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Bis(homopiperazinium) diaquapentakis(nitrato-κ^2O,O')lanthanate(III) dinitrate

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The title compound, $(C_5H_{14}N_2)_2[La(NO_3)_5(H_2O)_2](NO_3)_2$, contains a network of doubly protonated homopiperazinium (1,4-diazoniacycloheptane) cations, diaquapentanitratolanthanate(III) dianions and nitrate anions. In the complex anion, the 12 O atoms surround La in a distorted icosahedral arrangement. A network of N—H···O and O—H···O hydrogen bonds help to consolidate the crystal packing, resulting in a three-dimensional network. The La atom and one N and one O atom lie on a twofold axis.

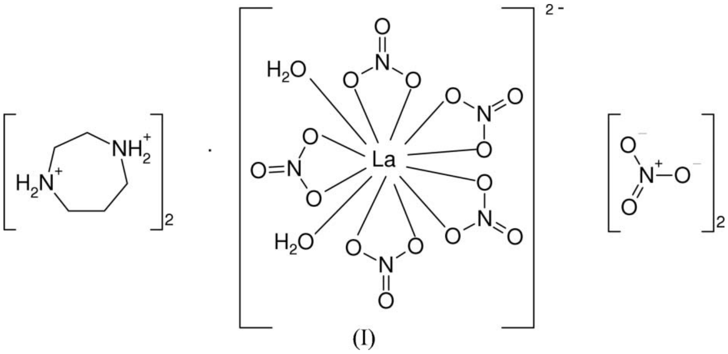
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.062
Data-to-parameter ratio = 24.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I) (Fig. 1), contains organic dications, lanthanum/nitrate/water complex anions and non-coordinated nitrate anions. The La^{III} cation, which occupies a twofold symmetry axis, is surrounded by five bidentate nitrate groups [mean La—O = 2.681 (2) Å] and two water molecules (Table 1). The resulting O_{12} grouping (Fig. 2) surrounding the La ion is a distorted icosahedron. As expected, the icosahedral O···O contacts associated with O atoms that are part of the same nitrate ion are much shorter (O···O < 2.17 Å) than the other contacts (O···O > 2.8 Å). Atoms O1, O5, O2^i, O4^i and O7^i [symmetry code (i) $-x$, y, $\frac{1}{2} - z$] are approximately coplanar (r.m.s. deviation from the mean plane = 0.052 Å) and the symmetry-equivalent set of atoms O2, O4, O7, O1^i and O5^i have the same r.m.s. deviation. The La cation is displaced by 1.0046 (6) Å from each set of five O atoms. The dihedral angle between the two pentagons of O atoms is 1.42 (4)°. A very similar complex anion was seen in $(CH_6N_3)_2[La(H_2O)_2(NO_3)_5]$ (Fowkes & Harrison, 2004).



(I)

The conformation of the homopiperazinium cation in (I) approximates to a chair, with atoms N1, C2, C3 and C5 almost coplanar (r.m.s. deviation from the mean plane = 0.033 Å) and C1, C4 and N2 displaced from the plane by −0.672 (3), 1.183 (3) and 1.028 (3) Å, respectively. A similar conformation for the same species was observed by Almond *et al.* (2000)

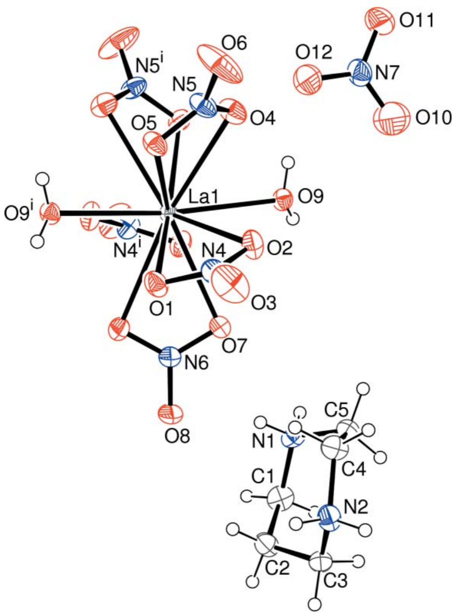


Figure 1

Component units of (I) (40% probability displacement ellipsoids; H atoms are drawn as small spheres of arbitrary radii). [Symmetry code (i) $-x, y, \frac{1}{2} - z$.]

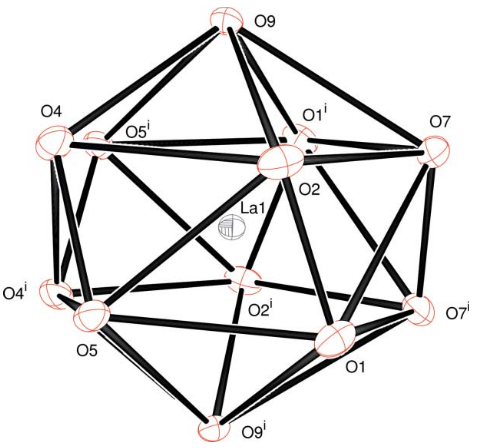


Figure 2

The LaO_{12} icosahedron in (I) with O···O contacts shown as solid lines (30% probability displacement ellipsoids). [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

with the interesting difference that the 'seat' of the chair was defined by four C atoms rather than three C atoms and one N atom as found here.

As well as coulombic and van der Waals forces, the component species in (I) interact by way of O—H···O and N—H···O hydrogen bonds (Table 2). The O9—H91···O1(x, $1 - y$, $z - \frac{1}{2}$) bonds link adjacent $[La(H_2O)_2(NO_3)_5]^{2-}$ anions into infinite [100] chains (Fig. 3) and the O9—H92···O12 bond attaches a pendant nitrate ion to the chain. The organic cations cross-link the chains into a three-dimensional network by way of the N—H···O interactions (Fig. 4). In $(CH_6N_3)_2[La(H_2O)_2(NO_3)_5]$ (Fowkes & Harrison, 2004), the anions form a two-dimensional hydrogen-bonded array, rather than the chains seen here.

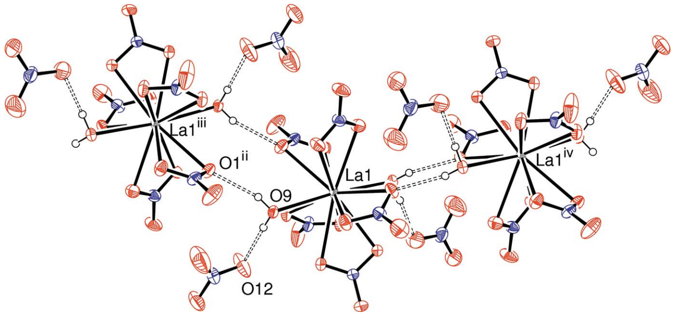


Figure 3

Detail of a hydrogen-bonded anionic chain in (I). Drawing conventions as in Fig. 1, with hydrogen bonds indicated by dashed lines. [Symmetry codes: (ii) $x, 1 - y, z - \frac{1}{2}$, (iii) $-x, 1 - y, -z$; (iv) $-x, 1 - y, 1 - z$.]

Experimental

The following solutions were mixed at 293 K in a Petri dish to result in a clear solution: 5 ml of 0.1 *M* homopiperazine, 5 ml of 0.1 *M* lanthanum nitrate and 1 ml of 1 *M* HCl. Colourless blocks and slabs of (I) grew over the course of a few days as the water evaporated at 293 K.

Crystal data

$(C_5H_{14}N_2)_2[La(NO_3)_5(H_2O)_2]$-$(NO_3)_2$
$M_r = 813.38$
Monoclinic, $C2/c$
$a = 17.2458$ (5) Å
$b = 12.8660$ (4) Å
$c = 13.4908$ (4) Å
$\beta = 105.780$ (1)°
$V = 2880.59$ (15) Å^3
$Z = 4$
$D_x = 1.876$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.60$ mm^{-1}
$T = 293$ (2) K
Slab, colourless
0.40 × 0.24 × 0.09 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.568$, $T_{max} = 0.870$
16827 measured reflections
5192 independent reflections
4634 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 32.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.062$
$S = 1.00$
5192 reflections
211 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

La1—O1	2.6990 (12)	La1—O5	2.6780 (12)
La1—O2	2.6355 (13)	La1—O7	2.7076 (13)
La1—O4	2.6863 (14)	La1—O9	2.5996 (12)
C1—C2—C3—N2	85.3 (2)	C4—C5—N1—C1	−81.6 (2)
C2—C3—N2—C4	−54.1 (2)	C5—N1—C1—C2	60.2 (2)
C3—N2—C4—C5	−16.1 (3)	N1—C1—C2—C3	−67.0 (2)
N2—C4—C5—N1	76.5 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O9—H91$\cdots$O1^{ii}	0.79 (2)	2.08 (2)	2.8388 (17)	163 (2)
O9—H92$\cdots$O12	0.84 (2)	1.87 (2)	2.705 (2)	173 (2)
N1—H1$A\cdots$O8	0.90	2.11	2.9817 (17)	163
N1—H1$B\cdots$O5^{ii}	0.90	1.97	2.8531 (19)	165
N2—H2$A\cdots$O9^{v}	0.90	2.07	2.966 (2)	172
N2—H2$B\cdots$O11^{vi}	0.90	1.95	2.797 (2)	155

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

The water H atoms were located in a difference map and their positions were freely refined The other H atoms were placed in idealized locations [C—H = 0.97 Å and N—H = 0.90 Å] and refined as riding. The constraint $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atom) was applied in all cases.

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* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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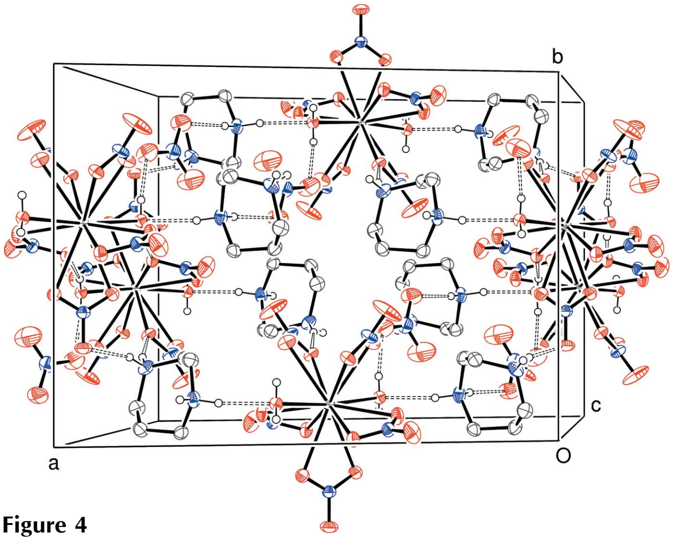

Figure 4
The packing in (I). Drawing conventions as in Fig. 1. C-bound H atoms have been omitted for clarity and hydrogen bonds are indicated by dashed lines.

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