

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

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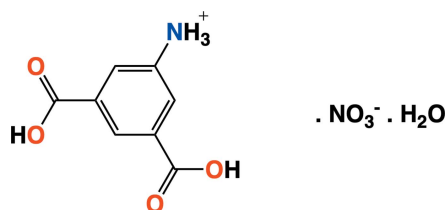
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The title compound, $C_8H_8NO_4^+ \cdot NO_3^- \cdot H_2O$, crystallizes in the same space group ($P2_1/c$) as the previously reported dihydrate form [Liang & Zhu (2010). *Acta Cryst. E* **66**, o667], but with two formula units per asymmetric unit 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-aminoisophtalic 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

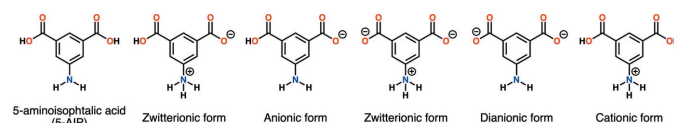
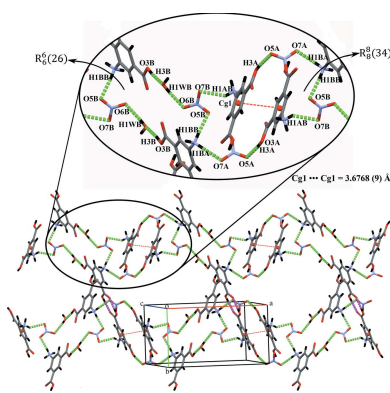


Figure 1
Different neutral and ionic forms of 5-aminoisophtalic acid



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Table 1
Selected geometric parameters (Å, °).

C6A—N1A	1.457 (2)	N1B—C6B	1.463 (2)
O1A—C1A	1.286 (2)	O1B—C1B	1.285 (2)
O2A—C1A	1.237 (2)	O2B—C1B	1.241 (2)
O3A—C8A	1.322 (2)	O3B—C8B	1.305 (2)
O4A—C8A	1.202 (2)	O4B—C8B	1.203 (2)
O2A—C1A—O1A	124.42 (17)	O2B—C1B—O1B	123.59 (17)
O4A—C8A—O3A	124.00 (16)	O4B—C8B—O3B	124.69 (18)

containing one water molecule per formula unit, instead of two. The asymmetric unit comprises two formula units, *i.e.*, two 3,5-dicarboxyanilinium cations (*A* and *B*), two nitrate anions (*A* and *B*) and two water molecules (Fig. 2*a*). All bond distances and angles fall within normal ranges as compared to similar molecules (Wang & Zhang, 2006; Dobson & Gerkin, 1998; Nath & Baruah, 2012; Singh *et al.*, 2019; Cai *et al.*, 2020). The cations have similar conformations that differ mainly in the opposite orientations of one carboxylic group, as seen by the torsion angles C5—C4—C8—O3 of 6.0 (2)° in cation *A* and −178.43 (18)° in cation *B*. *Mogul* (Bruno *et al.*, 2004) based on the Cambridge Structural Database (version 2022.2.0; Groom *et al.*, 2016), indicated the single character of the C6—N1 bonds [1.457 (2) Å for *A* and 1.462 (2) Å for *B*], which have lengths close to the median of the 2198 found fragments of the same chemical nature. The C=O double bonds in the carboxylic groups [1.202 (2) to 1.241 (2) Å] are shorter than the C—O single bonds [1.285 (2) to 1.322 (2) Å, Table 1]. The planarity of the cations varies slightly: the dihedral angles between the carboxylic group planes (C1, O1, O2) and (C8, O3, O4) and the ring plane are 7.85 (9) and 5.90 (9)°, respectively, in cation *A*, 5.93 (2) and 2.68 (2)° in cation *B*; all non-hydrogen atoms are coplanar within 0.083 Å in cation *A* and 0.052 Å in *B*.

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. 3*a*). In each layer, the 3,5-

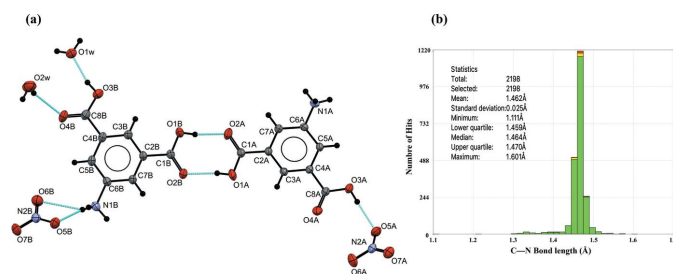


Figure 2
(*a*) ORTEP view of the asymmetric unit of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed cyan lines. (*b*) Histogram comparing the C—N bond lengths generating using *Mogul*.

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>
O2W—H2WA···O4B	0.93 (4)	2.11 (4)	2.911 (3)	143 (3)
O2W—H2WB···O1B ⁱ	0.88 (4)	2.14 (4)	2.913 (2)	147 (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···O2W ⁱⁱ	0.81 (3)	1.97 (3)	2.772 (2)	173 (3)
O1W—H1WB···O6B ⁱⁱⁱ	0.88 (3)	1.88 (3)	2.762 (2)	175 (3)
C7A—H7A···O5B ^{iv}	0.93	2.54	3.236 (2)	131
N1B—H1BA···O7A ^v	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—H1BC···O2W ^{vi}	0.86 (3)	2.64 (2)	3.056 (3)	111.2 (17)
N1B—H1BC···O1W ^{vi}	0.86 (3)	2.00 (3)	2.841 (2)	165 (2)
N1A—H1AA···O6A ^{vii}	0.81 (3)	2.38 (3)	3.104 (3)	150 (2)
N1A—H1AA···O5A ^{vii}	0.81 (3)	2.32 (3)	3.070 (2)	154 (2)
N1A—H1AB···O7B ^{iv}	0.90 (2)	2.25 (2)	2.934 (2)	132.1 (18)
N1A—H1AB···O5B ^{iv}	0.90 (2)	2.12 (2)	2.992 (2)	162.9 (19)
N1A—H1AC···O5A ^{viii}	0.86 (2)	2.34 (2)	3.000 (2)	133.8 (19)
N1A—H1AC···O7A ^{viii}	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) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y, -z + 1$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $-x + 2, y - \frac{3}{2}, -z + \frac{1}{2}$; (vi) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (vii) $x, -y + \frac{7}{2}, z + \frac{1}{2}$; (viii) $-x + 2, -y + 4, -z + 1$.

dicarboxyanilinium *A* cations and the nitrate *A* anions are linked through bifurcated hydrogen bonds, forming chains of $R_1^2(4)$ rings that propagate parallel to the *b* axis (Fig. 3*a,b*). In addition, the 3,5-dicarboxyanilinium *B* cations and water molecules form chains of $R_6^0(22)$ ring motifs that also extend along the *b*-axis direction (Fig. 3*a,c,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. 3*a,e*). Furthermore, we can distinguish, as illustrated in Fig. 4, that the nitrate *B* anions are involved in the formation of alternating $R_6^0(26)$ and $R_8^8(34)$ ring motifs, generating ribbons that propagate along the *a*-axis direction, which in turn leads to the formation of a three-dimensional supramolecular network.

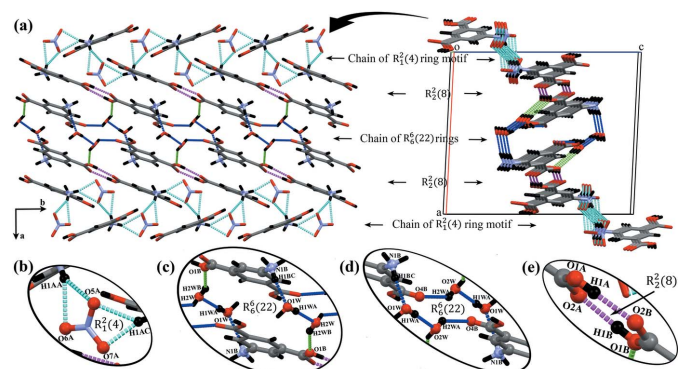


Figure 3
(*a*) Partial packing of (I) showing the two-dimensional layers (viewed down the *c* and *b* axes); (*b*) the $R_1^2(4)$ motif formed by a N—H···O bifurcated hydrogen bond; (*c*) and (*d*) the $R_6^0(22)$ motifs formed by a combination of N—H···O and O—H···O hydrogen bonds; (*e*) the dimeric $R_2^2(8)$ motifs formed by O—H···O hydrogen bonds.

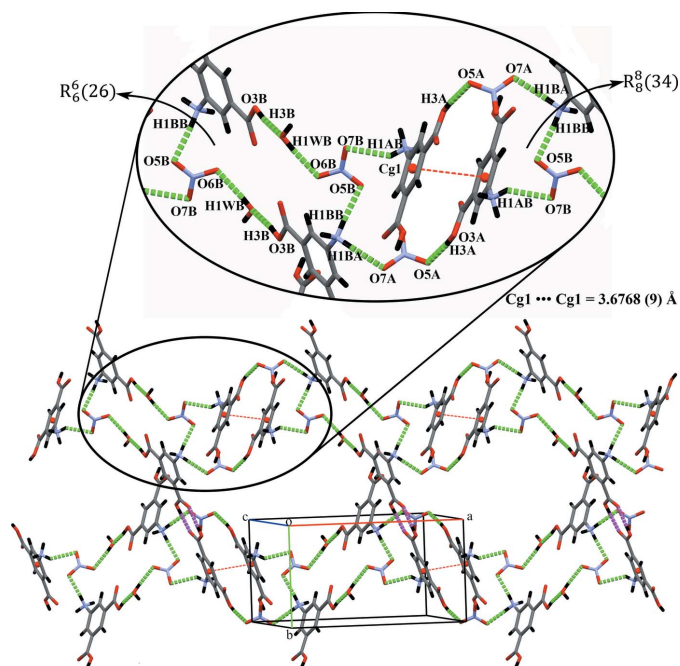


Figure 4
Partial packing of (I) showing the ribbons formed by alternating $R_6^c(26)$ and $R_8^c(34)$ ring motifs.

Further examination reveals that the cohesion in the crystal structure is enhanced by offset or slipped π - π 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 $Cg1 \cdots Cg1(2-x, 3-y, 1-z)$ of 3.6768 (9) Å, while rings *A* and *B* (forming an interplanar angle of 11.81°) contact with a $Cg1 \cdots Cg2(x, 1+y, z)$ distance of 3.7960 (9) Å. Note that the former π - π 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

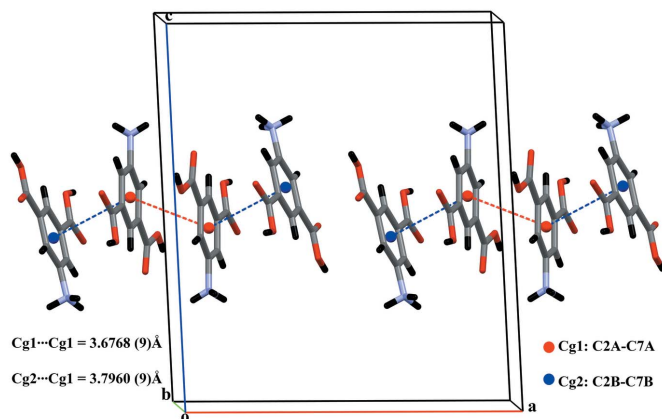


Figure 5
Part of the crystal structure of (I) showing the π - π stacking interactions, which appear parallel to the *a* axis.

(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_{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_{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...O and N—H...O hydrogen bonds in the crystal structure, whereas the faint-red spots (highlighted by red circles for clarity) represent weaker C—H...O interactions. The presence of characteristic red and blue triangles on the shape-index surface (Fig. 6b) clearly suggest the presence of π - π 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/H...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—

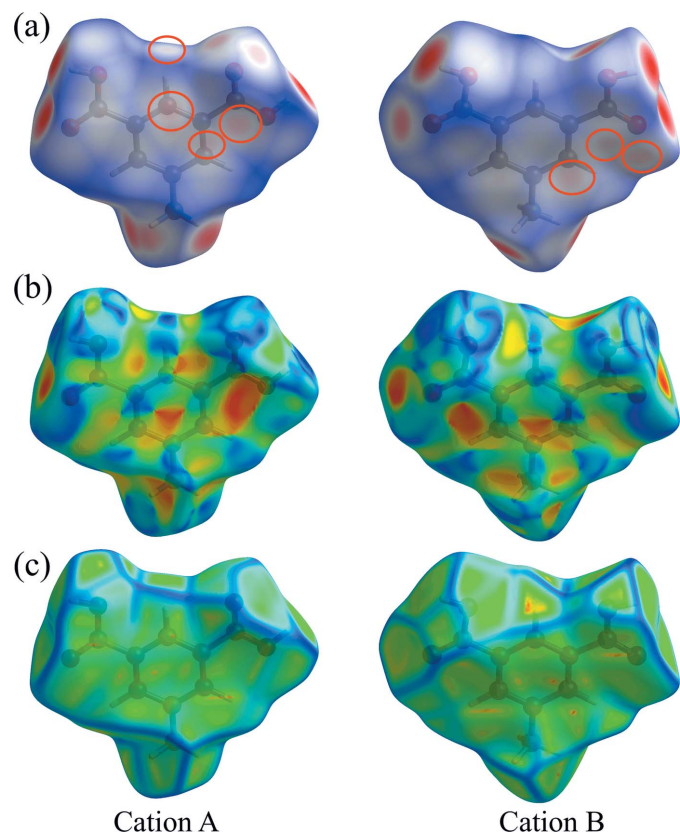
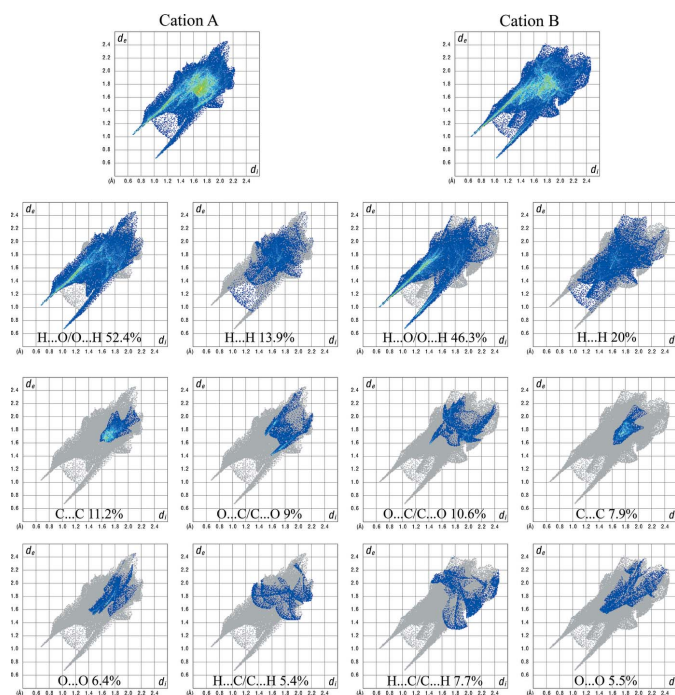


Figure 6
The Hirshfeld surfaces of the organic cations *A* and *B* mapped over: (a) d_{norm} in the range -0.7489 to 1.2298 a.u., (b) shape-index and (c) curvedness.

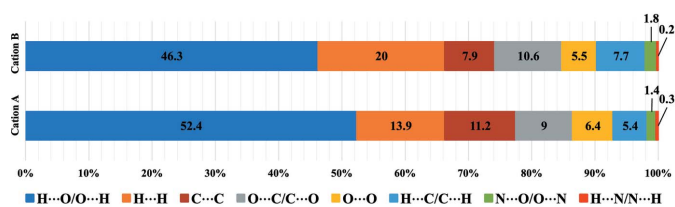

Figure 7

Two-dimensional fingerprint plots of (I), showing the percentage contributions of all contacts and those delineated into O...H/H...O, H...H, C...C, O...C/C...O, O...O and C...H/H...C contacts for the A and B organic cations.

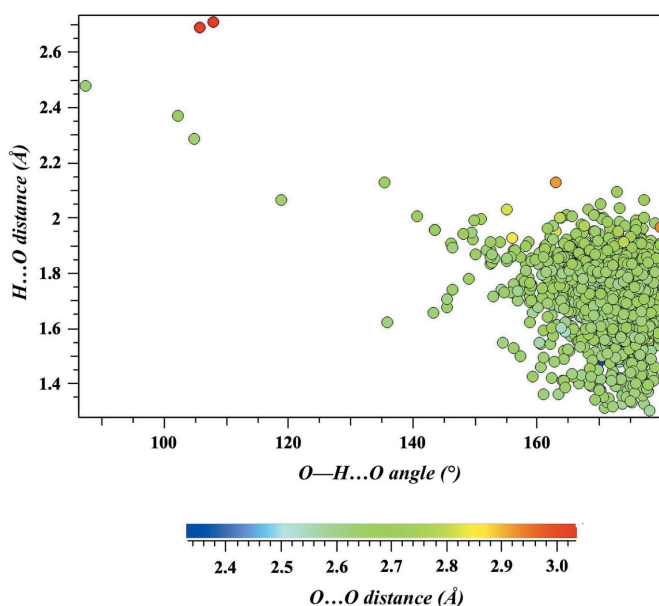
H...O and N—H...O hydrogen bonds. The second most important are H...H contacts, contributing 13.9% and 20% for cations A and B, respectively. These are followed for cation A by C...C contacts (11.2%), but for cation B by O...C/C...O contacts (10.6%), other contacts making less significant contributions.

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).


Figure 8

Percentage contributions of contacts to the Hirshfeld surface in the cations of (I).


Figure 9

Scatterplot of O—H...O angle (°) against H...O distance (Å) for carboxylic acid to carboxylic acid type hydrogen bonds, with the O...O distance (Å) shown using a color scale (bottom).

The geometries of O—H...O hydrogen bonds from an analysis of 2883 crystal structures deposited in the CSD are illustrated in Fig. 9. The relationship between the H...O distances and O—H...O angles is shown as a two-dimensional plot, the O...O distances being indicated by the color of the data points. The angle tends to increase as the O...O and H...O distances decrease. The greatest density of observed hydrogen bonds occurs in the range of 1.3–1.9 Å for the H...O distance, 2.6–2.8 Å for the O...O distances (indicated by green data points) and 160–180° for the O—H...O angle.

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 $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (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 NH_3^+ , carboxylic acid groups COOH and water molecules were localized in difference-Fourier maps and refined with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$ or $1.2U_{\text{eq}}(\text{N})$. 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 [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Table 3

Experimental details.

Crystal data	
Chemical formula	C ₈ H ₈ NO ₄ ⁺ ·NO ₃ ⁻ ·H ₂ O
<i>M_r</i>	262.18
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.7026 (4), 8.5449 (2), 16.9929 (4)
β (°)	92.800 (2)
<i>V</i> (Å ³)	2132.31 (9)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.15
Crystal size (mm)	0.14 × 0.12 × 0.1
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.627, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	20897, 4881, 3653
<i>R</i> _{int}	0.069
(sin θ/λ) _{max} (Å ⁻¹)	0.649
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	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
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.38, -0.36

Computer programs: *BIS*, *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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

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Computing details

Data collection: *BIS* (Bruker, 2014), *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (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

$C_8H_8NO_4^+ \cdot NO_3^- \cdot H_2O$
 $M_r = 262.18$
 Monoclinic, $P2_1/c$
 $a = 14.7026$ (4) Å
 $b = 8.5449$ (2) Å
 $c = 16.9929$ (4) Å
 $\beta = 92.800$ (2)°
 $V = 2132.31$ (9) Å³
 $Z = 8$

$F(000) = 1088$
 $D_x = 1.633$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 5578 reflections
 $\theta = 2.4$ – 28.9 °
 $\mu = 0.15$ mm⁻¹
 $T = 298$ K
 Plate, colorless
 0.14 × 0.12 × 0.1 mm

Data collection

Bruker APEXII CCD
 diffractometer
 Mirror optics monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2014)
 $T_{\min} = 0.627$, $T_{\max} = 0.746$
 20897 measured reflections

4881 independent reflections
 3653 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.069$
 $\theta_{\text{max}} = 27.5$ °, $\theta_{\text{min}} = 2.4$ °
 $h = -18$ → 19
 $k = -11$ → 10
 $l = -22$ → 20

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.142$
 $S = 1.02$
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.5757P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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)

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 (Å²)

	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)

C7A	0.0267 (9)	0.0198 (8)	0.0227 (8)	-0.0010 (7)	0.0032 (7)	0.0011 (6)
C8B	0.0361 (11)	0.0265 (10)	0.0339 (10)	-0.0055 (8)	0.0040 (8)	0.0051 (8)
C4B	0.0291 (9)	0.0212 (9)	0.0303 (9)	-0.0025 (7)	0.0017 (7)	0.0032 (7)
C3B	0.0282 (9)	0.0232 (9)	0.0273 (9)	-0.0019 (7)	0.0038 (7)	-0.0018 (7)
C2B	0.0230 (9)	0.0189 (8)	0.0288 (9)	-0.0012 (7)	0.0010 (7)	-0.0017 (7)
C1B	0.0281 (9)	0.0206 (8)	0.0277 (9)	0.0000 (7)	0.0027 (7)	-0.0018 (7)
C7B	0.0280 (9)	0.0189 (9)	0.0264 (9)	-0.0001 (7)	0.0034 (7)	0.0010 (7)
C6B	0.0247 (9)	0.0219 (9)	0.0254 (9)	-0.0004 (7)	0.0003 (7)	-0.0033 (7)
C5B	0.0300 (9)	0.0187 (8)	0.0324 (10)	-0.0045 (7)	0.0005 (7)	-0.0009 (7)

Geometric parameters (Å, °)

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—H1BC	0.86 (3)	C2A—C7A	1.388 (2)
O1A—C1A	1.286 (2)	C3A—H3AA	0.9300
O2A—C1A	1.237 (2)	C3A—C4A	1.390 (2)
O1A—H1A	0.77 (4)	C4A—C8A	1.496 (2)
O2W—H2WA	0.93 (4)	C4A—C5A	1.392 (2)
O2W—H2WB	0.88 (4)	C5A—H5A	0.9300
O3A—H3A	0.94 (3)	C5A—C6A	1.379 (2)
O3A—C8A	1.322 (2)	C6A—C7A	1.386 (2)
O4A—C8A	1.202 (2)	N1A—H1AA	0.81 (3)
N1B—C6B	1.463 (2)	N1A—H1AB	0.90 (2)
O1B—C1B	1.285 (2)	N1A—H1AC	0.86 (2)
O2B—C1B	1.241 (2)	C7A—H7A	0.9300
O3B—H3B	0.86 (3)	C8B—C4B	1.499 (2)
O3B—C8B	1.305 (2)	C4B—C3B	1.397 (3)
O1B—H1B	0.82 (3)	C4B—C5B	1.386 (3)
O4B—C8B	1.203 (2)	C3B—H3BA	0.9300
O6A—N2A	1.230 (2)	C3B—C2B	1.390 (2)
O5A—N2A	1.268 (2)	C2B—C1B	1.488 (2)
O7A—N2A	1.247 (2)	C2B—C7B	1.394 (2)
O1W—H1WA	0.81 (3)	C7B—H7B	0.9300
O1W—H1WB	0.88 (3)	C7B—C6B	1.378 (2)
O7B—N2B	1.237 (2)	C6B—C5B	1.381 (2)
O5B—N2B	1.255 (2)	C5B—H5B	0.9300
C6B—N1B—H1BA	112.8 (13)	C5A—C6A—N1A	119.66 (15)
C6B—N1B—H1BB	115.3 (14)	C5A—C6A—C7A	121.50 (15)
C6B—N1B—H1BC	107.5 (15)	C7A—C6A—N1A	118.84 (15)
H1BA—N1B—H1BB	101.1 (19)	C6A—N1A—H1AA	116.1 (16)
H1BA—N1B—H1BC	117 (2)	C6A—N1A—H1AB	107.9 (14)
H1BB—N1B—H1BC	103 (2)	C6A—N1A—H1AC	114.0 (15)
C1A—O1A—H1A	107 (3)	H1AA—N1A—H1AB	107 (2)
H2WA—O2W—H2WB	103 (3)	H1AA—N1A—H1AC	112 (2)
C8A—O3A—H3A	109.6 (16)	H1AB—N1A—H1AC	98 (2)

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—O3B	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—H3BA	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, °)

<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>
O2 <i>W</i> —H2 <i>WA</i> ···O4 <i>B</i>	0.93 (4)	2.11 (4)	2.911 (3)	143 (3)
O2 <i>W</i> —H2 <i>WB</i> ···O1 <i>B</i> ⁱ	0.88 (4)	2.14 (4)	2.913 (2)	147 (3)
O2 <i>W</i> —H2 <i>WB</i> ···O7 <i>B</i> ⁱⁱ	0.88 (4)	2.79 (4)	3.198 (3)	110 (3)
O3 <i>A</i> —H3 <i>A</i> ···O5 <i>A</i>	0.94 (3)	1.80 (3)	2.7399 (19)	173 (2)
O3 <i>B</i> —H3 <i>B</i> ···O1 <i>W</i>	0.86 (3)	1.76 (3)	2.604 (2)	165 (3)
O1 <i>W</i> —H1 <i>WA</i> ···O2 <i>W</i> ⁱⁱⁱ	0.81 (3)	1.97 (3)	2.772 (2)	173 (3)
O1 <i>W</i> —H1 <i>WB</i> ···O7 <i>B</i> ^{iv}	0.88 (3)	2.60 (3)	3.185 (2)	124 (2)
O1 <i>W</i> —H1 <i>WB</i> ···O6 <i>B</i> ^{iv}	0.88 (3)	1.88 (3)	2.762 (2)	175 (3)
C7 <i>A</i> —H7 <i>A</i> ···O5 <i>B</i> ^v	0.93	2.54	3.236 (2)	131
N1 <i>B</i> —H1 <i>BA</i> ···O6 <i>A</i> ^{vi}	0.94 (2)	2.60 (2)	3.197 (3)	121.7 (17)
N1 <i>B</i> —H1 <i>BA</i> ···O7 <i>A</i> ^{vi}	0.94 (2)	2.01 (2)	2.938 (2)	173 (2)
N1 <i>B</i> —H1 <i>BB</i> ···O5 <i>B</i>	0.90 (2)	1.96 (2)	2.842 (2)	168 (2)
N1 <i>B</i> —H1 <i>BB</i> ···O6 <i>B</i>	0.90 (2)	2.53 (2)	3.142 (2)	125.9 (18)
N1 <i>B</i> —H1 <i>BC</i> ···O2 <i>W</i> ^{vii}	0.86 (3)	2.64 (2)	3.056 (3)	111.2 (17)
N1 <i>B</i> —H1 <i>BC</i> ···O1 <i>W</i> ^{vii}	0.86 (3)	2.00 (3)	2.841 (2)	165 (2)
N1 <i>A</i> —H1 <i>AA</i> ···O6 <i>A</i> ^{viii}	0.81 (3)	2.38 (3)	3.104 (3)	150 (2)
N1 <i>A</i> —H1 <i>AA</i> ···O5 <i>A</i> ^{viii}	0.81 (3)	2.32 (3)	3.070 (2)	154 (2)
N1 <i>A</i> —H1 <i>AB</i> ···O7 <i>B</i> ^v	0.90 (2)	2.25 (2)	2.934 (2)	132.1 (18)
N1 <i>A</i> —H1 <i>AB</i> ···O5 <i>B</i> ^v	0.90 (2)	2.12 (2)	2.992 (2)	162.9 (19)
N1 <i>A</i> —H1 <i>AC</i> ···O4 <i>A</i> ^{viii}	0.86 (2)	2.53 (2)	2.899 (2)	107.3 (17)
N1 <i>A</i> —H1 <i>AC</i> ···O5 <i>A</i> ^{ix}	0.86 (2)	2.34 (2)	3.000 (2)	133.8 (19)
N1 <i>A</i> —H1 <i>AC</i> ···O7 <i>A</i> ^{ix}	0.86 (2)	2.10 (3)	2.942 (2)	167 (2)
O1 <i>A</i> —H1 <i>A</i> ···O2 <i>B</i>	0.77 (4)	1.91 (4)	2.669 (2)	174 (4)
O1 <i>B</i> —H1 <i>B</i> ···O2 <i>A</i>	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) $-x+2, -y+4, -z+1$.