

trans-2,5-Dimethylpiperazine-1,4-diium bis(perchlorate) dihydrate: crystal structure and Hirshfeld surface analysis

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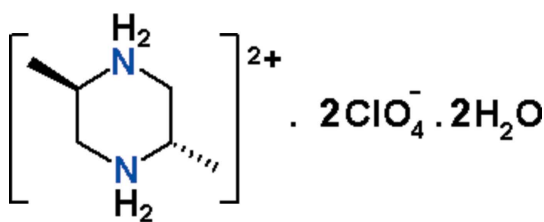
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The asymmetric unit of the title hydrated molecular salt, $C_6H_{16}N_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$, contains a half dication (completed by inversion symmetry), a perchlorate anion and a water molecule. The extended structure consists of infinite chains of formula $[(ClO_4)H_2O]_n^{n-}$ ions extending along the *b* axis linked by $O_w-H \cdots O$ (*w* = water) hydrogen bonds. These chains are cross-linked by the dications *via* $N-H \cdots O_w$ and weak $C-H \cdots O$ hydrogen bonds, thus forming a three-dimensional supramolecular network. Three-dimensional Hirshfeld surface analysis and two-dimensional fingerprint maps reveal that the structure is dominated by $H \cdots O/O \cdots H$ and $H \cdots H$ contacts.

1. Chemical context

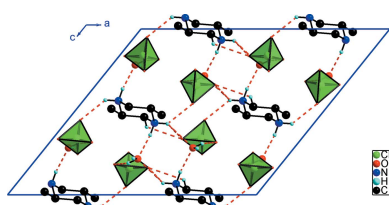
Piperazine ($C_4H_{10}N_2$) and its derivatives are a family of strongly basic amines able to form dications, in which all of the $N-H$ bonds are generally active in hydrogen-bond formation. They are used in pharmacology and found in biologically active compounds across a number of different therapeutic areas, displaying antibacterial, antifungal, antimalarial, antipsychotic, antidepressant and antitumor activity (Brockunier *et al.*, 2004; Bogatcheva *et al.*, 2006).



In this work, as part of our studies in this area, we report the preparation and structural investigation of a new hydrated perchlorate salt, $C_6H_{16}N_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$ (I).

2. Structural commentary

The asymmetric unit of (I) is composed of a half of a *trans*-2,5-dimethylpiperazine-1,4-diium dication, one perchlorate anion and one water molecule (Fig. 1). The complete dication is generated by crystallographic inversion symmetry, leading to a typical chair conformation, with the methyl groups occupying equatorial positions [puckering parameters: $Q = 0.7341$ Å, $\theta = 90^\circ$ and $\varphi = -16^\circ$], which is similar the conformation of the same species in its nitrate salt (Gatfaoui *et al.*, 2014). Other-



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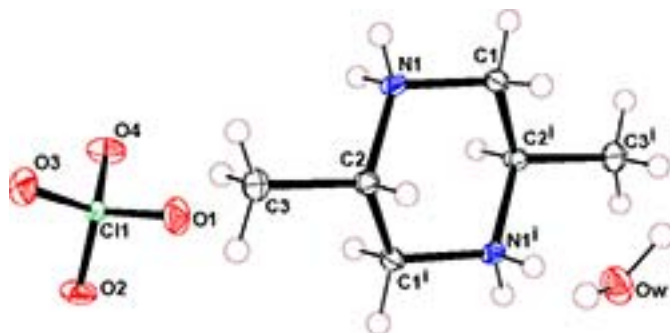


Figure 1
An ORTEP view of (I) with displacement ellipsoids drawn at the 30% probability level. Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

wise, the bond lengths and angle in the dication are normal (Rother *et al.*, 1997; Gatfaoui *et al.*, 2014; Essid *et al.*, 2015).

The perchlorate anion displays its expected tetrahedral geometry around the chlorine atom. Interatomic bond lengths and angles of the perchlorate anion lie respectively within the ranges [1.4327 (10)–1.4452 (11) Å] and [109.01 (7)–110.28 (7)°]. Similar geometrical features have also been noticed in other crystal structures (Toumi Akriche *et al.*, 2010; Berrah *et al.*, 2012).

3. Supramolecular features

In the extended structure, the anions are connected to the water molecules through $O_w-H\cdots O$ hydrogen bonds (Table 1), generating a corrugated $C_2^2(5)$ chain running along the [010] direction (Fig. 2). These chains are linked *via* the *trans*-2,5-dimethylpiperazine-1,4-diium cations through $N-H\cdots O$, $N-H\cdots O_w$ and weak $C-H\cdots O$ hydrogen bonds,

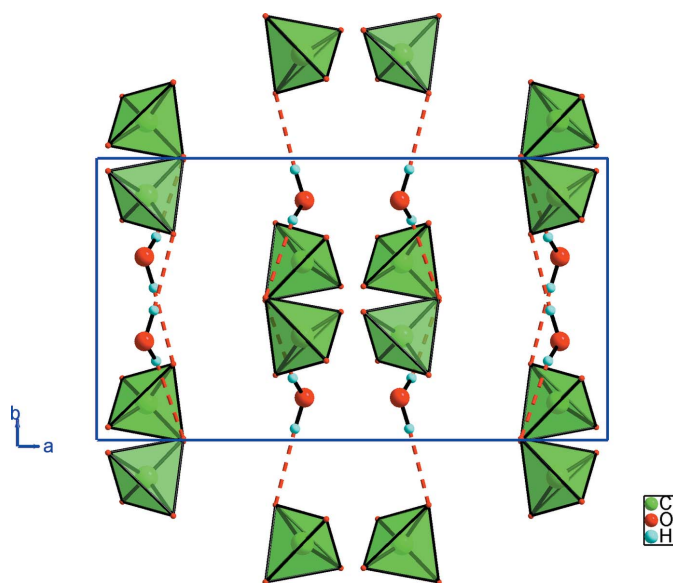


Figure 2
Hydrogen-bonded supramolecular chains involving anions and water molecules of compound (I), represented through the *ab* plane.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
OW–H1W \cdots O1 ⁱ	0.85 (1)	2.03 (1)	2.8637 (16)	167 (2)
OW–H2W \cdots O2 ⁱⁱ	0.85 (1)	2.23 (1)	2.9932 (16)	150 (2)
N1–H1N \cdots O4 ⁱⁱⁱ	0.90	2.18	2.9067 (15)	137
N1–H1N \cdots O3 ^{iv}	0.90	2.42	3.0293 (15)	125
N1–H1N \cdots OW ^v	0.90	2.55	3.1994 (16)	130
N1–H2N \cdots OW ⁱ	0.90	1.91	2.8019 (15)	172
C1–H1B \cdots O3 ^{iv}	0.97	2.56	3.1007 (17)	116

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

forming a three-dimensional supramolecular network (Fig. 3). These data show that each organic cation is connected to six inorganic chains.

4. Hirshfeld surface analysis

The three-dimensional Hirshfeld surfaces and two-dimensional fingerprint plots of (I) were prepared using *Crystal-Explorer* (Wolff *et al.*, 2012) and are shown in Figs. 4 and 5, respectively. The interaction between N–H and oxygen atoms can be seen in the Hirshfeld surface as the bright-red area in Fig. 4 (labeled *a*). The light-red spots are due to $O_w-H\cdots O$ interactions (labeled *b*). For the salt, $O\cdots H/H\cdots O$ contacts, which are attributed to $N-H\cdots O_w$ and $O_w-H\cdots O$ hydrogen-bonding interactions, appear as two sharp symmetric spikes in the two-dimensional fingerprint maps. They have the most significant contribution to the total Hirshfeld surfaces. The H \cdots H contacts appear in the middle of the scattered points in the two-dimensional fingerprint maps. For further information on Hirshfeld surfaces, see: Spackman & McKinnon (2002) and Spackman & Jayatilaka (2009).

5. Synthesis and crystallization

The title compound was prepared from an alcoholic solution containing *trans*-2,5-dimethylpiperazine (0.1 g, 1 mmol, purity

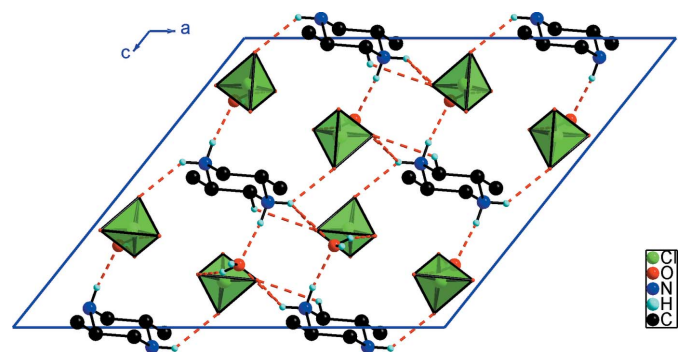


Figure 3
Projection of (I) along the *b* axis. The H-atoms not involved in hydrogen bonding are omitted.

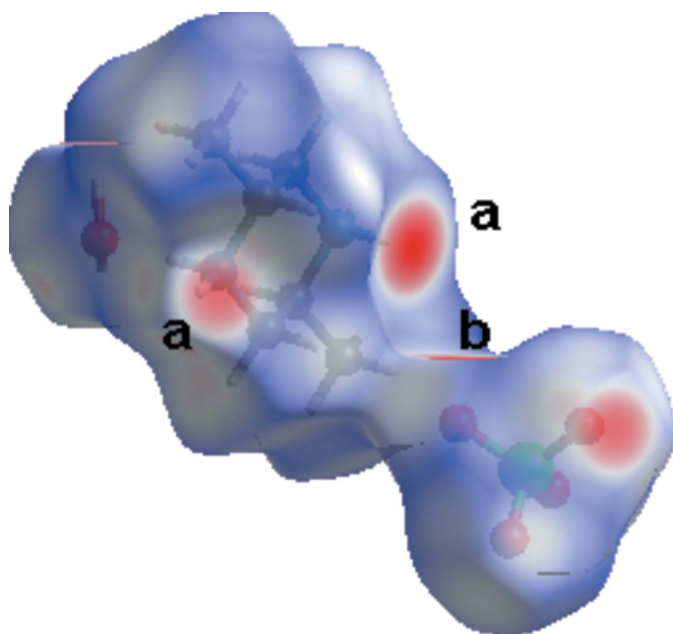


Figure 4
Hirshfeld surface around the constituents of (I) coloured according to d_{norm} . The surfaces are shown as transparent to allow visualization of the orientation and conformation of the functional groups.

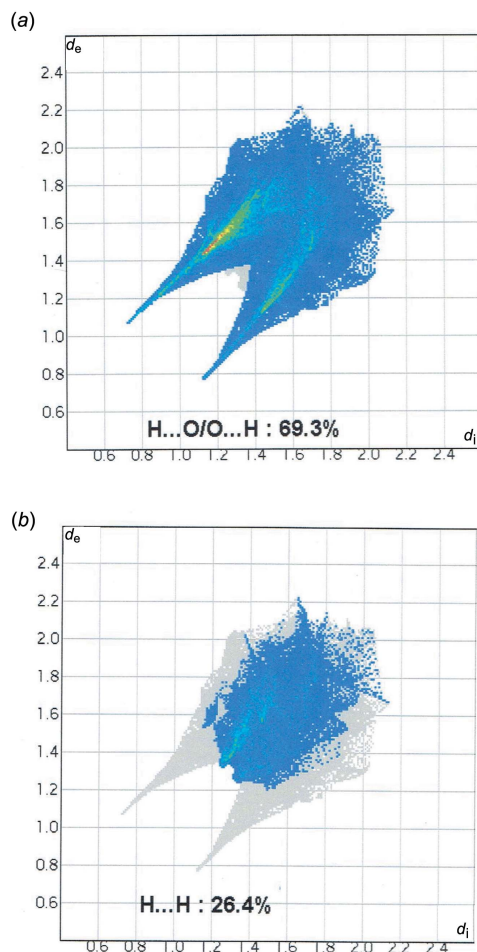


Figure 5
Fingerprint plots of the major contacts: (a) H...O and (b) H...H.

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_6\text{H}_{16}\text{N}_2^{2+} \cdot 2\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$
M_r	351.14
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	150
a, b, c (Å)	16.8603 (8), 7.2655 (3), 14.4534 (6)
β (°)	128.751 (1)
V (Å ³)	1380.78 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.52
Crystal size (mm)	0.44 × 0.29 × 0.25
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Multi-scan (SADABS; Bruker, 2014)
$T_{\text{min}}, T_{\text{max}}$	0.775, 0.878
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7760, 1557, 1457
R_{int}	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.074, 1.13
No. of reflections	1557
No. of parameters	100
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.34, -0.41

Computer programs: APEX2 and SAINT (Bruker, 2014), SIR97 (Altomare *et al.*, 1999), SHELXL2014/7 (Sheldrick, 2015), ORTEP-3 for Windows and WinGX publication routines (Farrugia, 2012).

99%, Aldrich) dissolved in ethanol (20 ml) and perchloric acid HClO_4 (0.2 g, 2 mmol, purity 96%, Aldrich) with a molar ratio of 1:2. This mixture was stirred for 1 h. After a week of evaporation at room temperature, colorless single crystals of suitable dimensions for crystallographic study were formed, and were isolated by filtration and washed with a small amount of distilled water. The crystals can be stable for months under normal conditions of temperature and humidity.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in a difference map but were placed geometrically and refined using a riding model, with C—H = 0.96 Å (methyl), or 0.98 Å (methine), N—H = 0.90 Å (NH_2) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}$ or $\text{N})$. The H atoms of the water molecule were refined with a distance restraint of O—H = 0.85 (1) Å using DFIX and DANG commands (Sheldrick, 2015) with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Acknowledgements

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supporting information

Acta Cryst. (2016). E72, 593-596 [https://doi.org/10.1107/S205698901600520X]

***trans*-2,5-Dimethylpiperazine-1,4-dium bis(perchlorate) dihydrate: crystal structure and Hirshfeld surface analysis**

Cherifa Ben Mleh, Thierry Roisnel and Houda Marouani

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

***trans*-2,5-Dimethylpiperazine-1,4-dium bis(perchlorate) dihydrate**

Crystal data

$\text{C}_6\text{H}_{16}\text{N}_2^{2+} \cdot 2\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$

$M_r = 351.14$

Monoclinic, $C2/c$

$a = 16.8603$ (8) Å

$b = 7.2655$ (3) Å

$c = 14.4534$ (6) Å

$\beta = 128.751$ (1)°

$V = 1380.78$ (10) Å³

$Z = 4$

$F(000) = 736$

$D_x = 1.689$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7552 reflections

$\theta = 3.1\text{--}27.5^\circ$

$\mu = 0.52$ mm⁻¹

$T = 150$ K

Prism, colourless

$0.44 \times 0.29 \times 0.25$ mm

Data collection

D8 VENTURE Bruker AXS

diffractometer

Radiation source: Incoatec microfocus sealed tube

Multilayer monochromator

rotation images scans

Absorption correction: multi-scan (SADABS; Bruker, 2014)

$T_{\min} = 0.775$, $T_{\max} = 0.878$

7760 measured reflections

1557 independent reflections

1457 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -21 \rightarrow 21$

$k = -9 \rightarrow 9$

$l = -18 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.074$

$S = 1.13$

1557 reflections

100 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 1.9533P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$$

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.

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.09748 (2)	0.13197 (4)	0.16201 (3)	0.01195 (12)
O1	0.14991 (10)	0.26958 (16)	0.25415 (10)	0.0307 (3)
O2	0.16959 (8)	−0.00473 (16)	0.18348 (11)	0.0254 (3)
O3	0.02214 (9)	0.04530 (16)	0.16384 (10)	0.0239 (3)
O4	0.05035 (9)	0.21898 (16)	0.04934 (9)	0.0236 (3)
OW	0.40676 (9)	0.84994 (14)	0.78311 (9)	0.0203 (2)
H1W	0.3881 (18)	0.9600 (15)	0.780 (2)	0.046 (7)*
H2W	0.3837 (15)	0.780 (2)	0.8086 (18)	0.034 (6)*
N1	0.14181 (8)	0.75580 (15)	0.43347 (10)	0.0111 (2)
H2N	0.1201	0.7208	0.3612	0.013*
H1N	0.0867	0.7774	0.4286	0.013*
C1	0.20218 (10)	0.92935 (18)	0.46870 (12)	0.0119 (3)
H1A	0.2220	0.9720	0.5442	0.014*
H1B	0.1605	1.0239	0.4099	0.014*
C2	0.20319 (10)	0.60230 (18)	0.52072 (11)	0.0114 (3)
H2	0.2243	0.6396	0.5984	0.014*
C3	0.13915 (11)	0.42938 (19)	0.48147 (13)	0.0186 (3)
H3A	0.0801	0.4542	0.4754	0.028*
H3B	0.1785	0.3334	0.5385	0.028*
H3C	0.1183	0.3911	0.4056	0.028*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01181 (18)	0.01242 (18)	0.01379 (18)	−0.00022 (10)	0.00907 (14)	0.00166 (10)
O1	0.0321 (6)	0.0200 (6)	0.0225 (6)	−0.0075 (5)	0.0085 (5)	−0.0069 (5)
O2	0.0215 (6)	0.0256 (6)	0.0347 (6)	0.0119 (5)	0.0203 (5)	0.0101 (5)
O3	0.0246 (6)	0.0246 (6)	0.0358 (6)	−0.0064 (4)	0.0253 (5)	−0.0012 (5)
O4	0.0269 (6)	0.0308 (6)	0.0190 (5)	0.0105 (5)	0.0171 (5)	0.0119 (4)
OW	0.0272 (6)	0.0152 (5)	0.0174 (5)	−0.0013 (4)	0.0135 (5)	0.0000 (4)
N1	0.0077 (5)	0.0131 (5)	0.0124 (5)	0.0006 (4)	0.0062 (4)	0.0008 (4)
C1	0.0120 (6)	0.0101 (6)	0.0142 (6)	0.0011 (5)	0.0084 (5)	0.0006 (5)

C2	0.0110 (6)	0.0113 (6)	0.0122 (6)	0.0008 (5)	0.0074 (5)	0.0020 (5)
C3	0.0163 (6)	0.0139 (6)	0.0230 (7)	−0.0034 (5)	0.0111 (6)	0.0008 (5)

Geometric parameters (Å, °)

Cl1—O3	1.4327 (10)	C1—C2 ⁱ	1.5218 (17)
Cl1—O4	1.4363 (10)	C1—H1A	0.9700
Cl1—O1	1.4425 (11)	C1—H1B	0.9700
Cl1—O2	1.4452 (11)	C2—C3	1.5163 (18)
OW—H1W	0.850 (9)	C2—C1 ⁱ	1.5218 (17)
OW—H2W	0.850 (9)	C2—H2	0.9800
N1—C1	1.4955 (16)	C3—H3A	0.9600
N1—C2	1.5071 (16)	C3—H3B	0.9600
N1—H2N	0.9000	C3—H3C	0.9600
N1—H1N	0.9000		
O3—Cl1—O4	110.28 (7)	N1—C1—H1B	109.5
O3—Cl1—O1	109.01 (7)	C2 ⁱ —C1—H1B	109.5
O4—Cl1—O1	109.03 (7)	H1A—C1—H1B	108.1
O3—Cl1—O2	109.29 (7)	N1—C2—C3	110.17 (10)
O4—Cl1—O2	109.87 (7)	N1—C2—C1 ⁱ	108.88 (10)
O1—Cl1—O2	109.34 (7)	C3—C2—C1 ⁱ	111.63 (11)
H1W—OW—H2W	109.1 (17)	N1—C2—H2	108.7
C1—N1—C2	111.99 (10)	C3—C2—H2	108.7
C1—N1—H2N	109.2	C1 ⁱ —C2—H2	108.7
C2—N1—H2N	109.2	C2—C3—H3A	109.5
C1—N1—H1N	109.2	C2—C3—H3B	109.5
C2—N1—H1N	109.2	H3A—C3—H3B	109.5
H2N—N1—H1N	107.9	C2—C3—H3C	109.5
N1—C1—C2 ⁱ	110.74 (10)	H3A—C3—H3C	109.5
N1—C1—H1A	109.5	H3B—C3—H3C	109.5
C2 ⁱ —C1—H1A	109.5		

Symmetry code: (i) $-x+1/2, -y+3/2, -z+1$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
OW—H1W \cdots O1 ⁱ	0.85 (1)	2.03 (1)	2.8637 (16)	167 (2)
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N1—H1N \cdots O4 ⁱⁱⁱ	0.90	2.18	2.9067 (15)	137
N1—H1N \cdots O3 ^{iv}	0.90	2.42	3.0293 (15)	125
N1—H1N \cdots OW ^v	0.90	2.55	3.1994 (16)	130
N1—H2N \cdots OW ⁱ	0.90	1.91	2.8019 (15)	172
C1—H1B \cdots O3 ^{iv}	0.97	2.56	3.1007 (17)	116

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