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Synthesis and Structure of Lanthanide Complexes of a Mixed Donor Macrocyclic Ligand

ATA M. ARIF, COLIN J. GRAY, F. ALAN HART and MICHAEL B. HURSTHOUSE

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

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Abstract

Complexes of lanthanide nitrates and perchlorates with a hexadentate triamine-triether macrocyclic ligand L have been obtained either by template synthesis for La and Ce or by metal ion transfer for Nd and Sm. IR, NMR, mass spectra, and cyclic voltammograms are discussed. The X-ray crystal structure of $[La(NO_3)_3L]$ shows 12-coordinated La with La–O (nitrate) = 2.653–2.752 Å, La–O (macrocycle) = 2.634–2.781 Å, and La–N (macrocycle) = 2.680–2.755 Å.

Introduction

The complexes of the alkaline earth ions with 2,16-dimethyl-3,15,21-triaza-6,9,12-trioxabicyclo-[15,3,1]heneicosa-1(21),2,15,17,19-pentane (L, I) have been described [1], the ligand having been prepared by a template condensation of 2,6-diacetylpyridine with 1,11-diamino-3,6,9-trioxaundecane. In pursuance of our interest in lanthanide complexes with macrocycles [2–5] we have now prepared complexes of lanthanides with L and report their synthesis, properties and structure.

Preparation and General Properties of the Complexes

1,11-diamino-3,6,9-trioxaundecane was synthesised from tetraethylene glycol; the glycol was brominated with PBr_3 to give the 1,11-dibromo-compound, which was converted into the diamine by a Gabriel synthesis [6].

Preparation of $M(NO_3)_3L$*, M = La or Ce*

An ethanolic solution (20 cm^3) of hydrated lanthanum nitrate (0.52 g, 1.20 mmol) was treated with 2,6-diacetylpyridine (0.20 g, 1.22 mmol) and 1,11-diamino-3,6,9-trioxaundecane (0.25 g, 1.3 mmol) in ethanol (10 cm^3). A yellow cloudy precipitate formed and was removed by centrifuge. The remaining clear solution was boiled under reflux for 6 h, filtered, and allowed to cool overnight, giving pale yellow crystals which were collected by filtration, washed with ethanol, and air-dried (yield 0.12 g, 16%). *Anal.* Found: C, 31.5; H, 3.8; N, 13.1%. $C_{17}H_{25}N_6O_{12}La$ requires C, 31.7; H, 3.9; N, 13.0%. The corresponding golden yellow cerium complex was prepared in the same way in 10% yield. *Anal.* Found: C, 31.8; H, 3.8; N, 13.0%. $C_{17}H_{25}N_6O_{12}Ce$ requires C, 31.6; H, 3.9; N, 13.0%. A thermogravimetric analysis of $La(NO_3)_3L$ showed loss of 60% of its weight between 270 °C and 530 °C.

Preparation of $M(NO_3)_2(ClO_4)L \cdot H_2O$*, M = Nd or Sm*

Hydrated samarium nitrate (0.22 g, 0.50 mmol) in methanol (1.6 cm^3) was treated with finely powdered $Ba(ClO_4)_2L \cdot H_2O$ [1] (0.05 g, 0.075 mmol), shaken, and allowed to stand for 24 h in a thin stoppered horizontal glass tube. Cream needles were deposited, together with a fine white solid. The latter was removed by decantation and repeated washing with methanol. The needles were collected by filtration and dried in air. *Anal.* Found: C, 28.6; H, 3.6; N, 10.0%. $C_{17}H_{25}ClN_5O_{14}Sm$ requires C, 28.7; H, 3.8; N, 9.85% (yield, 0.035 g, 66%). The corresponding lilac neodymium complex was prepared in similar yield. *Anal.* Found: C, 28.3; H, 3.5; N, 10.1%. $C_{17}H_{27}ClN_5O_{14}Nd$ requires C, 29.0; H, 3.9; N, 9.9%.

The template preparation of $M(NO_3)_3L$ proceeded satisfactorily in ethanol as described above for M = La or Ce. For heavier lanthanides, products were obtained but their infrared spectra indicated that the ligand had been modified, almost certainly by hydration of an imido linkage as reported for $M(NO_3)_3L'$, where M = a lanthanide and L′ = II, R = H [7]. However, a metal-exchange reaction as described above proved capable of extending the series of lanthanide complexes beyond Ce, as is also the case for the series $M(NO_3)_3L''$, where L″ = II, R = Me [8]. Thus the barium complex $Ba(ClO_4)_2L \cdot H_2O$ slowly exchanged metal with samarium or neodymium nitrate in methanol to give the dinitratoperchlorates $M(NO_3)_2(ClO_4)L \cdot H_2O$,

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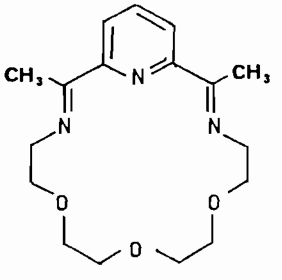
from whose infrared spectra absorption due to CO or NH is absent, indicating that the macrocycle has not suffered partial or complete hydration at an imide linkage.

The lanthanide complexes of L are considerably less stable in water than the analogous complexes of the hexaimine L″. Whereas the latter are stable for some min even in aqueous alkali [4], $La(NO_3)_3L$ and $Ce(NO_3)_3L$ deposit metal hydroxide within a few seconds when dissolved in water. Thus these triimide–triether complexes do not fall midway between the readily-dissociating hexaether complexes such as $La(NO_3)_3$(18-crown-6) and the very stable hexaimide complexes, but rather resemble the former. It is of interest that lanthanide complexes of the ligand **III**, with only two, separated, ether functions dissociate similarly in water [9]. Probably in the case of the complexes of L, dissociation proceeds by the initial breakage of three adjacent ether–metal bonds.



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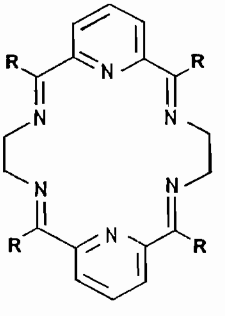
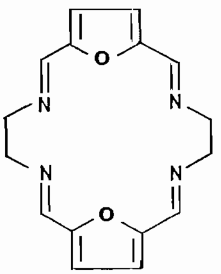


II



III

Structure of the Lanthanum Complex

The structure of the complex $[La(NO_3)_3L]$ was determined by X-ray crystallography. It has 12-coordinated La, the metal ion being coordinated to the three ether oxygen atoms, to the three imido nitrogen atoms, and to the three bidentate nitrate groups, two on one side of the macrocycle and one on the other. This type of arrangement has also been found in $[La(NO_3)_3$(18-crown-6)] [5] and in $[La(NO_3)_3L'']$, where L″ = **II**, R = Me [4]. However, in the present case the folding of the macrocycle away from the hemisphere containing the pair of nitrate groups and towards the lone nitrate, is rather greater (Fig. 1). Bond lengths and angles are given in Table I, least-squares plane data in Table II.

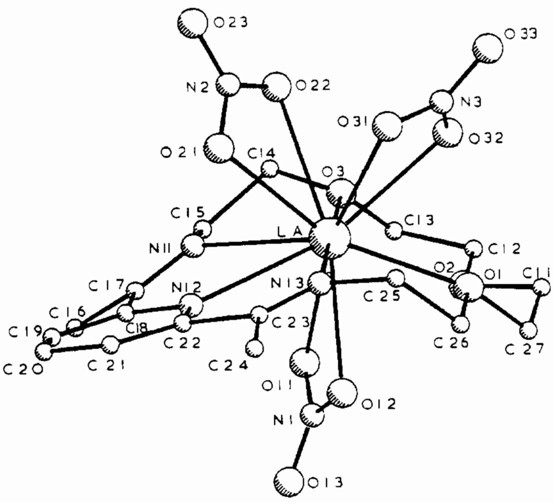


Fig. 1. Structure of $[La(NO_3)_3L]$.

TABLE I. Bond Lengths and Angles.

Bond Lengths (Å)			
O(11)–La	2.713(9)	O(21)–La	2.655(9)
O(12)–La	2.643(9)	O(22)–La	2.752(9)
O(31)–La	2.695(8)	O(32)–La	2.653(8)
O(11)–N(1)	1.258(9)	O(21)–N(2)	1.263(9)
O(12)–N(1)	1.259(9)	O(22)–N(2)	1.261(9)
O(13)–N(1)	1.219(11)	O(23)–N(2)	1.236(8)
O(31)–N(3)	1.260(9)	O(32)–N(3)	1.259(9)
O(33)–N(3)	1.230(8)		
O(1)–La	2.746(9)	N(11)–La	2.755(10)
O(2)–La	2.781(9)	N(12)–La	2.734(9)
O(3)–La	2.634(9)	N(13)–La	2.680(10)
C(27)–C(11)	1.521(14)	C(20)–C(19)	1.355(17)
C(13)–C(12)	1.516(17)	C(21)–C(20)	1.390(16)
C(15)–C(14)	1.520(14)	C(22)–C(21)	1.385(14)
C(17)–C(16)	1.526(13)	C(23)–C(22)	1.522(12)
C(18)–C(17)	1.530(11)	C(24)–C(23)	1.527(11)
C(19)–C(18)	1.402(13)	C(26)–C(25)	1.528(14)
O(1)–C(26)	1.442(9)	N(11)–C(15)	1.480(12)
C(27)–O(1)	1.437(10)	C(17)–N(11)	1.260(11)

(continued on facing page)

TABLE I *(continued)*

O(2)–C(11)	1.437(11)	N(12)–C(18)	1.328(11)
C(12)–O(2)	1.438(10)	C(22)–N(12)	1.335(11)
O(3)–C(13)	1.432(11)	C(25)–N(13)	1.469(12)
C(14)–O(3)	1.438(12)	N(13)–C(23)	1.258(11)
Bond Angles (deg.)			
O(1)–La–O(2)	59.2(2)	O(1)–La–O(3)	117.4(2)
O(1)–La–N(11)	158.8(2)	O(1)–La–N(12)	114.6(2)
O(2)–La–N(13)	62.0(2)	O(2)–La–O(3)	61.1(2)
O(2)–La–N(11)	109.7(2)	O(2)–La–N(12)	137.4(2)
O(2)–La–N(13)	118.5(2)	O(3)–La–N(11)	61.9(2)
O(3)–La–N(12)	121.1(2)	O(3)–La–N(13)	179.2(2)
N(11)–La–N(12)	59.5(2)	N(11)–La–N(13)	118.8(2)
N(12)–La–N(13)	59.6(2)		
O(11)–La–O(12)	47.0(2)	O(11)–La–O(21)	127.6(2)
O(11)–La–O(22)	125.0(2)	O(11)–La–O(31)	167.8(2)
O(11)–La–O(32)	125.0(2)	O(12)–La–O(21)	124.7(2)
O(12)–La–O(22)	165.3(2)	O(12)–La–O(31)	126.4(2)
O(12)–La–O(32)	128.5(2)	O(21)–La–O(22)	46.6(2)
O(21)–La–O(31)	64.3(2)	O(21)–La–O(32)	99.3(2)
O(22)–La–O(31)	63.8(2)	O(22)–La–O(32)	65.9(2)
O(31)–La–O(32)	47.9(2)		
N(1)–O(11)–La	95.8(4)	N(1)–O(12)–La	99.1(4)
N(2)–O(21)–La	100.9(4)	N(2)–O(22)–La	96.2(4)
N(3)–O(31)–La	95.4(4)	N(3)–O(32)–La	97.5(4)
C(26)–O(1)–La	117.3(5)	C(27)–O(1)–La	118.7(5)
C(11)–O(2)–La	118.3(5)	C(12)–O(2)–La	116.2(6)
C(13)–O(3)–La	123.0(5)	C(14)–O(3)–La	118.9(5)
C(15)–N(11)–La	117.5(5)	C(17)–N(11)–La	121.2(5)
C(18)–N(12)–La	121.4(5)	C(22)–N(12)–La	121.4(5)
C(23)–N(13)–La	125.1(5)	C(25)–N(13)–La	114.6(5)
O(11)–N(1)–O(12)	116.2(6)	O(11)–N(1)–O(13)	120.7(7)
O(13)–N(1)–O(12)	123.0(7)	O(21)–N(2)–O(22)	116.0(5)
O(21)–N(2)–O(23)	122.2(6)	O(22)–N(2)–O(23)	121.8(6)
O(31)–N(3)–O(32)	119.2(5)	O(31)–N(3)–O(33)	120.4(6)
O(32)–N(3)–O(33)	120.4(4)		
C(27)–C(11)–O(2)	105.9(1)	C(12)–O(2)–C(11)	108.5(7)
C(13)–C(12)–O(2)	113.5(5)	O(3)–C(13)–C(12)	108.4(8)
C(14)–O(3)–C(13)	108.2(7)	C(15)–C(14)–O(3)	110.4(7)
N(11)–C(15)–C(14)	109.1(7)	C(17)–N(11)–C(15)	114.9(7)
C(16)–C(17)–N(11)	127.5(7)	C(18)–C(17)–N(11)	116.8(6)
C(18)–C(17)–C(16)	115.7(7)	N(12)–C(18)–C(17)	116.6(7)
C(19)–C(18)–C(17)	120.4(7)	C(19)–C(18)–N(12)	123.0(7)
C(22)–N(12)–C(18)	116.8(6)	C(20)–C(19)–C(18)	119.1(9)
C(21)–C(20)–C(19)	119.0(10)	C(22)–C(21)–C(20)	117.9(10)
C(21)–C(22)–N(12)	124.0(8)	C(23)–C(22)–N(12)	115.6(6)
C(24)–C(23)–C(22)	116.1(7)	N(13)–C(23)–C(22)	117.8(6)
N(13)–C(23)–C(24)	126.1(8)	C(25)–N(13)–C(23)	119.8(7)
C(26)–C(25)–N(13)	108.2(7)	O(1)–C(26)–C(25)	107.2(6)
C(27)–O(1)–C(26)	108.7(6)	O(1)–C(27)–C(11)	108.3(6)

TABLE II. Least-Squares Planes and Deviations (Å) of Individual Atoms.

Plane 1: $(-14.6774)x + 12.7146y + (-0.0192)z = -1.4263$

O2	−0.5950	N12	−0.4113
O3	0.5979	N13	0.4169
N11	−0.0823	O1	0.0738
La*	0.4988		

WRMSD = 0.4216

Plane 2: $(-15.503)x + 12.0645y + 0.1351z = -1.2543$

O3	0.2601	N13	0.2533
N11	−0.2555	O1	−0.2578
La*	0.2481		

WRMSD = 0.2567

Plane 3: $19.2287x + (-7.8958)y + (-0.7209)z = 1.6953$

La	0.0678	N12	0.0686
N11	−0.0673	N13	−0.0691

WRMSD = 0.0682

Plane 4: $(-7.0000)x + 16.2851y + (-1.1804)z = 0.3355$

La	−0.2080	O3	0.2027
O2	−0.1925	O1	0.1978

WRMSD = 0.2003

Angles between normals to planes (deg.)

Plane 1 Plane 2	Plane 3 Plane 4
2.49	135.38

The triimide portion of the macrocycle is approximately coplanar, with deviation of the atoms of this unit of about ±0.07 Å from the plane defined by N11, N12, N13 and La. The triether portion has a similar conformation to that found in crown ether complexes. However, the ligand as a whole is considerably folded, the dihedral angle between the best planes defined by N11, N12, N13, La and O1, O2, O3, La being 135.38°. This conformation results from the ability of the flexible non-conjugated half of the ligand to fold away from the pair of nitrate anions to equalise inter-ligand atom contacts. Minimum interatomic distances of oxygen atoms of the lone nitrate group from N or O atoms of the macrocycle are 2.707 Å from N11 and 2.904 Å from O1. Similar distances for the paired nitrate groups are 2.866 Å from O2 and 2.714 Å from N12, while the two shortest nitrate–nitrate contacts are O21–O31 at 2.849 Å and O22–O31 at 2.879 Å. These distances show that interactions have been fairly efficiently equalised.

Lanthanum–ligand interatomic distances are 2.634–2.781 Å for oxygen ligand atoms and 2.680–2.755 Å for nitrogen. These values appear very similar when the small difference in radii between O and N is allowed for and would seem to suggest the possibility that the greater stability of imide macrocycles in water as compared with ether macrocycles may not be caused by differences in bond dissociation energy but rather by more effective hydrogen bonding to the more electronegative oxygen atoms after dissociation. These La–O and La–N distances are very closely similar to those for [La$(NO_3)_3$(18-crown-6)], 2.672–

2.780 Å, and for [La$(NO_3)_3$L′] (L′ = II, R = Me), 2.672–2.764 Å.

The La–O (nitrate) interatomic distances are in the range 2.643–2.752 Å. Thus all nitrates are fully bidentate and compare well with the corresponding distances for [La$(NO_3)_3$(18-crown-6)], 2.644–2.680 Å, and those for [La$(NO_3)_3$L′] (L′ = **II**, R = Me), 2.689–2.767 Å.

X-ray Crystallography

The crystal was air-stable and was mounted on a glass fibre for X-ray study. Preliminary cell dimensions were obtained photographically; systematic absences uniquely defined the space group as *Pbca*. Accurate cell dimensions were obtained by least-squares refinement of diffractometer setting angles (25 reflections in the range $11 < \theta < 18°$). Intensity data were recorded as previously described [10], corrected for Lorentz polarisation factors but not for absorption. The structure was solved by the heavy atom method and refined by least squares. A summary of the crystal data, intensity data measurement parameters, and refinement details are given below. Final coordinates for non-hydrogen atoms are given in Table III.†

TABLE III. Atom Co-ordinates ($\times 10^4$).

	x	y	z
La	1341(0.5)	822(0.5)	2308(0.5)
N(1)	2237(3)	−578(4)	2326(4)
O(11)	1996(3)	−366(4)	1478(4)
O(12)	2192(3)	−113(3)	3080(5)
O(13)	2476(4)	−1213(4)	2405(7)
N(2)	−70(2)	1248(4)	2172(4)
O(21)	161(3)	822(3)	2872(4)
O(22)	290(3)	1449(3)	1446(4)
O(23)	−613(2)	1468(4)	2204(6)
N(3)	1161(3)	2583(3)	2509(4)
O(31)	927(3)	2141(3)	3185(4)
O(32)	1455(3)	2294(3)	1755(4)
O(33)	1106(3)	3289(3)	2587(6)
C(11)	2827(4)	1809(5)	1864(7)
O(2)	2448(3)	1238(3)	1360(4)
C(12)	2418(6)	1413(7)	263(5)
C(13)	1945(4)	935(7)	−325(8)
O(3)	1380(3)	942(4)	256(5)
C(14)	916(4)	557(5)	−355(7)
C(15)	850(6)	−280(5)	−9(7)
N(11)	764(3)	−303(4)	1138(5)
C(16)	602(6)	−1726(5)	912(8)
C(17)	660(4)	−965(4)	1510(5)
C(18)	601(4)	−1025(4)	2698(5)
N(12)	852(3)	−457(4)	3253(5)
C(19)	273(5)	−1639(5)	3153(9)
C(20)	192(5)	−1648(6)	4203(9)
C(21)	457(5)	−1066(6)	4803(9)
C(22)	792(4)	−498(4)	4290(6)
C(23)	1093(4)	155(4)	4904(5)
C(24)	1121(5)	48(7)	6088(5)
N(13)	1305(4)	719(4)	4398(6)
C(25)	1634(4)	1340(5)	4949(7)
C(26)	2294(4)	1374(5)	4530(5)
O(1)	2255(3)	1545(3)	3429(4)
C(27)	2869(3)	1566(7)	3004(7)

Crystal Data

$a = 21.657$ Å; $b = 17.291$ Å; $c = 12.792$ Å; $U = 4790.5$ Å^3; space group, *Pbca*; $D_m = 1.66$ g cm^{-3}; $D_c = 1.70$ g cm^{-3}; $Z = 8$; $F(000) = 2576$; μ (Mo-Kα) = 17.16 cm^{-1}.

Data Collection

Crystal size, 0.25 × 0.16 × 0.5 mm; θ min. and θ max., 1.5° and 27°; total data, 5147; total observed data, 3650; significance test, $I > 1.5\sigma(I)$.

Refinement

No. of parameters, 349. Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o) + g(F_o)^2]$; $g = 0.0008$. Final R $(=\Sigma\Delta F/\Sigma|F_o|)$; $R = 0.065$. R' $(=[\Sigma(w\Delta F^2)/\Sigma(wF_o{}^2)]^{1/2}$; $R' = 0.071$.

Infrared Spectra

[La$(NO_3)_3$L] shows broad strong bands of coordinated nitrate at 1475, 1448 cm^{-1} (B_1), and 1321, 1300 cm^{-1} (A_1). The 1350 cm^{-1} band of the free D_{3h} nitrate ion is absent, as are absorptions assignable to the carbonyl or hydroxyl groups. Absorption in the C–O–C stretching region is complex, occurring at 1095, 1089, 1071, 1064, 1040 and 1005 cm^{-1}. Bands at 1648 cm^{-1} (C=N– stretch) and 1590 cm^{-1} (pyridine stretch) are also present.

Nd$(NO_3)_2(ClO_4)$L·H_2O shows perchlorate absorption at 1085 and 632 cm^{-1}, the latter being a very sharp singlet which indicates the uncoordinated ion. Broad strong bands due to coordinated nitrate are present at 1505 and 1290 cm^{-1}, the 1350 cm^{-1} band of the free nitrate ion being absent in this case also. A weak broad absorption at 3550 cm^{-1} due to water may indicate uncoordinated water. Bands at 1650 cm^{-1} (C=N– stretch) and 1594 cm^{-1} (pyridine stretch) also

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† Lists of hydrogen atoms parameters (inserted in theoretical positions), thermal parameters, and observed and calculated structure-factor amplitudes have been deposited with the Editor-in-Chief as supplementary material; copies are also available from the authors.

appear; the C–O–C region is obscured by the perchlorate bands. The infrared evidence would thus tentatively formulate this complex as $[Nd(NO_3)_2L]ClO_4 \cdot H_2O$ with 10-coordination.

^1H NMR Spectra

These were obtained from acetonitrile solutions at 400 MHz using a Bruker WH-400 spectrometer or at 80 MHz using a Bruker WP-80 instrument.

The Lanthanum Complex

Assignments were relatively straightforward, being based on chemical shifts, integration, coupling constant values and comparison with spectra of $[La(NO_3)_3(18\text{-crown-6})]$ and $[La(NO_3)_3L'']$. Chemical shifts and assignments are as follows (δ, p.p.m.). Hβ, 8.17; Hγ, 8.30; CH_3, 2.53; NCH_2CH_2O, 4.12; NCH_2CH_2O, 3.90; OCH_2CH_2O, 3.86. Coupling constants are (Hz): pyridine, 8; NCH_2CH_2O, 5.5. The OCH_2CH_2O protons are not separately resolved even at 400 MHz.

The Cerium Complex

Paramagnetic broadening and shifting is present in this complex and while assignments are not seriously in doubt, some cannot be proved. The pyridine protons are certainly assigned at 9.75 δ but are not resolved. The downfield shifts are 1.45 p.p.m. (γ) and 1.58 p.p.m. (β); as would be expected from the relative Ce–H distances, the β shift is rather greater than the γ and the resonances become accidentally degenerate. The OCH_2CH_2O resonance is assigned by integration at 0.04 δ, an upfield paramagnetic shift of 3.82 p.p.m. Assignments of NCH_2CH_2O at 2.83 δ and NCH_2CH_2O at 0.56 δ, with upfield paramagnetic shifts of 1.29 and 3.34 p.p.m. respectively, are based on integration and the assignments are made as stated rather than in the reverse combination because the shift of NCH_2CH_2O is likely to be greater as it is located nearer the fairly strongly shifted OCH_2CH_2O protons. These assignments make the reasonable assumption of the predominance of a dipolar shift mechanism. Finally, a fairly sharp singlet at 1.78 δ (upfield shift, 0.75 p.p.m.) must be the CH_3 resonance.

The moderate range of paramagnetic shifts, −1.58 to +3.82 p.p.m., is what might be expected for these complexes which have twelve nitrogen or oxygen ligating atoms of probably rather similar bond strengths and crystal fields fairly uniformly distributed over the coordination sphere, thus introducing only moderate magnetic anisotropy.

Mass Spectra

These were recorded using an AEI MS902 spectrometer by electron impact at 70 eV. The following compounds were studied at the temperatures stated: $La(NO_3)_3L$, 220 °C; $Ce(NO_3)_3L$, 238 °C; $Sm(NO_3)_2(ClO_4)L \cdot H_2O$, 255 °C. In no case was the molecular ion observed, but it is of interest that the molecular ion of the free ligand was observed, strongly for the lanthanum complex and much more weakly for the two others. This dissociation has been observed before for alkaline earth macrocyclic complexes [11], and recently in the case of the lanthanides [9].

Cyclic Voltammetry

The cerium complex was examined by cyclic voltammetry at 10^{-3} mol dm^{-3} in 10^{-1} mol dm^{-3} Et_4NClO_4 in CH_3CN at a scan rate of 35 mV s^{-1}. Potentials are quoted versus S.C.E. It gave an initial oxidation at +0.77 V followed by a reversible oxidation-reduction at $E_{1/2}$ = +1.015 V. The first wave is assigned to the oxidation of Ce^{3+} to Ce^{4+} (compare +0.830 V for $Ce(NO_3)_3 \cdot 6H_2O$) and the second wave must be associated with oxidation of the ligand. It is of interest that the oxidation potential of Ce^{3+} is little influenced by complexation with the macrocycle. This type of complex might have been expected to show sensitivity to the ionic radius of the central metal ion with a consequent effect on the oxidation potential, as has indeed been observed for the Eu^{2+}/Eu^{3+} complex with 2,2,2-cryptate [12].

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