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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.

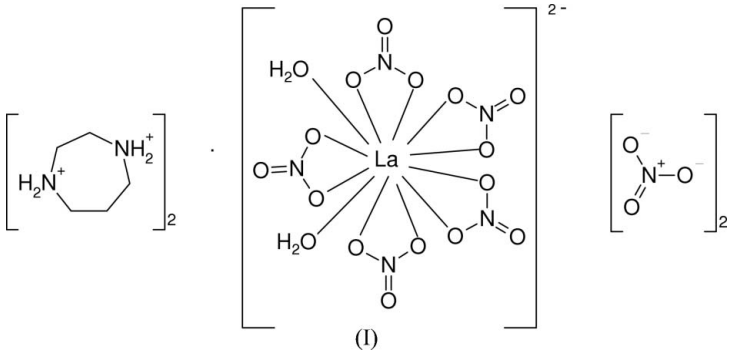
Key indicators

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)

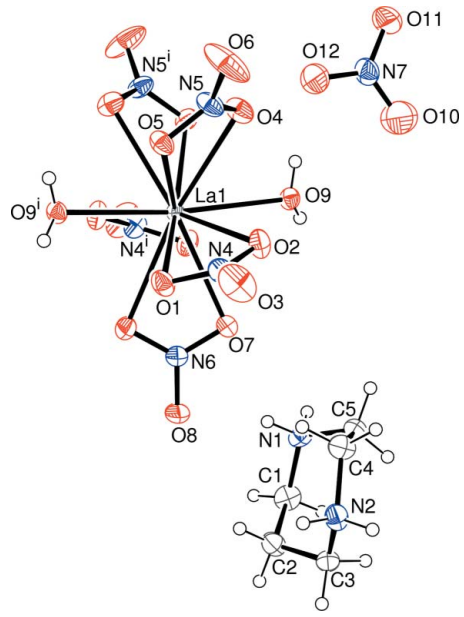


Figure 1
Component units of (I) (40% probability displacement ellipsoids; H atoms are drawn as small spheres of arbitrary radii). [Symmetry code (i) $-x, y, \frac{1}{2}-z$.]

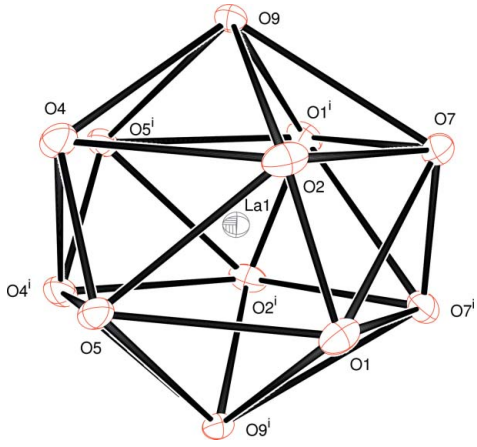


Figure 2
The LaO_{12} icosahedron in (I) with O···O contacts shown as solid lines (30% probability displacement ellipsoids). [Symmetry code: (i) $-x, y, \frac{1}{2}-z$.]

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.

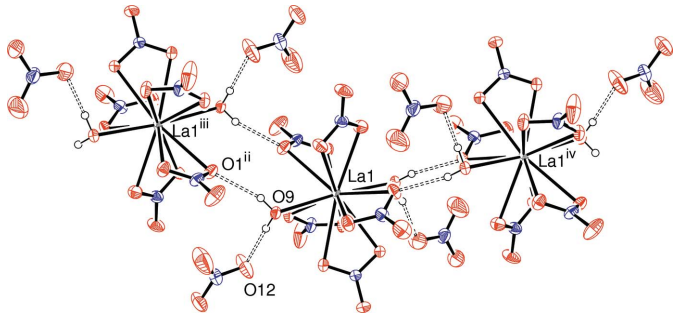


Figure 3
Detail of a hydrogen-bonded anionic chain in (I). Drawing conventions as in Fig. 1, with hydrogen bonds indicated by dashed lines. [Symmetry codes: (ii) $x, 1-y, z-\frac{1}{2}$, (iii) $-x, 1-y, -z$; (iv) $-x, 1-y, 1-z$.]

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
$\beta = 105.780\ (1)^\circ$
$V = 2880.59\ (15)$ 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 $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 32.5^\circ$

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···A	D—H	H···A	D···A	D—H···A
O9—H91···O1^{ii}	0.79 (2)	2.08 (2)	2.8388 (17)	163 (2)
O9—H92···O12	0.84 (2)	1.87 (2)	2.705 (2)	173 (2)
N1—H1A···O8	0.90	2.11	2.9817 (17)	163
N1—H1B···O5^{ii}	0.90	1.97	2.8531 (19)	165
N2—H2A···O9^{v}	0.90	2.07	2.966 (2)	172
N2—H2B···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_{iso}(H) = 1.2U_{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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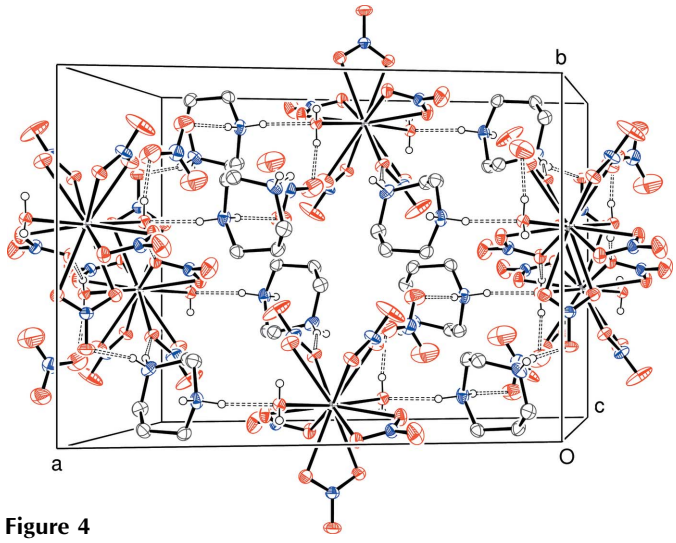

Figure 4
The packing in (I). Drawing conventions as in Fig. 1. C-bound H atoms have been omitted for clarity and hydrogen bonds are indicated by dashed lines.

References

Almond, P. M., Talley, C. E., Bean, A. C., Peper, S. M. & Albrecht-Smith, T. E. (2000). *J. Solid State Chem.* **154**, 635–641.
Bruker (1999). *SMART* (Version 5.624), *SAINT-Plus* (Version 6.02A) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. App. Cryst.* **30**, 565.
Fowkes, A. & Harrison, W. T. A. (2004). *Acta Cryst.* E**60**, m1647–m1649.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

Acta Cryst. (2006). E**62**, m1301–m1303 [https://doi.org/10.1107/S1600536806017235]

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Bis(1,4-diazoniacycloheptane) diaquapentakis(nitrato-κ^2O,O')lanthanum(III) dinitrate ?

Crystal data

$(C_5H_{14}N_2)_2[La(NO_3)_5(H_2O)_2](NO_3)_2$
$M_r = 813.38$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 17.2458$ (5) Å
$b = 12.8660$ (4) Å
$c = 13.4908$ (4) Å
$\beta = 105.780$ (1)°
$V = 2880.59$ (15) Å^3
$Z = 4$
$F(000) = 1640$
$D_x = 1.876$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9327 reflections
$\theta = 2.0$–$32.5°$
$\mu = 1.60$ mm^{-1}
$T = 293$ K
Slab, colourless
0.40 × 0.24 × 0.09 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 32.5°$, $\theta_{min} = 2.0°$
$h = -26\rightarrow26$
$k = -19\rightarrow14$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.062$
$S = 1.00$
5192 reflections
211 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difmap (O-H) and geom (others)
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}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
La1	0.0000	0.589697 (10)	0.2500	0.01899 (4)
N4	0.14572 (9)	0.53102 (13)	0.43198 (12)	0.0315 (3)
O1	0.07532 (8)	0.50627 (11)	0.43465 (10)	0.0339 (3)
O2	0.15348 (8)	0.56177 (12)	0.34585 (10)	0.0363 (3)
O3	0.20254 (10)	0.52783 (16)	0.50843 (13)	0.0609 (5)
N5	0.09740 (10)	0.78175 (12)	0.35558 (11)	0.0333 (3)
O4	0.08949 (9)	0.76256 (11)	0.26240 (9)	0.0367 (3)
O5	0.06011 (8)	0.72372 (10)	0.40356 (9)	0.0308 (3)
O6	0.13956 (15)	0.85228 (16)	0.40015 (13)	0.0792 (7)
N6	0.0000	0.34742 (17)	0.2500	0.0313 (4)
O7	0.05025 (9)	0.39674 (10)	0.21651 (12)	0.0357 (3)
O8	0.0000	0.25002 (16)	0.2500	0.0495 (6)
O9	0.08881 (8)	0.60093 (11)	0.12251 (9)	0.0262 (2)
H91	0.0813 (13)	0.5617 (18)	0.0762 (18)	0.031*
H92	0.0838 (13)	0.6601 (19)	0.0959 (17)	0.031*
N1	0.09602 (10)	0.18968 (13)	0.10566 (12)	0.0339 (3)
H1A	0.0709	0.2210	0.1480	0.041*
H1B	0.0757	0.2165	0.0423	0.041*
N2	0.23276 (10)	0.11081 (14)	0.30716 (13)	0.0355 (4)
H2A	0.2865	0.1013	0.3267	0.043*
H2B	0.2164	0.1134	0.3650	0.043*
C1	0.07662 (14)	0.07671 (17)	0.10186 (16)	0.0392 (4)
H1C	0.1011	0.0430	0.0535	0.047*
H1D	0.0187	0.0681	0.0763	0.047*
C2	0.10535 (12)	0.02359 (17)	0.20505 (16)	0.0374 (4)
H2C	0.0834	−0.0463	0.1987	0.045*
H2D	0.0835	0.0606	0.2540	0.045*
C3	0.19600 (12)	0.01657 (16)	0.24868 (16)	0.0355 (4)
H3A	0.2086	−0.0433	0.2939	0.043*
H3B	0.2202	0.0054	0.1925	0.043*
C4	0.21694 (13)	0.21552 (16)	0.25651 (15)	0.0382 (4)
H4A	0.2670	0.2543	0.2739	0.046*
H4B	0.1794	0.2524	0.2859	0.046*
C5	0.18364 (12)	0.21604 (16)	0.14100 (15)	0.0363 (4)
H5A	0.1918	0.2844	0.1152	0.044*
H5B	0.2135	0.1664	0.1117	0.044*
N7	0.12793 (11)	0.80286 (16)	−0.01623 (13)	0.0422 (4)
O10	0.1615 (2)	0.7241 (2)	−0.0376 (2)	0.1139 (12)
O11	0.13743 (14)	0.88747 (15)	−0.05498 (17)	0.0651 (6)
O12	0.08566 (15)	0.79433 (16)	0.04290 (19)	0.0805 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.01944 (6)	0.02038 (7)	0.01708 (6)	0.000	0.00484 (4)	0.000
N4	0.0255 (7)	0.0354 (9)	0.0301 (7)	0.0002 (6)	0.0014 (5)	0.0080 (6)
O1	0.0279 (6)	0.0412 (8)	0.0323 (6)	−0.0002 (6)	0.0075 (5)	0.0128 (6)
O2	0.0271 (6)	0.0510 (9)	0.0319 (6)	0.0004 (6)	0.0100 (5)	0.0086 (6)
O3	0.0400 (9)	0.0812 (14)	0.0452 (9)	−0.0110 (9)	−0.0161 (7)	0.0229 (9)
N5	0.0442 (9)	0.0305 (8)	0.0249 (6)	−0.0137 (7)	0.0090 (6)	−0.0031 (6)
O4	0.0540 (8)	0.0357 (7)	0.0226 (5)	−0.0117 (6)	0.0141 (5)	−0.0023 (5)
O5	0.0385 (7)	0.0318 (7)	0.0242 (5)	−0.0106 (6)	0.0121 (5)	−0.0038 (5)
O6	0.1314 (19)	0.0706 (13)	0.0381 (8)	−0.0730 (14)	0.0272 (10)	−0.0199 (9)
N6	0.0340 (11)	0.0245 (10)	0.0379 (11)	0.000	0.0140 (9)	0.000
O7	0.0358 (7)	0.0296 (7)	0.0473 (8)	0.0002 (5)	0.0211 (6)	0.0054 (6)
O8	0.0635 (14)	0.0211 (10)	0.0784 (16)	0.000	0.0440 (13)	0.000
O9	0.0293 (6)	0.0295 (7)	0.0214 (5)	0.0000 (5)	0.0096 (5)	−0.0027 (5)
N1	0.0394 (8)	0.0374 (9)	0.0239 (6)	0.0124 (7)	0.0065 (6)	0.0044 (6)
N2	0.0260 (7)	0.0480 (10)	0.0300 (7)	0.0019 (7)	0.0034 (6)	0.0098 (7)
C1	0.0393 (10)	0.0423 (12)	0.0312 (9)	0.0004 (8)	0.0013 (8)	−0.0025 (8)
C2	0.0345 (9)	0.0384 (11)	0.0384 (9)	−0.0047 (8)	0.0083 (8)	0.0056 (8)
C3	0.0348 (9)	0.0326 (10)	0.0404 (9)	0.0067 (8)	0.0124 (8)	0.0113 (8)
C4	0.0376 (10)	0.0359 (11)	0.0374 (9)	−0.0026 (8)	0.0037 (8)	0.0022 (8)
C5	0.0391 (10)	0.0356 (10)	0.0370 (9)	0.0029 (8)	0.0153 (8)	0.0101 (8)
N7	0.0451 (9)	0.0487 (11)	0.0360 (8)	0.0017 (8)	0.0167 (7)	0.0105 (8)
O10	0.174 (3)	0.0730 (17)	0.140 (3)	0.0222 (18)	0.119 (2)	0.0206 (16)
O11	0.0918 (15)	0.0487 (10)	0.0728 (13)	0.0027 (10)	0.0528 (12)	0.0167 (9)
O12	0.1119 (17)	0.0625 (13)	0.0973 (16)	0.0236 (12)	0.0797 (15)	0.0343 (11)

Geometric parameters (Å, º)

La1—O1^{i}	2.6990 (12)	N1—C5	1.495 (3)
La1—O1	2.6990 (12)	N1—H1A	0.9000
La1—O2^{i}	2.6355 (13)	N1—H1B	0.9000
La1—O2	2.6355 (13)	N2—C3	1.491 (3)
La1—O4	2.6863 (14)	N2—C4	1.502 (3)
La1—O4^{i}	2.6863 (14)	N2—H2A	0.9000
La1—O5	2.6780 (12)	N2—H2B	0.9000
La1—O5^{i}	2.6780 (12)	C1—C2	1.508 (3)
La1—O7^{i}	2.7076 (13)	C1—H1C	0.9700
La1—O7	2.7076 (13)	C1—H1D	0.9700
La1—O9^{i}	2.5996 (12)	C2—C3	1.516 (3)
La1—O9	2.5996 (12)	C2—H2C	0.9700
N4—O3	1.215 (2)	C2—H2D	0.9700
N4—O1	1.2651 (19)	C3—H3A	0.9700
N4—O2	1.2686 (19)	C3—H3B	0.9700
N5—O6	1.215 (2)	C4—C5	1.507 (3)
N5—O4	1.2516 (18)	C4—H4A	0.9700
N5—O5	1.2713 (18)	C4—H4B	0.9700

N6—O8	1.253 (3)	C5—H5A	0.9700
N6—O7	1.2533 (17)	C5—H5B	0.9700
N6—O7^{i}	1.2532 (17)	N7—O12	1.223 (2)
O9—H91	0.79 (2)	N7—O11	1.238 (2)
O9—H92	0.84 (2)	N7—O10	1.238 (3)
N1—C1	1.489 (3)		

O9^{i}—La1—O9	173.63 (6)	O1—La1—O7	72.17 (5)
O9^{i}—La1—O2^{i}	68.80 (4)	O7^{i}—La1—O7	47.05 (6)
O9—La1—O2^{i}	112.14 (4)	O3—N4—O1	121.74 (16)
O9^{i}—La1—O2	112.14 (4)	O3—N4—O2	121.77 (17)
O9—La1—O2	68.80 (4)	O1—N4—O2	116.47 (14)
O2^{i}—La1—O2	164.33 (7)	N4—O1—La1	95.65 (9)
O9^{i}—La1—O5	68.05 (4)	N4—O2—La1	98.62 (10)
O9—La1—O5	107.59 (4)	O6—N5—O4	122.11 (16)
O2^{i}—La1—O5	126.38 (4)	O6—N5—O5	120.28 (15)
O2—La1—O5	65.32 (4)	O4—N5—O5	117.61 (14)
O9^{i}—La1—O5^{i}	107.59 (4)	N5—O4—La1	97.45 (10)
O9—La1—O5^{i}	68.05 (4)	N5—O5—La1	97.31 (9)
O2^{i}—La1—O5^{i}	65.32 (4)	O8—N6—O7	120.42 (11)
O2—La1—O5^{i}	126.38 (4)	O8—N6—O7^{i}	120.42 (11)
O5—La1—O5^{i}	99.83 (6)	O7—N6—O7^{i}	119.2 (2)
O9^{i}—La1—O4	110.16 (4)	N6—O7—La1	96.89 (11)
O9—La1—O4	64.10 (4)	La1—O9—H91	119.4 (17)
O2^{i}—La1—O4	128.81 (5)	La1—O9—H92	108.9 (15)
O2—La1—O4	66.36 (5)	H91—O9—H92	106 (2)
O5—La1—O4	47.45 (4)	C1—N1—C5	115.51 (16)
O5^{i}—La1—O4	67.05 (4)	C1—N1—H1A	108.4
O9^{i}—La1—O4^{i}	64.10 (4)	C5—N1—H1A	108.4
O9—La1—O4^{i}	110.16 (4)	C1—N1—H1B	108.4
O2^{i}—La1—O4^{i}	66.36 (5)	C5—N1—H1B	108.4
O2—La1—O4^{i}	128.81 (5)	H1A—N1—H1B	107.5
O5—La1—O4^{i}	67.05 (4)	C3—N2—C4	119.36 (15)
O5^{i}—La1—O4^{i}	47.45 (4)	C3—N2—H2A	107.5
O4—La1—O4^{i}	68.22 (6)	C4—N2—H2A	107.5
O9^{i}—La1—O1^{i}	114.24 (4)	C3—N2—H2B	107.5
O9—La1—O1^{i}	68.51 (4)	C4—N2—H2B	107.5
O2^{i}—La1—O1^{i}	47.62 (4)	H2A—N2—H2B	107.0
O2—La1—O1^{i}	124.45 (4)	N1—C1—C2	113.34 (16)
O5—La1—O1^{i}	163.32 (5)	N1—C1—H1C	108.9
O5^{i}—La1—O1^{i}	63.53 (4)	C2—C1—H1C	108.9
O4—La1—O1^{i}	120.72 (4)	N1—C1—H1D	108.9
O4^{i}—La1—O1^{i}	98.49 (4)	C2—C1—H1D	108.9
O9^{i}—La1—O1	68.51 (4)	H1C—C1—H1D	107.7
O9—La1—O1	114.24 (4)	C1—C2—C3	115.50 (17)
O2^{i}—La1—O1	124.45 (4)	C1—C2—H2C	108.4
O2—La1—O1	47.62 (4)	C3—C2—H2C	108.4
O5—La1—O1	63.53 (4)	C1—C2—H2D	108.4

O5^{i}—La1—O1	163.32 (5)	C3—C2—H2D	108.4
O4—La1—O1	98.49 (4)	H2C—C2—H2D	107.5
O4^{i}—La1—O1	120.72 (4)	N2—C3—C2	113.72 (16)
O1^{i}—La1—O1	133.13 (6)	N2—C3—H3A	108.8
O9^{i}—La1—O7^{i}	70.59 (4)	C2—C3—H3A	108.8
O9—La1—O7^{i}	115.74 (4)	N2—C3—H3B	108.8
O2^{i}—La1—O7^{i}	68.44 (5)	C2—C3—H3B	108.8
O2—La1—O7^{i}	96.75 (5)	H3A—C3—H3B	107.7
O5—La1—O7^{i}	122.37 (4)	N2—C4—C5	116.45 (17)
O5^{i}—La1—O7^{i}	130.19 (5)	N2—C4—H4A	108.2
O4—La1—O7^{i}	162.41 (5)	C5—C4—H4A	108.2
O4^{i}—La1—O7^{i}	124.40 (4)	N2—C4—H4B	108.2
O1^{i}—La1—O7^{i}	72.17 (5)	C5—C4—H4B	108.2
O1—La1—O7^{i}	64.97 (5)	H4A—C4—H4B	107.3
O9^{i}—La1—O7	115.74 (4)	N1—C5—C4	113.38 (15)
O9—La1—O7	70.59 (4)	N1—C5—H5A	108.9
O2^{i}—La1—O7	96.75 (5)	C4—C5—H5A	108.9
O2—La1—O7	68.44 (5)	N1—C5—H5B	108.9
O5—La1—O7	130.19 (5)	C4—C5—H5B	108.9
O5^{i}—La1—O7	122.37 (4)	H5A—C5—H5B	107.7
O4—La1—O7	124.40 (4)	O12—N7—O11	121.7 (2)
O4^{i}—La1—O7	162.41 (5)	O12—N7—O10	118.5 (2)
O1^{i}—La1—O7	64.97 (5)	O11—N7—O10	119.8 (2)

O3—N4—O1—La1	165.63 (19)	O1—La1—O4—N5	−39.07 (12)
O2—N4—O1—La1	−12.69 (18)	O7^{i}—La1—O4—N5	−58.18 (19)
O9^{i}—La1—O1—N4	−147.79 (12)	O7—La1—O4—N5	−113.23 (12)
O9—La1—O1—N4	25.97 (12)	O6—N5—O5—La1	−175.0 (2)
O2^{i}—La1—O1—N4	170.05 (10)	O4—N5—O5—La1	4.27 (18)
O2—La1—O1—N4	7.36 (10)	O9^{i}—La1—O5—N5	−153.38 (12)
O5—La1—O1—N4	−72.44 (11)	O9—La1—O5—N5	21.68 (11)
O5^{i}—La1—O1—N4	−68.28 (18)	O2^{i}—La1—O5—N5	−114.76 (11)
O4—La1—O1—N4	−39.39 (12)	O2—La1—O5—N5	77.40 (11)
O4^{i}—La1—O1—N4	−109.04 (11)	O5^{i}—La1—O5—N5	−48.26 (10)
O1^{i}—La1—O1—N4	108.57 (11)	O4—La1—O5—N5	−2.39 (10)
O7^{i}—La1—O1—N4	134.35 (12)	O4^{i}—La1—O5—N5	−83.30 (11)
O7—La1—O1—N4	84.12 (11)	O1^{i}—La1—O5—N5	−52.03 (19)
O3—N4—O2—La1	−165.23 (18)	O1—La1—O5—N5	130.53 (11)
O1—N4—O2—La1	13.09 (18)	O7^{i}—La1—O5—N5	159.45 (10)
O9^{i}—La1—O2—N4	17.58 (13)	O7—La1—O5—N5	100.81 (11)
O9—La1—O2—N4	−169.21 (13)	O8—N6—O7—La1	180.0
O2^{i}—La1—O2—N4	−72.69 (11)	O7^{i}—N6—O7—La1	0.0
O5—La1—O2—N4	68.44 (11)	O9^{i}—La1—O7—N6	17.68 (10)
O5^{i}—La1—O2—N4	152.40 (11)	O9—La1—O7—N6	−163.14 (10)
O4—La1—O2—N4	120.76 (12)	O2^{i}—La1—O7—N6	−52.00 (9)
O4^{i}—La1—O2—N4	91.44 (12)	O2—La1—O7—N6	122.71 (9)
O1^{i}—La1—O2—N4	−127.15 (11)	O5—La1—O7—N6	99.86 (8)
O1—La1—O2—N4	−7.39 (10)	O5^{i}—La1—O7—N6	−116.98 (8)

O7^{i}—La1—O2—N4	−54.17 (12)	O4—La1—O7—N6	160.22 (7)
O7—La1—O2—N4	−92.51 (12)	O4^{i}—La1—O7—N6	−67.52 (17)
O6—N5—O4—La1	175.0 (2)	O1^{i}—La1—O7—N6	−88.45 (9)
O5—N5—O4—La1	−4.26 (18)	O1—La1—O7—N6	72.07 (8)
O9^{i}—La1—O4—N5	31.07 (12)	O7^{i}—La1—O7—N6	0.0
O9—La1—O4—N5	−151.96 (13)	C1—C2—C3—N2	85.3 (2)
O2^{i}—La1—O4—N5	109.59 (11)	C2—C3—N2—C4	−54.1 (2)
O2—La1—O4—N5	−75.04 (11)	C3—N2—C4—C5	−16.1 (3)
O5—La1—O4—N5	2.43 (10)	N2—C4—C5—N1	76.5 (2)
O5^{i}—La1—O4—N5	132.26 (12)	C4—C5—N1—C1	−81.6 (2)
O4^{i}—La1—O4—N5	80.70 (11)	C5—N1—C1—C2	60.2 (2)
O1^{i}—La1—O4—N5	167.69 (10)	N1—C1—C2—C3	−67.0 (2)

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

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

Symmetry codes: (ii) *x*, −*y*+1, *z*−1/2; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) *x*, −*y*+1, *z*+1/2.