A new (monohydrate) form of 3,5-dicarboxyanilinium nitrate: crystal structure and Hirshfeld surface analysis

Mehdi Boutebdja,a,b* Nesrine Benarous,a Ahlem Linda Boukedid,a Asma Lehlehanda and Adel Beghidja,a

aUnite de Recherche de Chimie de l’Environnement et Moléculaire Structurale (CHEMS), Université Frères Mentouri Constantine 1, 25017 Constantine, Algeria, and bLaboratoire de Technologie des Matériaux Avancés, École Nationale Polytechnique de Constantine Nouvelle Ville Universitaire, Ali Mendjeli, Constantine 25000, Algeria. *Correspondence e-mail: mboutebdja@gmail.com

The title compound, C8H8NO4+·NO3−·H2O, crystallizes in the same space group (P21/c) as the previously reported dihydrate form [Liang & Zhu (2010). Acta Cryst. E 66, o667], but with two formula units per asymmetric unit instead of one. In the crystal, the components are linked into a three-dimensional network by classical intermolecular O—H⋯O and N—H⋯O hydrogen bonds and π–π stacking interactions. A Hirshfeld surface (HS) analysis indicated that the most important contributions to the crystal packing are from H⋯O/O⋯H (52.4%), H⋯H (13.9%) and C⋯C (11.2%) for one cation and H⋯O/O⋯H (46.3%), H⋯H (20%) and O⋯C/C⋯O (10.6%) for the other.

1. Chemical context

The amphoteric 5-aminoisophthalic acid (5-AIP) has a well known ability to form supramolecular assemblies with metal ions (Xin et al., 2021; Luo et al., 2011). As a result, it can operate like nodes similar to natural amino acids (Singh et al., 2019) (Fig. 1). In addition, 5-AIP may self-assemble as a result of many hydrogen-bonding patterns. It forms salts with a Brønsted acid or base and its structural characteristics enable it to take on a variety of ionic forms (Nath & Baruah, 2012; McGuire et al., 2016). Herein, we report on the synthesis and crystal structure of a new 3,5-dicarboxyanilinium nitrate hydrate, (I).

2. Structural commentary

Compound (I) differs from the previously reported crystal form of 3,5-dicarboxyanilinium nitrate (Liang & Zhu, 2010) by
3. Supramolecular features

An extensive network of moderate-to-strong N−H⋯O and O−H⋯O hydrogen bonds (Steiner, 2002) exists in the crystal structure of (I) (Table 2). The supramolecular motif can be described as two-dimensional layers that extend parallel to the crystallographic (101) plane (Fig. 3a). In each layer, the 3,5-
dicarboxyloxyanilinium A cations and the nitrate A anions are linked through bifurcated hydrogen bonds, forming chains of $R_2^2(4)$ rings that propagate parallel to the b axis (Fig. 3a,b). In addition, the 3,5-dicarboxyloxyanilinium B cations and water molecules form chains of $R_2^2(22)$ ring motifs that also extend along the b-axis direction (Fig. 3a,d). These two types of chains are interconnected via dimeric O−H⋯O hydrogen bonds, which occur between one of the carboxylate groups of each of the A and B cations (within the asymmetric unit as defined here) and enclosing an $R_2^2(8)$ graph-set motif (Fig. 3a,e). Furthermore, we can distinguish, as illustrated in Fig. 4, that the nitrate B anions are involved in the formation of alternating $R_2^2(26)$ and $R_2^2(34)$ ring motifs, generating ribbons that propagate along the a-axis direction, which in turn leads to the formation of a three-dimensional supermolecular network.

Table 1

| Symbol | Value |
|--------|-------|
| C6A−N1A | 1.457 (2) |
| O1A−C1A | 1.286 (2) |
| O2A−C1A | 1.237 (2) |
| O3A−C6A | 1.322 (2) |
| O4A−C8A | 1.202 (2) |
| O2A−ClA−O1A | 124.42 (17) |
| O4A−C8A−O3A | 124.00 (16) |

Table 2

| Bond | A−A | B−B | C−C | D−D | E−E |
|------|-----|-----|-----|-----|-----|
| O2W−H2WA⋯O4B | 0.93 (4) |
| O2W−H2WB⋯O1B | 0.88 (4) |
| O3A−H3A⋯O5A | 0.94 (3) |
| O3B−H3B⋯O1W | 0.86 (3) |
| O1W−H1WA⋯O2Ww | 0.81 (3) |
| O1W−H1WB⋯O6Bw | 0.88 (3) |
| C7A−H7A⋯O5B | 0.93 |
| N1B−H1BA⋯O7A′ | 0.94 (2) |
| N1B−H1BB⋯O5B | 0.90 (2) |
| N1B−H1BC⋯O2Wwi | 0.86 (3) |
| N1B−H1BC⋯O1Wwii | 0.86 (3) |
| N1A−H1AA⋯O6Awii | 0.81 (3) |
| N1A−H1AA⋯O5Awii | 0.81 (3) |
| N1A−H1AB⋯O7Awii | 0.90 (2) |
| N1A−H1AB⋯O5Bwii | 0.90 (2) |
| N1A−H1AC⋯O5A′wii | 0.86 (2) |
| N1A−H1AC⋯O7A′wii | 0.86 (2) |
| O1B−H1BB⋯O2A | 0.77 (4) |
| O1B−H1BB⋯O2A | 0.82 (3) |

Symmetry codes: (i) x, y, z; (ii) −x+1, y−1/z+1; (iii) −x+1, y−z+1; (iv) x, −y+1/z, −z+1; (v) −x+2, y−2/z, −z+1; (vi) x, −y+1/z, −z+1; (vii) x, −y+1/z, −z+1; (viii) x, −y+1/z, −z+1.
Further examination reveals that the cohesion in the crystal structure is enhanced by offset or slipped $\pi$–$\pi$ stacking interactions, involving the aromatic rings of the A and B cations, which appear in the direction of the crystallographic a axis (Fig. 5). Two parallel rings A contact with a centroid-to-centroid distance $Cg1\cdot\cdot\cdot Cg1(2-x,3-y,1-z)$ of 3.6768 (9) Å, while rings A and B (forming an interplanar angle of 11.81°) contact with a $Cg1\cdot\cdot\cdot Cg2(x,1+y,z)$ distance of 3.7960 (9) Å. Note that the former $\pi$–$\pi$ stacking interaction reinforces the $R^2_2(8)$ ring described earlier.

4. Hirshfeld surface analysis

In order to visualize and quantify the intermolecular interactions in compound (I), we carried out a Hirshfeld surface (HS) analysis (Spackman & Jayatilaka, 2009) using Crystal-Explorer21 (Spackman et al., 2021) and the associated two-dimensional fingerprint plots (McKinnon et al., 2007) mapped in color with a normalized contact distance, $d_{\text{norm}}$, varying from red through white to blue depending on the distances compared to the sum of the van der Waals radii. The Hirshfeld surfaces mapped over $d_{\text{norm}}$ were calculated separately for cations A and B using a standard high surface resolution (Fig. 6a). The red spots correspond to contacts shorter than the van der Waals radii sum of the closest atoms and relate to the presence of $O-H\cdot\cdot\cdot O$ and $N-H\cdot\cdot\cdot O$ hydrogen bonds in the crystal structure, whereas the faint-red spots (highlighted by red circles for clarity) represent weaker $C-H\cdot\cdot\cdot O$ interactions. The presence of characteristic red and blue triangles on the shape-index surface (Fig. 6b) clearly suggest the presence of $\pi$–$\pi$ interactions between the neighboring organic cations and the curvedness plots (Fig. 6c) show flat surface patches characteristic of planar stacking.

The overall two-dimensional fingerprint plot and those delineated into O···H/O/O, H···H, C···C, O···C/C···O, O···O and C···H/H···C contacts for cations A and B are shown in Fig. 7 and their relative contributions to the HS are illustrated graphically in Fig. 8. The most important contributions for both cations come from H···O/O/H contacts (52.4% for cation A and 46.3% for B), with characteristic ‘spikes’ in the plots related to the presence of strong O–...
H··O and N—H··O hydrogen bonds. The second most important are H··H contacts, contributing 13.9% and 20% for cations A and B, respectively. These are followed for cation A by C··C contacts (11.2%), but for cation B by O··C/ C··O contacts (10.6%), other contacts making less significant contributions.

5. Database survey

The Cambridge Structural Database (Version 2022.2.0 updated to June 2022; Groom et al., 2016), was searched for structures with carboxyl–carboxyl \( R_2^2(8) \) graph-set motifs using ConQuest (Bruno et al., 2002) for all searches, and filters were applied to ensure that only organic compounds and non-disordered molecules were included. In addition, the searches were also limited to structures with low \( R \)-factor values (\( R < 0.05 \)). The results of the searches were analyzed using Mercury (CSD Version 2022.2.0; Macrae et al., 2020).

6. Synthesis and crystallization

5-Aminoisophthalic acid (0.181 g, 1 mmol) dissolved in methanol (10 mL) was added under stirring to a methanolic solution of Er(NO₃)₃·5H₂O (0.110 g, 0.25 mmol). After several minutes of stirring, a brighter orange precipitate appeared and was filtered. After slowly evaporating the filtrate over one week, colorless single crystals of the title compound suitable for X-ray diffraction analysis were isolated.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms of the ammonium NH₃⁺, carboxylic acid groups COOH and water molecules were localized in difference-Fourier maps and refined with \( U_{iso}(H) \) set to 1.5\( U_{eq}(O) \) or 1.2\( U_{eq}(N) \). The C-bound H atoms were placed in calculated positions with a C—H distance of 0.93 Å and refined using a riding model with fixed isotropic displacement parameters \( [U_{iso}(H) = 1.2U_{eq}(O)] \).
Funding information

The authors acknowledge the Algerian Ministry of Higher Education and Scientific Research, the Algerian Directorate-General for Scientific Research and Technological Development for support.

Table 3

Experimental details.

| Crystal data | Chemical formula | C₈H₈NO₄⁺·NO₃⁻·H₂O |
|--------------|------------------|---------------------|
| Mₙ           |                  | 262.18              |
| Crystal system, space group | Monoclinic, P2₁/c |
| Temperature (K) | 298             |
| a, b, c (Å) | 14.7026 (4), 8.5449 (2), 16.9929 (4) |
| β (°) | 92.800 (2) |
| V (Å³) | 2132.31 (9) |
| Z | 8 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.15 |
| Crystal size (mm) | 0.14 × 0.12 × 0.1 |

Data collection

Diffractometer Bruker APEXII CCD
Absorption correction Multi-scan (SADABS; Bruker, 2014)
T_min, T_max 0.627, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections 20897, 4881, 3653
R_int 0.069
(sin θ/λ)max (Å⁻¹) 0.649
Refinement

R[F² > 2σ(F²)], wR(F²), S 0.048, 0.142, 1.02
No. of reflections 4881
No. of parameters 368
H-atom treatment H atoms treated by a mixture of independent and constrained refinement
Δρ_max, Δρ_min (e Å⁻³) 0.38, −0.36

Computer programs: BIS, APEX2 and SAINT (Bruker, 2014), SHELXT (Sheldrick, 2015a), SHELXL2018/5 (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).

Research communications

References

Bruker (2014). BIS, APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). Acta Cryst. B58, 389–397.
Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). J. Chem. Inf. Comput. Sci. 44, 2133–2144.
Cai, B., Li, S.-J., Zhu, M.-E., Li, M.-Q. & Meng, Y. (2020). Z. Kristallogr. New Cryst. Struct. 235, 1–2.
Dobson, A. J. & Gerkin, R. E. (1998). Acta Cryst. C54, 1503–1505.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Liang, W.-X. & Zhu, Y.-T. (2010). Acta Cryst. E66, o667.
Luo, Y., Calvez, G., Freslon, S., Bernot, K., Daiguebonne, C. & Guillou, O. (2011). Eur. J. Inorg. Chem. 2011, 3705–3716.
Luo, Y., Calvez, G., Freslon, S., Bernot, K., Daiguebonne, C. & Guillou, O. (2011). Eur. J. Inorg. Chem. 2011, 3705–3716.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.
McGuire, S. C., Travis, S. C., Tuohey, D. W., Deering, T. J., Martin, B., Cox, J. M. & Benedict, J. B. (2016). Acta Cryst. E72, 639–642.
McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). Chem. Commun. pp. 3814–3816.
Nath, B. & Baruah, J. B. (2012). Mol. Cryst. Liq. Cryst. 562, 242–253.
Sheldrick, G. M. (2015a). Acta Cryst. C71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. A71, 3–8.
Singh, M. P., Tarai, A. & Baruah, J. B. (2019). ChemistrySelect, 4, 5427–5436.
Spackman, M. A. & Jayatilaka, D. (2009). CrystEngComm, 11, 19–32.
Steiner, T. (2002). Angew. Chem. Int. Ed. 41, 48–76.
Wang, G. X. & Zhang, Q. W. (2006). Z. Kristallogr. New Cryst. Struct. 221, 453–454.
Xin, Y., Zhou, J., Xing, Y. H., Bai, F. Y. & Sun, L. X. (2021). New J. Chem. 45, 3432–3440.

Acta Cryst. (2022). E78
supporting information

Acta Cryst. (2022). E78  [https://doi.org/10.1107/S2056989022010167]

A new (monohydrate) form of 3,5-dicarboxyanilinium nitrate: crystal structure and Hirshfeld surface analysis

Mehdi Boutebdja, Nesrine Benarous, Ahlem Linda Boulkedid, Asma Lehleh and Adel Beghidja

Computing details

Data collection: BIS (Bruker, 2014), APEX2 (Bruker, 2014); cell refinement: SAINT (Bruker, 2014); data reduction: SAINT (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

3,5-Dicarboxyanilinium nitrate monohydrate

Crystal data

C₈H₈NO₄+·NO₃⁻·H₂O  
Mr = 262.18
Monoclinic, P2₁/c  
a = 14.7026 (4) Å  
b = 8.5449 (2) Å  
c = 16.9929 (4) Å  
β = 92.800 (2)°  
V = 2132.31 (9) Å³  
Z = 8

Data collection

Bruker APEXII CCD diffractometer  
Mirror optics monochromator  
φ and ω scans  
Absorption correction: multi-scan (SADABS; Bruker, 2014)  
Tmin = 0.627, Tmax = 0.746  
20897 measured reflections  

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.048  
wR(F²) = 0.142  
S = 1.02  
4881 reflections  
368 parameters  
0 restraints  
Primary atom site location: heavy-atom method  
Secondary atom site location: other  
Hydrogen site location: mixed  
H atoms treated by a mixture of independent and constrained refinement

Δρmax = 0.38 e Å⁻³  
Δρmin = −0.36 e Å⁻³
**Special details**

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

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

|    | x          | y          | z          | Uiso*/Ueq |
|----|------------|------------|------------|-----------|
| N1B | 0.67893 (13) | 0.3682 (2) | 0.28611 (10) | 0.0301 (4) |
| O1A | 0.82519 (13) | 1.17198 (18) | 0.43486 (9) | 0.0423 (4) |
| O2W | 0.58027 (15) | −0.0690 (2) | 0.65998 (12) | 0.0603 (5) |
| H2WA | 0.546 (3) | −0.012 (5) | 0.622 (2) | 0.090* |
| H2WB | 0.615 (3) | −0.127 (4) | 0.631 (2) | 0.090* |
| O3A | 0.97439 (10) | 1.86406 (16) | 0.43414 (8) | 0.0346 (3) |
| H3A | 0.9913 (18) | 1.922 (3) | 0.3898 (16) | 0.052* |
| O2A | 0.78909 (12) | 1.14271 (17) | 0.56010 (9) | 0.0452 (4) |
| O4A | 0.92628 (11) | 1.69085 (17) | 0.34332 (8) | 0.0396 (4) |
| O3B | 0.56209 (12) | 0.38877 (19) | 0.62141 (9) | 0.0465 (4) |
| H3B | 0.539 (2) | 0.324 (4) | 0.6536 (18) | 0.070* |
| O1B | 0.70854 (12) | 0.86590 (18) | 0.53880 (9) | 0.0418 (4) |
| O4B | 0.55015 (15) | 0.17909 (18) | 0.54420 (10) | 0.0574 (5) |
| O2B | 0.75437 (11) | 0.88596 (16) | 0.41625 (8) | 0.0362 (3) |
| O6A | 1.10763 (13) | 1.85507 (18) | 0.24130 (10) | 0.0503 (4) |
| O5A | 1.03844 (10) | 2.02758 (17) | 0.30967 (9) | 0.0380 (4) |
| O7A | 1.18270 (10) | 2.05003 (17) | 0.29317 (9) | 0.0389 (4) |
| O1W | 0.49992 (10) | 0.22720 (19) | 0.73709 (9) | 0.0357 (3) |
| H1WA | 0.4800 (19) | 0.284 (3) | 0.7699 (16) | 0.053* |
| H1WB | 0.4622 (19) | 0.147 (3) | 0.7312 (15) | 0.053* |
| O7B | 0.70536 (11) | −0.14901 (17) | 0.22552 (10) | 0.0450 (4) |
| O5B | 0.76172 (10) | 0.07156 (17) | 0.26536 (9) | 0.0403 (4) |
| O6B | 0.62322 (10) | 0.01340 (18) | 0.28938 (9) | 0.0410 (4) |
| N2A | 1.11052 (12) | 1.97532 (18) | 0.28112 (9) | 0.0295 (4) |
| N2B | 0.69618 (11) | −0.02251 (18) | 0.25969 (10) | 0.0299 (4) |
| C1A | 0.82076 (13) | 1.2200 (2) | 0.50630 (11) | 0.0254 (4) |
| C2A | 0.85560 (12) | 1.3807 (2) | 0.52255 (10) | 0.0225 (4) |
| C3A | 0.88063 (11) | 1.4777 (2) | 0.46159 (10) | 0.0218 (4) |
| H3AA | 0.876949 | 1.441662 | 0.409886 | 0.026* |
| C4A | 0.91116 (11) | 1.62859 (19) | 0.47816 (10) | 0.0206 (3) |
| C8A | 0.93717 (12) | 1.7299 (2) | 0.41105 (10) | 0.0244 (4) |
| C5A | 0.91825 (12) | 1.68168 (19) | 0.55568 (10) | 0.0219 (3) |
| H5A | 0.939205 | 1.782250 | 0.567040 | 0.026* |
| C6A | 0.89382 (11) | 1.5833 (2) | 0.61539 (10) | 0.0212 (3) |
| N1A | 0.90040 (13) | 1.6379 (2) | 0.69669 (9) | 0.0267 (3) |
| C7A | 0.86173 (12) | 1.4334 (2) | 0.59991 (10) | 0.0230 (4) |
| H7A | 0.844537 | 1.369037 | 0.640745 | 0.028* |
| C8B | 0.57193 (14) | 0.3132 (2) | 0.55560 (12) | 0.0321 (4) |
| C4B | 0.61297 (13) | 0.4121 (2) | 0.49363 (11) | 0.0268 (4) |
supporting information

|     | U^11 | U^22 | U^33 | U^12 | U^13 | U^23 |
|-----|------|------|------|------|------|------|
| C3B | 0.64094 (13) | 0.5653 (2) | 0.51020 (11) | 0.0261 (4) |
| H3BA | 0.633618 | 0.607888 | 0.559853 | 0.031* |
| C2B | 0.67981 (12) | 0.6536 (2) | 0.45190 (11) | 0.0236 (4) |
| C1B | 0.71606 (12) | 0.8134 (2) | 0.46854 (11) | 0.0254 (4) |
| C7B | 0.69130 (12) | 0.5897 (2) | 0.37756 (10) | 0.0244 (4) |
| H7B | 0.716729 | 0.648905 | 0.338290 | 0.029* |
| C6B | 0.66436 (12) | 0.4375 (2) | 0.36321 (10) | 0.0240 (4) |
| C5B | 0.62522 (13) | 0.3476 (2) | 0.42002 (11) | 0.0271 (4) |
| H5B | 0.607314 | 0.245226 | 0.409039 | 0.033* |
| H1B | 0.7317 (17) | 0.954 (3) | 0.5397 (14) | 0.041* |
| H1BA | 0.7200 (16) | 0.426 (3) | 0.2570 (13) | 0.033* |
| H1BB | 0.7054 (15) | 0.273 (3) | 0.2872 (13) | 0.033* |
| H1BC | 0.6263 (18) | 0.350 (3) | 0.2638 (13) | 0.033* |
| H1AA | 0.9473 (17) | 1.618 (3) | 0.7214 (13) | 0.033* |
| H1AB | 0.8549 (16) | 1.593 (3) | 0.7224 (13) | 0.033* |
| H1AC | 0.8850 (15) | 1.734 (3) | 0.7023 (13) | 0.033* |
| H1A | 0.804 (3) | 1.090 (5) | 0.433 (2) | 0.087 (12)* |

Atomic displacement parameters (Å\(^2\))

|     | U^11  | U^22  | U^33  | U^12  | U^13  | U^23  |
|-----|-------|-------|-------|-------|-------|-------|
| N1B | 0.0342 (9) | 0.0260 (9) | 0.0305 (9) | −0.0018 (7) | 0.0048 (7) | −0.0073 (7) |
| O1A | 0.0685 (11) | 0.0235 (8) | 0.0348 (8) | −0.0118 (7) | 0.0009 (7) | −0.0098 (6) |
| O2W | 0.0750 (14) | 0.0476 (11) | 0.0614 (12) | 0.0152 (9) | 0.0353 (10) | 0.0080 (9) |
| O3A | 0.0509 (9) | 0.0253 (7) | 0.0279 (7) | −0.0142 (6) | 0.0051 (6) | 0.0020 (6) |
| O2A | 0.0679 (11) | 0.0298 (8) | 0.0381 (8) | −0.0217 (7) | 0.0046 (7) | 0.0034 (6) |
| O4A | 0.0628 (10) | 0.0343 (8) | 0.0219 (7) | −0.0123 (7) | 0.0033 (6) | 0.0008 (6) |
| O3B | 0.0690 (11) | 0.0400 (9) | 0.0318 (8) | −0.0176 (8) | 0.0154 (7) | 0.0013 (7) |
| O1B | 0.0616 (10) | 0.0277 (8) | 0.0375 (8) | −0.0182 (7) | 0.0179 (7) | −0.0130 (6) |
| O4B | 0.0931 (14) | 0.0302 (9) | 0.0507 (10) | −0.0227 (8) | 0.0230 (9) | 0.0021 (7) |
| O2B | 0.0534 (9) | 0.0237 (7) | 0.0320 (7) | −0.0118 (6) | 0.0081 (6) | −0.0002 (5) |
| O6A | 0.0677 (12) | 0.0278 (8) | 0.0560 (10) | 0.0005 (7) | 0.0081 (8) | −0.0119 (7) |
| O5A | 0.0419 (8) | 0.0315 (8) | 0.0419 (8) | 0.0004 (6) | 0.0170 (6) | 0.0065 (6) |
| O7A | 0.0353 (8) | 0.0388 (8) | 0.0425 (9) | −0.0050 (6) | 0.0013 (6) | 0.0046 (6) |
| O1W | 0.0359 (8) | 0.0355 (8) | 0.0365 (8) | −0.0048 (6) | 0.0102 (6) | −0.0007 (6) |
| O7B | 0.0558 (10) | 0.0263 (8) | 0.0541 (10) | 0.0004 (7) | 0.0153 (8) | −0.0108 (7) |
| O5B | 0.0417 (9) | 0.0335 (8) | 0.0467 (9) | −0.0101 (6) | 0.0127 (7) | −0.0036 (6) |
| O6B | 0.0338 (8) | 0.0393 (8) | 0.0508 (9) | 0.0046 (6) | 0.0117 (7) | −0.0038 (7) |
| N2A | 0.0394 (9) | 0.0220 (8) | 0.0273 (8) | −0.0009 (7) | 0.0050 (6) | 0.0059 (6) |
| N2B | 0.0354 (9) | 0.0247 (8) | 0.0298 (8) | 0.0019 (7) | 0.0050 (6) | 0.0011 (6) |
| C1A | 0.0306 (9) | 0.0202 (9) | 0.0254 (9) | −0.0024 (7) | 0.0009 (7) | −0.0008 (7) |
| C2A | 0.0251 (9) | 0.0176 (8) | 0.0248 (9) | −0.0016 (6) | 0.0005 (6) | 0.0004 (6) |
| C3A | 0.0233 (8) | 0.0218 (8) | 0.0202 (8) | −0.0007 (6) | −0.0006 (6) | −0.0023 (6) |
| C4A | 0.0219 (8) | 0.0199 (8) | 0.0202 (8) | 0.0008 (6) | 0.0012 (6) | 0.0019 (6) |
| C8A | 0.0286 (9) | 0.0210 (9) | 0.0236 (9) | −0.0010 (7) | 0.0022 (7) | 0.0024 (7) |
| C5A | 0.0253 (9) | 0.0166 (8) | 0.0236 (8) | −0.0017 (6) | 0.0007 (6) | −0.0017 (6) |
| C6A | 0.0229 (8) | 0.0219 (8) | 0.0188 (8) | 0.0020 (6) | 0.0013 (6) | −0.0025 (6) |
| N1A | 0.0345 (9) | 0.0258 (8) | 0.0200 (8) | −0.0003 (7) | 0.0030 (6) | −0.0031 (6) |
### Geometric parameters (Å, °)

| Bond/Angle | Length (Å) | Angle (°) | Length (Å) | Angle (°) | Length (Å) | Angle (°) | Length (Å) | Angle (°) | Length (Å) | Angle (°) |
|------------|------------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|-----------|
| C6A—N1A    | 1.457 (2)  | O6B—N2B   | 1.246 (2)  | N1B—H1BA  | 0.94 (2)   | C1A—C2A   | 1.486 (2)  | N1B—H1BB  | 0.90 (2)   | C2A—C3A   | 1.390 (2) |
| N1B—C6B    | 1.202 (2)  | C4A—C3A   | 1.390 (2)  | C2A—C7A   | 1.388 (2)  | O2W—H2WA  | 0.930 (3)  | C6B—C5B   | 1.381 (2)  | C5A—C6A   | 1.379 (2) |
| N1B—H1BC   | 0.86 (3)   | C3A—H3AA  | 0.930      | C1A—O1A   | 1.286 (2)  | C3A—H7A   | 0.930      | C4A—O4A   | 1.203 (2)  | C5A—C6A   | 1.379 (2) |
| N1B—H1A    | 0.77 (4)   | C4A—C8A   | 1.496 (2)  | O2W—H2WB  | 0.88 (4)   | C5A—H5A   | 0.930      | O3A—O4A   | 1.230 (2)  | C3B—C4B   | 1.499 (2) |
| N1B—C6B    | 1.463 (2)  | C4B—C3B   | 1.397 (3)  | C3B—H3BA  | 0.930      | O3B—H3B   | 0.86 (3)   | C4B—C8B   | 1.305 (2)  | C4B—C5B   | 1.386 (3) |
| O1A—C1A    | 1.285 (2)  | C7B—H7B   | 0.930      | C6B—N1B   | 1.203 (2)  | O1W—H1WA  | 0.81 (3)   | C7B—H7B   | 0.930      | C5A—C6A   | 1.379 (2) |
| O2A—C1A    | 1.237 (2)  | C7B—C6B   | 1.378 (2)  | C5A—C6A   | 1.230 (2)  | O1W—H1WB  | 0.88 (3)   | C5A—C6A   | 1.237 (2)  | C5A—C6A   | 1.378 (2) |
| O3A—C8A    | 1.322 (2)  | C3B—C4B   | 1.499 (2)  | C6B—N1B   | 1.235 (2)  | O7B—N2B   | 1.237 (2)  | C5A—C6A   | 1.235 (2)  | C5A—C6A   | 1.378 (2) |
| O4A—C8A    | 1.202 (2)  | O6A—N2A   | 1.390 (2)  | C6B—N1B   | 1.255 (2)  | O5B—N2B   | 0.930      | C6B—N1B   | 1.255 (2)  | C6B—N1B   | 0.930      |
| O5A—N2A    | 1.268 (2)  | C3B—C4B   | 1.390 (2)  | C6B—N1B   | 1.128 (13) | C5A—C6A   | 119.66 (15)| C6B—N1B   | 115.3 (14) | C5A—C6A   | 115.3 (14) |
| O6A—N2A    | 1.230 (2)  | C2B—C1B   | 1.390 (2)  | C6B—N1B   | 107.5 (15) | C7A—C6A   | 118.84 (15)| C6B—N1B   | 107.5 (15) | C7A—C6A   | 118.84 (15) |
| O7A—N2A    | 1.247 (2)  | C1B—N1B   | 112.8 (13) | C6B—N1B   | 101.1 (19) | C6A—N1A   | 116.1 (16) | C6B—N1B   | 101.1 (19) | C6A—N1A   | 116.1 (16) |
| O1W—H1WA   | 0.81 (3)   | H1A—N1B   | 117 (2)    | C6B—N1B   | 117 (2)    | C6A—N1A   | 107.9 (14) | C6B—N1B   | 117 (2)    | C6A—N1A   | 107.9 (14) |
| O1W—H1WB   | 0.88 (3)   | H1A—N1B   | 103 (2)    | C6B—N1B   | 103 (2)    | C6A—N1A   | 114.0 (15) | C6B—N1B   | 103 (2)    | C6A—N1A   | 114.0 (15) |
| O7B—N2B    | 1.237 (2)  | H1A—N1B   | 107 (3)    | C6B—N1B   | 107 (3)    | H1AA—N1A  | 112 (2)    | C6B—N1B   | 107 (3)    | H1AA—N1A  | 112 (2)    |
| C8A—O3A    | 109.6 (16) | H1A—N1B   | 103 (3)    | C6B—N1B   | 103 (3)    | H1AA—N1A  | 98 (2)     | C6B—N1B   | 103 (3)    | H1AA—N1A  | 98 (2)     |
| Bond                  | Bond Angle (degrees) | Bond Angle (degrees) | Bond Angle (degrees) | Bond Angle (degrees) |
|----------------------|----------------------|----------------------|----------------------|----------------------|
| C8B—O3B—H3B         | 107 (2)              | C2A—C7A—H7A         | 120.5                |
| C1B—O1B—H1B         | 106.3 (17)           | C6A—C7A—C2A         | 119.04 (16)          |
| H1WA—O1W—H1WB       | 107 (3)              | C6A—C7A—H7A         | 120.5                |
| O6A—N2A—O5A         | 119.84 (18)          | O3B—C8B—C4B         | 112.86 (16)          |
| O6A—N2A—O7A         | 121.63 (17)          | O2B—C1B—O1B         | 123.59 (17)          |
| O7A—N2A—O5A         | 118.51 (16)          | O4B—C8B—C4B         | 124.69 (18)          |
| O7B—N2B—O5B         | 119.63 (16)          | O4B—C8B—C4B         | 122.45 (18)          |
| O7B—N2B—O6B         | 121.39 (17)          | C3B—C4B—C8B         | 120.73 (17)          |
| O6B—N2B—O5B         | 118.97 (16)          | C5B—C4B—C8B         | 118.98 (16)          |
| O1A—C1A—C2A         | 115.93 (16)          | C5B—C4B—C3B         | 120.27 (16)          |
| O2A—C1A—O1A         | 124.42 (17)          | C4B—C3B—H3BA        | 120.3                |
| O2A—C1A—C2A         | 119.64 (16)          | C2B—C3B—C4B         | 119.49 (17)          |
| C3A—C2A—C1A         | 120.90 (16)          | C2B—C3B—C4B         | 120.3                |
| C7A—C2A—C1A         | 118.78 (15)          | C3B—C2B—C1B         | 121.24 (16)          |
| C7A—C2A—C3A         | 120.32 (16)          | C3B—C2B—C7B         | 120.38 (16)          |
| C2A—C3A—H3AA        | 120.1                | C7B—C2B—C1B         | 118.24 (16)          |
| C4A—C3A—C2A         | 119.79 (15)          | O1B—C1B—C2B         | 116.78 (16)          |
| C4A—C3A—H3AA        | 120.1                | O2B—C1B—C2B         | 119.57 (16)          |
| C3A—C4A—C8A         | 118.33 (15)          | C2B—C7B—H7B         | 120.6                |
| C3A—C4A—C5A         | 120.17 (15)          | C6B—C7B—C2B         | 118.89 (16)          |
| C5A—C4A—C8A         | 121.49 (15)          | C6B—C7B—H7B         | 120.6                |
| O3A—C8A—C4A         | 113.16 (15)          | C7B—C6B—N1B         | 119.14 (16)          |
| O4A—C8A—O3A         | 124.00 (16)          | C7B—C6B—C5B         | 121.83 (16)          |
| O4A—C8A—C4A         | 122.84 (16)          | C5B—C6B—N1B         | 119.03 (16)          |
| C4A—C5A—H5A         | 120.4                | C4B—C5B—H5B         | 120.4                |
| C6A—C5A—C4A         | 119.17 (15)          | C6B—C5B—C4B         | 119.13 (16)          |
| C6A—C5A—H5A         | 120.4                | C6B—C5B—H5B         | 120.4                |
| N1B—C6B—C5B—C4B     | 178.76 (17)          | C5A—C4A—C8A—O3A     | 6.0 (2)              |
| O1A—C1A—C2A—C3A     | 7.5 (3)              | C5A—C4A—C8A—O4A     | −175.09 (18)         |
| O1A—C1A—C2A—C7A     | −173.26 (17)         | C5A—C6A—C7A—C2A     | 1.1 (3)              |
| O2A—C1A—C2A—C3A     | −171.65 (18)         | N1A—C6A—C7A—C2A     | −179.81 (16)         |
| O2A—C1A—C2A—C7A     | 7.6 (3)              | C7A—C2A—C3A—C4A     | −0.6 (3)             |
| O3B—C8B—C4B—C3B     | 3.4 (3)              | C8B—C4B—C3B—C2B     | 179.20 (17)          |
| O3B—C8B—C4B—C5B     | −178.43 (18)         | C8B—C4B—C5B—C6B     | −178.95 (17)         |
| O4B—C8B—C4B—C3B     | −177.3 (2)           | C4B—C3B—C2B—C1B     | −175.94 (17)         |
| O4B—C8B—C4B—C5B     | 0.9 (3)              | C4B—C3B—C2B—C7B     | −0.3 (3)             |
| C1A—C2A—C3A—C4A     | 178.62 (16)          | C3B—C4B—C5B—C6B     | −0.8 (3)             |
| C1A—C2A—C7A—C6A     | −179.75 (16)         | C3B—C2B—C1B—O1B     | −0.9 (3)             |
| C2A—C3A—C4A—C8A     | −179.76 (16)         | C3B—C2B—C1B—O2B     | 176.44 (18)          |
| C2A—C3A—C4A—C5A     | 1.2 (3)              | C3B—C2B—C7B—C6B     | −0.6 (3)             |
| C3A—C2A—C7A—C6A     | −0.5 (3)             | C2B—C7B—C6B—N1B     | −178.06 (17)         |
| C3A—C4A—C8A—O3A     | −173.07 (16)         | C2B—C7B—C6B—C5B     | 0.9 (3)              |
| C3A—C4A—C8A—O4A     | 5.8 (3)              | C1B—C2B—C7B—C6B     | 175.10 (16)          |
| C3A—C4A—C5A—C6A     | −0.6 (3)             | C7B—C2B—C1B—O1B     | −176.57 (17)         |
| C4A—C5A—C6A—N1A     | −179.61 (16)         | C7B—C2B—C1B—O2B     | 0.7 (3)              |
| C4A—C5A—C6A—C7A     | −0.5 (3)             | C7B—C6B—C5B—C4B     | −0.2 (3)             |
| C8A—C4A—C5A—C6A     | −179.67 (16)         | C5B—C4B—C3B—C2B     | 1.1 (3)              |
**Hydrogen-bond geometry (Å, °)**

| D—H···A | D—H  | H···A  | D···A  | D—H···A  |
|---------|------|--------|--------|-----------|
| O2W—H2WA···O4B | 0.93 (4) | 2.11 (4) | 2.911 (3) | 143 (3)   |
| O2W—H2WB···O1Bi | 0.88 (4) | 2.14 (4) | 2.913 (2) | 147 (3)   |
| O2W—H2WB···O7Bi | 0.88 (4) | 2.79 (4) | 3.198 (3) | 110 (3)   |
| O3A—H3A···O5A | 0.94 (3) | 1.80 (3) | 2.7399 (19) | 173 (2)  |
| O3B—H3B···O1W | 0.86 (3) | 1.76 (3) | 2.604 (2) | 165 (3)   |
| O1W—H1WA···O2Wii | 0.81 (3) | 1.97 (3) | 2.772 (2) | 173 (3)   |
| O1W—H1WB···O7Bi | 0.88 (3) | 2.60 (3) | 3.185 (2) | 124 (2)   |
| O1W—H1WB···O6Bi | 0.88 (3) | 1.88 (3) | 2.762 (2) | 175 (3)   |
| C7A—H7A···O5B | 0.93 | 2.54 | 3.236 (2) | 131       |
| N1B—H1B4···O6Aiv | 0.94 (2) | 2.60 (2) | 3.197 (3) | 121.7 (17) |
| N1B—H1B4···O7Aiv | 0.94 (2) | 2.01 (2) | 2.938 (2) | 173 (2)   |
| N1B—H1BB···O5B | 0.90 (2) | 1.96 (2) | 2.842 (2) | 168 (2)   |
| N1B—H1BB···O6B | 0.90 (2) | 2.53 (2) | 3.142 (2) | 125.9 (18) |
| N1B—H1BC···O2Wvii | 0.86 (3) | 2.64 (2) | 3.056 (3) | 111.2 (17) |
| N1B—H1BC···O1Wvii | 0.86 (3) | 2.00 (3) | 2.841 (2) | 165 (2)   |
| N1A—H1A4···O6Aiii | 0.81 (3) | 2.38 (3) | 3.104 (3) | 150 (2)   |
| N1A—H1A4···O5Aiii | 0.81 (3) | 2.32 (3) | 3.070 (2) | 154 (2)   |
| N1A—H1AB···O7Aix | 0.90 (2) | 2.25 (2) | 2.934 (2) | 132.1 (18) |
| N1A—H1AB···O5Bv | 0.90 (2) | 2.12 (2) | 2.992 (2) | 162.9 (19) |
| N1A—H1AC···O4Aviii | 0.86 (2) | 2.53 (2) | 2.899 (2) | 107.3 (17) |
| N1A—H1AC···O5Ax | 0.86 (2) | 2.34 (2) | 3.000 (2) | 133.8 (19) |
| N1A—H1AC···O7Ax | 0.86 (2) | 2.10 (3) | 2.942 (2) | 167 (2)   |
| O1A—H1A···O2B | 0.77 (4) | 1.91 (4) | 2.669 (2) | 174 (4)   |
| O1B—H1B···O2A | 0.82 (3) | 1.85 (3) | 2.662 (2) | 170 (3)   |

Symmetry codes: (i) x, y−1, z; (ii) x, −y−1/2, z+1/2; (iii) −x+1, y+1/2, −z+3/2; (iv) −x+1, −y, −z+1; (v) x, −y+3/2, z+1/2; (vi) −x+2, y−3/2, −z+1/2; (vii) x, −y+1/2, z−1/2; (viii) x, −y+7/2, z+1/2; (ix) −x+2, −y+4, −z+1.