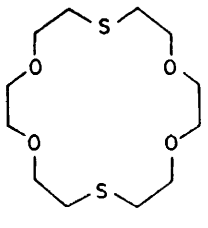
Synthesis and Properties of Some Lanthanoid(III) Perchlorates with Macrocyclic Polythioethers of the [18]-Crown-6 Type. Crystal Structure of Aquadiperchlorato(1,4,10,13-tetraoxa-7,16-dithiacyclo-octadecane)-lanthanum(III) Perchlorate

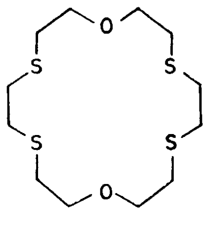
By **Mario Ciampolini,* Carlo Mealli, and Nicoletta Nardi**, Istituto di Chimica Generale ed Inorganica dell' Università, Laboratorio C.N.R., Via J. Nardi, 39, Florence, Italy

Some complexes of lanthanoid(III) perchlorates have been prepared with three polythia macrocycles of the [18]-crown-6 type. By using the ligand 1,4,10,13-tetraoxa-7,16-dithiacyclo-octadecane, L^1, in methyl cyanide, three series of complexes have been obtained with formulae (*i*) $Ln[ClO_4]_3{\cdot}L^1{\cdot}H_2O$ (Ln = La, Ce, or Pr), (*ii*) $Ln[ClO_4]_3{\cdot}L^1{\cdot}H_2O{\cdot}x$MeCN (Ln = Ce, Pr, Nd, Sm, Eu, Ho, or Yb; x = 1.5 or 2), and (*iii*) $Nd[ClO_4]_3{\cdot}L^1$. The crystal and molecular structure of the title complex has been determined by X-ray diffractometric data. The structure has been refined by least-squares techniques to R = 0.036 for 4 635 observed reflections. The lanthanum(III) ion is ten-co-ordinated to the six donor atoms of L^1, to two oxygen atoms of a $[ClO_4]^-$ ion, to an oxygen atom of a second $[ClO_4]^-$, and to an oxygen atom of a water molecule. The co-ordination polyhedron can be described as a decatetrahedron. The macrocycles 1,10-dioxa-4,7,13,16-tetrathiacyclo-octadecane, L^2, and 1,4,7,10,13,16-hexathiacyclo-octadecane, L^3, do not co-ordinate to lanthanoid(III) perchlorates in methyl cyanide but in dichloromethane the complexes $Eu[ClO_4]_3{\cdot}L^2{\cdot}H_2O$ and $Ln[ClO_4]_3{\cdot}L^3{\cdot}H_2O$ (Ln = Sm, Eu, or Yb) can be isolated. The i.r. and electronic spectra of all the complexes are discussed. The electron-transfer transitions are consistent with an optical electronegativity value of 2.8 for ligand L^1 and 2.7 for L^2 and L^3.

LANTHANOID(III) cations rarely form compounds with soft donors on account of their marked A-type behaviour.[1] In particular, the compounds known to contain sulphur–lanthanoid(III) linkages are limited to sulphides,[2] monothiolates,[3] and 1,1-dithiolates,[4,5] all having negatively charged sulphur atoms, and to a few thioamidic[6] complexes. So far the structures of no thioether lanthanoid complexes have been determined by X-ray crystallography.

Following the idea that such complexes can be stabilized by the macrocyclic effect, we have examined the macrocycles L^1—L^3 of the [18]-crown-6 type; ligand (L^4) is mainly used for comparative purposes. This paper reports the synthesis and characterization of complexes of some lanthanoid(III) perchlorates with these ligands, and the crystal structure of $[La(ClO_4)_2(OH_2)L^1][ClO_4]$, determined by X-ray analysis. Some lanthanoid complexes of L^4 have already been described.[7]


L^1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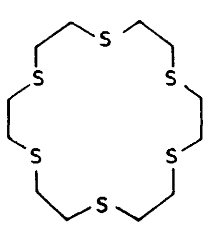
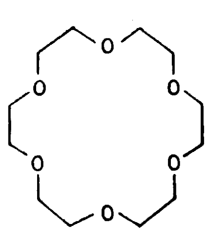

L^3


L^4

EXPERIMENTAL

Ligands L^1,[8] L^2,[8] and L^3 (ref. 9) were prepared according to the literature methods; L^4 was obtained from Fluka, Switzerland.

Preparation of the Complexes.—With ligand L^1. No complex of this ligand with lanthanoid(III) perchlorates was formed in the presence of ethanol or other solvents of comparable co-ordinating properties. A solution of the anhydrous lanthanoid perchlorate (1 mmol) in MeCN (10 cm^3) was added to a solution of L^1 (1.10 mmol) in CH_2Cl_2 (10 cm^3). After a few minutes, a crystalline compound separated, which was filtered off, washed with a mixture of methyl cyanide and dichloromethane, and dried *in vacuo* (10 Pa) at room temperature for 4 h. Table 1 gives analytical data, colours, and molar conductances of the complexes. The isolated MeCN adducts of Ce, Pr, and Nd lose all the MeCN (the Nd adduct also loses H_2O) at room temperature and normal pressures within a few weeks. These crystalline solids are transformed into a mixture of the ligand and hydrated lanthanoid perchlorate when exposed to air for a few minutes.

With ligands L^2 *and* L^3. No complex of these ligands with anhydrous lanthanoid(III) perchlorates was obtained by using MeCN or solvents of higher co-ordinating ability. Solid anhydrous europium perchlorate was digested with a strong solution of a 20% excess of the ligand in CH_2Cl_2 at room temperature for 3 d. Crystals were formed which appeared homogeneous under a microscope. These were filtered off, washed repeatedly with CH_2Cl_2, and dried *in vacuo* (10 Pa) at room temperature. They are indefinitely stable in closed vessels but, in air, are transformed to a white mixture of the ligand and hydrated perchlorate in a few minutes.

With ligand L^4. A solution of anhydrous europium(III) perchlorate (2 mmol) in anhydrous MeCN (10 cm^3) was added to a solution of L^4 (2.2 mmol) in CH_2Cl_2 (20 cm^3). After a few minutes, crystals of the complex separated, which were filtered off, washed with a mixture of methyl cyanide and dichloromethane, and dried *in vacuo* at room temperature.

Spectral Measurements.—Electronic spectra both in solution and by reflectance were recorded with a Cary 17 spectrophotometer. The i.r. spectra were obtained as Nujol mulls on a Perkin-Elmer model 283 spectrophotometer. All the manipulations were performed under pure nitrogen in a dry-box.

TABLE 1

Analytical and physical data for $Ln[ClO_4]_3 \cdot L$ complexes [a]

Complex	Colour	Analysis (%) C	H	N[S]	M	Λ[b] S cm^2 mol^{-1}
$La[ClO_4]_3 \cdot L^1 \cdot H_2O$	White	19.1 (19.2)	3.6 (3.5)		18.6 (18.5)	285
$Ce[ClO_4]_3 \cdot L^1 \cdot H_2O$	White	19.2 (19.1)	3.3 (3.5)		18.4 (18.6)	302
$Ce[ClO_4]_3 \cdot L^1 \cdot 2MeCN \cdot H_2O$	White	22.8 (23.0)	3.8 (3.9)	3.3 (3.3)	16.6 (16.8)	304
$Pr[ClO_4]_3 \cdot L^1 \cdot H_2O$	Pale green	19.2 (19.1)	3.4 (3.5)		18.8 (18.7)	275-
$Pr[ClO_4]_3 \cdot L^1 \cdot 1.5MeCN \cdot H_2O$	Pale green	22.0 (22.0)	3.7 (3.8)	2.8 (2.6)	17.4 (17.3)	295
$Nd[ClO_4]_3 \cdot L^1$	Pale lilac	19.4 (19.5)	3.5 (3.3)		19.2 (19.5)	265
$Nd[ClO_4]_3 \cdot L^1 \cdot 1.5MeCN \cdot H_2O$	Pale lilac	21.8 (22.0)	3.8 (3.7)	2.6 (2.6)	17.4 (17.6)	285
$Sm[ClO_4]_3 \cdot L^1 \cdot 1.5MeCN \cdot H_2O$	Creamy white	21.8 (21.8)	3.9 (3.7)	2.9 (2.6)	18.5 (18.2)	289
$Eu[ClO_4]_3 \cdot L^1 \cdot 2MeCN \cdot H_2O$	Yellow	22.4 (22.7)	3.7 (3.8)	3.3 (3.3)	17.8 (17.9)	295
$Ho[ClO_4]_3 \cdot L^1 \cdot 1.5MeCN \cdot H_2O$	Pink	21.5 (21.5)	3.8 (3.7)	2.6 (2.5)	19.5 (19.7)	301
$Yb[ClO_4]_3 \cdot L^1 \cdot 1.5MeCN \cdot H_2O$	White	21.5 (21.3)	3.9 (3.6)	2.8 (2.5	20.2 (20.4)	304
$Eu[ClO_4]_3 \cdot L^2 \cdot H_2O$	Yellow-orange	18.1 (18.1)	3.8 (3.3)		19.0 (19.0)	
$Sm[ClO_4]_3 \cdot L^3 \cdot H_2O$	Creamy white	17.6 (17.4)	3.3 (3.2)		18.1 (18.2)	
$Eu[ClO_4]_3 \cdot L^3 \cdot H_2O$	Orange	17.3 (17.4)	3.0 (3.0)	[23.2 (23.1)]	18.6 (18.3)	
$Yb[ClO_4]_3 \cdot L^3 \cdot H_2O$	White	16.7 (16.9)	3.2 (3.1)	[22.9 (22.6)]	20.1 (20.3)	
$Eu[ClO_4]_3 \cdot L^4 \cdot H_2O$	White	19.5 (19.7)	3.9 (3.6)		20.8 (20.7)	

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

X-*Ray Crystallography.*—*Crystal data.* $C_{12}H_{26}Cl_3LaO_{17}S_2$, $M = 751.72$, Monoclinic, space group $P2_1/a$, $a = 14.117(4)$, $b = 21.302(5)$, $c = 8.844(3)$ Å, $\beta = 104.62(3)°$, $U = 2\,573.1$ Å^3, $Z = 4$, $D_c = 1.94$ g cm^{-3}, λ(Mo-K_α) = 0.710 7 Å, μ(Mo-K_α) = 18.2 cm^{-1}.

Data collection. A prismatic crystal with dimensions 0.2 × 0.2 × 0.4 mm was used throughout the determination of lattice constants and data collection. All measurements were made with Mo-K_α radiation monochromatized with a flat graphite crystal, on a Philips PW 1 100 automatic diffractometer. The centred positions of 18 reflections in the 2θ range 16—24° and the setting angles thus obtained were used in the least-squares refinement of the cell parameters. The θ—2θ scan procedure was employed with a scan range 0.88° in θ (corrected for dispersion) at a scan rate of 0.08° s^{-1}. The background measurement time at each side of the scan was determined as (scan time)/2. 6 633 Unique reflections were measured up to $\theta = 28°$, 4 635 of which were considered observed having $I \geqslant 3\sigma(I)$. The σ values were calculated as described previously [10] with a value of 0.03 for the instability factor. The intensities of the standard reflections were monitored every 100 min and were subsequently used to establish all the reflections on a common scale.

Structure determination and refinement. Computation was carried out either on a CII 10 070 computer or on a CDC 7 600 using the SHELX-76 system of programs.[11] Scattering factors were taken from ref. 12. The usual corrections (including one for absorption) were applied to the data. The structure was solved by direct methods. Full-matrix least-squares refinement was initiated after a number of F_o and ΔF maps had enabled us to determine the positions of all the non-hydrogen atoms. After two cycles using an isotropic thermal model for all the atoms, the R factor ($= \Sigma|\Delta F|/\Sigma|F_o|$) dropped to 0.12. In the following cycles the hydrogen atoms (except those of the water molecule) were geometrically positioned (C–H 1.08 Å) and constrained to ride on the bonded carbon atom. All the other atoms (except for carbon) were refined anisotropically. Three cycles lowered R to 0.036 and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/|\Sigma w|F_o^2]^{\frac{1}{2}}\}$ to 0.038. The statistical validity of the least-squares refinement was checked by a weighting analysis to ensure that the average value of $w\Delta F^2$ was the same for various ranges of $|F_o|$ and of $(\sin\theta)/\lambda$. No obvious trends were found. Final parameters are given in Table 2.

TABLE 2

Fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
La	7 815.7(2)	1 204.3(2)	4 466.5(4)
Cl(1)	5 989(1)	1 671(1)	6 001(2)
Cl(2)	10 080(1)	1 476(1)	2 895(2)
Cl(3)	2 968(2)	1 065(1)	9 346(3)
S(1)	7 259(1)	1 356(1)	928(2)
S(2)	9 471(1)	724(1)	7 101(2)
O(1)	6 414(3)	467(2)	2 921(5)
O(2)	7 390(3)	217(2)	5 942(5)
O(3)	8 725(3)	2 055(2)	6 388(5)
O(4)	7 616(3)	2 358(2)	3 455(5)
O(5)	6 016(4)	1 635(3)	4 375(6)
O(6)	6 976(4)	1 486(3)	6 855(6)
O(7)	5 279(5)	1 253(3)	6 278(7)
O(8)	5 782(4)	2 283(3)	6 402(7)
O(9)	9 370(4)	1 511(2)	3 811(2)
O(10)	9 907(4)	907(3)	1 982(6)
O(11)	9 916(6)	2 007(4)	1 862(9)
O(12)	11 026(5)	1 500(3)	3 857(9)
O(13)	3 376(6)	1 054(4)	11 036(10)
O(14)	2 282(7)	577(5)	9 021(11)
O(15)	2 505(6)	1 643(4)	8 937(9)
O(16)	3 743(6)	971(4)	8 640(10)
O(17)	8 496(4)	254(2)	3 364(6)
C(1)	6 237(6)	825(4)	302(10)
C(2)	5 711(6)	691(4)	1 529(9)
C(3)	5 953(5)	81(4)	3 867(9)
C(4)	6 745(5)	−245(4)	5 050(9)
C(5)	8 012(6)	−64(4)	7 334(10)
C(6)	8 687(6)	411(4)	8 282(9)
C(7)	9 947(6)	1 436(4)	8 120(9)
C(8)	9 201(6)	1 943(4)	8 025(9)
C(9)	8 312(5)	2 680(3)	6 087(9)
C(10)	8 230(6)	2 826(4)	4 415(9)
C(11)	7 374(5)	2 564(4)	1 843(8)
C(12)	6 662(5)	2 108(3)	871(9)

Calculated and observed structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22667 (30 pp.).*

RESULTS AND DISCUSSION

Complexes of Ligand (L^1).—*Description of the structure.* The structure of the compound $[La(ClO_4)_2(OH_2)L^1][ClO_4]$ consists of perchlorate anions and cationic complex molecules (see stereoscopic view in Figure 1), with the lanthanum atom ten-co-ordinated by two sulphur and by eight oxygen atoms. The macrocyclic ligand L^1 supplies six of the ten donor atoms, namely two sulphur and four oxygen atoms. The remaining ligating atoms belong to one water molecule and to two perchlorate groups. The perchlorates differ from each other, one behaving as a unidentate ligand, the other as a bidentate ligand. Bond distances and angles within the macrocycle ligand are shown in Figure 2. Selected bond distances and angles in the complex are given in Table 3.

TABLE 3

Molecular geometry

(*a*) Selected bond lengths (Å). Standard deviations calculated from the inverted least-squares matrix

La–S(1)	3.045(1)	La–O(4)	2.605(4)
La–S(2)	3.030(1)	La–O(5)	2.683(4)
La–O(1)	2.623(3)	La–O(6)	2.738(4)
La–O(2)	2.623(4)	La–O(9)	2.494(4)
La–O(3)	2.591(4)	La–O(17)	2.539(4)

(*b*) Selected bond angles (°) with standard deviations

S(1)–La–O(1)	64.1(1)	O(2)–La–O(17)	73.0(1)
S(1)–La–O(2)	124.4(1)	S(2)–La–O(3)	64.8(1)
S(1)–La–S(2)	140.7(0)	S(2)–La–O(4)	125.3(1)
S(1)–La–O(3)	123.8(1)	S(2)–La–O(5)	132.8(1)
S(1)–La–O(4)	64.5(1)	S(2)–La–O(6)	83.2(1)
S(1)–La–O(5)	86.4(1)	S(2)–La–O(9)	73.4(1)
S(1)–La–O(6)	136.1(1)	S(2)–La–O(17)	74.5(1)
S(1)–La–O(9)	75.3(1)	O(3)–La–O(4)	63.8(1)
S(1)–La–O(17)	73.4(1)	O(3)–La–O(5)	95.1(1)
O(1)–La–O(2)	112.5(1)	O(3)–La–O(6)	65.1(1)
O(1)–La–S(2)	122.2(1)	O(3)–La–O(9)	69.5(1)
O(1)–La–O(3)	160.6(1)	O(3)–La–O(17)	129.6(1)
O(1)–La–O(4)	112.5(1)	O(4)–La–O(5)	69.4(1)
O(1)–La–O(5)	66.7(1)	O(4)–La–O(6)	91.6(1)
O(1)–La–O(6)	96.7(1)	O(4)–La–O(9)	72.4(1)
O(1)–La–O(9)	128.9(1)	O(4)–La–O(17)	129.7(1)
O(1)–La–O(17)	68.4(1)	O(5)–La–O(6)	50.0(1)
O(2)–La–S(2)	64.9(1)	O(5)–La–O(9)	141.8(1)
O(2)–La–O(3)	118.8(1)	O(5)–La–O(17)	135.1(1)
O(2)–La–O(4)	155.2(1)	O(6)–La–O(9)	134.4(1)
O(2)–La–O(5)	87.4(1)	O(6)–La–O(17)	138.7(1)
O(2)–La–O(6)	66.0(1)	O(9)–La–O(17)	71.3(1)
O(2)–La–O(9)	130.6(1)		

(*c*) Average bond distances (Å) in perchlorate groups. Standard deviations given as sample standard deviations

Cl(1)–O	1.430(30)	Cl(3)–O	1.416(29)
Cl(2)–O	1.428(25)		

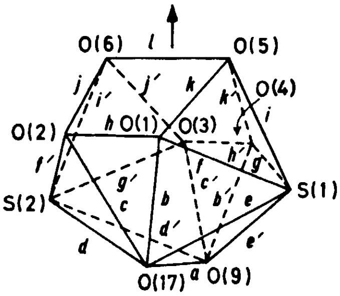
(*d*) Average bond angles (°) in the macrocycle and in perchlorate groups with standard deviations calculated as sample standard deviations

C–S–C	102.7(3)	La–S–C	99.7(3.9)
C–O–C	111.1(1.9)	O–Cl(1)–O	109.5(2.9)
O–C–C	108.8(1.1)	O–Cl(2)–O	109.5(1.7)
S–C–C	111.3(3.2)	O–Cl(3)–O	109.4(2.6)
La–O–C	120.4(5.0)		

The two La–S bond distances are similar, with an average value of 3.037(7) Å which falls inside the range (2.93—3.08 Å) [4a,5b,13] determined for complexes containing negatively charged sulphur atoms. The eight La–O distances are scattered over the range 2.494(4)—2.738(4) Å, the individual differences being expected, due to the different nature of the groups to which the oxygen atoms belong and to the different bonding modes of identical groups. The M–O(perchlorate) distances differ by up to 0.24 Å as already found in another lanthanoid complex [14] containing both uni- and bi-dentate perchlorate groups. The average La–O(ether) distance is 2.61(2) Å, close to the La–O(water) distance [2.539(4) Å]. Interestingly, the difference between average La–S and La–O(ether) distances (0.43 Å) is about the same as the difference (0.45 Å) between the ionic radii of sulphide and oxide anions.[15] The four oxygen atoms of the macrocyclic ligand are almost coplanar (largest deviations from the least-squares plane 0.06 Å). Displaced in the same direction out of the plane are the lanthanum (0.50 Å) and the two sulphur atoms (1.47 and 1.57 Å).

TABLE 4

Dihedral angles (°) of the decatetrahedron at each edge and the edge lengths (Å)



Edge	Dihedral angle (δ)	Length
a	39.4	2.94
b	39.2	2.90
b′	35.4	3.02
c	34.1	3.07
c′	37.9	2.90
d	52.3	3.40
d′	50.5	3.33
e	51.2	3.36
e′	50.1	3.41
f	63.0	3.03
f′	62.1	3.05
g	65.9	3.03
g′	60.2	3.03
h	63.2	2.73
h′	63.6	2.75
i	32.8	3.93
i′	35.5	3.86
j	59.4	2.93
j′	60.4	2.87
k	59.0	2.92
k′	58.3	3.01
l	84.1	2.28

Thus, the overall conformation of the co-ordinated sexidentate ligand resembles that of a boat.

Concerning the geometry of the whole co-ordination polyhedron, two idealised polyhedra (polytopes) are the most common references for ten-co-ordination, *i.e.* the bicapped square antiprism (b.s.a.p.) and the decatetrahedron (d.t.h.).[16] In the present structure no bond angle at the lanthanum atom is close to 180°, thus excluding the former geometry. Indeed, d.t.h. seems to be the closest idealised geometry, for the required C_{2v} symmetry is approximated. A two-fold axis joins the midpoint between the two co-ordinating oxygen atoms [O(5), O(6)] of the bidentate perchlorate group and the midpoint between the oxygen atom [O(17)] of the water molecule and that [O(9)] of the unidentate perchlorate group. The two required mirror planes are

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

approximately defined as that through the atoms S(1), S(2), O(5), O(6) and that through the atoms O(9), O(17), and the midpoint between the atoms O(5) and O(6). Table 4 gives the dihedral angles (δ) formed by the pairs of faces that meet at each edge of the decatetrahedron, as well as the lengths of the edges. The agreement with the δ values calculated by Robertson[16] for unidentate ligands and based on repulsion potentials is poor; however, one can conclude that the C_{2v} geometry holds well and that the identification of the polyhedron as d.t.h. is appropriate.

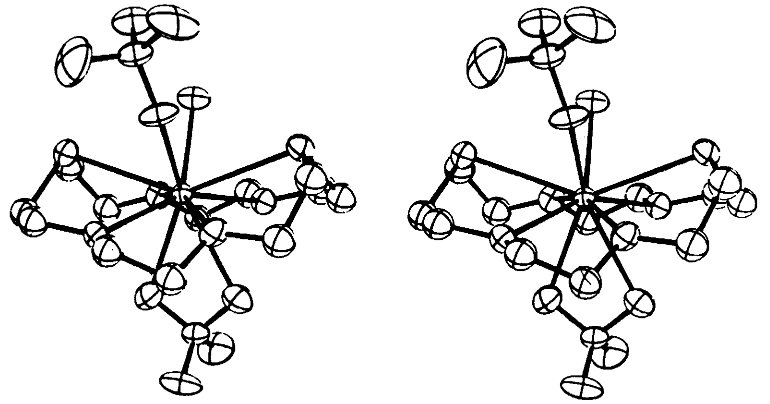

FIGURE 1 Stereoscopic view of the complex cation $[La(ClO_4)_2(OH_2)L^1]^+$

Spectral and conductivity data. As is well known, the lowering of the symmetry of a bonded perchlorate group with respect to the T_d free anion results in the splitting of both ν_4 (T_d) (*ca.* 620 cm^{-1}) and ν_3 (T_d) (1 080—1 100 cm^{-1}) into two or three components for C_{3v} (unidentate) or C_{2v} (bidentate) perchlorate, respectively.[17] The i.r. spectrum of $[La(ClO_4)_2(OH_2)L^1][ClO_4]$ displays a strong composite band with peaks at 610, 618, 620, and 640 cm^{-1} (Figure 3) which are assigned to bending vibrations of the ClO_4 groups. The complex nature of this band reflects the envelopes of absorptions due to free, uniden-

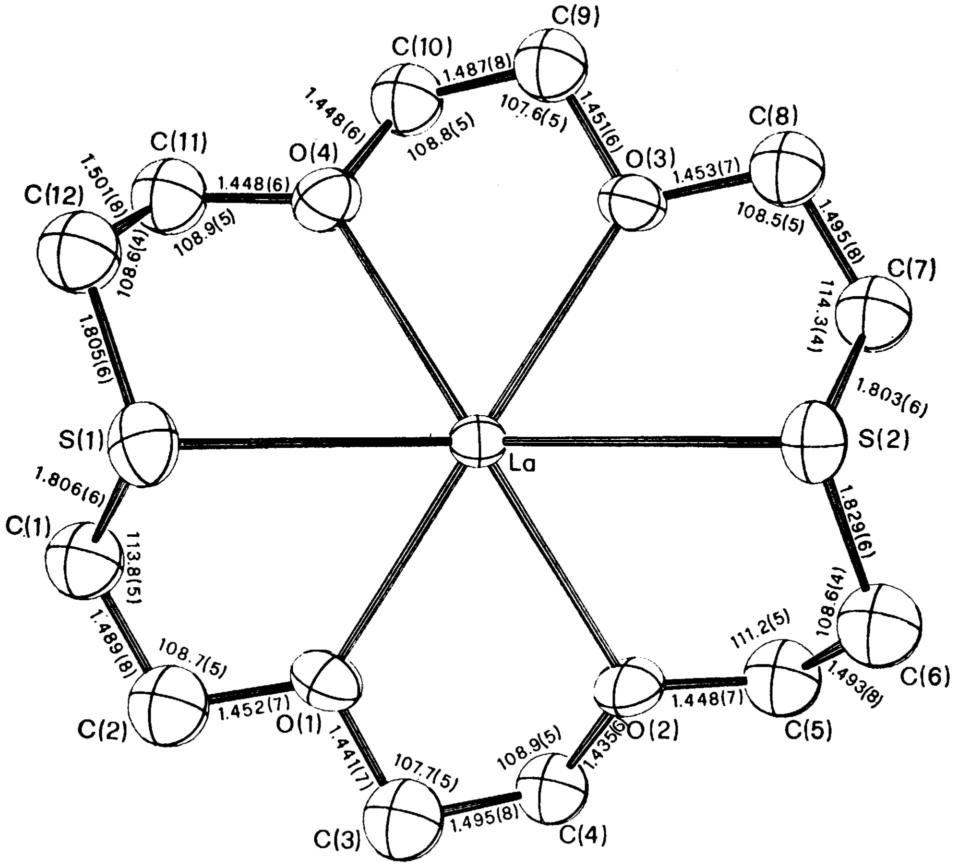

FIGURE 2 Summary of bond distances (Å) and angles (°) within the macrocycle

tate, and bidentate perchlorates. The split components of the ν_3 vibrations fall in the region 1 040—1 180 cm^{-1}, partially superimposed on the C–O–C vibrations of the polyether. Bands attributable to the co-ordinated water molecule are at 1 640 and 3 250, 3 380, and 3 480 cm^{-1}. The bands of the macrocyclic ligand, especially those in the region 700—950 cm^{-1}, undergo marked changes upon co-ordination (Figure 3).

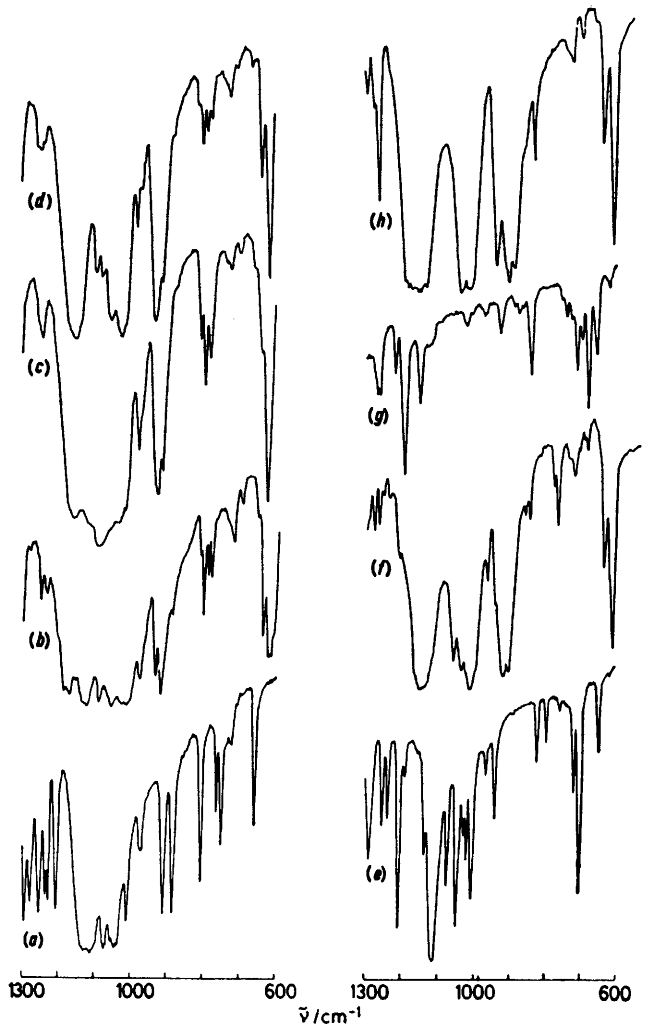

FIGURE 3 Infrared spectra in the 600—1 300 cm^{-1} region of the compounds: (a) L^1; (b) [La(ClO$_4$)$_2$(OH$_2$)L^1][ClO$_4$]; (c) Nd[ClO$_4$]$_3$·L^1·1.5MeCN·H$_2$O; (d) Nd[ClO$_4$]$_3$·L^1; (e) L^2; (f) Eu[ClO$_4$]$_3$·L^2·H$_2$O; (g) L^3; (h) Eu[ClO$_4$]$_3$·L^3·H$_2$O

The methyl cyanide adducts exhibit a simplified band envelope for the perchlorate ν_4 vibrations, showing only a sharp strong peak at 620 cm^{-1} and a peak of low relative intensity (or a shoulder) at 640 cm^{-1} (Figure 3). The peak at 1 100 cm^{-1}, due to the ν_3 vibrations of the free ClO$_4^-$, is very pronounced with respect to its split components for bonded perchlorate at 1 040 and 1 180 cm^{-1}. This suggests an increase of the ratio of free to bound perchlorate with respect to the lanthanum complex and presumably the absence of bidentate perchlorate, for which a three-fold splitting of ν_4 is expected. The two bands at 2 250 and 2 290 cm^{-1} found for free methyl cyanide are blue-shifted in the present adducts, by *ca.* 20 (Ce) to 40 (Yb) cm^{-1}, suggesting that the metal ions are co-ordinated to methyl cyanide *via* its nitrogen atom.[18] In the region 700—950 cm^{-1} the spectrum is somewhat different from that of the free macrocyclic ligand and that of the lanthanum complex (Figure 3). A plausible interpretation may be made in terms of a different conformation of the macrocycle around the metal, depending both on methyl cyanide co-ordination and metal ionic size. The bands due to water are the same as observed for the lanthanum complex. Finally, the i.r. spectra of the compounds Ce[ClO$_4$]$_3$·L^1·H$_2$O, Pr[ClO$_4$]$_3$·L^1·H$_2$O, and Nd[ClO$_4$]$_3$·L^1 are consistent with the presence of exclusively unidentate perchlorates (Figure 3). Indeed, the characteristic absorptions of ionic ClO$_4^-$ at 620 and 1 100 cm^{-1} are absent, whereas the two-fold splitting of $\nu_4(T_d)$, with peaks at 615 and 635 cm^{-1}, points to a C_{3v} symmetry for the perchlorate groups. The absorption bands of the macrocyclic ligand for these complexes are virtually identical to those of the lanthanum complex, suggesting an essentially similar conformation of the macrocycle around the metal.

The electronic spectra of the complexes of the three most reducible lanthanoids(III) (Eu, Yb, and Sm) exhibit broad bands beside feeble, sharp, *f–f* transitions (Figure 4). Such broad bands can be unambiguously assigned as electron-transfer transitions from the highest occupied molecular orbitals (h.o.m.o.s) of ligand L^1 to 4*f* metal orbitals. These h.o.m.o.s are essentially sulphur lone-pair orbitals suited for π overlap with the metal orbitals. In fact, by using the uncorrected electronegativities[19] of 1.9, 1.8, and 1.6 and the peak frequencies of 28 300, 30 700, and 37 200 cm^{-1} for Eu, Yb, and Sm, respectively, one can derive a value of 2.8 for the optical electronegativity of ligand L^1, close to the literature value of 2.9 for thioethers.[19] By contrast, the optical electronegativity of polyether L^4, calculated from the first electron-transfer band at 39 600 cm^{-1} (ε 190 dm^3 mol^{-1} cm^{-1}) of the complex Eu[ClO$_4$]$_3$·L^4·H$_2$O, is 3.2. On the basis of the above interpretation of the electron-transfer bands one can infer that a direct metal–sulphur interaction is operative in the methyl cyanide adducts too.

Finally, co-ordination of ligand L^1 is retained also in methyl cyanide solution as shown by the presence of the electron-transfer bands. For the complexes of L^1 these bands fall at 37 100 (ε 190) with Sm, at 27 800 (ε 88) and 38 500 (ε 130) with Eu, and 30 500 cm^{-1} (ε 30 dm^3 mol^{-1} cm^{-1}) with Yb.

The europium complex of L^1, having electron-transfer transitions at energies lower than those of the other lanthanoid complexes, exhibits an extra band at higher frequency. This band, which falls at 38 500 cm^{-1} (ε 130) in methyl cyanide, is probably attributable to electron transfers involving lone pairs of the ether oxygen atoms whose orbitals participate in π overlap with the metal orbitals, although the involvement of sulphur lone pairs engaged in Ln–S σ bonds cannot be excluded.

The electric conductivity values for *ca.* 10^{-3} mol dm^{-3} solutions of the present complexes in anhydrous methyl cyanide are those expected for 1 : 2 electrolytes (Table 1). Consequently, only one perchlorate group seems to be bound to the metal ion in MeCN solution, this being presumably also true for the solid methyl cyanide adducts.

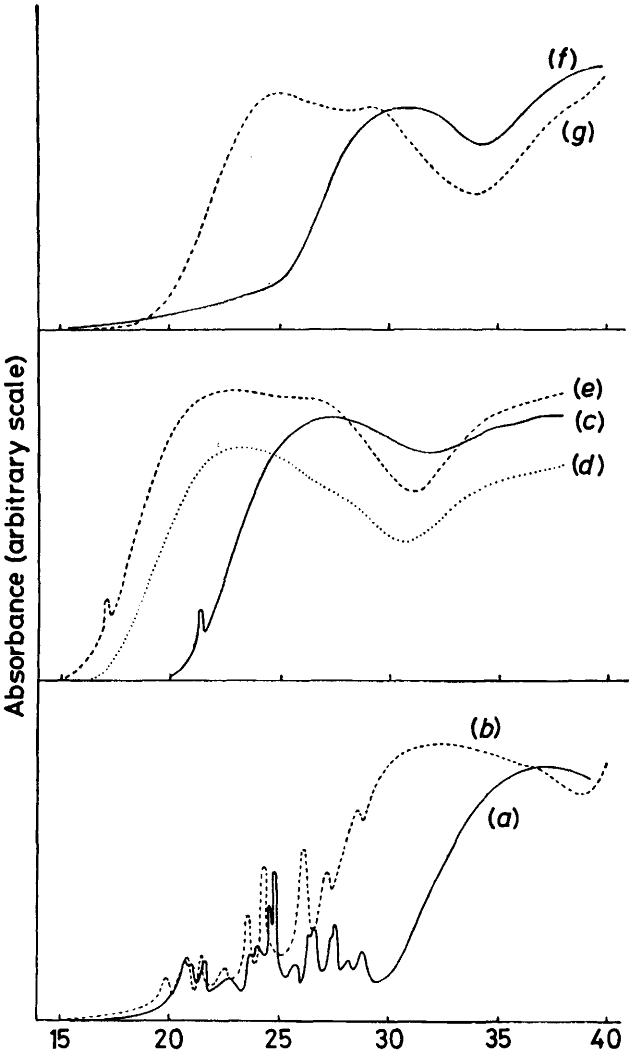

FIGURE 4 Reflectance spectra of the compounds: (*a*) $Sm[ClO_4]_3 \cdot L^1 \cdot 1.5MeCN \cdot H_2O$; (*b*) $Sm[ClO_4]_3 \cdot L^3 \cdot H_2O$; (*c*) $Eu[ClO_4]_3 \cdot L^1 \cdot 2MeCN \cdot H_2O$; (*d*) $Eu[ClO_4]_3 \cdot L^2 \cdot H_2O$; (*e*) $Eu[ClO_4]_3 \cdot L^3 \cdot H_2O$; (*f*) $Yb[ClO_4]_3 \cdot L^1 \cdot 1.5MeCN \cdot H_2O$; (*g*) $Yb[ClO_4]_3 \cdot L^3 \cdot H_2O$

Complexes of Ligands (L^2 *and* L^3).—Since the compounds decompose in methyl cyanide and are almost insoluble in dichloromethane and similar non-coordinating solvents, only measurements in the solid state can be performed.

The i.r. spectra of these complexes show no band attributable to ionic perchlorate (Figure 3). The presence of only two bands at 610 and 635 cm^{-1} is suggestive of exclusively unidentate perchlorate groups. As in the lanthanum complex, bands due to H_2O are detectable. The i.r. features of the macrocyclic ligands are markedly modified upon complexation.

Conclusive evidence for lanthanoid–sulphur interaction is afforded by the electronic spectra. The lanthanoid complexes of ligands L^2 and L^3 also show electron-transfer bands at rather low frequencies (Figure 4). The bands are very broad with a shoulder at about the same frequency as that found for the complexes of ligand L^1, the main peak being shifted by *ca.* 4 000—6 000 cm^{-1} toward lower frequencies. For low-symmetry chromophores, electron-transfer bands with several components are not unprecedented and are suggestive of non-degenerate h.o.m.o.s.[4b] With the present complexes, the energies of these non-degenerate h.o.m.o.s range over at least 4 000 cm^{-1} which may be due to non-equivalent Ln–S bonds or, more probably, interactions between the sulphur atoms, either of a direct type or *via* the metal, as was suggested for lanthanoid *OO'*-diethyl dithiophosphates.[4b]

Summarizing, ligands L^2 and L^3 appear to be coordinated to the lanthanoid(III) ions with a greater number of sulphur atoms than ligand L^1.

For the tetrathia and hexathia macrocycles, an optical electronegativity value of 2.7 can be calculated from the main peak of the first electron-transfer band. This value reflects the bathochromic colour changes observed when the complexes of the above ligands are compared with those of ligand L^1. Moreover, these europium complexes show a group of electron-transfer bands at a higher frequency in both cases. The first shoulder is at *ca.* 35 000 cm^{-1}, *i.e. ca.* 12 000 cm^{-1} beyond the main peak of the first group of bands. These transitions may be tentatively attributed to electron transfers from the σ-type sulphur lone pairs to 4*f* metal orbitals, as is usually found for halide ligands.[19]

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