Structure and Properties of Some Lanthanoid(III) Perchlorate Complexes with the Crown Polyether 5,6,14,15-Tetrahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclo-octadecin

By **Mario Ciampolini** * and **Nicoletta Nardi**, Istituto di Chimica Generale ed Inorganica dell'Università, Laboratorio C.N.R., Via J. Nardi, 39 Florence, Italy
Renzo Cini, **Stefano Mangani**, and **Pierluigi Orioli**, Istituto di Chimica Generale dell'Università, Siena, Italy

Some lanthanoid(III) perchlorate complexes with the title ligand (dbc-6) have been prepared in methyl cyanide. Two series have been obtained with formulae $Ln[ClO_4]_3.(dbc\text{-}6)$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Dy, or Ho) and $Ln[ClO_4]_3.(dbc\text{-}6).H_2O$ (Ln = Er or Yb). The crystal and molecular structure of the $[Sm(ClO_4)_3(dbc\text{-}6)]$ complex has been determined from *X*-ray diffractometric data. Crystals are orthorhombic, space group *Fdd*2, with a = 37.130(12), b = 12.987(5), c = 11.312(5) Å, and Z = 8. The structure has been refined by least-squares techniques to R 0.047 for 1 115 reflections. The structure shows the samarium(III) ion to be ten-co-ordinated by the six oxygen atoms of dbc-6, by two oxygen atoms of a bidentate $[ClO_4]^-$ ion, and by two oxygen atoms of the other unidentate $[ClO_4]^-$ ions. The complex has C_2 crystallographic symmetry. Conductivity data and i.r. and electronic spectra are discussed. The spectra of the complexes of Sm, Eu, and Yb show electron-transfer transitions in agreement with the optical electronegativity value of 2.7 for the present polyether.

INCREASING interest is being devoted to the study of co-ordination compounds formed between lanthanoid ions and crown polyethers or cryptands.[1-5] The aims are to utilize the macrocyclic effect in order to obtain lanthanoid compounds having both high thermodynamic stability as well as kinetic inertness in solution towards donor atoms which do not usually bind strongly to these metals.

As part of a systematic investigation on the co-ordination compounds of lanthanoids with macrocycles,[4,5] this paper reports the synthesis and characterization of the complexes of some lanthanoid(III) perchlorates with the polyether 5,6,14,15-tetrahydrodibenzo[*b*,*k*]-[1,4,7,10,13,16]hexaoxacyclo-octadecin, nicknamed dibenzo-[18]-crown-6 and here abbreviated as dbc-6. The crystal structure of the complex $[Sm(ClO_4)_3(dbc\text{-}6)]$ is described. Previously, Cassol *et al.*[1] isolated the complexes between dbc-6 and lanthanoid nitrates and thiocyanates. At variance with their results, King and Heckley as well as Desreux *et al.* could not isolate dbc-6 complexes with the lanthanoids heavier than neodymium.[2]

EXPERIMENTAL

Preparation of the Compounds.—No complex compound of dbc-6 with lanthanoid perchlorates was obtained by using methanol or ethanol as solvent but methyl cyanide proved to be a suitable reaction medium. Anhydrous lanthanoid perchlorates were used (Ln = La, Ce, Pr, Nd, Sm, or Eu) which were obtained by slowly heating the hydrated salts up to 200 °C at 0.1 mmHg.[6,†] With the heavier lanthanoids (Ln = Dy, Ho, Er, or Yb) the methyl cyanide solutions of the hydrated perchlorates were refluxed for 20 h through a Soxhlet extractor packed with molecular sieves.

To a solution of the given lanthanoid perchlorate (2 mmol) in anhydrous methyl cyanide (15 cm^3) was added dbc-6 (2.2 mmol) at room temperature. In a few minutes, crystals of the complexes separated from the solution, and were filtered off, washed with a $MeCN\text{–}CH_2Cl_2$ mixture, and dried *in vacuo* (0.2 mmHg) at room temperature. Recrystallization can be accomplished by dissolving the complexes in methyl cyanide and reprecipitating them with diethyl ether.

By careful exclusion of water from reagents, solvents, and the atmosphere, anhydrous compounds of formula $Ln[ClO_4]_3\cdot(dbc\text{-}6)$ are obtained with Ln = La, Ce, Pr, Nd, Sm, Eu, Dy, or Ho. These crystalline solids are stable indefinitely in closed vessels, but transform to the trihydrates $Ln[ClO_4]_3\cdot(dbc\text{-}6)\cdot 3H_2O$ when exposed to the air for a few hours. Under our experimental conditions the monohydrates $Ln[ClO_4]_3\cdot(dbc\text{-}6)\cdot H_2O$ were obtained with the heavier lanthanoids erbium and ytterbium. If the drying of the reaction mixture is less effective, compounds of the limiting formula $Ln[ClO_4]_3\cdot(dbc\text{-}6)\cdot 3H_2O\cdot 1.5MeCN$ are obtained with Ln = Er and Yb. In the air the yellow ytterbium complexes decompose to a white mixture of the ligand and hydrated ytterbium perchlorate.

Table 1 reports analytical data, colours, and molar conductances of the compounds.

Spectral Measurements.—The solution- and reflectance-electronic spectra were recorded with a Cary 17 spectrophotometer. The i.r. spectra were obtained for Nujol mulls on a Perkin-Elmer model 283 spectrophotometer.

Crystal Data.—$C_{20}H_{24}Cl_3O_{18}Sm$, M = 809.11, Orthorhombic, space group *Fdd*2 uniquely determined, a = 37.130(15), b = 12.987(5), c = 11.312(5) Å, U = 5 454.73 Å^3, D_c = 1.97 g cm^{-3}, Z = 8, $F(000)$ = 3 208, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 7 Å, $\mu(\text{Mo-}K_\alpha)$ = 25.7 cm^{-1}.

Data Collection.—For intensity measurements a small prismatic crystal (*ca.* 0.1 × 0.1 × 0.1 mm) was sealed in a glass capillary and mounted on a Philips automatic diffractometer. Mo-K_α radiation was monochromatized by means of a flat graphite crystal. The θ—2θ scan rate was 0.05° s^{-1}, the scan width 1.20°, and the background was counted 10 s on each side of the reflection. 1 140 Independent reflections were measured within $6 \leqslant 2\theta \leqslant 50°$ and 25 of these having $I < 2\sigma(I)$ were considered unobserved. The standard deviation of an intensity was calculated as follows: $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.02I)^2]^{\frac{1}{2}}$, where P is the total integrated count obtained in time T_p, B_1 and B_2 are the background counts, each obtained in time T_b, $I = P - 0.5(T_c/T_b)(B_1 + B_2)$, and $0.02I$ is an empirical correction for unrealistically small standard deviations in

---

† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

Analytical and physical data for $Ln[ClO_4]_3\cdot(dbc\text{-}6)$ complexes

Compound	Colour	Analysis (%) [a] C	H	Me	Λ [b] S cm² mol⁻¹
$La[ClO_4]_3\cdot$(dbc-6)	White	30.4 (30.15)	3.0 (3.05)	17.3 (17.45)	295 (156)
$Ce[ClO_4]_3\cdot$(dbc-6)	White	30.2 (30.05)	3.4 (3.05)	17.3 (17.55)	256 (169)
$Pr[ClO_4]_3\cdot$(dbc-6)	Pale green	30.2 (30.05)	3.2 (3.05)	17.4 (17.6)	242
$Nd[ClO_4]_3\cdot$(dbc-6)	Pale lilac	30.1 (29.9)	3.2 (3.0)	17.8 (17.95)	247
$Sm[ClO_4]_3\cdot$(dbc-6)	White	30.0 (29.7)	3.2 (3.0)	18.4 (18.6)	271
$Eu[ClO_4]_3\cdot$(dbc-6)	Orange	30.1 (29.65)	3.0 (3.0)	18.4 (18.75)	269
$Dy[ClO_4]_3\cdot$(dbc-6)	White	29.2 (29.25)	3.1 (2.95)	19.9 (19.8)	261 (189)
$Ho[ClO_4]_3\cdot$(dbc-6)	Pink	29.1 (29.15)	3.0 (2.95)	20.0 (20.0)	265 (188)
$Er[ClO_4]_3\cdot$(dbc-6)$\cdot H_2O$	Pink	28.7 (28.45)	3.1 (3.1)	19.8 (19.8)	259 (190)
$Yb[ClO_4]_3\cdot$(dbc-6)$\cdot H_2O$	Yellow	28.6 (28.25)	3.3 (3.1)	20.5 (20.35)	258

[a] Calculated values are given in parentheses. [b] For *ca.* 10^{-3} mol dm^{-3} solutions in methyl cyanide at 25 °C; values in parentheses are for *ca.* 10^{-2} mol dm^{-3} solutions. Under the same conditions literature values are 159 (129) for $[NBu_4][ClO_4]$ and 293 (163) S cm^2 mol^{-1} for $[NEt_4]_2[CoBr_4]$.

strong reflections. The intensities of two reference reflections were periodically checked and did not show any drift during data collection. Intensities were corrected for Lorentz-polarization effects; absorption effects were neglected.

Structure Determination and Refinement.—The space group being *Fdd*2, the eight samarium atoms must lie in the equivalent positions 8*a* along the two-fold symmetry axes.[7] The *z* co-ordinate was arbitrarily set at 0 and an electron-density map was calculated with phases from the samarium atom at 0,0,0. This map showed clearly the three perchlorate ions, together with their mirror images. An arbitrary choice was made between the two possibilities (which meant fixing the direction of the polar axis) and a new electron-density map was calculated with the contribution of the samarium atom and of the perchlorate ions. The resulting map showed unambiguously the positions of all the non-hydrogen atoms. The *R* factor was at this point 0.205.

Refinement was continued by means of full-matrix least squares. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = 4F^2/\sigma^2(F^2)$. Two cycles of refinement on the co-ordinates and isotropic temperature factors for all the atoms, followed by two cycles with anisotropic temperature factors for the non-carbon atoms, reduced the *R* factor to 0.041 for 1 115 observed reflections. Carbon atoms were refined only isotropically in order to retain a rather high ratio between the number of observations and parameters. A difference-Fourier synthesis calculated at this point did not show any anomalous peak except for those attributable to some of the hydrogen atoms. These atoms, however, were not introduced in the calculations.

TABLE 2

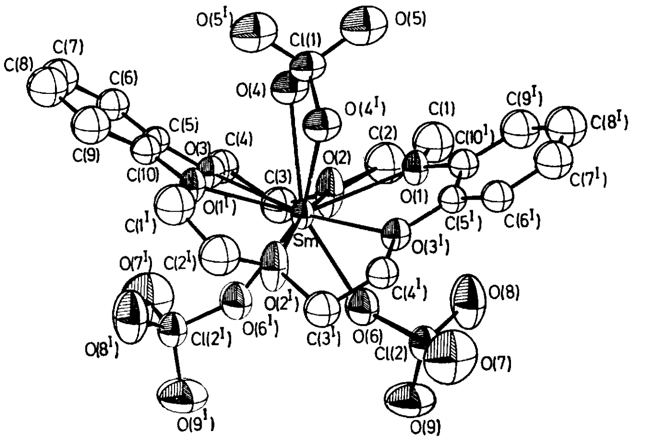
Positional parameters for the complex $[Sm(ClO_4)_3(dbc\text{-}6)]$ with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Sm	0.0	0.0	0.0
Cl(1)	0.0	0.0	0.288 1(5)
Cl(2)	−0.060 8(1)	0.097 1(3)	−0.239 1(5)
O(1)	−0.064 1(3)	0.023 4(8)	0.072 8(12)
O(2)	−0.040 4(3)	−0.143 6(7)	−0.029 8(12)
O(3)	0.026 4(3)	−0.183 8(6)	0.021 1(10)
O(4)	0.004 7(3)	0.088 5(8)	0.209 7(10)
O(5)	−0.031 1(5)	0.014 8(9)	0.360 4(11)
O(6)	−0.030 8(3)	0.046 6(10)	−0.174 9(12)
O(7)	−0.058 9(5)	0.204 2(10)	−0.222 9(17)
O(8)	−0.057 9(4)	0.069 7(13)	−0.358 9(13)
O(9)	−0.093 4(3)	0.058 4(12)	−0.186 3(16)
C(1)	−0.089 4(5)	−0.062 8(16)	0.078 7(21)
C(2)	−0.075 6(5)	−0.151 6(16)	0.008 9(24)
C(3)	−0.025 4(5)	−0.234 7(15)	−0.084 3(18)
C(4)	0.003 9(5)	−0.273 1(11)	−0.010 3(24)
C(5)	0.056 9(4)	−0.204 9(12)	0.086 1(14)
C(6)	0.067 8(4)	−0.301 0(13)	0.123 6(15)
C(7)	0.099 6(5)	−0.311 4(15)	0.185 7(19)
C(8)	0.120 9(6)	−0.226 6(15)	0.209 2(17)
C(9)	0.110 3(5)	−0.125 4(15)	0.169 5(19)
C(10)	0.077 7(4)	−0.116 3(13)	0.111 1(14)

Atomic scattering factors were from Cromer and Waber,[8] that of samarium being corrected for the real and imaginary part of anomalous dispersion effects. The '*X*-Ray '72' system of programs was used for all calculations.[9] Final atom parameters with their standard deviations estimated from the inverse least-squares matrix are reported in Table 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22617 (9 pp.).*

RESULTS AND DISCUSSION

Description of the Structure.—The structure of $[Sm(ClO_4)_3(dbc\text{-}6)]$ consists of neutral molecules in which the samarium atom is ten-co-ordinated by the six oxygen atoms of the polyether and four oxygen atoms of the perchlorate ions (Figure). Two perchlorate ions behave as unidentate ligands, the third one as a bidentate ligand. The co-ordination polyhedron is more easily described as an hexagonal bipyramid, where the six



An ORTEP drawing of the molecule $[Sm(ClO_4)_3(dbc\text{-}6)]$

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

oxygen atoms of the ligand form the equatorial plane and the two apices are defined by the baricentres of the bound perchlorate oxygen pairs. There is a two-fold crystallographic axis going through the samarium atom. Bond lengths and angles in the molecule are reported in Table 3. The equations of the least-squares planes through the equatorial oxygen atoms and the benzene rings are respectively: $11.312z + 0.242 = 0$ and $18.040x - 1.760y - 9.767z + 0.539 = 0$ with x, y, and z fractional orthorhombic co-ordinates. The ether oxygen atoms are not coplanar, O(1) and O(1$^{\mathrm{I}}$) being displaced 0.58 Å on one side of the plane towards the bidentate perchlorate group, O(2) and O(2$^{\mathrm{I}}$) by the same amount on the other side. The samarium atom is 0.24 Å out of the plane on the same side as the two unidentate perchlorate groups. The planes through the benzene rings form an angle of 119.6°, the bidentate perchlorate group being on the more hindered side. The plane through O(4)–Sm–O(4$^{\mathrm{I}}$) bisects the angle between the planes through the benzene rings and is approximately perpendicular to the plane formed by O(6)–Sm–O(6$^{\mathrm{I}}$), the angle being 70.9°.

TABLE 3

Bond lengths (Å) and angles (°) for the complex [Sm$(ClO_4)_3$-(dbc-6)] with estimated standard deviations in parentheses *

(*a*) Distances

Sm–O(1)	2.54(1)	C(1)–C(2)	1.49(3)
Sm–O(2)	2.42(1)	C(1)–O(1)	1.46(2)
Sm–O(3)	2.59(1)	C(2)–O(2)	1.38(2)
Sm–O(4)	2.64(1)	C(3)–C(4)	1.46(3)
Sm–O(6)	2.36(1)	C(3)–O(2)	1.45(2)
		C(4)–O(3)	1.47(2)
Cl(1)–O(4)	1.46(1)	C(5)–C(6)	1.38(2)
Cl(1)–O(5)	1.43(2)	C(5)–C(10)	1.41(2)
Cl(2)–O(6)	1.48(1)	C(5)–O(3)	1.38(2)
Cl(2)–O(7)	1.40(2)	C(6)–C(7)	1.38(3)
Cl(2)–O(8)	1.40(2)	C(7)–C(8)	1.38(3)
Cl(2)–O(9)	1.44(1)	C(8)–C(9)	1.44(3)
		C(9)–C(10)	1.38(3)
		C(10)–O(1$^{\mathrm{I}}$)	1.38(2)

(*b*) Angles

O(1)–Sm–O(1$^{\mathrm{I}}$)	142.1(4)	O(2)–Sm–O(6)	77.3(4)
O(1)–Sm–O(2)	63.6(3)	O(2)–Sm–O(6$^{\mathrm{I}}$)	89.2(4)
O(1)–Sm–O(3$^{\mathrm{I}}$)	60.3(3)	O(3)–Sm–O(3$^{\mathrm{I}}$)	169.4(4)
O(1)–Sm–O(4)	73.6(4)	O(3)–Sm–O(4)	107.0(3)
O(1)–Sm–O(4$^{\mathrm{I}}$)	72.4(4)	O(3)–Sm–O(4$^{\mathrm{I}}$)	62.7(3)
O(1)–Sm–O(6)	77.7(4)	O(3)–Sm–O(6)	119.7(4)
O(1)–Sm–O(6$^{\mathrm{I}}$)	139.1(4)	O(3)–Sm–O(6$^{\mathrm{I}}$)	70.0(4)
O(2)–Sm–O(2$^{\mathrm{I}}$)	164.0(4)	O(4)–Sm–O(4$^{\mathrm{I}}$)	52.2(3)
O(2)–Sm–O(3)	62.4(3)	O(4)–Sm–O(6)	132.2(4)
O(2)–Sm–O(4)	120.1(4)	O(4)–Sm–O(6$^{\mathrm{I}}$)	146.2(4)
O(2)–Sm–O(4$^{\mathrm{I}}$)	75.4(4)	O(6)–Sm–O(6$^{\mathrm{I}}$)	66.4(4)
O(4)–Cl(1)–O(4$^{\mathrm{I}}$)	105.3(0.7)	O(6)–Cl(2)–O(8)	107.6(0.9)
O(4)–Cl(1)–O(5)	109.8(0.7)	O(6)–Cl(2)–O(9)	105.8(0.8)
O(4)–Cl(1)–O(5$^{\mathrm{I}}$)	110.9(0.7)	O(7)–Cl(2)–O(8)	111.9(1.1)
O(5)–Cl(1)–O(5$^{\mathrm{I}}$)	110.1(0.9)	O(7)–Cl(2)–O(9)	109.4(1.0)
O(6)–Cl(2)–O(7)	109.7(0.9)	O(8)–Cl(2)–O(9)	112.1(1.0)
C(1)–O(1)–Sm	121.7(1.0)	C(6)–C(5)–C(10)	121.0(1.4)
C(1)–O(1)–C(10$^{\mathrm{I}}$)	114.8(1.2)	O(3)–C(5)–C(6)	125.8(1.4)
C(10$^{\mathrm{I}}$)–O(1)–Sm	123.4(0.9)	O(3)–C(5)–C(10)	113.2(1.3)
C(2)–C(1)–O(1)	110.3(1.6)	C(5)–C(6)–C(7)	119.8(1.6)
O(2)–C(2)–C(1)	115.8(1.7)	C(6)–C(7)–C(8)	120.7(1.8)
C(2)–O(2)–Sm	127.0(1.1)	C(7)–C(8)–C(9)	120.6(1.9)
C(3)–O(2)–Sm	116.8(0.9)	C(8)–C(9)–C(10)	117.7(1.7)
C(3)–O(2)–C(2)	115.9(1.3)	C(9)–C(10)–O(1$^{\mathrm{I}}$)	123.1(1.5)
C(4)–C(3)–O(2)	108.8(1.6)	C(5)–C(10)–C(9)	120.2(1.5)
O(3)–C(4)–C(3)	107.0(1.3)	O(1$^{\mathrm{I}}$)–C(10)–C(5)	116.7(1.3)
C(4)–O(3)–Sm	119.2(0.9)	Cl(1)–O(4)–Sm	101.2(0.5)
C(5)–O(3)–Sm	122.9(0.8)	Cl(2)–O(6)–Sm	152.5(0.8)
C(5)–O(3)–C(4)	116.0(1.2)		

* Roman numeral superscripts refer to atoms in the position $\bar{x}, \bar{y}, z$.

TABLE 4

Contact distances <3.5 Å *

(*a*) Intramolecular distances

O(1) · · · O(5)	3.48	O(6) · · · C(3$^{\mathrm{I}}$)	3.37
O(1) · · · O(9)	3.16	O(7) · · · C(4$^{\mathrm{I}}$)	3.28
O(3$^{\mathrm{I}}$) · · · O(7)	3.02	O(7) · · · C(5$^{\mathrm{I}}$)	3.49
O(4) · · · C(10$^{\mathrm{I}}$)	3.28	O(9) · · · C(1)	3.39
O(4$^{\mathrm{I}}$) · · · C(4)	3.47		

(*b*) Intermolecular distances

O(4) · · · C(3$^{\mathrm{III}}$)	3.46	O(5) · · · C(4$^{\mathrm{III}}$)	3.38
O(4) · · · O(7$^{\mathrm{IV}}$)	3.45	O(9) · · · C(1$^{\mathrm{IV}}$)	3.01
O(5) · · · O(8$^{\mathrm{II}}$)	3.40	O(9) · · · C(2$^{\mathrm{VI}}$)	3.11
O(5) · · · C(3$^{\mathrm{III}}$)	3.32	C(9) · · · C(7$^{\mathrm{V}}$)	3.46

* Roman numeral superscripts refer to equivalent positions relative to the reference molecule at x,y,z: I $\bar{x}, \bar{y}, z$; II $\bar{x}, y, z + 1$; III $x, \frac{1}{2} + y, \frac{1}{2} + z$; IV $-x, \frac{1}{2} - y, -\frac{1}{2} + z$; V $\frac{1}{4} - x, \frac{1}{4} + y, \frac{1}{4} + z$; VI $-\frac{1}{4} - x, \frac{1}{4} + y, -\frac{1}{4} + z$.

As far as bond distances are concerned, the present samarium–ether oxygen distances range from 2.42 to 2.59 Å with an average of 2.52(1) Å. This value compares well with the mean Eu–O(ether) distance 2.49 Å found in the ten-co-ordinate [Eu(ClO_4)L]$^{2+}$ cation,[4] where L is the macrobicycle 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane. It also compares well with the La–O(water) distances of 2.59 Å in the ten-co-ordinate lanthanum hydrogenethylenediamine-tetra-acetate of composition [La(Hedta)$(OH_2)_4$]·$7H_2O$.[10] Indeed, the ionic radius of samarium(III) is 0.02 Å longer and 0.09 Å shorter than europium and lanthanum radii respectively.[11] It is interesting to point out that the samarium–perchlorate oxygen distances are much shorter for the unidentate (2.36 Å) than for the bidentate (2.64 Å) groups. Inspection of Table 4 shows the presence of several contact distances significantly shorter than 3.5 Å, involving especially the perchlorate groups.

Spectral and Electric Conductivity Data.—The i.r. spectrum of the complex [Sm$(ClO_4)_3$(dbc-6)] deserves some comments since it can be used as a diagnostic tool for the structures of the other compounds. First, it exhibits bands at 610 (sh), 620 (sh), 635m, and 645m cm^{-1} which must be attributed to the bending vibrations (ν_4 in the T_d limit symmetry) of co-ordinated perchlorate groups. In fact, no polyether band is present in the range 610—700 cm^{-1}. Other bands, attributable to split ν_3 vibrations of $[ClO_4]^-$, are present in the range 1 000—1 200 cm^{-1}, but they strongly interfere with the macrocycle absorptions. Secondly, the polyether bands in the present compound show definite changes with respect to those of the free polyether, especially in the 1 600 and 700—1 000 cm^{-1} regions. Thus, the free-ligand band at 1 600 cm^{-1}, which is attributable to the stretching vibrations of the benzene rings, is split into two bands at 1 595 and 1 615 cm^{-1}. This fact may suggest coupling between the two benzene rings *via* the lanthanoid ion, since these rings are equivalent due to the presence of the C_2 axis.

The i.r. spectra of all the present unsolvated complexes are indistinguishable from that of the [Sm$(ClO_4)_3$-

(dbc-6)] complex. An essentially similar molecular structure, therefore, can be assigned to such a class of compounds, *i.e.* a structure with co-ordinated dbc-6 and perchlorate groups.

With the trihydrate complexes, on the other hand, the ν_4 vibrations are degenerate, only one sharp strong band being found at 620 cm^{-1} over the region 610—700 cm^{-1}. Thus only unco-ordinated perchlorate ions are present in these compounds. The polyether absorption bands are essentially the same as with the anhydrous compounds.

Finally, with the erbium and ytterbium monohydrate complexes the polyether bands are still the same as with the anhydrous compounds but perchlorate bands occur at 610m, 620s, and 650s cm^{-1}. Thus, differences in the bonding modes of the perchlorate groups should occur in these compounds. The absorption band at 650 cm^{-1} could tentatively be attributed to the presence of bidentate perchlorates. In fact, the $[Eu(ClO_4)L]^{2+}$ cation, which has a bidentate perchlorate, exhibits a band at 645 cm^{-1}.[4]

As far as the electronic spectra of the present complexes are concerned, the *f–f* bands in methyl cyanide solution show only small changes with respect to those of the anhydrous metal perchlorate in the same solvent. In addition, the compounds with the more reducible lanthanoid(III) ions, *i.e.* samarium, europium, and ytterbium exhibit broad bands with maxima at 32 100, 22 500, and 27 400 cm^{-1}, respectively in the solid state. These transitions can be safely attributed to electron transfer transitions from the loosest bound molecular orbitals of the polyether (probably those localized chiefly on the $-O-C_6H_4-O-$ moieties) to 4*f* orbitals of the lanthanoid ions. Using the values of the band maxima and values for the uncorrected optical electronegativities of 1.6 (Sm), 1.9 (Eu), and 1.8 (Yb),[12] a value of 2.7 for the optical electronegativity of dbc-6 is obtained. These electron-transfer bands persist in the methyl cyanide solutions, indicating that dbc-6 is still co-ordinated to the metal in this solvent. The wavenumbers and molar absorbances (in parentheses) are 32 800 [110 (sh)], 23 800 (40), and 22 900 cm^{-1} (15 dm^3 mol^{-1} cm^{-1}), respectively, for 3×10^{-3} mol dm^{-3} solutions. Nonetheless, the molar absorbances of these transitions are moderately sensitive to complex concentration and to a ligand excess, indicating that partial dissociation and/or solvolysis should take place.

The electric conductivity values for 10^{-3} mol dm^{-3} solutions of the present complexes in anhydrous methyl cyanide are those expected for 1 : 2 electrolytes, whereas they approach those for 1 : 1 electrolytes in 10^{-2} mol dm^{-3} solutions (Table 1). Ionization of the bound perchlorate anions is presumably favoured by solvent co-ordination.

We thank Mr. Giancarlo Vignozzi for microanalyses.

[9/147 *Received*, 30*th January*, 1979]

REFERENCES

[1] A. Cassol, A. Seminaro, and G. De Paoli, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1163.

[2] R. B. King and P. R. Heckley, *J. Amer. Chem. Soc.*, 1974, **96**, 3118; J. F. Desreux, A. Renard, and G. Duyckaerts, *J. Inorg. Nuclear Chem.*, 1977, **39**, 1587.

[3] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 2495; E. Shchori, N. Nae, and J. Jagur-Grodzinski, *J.C.S. Dalton*, 1975, 2381; M. E. Harman, F. A. Hart, M. B. Hursthouse, G. P. Moss, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1976, 396; R. M. Izatt, J. D. Lamb, J. J. Christensen, and B. L. Haymore, *J. Amer. Chem. Soc.*, 1977, **99**, 8344; O. A. Gansow, A. R. Kansar, K. M. Triplett, M. J. Weaver, and E. L. Yee, *ibid.*, p. 7087; G. A. Catton, M. E. Harman, F. A. Hart, G. E. Hawkes, and G. P. Moss, *J.C.S. Dalton*, 1978, 181.

[4] M. Ciampolini, P. Dapporto, and N. Nardi, *J.C.S. Chem. Comm.*, 1978, 788; *J.C.S. Dalton*, 1979, 974.

[5] M. Ciampolini and N. Nardi, *Inorg. Chim. Acta Letters*, 1979, **32**, L9.

[6] J. H. Forsberg and T. Moeller, *Inorg. Chem.*, 1969, **8**, 883.

[7] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[9] '*X*-Ray '72,' Technical Report TR 192, 1972, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland.

[10] M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1965, **87**, 1611.

[11] See, for example, S. P. Sinha, *Structure and Bonding*, 1976, **25**, 69.

[12] See, for example, C. K. Jørgensen, in 'Oxidation Numbers and Oxidation States,' Springer-Verlag, Berlin, 1969, p. 141.