Complexes of Lanthanide Ions with the Crown Ether 1,4,7,10,13,16-Hexaoxacyclo-octadecane

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The title crown ether forms three types of compound with lanthanide ions, [$M(NO_3)_3$(crown)] (M = La—Nd), $M_4(NO_3)_{12}$(crown)$_3$ (M = La—Gd), and [$M(NO_3)_3(OH_2)_3$]·crown (M = Gd—Lu). Crystal structures of the first and third types have been determined by *X*-ray diffraction. The complex [$La(NO_3)_3$(crown)] is orthorhombic, space group *Pbca*, with a = 12.249, b = 15.618, c = 21.852 Å, and Z = 8. Least-squares refinement using 3 607 observed [$I > 1.5\sigma(I)$] intensity data has given R = 0.039 9. The lanthanum co-ordination comprises the six crown oxygens [La–O = 2.627—2.771(3) Å] and two oxygens from each of the three bidentate nitrates [La–O = 2.644—2.675(3) Å]. The complex [$Gd(NO_3)_3(OH_2)_3$]·crown is also orthorhombic, space group probably $Pn2_1a$, with a = 15.259, b = 14.302, c = 11.094 Å, and Z = 4. The structure has been refined to R = 0.029 using 2 314 observed data. Here the crown is not co-ordinated to the metal ion but is linked to the [$Gd(NO_3)_3(OH_2)_3$] molecule by O · · · HO bonds. The Gd–O bond lengths are 2.41—2.53(1) Å for nitrato- and 2.30—2.46(1) Å for water oxygens.

MACROCYCLIC multidentate complexes of lanthanides may be expected to differ from most other lanthanide complexes in several interesting respects, including the following. Ligand atoms such as dialkyl oxide or sulphide, which do not normally form stable lanthanide complexes, may be forced into co-ordination. Unusually high, though possibly not uniquely high, co-ordination numbers may be obtained. The complexes may be non-labile in solution. The magnetic anisotropy produced by the ligand field of the macrocycle may give unusual paramagnetically shifted n.m.r. spectra.

There has consequently been considerable recent interest in complexes formed between lanthanide salts and crown ethers (cyclic polyethers). Thus complexes such as $M(NO_3)_3$(dibenzo-18-crown-6), $M(NO_3)_3$(benzo-15-crown-5)$(OH_2)_x(OCMe_2)_y$ (M = a lanthanide; $x = y = 0$ or $x = 3$, $y = 1$),[1] and PrX_3(crown) (X = Cl, NCS, or ClO_4; crown = 18-crown-6 or 15-crown-5) [2] have been described, as have the 2 : 1 complexes $Pr(ClO_4)_3$(15-crown-5)$_2$ and $Pr(ClO_4)_3$(15-crown-5)(12-crown-4),[2] while a brief account has appeared of $M(ClO_4)_3$(12-crown-4)$_2$ (M = La, Pr, Eu, Ho, Er, Tm, or Yb).[3] The *X*-ray crystal structure of [$La(NO_3)_3$(*cis*, *syn*, *cis*-dicyclohexyl-18-crown-6)] [4] has shown co-ordination by all six crown oxygen atoms and by three bidentate nitrate ions, while a ^1H and ^{13}C n.m.r. study of complexes of the same ligand with praseodymium and other lanthanide perchlorates has demonstrated by analysis of the paramagnetically shifted spectra that the metal–crown co-ordination geometry is preserved in solution.[5] In addition, while our present work was in progress, there appeared [6] a study of the complexes formed between lanthanide (La—Gd) nitrates and 18-crown-6 (L). Our presently reported work in many respects confirms, and considerably extends, the results of Bünzli and Wessner,[6] who prepared complexes $M(NO_3)_3L$ (M = La—Nd) and $M_4(NO_3)_{12}L_3$ (M = La—Gd) and recorded thermogravimetric and differential thermal analyses, *X*-ray powder patterns, magnetic moments, and i.r. spectra. After our present work had been completed, the *X*-ray crystal structure of [$Nd(NO_3)_3L$] was reported.[7]

RESULTS AND DISCUSSION

By treating hydrated lanthanide nitrates with 1.1—1.2 mol equivalents L in hot acetone, three types of analytically pure crystalline complexes were obtained, (*i*) $M(NO_3)_3L$ (M = La—Nd), (*ii*) $M_4(NO_3)_{12}L_3$ (M = Nd—Gd), and (*iii*) $M(NO_3)_3L(OH_2)_3$ (M = Gd—Lu). At the borders between the three series of complexes, the nature of the product obtained is very sensitive to the exact conditions (temperature, period of crystallisation) of the preparation. For M = Nd or M = Gd, two alternative com-

(*i*) $[M(NO_3)_3L] \xrightarrow{(a)} \frac{1}{4}M_4(NO_3)_{12}L_3 \xrightarrow{(b)} M\ oxide$

La: (*a*) 185—250, (*b*) 310—320; Ce: (*a*) 180—230, (*b*) 250—260; Pr: (*a*) 155—250, (*b*) 305—320; Nd: (*a*) 160—250, (*b*) 310—325

(*ii*) $M_4(NO_3)_{12}L_3 \xrightarrow{(b)} M\ oxide$

Nd: 310—325; Sm: 305—340; Eu: 300—335; Gd: 295—330

(*iii*) $M(NO_3)_3(OH_2)_3L \xrightarrow{(c)} M(NO_3)_3L \xrightarrow{(d)} \frac{1}{4}M_4(NO_3)_{12}L_3 \xrightarrow{(b)} M\ oxide$

	(*c*)	(*d*)	(*b*)		(*c*)	(*d*)	(*b*)
Gd:	95—120	160—200	295—310	Tb:	100—120	160—225	295—305
Dy:	95—130	160—265	280—290	Ho:	100—130	150—230	270—285
Er:	105—135	155—240	260—270	Tm:	105—140	160—230	245—255
Yb:	110—145	170—240	240—255	Lu:	120—140	160—225	240—250

SCHEME Temperature ranges (°C) for thermolysis reactions plexes could be obtained in each instance. Types (i) (M = La—Nd) and (ii) (M = Nd—Gd) were obtained previously,[6] microcrystalline from acetonitrile, and the conversion of $M(NO_3)_3L$ into $M_4(NO_3)_{12}L$ (M = La—Nd) at 110—170 °C was noted.[6] The results of our thermogravimetric analyses, carried out in air, are shown in the Scheme. The temperatures for reaction (*a*) are very considerably higher than previously reported [6] for M = Nd (the only instance where a thermogravimetric result is quoted).

The temperature of commencement of reaction falls by *ca.* 25 °C along the series La—Nd, which may be correlated with the fact that the complexes $M(NO_3)_3L$ (M = Sm—Gd) are not obtained from solution, $M_4(NO_3)_{12}L_3$ being obtained instead. Although we have no *X*-ray structural data for $M_4(NO_3)_{12}L_3$, the reaction can be explained on the basis of steric overcrowding of the 12-co-ordinated $M(NO_3)_3L$ (for which *X*-ray data are available, see below). The complex $M_4(NO_3)_{12}L_3$ is most probably to be formulated as $[M(NO_3)_2L]_3[M(NO_3)_6]$, with three 10-co-ordinated metal ions and one, which while 12-co-ordinated, incorporates much of the interligand steric repulsion within the six bidentate anions. A plausible mechanism for this solid-state reaction would involve dissociation of L from individual metal ions followed by, or concurrent with, transfer of nitrate ions to these metal ions perhaps through a transition state involving nitrate bridges.

In order to investigate the persistence of the structure along the series $M_4(NO_3)_{12}L_3$, *X*-ray powder photographs were obtained for the compounds M = Nd*, Sm, Eu, Gd, Tb*, Dy*, Ho*, Er*, or Lu*. The asterisks indicate that the specimen was obtained by thermal decomposition; the remaining specimens were obtained by direct preparation. The patterns fell into two groups, Nd—Tb and Dy—Lu, compounds within each group being powder-pattern isomorphous with each other. The break after Tb is not accompanied by any significant changes in the i.r. spectrum, and it is likely to be caused by a change in crystal packing leading to a different space group, rather than a fundamental structural change.

The final decomposition (*b*) occurs at nearly the same temperature from La (310—320 °C) to Tb (295—305 °C) and thence falls more sharply to Lu (240—250 °C); the cerium compound (250—260 °C) is not surprisingly out of sequence. The final product of decomposition is the metal oxide. The compound $NdO(NO_3)$ was previously reported [6] as the product of decomposition at 290 °C in an argon atmosphere. The hydrated complexes $[M(NO_3)_3(OH_2)_3]\cdot L$ decompose in two stages, (*c*) and (*d*), giving $M_4(NO_3)_{12}L_3$. Stage (*c*) shows a rising trend from Gd (95—120 °C) to Lu (120—140 °C), while stage (*d*) is fairly constant at around 180—230 °C.

It is of interest that the molecular ions $[M(NO_3)_2L]^+$ (M = La—Nd) correspond with the highest-mass peaks in the ^{252}Cf plasma desorption mass spectra [8] of $[M(NO_3)_3L]$; these observations may be related to the stability of $[M(NO_3)_2L]^+$ relative to $[M(NO_3)_3L]$ indicated by the thermogravimetric measurements.

Electronic Spectra.—These were obtained from the solid compounds by diffuse reflectance. They show only very minor differences from spectra of the corresponding hydrated nitrates, obtained under similar conditions for comparison purposes. The compounds studied were $[M(NO_3)_3L]$ (M = Pr or Nd), $M_4(NO_3)_{12}L_3$ (M = Sm or Eu), and $[M(NO_3)_3(OH_2)_3]\cdot L$ (M = Dy or Ho). Compared with corresponding values for hydrated nitrates, wavelengths differ by only 0—3 nm and relative intensities are closely similar, except for the 350 nm band ($^6P_{\frac{5}{2}}$) of the Dy complex which is 25% less intense than expected by comparison with the other maxima of that complex. It was previously stated [6] that upon complexation the splitting of the *f–f* transitions and their intensities change, and inferred from this premise, from magnetic susceptibility measurements which lead to low values for magnetic moments, and from i.r. data, that there is a large lanthanide–polyether interaction which produces these effects. This, if correct, would be of much importance in understanding the bonding in lanthanide complexes. However, we have recalculated the magnetic moments [6] after correcting the observed susceptibilities for molecular diamagnetism using Pascal's constants. The new values of μ for $[M(NO_3)_3L]$ are: M = Ce, 2.43; M = Pr, 3.37; M = Nd, 3.39 B.M.* Those for $M_4(NO_3)_{12}L_3$ are: M = Ce, 2.36; M = Pr, 3.37; M = Nd, 3.35; M = Sm, 1.61; M = Eu, 3.32; M = Gd, 7.93 B.M. These values are rather similar to values previously determined for lanthanide complexes.[9,10] Furthermore, the value of the semi-empirical covalency indicator β,[11] where $\beta = [\sigma(\text{complex})/\sigma(\text{free ion})]$ and σ = transition energy, may be calculated from the electronic spectra and is equal to 0.981, as calculated from the $^3H_4 \rightarrow {}^3P_2$, $^3P_1$, $^3P_0$ transitions of $Pr(NO_3)_3L$ in conjunction with the free-ion terms [12] of Pr^{3+}. This β value indicates a nephelauxetic effect which is considerably smaller than that indicated (0.959) by the spectrum of anhydrous $PrCl_3$.[13]

Finally, an i.r. shift of -29 cm^{-1} in the crown ether C–O–C stretching mode which occurs upon complexation is adduced [6] as evidence for a strong metal–ligand interaction. However, the corresponding stretching mode of tetrahydrofuran is shifted -58 cm^{-1} by complexation [14] with Ca^{2+} although this ether interaction with a less highly charged cation of equal radius should be weaker. Hence ether C–O i.r. shifts appear not to be quantitative indicators of bond strength. There is thus no evidence for an interaction any stronger than the very weak interaction observed [15] between unidentate ethers and lanthanides, although the stability constant is raised sufficiently (in non-aqueous solvents only) by the chelate effect for crown ether complexes to be isolated. Furthermore, these crown ether complexes, of all three types, immediately dissociate in aqueous solution, as shown by n.m.r. (Table 1), demonstrating the kinetic and thermodynamic instability of the lanthanide–polyether linkage. This instability contrasts strikingly with the great

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2; 1 mmHg $\approx 13.6 \times 9.8$ Pa.

stability, even in water solution, of lanthanide complexes of a macrocyclic hexaimine.[16]

Infrared Spectra.—These were obtained from Nujol and hexachlorobutadiene mulls. The nitrate bands are typical of co-ordinated groups in all cases (Table 2). The *E* stretching mode at 1 350—1 390 cm^{-1} characteristic of non-bonded nitrate ion is nowhere present. The nitrate groups are known from *X*-ray structural data to be co-ordinated in [M(NO$_3$)$_3$L] and [M(NO$_3$)$_3$(OH$_2$)$_3$]·L, and would be co-ordinated in M$_4$(NO$_3$)$_{12}$L$_3$ if the formulation [M(NO$_3$)$_2$L]$_3$[M(NO$_3$)$_6$] should be correct. The extensive splitting of the nitrate frequencies in M$_4$(NO$_3$)$_{12}$L$_3$ indicates that in this structure there are a number of nitrate groups which differ in their local symmetry. The bands caused by the crown ether are unremarkable except that the C–O stretch at 1 105 cm^{-1} in the free ligand is a good indicator of whether co-ordination occurs. Thus in [M(NO$_3$)$_3$L] and M$_4$(NO$_3$)$_{12}$L$_3$, this band occurs in the range 1 072—1 082 cm^{-1} while in [M(NO$_3$)$_3$(OH$_2$)$_3$]·L there is an almost unshifted band at 1 098 cm^{-1}. The lowering of *ca.* 23—33 cm^{-1} is doubtless caused by the inductive effect of the metal cation on the C–O bond.

TABLE 1

Hydrogen-1 n.m.r. spectra of lanthanide nitrate complexes with L = 18-crown-6. Values (p.p.m.) relate to CD$_3$CN solutions except τ_{D_2O} which relates to D$_2$O solutions

	τ	$\Delta\tau$ [a]	$\Delta\tau/A$	τ_{D_2O}
L	6.48			6.5
La(NO$_3$)$_3$L	6.20	0		
Ce(NO$_3$)$_3$L	12.75	6.55	−0.555	
Pr(NO$_3$)$_3$L	17.83	11.63	−0.562	6.5
Nd(NO$_3$)$_3$L [b]	10.14	3.94	−0.488	
Nd$_4$(NO$_3$)$_{12}$L$_3$	9.33	3.13	−0.387	
Sm$_4$(NO$_3$)$_{12}$L$_3$	6.99	0.79	*c*	6.5
Eu$_4$(NO$_3$)$_{12}$L$_3$ [b]	1.92	−4.28	*c*	6.5
Yb(NO$_3$)$_3$(OH$_2$)$_3$L [b]	−23.9	−30.1	−0.768	6.5
Lu(NO$_3$)$_3$(OH$_2$)$_3$L [b]	6.08	−0.12		

[a] $\Delta\tau$ is the shift relative to [La(NO$_3$)$_3$L]. [b] Peak due to uncomplexed L also present. [c] First-order theory not valid.

Structures of the Complexes.—The complex [La(NO$_3$)$_3$L] has 12-co-ordinated La, the metal ion being co-ordinated to the six ether oxygen atoms and to two bidentate nitrate ions on one side of the crown ring and to the remaining bidentate nitrate ion on the other (see Figures 1 and 2). Bond lengths and angles are given in Table 3, least-squares plane data in Table 4. The crown ether ring is folded away from the pair of nitrate ions; such an arrangement clearly results in greater equalisation of O(nitrate)–O(ether) interligand contacts. Thus, relative to the O(1) ··· O(6) mean plane, La, O(2), and O(5) are almost equidistant below it (−0.466, −0.519, and −0.484 Å respectively) with O(2)–La–O(5) = 178.4°, while O(3) and O(6) are almost in the plane (−0.026 and −0.062 Å with O(3)–La–O(6) = 162.5°, and O(1) and O(4) are above it (0.564 and 0.528 Å) with O(1)–La–O(4) = 136.4°.

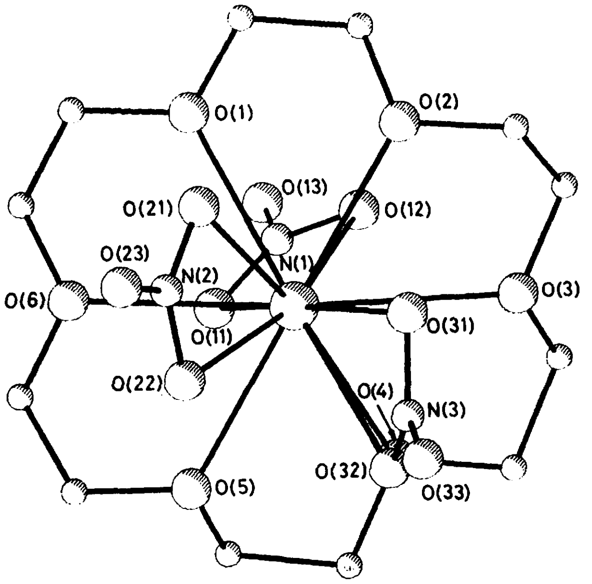

FIGURE 1 The molecular structure of [La(NO$_3$)$_3$(C$_{12}$H$_{24}$O$_6$)] showing atom-numbering scheme

The La–O(nitrate) distances are closely similar (2.644—2.680 Å) but the La–O(ether) distances cover a range of 0.118 Å (2.662—2.780 Å). It is possibly significant that the two shortest La–O(ether) distances relate to the only two oxygen atoms [O(2) and O(5)] which do not have close (< 2.9 Å) interligand approach to a nitrate oxygen atom, implying that in the case of a close approach, *e.g.* O(6)–O(11) = 2.772 Å, it is the ether oxygen which has to some extent relieved repulsion by an increase in its bond distance [La–O(6) = 2.771 Å]. This would further imply that the La–O(ether) force constant is smaller than that of La–O(nitrate), which is in accord with the observed extreme weakness of lanthanide–

TABLE 2

Infrared frequencies (cm^{-1}) of a selection of complexes of lanthanide nitrates with L = 18-crown-6

		NO$_3$					
		B_1	A_1	A_1	B_2	ν(C–O)	H$_2$O
[M(NO$_3$)$_3$L]	M = La	1 494, 1 464, 1 443	1 328, 1 318	1 049	827	1 082	
	M = Nd	1 498, 1 465, 1 447	1 332, 1 323	1 050	825	1 082	
[M$_4$(NO$_3$)$_{12}$L$_3$]	M = Sm	1 532, 1 515, 1 480, 1 461, 1 438	1 332, 1 295, 1 277	1 050, 1 029	828, 821	1 072	
	M = Gd	1 534, 1 520, 1 515, 1 483, 1 465, 1 442	1 337, 1 298, 1 282	1 053, 1 032	829, 822	1 072	
[M(NO$_3$)$_3$(OH$_2$)$_3$]·L	M = Gd	1 544, 1 510	1 292, 1 277	1 026	822	1 098	3 360, 3 240, 1 635
	M = Lu	1 546, 1 512	1 306, 1 287	1 029	822	1 098	3 360, 3 240, 1 635

ether interactions. There is no evidence that the crown ring as a whole is under significant stress caused by incompatible La–O(ether) and intra-annular bonding requirements. Thus C–O distances all lie in the range 1.427—1.447 Å, C–C within 1.473—1.488 Å, with C–O–C within 110.0—114.5° and O–C–C within 106.6—110.8°.

TABLE 3

Selected molecular geometry parameters for $[La(NO_3)_3(C_{12}H_{24}O_6)]$ with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

O(1)–La	2.741(6)	C(42)–O(5)	1.448(6)
O(2)–La	2.661(6)	C(51)–O(5)	1.443(6)
O(3)–La	2.780(6)	C(52)–O(6)	1.440(7)
O(4)–La	2.712(6)	C(61)–O(6)	1.431(6)
O(5)–La	2.627(6)	N(1)–O(11)	1.253(5)
O(6)–La	2.772(6)	N(1)–O(12)	1.270(5)
O(11)–La	2.644(6)	N(1)–O(13)	1.214(6)
O(12)–La	2.680(6)	N(2)–O(21)	1.252(6)
O(21)–La	2.670(6)	N(2)–O(22)	1.271(6)
O(22)–La	2.650(6)	N(2)–O(23)	1.219(6)
O(31)–La	2.665(6)	N(3)–O(31)	1.271(6)
O(32)–La	2.675(6)	N(3)–O(32)	1.257(5)
C(11)–O(1)	1.443(7)	N(3)–O(33)	1.222(5)
C(62)–O(1)	1.446(8)	C(12)–C(11)	1.473(11)
C(12)–O(2)	1.439(8)	C(22)–C(21)	1.487(9)
C(21)–O(2)	1.430(7)	C(32)–C(31)	1.483(9)
C(22)–O(3)	1.440(8)	C(42)–C(41)	1.485(8)
C(31)–O(3)	1.427(7)	C(52)–C(51)	1.483(8)
C(32)–O(4)	1.436(7)	C(62)–C(61)	1.474(8)
C(41)–O(4)	1.429(7)		

(*b*) Bond angles (°) in co-ordination sphere

O(1)–La–O(2)	61.7(1)	O(2)–La–O(3)	60.8(1)
O(3)–La–O(4)	59.5(1)	O(4)–La–O(5)	61.4(1)
O(1)–La–O(6)	59.6(1)	O(5)–La–O(6)	61.6(1)
O(11)–La–O(12)	47.5(1)	O(21)–La–O(22)	47.6(1)
O(31)–La–O(32)	47.4(1)		
O(1)–La–O(11)	71.1(1)	O(4)–La–O(11)	69.6(1)
O(5)–La–O(11)	69.3(1)	O(6)–La–O(11)	61.5(1)
O(1)–La–O(12)	67.1(1)	O(2)–La–O(12)	70.1(1)
O(3)–La–O(12)	62.5(1)	O(4)–La–O(12)	72.8(1)
O(1)–La–O(21)	62.4(1)	O(2)–La–O(21)	70.2(1)
O(6)–La–O(21)	69.7(1)	O(5)–La–O(22)	66.7(1)
O(6)–La–O(22)	66.7(1)	O(2)–La–O(31)	66.3(1)
O(3)–La–O(31)	68.7(1)	O(21)–La–O(31)	64.9(1)
O(22)–La–O(31)	64.9(1)	O(3)–La–O(32)	72.4(1)
O(4)–La–O(32)	63.3(1)	O(5)–La–O(32)	70.0(1)
O(22)–La–O(32)	64.3(1)		

(*c*) Co-ordination sphere O · · · O close contacts (Å) <3.0 Å

O(1) · · · O(2)	2.77	O(12) · · · O(3)	2.84
O(3) · · · O(4)	2.73	O(22) · · · O(5)	2.90
O(11) · · · O(6)	2.77	O(22) · · · O(32)	2.83
O(21) · · · O(31)	2.86	O(2) · · · O(8)	2.75
O(22) · · · O(31)	2.95	O(5) · · · O(6)	2.77
O(32) · · · O(4)	2.83	O(21) · · · O(1)	2.81
O(1) · · · O(6)	2.74	O(22) · · · O(6)	2.98
O(4) · · · O(5)	2.73	O(31) · · · O(2)	2.92

It is of considerable interest to compare this structure with that of $[Nd(NO_3)_3L]$, reported [7] after this work was completed. These constitute an isostructural pair of lanthanide complexes, and there are few cases where the detailed structures of such pairs have been determined. There would be expected to be considerable crowding of the neodymium complex (ionic radius 0.99 Å) compared with that of lanthanum (1.06 Å) as Nd^{3+} is the smallest ion which gives $[M(NO_3)_3L]$ and indeed gives $Nd_4(NO_3)_{12}L_3$ under slightly different preparative conditions. It is noteworthy that the co-ordination of the pair of crown oxygen atoms which are furthest from the La ion is at least as close (La–O = 2.771 and 2.780 Å) as the corresponding pair in the neodymium complex (2.771 and 2.788 Å). The remaining La–O(crown) and the La–O(nitrate) distances are an average of 0.047 Å greater than the corresponding Nd–O distances, in good agreement with the difference in ionic radii. It therefore appears that the effects of steric crowding are absorbed by just two crown oxygen atoms, in *trans* positions in the crown ring.

TABLE 4

Least-squares plane for $[La(NO_3)_3L]$ in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates, and deviations (Å) of the relevant atoms are in square brackets

Plane: O(1), O(2), O(3), O(4), O(5), O(6)

$$9.977x + 9.060y + 0.041z = 7.258$$

[La(1) −0.466, O(1) 0.564, O(2) −0.519, O(3) −0.026, O(4) 0.528, O(5) −0.484, O(6) −0.062]

The complex $[Gd(NO_3)_3(OH_2)_3]\cdot L$ does not contain co-ordinated crown ether (Figure 3). The Gd^{3+} ions are co-ordinated by three bidentate nitrate groups and three water molecules in an irregular co-ordination polyhedron. The crown ether is bound to co-ordinated water molecules by O(crown) · · · H–O(water) hydrogen bonds. Thus, each crown ether oxygen atom is hydrogen-bonded to one of the water molecules: all the ether oxygen atoms and all the water hydrogen atoms form one hydrogen bond each. They are of moderate strength with O–O internuclear distances of 2.780—2.934 Å. This rather elegant arrangement, whereby the lanthanide co-ordinates with just sufficient water molecules to provide six hydrogen bonds per molecule of 18-crown-6, is doubtless the driving force for the formation of the stable 1 : 1 adduct. Bond lengths and angles for both molecules are given in Table 5.

The Gd^{3+} nine-co-ordinated polyhedron in $[Gd(NO_3)_3(OH_2)_3]$ is quite appreciably less crowded than that of the 12-co-ordinated La^{3+} polyhedron in $[La(NO_3)_3L]$ despite the smaller ionic radius (0.94 Å as against 1.06 Å). Thus of the interligand distances, only four contacts are within the range 2.79—2.90 Å; the remainder extend up to 3.25 Å. These four distances comprise one O(nitrate)–O(nitrate) (2.793 Å) contact, two O(nitrate)–O(water) (2.848, 2.876 Å), and one O(water)–O(water) (2.868 Å). They are approximately 0.15—0.2 Å greater than the corresponding smallest distances in $[La(NO_3)_3L]$.

Nuclear Magnetic Resonance Data.—Hydrogen-1 n.m.r. spectra obtained in CD_3CN (Table 1) show chemical shifts which are approximately proportional to A, where $A = g^2J(J + 1)(2J - 1)(2J + 3)\langle J||\alpha||J\rangle$, in the case of the series $[M(NO_3)_3L]$(M = Ce, Pr, or Nd). The shifts depart from this proportionality in the case of $Nd_4(NO_3)_{12}L_3$ and $[Yb(NO_3)_3(OH_2)_3]\cdot L$, which have different stoicheiometries, structures, and yield different

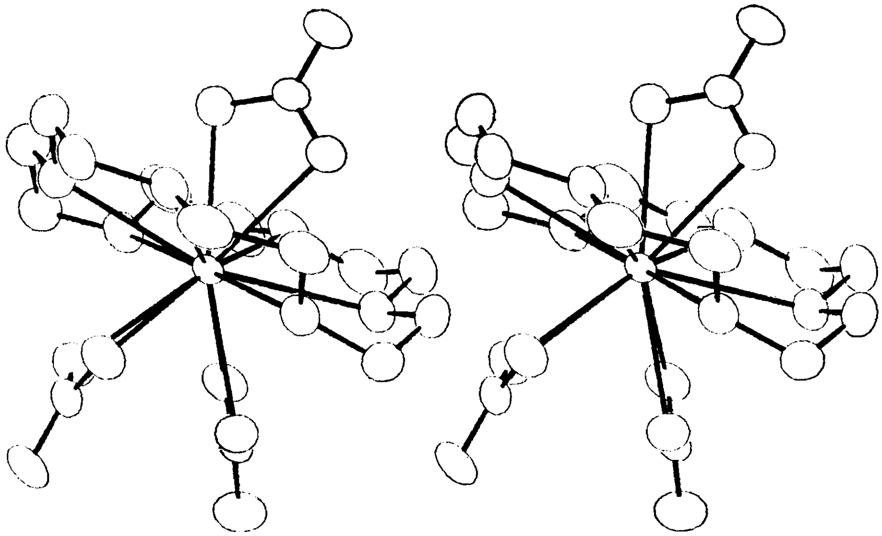

FIGURE 2 A stereodiagram of molecules of $[La(NO_3)_3(C_{12}H_{24}O_6)]$

species in solution as shown by the conductance results. The value of $\Delta\tau/A$ should be constant for a series having identical structures in solution if a purely dipolar shift mechanism operates.[17]

The compound $[Yb(NO_3)_3(OH_2)_3]\cdot L$ showed both complexed and free L in the spectrum and was investigated at 292—343 K over which range the dissociation was constant within experimental error, lying between 36 and 38.1%. It follows that the enthalpy of dissociation of the crown ligand is close to zero; we estimate $\Delta H_{dis.} = 0(\pm 2)$ kJ mol^{-1}. The value of the concentration stability constant K is 655 ($\pm$ 60) dm^3 mol^{-1}. Low solubility precluded extension of these measurements to lower temperatures, but values of τ were determined over the range $T = 232$—343 K at lower concentrations. A straight-line plot was obtained for $\Delta\tau$ against $T^{-\frac{3}{2}}$; this fit is a close one, $(\Delta\tau)\cdot T^{\frac{3}{2}}$ being constant within $\pm 1\%$. Theory [17] indicates that $\Delta\tau$ should vary as T^{-2}; an alternative treatment [18] however supports a less simple temperature dependence. The $\Delta\tau$ against T^{-2} plot shows some curvature, with the tangents at $T = 232$ and $T = 343$ K having slopes differing by 20%.

Conductance Data.—At 0.001 mol dm^{-3} concentration, the complexes $[M(NO_3)_3L]$ (M = La, Ce, Pr, or Nd) are

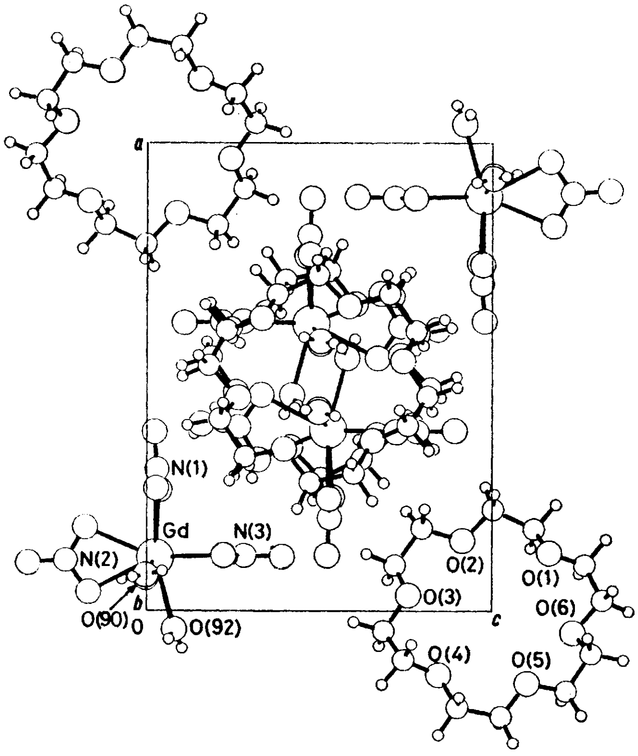

FIGURE 3 Packing diagram of the crystal structure of $[Gd(NO_3)_3(OH_2)_3]\cdot C_{12}H_{24}O_6$

TABLE 5

Selected bond lengths and angles for $[Gd(NO_3)_3(OH_2)_3]\cdot C_{12}H_{24}O_6$

(*a*) Bond lengths (Å)

Gd–O(11)	2.411(11)	Gd–O(21)	2.422(4)
Gd–O(12)	2.533(13)	Gd–O(22)	2.454(6)
Gd–O(31)	2.448(14)	Gd–O(32)	2.440(14)
Gd–O(90)	2.459(11)	Gd–O(91)	2.308(11)
Gd–O(92)	2.417(5)		

(*b*) Angles (°)

O(12)–Gd–O(11)	51.4(4)	O(22)–Gd–O(21)	51.4(2)
O(32)–Gd–O(31)	52.1(4)		
O(22)–Gd–O(11)	70.2(5)	O(22)–Gd–O(12)	71.8(5)
O(31)–Gd–O(12)	76.0(4)	O(32)–Gd–O(11)	75.2(5)
O(90)–Gd–O(12)	76.4(4)	O(90)–Gd–O(21)	77.1(4)
O(90)–Gd–O(31)	71.7(4)	O(91)–Gd–O(11)	83.4(5)
O(91)–Gd–O(21)	75.8(5)	O(91)–Gd–O(22)	86.0(7)
O(91)–Gd–O(32)	73.7(5)	O(92)–Gd–O(21)	77.0(2)
O(92)–Gd–O(31)	78.9(4)	O(92)–Gd–O(32)	78.3(4)
O(92)–Gd–O(90)	79.7(4)	O(92)–Gd–O(91)	75.0(5)

(*c*) N–O(nitrate) distances range over 1.22—1.29(3) Å
C–O(crown) distances range over 1.32—1.45(3) Å
C–C(crown) distances range over 1.47—1.53(3) Å

(*d*) O · · · O close contacts in co-ordination sphere (Å)

O(22) · · · O(11)	2.80	O(31) · · · O(12)	3.07
O(32) · · · O(11)	2.96	O(90) · · · O(12)	3.09
O(91) · · · O(11)	3.14	O(91) · · · O(32)	2.85
O(90) · · · O(31)	2.88	O(92) · · · O(32)	3.07
O(92) · · · O(31)	3.10	O(90) · · · O(21)	3.04
O(92) · · · O(90)	3.13	O(91) · · · O(21)	2.91
O(22) · · · O(12)	2.93	O(92) · · · O(21)	3.01

essentially non-conductors in CH_3CN (Table 6) but the neodymium complex shows some dissociation ($\Lambda_M = 67$ against $\Lambda_M = 175\ \Omega^{-1}\ cm^2\ mol^{-1}$ for a 1 : 1 electrolyte) which is probably caused by co-ordinative over-saturation of the smaller Nd^{3+} ion. The compounds $M_4(NO_3)_{12}L_3$ (M = Sm, Eu, or Gd) have a conductance in accord with that expected for a 3 : 1 electrolyte but the corresponding neodymium complex has a rather lower value possibly caused by the equilibrium (1) where some charge neutralisation occurs.

$$[Nd(NO_3)_2L]^+ + [Nd(NO_3)_6]^{3-} \rightleftharpoons [Nd(NO_3)_3L] + [Nd(NO_3)_5]^{2-} \quad (1)$$

The complexes $[M(NO_3)_3(OH_2)_3]\cdot L$ (M = Gd, Tb, Dy, Ho, or Er) have conductances of *ca.* 100 $\Omega^{-1}\ cm^2\ mol^{-1}$ dropping during the sequence M = Tm, Yb, Lu to 51 $\Omega^{-1}\ cm^2\ mol^{-1}$ at Lu. These values would be in accord with partial co-ordination of L, which is demonstrated by the n.m.r. results. The left-hand side components of

$$[M(NO_3)_3(NCCH_3)_n] + L \rightleftharpoons [M(NO_3)_2L]^+ + NO_3^- + nCH_3CN \quad (2)$$

equilibrium (2) are non-conductors, demonstrated by a conductance of 5 $\Omega^{-1}\ cm^2\ mol^{-1}$ for $Yb(NO_3)_3\cdot 6H_2O$ in 0.007 mol dm^{-3} CH_3CN; the H_2O is displaced from co-ordination by solvent CH_3CN as shown by the nearly equal τ values for the water protons in the n.m.r. spectra of $[M(NO_3)_3(OH_2)_3]\cdot L$ (M = Yb or Lu) in CD_3CN.

TABLE 6

Analysis and conductance data

Complex	Colour	Found (%) C	H	N	M	Calculated (%) C	H	N	M	$\Lambda_M/^a$ $\Omega^{-1}\ cm^2\ mol^{-1}$
$[La(NO_3)_3L]$	White	25.06	4.28	6.97	23.30	24.46	4.11	7.13	23.57	6.8
$[Ce(NO_3)_3L]$	White	24.84	4.30	6.93	23.81	24.41	4.10	7.12	23.73	27
$[Pr(NO_3)_3L]$	Pale green	24.56	4.03	6.71	24.03	24.38	4.09	7.11	23.83	24
$[Nd(NO_3)_3L]$	Lilac	24.66	4.11	6.67	24.01	24.24	4.07	7.07	24.26	67
$Nd_4(NO_3)_{12}L_3$	Lilac	20.62	3.48	7.93	27.71	20.45	3.43	7.95	27.29	260 [b]
$Sm_4(NO_3)_{12}L_3$	Cream	20.10	3.56	7.49	28.22	20.22	3.39	7.86	28.13	382
$Eu_4(NO_3)_{12}L_3$	White	20.09	3.42	7.41	28.39	20.16	3.38	7.84	28.34	415
$Gd_4(NO_3)_{12}L_3$	White	19.92	3.42	7.64	29.16	19.96	3.35	7.76	29.04	390
$[Gd(NO_3)_3(OH_2)_3]\cdot L$	White	22.10	4.74	6.34	24.50	21.78	4.57	6.35	23.77	106
$[Tb(NO_3)_3(OH_2)_3]\cdot L$	White	21.92	4.54	6.27	24.35	21.73	4.56	6.33	23.96	104
$[Dy(NO_3)_3(OH_2)_3]\cdot L$	Cream	21.82	4.62	6.24	24.54	21.61	4.53	6.30	24.37	117
$[Ho(NO_3)_3(OH_2)_3]\cdot L$	Pale yellow	21.68	4.63	6.48	24.93	21.53	4.52	6.28	24.64	107
$[Er(NO_3)_3(OH_2)_3]\cdot L$	Pale pink	21.52	4.64	6.18	25.03	21.46	4.50	6.26	24.90	101
$[Tm(NO_3)_3(OH_2)_3]\cdot L$	White	21.58	4.64	6.23	25.09	21.41	4.49	6.24	25.09	92
$[Yb(NO_3)_3(OH_2)_3]\cdot L$	White	21.38	4.64	6.15	25.66	21.28	4.46	6.20	25.54	84
$[Lu(NO_3)_3(OH_2)_3]\cdot L$	White	21.37	4.62	6.07	26.30	21.22	4.45	6.19	25.76	51

[a] In CH_3CN at 0.001 mol dm^{-3} and 25 °C except where noted. [b] $M_4(NO_3)_{12}L_3$ at 0.000 25 mol dm^{-3}.

In order to provide more direct correlation with our n.m.r. experiments, Λ_M values of some representative compounds, *viz.* $[La(NO_3)_3L]$, $Sm_4(NO_3)_{12}L_3$, and $[Yb(NO_3)_3(OH_2)_3]\cdot L$, were determined at concentrations comparable with those employed in the n.m.r. experiments. The Λ_M values were essentially unchanged compared with the values at 0.001 mol dm^{-3} concentration just discussed.

EXPERIMENTAL

Materials.—Lanthanides were obtained as their oxides 99.9 or 99.99% pure from Johnson–Matthey and Co. Ltd. The ligand (1,4,7,10,13,16-hexaoxacyclo-octadecane) was prepared [19,20] from triethylene glycol and 1,8-dichloro-3,6-dioxaoctane (obtained by treating triethylene glycol with thionyl chloride [21]).

Analyses.—Elemental (C, H, and N) analyses were by the University College, London, microanalytical service. Lanthanides were determined by titration against ethylenediaminetetra-acetic acid solution, using xylenol orange as indicator.[22]

Instrumentation.—Infrared spectra. These were obtained from Nujol or hexachlorobutadiene mulls between KBr discs, using a Perkin-Elmer 577 grating infrared spectrophotometer.

Reflectance spectra. These were obtained from powdered samples smeared on filter papers, using a Beckman DK2A ratio recording spectrophotometer.

Nuclear magnetic resonance spectra. These were obtained from CD_3CN solutions, using Varian EM360 (60 MHz), or Bruker HFX 90 spectrometers. In the latter case we are indebted to the King's College section of the London University Intercollegiate Research Service.

Thermogravimetric data. These were obtained in the air, using a Stanton–Redcroft TR-02 automatic thermorecording balance with Pt against 13% Rh-Pt thermocouples. A linear heating rate of 4° min^{-1} was used.

Conductivity data. These were obtained from CH_3CN solutions (at 25 °C except for variable-temperature studies) using a Mullard E7566 conductivity bridge.

X-*Ray powder data.* These were recorded using a Philips 1 050 vertical diffractometer. The *X*-rays (nickel-filtered Cu-K_α radiation, λ = 1.541 8 Å) were from a Phillips 1 010 generator. Each powdered sample was smeared on one side of double-sided Sellotape, which was then mounted on a microscope slide for insertion into the diffractometer.

Preparations.—$[M(NO_3)_3L]$. For M = La, Ce, or Pr, a hot solution of L (0.2 g, 0.76 mmol) in acetone (10 cm^3) was added to a hot solution of the hydrated lanthanide nitrate

(0.3 g, *ca.* 0.71 mmol) in acetone (10 cm^3). In this and other preparations the mixture was covered in order to prevent solvent evaporation causing premature crystallisation. The crystalline product was collected after 16 h, washed with acetone, and dried over P_4O_{10} at 50 °C (0.1 mmHg) for 16 h. Yields: 70—80%.

For M = Nd, the above procedure was used, except that the acetone solutions were cold when mixed. Yield: 49%.

$M_4(NO_3)_{12}L_3$. For M = Sm or Eu, a hot solution of L (0.2 g, 0.76 mmol) in acetone (10 cm^3) was added to a hot solution of the hydrated lanthanide nitrate (0.3 g, *ca.* 0.67 mmol) in acetone (10 cm^3). The product was collected after 16 h, washed with acetone, and dried over P_4O_{10} at 110 °C (0.1 mmHg) for 16 h. Yield: *ca.* 70%.

For M = Nd, the above procedure was used, except that the product was collected 1 min after the hot acetone solutions were mixed, otherwise [Nd$(NO_3)_3$L] may be co-precipitated. Yield: 69%.

For M = Gd, the above procedure was used, except that the product was collected only 30 min after the acetone solutions were mixed; otherwise the product is slowly converted into [Gd$(NO_3)_3(OH_2)_3$]·L. Yield: 59%.

TABLE 7

X-Ray data for [La$(NO_3)_3(C_{12}H_{24}O_6)$] and [Gd$(NO_3)_3(OH_2)_3$]·$C_{12}H_{24}O_6$

(*a*) Crystal data	[La$(NO_3)_3(C_{12}H_{24}O_6)$]	[Gd$(NO_3)_3(OH_2)_3$]· $C_{12}H_{24}O_6$
a/Å	12.249(2)	15.259(3)
b/Å	15.618(2)	14.302(3)
c/Å	21.852(3)	11.094(2)
U/Å^3	4 180.2	2 421.2
Space group	*Pbca*	$Pn2_1a$
D_m/g cm^{-3}	1.85	1.80
Z	8	4
D_c/g cm^{-3}	1.872	1.813
F(000)	2 352	1 364
μ(Mo-K_α)/cm^{-1}	19.7	26.7
(*b*) Data collection		
Crystal size/mm	0.75 × 0.5 × 0.25	0.40 × 0.32 × 0.25
$\theta_{min.}/\theta_{max.}$	1.5, 25.0	1.5, 25.0
Scan width parameters		
A,B in width = $A + B \tan\theta$	0.75, 0.35	0.8, 0.35
Horizontal aperture		
parameters A,B in aperture = $A + B \tan\theta$	4.0, 0.0	4.0, 0.0
Total data	5 158	3 154
Total unique data	4 543	2 835
Observed data	3 607	2 314
Significance test	$I > 1.5\sigma(I)$	$I > 1.5\sigma(I)$
(*c*) Refinement		
No. of parameters	379	168
Weighting scheme		
coefficient g in $w = 1/[\sigma^2(F_o) + g(F_o)^2]$	0.000 3	0.000 5
Final R $(= \Sigma\Delta F/\Sigma\lvert F_o\rvert)$	0.039 9	0.028 9
$R'\{= [\Sigma(w\Delta F^2)/\Sigma(wF_o^2)]^{\frac{1}{2}}\}$	0.045 8	0.032 7

[M$(NO_3)_3(OH_2)_3$]·L. For M = Tb, Dy, Ho, Er, Tm, Yb, or Lu, a hot solution of L (0.2 g, 0.76 mmol) in acetone (10 cm^3) was added to a hot solution of the hydrated lanthanide nitrate (0.3 g, *ca.* 0.65 mmol) in acetone (10 cm^3). The crystalline product was collected after 16 h, washed with acetone, and dried at 20 °C (0.1 mmHg) for 16 h. Yields: 80—95%.

For M = Gd, the above procedure was used, except that the product was collected 72 h after the acetone solutions were mixed. Yield: *ca.* 70%. Analytical data for all the compounds are given in Table 6.

X-Ray Crystallography.—Crystals of both compounds are air-stable and were mounted on glass fibres for *X*-ray study. Preliminary cell dimensions were obtained photographically and accurate values by least-squares refinement of diffractometer setting angles (25 reflections in the range $11 < \theta < 18°$ in each case). Intensity data were recorded as previously described,[23] corrected for Lorentz polarization factors but not for absorption. The structures were 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 in Table 7.

TABLE 8

Atomic fractional co-ordinates for [La$(NO_3)_3(C_{12}H_{24}O_6)$] (La × 10^5, others × 10^4)

Atom	x	y	z
La	51 068(2)	18 559(2)	38 259(1)
O(1)	6 199(2)	1 794(2)	2 732(1)
O(2)	4 281(2)	2 711(2)	2 879(1)
O(3)	4 115(2)	3 432(2)	4 025(2)
O(4)	5 353(2)	2 677(2)	4 911(1)
O(5)	5 870(2)	992(2)	4 764(1)
O(6)	6 655(2)	597(2)	3 612(1)
O(11)	7 185(2)	2 227(2)	4 017(1)
O(12)	6 298(2)	3 263(2)	3 611(2)
O(13)	8 060(3)	3 327(2)	3 665(2)
O(21)	4 386(2)	755(2)	2 982(1)
O(22)	4 311(2)	282(2)	3 904(1)
O(23)	3 671(3)	−488(2)	3 164(2)
O(31)	2 942(3)	1 739(2)	3 736(1)
O(32)	3 530(2)	1 626(2)	4 657(1)
O(33)	1 945(2)	1 096(2)	4 416(2)
N(1)	7 214(3)	2 946(2)	3 762(1)
N(2)	4 119(3)	164(2)	3 339(2)
N(3)	2 779(2)	1 481(2)	4 280(2)
C(11)	5 601(5)	2 120(5)	2 213(2)
C(12)	5 041(4)	2 914(5)	2 398(3)
C(21)	3 506(4)	3 371(3)	3 008(3)
C(22)	3 929(4)	3 953(3)	3 491(3)
C(31)	4 532(4)	3 929(3)	4 521(3)
C(32)	4 627(4)	3 365(3)	5 065(3)
C(41)	5 535(4)	2 147(4)	5 434(2)
C(42)	6 337(4)	1 474(3)	5 266(2)
C(51)	6 417(4)	192(3)	4 642(2)
C(52)	7 229(4)	294(3)	4 144(2)
C(61)	7 400(4)	724(3)	3 115(2)
C(62)	6 754(4)	1 004(4)	2 583(2)

The lanthanum compound behaved normally during structure refinement but pseudo-symmetry problems occurred with the gadolinium complex. Systematic absences in the data indicated the two possible space groups *Pnma* and $Pn2_1a$. Refinement in the former, where the [Gd$(NO_3)_3(OH_2)_3$] group is required to have $C_s(m)$ symmetry and the crown ether molecule $C_i(\bar{1})$ symmetry gave a final R $(= \Sigma\Delta F/\Sigma\lvert F_0\rvert)$ of 0.039 $\{R' = [\Sigma(w\Delta F^2)/\Sigma(wF_0^2)]^{\frac{1}{2}} = 0.048\}$, some non-positive definite temperature factors, and some unacceptable bond lengths and angles in both units. Refinement in $Pn2_1a$ was also unstable but gave $R = 0.029$, $R' = 0.033$, still some high U_{ii} values (although none physically unreasonable) but acceptable bond lengths and angles. We have chosen the latter space group therefore, although it is possible that a disordered *Pnma* model could still be correct. However, with such a low R value already and with such a dominating heavy atom, we consider it to be rather futile and expensive in computer time to explore this aspect further.

Final co-ordinates for non-hydrogen atoms are given in Tables 8 and 9. Lists of hydrogen-atom parameters (determined experimentally in the lanthanum complex; inserted in theoretical positions for the CH_2 groups but experimentally determined for the water molecules in the gadolinium compound), thermal parameters, and observed and calculated structure-factor amplitudes are given in Supplementary Publication No. SUP 22849 (30 pp.).* Details of computers, programs, and scattering-factor data are as given in ref. 23.

TABLE 9

Atomic fractional co-ordinates for $[Gd(NO_3)_3(OH_2)_3]\cdot C_{12}H_{24}O_6$ (Gd × 10^5, others × 10^4)

Atom	*x*	*y*	*z*
Gd(1)	1 134	2 500	244
N(1)	3 017(4)	2 589(19)	291(5)
O(11)	2 576(7)	1 815(10)	364(14)
O(12)	2 609(8)	3 313(10)	269(12)
O(13)	3 815(3)	2 659(9)	219(7)
N(2)	1 068(4)	2 588(28)	−2 344(5)
O(21)	394(3)	2 507(11)	−1 688(4)
O(22)	1 773(3)	2 376(20)	−1 780(5)
O(23)	1 013(4)	2 455(25)	−3 427(5)
N(3)	1 177(3)	2 530(9)	2 822(4)
O(31)	1 189(9)	3 267(9)	2 217(13)
O(32)	1 181(8)	1 765(9)	2 225(13)
O(33)	1 154(4)	2 482(13)	3 913(4)
O(90)	759(9)	4 161(7)	−29(10)
H(01)	846(45)	4 616(32)	449(51)
H(02)	743(69)	4 664(42)	−434(82)
O(91)	698(9)	972(7)	−31(13)
H(03)	653(38)	708(45)	−716(28)
H(04)	1 032(114)	731(180)	506(157)
O(92)	−398(3)	2 469(10)	798(5)
H(05)	−782(58)	2 084(58)	1 056(100)
H(06)	−624(77)	2 997(37)	627(111)
O(1)	3 749(12)	4 596(11)	6 666(20)
C(1)	3 241(14)	3 847(13)	6 219(18)
C(2)	2 829(12)	4 038(15)	5 031(20)
O(2)	3 492(7)	4 064(8)	4 144(15)
C(3)	3 231(12)	4 395(17)	2 964(16)
C(4)	4 023(10)	4 643(14)	2 190(19)
O(3)	4 665(7)	5 181(6)	2 580(10)
C(5)	5 422(8)	5 333(9)	1 868(10)
C(6)	6 048(11)	5 979(8)	2 445(16)
O(4)	6 370(6)	5 566(7)	3 466(11)
C(7)	7 069(9)	6 140(10)	4 016(18)
C(8)	7 261(8)	5 761(12)	5 280(18)
O(5)	6 547(9)	5 908(8)	6 030(10)
C(9)	6 711(9)	5 515(11)	7 157(14)
C(10)	5 906(11)	5 554(10)	7 888(9)
O(6)	5 455(10)	4 800(8)	7 358(11)
C(11)	4 758(15)	4 721(19)	8 212(18)
C(12)	4 004(9)	4 222(17)	7 695(15)

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

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