

## 58. Complexes of Lanthanoid Nitrates with 15-Crown-5 and 18-Crown-6 Ethers<sup>1)2)</sup>

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### Summary

Complexes between the heavier lanthanoid nitrates  $\text{Ln}(\text{NO}_3)_3$  and 15-crown-5 (**1**) and 18-crown-6 (**2**) ethers were isolated and characterized. Both 1:1 and 4:3 complexes are formed with each Ln(III) ion, except in the case of Gd and **2**. The thermal transformation of the 1:1 complexes into the corresponding 4:3 complexes was studied by thermogravimetry and by DSC. X-ray and vibrational data provide information about the structure of these complexes. The interaction between Ln(III) ions and ligands **1** and **2** in non-aqueous solutions is discussed on the basis of conductometric, fluorescence, UV./VIS. and <sup>1</sup>H-NMR. data. Only 1:1 complexes of **2** formed in solution and their formation constants range from  $\log K_f = 4.4$  (Ln=La) to 2.4 (Ln=Yb); for Eu,  $K_f$  of the 15-crown-5 and 18-crown-6 ether complexes are of the same order of magnitude. For La, Pr, Nd, Eu, Yb, a variable temperature NMR. study gave some indications about the chemical exchanges in solution.

The factors which determine the stoichiometry of the complexes are discussed.

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**Introduction.** - Complexes between lanthanoid salts and multidentate macrocyclic ligands, namely crown ethers [1] and cryptands [2], attract considerable interest [3], which was initiated by the work of *Cassol et al.* and *King & Heckley* [4]. Indeed, these ligands may be used to study high coordination numbers (10, 11, 12) of the rare-earth ions [5] and to stabilize divalent ions such as Sm(II), Eu(II) and Yb(II) [6-8]. Moreover, macrocyclic ligands facilitate the study of the chemical bond between Ln(III) ions and soft donor atoms; the macrocyclic effect may be used to stabilize complexes with polyethers in which one or more of the O-atoms are replaced by S-atoms [9]. We have reported the isolation of three types of complexes: (i) 1:1 complexes between  $\text{Ln}(\text{NO}_3)_3$  and 12-crown-4 (La-Lu) [10], 15-crown-5 (**1**) (La-Gd) [11], and 18-crown-6 (**2**) (La-Nd) [11] ethers<sup>4)</sup>, (ii) 4:3 com-

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<sup>1)</sup> Part 10 of the series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'. Part 9 [22].

<sup>2)</sup> Abstracted in part from the Ph.D. Thesis of D. W.

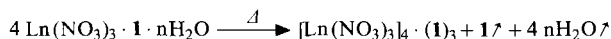
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<sup>4)</sup> The nomenclature proposed in [1] is used; systematic names are: 1,4,7,10-tetraoxacyclododecane, 1,4,7,10,13-pentaoxacyclpentadecane (**1**), and 1,4,7,10,13,16-hexaoxacyclooctadecane (**2**).

plexes between  $\text{Ln}(\text{NO}_3)_3$  and **2** (La-Gd), and (iii) 1:2 sandwich complexes between  $\text{Ln}(\text{ClO}_4)_3$  and 12-crown-4 and 15-crown-5 ethers (La-Gd) [12] [13]. We report here the synthesis and characterization of the 1:1 and 4:3 complexes between the heavier lanthanoid nitrates (Dy-Lu) and the polyethers **1** and **2**. We also discuss the interaction, both in the solid state and in anhydrous solutions, between these ligands and the Ln (III) ions.

**Experimental Part.** - 1. *Syntheses.* 1.1. *The 1:1 complexes of 1* were prepared by adding dropwise a solution of 5 mmol of **1** (*Fluka, purum*) in 50 ml  $\text{CH}_3\text{CN}$  (*Fluka, puriss.*) to a solution of 5 mmol  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  ( $1 < x < 5$ ) [14] in 50 ml  $\text{CH}_3\text{CN}$ . The resulting solution was stirred 24 h at 60°, cooled at RT, and concentrated to 25-50 ml. The crystalline complexes were filtered off and dried in a desiccator with  $\text{P}_2\text{O}_5$ ; they still contained 3-4 molecules  $\text{H}_2\text{O}$  per formula weight. Completely anhydrous complexes could be obtained for Tb-Er after drying for 3-5 days at  $-5^\circ/2 \cdot 10^{-5}$  Torr. For Tm-Lu, part of the ligand is lost under high vacuum and unsolvated complexes could not be obtained.

1.2. *The 4:3 complexes of 1 (Ln = Gd-Lu)* were obtained by quantitative thermal decomposition of the corresponding 1:1 complexes:



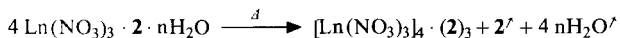
The experimental conditions are reported in *Table 1*.

Table 1. *Conditions for the quantitative thermal transformation of  $\text{Ln}(\text{NO}_3)_3 \cdot \mathbf{1}$  into  $[\text{Ln}(\text{NO}_3)_3]_4 \cdot (\mathbf{1})_3$  at  $10^{-5}$  Torr*

Ln	t (h)	T (°C)	Ln	t (h)	T (°C)
Gd	24	160	Er	96	25
Tb	5	120	Tm	24	40
Dy	120	25	Yb	96	25
Ho	3	80	Lu	72	40

1.3. *The 1:1 complexes of 2* were synthesized as described above, (§ 1.1) with the following modifications. With  $\text{Ln} = \text{Eu, Dy}$ : 5 mmol  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  in 80 ml  $\text{CH}_3\text{CN}$  were added at 0° to 5 mmol **2** in 75 ml  $\text{CH}_3\text{CN}$ ; the resulting solution was stirred 24 h at 0°, filtered, stirred 72 h at  $-20^\circ$ , and filtered; the complexes were dried for a few days in a desiccator with  $\text{P}_2\text{O}_5$  and for 3-4 days at  $\text{RT}/2 \cdot 10^{-5}$  Torr; for  $\text{Ln} = \text{Sm, Gd}$ , such a procedure led to 4:3 complexes  $[\text{Ln}(\text{NO}_3)_3]_4 \cdot (\mathbf{2})_3$ . With  $\text{Ln} = \text{Tb, Ho}$ : 5 mmol  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  in 20-40 ml  $\text{CH}_3\text{CN}$  were added at 0° to 5 mmol **2** in 75 ml  $\text{CH}_3\text{CN}$ ; the resulting solution was stirred 24 h at 0° and filtered; the complexes were dried as described for  $\text{Ln} = \text{Eu, Dy}$ . With  $\text{Ln} = \text{Er-Lu}$ : 5 mmol **2** in 50 ml  $\text{CH}_3\text{CN}$  were added to 5 mmol  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  in 50 ml; the resulting solution was stirred 24 h at 60°, cooled at RT, and filtered; the complexes were dried as described for  $\text{Ln} = \text{Eu, Dy}$ .

1.4. *The 4:3 complexes of 2 (Ln = Tb, Ho-Lu)* were obtained by quantitative thermal decomposition of the corresponding 1:1 complexes:



The experimental conditions are reported in *Table 2*. The complex with  $\text{Ln} = \text{Dy}$  was synthesized as described in [11] for Gd.

Table 2. *Conditions for the quantitative thermal transformation of  $\text{Ln}(\text{NO}_3)_3 \cdot \mathbf{2}$  into  $[\text{Ln}(\text{NO}_3)_3]_4 \cdot (\mathbf{2})_3$*

Ln	t (h)	T (°C)	P (Torr)	Ln	t (h)	T (°C)	P (Torr)
Tb	48	60	$5 \cdot 10^{-5}$	Tm	96	40	$5 \cdot 10^{-5}$
Ho	24	110	$2 \cdot 10^{-2}$	Yb	96	70	$2 \cdot 10^{-2}$
Er	16	180	$2 \cdot 10^{-2}$	Lu	48	40	$5 \cdot 10^{-5}$

2. *Analysis of the complexes.* The metal content was determined as described in [11]. C, H, N elemental analyses were performed by *W. Manser* (Mikroanalytisches Laboratorium der ETH Zürich). Good values were difficult to obtain for highly hygroscopic complexes; we therefore report the analyses for complexes with a relatively stable hydration number. The results are listed in *Table 3*. For  $[\text{Ln}(\text{NO}_3)_3]_4 \cdot (1)_3$ , the metal content is: Gd (MW=2,033.85), found 31.54% (Calc. 30.93%); Tb (2,040.53), 31.56 (31.15); Dy (2,054.85), 31.47 (31.63); Ho (2,064.57), 31.76 (31.95); Er (2,073.89), 32.13 (32.26); Tm (2,080.57), 32.87 (32.48); Yb (2,097.01), 33.17 (33.01); Lu (2,104.61), 33.42 (33.25).

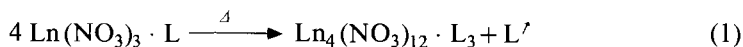
3. *Other measurements.* Hygroscopic samples were handled under controlled atmosphere ( $\text{N}_2$  with less than 10 ppm water). X-ray powder diagrams were recorded on an *Ital* Structure diffractometer equipped with a *Guignier* camera, using the Ni-filtered  $\text{CuK}_\alpha$  line ( $\lambda = 1.54056 \text{ \AA}$ ). Thermogravimetric

Table 3. *Elemental analyses of the complexes and yields of the syntheses*

Ln	n	MW	$\eta$ %	% C		% H		% N		% Ln	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$\text{Ln}(\text{NO}_3)_3 \cdot (1) \cdot n\text{H}_2\text{O}$											
Tb	0	565.20	27	21.25	-	3.57	-	7.43	-	28.12	28.30
	2	601.23		19.98	20.21	4.02	3.97	6.99	6.88	26.43	26.77
Dy	0	568.78	35	21.12	-	3.54	-	7.39	-	28.57	28.42
	2	604.81		19.86	19.76	4.00	4.05	6.95	7.00	26.87	26.60
Ho	0	571.21	21	21.03	-	3.53	-	7.36	-	28.87	28.96
	2	607.24		19.78	19.87	3.98	4.07	6.92	6.89	27.16	27.25
Er	0	573.54	43	20.94	20.74	3.51	3.68	7.33	7.30	29.16	29.15
	3	627.59		19.14	18.83	4.18	4.09	6.70	6.67	26.65	26.67
Tm	3	629.56	58	19.09	18.92	4.16	4.02	6.68	6.52	26.85	26.61
Yb	3	633.37	68	18.96	19.23	4.14	4.19	6.63	6.40	27.32	27.17
Lu	3	635.27	66	18.91	18.95	4.13	4.01	6.61	6.46	27.54	27.34
$\text{Ln}(\text{NO}_3)_3 \cdot (2) \cdot n\text{H}_2\text{O}$											
Eu	0	602.29	32	23.93	23.92	4.02	4.09	6.98	7.07	25.23	25.03
Tb	0	609.26	34	23.66	-	3.97	-	6.90	-	26.08	25.98
	1	627.27		22.98	22.86	4.18	4.34	6.70	6.90	25.34	25.24
Dy	0	612.83	29	23.52	-	3.95	-	6.86	-	26.52	26.42
	1	630.84		22.85	22.72	4.15	4.10	6.66	6.40	25.76	25.68
Ho	0	615.27	37	23.43	23.51	3.93	4.01	6.83	6.67	26.81	26.65
	1	633.28		22.76	22.68	4.14	4.05	6.64	6.96	26.04	25.88
Er	0	617.58	40	23.34	23.18	3.92	4.10	6.80	6.70	27.08	26.86
	1	635.59		22.67	22.72	4.12	4.32	6.61	6.49	26.32	26.25
Tm	0	619.26	77	23.27	-	3.91	-	6.79	-	27.30	27.16
	1	637.27		22.62	22.94	4.11	4.38	6.59	6.44	26.51	26.53
Yb	0	623.38	63	23.12	-	3.88	-	6.74	-	27.76	27.59
	1	641.39		22.47	22.47	4.09	4.16	6.55	6.37	26.98	26.82
Lu	0	625.27	89	23.05	-	3.87	-	6.72	-	27.98	28.01
	1	643.28		22.40	22.42	4.07	4.05	6.53	6.36	27.20	27.21
$[\text{Ln}(\text{NO}_3)_3]_4 \cdot (2)_3$											
Tb	0	2172.72	100	19.90	20.01	3.34	3.45	7.74	7.64	29.26	29.03
Dy	0	2187.02	34	19.77	19.52	3.32	3.47	7.69	7.51	29.72	29.69
Ho	0	2196.74	100	19.68	19.68	3.30	3.48	7.65	7.46	30.03	29.71
Er	0	2206.06	100	19.60	19.51	3.29	3.51	7.62	7.38	30.33	30.53
Tm	0	2212.72	100	19.54	-	3.28	-	7.60	-	30.54	30.14
Yb	0	2229.16	100	19.40	-	3.26	-	7.54	-	31.05	31.10
Lu	0	2236.76	100	19.33	-	3.24	-	7.51	-	31.29	31.45

analyses were performed by *P. Comte*, Institut de radiochimie de l'EPF Lausanne (Prof. *P. Lerch*) and by *P. Tissot*, Département de chimie technique de l'Université de Genève. *Mettler* TA-1 thermo-analyzers with Pt/Pt-Rh 10% thermocouples were used. Samples of 9–12 mg in Pt-crucibles were heated under a dynamic atmosphere of Ar at a rate of 2°/min. All the thermograms were baseline corrected. The enthalpy of the transformation of 1:1 complexes into 4:3 complexes was measured using a *Setaram* C-80 scanning calorimeter. The samples (20–40 mg) were sealed under vacuum and heated at a rate of 0.5°/min. IR. spectra were recorded using Nujol (*Fluka, puriss.*) mulls with a *Perkin-Elmer* 577 spectrometer or with a *Bruker* IFS-113c *Fourier-transform* spectrometer. Raman spectra of finely powdered samples were recorded with a *Spex* Ramalog-4 laser-spectrometer (Ar line,  $\lambda = 514.5$  nm, 200–400 mW). Conductometric measurements were performed at  $25.0 \pm 0.1^\circ$  on 0.001M solutions in CH<sub>3</sub>CN, using a *Metrohm* E-365 conductometer. UV/VIS. spectra were recorded on a *Perkin-Elmer* 340 spectrophotometer equipped with a microprocessor-controlled data station, using quartz cells with 1, 5 or 10 cm path. The water content of CH<sub>3</sub>CN (*Merck*, spectroscopic quality) was less than 0.026 mol l<sup>-1</sup>, as determined by *Karl-Fischer* titration. <sup>1</sup>H-NMR. spectra (60 MHz) were recorded on a *Bruker* WP-60 FT-spectrometer. The water content of CD<sub>3</sub>CN (*Ciba-Geigy AG*, 99.9%) was less than 0.1 mol l<sup>-1</sup>.

**Results and discussion.** - 1. *The 1:1 and 4:3 stoichiometries.* All complexes were microcrystalline, hygroscopic powders with the characteristic colour of the lanthanoid ions. Both 1:1 and 4:3 complexes of **1** and **2** were isolated for each lanthanide ion (Gd-Lu), either directly or by thermal decomposition, except for **2** and Ln = Gd. The 4:3 stoichiometry is rather unusual for the rare earths. To our knowledge, the only other examples are Ln[Ln(EDTA)]<sub>3</sub> (Ln = Nd, Sm), described by *Möller et al.* [15], the complexes between lanthanum nitrate and the [2.2.1] and [2.2.2] cryptands [16] [17], and those we have previously reported [11] [18]. Since many of the 4:3 complexes we isolated could be obtained from thermal decomposition of the corresponding 1:1 species,



we recorded their thermogravimetric data.

Non-hygroscopic complexes of the lighter lanthanoid nitrates with **1** were thermally stable up to 240–260°. Similarly to the Ln(NO<sub>3</sub>)<sub>3</sub> · (12-crown-4) complexes [10], they decomposed completely into a mixture of oxinitrate, oxide, and organic residue. Complexes of lanthanoids heavier than Eu started to decompose at lower temperature, and an intermediate compound of limited thermal stability was observed (*Table 4, Fig. 1a*). This trend was confirmed for Gd(NO<sub>3</sub>)<sub>3</sub> · **1** · 4 H<sub>2</sub>O; loss of water occurred above 50° and led to the monohydrated complex which in turn decomposed into the anhydrous complex; this compound was stable up to 160° and finally transformed into the 4:3 complex. The ligand could be recovered unchanged (IR.). A similar situation occurred for Ln = Tb, with a much more unstable 1:1 complex, as well as for the other heavier Ln(III) ions. The 4:3 complexes all decomposed within a narrow temperature range (275–285°). From Gd to Yb, the starting complexes were extremely hygroscopic and the degree of hydration was difficult to determine. Consequently, a slight doubt was left whether the observed plateaux correspond to 4:3 complexes or not. Heating the 1:1 hydrated complexes (*cf. exper. part*), led, however, to the formation of analytically pure 4:3 complexes.

Table 4. Thermogravimetric data of some complexes  $\text{Ln}(\text{NO}_3)_3 \cdot L \cdot n\text{H}_2\text{O}$ ,  $L = 1, 2$ 

Ln	n	1:1 Complex stab. range (°C)	1:1 Complex			4:3 Complex stab. range (°C)	4:3 Complex	
			% Calc. <sup>a)</sup> <sup>b)</sup>	% Calc. <sup>a)</sup> <sup>c)</sup>	% Found		% Calc. <sup>a)</sup>	% Found
15-Crown-5 complexes								
La	0	→ 260						
Pr	0	→ 240						
Eu	0	→ 170						
Gd	4.2	100–160	88.1		88.9	195–250	79.5	77.7
Tb	2.0	100–110	94.0		94.6	155–260	84.8	83.1
Dy	4.6	(90)	87.4	90.1	89.4	150–260	78.9	78.9 <sup>d)</sup>
Ho	5.1	(90)	86.2	88.9	89.0	150–270	77.9	77.9 <sup>d)</sup>
Er	3.4	105–110	90.4	93.2	91.7	170–275	81.6	81.6 <sup>d)</sup>
Yb	3.9	(105)	89.2	92.0	91.0	165–270	80.7	80.7 <sup>d)</sup>
18-Crown-6 complexes								
La	0	→ 210				230–305	88.8	88.7
Pr	0	→ 130				220–290	88.8	88.8
Nd	0	→ 110				180–250	88.9	89.6
Eu	0.4	50–110	98.8		98.8	<sup>e)</sup>	88.0	87.7
Tb	3.5	100–110	90.6		91.5	<sup>e)</sup>	80.8	76.9
Er	3.1	105–135	92.0		93.2	200–270	82.1	81.9
Yb	3.5	105–120	90.9		92.2	195–235	81.2	79.6

<sup>a)</sup> % weight of the sample. <sup>b)</sup> Anhydrous 1:1 complex. <sup>c)</sup> Monohydrated 1:1 complex. <sup>d)</sup> Calculated assuming the plateau corresponds to the 4:3 complex. <sup>e)</sup> Undefined plateau.

With **2**, a 1:1 → 4:3 transformation occurred for all the lanthanoid ions (*Fig. 1b*). The stability range of the 4:3 complexes was usually smaller than for the complexes of **1**: 35–75°, as compared to 55–120°. Except for La–Pr, Er, the plateaux corresponding to the 4:3 complexes were not perfectly horizontal, indicating a slight decomposition even at relatively low temperature. Moreover, the decomposition temperature of the 4:3 complexes was not reproducible; differences of up to 20° were found between two runs. The influence of the anion on the 1:1 → 4:3 transformation was studied using complexes with Pr salts (*Fig. 2*). With the chloride, the 1:1 complex decomposed at 210° and the plateau corresponding to the 4:3 complex was perfectly horizontal up to 300°. With the isothiocyanate, the 4:3 complex did not form, the 1:1 complex being completely decomposed at 300°.

Reaction 1 was endothermic for 18-crown-6 complexes of  $\text{Ln}(\text{NO}_3)_3$  (La–Nd) and of  $\text{PrCl}_3$ . The uncorrected heat of reaction, measured by differential scanning calorimetry (DSC.) amounted to 57 (La), 47 (Ce), 43 ( $\text{Pr}(\text{NO}_3)_3$ ), 40 ( $\text{PrCl}_3$ ), and 38 (Nd) kJ mol<sup>-1</sup>. No heat of transformation could be measured for the other complexes, neither by DSC., nor by differential thermal analysis performed simultaneously with the thermogravimetric experiment.

These thermal data demonstrate that 4:3 complexes are formed between **1** and the heavier rare-earth ions (Gd–Lu) and between **2** and all the lanthanoid ions. Similar compounds are not formed with the more rigid benzo-15-crown-5 and dibenzo-18-crown-6 ethers [4] [19].

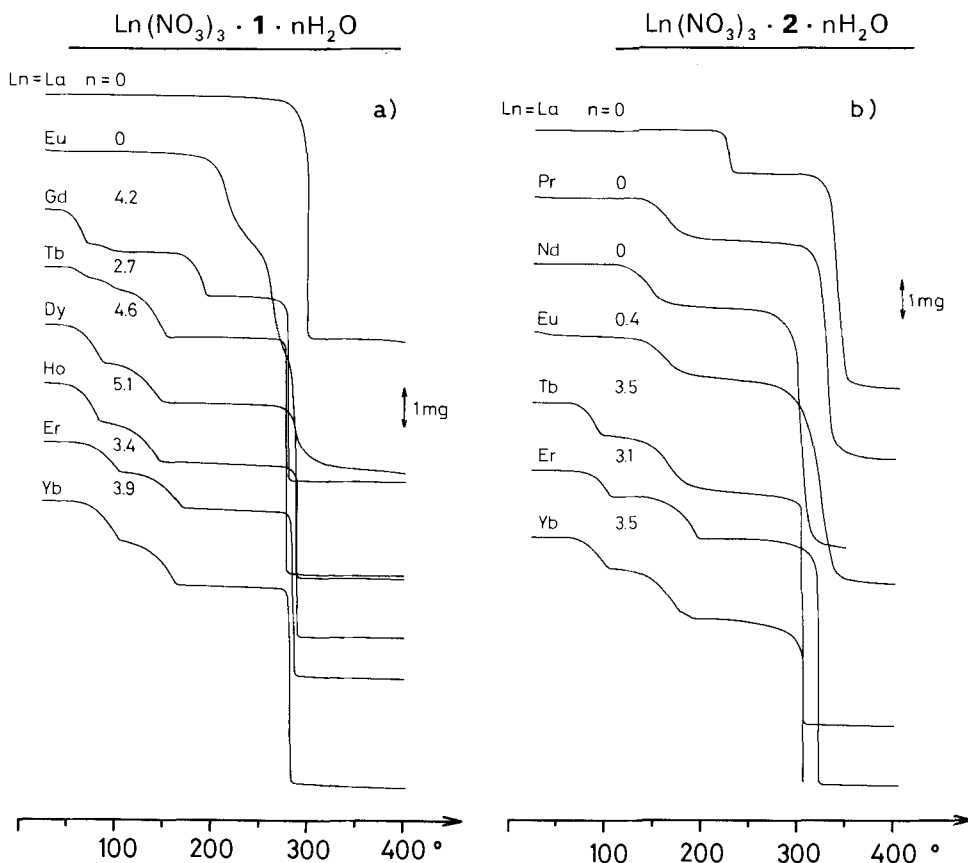
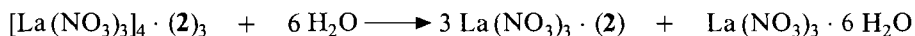


Fig. 1. Thermogravimetric analyses. (a)  $\text{Ln}(\text{NO}_3)_3 \cdot 1 \cdot n\text{H}_2\text{O}$  complexes: Ln=La (9.60 mg), Eu (11.36), Gd (9.77), Tb (10.67), Dy (9.57), Er (9.54), Yb (11.25). (b)  $\text{Ln}(\text{NO}_3)_3 \cdot 2 \cdot n\text{H}_2\text{O}$  complexes: Ln=La (9.88 mg), Pr (9.61), Nd (10.95), Eu (9.26), Tb (9.80), Er (9.73), Yb (10.32).

2. *Structural and vibrational data.* X-ray powder photographs of the less hygroscopic complexes indicated at least three types of structure within the series  $\text{Ln}(\text{NO}_3)_3 \cdot 1$ : Ln=La-Nd, Ln=Sm, Eu, and Ln=Ho. Both the 1:1 and 4:3 complexes of holmium nitrate gave the same powder pattern. The 1:1 complexes of **2** were isomorphous for La-Nd, and so were 4:3 complexes for Ce, Nd, Eu, Ho. Again, both the 1:1 and 4:3 complexes of holmium nitrate gave the same powder pattern (*vide infra*). The powder photograph of  $[\text{La}(\text{NO}_3)_3]_4 \cdot (\mathbf{2})_3$  was more complex; IR. and elemental analyses indicated the decomposition of this complex according to



Some complexes yielded suitable monocrystals for crystallographic investigations and we have solved the structure of three of them. In  $\text{Eu}(\text{NO}_3)_3 \cdot 1$ , the Eu(III) ion is undecacoordinated to the five O-atoms of the crown ether and to

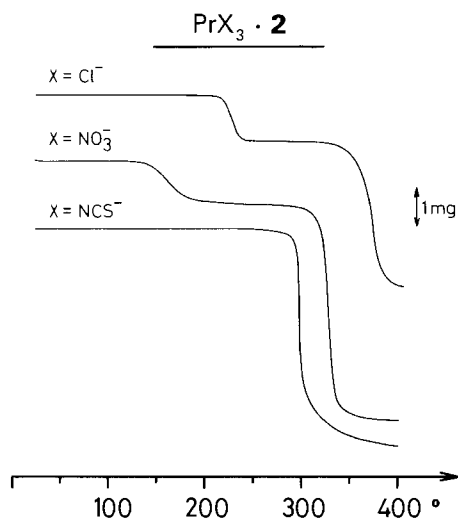


Fig. 2. Thermogravimetric analyses of praseodymium complexes: X = Cl (9.63 mg), NO<sub>3</sub> (9.61), NCS (10.93).

three bidentate nitrate groups which all lie on the same side [20]. In Nd(NO<sub>3</sub>)<sub>3</sub> · 2, the Nd(III) ion is dodecaordinated to the six O-atoms of the polyether and to three bidentate nitrate groups, one on the more sterically hindered side of the macrocycle and two on the opposite side [21]. The 4:3 complex contains three crystallographically distinct ions; one hexanitrate ion Nd(NO<sub>3</sub>)<sub>6</sub><sup>3-</sup> and three cations [Nd(NO<sub>3</sub>)<sub>2</sub> · 2]<sup>+</sup> of two different symmetries [22]; all the nitrate groups are bidentate.

The vibrational spectra of the complexes can now be discussed on the basis of this structural information. Typical data for the nitrate ions are summarized in Table 5. Since the crystallographic structures indicated that all the nitrate ions are planar and of approximate C<sub>2v</sub> symmetry, we labelled the six observed vibrations according to this point group of symmetry [14]. The IR. absorptions of both Ln(NO<sub>3</sub>)<sub>3</sub> · 2 (Eu, Tb-Lu) and [Ln(NO<sub>3</sub>)<sub>3</sub>]<sub>4</sub> · (2)<sub>3</sub> (La-Lu) were very similar. Systematic shifts were observed for ν<sub>6</sub>, from 735 (La) to 754 cm<sup>-1</sup> (Lu), and for one component of ν<sub>4</sub>, from 1263 (La) to 1280 cm<sup>-1</sup> (Lu). This component probably arose from a [Ln(NO<sub>3</sub>)<sub>6</sub>]<sup>3-</sup> species; the corresponding vibration of (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> and K<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> occurred at 1275 and 1290 cm<sup>-1</sup> (nujol mulls) respectively [23]. The other component of ν<sub>4</sub>, at about 1330 cm<sup>-1</sup>, may therefore be assigned to complex species [Ln(NO<sub>3</sub>)<sub>2</sub> · 2]<sup>+</sup>. The neutral complexes Ln(NO<sub>3</sub>)<sub>3</sub> · 2 (La-Nd) displayed only one ν<sub>4</sub> vibration. A similar situation was met with the complexes of **1**. The 1:1 complexes of the lighter lanthanoid (La-Eu) nitrates were characterized by one ν<sub>4</sub> vibration, whereas the 1:1 complexes of the heavier rare-earth ions (Gd-Er) and the 4:3 complexes (Gd-Lu) displayed two ν<sub>4</sub> vibrations, at ~1320 and at ~1280 cm<sup>-1</sup>; the latter vibration could be assigned to a hexanitrate species. Regarding the bonding mode of the nitrate groups, both criteria proposed by Curtis & Curtis [24] and by Lever *et al.* [25] indicate that these groups are bidentate in all the complexes; ν<sub>1</sub>-ν<sub>4</sub> ranges between

Table 5. *Typical vibrational data (cm<sup>-1</sup>) for the nitrate ions<sup>a</sup>*

Complex		$\nu_2 + \nu_5, \nu_6$ b)	$\nu_1(A_1)$	$\nu_4(B_2)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_6(B_1)$	$\nu_5(B_2)$
Pr(NO <sub>3</sub> ) <sub>3</sub> · 1	IR.:	4	1500 <sub>vs</sub>	1310 <sub>vs</sub>	1035 <sub>s</sub>	821 <sub>m</sub>	746sh. 741 <sub>m</sub>	725 <sub>m</sub>
	R.:	-	c)	1300 <sub>w</sub>	1034 <sub>vs</sub> 1031 <sub>s</sub>	c)	732 <sub>m</sub>	707 <sub>vw</sub>
Ho(NO <sub>3</sub> ) <sub>3</sub> · 1	IR.:	3	1500 <sub>vs</sub>	1320 <sub>vs</sub> 1278 <sub>vs</sub>	1025 <sub>s</sub>	819 <sub>m</sub>	751 <sub>m</sub>	715
Ho <sub>4</sub> (NO <sub>3</sub> ) <sub>12</sub> · (1) <sub>3</sub>	R.:	-	c)	c)	1032 <sub>vs</sub> 1024 <sub>s</sub>	802 <sub>w</sub>	742 <sub>w</sub>	702 <sub>w</sub>
Pr(NO <sub>3</sub> ) <sub>3</sub> · 2	IR.:	4	1490 <sub>vs</sub>	1310 <sub>vs</sub>	1048 <sub>s</sub> 1032sh.	821 <sub>m</sub>	745 <sub>m</sub>	715
	R.:	-	c)	c)	1045 <sub>vs</sub>	c)	741 <sub>m</sub> 737sh.	706 <sub>vw</sub>
Pr <sub>4</sub> (NO <sub>3</sub> ) <sub>12</sub> · (2) <sub>3</sub>	IR.:	4	1510 <sub>vs</sub>	1319 <sub>vs</sub> 1263 <sub>vs</sub> <sup>d)</sup>	1040 <sub>m</sub> 1020 <sub>s</sub>	822 <sub>m</sub> 817sh.	738 <sub>s</sub> 725sh.	707
Ho(NO <sub>3</sub> ) <sub>3</sub> · 2	IR.:	3	1512 <sub>vs</sub>	1333 <sub>s</sub> 1292sh.	1046sh. 1027 <sub>m</sub>	821 <sub>m</sub> 815sh.	747 <sub>m</sub>	709
	Ho <sub>4</sub> (NO <sub>3</sub> ) <sub>12</sub> · (2) <sub>3</sub>	R.:	-	c)	c) 1279 <sub>vs</sub>	1045 <sub>s</sub> 1027 <sub>s</sub>	c)	749 <sub>w</sub>

<sup>a</sup>) Key: IR. = infrared, R. = Raman; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh. = shoulder. <sup>b</sup>) Number of weak components between 1720 and 1790 cm<sup>-1</sup>. <sup>c</sup>) Masked by ligand vibrations. <sup>d</sup>) Partially masked by ligand vibrations.

180 and 200 cm<sup>-1</sup> and the separation of the combinations  $\nu_2 + \nu_5, \nu_6$  in the spectral range 1700–1800 cm<sup>-1</sup> varied from 32 to 49 cm<sup>-1</sup>. However, the presence of one monodentate nitrate group in Ln(NO<sub>3</sub>)<sub>3</sub> · 1 (La–Nd) could be completely ruled out [12].

The vibrations of the polyethers were assigned according to [11] and [26–31]. The IR. absorptions of the complexes [Ln(NO<sub>3</sub>)<sub>3</sub>]<sub>4</sub> · (2)<sub>3</sub> were almost identical for La–Eu, but for small energy shifts vs. the atomic number of the rare earth. The spectra of the complexes with the heavier lanthanide ions were only slightly different (*cf.* Fig. 3). The  $\nu(\text{CCO})$  vibration at ~1100 cm<sup>-1</sup> was split into two components, the more intense being displaced by –40 cm<sup>-1</sup> towards lower wave numbers, with respect to the free ligand vibration. Subtle changes appeared in the weak bands around 520–580 cm<sup>-1</sup> arising from the ring deformation modes; for Ln=Lu, only one band was observed whereas complexes of the lighter rare earth ions displayed 3 bands in this spectral range. Since the X-ray powder diagrams and the IR. spectra of the complexes [Ln(NO<sub>3</sub>)<sub>3</sub>]<sub>4</sub> · (2)<sub>3</sub> were very similar for Ce to Eu, the structure of these complexes must be closely related to the structure determined for the neodymium complex, which implies the presence of Sm(NO<sub>3</sub>)<sub>6</sub><sup>3-</sup> and Eu(NO<sub>3</sub>)<sub>6</sub><sup>3-</sup> species<sup>5)</sup>. According to Walker & Weeden, hexa-

<sup>5)</sup> The fluorescence spectrum of the Eu complex, recorded at 77 K, is indeed consistent with [Eu(NO<sub>3</sub>)<sub>2</sub> · 2]<sub>3</sub>Eu(NO<sub>3</sub>)<sub>6</sub> [20].



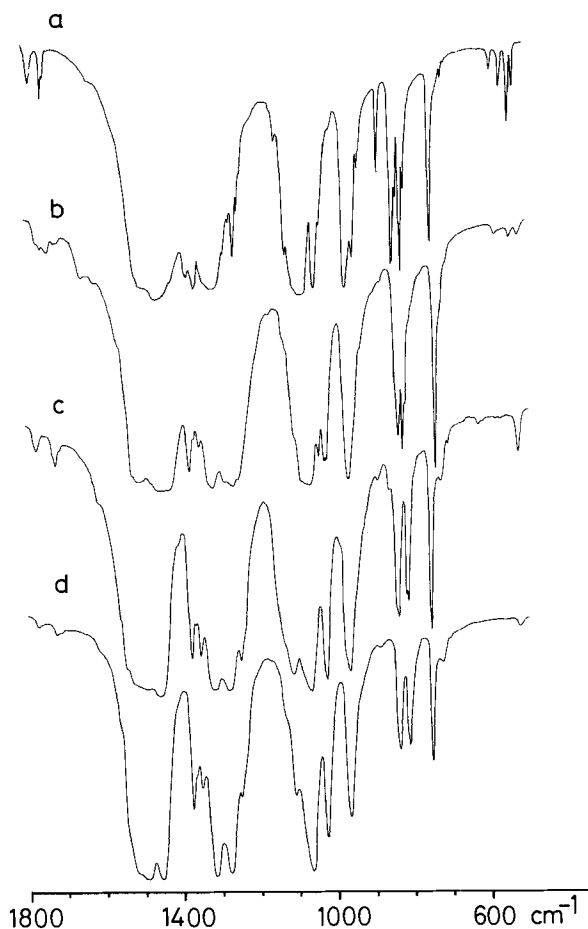


Fig. 3. Typical IR. spectra of complexes with 18-crown-6 ether (2). (a)  $\text{Pr}(\text{NO}_3)_3 \cdot 2$ , (b)  $[\text{Pr}(\text{NO}_3)_3]_4 \cdot (2)_3$ , (c)  $\text{Lu}(\text{NO}_3)_3 \cdot 2$ , and (d)  $[\text{Lu}(\text{NO}_3)_3]_4 \cdot (2)_3$ .

nitrate complexes  $(\text{C}_4\text{H}_9\text{N})_3\text{Ln}(\text{NO}_3)_6$  can indeed be prepared for all the lighter rare-earth ions, from La to Sm, whereas pentanitrate complexes are isolated from Ho to Lu [32]<sup>6</sup>). The 4:3 complexes of the heavier rare-earth ions could therefore contain  $\text{Ln}(\text{NO}_3)_5^{2-}$  species. This is, however, not consistent with the available X-ray and IR. data. For instance, the  $\nu_4(\text{NO}_3^-)$  vibration occurred at 1300–1310  $\text{cm}^{-1}$  in  $\text{M}_2\text{Ln}(\text{NO}_3)_5$  [20], that is at a wavenumber 30–40  $\text{cm}^{-1}$  higher than observed for the  $\nu_4$  component at 1270–1280  $\text{cm}^{-1}$ . Moreover, the presence of a pentanitrate species would rather correspond to a different stoichiometry, as it is the case for the complex between samarium nitrate and the cryptand [2.2.2] [33].

<sup>6</sup>) The complexes with Eu-Dy were not studied by these authors.

We conclude that the 4:3 complexes of the heavier rare-earth ions may also be formulated as  $[\text{Ln}(\text{NO}_3)_2 \cdot (\mathbf{2})_3]\text{Ln}(\text{NO}_3)_6$ .

The 'ring breathing' mode [29] of  $\mathbf{2}$ , at  $\sim 880 \text{ cm}^{-1}$ , is active in the *Raman* spectra of all the 1:1 and 4:3 complexes of  $\mathbf{2}$  and inactive in the IR. spectra of the 1:1 complexes with Eu, Tb-Lu, and of all the 4:3 complexes. Inspection of the character tables [34] allowed us to extend the conclusions *Fouassier & Lassègues* [29] reached for K and Cs complexes of  $D_{3d}$ -symmetry: the presence of this vibration in the IR. spectrum of an 18-crown-6 complex implies that the polyether does not possess a center of inversion (*cf.* the crystal structure of  $\text{Nd}(\text{NO}_3)_3 \cdot \mathbf{2}$  [21]). On the contrary, the presence of this vibration does not necessarily imply the presence of an inversion center.

The IR. spectra of the 1:1 and 4:3 complexes between  $\mathbf{2}$  and the heavier lanthanide (Eu, Tb-Lu) nitrates were very similar, except for one component of the  $\nu(\text{CCO})$  vibration at  $\sim 1110 \text{ cm}^{-1}$  which was more intense for the 1:1 complexes. The spectrum of the uncomplexed ether also displayed a vibrational mode at  $1100 \text{ cm}^{-1}$ . A close inspection of the IR. and *Raman* spectra of the complexes of holmium and lutetium revealed that most of the free polyether vibrations appear as weak bands or as shoulders in the spectra of the 1:1 complexes, but not in the spectra of the 4:3 complexes. Since both 1:1 and 4:3 complexes of Ho displayed similar X-ray powder patterns (*vide supra*), we conclude that hydrated 1:1 complexes of the heavier lanthanide nitrates are probably 4:3 complexes with one uncomplexed crown ether held in the lattice by hydrogen bonds from the water molecules. This is supported by the absence of heat of reaction for the 1:1  $\rightarrow$  4:3 transformation when  $\text{Ln} = \text{Eu, Tb, Ho, Er, Yb}$  (*cf.* § 1 of this chapter).

Typical IR. spectra of complexes with  $\mathbf{1}$  are displayed in *Figure 4*<sup>7)</sup>. Since no structure determination is available for a 4:3 complex, these spectra could not be interpreted in great detail. However, two facts are of some interest: (i) the IR. spectra of both 1:1 and 4:3 complexes of the heavier lanthanide ions showed an absorption band at  $1275 \text{ cm}^{-1}$ , which was assigned to a hexanitrate species; (ii) the spectra of the 1:1 complexes for  $\text{Ln} = \text{Gd-Lu}$  seemed to be the superposition of the spectra of the corresponding 4:3 complexes and the free ligand; in particular, the component at  $\sim 1130 \text{ cm}^{-1}$  of the  $\nu(\text{CCO})$  vibration, which appears at the same frequency in the spectrum of the free ligand, was much more intense for the 1:1 complexes than for the 4:3 complexes. This pointed to structures for 1:1 and 4:3 complexes of  $\mathbf{1}$  similar to the structures discussed above for the complexes of  $\mathbf{2}$ .

The presence of uncomplexed crown ether molecules in the lattice of inorganic salts or complexes is not uncommon. Known examples are, for instance,  $[\text{U}(\text{NCS})_4 \cdot 4 \text{H}_2\text{O}]_2 \cdot (\mathbf{2})_3 \cdot 6 \text{H}_2\text{O} \cdot (\text{CH}_3\text{COC}_4\text{H}_9)_2$  [27],  $[\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}] \cdot 2 \text{H}_2\text{O} \cdot \mathbf{2}$  [35], and  $[\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}] \cdot \mathbf{2}$  [36] in which the crown ether is held in the lattice by hydrogen bonding. In  $(\text{MNCS})_2 \cdot (\text{dibenzo-18-crown-6})_3$  ( $\text{M} = \text{Na, Rb}$ ) [37] and  $\text{Ca}(\text{DNB})_2 \cdot (\text{benzo-15-crown-5})_2 \cdot 3 \text{H}_2\text{O}$  [38]<sup>8)</sup> both complexed and uncomplexed crown ethers are present.

<sup>7)</sup> Tables of IR. and *Raman* frequencies for the complexes of  $\mathbf{1}$  and  $\mathbf{2}$  are available upon request.

<sup>8)</sup> DNB = 3,5-dinitrobenzoate.

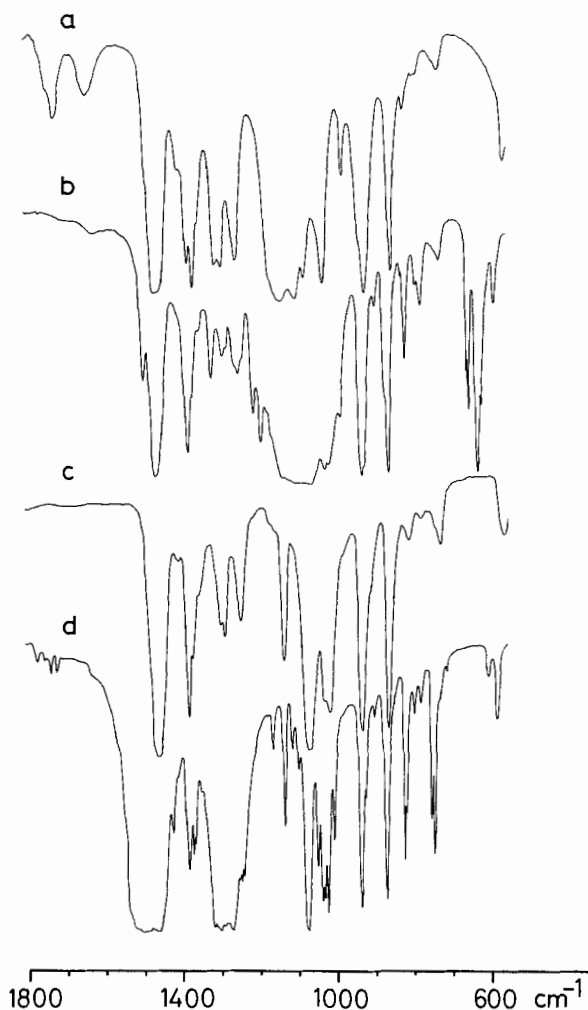


Fig.4. Typical IR. spectra of complexes with 15-crown-5 (I). (a) Ligand alone, (b)  $\text{Pr}(\text{NO}_3)_3 \cdot \mathbf{1}$ , (c)  $\text{Ho}(\text{NO}_3)_3 \cdot \mathbf{1}$ , and (d)  $[\text{Ho}(\text{NO}_3)_3]_4 \cdot (\mathbf{1})_3$ .

3. *Solutions.* Despite their low solubility, usually  $< 0.02 \text{ mol l}^{-1}$ , a few complexes were studied in anhydrous acetonitrile in order to determine the species present in solution and to evaluate their formation constant. The molar conductances of  $10^{-3} \text{ M}$  solutions indicated that the 1:1 complexes of the lighter rare earth nitrates are essentially non-conductors; for example,  $\Lambda = 9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for  $\text{Pr}(\text{NO}_3)_3 \cdot \mathbf{1}$ , 28 for  $\text{Pr}(\text{NO}_3)_3 \cdot \mathbf{2}$  and 57 for  $\text{Nd}(\text{NO}_3)_3 \cdot \mathbf{2}$ . As expected, the molar conductance of the 4:3 complexes of  $\mathbf{2}$  is larger: 44 and  $66 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for Pr and Nd, respectively. However, these values are rather low considering the structure of the 4:3 complexes (e.g. 1:1 electrolytes have  $\Lambda = 120$ –

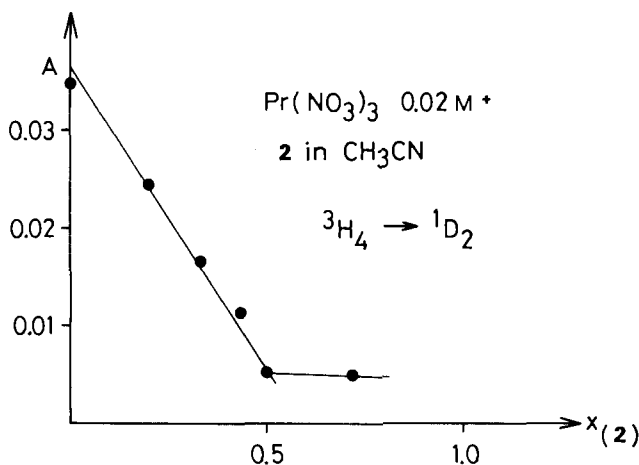
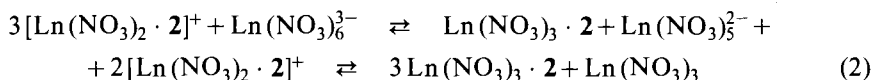


Fig. 5. Absorbance at 593 nm ( $^3H_4 \rightarrow ^1D_2$  transition) of 0.02 M praseodymium nitrate in CH<sub>3</sub>CN vs. the molar fraction of added 18-crown-6 ether (2). The break at  $x=0.5$  corresponds to the formation of the 1:1 complex.

160 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in CH<sub>3</sub>CN) and they can only be explained by the following equilibria:



Walker & Weeden have already noticed the dissociation of hexanitrate species into pentanitrate species [32].

The electronic spectra of 0.02 M solutions of Pr(NO<sub>3</sub>)<sub>3</sub> containing increasing amounts of 2 (Fig. 5) clearly indicated the formation of a 1:1 complex in acetonitrile. Since both the solubility of the complexes and the molar absorption coefficients of the f-f transitions are small, we investigated the Ln(III)/2 interaction by means of <sup>1</sup>H-NMR. spectroscopy for La-Nd, Eu and Yb. At RT., the exchange reaction between free and coordinated polyether was very slow and two singlets were observed (Table 6). One signal at 3.6 ppm was narrow and assigned to the free ligand. The other one was broader and shifted, and therefore corresponds to the coordinated polyether. Solutions of 1:1 and 4:3 complexes gave essentially the same spectra, except for Nd and, to a lesser extent, for Pr. This probably reflects the presence of the equilibria 2 in solutions of the 4:3 complexes<sup>9)</sup>. The formation constants listed in Table 6 were determined by integration of the signals of the free and coordinated ligand, assuming the formation of 1:1 complexes only. The intensities of the resonances observed in presence of an excess of ligand or salt are indeed only compatible with the formation of 1:1 complexes. The complexes were destroyed when dissolved in water; since the solvent was not completely anhydrous ([H<sub>2</sub>O]:[Ln-salt]

<sup>9)</sup> Solutions were heated at 40° during 4 h before measurements, to allow possible equilibria between different species.

Table 6.  $^1\text{H}$  chemical shifts (ppm with respect to TMS) of the free ( $\delta_{\text{L}}$ ) and complexed ( $\delta_{\text{C}}$ ) 18-crown-6 ether in solutions of 1:1 and 4:3 complexes in  $\text{CD}_3\text{CN}$ . The formation constants  $K_{\text{f}}$  are calculated for 1:1 complexes.

Ln	$10^2 \cdot [\text{Ln}^{3+}]$ mol $\text{l}^{-1}$	Ln:L	T = 25°				T = -38°		
			$\delta_{\text{L}}$	$\delta_{\text{C}}$	$\log K_{\text{f}}$ a)	$\delta_{\text{L}}$ b)	$\delta_{\text{L}}$	$\delta_{\text{C}}$	
La	0.86	1:1	3.62	3.85	4.4	3.29	3.58	3.83	
	0.46	4:3	c)	3.85	-	-	c)	3.82	
Ce	0.94	1:1	3.62	-2.95	4.5	3.57	3.58	-2.31	-10.59
	1.34	1:1	3.62	-8.05	3.7	2.63	3.7	-5.6	-19.0
4:3		3.63	-8.30	-	-	3.6	-5.7	-19.1	
Nd	1.70	1:1	3.57	-0.53	3.5	2.44	3.58	0.1	-7.1
	1.14	4:3	3.62	0.47	3.4	-	3.62	0.0	-6.6
Eu	1.45	1:1	3.55	8.57	2.6	1.84	3.50	10.85	
	0.84	4:3	3.62	8.60	2.9	-	3.55	10.87	
Yb	0.81	1:1	3.62	36.0	2.3	d)	3.5	49.5	
	0.71	4:3	3.62	35.9	2.5	-	3.5	49.5	

a) This work,  $\pm 0.2$ . b) From [39]. c) Too weak to be observed. d) No Ln(III)/crown ether interaction was observed for Ln = Tb-Lu.

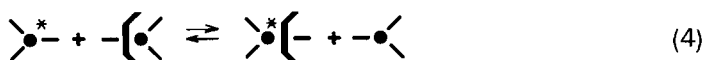
$\leq 10$ ) we have checked the influence of the water content on the formation constant of  $\text{Nd}(\text{NO}_3)_3 \cdot 2$ :  $K_{\text{f}}$  does not vary up to a  $[\text{H}_2\text{O}]/[\text{Nd-salt}]$  ratio of 20.

The formation constants decreased when the atomic number increased. The  $\text{LnCl}_3/2$  interaction in methanol/water was studied by *Izatt et al.* [39] by means of titration calorimetry. They found no interaction between **2** and the heavier lanthanoid ions (Tb-Lu). Working with a poorer *Lewis* base as solvent allowed us to observe an appreciable interaction between **2** and, for instance, Yb(III), the formation constant of the corresponding complex being around 250. On average, the formation constants we found in acetonitrile are 10 times larger than in the  $\text{LnCl}_3/\text{CH}_3\text{OH}/\text{H}_2\text{O}$  system. Owing to solubility problems and to highly hygroscopic compounds, reliable data could not be obtained for 1-complexes. An estimate of  $K_{\text{f}}$  could, however, be made by spectrofluorimetry for Eu; semi-quantitative deconvolution of the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transitions, at 5790 Å for  $\text{Eu}(\text{NO}_3)_3 \cdot (\text{CH}_3\text{CN})_x$  and at 5798 Å for  $\text{Eu}(\text{NO}_3)_3 \cdot 1$ , indicated that  $K_{\text{f}}$  is of the same order of magnitude than for  $\text{Eu}(\text{NO}_3)_3 \cdot 2$  ( $K_{\text{f}} \approx 2.5$ ).

At lower temperatures, the  $^1\text{H}$ -NMR. spectra of **2**-complexes fell into two categories. For La, Eu, Yb, the resonance of the coordinated polyether was broadened and shifted. For Ce, Pr, Nd, this resonance was split into two components of approximately same intensity (*Fig. 6*). The coalescence temperature of these signals was  $-5^\circ$  for Pr,  $-15^\circ$  for Nd, and was lowered by addition of an excess lanthanide nitrate. The chemical shifts corresponding to the coordinated ligand, linear function of  $1/T$ , were not modified upon addition of an excess of ligand. On the contrary, addition of lanthanide nitrate induced shifts towards lower (Nd) and higher (Pr) field, respectively.

Possible inter- and intramolecular exchange reactions are pictured in the following scheme. The ligand exchange reaction is completely frozen at RT. The exchange

## Scheme



rate is independent of both the concentration of the 1:1 complex and of the ligand, which points to a dissociative-type mechanism. For Ln = Nd, heating the solution to 70° results in a broadening of the free-ligand resonance which corresponds to an exchange rate of *ca.* 12 s<sup>-1</sup>. Exchange reaction 4 takes place below RT. The width at half-height of the complexed ligand resonance indicated an increase in the rate of exchange with increasing atomic number, that is, since *K<sub>f</sub>* decreases with *Z*, with an increase of the concentration of free Ln(NO<sub>3</sub>)<sub>3</sub> in the solution. Indeed, addition of lanthanide nitrate increased the rate of exchange. This means the mechanism of reaction 4 is associative or that reaction 5 is catalyzed by uncomplexed lanthanide nitrate. The experiments we could perform did not allow us to decide whether the two resonances observed at low temperature for the coordinated polyether arose from complexes with two different conformations of the polyether or from two chemically different types of protons belonging to the same conformation of the macrocycle. Low temperature spectra of solutions of **2** in CD<sub>3</sub>CN (–38°) and CD<sub>2</sub>Cl<sub>2</sub> (–95°) did not show any freezing of the fast conformational ring movements.

**Conclusion.** – The stoichiometries of the complexes between lanthanoid salts and unsubstituted crown ethers are summarized in *Table 7*. To rationalize these findings

Table 7. Complexes between lanthanoid salts and unsubstituted crown ethers for which elemental analyses have been reported

LnX <sub>3</sub>	12-crown-4		15-crown-5			18-crown-6		21-crown-7 <sup>a</sup> )		
	1:2	1:1	1:2	1:1	4:3	1:1	4:3	1:1	4:3	
Ln(NO <sub>3</sub> ) <sub>3</sub>		La-Lu <sup>b</sup> )		La-Eu <sup>c</sup> ) Gd-Lu <sup>d</sup> )	Gd-Lu <sup>c</sup> ) <sup>d</sup> )	La-Nd <sup>e</sup> ) Eu, Tb-Lu <sup>d</sup> )		La-Lu <sup>c</sup> ) <sup>d</sup> )	Er	La-Eu
Ln(ClO <sub>4</sub> ) <sub>3</sub>	La-Gd <sup>e</sup> ) La-Lu <sup>f</sup> )		La-Gd <sup>e</sup> )			Pr <sup>g</sup> ), Eu <sup>h</sup> )				
LnCl <sub>3</sub> <sup>g</sup> )		Pr, Eu <sup>h</sup> )		Pr, Eu <sup>h</sup> )		Pr		Pr		
Ln(NCS) <sub>3</sub> <sup>g</sup> )				Pr		Pr				

<sup>a</sup>) [40]. <sup>b</sup>) [10]. <sup>c</sup>) [11]. <sup>d</sup>) This work. <sup>e</sup>) [13], mixed complexes Ln(ClO<sub>4</sub>)<sub>3</sub> · (12-4) · (15-5) were also isolated for Ln = Pr-Gd. <sup>f</sup>) [41]. <sup>g</sup>) [12]. <sup>h</sup>) Unpublished results.

we consider the influence of both the crown ether and the anion on the stoichiometries of these complexes.

In  $\text{Nd}(\text{NO}_3)_3 \cdot 2$ , the diameter of the polyether cavity,  $D_e$ , is 2.5 Å [21], *i.e.* slightly smaller than in the uncomplexed macrocycle (2.7 Å [42]), and the ratio  $D_i/D_e$ ,  $D_i$  being the effective ionic diameter of the 12-coordinated Nd ion [43], is 1.0. According to *Izatt et al.* [44] this value is close to the optimum value for a complex in which the metal ion lies inside the cavity. In our case however, the electrostatic asymmetry caused by the presence of two nitrate groups coordinated on the same side of the polyether [21] pulls the Nd(III) ion out of the cavity. When the electrostatic asymmetry is removed, *e.g.* in  $[\text{Nd}(\text{NO}_3)_2 \cdot 2]^+$ , the Ln(III) ion lies exactly in the center of the polyether cavity [22]. This could explain why 4:3 complexes are formed with the larger crown ethers or, more exactly, when  $D_i/D_e \leq 1.0$ . For instance, the 1:1 complex  $\text{Eu}(\text{NO}_3)_3 \cdot 1$  ( $D_i/D_e \sim 1.1$  [20]) cannot be transformed into a 4:3 complex. Another important factor for obtaining a given stoichiometry, besides the ring flexibility already discussed in [11], is the nature of the anion. The formation of a 4:3 complex implies the formation of  $\text{LnX}_6^{3-}$  species and we can therefore expect that such complexes will form only if these species are stable enough.

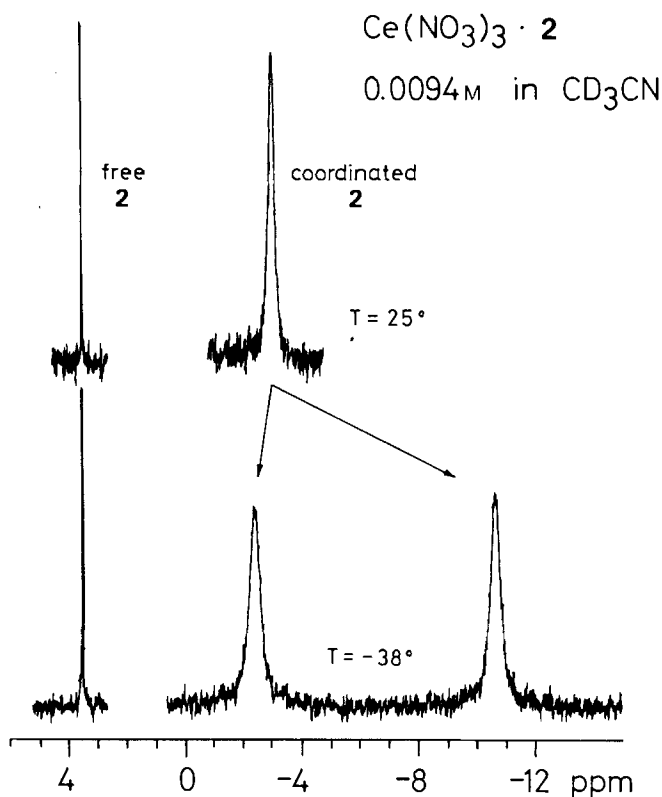


Fig. 6.  $^1\text{H}$ -NMR. spectra at 60 MHz of  $\text{Ce}(\text{NO}_3)_3 \cdot 2$ , 0.0094M in  $\text{CD}_3\text{CN}$

This is the case for  $\text{Ln}(\text{NO}_3)_6^{3-}$ , at least in the solid state and for the lighter lanthanoid ions [32], for  $\text{LnCl}_6^{3-}$  [45] and, to a lesser extent, for  $\text{Ln}(\text{NCS})_6^{3-}$  [46]. We have isolated 4:3 complexes of **2** with some chlorides (*cf.* Table 7) but we were unable to obtain such complexes with isothiocyanates, either by crystallization from a solution, or by thermal decomposition of the corresponding 1:1 complexes. With lanthanoid perchlorates, both 1:1 and 1:2 sandwich complexes can be obtained, depending on the ring size of the macrocycle. Considering Table 7, we can make the following generalizations for the stoichiometry of complexes between lanthanoid salts and unsubstituted crown ethers: (i) in presence of poorly complexing anions, sandwich 1:2 complexes are formed when  $\text{Di}/\text{De} > 1$ , whereas 1:1 complexes are isolated when  $\text{Di}/\text{De} < 1$ ; (ii) in presence of strongly complexing anions, 1:1 complexes are formed when  $\text{Di}/\text{De} > 1$ , whereas complexes with a metal:ligand ratio  $\geq 1$  are isolated when  $\text{Di}/\text{De} < 1$ .

It is therefore possible to design complexes with a given stoichiometry by a judicious choice of the crown ether and of the anion. In fact complexes in which the rare-earth ion has a coordination number of 7, 8, 9, 10, 11 and 12 have been isolated [5].

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*Note added in proof.* A recent paper by *J. D. J. Baker-Dirks et al.* (*J. Chem. Soc. Dalton 1980*, 2191) confirms some of the results we obtained with **2**.

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