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Melaminium sulfate

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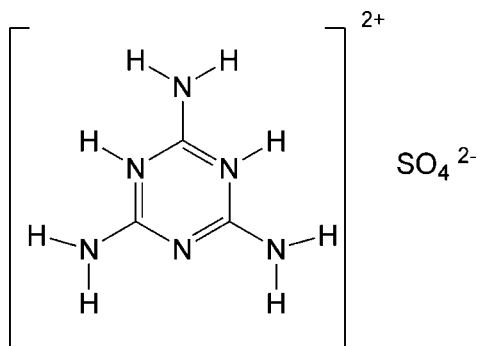
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{N}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.089; data-to-parameter ratio = 13.2.

In the title compound, $\text{C}_3\text{H}_8\text{N}_6^{2+}\cdot\text{SO}_4^{2-}$, the melaminium cations and sulfate anions are interconnected by $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a layer in the (101) plane. The layers are connected through multiple hydrogen bonds and $\pi-\pi$ stacking interactions (centroid-centroid distance of about 3.4 Å).

Related literature

For related literature, see: Janczak & Perpétuo (2001*a,b*); Martin & Pinkerton (1995); Dewar *et al.* (1985).



Experimental

Crystal data

 $\text{C}_3\text{H}_8\text{N}_6^{2+}\cdot\text{SO}_4^{2-}$
 $M_r = 224.21$

 Monoclinic, $C2/c$
 $a = 18.5787$ (3) Å

 $b = 8.6272$ (2) Å

 $c = 12.7945$ (4) Å

 $\beta = 129.739$ (1)°

 $V = 1576.94$ (7) Å³
 $Z = 8$

 Mo $K\alpha$ radiation

 $\mu = 0.42$ mm⁻¹
 $T = 293$ (2) K

 $0.32 \times 0.27 \times 0.26$ mm

Data collection

Bruker APEXII CCD diffractometer

Absorption correction: multi-scan (APEX2; Bruker, 2005)

 $T_{\min} = 0.878$, $T_{\max} = 0.900$

3793 measured reflections

1794 independent reflections

 1672 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.088$
 $S = 1.00$

1794 reflections

136 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N6}-\text{H6}\cdots\text{O2}^{\text{i}}$	0.87 (3)	1.76 (3)	2.622 (2)	171 (3)
$\text{N5}-\text{H5}\cdots\text{O4}^{\text{ii}}$	0.85 (3)	1.76 (3)	2.608 (2)	176 (3)
$\text{N3}-\text{H3B}\cdots\text{O2}^{\text{i}}$	0.86	2.59	3.244 (2)	134
$\text{N3}-\text{H3B}\cdots\text{O1}^{\text{iii}}$	0.86	2.44	2.944 (2)	118
$\text{N3}-\text{H3A}\cdots\text{N4}^{\text{iv}}$	0.86	2.14	3.000 (2)	176
$\text{N2}-\text{H2B}\cdots\text{O3}^{\text{i}}$	0.86	1.97	2.822 (2)	172
$\text{N2}-\text{H2A}\cdots\text{O3}^{\text{v}}$	0.86	2.02	2.836 (2)	159
$\text{N1}-\text{H1B}\cdots\text{O2}^{\text{ii}}$	0.86	1.99	2.838 (2)	169
$\text{N1}-\text{H1A}\cdots\text{O1}^{\text{vi}}$	0.86	2.43	2.992 (2)	123
$\text{N1}-\text{H1A}\cdots\text{O1}^{\text{vii}}$	0.86	2.11	2.887 (2)	151

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

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

We thank Professor Wen-Tao Yu and Mr Jian-Dong Fan for the data collection and helpful discussions. This work was supported by the Science and Technology Research Program of the Ministry of Education, China (grant No. 305010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2656).

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supporting information

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Melaminium sulfate

Bao-Yong Zhu, De-Liang Cui and Hai-Peng Jing

S1. Comment

Salts of melamine and its derivatives can develop supramolecular structures *via* hydrogen bonding by self assembly. Monoprotonated melaminium sulfate hydrate, $(C_3H_7N_6)_2 SO_4 \cdot H_2O$, has been structurally investigated (Janczak & Perpétuo, 2001*b*). We present here the solid state structure of anhydrous diprotonated melaminium salt.

The internal C—N—C angle at the protonated N atoms [C2—N6—C3 120.35 (15) ° and C2—N5—C1 120.25 (15) °] is significantly larger than the C—N—C angle at the non-protonated N atom [C1—N4—C3 116.79 (15) °]. These differences are due to the steric effect of the lone-pair electrons and are fully consistent with the valence-shell electron-pair repulsion theory (Janczak & Perpétuo, 2001*a*). The two shortest bonds [N4—C3 1.333 (2) Å and N4—C1 1.338 (2) Å] are those furthest from the protonated ring N atoms. The two longest bonds [N6—C3 1.367 (2) Å and N5—C1 1.373 (2) Å] are those connected to the shortest bonds. This has the effect of opening up the ring bond angles at atoms C1 and C3, thus creating the largest bond angles in the ring [N4—C3—N6 122.4 (1) ° and N4—C1—N5 122.1 (1) °]. A semi-empirical calculation, with the AM1 parameter set (Dewar *et al.*, 1985) on the melaminium residue diprotonated at two ring N atoms, results in almost the same geometrical features as being found in the title compound. The distortion of the aromatic ring is quite similar to that reported for the melaminium diperchlorate monohydrate salt (Martin & Pinkerton, 1995), as well as for melaminium bis(4-hydroxybenzene-sulfonate) dihydrate (Janczak & Perpétuo, 2001*a*).

The melaminium residue is involved in eleven hydrogen bonds, two N—H···N bonds with the neighbouring melaminium residue and nine N—H···O bonds with six neighbouring SO_4^{2-} anions. Two of the SO_4^{2-} anions are acceptors of two and three hydrogen bonds, respectively, while the other four are acceptors of one hydrogen bond each (Fig. 2). The H atoms at the protonated N atoms of the melaminium residue are involved in almost linear N—H···O hydrogen bonds.

Each SO_4^{2-} ion is involved as an acceptor in nine hydrogen bonds connecting to six melaminium residues. The O1 and O2 atoms are the most interesting ones as they all accept three hydrogen atoms each. O3 forms two hydrogen bonds with melaminium residues *via* the H atoms of the amino groups, and O4 forms only one hydrogen bond *via* H5 atom at the protonated N atom of the melaminium residue.

The melaminium residues are interconnected by two almost linear N—H···N hydrogen bonds and five N—H···O hydrogen bonds. The distance between the centroids of the aromatic rings in adjacent layers (symmetry operator $2 - x, +y, 1.5 - z$) is about 3.4 Å, which is much shorter than the maximum distance for the π - π stacking interaction (3.8 Å for centroid-centroid distance), indicating strong π - π stacking interactions. The two-dimensional layers are extensively interconnected by multiple hydrogen bonds with sulfate anions and π - π stacking interactions (Fig. 3).

S2. Experimental

0.126 g (0.001 mol) of melamine was dissolved in 50 ml hot water. To this solution 4 ml 98% sulfate acid was slowly added. After several days, colorless crystals of (I) appeared.

S3. Refinement

The H atoms bonded to the ring N atoms were located in difference Fourier map and their positions and displacement parameters were refined freely. The amino H atoms were added geometrically and treated as riding, with $N-H = 0.86 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(N)$.

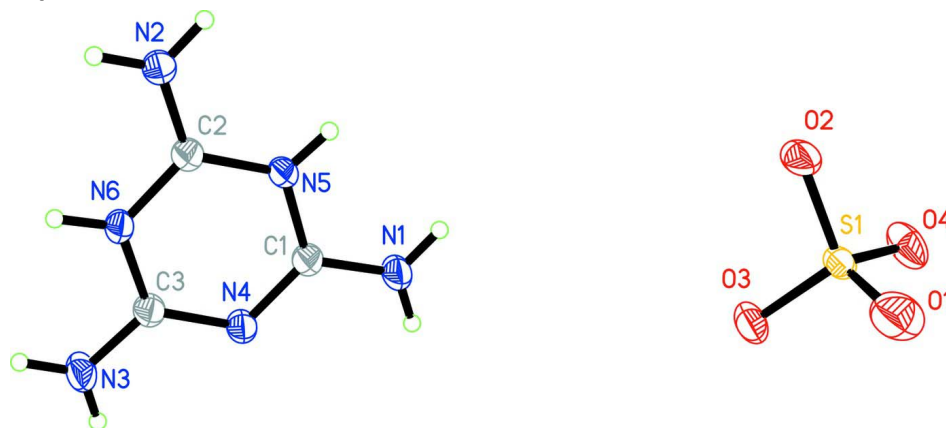


Figure 1

View of the asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

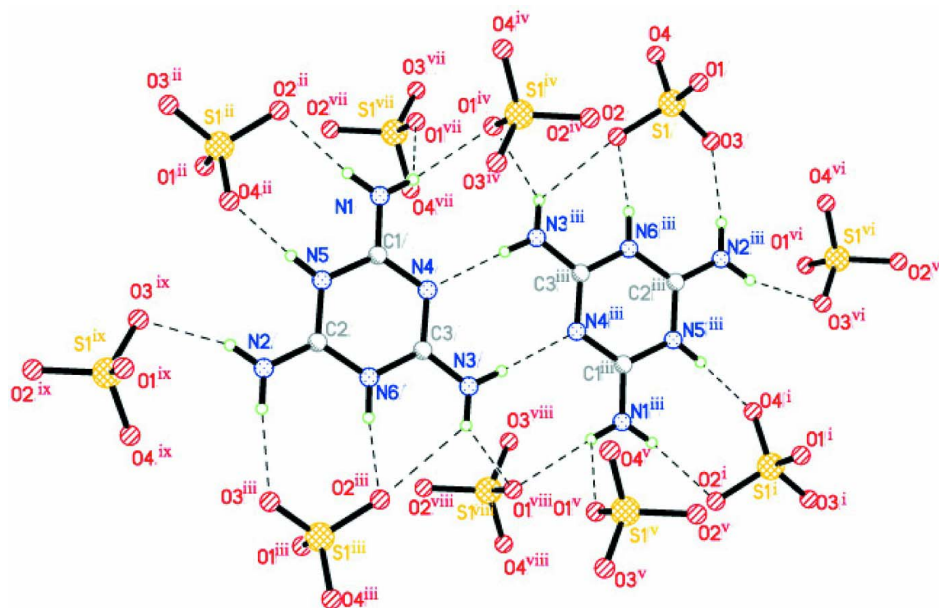
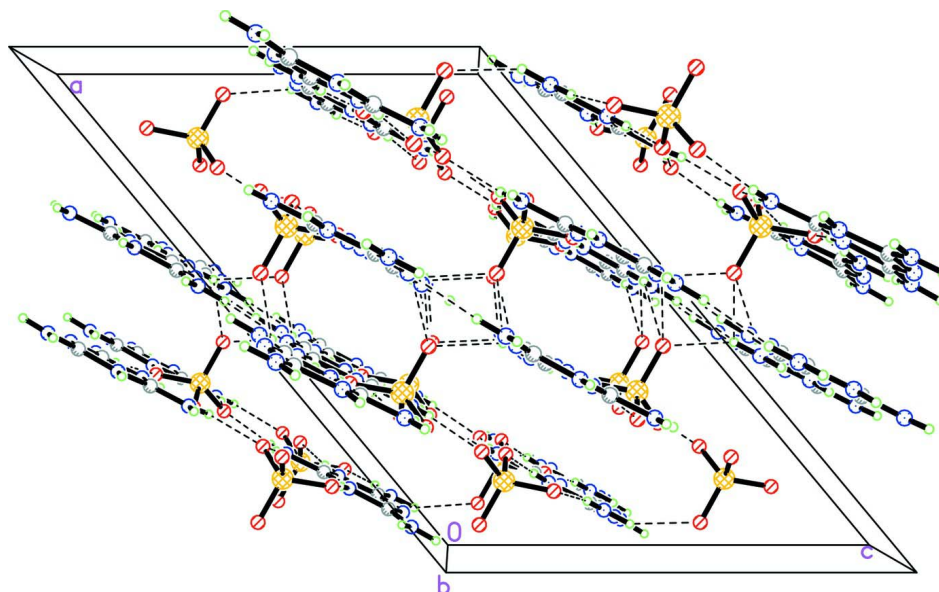


Figure 2

Diagram showing the hydrogen bonds of the melaminium cation. symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, y, -z + 1/2$; (v) $-x + 1, y + 1, -z + 1/2$; (vi) $-x + 3/2, y + 1/2, -z + 1/2$; (vii) $x, -y, z + 1/2$; (viii) $x, -y + 1, z + 1/2$; (ix) $x - 1/2, -y + 1/2, z + 1/2$.

**Figure 3**

The molecular packing of (I) in the unit cell showing the hydrogen-bonding interaction (dashed lines).

Melaminium sulfate

Crystal data

$C_3H_8N_6^{2+} \cdot SO_4^{2-}$
 $M_r = 224.21$
 Monoclinic, $C2/c$
 $a = 18.5787$ (3) Å
 $b = 8.6272$ (2) Å
 $c = 12.7945$ (4) Å
 $\beta = 129.739$ (1)°
 $V = 1576.94$ (7) Å³
 $Z = 8$

$F(000) = 928$
 $D_x = 1.889$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2920 reflections
 $\theta = 2.8$ – 27.5 °
 $\mu = 0.42$ mm⁻¹
 $T = 293$ K
 Prism, colorless
 $0.32 \times 0.27 \times 0.26$ mm

Data collection

Bruker APEX2 CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (APEX2; Bruker, 2005)
 $T_{\min} = 0.879$, $T_{\max} = 0.900$

3793 measured reflections
 1794 independent reflections
 1672 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$
 $\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.8$ °
 $h = -24 \rightarrow 19$
 $k = -6 \rightarrow 11$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.089$
 $S = 1.00$
 1794 reflections
 136 parameters
 0 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

$$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 3.6165P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$

$$\Delta\rho_{\min} = -0.45 \text{ e } \text{Å}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 1997), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0037 (5)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.65733 (3)	0.06360 (5)	0.27385 (4)	0.02105 (15)
O2	0.63929 (12)	0.11467 (16)	0.36667 (16)	0.0369 (4)
O4	0.70593 (10)	-0.08710 (15)	0.32413 (17)	0.0348 (4)
C2	0.84604 (12)	0.9717 (2)	0.65207 (17)	0.0210 (3)
N5	0.86032 (10)	0.82418 (17)	0.63479 (15)	0.0215 (3)
N3	0.95352 (12)	1.16685 (18)	0.54108 (18)	0.0312 (4)
H3A	0.9834	1.1488	0.5118	0.037*
H3B	0.9448	1.2607	0.5534	0.037*
O3	0.71951 (10)	0.17704 (15)	0.28119 (15)	0.0309 (3)
N2	0.80592 (11)	1.00382 (18)	0.70342 (17)	0.0277 (3)
H2A	0.7879	0.9301	0.7272	0.033*
H2B	0.7974	1.0988	0.7136	0.033*
C3	0.92125 (12)	1.0513 (2)	0.56700 (18)	0.0222 (3)
N4	0.93490 (11)	0.90603 (17)	0.54780 (16)	0.0236 (3)
N1	0.91024 (13)	0.64908 (18)	0.55885 (18)	0.0317 (4)
H1A	0.9372	0.6259	0.5259	0.038*
H1B	0.8889	0.5768	0.5787	0.038*
O1	0.56934 (11)	0.0514 (2)	0.13681 (16)	0.0440 (4)
N6	0.87638 (11)	1.08607 (18)	0.61675 (16)	0.0232 (3)
C1	0.90174 (12)	0.7934 (2)	0.57868 (17)	0.0219 (3)
H6	0.8684 (18)	1.183 (3)	0.626 (2)	0.042 (7)*
H5	0.8388 (18)	0.749 (3)	0.651 (3)	0.044 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0277 (2)	0.0160 (2)	0.0288 (2)	0.00029 (15)	0.0224 (2)	0.00143 (15)
O2	0.0657 (10)	0.0212 (7)	0.0574 (9)	-0.0009 (7)	0.0549 (9)	-0.0015 (6)
O4	0.0425 (8)	0.0182 (6)	0.0605 (10)	0.0067 (6)	0.0408 (8)	0.0085 (6)
C2	0.0228 (8)	0.0197 (8)	0.0233 (8)	-0.0007 (6)	0.0160 (7)	-0.0004 (6)
N5	0.0284 (7)	0.0166 (7)	0.0289 (7)	-0.0010 (6)	0.0226 (7)	0.0004 (6)

N3	0.0438 (9)	0.0183 (7)	0.0528 (10)	-0.0030 (7)	0.0407 (9)	-0.0011 (7)
O3	0.0416 (8)	0.0189 (6)	0.0502 (8)	-0.0047 (5)	0.0377 (7)	-0.0022 (6)
N2	0.0395 (9)	0.0202 (7)	0.0418 (9)	-0.0002 (6)	0.0345 (8)	-0.0006 (6)
C3	0.0246 (8)	0.0201 (8)	0.0274 (8)	-0.0013 (6)	0.0191 (7)	-0.0010 (6)
N4	0.0296 (8)	0.0185 (7)	0.0345 (8)	-0.0010 (6)	0.0259 (7)	-0.0010 (6)
N1	0.0519 (10)	0.0172 (7)	0.0516 (10)	-0.0016 (7)	0.0449 (9)	-0.0018 (7)
O1	0.0361 (8)	0.0554 (10)	0.0329 (8)	-0.0085 (7)	0.0185 (7)	0.0045 (7)
N6	0.0320 (8)	0.0156 (7)	0.0330 (8)	-0.0002 (6)	0.0259 (7)	-0.0012 (6)
C1	0.0254 (8)	0.0194 (8)	0.0262 (8)	-0.0003 (6)	0.0188 (7)	-0.0007 (6)

Geometric parameters (Å, °)

S1—O1	1.447 (1)	N3—H3B	0.8600
S1—O3	1.471 (1)	N2—H2A	0.8600
S1—O4	1.475 (1)	N2—H2B	0.8600
S1—O2	1.492 (1)	C3—N4	1.333 (2)
C2—N2	1.300 (2)	C3—N6	1.367 (2)
C2—N5	1.347 (2)	N4—C1	1.338 (2)
C2—N6	1.350 (2)	N1—C1	1.300 (2)
N5—C1	1.373 (2)	N1—H1A	0.8600
N5—H5	0.85 (3)	N1—H1B	0.8600
N3—C3	1.310 (2)	N6—H6	0.87 (3)
N3—H3A	0.8600		
O1—S1—O3	111.02 (9)	C2—N2—H2B	120.0
O1—S1—O4	111.51 (10)	H2A—N2—H2B	120.0
O3—S1—O4	108.77 (8)	N3—C3—N4	119.80 (16)
O1—S1—O2	109.36 (10)	N3—C3—N6	117.71 (16)
O3—S1—O2	108.65 (8)	N4—C3—N6	122.46 (16)
O4—S1—O2	107.42 (9)	C3—N4—C1	116.79 (15)
N2—C2—N5	121.41 (16)	C1—N1—H1A	120.0
N2—C2—N6	120.69 (16)	C1—N1—H1B	120.0
N5—C2—N6	117.88 (15)	H1A—N1—H1B	120.0
C2—N5—C1	120.25 (15)	C2—N6—C3	120.35 (15)
C2—N5—H5	120.6 (18)	C2—N6—H6	120.8 (17)
C1—N5—H5	118.9 (19)	C3—N6—H6	118.8 (17)
C3—N3—H3A	120.0	N1—C1—N4	120.09 (16)
C3—N3—H3B	120.0	N1—C1—N5	117.76 (16)
H3A—N3—H3B	120.0	N4—C1—N5	122.13 (15)
C2—N2—H2A	120.0		
N2—C2—N5—C1	179.14 (16)	N3—C3—N6—C2	-176.50 (17)
N6—C2—N5—C1	-2.1 (2)	N4—C3—N6—C2	1.8 (3)
N3—C3—N4—C1	178.76 (17)	C3—N4—C1—N1	178.06 (18)
N6—C3—N4—C1	0.5 (3)	C3—N4—C1—N5	-3.6 (3)
N2—C2—N6—C3	177.84 (17)	C2—N5—C1—N1	-177.10 (17)
N5—C2—N6—C3	-0.9 (3)	C2—N5—C1—N4	4.6 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N6—H6 \cdots O2 ⁱ	0.87 (3)	1.76 (3)	2.622 (2)	171 (3)
N5—H5 \cdots O4 ⁱⁱ	0.85 (3)	1.76 (3)	2.608 (2)	176 (3)
N3—H3B \cdots O2 ⁱ	0.86	2.59	3.244 (2)	134
N3—H3B \cdots O1 ⁱⁱⁱ	0.86	2.44	2.944 (2)	118
N3—H3A \cdots N4 ^{iv}	0.86	2.14	3.000 (2)	176
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N2—H2A \cdots O3 ^v	0.86	2.02	2.836 (2)	159
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N1—H1A \cdots O1 ^{vi}	0.86	2.43	2.992 (2)	123
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Symmetry codes: (i) $-x+3/2, -y+3/2, -z+1$; (ii) $-x+3/2, -y+1/2, -z+1$; (iii) $x+1/2, -y+3/2, z+1/2$; (iv) $-x+2, -y+2, -z+1$; (v) $x, -y+1, z+1/2$; (vi) $x+1/2, -y+1/2, z+1/2$; (vii) $-x+3/2, y+1/2, -z+1/2$.