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Synthesis and Characterization of Pr(III) Complexes with 15-Crown-5 and 18-Crown-6 Ethers*

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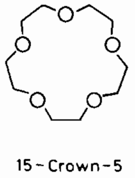
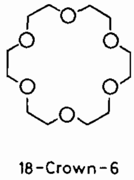
Crown ethers and related macrocyclic and macropolycyclic molecules show a high complexation selectivity which makes them adequate ligands for the investigation of the coordinative properties of lanthanoid ions [1–7]. In Part I of this series [8] we have shown that stable and unsolvated complexes of the lighter lanthanoid nitrates (Ln = La–Gd) can be isolated with the crown ethers 1 and 2. The Ln(III)/crown ether ratio is 1:1 for the complexes with ligand 1 whereas complexes of ligand 2 may have two different stoichiometries, 1:1 complexes for Ln = La–Nd and the thermally more stable 4:3 complexes for Ln = La–Gd. Two important factors influencing the complexation process are: the ratio ionic diameter/ligand cavity diameter and the ligand flexibility. In this communication we investigate the influence of the coordination number of the lanthanoid ion on the complex formation between PrX$_3$ (X = NO$_3^-$ [8], NCS$^-$, ClO$_4^-$, Cl$^-$) and the crown ethers 1 and 2; moreover a complex containing ligand 3 is also described.



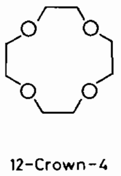
1

15-crown-5



2

18-crown-6



3

12-crown-4

Experimental

Synthesis of the Complexes

A solution of 5 mmol (for 1:1 complexes), respectively 10 (for 1:2 complexes), of ligand(s) in 20–35 ml of CH$_3$CN (or in CH$_3$OH:CH$_3$CN 1:3 for X = Cl$^-$) was added dropwise to a solution of 5 mmol of PrX$_3$·nH$_2$O (n between 0.5 and 5, X = Cl$^-$, NCS$^-$, ClO$_4^-$) in 20–35 ml of the corresponding solvent. The mixture was stirred at 60 °C for 5–20 h; after cooling and partial evaporation of the solvent for complexes with ligand 2, the complexes were filtered off and dried for 3–4 days in a dessicator over P$_2$O$_5$. The complexes with X = NCS$^-$ and ClO$_4^-$ were further dried for 1 day at 50 °C/10^{-2} Torr. Yields: 70–90% for the complexes with ligand 1, and 75% (X = Cl$^-$) or 30% (X = NCS$^-$, ClO$_4^-$) for the complexes of ligand 2.

The results of C, H, N elemental analyses (performed by Mr. W. Manser, Mikroanalytisches Laboratorium der ETH-Zürich) and complexometric analyses of lanthanoid ions by EDTA of the isolated complexes are given in Table I.

Raman Spectra

They were obtained on finely powdered samples using a Spex Ramalog-4 spectrometer and an Ar laser as excitation source (514.5 nm, 200–400 mW).

Magnetic Moments

Effective magnetic moments were calculated from the measured mass susceptibility, corrected for diamagnetic contributions. The connection for the ligands 1, 2 and 3 was evaluated from the measured susceptibility of 2 and from Pascal's constants [9]. The corrections for Pr(III) and the anions were taken from [9]. Other experimental details: see [8].

Results and Discussion

The isolated complexes are microcrystalline powders of pale green colour. Complexes with 15-crown-5 ether form more rapidly and in a better yield than those with 18-crown-6 ether, which reflects the more favourable ratio ionic diameter/ligand cavity diameter for ligand 1 than for 2, This ratio, ~ 0.9 for ligand 1, is close to the optimum value observed for main and transition metal complexes [10], whereas the value for 2 is ~ 0.7. Attempts to synthesize the 1:1 complex Pr(ClO$_4$)$_3$·1 failed: the only compounds formed from Pr(ClO$_4$)$_3$ and ligand 1 are either the 1:2 complex (even in the presence of an excess of salt) or mixed complexes such as Pr(ClO$_4$)$_3$·1·3. The 12-crown-4 ether 3 also yields a 1:2 complex with Pr(ClO$_4$)$_3$ [11].

Bond formation between Pr(III) and the polyethers is evidenced in the IR and Raman spectra. The ligand vibrational modes undergo substantial shifts and splittings upon complexation. These shifts, defined as $\tilde{\nu}$(complex) – $\tilde{\nu}$(ligand), depend on both the ligand and the kind of anion (*cf.* Fig.). They may be summarized in the following simplified way.

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*Part 2 of the series "Complexes of Lanthanoid Salts with Macrocyclic Ligands". For Part 1 see ref. [8].

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TABLE I. Elemental Analysis of the Isolated Complexes.

Complex	MW	Hygroscopic	%C		%H		%N		%Pr	
			calc.	found	calc.	found	calc.	found	calc.	found
$PrCl_3 \cdot 1$	467.54	yes	25.69	25.35	4.31	4.16	–	–	30.14	30.35
$PrCl_3 \cdot 2$	511.59	yes	28.17	27.82	4.73	4.70	–	–	27.54	27.26
$Pr(NCS)_3 \cdot 1$	535.42	very	29.16	29.02	3.76	3.83	7.85	7.71	26.32	26.17
$Pr(NCS)_3 \cdot 1 \cdot H_2O$	553.44	no	28.21	28.41	4.01	4.05	7.59	7.53	25.45	a
$Pr(NCS)_3 \cdot 2$	579.47	no	31.09	31.03	4.17	4.14	7.25	7.09	24.32	24.34
$Pr(ClO_4)_3 \cdot (1)_2$	879.80	no	27.30	27.11	4.58	4.44	–	–	16.02	15.96
$Pr(ClO_4)_3 \cdot 2$	703.58	yes	20.49	20.60	3.44	3.57	–	–	20.03	20.14
$Pr(ClO_4)_3 \cdot 1 \cdot 3$	835.74	yes	25.87	25.58	4.34	4.40	–	–	16.86	16.74

[a]Not analyzed.

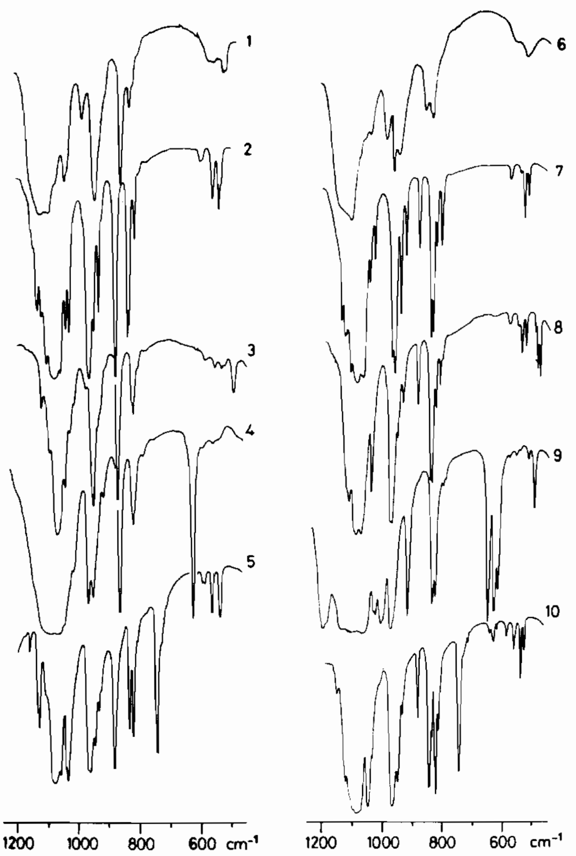

Figure. Part of the IR spectra (Nujol mulls) of some complexes. 1) 15-crown-5 1, 2) $PrCl_3 \cdot 1$, 3) $Pr(NCS)_3 \cdot 1$, 4) $Pr(ClO_4)_3 \cdot (1)_2$, (5) $Pr(NO_3)_3 \cdot 1$, 6) 18-crown-6 2, 7) $PrCl_3 \cdot 2$, 8) $Pr(NCS)_3 \cdot 2$, 9) $Pr(ClO_4)_3 \cdot 2$, 10) $Pr(NO_3)_3 \cdot 2$.

For 1:1 complexes the $\tilde{\nu}(C\text{–}O\text{–}C)_n$ at ~ 1100 cm^{-1} in the free ligands is shifted by –20 to –40 cm^{-1}; other ligand vibrations, at 940–990 cm^{-1} and ~ 860 cm^{-1} in the free ligands are shifted by ±10 to 25 cm^{-1} and +15 to +20 cm^{-1}, respectively. This latter IR absorption is characteristic of most 1:1 complexes: it appears in the spectra of all the lighter lanthanoid nitrate 1:1 complexes [8], but not in the spectra of both the 4:3 complexes $[Ln(NO_3)_3]_4 \cdot (2)_3$ and the 1:2 complex $Pr(ClO_4)_3 \cdot (1)_2$ in which it occurs at ~ 865 cm^{-1}. An exception to this rule is $Pr(ClO_4)_3 \cdot 2$ for which no IR absorption is detected at 880 cm^{-1}; however, its Raman spectrum shows an emission band at 874 cm^{-1}.

Information about the bonding mode of the anions, and thus about the coordination number of Pr(III), may also be obtained from the vibrational spectra (Table II). The data for the complexes of $Pr(NO_3)_3$ indicate that the nitrate groups are not tetrahedral since six vibration modes are observed [12]. The distinction between monodentate, bidentate or bridging nitrato moieties is difficult. Lever *et al.* [13] have proposed that the number and relative energies of the nitrate combination frequencies in the 1700–1800 cm^{-1} region of the IR spectra may be used as an aid to establish the coordination mode of the nitrato groups: mono- and bidentate nitrates exhibit two bands separated from each other by 5–26 cm^{-1} and 20–66 cm^{-1}, respectively. The complexes of $Pr(NO_3)_3$ with ligands 1 and 2 show two combination bands in this region; they are separated by 37 cm^{-1} but each of them is further split into two components. For $Pr(NO_3)_3 \cdot 2$ this latter splitting is small (4–7 cm^{-1}) and we conclude to the presence of bidentate, although not equivalent NO_3^- groups, like in $La(NO_3)_3$·dicyclohexyl-18-crown-6 for instance [7]. For $Pr(NO_3)_3 \cdot 1$ the situation is different (see Table II), and we cannot rule out the presence of one monodentate nitrato group.

The observed vibrational frequencies of the $Pr(NCS)_3$ complexes are consistent with N-bonded NCS^- anions [14]. Most of the bands are split, reflecting the presence of two or even three (complex with ligand 2) non equivalent isothiocyanates. The assignment for the perchlorate vibrations [15] may be summarized as follows. The three ClO_4^- groups of the 1:2 and 1:1:1 complexes are ionic (symmetry T_d) whereas $Pr(ClO_4)_3$ 2 contains bidentate perchlorate(s) although the presence in this complex of ionic ClO_4^- group(s) cannot be ruled out. In acetonitrile as solvent, this complex is a 2:1 electrolyte as indicated by

TABLE II. IR and Raman Data for the Anion Vibration Modes (cm^{-1}).

Compound	Wavenumbers and assignments								
$Pr(ClO_4)_3\cdot(1)_2$	T_d:	$\nu_3(F_2)$	$\nu_1(A_1)$	$\nu_4(F_2)$	$\nu_2(E)$				
	IR:	1040–1120[a]	inactive	630s	inactive				
	R:	1060–1120[a]	929s	623s	458s				
$Pr(ClO_4)_3\cdot 1\cdot 3$	IR:	1052s[a]	inactive	625s	inactive				
	R:	1063w 1095w	928s	622s	456s				
$Pr(ClO_4)_3\cdot 2$	C_{2v}:	$\nu_8(B_2)$	$\nu_6(B_1), \nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_7(B_1)$	$\nu_9(B_2)$	$\nu_4(A_1)$	$\nu_5(A_2)$
	IR:	1200s 1190sh	1010–1135[b]	920s	651s	630s	620s	–	inactive
	R:	1199w	1105w	911vs 928s	640w	620m	610m	456w	435w
$Pr(NCS)_3\cdot 1$		ν(CN)		ν(CS)		δ(NCS)			
	IR:	2060vs, 2030vs		–		490w			
	R:	2059sh, 2047s, 2028s		820s, 783w		483w			
$Pr(NCS)_3\cdot 2$	IR:	2070vs, 2040vs, 1992vs		–		495vw, 488w, 480w			
	R:	2061vs, 2049vs, 2035vs		819vs, 807m, 794m		479w			
	C_{2v}:	$\nu_2+\nu_5$ or ν_6	$\nu_1(A_1)$	$\nu_4(B_2)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_6(B_1)$	$\nu_5(B_2)$	
$Pr(NO_3)_3\cdot 1$	IR:	1736w 1748w 1770w 1774sh	~1500vs	~1310vs	1035vs	821s	745sh 741s	725?	
	R:	–	b	1300m	1031s 1034s	b	732m	707vw	
$Pr(NO_3)_3\cdot 2$	IR:	1747sh 1754w 1780sh 1784w	~1490vs	~1310vs	1048vs	820s	744s	725?	
	R:	–	b	b	1045s	b	737sh 741s	706vw	

[a] Broad, strong band containing C–O–C vibrations. [b] Masked by ligand vibrations.

TABLE III. Magnetic Moments (21 ± 1 °C, ± 0.02 Bohr Magneton)[a] of the Isolated Complexes and of the Anhydrous Salts PrX_3[b].

X	Salt μ_{eff}	15-crown-5 Complexes		18-crown-6 Complexes	
		Stoech.	μ_{eff}	Stoech.	μ_{eff}
NO_3^- [c]	3.35	1:1	3.32	1:1	3.32
NCS^- [d]	3.64	1:1	3.48	1:1	3.41
Cl^-	3.57	1:1	3.49	1:1	3.48
ClO_4^-	3.50	1:2 1:1:1[e]	3.37 3.46	1:1	3.45

[a] Averages of 10 determinations on two independent samples. [b] Free ion moment: 3.62 [9]; literature data for Pr(III)-containing compounds: 3.47–3.70 [9]. [c] From [8], but corrected for diamagnetic contribution. [d] $Pr(NCS)_3\cdot 2EtOH$. [e] $Pr(ClO_4)_3\cdot 1\cdot 3$.

conductimetric measurements in the concentration range 10^{-3} to 10^{-4} *M*.

The coordination number CN of the Pr(III) ion ranges between 8 and 12 in the studied compounds. Nitrato-complexes have CN = 10 or 11 with ligand **1**, depending on the presence of one monodentate NO_3^- or not, and CN = 12 with ligand **2**. Such a high CN is usually observed for nitrato-compounds, *e.g.* CN = 10 in $Pr(NO_3)_3\cdot 6H_2O$ [16] or $Ln(NO_3)_3\cdot$**3** [11], and CN = 12 in $K_3Pr_2(NO_3)_3$ [17] or in $La(NO_3)_3\cdot$dicyclohexyl-18-crown-6 [7]. When the anion is a small and fairly good complexing agent like NCS^-, a minimum coordination number of 9 is required to get stable compounds: $Pr(NCS)_3\cdot$**2** (CN = 9) is not hygroscopic whereas $Pr(NCS)_3\cdot$**1** (CN = 8) is very hygroscopic and gives readily the monohydrate. With a bulkier and less good complexing anion like ClO_4^- it seems that a minimum CN of 10 is required: $Pr(ClO_4)_3\cdot(\mathbf{1})_2$ (CN = 10) is stable to air and moisture, $Pr(ClO_4)_3\cdot$**1**$\cdot$**3** (CN = 9) is hygroscopic and forms the monohydrate, and so is $Pr(ClO_4)_3\cdot(\mathbf{3})_2$ (CN = 8) which yields a dihydrate [11]. That $Pr(ClO_4)_3\cdot$**2** (CN = 8 to 12) is hygroscopic may be explained either because one ClO_4^- group only is bound to Pr(III) or because the interaction between ClO_4^- and Pr(III) is weak due to steric hindrance.

The corrected magnetic moments reported in Table III are a measure of the ligand-field strength in the studied Pr(III) complexes and they confirm the above qualitative discussion. In non hygroscopic, that is strongly bonded, complexes Pr(III) has an effective magnetic moment 0.21 to 0.30 B.M. unit lower than the free ion moment. In the other complexes, the magnetic moment of Pr(III) is closer to the free ion value, being only 0.12 to 0.16 B.M. unit lower.

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