



Crystal structure of poly[μ_2 -aqua-aqua(μ_2 -4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olato)-hemi- μ_4 -oxalato-barium(II)]

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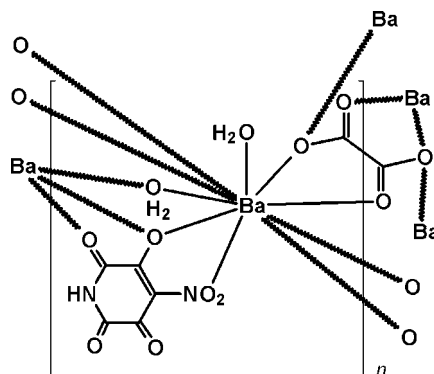
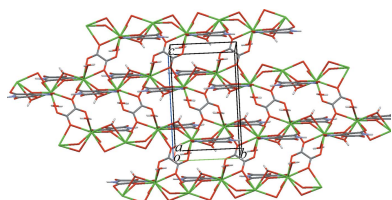
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In the title coordination polymer, $[\text{Ba}(\text{C}_5\text{HN}_2\text{O}_6)(\text{C}_2\text{O}_4)_{0.5}(\text{H}_2\text{O})_2]_n$, the tenfold coordination of the Ba centre consists of four O atoms from the two 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate (*L*) anions, three O atoms of two oxalate anions and three water molecules. The Ba—O bond lengths fall in the range 2.698 (3)–2.978 (3) Å. The *L* ligand chelates two Ba atoms related by a screw axis, leading to formation of fused five- and six-membered chelate rings. Due to the bridging function of the ligands and water molecules, the complex monomers are connected into polymeric two-dimensional layers parallel to the *bc* plane. Intermolecular O—H...O hydrogen bonds link these layers into a three-dimensional supramolecular framework.

1. Chemical context

Mixed ligand coordination polymers containing bridging oxalate anions and 1,2-dicarbonyl carbocyclic or heterocyclic compounds exhibit high reactivity and different types of magnetism (Aldoshin, 2008; Coronado *et al.*, 2007; Kitagawa & Kawata, 2002; Kovalchukova & Strashnova, 2014; Ohba & Okawa, 2000). Such compounds are of chemical interest, since a large number of potential donors available in the ligands predetermine a variety of coordination modes, which afford different geometries and dimensionalities of coordination polymers. Recently, we reported the synthesis, crystal structure and some properties of metal complexes of the 2,3,5,6-tetraoxo-4-nitro-4-idene anion (Kovalchukova *et al.*, 2014, 2014; Dinh Do *et al.*, 2013). The above-mentioned anion does not replace the water molecules from the inner sphere of the hydrated metal cations $[M(\text{H}_2\text{O})_6]^{n+}$, but can coordinate metal centres like sodium and silver(I). In the present paper, we report the molecular and crystal structure of a mixed-ligand barium complex containing 4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olate (*L*) and oxalate anions as ligands.



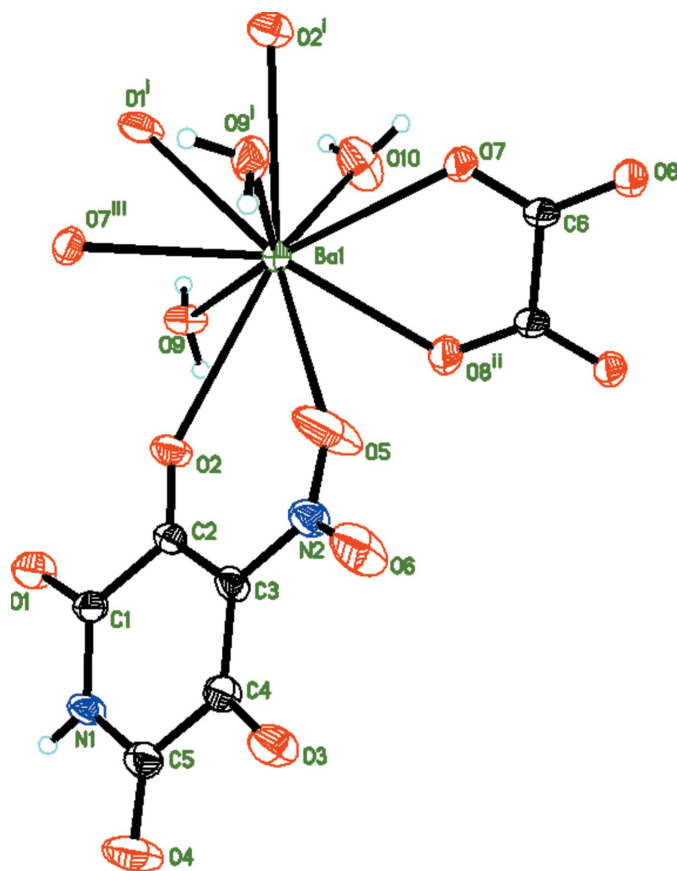


Figure 1
View of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. [Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$]

2. Structural commentary

In the title compound, $[\text{Ba}(\text{C}_5\text{HN}_2\text{O}_6)(\text{C}_2\text{O}_4)_{0.5}(\text{H}_2\text{O})_2]_n$, (I) (Fig. 1), the tenfold coordination of the Ba1 atom (Table 1) is formed by the O2, O5, O1 and O2 atoms of two 4-nitro-2,3,5,6-tetraoxypyridine-4-ide anions (*L*), the O7, O8 and O7A atoms of two oxalate anions, and the O9, O9A and O10 atoms of water molecules. The Ba—O bond lengths fall in the range 2.698 (3)–2.978 (3) Å, which is typical for ten-coordinate barium complexes containing oxalate anions (Viciano-Chumillas *et al.*, 2010; Hehl *et al.*, 2002; Marinescu *et al.*, 2005; Belombe *et al.*, 2003, 2012; Larsson, 2001; Bouayad *et al.*, 1995; Iveson *et al.*, 2011). The *L* anion has a flattened skeleton. The r.m.s. deviation of the six ring atoms from their mean plane is 0.0256 Å; the O2 and O4 atoms lie in this plane deviating by 0.049 (3) and 0.010 (3) Å, respectively, whereas the O1 and O3 atoms deviate from it by 0.171 (3) and 0.077 (3) Å, respectively. The plane of the nitro group is rotated by 11.9 (8)° with respect to the ring plane. The *L* ligand chelates two Ba atoms related by a screw axis forming fused chelate rings. The six-membered ring is almost planar (r.m.s. deviation = 0.0353 Å) and the five-membered ring is folded along the O1—O2 line by 19.0°. The geometry of the *L* anion in the Ba complex is close to that in the compounds studied earlier (Kovalchukova *et al.*, 2014; Dinh Do *et al.*, 2013). All C=O bonds are of the

Table 1
Selected bond lengths (Å).

| | | | |
|-----------------------|-----------|-----------------------|-----------|
| Ba1—O8 ⁱ | 2.698 (3) | Ba1—O10 | 2.882 (4) |
| Ba1—O7 | 2.728 (3) | Ba1—O1 ⁱⁱⁱ | 2.889 (3) |
| Ba1—O9 | 2.755 (3) | Ba1—O5 | 2.914 (4) |
| Ba1—O7 ⁱⁱⁱ | 2.805 (3) | Ba1—O2 | 2.931 (3) |
| Ba1—O9 ⁱⁱⁱ | 2.860 (3) | Ba1—O2 ⁱⁱⁱ | 2.978 (3) |

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

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

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1...O6 ⁱ | 0.86 | 2.21 | 3.052 (5) | 166 |
| O9—H2...O3 ⁱⁱ | 0.82 | 2.10 | 2.877 (4) | 158 |
| O9—H3...O8 ⁱ | 0.82 | 1.84 | 2.639 (4) | 163 |
| O10—H4...O3 ⁱⁱ | 0.82 | 2.14 | 2.828 (5) | 141 |
| O10—H4...O6 ⁱⁱ | 0.82 | 2.30 | 3.010 (5) | 146 |
| O10—H5...O4 ⁱⁱⁱ | 0.82 | 2.41 | 3.210 (5) | 165 |

Symmetry codes: (i) $x, y - 1, z$; (ii) $x - 1, y, z$; (iii) $x - 1, y + 1, z$.

double-bond type [1.200 (5)–1.229 (5) Å]. The monodentate coordination of *L* via the O atom of a nitro group attached to a benzene ring is in accordance with Venkatasubramanian *et al.* (1984), Harrowfield *et al.* (1998) and Chantrapromma *et al.* (2002). The centrosymmetric oxalate anion connects four Ba atoms closing two almost planar five-membered rings (r.m.s. deviation of rings = 0.0415 Å).

3. Supramolecular features

Due to the bridging function of the *L* ligand and the O9 water molecule, the hydrated complex cations $[\text{Ba}(\text{L})(\text{H}_2\text{O})_2]^+$ form wide zigzag bands running along the screw axes in the *b*-axis direction (Fig. 2). Oxalate anions connect the bands into thick two-dimensional networks parallel to *bc*. The networks have corrugated surfaces with terminal O3, O4 and O6 atoms of the *L* ligand on the ‘hills’ and water molecules in the ‘hollows’. In the packing (Fig. 3), the ‘hills’ enter the ‘hollows’ of adjacent networks. Two-centre hydrogen bonds O9—H2...O3 and

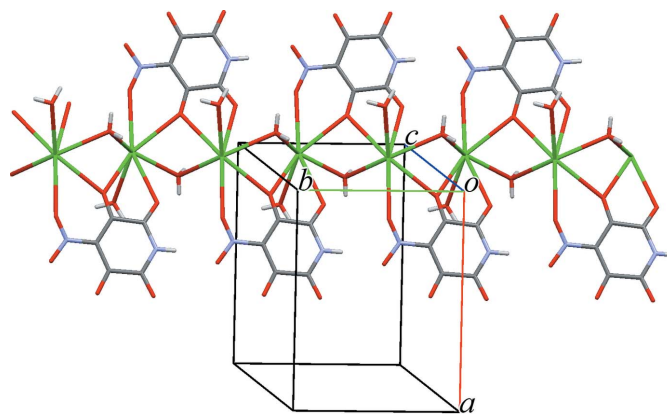


Figure 2
One-dimensional polymeric chain in (I). Oxalato ligands omitted for clarity.

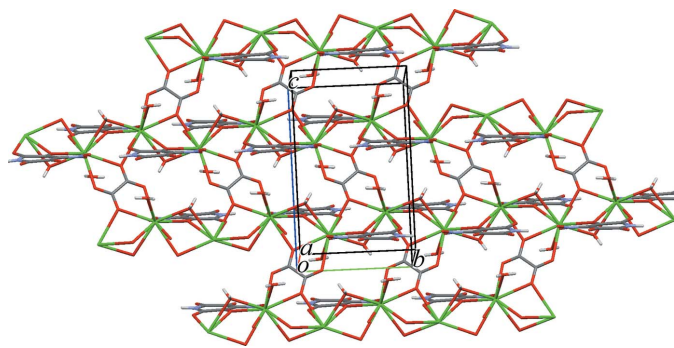


Figure 3
two-dimensional polymeric layer in (I) viewed approximately along the *a* axis.

O10—H5···O4 and three-centre bonds O10—H4···(O3,O6) (Table 2) link the networks into a three-dimensional framework. Hydrogen bonds N1—H1···O6 and O9—H3···O8 link the elements of a band and a network, respectively.

4. Database survey

The synthesis, crystal structure and some properties of metal complexes of the 4-nitro-2,3,5,6-tetraoxo-4-ide anion are described in Kovalchukova *et al.* (2014) and Dinh Do *et al.* (2013). Model structures of complexes containing carbocyclic polyoxo compounds are reviewed in Kitagawa & Kawata (2002) and Kovalchukova & Strashnova (2014). Ten coordinated structures of Ba cations with oxalate anions containing other *O*-donating ligands have been described (Viciano-Chumillas *et al.*, 2010; Marinescu *et al.*, 2005; Belombe *et al.*, 2003, 2012; Larsson, 2001; Bouayad *et al.*, 1995; Iveson *et al.*, 2011). Monodentate coordination *via* the O atom of a nitro aromatic group is described by Venkatasubramanian *et al.* (1984), Harrowfield *et al.* (1998) and Chantrapromma *et al.* (2002).

5. Synthesis and crystallization

Single crystals of (I) were grown by the slow evaporation of an ethanol solution of a 1:1:1 molar mixture of barium chloride, ammonium oxalate and ammonium 2,3,5,6-tetraoxo-4-nitro-4-inide.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms of water molecules were localized in a difference map; O—H distances were normalized. The position of the amino H atom was calculated. All H atoms were refined within the riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom. The crystal studied was a twin without superposition of reciprocal lattices. Apparently, an accidental overlapping of reflections of two domains is responsible for increased displacement ellipsoids of some

Table 3
Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | [Ba(C ₅ HN ₂ O ₆)(C ₂ O ₄) _{0.5} (H ₂ O) ₂] |
| <i>M_r</i> | 804.92 |
| Crystal system, space group | Monoclinic, <i>P</i> ₂ ₁ / <i>c</i> |
| Temperature (K) | 296 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 10.3283 (11), 7.9868 (8), 13.0760 (14) |
| β (°) | 96.419 (2) |
| <i>V</i> (Å ³) | 1071.88 (19) |
| <i>Z</i> | 2 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ^{−1}) | 3.76 |
| Crystal size (mm) | 0.16 × 0.12 × 0.03 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Bruker, 2004) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.586, 0.746 |
| No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 11240, 3410, 2692 |
| <i>R</i> _{int} | 0.036 |
| (sin θ/λ) _{max} (Å ^{−1}) | 0.736 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.038, 0.093, 1.05 |
| No. of reflections | 3410 |
| No. of parameters | 172 |
| No. of restraints | 6 |
| H-atom treatment | H-atom parameters constrained |
| Δρ _{max} , Δρ _{min} (e Å ^{−3}) | 2.31, −1.67 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *ORTEP* (Johnson & Burnett, 1996) and *Mercury* (Macrae *et al.*, 2008).

atoms. The U_{ij} components of atom O5 were restrained to approximate the isotropic behaviour.

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Acta Cryst. (2015). E71, 459-462 [https://doi.org/10.1107/S2056989015006520]

Crystal structure of poly[μ_2 -aqua-aqua(μ_2 -4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olato)hemi- μ_4 -oxalato-barium(II)]

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Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *ORTEP* (Johnson & Burnett, 1996) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Poly[μ_2 -aqua-aqua(μ_4 -4-nitro-2,5,6-trioxo-1,2,5,6-tetrahydropyridin-3-olato)hemi- μ_6 -oxalato-barium(II)]

Crystal data

[Ba(C₅HN₂O₆)(C₂O₄)_{0.5}(H₂O)₂]
 $M_r = 804.92$
 Monoclinic, $P2_1/c$
 $a = 10.3283$ (11) Å
 $b = 7.9868$ (8) Å
 $c = 13.0760$ (14) Å
 $\beta = 96.419$ (2)°
 $V = 1071.88$ (19) Å³
 $Z = 2$

$F(000) = 764$
 $D_x = 2.494$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3977 reflections
 $\theta = 3.0\text{--}31.4^\circ$
 $\mu = 3.76$ mm⁻¹
 $T = 296$ K
 Plate, brown
 $0.16 \times 0.12 \times 0.03$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: sealed tube
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2004)
 $T_{\min} = 0.586$, $T_{\max} = 0.746$
 11240 measured reflections

3410 independent reflections
 2692 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 31.5^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -15 \rightarrow 14$
 $k = -11 \rightarrow 11$
 $l = -19 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.093$
 $S = 1.05$
 3410 reflections
 172 parameters
 6 restraints

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.9998P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 2.31 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.67 \text{ e } \text{\AA}^{-3}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|-------------|----------------------------------|
| Ba1 | −0.00361 (2) | 0.20711 (3) | 0.69482 (2) | 0.01991 (8) |
| O1 | 0.2105 (3) | −0.4097 (4) | 0.6917 (3) | 0.0343 (8) |
| O2 | 0.1678 (3) | −0.0830 (4) | 0.6825 (3) | 0.0295 (7) |
| O3 | 0.6026 (3) | −0.0297 (4) | 0.6022 (3) | 0.0344 (8) |
| O4 | 0.6113 (4) | −0.3626 (5) | 0.5935 (4) | 0.0489 (10) |
| O5 | 0.2660 (4) | 0.2124 (5) | 0.6490 (5) | 0.0711 (16) |
| O6 | 0.4673 (4) | 0.2379 (4) | 0.6424 (4) | 0.0446 (10) |
| O7 | −0.0517 (3) | 0.5240 (4) | 0.6225 (2) | 0.0259 (6) |
| O8 | −0.0324 (4) | 0.7141 (4) | 0.5006 (3) | 0.0380 (9) |
| O9 | −0.1222 (3) | −0.0942 (4) | 0.6412 (2) | 0.0277 (7) |
| H2 | −0.2018 | −0.1018 | 0.6364 | 0.033* |
| H3 | −0.1064 | −0.1457 | 0.5898 | 0.033* |
| O10 | −0.2582 (4) | 0.2730 (5) | 0.5886 (4) | 0.0452 (10) |
| H4 | −0.3231 | 0.2206 | 0.6007 | 0.054* |
| H5 | −0.2776 | 0.3726 | 0.5862 | 0.054* |
| N1 | 0.4071 (3) | −0.3879 (4) | 0.6348 (3) | 0.0236 (7) |
| H1 | 0.4119 | −0.4950 | 0.6295 | 0.028* |
| N2 | 0.3712 (4) | 0.1478 (5) | 0.6435 (3) | 0.0258 (7) |
| C1 | 0.2940 (4) | −0.3217 (5) | 0.6640 (3) | 0.0211 (8) |
| C2 | 0.2754 (4) | −0.1295 (5) | 0.6620 (3) | 0.0196 (7) |
| C3 | 0.3832 (4) | −0.0309 (5) | 0.6406 (3) | 0.0201 (7) |
| C4 | 0.5038 (4) | −0.1026 (5) | 0.6192 (3) | 0.0217 (8) |
| C5 | 0.5130 (4) | −0.2959 (6) | 0.6135 (4) | 0.0250 (8) |
| C6 | −0.0251 (4) | 0.5680 (5) | 0.5350 (3) | 0.0218 (8) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|-------------|--------------|
| Ba1 | 0.02335 (13) | 0.01750 (12) | 0.01979 (12) | 0.00255 (10) | 0.00648 (8) | 0.00287 (9) |
| O1 | 0.0313 (17) | 0.0196 (16) | 0.056 (2) | −0.0044 (13) | 0.0208 (15) | 0.0017 (14) |
| O2 | 0.0223 (15) | 0.0213 (16) | 0.048 (2) | 0.0046 (12) | 0.0156 (13) | 0.0036 (13) |
| O3 | 0.0191 (15) | 0.0244 (17) | 0.061 (2) | −0.0021 (13) | 0.0110 (14) | 0.0034 (15) |
| O4 | 0.0296 (18) | 0.0305 (19) | 0.091 (3) | 0.0069 (16) | 0.0260 (19) | 0.000 (2) |
| O5 | 0.037 (2) | 0.026 (2) | 0.157 (5) | 0.0086 (17) | 0.038 (3) | 0.007 (2) |
| O6 | 0.0302 (18) | 0.0179 (17) | 0.087 (3) | −0.0070 (14) | 0.0102 (19) | 0.0005 (18) |
| O7 | 0.0408 (18) | 0.0192 (14) | 0.0193 (14) | 0.0009 (13) | 0.0101 (13) | −0.0011 (11) |
| O8 | 0.068 (3) | 0.0215 (16) | 0.0281 (17) | 0.0077 (17) | 0.0221 (17) | 0.0028 (13) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O9 | 0.0241 (15) | 0.0280 (16) | 0.0318 (16) | 0.0028 (13) | 0.0063 (12) | −0.0083 (13) |
| O10 | 0.0294 (18) | 0.032 (2) | 0.072 (3) | −0.0050 (16) | −0.0021 (18) | 0.0092 (18) |
| N1 | 0.0228 (17) | 0.0139 (15) | 0.035 (2) | 0.0023 (13) | 0.0096 (14) | 0.0000 (14) |
| N2 | 0.0228 (17) | 0.0192 (17) | 0.036 (2) | 0.0005 (14) | 0.0066 (15) | 0.0007 (15) |
| C1 | 0.0216 (19) | 0.0184 (19) | 0.0245 (19) | 0.0014 (14) | 0.0075 (15) | 0.0000 (14) |
| C2 | 0.0198 (18) | 0.0168 (18) | 0.0227 (18) | 0.0023 (15) | 0.0049 (14) | 0.0005 (15) |
| C3 | 0.0187 (18) | 0.0146 (17) | 0.027 (2) | −0.0003 (14) | 0.0032 (15) | 0.0012 (14) |
| C4 | 0.0191 (18) | 0.0180 (18) | 0.028 (2) | −0.0019 (15) | 0.0043 (15) | 0.0003 (15) |
| C5 | 0.0211 (19) | 0.024 (2) | 0.031 (2) | 0.0023 (17) | 0.0056 (16) | 0.0027 (17) |
| C6 | 0.027 (2) | 0.0183 (19) | 0.0211 (19) | 0.0020 (15) | 0.0073 (15) | −0.0044 (14) |

Geometric parameters (Å, °)

| | | | |
|---|-------------|---------------------------|------------|
| Ba1—O8 ⁱ | 2.698 (3) | O7—C6 | 1.257 (5) |
| Ba1—O7 | 2.728 (3) | O7—Ba1 ⁱⁱⁱ | 2.805 (3) |
| Ba1—O9 | 2.755 (3) | O8—C6 | 1.250 (5) |
| Ba1—O7 ⁱⁱ | 2.805 (3) | O8—Ba1 ⁱ | 2.698 (3) |
| Ba1—O9 ⁱⁱⁱ | 2.860 (3) | O9—Ba1 ⁱⁱ | 2.860 (3) |
| Ba1—O10 | 2.882 (4) | O9—H2 | 0.8200 |
| Ba1—O1 ⁱⁱⁱ | 2.889 (3) | O9—H3 | 0.8200 |
| Ba1—O5 | 2.914 (4) | O10—H4 | 0.8201 |
| Ba1—O2 | 2.931 (3) | O10—H5 | 0.8200 |
| Ba1—O2 ⁱⁱⁱ | 2.978 (3) | N1—C5 | 1.372 (5) |
| O1—C1 | 1.199 (5) | N1—C1 | 1.375 (5) |
| O1—Ba1 ⁱⁱ | 2.889 (3) | N1—H1 | 0.8600 |
| O2—C2 | 1.229 (5) | N2—C3 | 1.433 (5) |
| O2—Ba1 ⁱⁱ | 2.978 (3) | C1—C2 | 1.547 (6) |
| O3—C4 | 1.217 (5) | C2—C3 | 1.417 (5) |
| O4—C5 | 1.202 (5) | C3—C4 | 1.427 (5) |
| O5—N2 | 1.212 (5) | C4—C5 | 1.549 (6) |
| O6—N2 | 1.227 (5) | C6—C6 ⁱ | 1.546 (8) |
| O8 ⁱ —Ba1—O7 | 59.61 (9) | O2—Ba1—O2 ⁱⁱⁱ | 149.14 (6) |
| O8 ⁱ —Ba1—O9 | 93.86 (10) | C1—O1—Ba1 ⁱⁱ | 124.3 (3) |
| O7—Ba1—O9 | 131.58 (10) | C2—O2—Ba1 | 144.8 (3) |
| O8 ⁱ —Ba1—O7 ⁱⁱ | 153.12 (10) | C2—O2—Ba1 ⁱⁱ | 122.0 (3) |
| O7—Ba1—O7 ⁱⁱ | 142.27 (8) | Ba1—O2—Ba1 ⁱⁱ | 91.81 (8) |
| O9—Ba1—O7 ⁱⁱ | 78.67 (9) | N2—O5—Ba1 | 152.8 (3) |
| O8 ⁱ —Ba1—O9 ⁱⁱⁱ | 118.77 (10) | C6—O7—Ba1 | 121.7 (3) |
| O7—Ba1—O9 ⁱⁱⁱ | 78.16 (9) | C6—O7—Ba1 ⁱⁱⁱ | 125.8 (3) |
| O9—Ba1—O9 ⁱⁱⁱ | 145.81 (7) | Ba1—O7—Ba1 ⁱⁱⁱ | 100.18 (9) |
| O7 ⁱⁱ —Ba1—O9 ⁱⁱⁱ | 67.59 (9) | C6—O8—Ba1 ⁱ | 123.3 (3) |
| O8 ⁱ —Ba1—O10 | 73.50 (13) | Ba1—O9—Ba1 ⁱⁱ | 98.17 (9) |
| O7—Ba1—O10 | 62.78 (10) | Ba1—O9—H2 | 119.8 |
| O9—Ba1—O10 | 71.41 (10) | Ba1 ⁱⁱ —O9—H2 | 112.6 |
| O7 ⁱⁱ —Ba1—O10 | 126.42 (11) | Ba1—O9—H3 | 121.6 |
| O9 ⁱⁱⁱ —Ba1—O10 | 125.00 (11) | Ba1 ⁱⁱ —O9—H3 | 102.8 |
| O8 ⁱ —Ba1—O1 ⁱⁱⁱ | 138.61 (12) | H2—O9—H3 | 100.9 |

| | | | |
|--|-------------|-----------------------|-----------|
| O7—Ba1—O1 ⁱⁱⁱ | 111.17 (9) | Ba1—O10—H4 | 122.3 |
| O9—Ba1—O1 ⁱⁱⁱ | 61.02 (9) | Ba1—O10—H5 | 113.6 |
| O7 ⁱⁱ —Ba1—O1 ⁱⁱⁱ | 59.07 (10) | H4—O10—H5 | 107.6 |
| O9 ⁱⁱⁱ —Ba1—O1 ⁱⁱⁱ | 95.40 (9) | C5—N1—C1 | 124.8 (4) |
| O10—Ba1—O1 ⁱⁱⁱ | 67.61 (11) | C5—N1—H1 | 117.6 |
| O8 ⁱ —Ba1—O5 | 64.24 (16) | C1—N1—H1 | 117.6 |
| O7—Ba1—O5 | 93.23 (11) | O5—N2—O6 | 118.8 (4) |
| O9—Ba1—O5 | 111.61 (11) | O5—N2—C3 | 120.4 (4) |
| O7 ⁱⁱ —Ba1—O5 | 94.27 (14) | O6—N2—C3 | 120.8 (4) |
| O9 ⁱⁱⁱ —Ba1—O5 | 77.39 (14) | O1—C1—N1 | 121.4 (4) |
| O10—Ba1—O5 | 137.72 (16) | O1—C1—C2 | 119.6 (4) |
| O1 ⁱⁱⁱ —Ba1—O5 | 152.77 (13) | N1—C1—C2 | 119.0 (3) |
| O8 ⁱ —Ba1—O2 | 89.10 (10) | O2—C2—C3 | 128.6 (4) |
| O7—Ba1—O2 | 143.31 (9) | O2—C2—C1 | 114.2 (4) |
| O9—Ba1—O2 | 63.24 (9) | C3—C2—C1 | 117.1 (3) |
| O7 ⁱⁱ —Ba1—O2 | 64.40 (9) | C2—C3—C4 | 122.6 (4) |
| O9 ⁱⁱⁱ —Ba1—O2 | 104.67 (9) | C2—C3—N2 | 118.4 (4) |
| O10—Ba1—O2 | 129.95 (11) | C4—C3—N2 | 119.0 (3) |
| O1 ⁱⁱⁱ —Ba1—O2 | 105.01 (9) | O3—C4—C3 | 127.7 (4) |
| O5—Ba1—O2 | 53.35 (10) | O3—C4—C5 | 114.3 (4) |
| O8 ⁱ —Ba1—O2 ⁱⁱⁱ | 121.74 (10) | C3—C4—C5 | 117.9 (3) |
| O7—Ba1—O2 ⁱⁱⁱ | 64.65 (9) | O4—C5—N1 | 121.2 (4) |
| O9—Ba1—O2 ⁱⁱⁱ | 111.41 (8) | O4—C5—C4 | 120.7 (4) |
| O7 ⁱⁱ —Ba1—O2 ⁱⁱⁱ | 84.77 (9) | N1—C5—C4 | 118.0 (3) |
| O9 ⁱⁱⁱ —Ba1—O2 ⁱⁱⁱ | 61.45 (9) | O8—C6—O7 | 125.3 (4) |
| O10—Ba1—O2 ⁱⁱⁱ | 67.23 (11) | O8—C6—C6 ⁱ | 117.0 (5) |
| O1 ⁱⁱⁱ —Ba1—O2 ⁱⁱⁱ | 53.60 (8) | O7—C6—C6 ⁱ | 117.7 (5) |
| O5—Ba1—O2 ⁱⁱⁱ | 135.85 (12) | | |

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, y-1/2, -z+3/2$; (iii) $-x, y+1/2, -z+3/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| N1—H1 \cdots O6 ^{iv} | 0.86 | 2.21 | 3.052 (5) | 166 |
| O9—H2 \cdots O3 ^v | 0.82 | 2.10 | 2.877 (4) | 158 |
| O9—H3 \cdots O8 ^{iv} | 0.82 | 1.84 | 2.639 (4) | 163 |
| O10—H4 \cdots O3 ^v | 0.82 | 2.14 | 2.828 (5) | 141 |
| O10—H4 \cdots O6 ^v | 0.82 | 2.30 | 3.010 (5) | 146 |
| O10—H5 \cdots O4 ^{vi} | 0.82 | 2.41 | 3.210 (5) | 165 |

Symmetry codes: (iv) $x, y-1, z$; (v) $x-1, y, z$; (vi) $x-1, y+1, z$.