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Syntheses and Properties of Lanthanoid Perchlorate Complexes with the Crown Ether 2,3:17,18-dibenzo-1,4,7,10,13,16,19,22,25,28-decaoxacyclotriaconta-2,17-diene

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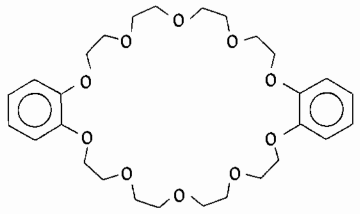
The coordination compounds of alkali and alkaline earth ions with macrocycles of the types crown-polyethers and cryptands have been extensively studied in recent years [1]. On the contrary, the coordination behaviour of lanthanoids towards the above ligands has attracted little attention [2, 3]. As a part of a systematic investigation on the coordination compounds of lanthanoids with macrocycles [3, 4], this communication reports the preparation and properties of some complexes of 2,3:17,18-dibenzo-1,4,7,10,13,16,19,22,25,28-decaoxacyclotriaconta-2,17-diene (hereafter named dbc-10) with the perchlorates of La, Ce, Pr, Nd, Sm, Eu, Dy, Ho, Er, and Yb. So far, to our knowledge, no report on such systems has appeared. An X-ray structural analysis of [K(dbc-10)]I showed that the potassium cation is completely enclosed by the ligand [5].



dibenzo-[30]-crown-10

Experimental

No complex compound of dbc-10 was obtained by using methanol or ethanol as solvents but methyl cyanide proved to be a suitable reaction medium. Anhydrous lanthanoid perchlorates were used (Ln = La, Ce, Pr, Nd, Sm, and Eu) which were obtained by slowly heating the hydrated salts up to 200 °C at 0.1 mm Hg [6]. With the heavier lanthanoids (Ln = Dy, Ho, Er, and Yb) for which such a procedure fails [6], the MeCN solutions of the hydrated perchlorates were refluxed through a Soxhlet extractor packed with molecular Sieves for 20 hours. With Dy, Ho, and Er, however, water is present in the separated compounds.

A solution of the proper lanthanoid perchlorate (1 mmol) in anhydrous MeCN (15 cm^3) was added to dbc-10 (1.1 mmol). In a few minutes, crystals of the complexes separated, which were filtered off, washed with a MeCN–CH_2Cl_2 mixture and dried *in vacuo* at room temperature. Recrystallization can be carried out by dissolving the complexes in MeCN and reprecipitating them with CH_2Cl_2. Table I reports analytical data, colours, and molar conductances of the compounds. The presence of water and MeCN was confirmed by i.r. spectra.

The i.r. spectra were recorded as Nujol mulls on a Perkin-Elmer Spectrophotometer Model 283. The electronic spectra both on solution and by reflectance were recorded with a Cary 17 Spectrophotometer.

TABLE I. Analytical and Physical Data for $Ln(ClO_4)_3$(dbc-10) Complexes.

Compound	Colour	Analysis (%)[a]				Λ[b]
		C	H	Me	N	(S cm^2 mol^{-1})
$La(ClO_4)_3$(dbc-10)	White	34.3(34.5)	4.1(4.1)	14.5(14.3)		350
$Ce(ClO_4)_3$(dbc-10)	White	34.4(34.5)	4.0(4.0)	14.2(14.4)		356
$Pr(ClO_4)_3$(dbc-10)	Pale green	34.1(34.5)	4.3(4.1)	14.3(14.4)		340
$Nd(ClO_4)_3$(dbc-10)	Pale lilac	34.1(34.3)	4.1(4.1)	14.9(14.7)		351
$Sm(ClO_4)_3$(dbc-10)	White	34.3(34.1)	4.2(4.1)	15.6(15.3)		347
$Eu(ClO_4)_3$(dbc-10)	Orange	34.1(34.0)	3.8(4.1)	15.2(15.4)		370
$Dy(ClO_4)_3$(dbc-10)·$2H_2O$·2MeCN	White	34.5(34.4)	4.5(4.3)	14.5(14.6)	2.3(2.5)	357
$Ho(ClO_4)_3$(dbc-10)·$2H_2O$·1.5MeCN	Pink	33.8(33.9)	4.8(4.4)	14.8(15.0)	1.9(1.9)	350
$Ho(ClO_4)_3$(dbc-10)·$1H_2O$·2MeCN	Pink	34.4(34.9)	4.3(4.4)	14.8(15.0)	2.5(2.5)	359
$Er(ClO_4)_3$(dbc-10)·$2H_2O$·1.5MeCN	Pink	33.8(33.8)	4.3(4.4)	15.3(15.2)	2.0(1.9)	373
$Yb(ClO_4)_3$(dbc-10)·2MeCN	Yellow	35.3(35.2)	4.3(4.2)	16.0(15.9)	2.6(2.6)	350

[a] Calcd. values in parentheses. [b] For *ca.* 10^{-3} molar solutions in methyl cyanide at 25 °C. Under the same conditions reference values are: 159 S cm^2 mol^{-1} for $[Bu_4N](ClO_4)$ and 293 S cm^2 mol^{-1} for $[Et_4N]_2CoBr_4$.

Results and Discussion

All the present compounds are crystalline solids, which are indefinitely stable in closed vessels. They are very hygroscopic and transform to a mixture of the ligand and hydrated lanthanoid perchlorates when exposed to the open air for a few hours. The stoichiometry of the present compounds does not prove, by itself, true coordination of the polyether to the metal ions. Actually, co-crystallization occurs with the compound $UO_2(NO_3)_2(H_2O)_2$(18 crown-6) [7]. Nevertheless, direct evidence of true coordination by the polyether dbc-10 to metal ions follows from the electronic spectra of the samarium, europium, and ytterbium compounds. In fact, the reflectance spectra of these solid compounds exhibit broad bands with maxima at 32,800 (Sm), 24,100 (Eu), and 27,000 (Yb) cm^{-1} (Figure 1). These bands can be safely attributed to electron transfer transitions from the loosest bound molecular orbitals of the polyether (probably, those involving chiefly the $-O-C_6H_4-O-$ moieties) to 4*f* orbitals of the more reducible lanthanoid ions [8, 9]. By using the values of the band maxima and the values for the uncorrected optical electronegativities of 1.6 (Sm), 1.9 (Eu), and 1.8 (Yb) [8], the value of 2.7 for the optical electronegativity of dbc-10 can be obtained. The same value holds with the similar ligand dibenzo-[18]-crown-6 (dbc-6) for which an X-ray diffraction study has ascertained the anular coordination of the sexidentate ligand around the samarium ion in the complex $[Sm(ClO_4)_3(dbc\text{-}6)]$ [4].

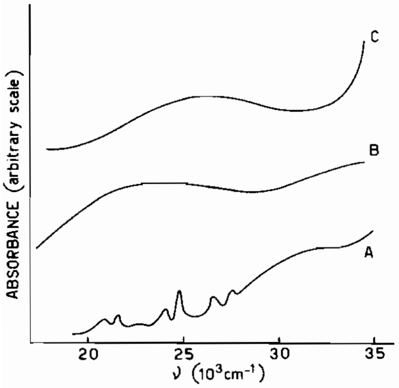


Figure. Diffuse reflectance spectra of: A, $Sm(ClO_4)_3$(dbc-10); B, $Eu(ClO_4)_3$(dbc-10); C, $Yb(ClO_4)_3$(dbc-10)·2MeCN.

These electron transfer transitions persist in the MeCN solutions of the above complexes (32,800 (Sm), 25,000 (Eu), and 28,200 (Yb) cm^{-1}). This indicates that the ligand is coordinated to the metal ions in solution. Nevertheless, the molar absorbances of these transitions are moderately sensitive to complex concentration and to ligand excess, indicating that partial dissociation and/or solvolysis takes place.

The uncoordinated nature of the perchlorate anion in these compounds can be easily inferred from their i.r. spectra. The ν_3 vibrations of ClO_4^- strongly interfere with the polyether absorptions but the ν_4 bending vibrations are clearly degenerate in all these complexes. Actually, only one sharp, strong band is present at 620 cm^{-1} over the 600–700 cm^{-1} frequency range. Hence, we can conclude that only free perchlorate anions are present in all these solid compounds. This is an indirect evidence of coordination of the polyether to the lanthanoid ions. Also in MeCN solution the perchlorate anions are not coordinated to the lanthanoid ions, since all complexes behave as 1:3 electrolytes.

Other features of the i.r. spectra of the present solid compounds deserve further comments. The polyether bands show small but definite changes with respect to those of the free polyether, especially in the 1600 and 700–1000 cm^{-1} regions. For instance, the free-ligand band at 1600 cm^{-1}, which is attributable to the stretching vibrations of the benzene rings, is split into two bands at 1595 and 1610 cm^{-1}. Such a splitting is also found with the above mentioned $[Sm(ClO_4)_3(dbc\text{-}6)]$ complex [4], and may be ascribed to coupling between the two benzene rings via the lanthanoid ion.

The two bands of liquid MeCN at 2250 and 2290 cm^{-1} are blue shifted of about 35 cm^{-1} in the present solid compounds. Such an upward shift is usually considered to indicate coordination of the MeCN to a metal ion through the nitrogen atom [11].

In conclusion, the potentially decadentate polyether dbc-10 is able to coordinate the lanthanoid ions and, at least with the unsolvated compounds, fully saturates their coordination sites. An X-ray structural study is in progress in order to ascertain the coordination geometry of these compounds.

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