been prepared and characterized. The complexes of lanthanide(III) nitrates and thiocyanates with the cyclic polyethers benzo-15-crown-5 and dibenzo-18-crown-6 [1] and some complexes with the cyclic polyethers 12-crown-4, 15-crown-5 and 18-crown-6 [2] have also been reported. Only the lanthanum nitrate and praseodymium perchlorate complexes with the polyether dicyclohexyl-18-crown-6 are known [3]; for these systems the authors emphasize the inclusion of the cation into the cycle of the polyether.

Recently a communication on the synthesis and properties of some lanthanide cryptates [4] and two X-ray crystal studies on the cryptates [La⟨cryp222⟩ (NO$_3$)$_2$]$^+$ [5] and [Eu⟨cryp222⟩ClO$_4$](ClO$_4$)$_2$·MeCN [6] (cryp222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8,8,8]-hexacosane) have been published.

In this paper we report the synthesis and properties of some lanthanide(III) nitrate and perchlorate complexes with the bicyclic macromolecules cryp222 and cryp221 (cryp221 = 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-[8,8,5]-tricosane) and of the complexes of the cyclic polyethers benzo-15-crown-5, dibenzo-18-crown-6 and dicyclohexyl-18-crown-6 with lanthanide(III) chlorides and perchlorates. The lanthanide(III) nitrate and thiocyanate complexes with the polyether diciclohexyl-18-crown-6 have also been prepared and characterized; the properties of

these complexes have been compared with the corresponding complexes with the polyethers benzo-15-crown-5 and dibenzo-18-crown-6.

Experimental

Materials

Hydrated lanthanide(III) nitrates, thiocyanates, chlorides and perchlorates were employed; as a starting material for the synthesis of the cryptates, anhydrous lanthanide(III) nitrate and perchlorate complexes with dimethylsulphoxide were also employed. The polyether benzo-15-crown-5 (L$_I$) was prepared following Pedersen [7]; the polyethers dibenzo-18-crown-6 (L$_{II}$) and dicyclohexyl-18-crown-6 (L$_{III}$) are Strem chemical products. The bicyclic macromolecules cryp222 and cryp221 are Merck products and were used as received. Methanol contained less than 0.03% of water (C. Erba).

Synthesis of the Cryptates

0.8 mmol of the cryptand macromolecule in 10 ml of methanol were added to 1.0 mmol of the cation in 20 ml of methanol. The resulting solution was refluxed under dry nitrogen for 10 min. The lanthanide cryptate slowly formed as crystalline powder. The precipitates were filtered off, washed with methanol and dried *in vacuo* at room temperature. Only the complexes of large cations (La–Eu) were prepared; in this case no exceptional precaution was necessary to avoid moisture. Attempts to obtain cryptate-type compounds employing nitrate of ligands were unsuccessful. Minute crystals were obtained by mixing and moderately heating solutions of the lanthanide(III) nitrates and the N-protonated cryptand in methanol (c = 2 × 10^{-2} *M*), but the following considerations suggest that coordination between the macromolecule and the cation does not occur and that these compounds consist of the ion pairs ([Ln(NO$_3$)$_{3+x}$]$^{x-}$)(x/2(H$_2$L)$^{2+}$) (x = 3, 2): (i) the strong bands arising from the ionic nitrate groups that appear in the IR spectra of the protonated ligand disappear in the spectra of the compounds

with lanthanide nitrates; the spectra show in fact only unsplit bands due to the C_{2v} symmetry nitrate group. (ii) The insignificant shift of the C–O–C and C–N–C modes with respect to the free ligand which indicates no lanthanide–cryptand bonding. (iii) An increase in the intensity of the f–f hypersensitive transitions caused by the addition to the tripositive cation in methanol of the protonated ligand, the same as caused by the addition of an ionic nitrate. La$_2$-(cryp222H$_2$)$_3$(NO$_3$)$_{12}$ requires: N, 11.69%; La, 12.88%; found: N, 11.37%; La, 13.51%. Nd-(cryp222H$_2$)(NO$_3$)$_5$ requires: N, 11.77%; Nd, 17.32%; found: N, 11.80%; Nd, 16.94%.

Synthesis of the Complexes with Polyethers

Complexes of lanthanide(III) nitrates and thiocyanates with L$_I$ and L$_{II}$ were prepared following ref. [1]. The complexes of lanthanide(III) nitrates and thiocyanates with L$_{III}$ and the chloride complexes with L$_I$, L$_{II}$ and L$_{III}$ were obtained by adding 1 mmol of the crystalline polyether to 1 mmol of the cation in acetonitrile (nitrates and thiocyanates) or anhydrous ethanol (chlorides). The complexes of large nitrates and chlorides (La–Eu) and the complexes of the thiocyanates (La–Ho) with L$_{III}$ precipitated slowly as crystalline powder on heating the solution (method *a*).

1 mmol of the crystalline polyether L$_{II}$ or L$_{III}$ was added to 1 mmol of the lanthanide(III) perchlorate (La–Eu), previously heated at 200 °C under reduced pressure (~10^{-3} mm Hg) in a vacuum thermoanalyzer and immediately dissolved in anhydrous acetonitrile; the solution was moderately heated. From the cooled solution microcrystalline products formed.

To obtain the compounds EuL$_I$Cl$_3$·4H$_2$O, EuL$_{III}$-(ClO$_4$)$_3$·2H$_2$O and HoL$_{III}$(NO$_3$)$_3$·4H$_2$O it was necessary to concentrate the solution containing rigorously stoichiometric proportions of the cation and polyether and add successively small amounts of carbon tetrachloride or anhydrous diethyl ether until turbidity settled; the compounds precipitated slowly from the cooled solutions by prolonged stirring or on standing overnight (method *b*).

All precipitates were filtered off, washed with acetonitrile or anhydrous ethanol and dried *in vacuo* at room temperature.

Viscous oils, which difficulty crystallized, formed with the heaviest cations.

Measurements

IR spectra were obtained by a Perkin-Elmer 577 spectrophotometer from KBr pellets and nujol mulls. The integrated absorption intensity (A, M^{-1} cm^{-2}) of the CN stretching mode for the thiocyanate complexes was determined by Ramsay's method of direct integration [8]. Electronic absorption spectra were recorded with an Optica CF4NI spectrophotometer

equipped with 5 cm quartz cells; the diffuse reflectance spectra were obtained with the same instrument equipped with a single-beam reflectance attachment using solid compounds pasted with nujol and spread on a disk of filter paper. The absorption intensity, presented as oscillator strength, was calculated from the expression:

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2 + 2)^2} \right] \int \epsilon(\nu)\delta\nu,$$

where η is the refractive index of the solution and ϵ the molar extinction coefficient at the wavelength ν. The molar conductivity was measured with an Amel 951 conductivity bridge, at 25 ± 0.1 °C, equipped with a conventional closed cell. Spectral and conductivity measurements were carried out in acetonitrile or methanol solutions of the complexes or by addition of successive known amounts of the crystalline polyether or cryptand molecule to the solution. Thermal analysis was performed with a Mettler vacuum thermoanalyzer in dynamic nitrogen (10 l h^{-1}) and with an heating rate of 2 °C min^{-1}. Fluorescence spectra were obtained by a Perkin-Elmer MPF-3L fluorescence spectrophotometer from solid state compounds and methanol or acetonitrile solutions exciting with 395 mm radiation at room and liquid nitrogen temperatures. Resolution was better than 10 cm^{-1}.

Analysis

Lanthanides were determined by gravimetric (oxalate) method. The water molecules content was determined by the Karl Fisher method; the results were compared with the thermal analysis.

Results and Discussion

Selected analytical data and properties of the complexes satisfactorily isolated are reported in Tables I, II. All complexes with polyethers have 1:1 stoichiometry and are soluble in acetonitrile, nitromethane and alcohols. Since the two cryptand macromolecules have relatively strong basic properties, the synthesis of the lanthanide cryptates starting from hydrated cations is strongly hampered by formation of hydroxo-compounds and N-protonated species. Rigorously anhydrous conditions are required to prepare analytically pure compounds; however, traces of moisture are tolerated and it was not necessary to take particular precaution to avoid moisture in the case of the cryptates of large cations (La–Eu). The cryptates are soluble in methanol and acetonitrile.

The conductivity of the light lanthanide nitrates in acetonitrile and chlorides in acetonitrile–ethanol mixture (5:1) increases and tends to 1:1 electrolytic behaviour [9] on complexation with L$_{II}$ and L$_{III}$, but the conductivity of the nitrates decreases if L$_I$ is the polyether.

TABLE I. Selected Analytical Data, Conductivity and Temperature of Thermal Decomposition of Lanthanide(III) Complexes with Cyclic Polyethers (L_I = Benzo-15-crown-5; L_{II} = Dibenzo-18-crown-6; L_{III} = dicyclohexyl-18-crown-6). In parenthesis the calcd. values.

Complex	% C	% H	% X (X = Cl, N)	% Ln	Λ_M[a]	$(M \times 10^3)^c$	t_i, °C[b]	Method
$NdL_ICl_3 \cdot 2H_2O$	(30.30)31.00	(4.36)4.50	(19.17)19.29	(26.00)26.45	33	2.2	230	a
$EuL_ICl_3 \cdot 4H_2O$	(28.09)29.45	(4.73)4.61	(17.75)18.06	(25.38)25.89	39	1.8	225	b
$PrL_{II}Cl_3$	(39.53)38.95	(3.98)4.03	(17.50)17.63	(23.19)23.36	48	1.9	260	a
$SmL_{II}Cl_3 \cdot 2H_2O$	(36.78)36.03	(4.32)4.50	(16.29)16.12	(23.02)22.70	46	2.1	250	a
$LaL_{III}Cl_3$	(39.14)38.70	(5.26)5.15	(17.32)16.99	(22.64)22.85	75	2.2	270	a
$NdL_{III}Cl_3$	(38.80)39.12	(5.21)5.37	(17.17)17.51	(23.30)23.63	72	1.9	270	a
$EuL_{III}Cl_3 \cdot H_2O$	(37.25)36.86	(5.32)5.18	(16.49)16.74	(23.57)24.03	80	1.7	260	a
$LaL_{II}(ClO_4)_3$	(30.11)28.95	(3.03)3.10		(17.42)17.63	220	1.8	300	a
$NdL_{II}(ClO_4)_3$	(29.91)30.07	(3.01)2.95		(17.97)18.10	225	1.7	305	a
$LaL_{III}(ClO_4)_3$	(29.81)30.00	(4.00)4.13		(17.24)17.35	220	1.8	300	a
$NdL_{III}(ClO_4)_3$	(29.62)28.90	(3.98)3.77		(17.79)18.01	225	1.9	295	a
$EuL_{III}(ClO_4)_3 \cdot 2H_2O$	(28.20)27.15	(4.22)4.38		(17.80)18.35	245	1.5	285	b
$LaL_{III}(NO_3)_3$	(34.64)35.03	(4.65)4.70	(6.06)6.12	(20.03)20.48	90	2.9	270	a
$NdL_{III}(NO_3)_3$	(34.38)34.07	(4.62)4.48	(6.01)5.89	(20.65)20.91	95	2.4	270	a
$EuL_{III}(NO_3)_3 \cdot 2H_2O$*	(32.35)31.22	(4.89)4.95	(5.66)5.54	(20.47)21.06	75	1.8	265	a
$HoL_{III}(NO_3)_3 \cdot 4H_2O$ §	(30.35)29.54	(5.09)5.17	(5.31)5.47	(20.84)21.38	45	2.0	235	b
$LaL_{III}(NCS)_3$	(40.52)40.37	(4.73)4.68	(6.17)6.22	(20.38)20.50	38	2.1	270	a
$NdL_{III}(NCS)_3$	(40.21)40.53	(4.70)4.86	(6.12)6.07	(21.00)21.33	35	2.1	275	a
$EuL_{III}(NCS)_3$	(39.76)40.02	(4.64)4.71	(6.05)5.88	(21.88)21.75	38	2.0	265	a
$TbL_{III}(NCS)_3$	(39.37)38.25	(4.60)4.43	(5.99)5.71	(22.65)23.07	32	1.9	255	a

[a] ohm^{-1} cm^2 M^{-1}, at 25 ± 0.1 °C, in acetonitrile (nitrates, thiocyanates, perchlorates) or acetonitrile—ethanol mixture (5:1) (chlorides). The average values measured in acetonitrile for 1:1, 1:2 and 1:3 electrolytes are respectively 140, 260 and 390 ohm^{-1} cm^2 M^{-1} [9]; the values measured in acetonitrile for the hydrated lanthanide(III) nitrates and thiocyanates vary, respectively, between 11–18 and 22–29 (c = $1–3 \times 10^{-3}$ M), and for lanthanide(III) perchlorates (hydrated) between 280 and 310 ohm^{-1} cm^2 M^{-1} for $1–1.3 \times 10^{-3}$ M concentration and between 370 and 390 ohm^{-1} cm^2 M^{-1} for $1–1.3 \times 10^{-4}$ M concentration. The molar conductivity measured for hydrated lanthanide(III) chlorides in acetonitrile—ethanol mixture (5:1) vary between 26 and 32 ohm^{-1} cm^2 M^{-1} (c = $1–3 \times 10^{-3}$ M). [b] Temperature of incipient thermal decomposition. *This complex heated at 50 °C for a night under reduced pressure ($\sim 10^{-3}$ mm Hg) loses the water molecules; the thermoanalytical curves do not show any step with mass-loss until thermal decomposition begins at 265 °C. § This complex undergoes dehydration between 110 and 155 °C; no step with mass-loss occurs successively until thermal decomposition begins at 235 °C.

The complexation of lanthanide chlorides with L_I and thiocyanates with all these polyethers does not cause any pronounced change in the conductivity. The anhydrous lanthanide perchlorate complexes, the complex $EuL_{III}(ClO_4)_3 \cdot 2H_2O$ and the complexes of the two cryptand molecules with lanthanide perchlorates exhibit in acetonitrile molar conductivity values which are too small to be simply attributed to ion association and suggest contribution of coordinative effects. The molar conductivity values measured for the lanthanide nitrate complexes with cryptands in acetonitrile—methanol mixture (1:1) vary between those obtained for 1:1 and 1:3 electrolytes in the same mixture of solvents (Table II, note a). Conductivity measurements were performed also by addition of known amounts of the polyether to the cation in acetonitrile or acetonitrile—ethanol mixture (5:1). In the case of large nitrates and chlorides the conductivity becomes constant and reaches the value measured for the corresponding complex dissolved in the same

solvent after the addition of 1 mmol of the polyether to 1 mmol of the cation; this trend has been previously observed [10] and is a clear indication of the occurred complexation. For most of the systems, however, the conductivity unceasingly changes by addition of the polyether. This trend is more likely due to the equilibrium that occurs between un-complexed and mono-complexed species or, simply, to the fact that no true complexation occurs, rather than to the formation of systems containing more than one molecule of polyether [11].

IR Spectra
Ligand modes
The IR bands exhibited by these molecules which undergo significant changes on complexation with lanthanides are those arising from C–O–C and C–N–C stretching and CH bending modes. The C–O–C and C–N–C stretching modes which appear as strong and broad bands around 1250 and 1100 cm^{-1} in the

TABLE II. Analytical Data, Conductivity and Temperature of Thermal Decomposition of Lanthanide(III) Cryptates (cryp222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8,8,8]-hexacosane; cryp221 = 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-[8,8,5]-tricosane). In parenthesis the calcd. values.

Complex	% C	% H	% N	% Ln	Λ_M[a]	$(M \times 10^4)$[c]	$t_i,°C$[b]
$La_4(cryp221)_3(NO_3)_{12} \cdot 2MeOH$	(25.43)26.01	(4.44)4.35	(10.68)10.75	(23.53)23.65	385	5.8	220
$Nd_2(cryp221)(NO_3)_6 \cdot H_2O \cdot MeOH$	(19.57)20.41	(3.67)3.81	(10.74)10.63	(27.66)26.54	235	8.6	205
$Sm_2(cryp221)(NO_3)_6 \cdot H_2O \cdot MeOH$	(19.46)20.07	(3.65)3.74	(10.68)10.87	(28.66)27.79	248	5.7	200
$La(cryp221)(ClO_4)_3 \cdot H_2O \cdot MeOH$	(24.99)24.78	(4.67)4.50	(3.42)3.39	(16.96)17.08	265	7.3	190
$Pr(cryp221)(ClO_4)_3 \cdot H_2O \cdot MeOH$	(24.85)25.03	(4.66)4.74	(3.41)3.53	(17.15)16.94	260	8.0	185
$Nd(cryp221)(ClO_4)_3 \cdot H_2O \cdot MeOH$	(24.75)25.17	(4.64)4.57	(3.40)3.29	(17.49)17.15	275	6.5	185
$Sm(cryp221)(ClO_4)_3 \cdot H_2O \cdot MeOH$	(24.57)24.12	(4.61)4.70	(3.37)3.44	(18.09)17.85	280	7.3	180
$Pr_2(cryp222)(NO_3)_6 \cdot MeOH$	(21.48)22.05	(3.80)3.85	(10.55)10.31	(26.53)26.04	205	10.5	215
$Nd_2(cryp222)(NO_3)_6 \cdot MeOH$	(21.35)21.54	(3.77)3.68	(10.48)10.42	(26.99)26.75	215	9.8	215
$Sm_2(cryp222)(NO_3)_6 \cdot MeOH$	(21.11)21.63	(3.73)3.60	(10.36)10.11	(27.81)28.35	210	10.6	200
$Eu_2(cryp222)(NO_3)_6 \cdot MeOH \cdot H_2O$	(20.70)20.58	(3.84)3.76	(10.16)10.41	(27.57)28.65	265	10.3	210

[a] ohm^{-1} cm^2 M^{-1}, at 25 ± 0.1 °C, in acetonitrile—methanol mixture (1:1). The molar conductivity values measured for pyridinium nitrate and perchlorate are 138 and 151 ohm^{-1} cm^2 M^{-1}, respectively; the values measured for $(cryp222H_2)(NO_3)_2$ and $(cryp222H_2)(ClO_4)_2$ are 253 and 265 ohm^{-1} cm^2 M^{-1}, respectively; the values measured for lanthanide(III) trifluoromethane-sulfonates vary between 240–280 ohm^{-1} cm^2 M^{-1} for 1–2 × 10^{-3} M concentration and 365–385 ohm^{-1} cm^2 M^{-1} for 1–2 × 10^{-4} M concentration. All measurements in acetonitrile—methanol mixture (1:1) (c = 4–6 × 10^{-3} M). [b] Temperature of incipient thermal decomposition.

spectra of the free ligands shift upon complexation 20–40 cm^{-1} to lower frequencies; the CH bending mode which appears at 950–900 cm^{-1} in the spectra of the ligands shifts 10–30 cm^{-1} to higher frequencies. These spectral changes are similar to those reported for the complexes of lanthanide(III) nitrates with a tetraoxadiaza macromolecule; for these complexes the authors emphasize that a complete inclusion of the cation into the cavity of the ligand occurs [12]. However, pronounced changes are observed, independently of the anion present, only for the complexes of large nitrates, chlorides and perchlorates (La—Eu) with each of these polyethers and for all the thiocyanate complexes; otherwise the spectra appear slightly changed with respect to the free ligand. This suggests that true coordination does not occur in some cases, but interactions of the outer-sphere type only or hydrogen bonds act between the polyether and water molecules of adjacent entities [13, 14].

Anion modes

No band attributable to the D_{3h} symmetry nitrate group appears in the IR spectra of the larger lanthanide nitrate complexes (La—Nd) with L_{II} and L_{III} in the solid state where three bidentate nitrate groups act; however, the appearance in acetonitrile solution of a band at 1380 cm^{-1} due to the ν_3 mode suggests ionization of nitrate groups. The nitrate complexes with L_I do not exhibit in any case ionic nitrate bands. Only bands arising from the C_{2v} symmetry nitrate group appear in the IR spectra of the

nitrate complexes with the two cryptand molecules; however, splitting occurs for the ν_2, ν_3 and ν_6 modes while more than one peak appear in the regions of the combination bands $\nu_2 + \nu_5$ and $\nu_2 + \nu_6$ (Table III). The spectral patterns shown by the cryptates here reported are similar to that shown by the lanthanum nitrate complex with the cryp222 and suggest that two different entities, both containing bidentate nitrate groups, act in these systems.

Parson *et al.* [15] attribute the splitting of perchlorate modes observed in the IR spectra of the alkaline earth metal complexes with the polyethers benzo-18-crown-6 and dibenzo-18-crown-6 to coordinative effects. Ciampolini *et al.* [6], Sinha *et al.* [16] find perchlorate groups bidentate to the cation in some europium complexes. In the IR spectra of the anhydrous perchlorate complexes with polyethers and perchlorate cryptates the degeneracy of the asymmetric stretching and bending modes of the perchlorate group appears removed and triplets are exhibited in the ranges 1160–1070 and 650–620 cm^{-1}, respectively; furthermore, the ν_1 mode (T_d symmetry) is activated and appears as a medium intensity band around 935 cm^{-1}. This behaviour is due to lowering from the T_d symmetry and can be reasonably attributed to coordinative effects.

The IR spectra of the thiocyanate complexes with polyethers show the CN stretching mode split into two or three components between 2090 and 2040 cm^{-1}. This splitting is too high to be attributed to crystalline perturbations alone (40–30 cm^{-1}) and arises also from inequivalence (different M—N—C bond

TABLE III. Lanthanide Cryptates. IR Data for Nitrate and Perchlorate Groups.

Complex[a]	$\nu_2 + \nu_5$	$\nu_2 + \nu_6$	ν_1	ν_4	ν_2	ν_3	ν_6	ν_5	(C_{2v})
$La_4(cryp222)_3(NO_3)_{12} \cdot 2MeOH*$	1775w	1735br	1480vs	1320s	1042w	825m	746m	720vw	
	1770w				1038m	820w	742m		
$Pr_2(cryp222)(NO_3)_6 \cdot MeOH$	1780w	1740br	1490vs	1320s	1042sh	826m	747m	720vw	
	1775w				1038m	822w	743m		
$Sm_2(cryp222)(NO_3)_6 \cdot MeOH$	1780br	1740br	1490vs	1320s	1040sh	825m	748m	720vw	
					1037m	822sh	744m		
$La_4(cryp221)_3(NO_3)_{12} \cdot 2MeOH$	1775w	1740w	1485vs	1315s	1042w	825m	745m	720w	
	1770w	1735w			1038m	820w	742m		
$Nd_2(cryp221)(NO_3)_6 \cdot H_2O \cdot MeOH$	1780w	1740br	1490vs	1320s	1043m	827m	747m	720vw	
	1775w				1038w	823sh	743m		

	ν_3	ν_1	ν_4	(T_d)
$Eu(cryp222)(ClO_4)_3 \cdot H_2O \cdot 0.5MeCN$[§]	1155s, 1025s, 1080s	935m	645m, 635m, 630m	
$Nd(cryp221)(ClO_4)_3 \cdot H_2O \cdot MeOH$	1155s, 1025s, 1080s	932m	643m, 635m, 632m	

*Prepared following ref. [5].   § Prepared following ref. [6].   [a]The $Nd(NO_3)_5 \cdot (cryp222H_2)$ exhibits the $\nu_2 + \nu_5$, $\nu_2 + \nu_6$, ν_1, ν_4, ν_2, ν_3, ν_5, ν_6 modes respectively at 1780w, 1745w, 1480s, 1325s, 1042m, 825m, 743m, 715w.

angles and M–N bond length) of the three thiocyanate groups. The measured intensity values for the single thiocyanate group (A = 11–13×10^{-4}, M^{-1} cm^{-2}) are in the range of values found in acetonitrile for the N-coordination of the thiocyanate group.

Electronic Spectra
  Ligand Spectra
  The polyethers L_I and L_{II} exhibit intraligand bands at 227–228 and 275–276 nm. Complexation with lanthanides causes a blue-shift and a decrease in the intensity for both transitions (Fig. 1). This trend has been previously observed [1, 7] and is a clear indication of oxygen atoms of the polyether involved in bonding with metal ions. The spectra of the complexes of the heavy nitrates and perchlorates do not show any marked intensity or band shape change; this can mean that no bond occurs between the oxygen atoms of the polyether and the cation.

f–f spectra
  Changes with respect to the solvated cation of the intensity and shape of the bands associated with the hypersensitive transitions in lanthanide(III) ions occur on complexation with these polyethers and cryptand molecules. The intensity decreases and the baricenter of the band group shifts to higher frequencies in the case of the thiocyanate complexes with L_{II} and L_{III} and of all chloride and nitrate complexes; the intensity increases and the band shifts to lower frequencies for all the perchlorate complexes and for the thiocyanate complexes with L_I (Table IV and Fig. 2).
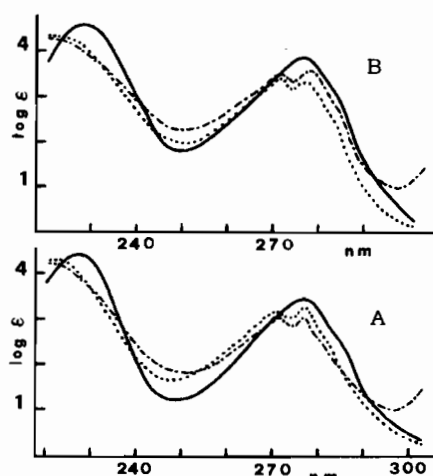

Fig. 1. UV spectra. A: (——) L_I; (...) $NdL_ICl_3 \cdot 2H_2O$; (–.–.) $EuL_I(NCS)_3 \cdot H_2O$. B: (——) L_{II}; (...) $LaL_{II}Cl_3$; (–.–.) $NdL_{II}(NCS)_3$.

The shape of the band associated with the $^4I_{9/2} \rightarrow$ $^4G_{5/2}$ hypersensitive transition in the neodymium complexes with these ligands is independent of the ligand, anion and coordination number; moreover, the absorption spectra are similar to the reflectance ones. This trend indicates that complexation occurs in any case; however, the higher the ionic dissociation degree the lower the intensity of the hypersensitive transition.

Recently the red-shift of the main peak associated with the $^4I_{9/2} \rightarrow ^2P_{1/2}$ transition and the intensity of

TABLE IV. f–f Spectra of Lanthanide(III) Complexes in Acetonitrile (nitrates, thiocyanates, perchlorates) or Acetonitrile–Ethanol Mixture (5:1) (chlorides).

	Transition		Solvated Cation	Complexes				
				L_I	L_{II}	L_{III}	cryp222	cryp221
$Nd(NO_3)_3 \cdot 5H_2O$	$^4I_{9/2} \rightarrow {}^4G_{5/2}$	$10^6 \cdot P$	26.15	25.06	23.70	22.95	21.88	25.62
		kK^*	17.18	17.18	17.18	17.24	17.21	17.18
$Nd(NCS)_3 \cdot nH_2O$	$^4I_{9/2} \rightarrow {}^4G_{5/2}$	$10^6 \cdot P$	22.07	23.62	19.48	21.33		
		kK^*	17.09	17.06	17.12	17.09		
$NdCl_3 \cdot 6H_2O$	$^4I_{9/2} \rightarrow {}^4G_{5/2}$	$10^6 \cdot P$	18.85	17.02	15.48	14.80		
		kK^*	17.05	17.05	17.07	17.07		
$Nd(ClO_4)_3 \cdot nH_2O$	$^4I_{9/2} \rightarrow {}^4G_{5/2}$	$10^6 \cdot P$	11.49		12.80	14.95	15.44	15.63
		kK^*	17.33		17.30	17.27	17.27	17.27
$Ho(NCS)_3 \cdot nH_2O$	$^5I_8 \rightarrow {}^5G_6$	$10^6 \cdot P$	23.08	29.60		21.45		
		kK^*	22.08	22.05		22.10		

*Baricenter of the band group.

TABLE V. Partial Energy Level Scheme for Solid Europium(III) Complexes with Cyclic Macromolecules. The values refer to the baricenter of the band group (cm^{-1}, ± 7).

Complex	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^5D_0$	$^5D_1$	$^5D_2$
$EuL_ICl_3 \cdot 4H_2O$	0	388	988	1863*	17280	18956	21505
$EuL_{III}Cl_3 \cdot H_2O$	0	365	1017	1945*	17286	18975	21515
$EuL_{III}(NO_3)_3 \cdot 2H_2O$	0	341	1025	1915	17247	19065	21510
$EuL_{III}(NCS)_3$	0	428	1049	1984*	17283	19055*	21491
$Eu(cryp222)(ClO_4)_3 \cdot H_2O \cdot O \cdot 5MeCN$ §	0	345	960	1893	17265	19173	21495

§ See ref. [6]. *±10.
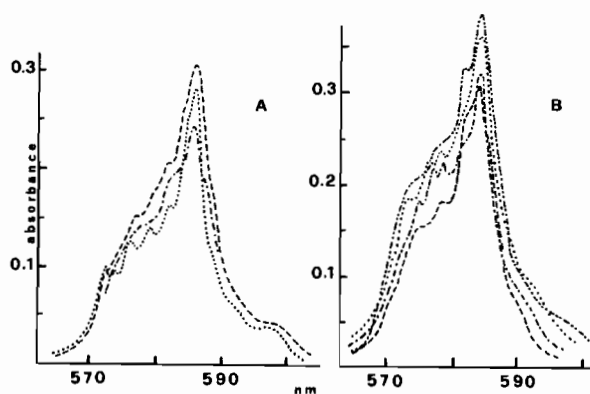
Fig. 2. The $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition in Nd^{3+} ion. Absorption spectra in acetonitrile. A: (——) $NdL_I(NCS)_3 \cdot H_2O$; (...) $NdL_{III}(NCS)_3$; (–.–.) $NdL_{II}(NCS)_3$. B: (...) $NdL_I(NO_3)_3$; (–.–.) $NdL_{III}(NO_3)_3$; (– – –) $Nd_2(cryp222)(NO_3)_6 \cdot MeOH$; (–..–..) $Nd_2(cryp221)(NO_3)_6 \cdot MeOH \cdot H_2O$.

the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition in Nd^{3+} ion have been correlated with the stability constants of some inner-sphere complexes of neodymium [17, 18]. The complexes of the alkali and alkaline earth metals with L_{III} have stability constants greater than the corre-

sponding complexes with L_{II} [19]. Here it occurs that the intensity of the hypersensitive transitions increases on passing from the complexes of large perchlorates and thiocyanates with L_{II} to the corresponding complexes with L_{III}, but the intensity decreases for the complexes of nitrates and chlorides. It is probable that this trend arises from a different degree of ionic dissociation, but the intensity decreases also for the nitrate complexes with L_I for which no ionic dissociation occurs. An explanation is connected with the contribution which can arise from a generalized lengthening of the Ln–O bonds owing to the complexation of the nitrates.

The intensity of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition measured for the neodymium nitrate increases on passing from the complex with the cryp 222 to the complex with cryp 221; the values are comparable with those of the complexes $NdL_{III}(NO_3)_3$ and $NdL_I(NO_3)_3$, respectively.

From the absorption and emission spectra it is possible to construct a partial energy level scheme for the europium(III) ion in some of these complexes (Table V).

It is known that information concerning the symmetry at the europium(III) ion can be obtained by a study of the fluorescence spectra. The fluorescence
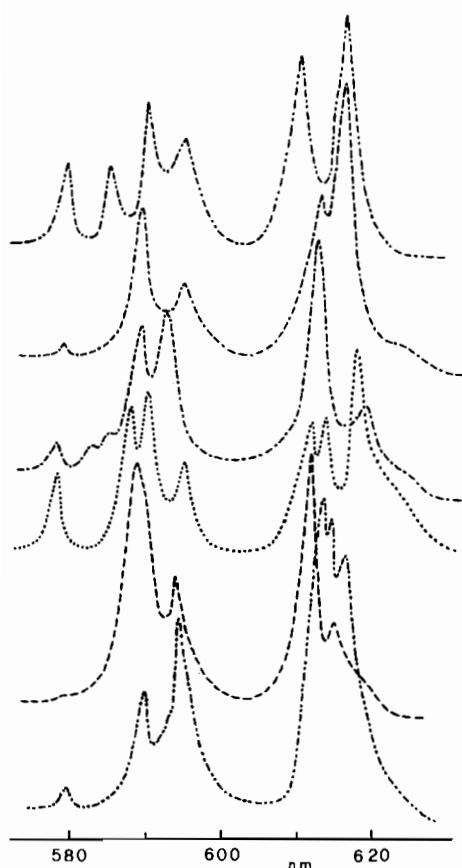
Fig. 3. Solid state fluorescence spectra at 77 K. (– – –) $Eu(cryp222)(ClO_4)_3 \cdot 0.5MeCN \cdot H_2O$; (– .. – ..) $Eu_2(cryp222)$ $(NO_3)_6 \cdot MeOH$; (...) $EuL_{III}Cl_3 \cdot H_2O$; (– – . – – .) EuL_{III}-$(NO_3)_3 \cdot 2H_2O$; (– – ..) $EuL_{III}(NCS)_3$; (– . – .) $EuL_ICl_3 \cdot$ $4H_2O$.

spectra of some complexes here reported are depicted in Fig. 3. Fluorescence arises mainly from the $^5D_0$ level by excitation to the $^5L_6$ level.

The europium trichloride hexahydrate in the solid state has been described in terms of octacoordinated $[Eu(OH_2)_6Cl_2]^+$ units with highly distorted square antiprismatic geometry [20]. The emission spectrum of the solid complex $EuL_{III}Cl_3 \cdot H_2O$ consists of two weak lines at 611.0 and 612.5 nm and a more intense line at 618.0 nm, broadened to lower frequencies, all associated with the $^5D_0 \rightarrow {}^7F_2$ transition (Fig. 3). Two almost equal intensity lines at 588.8 and 591.3 nm and a weaker line at 596.5 nm arise from the $^5D_0 \rightarrow {}^7F_1$ transition. The $^5D_0 \rightarrow {}^7F_0$ transition is allowed and appears as a relatively intense line at 578.5 nm. There is little doubt both from synthetic and spectroscopic data that this complex consists of 8-coordinated arrangement. The spectral pattern suggests C_{2v} site symmetry for the europium(III) ion in this complex. The emission spectrum of the solid complex $EuL_ICl_3 \cdot 4H_2O$ at 77 K shows two lines at 590.0 and 593.5 nm associated with the $^5D_0 \rightarrow {}^7F_1$

transition. Two lines arise from the $^5D_0 \rightarrow {}^7F_2$ transition; the first appears at 613.0 nm, the second is exhibited as a very weak line at 619.0 nm. A weak line appears at 578.7 nm arising from the $^5D_0 \rightarrow {}^7F_0$ transition. Two weak lines at 584 and 586.5 nm are assigned to the $^5D_1 \rightarrow {}^7F_3$ transition. This spectral pattern is similar to that shown by the solid europium trichloride hexahydrate and suggests the same site symmetry for the europium(III) ion.

A decacoordinated $[LnO_{10}]$ chromophore acquired by three bidentate nitrate groups and four water molecules in bicapped dodecahedral geometry has been established for hydrated lanthanide nitrates in the solid state [21]. The emission spectrum of the solid europium nitrate complex with L_{III} at 77 K shows two lines, one sharp at 590.5 nm and one broad at 596.2 nm, both associated with the $^5D_0 \rightarrow {}^7F_1$ transition; the sharp line can be assigned to a non-degenerate and the broad one to a doubly degenerate representation. Two relatively intense lines appearing at 614.2 and 618 nm and a very weak line at 622 nm are associated with the $^5D_0 \rightarrow {}^7F_2$ transition. A line appearing at 579.8 nm is assigned to the $^5D_0 \rightarrow {}^7F_0$ transition; its intensity is, however, less than 2% of the most intense $^5D_0 \rightarrow {}^7F_2$ transition. This spectral pattern suggests D_{2d} site symmetry for the europium(III) ion. Conductivity measurements indicate that in acetonitrile the nitrate complexes with L_{III} ionize one nitrate group with the cation, possibly, surrounded by ten oxygen atoms from two bidentate nitrate groups and one hexadentate molecule of L_{III}. The emission spectrum of the europium complex in acetonitrile is similar to that of the solid complex and, both, to the spectrum of the solid europium(III) nitrate pentahydrate, but indicate deviations from the idealized polyhedron.

The structure of lanthanide(III) thiocyanate heptahydrates consists of 9-coordinated arrangements in monocapped square antiprismatic geometry [22]. Conductivity measurements, analytical data and IR spectra indicate that 9-coordinated arrangements are maintained in any case upon complexation with these polyethers. There is a marked similarity between the IR spectra of the lanthanide thiocyanate complexes with L_I and the calcium thiocyanate monohydrate complex or the sandwich complexes of sodium and potassium tetraphenylborates with this polyether [15, 23, 24] (Fig. 4). The radical ratio is unfavourable to the inclusion into the cycle of this polyether of large cations, these lying out of the molecular plane of the ligand. In the case of the lanthanide complexes the environment could be completed by three N-coordinated thiocyanate groups and one water molecule. On the other hand, large cations may get into the cycle of the 18-membered ring and heavy cations into the cycle of the 15-membered ring polyethers. The emission spectrum of the complex $EuL_{III}(NCS)_3$ consists of two lines at 612.5 and
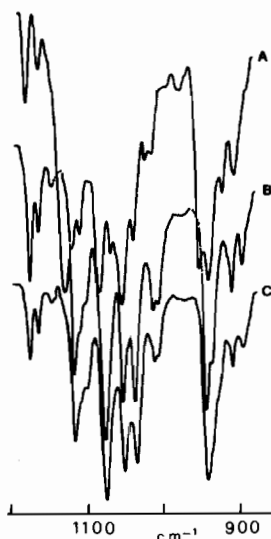
Fig. 4. IR spectra of: A, CaL$_I$(NCS)$_2 \cdot$H$_2$O (prepared following ref. 24); B, NdL$_I$(NCS)$_3 \cdot$H$_2$O; C, HoL$_I$(NCS)$_3 \cdot$H$_2$O.

618.5 nm arising from the $^5D_0 \rightarrow {}^7F_2$ transition; the last is broad and could originate from an E-component. Two lines, one sharp at 592.5 nm and one broad at 597.5 nm, appear in the region of the $^5D_0 \rightarrow {}^7F_1$ transition. The $^5D_0 \rightarrow {}^7F_0$ transition is allowed and appears as a relatively intense line at 578.6 nm; an almost equal intensity line appearing at 586 nm is assigned to the $^5D_1 \rightarrow {}^7F_3$ transition. This spectral pattern agrees well with C$_{4v}$ site symmetry for the europium(III) ion in this complex.

The emission spectrum of the europium nitrate complex with the 222cryptand shows two components of the $^5D_0 \rightarrow {}^7F_1$ transition at 588.3 and 594.5 nm; the latter is, however, broad. Two relatively intense lines arising from the $^5D_0 \rightarrow {}^7F_2$ transition appear at 613.0 and 614.5 nm; a third but weak and broad component of this transition appears at 617 nm. A line arising from the $^5D_0 \rightarrow {}^7F_0$ transition is exhibited at 579.2 nm; its intensity is, however, about 2.5% of the most intense $^5D_0 \rightarrow {}^7F_2$ transition. The diameter of both cycles of this molecule is approximately 2.8 Å and is adequate to include only large cations as K$^+$ or Cs$^+$; moreover, the presence of two cycles helds the molecule to be more rigid than the monocyclic 18-membered ring molecules. Nevertheless, the high number of potential donor atoms, the presence of cycles having smaller diameters (2.2 Å for the 221cryptand) and the possibilities that these molecules have of existing in different configurations rapidly interconverting *via* nitrogen inversion (*exo–exo, exo–endo, endo–endo*) [25] make them able to including into the cavity also lanthanide(III) cations. That lanthanum ion in nitrate and europium ion in perchlorate systems get into the cavity of the 222cryptand has been demonstrated by X-ray crystal

studies [5, 6]. Here is, indeed, evidence that other lanthanides (Ce–Eu) lie into the cavity of both these cryptand macromolecules and that ion pairs form in the case of the nitrate systems (m[Ln(cryp)-(NO$_3$)$_{3-x}$]$^{x+}$)(n[Ln(NO$_3$)$_{3+y}$]$^{y-}$) (x = 1, 2; y = 2, 3). The formation of the cryptate occurs in fact through the ionization of nitrate groups, which, in alcohols, may coordinate with another nitrate entity. The system La$_4$(cryp222)$_3$(NO$_3$)$_{12}$ ·2MeOH has been described in terms of the ion pair (3[La(cryp222)-(NO$_3$)$_2$]$^+$)([La(NO$_3$)$_6$]$^{3-}$) [5]. However, reduced cation size allows the cation, in the cryptate entity, to coordinate only one nitrate group; on the other hand, the minor depth of the *tomb* of the cryp 221 could favour the coordination of a greater number of nitrate groups than the 222cryp.

The complex [Eu(cryp222)ClO$_4$]$^{2+}$ has been described in terms of bicapped square antiprismatic geometry [6]. The emission spectrum of the monohydrated species shows a broad line at 590. 5 nm and a sharp one at 594.5 nm, both arising from the $^5D_0 \rightarrow {}^7F_1$ transition. The $^5D_0 \rightarrow {}^7F_2$ transition consists of a line at 611.0 nm and a very weak and broad component at 615 nm. The $^5D_0 \rightarrow {}^7F_0$ transition can be taken as forbidden, the spectrum showing only a weak line at 579.2 nm. This spectral pattern indicates deviation from the idealized polyhedron and lower than D$_{4d}$ site symmetry for the europium(III) ion.

References

1 (a) A. Cassol, A. Seminara and G. De Paoli, *Inorg. Nucl. Chem. Letters, 9,* 1163 (1973). (b) R. B. King and P. R. Heckley, *J. Am. Chem. Soc., 96,* 3118 (1974).

2 (a) J.-C. G. Bunzli and D. Wessner, *Helv. Chim. Acta, 61,* 1454 (1978); (b) J.-C. G. Bunzli, D. Wessner and H. T. T. Oanh, *Inorg. Chim. Acta, 32,* L33 (1979).

3 (a) M. E. Harman, F. A. Hart, M. B. Hursthouse, G. P. Moss and P. R. Raithby, *Chem. Comm.,* 396 (1976). (b) G. A. Catton, M. E. Harman, F. A. Hart, G. E. Hawkes and G. P. Moss, *J. Chem. Soc. Dalton,* 181 (1978).

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

5 F. A. Hart, M. B. Hursthouse, K. M. A. Malik and S. Moorhouse, *Chem. Comm.,* 549 (1978).

6 M. Ciampolini, P. Dapporto and N. Nardi, *Chem. Comm.,* 788 (1978).

7 C. J. Pedersen, *J. Am. Chem. Soc., 89,* 2945 (1967); *89* 7017 (1967).

8 D. A. Ramsay, *J. Am. Chem. Soc., 74,* 72 (1952).

9 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).

10 C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Internat. Edit., 11,* 16 (1972).

11 D. F. Evans, S. L. Ellington, J. A. Nadis and E. L. Cussler, *J. Solution Chem., 1,* 499 (1972).

12 J. E. Desreux, A. Renard and G. Duyckaerts, *J. Inorg. Nucl. Chem., 39,* 1587 (1977).

13 G. Bombieri, G. De Paoli, A. Cassol and A. Immirzi, *Inorg. Chim. Acta, 18,* L 23 (1976).

14 P. G. Eller and R. A. Penneman, *Inorg. Chem., 15,* 2439 (1976).

15 D. G. Parson and J. N. Wingfield, *Inorg. Chim., Acta, 18,* 263 (1976).

16 S. P. Sinha and A. Bartecki, *Inorg. Chim. Acta, 28,* 145 (1978).

17 R. B. Gayhart and T. Moeller, *J. Inorg. Nucl. Chem., 39,* 49 (1977).

18 K. Bukietynska, A. Mondry and E. Osmeda, *J. Inorg. Nucl. Chem., 39,* 483 (1977).

19 H. K. Frensdorff, *J. Am. Chem. Soc., 93,* 600 (1971).

20 N. K. Bel'skii and Yu. T. Struchkov, *Crystallography (Soviet. Phys.), 10,* 15 (1965).

21 I. M. Rumanova, G. F. Volodina and N. V. Belov, *Crystallography (Soviet. Phys.), 9,* 545 (1965).

22 P. I. Lazarev, M. A. Porai Koshits, L. A. Aslanov and V. I. Ivanov, *Zh. Strukt. Khim., 13,* 543 (1972); *13,* 740 (1972).

23 D. G. Parson, M. R. Truter and J. N. Wingfield, *Inorg. Chim. Acta, 14,* 45 (1975).

24 J. D. Owen, *J. Chem. Soc. Dalton,* 1418 (1978).

25 B. Dietrich, J. M. Lehn and J. P. Sauvage, *Tetrahedron Letters, 34,* 2889 (1969).