

5-Amino-1*H*-1,2,4-triazol-4-ium-3-carboxylate hemihydrate

José A. Fernandes,^a Bing Liu,^{a,b} João P. C. Tomé,^c Luís Cunha-Silva^b and Filipe A. Almeida Paz^{a*}

^aDepartment of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal, ^bREQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal, and ^cDepartment of Chemistry, University of Aveiro, QOPNA, 3810-193 Aveiro, Portugal

Correspondence e-mail: filipe.paz@ua.pt

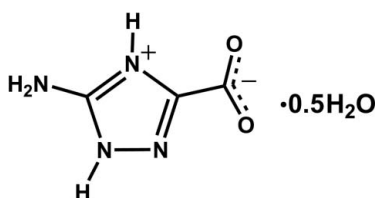
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.066; wR factor = 0.202; data-to-parameter ratio = 8.9.

The asymmetric unit of the title compound, $\text{C}_3\text{H}_4\text{N}_4\text{O}_2 \cdot 0.5\text{H}_2\text{O}$, comprises two whole molecules of 5-amino-1*H*-1,2,4-triazole-3-carboxylic acid in its zwitterionic form (proton transfer occurs from the carboxylic acid group to the N heteroatom at position 1), plus one water molecule of crystallization. The organic moieties are disposed into supramolecular layers linked by $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds parallel to the *bc* plane. Additional $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds involving the water molecules and the organic molecules lead to the formation of double-deck supramolecular arrangements which are interconnected along the *a* axis via $\pi-\pi$ stacking [centroid-centroid distance = 3.507 (3) Å].

Related literature

For related compounds with 5-amino-1*H*-1,2,4-triazole-3-carboxylic acid residues, see: Masiukiewicz *et al.* (2007); Ouakkaf *et al.* (2011); Sun *et al.* (2011); Wawrzycka-Gorczyca *et al.* (2003). For previous work in crystal engineering, see: Amarante, Gonçalves *et al.* (2009); Amarante, Figueiredo *et al.* (2009); Shi *et al.* (2008); Paz & Klinowski (2004, 2007); Paz *et al.* (2005). For graph-set notation, see: Grell *et al.* (1999). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$\text{C}_3\text{H}_4\text{N}_4\text{O}_2 \cdot 0.5\text{H}_2\text{O}$
 $M_r = 137.11$
 Triclinic, $P\bar{1}$
 $a = 6.5440$ (11) Å
 $b = 6.9490$ (8) Å
 $c = 12.0723$ (17) Å
 $\alpha = 93.976$ (7)°
 $\beta = 105.012$ (9)°

$\gamma = 99.703$ (8)°
 $V = 518.96$ (13) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.15$ mm⁻¹
 $T = 150$ K
 $0.10 \times 0.07 \times 0.04$ mm

Data collection

Bruker X8 KappaCCD APEXII diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
 $T_{\text{min}} = 0.985$, $T_{\text{max}} = 0.994$

4474 measured reflections
 1797 independent reflections
 1433 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.202$
 $S = 1.24$
 1797 reflections
 202 parameters
 13 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i> ⋯ <i>A</i>
N1—H1⋯O1 ^W	0.95 (1)	1.87 (2)	2.799 (5)	167 (5)
N3—H3⋯O1 ^W ⁱ	0.95 (1)	1.87 (3)	2.758 (5)	154 (5)
N4—H4A⋯O4	0.94 (1)	1.86 (2)	2.777 (5)	163 (4)
N4—H4B⋯N6 ⁱ	0.94 (1)	2.29 (3)	3.125 (6)	146 (4)
N5—H5⋯O1 ⁱⁱ	0.95 (1)	1.75 (1)	2.699 (5)	178 (5)
N7—H7⋯O3 ⁱⁱⁱ	0.95 (1)	1.66 (2)	2.579 (5)	161 (5)
N8—H8A⋯O2 ⁱⁱ	0.94 (1)	2.10 (2)	2.989 (5)	155 (4)
N8—H8B⋯O1 ^{iv}	0.94 (1)	2.17 (1)	3.117 (5)	178 (5)
O1 ^W —H1 ^X ⋯O1 ^v	0.95 (1)	1.94 (2)	2.839 (5)	159 (5)
O1 ^W —H1 ^Y ⋯O4	0.95 (1)	1.70 (2)	2.634 (5)	170 (5)

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2764).

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supporting information

Acta Cryst. (2011). E67, o2073–o2074 [doi:10.1107/S160053681102811X]

5-Amino-1*H*-1,2,4-triazol-4-ium-3-carboxylate hemihydrate

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S1. Comment

5-Amino-1*H*-1,2,4-triazole-3-carboxylic acid (H₂Atrc) arises as a promising ligand which can be employed in the preparation of coordination compounds as a consequence of its multiple available sites to establish direct connections with metallic centres. However, surveying the Cambridge Structural Database (Allen, 2002) showed only a handful of crystalline compounds reported to date, namely organic derivatives (Masiukiewicz *et al.*, 2007; Wawrzycka-Gorczyca *et al.*, 2003), the sulfate salt (Ouakkaf *et al.*, 2011) and a three-dimensional metal-organic framework (MOF) with Dy³⁺, very recently reported by Sun *et al.* (2011). Following our on-going interest on crystal engineering approaches of both organic crystals (Amarante, Gonçalves *et al.*, 2009; Amarante, Figueiredo *et al.*, 2009) and metal-organic frameworks (Shi *et al.*, 2008; Paz & Klinowski, 2007; Paz *et al.*, 2005; Paz & Klinowski, 2004), we are currently interested in exploring the coordination capabilities of H₂Atrc and its residues. The title compound was isolated as a secondary minor product for which we wish to report its crystal structure at the low temperature of 150 K.

The asymmetric unit of title compound comprises two whole molecules of H₂Atrc in its zwitterionic form (proton transference occurs from the carboxylic acid group to the *N* heteroatom at position 1) and a water molecule of crystallization as depicted in Fig. 1. The two individual molecular units are almost planar, with the observed deviations being smaller than 0.037 Å. The two organic moieties are also mutually located in the same average plane, with the average planes subtending an angle of *ca* 7.2°. This planarity is extended throughout the entire crystal structure with the organic moieties being disposed in layers placed in the *bc* plane of the unit cell.

Due to the presence of a considerable number of proton donors and acceptors, the crystal structure is rich in hydrogen bonding interactions (see Table 1 for further details). In this context, the structural function of the two non-equivalent organic molecules composing the asymmetric unit is not the same since the hydrogen bonding interactions in which each moiety is involved differ considerably. While the moiety coined as A interacts with other symmetry-related moieties and also with B, the residue coined as B only interacts with A and with water molecules of crystallization. Given the coplanarity of the two non-equivalent H₂Atrc molecules, mutual interactions occur solely along the aforementioned layers, forming several fused hydrogen-bonded rings (green dashed lines in Figs 2 and 3), best described by the graph set motifs $R_2^2(8)$, $R_3^3(9)$ and $R_3^2(11)$ (Grell *et al.*, 1999). Because of the hydrogen bonds directly involving the crystallographically independent water molecule of crystallization (pink dashed lines in Fig. 3), individual moieties are arranged into double decker layers as depicted in Fig. 3. These supramolecular arrays interact between each other along the *a*-axis of the unit cell *via* weak interactions such as π - π stacking. The most structurally relevant of such interactions occurs between two symmetry-equivalent A moieties with an inter-centroid distance of 3.507 (3) Å (orange dashed lines in Figure 3).

S2. Experimental

5-Amino-1*H*-1,2,4-triazole-3-carboxylic acid (H₂Atrc) and MnSO₄ were purchased from Sigma-Aldrich and they were used as received without purification.

H₂Atrc (0.1 mmol, 12.8 mg) was dissolved in *ca* 15 ml of hot water (*ca* 358 K). The solution was then cooled to ambient temperature. A second aqueous solution of MnSO₄ (0.1 mmol, 11.7 mg in *ca* 2 ml) was added drop wise to that containing the dissolved H₂Atrc ligand. The resulting mixture solution was allowed to stand still over a period of one week and small colourless blocks were formed as a secondary product.

S3. Refinement

All hydrogen atoms bound to nitrogen (organic molecules) and to oxygen (water molecule of crystallization) were directly located from difference Fourier maps and included in the structural model with the O—H and N—H distances restrained to 0.95 (1) Å. The H···H distances in the water molecule and in the —NH₂ groups were further restrained to 1.55 (1) Å in order to ensure a chemically reasonable geometry for these moieties. The U_{iso} of these hydrogen atoms were fixed at $1.5 \times U_{\text{eq}}$ of the parent nitrogen or oxygen atoms.

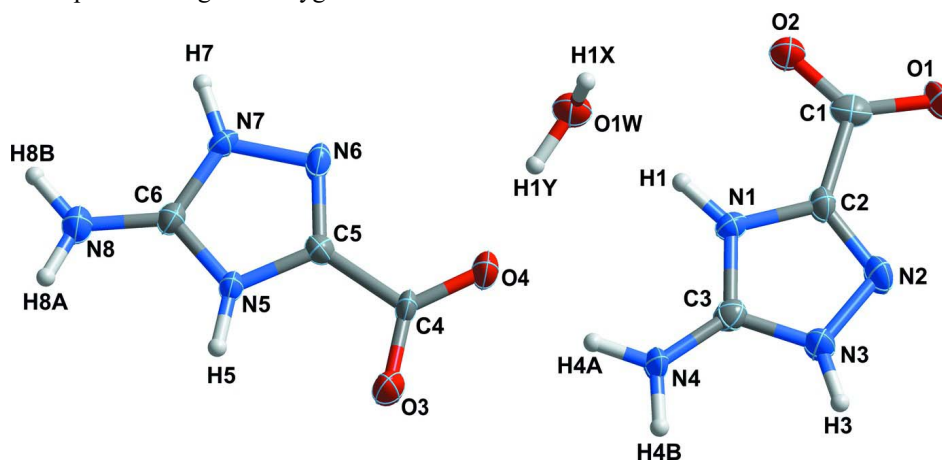
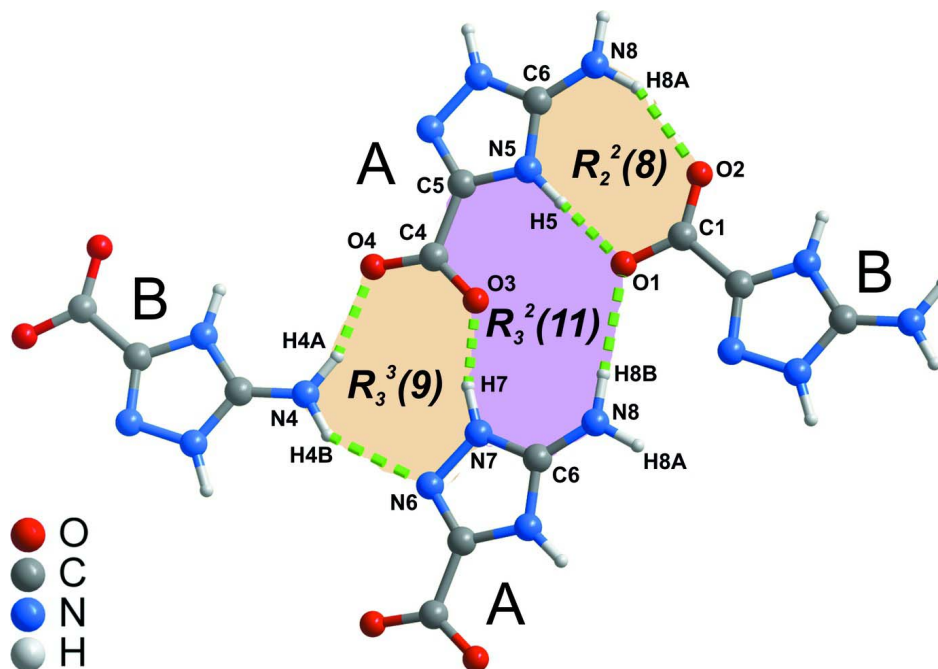
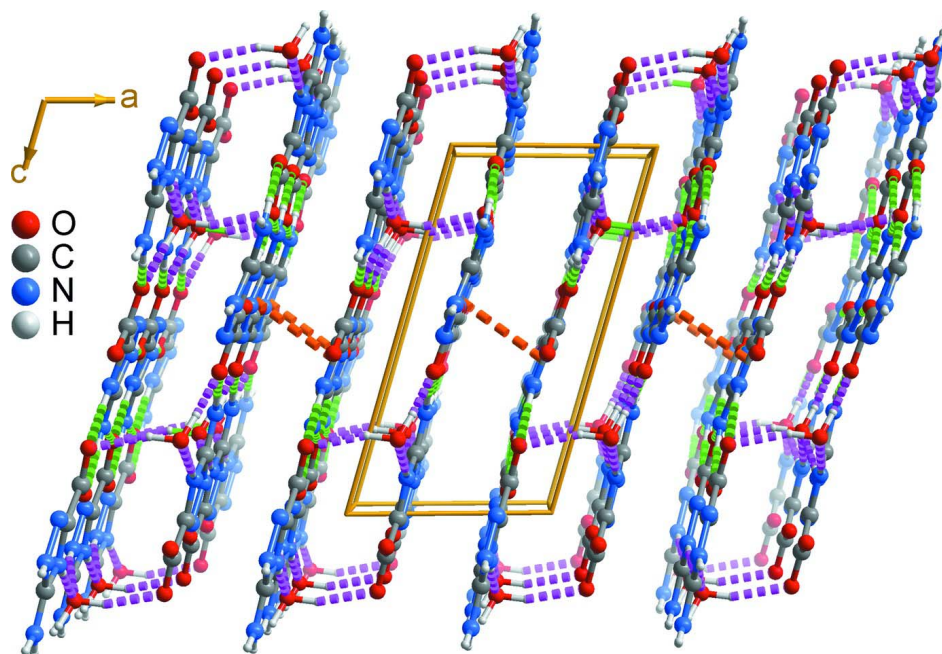


Figure 1

Molecular structures of the units composing the asymmetric unit of the title compound, showing the atomic labelling for all atoms. Non-hydrogen atoms are represented as displacement ellipsoids drawn at the 70% probability level. Hydrogen atoms are depicted as small spheres with arbitrary radii.

**Figure 2**

N—H \cdots N and N—H \cdots O interactions (dashed green lines) forming the supramolecular layer placed in the *bc* plane of the unit cell. The two distinct H₂Atrc residues are depicted as molecules A and B. Supramolecular arrangements are described by their graph set notation following Grell *et al.* (1999). For geometric details on the represented supramolecular contacts see Table 1. Symmetry transformations used to generate equivalent atoms have been omitted for clarity.

**Figure 3**

Crystal packing of the title compound viewed in perspective along the [010] direction of the unit cell. Hydrogen bonding interactions between H₂Atrc moieties are depicted as dashed green lines, while those involving the water molecules of crystallization are represented as dashed pink lines. π - π stacking interactions are represented as dashed orange lines.

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Crystal data

C₃H₄N₄O₂·0.5H₂O
M_r = 137.11
 Triclinic, *P*1̄
 Hall symbol: -P 1
a = 6.5440 (11) Å
b = 6.9490 (8) Å
c = 12.0723 (17) Å
 α = 93.976 (7)°
 β = 105.012 (9)°
 γ = 99.703 (8)°
V = 518.96 (13) Å³

Z = 4
F(000) = 284
D_x = 1.755 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 2284 reflections
 θ = 3.0–26.5°
 μ = 0.15 mm⁻¹
T = 150 K
 Block, colourless
 0.10 × 0.07 × 0.04 mm

Data collection

Bruker X8 KappaCCD APEXII
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω and ϕ scans
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1997)
T_{min} = 0.985, *T_{max}* = 0.994

4474 measured reflections
 1797 independent reflections
 1433 reflections with *I* > 2 σ (*I*)
R_{int} = 0.032
 θ_{\max} = 25.3°, θ_{\min} = 3.7°
h = -7→7
k = -8→8
l = -14→14

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.202$
 $S = 1.24$
 1797 reflections
 202 parameters
 13 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
 $w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 2.637P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{Å}^{-3}$

Special details

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

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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.2627 (6)	0.4287 (5)	1.1942 (3)	0.0210 (8)
O2	0.2494 (6)	0.6539 (5)	1.0686 (3)	0.0204 (8)
C1	0.2566 (8)	0.4869 (7)	1.0970 (4)	0.0181 (11)
C2	0.2597 (8)	0.3319 (7)	1.0033 (4)	0.0145 (10)
C3	0.2551 (8)	0.2009 (7)	0.8332 (4)	0.0151 (10)
N1	0.2483 (7)	0.3692 (6)	0.8926 (3)	0.0156 (9)
H1	0.230 (9)	0.492 (4)	0.867 (5)	0.023*
N2	0.2760 (7)	0.1506 (6)	1.0170 (3)	0.0190 (10)
N3	0.2736 (7)	0.0699 (6)	0.9090 (3)	0.0180 (9)
H3	0.262 (9)	-0.066 (2)	0.887 (5)	0.027*
N4	0.2452 (7)	0.1709 (6)	0.7223 (3)	0.0185 (10)
H4A	0.234 (9)	0.266 (5)	0.670 (3)	0.028*
H4B	0.251 (9)	0.049 (3)	0.685 (3)	0.028*
O3	0.2553 (6)	0.3765 (5)	0.4390 (3)	0.0227 (9)
O4	0.2348 (6)	0.5057 (5)	0.6096 (3)	0.0219 (9)
C4	0.2476 (8)	0.5132 (7)	0.5087 (4)	0.0151 (10)
C5	0.2534 (8)	0.7084 (7)	0.4618 (4)	0.0146 (10)
C6	0.2720 (8)	0.9152 (7)	0.3368 (4)	0.0146 (10)
N5	0.2730 (7)	0.7267 (6)	0.3525 (3)	0.0149 (9)
H5	0.272 (9)	0.622 (5)	0.298 (4)	0.022*
N6	0.2409 (7)	0.8740 (6)	0.5147 (3)	0.0167 (9)
N7	0.2527 (7)	1.0044 (6)	0.4344 (3)	0.0157 (9)
H7	0.248 (9)	1.139 (3)	0.452 (5)	0.024*
N8	0.2862 (8)	0.9965 (6)	0.2414 (4)	0.0232 (10)

H8A	0.274 (10)	0.918 (6)	0.172 (2)	0.035*
H8B	0.276 (10)	1.127 (3)	0.228 (4)	0.035*
O1W	0.1593 (6)	0.7013 (5)	0.7849 (3)	0.0225 (9)
H1X	0.009 (2)	0.672 (8)	0.775 (4)	0.034*
H1Y	0.194 (7)	0.645 (8)	0.720 (3)	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.036 (2)	0.0223 (19)	0.0072 (17)	0.0083 (16)	0.0077 (15)	0.0024 (14)
O2	0.030 (2)	0.0150 (18)	0.0164 (18)	0.0058 (15)	0.0074 (16)	0.0005 (14)
C1	0.016 (3)	0.018 (3)	0.020 (3)	0.004 (2)	0.005 (2)	−0.002 (2)
C2	0.018 (3)	0.016 (2)	0.010 (2)	0.004 (2)	0.0032 (19)	0.0037 (19)
C3	0.016 (3)	0.014 (2)	0.014 (2)	0.004 (2)	0.002 (2)	0.0019 (19)
N1	0.023 (2)	0.0101 (19)	0.015 (2)	0.0050 (17)	0.0064 (17)	0.0020 (16)
N2	0.029 (2)	0.019 (2)	0.009 (2)	0.0048 (19)	0.0049 (18)	0.0018 (17)
N3	0.030 (2)	0.013 (2)	0.012 (2)	0.0046 (18)	0.0065 (18)	0.0002 (17)
N4	0.035 (3)	0.015 (2)	0.009 (2)	0.0097 (19)	0.0079 (19)	0.0047 (17)
O3	0.040 (2)	0.0126 (17)	0.0193 (19)	0.0071 (16)	0.0121 (17)	0.0045 (15)
O4	0.037 (2)	0.0174 (18)	0.0149 (19)	0.0090 (16)	0.0099 (16)	0.0077 (14)
C4	0.022 (3)	0.013 (2)	0.011 (3)	0.005 (2)	0.005 (2)	0.0067 (19)
C5	0.018 (3)	0.014 (2)	0.012 (2)	0.004 (2)	0.006 (2)	0.0017 (19)
C6	0.018 (2)	0.013 (2)	0.014 (2)	0.005 (2)	0.004 (2)	0.0044 (19)
N5	0.025 (2)	0.011 (2)	0.011 (2)	0.0052 (17)	0.0065 (17)	0.0043 (16)
N6	0.023 (2)	0.015 (2)	0.013 (2)	0.0035 (17)	0.0045 (18)	0.0066 (17)
N7	0.024 (2)	0.0088 (19)	0.015 (2)	0.0058 (17)	0.0059 (18)	0.0024 (16)
N8	0.038 (3)	0.018 (2)	0.017 (2)	0.009 (2)	0.011 (2)	0.0064 (18)
O1W	0.033 (2)	0.0174 (18)	0.0194 (19)	0.0064 (16)	0.0098 (16)	−0.0001 (15)

Geometric parameters (Å, °)

O1—C1	1.260 (6)	O4—C4	1.246 (6)
O2—C1	1.238 (6)	C4—C5	1.504 (6)
C1—C2	1.513 (7)	C5—N6	1.302 (6)
C2—N2	1.300 (6)	C5—N5	1.370 (6)
C2—N1	1.364 (6)	C6—N8	1.335 (6)
C3—N4	1.324 (6)	C6—N5	1.337 (6)
C3—N3	1.332 (6)	C6—N7	1.339 (6)
C3—N1	1.343 (6)	N5—H5	0.947 (10)
N1—H1	0.946 (11)	N6—N7	1.380 (5)
N2—N3	1.378 (6)	N7—H7	0.948 (10)
N3—H3	0.947 (11)	N8—H8A	0.944 (10)
N4—H4A	0.943 (10)	N8—H8B	0.944 (10)
N4—H4B	0.944 (10)	O1W—H1X	0.946 (10)
O3—C4	1.241 (6)	O1W—H1Y	0.945 (10)
O2—C1—O1	128.4 (4)	O3—C4—C5	114.0 (4)
O2—C1—C2	116.0 (4)	O4—C4—C5	118.2 (4)

O1—C1—C2	115.5 (4)	N6—C5—N5	112.4 (4)
N2—C2—N1	111.7 (4)	N6—C5—C4	126.8 (4)
N2—C2—C1	125.4 (4)	N5—C5—C4	120.8 (4)
N1—C2—C1	122.9 (4)	N8—C6—N5	126.1 (4)
N4—C3—N3	127.0 (5)	N8—C6—N7	127.1 (4)
N4—C3—N1	127.2 (4)	N5—C6—N7	106.7 (4)
N3—C3—N1	105.8 (4)	C6—N5—C5	106.3 (4)
C3—N1—C2	107.2 (4)	C6—N5—H5	128 (3)
C3—N1—H1	130 (3)	C5—N5—H5	126 (3)
C2—N1—H1	123 (3)	C5—N6—N7	103.5 (4)
C2—N2—N3	103.7 (4)	C6—N7—N6	111.1 (4)
C3—N3—N2	111.6 (4)	C6—N7—H7	128 (3)
C3—N3—H3	123 (3)	N6—N7—H7	121 (3)
N2—N3—H3	125 (3)	C6—N8—H8A	121 (3)
C3—N4—H4A	126 (3)	C6—N8—H8B	127 (3)
C3—N4—H4B	123 (3)	H8A—N8—H8B	111 (4)
H4A—N4—H4B	110.9 (16)	H1X—O1W—H1Y	111 (4)
O3—C4—O4	127.8 (4)		
O2—C1—C2—N2	177.0 (5)	O3—C4—C5—N6	177.7 (5)
O1—C1—C2—N2	-2.7 (7)	O4—C4—C5—N6	-1.9 (8)
O2—C1—C2—N1	-2.0 (7)	O3—C4—C5—N5	-2.0 (7)
O1—C1—C2—N1	178.2 (5)	O4—C4—C5—N5	178.3 (5)
N4—C3—N1—C2	179.0 (5)	N8—C6—N5—C5	-179.5 (5)
N3—C3—N1—C2	-1.0 (5)	N7—C6—N5—C5	0.1 (5)
N2—C2—N1—C3	0.8 (6)	N6—C5—N5—C6	-0.1 (6)
C1—C2—N1—C3	180.0 (4)	C4—C5—N5—C6	179.7 (4)
N1—C2—N2—N3	-0.3 (6)	N5—C5—N6—N7	0.1 (5)
C1—C2—N2—N3	-179.5 (5)	C4—C5—N6—N7	-179.7 (5)
N4—C3—N3—N2	-179.1 (5)	N8—C6—N7—N6	179.6 (5)
N1—C3—N3—N2	0.8 (6)	N5—C6—N7—N6	0.0 (5)
C2—N2—N3—C3	-0.3 (6)	C5—N6—N7—C6	-0.1 (5)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O1W	0.95 (1)	1.87 (2)	2.799 (5)	167 (5)
N3—H3 \cdots O1W ^a	0.95 (1)	1.87 (3)	2.758 (5)	154 (5)
N4—H4A \cdots O4	0.94 (1)	1.86 (2)	2.777 (5)	163 (4)
N4—H4B \cdots N6 ⁱ	0.94 (1)	2.29 (3)	3.125 (6)	146 (4)
N5—H5 \cdots O1 ⁱⁱ	0.95 (1)	1.75 (1)	2.699 (5)	178 (5)
N7—H7 \cdots O3 ⁱⁱⁱ	0.95 (1)	1.66 (2)	2.579 (5)	161 (5)
N8—H8A \cdots O2 ⁱⁱ	0.94 (1)	2.10 (2)	2.989 (5)	155 (4)
N8—H8B \cdots O1 ^{iv}	0.94 (1)	2.17 (1)	3.117 (5)	178 (5)
O1W—H1X \cdots O1 ^v	0.95 (1)	1.94 (2)	2.839 (5)	159 (5)
O1W—H1Y \cdots O4	0.95 (1)	1.70 (2)	2.634 (5)	170 (5)

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