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Crystal structure of 2,4-diamino-7-(hydroxymethyl)pteridin-1-ium nitrate

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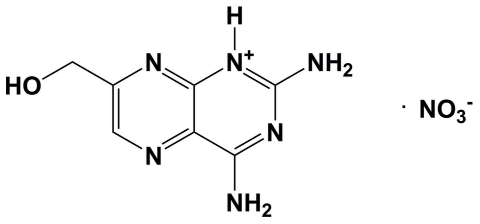
In the crystal of the title molecular salt, $C_7H_9N_6O^+ \cdot NO_3^-$, the cations and anions are linked *via* N—H···O and O—H···O hydrogen bonds, forming sheets parallel to (100). Within the sheets there are numerous hydrogen-bonding ring motifs.

Keywords: crystal structure; pteridine; 2,4-diaminopteridinium; pteridin-1-ium nitrate; hydrogen bonding; ring motifs.

CCDC reference: 1062258

1. Related literature

For background to and the biological activity of pteridine derivatives, see: Benkovic Annu (1980); Blakeley (1969); Van Beelen *et al.* (1984); Dolphin (1980); Pfleiderer (1982); Blakely & Cocco (1985); Pfleiderer & Taylor (1964); Müller *et al.* (1991); Weinstock *et al.* (1968). For related structures, see: Kuyper (1990); Schwalbe & Williams (1986); Robertson *et al.* (1998). For hydrogen-bond motifs, see: Etter (1990); Bernstein *et al.* (1995); Allen *et al.* (1998).



2. Experimental

2.1. Crystal data

$C_7H_9N_6O^+ \cdot NO_3^-$
$M_r = 255.21$
Orthorhombic, $Cmc2_1$
$a = 6.4060$ (17) Å
$b = 14.960$ (6) Å
$c = 10.867$ (3) Å
$V = 1041.4$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.14$ mm^{-1}
$T = 294$ K
0.27 × 0.10 × 0.07 mm

2.2. Data collection

Bruker SMART APEXII Duo CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.964$, $T_{max} = 0.991$
2866 measured reflections
862 independent reflections
720 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.074$
$S = 1.03$
862 reflections
127 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.09$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N3*···O2	1.03 (5)	1.82 (5)	2.831 (5)	167 (4)
N6—H2*N6*···O4	0.98 (3)	2.06 (3)	3.019 (6)	167 (3)
O1—H1*O1*···O2^{i}	0.95 (6)	1.93 (6)	2.846 (4)	163 (6)
N5—H1*N5*···O3^{ii}	0.92 (4)	2.09 (4)	2.983 (6)	164 (4)
N5—H2*N5*···O1^{i}	0.91 (5)	2.15 (5)	2.913 (5)	141 (4)
N6—H1*N6*···O3^{iii}	0.78 (5)	2.35 (4)	3.015 (5)	145 (5)
N6—H1*N6*···O4^{iii}	0.78 (5)	2.44 (5)	3.190 (6)	162 (5)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5127).

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‡ Thomson Reuters ResearcherID: A-5599-2009.

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Acta Cryst. (2015). E**71**, o376–o377 Sivajeyanthi *et al.* • $C_7H_9N_6O^+\cdot NO_3^-$ **o377**

supporting information

Acta Cryst. (2015). E**71**, o376–o377   [doi:10.1107/S2056989015008397]

Crystal structure of 2,4-diamino-7-(hydroxymethyl)pteridin-1-ium nitrate

Palaniyappan Sivajeyanthi, Kasthuri Balasubramani, Muthaiah Jeevaraj, Kaliyaperumal Thanigaimani, Nuridayanti Che Khalib and Ibrahim Abdul Razak

S1. Structural commentary

Pteridine derivatives are found as the core structure of folic acid flavin adenine dinucleotide (FAD) and function as cofactors for enzymes involved in hydroxylation (Benkovic & Annu,1980) and methyl transfer (Blakeley, 1969; Van Beelen *et al.*, 1984), as redox mediators (Dolphin, 1980) and as pigments for eyes and wings in certain insects (Pfleiderer, 1982). Variation of the substituents on the pteridine core of folates has provided synthetic anticancer drugs (Blakely & Cocco, 1985; Pfleiderer & Taylor, 1964). Pterdines are metabolites formed by a bicyclic pyrimidine-pyrazine moiety that occurs in a wide range of living systems and contributes in relevant biological functions (Muller *et al.*, 1991). Pteridine derivatives have good diuretic activity and are also used as simple models for therapeutically valuable antifolate drugs (Weinstock *et al.*, 1968). In order to study potential hydrogen bonding interactions, the title compound was synthesized and we report herein on its crystal structure.

The title molecular salt, Fig. 1, consists of a 2,4-diamino-7-(hydroxymethyl)pteridinum cation and a nitrate anion. During the synthesis of the molecular salt a proton was transferred from the hydroxyl group of nitric acid to atom N3 of the pteridine ring. The pteridine ring system (C1—C7/N1—N6/O1) is planar with a maximum deviation of 0.001 (1) Å for all the non H atoms. The bond lengths and angles are close to those found for similar compounds, *viz.* 2,4-diamino-6,7-dimethylpteridine hydrochloride monohydrate (Schwalbe & Williams, 1986) and triamterenium tetraphenylborate acetonitrile solvate (Robertson *et al.*, 1998).

In the crystal, Fig. 2, the protonated N3 atom and the protonated 2-amino group (N6) are hydrogen-bonded to the nitrate O atoms (O2 and O4) *via* a pair of N3—H1N3···O2 and N6—H2N6···O4 hydrogen bonds, forming an $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995). This type of interaction is similar to the carboxylate-trimethoprim interaction observed in the trimethoprim cation-dihydrofolate reductase complex (Kuyper, 1990) and to the cyclic hydrogen bonded motif observed in many organic crystal structures (Allen *et al.*, 1998). An $R_1^2(4)$ ring motif indicates a bifurcated hydrogen bond formed by N6–H1N6 to the two acceptors (O3 and O4). The 4-amino group and the hydroxyl group form hydrogen bonds with the O atoms of the nitrate ion leading to an $R_3^3(8)$ ring. The three center and bifurcated hydrogen bonds and fork like interaction form an $R_4^4(12)$ ring. Two $R_3^3(8)$ motifs and an $R_2^2(8)$ ring motif generate a new $R_3^2(18)$ ring motif. The above interactions lead to the formation a two dimensional network parallel to the *bc* plane (Table 1 and Fig. 2).

S2. Synthesis and crystallization

A few drops of nitric acid were added to a hot methanol solution (20 ml) of 2,4-diamino-6-(hydroxymethyl)pteridine (43 mg, Aldrich) which had been warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title molecular salt appeared after a few days.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The O– and N-bound H atoms were located in a difference Fourier map and freely refined (O–H = 0.94 (6) Å and N–H = 0.78 (5)– 1.03 (5) Å). The C-bound H atoms were positioned geometrically (C–H = 0.93–0.97 Å) and refined using a riding model with U_{iso}(H) = 1.2 U_{eq}(C).

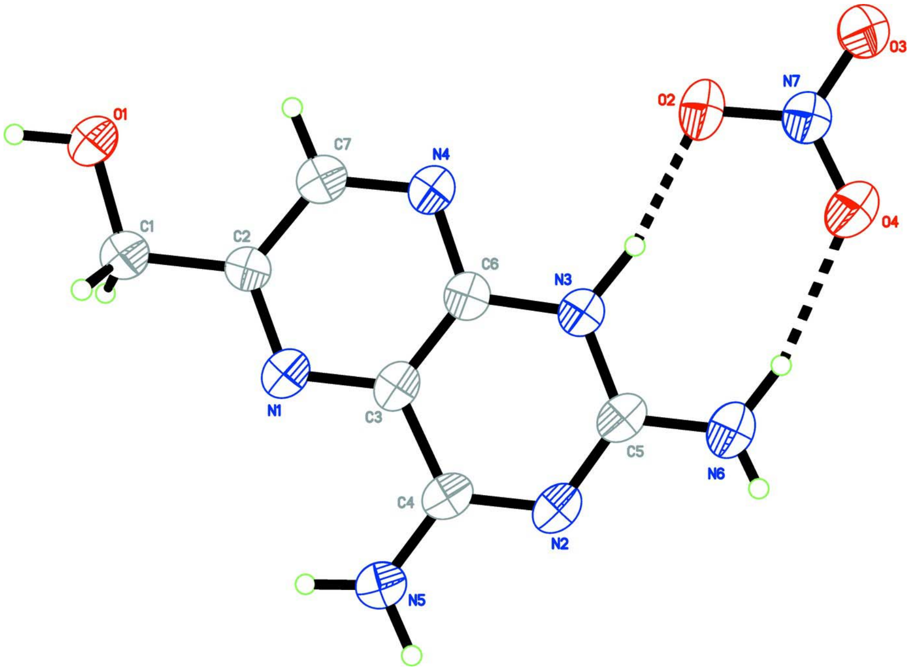

Figure 1

The molecular structure of the title salt, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The N-H···O hydrogen bonds are shown as dashed lines (see Table 1 for details).

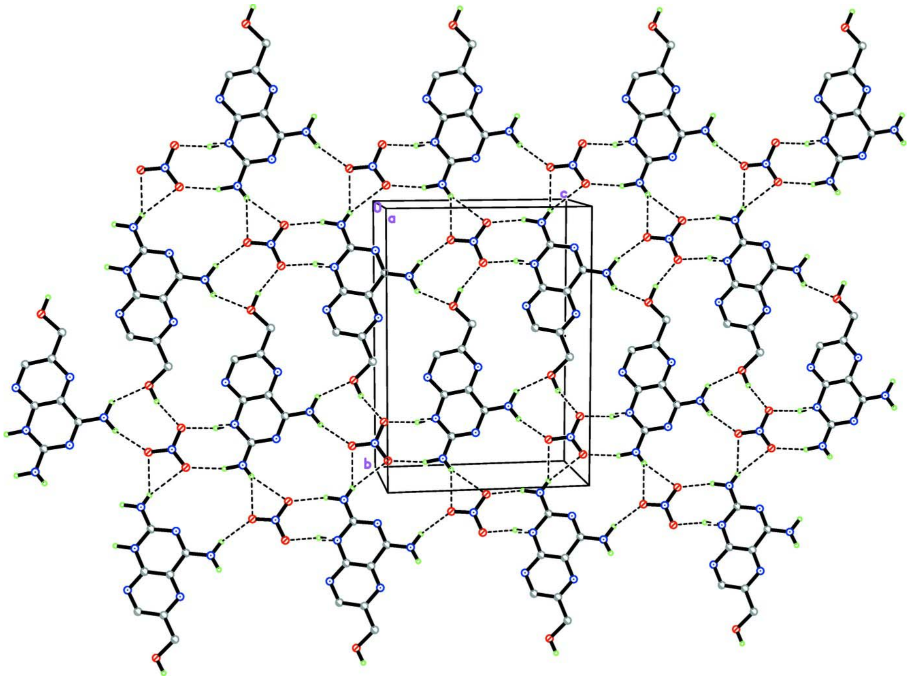

Figure 2

A view along the *a* axis of the crystal packing of the title molecular salt. The N-H···O hydrogen bonds are shown as dashed lines (see Table 1 for details).

2,4-Diamino-7-(hydroxymethyl)pteridin-1-ium nitrate

Crystal data

$C_7H_9N_6O^+\cdot NO_3^-$
$M_r = 255.21$
Orthorhombic, $Cmc2_1$
Hall symbol: C 2c -2
$a = 6.4060$ (17) Å
$b = 14.960$ (6) Å
$c = 10.867$ (3) Å
$V = 1041.4$ (6) Å^3
$Z = 4$
$F(000) = 528$
$D_x = 1.628$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1083 reflections
$\theta = 2.7$–24.6°
$\mu = 0.14$ mm^{-1}
$T = 294$ K
Block, bronze
0.27 × 0.10 × 0.07 mm

Data collection

Bruker SMART APEXII Duo CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{\min} = 0.964$, $T_{\max} = 0.991$
2866 measured reflections
862 independent reflections
720 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 25.0°$, $\theta_{\min} = 2.7°$
$h = -5 \rightarrow 7$
$k = -17 \rightarrow 17$
$l = -8 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.074$
$S = 1.03$
862 reflections
127 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.1935P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.09$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e 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_{iso}*/U_{eq}	Occ. (<1)
O1	0.5000	0.63088 (17)	0.8666 (3)	0.0557 (8)	
O2	0.5000	0.2129 (2)	0.5161 (3)	0.0585 (9)	
O3	0.5000	0.12875 (19)	0.3553 (3)	0.0584 (9)	
O4	0.5000	0.06903 (19)	0.5342 (3)	0.0608 (9)	
N1	0.5000	0.4061 (2)	0.9909 (3)	0.0415 (9)	
N2	0.5000	0.1632 (3)	0.9791 (4)	0.0451 (9)	
N3	0.5000	0.2207 (2)	0.7764 (3)	0.0447 (9)	
N4	0.5000	0.3731 (2)	0.7360 (4)	0.0499 (10)	
N5	0.5000	0.2581 (3)	1.1464 (4)	0.0524 (10)	
H1N5	0.5000	0.210 (3)	1.199 (4)	0.042 (13)*	
H2N5	0.5000	0.312 (3)	1.185 (5)	0.062 (14)*	
N6	0.5000	0.0703 (3)	0.8120 (4)	0.0546 (11)	
H1N6	0.5000	0.028 (3)	0.854 (5)	0.056 (15)*	
H2N6	0.5000	0.060 (2)	0.723 (3)	0.020 (9)*	
N7	0.5000	0.1359 (2)	0.4687 (4)	0.0448 (9)	
C1	0.5000	0.5648 (3)	0.9606 (5)	0.0467 (11)	
H1A	0.3776	0.5726	1.0120	0.056*	0.50
H1B	0.6224	0.5726	1.0120	0.056*	0.50
C2	0.5000	0.4726 (2)	0.9092 (4)	0.0390 (10)	
C3	0.5000	0.3228 (3)	0.9449 (4)	0.0384 (11)	
C4	0.5000	0.2451 (2)	1.0250 (4)	0.0401 (10)	
C5	0.5000	0.1519 (2)	0.8573 (5)	0.0408 (11)	
C6	0.5000	0.3074 (2)	0.8204 (5)	0.0391 (10)	
C7	0.5000	0.4546 (3)	0.7834 (4)	0.0498 (13)	

H7A	0.5000	0.5028	0.7293	0.060*
H1O1	0.5000	0.689 (4)	0.901 (6)	0.072 (14)*
H1N3	0.5000	0.208 (3)	0.683 (5)	0.046 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0954 (19)	0.0284 (13)	0.0435 (17)	0.000	0.000	0.0045 (16)
O2	0.090 (2)	0.0310 (14)	0.054 (2)	0.000	0.000	−0.0078 (16)
O3	0.096 (2)	0.0401 (17)	0.039 (2)	0.000	0.000	−0.0029 (17)
O4	0.093 (2)	0.0323 (15)	0.057 (2)	0.000	0.000	0.0045 (15)
N1	0.0534 (19)	0.0299 (17)	0.041 (2)	0.000	0.000	0.0027 (15)
N2	0.062 (2)	0.0276 (17)	0.046 (2)	0.000	0.000	0.0055 (15)
N3	0.068 (2)	0.0304 (18)	0.035 (2)	0.000	0.000	0.0005 (14)
N4	0.082 (3)	0.0300 (15)	0.038 (2)	0.000	0.000	0.0011 (17)
N5	0.086 (2)	0.035 (2)	0.036 (2)	0.000	0.000	0.0041 (18)
N6	0.082 (3)	0.0308 (18)	0.051 (3)	0.000	0.000	−0.001 (2)
N7	0.058 (2)	0.036 (2)	0.040 (2)	0.000	0.000	−0.0012 (17)
C1	0.069 (3)	0.034 (2)	0.037 (2)	0.000	0.000	0.0015 (19)
C2	0.056 (2)	0.032 (2)	0.029 (2)	0.000	0.000	0.0006 (18)
C3	0.046 (2)	0.027 (2)	0.041 (3)	0.000	0.000	0.0013 (15)
C4	0.049 (2)	0.032 (2)	0.040 (3)	0.000	0.000	0.007 (2)
C5	0.049 (2)	0.029 (2)	0.044 (3)	0.000	0.000	0.006 (2)
C6	0.050 (2)	0.0322 (19)	0.035 (2)	0.000	0.000	−0.0005 (18)
C7	0.075 (3)	0.036 (2)	0.038 (3)	0.000	0.000	0.003 (2)

Geometric parameters (Å, º)

O1—C1	1.422 (6)	N5—C4	1.333 (7)
O1—H1O1	0.94 (6)	N5—H1N5	0.92 (5)
O2—N7	1.262 (5)	N5—H2N5	0.91 (5)
O3—N7	1.237 (5)	N6—C5	1.317 (5)
O4—N7	1.228 (5)	N6—H1N6	0.78 (5)
N1—C2	1.334 (5)	N6—H2N6	0.98 (4)
N1—C3	1.342 (5)	C1—C2	1.487 (6)
N2—C4	1.322 (5)	C1—H1A	0.9700
N2—C5	1.334 (7)	C1—H1B	0.9700
N3—C5	1.353 (6)	C2—C7	1.394 (5)
N3—C6	1.383 (5)	C3—C6	1.372 (6)
N3—H1N3	1.03 (5)	C3—C4	1.454 (5)
N4—C7	1.323 (5)	C7—H7A	0.9300
N4—C6	1.344 (6)		
C1—O1—H1O1	111 (4)	C2—C1—H1B	109.2
C2—N1—C3	116.4 (4)	H1A—C1—H1B	107.9
C4—N2—C5	119.5 (4)	N1—C2—C7	120.6 (3)
C5—N3—C6	119.3 (4)	N1—C2—C1	116.2 (4)
C5—N3—H1N3	120 (2)	C7—C2—C1	123.3 (3)

C6—N3—H1N3	121 (2)	N1—C3—C6	121.6 (4)
C7—N4—C6	114.1 (5)	N1—C3—C4	121.3 (4)
C4—N5—H1N5	120 (3)	C6—C3—C4	117.2 (4)
C4—N5—H2N5	126 (3)	N2—C4—N5	120.6 (3)
H1N5—N5—H2N5	114 (4)	N2—C4—C3	121.0 (5)
C5—N6—H1N6	122 (4)	N5—C4—C3	118.4 (4)
C5—N6—H2N6	121 (2)	N6—C5—N2	119.3 (4)
H1N6—N6—H2N6	117 (4)	N6—C5—N3	117.5 (5)
O4—N7—O3	120.5 (4)	N2—C5—N3	123.2 (4)
O4—N7—O2	120.4 (4)	N4—C6—C3	123.4 (4)
O3—N7—O2	119.0 (4)	N4—C6—N3	116.8 (4)
O1—C1—C2	112.0 (4)	C3—C6—N3	119.9 (4)
O1—C1—H1A	109.2	N4—C7—C2	124.1 (4)
C2—C1—H1A	109.2	N4—C7—H7A	118.0
O1—C1—H1B	109.2	C2—C7—H7A	118.0

C3—N1—C2—C7	0.000 (2)	C6—N3—C5—N6	180.000 (1)
C3—N1—C2—C1	180.000 (2)	C6—N3—C5—N2	0.000 (2)
O1—C1—C2—N1	180.000 (2)	C7—N4—C6—C3	0.000 (2)
O1—C1—C2—C7	0.000 (2)	C7—N4—C6—N3	180.000 (1)
C2—N1—C3—C6	0.000 (2)	N1—C3—C6—N4	0.000 (2)
C2—N1—C3—C4	180.000 (2)	C4—C3—C6—N4	180.000 (2)
C5—N2—C4—N5	180.000 (2)	N1—C3—C6—N3	180.000 (2)
C5—N2—C4—C3	0.000 (2)	C4—C3—C6—N3	0.000 (2)
N1—C3—C4—N2	180.000 (2)	C5—N3—C6—N4	180.000 (1)
C6—C3—C4—N2	0.000 (2)	C5—N3—C6—C3	0.000 (2)
N1—C3—C4—N5	0.000 (2)	C6—N4—C7—C2	0.000 (2)
C6—C3—C4—N5	180.000 (2)	N1—C2—C7—N4	0.000 (2)
C4—N2—C5—N6	180.000 (2)	C1—C2—C7—N4	180.000 (2)
C4—N2—C5—N3	0.000 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N*3···O2	1.03 (5)	1.82 (5)	2.831 (5)	167 (4)
N6—H2*N*6···O4	0.98 (3)	2.06 (3)	3.019 (6)	167 (3)
O1—H1*O*1···O2^{i}	0.95 (6)	1.93 (6)	2.846 (4)	163 (6)
N5—H1*N*5···O3^{ii}	0.92 (4)	2.09 (4)	2.983 (6)	164 (4)
N5—H2*N*5···O1^{i}	0.91 (5)	2.15 (5)	2.913 (5)	141 (4)
N6—H1*N*6···O3^{iii}	0.78 (5)	2.35 (4)	3.015 (5)	145 (5)
N6—H1*N*6···O4^{iii}	0.78 (5)	2.44 (5)	3.190 (6)	162 (5)

Symmetry codes: (i) −*x*+1, −*y*+1, *z*+1/2; (ii) *x*, *y*, *z*+1; (iii) −*x*+1, −*y*, *z*+1/2.