

## 145. Complexes of the Lighter Lanthanoid Nitrates with 15-Crown-5 and 18-Crown-6 Ethers: Synthesis and Characterization

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### Summary

Complexes of lanthanoid trinitrates  $\text{Ln}(\text{NO}_3)_3$  with 15-crown-5 ether **1** ( $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd}$ ) and with 18-crown-6 ether **2** ( $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd}$ ) have been synthesized and characterized. All the isolated complexes are solvent free. At 170–220° the 1:1 complexes of **2** are quantitatively transformed into 4:3 complexes. X-Ray powder diagrams of the neodymium complexes with **2** indicate that both the 1:1 and 4:3 complexes are genuine compounds. All the 1:1 complexes show a characteristic IR. absorption band at 875–880  $\text{cm}^{-1}$  absent from both the spectra of the free ligands and of the 4:3 complexes.

The spectroscopic properties (IR. and electronic spectra, fluorescence lifetimes) of the complexes and the low magnetic moments of the Ln(III) ions in the complexes with  $\text{Ln} = \text{Ce-Eu}$  are indicative of a strong interaction between the lanthanoid ions and the crown ethers **1** and **2**.

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**1. Introduction.** - Most earlier work on the complexation of metal cations by crown ethers has been devoted to mono- and divalent ions [1],[2]. The only known lanthanoid complexes were those of  $\text{Ln}(\text{NO}_3)_3$  and  $\text{Ln}(\text{NCS})_3$  with benzo-15-crown-5<sup>2)</sup> and dibenzo-18-crown-6 ethers [4] [5] and some complexes of La(III) [1-3]. The high complexation selectivity of the crown ethers and related macrocyclic and macropolycyclic molecules make them attractive ligands for the systematic study of the coordinative properties of the Ln(III) ions and for the elaboration of efficient liquid-liquid extraction processes. Indeed, there has been a recent surge of interest in such systems: *Desreux et al.* [6] have synthesized 1:1 complexes of  $\text{Ln}(\text{NO}_3)_3$  with an 18-membered diazatetraoxa-macrocyclic, *Gansow et al.* [7] have investigated the chemical properties of  $\text{LnCl}_3$  ( $\text{Ln} = \text{La, Pr, Eu, Gd, Yb}$ ) complexes with 2:2:1 and 2:2:2 cryptates, *Izatt et al.* [8] have studied the stability sequence of  $\text{LnCl}_3$  complexes with 18-crown-6 ether in methanolic solutions, and *Catton et al.* [9] have investigated the <sup>1</sup>H- and <sup>13</sup>C-NMR. spectra of  $\text{Ln}(\text{NO}_3)_3$  and  $\text{Ln}(\text{ClO}_4)_3$  ( $\text{Ln} = \text{La, Pr, Sm}$ ) complexes with dicyclohexyl-18-crown-6 ether.

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<sup>2)</sup> For concision the nomenclature proposed in [3] for crown ethers is used.



As part of an investigation on the solvation of anhydrous lanthanoid nitrates, we synthesize model complexes in which the Ln(III) ion has a high coordination number and should be protected against further solvent coordination. Such an environment for Ln(III) may be provided by crown ethers: indeed, a recent crystal structure determination has shown that La(III) is 12-coordinated in its trinitrato-*cis, syn, cis*-dicyclohexyl-18-crown-6 complex [10]. We now report the synthesis and characterization of complexes of Ln(NO<sub>3</sub>)<sub>3</sub> (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) with the crown ethers **1** and **2**. This choice of Ln(III) and ligands allows the estimation of the influence on the complexation of the ratio ionic diameter/ligand cavity diameter, and of the crown ether flexibility (larger for **1** and **2** than for the corresponding benzo-substituted ligands).

**2. Experimental part**<sup>3)</sup>. - 2.1 *The 1:1 complexes with 1* were prepared according to [4] using acetonitrile (Fluka, puriss.) and the partially dehydrated lanthanoid nitrates containing 0.5-1.5 mol H<sub>2</sub>O per formula weight (for Ln = Pr-Gd) [12]. After partial evaporation of the solvent the crystalline complexes were collected and dried for 3-4 days either in a desiccator with P<sub>2</sub>O<sub>5</sub> (Ln = La-Eu) or in high vacuum at 5°/10<sup>-5</sup> Torr (Ln = Gd). Yields: 90% for Ln = La-Nd, 70% for Ln = Sm, Eu, and 20% for Ln = Gd.

2.2 *Synthesis of the complexes with 2*. 1:1 Complexes (Ln = La-Pr) were obtained as described above in ca. 55% yield. For Ln = Nd-Gd the same procedure lead to a crystalline precipitate of [Ln(NO<sub>3</sub>)<sub>3</sub>]<sub>4</sub> · (2)<sub>3</sub>. These 4:3 complexes could be recrystallized unchanged from EtOH. Yields: 15% for Ln = Nd, 40% for Sm, 65% for Eu, and 30% for Gd.

For Ln = Nd, partial solvent evaporation from the filtrate of the solid 4:3 complex yielded a second crystalline fraction corresponding to the 1:1 complex (30%).

The 4:3 complexes of the lightest rare earths (Ln = La-Pr) were obtained in quantitative yield by heating the corresponding 1:1 complexes for 24 h at 225°/2 · 10<sup>-2</sup> Torr (Ln = La), 22 h at 190°/2 · 10<sup>-2</sup> Torr (Ce), and 16 h at 170°/720 Torr (Pr).

2.3 *Analysis of the complexes*. The metal content was determined by complexometric titration with EDTA (Titriplex III, Merck) in the presence of urotropine (pH ≈ 5) and xylenol orange. C, H, N elemental analyses were performed by Mr. W. Manser (Mikroanalytisches Laboratorium des ETHZ); the results are summarized in Table 1.

The thermogravimetric analyses were performed by Mr. J. P. Kummer at the Institut de Radiochimie et d'Electrochimie appliquée de l'EPFL (Head Prof. Dr. P. Lerch) using a Mettler thermoanalyser with Pt/Pt-Rh 10% thermocouples. Samples of 10-11 mg in Pt-crucibles were heated under Ar at a rate of 1°/min. The thermograms were baseline corrected. The complex [Nd(NO<sub>3</sub>)<sub>3</sub>]<sub>4</sub> · (2)<sub>3</sub> decomposed exothermally at ca. 290° losing 61% of its mass; the calculated value for a quantitative transformation into NdONO<sub>3</sub> is 58%. Nd(NO<sub>3</sub>)<sub>3</sub> · 2 showed first an endothermic decomposition at 110-170° with a mass loss of 10.9% corresponding to 98.2% transformation into the 4:3 complex. A second, exothermic decomposition occurred at ca. 290° with a mass loss of 56%; the calculated value for the quantitative formation of NdONO<sub>3</sub> is 51.5%. A sample of Nd(NO<sub>3</sub>)<sub>3</sub> · H<sub>2</sub>O was analysed for comparison: water loss occurred at ca. 100° and decomposition into oxynitrate started at 330°.

X-Ray powder diagrams of Nd(NO<sub>3</sub>)<sub>3</sub> · H<sub>2</sub>O and of its 1:1 and 4:3 complexes with **2** were recorded on a Philips PW 1008 spectrometer using the CrK<sub>α</sub> line.

<sup>3)</sup> Preliminary work on Pr and Eu complexes by Mr. C. Taillens [11] is acknowledged.

Table. Elemental analysis of the isolated complexes and magnetic moments  $\mu$  (Bohr Magneton) at 21° of the corresponding  $Ln^{3+}$ 

Compound	MW	$\mu^a)$		% C	% H	% N	% Ln
$C_{10}H_{20}N_3O_{14}La$	545.19	b)	Calc.	22.03	3.70	7.71	25.48
			Found	22.17	3.68	7.62	25.45
$C_{10}H_{20}N_3O_{14}Ce$	546.40	$2.26 \pm 0.01$	Calc.	21.98	3.69	7.69	25.64
			Found	22.05	3.77	7.61	25.56
$C_{10}H_{20}N_3O_{14}Pr$	547.19	$3.26 \pm 0.02^c)$	Calc.	21.95	3.68	7.68	25.75
			Found	22.10	3.67	7.74	25.49
$C_{10}H_{20}N_3O_{14}Nd$	550.52	$3.28 \pm 0.02$	Calc.	21.82	3.66	7.63	26.20
			Found	21.94	3.66	7.70	26.12
$C_{10}H_{20}N_3O_{14}Sm$	556.63	$1.42 \pm 0.01$	Calc.	21.58	3.62	7.55	27.01
			Found	21.73	3.62	7.65	26.82
$C_{10}H_{20}N_3O_{14}Eu$	558.24	$3.25 \pm 0.02$	Calc.	21.52	3.61	7.53	27.22
			Found	21.36	3.63	7.42	27.24
$C_{10}H_{20}N_3O_{14}Gd$	563.53	$7.89 \pm 0.03$	Calc.	21.31	3.58	7.46	27.90
			Found	21.17	3.70	7.47	27.54
$C_{12}H_{24}N_3O_{15}La$	589.24	b)	Calc.	24.46	4.11	7.13	23.57
			Found	24.55	4.10	7.16	23.43
$C_{12}H_{24}N_3O_{15}Ce$	590.45	$2.30 \pm 0.02$	Calc.	24.41	4.10	7.12	23.73
			Found	24.47	4.06	7.11	23.78
$C_{12}H_{24}N_3O_{15}Pr$	591.24	$3.28 \pm 0.02$	Calc.	24.38	4.09	7.11	23.83
			Found	24.43	4.03	7.17	23.81
$C_{12}H_{24}N_3O_{15}Nd$	594.57	$3.30 \pm 0.02$	Calc.	24.24	4.07	7.07	24.26
			Found	24.31	4.00	7.21	24.19
$C_{36}H_{72}N_{12}O_{54}La_4$	2,092.66	b)	Calc.	20.66	3.47	8.03	26.55
			Found	20.48	3.42	8.06	26.63
$C_{36}H_{72}N_{12}O_{54}Ce_4$	2,097.50	$2.25 \pm 0.02$	Calc.	20.62	3.46	8.01	26.72
			Found	20.71	3.50	7.97	26.53
$C_{36}H_{72}N_{12}O_{54}Pr_4$	2,100.65	$3.29 \pm 0.02$	Calc.	20.58	3.45	8.00	26.83
			Found	20.65	3.46	8.04	26.70
$C_{36}H_{72}N_{12}O_{54}Nd_4$	2,113.96	$3.27 \pm 0.02$	Calc.	20.45	3.43	7.95	27.29
			Found	20.46	3.39	8.03	27.32
$C_{36}H_{72}N_{12}O_{54}Sm_4$	2,138.42	$1.44 \pm 0.01$	Calc.	20.22	3.39	7.86	28.12
			Found	20.29	3.53	7.91	28.20
$C_{36}H_{72}N_{12}O_{54}Eu_4$	2,144.86	$3.24 \pm 0.02$	Calc.	20.16	3.38	7.84	28.34
			Found	20.29	3.40	7.79	28.37
$C_{36}H_{72}N_{12}O_{54}Gd_4$	2,165.98	$7.90 \pm 0.03$	Calc.	19.96	3.35	7.76	29.04
			Found	20.26	3.49	7.53	28.55

a) Averages of 2 determinations on independent samples, each sample being measured 5 times.

b) All the La compounds are diamagnetic with a mass susceptibility of  $-0.35 \cdot 10^{-6}$  c.g.s. unit.

c)  $\mu = 3.34 \pm 0.02$  for anhydrous  $Pr(NO_3)_3$ .

IR. spectra were recorded using Nujol (*Fluka, puriss.*) mulls or KBr pellets with a *Perkin-Elmer 577* spectrometer or with a *Bruker IFS-113c* Fourier-transform spectrometer.

2.4 *Magnetic susceptibility measurements.* Paramagnetic mass susceptibilities were determined by the *Faraday* method at  $21 \pm 1^\circ$  on finely powdered samples under reduced pressure of He ( $5 \cdot 10^{-2}$  Torr), using a *Bruker* BE-10 magnet and a *Mettler* ME-21 electronic microbalance. The product of the magnetic induction field by its gradient  $B \cdot dB/dx$  was determined with a standard of known mass susceptibility,  $HgCo(SCN)_4$  [13]. It usually ranged between  $7$  and  $8 \cdot 10^6$   $G^2 \cdot cm^{-1}$ . The reproducibility of measurements on independent samples was better than 0.5%. The magnetic moments listed in the *Table* were calculated using the uncorrected paramagnetic susceptibilities.

**3. Results and discussion.** - All the complexes isolated were microcrystalline powders with the characteristic colour of the lanthanoid ions. They were stable to air and moisture, except the hygroscopic gadolinium complexes. 1:1 Complexes of 15-crown-5 ether are formed more rapidly and in a better yield than 1:1 18-crown-6 complexes. In general, the complexes form more easily with the larger lanthanoid ions than with the smaller ones. With the less flexible, substituted crown ethers and main or transition metal ions the optimum ratio  $D/d$  ( $D$ =metallic ion diameter,  $d$ =polyether cavity diameter) usually lies around 0.9 [14]. This value corresponds to the ratio calculated for  $\text{Ln}^{3+}$  ( $D=2.12 \text{ \AA}$  for  $\text{La}^{3+}$  to  $1.88 \text{ \AA}$  for  $\text{Gd}^{3+}$  [15]) and ligand **1** ( $d=ca. 2.2 \text{ \AA}$  [14]) which explains the easy formation of the complexes  $\text{Ln}(\text{NO}_3)_3 \cdot \mathbf{1}$ . However  $D/d$  is only *ca.* 0.7 for the 18-crown-6 ether complexes; the formation of 1:1 complexes occurs only with the larger lanthanoid ions ( $\text{Ln}=\text{La-Nd}$ ) which may be due to the following reasons. First, the coordination number of  $\text{Ln}^{3+}$  is increased from 11 in  $\text{Ln}(\text{NO}_3)_3 \cdot \mathbf{1}$  to  $12^4$ , a value often met in complexes of  $\text{Ln}(\text{NO}_3)_3$  [16]. Second, the 18-membered macrocycle is flexible enough to wrap around the metallic ion, as for instance in  $\text{NaNCS} \cdot \mathbf{2}$  [17].

The 4:3 18-crown-6 complexes are, to our knowledge, the first crown ether complexes isolated with such stoichiometry. Complexes of main and transition metal ions with crown ethers have 1:1, 1:2 or 2:3 metal ion/polyether ratios [1]. A monohydrated 3:2 complex of  $\text{ScCl}_3$  with benzo-15-crown-5 ether [18] and 3:2 complexes of  $\text{Pr}(\text{NO}_3)_3$  and  $\text{Nd}(\text{NO}_3)_3$  with 1,13-di(8-quinolyl)-1,4,7,10,13-pentaoxa-tridecane [19] have also been isolated. The question arises whether this 4:3 metal ion/polyether ratio simply results from a co-crystallization of an equimolar mixture of 1:1 complex and  $\text{Ln}(\text{NO}_3)_3$  or whether it corresponds to genuine complexes. The following considerations support the latter hypothesis.

(i) The 4:3 complexes may be recrystallized unchanged from ethanol. They are not sensitive to moisture ( $[\text{Gd}(\text{NO}_3)_3]_4 \cdot (\mathbf{2})_3$  being an exception), in contrast to  $\text{Ln}(\text{NO}_3)_3$  which are very hygroscopic.

(ii) The X-ray powder diagram of  $[\text{Nd}(\text{NO}_3)_3]_4 \cdot (\mathbf{2})_3$  (*cf. Fig. 1*) shows diffraction lines at angles different from the diffraction angles of both the 1:1 complex and the neodymium nitrate, at  $2\theta = 19.2^\circ, 20.2^\circ, 22.2^\circ, 23.7^\circ, \text{etc.}$  *Vice-versa*, strong lines in the powder diagrams of  $\text{Nd}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , at  $2\theta = 16.6^\circ, 24.3^\circ, 25.8^\circ, 35.4^\circ, \text{etc.}$ , and of the 1:1 complex, at  $2\theta = 23.0^\circ, 24.4^\circ, \text{etc.}$ , are absent from the diffraction pattern of the 4:3 complex.

(iii) The IR. spectra afford evidence for the complexation of  $\text{Ln}(\text{NO}_3)_3$  by the crown ethers **1** and **2**. The main features of the spectra of the 1:1 complexes may be summarized as follows. Upon complexation the 2 components of the 15-crown-5  $\tilde{\nu}(\text{CCO})$  stretch at  $1,120$  and  $1,092 \text{ cm}^{-1}$  undergo an average shift towards lower wavenumbers of  $-43$  and  $-18 \text{ cm}^{-1}$ , respectively. A similar shift ( $-29 \text{ cm}^{-1}$ ) is observed for the 1:1 complexes of **2** (free ligand:  $\tilde{\nu}(\text{CCO})$  at  $1,107 \text{ cm}^{-1}$ ). These shifts are comparable to those reported for the complexes with benzo-substituted crown ethers ( $-20$  to  $-40 \text{ cm}^{-1}$  [4]) and for uranyl nitrate complexes with

<sup>4</sup>) X-Ray structure determinations show that  $\text{NO}_3^-$  groups are usually bidentate or bridging in lanthanoid nitrate complexes, *cf.* [10] [12] [16]. The IR. spectra of all the complexes isolated are in agreement with bidentate nitrate groups.

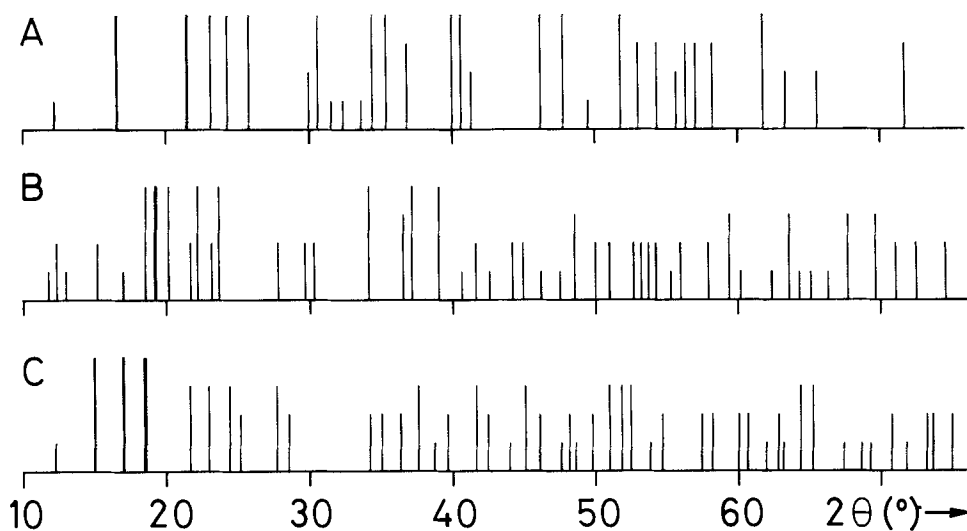


Fig. 1. Schematic representation of the X-ray powder diagrams of  $\text{Nd}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  (A),  $[\text{Nd}(\text{NO}_3)_3]_4 \cdot (2)_3$  (B) and  $\text{Nd}(\text{NO}_3)_3 \cdot 2$  (C)

unsubstituted crown ethers ( $-20$  to  $-25 \text{ cm}^{-1}$  [20]). They indicate a strong lanthanoid/polyether interaction. Non-systematic shifts ( $\pm 10$  to  $30 \text{ cm}^{-1}$ ) and intensity changes of the polyether ring stretching and deformation modes occur in the  $510$ – $990 \text{ cm}^{-1}$  region<sup>5</sup>). Nevertheless all the 1:1 complexes of both **1** and **2** show a sharp, characteristic absorption band at  $875$ – $880 \text{ cm}^{-1}$ .

The situation is somewhat different for the 4:3 complexes of **2**. The  $\tilde{\nu}(\text{CCO})$  band of the polyether is more shifted towards lower wavenumbers ( $-41 \text{ cm}^{-1}$ ) than for the corresponding 1:1 complexes, and there is no absorption band at  $875$ – $880 \text{ cm}^{-1}$ , as illustrated in *Figure 2*. Upon complexation the  $863 \text{ cm}^{-1}$  band of the free ligand is shifted by  $-25 \text{ cm}^{-1}$  towards lower wavenumbers and it is then superimposed with the methylene rocking mode at  $838 \text{ cm}^{-1}$ . Finally, subtle differences are observed for the weak bands between  $520$  and  $590 \text{ cm}^{-1}$  of the ring deformation modes. The free ligand **2** exhibits 2 absorption bands at  $542$  and  $575 \text{ cm}^{-1}$ ; 1:1 complexes show 4 bands at  $527$ ,  $540$ ,  $561$  and  $584 \text{ cm}^{-1}$ , whereas 4:3 complexes have only 3 bands at  $522$ ,  $544$ , and  $580 \text{ cm}^{-1}$ .

(iv) 4:3 Complexes are thermally more stable than the corresponding 1:1 complexes as illustrated by the thermogravimetric curves for the neodymium compounds (*Fig. 3*). The 4:3 complex decomposes at  $290^\circ$  mainly into oxynitrate whereas the 1:1 complex undergoes already at  $110$ – $170^\circ$  a first quantitative transformation into the 4:3 complex before decomposing at  $290^\circ$ . The higher thermal stability of the 4:3 complexes ( $\text{Ln} = \text{La-Pr}$ ) is further demonstrated by the synthesis of these complexes which may be obtained simply by thermolysis of the corresponding 1:1 complexes (*cf. chap. 2.2*).

<sup>5</sup>) A precise assignment is difficult to make since methylene group vibrations also occur in this region.

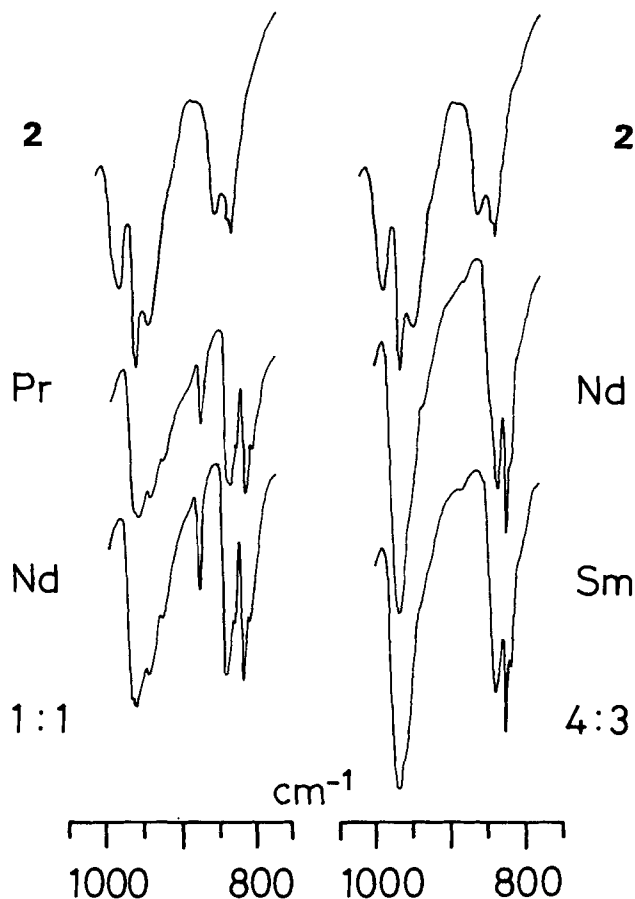


Fig. 2. 750-1000  $\text{cm}^{-1}$  region of the IR. spectra of 18-crown-6 ether (2) and of some of its 1:1 and 4:3 complexes with  $\text{Ln}(\text{NO}_3)_3$

The IR. spectra discussed above point to a large lanthanoid/polyether interaction in all the isolated complexes. In order to verify this, we have measured the magnetic moments of the Ln(III) ions in these complexes (*cf.* Table 1). The 4*f* electrons responsible for the paramagnetism of  $\text{Ln}^{3+}$  are well shielded from external interactions by the 5*s* and 5*p* subshells. However, in strongly bonded compounds and complexes the influence of the ligand field may be large enough to induce a decrease of the magnetic moment [21] [22]. Table 1 shows that the magnetic moment of a given ion does not depend on the type of complex nor on its stoichiometry. Moreover all the measured moments are consistently lower than those reported for most Ln(III) compounds [22]. The decrease compared to the theoretical free ion values [22] is 10-11% for Ln=Ce-Sm and 6% for Ln=Eu, reflecting a large lanthanoid/polyether interaction.  $\text{Gd}^{3+}$  has a moment close to its theoretical value of 7.94 B.M., as usually observed [22].

The electronic spectra of the Pr(III) and Eu(III) complexes further reflect the lanthanoid/crown ether interaction: upon complexation the splitting of the *f-f*

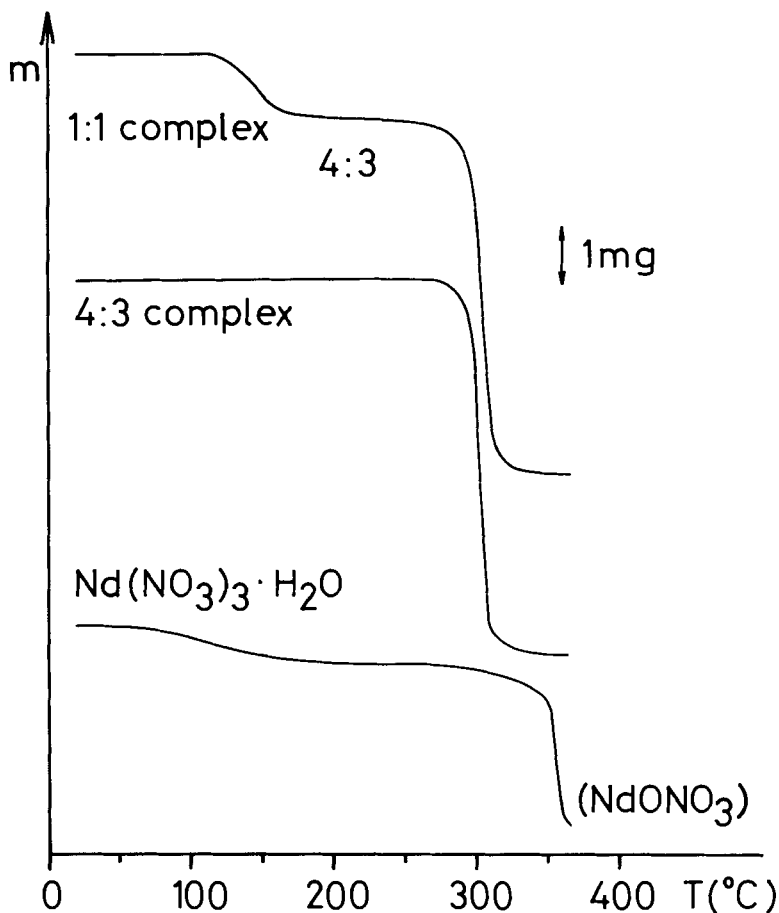


Fig. 3. Thermogravimetric curves for  $\text{Nd}(\text{NO}_3)_3 \cdot 2$ ,  $[\text{Nd}(\text{NO}_3)_3]_4 \cdot (2)_3$  and  $\text{Nd}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$

transitions and their intensities change [11]. Solutions containing equimolar mixtures of Eu(III) nitrate, crown ether and water in acetonitrile have fluorescence lifetimes of *ca.* 500  $\mu\text{s}$  (15-crown-5 ether) and *ca.* 600  $\mu\text{s}$  (18-crown-6 ether) compared to 1 ms for anhydrous  $\text{Eu}(\text{NO}_3)_3$  and 410  $\mu\text{s}$  for  $\text{Eu}(\text{NO}_3)_3 \cdot 1 \text{H}_2\text{O}$ , both in acetonitrile [23]. This means that the fluorescence quenching [24] by the CCO and CH vibrational modes of the macrocycle is weak and that the Eu(III) ion is effectively protected against solvent (here water) interaction.

**4. Conclusion.** - Stable and unsolvated complexes of the lighter lanthanoid nitrates with **1** and **2** can be isolated. The lanthanoid ion/polyether ratio is 1:1 for all the complexes of ligand **1** whereas complexes of ligand **2** may have 2 different stoichiometries, 1:1 complexes for Ln=La-Nd, and the thermally more stable 4:3 complexes for Ln=La-Gd. *King & Heckley* [4] have obtained different results with benzo-15-crown-5 (**1a**) and dibenzo-18-crown-6 (**2a**) ethers. With **1a** these authors have isolated solvent-free 1:1 complexes with Ln=La-Nd and solvated 1:1

complexes with Ln = Eu-Lu. With **2a** they have obtained solvent-free 1:1 complexes with Ln = La-Nd only. These differences may be related to the greater flexibility of **1** and **2** compared to **1a** and **2a**. A similar conclusion is reached by *Desreux et al.* [6] who isolated 1:1 complexes of Ln(NO<sub>3</sub>)<sub>3</sub> (Ln = La-Lu) with 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (**2b**). On the other hand, the different stoichiometries of the complexes obtained with **2** and **2b** may be tentatively explained as follows. In the case of **2b** the strain induced when the ligand rearranges around the central lanthanoid ion is partially compensated by the stabilizing process of hydrogen-bond formation between the N-H and NO<sub>3</sub><sup>-</sup> moieties. This is not possible for **2**: in this case 4:3 complexes are formed when the lanthanoid ion becomes too small.

Work concerning the properties of the isolated complexes of **1** and **2** in solution and their formation constants is in progress. Our study is also being extended to the heavier lanthanoid nitrates, to other lanthanoid salts and to other macrocyclic ligands.

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