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Sandwich Complexes of the Lighter Lanthanoid Perchlorates with 12-Crown-4 and 15-Crown-5 Ethers*

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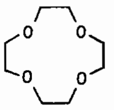
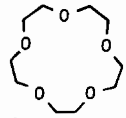
Introduction

Crown ethers react in organic solvents with trivalent lanthanide ions to yield stable complexes. Since the original work of de Paoli and King [1] there has been a large interest in these complexes especially because they can be used to stabilize Ln(II) oxidation states [2]. In previous papers of this series, we have reported the isolation of both 1:1 and 4:3 complexes of $Ln(NO_3)_3$ with 15-crown-5 and 18-crown-6 ethers [3]. It has been found that 12-crown-4 ether forms 1:1 complexes with $Ln(NO_3)_3$ [4] and a 1:2 complex with $Pr(ClO_4)_3$ [5]. Desreux has recently discussed the ^{1}H-NMR spectra of the sandwich complexes $Ln(ClO_4)_3 \cdot (1)_2$ (Ln = La–Yb) [6]. In this communication, we discuss the properties of three series of complexes: $Ln(ClO_4)_3 \cdot (1)_2$, Ln = La–Gd, $Ln(ClO_4)_3 \cdot 1 \cdot 2$, Ln = Pr–Gd, and $Ln(ClO_4)_3 \cdot (2)_2$, Ln = La–Eu.


12-crown-4
1


15-crown-5
2

Experimental

A solution of 7.5 mmol of ligand(s) (Fluka, *purum*) in 5–30 ml CH_3CN (Fluka, *puriss*) was added dropwise to a solution of 3 mmol $Ln(ClO_4)_3 \cdot xH_2O$ (x = 0.2–1) in 5–15 ml CH_3CN, under nitrogen atmosphere. The mixture was stirred at 60 °C during 24 h and the solvent was then partially evaporated. The polycrystalline complex was filtered, washed with 3 × 10 ml CH_2Cl_2, dried in a dessicator over P_2O_5 during 2 days, and under vacuum (10^{-2} Torr) during 3–10 days. Yield: 15–40% for complexes with *1* or *2* and 50–80% for the mixed complexes. The elemental analyses are reported in Table I. The solutions for ^{1}H NMR measurements (WP-60 and WH-360 Bruker spectrometers) were prepared under controlled atmosphere (<30 ppm water); they were

TABLE I. Elemental Analysis of the Isolated $Ln(ClO_4)_3 \cdot L \cdot L' \cdot nH_2O$ Complexes.

Ln	n	MW	Hygroscopic?	%C		%H		%Ln	
				calc.	found	calc.	found	calc.	found
L = L' = 12-Crown-4[a]									
La	2	825.711	a little	23.27	23.34	4.39	4.44	16.82	16.78
L = L' = 15-Crown-5									
La	0	877.79	no	27.37	27.50	4.59	4.74	15.82	15.97
Ce	0	879.00	no	27.33	27.36	4.59	4.50	15.94	15.98
Pr	0	879.80	no	27.30	27.11	4.58	4.44	16.02	15.96
Nd	0	883.12	no	27.20	26.79	4.56	4.50	16.33	16.45
Sm	0	889.23	yes	27.10	27.19	4.53	4.63	16.91	17.08
Eu	1	908.85	no	26.43	26.30	4.66	4.68	16.72	16.74
L = 12-Crown-4, L' = 15-Crown-5									
Pr	1	835.74	a little	25.87	25.58	4.34	4.40	16.86	16.74
Nd	1	857.08	a little	25.22	24.89	4.47	4.30	16.82	16.74
Sm	1	863.19	a little	25.05	24.09	4.44	4.04	17.52	17.35
Eu	1	964.80	a little	25.00	24.94	4.43	4.37	17.57	17.51
Gd	1	870.09	a little	24.85	24.65	4.40	4.38	18.07	18.16

[a] The elemental analyses for Ln = La–Yb are reported in [5].

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[*] Part 8 of the series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'. For part 7, see [7].

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TABLE II. Main IR Absorptions for Ligands *1* and *2* and for the Isolated Complexes (cm^{-1}).

Proposed Assignment	12-Crown-4 *1*	15-Crown-5 *2*	$Ln(ClO_4)_3\cdot(1)_2$ Ln = La–Gd	$Ln(ClO_4)_3\cdot(2)_2$ Ln = La–Eu	$Ln(ClO_4)_3\cdot 1\cdot 2$ Ln = Pr–Gd
$\nu_4(ClO_4^-)$			620–625[a]	630	625–632
			627–635		
Bound ClO_4^-			648–658		
$r(CH_2)$	848	860	858–869	866–870	863–867
$\nu_s(CCO)$	919	943	920–930	952–956	935–938
			935–940	967–970	960–965
	1025	1042	995–1200	1015–1150	1015–1135
$\nu_{as}(CCO)$ +	1074	1075	b	b	b
$\nu_3(ClO_4^-)$	1095	1093			
	1135	1120			
Bound ClO_4^-			1208–1215		
$t(CH_2)$	1252	1248	1250–1260	1250–1260	1250–1255
	1289	1305	1280–1300	1300–1305	1295–1305
	1307		1315–1325		

[a] From bound perchlorate. [b] Broad band with several maxima.

heated 3–5 h at 50 °C before measurement, to allow possible equilibria between different species to be attained. See [5] for other experimental details.

Results and Discussion

The complexes of 12-crown-4 ether are hygroscopic and readily form dihydrates. The mixed complexes are also hygroscopic and form monohydrates, whereas the complexes of 15-crown-5 ether with Ln = La–Nd are not hygroscopic. Mixed complexes could not be isolated for Ln = La and Ce: the sandwich complexes $Ln(ClO_4)_3\cdot(2)_2$ crystallized out of the solution even in presence of a threefold excess of 12-crown-4 ether.

The IR spectra (Table II) of a series of complexes are very similar, with frequency shifts of ±5 to ±10 cm^{-1} upon going from La to Gd. The assignment of the spectra in the 1000–1200 cm^{-1} range and around 900 cm^{-1} is not always clear cut since both perchlorate and crown ether vibrations absorb in these regions. Two comments may however be made. (i) The perchlorate groups of the two series of complexes $Ln(ClO_4)_3\cdot 1\cdot 2$ and $Ln(ClO_4)_3\cdot(2)_2$ have two IR active modes only (~630 and ~1100 cm^{-1}); they are therefore ionic. Additional bands at 625, 650, and 1210 cm^{-1} are observed for $Ln(ClO_4)_3\cdot(1)_2$; this points to the presence of bonded perchlorate groups. Provided all the oxygen atoms of the crown ether molecules are coordinated to the metal ion, which is a reasonable assumption in view of the published crystal structures of lanthanide complexes with crown ethers [7, 8], the coordination number of the rare earth ions in these series of complexes ranges between 9 and 10. (ii) Figure 1 displays the 800–1000 cm^{-1} region of the IR spectra of the ligands and of the samarium complexes, where one of the $\nu(CCO)$ vibrations absorbs, at 919 and 943 cm^{-1} for *1* and *2*, respectively. This vibration is displaced by 15–25 cm^{-1} towards higher wavenumbers upon complexation; for both $Ln(ClO_4)_3\cdot(1)_2$ and $Ln(ClO_4)_3\cdot(2)_2$ complexes, the presence of a splitting indicates that the two macrocycles are probably not equivalent in the solid state. For comparison, neither of the 12-crown-4 and 15-crown-5 $\nu(CCO)$ absorptions are split in the spectra of the mixed complexes.

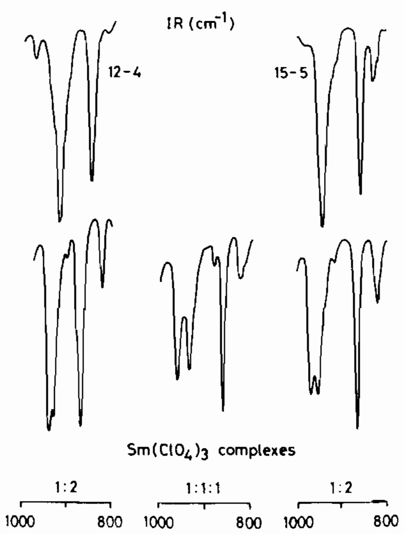

Fig. 1. Part of the IR spectra of 12-Crown-4, 15-Crown-5 and $Sm(ClO_4)_4\cdot L\cdot L'$.

TABLE III. ^{1}H NMR Chemical Shifts (ppm, from TMS) for Free (δ_F) and Bound (δ_B) 15-Crown-5 Ether in Some of the Lanthanum Perchlorate Solutions Studied. Solvent: CD_3CN 99.9% D; $[La^{3+}] = 6.7 \times 10^{-3}$ *M*.

$[2]_t/[La^{3+}]_t$	δ_F			δ_B		
	−30 °C	+25 °C	+40 °C	−30 °C	+25 °C	+40 °C
0.5				4.17	4.21	4.2^a
1.0				4.17	4.20	4.22
1.5				4.16	4.21	4.21
2.0	3.72	^{b}	^{c}	4.15	4.19	^{c}
2.2	3.62	3.66	3.68	4.17	4.21	4.21
2.5	3.58	3.63	3.64	4.16	4.20	4.21

^{a}Center of a multiplet. ^{b}Not observed. ^{c}Not measured.

The molar conductivities at 25.0 °C of 10^{-3} *M* solutions in anhydrous acetonitrile are 370, 400 and 400 ohm^{-1} cm^2 mol^{-1} for $Ln(ClO_4)_3\cdot(1)_2$, $Ln(ClO_4)_3\cdot(2)_2$ and $Ln(ClO_4)_3\cdot 1\cdot 2$, respectively. They lie in the range reported for 3:1 electrolytes [9] although the smaller value observed for the 12-crown-4 complexes may reflect a Ln^{3+}/ClO_4^- interaction similar to the one observed in anhydrous solutions of europium perchlorate [10]. ^{1}H NMR spectra of lanthanum perchlorate solutions were recorded for ligand to metal ratios R ranging from 0.5 to 2.5. Both free and bound ligands give rise to well separated signals. Inspection of the data reported in Table III indicates no signal attributable to the free ligand ($\delta \sim 3.6$ ppm) when $R < 1.5$. For $R = 2$ the free ligand signal is only observed at −30 °C when the ligand exchange reaction is slow and it is very weak: only about 5% of the total ligand is dissociated. The formation constant of the 1:2 complex is therefore larger than 10^4. The addition of up to 15 water molecules per lanthanum ion does not produce an increase of the free ligand signal. Upon heating, both resonances from the free ligand (singlet) and the coordinated ligand (singlet with a broader base, except for $R = 0.5$, where an AA′BB′ spectrum is obtained at 40 °C) are broadened because of the ligand exchange reaction:

$$Ln(ClO_4)_3\cdot(2)_2 + 2^* \rightleftharpoons Ln(ClO_4)_3\cdot 2\cdot 2^* + 2$$

The exchange rate is independent of the ligand concentration ($k_e \sim 4$ s^{-1} at 25 °C) which points to a dissociative exchange mechanism. In the case of $Nd(ClO_4)_3$ solutions, two resonances are obtained at 25 °C for the bound ligand at 5.1 and 7.6 ppm. Similarly to what was observed for $Nd(NO_3)_3\cdot$(18-crown-6) [3] the latter resonance is split into two singlets (6.95 and 8.9 ppm) upon cooling to −40 °C. A systematic study of the corresponding exchange reactions will be reported elsewhere. The crystal structure of $Nd(ClO_4)_3\cdot(2)_2$ is also currently being investigated.

Acknowledgement

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