

(Nitrato- κ^2O,O')bis(triethanolamine- κ^4N,O,O',O'')lanthanum(III) dinitrate

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The title compound, $[\text{La}(\text{NO}_3)(\text{C}_6\text{H}_{15}\text{NO}_3)_2](\text{NO}_3)_2$, contains a network of $[\text{La}(\text{NO}_3)(\text{C}_6\text{H}_{15}\text{NO}_3)_2]^{2+}$ cations and nitrate counter-ions. The crystal packing is influenced by cation-to-anion $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, resulting in a structure with one-dimensional character. The ten-coordinate La atom and a nitrate anion have site symmetry 2. The fact that triethanolamine can bind to such diverse cations as Li^+ and La^{3+} militates against possible applications that require selective binding of ligand to metal.

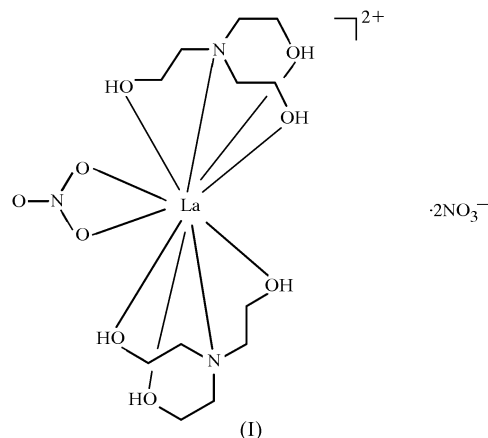
Comment

Triethanolamine (TEA) is a versatile polyfunctional ligand (Naiini *et al.*, 1995) that may bond to metals in tridentate (Gao *et al.*, 2004) or tetradentate mode (Kazak *et al.*, 2003) through its N and/or O atoms. TEA can be protonated at its central N atom (Long *et al.*, 2004) or various numbers of protons can be lost from the terminal OH groups (Johnstone & Harrison, 2004). In some complexes, TEA can show more than one binding mode simultaneously (Topcu *et al.*, 2002). A survey of the Cambridge Structural Database (Allen, 2002) revealed that crystal structures have been reported for complexes of TEA with many metal ions, including lithium, zinc, copper, barium, nickel, manganese, mercury, lead, cadmium, yttrium, praseodymium and ytterbium.

We report here the synthesis and structure of the title compound, $[\text{La}(\text{NO}_3)(\text{TEA})_2](\text{NO}_3)_2$, (I) (Fig. 1), the first reported crystal structure of a complex of La^{3+} and TEA. In (I), the La atom is bonded to two symmetry-related neutral TEA molecules, which act as N,O,O',O'' -tetradentate ligands. In addition, a nitrate group bonds to the La atom in bidentate mode, and a further non-coordinated nitrate group provides charge compensation for the cationic complex.

The $[\text{La}(\text{NO}_3)(\text{TEA})_2]^{2+}$ ion has twofold symmetry, with atom La1 and nitrate atoms N1 and O2 occupying the rotation axis. One of the methylene groups of the TEA species shows positional disorder over two orientations, which is not unusual for this species (Demir *et al.*, 2003). The average La—O distance in (I) of 2.571 (2) Å (Table 1) and the fact that the

La—N bonds are notably longer than the La—O vertices are consistent with the situation in other O,N-bonded lanthanum complexes (Thomas *et al.*, 1979; Zhang *et al.*, 2004). Overall, the LaO_8N_2 polyhedron in (I) is irregular.



As well as electrostatic attractions, the component species in (I) interact by means of three cation-to-anion $\text{O}-\text{H}\cdots\text{O}$ links (Table 2). Each TEA OH group makes a strong near linear hydrogen bond (mean $\text{H}\cdots\text{O} = 1.87$ Å) to a nearby non-coordinated nitrate O atom. This results in [110] chains of $[\text{La}(\text{NO}_3)(\text{TEA})_2]^{2+}$ ions bonded to their neighbours by a pair of bridging nitrate groups (Fig. 2). The hydrogen-bond acceptor behaviour for the nitrate ion is unbalanced, with atom O6 accepting two hydrogen bonds, O7 one and O8 none. This possibly correlates with the fact that the N3—O8 bond [1.214 (3) Å] is noticeably shorter than N3—O6 or N3—O7 [1.267 (3) and 1.256 (3) Å, respectively]. Finally, the [110] chains in (I) interact by way of van der Waals forces, resulting in a pseudo-layered unit-cell packing, such that the cations are arranged in (001) sheets and their attached nitrate groups point in alternating directions with respect to the *c* axis.

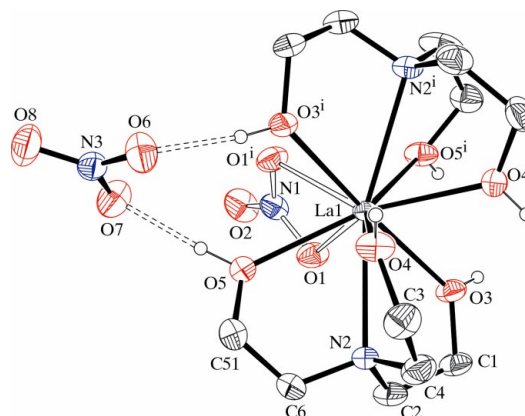
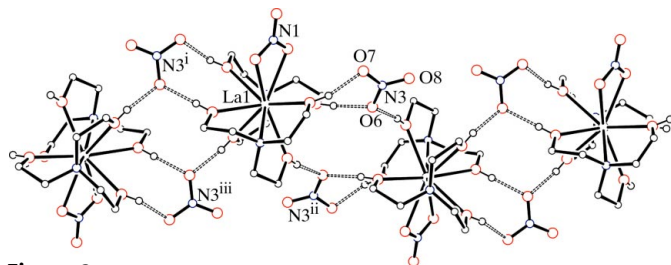


Figure 1

The component species in (I) (30% probability displacement ellipsoids; C-bound H atoms and minor disorder components of the TEA ligands have been omitted for clarity), with O-bound H atoms drawn as small spheres of arbitrary radii and hydrogen bonds shown as dashed lines. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]


Figure 2

A detail of a hydrogen-bonded chain in (I). Atoms are represented by arbitrary spheres; minor disorder components and all C-bound H atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-\frac{1}{2} + x, -y + \frac{1}{2}, -\frac{1}{2} + z$.]

The fact that TEA can bind effectively to metal cations ranging in size from Li^+ [as a five-coordinate $[\text{Li}(\text{TEA})(\text{H}_2\text{O})]^+$ ion with mean $\text{Li}-\text{O}_{\text{TEA}} = 2.003$ (9) Å and $\text{Li}-\text{N} = 2.206$ (8) Å (Padmanabhan *et al.*, 1987)], to Y^{3+} [as an eight-coordinate $[\text{Y}(\text{TEA})_2]^{3+}$ complex cation with mean $\text{Y}-\text{O} = 2.312$ (5) Å and mean $\text{Y}-\text{N} = 2.685$ (9) Å (Naiini *et al.*, 1995)], Pr^{3+} [as a nine-coordinate $[\text{Pr}(\text{TEA})_2(\text{C}_4\text{H}_8\text{O})]^{3+}$ complex cation, with mean $\text{Pr}-\text{O}_{\text{TEA}} = 2.465$ (5) Å and mean $\text{Pr}-\text{N} = 2.716$ (5) Å (Hahn & Mohr, 1990)] and the ten-coordinate $[\text{La}(\text{NO}_3)(\text{TEA})_2]^{2+}$ species seen here presumably correlates with the flexible ‘gripping’ nature of TEA, making it a poor candidate for possible applications requiring a multi-dentate ligand to bind selectively to particular metals.

Experimental

Triethanolamine (1 ml), 0.1 M lanthanum nitrate (5 ml) and 1 M HCl (2 ml) were mixed at 293 K in a Petri dish. This resulted in a clear solution, and colourless block-like crystals of (I) grew as the water evaporated at 293 K over the course of a few days.

Crystal data

$[\text{La}(\text{NO}_3)(\text{C}_6\text{H}_{15}\text{NO}_3)_2](\text{NO}_3)_2$	$Z = 4$
$M_r = 623.32$	$D_x = 1.780 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 11.6451$ (4) Å	$\mu = 1.92 \text{ mm}^{-1}$
$b = 14.7287$ (6) Å	$T = 293$ (2) K
$c = 14.2679$ (6) Å	Block, colourless
$\beta = 108.090$ (1)°	$0.42 \times 0.25 \times 0.21 \text{ mm}$
$V = 2326.22$ (16) Å ³	

Data collection

Bruker SMART 1000 CCD diffractometer	11819 measured reflections
ω scans	4186 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	3722 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.500, T_{\max} = 0.689$	$R_{\text{int}} = 0.019$
	$\theta_{\text{max}} = 32.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.0997P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.10 \text{ e \AA}^{-3}$
4186 reflections	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
161 parameters	
H-atom parameters constrained	

Table 1

Selected bond lengths (Å).

La1—O3	2.5402 (17)	La1—O1	2.6228 (18)
La1—O5	2.5570 (17)	La1—N2	2.8008 (18)
La1—O4	2.5626 (16)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3 \cdots O6 ⁱ	0.86	1.84	2.691 (3)	173
O4—H4 \cdots O6 ⁱⁱ	0.82	1.91	2.725 (3)	172
O5—H5 \cdots O7	0.87	1.86	2.712 (3)	166

 Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

The site occupancies of the disordered CH_2 groups (C51/C52) were constrained to sum to unity, resulting in almost equal occupancies for the two components [0.465 (12) and 0.535 (12)]. Disorder for the other TEA arms cannot be ruled out but could not be resolved with the present data. O-bound H atoms were located in difference maps and refined as riding from their starting locations, while C-bound H atoms were placed in idealized positions ($\text{C}-\text{H} = 0.97$ Å) and refined as riding; the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3009). Services for accessing these data are described at the back of the journal.

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