

Crystal structure of melaminium cyanoacetate monohydrate

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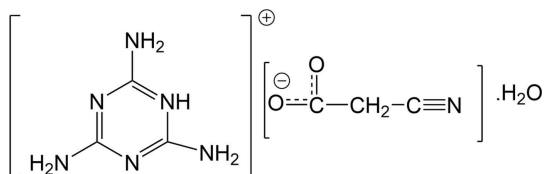
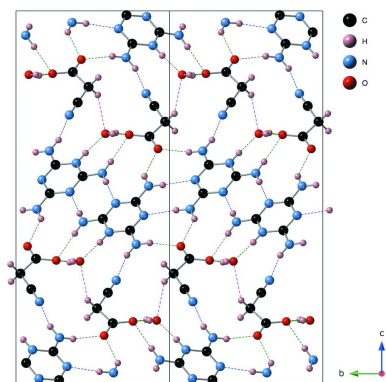
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The asymmetric unit of the title compound, 2,4,6-triamino-1,3,5-triazin-1-ium cyanoacetate monohydrate, $C_3H_7N_6^+ \cdot NCCH_2COO^- \cdot H_2O$, consists of a melaminium cation, a cyanoacetate anion and a water molecule, which are connected to each other *via* $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds, generating an eight-membered ring. In the crystal, the melaminium cations are connected by two pairs of $N-H \cdots N$ hydrogen bonds, forming tapes along [110]. These tapes develop a three-dimensional network through $N-H \cdots O$, $O-H \cdots O$, $N-H \cdots N$ and $C-H \cdots O$ hydrogen bonds between the cations, anions and water molecules.

1. Chemical context

Melamine (systematic name: 2,4,6-triamino-1,3,5-triazine), a trimer of cyanamide, has many industrial applications. The cross-linked resins of melamine with formaldehyde have applications in adhesive coatings, laminations and flame retardants (Billmeyer, 1984). In the past, various organic melamine salts were tested as potential melamine substitutes for melamine urea formaldehyde resins (Weinstabl *et al.*, 2001). In general, protonation of melamine with organic and inorganic acids has been found to yield compounds with extensive hydrogen-bonding networks involving both $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds. This paper is a part of our investigation of the chemistry of cyanoacetate with nitrogen-based cations and their potential application as flame retardants since cyanoacetic acid is an analogue to polyacrylonitrile. It is well known that polyacrylonitrile is used in industry to manufacture carbon fibers because of its ability to produce carbon char (Bacon & Hoses, 1986). Cyanoacetic acid has a nitrile group and also can act as acid source, both of which could enhance the flame-retarding properties.



2. Structural commentary

The asymmetric unit of the title compound consists of a melaminium cation, a cyanoacetate anion and a water molecule, which are connected to each other *via* $N-H \cdots O$ and

O—H···O hydrogen bonds, generating an eight-membered ring (Fig. 1). The six-membered ring of the melaminium cation shows significant distortion from a hexagonal shape. The bond distances [C—N = 1.322 (2)–1.368 (2) Å] and the angles [C—N—C = 115.76 (15)–119.08 (14)° and N—C—N = 121.44 (15)–125.42 (15)°] fall within similar ranges to those reported for similar singly protonated melaminium salts of simple alkyl mono- and dicarboxylic acids, namely, melaminium acetate acetic acid solvate (Perpétuo & Janczak, 2002), melaminium maleate (Janczak & Perpétuo, 2004), melaminium formate (Perpétuo *et al.*, 2005), melaminium tartarate (Su *et al.*, 2009), bis(melaminium) succinate (Froschauer & Weil, 2012*a*) and melaminium hydrogen malonate (Froschauer & Weil, 2012*b*). On the other hand, the angles in the six-membered ring of unprotonated melamine (Adam *et al.*, 2010) are in the range 124.86 (17) to 125.51 (17)°.

In the anion, both O atoms of the carboxylate group are involved in hydrogen bonds to amino groups of adjacent melaminium ions. The nitrile group has a bond length of 1.145 (2) Å that is typical of a nitrile (Kanters *et al.*, 1978). The angle at the nitrile carbon, N≡C—C, is 179.30 (19)° which is close to the theoretical value of 180°. The O atom of the water molecule acts as a lone-pair donor to the protonated nitrogen

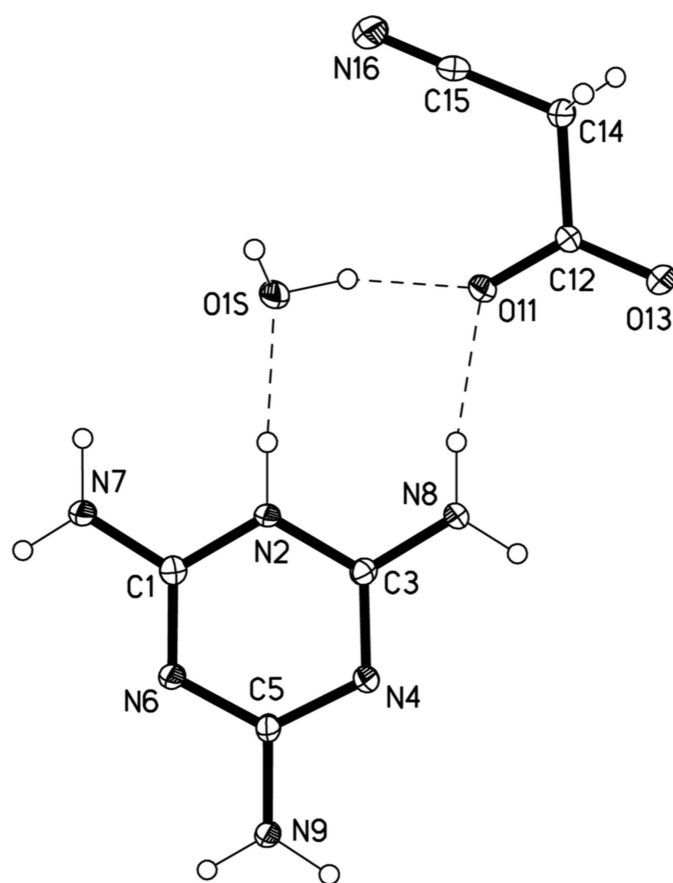


Figure 1
Molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen atoms are shown as spheres of arbitrary radius and hydrogen bonds as dashed lines.

Table 1
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>
N2—H2···O1S	0.90 (2)	1.81 (2)	2.7067 (19)	176.4 (19)
N7—H7A···O13 ⁱ	0.89 (2)	2.00 (2)	2.881 (2)	168 (2)
N7—H7B···N16 ⁱⁱⁱ	0.92 (2)	2.13 (2)	3.001 (2)	155.6 (18)
N8—H8A···O11	0.91 (2)	2.01 (2)	2.891 (2)	164.6 (19)
N8—H8B···N4 ⁱⁱⁱ	0.88 (2)	2.07 (2)	2.952 (2)	176 (2)
N9—H9A···O13 ⁱⁱⁱ	0.90 (2)	2.08 (2)	2.792 (2)	135.7 (19)
N9—H9B···N6 ^{iv}	0.90 (2)	2.08 (2)	2.980 (2)	174 (2)
C14—H14B···O1S ^v	0.99	2.46	3.233 (2)	134
O1S—H1SA···O11	0.93 (2)	1.78 (2)	2.6860 (19)	163.3 (19)
O1S—H1SB···O11 ^{vi}	0.87 (2)	1.97 (2)	2.8351 (19)	178 (2)

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

of the melaminium ion that is present in the same eight-membered ring. The presence of the water molecule in the structure of melaminium cyanoacetate can be expected to contribute to fire retardancy as its release and evaporation will provide cooling.

3. Supramolecular features

The melaminium cation in the crystal is involved in altogether nine hydrogen bonds: for each melaminium cation, seven of them are of the hydrogen-bond donor type while the remaining two are of the acceptor type (Table 1). Neighbouring cations are connected by two pairs of N—H···N hydrogen bonds (N8—H8B···N4ⁱⁱⁱ and N9—H9B···N6^{iv};

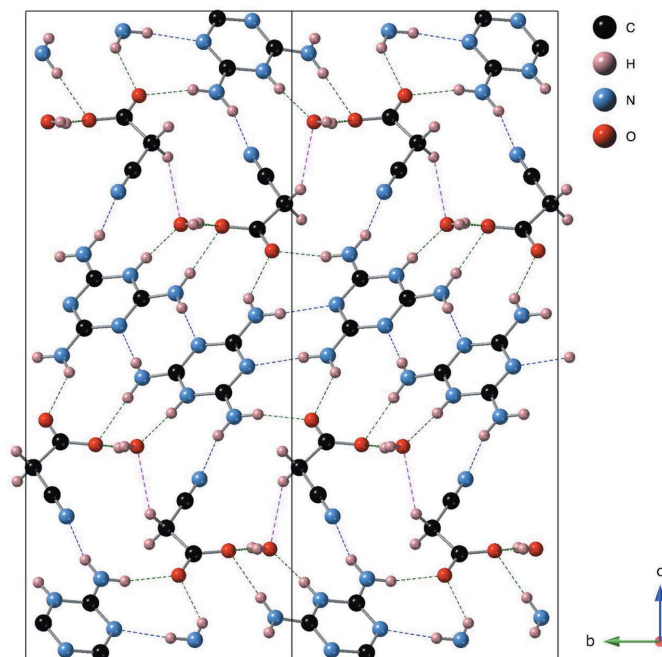


Figure 2
A packing diagram of the title compound, viewed down the *a* axis, showing the O—H···O and N—H···O hydrogen bonds (green dashed lines), the N—H···N hydrogen bonds (blue dashed lines) and the C—H···O hydrogen bonds (magenta dashed lines).

symmetry codes as in Table 1) to form a tape-like structure propagating along [110] and running between the cyanoacetate anions. Three N—H···O hydrogen bonds (N7—H7A···O13ⁱ, N8—H8A···O11 and N9—H9A···O13ⁱⁱⁱ; Table 1) link the cation with three different cyanoacetate anions. Furthermore, the cation is also connected with a water molecule *via* an N—H···O hydrogen bond (N2—H2···O15) between the protonated imine and the water O atom. Finally, the cation is linked with the nitrile group of the anion *via* an N—H···N hydrogen bond (N7—H7B···N16ⁱⁱ; Table 1). There also exist O—H···O (O1S—H1SA···O11 and O1S—H1SB···O11^{vi}) hydrogen bonds between the water molecule and the anion. In addition, a C—H···O hydrogen bond between the methylene H and water O atoms is observed as the C—H group is activated because of the electron-withdrawing cyano group adjacent to it. Altogether, these hydrogen bonds existing between the cations, anions and water molecules generate a three-dimensional network (Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (Version 5.40, update of May 2020; Groom *et al.*, 2016) for 2,4,6-triamino-1,3,5-triazin-1-ium showed more than 30 records; however, for 2,4,6-triamino-1,3,5-triazin-1-ium forming only single protonated salts with purely organic aliphatic carboxylic acids the search gave the following crystal structures: melamine with maleic acid (refcode ARUDAS; Janczak & Perpétuo, 2004), with formic acid (FONMEB; Perpétuo *et al.*, 2005), with acetic acid (EFAZOA; Perpétuo & Janczak, 2002), with malonic acid (HOWRIV01; Froschauer & Weil, 2012*b*), with succinic acid (LEGZEE; Froschauer & Weil, 2012*a*), with nitrilotriacetic acid (MIHYAF; Hoxha *et al.*, 2013) and with tartaric acid (VORSUR; Su *et al.*, 2009). A search for organic co-crystals/salts of cyanoacetic acid gave one structure, 4,4'-bipyridine bis(cyanoacetic acid) (Song *et al.*, 2008). For metal complexes with cyanoacetic acid or cyanoacetate, 24 structures were reported, such as silver cyanoacetate (Edwards *et al.*, 1997) and cadmium cyanoacetate (Post & Trotter, 1974). In these metal salts, the metal is coordinated by the acetate group as well as the cyano group.

5. Synthesis and crystallization

A solution of cyanoacetic acid (1.7g, 20 mmol) in 100 ml of deionized water was added to a solution of melamine (2.5 g, 20 mmol) in 100 ml of deionized water. The reaction mixture was heated to 353 K for 3 h. The resulting clear solution was cooled to room temperature and then was allowed to slowly evaporate. Single crystals of the title compound formed after several days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were initially

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₃ H ₇ N ₆ ⁺ ·C ₃ H ₂ NO ₂ ⁻ ·H ₂ O
<i>M_r</i>	229.22
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.6928 (6), 9.3881 (13), 22.918 (3)
β (°)	91.646 (3)
<i>V</i> (Å ³)	1009.3 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.12
Crystal size (mm)	0.44 × 0.17 × 0.04
Data collection	
Diffractometer	Bruker <i>APEX</i> CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2007)
<i>T</i> _{min} , <i>T</i> _{max}	0.948, 0.995
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	12615, 2517, 1856
<i>R</i> _{int}	0.058
(sin θ / λ) _{max} (Å ⁻¹)	0.668
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.047, 0.126, 1.00
No. of reflections	2517
No. of parameters	172
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.28, -0.29

Computer programs: *SMART* and *SAINT* (Bruker, 2007), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *SHELXTL* (Sheldrick, 2008) and *CrystalMaker* (Palmer, 2014).

determined by geometry (C—H = 0.99 Å) and were refined using a riding model, with *U*_{iso}(H) = 1.2*U*_{eq}(C). H atoms bonded to N and O were located in a difference map, and their positions were refined freely, with *U*_{iso}(H) = 1.2*U*_{eq}(N or O).

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Computing details

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *CrystalMaker* (Palmer, 2014); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

2,4,6-Triamino-1,3,5-triazin-1-ium cyanoacetate monohydrate

Crystal data


 $M_r = 229.22$

Monoclinic, $P2_1/c$

 $a = 4.6928$ (6) Å

 $b = 9.3881$ (13) Å

 $c = 22.918$ (3) Å

 $\beta = 91.646$ (3)°

 $V = 1009.3$ (2) Å³
 $Z = 4$
 $F(000) = 480$
 $D_x = 1.509$ Mg m⁻³

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

Cell parameters from 3720 reflections

 $\theta = 2.3$ – 28.1 °

 $\mu = 0.12$ mm⁻¹
 $T = 100$ K

Needle, colourless

 $0.44 \times 0.17 \times 0.04$ mm

Data collection

Bruker APEX CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2007)

 $T_{\min} = 0.948$, $T_{\max} = 0.995$

12615 measured reflections

2517 independent reflections

1856 reflections with $I > 2\sigma(I)$

 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 28.4$ °, $\theta_{\min} = 1.8$ °

 $h = -5$ → 6
 $k = -12$ → 12
 $l = -30$ → 30

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.126$
 $S = 1.00$

2517 reflections

172 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.320P]$

where $P = (F_o^2 + 2F_c^2)/3$

 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.28$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3297 (4)	0.25701 (18)	0.41214 (7)	0.0117 (4)
N2	0.4321 (3)	0.39286 (15)	0.40750 (6)	0.0121 (3)
H2	0.359 (4)	0.453 (2)	0.3804 (9)	0.014*
C3	0.6562 (4)	0.43434 (17)	0.44283 (7)	0.0111 (4)
N4	0.7614 (3)	0.35064 (14)	0.48477 (6)	0.0126 (3)
C5	0.6396 (4)	0.21954 (17)	0.48861 (8)	0.0125 (4)
N6	0.4316 (3)	0.16816 (15)	0.45231 (6)	0.0135 (3)
N7	0.1226 (3)	0.21696 (16)	0.37493 (7)	0.0151 (3)
H7A	0.059 (4)	0.128 (2)	0.3786 (9)	0.018*
H7B	0.055 (4)	0.277 (2)	0.3458 (9)	0.018*
N8	0.7672 (3)	0.56251 (15)	0.43490 (7)	0.0137 (3)
H8A	0.711 (4)	0.617 (2)	0.4041 (9)	0.016*
H8B	0.914 (5)	0.586 (2)	0.4577 (9)	0.016*
N9	0.7332 (4)	0.13535 (16)	0.53094 (7)	0.0202 (4)
H9A	0.870 (5)	0.163 (2)	0.5569 (10)	0.024*
H9B	0.673 (5)	0.044 (3)	0.5337 (9)	0.024*
O11	0.6998 (3)	0.73778 (13)	0.33172 (5)	0.0157 (3)
C12	0.7511 (4)	0.87001 (18)	0.33632 (8)	0.0129 (4)
O13	0.9314 (3)	0.92554 (14)	0.36958 (6)	0.0224 (3)
C14	0.5789 (4)	0.97232 (18)	0.29669 (8)	0.0163 (4)
H14A	0.465226	1.035861	0.321467	0.020*
H14B	0.713248	1.032642	0.275142	0.020*
C15	0.3874 (4)	0.90159 (18)	0.25472 (8)	0.0156 (4)
N16	0.2366 (4)	0.84731 (17)	0.22144 (7)	0.0237 (4)
O1S	0.2181 (3)	0.58309 (13)	0.32906 (6)	0.0163 (3)
H1SA	0.363 (5)	0.650 (2)	0.3269 (9)	0.020*
H1SB	0.059 (5)	0.630 (2)	0.3289 (9)	0.020*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0117 (8)	0.0117 (8)	0.0118 (8)	-0.0003 (6)	0.0012 (6)	-0.0011 (6)
N2	0.0141 (8)	0.0088 (7)	0.0131 (7)	-0.0006 (6)	-0.0040 (6)	0.0023 (6)
C3	0.0116 (9)	0.0105 (8)	0.0110 (8)	0.0009 (6)	-0.0005 (6)	-0.0011 (6)
N4	0.0140 (8)	0.0095 (7)	0.0141 (7)	-0.0014 (6)	-0.0023 (6)	0.0011 (5)
C5	0.0123 (9)	0.0104 (7)	0.0148 (9)	-0.0017 (6)	-0.0024 (7)	0.0005 (6)
N6	0.0161 (8)	0.0099 (7)	0.0144 (8)	-0.0012 (6)	-0.0048 (6)	0.0016 (6)
N7	0.0184 (8)	0.0109 (7)	0.0155 (8)	-0.0025 (6)	-0.0063 (6)	0.0025 (6)
N8	0.0148 (8)	0.0108 (7)	0.0152 (8)	-0.0039 (6)	-0.0036 (6)	0.0036 (6)

N9	0.0257 (9)	0.0117 (7)	0.0222 (9)	-0.0067 (7)	-0.0141 (7)	0.0064 (6)
O11	0.0150 (7)	0.0108 (6)	0.0208 (7)	-0.0009 (5)	-0.0040 (5)	0.0034 (5)
C12	0.0135 (9)	0.0115 (8)	0.0136 (9)	-0.0024 (7)	-0.0013 (7)	0.0022 (6)
O13	0.0269 (8)	0.0163 (6)	0.0231 (7)	-0.0048 (6)	-0.0135 (6)	0.0034 (5)
C14	0.0197 (10)	0.0113 (8)	0.0174 (9)	-0.0010 (7)	-0.0069 (7)	-0.0001 (7)
C15	0.0164 (9)	0.0128 (8)	0.0174 (9)	0.0025 (7)	-0.0027 (7)	0.0037 (7)
N16	0.0273 (10)	0.0198 (8)	0.0235 (9)	-0.0010 (7)	-0.0104 (7)	0.0012 (7)
O1S	0.0129 (7)	0.0126 (6)	0.0232 (7)	-0.0003 (5)	-0.0031 (5)	0.0052 (5)

Geometric parameters (Å, °)

C1—N6	1.322 (2)	N8—H8B	0.88 (2)
C1—N7	1.329 (2)	N9—H9A	0.90 (2)
C1—N2	1.368 (2)	N9—H9B	0.90 (2)
N2—C3	1.365 (2)	O11—C12	1.268 (2)
N2—H2	0.90 (2)	C12—O13	1.238 (2)
C3—N4	1.326 (2)	C12—C14	1.536 (2)
C3—N8	1.326 (2)	C14—C15	1.458 (2)
N4—C5	1.361 (2)	C14—H14A	0.9900
C5—N9	1.317 (2)	C14—H14B	0.9900
C5—N6	1.353 (2)	C15—N16	1.145 (2)
N7—H7A	0.89 (2)	O1S—H1SA	0.93 (2)
N7—H7B	0.92 (2)	O1S—H1SB	0.87 (2)
N8—H8A	0.91 (2)		
N6—C1—N7	120.78 (16)	C3—N8—H8A	121.0 (13)
N6—C1—N2	121.44 (15)	C3—N8—H8B	117.0 (14)
N7—C1—N2	117.77 (15)	H8A—N8—H8B	121.5 (19)
C3—N2—C1	119.08 (14)	C5—N9—H9A	122.0 (14)
C3—N2—H2	120.1 (13)	C5—N9—H9B	121.5 (14)
C1—N2—H2	120.8 (13)	H9A—N9—H9B	116 (2)
N4—C3—N8	119.86 (16)	O13—C12—O11	126.04 (16)
N4—C3—N2	121.68 (15)	O13—C12—C14	116.09 (15)
N8—C3—N2	118.45 (15)	O11—C12—C14	117.87 (15)
C3—N4—C5	115.76 (15)	C15—C14—C12	114.17 (14)
N9—C5—N6	117.29 (15)	C15—C14—H14A	108.7
N9—C5—N4	117.30 (16)	C12—C14—H14A	108.7
N6—C5—N4	125.42 (15)	C15—C14—H14B	108.7
C1—N6—C5	116.32 (15)	C12—C14—H14B	108.7
C1—N7—H7A	116.4 (13)	H14A—C14—H14B	107.6
C1—N7—H7B	121.4 (13)	N16—C15—C14	179.30 (19)
H7A—N7—H7B	122.1 (19)	H1SA—O1S—H1SB	106.4 (19)
N6—C1—N2—C3	4.1 (2)	C3—N4—C5—N6	2.5 (3)
N7—C1—N2—C3	-176.16 (16)	N7—C1—N6—C5	-179.16 (16)
C1—N2—C3—N4	-5.8 (2)	N2—C1—N6—C5	0.6 (2)
C1—N2—C3—N8	174.98 (16)	N9—C5—N6—C1	176.40 (17)
N8—C3—N4—C5	-178.19 (16)	N4—C5—N6—C1	-4.1 (3)

N2—C3—N4—C5	2.6 (2)	O13—C12—C14—C15	174.83 (17)
C3—N4—C5—N9	-177.98 (17)	O11—C12—C14—C15	-4.3 (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>
N2—H2...O1S	0.90 (2)	1.81 (2)	2.7067 (19)	176.4 (19)
N7—H7A...O13 ⁱ	0.89 (2)	2.00 (2)	2.881 (2)	168 (2)
N7—H7B...N16 ⁱⁱ	0.92 (2)	2.13 (2)	3.001 (2)	155.6 (18)
N8—H8A...O11	0.91 (2)	2.01 (2)	2.891 (2)	164.6 (19)
N8—H8B...N4 ⁱⁱⁱ	0.88 (2)	2.07 (2)	2.952 (2)	176 (2)
N9—H9A...O13 ⁱⁱⁱ	0.90 (2)	2.08 (2)	2.792 (2)	135.7 (19)
N9—H9B...N6 ^{iv}	0.90 (2)	2.08 (2)	2.980 (2)	174 (2)
C14—H14B...O1S ^v	0.99	2.46	3.233 (2)	134
O1S—H1SA...O11	0.93 (2)	1.78 (2)	2.6860 (19)	163.3 (19)
O1S—H1SB...O11 ^{vi}	0.87 (2)	1.97 (2)	2.8351 (19)	178 (2)

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