Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Amino-1-(2-carboxylatoethyl)-pyrimidin-1-ium monohydrate

Christopher R. Sparrow,[a] Edwin H. Walker Jr[a] and Frank R. Fronczek[b]*

[a]Department of Chemistry, Southern University, Baton Rouge, LA 70813, USA, and [b]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA
Correspondence e-mail: ffroncz@lsu.edu

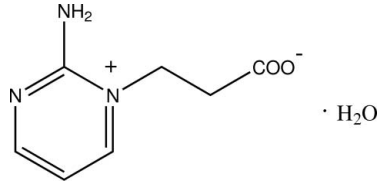
Received 21 October 2010; accepted 4 November 2010

Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.003 Å; R factor = 0.050; wR factor = 0.119; data-to-parameter ratio = 13.5.

In the title structure, $C_7H_9N_3O_2\cdot H_2O$, there are two formula units in the asymmetric unit. The molecule is a zwitterion, containing a quaternary N atom and a deprotonated carboxyl group, with C—O distances in the range 1.256 (2)–1.266 (3) Å. The two independent molecules form a hydrogen-bonded $R_2^2(16)$ dimer about an approximate inversion center *via* N—H···O hydrogen bonds, with N···O distances of 2.766 (2) and 2.888 (2) Å. O—H···O hydrogen bonds involving the water molecules and additional N—H···O hydrogen bonds link these dimers, forming double chains.

Related literature

For background information on deep eutectic solvents, see: Abbott *et al.* (2003, 2004); Reddy (2006); Santos *et al.* (2007); Walker *et al.* (2004). For graph sets, see: Etter (1990). For a description of the Cambridge Structural Database, see: Allen (2002). For related structures, see: Holy *et al.* (1999); Slouf *et al.* (2002).



Experimental

Crystal data

$C_7H_9N_3O_2\cdot H_2O$
M_r = 185.19
Monoclinic, $P2_1/c$
a = 10.075 (2) Å
b = 15.576 (5) Å
c = 10.810 (3) Å
β = 107.741 (16)°
V = 1615.7 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 90 K
0.17 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer with Oxford Cryostream cooler
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.980, T_{max} = 0.994
10202 measured reflections
3518 independent reflections
2418 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.119
S = 1.02
3518 reflections
260 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31*N*···O4^{i}	0.85 (3)	2.05 (3)	2.882 (3)	170 (2)
N3—H32*N*···O3	0.91 (2)	1.99 (2)	2.888 (2)	166 (2)
N6—H61*N*···O2^{ii}	0.85 (3)	2.12 (3)	2.960 (3)	170 (2)
N6—H62*N*···O1	0.90 (2)	1.88 (2)	2.766 (2)	169 (2)
O1*W*—H11*W*···O3	0.89 (3)	1.93 (3)	2.794 (2)	165 (3)
O1*W*—H12*W*···O2^{iii}	0.84 (3)	2.04 (3)	2.867 (2)	170 (3)
O2*W*—H21*W*···O1	0.90 (3)	2.00 (3)	2.863 (2)	159 (2)
O2*W*—H22*W*···O4^{iv}	0.86 (3)	2.10 (3)	2.923 (2)	159 (3)

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

This research was made possible by a grant supplied by the National Science Foundation's Early CAREER program (Cooperative Agreement DMR-0449886) at Southern University. The purchase of the NMR was made possible by the National Science Foundation's Major Research Instrument program (Cooperative Agreement CHE-0321591) at Southern University. The purchase of the FTIR was made possible by grant No. LEQSF(2005–2007)-ENH-TR-65, and the purchase of the diffractometer at LSU was made possible by grant No. LEQSF (1999–2000)-ENH-TR-13, both administered by the Louisiana Board of Regents.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2345).

References

Abbott, A. P., Boothby, D., Capper, G., Davies, D. L. & Rasheed, R. K. (2004). *J. Am. Chem. Soc.* **126**, 9142–9147.
Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K. & Tambyrajah, V. (2003). *Chem. Commun.* pp. 70–71.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Holy, A., Budesinski, M., Podlaha, J. & Cisarova, I. (1999). *Collect. Czech. Chem. Commun.* **84**, 242–256.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Reddy, R. G. (2006). *J. Phase Equil. Diffusion*, **27**, 210–211.
Santos, L. M. N. B. F., Lopes, J. N. C., Coutinho, J. A. P., Esperanca, J. M. S. S., Gomes, L. R., Marrucho, I. M. & Rebelo, L. P. N. (2007). *J. Am. Chem. Soc.* **129**, 284–285.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Slouf, M., Holy, A., Petříček, V. & Cisarova, I. (2002). *Acta Cryst.* B**58**, 519–529.
Walker, E. H. Jr, Apblett, A. W., Walker, R. & Zachary, A. (2004). *Chem. Mater.* **16**, 5336–5343.

supporting information

Acta Cryst. (2010). E**66**, o3156–o3157 [https://doi.org/10.1107/S1600536810045332]

2-Amino-1-(2-carboxylatoethyl)pyrimidin-1-ium monohydrate

Christopher R. Sparrow, Edwin H. Walker and Frank R. Fronczek

S1. Comment

With the growing environmental awareness of the global economy, there has been an increased interest in "green" solvents. Since ionic liquids or ionic solvents are considered nonvolatile substances with negligible vapor pressure, they can be utilized in establishing novel "green" synthetic routes (Santos *et al.*, 2007). Deep eutectic solvents (DES) are considered a designated group within the broad range of ionic solvents, more specifically, they are a type of ionic solvent with special properties composed of a mixture that forms a eutectic with a melting point much lower than either of the individual components. The first generation eutectic solvents were based on mixtures of quaternary ammonium salts with hydrogen donors such as amines and carboxylic acids. The deep eutectic solvent concept was first described by Abbot *et al.* (2003, 2004) for a mixture of choline chloride and urea. The mixture resulted in a eutectic that melts at 285 K.

DES are capable of dissolving many metal salts. Since the solvents are conductive, DES have a potential application as battery electrolytes. Compared to ionic liquids, deep eutectic solvents are cheaper to make, much less toxic, and are sometimes biodegradable. Production of 3-(2-aminopyrimidin-1-yl) propanoate by quaternerization of the amine within the aromatic system presents a new molecular construct for deep eutectic solvents. DES can be modified in order to control factors such as conductivity, viscosity, and surface tension (Reddy, 2006). The synthesis of of 3-(2-amino-pyrimidin-1-yl) propanoate takes advantage of the self-initiating condensation of 2-aminopyrimidine with the vinyl group of the *αβ*-unsaturated acrylic acid *via* anti-Markovnikov addition, which is similar to chemistry involved in the synthesis of the novel 3,3′,3"-nitrilotripropionic acid precursor gel, that we have recently developed (Walker *et al.*, 2004).

The asymmetric unit of the title compound, consisting of two 2-aminopyrimidinium carboxylate molecules and two water molecules, is shown in Fig. 1. The two main molecules form a hydrogen-bonded dimer of graph set (Etter, 1990) $R^2_2(16)$ about an approximate inversion center located near 0.186, 0.632, 0.281. The carboxyl group is deprotonated, as evidenced by all C—O distances falling within a narrow range 1.256 (2) - 1.266 (3) Å. The propionate side chains are extended, with N—C—C—C torsion angles 179.52 (17)° about C5—C6 and -175.40 (17)° about C12—C13. The 18-membered hydrogen-bonded rings are linked by centrosymmetric $R^4_4(12)$ rings involving both H atoms on N3 and both O atoms O3 and O4 of the same carboxylate, as can been seen in the unit-cell diagram, Figure 2. Both water molecules link the 18-membered rings *via* O—H···O hydrogen bonds, forming double chains in which N6—H···O2 (at *x*, 3/2 - *y*, *z* - 1/2) are also involved, as illustrated in Fig. 3.

We find no previous examples of 2-aminopyrimidine with a C atom on a ring N in the Cambridge Structural Database (Allen, 2002, version 5.31, Nov. 2009), although there are a few examples of N—-C substituted 2,4-diaminopyrimidine structures (Holy *et al.*, 1999; Slouf *et al.*, 2002).

S2. Experimental

2-Aminopyrimidine (1.001 g, 10.52 mmol) was dissolved in 10 ml deionized water. The solution was charged with acrylic acid (1.5 ml, 21.9 mmol) and refluxed at 343–348 K for 2 h. After heating, the mixture was stirred continuously

until the temperature gradually cooled to room temperature (299 K). A light yellow aqueous slurry was obtained. In a 125 ml separatory funnel, the aqueous slurry was combined with 15 ml of benzene and shaken for several minutes. The aqueous layer was isolated and filtered. The resulting white crystalline material product was isolated by gravimetric filtration, washed with three 20 ml aliquots of cold ethanol, and allowed to air-dry overnight, yielding 1.217 g (69.36%) of white solid material.

S3. Refinement

H atoms on C were placed in idealized positions with C—H distances 0.95 - 0.99 Å and thereafter treated as riding. Coordinates for the H atoms on N and H_2O were refined. U_{iso} for H was assigned as 1.2 times $U_{eq}$of the attached atoms (1.5 for methyl and H_2O).

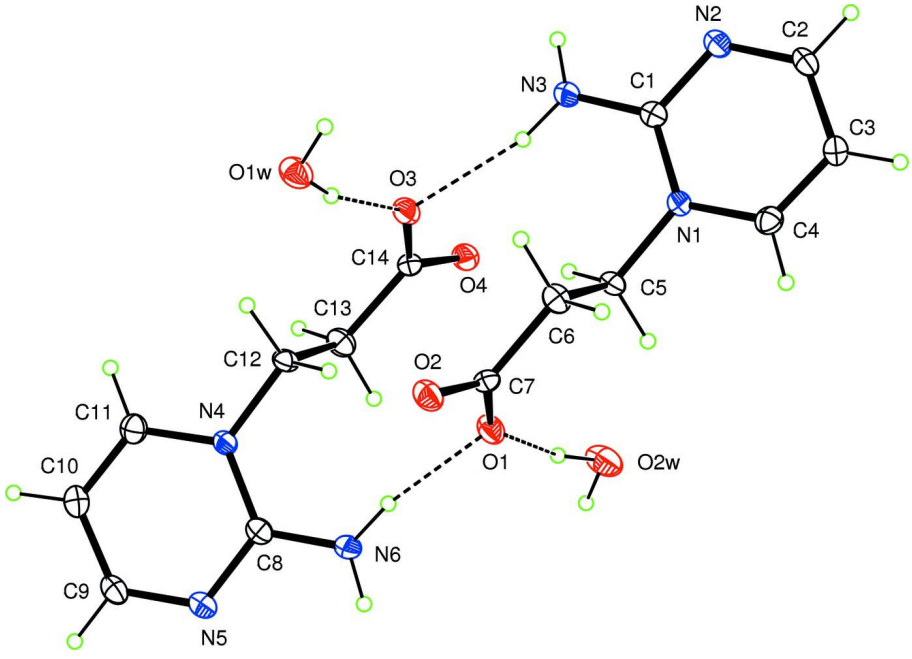


Figure 1

The asymmetric unit, with ellipsoids at the 50% level and H atoms having arbitrary radius. Dotted lines are hydrogen bonds.

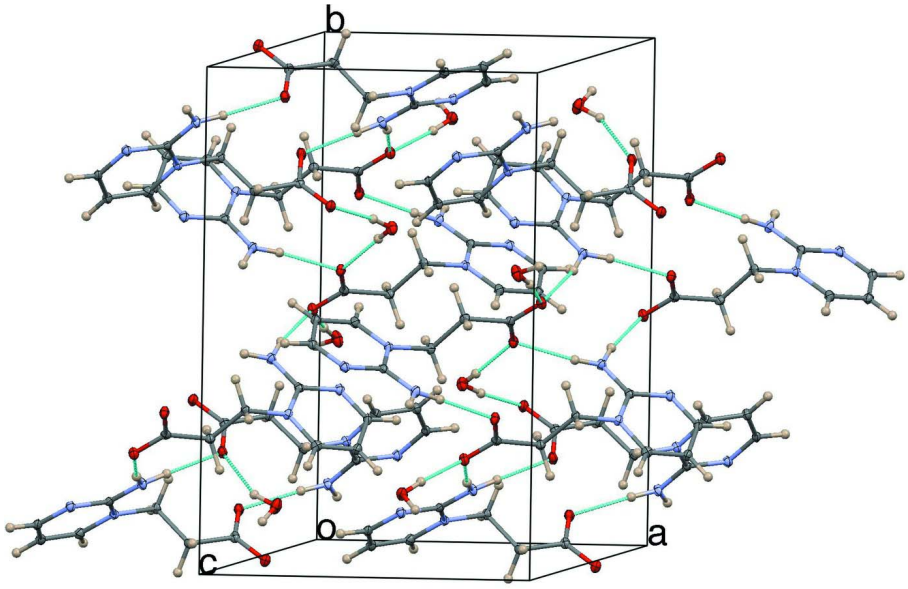


Figure 2
The unit cell.

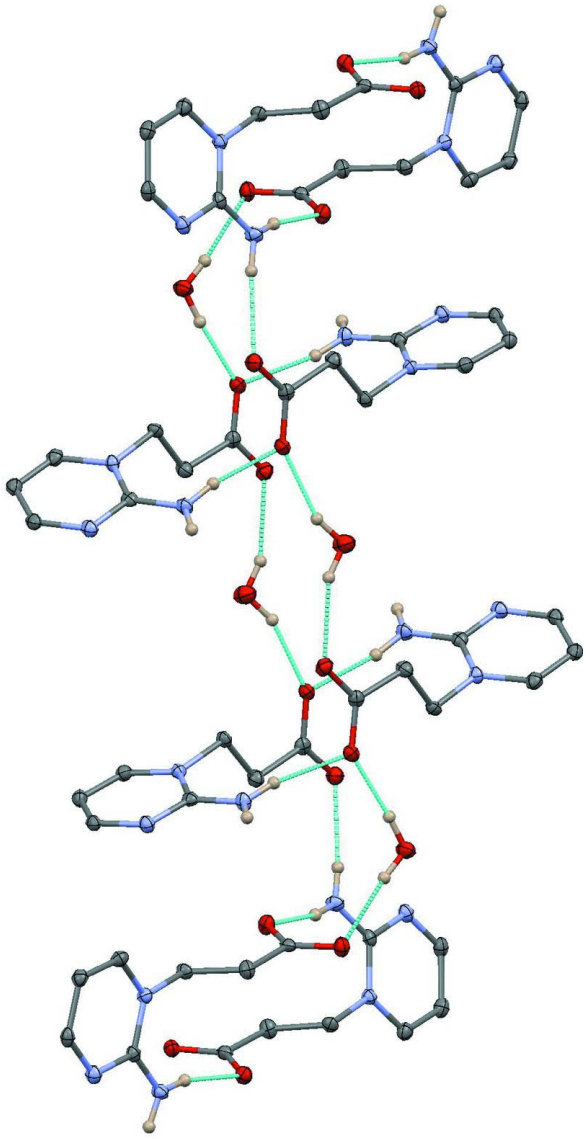


Figure 3

A portion of the hydrogen-bonded double chain.

2-Amino-1-(2-carboxylatoethyl)pyrimidin-1-ium monohydrate

Crystal data

$C_7H_9N_3O_2·H_2O$
M_r = 185.19
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 10.075 (2) Å
b = 15.576 (5) Å
c = 10.810 (3) Å
β = 107.741 (16)°
V = 1615.7 (8) Å^3
Z = 8
$F(000)$ = 784
D_x = 1.523 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3071 reflections
θ = 2.5–27.1°
μ = 0.12 mm^{-1}
T = 90 K
Plate, colorless
0.17 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer with Oxford Cryostream cooler
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.980, T_{max} = 0.994
10202 measured reflections
3518 independent reflections
2418 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 27.1°, θ_{min} = 2.7°
h = −12→12
k = −19→16
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.119
S = 1.02
3518 reflections
260 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
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 1.0034P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0052 (10)

Special details

Experimental. ^{1}H (D_2O): δ(p.p.m.) 2.72 (t, 2H, J = 6.14 Hz), 4.33 (t, 2H, J = 6.14 Hz), 7.01 (t, 1H, J = 5.6 Hz), 8.32 (d, 1H, J = 5.6 Hz), and 8.69 (d, 1H, J = 5.6 Hz). ^{13}C (D_2O): δ(p.p.m.) 34.2, 51.9, 111.3, 150.5, 155.8, 166.2, and 177.5. IR (thin film, KBr plates, cm^{-1}): 3428.76 (m, br), 3093.35 (br), 2363.8 (*m*), 1675.0 (*m*), 1386.82 (*s*), 1262.48 (*s*), 1193.82 (w, sh), 1094.27 (w), 1024.62 (w), and 931.94 (w, sh).

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}
O1	0.16601 (14)	0.69376 (10)	0.15055 (14)	0.0176 (4)
O2	0.30612 (14)	0.78552 (10)	0.28952 (15)	0.0188 (4)
N1	−0.14185 (16)	0.70633 (11)	0.33727 (16)	0.0135 (4)
N2	−0.23793 (17)	0.66797 (12)	0.50401 (18)	0.0161 (4)
N3	−0.02988 (18)	0.60908 (12)	0.50172 (19)	0.0159 (4)
H31N	−0.036 (2)	0.5803 (16)	0.566 (2)	0.019*
H32N	0.038 (2)	0.5978 (15)	0.464 (2)	0.019*
C1	−0.1350 (2)	0.66116 (13)	0.4473 (2)	0.0134 (4)
C2	−0.3421 (2)	0.72143 (14)	0.4525 (2)	0.0152 (5)
H2	−0.4151	0.7250	0.4909	0.018*
C3	−0.3504 (2)	0.77295 (14)	0.3446 (2)	0.0159 (5)

H3	−0.4249	0.8122	0.3112	0.019*
C4	−0.2464 (2)	0.76392 (14)	0.2900 (2)	0.0161 (5)
H4	−0.2467	0.7985	0.2175	0.019*
C5	−0.0369 (2)	0.69512 (14)	0.2672 (2)	0.0143 (5)
H5A	−0.0817	0.7058	0.1734	0.017*
H5B	−0.0029	0.6351	0.2774	0.017*
C6	0.0857 (2)	0.75559 (14)	0.3174 (2)	0.0164 (5)
H6A	0.1298	0.7452	0.4113	0.020*
H6B	0.0516	0.8156	0.3065	0.020*
C7	0.1944 (2)	0.74413 (14)	0.2470 (2)	0.0142 (5)
O3	0.20974 (14)	0.56176 (10)	0.42323 (14)	0.0169 (3)
O4	0.07476 (14)	0.47312 (10)	0.27549 (14)	0.0175 (4)
N4	0.51826 (16)	0.56177 (11)	0.22871 (16)	0.0132 (4)
N5	0.58362 (17)	0.58906 (12)	0.03946 (17)	0.0159 (4)
N6	0.37231 (18)	0.63627 (12)	0.05084 (19)	0.0161 (4)
H61N	0.362 (2)	0.6558 (16)	−0.025 (3)	0.019*
H62N	0.313 (2)	0.6537 (15)	0.094 (2)	0.019*
C8	0.4900 (2)	0.59599 (13)	0.1067 (2)	0.0137 (4)
C9	0.7023 (2)	0.54856 (14)	0.0946 (2)	0.0164 (5)
H9	0.7685	0.5450	0.0483	0.020*
C10	0.7352 (2)	0.51078 (14)	0.2174 (2)	0.0172 (5)
H10	0.8202	0.4807	0.2535	0.021*
C11	0.6406 (2)	0.51888 (14)	0.2830 (2)	0.0169 (5)
H11	0.6595	0.4946	0.3672	0.020*
C12	0.4179 (2)	0.56957 (14)	0.3045 (2)	0.0140 (5)
H12A	0.3793	0.6285	0.2953	0.017*
H12B	0.4672	0.5594	0.3976	0.017*
C13	0.2994 (2)	0.50517 (14)	0.2575 (2)	0.0171 (5)
H13A	0.3384	0.4464	0.2729	0.021*
H13B	0.2565	0.5123	0.1627	0.021*
C14	0.1859 (2)	0.51433 (14)	0.3239 (2)	0.0144 (5)
O1W	0.42213 (16)	0.65900 (11)	0.59146 (17)	0.0215 (4)
H11W	0.359 (3)	0.6329 (17)	0.527 (3)	0.032*
H12W	0.384 (3)	0.6801 (18)	0.643 (3)	0.032*
O2W	−0.06112 (17)	0.60258 (12)	−0.02453 (18)	0.0270 (4)
H21W	0.023 (3)	0.6207 (18)	0.026 (3)	0.040*
H22W	−0.043 (3)	0.5764 (19)	−0.088 (3)	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0148 (7)	0.0222 (9)	0.0171 (8)	0.0004 (6)	0.0067 (6)	−0.0044 (7)
O2	0.0152 (7)	0.0226 (9)	0.0200 (9)	−0.0030 (6)	0.0072 (6)	−0.0027 (7)
N1	0.0126 (8)	0.0152 (9)	0.0133 (10)	0.0016 (7)	0.0050 (7)	0.0000 (8)
N2	0.0147 (8)	0.0181 (10)	0.0170 (10)	−0.0001 (7)	0.0070 (7)	−0.0013 (8)
N3	0.0152 (9)	0.0178 (10)	0.0164 (10)	0.0020 (8)	0.0073 (8)	0.0037 (8)
C1	0.0138 (9)	0.0130 (11)	0.0136 (11)	−0.0026 (8)	0.0044 (8)	−0.0024 (9)
C2	0.0116 (9)	0.0182 (12)	0.0169 (12)	−0.0017 (9)	0.0061 (9)	−0.0049 (9)

C3	0.0129 (10)	0.0168 (12)	0.0177 (12)	0.0018 (8)	0.0042 (9)	0.0004 (9)
C4	0.0167 (10)	0.0168 (12)	0.0137 (12)	0.0002 (9)	0.0030 (9)	−0.0010 (9)
C5	0.0145 (10)	0.0168 (11)	0.0138 (11)	0.0016 (9)	0.0073 (8)	0.0005 (9)
C6	0.0153 (10)	0.0163 (12)	0.0186 (12)	−0.0011 (9)	0.0065 (9)	−0.0016 (9)
C7	0.0158 (10)	0.0150 (11)	0.0127 (11)	0.0019 (9)	0.0056 (9)	0.0047 (9)
O3	0.0154 (7)	0.0205 (8)	0.0159 (8)	0.0005 (6)	0.0063 (6)	−0.0019 (7)
O4	0.0141 (7)	0.0216 (9)	0.0168 (8)	−0.0026 (6)	0.0050 (6)	0.0005 (7)
N4	0.0123 (8)	0.0142 (9)	0.0143 (9)	0.0001 (7)	0.0057 (7)	0.0010 (7)
N5	0.0156 (8)	0.0172 (10)	0.0167 (10)	−0.0018 (7)	0.0077 (7)	−0.0012 (8)
N6	0.0170 (9)	0.0196 (10)	0.0135 (10)	0.0025 (8)	0.0074 (8)	0.0011 (8)
C8	0.0138 (9)	0.0118 (11)	0.0163 (11)	−0.0029 (8)	0.0059 (8)	−0.0019 (9)
C9	0.0134 (10)	0.0187 (12)	0.0183 (12)	−0.0029 (9)	0.0068 (9)	−0.0050 (10)
C10	0.0134 (10)	0.0169 (12)	0.0202 (12)	0.0003 (9)	0.0037 (9)	−0.0025 (9)
C11	0.0149 (10)	0.0168 (12)	0.0180 (12)	−0.0019 (9)	0.0035 (9)	−0.0010 (9)
C12	0.0146 (10)	0.0174 (12)	0.0116 (11)	0.0001 (8)	0.0064 (8)	−0.0013 (9)
C13	0.0178 (10)	0.0161 (11)	0.0190 (12)	−0.0009 (9)	0.0080 (9)	−0.0032 (9)
C14	0.0141 (10)	0.0168 (12)	0.0132 (11)	0.0020 (9)	0.0055 (8)	0.0040 (9)
O1W	0.0201 (8)	0.0266 (10)	0.0194 (9)	−0.0030 (7)	0.0083 (7)	−0.0066 (7)
O2W	0.0221 (8)	0.0396 (11)	0.0215 (10)	−0.0092 (8)	0.0100 (7)	−0.0071 (8)

Geometric parameters (Å, º)

O1—C7	1.266 (3)	N4—C11	1.367 (3)
O2—C7	1.256 (2)	N4—C8	1.370 (3)
N1—C4	1.359 (3)	N4—C12	1.487 (2)
N1—C1	1.365 (3)	N5—C9	1.322 (3)
N1—C5	1.487 (3)	N5—C8	1.359 (3)
N2—C2	1.322 (3)	N6—C8	1.315 (3)
N2—C1	1.360 (3)	N6—H61N	0.85 (3)
N3—C1	1.322 (3)	N6—H62N	0.90 (2)
N3—H31N	0.85 (3)	C9—C10	1.397 (3)
N3—H32N	0.91 (2)	C9—H9	0.9500
C2—C3	1.397 (3)	C10—C11	1.356 (3)
C2—H2	0.9500	C10—H10	0.9500
C3—C4	1.358 (3)	C11—H11	0.9500
C3—H3	0.9500	C12—C13	1.523 (3)
C4—H4	0.9500	C12—H12A	0.9900
C5—C6	1.516 (3)	C12—H12B	0.9900
C5—H5A	0.9900	C13—C14	1.531 (3)
C5—H5B	0.9900	C13—H13A	0.9900
C6—C7	1.522 (3)	C13—H13B	0.9900
C6—H6A	0.9900	O1W—H11W	0.89 (3)
C6—H6B	0.9900	O1W—H12W	0.84 (3)
O3—C14	1.265 (3)	O2W—H21W	0.90 (3)
O4—C14	1.258 (2)	O2W—H22W	0.86 (3)
C4—N1—C1	119.69 (17)	C11—N4—C12	118.61 (17)
C4—N1—C5	118.41 (17)	C8—N4—C12	121.46 (16)

C1—N1—C5	121.90 (17)	C9—N5—C8	118.44 (19)
C2—N2—C1	118.38 (19)	C8—N6—H61N	116.1 (16)
C1—N3—H31N	116.4 (16)	C8—N6—H62N	123.7 (15)
C1—N3—H32N	121.7 (15)	H61N—N6—H62N	119 (2)
H31N—N3—H32N	121 (2)	N6—C8—N5	117.9 (2)
N3—C1—N2	117.7 (2)	N6—C8—N4	121.43 (18)
N3—C1—N1	121.68 (18)	N5—C8—N4	120.66 (18)
N2—C1—N1	120.64 (18)	N5—C9—C10	123.34 (19)
N2—C2—C3	123.45 (19)	N5—C9—H9	118.3
N2—C2—H2	118.3	C10—C9—H9	118.3
C3—C2—H2	118.3	C11—C10—C9	117.2 (2)
C4—C3—C2	116.5 (2)	C11—C10—H10	121.4
C4—C3—H3	121.8	C9—C10—H10	121.4
C2—C3—H3	121.8	C10—C11—N4	120.4 (2)
C3—C4—N1	121.1 (2)	C10—C11—H11	119.8
C3—C4—H4	119.4	N4—C11—H11	119.8
N1—C4—H4	119.4	N4—C12—C13	110.99 (17)
N1—C5—C6	111.90 (17)	N4—C12—H12A	109.4
N1—C5—H5A	109.2	C13—C12—H12A	109.4
C6—C5—H5A	109.2	N4—C12—H12B	109.4
N1—C5—H5B	109.2	C13—C12—H12B	109.4
C6—C5—H5B	109.2	H12A—C12—H12B	108.0
H5A—C5—H5B	107.9	C12—C13—C14	113.84 (18)
C5—C6—C7	112.33 (18)	C12—C13—H13A	108.8
C5—C6—H6A	109.1	C14—C13—H13A	108.8
C7—C6—H6A	109.1	C12—C13—H13B	108.8
C5—C6—H6B	109.1	C14—C13—H13B	108.8
C7—C6—H6B	109.1	H13A—C13—H13B	107.7
H6A—C6—H6B	107.9	O4—C14—O3	124.47 (19)
O2—C7—O1	124.89 (19)	O4—C14—C13	117.05 (19)
O2—C7—C6	117.22 (19)	O3—C14—C13	118.48 (18)
O1—C7—C6	117.88 (18)	H11W—O1W—H12W	110 (2)
C11—N4—C8	119.92 (17)	H21W—O2W—H22W	104 (2)

C2—N2—C1—N3	178.36 (19)	C9—N5—C8—N6	−179.88 (19)
C2—N2—C1—N1	−2.2 (3)	C9—N5—C8—N4	0.0 (3)
C4—N1—C1—N3	−175.13 (19)	C11—N4—C8—N6	178.78 (19)
C5—N1—C1—N3	4.3 (3)	C12—N4—C8—N6	−0.8 (3)
C4—N1—C1—N2	5.4 (3)	C11—N4—C8—N5	−1.1 (3)
C5—N1—C1—N2	−175.12 (18)	C12—N4—C8—N5	179.27 (18)
C1—N2—C2—C3	−1.6 (3)	C8—N5—C9—C10	1.5 (3)
N2—C2—C3—C4	2.1 (3)	N5—C9—C10—C11	−1.8 (3)
C2—C3—C4—N1	1.2 (3)	C9—C10—C11—N4	0.6 (3)
C1—N1—C4—C3	−4.9 (3)	C8—N4—C11—C10	0.8 (3)
C5—N1—C4—C3	175.6 (2)	C12—N4—C11—C10	−179.63 (19)
C4—N1—C5—C6	90.1 (2)	C11—N4—C12—C13	−101.4 (2)
C1—N1—C5—C6	−89.4 (2)	C8—N4—C12—C13	78.2 (2)
N1—C5—C6—C7	179.52 (17)	N4—C12—C13—C14	−175.40 (17)

C5—C6—C7—O2	−173.50 (18)	C12—C13—C14—O4	168.71 (18)
C5—C6—C7—O1	6.4 (3)	C12—C13—C14—O3	−11.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H31*N*···O4^{i}	0.85 (3)	2.05 (3)	2.882 (3)	170 (2)
N3—H32*N*···O3	0.91 (2)	1.99 (2)	2.888 (2)	166 (2)
N6—H61*N*···O2^{ii}	0.85 (3)	2.12 (3)	2.960 (3)	170 (2)
N6—H62*N*···O1	0.90 (2)	1.88 (2)	2.766 (2)	169 (2)
O1*W*—H11*W*···O3	0.89 (3)	1.93 (3)	2.794 (2)	165 (3)
O1*W*—H12*W*···O2^{iii}	0.84 (3)	2.04 (3)	2.867 (2)	170 (3)
O2*W*—H21*W*···O1	0.90 (3)	2.00 (3)	2.863 (2)	159 (2)
O2*W*—H22*W*···O4^{iv}	0.86 (3)	2.10 (3)	2.923 (2)	159 (3)

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