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Synthesis and Crystal Structure of a Complex between Lanthanum Nitrate and a Bicyclic Polyether

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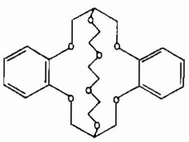
Abstract

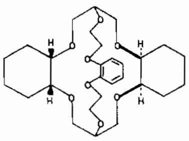
Reaction between lanthanum nitrate hexahydrate and a macrobicyclic polyether in ethanol has yielded a product of overall stoichiometry 3:2. The ligand, 21R, 26S, 29R, 34S-21, 22, 23, 24, 25, 26, 29, 30, 31,32,33,34-dodecahydro-1,4,7,14,17,20,28,35-octaoxa$(2^{3,29}\mathit{syn}2^{18,34}\mathit{syn})$ (7.7) orthocyclophane, L, provides 8 oxygen donor atoms. Crystals were obtained from MeOH/EtOH (50/50). Crystal structure determination on 9590 observations, $R = 0.059$, has shown the triclinic unit cell, $a = 26.562(6)$, $b = 13.486(3)$, $c = 12.154(3)$ Å, $\alpha = 63.9(1)$, $\beta = 100.0(1)$, $\gamma = 102.0(1)°$ space group $P\bar{1}$, $V = 3806$ Å to contain, as the asymmetric unit, two complex cations $(La(NO_3)_2L)^+$ and one complex anion $(La(NO_3)_5MeOH)^{2-}$. The lanthanum is 11-coordinated in the anion and one of the cations, in which there is one bidentate and one monodentate nitrate ion, and 12-coordinated in the other cation. For the monodentate nitrate La–O = 2.448(9) Å, all other nitrate ions are bidentate (La–O = 2.594(9)–2.743(10) Å). Most La–O bonds are shorter in the 11 than in the 12-coordinated cation. There are large differences in La–O bond lengths according to the nature of the carbon atoms to which the oxygen is attached. The methanol molecule forms a hydrogen bond to one oxygen atom of the monodentate nitrate group.

Introduction

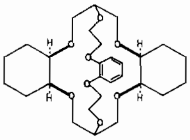
As part of an investigation on the effect of small changes in radius of the cation on complexes formed by bicyclic polyethers, we have already made and reported [1] on the structure of the 1:1 complex between lanthanum chloride and **I**. This, while interesting in itself, indicated that the required comparison could not be achieved by making the corresponding complexes of the other lanthanides. The crystal structure contained disordered water in channels and also showed that some hydrolysis had taken place so that the formula was $C_{24}H_{30}O_8 \cdot LaCl_x(OH)_{3-x} \cdot yH_2O$ with neither x nor y being exactly determinable. This limited the reliability with which the whole electron density could be matched and, hence, the true accuracy of the La–O bond lengths. To reduce the risk of hydrolysis we have now used lanthanum nitrate and taken the opportunity to investigate three isomers, bicyclic polyethers **II**, which have very different formation constants with alkali metals [2]. Here we describe the synthesis and crystal structure of the complex with the isomer of **II**, *viz.* **L** which has the highest formation constant and for which the crystal structure of the potassium perchlorate complex, $[LKOClO_3]°$, is known [3].



I



II



L

Experimental

The complex was prepared by mixing an ethanolic solution of the ligand, **L**, with an ethanolic solution of $La(NO_3)_3 \cdot 6H_2O$ (Ventron). Salt/ligand = 1.5. A white solid precipitated immediately. The crude product was recrystallized from a mixture of MeOH/EtOH (50:50). Calcd. for $La_3(NO_3)_9(C_{28}H_{42}O_8)_2$-$CH_3OH$: C, 33.88; H, 4.39; N, 6.24. Found C, 34.05; H, 4.39, N, 6.08%. The compound turned brown but did not melt below 270 °C. In the infrared spectrum a broad band at 3380 cm^{-1} indicated the presence of a hydrogen-bonded hydroxy group, overlap between ligand and nitrate frequencies precluded any conclusions about either.

Crystal Structure Determination

Crystal Data

$2[La(NO_3)_2C_{28}H_{42}O_8]^+[La(NO_3)_5CH_3OH]^=$, $C_{57}H_{88}La_3N_9O_{44}$, M = 2020, triclinic, space group $P\bar{1}$ (no. 2) $a = 26.562(6)$, $b = 13.486(3)$, $c = 12.154(3)$ Å, $\alpha = 63.9(1)$, $\beta = 100.0(1)$, $\gamma = 102.0(1)°$, $V = 3806$ Å^3, $F(000) = 2032$, $D_c = 1.75$ g cm^{-3}, $Z = 2$, μ(Mo K$_\alpha$) 16.25 cm^{-1}, λ(Mo K$_\alpha$) = 0.71069 Å.

The crystals are colourless prisms and are moisture sensitive. One 0.08 × 0.18 × 0.35 mm was mounted on a fibre and coated with epoxy resin for intensity measurements on a Philips PW 1100 4-circle diffractometer with graphite-monochromated MoK$_\alpha$ radiation.

The unit cell was determined on the basis of 25 strong reflections found by mounting the crystal at random, varying the orientation angles ϕ and χ over a range of 120° each, with the detector position varying between $\theta = 6$ and $\theta = 10°$. For the determination of precise lattice parameters 20 strong reflections with $10 \leqslant \theta \leqslant 14°$ were considered. The intensities of two standard reflections, $-7, 4, 2$ and $5, 3, 2$, monitored at 180 min intervals showed a slight but constant decay in intensity and, at the end of data collection, the decrease in intensity of the two standard reflections was of the order of 8%.

A $\theta/2\theta$ scan was used with scan speed 1.8° min^{-1} and scan width of 1.2°; stationary backgrounds were counted for 20 s. A total of 13372 reflections were measured out to $2\theta = 50°$ yielding 9590 unique observations with $I \geqslant 3\sigma(I)$. Lorentz, polarization and absorption corrections were applied following the method of North *et al.* [4]. The phase problem was solved with difficulty by a mixture of Patterson and direct methods. There are three independent lanthanum atoms in the asymmetric unit. Successive difference electron density syntheses eventually revealed all the non-hydrogen atoms and showed the structure to consist of cat. (1) $(La(1)L(NO_3)_2)^+$, cat. (2) $(La(2)L(NO_3)_2)^+$, and an. (3) $(La(3)(NO_3)_5$-(CH_3OH). SHELX-76 programs [5] were used for refinement allowing anisotropic vibration for the $[La(NO_3)_5(CH_3OH)]^{2-}$ moiety and for the other two lanthanum ions and individual isotropic vibration parameters for the others. It was necessary to use block matrices with the sequence: (i) cat. (1) and an. (3), (ii) cat. (2) and an. (3), (iii) cat. (1) and (iv) cat. (2) for isotropic refinement; this was modified to: (i) cat. (1), (ii) an. (3) and (iii) cat. (2) for the partial anisotropic refinement in the last refinement cycles. Only the hydrogen atoms defining the isomer of the macrocycle were introduced in calculated positions (C–H 0.98 Å) with a common isotropic temperature factor $U = 0.08$ Å^2. The weighting scheme was $w = 4.58\ (\sigma^2(F_o) + 0.0004(F_o)^2)^{-1}$ and refinement concluded with $R = 0.059$, $R_w = 0.063$.

On the final difference map, two peaks of the order of 1 e/Å^3 were close to La(1) and La(3), while a peak of the same order was 0.56 Å from C(17) indicating a possible alternative position of the atom of 1.33 Å from O(1) and 1.45 Å from C(16). Other residuals of about 0.5 e/Å^3 near the nitrate groups in the complex cations were probably due to the isotropic refinement of the atoms (the number of hydrogen atoms and anisotropic vibration parameters were limited by the capacity of our version of the SHELX-76 program). The most significant parameter shift was 0.8 of the corresponding standard deviation. Scattering factors for La, C, N, O and H were from ref. 6, that for La making allowance for anomalous dispersion.

Computation for structure solution and refinement was carried out on the CYBER 76 computer of Centro di Calcolo Interuniversitario, Italia Nord-Orientale. The molecular geometry was calculated on a VAX 11/750 computer.

Final parameters for the atoms are in Table I, bond lengths and bond angles around the lanthanum atoms are in Table II. Table III summarises the bond lengths in the nitrate and the organic ligands.

Torsion angles for the bicyclic ligands and the atom numbering scheme are displayed in Fig. 1.

Results and Discussion

The overall stoichiometry $3La(NO_3)_3$:2L:1MeOH has been established by crystal structure determination. It is achieved by the formation of an anion and the two complex +1 cations with a low charge density. In this, the behaviour is reminiscent of the 4:3 $Ln(NO_3)_3$:18-crown-6 [7] and $La(NO_3)_3$:penta ethylene glycol dimethyl ether [8] and $La(NO_3)_3$: 222 cryptand [9] systems in which there are three complex +1 cations with a $(Ln(NO_3)_6)^{3-}$ anion. The relative stability of the +1 cation compared with the neutral $[Ln(NO_3)_3(18\text{-crown-}6)]$ molecule in thermogravimetric analyses and ^{252}Cf desorption mass spectra was noted [10] although the neutral entity was isolated in crystalline form for the large cations in that system.

TABLE I. Fractional Coordinates ($\times10^4$) with e.s.d.s in Parentheses, Hydrogen ($\times10^3$) and $U_{iso\ or\ eq}$.

	x	*y*	*z*	$U_{eq\ or\ iso}$ [a]		*x*	*y*	*z*
La(1)	8846.0(2)	6091.8(4)	2133.7(5)	35.6(2)*				
N(1)	7919(4)	4729(8)	1312(9)	72(3)				
N(11)	10037(3)	6428(7)	2434(8)	56(2)				
O(110)	7465(3)	4360(7)	997(8)	84(2)				
O(111)	9790(3)	7131(6)	1566(6)	54(2)				
O(112)	9785(3)	5616(6)	3212(6)	58(2)				
O(113)	10519(4)	6546(8)	2499(8)	94(3)				
O(18)	8211(3)	5310(7)	562(8)	87(2)				
O(19)	8038(3)	4551(7)	2438(8)	76(2)				
O(1)	8828(2)	4716(5)	4380(6)	49(2)				
O(11)	9304(2)	5502(5)	625(6)	45(2)				
O(12)	9058(3)	4010(6)	2825(6)	57(2)				
O(13)	8847(2)	7348(5)	−138(6)	51(2)				
C(1)	9272(4)	4371(8)	878(9)	48(2)				
C(11)	9379(4)	4034(9)	−6(10)	59(3)				
C(12)	9314(5)	2867(10)	331(11)	68(3)				
C(13)	9167(5)	2141(10)	1424(11)	73(3)				
C(14)	9069(4)	2457(9)	2321(10)	60(3)				
C(15)	9134(4)	3592(8)	2024(9)	51(2)				
C(16)	9002(4)	3202(9)	4089(10)	58(3)				
C(17)	9040(6)	3704(12)	4878(14)	99(4)				
C(18)	8759(4)	5212(8)	5180(9)	47(2)				
C(19)	9219(4)	6152(9)	5088(10)	56(3)				
C(110)	8221(4)	5541(8)	4776(9)	50(2)				
O(16)	9252(2)	6998(5)	3842(6)	48(2)				
C(111)	9092(4)	8056(9)	3571(9)	55(3)	H(111)	872	792	366
C(112)	9374(5)	8583(10)	4490(11)	74(3)				
C(116)	9206(4)	8833(9)	2281(10)	59(3)	H(116)	907	952	208
C(115)	9791(5)	9249(10)	2083(11)	73(3)				
O(17)	8965(2)	8273(5)	1509(6)	50(2)				
C(113)	9959(5)	8904(11)	4308(12)	84(4)				
C(114)	10065(5)	9737(11)	3043(13)	83(4)				
C(117)	8936(4)	9010(10)	208(11)	63(3)				
C(118)	8620(4)	8352(8)	−496(9)	53(2)				
C(119)	8056(4)	7926(9)	−266(10)	61(3)				
O(14)	7984(2)	7145(5)	1011(6)	49(2)				
C(120)	7752(4)	7543(8)	1710(9)	52(2)	H(120)	799	819	175
C(121)	7226(5)	7941(10)	1113(11)	75(3)				
C(125)	7690(3)	6611(7)	2982(8)	43(2)	H(125)	758	690	350
C(124)	7263(4)	5640(9)	3013(10)	61(3)				
O(15)	8191(2)	6216(5)	3461(5)	41(1)				
C(122)	6811(5)	6995(11)	1109(11)	74(3)				
C(123)	6745(5)	6092(10)	2447(11)	69(3)				
C(126)	9250(4)	7404(8)	−872(9)	52(2)				
C(127)	9254(4)	6248(9)	−705(10)	58(3)				
La(3)	2466.2(2)	772.5(4)	4746.6(5)	43.0(2)*				
N(3)	1612(3)	−543(7)	3684(8)	56(4)*				
N(31)	3158(4)	1733(8)	2658(8)	62(4)*				
N(32)	2036(3)	101(7)	7212(8)	60(4)*				
N(33)	3430(4)	1520(8)	6118(7)	63(4)*				
N(34)	1803(4)	2687(7)	3526(7)	63(4)*				
O(3)	2001(3)	52(6)	3097(6)	61(4)*				
O(31)	1624(3)	−633(6)	4772(7)	64(4)*				
O(32)	1248(3)	−996(7)	3204(8)	87(5)*				
O(33)	3184(3)	811(6)	3522(8)	76(4)*				
O(34)	2823(3)	2254(6)	2672(7)	76(4)*				
O(35)	3443(4)	2147(8)	1828(8)	103(5)*				

(continued overleaf)

TABLE I. *(continued)*

	x	y	z	U_{eq} or $_{iso}$[a]		x	y	z
O(36)	1968(4)	967(7)	6306(8)	118(5)*				
O(37)	2285(4)	−497(8)	7085(8)	108(5)*				
O(38)	1883(3)	−141(7)	8225(7)	79(4)*				
O(39)	3325(4)	545(7)	6249(8)	96(5)*				
O(310)	3149(3)	2178(6)	5345(8)	93(4)*				
O(311)	3809(3)	1843(7)	6703(8)	87(4)*				
O(312)	2227(3)	2794(6)	4101(7)	68(4)*				
O(313)	1653(3)	1755(7)	3442(8)	82(4)*				
O(314)	1521(3)	3411(6)	3094(7)	79(4)*				
O(315)	2752(3)	−1101(5)	5377(7)	63(4)*				
C(3)	2551(5)	−2192(10)	6178(15)	101(8)*				
La(2)	6031.5(2)	2642.8(4)	8007.8(4)	33.6(2)*				
N(2)	6539(4)	2384(8)	5639(9)	67(2)				
N(21)	4929(3)	2844(7)	8177(8)	56(2)				
O(28)	6555(3)	2563(6)	6586(6)	57(2)				
O(29)	6504(4)	1419(8)	5749(9)	98(3)				
O(210)	6511(4)	3151(8)	4601(9)	101(3)				
O(211)	5266(3)	3707(6)	7696(6)	56(2)				
O(212)	5058(3)	1925(6)	8419(6)	56(2)				
O(213)	4504(3)	2950(7)	8366(8)	87(2)				
O(2)	5622(2)	3517(5)	5626(5)	45(2)				
O(21)	5530(2)	1369(5)	6784(6)	48(2)				
O(22)	5814(2)	498(5)	9133(5)	43(1)				
O(27)	6245(2)	4730(5)	6703(5)	41(1)				
C(2)	5215(4)	2936(8)	5187(8)	45(2)				
C(21)	5167(4)	1780(8)	5796(8)	44(2)				
C(22)	4767(4)	1076(9)	5448(10)	57(3)				
C(23)	4409(5)	1601(10)	4435(11)	69(3)				
C(24)	4455(4)	2725(10)	3833(10)	65(3)				
C(25)	4863(4)	3439(9)	4181(10)	58(3)				
C(26)	5513(4)	164(9)	7379(10)	58(3)				
C(27)	5929(4)	−75(8)	8464(9)	55(2)				
C(28)	6027(4)	94(8)	10423(9)	47(2)				
C(29)	5758(4)	616(8)	10989(8)	47(2)				
C(210)	6612(4)	385(8)	10473(9)	54(2)				
O(23)	5864(2)	1839(5)	10405(5)	40(1)				
C(211)	6202(4)	2387(8)	11128(8)	47(2)	H(211)	654	216	1.127
C(212)	6029(4)	2029(9)	12424(10)	59(3)				
C(216)	6197(4)	3617(8)	10401(8)	45(2)	H(216)	645	401	1.082
C(215)	5685(4)	3999(9)	10328(10)	58(3)				
O(24)	6330(2)	3898(5)	9178(5)	43(1)				
C(213)	5505(4)	2345(10)	12369(10)	67(3)				
C(214)	5531(5)	3610(10)	11671(11)	70(3)				
C(217)	6497(4)	5085(8)	8490(9)	53(2)				
C(218)	6676(4)	5262(8)	7271(9)	48(2)				
C(219)	7177(4)	4812(9)	7431(10)	61(3)				
O(25)	7076(2)	3588(5)	8043(6)	46(2)				
C(220)	7410(4)	3094(8)	9144(9)	51(2)	H(220)	734	332	976
C(221)	7987(4)	3502(9)	8990(10)	62(3)				
C(225)	7291(4)	1845(8)	9542(9)	49(2)	H(225)	748	146	1.035
C(224)	7482(4)	1449(9)	8697(10)	60(3)				
O(26)	6744(2)	1535(5)	9607(5)	42(1)				
C(222)	8183(5)	3161(10)	8120(11)	74(3)				
C(223)	8072(5)	1889(10)	8562(11)	73(3)				
C(226)	6258(4)	5111(8)	5387(9)	50(2)				
C(227)	5729(4)	4698(8)	4919(9)	50(2)				

[a] U_{eq} is denoted by an asterisk.

TABLE IIa. Lanthanum–Oxygen Bond Lengths (Å).

In the cations			
La(1)–O(1)	2539(6)	La(2)–O(27)	2.545(5)
La(1)–O(11)	2.817(8)	La(2)–O(21)	2.746(8)
La(1)–O(12)	2.707(8)	La(2)–O(2)	2.718(6)
La(1)–O(13)	2.525(6)	La(2)–O(22)	2.581(6)
La(1)–O(14)	2.772(6)	La(2)–O(23)	2.707(6)
La(1)–O(15)	2.644(7)	La(2)–O(24)	2.586(8)
La(1)–O(16)	2.807(8)	La(2)–O(25)	2.803(6)
La(1)–O(17)	2.656(7)	La(2)–O(26)	2.634(6)
La(1)–O(18)$_{nit}$	2.743(10)	La(2)–O(211)$_{nit}$	2.611(8)
La(1)–O(19)$_{nit}$	2.607(8)	La(2)–O(212)$_{nit}$	2.618(7)
La(1)–O(111)$_{nit}$	2.648(6)	La(2)–O(28)$_{nit}$	2.448(9)
La(1)–O(112)$_{nit}$	2.673(7)		
In the anion			
La(3)–O(3)	2.616(9)		
La(3)–O(31)	2.609(7)		
La(3)–O(33)	2.594(10)		
La(3)–O(34)	2.616(7)		
La(3)–O(36)	2.620(12)		
La(3)–O(37)	2.662(8)		
La(3)–O(39)	2.644(9)		
La(3)–O(310)	2.595(9)		
La(3)–O(312)	2.668(8)		
La(3)–O(313)	2.663(8)		
La(3)–O(315)[a]	2.538(8)		

[a] methanol oxygen.

TABLE IIb. Bond Angles (°) Subtended at the Lanthanum Atoms in the Complex Cations, in the Form O_a–La–O_b. Standard Deviations are 0.2–0.3°. The Arrangement Corresponds to the Same Orientation of the Ligand for each La and for the $KClO_4$ Complex (Bandy and Truter, 1982).

La(1)

O(b)	O(a)	O(14)	O(13)	O(11)	O(12)	O(1)	O(15)	O(17)	O(16)	O(18)	O(19)	O(111)
O(13)		63.4	–									
O(11)		114.7	60.8	–								
O(12)		134.5	115.7	56.9	–							
O(1)		117.3	176.1	116.3	60.9	–						
O(15)		59.2	120.5	163.3	114.6	61.3	–					
O(17)		63.1	63.6	114.5	161.6	120.2	77.8	–				
O(16)		102.3	119.3	133.1	113.8	64.6	62.5	58.2	–			
O(18)		64.7	63.4	61.7	74.8	113.4	103.1	117.1	165.0	–		
O(19)		72.1	107.8	95.3	65.1	69.4	68.2	133.3	123.8	47.0	–	
O(111)		121.5	69.1	63.6	95.8	112.4	133.1	66.4	73.1	119.5	157.8	–
O(112)		164.4	112.9	72.2	61.1	67.5	118.0	101.5	65.5	128.6	122.2	47.4

La(2)

O(b)	O(a)	O(23)	O(22)	O(21)	O(2)	O(27)	O(24)	O(26)	O(25)	O(211)	O(212)
O(22)		64.5	–								
O(21)		116.1	58.4	–							
O(2)		146.6	114.3	56.4	–						
O(27)		121.3	174.2	116.4	60.9	–					
O(24)		60.1	122.3	169.2	120.3	63.3	–				
O(26)		64.4	61.7	107.2	147.2	120.2	80.7	–			
O(25)		101.6	117.5	128.0	107.0	63.0	62.3	58.1	–		

(continued overleaf)

TABLE IIb. *(continued)*

O(211)	82.3	114.2	96.3	67.6	67.7	73.4	145.1	124.2	–		
O(212)	66.3	66.0	66.5	82.5	115.0	103.4	119.0	165.4	48.5	–	
O(28)	144.3	93.6	66.2	66.9	81.6	123.2	80.6	62.3	133.3	132.3	–

TABLE IIc. Bond Angles (°) Subtended at Lanthanum in the Anion. Standard Deviations are 0.3–0.4°.

La(3)	O(a)	O(3)	O(31)	O(33)	O(34)	O(36)	O(37)	O(39)	O(310)	O(312)	O(313)	
O(b)												
O(31)		48.8	–									
O(33)		73.6	116.1	–								
O(34)		75.1	121.1	47.7	–							
O(36)		122.8	79.2	163.5	131.3	–						
O(37)		117.7	72.1	129.9	166.7	46.1	–					
O(39)		137.8	131.2	73.5	100.8	91.9	67.7	–				
O(310)		150.1	159.4	84.0	75.1	80.4	91.8	47.2	–			
O(312)		108.2	109.8	112.9	67.4	63.9	108.8	108.6	62.4	–		
O(313)		65.5	66.5	116.9	76.0	73.7	111.4	155.5	109.7	47.5	–	
O(315)		74.1	73.7	65.0	111.1	117.3	71.9	68.3	114.3	176.5	135.8	–

TABLE III. Ranges and Means of Bond Lengths (Å), in the Bicyclic Polyethers.

Type of bond	Range (e.s.d. from [5])	Mean	σ_{mean}	$\sigma_{individual}$
C–C aromatic	1.323(16)–1.430(17)	1.396	(10)	(33)
C–C cyclohexano	1.484(17)–1.583(22)	1.536	(6)	(27)
C–C aliphatic[a]	1.483(17)–1.546(14)	1.520	(6)	(21)
O–C aromatic	1.372(12)–1.404(13)	1.383	(6)	(13)
O–C aliphatic[b]	1.422(18)–1.480(17)	1.453	(3)	(14)
N–O coordinated	1.187(13)–1.283(10)	1.248	(6)	(26)
N–O non-coordinated	1.223(14)–1.267(13)	1.239	(4)	(14)

[a] C(16)–C(17) 1.378(25) omitted. [b] O(315)–C(3) 1.410(13) omitted. Numbers in parentheses correspond to the least significant digits.

The asymmetric unit consists of one complex cation in which the lanthanum, La(1), is 12-coordinated by the eight oxygen atoms of the ligand L(1) and two bidentate nitrate ions as shown in Fig. 2(a), one complex cation in which La(2) is 11-coordinated by the eight oxygen atoms of the ligand L(2), one bidentate and one monodentate nitrate ion as shown in Fig. 2(b) and one complex anion (shown with its atomic numbering scheme in Fig. 2(c). In the latter, La(3) is 11-coordinated by five bidentate nitrate anions and one methanol molecule. Each anion is surrounded by six cations, three each of cat. (1) and cat. (2); one of the latter is an acceptor of the hydrogen bond; see below. Each cat. (1) is in contact with three anions, one cat. (2), and two cat. (1) cations, while each cat. (2) is in contact with three anions, one cat. (1), and two cat. (2) cations. Cation–cation contact is not uncommon in complexes with very low charge density. There are only two interionic contacts less than 3.0 Å, from the methanol oxygen O(315) to O(29^{I}), (I is at $1-x, -y, 1-z$) 2.788(16) Å, and the other between O(33) and O(29^{I}) 2.992(14) Å. The latter is a contact between two nitrate oxygen atoms, the former probably being a hydrogen bond, the acceptor oxygen atom being one of the two uncoordinated ones of the monodentate nitrate group La(3)–O(315)···O(29^{I}) 123.5(4)° and O(315)···O(29^{I})–N(2^{I}) 114.0(8)°. About the same centre of symmetry, ½, 0, ½, the related hydrogen bond is O(29)···O(315^{I}). (see Fig. 3). This hydrogen bond between the coordinated methanol and the oxygen of the monodentate nitrate group seems to stabilize the lower coordination number 11 in the two complex species.

Before discussing the molecular dimensions, the validity of the standard deviations were considered. It was necessary to carry out refinement in blocks so the e.s.d.s may be underestimated if there

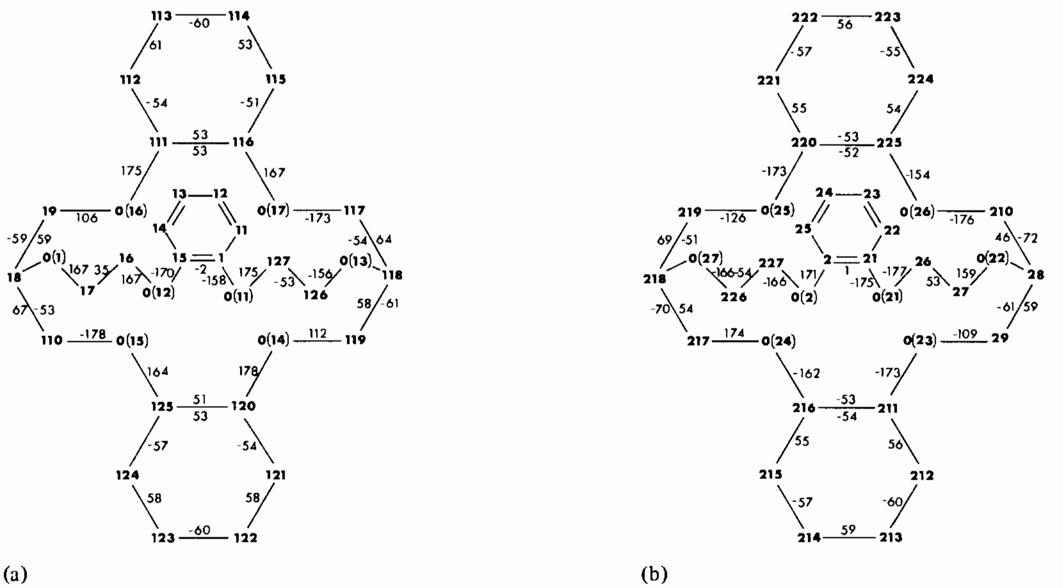


Fig. 1. The numbering schemes for the atoms of the bicyclic ligands. Oxygen atoms are designated specifically and carbon atoms by numbers only. Most of the torsion angles are also shown, e.s.d.s' range from 0.9° (at 180°) to 2.5° (at 0°); for the benzene rings angles are 0 or 180° to within 3.6°. Molecule (a) is coordinated to La(1) as are the bidentate nitrate ions N(1), O(18), O(19), O(110) and N(11), O(111), O(112) and O(113); with O(110) and O(113) not coordinated. Additional torsion angles are C(117)–C(118)–O(13)–C(126) –91°, C(119)–C(118)–O(13)–C(126) 143°, C(110)–C(18)–O(1)–C(17) –135°, C(19)–C(18)–O(1)–C(17) 99°. Molecule (b) is coordinated to La(2) as are the bidentate nitrate ion N(21), O(211), O(212), O(213) with O(213) not coordinated and the monodentate nitrate ion N(2), O(28), O(29), O(210) with O(28) coordinated. Additional torsion angles are C(210)–C(28)–O(22)–C(27) 68°, C(29)–C(28)–O(22)–C(27) –167°, C(217)–C(218)–O(27)–C(226) 160°, C(219)–C(218)–O(27)–C(226) –76°. The torsion angles given correspond to the coordinates in Table I; for the centrosymmetrically related cations all the signs are reversed.

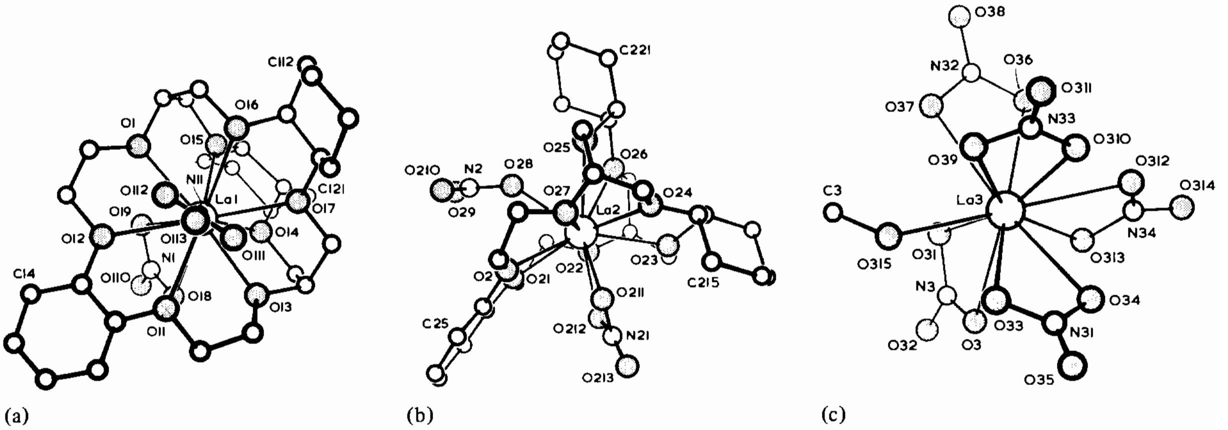


Fig. 2. (a) Cation (1) viewed approximately along the normal to the plane of the benzene ring. (b) Cation (2) showing the mono- and bidentate coordination of the nitrate ligands. The view is normal to the triangular faces of the approximate trigonal prism. (c) The complex anion with numbering for the atoms.

are large correlation coefficients. The actual values are close to those calculated from Cruickshank's formula [11]. For chemically similar bonds the spread about the mean values gives an estimate of the standard deviation. Table III gives the mean values of the various kinds of bond; for the individual values, the underestimate appears to be a factor of two. Within the nitrate ions, the N–O bond lengths average 1.245(5) Å whether the oxygen atoms are coordinated or not. The values of the means of the C–O and C–C bonds are normal. Because it is frequently found in polyethers that the CH_2–CH_2-bonds are signifi-

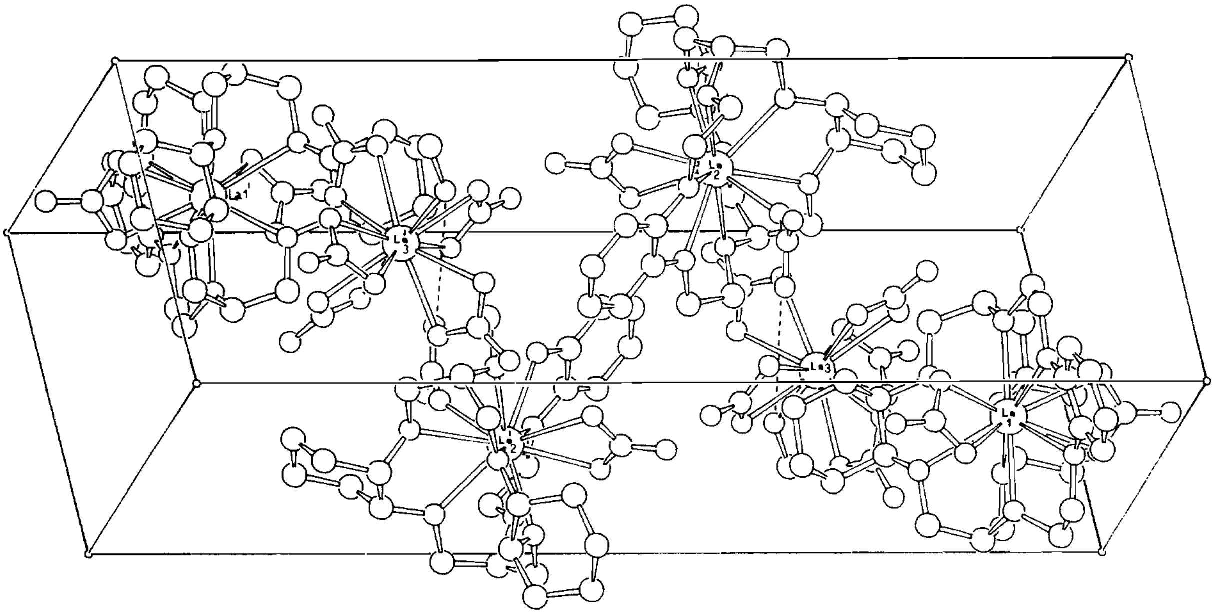


Fig. 3. Perspective view of the unit cell content. Dotted lines indicate hydrogen bonds; primed atoms are centrosymmetrically related to the unprimed.

cantly less than 1.54 Å these have been distinguished from those of the cyclohexane rings.

Comparison of the La–O(nitrate) distances in the 12- and 11-coordinated ions shows, most strikingly; La–O(28) (monodentate) to be significantly shorter than any of the La–O (bidentate) distances. In the 11-coordinated anion the range 2.594–2.668 Å suggests a shortening of about 0.03 Å compared with the 12-coordinated anionic species, e.g. 2.663(8)–2.731(7) Å and 2.675(5)–2.716(6) Å in $[La(NO_3)_5(H_2O)_2]^{2-}$ [12], 2.615–2.709 Å in $[La(NO_3)_6]^{3-}$ [10]. There is a wide spread in the four distances in the 12-coordinated cat. (**1**), 2.607(8) to 2.743(10) Å, the mean 2.668 Å being similar to that for other chelate nitrates; a truly comparable arrangement is that in the 222 cryptand [9] in which the ligand provides eight donor atoms. The La–O bidentate nitrate distances, in cat. (**2**) 2.611(8) and 2.618(8) Å, are smaller than the average for cat. (**1**), indicating a shortening with a lower overall coordination number.

For the organic ligand there is a wide range of La–O distances in each cation. The ligand occupies approximately an end-capped trigonal prism about the lanthanum. Each triangular face is formed by one oxygen atom from each of the six-membered (benzene or cyclohexano) rings, *i.e.* for La(1) these atoms are O(12), O(15), O(16) and O(11), O(14), O(17); for La(2) these atoms are O(2), O(24), O(25) and O(21), O(23), O(26). The angles between the normals to the pairs of planes are 0.2° and 0.4° for cations (**1**) and (**2**), respectively. The skew angle is 12(1)° in each cation compared with 0° for a trigonal prism. The end capping atoms are O(1) and O(13) for La(1) and O(27) and O(22) for La(2). As shown in Table IIa, the La–O bonds to end capping oxygen atoms are the shortest but, surprisingly, are longer for La(2) than for La(1). The next shortest distances are to the oxygen atoms which occupy equatorial positions on the cyclohexano rings O(17), O(15), O(24) and O(26) and, for these, La(1) bonds are longer than those to La(2). The remaining distances are to aromatic oxygen atoms and to the axial oxygen atoms of the cyclohexano rings. The longer bonds to axial than to equatorial oxygen atoms are a common feature of monocyclic and macrobicyclic rings substituted by cyclohexano rings and have been attributed to steric interactions [13].

The general pattern of metal–oxygen bond lengths from L is similar to that shown by the potassium perchlorate complex [3] but in that case there was only one coordinated anion and the potassium ion appeared to be drawn towards it, giving rise to relatively longer bonds to one pair of cyclohexano oxygen atoms. The remaining six oxygen atoms and the potassium ion were roughly coplanar (±0.3 Å) giving an approximate benzo–cyclohexano 18-crown-6 entity. As there are two coordinated anions for each lanthanum in the present complexes neither shows a pseudo 18-crown-6 ring, nor significant differences between bond lengths to the two sets of cyclohexano oxygen atoms (see Figs. 2(a) and 2(b)).

The quantitative differences attributable to the requirements of accommodating bidentate and monodentate nitrate ions are in the torsion angles, Figs. 1(a) and 1(b) and in the bond angles at the lanthanum atoms (Table IIb,c). As Figs. 1(a) and 1(b) show, the dicyclohexano–14-crown-4 rings have approximate 2-fold axes of symmetry essentially normal to the plane of the four oxygens of the 14-crown-4 moieties. The maximum deviation of about 17° from C_2 symmetry is in La(2) and involves the C(219) and C(29) atoms. At C(219) there is also the maximum difference of 20° between the two ligands (the corresponding torsion angles at C(19) and C(219) are 106 and 126°, respectively). But it is at the C–O bonds at the bridge-head carbon atoms, e.g. C(18)–O(1), that there are largest differences ranging from a minimum of 23° to a maximum of 25° (see caption to Fig. 1). Furthermore, there is not a 2-fold symmetry across the C(18) to C(118) and C(28) to C(218) links because central $O–CH_2–CH_2–O$ torsion angles have opposite signs (the small value for C(16)–C(17), as its improbable bond length, 1.38 Å indicates some disorder).

Each benzene ring and attached oxygen atoms are coplanar, La(1) is 0.78(1) and La(2) is 1.04(1) Å out of their respective planes, and the normals to the benzene rings are at 72.0(3)° and 74.5(3)° to the normals to the planes of the oxygen atoms of the 14-crown-4 rings. However, the plane of the four link oxygen atoms O(1), O(12), O(11) and O(13) is 87.2(2)°, *i.e.* nearly normal to that of the other four, while that of O(2), O(27), O(21), O(22) is 81.7(2) to that of O(23), O(24), O(25) and O(26). The deviation from 90° reflects the difference in the two rectangular faces of the trigonal prism to accomodate a monodentate nitrate on O(2), O(21), O(25), O(26); comparable angles subtended at lanthanum across the diagonals of the rectangular faces are in Table IIb, e.g. O(2)–La(2)–O(26) 147.2° while on the bidentate side O(21)–La(2)–O(24) is 169.2° slightly larger than the corresponding values, 161.6 and 163.3° for La(1).

A comparison with the structure of $(C_{20}H_{30}O_8)$-$LaCl_x(OH)_{3-x}\cdot yH_2O$ [1] shows that in the chloro complex, the large cations of low charge density pack together leaving channels in which disordered chloride ions and water molecules are held by hydrogen bonds which stabilize the crystal. In the nitrate complex it is the stability of the large complex anion $[La(NO_3)_5CH_3OH]^{2-}$ which allows two complex cations to be formed and gives rise to a structure with the whole volume of the crystal filled with ordered entities. An additional stabilizing factor is the CH_3OH––O hydrogen bond to one oxygen atom of a nitrate ligand on La(2), this nitro group then coordinating to the lanthanum through only one oxygen atom. In general it seems that with acyclic, monocyclic and bicyclic polyether ligands the lanthanide nitrates form systems which depend, in part on the radius of the lanthanide and hence on the number of chelate nitro groups in complex anions, these then being counterbalanced by complex cations. For the larger lanthanides including La, itself, six chelate nitrato groups can be accomodated or, as in the present work, five chelate nitrato groups and a solvent molecule. It is this tendency which gives rise to stoichiometries $Ln(NO_3)_3$:L other than 1:1.

Acknowledgements

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