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Complexes of Lanthanoid Nitrates with 21-crown-7 Ether*

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Introduction

Lanthanoid ions react with crown ethers in organic solvents to yield stable complexes of various compositions [1, 2]. In previous work, we have reported the isolation and the properties of complexes with 12, 15, and 18-membered polyethers having metal: ligand ratios of 1·2, 1.1, 4 3, 3:2 and 2 1 [3–5]. To our knowledge, the only work with a larger polyether deals with the complexes of $Ln(ClO_4)_3$ (Ln = La–Eu, Dy–Er, Yb) with dibenzo-30-crown-10 ether [6]. In this communication, we report the synthesis and the characterization of the complexes between $Ln(NO_3)_3$ (Ln = La–Lu) and 1,4,7,10,13,16-19-heptaoxacyclohenicosane (21-crown-7 ether [7]).

Experimental

A solution of 5 mmol of 21-crown-7 (Parish) in 50 ml CH_3CN was added dropwise to a solution of 5 mmol $Ln(NO_3)_3 \cdot xH_2O$ ($0.5 \leqslant x \leqslant 6$) in 50 ml CH_3CN (6.7 mmol in 70 ml CH_3CN for Ln = Eu, Ho) The resulting mixture was stirred at 70 °C during 24 h, cooled and evaporated to a small volume (25 ml for Ln = La–Nd, 12–8 ml for Ln = Sm, Eu, Er, Yb, Lu and 4–5 ml for Ln = Gd, Tb, Ho, Tm). After 24 h stirring at room temperature, the polycrystalline complexes were filtered off and dried 24 h over P_2O_5. For Ln = La–Nd, the complexes were anhydrous and non hygroscopic. For the heavier lanthanoids, the complexes were further dried at room temperature under high vacuum (2×10^{-5} mm Hg, 1 day for Ln = Sm–Gd, Er, 3 days for Ln = Tb, Tm, 6 days for Ln = Ho, Yb and 11 days for Ln = Lu). For Ln = Dy, no crystallization occured. The results of C, H, N elemental analyses (performed by Mr. W. Manser, Mikroanalytisches Laboratorium der ETH-Zurich) and complexometric analysis of Ln(III) ions by EDTA are given in Table I.

X-ray powder diagrams were recorded on a Philips PW 1008 spectrometer using Cr, Co or CuK_α lines. Emission and excitation spectra of a solid sample and of solutions of the Eu(III) complex were measured

TABLE I. Yields of the Syntheses and Elemental Analyses of the $[Ln(NO_3)_3]_4 \cdot (21\text{-}7)_3$ Complexes.

Ln	MM	η %	% C		% H		% N		% Ln	
			calc	found	calc	found	calc	found	calc	found
La	2224 77	52	22.67	22.82	3.81	3.82	7.55	7.46	24.97	24.72
Ce	2229.65	37	22.63	22.59	3.80	3 71	7.54	7.42	25.14	25.44
Pr	2232 81	47	22.59	22.50	3.79	3.87	7.53	7.49	25.24	25.37
Nd	2246.13	68	22.46	22.37	3.77	3.84	7.48	7.46	25.69	25.64
Sm	2270.57	27	22.22	21.23	3.73	3.70	7.40	7.26	26.49	26.22
Eu	2277 01	20	22.15	22.41	3 72	3.76	7.38	7.43	26.69	26.53
Gd	2298.14	9	21.95	–	3.68	–	7.31	–	27.37	26.70
Tb	2304.86	5	21.89	21.70	3.67	3.83	7.29	7.12	27.58	26.19
Ho	2328.90	20	21.66	21.71	3.63	3.81	7.22	7.30	28.33	28.61
Er[a]	661.62	20	25.41	25 51	4 27	4.22	6.35	6.43	25.28	25.66
Tm	2344.90	41	21.51	21.43	3.61	3.71	7.17	7.09	28.82	28.73
Yb[a]	667.43	25	25.19	–	4.23	–	6.29	–	25.93	26.21
Yb[b]	721.48		23 30	23.46	4.75	4 90	5.82	5.96	23 98	24.11
Yb	2361.34	40	21.36	20.45	3.58	3.75	7.12	7.26	29.31	29.50
Lu	2368.94	28	21.29	21.14	3.57	3.59	7.09	7.00	29.54	29.08

[a] For 1:1 complexes. [b] For the trihydrated 1:1 complex.

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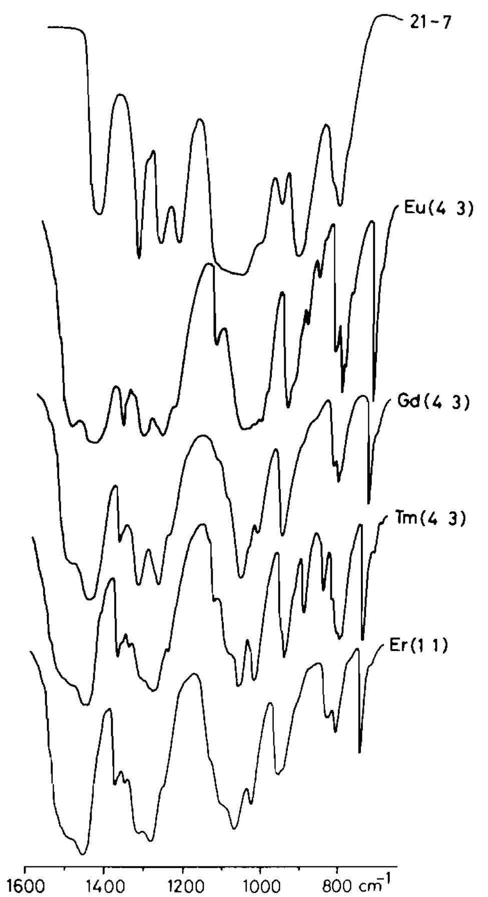

Fig. 1. Part of the IR spectra of (from top to bottom) 21-crown-7 ether (neat), $[Ln(NO_3)_3]_4\cdot(21\text{-}7)_3$, Ln = Eu, Gd, Tm, $Er(NO_3)_3\cdot(21\text{-}7)$ (nujol mulls)

as previously described [8] See [4] for other experimental details.

Results and Discussion

For Ln = La–Tb, Ho, Tm and Lu, complexes having a metal ligand ratio equal to 4 3 are isolated. Such a stoichiometry has been observed for $Ln(NO_3)_3$ complexes with 15-crown-5 and 18-crown-6 ethers [3–5] and with the [2,2,2] cryptand [9], as well as for one complex between $PrCl_3$ and the 18-crown-6 ether [4]. For Ln = Er, a 1 1 complex is obtained, whereas both 1.1 and 4 3 complexes can be isolated for Ln = Yb X-ray powder diagrams indicate the presence of at least two series of isomorphous 4 3 complexes I, Ln = La–Eu and III, Ln = Tm–Lu. The 1·1 complex of erbium only displays hazy lines, different from those of series I and III, indicating a not well-crystallized compound. The thermogram of this hydrated complex (under Ar flow) does not present evidence of a transformation into the 4 3 complex, as was observed for the corresponding complexes of 15-crown-5 and 18-crown-6 ethers [4]; loss of water occurs between 50 and 110 °C, followed by a complete decomposition at ~170 °C. However, due to the high boiling point of 21-crown-7 ether (>140 °C/2 × 10^{-2} mm Hg) it is well possible that such a transformation does not induce a loss of weight. Heating the complex at 110 °C under high vacuum (24 h/2 × 10^{-5} mm Hg) yields a compound having an X-ray powder diagram which is identical with those of series III, and the elemental analysis of which is close to the calculated values for a 4 3 complex % C = 19.86 (calc. 21.57), % H = 3.96 (3.62), % N = 7.01 (7.19), and % Er = 29.33 (28.61).

The IR spectra (Fig. 1) are in agreement with the X-ray data They can be divided in four series I, Ln = La–Eu; II, Ln = Gd, Tb, Ho, III, Ln = Tm–Lu, IV, Ln = Er, Yb, (1 1 complexes). The spectra inside each series are identical but for small shifts in the position of the absorption bands. The main features are the following:

(i) In the region of the unsymmetrical stretch of the nitrato groups (ν_4, B_2, assuming a C_{2v} point group of symmetry), two distinct vibrations are observed for both series I and II, at ~1320 and 1275 cm^{-1}. This last vibration may be assigned to an $[Ln(NO_3)_6]^{3-}$ species as in the 4.3 complexes of the 18-crown-6 ether [4] One band at ~1285 cm^{-1} with a shoulder at 1315 cm^{-1} is observed for series III and IV The other nitrate vibrations occur around 1500, 1030, 820 and 750 cm^{-1}. The first three interfere with ligand vibrations so that a detailed analysis is difficult to carry out. However, the observation of six absorption bands and a $\tilde{\nu}_1-\tilde{\nu}_4$ difference ranging between 170 and 230 cm^{-1} indicate the presence of bidentate nitrates in all the complexes [10].

(ii) For all the complexes, the symmetrical C–C–O stretching ν_s(CCO) appears at ~955 cm^{-1}. In addition, two bands of medium intensity are observed in series III at 910 and 860 cm^{-1}. In the spectra of series I, these bands are very weak. The other C–C–O vibration, ν_{as}(CCO) occurs at ~1070 cm^{-1}. With respect to the free ligand, the shifts of these two vibrations upon complexation amount to +10 to +22 cm^{-1} and to –15 to –25 cm^{-1} for ν_s and ν_{as}, respectively. They are smaller than the values observed for the complexes of the 15-crown-5 and 18-crown-6 ethers [3, 4], which points to a slightly weaker Ln(III)/ether interaction.

The corrected magnetic moments of the lighter Ln(III) ions in the 21-crown-7 ether complexes are similar to those found in the 15-crown-5 and 18-crown-6 complexes [3]. they amount to 2.36, 3.36, 3.35 and 3.38 (Bohr magnetons, at 21 ± 1 °C) for Ln = Ce, Pr, Nd and Eu, respectively.

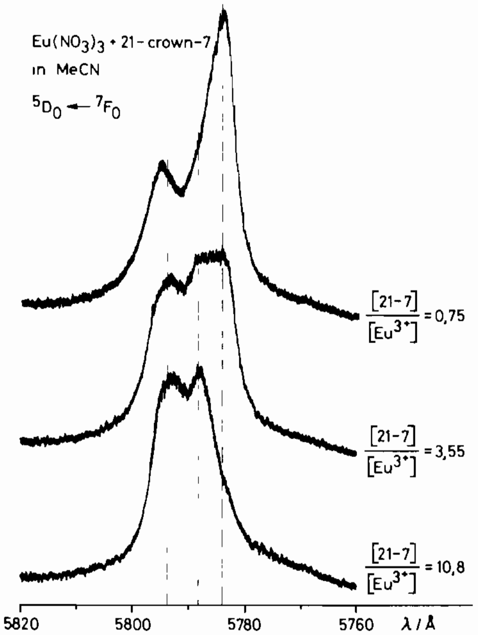

Fig. 2. Part of the excitation spectra of solutions of Eu$(NO_3)_3$ in acetonitrile containing various concentrations of 21-crown-7 ether; λ_{anal} = 6852.5 Å (bandpass: 0.7 Å); excitation by a Coherent CR-599 dye laser (100 mW, bandpass 0.2 Å) pumped by a Coherent CR-8 argon laser.

The 4.3 complex $[Nd(NO_3)_3]_4 \cdot (18\text{-crown-}6)_3$ contains one anionic species $[Nd(NO_3)_6]^{3-}$ and three cationic species $[Nd(NO_3)_2 \cdot (18\text{-crown-}6)]^+$ in which the metal ion lies fairly exactly in the center of the polyether cavity [11]. A similar structure may be postulated for the complexes of 21-crown-7 with the lighter lanthanoid ions for the following reasons.

(i) The IR spectra indicate the presence of an hexanitrato species.

(ii) The cavity diameter of 21-crown-7 ether is estimated to 3.4–4.3 Å [12], so that the ratio ionic diameter/cavity diameter will range between 0.7 (La) and 0.6 (Eu) for highly coordinated Ln(III) ions [8, 13]; the flexible ligand can wrap around the metal ion, as in the complex between KI and dibenzo-30-crown-10 ether [14].

(iii) The emission spectrum of the europium complex displays two $^5D_0 \rightarrow {}^7F_0$ transitions, corresponding to two different environments for the Eu(III) ion, similarly to what is observed with the 4:3 complex of 18-crown-6 ether [4].

The molar conductances at 25 °C of solutions containing 10^{-3} ion-g l^{-1} indicate that the complexes are dissociated in methanol, being 1:1 electrolytes (Λ = 101 ohm^{-1} cm^2 eq^{-1} for Ln = Nd, Eu and 80 ohm^{-1} cm^2 eq^{-1} for Ln = Tm and for the 1:1 complex of erbium), whereas they are essentially non-electrolytes in acetonitrile (Λ = 66, 66, 65, 29, and 36 ohm^{-1} cm^2 eq^{-1} for Ln = Pr, Nd, Eu, Tm and for the 1:1 complex of erbium, respectively). As in the case of 18-crown-6 ether these latter values for the lighter Ln(III) ions can be explained by the presence of the following equilibria, since the hexanitrate anion is not stable in solution [15]:

$$3[Ln(NO_3)_2 \cdot L]^+ + Ln(NO_3)_6^{3-} \rightleftarrows Ln(NO_3)_3 \cdot L +$$

$$+ Ln(NO_3)_5^{2-} + 2[Ln(NO_3)_2 \cdot L]^+ \rightleftarrows 3Ln(NO_3)_3 \cdot L +$$

$$+ Ln(NO_3)_3$$

where L stands for 21-crown-7 ether. High resolution excitation spectra of solutions containing $Eu(NO_3)_3$ and various concentrations of the polyether in acetonitrile are displayed in Fig. 2. There are clearly three $^5D_0 \leftarrow {}^7F_0$ transitions occurring at 5794, 5788, and 5784 Å, respectively, which correspond to three different Eu-containing species. The intensity of the band at 5784 Å strongly decreases upon addition of ligand and is therefore assigned to uncomplexed nitrato species (the $^5D_0 \rightarrow {}^7F_0$ transition of $Eu(NO_3)_3$ and $Eu(NO_3)_5^{2-}$ in CH_3CN appear almost at the same wavelength [16]), the two other bands are therefore assigned to complexed species. These data are consistent with the assumption made above on the structure of the 4:3 complexes. Finally, it is relevant to mention that the ^1H NMR spectrum of a solution of the 4:3 complex of lanthanum (3.92 × 10^{-3} *M* in CD_3CN, 25 °C) displays only one peak at 3.85 ppm (from TMS), which corresponds to a downfield shift of 0.33 ppm with respect to the free ligand and which can be assigned to coordinated crown ether Again, these data are similar to those obtained with the 18-crown-6 ether [4], which means that the formation constants of both 1:1 complexes are of the same order of magnitude.

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