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Bis(piperazinediium) benzene-1,2,4,5-tetracarboxylate hexahydrate

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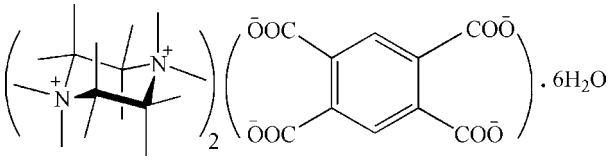
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; H-atom completeness 90%; disorder in solvent or counterion; R factor = 0.059; wR factor = 0.160; data-to-parameter ratio = 18.1.

The title compound, $2C_4H_{12}N_2^{2+}\cdot C_{10}H_2O_8^{4-}\cdot 6H_2O$ or $(pipzH_2)_2(btc)\cdot 6H_2O$, was formed from the reaction between benzene-1,2,4,5-tetracarboxylic acid ($btcH_4$) as a proton donor and piperazine (pipz) as a proton acceptor. A variety of O—H···O, N—H···O and C—H···O hydrogen bonds, as well as C—H···π interactions, are present in the crystal structure. Two water O atoms are each disordered over two positions; for both the site occupany factors are *ca* 0.66 and 0.34.

Related literature

For related literature, see: Aghabozorg *et al.* (2006, 2007); Arora & Pedireddi (2003); Biradha & Zaworotko (1998).



Experimental

Crystal data

$2C_4H_{12}N_2^{2+}\cdot C_{10}H_2O_8^{4-}\cdot 6H_2O$
M_r = 534.52
Triclinic, $P\overline{1}$
a = 6.7420 (4) Å
b = 12.4636 (7) Å
c = 16.0100 (9) Å
α = 99.0920 (10)°
β = 90.3470 (10)°
γ = 105.5280 (10)°
V = 1278.27 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 100 (2) K
0.23 × 0.21 × 0.17 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.970, T_{max} = 0.982
13995 measured reflections
5839 independent reflections
4805 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.159
S = 1.02
5839 reflections
323 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*C*···O5^{i}	0.92	1.74	2.642 (2)	166
N1—H1*D*···O7^{ii}	0.92	1.84	2.763 (2)	178
N2—H2*C*···O1^{iii}	0.92	1.82	2.723 (2)	165
N2—H2*D*···O4	0.92	1.72	2.635 (2)	179
N3—H3*C*···O2^{iii}	0.92	1.90	2.787 (2)	163
N3—H3*D*···O6	0.92	1.92	2.690 (2)	141
N4—H4*C*···O8^{iv}	0.92	1.85	2.753 (2)	168
N4—H4*D*···O3	0.92	2.00	2.748 (2)	138
O1*S*—H1*SA*···O5*SA*	0.82	2.02	2.837 (2)	172
O1*S*—H1*SA*···O5*SA*	0.82	2.02	2.837 (2)	172
O1*S*—H1*SB*···O2^{v}	0.82	1.95	2.763 (2)	172
O2*S*—H2*SA*···O4*S*^{iii}	0.82	2.04	2.839 (2)	165
O2*S*—H2*SB*···O8^{vi}	0.82	2.05	2.835 (2)	160
O3*S*—H3*SA*···O2*S*	0.82	1.90	2.722 (2)	176
O3*S*—H3*SB*···O5^{ii}	0.82	2.00	2.817 (2)	171
O4*S*—H4*SA*···O1	0.82	1.95	2.772 (2)	175
O4*S*—H4*SB*···O3*S*	0.82	1.95	2.764 (2)	170
C5—H5*A*···O6*SA*	0.99	2.50	3.288 (4)	136
C5—H5*B*···O7^{iv}	0.99	2.35	3.272 (3)	154
C7—H7*A*···O1^{iii}	0.99	2.48	3.414 (3)	156
C8—H8*B*···O4*S*^{iii}	0.99	2.51	3.299 (3)	137
C4—H4*B*···*Cg*1^{ii}	0.99	2.64	3.518 (2)	148
C4—H4*B*···*Cg*1^{vi}	0.99	2.64	3.518 (2)	148

Symmetry codes: (i) $x-1, y-1, z$; (ii) $x, y-1, z$; (iii) $x-1, y, z$; (iv) $x+1, y, z$; (v) $-x+2, -y+1, -z+1$; (vi) $-x, -y+1, -z+1$. *Cg*1 is the centroid of the C14,C15,C16,C14′,C15′,C16′ benzene ring.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2674).

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Acta Cryst. (2008). E**64**, o740 [doi:10.1107/S1600536808007332]

Bis(piperazinediium) benzene-1,2,4,5-tetracarboxylate hexahydrate

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S1. Comment

Continuing the path to synthesize proton transfer compounds, our team works have recently been focused on forming ion pairs between benzene-1,2,4,5-tetracarboxylic acid and various organic bases such as propane-1,3-diamine (Aghabozorg *et al.*, 2007) and 1,10-phenanthroline (Aghabozorg *et al.*, 2006). Due to its flat and symmetric structure and four proton donor sites, benzene-1,2,4,5-tetracarboxylic acid has a potential of constructing a supramolecular network. Supramolecular assemblies of 1,2,4,5-benzenetetracarboxylic acid, with aza donor molecules such as 1,10-phenanthroline, 1,7-phenanthroline, phenazine, 4-(*N*,*N*-dimethylamino)pyridine, 1,2-bis(4-pyridyl)ethene, and 1,2-bis(4-pyridyl)ethane have been synthesized and characterized by single-crystal X-ray diffraction methods (Arora *et al.*, 2003). Among the known structures, cyclic network mediated supramolecular assemblies of benzene-1,2,4,5-tetracarboxylic acid with pyridine and some of its derivatives is quite significant (Biradha *et al.*, 1998). The title compound has a structure constituted of one fully deprotonated benzene-1,2,4,5-tetracarboxylic acid unit, two doubly protonated piperazine units and six water molecules, two of which are disordered.

Various hydrogen bonds are formed between the named fragments, the water molecules are hydrogen bonded to each other and to carboxylate groups by O—H···O bonds, piperazinium ions are linked to carboxylate groups by N—H···O bonds, also the carbon atoms of piperaziniedium ion have C—H···O hydrogen bonds to oxygen atoms of water molecules and carboxyl groups. It is notable that the shortest hydrogen bond N2—H2D···O4 has the least deviation *i.e.* 1° from linearity. As shown in Fig. 2, in the cell packing there are six water molecules surrounded by cationic and anionic fragments. So if the structure expanded and the layers appeared, it can be seen a channel in which water molecules are trapped. This is previously observed for ion pairs of the tetraacid (Arora *et al.*, 2003), in which the three-dimensional arrangement of the layers are stacked such that the cavities align to yield channels. It appears that the size and direction of water molecules plays an important role in constructing of channel structures in the supramolecular assemblies of acid.

As shown in Fig. 3, there are C—H···π interactions between C4—H4B bond of piperazinium ion and two benzene rings containing C14, C15 and C16 atoms with different symmetry codes [(x, y - 1, z), (-x, -y + 1, 1 - z)] for which the C—H···π distance and angle are 3.518 (2) Å and 148°, respectively.

Finally in Fig. 4, it can be seen how ribbons of constituents of the compound are arranged.

S2. Experimental

For synthesizing the title compoud, a solution of 2540 mg (10 mmol) benzene-1,2,4,5-tetracarboxylic acid in 10 ml tetrahydrofuran and another solution of 860 mg (10 mmol) of piperazine in 10 ml of the same solvent were prepared and mixed. By heating, a white precipitate was obtained. The colorless prisms of the compound were obtained by recrystallization from water solution.

S3. Refinement

The hydrogen atoms of NH_2 groups and water molecules (with exception of disordered ones) were found in difference Fourier synthesis. The positions of the H atoms bonded to C were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with with the U_{iso}(H) parameters equal to 1.2 U_{eq}(C), 1.2 U_{eq}(N) and 1.2 U_{eq}(O) where U(C), U(N), U(O) are respectively the equivalent thermal parameters of the carbon, nitrogen and oxygen atoms to which corresponding H atoms are bonded.

Two water molecules are disordered over two positions with site occupation factor ratios of 0.663 (9)/0.337 (9) and 0.666 (6)/0.334 (6). It was impossible to locate hydrogen atoms on disordered water molecules.

There are two residual electron density peaks of 2.20 and 1.84 e Å^{-3} at 1.05 and 0.78%A near O6SB and O6SA atoms, respectively. It was impossible to refine these peaks as disordered water molecules.

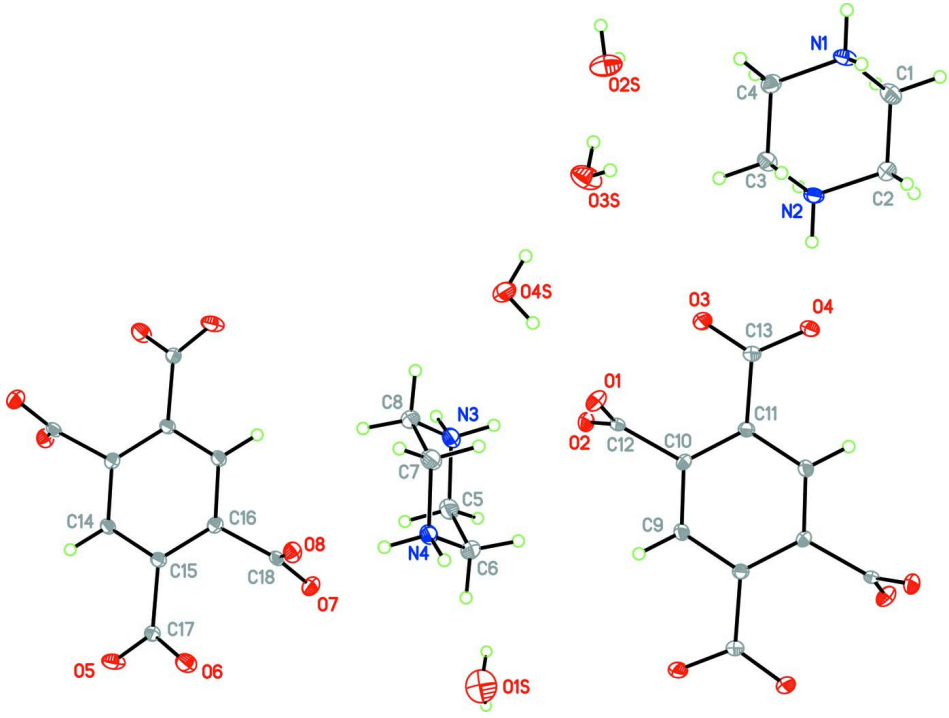

Figure 1

Molecular structure of the ion pair $(C_4H_{12}N_2)_2^{4+}(C_{10}H_2O_8)^{4-}.6H_2O$. Displacement ellipsoids are drawn at 50% probability level.

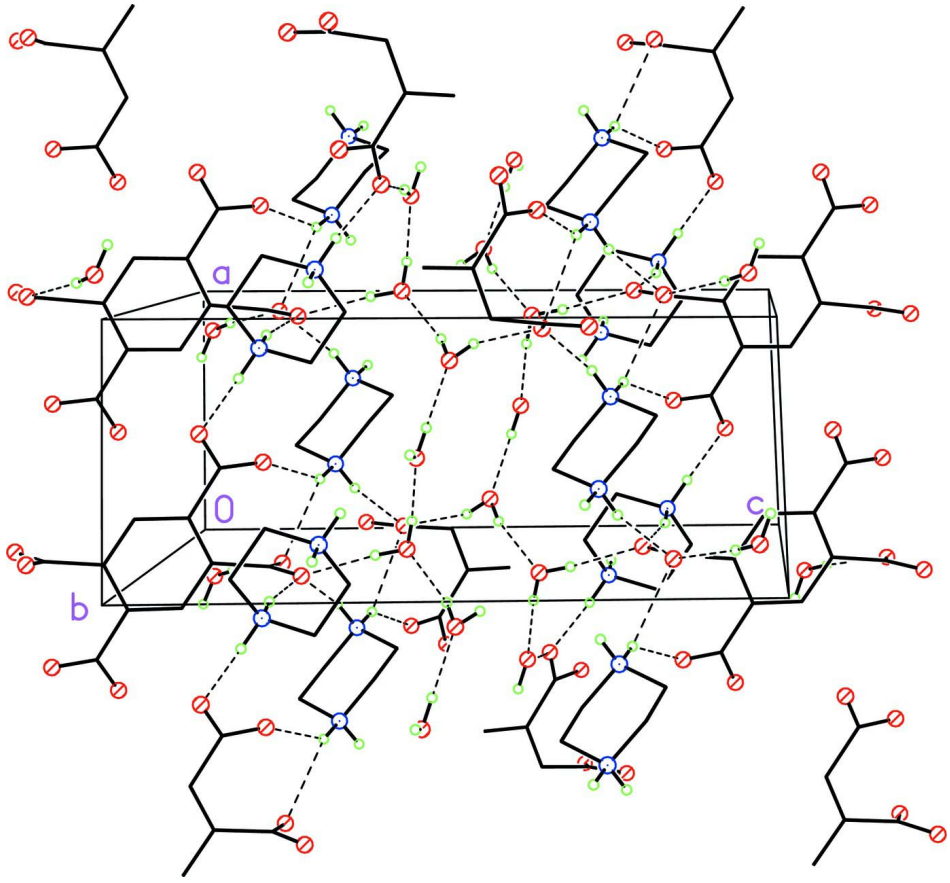

Figure 2

Unit cell packing of the title compound, hydrogen bonds are shown as dashed lines and disordered atoms are omitted.

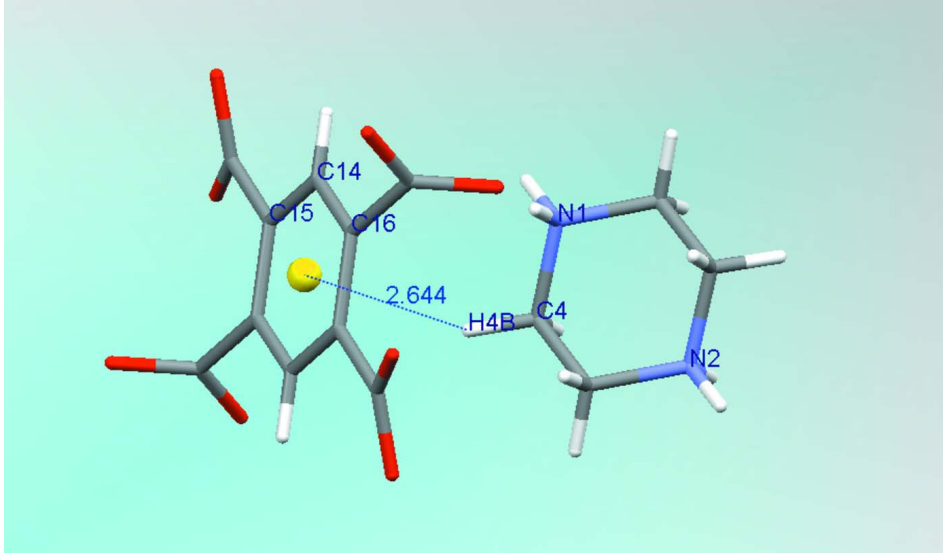

Figure 3

The C—H···π interaction between C4—H4B and benzene ring, distance from the H atom to the ring centroid is drawn as a dashed line.

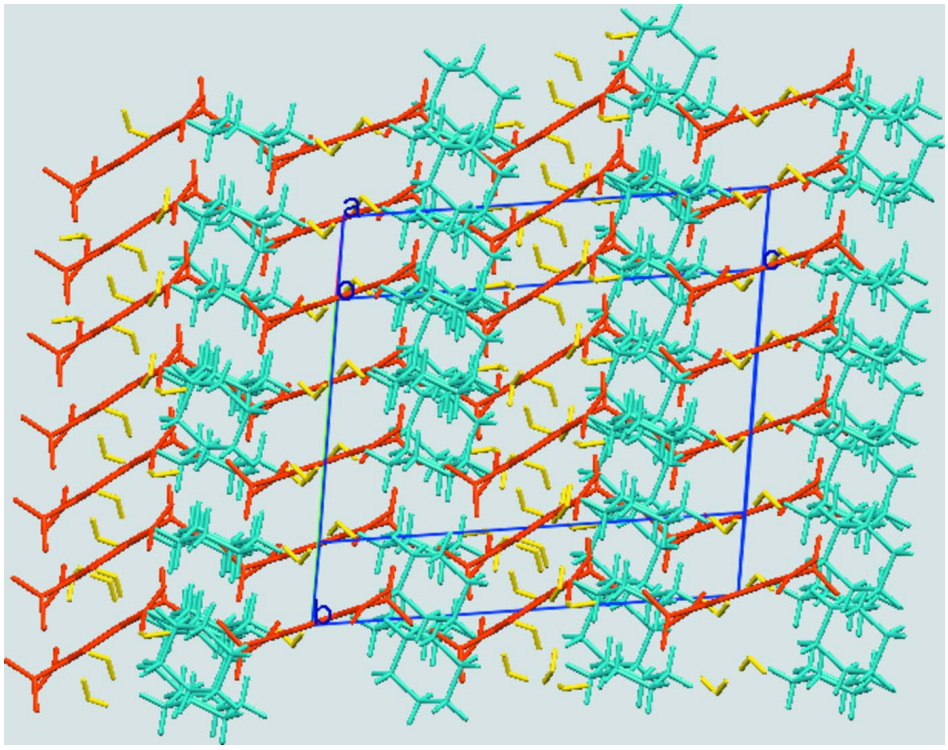

Figure 4

Crystal packing of the title compound, Anions, cations and water molecules are shown in different colours.

Bis(piperazinediium) benzene-1,2,4,5-tetracarboxylate hexahydrate

Crystal data

$2C_4H_{12}N_2^{2+}\cdot C_{10}H_2O_8^{4-}\cdot 6H_2O$
$M_r = 534.52$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.7420\ (4)$ Å
$b = 12.4636\ (7)$ Å
$c = 16.0100\ (9)$ Å
$\alpha = 99.092\ (1)°$
$\beta = 90.347\ (1)°$
$\gamma = 105.528\ (1)°$
$V = 1278.27\ (13)$ Å^3
$Z = 2$
$F(000) = 572$
$D_x = 1.389$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 614 reflections
$\theta = 3–29°$
$\mu = 0.12$ mm^{-1}
$T = 100$ K
Prism, colorless
0.23 × 0.21 × 0.17 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.970$, $T_{max} = 0.982$
13995 measured reflections
5839 independent reflections
4805 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -8\rightarrow8$
$k = -16\rightarrow16$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.159$
$S = 1.02$
5839 reflections
323 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.20$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	−0.1642 (3)	0.13752 (14)	0.70314 (11)	0.0148 (4)	
H1C	−0.2812	0.1173	0.6680	0.018*	
H1D	−0.1227	0.0735	0.7058	0.018*	
N2	0.1462 (3)	0.30353 (14)	0.81088 (11)	0.0141 (3)	
H2C	0.1056	0.3677	0.8077	0.017*	
H2D	0.2632	0.3239	0.8460	0.017*	
C1	−0.2126 (3)	0.18509 (18)	0.78933 (14)	0.0179 (4)	
H1A	−0.3195	0.1274	0.8122	0.022*	
H1B	−0.2674	0.2506	0.7862	0.022*	
C2	−0.0202 (3)	0.22196 (18)	0.84771 (13)	0.0163 (4)	
H2A	−0.0515	0.2580	0.9039	0.020*	
H2B	0.0267	0.1552	0.8555	0.020*	
C3	0.1944 (3)	0.25478 (18)	0.72488 (13)	0.0158 (4)	
H3A	0.2459	0.1882	0.7282	0.019*	
H3B	0.3032	0.3114	0.7018	0.019*	
C4	0.0012 (3)	0.22030 (17)	0.66729 (13)	0.0150 (4)	
H4A	−0.0454	0.2877	0.6615	0.018*	
H4B	0.0312	0.1860	0.6103	0.018*	
N3	0.3335 (3)	0.76396 (16)	0.71554 (12)	0.0178 (4)	
H3C	0.2266	0.7216	0.7419	0.021*	
H3D	0.2885	0.8194	0.6960	0.021*	
N4	0.6573 (3)	0.65653 (16)	0.73462 (11)	0.0171 (4)	
H4C	0.7631	0.6995	0.7082	0.021*	
H4D	0.7039	0.6016	0.7541	0.021*	
C5	0.5109 (3)	0.81764 (19)	0.77813 (14)	0.0194 (4)	

H5A	0.4648	0.8619	0.8274	0.023*	
H5B	0.6199	0.8701	0.7517	0.023*	
C6	0.5976 (3)	0.7297 (2)	0.80781 (14)	0.0201 (4)	
H6A	0.7200	0.7675	0.8465	0.024*	
H6B	0.4933	0.6823	0.8396	0.024*	
C7	0.4797 (3)	0.60208 (18)	0.67239 (14)	0.0185 (4)	
H7A	0.3712	0.5496	0.6991	0.022*	
H7B	0.5257	0.5577	0.6232	0.022*	
C8	0.3916 (3)	0.69016 (19)	0.64249 (14)	0.0185 (4)	
H8A	0.4950	0.7371	0.6101	0.022*	
H8B	0.2684	0.6521	0.6043	0.022*	
O1	1.0470 (2)	0.48871 (13)	0.77274 (9)	0.0169 (3)	
O2	1.0471 (2)	0.66537 (12)	0.82508 (9)	0.0148 (3)	
O3	0.6122 (2)	0.48861 (14)	0.83124 (10)	0.0204 (3)	
O4	0.4782 (2)	0.36214 (14)	0.91348 (10)	0.0233 (4)	
C9	1.1854 (3)	0.55782 (16)	0.97230 (12)	0.0115 (4)	
H9A	1.3129	0.5973	0.9530	0.014*	
C10	1.0075 (3)	0.53211 (15)	0.91992 (12)	0.0100 (4)	
C11	0.8194 (3)	0.47309 (16)	0.94750 (12)	0.0109 (4)	
C12	1.0312 (3)	0.56437 (16)	0.83241 (12)	0.0113 (4)	
C13	0.6225 (3)	0.44016 (17)	0.89245 (12)	0.0131 (4)	
O5	0.5182 (2)	1.11219 (12)	0.59735 (10)	0.0182 (3)	
O6	0.3881 (2)	0.94917 (13)	0.64244 (10)	0.0197 (3)	
O7	−0.0392 (2)	0.94673 (12)	0.71610 (9)	0.0152 (3)	
O8	−0.0657 (2)	0.77912 (12)	0.63610 (9)	0.0145 (3)	
C14	0.1873 (3)	1.06607 (16)	0.47969 (12)	0.0108 (4)	
H14A	0.3161	1.1113	0.4657	0.013*	
C15	0.1797 (3)	1.00875 (16)	0.54829 (12)	0.0105 (4)	
C16	−0.0101 (3)	0.94157 (16)	0.56864 (12)	0.0104 (4)	
C17	0.3760 (3)	1.02308 (17)	0.60026 (12)	0.0121 (4)	
C18	−0.0362 (3)	0.88465 (17)	0.64644 (12)	0.0116 (4)	
O1S	0.8540 (4)	0.15919 (16)	0.03938 (14)	0.0422 (5)	
H1SA	0.7441	0.1645	0.0207	0.051*	
H1SB	0.8898	0.2148	0.0766	0.051*	
O2S	0.2052 (3)	0.36605 (15)	0.52006 (11)	0.0276 (4)	
H2SA	0.1274	0.4049	0.5358	0.033*	
H2SB	0.1364	0.3266	0.4783	0.033*	
O3S	0.5686 (3)	0.33661 (14)	0.57282 (12)	0.0276 (4)	
H3SA	0.4566	0.3418	0.5565	0.033*	
H3SB	0.5433	0.2694	0.5763	0.033*	
O4S	0.9503 (3)	0.49208 (14)	0.60483 (10)	0.0234 (4)	
H4SA	0.9722	0.4923	0.6553	0.028*	
H4SB	0.8329	0.4518	0.5922	0.028*	
O5SA	0.4646 (6)	0.1816 (3)	−0.0094 (3)	0.0453 (12)*	0.663 (9)
O6SA	0.2705 (5)	1.0084 (3)	0.8494 (2)	0.0431 (10)*	0.666 (6)
O5SB	0.5326 (8)	0.1596 (4)	−0.0451 (4)	0.0246 (18)*	0.337 (9)
O6SB	0.8058 (10)	0.9423 (5)	0.9689 (4)	0.0419 (19)*	0.334 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0127 (8)	0.0119 (8)	0.0179 (9)	0.0019 (6)	−0.0054 (6)	0.0000 (6)
N2	0.0115 (8)	0.0146 (8)	0.0145 (8)	0.0011 (6)	−0.0032 (6)	0.0012 (6)
C1	0.0127 (9)	0.0178 (10)	0.0215 (10)	0.0020 (8)	0.0012 (8)	0.0017 (8)
C2	0.0164 (10)	0.0172 (10)	0.0144 (9)	0.0025 (8)	−0.0003 (8)	0.0038 (8)
C3	0.0131 (9)	0.0173 (10)	0.0163 (10)	0.0030 (8)	0.0007 (7)	0.0023 (8)
C4	0.0180 (10)	0.0130 (9)	0.0135 (9)	0.0035 (8)	−0.0020 (7)	0.0019 (7)
N3	0.0121 (8)	0.0212 (9)	0.0236 (9)	0.0048 (7)	0.0015 (7)	0.0137 (7)
N4	0.0123 (8)	0.0236 (9)	0.0200 (9)	0.0068 (7)	0.0031 (7)	0.0133 (7)
C5	0.0163 (10)	0.0213 (11)	0.0205 (10)	0.0024 (8)	0.0016 (8)	0.0082 (8)
C6	0.0148 (10)	0.0303 (12)	0.0172 (10)	0.0063 (9)	−0.0003 (8)	0.0094 (9)
C7	0.0141 (10)	0.0201 (10)	0.0224 (11)	0.0034 (8)	0.0007 (8)	0.0088 (8)
C8	0.0143 (10)	0.0240 (11)	0.0184 (10)	0.0032 (8)	−0.0008 (8)	0.0103 (8)
O1	0.0226 (8)	0.0186 (7)	0.0100 (7)	0.0064 (6)	−0.0002 (6)	0.0027 (5)
O2	0.0152 (7)	0.0153 (7)	0.0152 (7)	0.0032 (5)	0.0020 (5)	0.0080 (5)
O3	0.0152 (7)	0.0261 (8)	0.0202 (8)	0.0006 (6)	−0.0046 (6)	0.0138 (6)
O4	0.0137 (7)	0.0287 (9)	0.0237 (8)	−0.0066 (6)	−0.0078 (6)	0.0154 (7)
C9	0.0104 (9)	0.0118 (9)	0.0125 (9)	0.0025 (7)	0.0007 (7)	0.0037 (7)
C10	0.0117 (9)	0.0095 (8)	0.0095 (8)	0.0032 (7)	0.0007 (7)	0.0031 (7)
C11	0.0110 (9)	0.0102 (8)	0.0117 (9)	0.0025 (7)	−0.0009 (7)	0.0027 (7)
C12	0.0064 (8)	0.0153 (9)	0.0117 (9)	0.0010 (7)	−0.0013 (7)	0.0042 (7)
C13	0.0109 (9)	0.0155 (9)	0.0127 (9)	0.0026 (7)	−0.0007 (7)	0.0038 (7)
O5	0.0132 (7)	0.0163 (7)	0.0238 (8)	−0.0008 (6)	−0.0068 (6)	0.0082 (6)
O6	0.0133 (7)	0.0232 (8)	0.0260 (8)	0.0039 (6)	−0.0004 (6)	0.0162 (6)
O7	0.0181 (7)	0.0159 (7)	0.0118 (7)	0.0040 (6)	0.0007 (5)	0.0042 (5)
O8	0.0153 (7)	0.0127 (7)	0.0169 (7)	0.0040 (5)	0.0023 (5)	0.0066 (5)
C14	0.0093 (8)	0.0107 (8)	0.0126 (9)	0.0022 (7)	0.0010 (7)	0.0034 (7)
C15	0.0092 (9)	0.0105 (8)	0.0121 (9)	0.0028 (7)	−0.0002 (7)	0.0023 (7)
C16	0.0129 (9)	0.0095 (8)	0.0098 (8)	0.0041 (7)	0.0009 (7)	0.0023 (7)
C17	0.0109 (9)	0.0157 (9)	0.0107 (9)	0.0049 (7)	0.0010 (7)	0.0033 (7)
C18	0.0066 (8)	0.0154 (9)	0.0142 (9)	0.0027 (7)	0.0003 (7)	0.0073 (7)
O1S	0.0552 (13)	0.0269 (10)	0.0427 (12)	0.0156 (9)	0.0075 (10)	−0.0071 (8)
O2S	0.0277 (9)	0.0299 (9)	0.0262 (9)	0.0132 (7)	−0.0097 (7)	−0.0012 (7)
O3S	0.0208 (8)	0.0188 (8)	0.0422 (10)	0.0022 (6)	−0.0072 (7)	0.0076 (7)
O4S	0.0250 (8)	0.0263 (8)	0.0159 (7)	−0.0003 (7)	−0.0050 (6)	0.0069 (6)

Geometric parameters (Å, º)

N1—C1	1.488 (3)	C7—H7B	0.9900
N1—C4	1.489 (3)	C8—H8A	0.9900
N1—H1C	0.9200	C8—H8B	0.9900
N1—H1D	0.9200	O1—C12	1.258 (2)
N2—C3	1.489 (3)	O2—C12	1.259 (2)
N2—C2	1.492 (3)	O3—C13	1.241 (2)
N2—H2C	0.9200	O4—C13	1.268 (2)
N2—H2D	0.9200	C9—C10	1.393 (3)

C1—C2	1.516 (3)	C9—C11^{i}	1.396 (3)
C1—H1A	0.9900	C9—H9A	0.9500
C1—H1B	0.9900	C10—C11	1.398 (3)
C2—H2A	0.9900	C10—C12	1.515 (3)
C2—H2B	0.9900	C11—C9^{i}	1.396 (3)
C3—C4	1.514 (3)	C11—C13	1.512 (3)
C3—H3A	0.9900	O5—C17	1.266 (2)
C3—H3B	0.9900	O6—C17	1.244 (2)
C4—H4A	0.9900	O7—C18	1.256 (2)
C4—H4B	0.9900	O8—C18	1.260 (2)
N3—C8	1.492 (3)	C14—C16^{ii}	1.392 (3)
N3—C5	1.493 (3)	C14—C15	1.396 (3)
N3—H3C	0.9200	C14—H14A	0.9500
N3—H3D	0.9200	C15—C16	1.401 (3)
N4—C7	1.491 (3)	C15—C17	1.513 (3)
N4—C6	1.494 (3)	C16—C14^{ii}	1.392 (3)
N4—H4C	0.9200	C16—C18	1.517 (3)
N4—H4D	0.9200	O1S—H1SA	0.8201
C5—C6	1.508 (3)	O1S—H1SB	0.8200
C5—H5A	0.9900	O2S—H2SA	0.8197
C5—H5B	0.9900	O2S—H2SB	0.8206
C6—H6A	0.9900	O3S—H3SA	0.8199
C6—H6B	0.9900	O3S—H3SB	0.8201
C7—C8	1.516 (3)	O4S—H4SA	0.8201
C7—H7A	0.9900	O4S—H4SB	0.8201

C1—N1—C4	111.54 (15)	H5A—C5—H5B	108.0
C1—N1—H1C	109.3	N4—C6—C5	111.00 (17)
C4—N1—H1C	109.3	N4—C6—H6A	109.4
C1—N1—H1D	109.3	C5—C6—H6A	109.4
C4—N1—H1D	109.3	N4—C6—H6B	109.4
H1C—N1—H1D	108.0	C5—C6—H6B	109.4
C3—N2—C2	111.88 (16)	H6A—C6—H6B	108.0
C3—N2—H2C	109.2	N4—C7—C8	110.76 (18)
C2—N2—H2C	109.2	N4—C7—H7A	109.5
C3—N2—H2D	109.2	C8—C7—H7A	109.5
C2—N2—H2D	109.2	N4—C7—H7B	109.5
H2C—N2—H2D	107.9	C8—C7—H7B	109.5
N1—C1—C2	110.14 (17)	H7A—C7—H7B	108.1
N1—C1—H1A	109.6	N3—C8—C7	111.08 (17)
C2—C1—H1A	109.6	N3—C8—H8A	109.4
N1—C1—H1B	109.6	C7—C8—H8A	109.4
C2—C1—H1B	109.6	N3—C8—H8B	109.4
H1A—C1—H1B	108.1	C7—C8—H8B	109.4
N2—C2—C1	109.93 (16)	H8A—C8—H8B	108.0
N2—C2—H2A	109.7	C10—C9—C11^{i}	121.56 (18)
C1—C2—H2A	109.7	C10—C9—H9A	119.2
N2—C2—H2B	109.7	C11^{i}—C9—H9A	119.2

C1—C2—H2B	109.7	C9—C10—C11	119.63 (17)
H2A—C2—H2B	108.2	C9—C10—C12	117.35 (17)
N2—C3—C4	109.19 (16)	C11—C10—C12	122.92 (17)
N2—C3—H3A	109.8	C9^{i}—C11—C10	118.81 (17)
C4—C3—H3A	109.8	C9^{i}—C11—C13	119.25 (17)
N2—C3—H3B	109.8	C10—C11—C13	121.93 (17)
C4—C3—H3B	109.8	O1—C12—O2	124.58 (18)
H3A—C3—H3B	108.3	O1—C12—C10	116.78 (17)
N1—C4—C3	109.85 (16)	O2—C12—C10	118.47 (17)
N1—C4—H4A	109.7	O3—C13—O4	124.84 (18)
C3—C4—H4A	109.7	O3—C13—C11	119.64 (17)
N1—C4—H4B	109.7	O4—C13—C11	115.51 (17)
C3—C4—H4B	109.7	C16^{ii}—C14—C15	121.44 (17)
H4A—C4—H4B	108.2	C16^{ii}—C14—H14A	119.3
C8—N3—C5	111.59 (16)	C15—C14—H14A	119.3
C8—N3—H3C	109.3	C14—C15—C16	119.25 (17)
C5—N3—H3C	109.3	C14—C15—C17	119.16 (17)
C8—N3—H3D	109.3	C16—C15—C17	121.57 (17)
C5—N3—H3D	109.3	C14^{ii}—C16—C15	119.31 (17)
H3C—N3—H3D	108.0	C14^{ii}—C16—C18	117.57 (17)
C7—N4—C6	111.34 (16)	C15—C16—C18	122.87 (17)
C7—N4—H4C	109.4	O6—C17—O5	124.55 (18)
C6—N4—H4C	109.4	O6—C17—C15	119.42 (17)
C7—N4—H4D	109.4	O5—C17—C15	116.03 (16)
C6—N4—H4D	109.4	O7—C18—O8	125.13 (18)
H4C—N4—H4D	108.0	O7—C18—C16	116.50 (17)
N3—C5—C6	110.95 (18)	O8—C18—C16	118.21 (17)
N3—C5—H5A	109.4	H1SA—O1S—H1SB	102.8
C6—C5—H5A	109.4	H2SA—O2S—H2SB	98.8
N3—C5—H5B	109.4	H3SA—O3S—H3SB	102.2
C6—C5—H5B	109.4	H4SA—O4S—H4SB	106.6

C4—N1—C1—C2	−57.4 (2)	C9—C10—C12—O2	−79.7 (2)
C3—N2—C2—C1	−57.4 (2)	C11—C10—C12—O2	103.9 (2)
N1—C1—C2—N2	55.7 (2)	C9^{i}—C11—C13—O3	162.78 (19)
C2—N2—C3—C4	58.4 (2)	C10—C11—C13—O3	−18.3 (3)
C1—N1—C4—C3	58.7 (2)	C9^{i}—C11—C13—O4	−17.7 (3)
N2—C3—C4—N1	−57.9 (2)	C10—C11—C13—O4	161.22 (19)
C8—N3—C5—C6	−55.5 (2)	C16^{ii}—C14—C15—C16	0.4 (3)
C7—N4—C6—C5	−56.4 (2)	C16^{ii}—C14—C15—C17	−178.07 (17)
N3—C5—C6—N4	55.7 (2)	C14—C15—C16—C14^{ii}	−0.4 (3)
C6—N4—C7—C8	56.0 (2)	C17—C15—C16—C14^{ii}	178.04 (17)
C5—N3—C8—C7	55.3 (2)	C14—C15—C16—C18	−174.45 (18)
N4—C7—C8—N3	−55.3 (2)	C17—C15—C16—C18	3.9 (3)
C11^{i}—C9—C10—C11	−0.6 (3)	C14—C15—C17—O6	−157.34 (19)
C11^{i}—C9—C10—C12	−177.06 (17)	C16—C15—C17—O6	24.3 (3)
C9—C10—C11—C9^{i}	0.6 (3)	C14—C15—C17—O5	22.9 (3)
C12—C10—C11—C9^{i}	176.84 (17)	C16—C15—C17—O5	−155.48 (18)

C9—C10—C11—C13	−178.33 (17)	C14^{ii}—C16—C18—O7	−97.7 (2)
C12—C10—C11—C13	−2.1 (3)	C15—C16—C18—O7	76.5 (2)
C9—C10—C12—O1	95.7 (2)	C14^{ii}—C16—C18—O8	78.0 (2)
C11—C10—C12—O1	−80.6 (2)	C15—C16—C18—O8	−107.8 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···O5^{iii}	0.92	1.74	2.642 (2)	166
N1—H1*D*···O7^{iv}	0.92	1.84	2.763 (2)	178
N2—H2*C*···O1^{v}	0.92	1.82	2.723 (2)	165
N2—H2*D*···O4	0.92	1.72	2.635 (2)	179
N3—H3*C*···O2^{v}	0.92	1.90	2.787 (2)	163
N3—H3*D*···O6	0.92	1.92	2.690 (2)	141
N4—H4*C*···O8^{vi}	0.92	1.85	2.753 (2)	168
N4—H4*D*···O3	0.92	2.00	2.748 (2)	138
O1*S*—H1*SA*···O5*SA*	0.82	2.02	2.837 (2)	172
O1*S*—H1*SA*···O5*SA*	0.82	2.02	2.837 (2)	172
O1*S*—H1*SB*···O2^{vii}	0.82	1.95	2.763 (2)	172
O2*S*—H2*SA*···O4*S*^{v}	0.82	2.04	2.839 (2)	165
O2*S*—H2*SB*···O8^{viii}	0.82	2.05	2.835 (2)	160
O3*S*—H3*SA*···O2*S*	0.82	1.90	2.722 (2)	176
O3*S*—H3*SB*···O5^{iv}	0.82	2.00	2.817 (2)	171
O4*S*—H4*SA*···O1	0.82	1.95	2.772 (2)	175
O4*S*—H4*SB*···O3*S*	0.82	1.95	2.764 (2)	170
C5—H5*A*···O6*SA*	0.99	2.50	3.288 (4)	136
C5—H5*B*···O7^{vi}	0.99	2.35	3.272 (3)	154
C7—H7*A*···O1^{v}	0.99	2.48	3.414 (3)	156
C8—H8*B*···O4*S*^{v}	0.99	2.51	3.299 (3)	137
C4—H4*B*···*Cg*1^{iv}	0.99	2.64	3.518 (2)	148
C4—H4*B*···*Cg*1^{viii}	0.99	2.64	3.518 (2)	148

Symmetry codes: (iii) *x*−1, *y*−1, *z*; (iv) *x*, *y*−1, *z*; (v) *x*−1, *y*, *z*; (vi) *x*+1, *y*, *z*; (vii) −*x*+2, −*y*+1, −*z*+1; (viii) −*x*, −*y*+1, −*z*+1.