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Bis(guanidinium) diaquapentakis(nitrato-κ^2O,O')-lanthanum

Adrian Fowkes and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: w.harrison@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.003 Å
R factor = 0.029
wR factor = 0.046
Data-to-parameter ratio = 25.9

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

The title compound, $(CH_6N_3)_2[La(NO_3)_5(H_2O)_2]$, 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 N—H···O and O—H···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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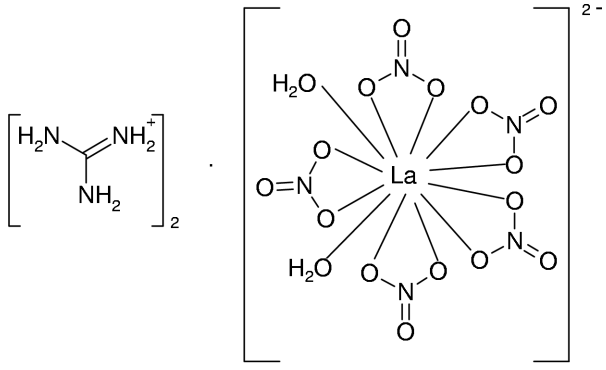
Comment

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 La—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 O···O contacts associated with the nitrate ions [2.149 (2)–2.1627 (19) Å] are much shorter than the other contacts (O···O > 2.8 Å). Atoms O1, O4, O7, O3^{i} and O6^{i} [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/O1^{i}/O4^{i}/O7^{i} 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.



(I)

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 O—H···O bonds link adjacent $[La(H_2O)_2(NO_3)_5]^{2-}$ anions into an infinite (001) sheet (Fig. 3). The guanidinium cations crosslink the (001)

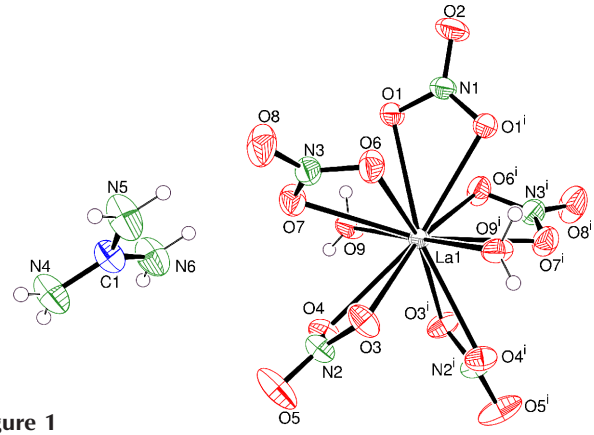


Figure 1
The component ions of (I) (40% displacement ellipsoids; H atoms are drawn as small spheres of arbitrary radius). [Symmetry code: (i) $-x, y, \frac{1}{2}-z$.]

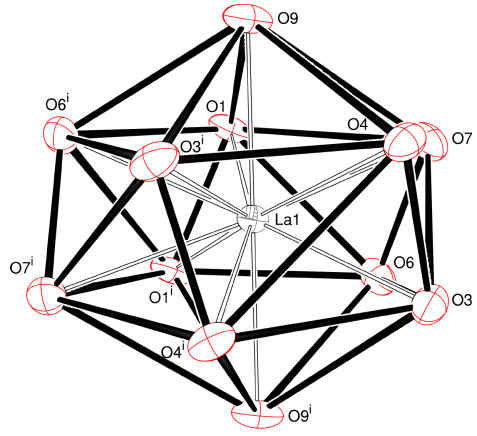


Figure 2
The LaO_{12} icosahedron in (I), with O···O contacts shown as solid lines. [Symmetry code: (i) $-x, y, \frac{1}{2}-z$.]

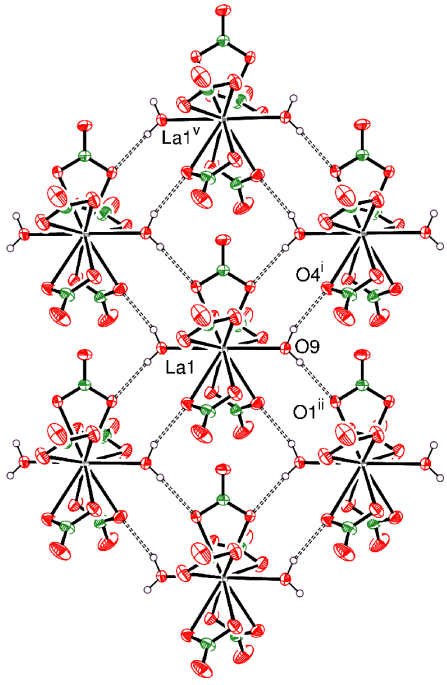


Figure 3
Detail of a hydrogen-bonded (dotted lines) anionic sheet in (I). [Symmetry codes as in Table 2; in addition, (v) $x, 1+y, z$.]

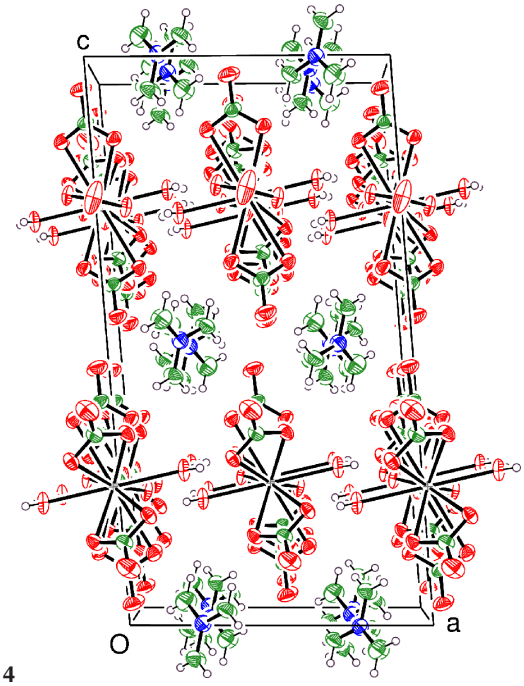


Figure 4
A [010] projection of the unit-cell packing in (I).

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

La/nitrate/water anions related to the $[La(H_2O)_2(NO_3)_5]^{2-}$ species seen in (I) include $[La(H_2O)(NO_3)_5]^{2-}$ (Evans *et al.*, 2002) and a number of examples of the hexakis(nitrato) $[La(NO_3)_6]^{3-}$ species (Cui *et al.*, 1999; Drew *et al.*, 2000). The $[La_2(H_2O)_7(NO_3)_6]$ 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 ($[CH_6N_3]^+Cl^-$), 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

$(CH_6N_3)_2[La(NO_3)_5(H_2O)_2]$
$M_r = 605.16$
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) Å^3
$Z = 4$
$D_x = 1.965$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3673 reflections
$\theta = 2.9$–28.5°
$\mu = 2.19$ 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 $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 32.5°$
$h = -16 \rightarrow 15$
$k = -13 \rightarrow 12$
$l = -30 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.046$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.91$	$\Delta\rho_{max} = 1.15$ e Å^{-3}
3682 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}
142 parameters	

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···A	D—H	H···A	D···A	D—H···A
O9—H1···O4^{i}	0.81	2.13	2.9157 (18)	163
O9—H2···O1^{ii}	0.80	2.14	2.9060 (18)	161
N4—H4···O8^{iii}	0.86	2.26	3.069 (3)	156
N5—H5···O8	0.86	2.06	2.908 (3)	169
N5—H6···O3^{iv}	0.86	2.02	2.863 (3)	166
N6—H7···O7	0.86	2.22	3.037 (3)	159
N6—H8···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 $U_{iso}(H) = 1.2U_{eq}$(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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL*97.

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$V = 2045.68$ (19) Å^3
$Z = 4$
$F(000) = 1192$
$D_x = 1.965$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
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$h = -16\rightarrow15$
$k = -13\rightarrow12$
$l = -30\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.046$
$S = 0.91$
3682 reflections
142 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 (N-H)
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.15$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ 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	0.642098 (17)	0.2500	0.02453 (5)
O1	0.09473 (12)	0.90974 (15)	0.23924 (8)	0.0411 (4)
O2	0.0000	1.1137 (2)	0.2500	0.0877 (12)
N1	0.0000	0.9816 (3)	0.2500	0.0422 (7)
O3	−0.06367 (13)	0.45066 (16)	0.15884 (8)	0.0439 (4)
O4	0.11411 (13)	0.40085 (15)	0.20462 (8)	0.0401 (4)
O5	0.04385 (18)	0.2771 (2)	0.11957 (10)	0.0734 (6)
N2	0.03253 (16)	0.37254 (19)	0.15993 (9)	0.0400 (4)
O6	−0.06808 (13)	0.77556 (17)	0.13453 (8)	0.0453 (4)
O7	0.11162 (14)	0.68127 (17)	0.13578 (8)	0.0474 (4)
O8	0.02837 (17)	0.7806 (2)	0.04701 (9)	0.0689 (6)
N3	0.02408 (17)	0.74586 (19)	0.10504 (10)	0.0413 (4)
O9	0.22927 (11)	0.64245 (15)	0.27811 (8)	0.0439 (4)
H1	0.2596	0.7239	0.2810	0.053*
H2	0.2820	0.5820	0.2825	0.053*
C1	0.2587 (2)	0.5006 (3)	−0.00306 (13)	0.0488 (6)
N4	0.3114 (2)	0.4031 (2)	−0.03940 (13)	0.0725 (7)
H3	0.2902	0.3972	−0.0805	0.087*
H4	0.3668	0.3455	−0.0220	0.087*
N5	0.1742 (2)	0.5887 (3)	−0.02918 (11)	0.0680 (7)
H5	0.1402	0.6519	−0.0053	0.082*
H6	0.1526	0.5833	−0.0702	0.082*
N6	0.29067 (19)	0.5099 (2)	0.05970 (11)	0.0626 (6)
H7	0.2562	0.5735	0.0832	0.075*
H8	0.3461	0.4525	0.0773	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.02193 (7)	0.02200 (7)	0.02968 (9)	0.000	0.00206 (5)	0.000
O1	0.0245 (7)	0.0307 (7)	0.0700 (12)	0.0031 (5)	0.0152 (7)	0.0022 (7)
O2	0.0606 (16)	0.0235 (12)	0.186 (4)	0.000	0.058 (2)	0.000
N1	0.0354 (14)	0.0252 (12)	0.068 (2)	0.000	0.0143 (13)	0.000
O3	0.0401 (8)	0.0459 (9)	0.0439 (10)	0.0142 (7)	−0.0086 (7)	−0.0129 (7)
O4	0.0379 (8)	0.0342 (8)	0.0461 (10)	0.0061 (6)	−0.0091 (7)	−0.0047 (7)
O5	0.0835 (13)	0.0677 (12)	0.0659 (14)	0.0328 (10)	−0.0143 (11)	−0.0387 (11)
N2	0.0455 (10)	0.0347 (9)	0.0389 (11)	0.0099 (8)	−0.0019 (8)	−0.0067 (9)
O6	0.0411 (9)	0.0547 (9)	0.0413 (10)	0.0142 (7)	0.0111 (7)	0.0106 (8)
O7	0.0430 (9)	0.0529 (9)	0.0474 (10)	0.0163 (7)	0.0105 (8)	0.0101 (8)
O8	0.0791 (13)	0.0894 (13)	0.0408 (11)	0.0313 (11)	0.0209 (10)	0.0240 (10)

N3	0.0477 (11)	0.0401 (10)	0.0374 (11)	0.0101 (8)	0.0109 (9)	0.0073 (9)
O9	0.0221 (6)	0.0295 (7)	0.0797 (12)	0.0005 (6)	0.0022 (7)	−0.0084 (8)
C1	0.0469 (14)	0.0483 (13)	0.0512 (17)	0.0087 (10)	0.0032 (12)	−0.0092 (12)
N4	0.0796 (17)	0.0672 (15)	0.0711 (17)	0.0217 (12)	0.0088 (13)	−0.0218 (13)
N5	0.0658 (14)	0.0906 (17)	0.0450 (13)	0.0346 (13)	−0.0120 (12)	−0.0131 (12)
N6	0.0671 (14)	0.0702 (15)	0.0486 (14)	0.0335 (11)	−0.0087 (11)	−0.0024 (12)

Geometric parameters (Å, º)

La1—O9	2.5409 (12)	O4—N2	1.259 (2)
La1—O3	2.6112 (14)	O5—N2	1.213 (2)
La1—O1	2.6603 (14)	O6—N3	1.250 (2)
La1—O6	2.7174 (15)	O7—N3	1.254 (2)
La1—O4	2.7254 (14)	O8—N3	1.238 (2)
La1—O7	2.7562 (16)	O9—H1	0.8114
La1—O9^{i}	2.5409 (12)	O9—H2	0.7982
La1—O3^{i}	2.6112 (14)	C1—N5	1.309 (3)
La1—O1^{i}	2.6603 (13)	C1—N6	1.313 (3)
La1—O6^{i}	2.7174 (15)	C1—N4	1.321 (3)
La1—O4^{i}	2.7254 (14)	N4—H3	0.8600
La1—O7^{i}	2.7562 (16)	N4—H4	0.8600
O1—N1	1.2632 (16)	N5—H5	0.8600
O2—N1	1.200 (3)	N5—H6	0.8600
N1—O1^{i}	1.2632 (16)	N6—H7	0.8600
O3—N2	1.272 (2)	N6—H8	0.8600
O9^{i}—La1—O9	179.86 (7)	O3^{i}—La1—O7	125.81 (5)
O9^{i}—La1—O3	68.43 (5)	O1—La1—O7	66.92 (5)
O9—La1—O3	111.67 (5)	O1^{i}—La1—O7	98.98 (5)
O9^{i}—La1—O3^{i}	111.67 (5)	O6^{i}—La1—O7	125.17 (5)
O9—La1—O3^{i}	68.43 (5)	O6—La1—O7	46.28 (4)
O3—La1—O3^{i}	96.51 (7)	O4^{i}—La1—O7	130.01 (5)
O9^{i}—La1—O1	111.57 (4)	O4—La1—O7	64.19 (5)
O9—La1—O1	68.29 (4)	O9^{i}—La1—O7^{i}	72.16 (5)
O3—La1—O1	129.30 (5)	O9—La1—O7^{i}	107.82 (5)
O3^{i}—La1—O1	125.69 (5)	O3—La1—O7^{i}	125.81 (5)
O9^{i}—La1—O1^{i}	68.29 (4)	O3^{i}—La1—O7^{i}	65.59 (5)
O9—La1—O1^{i}	111.57 (4)	O1—La1—O7^{i}	98.98 (5)
O3—La1—O1^{i}	125.69 (5)	O1^{i}—La1—O7^{i}	66.92 (5)
O3^{i}—La1—O1^{i}	129.30 (5)	O6^{i}—La1—O7^{i}	46.28 (4)
O1—La1—O1^{i}	47.96 (6)	O6—La1—O7^{i}	125.17 (5)
O9^{i}—La1—O6^{i}	113.47 (5)	O4^{i}—La1—O7^{i}	64.19 (5)
O9—La1—O6^{i}	66.46 (5)	O4—La1—O7^{i}	130.01 (5)
O3—La1—O6^{i}	164.53 (5)	O7—La1—O7^{i}	165.17 (6)
O3^{i}—La1—O6^{i}	68.30 (5)	N1—O1—La1	97.15 (12)
O1—La1—O6^{i}	65.31 (5)	O2—N1—O1^{i}	121.13 (11)
O1^{i}—La1—O6^{i}	66.58 (5)	O2—N1—O1	121.13 (11)
O9^{i}—La1—O6	66.46 (5)	O1^{i}—N1—O1	117.7 (2)

O9—La1—O6	113.47 (5)	N2—O3—La1	100.55 (11)
O3—La1—O6	68.30 (5)	N2—O4—La1	95.36 (11)
O3^{i}—La1—O6	164.53 (5)	O5—N2—O4	122.66 (18)
O1—La1—O6	66.58 (5)	O5—N2—O3	121.08 (18)
O1^{i}—La1—O6	65.31 (5)	O4—N2—O3	116.26 (17)
O6^{i}—La1—O6	127.02 (7)	N3—O6—La1	98.58 (12)
O9^{i}—La1—O4^{i}	66.67 (4)	N3—O7—La1	96.56 (12)
O9—La1—O4^{i}	113.46 (4)	O8—N3—O6	120.37 (19)
O3—La1—O4^{i}	66.78 (5)	O8—N3—O7	121.2 (2)
O3^{i}—La1—O4^{i}	47.45 (4)	O6—N3—O7	118.39 (19)
O1—La1—O4^{i}	163.06 (5)	La1—O9—H1	114.4
O1^{i}—La1—O4^{i}	120.83 (4)	La1—O9—H2	136.4
O6^{i}—La1—O4^{i}	99.34 (5)	H1—O9—H2	109.1
O6—La1—O4^{i}	123.71 (5)	N5—C1—N6	119.4 (2)
O9^{i}—La1—O4	113.46 (4)	N5—C1—N4	120.4 (3)
O9—La1—O4	66.67 (4)	N6—C1—N4	120.2 (2)
O3—La1—O4	47.45 (4)	C1—N4—H3	120.0
O3^{i}—La1—O4	66.78 (5)	C1—N4—H4	120.0
O1—La1—O4	120.83 (4)	H3—N4—H4	120.0
O1^{i}—La1—O4	163.06 (5)	C1—N5—H5	120.0
O6^{i}—La1—O4	123.71 (5)	C1—N5—H6	120.0
O6—La1—O4	99.34 (5)	H5—N5—H6	120.0
O4^{i}—La1—O4	72.98 (7)	C1—N6—H7	120.0
O9^{i}—La1—O7	107.82 (5)	C1—N6—H8	120.0
O9—La1—O7	72.16 (5)	H7—N6—H8	120.0
O3—La1—O7	65.59 (5)		

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

Symmetry codes: (ii) $-x+1/2$, $y+1/2$, $-z+1/2$; (iii) $-x+1/2$, $y-1/2$, $-z+1/2$; (iv) $x+1/2$, $y-1/2$, z; (v) $-x$, $-y+1$, $-z$.