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The Crystal Structure of Tetraethylenglycoltrinitrato Lanthanum(III): An Example of Undecacoordination

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The title compound has been prepared by reacting La(NO_3)$_3$ with tetraethylenglycol. The structure was determined from counter-collected data and refined to R = 0.049 for 2310 reflections. The space group is P2_1/n, monoclinic, with cell dimensions $a = 12.75(1)$, $b = 16.84(1)$, $c = 8.15(1)$ Å, $\beta = 101.27(3)^\circ$, $D_x = 2.01$ g cm^{-3} *for* $Z = 4$.

The pentadentate organic ligand wraps around the metal ion which is also bound to three chelate nitrato groups, thus achieving the rather uncommon undecacoordination. Five La–O(nitrate) (mean 2.61 Å) compare well with the two La–O (alcohol) bond distances (mean 2.58 Å). One La–O (nitrate) (2.79 Å) and the three La–O(ether) bond distances (mean 2.70 Å) are significantly longer. Weak intra- and intermolecular hydrogen bonds are also present.

Introduction

Previous work on lanthanide complexes with polydentate ligands has been mainly devoted to coordination compounds with macrocyclic ligands such as crown ethers and cryptands, but little attention has been paid to the behaviour of these ions towards the acyclic polyethers [1, 2]. Recently, crystalline complexes of alkaline and alkaline earth metal ions with this type of ligands and glycols have been isolated [3–5]. We report here the crystal structure of tetraethylenglycoltrinitratolanthanum(III). The synthesis of this complex has been already reported [2].

Experimental

Preparation

A very diluted solution of La(NO_3)$_3$·6H_2O in anhydrous CH_3CN was added to an equimolecular solution of tetraethylenglycol in the same solvent and the resulting mixture was refluxed for 2–3 hr. After cooling and partial evaporation of the solvent pale pink crystals of the complex were obtained*. *Anal.* Calcd. for ($C_8H_{18}O_5$)(NO_3)$_3$La: C = 18.50, H = 3.63, N = 8.33%; found: C = 18.89, H = 3.49, N = 8.33%.

X-Ray Data

Crystal data: $C_8H_{18}N_3O_{14}La$; M = 519. Monoclinic, space group P2_1/n, a = 12.75(1), b = 16.84(1), c = 8.15(1) Å, β = 101.27(3)°; V = 1716 Å^3, D_x = 2.01 g cm^{-3} for Z = 4; F(000) = 1024; μ(MoKα) = 27.5 cm^{-1}.

The unit-cell parameters were determined by least-squares calculation based on the angular settings of 25 automatically centered reflections with 2θ between 10° and 34°. Data were collected from a crystal of approximate dimensions 0.1 X 0.2 X 0.1 mm, up to 2θ = 50° in the ω–2θ scan mode using the graphite-monochromated MoKα radiation. Two control reflections were monitored every 100 measured intensities with no significant variation in intensity observed. Only the intensities of 2310 reflections having I > 3σ(I) were used throughout the refinement, corrected for background and for Lorentz and polarization effects. Absorption correction was also applied using a local program.

The structure was solved by the heavy-atom method and refined to the final conventional R value of 0.049 by full-matrix least-squares with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for H atoms. C–H vectors were constrained to lie in geometrically idealized orientations with C–H = 1.00 Å but the H atoms bonded to O(1) and O(5) were

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*The pure complex must be colourless. The pale pink colour probably arises from excessive heating of the CH_3-CN–nitrate mixture.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$).

	x	y	z
La	2975(1)	3904(1)	1321(1)
N(1)	2600(8)	2276(6)	2695(14)
O(11)	3090(7)	2355(5)	1499(12)
O(12)	2201(7)	2900(5)	3171(12)
O(13)	2533(8)	1641(6)	3350(15)
N(2)	2792(9)	5379(6)	−888(14)
O(21)	3656(7)	5180(6)	−6(13)
O(22)	1986(7)	4959(6)	−773(14)
O(23)	2712(9)	5945(6)	−1822(14)
N(3)	5037(8)	3912(7)	4127(13)
O(31)	4364(7)	3373(6)	3860(12)
O(32)	4889(7)	4498(6)	3170(12)
O(33)	5812(7)	3843(7)	5273(13)
O(1)	4753(5)	3612(5)	315(12)
O(2)	2897(6)	3303(6)	−1735(9)
O(3)	1116(5)	3355(4)	−458(10)
O(4)	1073(5)	4346(4)	2138(11)
O(5)	2903(6)	4877(5)	3692(11)
C(1)	4711(11)	3432(9)	−1429(22)
C(2)	3849(14)	2946(12)	−2091(23)
C(3)	2031(12)	2760(7)	−2386(17)
C(4)	1056(11)	3156(9)	−2176(17)
C(5)	115(8)	3682(8)	−192(22)
C(6)	193(8)	3819(8)	1588(20)
C(7)	1160(11)	4577(9)	3809(20)
C(8)	1976(11)	5204(8)	4168(20)
H(11)	4618	3950	−2096
H(12)	5405	3187	−1588
H(21)	3816	2853	−3307
H(22)	3986	2404	−1498
H(31)	2010	2628	−3593
H(32)	2112	2246	−1726
H(41)	953	3664	−2870
H(42)	404	2813	−2574
H(51)	−31	4205	−821
H(52)	−493	3311	−640
H(61)	−482	4052	1817
H(62)	328	3294	2198
H(71)	453	4773	4021
H(72)	1386	4108	4586
H(81)	1729	5697	3496
H(82)	2129	5356	5392
H(1)	5459	3614	1144
H(2)	3614	5052	4365

Anisotropic thermal parameters ($\times 10^4$) in the form
$\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$

	U11	U22	U33	U12	U13	U23
La	201(2)	281(3)	299(3)	−10(2)	75(2)	10(3)
N(1)	238(52)	373(65)	448(68)	−57(47)	−5(50)	38(55)
O(11)	285(45)	411(50)	468(58)	−38(40)	90(43)	−7(47)
O(12)	379(50)	381(53)	559(63)	58(42)	204(47)	83(47)
O(13)	429(55)	520(66)	897(86)	−40(49)	182(58)	288(64)
N(2)	583(76)	246(57)	348(63)	−33(52)	188(57)	−24(50)
O(21)	289(49)	490(58)	565(63)	−57(41)	83(46)	140(51)

(continued on facing page)

TABLE I. *(continued)*

	U11	U22	U33	U12	U13	U23
O(22)	329(49)	424(54)	736(76)	–30(44)	52(50)	209(52)
O(23)	789(77)	419(63)	622(71)	1(54)	179(61)	99(56)
N(3)	293(52)	469(65)	395(61)	82(56)	65(48)	–23(63)
O(31)	449(54)	445(57)	499(61)	–116(47)	–78(48)	1(50)
O(32)	314(48)	451(56)	509(61)	–23(42)	14(45)	50(50)
O(33)	404(53)	660(69)	583(65)	51(53)	–160(49)	–35(62)
O(1)	258(37)	691(56)	845(64)	–40(35)	302(40)	–186(49)
O(2)	450(44)	849(62)	372(44)	88(45)	162(37)	–119(46)
O(3)	379(39)	446(48)	496(48)	–158(35)	–40(36)	0(40)
O(4)	322(38)	427(43)	693(56)	20(32)	273(38)	–5(41)
O(5)	468(45)	567(52)	655(57)	45(40)	142(42)	–242(46)
C(1)	701(89)	958(110)	1241(136)	–344(82)	805(97)	–650(103)
C(2)	895(120)	1389(158)	966(130)	257(110)	442(105)	–538(120)
C(3)	971(107)	441(71)	538(82)	–69(71)	–65(78)	–306(66)
C(4)	616(81)	748(97)	534(82)	–336(74)	–148(67)	9(74)
C(5)	189(52)	582(83)	1118(124)	–36(50)	–60(64)	–19(82)
C(6)	202(50)	634(82)	1062(112)	–82(55)	180(61)	8(85)
C(7)	659(88)	686(91)	881(109)	268(73)	512(84)	–16(82)
C(8)	745(91)	662(89)	943(117)	50(74)	552(88)	–298(82)

TABLE II. Interatomic Distances (A).

(a) *Bond distances*

Coordination

La–O(11)	2.61(1)	La–O(1)	2.60(1)
La–O(12)	2.59(1)	La–O(2)	2.67(1)
La–O(21)	2.63(1)	La–O(3)	2.69(1)
La–O(22)	2.61(1)	La–O(4)	2.74(1)
La–O(31)	2.60(1)	La–O(5)	2.55(1)
La–O(32)	2.79(1)		

Nitrate groups

N(1)–O(11)	1.26(1)	N(2)–O(21)	1.24(1)	N(3)–O(31)	1.24(1)
N(1)–O(12)	1.26(1)	N(2)–O(22)	1.27(1)	N(3)–O(32)	1.25(1)
N(1)–O(13)	1.20(2)	N(2)–O(23)	1.21(1)	N(3)–O(33)	1.22(1)

Organic ligand

O(1)–C(1)	1.44(2)	O(3)–C(5)	1.45(1)
C(1)–C(2)	1.39(2)	C(5)–C(6)	1.45(2)
C(2)–O(2)	1.43(2)	C(6)–O(4)	1.43(1)
O(2)–C(3)	1.45(2)	O(4)–C(7)	1.40(2)
C(3)–C(4)	1.45(2)	C(7)–C(8)	1.47(2)
C(4)–O(3)	1.43(2)	C(8)–O(5)	1.42(2)
O(1)–H(1)	1.01(3)	O(5)–H(2)	1.01(3)

(b) *Contact distances*

O(1)···O(32)	2.74(1)	O(5)···O(32)	2.72(1)
O(1)···O(2)	2.67(1)	O(5)···O(4)	2.59(1)
O(2)···O(3)	2.68(1)	O(4)···O(3)	2.70(1)

(continued overleaf)

TABLE II. *(continued)*

(c) Hydrogen contacts. Symmetry-operator superscripts: i, 1 − x, 1 − y, $\bar{z}$; ii, 1 − x, 1 − y, 1 − z.

O–H···O	O–H	H···O	O–H···O	O···O
O(1)–H(1)···O(32)	1.01	2.44	96	2.74
O(5)–H(2)···O(32)	1.01	2.25	107	2.72
O(1)–H(1)···O(23^{i})	1.01	2.41	148	3.31
O(5)–H(2)···O(33^{ii})	1.01	2.00	162	2.74

TABLE III. Angles (°).

Coordination			
O(1)–La–O(2)	60.7(2)	O(11)–La–O(12)	48.6(2)
O(2)–La–O(3)	59.9(2)	O(21)–La–O(22)	48.0(2)
O(3)–La–O(4)	59.7(2)	O(31)–La–O(32)	46.2(2)
O(4)–La–O(5)	58.4(2)	O(11)–La–O(31)	65.9(2)
O(1)–La–O(32)	61.0(2)	O(11)–La–O(32)	107.1(2)
O(5)–La–O(32)	61.2(2)	O(12)–La–O(32)	108.2(2)
O(1)–La–O(31)	71.8(2)	O(12)–La–O(31)	65.8(2)
O(5)–La–O(31)	74.8(2)	O(21)–La–O(32)	66.7(2)
O(2)–La–O(11)	70.4(2)	O(21)–La–O(31)	112.3(2)
O(3)–La–O(22)	67.6(2)	O(22)–La–O(32)	111.7(2)
O(4)–La–O(12)	65.1(2)	O(1)–La–O(5)	121.6(2)
Nitrate groups			
La–O(11)–N(1)	97(1)	La–O(21)–N(2)	97(1)
La–O(12)–N(1)	98(1)	La–O(22)–N(2)	98(1)
O(11)–N(1)–O(12)	116(1)	O(21)–N(2)–O(22)	117(1)
O(11)–N(1)–O(13)	122(1)	O(21)–N(2)–O(23)	122(1)
O(12)–N(1)–O(13)	122(1)	O(22)–N(2)–O(23)	121(1)
La–O(31)–N(3)	103(1)		
La–O(32)–N(3)	94(1)		
O(31)–N(3)–O(32)	117(1)		
O(31)–N(3)–O(33)	119(1)		
O(32)–N(3)–O(33)	124(1)		
Organic ligand			
La–O(1)–C(1)	119(1)	O(1)–C(1)–C(2)	112(1)
La–O(2)–C(2)	118(1)	O(2)–C(2)–C(1)	108(2)
La–O(2)–C(3)	118(1)	O(2)–C(3)–C(4)	106(1)
La–O(3)–C(4)	119(1)	O(3)–C(4)–C(3)	110(1)
La–O(3)–C(5)	120(1)	O(3)–C(5)–C(6)	108(1)
La–O(4)–C(6)	115(1)	O(4)–C(6)–C(5)	108(1)
La–O(4)–C(7)	114(1)	O(4)–C(7)–C(8)	108(1)
La–O(5)–C(8)	127(1)	O(5)–C(8)–C(7)	105(1)
La–O(1)–H(1)	120(2)	La–O(5)–H(2)	116(2)

located from a difference map. The atomic scattering factors for neutral non-hydrogen atoms were taken from ref. 6 and those for H atoms from ref. 7. Real and imaginary anomalous-dispersion corrections were included for the La atom [8].

Final atomic coordinates are listed in Table I, while interatomic distances and angles are reported in Tables II, III.

Selected mean planes are reported in Table IV. Computer programs used for the determination

TABLE IV. Selected Mean Planes with the Deviations (Å) of Relevant Atoms in Square Brackets. The equation of the plane is in the form AX + BY + CZ = D, where X, Y, Z are fractional unit-cell coordinates.

Plane I:	O(1), O(2), O(3), O(4), O(5), O(32) $0.29X + 14.16Y - 4.36Z = 5.23$ Å [O(1) −0.11, O(2) 0.29, O(3) −0.25, O(4) 0.02, O(5) 0.15, O(32) −0.10, La −0.19]
*Plane II:	N(1), O(11), O(12), O(13) $9.42X + 3.05Y + 4.01Z = 4.22$ Å
*Plane III:	N(2), O(21), O(22), O(23) $-4.26X + 9.95Y + 6.40Z = 3.59$ Å
*Plane IV:	N(3), O(31), O(32), O(33) $8.26X - 7.51Y - 5.96Z = -1.23$ Å

Angles between the planes

Planes	Angle (Deg)	Planes	Angle (Deg)
I–II	79.5	II–III	70.3
I–III	84.7	II–IV	89.8
I–IV	88.5	III–IV	21.0

*The atoms of the nitrate groups are coplanar within 0.06 Å.

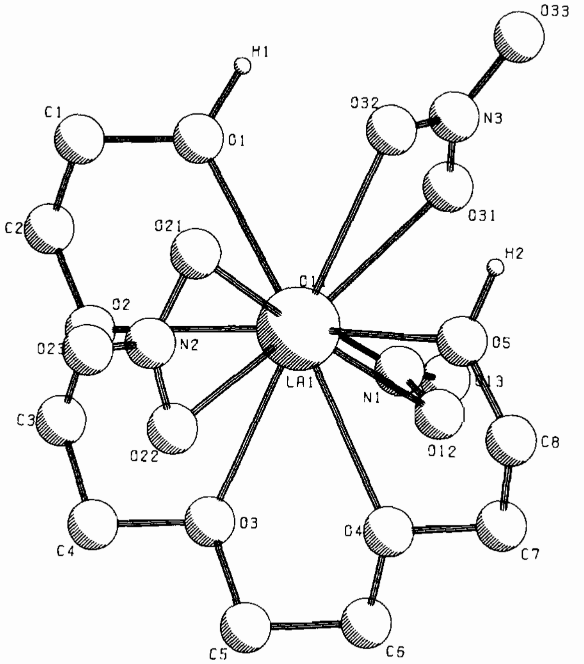

Fig. 1. The molecular structure of $La(NO_3)_3L$ with the numbering scheme used.

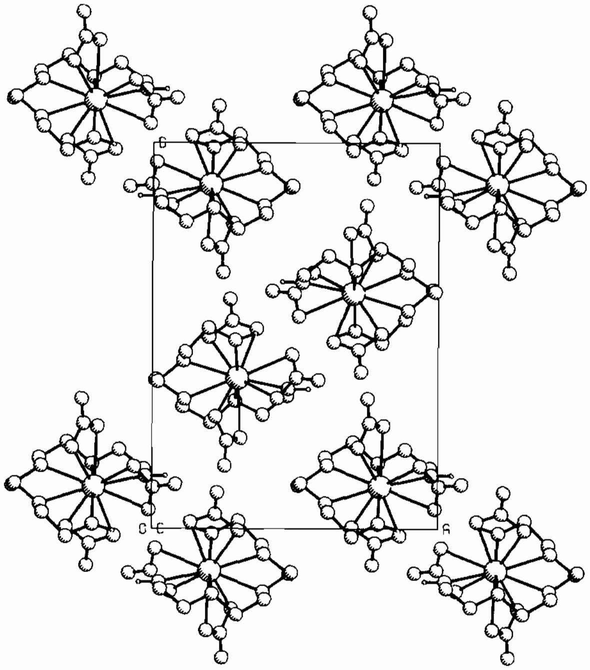

Fig. 2. Projection of the cell content down the *c* axis.

and refinement were those of the X-Ray 72 System [9].

Discussion

As shown in Figs. 1 and 2 the crystal structure of $La(NO_3)_3L$ is composed of discrete molecules where the lanthanum ion is 11-coordinated, being bonded to three bidentate nitrate groups and to the oxygen atoms of the tetraethylenglycol L. The five O (L) atoms form with one O (nitrate) atom a quasi regular hexagon around the metal ion in which the six O–La–O angles are comprised in a very small range of values. The two NO_3^- groups are

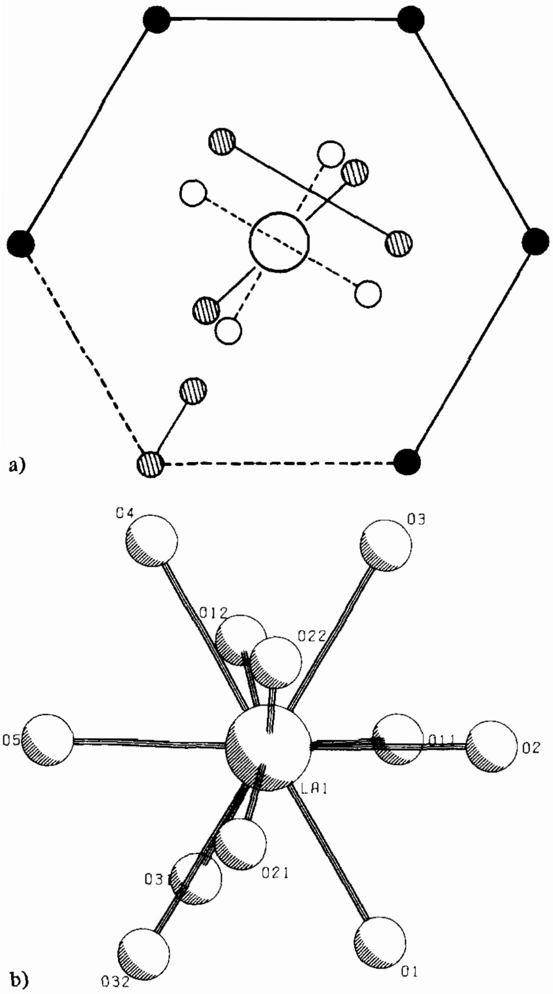

Fig. 3. a) Idealized (empty balls) and actual (filled balls) coordination geometry around La^{3+}. Chelating oxygens of the same NO_3^- group are joined by a line. Full black circles are oxygens of the pentadentate ligand. b) Coordination polyhedron. Projection on to the base plane.

chelated on the opposite sides of the 'base plane' in approximately bisphenoidal positions. The additional presence of the second oxygen atom of the first-mentioned nitrate group is the major asymmetry element in the coordination geometry, and probably causes the observed displacement of the neighbouring nitrate group from the idealized position, as shown in Fig. 3. All nitrate groups are strictly planar and are roughly perpendicular to the base plane.

Five La–O (nitrate) distances are comprised between 2.59 and 2.63 Å (mean 2.61 Å) while the La–O(32) distance involving the nitrate oxygen atom which completes the hexagonal base around the metal ion is considerably longer (2.79(1) Å). The La–O (L) distances are of two types: as expected, the three La–O (ether) distances (mean 2.70 Å) are significantly longer than the two terminal La–O (alcohol) ones (mean 2.58 Å). It is noteworthy that both the La–O (nitrate) and the La–O (alcohol) bond distances compare favourably with the sum of the atomic radii (2.55 Å) [10]. As already observed in many structures with coordinated bidentate nitrate groups, the terminal N–O bonds are shortened (average 1.215 Å) and the N–O bonds involving the chelating oxygen atoms are lengthened (average 1.253 Å) as compared with the values in a regular nitrate ion (1.245 Å [10]) [11]. In addition the O–N–O interbond angles involving the coordinated oxygen are smaller than 120° (average 116.6°), and the other two angles are correspondingly large. C–O(L) distances (mean 2.43 Å) have the normal values for single paraffinic bonds.

As shown in Table II(c), both alcoholic hydrogen atoms H(1) and H(2) are involved in two relatively short intramolecular contacts with the equatorial (nitrate) oxygen O(32), thus providing more completeness to the equatorial environment of the metal ion, and in two additional intermolecular contacts with (nitrate) oxygen of neighbouring molecules. These contacts are probably weak, bifurcated hydrogen bonds.

To our knowledge this is the third example of undecacoordinated lanthanum. The same coordination number was found in pentaaquotrinitratolanthanum(III) hydrate, $[La(NO_3)_3(H_2O)_5]\cdot H_2O$ [12], in trisnitrato 2,6-diacetylpyridinebis(benzoic acid hydrazone)lanthanum(III), $[La(NO_3)_3(C_{23}H_{21}N_5O_2)]$ [13], in the thorium nitrates $Th(NO_3)_4\cdot 5H_2O$ [14] and $[Th(OH)(NO_3)_2(H_2O)_4]_2$ [15], in the structure of the cerate(III) complexes $[Ce(NO_3)_4(H_2O)_2(NC_5H_4\cdot C_5H_4N)]$ [16] and $[Ce(NO_3)_3(H_2O)]\cdot H_2O$ [17], in the anion $[Sm(NO_3)_5H_2O]^{2-}$ [18], and in $[Y(BH_4)_3(THF)_3]$ [19]. In general the coordination polyhedra in these complexes are not easily definable nor comparable, and seem to be more determined by the shapes and characteristics of the bonded ligands than by the common coordination number.

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