

Adrian Fowkes and
William T. A. Harrison*Department of Chemistry, University of
Aberdeen, Meston Walk, Aberdeen AB24 3UE,
ScotlandCorrespondence e-mail:
w.harrison@abdn.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{N}-\text{C}) = 0.003$ Å
 R factor = 0.029
 wR factor = 0.046
Data-to-parameter ratio = 25.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(guanidinium) diaquapentakis(nitrato- κ^2O,O')-
lanthanum

The title compound, $(\text{CH}_6\text{N}_3)_2[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$, contains a network of guanidinium cations and the previously unseen diaquapentakis(nitrato)lanthanum dianion, in which 12 O atoms surround La in a distorted icosahedral arrangement. A network of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds helps to consolidate the crystal packing, resulting in a three-dimensional network. The La cation, one N atom and one O atom occupy a twofold axis.

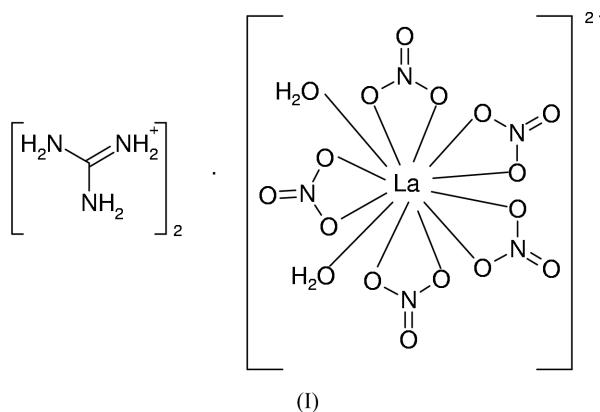
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Comment

The title compound, (I) (Fig. 1), contains a new lanthanum/nitrate/water complex anion. The La^{3+} cation, which occupies a twofold symmetry axis, is surrounded by five O,O' -bidentate nitrate groups [mean $\text{La}-\text{O} = 2.693$ (3) Å] and two water molecules (Table 1). The resulting O_{12} grouping (Fig. 2) surrounding the La atom is a distorted icosahedron. As expected, the icosahedral $\text{O}\cdots\text{O}$ contacts associated with the nitrate ions [2.149 (2)–2.1627 (19) Å] are much shorter than the other contacts ($\text{O}\cdots\text{O} > 2.8$ Å). Atoms O1, O4, O7, O3ⁱ and O6ⁱ [symmetry code: (i) $-x, y, \frac{1}{2} - z$] are approximately coplanar (r.m.s. deviation from the mean plane = 0.074 Å) and the symmetry-generated set O3/O6/O1ⁱ/O4ⁱ/O7ⁱ have the same r.m.s. deviation. The La cation is displaced by 0.9924 (7) Å from each set of five O atoms. The dihedral angle between the two sets of O atoms is 0.91 (2)°. The propeller-shaped guanidinium species in (I) is unexceptional, with a typical mean C–N bond length of 1.314 (4) Å, indicating that the usual model of electronic delocalization (Harrison, 2003), leading to a C–N bond order of 1.33, is applicable here.



As well as Coulombic and van der Waals forces, the component species in (I) interact by way of $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). The $\text{O}-\text{H}\cdots\text{O}$ bonds link adjacent $[\text{La}(\text{H}_2\text{O})_2(\text{NO}_3)_5]^{2-}$ anions into an infinite (001) sheet (Fig. 3). The guanidinium cations crosslink the (001)

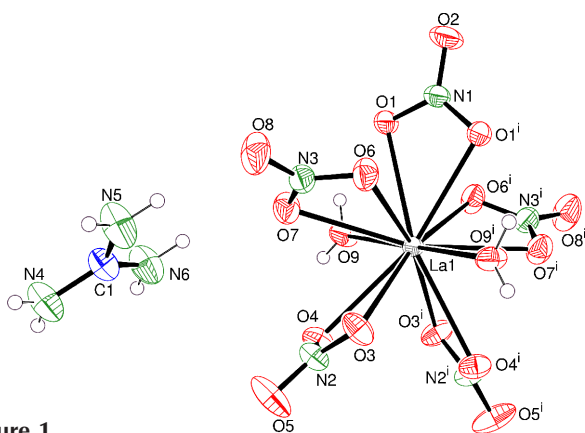


Figure 1
The component ions of (I) (40% displacement ellipsoids; H atoms are drawn as small spheres of arbitrary radius). [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

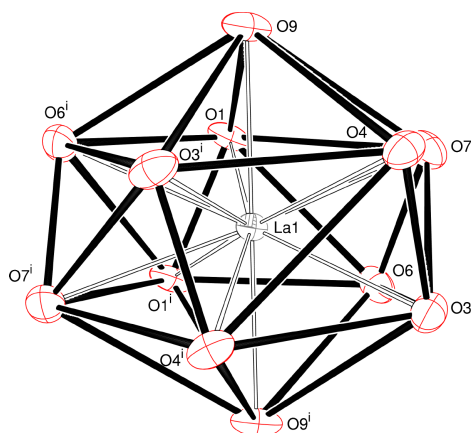


Figure 2
The LaO_{12} icosahedron in (I), with $\text{O} \cdots \text{O}$ contacts shown as solid lines. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

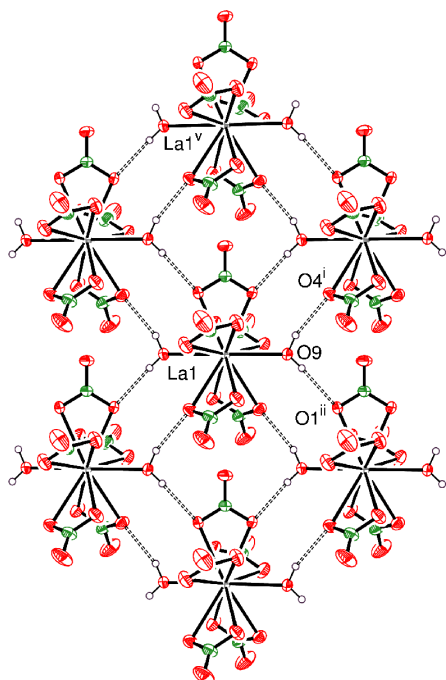


Figure 3
Detail of a hydrogen-bonded (dotted lines) anionic sheet in (I). [Symmetry codes as in Table 2; in addition, (v) $x, 1 + y, z$.]

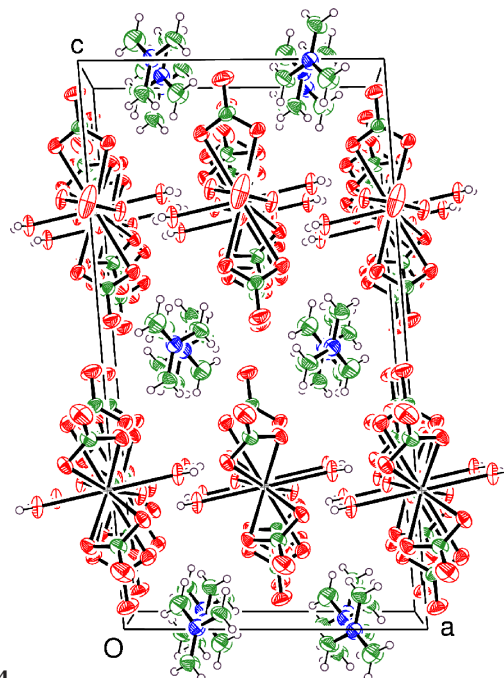


Figure 4
A [010] projection of the unit-cell packing in (I).

anionic sheets into a three-dimensional network (Fig. 4), with mean $\text{H} \cdots \text{O}$, $\text{N} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ values of 2.14 Å, 2.973 (5) Å and 162°, respectively. The guanidinium $\text{N4}-\text{H3}$ vertex does not participate in hydrogen bonds.

La/nitrate/water anions related to the $[\text{La}(\text{H}_2\text{O})(\text{NO}_3)_5]^{2-}$ species seen in (I) include $[\text{La}(\text{H}_2\text{O})(\text{NO}_3)_5]^{2-}$ (Evans *et al.*, 2002) and a number of examples of the hexakis(nitrate) $[\text{La}(\text{NO}_3)_6]^{3-}$ species (Cui *et al.*, 1999; Drew *et al.*, 2000). The $[\text{La}_2(\text{H}_2\text{O})_7(\text{NO}_3)_6]$ dinuclear cluster contains bridging nitrate groups (Weakley, 1982).

Experimental

The following solutions were mixed at 293 K in a Petri dish, resulting in a clear solution: 5 ml of 0.1 M guanidinium hydrochloride ($[\text{CH}_6\text{N}_3]^+\text{Cl}^-$), 5 ml of 0.1 M lanthanum nitrate, and 1 ml of 1 M HCl. Colourless block-like crystals of (I) grew over the course of a few days as the water evaporated at 293 K.

Crystal data

$(\text{CH}_6\text{N}_3)_2[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$
 $M_r = 605.16$
 Monoclinic, $C2/c$
 $a = 10.9918$ (6) Å
 $b = 9.0820$ (5) Å
 $c = 20.5555$ (11) Å
 $\beta = 94.500$ (1)°
 $V = 2045.68$ (19) Å³
 $Z = 4$

$D_x = 1.965$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3673 reflections
 $\theta = 2.9-28.5^\circ$
 $\mu = 2.19$ mm⁻¹
 $T = 293$ (2) K
 Block, colourless
 0.17 × 0.14 × 0.08 mm

Data collection

Bruker SMART1000 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.707$, $T_{\max} = 0.844$
 9927 measured reflections

3682 independent reflections
 3094 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 32.5^\circ$
 $h = -16 \rightarrow 15$
 $k = -13 \rightarrow 12$
 $l = -30 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.046$
 $S = 0.91$
 3682 reflections
 142 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0157P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (Å).

La1—O9	2.5409 (12)	La1—O6	2.7174 (15)
La1—O3	2.6112 (14)	La1—O4	2.7254 (14)
La1—O1	2.6603 (14)	La1—O7	2.7562 (16)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H1 \cdots O4 ⁱ	0.81	2.13	2.9157 (18)	163
O9—H2 \cdots O1 ⁱⁱ	0.80	2.14	2.9060 (18)	161
N4—H4 \cdots O8 ⁱⁱⁱ	0.86	2.26	3.069 (3)	156
N5—H5 \cdots O8	0.86	2.06	2.908 (3)	169
N5—H6 \cdots O3 ^{iv}	0.86	2.02	2.863 (3)	166
N6—H7 \cdots O7	0.86	2.22	3.037 (3)	159
N6—H8 \cdots O6 ⁱⁱⁱ	0.86	2.16	2.989 (2)	161

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

The water H atoms were located in a difference map and refined as riding on O9 in their as-found relative positions. The N—H H atoms were placed in idealized locations (N—H = 0.86 Å) and refined as riding. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$ was applied in all cases. The maximum difference peak is at La1 and the largest difference hole is 0.56 Å from La1.

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

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