IUCrData

ISSN 2414-3146

5-[2,4-Dihydroxy-5-(5-hydroxy-2,4,6-trioxo-3,5-dihydro-1*H*-pyrimidin-5-yl)-3-methoxyphenyl]-5-hydroxy-3,5-dihydro-1*H*-pyrimidine-2,4,6-trione pentahydrate

Ravell Bengiat,[a] Asne Klein,[a] Maayan Gil,[a] Benny Bogoslavsky,[a] Shmuel Cohen,[a] Guy Yardeni,[b] Israel Zilbermann[b] and Joseph Almog[a]*

[a]Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, 9190401, Israel, and [b]Department of Chemistry, The Nuclear Research Centre Negev, Beer Sheva, 84190, Israel. *Correspondence e-mail: almog@mail.huji.ac.il

Received 7 February 2016
Accepted 14 February 2016

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

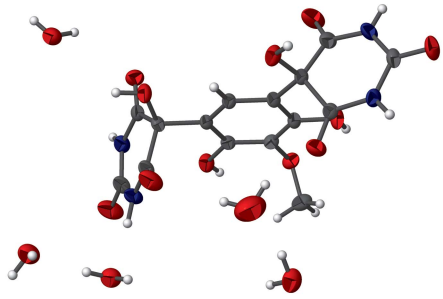
Keywords: crystal structure; ion-pair recognition; alloxan; vasarene analogues; supramolecular ligand; hydrogen bonding; three-dimensional supramolecular structure.

CCDC reference: 1451787

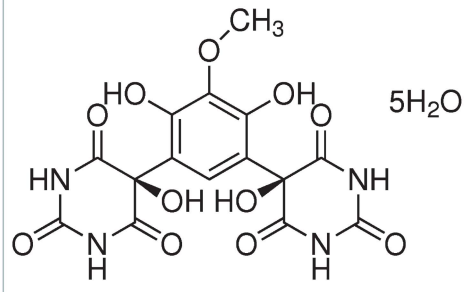
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{15}H_{12}N_4O_{11}\cdot 5H_2O$, has a 'propeller-like' structure. The two alloxan units have screw-boat conformations. Their mean planes are normal to the central aromatic ring with dihedral angles of 87.91 (7) and 88.27 (7)°, and they are inclined to one another by 40.86 (7)°. In the crystal, molecules are linked *via* O—H···O and N—H···O hydrogen bonds, forming a three-dimensional framework. There are also C—H···O hydrogen bonds present within the framework.

3D view



Chemical scheme



Structure description

Vasarene and analogues are prepared by a one-pot reaction between cyclic vicinal polycarbonyl compounds, such as ninhydrin and benzo[*f*]ninhydrin (Almog *et al.*, 2009), and polyhydroxy aromatics. Previous work by our group (Almog *et al.*, 2009) has shown that the reaction with alloxan (1,3-dihydropyrimidine-2,4,5,6-tetrone) results in a partially closed, 'propeller-like' structure, where the alloxan units are in a perpendicular and slightly tilted position (40–60°), due to the tetrahedral angle of the sp^3 carbon atom of the alloxan attached to the central aromatic ring. Attempts to prepare bis-adducts with other polyhydroxy aromatics have also been successful, following a similar pattern. These compounds have shown promising potential for the challenging task of selective precipitation of certain alkali fluorides from aqueous solutions.

The molecular structure of the title compound is illustrated in Fig. 1. A selective methylation on the central hydroxyl group of the 1,2,3-benzenetriol molecule was

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O1W^{i}	0.81 (3)	1.97 (2)	2.6935 (18)	148 (2)
O3—H3O···O2	0.75 (3)	2.41 (2)	2.7788 (16)	112 (2)
O3—H3O···O2W^{ii}	0.75 (3)	2.12 (3)	2.7849 (18)	147 (2)
O4—H4O···O9^{iii}	0.83 (2)	1.93 (2)	2.7520 (16)	168 (2)
O8—H8O···O6^{iv}	0.87 (3)	2.13 (2)	2.8495 (16)	140 (2)
O8—H8O···O4W^{v}	0.87 (3)	2.63 (3)	3.2504 (19)	129 (2)
N1—H1N···O2W	0.92 (2)	1.97 (2)	2.8746 (19)	169 (2)
N2—H2N···O1W^{vi}	0.89 (2)	1.92 (2)	2.8023 (18)	170.2 (18)
N3—H3N···O3W^{vii}	0.82 (3)	2.00 (3)	2.8026 (19)	167 (2)
N4—H4N···O4W^{vii}	0.82 (2)	2.13 (2)	2.9134 (19)	158 (2)
O1W—H11W···O10^{ii}	0.87 (2)	1.97 (2)	2.8006 (18)	161 (3)
O1W—H21W···O5W	0.90 (2)	1.77 (2)	2.651 (3)	164 (2)
O2W—H12W···O5^{viii}	0.85 (2)	2.23 (2)	3.0518 (19)	165 (3)
O2W—H22W···O4W	0.84 (2)	1.98 (2)	2.825 (2)	175 (3)
O3W—H13W···O7^{vi}	0.86 (2)	2.30 (2)	3.0573 (18)	147 (3)
O3W—H13W···O11	0.86 (2)	2.44 (2)	3.0292 (19)	126 (3)
O3W—H23W···O4^{ix}	0.83 (2)	2.10 (2)	2.9303 (18)	178 (3)
O4W—H14W···O3W^{v}	0.84 (2)	1.97 (2)	2.814 (2)	178 (3)
O4W—H24W···O11^{viii}	0.83 (2)	2.08 (2)	2.8937 (18)	168 (3)
O5W—H15W···O9	0.84	2.34	3.151 (3)	164
O5W—H25W···O7	0.87	2.21	2.918 (3)	139
C7—H7B···O7^{i}	0.96	2.63	3.501 (2)	151
C7—H7B···O11^{x}	0.96	2.59	3.242 (2)	125
C7—H7C···O10^{ii}	0.96	2.54	3.458 (2)	159

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

performed prior to the one-pot reaction with alloxan. It can be used as a model for potential binding to a solid phase for future separation techniques.

The title compound, contains several oxygen and nitrogen functional groups (hydroxyls, carbonyls and amides) that are capable of forming multiple hydrogen bonds with protic solvent molecules (Table 1 and Figs. 2 and 3). This greatly enhances its solubility in water, thus enabling the selective binding and precipitation of the highly soluble heavy alkali fluorides from aqueous solutions, as shall be reported in a forthcoming article, and exhibiting promising potential as a new analytical method for salt-separation techniques. The

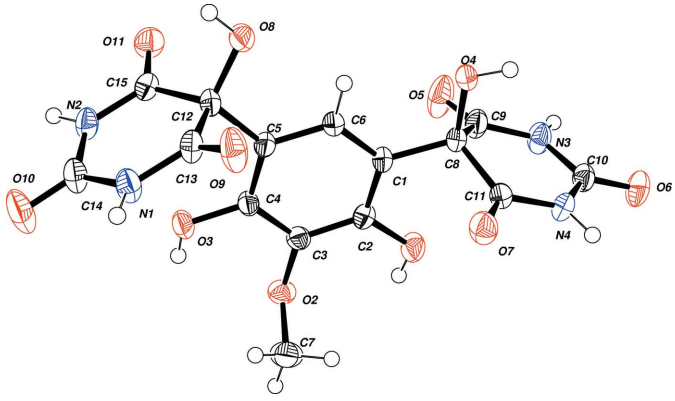


Figure 1
A view of the molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. All solvent molecules have been omitted for clarity.

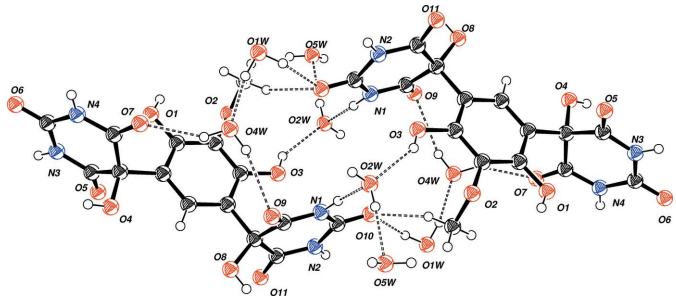


Figure 2
A partial view of the crystal packing of the title compound, showing some of the hydrogen bonds involving the water molecules (dashed lines; see Table 1). Displacement ellipsoids are drawn at the 50% probability level.

'propeller-like' structure is established as non-hemiketal ring closure is allowed with a second carbonyl group, unlike the ninhydrin-based vasarene analogues (Almog *et al.*, 2016). We suspect that this is due to two main factors: 1) the less reactive amidic carbonyls compared to the 'true' ketones on ninhydrin; 2) a greater ring strain when closing a six-membered ring compared to the five-membered ring of ninhydrin. Nevertheless, this structure is responsible for the greater flexibility of the ligand as opposed to the rigid ninhydrin-based vasarenes, assisting in the final complex formation with alkali fluoride ion-pairs.

Synthesis and crystallization

Alloxan monohydrate (329 mg, 2.05 mmol) and 2-methoxybenzene-1,3-diol (prepared according to a known procedure; Donnelly *et al.*, 2008) (142 mg, 1.01 mmol) were stirred at room temperature in glacial acetic acid (10 ml) for 24 h. The white precipitate that formed was collected by vacuum filtration. The filtrate was left sealed and after a few days colourless crystals were formed. They were filtered onto sintered glass

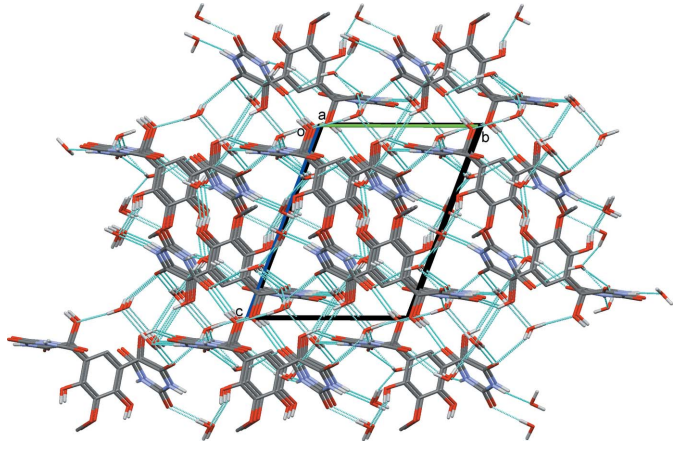


Figure 3
A perspective view along the *a* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1), and C-bound H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{12}N_4O_{11}\cdot 5H_2O$
M_r	514.36
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	295
a, b, c (Å)	9.4495 (6), 10.0608 (6), 12.3484 (8)
α, β, γ (°)	109.133 (1), 91.964 (1), 106.201 (1)
V (Å^3)	1054.79 (11)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.15
Crystal size (mm)	0.43 × 0.36 × 0.26
Data collection	
Diffractometer	Bruker APEXII CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2010)
T_{min}, T_{max}	0.939, 0.962
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12041, 4821, 4337
R_{int}	0.018
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.133, 1.04
No. of reflections	4821
No. of parameters	381
No. of restraints	12
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.44

Computer programs: *APEX2* (Bruker, 2010), *SAINT* (Bruker, 2010), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008), *SHELXTL* (Sheldrick, 2008).

and washed with AcOH followed by diethyl ether (yield: 103 mg, 24%). Recrystallization (MeOH/H_2O) afforded colourless crystals (m.p. > 473 K with decomposition). Analysis calculated for $C_{15}H_{12}N_4O_{11}$+2H_2O: C, 39.14; H, 3.50; N, 12.17; found: C, 39.35; H, 3.29; N, 11.90; ^{1}H NMR (DMSO-d_6) δ (p.p.m.): 3.49 (*s*, 3H), 7.35 (*br s*, 2H), 7.62 (*s*, 1H), 9.45 (*br s*, 2H), 11.31 (*br s*, 4H); UV/Vis (DMSO): λ_{max} = 282 nm. IR: ν = 494, 527, 606, 702, 793, 1020, 1132, 1246, 1348, 1411, 1479, 1699, 2842, 3101, 3209, 3300, 3373 cm^{-1}; MS/MS positive mode ESI (m/z): 407.05 $[(M + H) - H_2O]^+$, 442.08 $[M + NH_4]^+$, 447.04 $[M + Na]^+$, 871.09 $[2M + Na]^+$.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

This research was supported by the Pazy Research Foundation.

References

Almog, J., Bengiat, R., Gil, M., Klein, A., Cohen, O., Bogoslavski, B., Cohen, S. & Dubnikova, F. (2016). *Tetrahedron*. Submitted.
Almog, J., Rozin, R., Klein, A., Shamuilov-Levinton, G. & Cohen, S. (2009). *Tetrahedron*, **65**, 7954–7962.
Bruker (2010). *APEX2*, *SAINT*, and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Donnelly, A. C., Mays, J. R., Burlison, J., Nelson, J. T., Vielhauer, G., Holzbeierlein, J. & Blagg, B. S. J. (2008). *J. Org. Chem.* **73**, 8901–8920.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2016). **1**, x160261 [https://doi.org/10.1107/S2414314616002613]

5-[2,4-Dihydroxy-5-(5-hydroxy-2,4,6-trioxo-3,5-dihydro-1*H*-pyrimidin-5-yl)-3-methoxyphenyl]-5-hydroxy-3,5-dihydro-1*H*-pyrimidine-2,4,6-trione pentahydrate

Ravell Bengiat, Asne Klein, Maayan Gil, Benny Bogoslavsky, Shmuel Cohen, Guy Yardeni, Israel Zilbermann and Joseph Almog

5-[2,4-Dihydroxy-5-(5-hydroxy-2,4,6-trioxo-1,3-diazinan-5-yl)-3-methoxyphenyl]-5-hydroxy-1,3-diazinane-2,4,6-trione pentahydrate

Crystal data

$C_{15}H_{12}N_4O_{11}\cdot 5H_2O$
$M_r = 514.36$
Triclinic, $P\overline{1}$
$a = 9.4495\ (6)$ Å
$b = 10.0608\ (6)$ Å
$c = 12.3484\ (8)$ Å
$\alpha = 109.133\ (1)°$
$\beta = 91.964\ (1)°$
$\gamma = 106.201\ (1)°$
$V = 1054.79\ (11)$ Å^3
$Z = 2$
$F(000) = 536$
$D_x = 1.620$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6750 reflections
$\theta = 2.3–27.9°$
$\mu = 0.15$ mm^{-1}
$T = 295$ K
Plate, colourless
0.43 × 0.36 × 0.26 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2010)
$T_{min} = 0.939$, $T_{max} = 0.962$
12041 measured reflections
4821 independent reflections
4337 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.9°$, $\theta_{min} = 1.8°$
$h = -12\rightarrow12$
$k = -13\rightarrow13$
$l = -16\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.133$
$S = 1.04$
4821 reflections
381 parameters
12 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
$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 0.3761P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.21877 (13)	0.03575 (13)	0.36014 (11)	0.0352 (3)
H1O	−0.219 (3)	0.061 (3)	0.429 (2)	0.045 (6)*
O2	−0.01468 (13)	0.28905 (12)	0.52758 (9)	0.0303 (2)
O3	0.19179 (13)	0.48136 (12)	0.44958 (10)	0.0327 (3)
H3O	0.185 (3)	0.489 (3)	0.512 (2)	0.045 (6)*
O4	−0.20540 (13)	−0.03555 (12)	0.01383 (9)	0.0337 (3)
H4O	−0.252 (3)	−0.119 (3)	−0.034 (2)	0.043 (6)*
O5	−0.42159 (15)	0.08106 (14)	0.16241 (16)	0.0562 (4)
O6	−0.55723 (13)	−0.40618 (12)	0.09977 (11)	0.0396 (3)
O7	−0.06530 (12)	−0.16599 (13)	0.16113 (11)	0.0362 (3)
O8	0.15820 (12)	0.39213 (12)	0.08897 (9)	0.0313 (3)
H8O	0.220 (3)	0.451 (3)	0.061 (2)	0.052 (6)*
O9	0.37197 (14)	0.28800 (13)	0.16235 (12)	0.0441 (3)
O10	0.55171 (16)	0.72199 (15)	0.45658 (14)	0.0553 (4)
O11	0.12768 (13)	0.64877 (13)	0.23793 (11)	0.0368 (3)
N1	0.45466 (15)	0.49915 (14)	0.31528 (12)	0.0326 (3)
H1N	0.540 (3)	0.474 (3)	0.324 (2)	0.049 (6)*
N2	0.34045 (14)	0.68507 (14)	0.34510 (12)	0.0302 (3)
H2N	0.342 (2)	0.778 (2)	0.3814 (17)	0.032 (5)*
N3	−0.48738 (15)	−0.16430 (15)	0.12230 (13)	0.0335 (3)
H3N	−0.577 (3)	−0.174 (3)	0.114 (2)	0.048 (6)*
N4	−0.31095 (14)	−0.28503 (14)	0.12969 (11)	0.0277 (3)
H4N	−0.297 (3)	−0.363 (3)	0.128 (2)	0.045 (6)*
C1	−0.11481 (15)	0.11043 (15)	0.21253 (12)	0.0235 (3)
C2	−0.11630 (15)	0.13784 (15)	0.33064 (12)	0.0246 (3)
C3	−0.01410 (16)	0.26189 (15)	0.41090 (12)	0.0240 (3)
C4	0.08900 (15)	0.36102 (15)	0.37351 (12)	0.0234 (3)
C5	0.08942 (15)	0.33507 (14)	0.25529 (12)	0.0225 (3)
C6	−0.01113 (15)	0.20805 (15)	0.17600 (12)	0.0231 (3)
H6	−0.0086	0.1884	0.0972	0.028*
C7	0.0760 (2)	0.2224 (2)	0.57378 (15)	0.0398 (4)
H7A	0.0424	0.1174	0.5338	0.060*
H7B	0.0688	0.2435	0.6547	0.060*
H7C	0.1777	0.2617	0.5639	0.060*
C8	−0.22382 (15)	−0.02921 (15)	0.12904 (12)	0.0241 (3)
C9	−0.38477 (17)	−0.02905 (17)	0.14319 (15)	0.0322 (3)
C10	−0.45805 (16)	−0.29232 (16)	0.11523 (13)	0.0274 (3)
C11	−0.19071 (16)	−0.16394 (15)	0.14372 (12)	0.0246 (3)
C12	0.20492 (15)	0.43398 (15)	0.20782 (12)	0.0237 (3)

C13	0.35182 (16)	0.40093 (16)	0.22442 (14)	0.0288 (3)
C14	0.45360 (18)	0.64053 (17)	0.37814 (15)	0.0337 (3)
C15	0.21882 (16)	0.59811 (15)	0.26550 (13)	0.0259 (3)
O1W	0.31872 (17)	−0.02845 (14)	0.43957 (12)	0.0440 (3)
H11W	0.378 (3)	0.062 (2)	0.470 (2)	0.087 (10)*
H21W	0.275 (3)	−0.019 (3)	0.3773 (18)	0.066 (8)*
O2W	0.71624 (15)	0.40613 (14)	0.31264 (11)	0.0390 (3)
H12W	0.679 (3)	0.3131 (19)	0.283 (2)	0.080 (9)*
H22W	0.753 (3)	0.430 (3)	0.258 (2)	0.066 (8)*
O3W	0.21039 (14)	0.78324 (16)	0.05355 (12)	0.0430 (3)
H13W	0.146 (3)	0.780 (4)	0.101 (2)	0.090 (10)*
H23W	0.209 (4)	0.853 (3)	0.032 (3)	0.087 (10)*
O4W	0.82549 (15)	0.48740 (15)	0.12591 (14)	0.0452 (3)
H14W	0.814 (3)	0.405 (2)	0.0736 (19)	0.062 (7)*
H24W	0.916 (2)	0.526 (3)	0.149 (2)	0.072 (8)*
O5W	0.2259 (3)	0.0461 (3)	0.2693 (2)	0.0937 (7)
H15W	0.2655	0.1234	0.2549	0.141*
H25W	0.1306	0.0260	0.2546	0.141*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0381 (6)	0.0301 (6)	0.0288 (6)	−0.0037 (5)	0.0073 (5)	0.0110 (5)
O2	0.0382 (6)	0.0322 (6)	0.0221 (5)	0.0133 (5)	0.0054 (4)	0.0095 (4)
O3	0.0358 (6)	0.0262 (6)	0.0229 (5)	−0.0038 (4)	−0.0025 (4)	0.0035 (4)
O4	0.0439 (6)	0.0227 (5)	0.0230 (5)	−0.0050 (5)	−0.0045 (4)	0.0069 (4)
O5	0.0354 (7)	0.0264 (6)	0.1024 (13)	0.0103 (5)	−0.0032 (7)	0.0175 (7)
O6	0.0339 (6)	0.0251 (6)	0.0516 (7)	−0.0031 (5)	0.0112 (5)	0.0124 (5)
O7	0.0270 (6)	0.0313 (6)	0.0468 (7)	0.0080 (4)	−0.0018 (5)	0.0108 (5)
O8	0.0324 (6)	0.0303 (6)	0.0239 (5)	−0.0019 (4)	0.0030 (4)	0.0098 (4)
O9	0.0341 (6)	0.0246 (6)	0.0579 (8)	0.0095 (5)	−0.0037 (5)	−0.0049 (5)
O10	0.0433 (7)	0.0347 (7)	0.0624 (9)	0.0054 (6)	−0.0213 (6)	−0.0074 (6)
O11	0.0351 (6)	0.0326 (6)	0.0456 (7)	0.0140 (5)	0.0026 (5)	0.0148 (5)
N1	0.0246 (6)	0.0248 (6)	0.0415 (7)	0.0067 (5)	−0.0037 (5)	0.0042 (5)
N2	0.0304 (6)	0.0172 (6)	0.0357 (7)	0.0038 (5)	0.0015 (5)	0.0031 (5)
N3	0.0200 (6)	0.0261 (7)	0.0495 (8)	0.0021 (5)	0.0005 (5)	0.0116 (6)
N4	0.0300 (6)	0.0179 (6)	0.0345 (7)	0.0049 (5)	0.0050 (5)	0.0103 (5)
C1	0.0224 (6)	0.0179 (6)	0.0252 (7)	0.0007 (5)	−0.0002 (5)	0.0061 (5)
C2	0.0244 (7)	0.0208 (6)	0.0274 (7)	0.0039 (5)	0.0047 (5)	0.0094 (5)
C3	0.0275 (7)	0.0226 (6)	0.0210 (6)	0.0081 (5)	0.0024 (5)	0.0064 (5)
C4	0.0235 (6)	0.0188 (6)	0.0239 (6)	0.0040 (5)	−0.0013 (5)	0.0047 (5)
C5	0.0211 (6)	0.0186 (6)	0.0250 (6)	0.0023 (5)	0.0015 (5)	0.0076 (5)
C6	0.0234 (6)	0.0200 (6)	0.0218 (6)	0.0020 (5)	0.0005 (5)	0.0063 (5)
C7	0.0492 (10)	0.0416 (9)	0.0316 (8)	0.0178 (8)	−0.0002 (7)	0.0139 (7)
C8	0.0239 (6)	0.0182 (6)	0.0254 (7)	0.0000 (5)	−0.0009 (5)	0.0076 (5)
C9	0.0263 (7)	0.0224 (7)	0.0433 (9)	0.0029 (6)	−0.0030 (6)	0.0105 (6)
C10	0.0278 (7)	0.0216 (6)	0.0278 (7)	0.0011 (5)	0.0063 (5)	0.0073 (5)
C11	0.0257 (7)	0.0211 (6)	0.0234 (6)	0.0037 (5)	0.0009 (5)	0.0062 (5)

C12	0.0207 (6)	0.0190 (6)	0.0254 (7)	0.0007 (5)	0.0004 (5)	0.0050 (5)
C13	0.0238 (7)	0.0199 (6)	0.0366 (8)	0.0027 (5)	0.0019 (6)	0.0056 (6)
C14	0.0273 (7)	0.0242 (7)	0.0391 (8)	0.0019 (6)	−0.0016 (6)	0.0031 (6)
C15	0.0250 (7)	0.0220 (6)	0.0298 (7)	0.0047 (5)	0.0061 (5)	0.0096 (5)
O1W	0.0566 (8)	0.0268 (6)	0.0403 (7)	0.0062 (6)	0.0070 (6)	0.0066 (5)
O2W	0.0402 (7)	0.0338 (6)	0.0386 (7)	0.0114 (5)	0.0019 (5)	0.0075 (5)
O3W	0.0336 (6)	0.0498 (8)	0.0502 (8)	0.0137 (6)	0.0053 (6)	0.0228 (6)
O4W	0.0378 (7)	0.0322 (7)	0.0616 (9)	0.0099 (5)	−0.0003 (6)	0.0128 (6)
O5W	0.1022 (17)	0.0852 (15)	0.1002 (17)	0.0286 (13)	−0.0120 (13)	0.0437 (13)

Geometric parameters (Å, º)

O1—C2	1.3563 (17)	N4—H4N	0.82 (2)
O1—H1O	0.81 (3)	C1—C6	1.3827 (19)
O2—C3	1.3762 (17)	C1—C2	1.394 (2)
O2—C7	1.431 (2)	C1—C8	1.5059 (18)
O3—C4	1.3518 (17)	C2—C3	1.3869 (19)
O3—H3O	0.75 (3)	C3—C4	1.3955 (19)
O4—C8	1.4219 (17)	C4—C5	1.3966 (19)
O4—H4O	0.83 (2)	C5—C6	1.3904 (18)
O5—C9	1.205 (2)	C5—C12	1.5314 (18)
O6—C10	1.2133 (17)	C6—H6	0.9300
O7—C11	1.2042 (19)	C7—H7A	0.9600
O8—C12	1.4046 (17)	C7—H7B	0.9600
O8—H8O	0.87 (3)	C7—H7C	0.9600
O9—C13	1.2143 (19)	C8—C11	1.5369 (19)
O10—C14	1.210 (2)	C8—C9	1.537 (2)
O11—C15	1.2067 (19)	C12—C15	1.5339 (19)
N1—C13	1.357 (2)	C12—C13	1.537 (2)
N1—C14	1.382 (2)	O1W—H11W	0.867 (17)
N1—H1N	0.92 (2)	O1W—H21W	0.903 (16)
N2—C15	1.3602 (19)	O2W—H12W	0.846 (17)
N2—C14	1.367 (2)	O2W—H22W	0.843 (16)
N2—H2N	0.89 (2)	O3W—H13W	0.861 (17)
N3—C10	1.368 (2)	O3W—H23W	0.833 (17)
N3—C9	1.3692 (19)	O4W—H14W	0.840 (16)
N3—H3N	0.82 (3)	O4W—H24W	0.833 (17)
N4—C11	1.3714 (18)	O5W—H15W	0.8414
N4—C10	1.374 (2)	O5W—H25W	0.8652
C2—O1—H1O	111.7 (16)	O2—C7—H7C	109.5
C3—O2—C7	113.68 (12)	H7A—C7—H7C	109.5
C4—O3—H3O	113.0 (18)	H7B—C7—H7C	109.5
C8—O4—H4O	111.3 (15)	O4—C8—C1	109.26 (11)
C12—O8—H8O	108.8 (16)	O4—C8—C11	107.57 (12)
C13—N1—C14	125.29 (14)	C1—C8—C11	109.46 (11)
C13—N1—H1N	114.9 (14)	O4—C8—C9	106.24 (12)
C14—N1—H1N	118.6 (15)	C1—C8—C9	110.79 (12)

C15—N2—C14	126.12 (13)	C11—C8—C9	113.36 (11)
C15—N2—H2N	115.7 (13)	O5—C9—N3	121.38 (15)
C14—N2—H2N	118.0 (13)	O5—C9—C8	122.43 (14)
C10—N3—C9	126.54 (14)	N3—C9—C8	115.94 (13)
C10—N3—H3N	113.5 (16)	O6—C10—N3	121.61 (14)
C9—N3—H3N	119.9 (16)	O6—C10—N4	121.50 (14)
C11—N4—C10	126.23 (13)	N3—C10—N4	116.86 (12)
C11—N4—H4N	119.2 (16)	O7—C11—N4	121.48 (14)
C10—N4—H4N	114.6 (16)	O7—C11—C8	121.78 (13)
C6—C1—C2	119.54 (12)	N4—C11—C8	116.65 (12)
C6—C1—C8	122.37 (13)	O8—C12—C5	107.70 (11)
C2—C1—C8	118.05 (12)	O8—C12—C15	108.11 (12)
O1—C2—C3	123.45 (13)	C5—C12—C15	112.28 (11)
O1—C2—C1	116.33 (12)	O8—C12—C13	109.21 (12)
C3—C2—C1	120.20 (12)	C5—C12—C13	106.52 (11)
O2—C3—C2	120.41 (13)	C15—C12—C13	112.87 (11)
O2—C3—C4	119.60 (12)	O9—C13—N1	121.36 (14)
C2—C3—C4	119.98 (13)	O9—C13—C12	121.34 (13)
O3—C4—C3	121.33 (13)	N1—C13—C12	117.20 (13)
O3—C4—C5	118.67 (12)	O10—C14—N2	121.94 (15)
C3—C4—C5	119.98 (12)	O10—C14—N1	120.89 (16)
C6—C5—C4	119.25 (12)	N2—C14—N1	117.13 (14)
C6—C5—C12	117.72 (12)	O11—C15—N2	121.43 (14)
C4—C5—C12	122.83 (12)	O11—C15—C12	120.95 (13)
C1—C6—C5	121.01 (13)	N2—C15—C12	117.57 (13)
C1—C6—H6	119.5	H11W—O1W—H21W	97.9 (19)
C5—C6—H6	119.5	H12W—O2W—H22W	103 (2)
O2—C7—H7A	109.5	H13W—O3W—H23W	106 (2)
O2—C7—H7B	109.5	H14W—O4W—H24W	107 (2)
H7A—C7—H7B	109.5	H15W—O5W—H25W	107.1

C6—C1—C2—O1	−178.56 (13)	C9—N3—C10—N4	−0.5 (2)
C8—C1—C2—O1	−0.9 (2)	C11—N4—C10—O6	177.64 (14)
C6—C1—C2—C3	−0.2 (2)	C11—N4—C10—N3	−4.1 (2)
C8—C1—C2—C3	177.40 (13)	C10—N4—C11—O7	176.55 (14)
C7—O2—C3—C2	88.96 (17)	C10—N4—C11—C8	−6.9 (2)
C7—O2—C3—C4	−91.82 (17)	O4—C8—C11—O7	79.73 (16)
O1—C2—C3—O2	−1.5 (2)	C1—C8—C11—O7	−38.88 (18)
C1—C2—C3—O2	−179.69 (12)	C9—C8—C11—O7	−163.12 (14)
O1—C2—C3—C4	179.28 (13)	O4—C8—C11—N4	−96.79 (14)
C1—C2—C3—C4	1.1 (2)	C1—C8—C11—N4	144.60 (13)
O2—C3—C4—O3	2.1 (2)	C9—C8—C11—N4	20.35 (18)
C2—C3—C4—O3	−178.71 (13)	C6—C5—C12—O8	15.20 (17)
O2—C3—C4—C5	−179.37 (12)	C4—C5—C12—O8	−170.04 (13)
C2—C3—C4—C5	−0.1 (2)	C6—C5—C12—C15	134.11 (13)
O3—C4—C5—C6	176.98 (13)	C4—C5—C12—C15	−51.12 (18)
C3—C4—C5—C6	−1.6 (2)	C6—C5—C12—C13	−101.87 (14)
O3—C4—C5—C12	2.3 (2)	C4—C5—C12—C13	72.90 (16)

C3—C4—C5—C12	−176.31 (13)	C14—N1—C13—O9	168.41 (17)
C2—C1—C6—C5	−1.6 (2)	C14—N1—C13—C12	−15.2 (2)
C8—C1—C6—C5	−179.10 (13)	O8—C12—C13—O9	−40.9 (2)
C4—C5—C6—C1	2.5 (2)	C5—C12—C13—O9	75.12 (18)
C12—C5—C6—C1	177.45 (13)	C15—C12—C13—O9	−161.22 (15)
C6—C1—C8—O4	−3.02 (19)	O8—C12—C13—N1	142.66 (14)
C2—C1—C8—O4	179.41 (12)	C5—C12—C13—N1	−101.29 (15)
C6—C1—C8—C11	114.53 (15)	C15—C12—C13—N1	22.37 (19)
C2—C1—C8—C11	−63.03 (17)	C15—N2—C14—O10	−173.69 (17)
C6—C1—C8—C9	−119.74 (15)	C15—N2—C14—N1	8.6 (2)
C2—C1—C8—C9	62.70 (17)	C13—N1—C14—O10	−178.46 (17)
C10—N3—C9—O5	−170.40 (18)	C13—N1—C14—N2	−0.7 (3)
C10—N3—C9—C8	15.2 (2)	C14—N2—C15—O11	−176.55 (16)
O4—C8—C9—O5	−80.4 (2)	C14—N2—C15—C12	0.8 (2)
C1—C8—C9—O5	38.1 (2)	O8—C12—C15—O11	40.69 (18)
C11—C8—C9—O5	161.66 (17)	C5—C12—C15—O11	−77.98 (17)
O4—C8—C9—N3	93.87 (16)	C13—C12—C15—O11	161.60 (14)
C1—C8—C9—N3	−147.57 (14)	O8—C12—C15—N2	−136.70 (13)
C11—C8—C9—N3	−24.05 (19)	C5—C12—C15—N2	104.63 (14)
C9—N3—C10—O6	177.74 (16)	C13—C12—C15—N2	−15.78 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O1*W*^{i}	0.81 (3)	1.97 (2)	2.6935 (18)	148 (2)
O3—H3*O*···O2	0.75 (3)	2.41 (2)	2.7788 (16)	112 (2)
O3—H3*O*···O2*W*^{ii}	0.75 (3)	2.12 (3)	2.7849 (18)	147 (2)
O4—H4*O*···O9^{iii}	0.83 (2)	1.93 (2)	2.7520 (16)	168 (2)
O8—H8*O*···O6^{iv}	0.87 (3)	2.13 (2)	2.8495 (16)	140 (2)
O8—H8*O*···O4*W*^{v}	0.87 (3)	2.63 (3)	3.2504 (19)	129 (2)
N1—H1*N*···O2*W*	0.92 (2)	1.97 (2)	2.8746 (19)	169 (2)
N2—H2*N*···O1*W*^{vi}	0.89 (2)	1.92 (2)	2.8023 (18)	170.2 (18)
N3—H3*N*···O3*W*^{vii}	0.82 (3)	2.00 (3)	2.8026 (19)	167 (2)
N4—H4*N*···O4*W*^{vii}	0.82 (2)	2.13 (2)	2.9134 (19)	158 (2)
O1*W*—H11*W*···O10^{ii}	0.87 (2)	1.97 (2)	2.8006 (18)	161 (3)
O1*W*—H21*W*···O5*W*	0.90 (2)	1.77 (2)	2.651 (3)	164 (2)
O2*W*—H12*W*···O5^{viii}	0.85 (2)	2.23 (2)	3.0518 (19)	165 (3)
O2*W*—H22*W*···O4*W*	0.84 (2)	1.98 (2)	2.825 (2)	175 (3)
O3*W*—H13*W*···O7^{vi}	0.86 (2)	2.30 (2)	3.0573 (18)	147 (3)
O3*W*—H13*W*···O11	0.86 (2)	2.44 (2)	3.0292 (19)	126 (3)
O3*W*—H23*W*···O4^{ix}	0.83 (2)	2.10 (2)	2.9303 (18)	178 (3)
O4*W*—H14*W*···O3*W*^{v}	0.84 (2)	1.97 (2)	2.814 (2)	178 (3)
O4*W*—H24*W*···O11^{viii}	0.83 (2)	2.08 (2)	2.8937 (18)	168 (3)
O5*W*—H15*W*···O9	0.84	2.34	3.151 (3)	164
O5*W*—H25*W*···O7	0.87	2.21	2.918 (3)	139
C7—H7*B*···O7^{i}	0.96	2.63	3.501 (2)	151

C7—H7*B*···O11^{x}	0.96	2.59	3.242 (2)	125
C7—H7*C*···O10^{ii}	0.96	2.54	3.458 (2)	159

Symmetry codes: (i) −*x*, −*y*, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*, −*y*, −*z*; (iv) *x*+1, *y*+1, *z*; (v) −*x*+1, −*y*+1, −*z*; (vi) *x*, *y*+1, *z*; (vii) *x*−1, *y*−1, *z*; (viii) *x*+1, *y*, *z*; (ix) −*x*, −*y*+1, −*z*; (x) −*x*, −*y*+1, −*z*+1.