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Complexes of Lanthanoid Nitrates with 12-Crown-4 Ether: Synthesis and Characterization*

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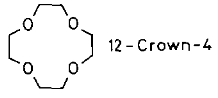
Introduction

Interest in electrically neutral ion-complexing agents like macrocyclic polyethers (crown ethers) has continually increased since the original work of Pedersen [1]. Indeed, their selective metal binding properties [2] make them useful ligands for the study of the coordinative properties of metallic ions, for catalyzing synthetic processes and for analytical purposes [3]. Recently, attention has been focused on lanthanoid/crown ether complexes since they can be used for lanthanoid ion separation [4], for stabilizing Ln(II) oxidation states [3, 5] and for studying high coordination numbers of the rare earths [6, 7]. The complexes are usually isolated from non-aqueous solutions since little Ln(III)/crown ether interaction occurs in water due to unfavorable energetics in removing water molecules from the inner coordination sphere of rary earth ions. In previous papers of this series we have reported the isolation of $Ln(NO_3)_3$ complexes with 15-crown-5 and 18-crown-6 ethers having two different Ln(III)/crown ratios, 1:1 and 4:3 [7 - 9]. A 4:3 complex of 18-crown-6 could also be isolated with $PrCl_3$, but we were not yet able to isolate them with thiocyanates or with perchlorates. With the latter, sandwich 1:2 complexes have been isolated with 15-crown-5 ether [10, 11] and with 12-crown-4 ether [10, 12]. Our study with lanthanoid nitrates is now being extended to both smaller and larger crown ethers in order to find out the conditions which are required to form 4:3 complexes. In this communication we present the results we obtained with 12-crown-4 ether.



Experimental

A solution of 5 mmol of 12-crown-4 (Fluka, *purum*) in 50 ml CH_3CN was added dropwise to a

TABLE I. Yields of the Synthesis and Elemental Analyses of $Ln(NO_3)_3 \cdot$(12-crown-4), $PrCl_3 \cdot$(12-crown-4), and $Pr(ClO_4)_3 \cdot$(12-crown-4)$_2$.

Ln	MW	η%	%C		%H		%N		%Ln	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
La	501.12	85	19.17	19.27	3.22	3.36	8.38	8.36	27.72	27.83
Ce	502.34	67	19.13	18.97	3.21	3.21	8.36	8.12	27.89	27.64
Pr	503.13	68	19.10	19.23	3.21	3.16	8.35	8.20	28.01	28.06
Nd	506.46	68	18.97	19.31	3.18	3.24	8.30	7.97	28.48	28.37
Sm	512.57	72	18.75	18.89	3.15	3.16	8.20	7.98	29.33	29.04
Eu	514.19	75	18.69	18.83	3.14	3.32	8.17	7.97	29.55	29.31
Gd	519.48	80	18.50	18.32	3.10	2.90	8.09	7.97	30.27	30.15
Tb	521.14	85	18.44	18.54	3.09	3.14	8.06	7.88	30.49	30.49
Dy	524.72	76	18.31	18.13	3.07	2.96	8.01	7.97	30.97	30.97
Ho	527.15	77	18.23	18.24	3.06	2.96	7.97	7.85	31.29	31.26
Er	529.49	78	18.15	18.17	3.05	2.95	7.94	7.79	31.59	31.62
Tm	531.15	50	18.09	17.90	3.04	2.97	7.91	7.83	31.80	31.83
Yb	535.26	58	17.95	17.91	3.01	2.93	7.85	7.78	32.33	32.20
Lu	537.20	34	17.89	17.71	3.00	2.92	7.82	7.61	32.57	32.37
$PrCl_3$[a]	441.40		21.76	21.83	4.11	4.14			31.92	32.06
$Pr(ClO_4)_3$[b]	827.72		23.21	23.37	4.38	4.49			17.02	16.90

[a] Monohydrate, anhydrous complex: Pr 33.27% (calc.), 33.20% (found). [b] Dihydrate, anhydrous complex: Pr 17.80% (calc.), 17.71% (found).

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*Part 6 of the series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'. For Part 5 see ref. [9].

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TABLE II. Vibrational Frequencies of 12-Crown-4 Ether between 100 and 2000 cm^{-1} [a,b], and Proposed Assignment.

Assignment	IR	Raman	Assignment	IR	Raman
Combinations	1935 m		Ring breathing	974 m	980 vw
	1740 sh		ν_s(CCO)	929 sh	
	1722 m			919 s	890 m
δ(CH$_2$)	1460 s	1442 s	r(CH$_2$)	848 s	838 m
w(CH$_2$)	1400 w	1398 vw		819 w	810 s
	1378 m	1372 w		790 vw	794 s
	1361 s			780 sh	780 sh
	1350 sh	1340 vw	δ(ring)	574 m	565 m
t(CH$_2$)	1307 s			538 m	538 w
	1289 s	1285 s		526 m	520 m
	1252 s	1245 m		510 sh	
ν_{as}(CCO)	1164 sh			488 sh	488 m
+ combinations	1150 sh			428 vw	
	1135 s	1140 m		353 m	344 s
		1110 m		320 w	
	1095 s	1095 m		290 w	308 m
	1074 s	1064 vw		260 w	252 m
	1025 s	1032 m		193 s	
				180 s	

[a] IR: Nujol mull; Raman: liquid sample. [b] Key: vw: very weak, w: weak, m: medium, s: strong, sh: shoulder.

solution of 5 mmol Ln(NO$_3$)$_3$·xH$_2$O ($0.5 \leqslant x \leqslant 6$) in 50 ml CH$_3$CN. The resulting mixture was stirred at 60 °C for 24 h. The polycrystalline complexes were filtered off after cooling, washed with CH$_2$Cl$_2$ and dried 24 h over P$_2$O$_5$. Anhydrous complexes were obtained for Ln = Nd–Lu. For Ln = La–Pr, monohydrated complexes were isolated, which could be further dried under high vacuum (48 h, 10^{-6} mm Hg). The 1:1 complex with PrCl$_3$ and the 1:2 complex with Pr(ClO$_4$)$_3$ were synthesized and dried as described in [10]. The results of C, H, N elemental analyses (performed by Mr. W. Manser, Mikroanalytisches Laboratorium der ETH-Zürich) and complexometric analysis of Ln(III) ions by EDTA are given in Table I.

Effective magnetic moments were calculated from the measured mass susceptibilities at 21 ± 1 °C, corrected for diamagnetic contributions; HgCo(NCS)$_4$ was used as standard [13].

See [8] and [10] for the other experimental details.

Results and Discussion

Lanthanoid nitrates yield 1:1 complexes with 12-crown-4 ether. The complexes with the larger ions, La(III) to Pr(III), are hygroscopic, contrary to the complexes with the other lanthanoid ions. The diameter of the 12-crown-4 cavity has been estimated to be less than 1.8 Å by Pedersen [1], so that the ratio ionic diameter/crown ether cavity diameter is about 1.3 for La(III) and 1.1 for a heavier rare earth ion like Er(III), for instance. Moreover, the Ln–O bond lengths are substantially longer for Ln = La (2.6–2.9 Å [6]) than for Ln = Er (2.4–2.5 Å [15]). That is, the La(III) ion must lie further apart from the ether which explains why its complex is more easily attacked by water. Conductometric measurements at 25 °C of 10^{-3} *M* solutions of the 12-crown-4 complexes indicate that all the nitrato groups are coordinated in acetonitrile: $\Lambda_M = 14$ ohm^{-1} cm^2 mol^{-1}. Depending on the coordination mode of the anions (*vide infra*) the coordination number of the Ln(III) ions is thus between 8 and 10 in these complexes.

X-ray powder diagrams of the complexes with Ln = Nd–Lu show that all these complexes are strictly isomorphous. This is confirmed by the similarity of both the middle and far infra-red spectra, and the Raman spectra of all the complexes (Ln = La–Lu): the vibrational frequencies of the ligand only undergo systematic shifts across the series, typically ±8 to ±15 cm^{-1} in going from Ln = La to Ln = Lu. The anion vibrations (710–745, 810–820, 1020–1030, 1260–1310, and ~1500 cm^{-1}) are consistent with the presence of bidentate, although not equivalent, nitrato groups. However, we cannot completely rule out the presence of monodentate nitrato groups since the combination region (1700–1800 cm^{-1}) which is commonly used to establish the coordination mode of these anions [16] is obscured by combinations arising from the ligand. The vibrational frequencies of the 12-crown-4 ether

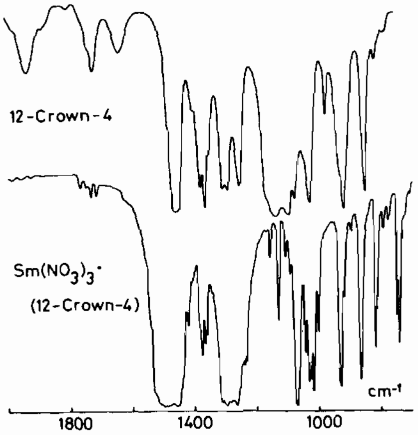

Fig. 1. Part of the IR spectra of 12-crown-4 ether and of the 1:1 complex with Samarium nitrate (Nujol mulls).

are reported in Table II and typical spectra are displayed in Figs. 1 and 2. Anet *et al.* [17] have shown that liquid and crystalline forms of 12-crown-4 ether have very similar IR spectra. Since the crystalline ether belongs to the C_i point group of symmetry [14] one can assume this geometry is retained in the conformationally homogeneous [17] liquid. Indeed, Table II shows that strong IR absorptions, at 1307, 1074, 919, and 193 cm^{-1} for instance, are Raman inactive, whereas strong Raman emission, at 810 and 794 cm^{-1} for instance, correspond to very weak IR absorptions. The question arises whether or not the inversion center of the ligand is retained in the lanthanoid complexes, as it is in the magnesium complex [18]. The ν(CCO) and δ(ring) vibrational modes undergo substantial shifts and splittings upon complexation. The shifts are similar to those observed for 15-crown-5 and 18-crown-6 complexes [8, 10]. The extended splittings of the bands and the presence of the nitrato group vibrations make difficult a detailed analysis of the spectra. Nevertheless, the IR and Raman spectra of the complexes are more similar than the spectra of the free ligand, and we think that the ligand geometry is perturbed upon complexation. We currently investigate this problem further by X-ray structure determination. In the far infrared region of the spectra, two distinct Ln–O vibrational frequencies can be assigned: ν(Ln–ONO$_2$) at ~220 cm^{-1} and ν(Ln–O ether) at ~210 cm^{-1}.

The corrected magnetic moments of the lighter Ln(III) ions in the 12-crown-4 complexes are 3–8% lower than the free ion moments, except for Sm and Gd. They are similar to those found in the 15-crown-5 and 18-crown-6 complexes [8, 10], which points to a similar Ln(III)/crown ether interaction. Expressed in Bohr magnetons these moments amount to 2.41, 3.42, 3.37, 1.66, 3.31, and 7.87 for Ln = Ce, Pr, Nd, Sm, Eu, Gd, respectively.

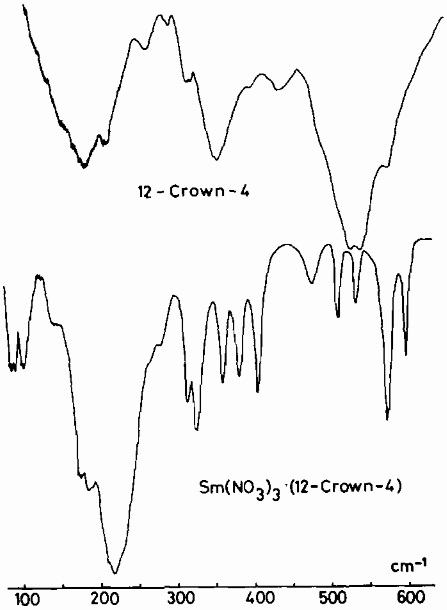

Fig. 2. Far IR spectra of 12-crown-4 ether and of the 1:1 complex with Samarium nitrate (Nujol mulls).

We have also studied the thermal stability of the 12-crown-4 complexes by recording the thermogravimetric curves of the neodymium and lutetium compounds. The complexes remain unchanged up to 270 °C and then decompose completely, mainly into oxinitrates, at 280 °C and 340 °C for Ln = Lu and Nd, respectively. Contrary to what we observed for the complexes of 18-crown-6 ether and for the complexes of 15-crown-5 ether with the heavier lanthanoid nitrates (Ln = Gd-Lu) [8, 9], no transformation into 4:3 complexes occurred.

In the case of praseodymium, a 1:1 complex is also isolated with chloride as anion. This complex is very hygroscopic and gives readily the di-hydrate. Its IR absorption bands are less split as compared to those of the nitrato complexes; its IR spectrum is in fact similar to the spectrum of the lithium bromide complex [17]. The Ln–O frequency occurs around 210 cm^{-1} and one Ln–Cl vibration can be assigned at 238 cm^{-1} (240 cm^{-1} in the Raman spectrum). Lanthanoid perchlorates give 1:2 complexes [11, 12] which will be discussed in a subsequent paper.

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