research communications

Crystal structure of 2-(azaniumylmethyl)pyridinium bis(hydrogen squarate)

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The asymmetric unit of the title compound, $C_6H_{10}N_2{}^{2+} \cdot 2C_4HO_4{}^-$, comprises two hydrogen squarate (Hsq$^-$; systematic name: 2-hydroxy-3,4-dioxocyclobutanolate) anions and a 2-(azaniumylmethyl)pyridinium dication. The squaric acid molecules each donate an H atom to the N atoms of the pyridine ring and the aminomethyl units of a 2-(aminomethyl)pyridine molecule, forming the 1:2 salt. The Hsq$^-$ anions are linked by strong O—H$\cdots$O hydrogen bonds and an N—H$\cdots$O hydrogen bond links the 2-(azaniumylmethyl)pyridinium cation to one of the squaric acid anions. The crystal structure features additional N—H$\cdots$O and O—H$\cdots$O hydrogen bonds, π–π stacking and unusual weak C—O$\cdots\pi$(ring) interactions.

1. Chemical context

Hydrogen bonding is the most common way of generating supramolecular organic systems in crystal engineering and molecular recognition. Hydrogen-bonded systems generated from organic cations and anions are of special interest as they would be expected to form stronger hydrogen bonds than those in neutral molecules (Reetz et al.,1994; Bertolasi et al., 2001). Squaric acid ($H_2C_4O_4$, H_2sq), has been of interest because of its cyclic structure and potential aromaticity and is used as a building block in crystal engineering due to the simplicity of the cyclic units. It can be found in three forms: uncharged H_2sq, the Hsq$^-$ monoanion and the sq^{2-} dianion. The mono- and dianions are often produced following deprotonation by amines (Lam & Mak, 2000; Mathew et al., 2002). The squarate derivatives are almost flat because of the π-conjugation of their C—C and C—O bonds, and therefore their four oxygen atoms behave as planar (sp^2) electron donors of one or two lone pairs of electrons. Recently, we reported the synthesis and characterization of the same organoammonium squarate as the title compound but as a hydrate in the triclinic space group $P\bar{1}$ (Korkmaz & Bulut, 2013). We report here the unsolvated form of this salt, which crystallizes in the monoclinic space group $P2_1/c$.
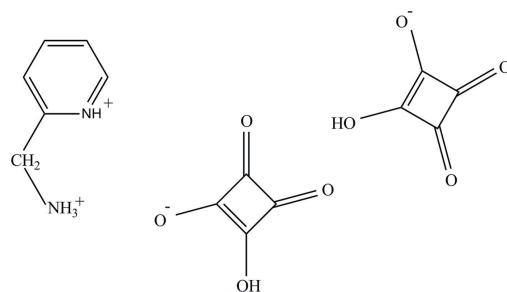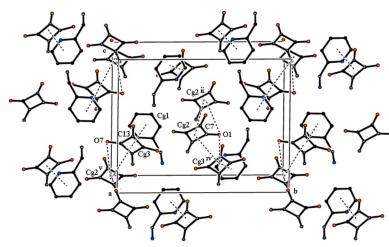
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2. Structural commentary

2-(Aminomethyl) pyridine forms a salt with two squaric acid molecules and each molecule of the acid loses one proton. One of these is transferred to the N atom of the pyridine ring, generating the 4-(aminomethyl)morpholinium mono-cation. The other from the second acid molecule is engaged in the formation of a homo-conjugated hydrogen squarate anion *via* a short, symmetric O5—H5A···O3 [2.4583 (14) Å] hydrogen bond (Fig. 1). The electron density associated with this H atom is shared by the O5 and O3 atoms, indicating a large degree of ionic character (Gilli & Gilli, 2000). Considering the range (2.38–2.50 Å) of Gilli's classification for such an interaction, this hydrogen bonding can be referred to as negative charge-assisted hydrogen bonding [(−) CAHB] (Gilli & Gilli, 2009; Gilli *et al.*, 2001; Becke, 1993; Lee *et al.*, 1988) and can be represented as [-O···H···O-]⁻.

N1/C1–C5, C7–C10 and C11–C14 are defined as rings 1, 2 and 3, respectively, with centroids $Cg1$, $Cg2$ and $Cg3$. The dihedral angles between the mean plane of ring 1 and those of rings 2 and 3 are 18.818 (8) and 31.564 (6)°, respectively. The dihedral angle between the two squarate anions is 29.19 (1)°. The angles between the C—C bonds in the Hsq⁻ anions are close to 90°, with the oxygen atoms directed almost along the diagonals.

The C—C distances in the planar squarate ring systems reflect partial double-bond character for C9—C10, C7—C10, C11—C12 and C11—C14 with distances of 1.4291 (17), 1.4357 (16), 1.4139 (17) and 1.4465 (18) Å, respectively. In contrast C7—C8, C8—C9, C12—C13 and C13—C14 display more single-bond character with distances of 1.4886 (17), 1.4929 (17), 1.4802 (18) and 1.5141 (17) Å, respectively. The Hsq⁻ ion has one C—O bond (C11—O5) at 1.3023 (17) Å, which is significantly longer than a normal single C—O bond. This most likely reflects the involvement in the negative charge-assisted hydrogen bonding mentioned earlier. At 1.3000 (15) Å, the C10—O4 bond is similarly extended. The remaining C—O bonds in both rings display a similar pattern with one obvious C=O double bond in each ring [C8=O2, 1.2268 (15) Å and C13=O7, 1.2141 (17) Å] and the others of intermediate length in the range 1.2356 (16) to 1.2658 (15) Å, indicating some delocalization occurring in both rings.
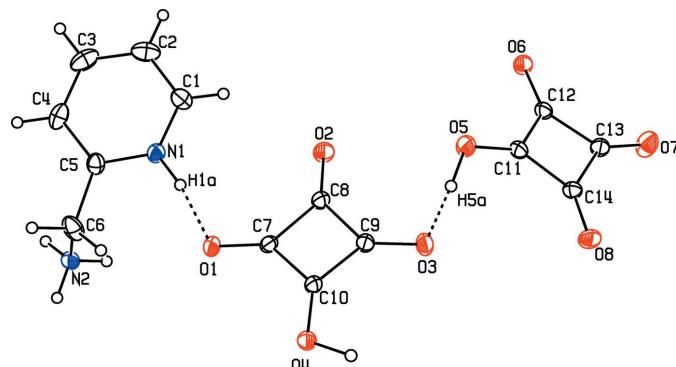

Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

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

$Cg2$ and $Cg3$ are the centroids of the C7–C10 and C11–C14 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.93 (2)	1.74 (2)	2.6598 (15)	166.7 (19)
N2—H2B···O2^i	0.89	2.05	2.8565 (16)	150
N2—H2B···O5^i	0.89	2.56	3.1613 (17)	126
N2—H2C···O6^i	0.89	2.02	2.8765 (16)	161
N2—H2A···O8^{ii}	0.89	1.90	2.7580 (15)	162
O4—H4A···O6^{iii}	0.99 (2)	1.51 (2)	2.4993 (14)	175 (2)
O5—H5A···O3	1.00 (2)	1.46 (2)	2.4583 (14)	175 (2)
C7—O1···$Cg2^{ii}$	1.25 (1)	3.38 (1)	3.3226 (14)	77 (1)
C7—O1···$Cg3^{iv}$	1.25 (1)	3.39 (1)	3.3297 (14)	76 (1)
C13—O7···$Cg2^v$	1.21 (1)	3.52 (1)	3.4188 (15)	75 (1)

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

3. Supramolecular features

The two hydrogen squarate anions are linked in the asymmetric unit by a short hydrogen-bonding interaction O5—H5A···O3 [2.4583 (14) Å] related to the proton-sharing interaction discussed earlier. This pair of anions is further linked to the 2-(azaniumylmethyl)pyridinium dication by an N1—H1A···O1 hydrogen bond, Fig. 1, Table 1. O5—H5A···O3, N2—H2B···O2^i and N2—H2B···O5^i hydrogen bonds form rings with an $R_3^2(7)$ graph-set motif while N2—H2C···O6^i and N2—H2B···O5^i hydrogen bonds combine to form $R_2^2(7)$ rings. In addition, heteronuclear N2—H2C···O6^i, and N2—H2A···O8^{ii} and homonuclear O4—H4A···O6^{iii} and O5—H5A···O3 hydrogen bonds generate a larger $R_3^4(14)$ ring motif (Fig. 2, Table 1). The crystal packing also features unusual weak C7—O1···$Cg2^{ii}$, C7—O1···$Cg3^{iv}$ and C13—O7···$Cg2^v$ interactions reinforced by π–π stacking interactions. These latter contacts [$Cg1$···$Cg3$ = 2.5382 (9) Å, $Cg2$···$Cg2^{ii}$ = 3.5997 (9) Å, $Cg2$···$Cg3^{iv}$ = 3.6406 (10) Å and $Cg3$···$Cg2^v$ = 3.6406 (10) Å; symmetry codes: (ii) $1 - x, 1 - y, 1 - z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$] also contribute to the stabilization of the crystal packing (Fig. 3).

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update February 2017; Groom *et al.*, 2016) revealed the structures of various organoammonium squarates (Georgopoulos *et al.*, 2005; Wang & Stucky, 1974; Kanters *et al.*, 1991; Kolev *et al.*, 2000; Karle *et al.*, 1996; Angelova *et al.*, 1996). In the squarate anion form, the anions are generally linked to amines by N—H···O hydrogen bonds (Gilli *et al.*, 2001; Korkmaz *et al.*, 2011; Dega-Szafran *et al.*, 2012). Structures of 2-(amoniomethyl) pyridinium, dihydrogen squarate and squaric acid derivatives are also known (Korkmaz *et al.*, 2011; Korkmaz & Bulut, 2013, 2014). Often, the supramolecular architectures of similar structures have been investigated together with their spectroscopic properties, including their potential non-linear optical (NLO) behaviour (Bosshard *et al.*, 1995; Kolev *et al.*, 2008). The literature also reveals that squarenes show photo-chemical, photo-conductive and NLO
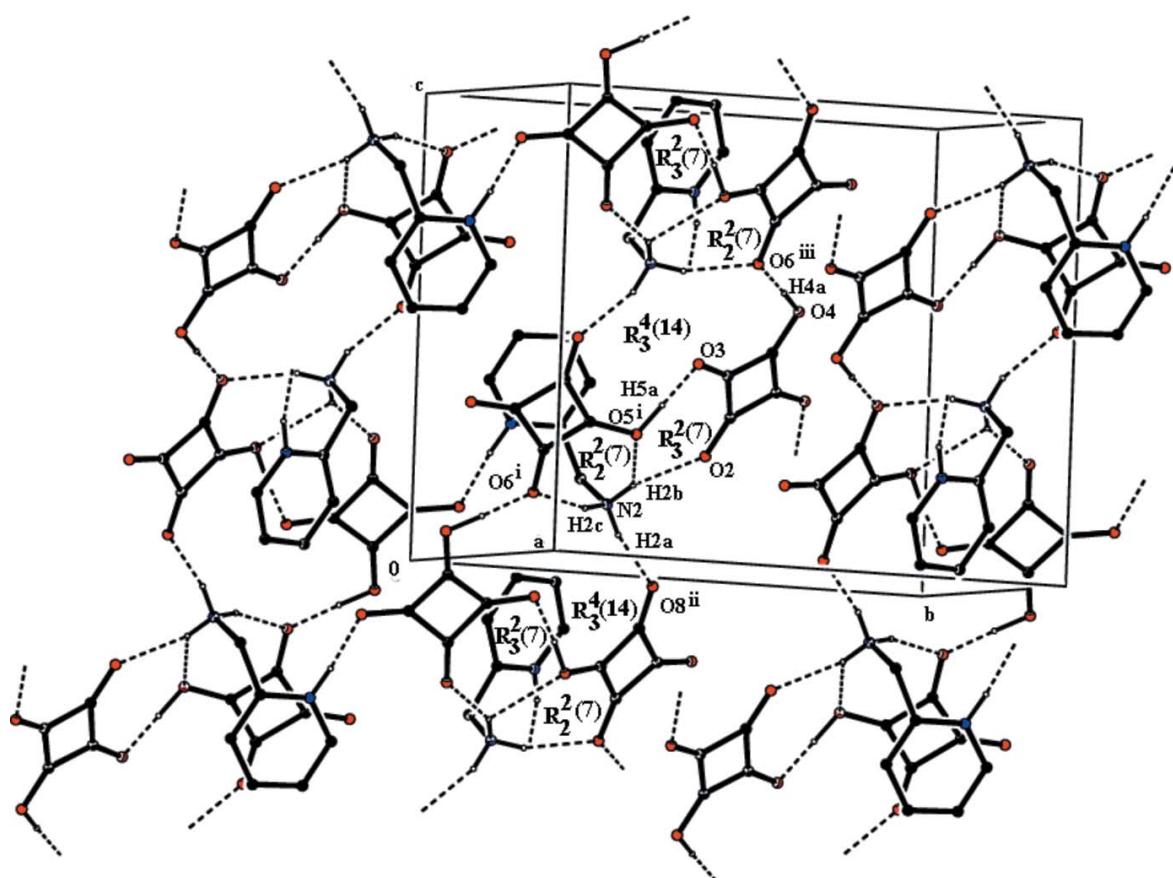
Figure 2
A view of the N—H···O and O—H···O interactions in the crystal of the title compound (hydrogen bonds are shown as dashed lines; see Table 1 for numerical details).
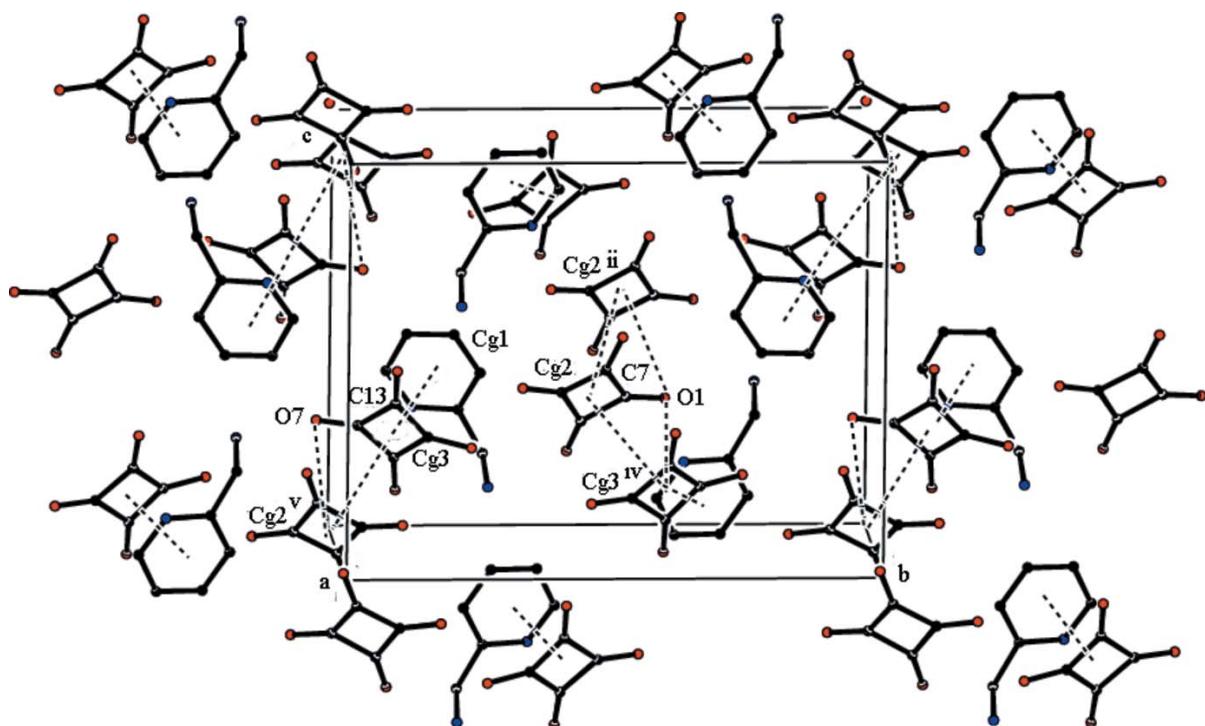
Figure 3
A packing diagram showing the C—O···π and π–π stacking interactions. [Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.] H atoms not involved in the interactions have been omitted for clarity.

Table 2
Experimental details.

|	
Crystal data	
Chemical formula	$C_6H_{10}N_2{}^{2+} \cdot 2C_4HO_4{}^-$
M_r	336.26
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	7.4653 (7), 15.4548 (14), 12.2095 (12)
β (°)	90.073 (4)
V (Å^3)	1408.7 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	$0.17 \times 0.13 \times 0.11$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2013)
T_{min}, T_{max}	0.672, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	70681, 3496, 3090
R_{int}	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.042, 0.118, 1.11
No. of reflections	3496
No. of parameters	227
H-atom treatment	H-atom parameters not refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.26, −0.28

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT2014* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

properties and that they can be used as electron acceptors in photo-sensitive devices (Korkmaz *et al.*, 2016).

5. Synthesis and crystallization

All chemical reagents were analytical grade commercial products. The solvent was purified by conventional methods. Squaric acid (H₂Sq; 0,46 g, 4 mmol) and 2-(aminomethyl)-pyridine (0,24 g; 2 mmol) were dissolved in water (25 cm³) to obtain a mixture in the molar ratio 2:1 and the solution was heated to 323 K in a temperature-controlled bath and stirred for one h. The reaction mixture was then slowly cooled to room temperature. The crystals formed were filtered and washed with 10 cm³ of methanol, and dried in air.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound hydrogen atoms were included in calculated positions with C—H = 0.93 Å (aromatic) and 0.97 Å (methylene) and allowed to ride, with $U_{iso}(H) = 1.2U_{eq}(C)$. The NH₃ group (N—H = 0.89 Å) was also allowed to ride in the refinement with $U_{iso}(H) = 1.5U_{eq}(N)$. The O-bound H atoms and N1-bound H atom were located in a difference-Fourier map and refined with $U_{iso}(H) = 1.2U_{eq}(O)$ and $U_{iso}(H) = 1.5U_{eq}(N)$.

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supporting information

Crystal structure of 2-(azaniumylmethyl)pyridinium bis(hydrogen squarate)

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

2-(Azaniumylmethyl)pyridinium bis(2-hydroxy-3,4-dioxocyclobutanolate)

Crystal data
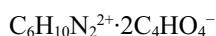
$C_6H_{10}N_2^{2+}\cdot 2C_4HO_4^-$	$F(000) = 696$
$M_r = 336.26$	$D_x = 1.586$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.4653$ (7) Å	Cell parameters from 9896 reflections
$b = 15.4548$ (14) Å	$\theta = 3.0–28.3°$
$c = 12.2095$ (12) Å	$\mu = 0.13$ mm^{-1}
$\beta = 90.073$ (4)°	$T = 296$ K
$V = 1408.7$ (2) Å^3	Block, bronze
$Z = 4$	$0.17 \times 0.13 \times 0.11$ mm

Data collection

Bruker APEXII CCD diffractometer	3496 independent reflections
φ and ω scans	3090 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2013)	$R_{int} = 0.042$
	$\theta_{max} = 28.3°$, $\theta_{min} = 3.0°$
$T_{min} = 0.672$, $T_{max} = 0.746$	$h = -9\rightarrow9$
70681 measured reflections	$k = -20\rightarrow20$
	$l = -16\rightarrow16$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.5691P]$
$wR(F^2) = 0.118$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
3496 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
227 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
0 restraints	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3472 (2)	0.59963 (10)	0.10814 (12)	0.0377 (3)
H1	0.376471	0.541181	0.111071	0.045*
C2	0.2856 (2)	0.63543 (13)	0.01196 (13)	0.0479 (4)
H2	0.270245	0.601292	−0.050069	0.058*
C3	0.2473 (2)	0.72223 (14)	0.00899 (14)	0.0507 (4)
H3	0.210063	0.747750	−0.056155	0.061*
C4	0.2640 (2)	0.77205 (11)	0.10321 (14)	0.0442 (4)
H4	0.236500	0.830733	0.101700	0.053*
C5	0.32152 (18)	0.73381 (8)	0.19877 (12)	0.0305 (3)
C6	0.3378 (2)	0.78078 (10)	0.30627 (14)	0.0419 (4)
H6A	0.424710	0.751293	0.352098	0.050*
H6B	0.381247	0.839005	0.293104	0.050*
C7	0.61186 (16)	0.53092 (8)	0.38741 (10)	0.0245 (2)
C8	0.59463 (17)	0.44771 (8)	0.32689 (10)	0.0273 (3)
C9	0.71303 (18)	0.40741 (8)	0.41129 (10)	0.0278 (3)
C10	0.72538 (16)	0.48889 (8)	0.46610 (10)	0.0247 (2)
C11	0.64141 (18)	0.16148 (8)	0.29601 (10)	0.0289 (3)
C12	0.54027 (17)	0.10155 (8)	0.23404 (10)	0.0271 (3)
C13	0.57553 (18)	0.03307 (9)	0.31604 (10)	0.0293 (3)
C14	0.67917 (17)	0.09946 (8)	0.38172 (10)	0.0272 (3)
N1	0.36494 (15)	0.64919 (7)	0.19743 (9)	0.0288 (2)
N2	0.16375 (17)	0.78523 (8)	0.36470 (10)	0.0346 (3)
H2A	0.177821	0.813962	0.427290	0.052*
H2C	0.125260	0.731888	0.378838	0.052*
H2B	0.083844	0.812501	0.322984	0.052*
O1	0.54865 (14)	0.60498 (6)	0.37564 (8)	0.0328 (2)
O2	0.51318 (15)	0.42458 (7)	0.24462 (8)	0.0387 (3)
O3	0.77376 (16)	0.33276 (6)	0.42957 (9)	0.0409 (3)
O4	0.80146 (14)	0.51691 (6)	0.55513 (8)	0.0331 (2)
O5	0.68219 (19)	0.24159 (7)	0.27431 (9)	0.0457 (3)
O6	0.45452 (15)	0.10825 (7)	0.14494 (8)	0.0380 (3)
O7	0.54053 (18)	−0.04333 (7)	0.32469 (10)	0.0514 (3)
O8	0.76167 (16)	0.09899 (7)	0.46951 (8)	0.0400 (3)
H1A	0.419 (3)	0.6260 (13)	0.2598 (17)	0.048*
H5A	0.725 (3)	0.2770 (14)	0.3380 (18)	0.060*
H4A	0.868 (3)	0.4687 (15)	0.5894 (17)	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0412 (7)	0.0344 (7)	0.0375 (8)	0.0016 (6)	0.0005 (6)	−0.0072 (6)
C2	0.0440 (8)	0.0679 (11)	0.0320 (7)	−0.0028 (8)	−0.0042 (6)	−0.0111 (7)
C3	0.0442 (9)	0.0732 (12)	0.0346 (8)	0.0039 (8)	−0.0084 (6)	0.0176 (8)
C4	0.0458 (8)	0.0362 (8)	0.0505 (9)	0.0057 (6)	−0.0058 (7)	0.0159 (7)
C5	0.0293 (6)	0.0253 (6)	0.0370 (7)	−0.0015 (5)	−0.0047 (5)	0.0011 (5)
C6	0.0383 (7)	0.0333 (7)	0.0540 (9)	−0.0031 (6)	−0.0126 (7)	−0.0137 (6)
C7	0.0285 (6)	0.0245 (6)	0.0207 (5)	−0.0021 (4)	−0.0029 (4)	0.0028 (4)
C8	0.0327 (6)	0.0254 (6)	0.0237 (6)	−0.0010 (5)	−0.0045 (5)	0.0012 (5)
C9	0.0344 (6)	0.0230 (6)	0.0259 (6)	−0.0008 (5)	−0.0073 (5)	−0.0009 (4)
C10	0.0297 (6)	0.0222 (5)	0.0223 (5)	−0.0007 (4)	−0.0045 (4)	0.0009 (4)
C11	0.0364 (6)	0.0242 (6)	0.0261 (6)	0.0020 (5)	−0.0054 (5)	−0.0052 (5)
C12	0.0307 (6)	0.0257 (6)	0.0248 (6)	0.0040 (5)	−0.0059 (5)	−0.0052 (5)
C13	0.0322 (6)	0.0280 (6)	0.0276 (6)	−0.0013 (5)	−0.0061 (5)	−0.0020 (5)
C14	0.0297 (6)	0.0287 (6)	0.0234 (6)	0.0000 (5)	−0.0039 (5)	−0.0035 (5)
N1	0.0310 (5)	0.0265 (5)	0.0287 (5)	0.0017 (4)	−0.0043 (4)	0.0019 (4)
N2	0.0473 (7)	0.0276 (6)	0.0288 (6)	0.0021 (5)	−0.0120 (5)	−0.0032 (4)
O1	0.0431 (5)	0.0240 (4)	0.0312 (5)	0.0049 (4)	−0.0081 (4)	0.0028 (4)
O2	0.0505 (6)	0.0340 (5)	0.0315 (5)	−0.0006 (4)	−0.0189 (4)	−0.0030 (4)
O3	0.0594 (7)	0.0227 (5)	0.0405 (6)	0.0071 (4)	−0.0227 (5)	−0.0051 (4)
O4	0.0452 (5)	0.0257 (5)	0.0282 (5)	0.0014 (4)	−0.0150 (4)	−0.0028 (4)
O5	0.0797 (9)	0.0227 (5)	0.0346 (5)	−0.0061 (5)	−0.0174 (5)	−0.0021 (4)
O6	0.0520 (6)	0.0309 (5)	0.0310 (5)	0.0043 (4)	−0.0204 (4)	−0.0050 (4)
O7	0.0700 (8)	0.0309 (6)	0.0532 (7)	−0.0154 (5)	−0.0214 (6)	0.0067 (5)
O8	0.0525 (6)	0.0386 (6)	0.0290 (5)	−0.0023 (5)	−0.0171 (4)	−0.0034 (4)

Geometric parameters (Å, °)

C1—N1	1.3388 (18)	C9—O3	1.2593 (16)
C1—C2	1.377 (2)	C9—C10	1.4291 (17)
C1—H1	0.9300	C10—O4	1.3000 (15)
C2—C3	1.372 (3)	C11—O5	1.3023 (17)
C2—H2	0.9300	C11—C12	1.4139 (17)
C3—C4	1.390 (3)	C11—C14	1.4465 (18)
C3—H3	0.9300	C12—O6	1.2658 (15)
C4—C5	1.376 (2)	C12—C13	1.4802 (18)
C4—H4	0.9300	C13—O7	1.2141 (17)
C5—N1	1.3475 (17)	C13—C14	1.5141 (17)
C5—C6	1.505 (2)	C14—O8	1.2356 (16)
C6—N2	1.485 (2)	N1—H1A	0.93 (2)
C6—H6A	0.9700	N2—H2A	0.8900
C6—H6B	0.9700	N2—H2C	0.8900
C7—O1	1.2462 (15)	N2—H2B	0.8900
C7—C10	1.4357 (16)	O3—H5A	1.46 (2)
C7—C8	1.4886 (17)	O4—H4A	0.99 (2)
C8—O2	1.2268 (15)	O5—H5A	1.00 (2)

C8—C9	1.4929 (17)		
N1—C1—C2	119.82 (15)	C10—C9—C8	89.62 (10)
N1—C1—H1	120.1	O4—C10—C9	135.48 (12)
C2—C1—H1	120.1	O4—C10—C7	131.74 (12)
C3—C2—C1	119.01 (15)	C9—C10—C7	92.73 (10)
C3—C2—H2	120.5	O5—C11—C12	129.70 (12)
C1—C2—H2	120.5	O5—C11—C14	137.03 (12)
C2—C3—C4	120.09 (15)	C12—C11—C14	93.24 (11)
C2—C3—H3	120.0	O6—C12—C11	132.49 (13)
C4—C3—H3	120.0	O6—C12—C13	136.82 (12)
C5—C4—C3	119.43 (15)	C11—C12—C13	90.68 (10)
C5—C4—H4	120.3	O7—C13—C12	135.73 (12)
C3—C4—H4	120.3	O7—C13—C14	136.29 (13)
N1—C5—C4	118.78 (14)	C12—C13—C14	87.94 (10)
N1—C5—C6	117.37 (12)	O8—C14—C11	136.71 (12)
C4—C5—C6	123.85 (14)	O8—C14—C13	135.18 (12)
N2—C6—C5	111.82 (11)	C11—C14—C13	88.10 (10)
N2—C6—H6A	109.3	C1—N1—C5	122.79 (12)
C5—C6—H6A	109.3	C1—N1—H1A	119.1 (12)
N2—C6—H6B	109.3	C5—N1—H1A	117.8 (12)
C5—C6—H6B	109.3	C6—N2—H2A	109.5
H6A—C6—H6B	107.9	C6—N2—H2C	109.5
O1—C7—C10	135.70 (12)	H2A—N2—H2C	109.5
O1—C7—C8	134.73 (11)	C6—N2—H2B	109.5
C10—C7—C8	89.54 (10)	H2A—N2—H2B	109.5
O2—C8—C7	134.48 (12)	H2C—N2—H2B	109.5
O2—C8—C9	137.39 (12)	C9—O3—H5A	108.5 (9)
C7—C8—C9	88.12 (9)	C10—O4—H4A	108.8 (12)
O3—C9—C10	134.53 (12)	C11—O5—H5A	115.9 (12)
O3—C9—C8	135.83 (12)		
N1—C1—C2—C3	1.5 (2)	O1—C7—C10—C9	177.87 (16)
C1—C2—C3—C4	−2.5 (3)	C8—C7—C10—C9	−0.11 (10)
C2—C3—C4—C5	0.9 (3)	O5—C11—C12—O6	−4.0 (3)
C3—C4—C5—N1	1.8 (2)	C14—C11—C12—O6	177.80 (15)
C3—C4—C5—C6	−177.64 (15)	O5—C11—C12—C13	176.91 (15)
N1—C5—C6—N2	−96.31 (15)	C14—C11—C12—C13	−1.33 (11)
C4—C5—C6—N2	83.15 (19)	O6—C12—C13—O7	4.0 (3)
O1—C7—C8—O2	0.6 (3)	C11—C12—C13—O7	−176.90 (19)
C10—C7—C8—O2	178.65 (16)	O6—C12—C13—C14	−177.79 (17)
O1—C7—C8—C9	−177.91 (15)	C11—C12—C13—C14	1.27 (10)
C10—C7—C8—C9	0.10 (10)	O5—C11—C14—O8	2.2 (3)
O2—C8—C9—O3	−0.3 (3)	C12—C11—C14—O8	−179.74 (17)
C7—C8—C9—O3	178.15 (17)	O5—C11—C14—C13	−176.71 (18)
O2—C8—C9—C10	−178.57 (17)	C12—C11—C14—C13	1.30 (10)
C7—C8—C9—C10	−0.11 (10)	O7—C13—C14—O8	−2.1 (3)
O3—C9—C10—O4	−0.8 (3)	C12—C13—C14—O8	179.77 (16)

C8—C9—C10—O4	177.53 (16)	O7—C13—C14—C11	176.91 (19)
O3—C9—C10—C7	−178.19 (17)	C12—C13—C14—C11	−1.24 (10)
C8—C9—C10—C7	0.11 (10)	C2—C1—N1—C5	1.3 (2)
O1—C7—C10—O4	0.3 (3)	C4—C5—N1—C1	−3.0 (2)
C8—C7—C10—O4	−177.69 (15)	C6—C5—N1—C1	176.53 (13)

Hydrogen-bond geometry (Å, º)

Cg2 and Cg3 are the centroids of the C7–C10 and C11–C14 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.93 (2)	1.74 (2)	2.6598 (15)	166.7 (19)
N2—H2*B*···O2[i]	0.89	2.05	2.8565 (16)	150
N2—H2*B*···O5[i]	0.89	2.56	3.1613 (17)	126
N2—H2*C*···O6[i]	0.89	2.02	2.8765 (16)	161
N2—H2*A*···O8[ii]	0.89	1.90	2.7580 (15)	162
O4—H4*A*···O6[iii]	0.99 (2)	1.51 (2)	2.4993 (14)	175 (2)
O5—H5*A*···O3	1.00 (2)	1.46 (2)	2.4583 (14)	175 (2)
C7—O1···*Cg*2[ii]	1.25 (1)	3.38 (1)	3.3226 (14)	77 (1)
C7—O1···*Cg*3[iv]	1.25 (1)	3.39 (1)	3.3297 (14)	76 (1)
C13—O7···*Cg*2[v]	1.21 (1)	3.52 (1)	3.4188 (15)	75 (1)

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