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Crystal structure of zwitterionic 3,3′-[1,1′-(butane-1,4-diyl)bis(1*H*-imidazol-3-ium-3,1-diyl)]bis(propane-1-sulfonate) dihydrate

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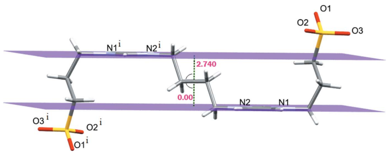
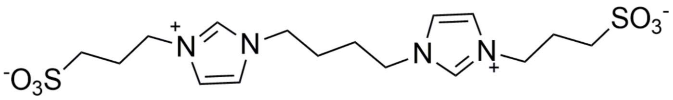
The crystal structure of the title compound, $C_{16}H_{26}N_4O_6S_2{\cdot}2H_2O$, a water-soluble di-*N*-heterocyclic carbene ligand precursor was determined using a single crystal grown by the slow cooling of a hot *N*,*N*-dimethylformamide solution of the compound. The dihydrate crystallizes in the monoclinic space group $P2_1/c$, with half of the zwitterionic molecule and one water molecule of crystallization in the asymmetric unit. The remaining part of the molecule is completed by inversion symmetry. In the molecule, the imidazole ring planes are parallel with a plane-to-plane distance of 2.741 (2) Å. The supramolecular network is consolidated by hydrogen bonds of medium strength between the zwitterionic molecules and the water molecules of crystallization, as well as by π–π stacking interactions between the imidazole rings of neighbouring molecules and C—H···O hydrogen-bonding interactions.



1. Chemical context

Imidazolium salt-based ionic liquids are versatile because of their unique properties and their use as green solvents, replacing volatile or toxic organic solvents (De *et al.*, 2019). Moreover, they are very often used as reaction media, or – the water-immiscible ones – for extraction. X-ray crystallographic studies of several crystalline imidazolium salts have been described. However, examples of zwitterionic imidazolium salts are limited in the literature, and only a few examples of zwitterionic imidazolium sulfonates, with their crystal structures determined, have been reported to date. The introduction of hydrophilic substituents (*e.g.* sulfonate groups) made possible the synthesis of water-soluble metal complexes, and subsequently, a range of catalytic applications (Kohmoto *et al.*, 2012).



Here we report the crystal structure of the title compound, 3,3′-[1,1′-(butane-1,4-diyl)bis(1*H*-imidazol-3-ium-3,1-diyl)]-bis(propane-1-sulfonate) (**1**; Fig. 1), which crystallizes as a

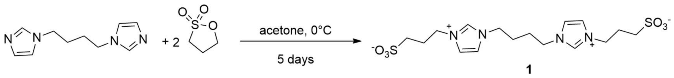


Figure 1
Synthesis scheme of **1**.

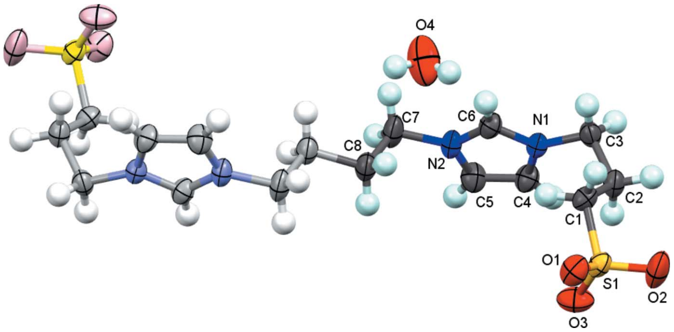


Figure 2
The molecular structure of **1** showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. The asymmetric unit of **1** is given in darker colours, and the symmetry-generated part (symmetry code: $1 - x, -y, -z$) of the molecule is given in lighter colours. The water molecule is also shown.

dihydrate (**1**·$2H_2O$). To the best of our knowledge, this is the first crystal structure determination of an alkylene-bridged di-imidazolium salt with ω-propylsulfonate wingtips. Compound **1** is known from the literature (Liu *et al.*, 2013; Xu *et al.*, 2012; Zeng *et al.*, 2013) and was prepared according to the method described by Papini *et al.* (2009), utilizing the reaction between 1,1′-(butane-1,4-diyl)di-1*H*-imidazole and 1,3-propanesultone (Fig. 1).

2. Structural commentary

The di-*N*-heterocyclic carbene precursor **1** crystallizes as a dihydrate, with one half of the molecule and one water molecule of crystallization being present in the asymmetric unit. The other half of the molecule is generated by the application of inversion symmetry (symmentry operation: $1 - x, -y, -z$). No molecules of the solvent, DMF, from which the crystals were obtained, are built into the lattice.

The zwitterionic molecule of **1** (Fig. 2) is composed of two imidazolium propane sulfonate fragments, which are linked by a butylene bridge. The N1—C6 and N2—C6 bond lengths are 1.327 (3) Å and 1.320 (4) Å, and the N1—C1—N2 angle is 108.9 (2)°. The length of the C2—C3 bond of 1.342 (4) Å indicates that these carbon atoms are sp^2 hybridized. The sulfonate moiety is rigid, with characteristic bond lengths of S1—C1 = 1.773 (3) Å, S1—O1 = 1.446 (2) Å, S1—O2 = 1.450 (2) Å, S1—O3 = 1.453 (2) Å, and angles O1—S1—O2 = 112.16 (14)°, O1—S1—O3 = 111.80 (14)°, and O2—S1—O3 = 112.80 (15)°. As a result of the point group symmetry $\overline{1}$ of the molecule, the imidazole planes are parallel and have a distance of 2.741 (2) Å (Fig. 3) from each other.

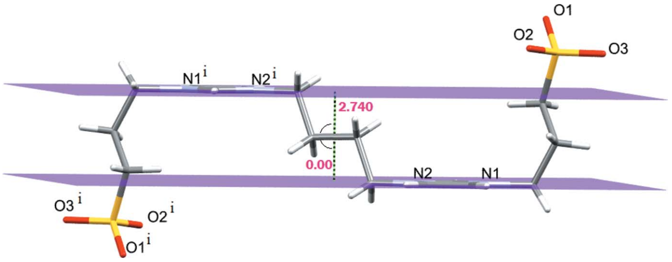


Figure 3
The imidazole ring planes in **1** displayed as capped sticks. The water molecules of crystallization are omitted for clarity [Symmetry code: (i) $1 - x, -y, -z$].

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O2^{i}	0.85	1.97	2.818 (4)	180
O4—H4*B*···O3^{ii}	0.85	2.04	2.821 (4)	152
C4—H4···O1^{iii}	0.93	2.40	3.217 (4)	146
C5—H5···O1^{iv}	0.93	2.40	3.321 (4)	170
C6—H6···O4	0.93	2.39	3.209 (4)	147

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

3. Supramolecular features

The water molecules bridge adjacent zwitterionic molecules through hydrogen bonds of medium strength with sulfonate O atoms as acceptor groups into ribbons aligned parallel to [001]

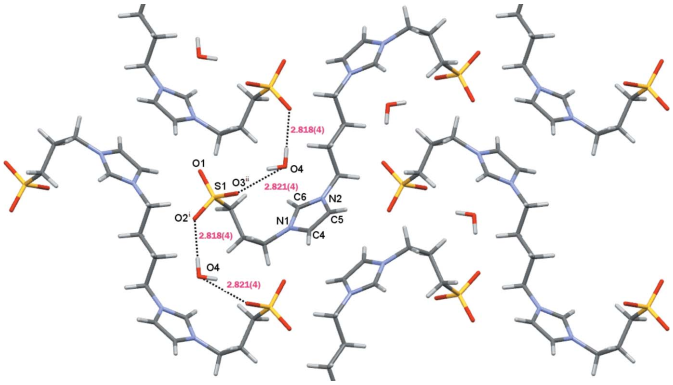


Figure 4
A partial packing diagram of **1**, showing the formation of ribbons through O—H···O hydrogen bonds. [Symmetry codes: (i) $x + 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + 1, y, z$].

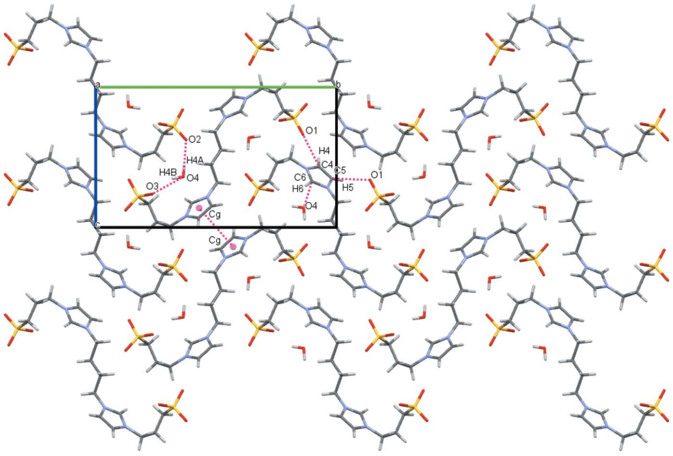


Figure 5
Packing diagram of **1** viewed along the *a* axis, showing selected hydrogen bonds (including weak C—H···O interactions) and π–π stacking interactions (*Cg* is the centroid of the: N1–N6–N2–C4–C5 ring).

(Table 1, Fig. 4). π–π stacking interactions involving the imidazole rings of neighbouring molecules (symmetry operation $2 - x$, $1 - y$, $1 - z$; centroid-to-centroid distance of 3.9541 (17) Å, slippage 1.622 Å, Fig. 5) lead to the formation of supramolecular layers extending parallel to (100). Additional weak C—H$\cdots$O hydrogen bonds (Table 1, Fig. 5) consolidate the three-dimensional network structure.

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.41, May 2020; Groom *et al.*, 2016) revealed no similar crystal structures of di-*N*-heterocyclic carbene ligand precursor molecules where two *N*-ω-sulfonatopropyl-imidazolium units are connected through an α,ω-alkylene bridge. Crystals of similar sulfoalkyl-imidazolium di-NHC precursors containing aromatic linkers have been grown by Kohmoto *et al.* (2012). Crystal structures of gold(III) (refcode: KOGGUK; Hung *et al.*, 2014) and palladium(II) (Asensio *et al.*, 2017) metal complexes with similar ligands with a methylene bridge (Fig. 6, **2**) were also reported.

The Pd complexes [PdCl$_2$(**2**)], refcode: YAVROF, and [Pd(**2**)$_2$], refcode: YAVXAX, crystallize in space group type $P\overline{1}$. In all other above-mentioned cases, the space-group type is $P2_1/c$.

5. Synthesis and crystallization

Compound **1** was synthesized according to the method of Papini *et al.* (2009). 4.4 mmol of 1,3-propanesultone were slowly added to a solution of 2 mmol of 1,1′-(butane-1,4-diyl)di-1*H*-imidazole in 30 ml of acetone at 273 K. Then the mixture was left to warm to room temperature and stirred for 5 d. The solvent was evaporated and the resulting white solid was recrystallized from methanol affording **1** as a white powder (yield: 617 mg, 71%). Analytical data: ^{13}C{^{1}H}-NMR (90 MHz, D$_2$O, 298 K) δ [ppm], 135.6, 122.5, 48.8, 47.8, 47.2, 26.2, 25.0; ESI–MS (CH$_3$OH, positive mode), *m*/*z* observed 435.1359, calculated value for $C_{16}H_{27}N_4O_6S_2$, ([*M* - H]$^+$): 435.1367). For recrystallization, **1** was suspended in DMF and heated to approximately 373 K, then filtered and left overnight to slowly cool down to room temperature. Single crystals, suitable for X-ray analysis, were obtained as colourless prisms after storing the solution in open glass vials in a refrigerator at 278 K. A possible source of water is the employed DMF, which is hygroscopic and easily adsorbs water from a humid atmosphere. The same type of prismatic crystals were also grown from hot water, revealing a very similar unit cell. However, these crystals were of poor quality, and the best $R_{\rm int}$ value was very high, 0.19.

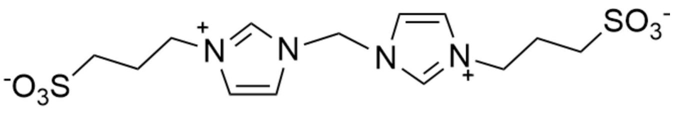


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Figure 6
Structural formula of 3,3′-[1,1′-methylenebis(1*H*-imidazole-3-ium-3,1-diyl)]bis(propane-1-sulfonate (**2**).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{26}N_4O_6S_2{\cdot}2H_2O$
M_r	470.56
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	300
a, b, c (Å)	5.6085 (4), 18.1641 (11), 10.6884 (7)
β (°)	97.860 (4)
V (Å^3)	1078.63 (12)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.69
Crystal size (mm)	0.20 × 0.12 × 0.07
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
$T_{\rm min}$, $T_{\rm max}$	0.702, 0.820
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8276, 1841, 1483
$R_{\rm int}$	0.052
(sin $\theta/\lambda)_{\rm max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.109, 1.11
No. of reflections	1841
No. of parameters	136
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.40, −0.29

Computer programs: *APEX3* and *SAINT* (Bruker 2017), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *WinGX* (Farrugia, 2012), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, and details of data collection and structure refinement are summarized in Table 2. Hydrogen atoms of the zwitterionic molecules were placed at idealized positions and refined using a riding model. The positions of hydrogen atoms of the water molecule were discernible in a difference-Fourier map. They were refined with a fixed bond length of 0.85 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

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supporting information

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Crystal structure of zwitterionic 3,3′-[1,1′-(butane-1,4-diyl)bis(1*H*-imidazol-3-ium-3,1-diyl)]bis(propane-1-sulfonate) dihydrate

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Computing details

Data collection: *APEX3* (Bruker, 2017); cell refinement: *SAINT* (Bruker, 2017); data reduction: *SAINT* (Bruker 2017); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *OLEX2* (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010).

3,3′-[1,1′-(Butane-1,4-diyl)bis(1*H*-imidazol-3-ium-3,1-diyl)]bis(propane-1-sulfonate) dihydrate

Crystal data

$C_{16}H_{26}N_4O_6S_2{\cdot}2H_2O$
$M_r = 470.56$
Monoclinic, $P2_1/c$
$a = 5.6085$ (4) Å
$b = 18.1641$ (11) Å
$c = 10.6884$ (7) Å
$\beta = 97.860$ (4)°
$V = 1078.63$ (12) Å^3
$Z = 2$
$F(000) = 500$
$D_x = 1.449$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 8513 reflections
$\theta = 4.8$–70.0°
$\mu = 2.69$ mm^{-1}
$T = 300$ K
Prism, colourless
0.20 × 0.12 × 0.07 mm

Data collection

Bruker D8 VENTURE diffractometer
Radiation source: microfocus sealed tube
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
$T_{min} = 0.702$, $T_{max} = 0.820$
8276 measured reflections
1841 independent reflections
1483 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 66.8°$, $\theta_{min} = 4.8°$
$h = -6 \rightarrow 6$
$k = -21 \rightarrow 21$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.109$
$S = 1.11$
1841 reflections
136 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.8877P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	−0.01051 (13)	0.32408 (4)	0.27909 (7)	0.0384 (2)
O1	0.0178 (4)	0.36082 (12)	0.1620 (2)	0.0515 (6)
O2	−0.0556 (5)	0.37554 (13)	0.3769 (2)	0.0684 (7)
O3	−0.1853 (4)	0.26460 (13)	0.2622 (2)	0.0605 (7)
N1	0.4379 (4)	0.12377 (12)	0.4186 (2)	0.0342 (5)
N2	0.4693 (4)	0.03758 (12)	0.2835 (2)	0.0397 (6)
C1	0.2680 (5)	0.28051 (15)	0.3317 (3)	0.0387 (7)
H1A	0.295761	0.242246	0.272092	0.046*
H1B	0.396416	0.316390	0.333023	0.046*
C2	0.2778 (5)	0.24673 (15)	0.4622 (3)	0.0407 (7)
H2A	0.126464	0.222028	0.468117	0.049*
H2B	0.296498	0.285719	0.524741	0.049*
C3	0.4824 (6)	0.19192 (15)	0.4923 (3)	0.0414 (7)
H3A	0.631092	0.214116	0.473993	0.050*
H3B	0.501309	0.180196	0.581604	0.050*
C4	0.2637 (5)	0.07226 (16)	0.4320 (3)	0.0442 (8)
H4	0.152627	0.074210	0.489045	0.053*
C5	0.2834 (6)	0.01861 (16)	0.3477 (3)	0.0470 (8)
H5	0.188704	−0.023476	0.335243	0.056*
C6	0.5586 (5)	0.10126 (15)	0.3272 (3)	0.0383 (7)
H6	0.685369	0.126268	0.298589	0.046*
C7	0.5562 (6)	−0.00487 (17)	0.1802 (3)	0.0516 (8)
H7A	0.517965	−0.056495	0.189484	0.062*
H7B	0.729934	−0.000435	0.187416	0.062*
C8	0.4471 (6)	0.02087 (17)	0.0518 (3)	0.0462 (8)
H8A	0.274204	0.013577	0.041893	0.055*
H8B	0.477584	0.073117	0.043983	0.055*
O4	0.9450 (6)	0.13610 (16)	0.1398 (3)	0.0982 (11)
H4A	0.944211	0.132449	0.060413	0.147*
H4B	0.898201	0.179850	0.150683	0.147*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0413 (4)	0.0408 (4)	0.0350 (4)	0.0084 (3)	0.0128 (3)	0.0048 (3)
O1	0.0632 (15)	0.0539 (13)	0.0404 (12)	0.0105 (11)	0.0174 (11)	0.0153 (10)
O2	0.097 (2)	0.0648 (15)	0.0463 (14)	0.0381 (14)	0.0195 (13)	−0.0033 (11)
O3	0.0407 (13)	0.0686 (15)	0.0714 (17)	−0.0097 (11)	0.0046 (12)	0.0164 (12)
N1	0.0408 (13)	0.0316 (12)	0.0313 (13)	0.0045 (10)	0.0087 (11)	−0.0006 (10)

N2	0.0527 (16)	0.0335 (13)	0.0344 (14)	0.0073 (11)	0.0114 (12)	−0.0036 (10)
C1	0.0362 (16)	0.0368 (15)	0.0447 (18)	0.0024 (12)	0.0116 (14)	0.0029 (13)
C2	0.0528 (19)	0.0371 (15)	0.0332 (16)	0.0063 (13)	0.0095 (14)	−0.0037 (12)
C3	0.0488 (18)	0.0397 (16)	0.0340 (16)	0.0047 (13)	−0.0008 (14)	−0.0071 (13)
C4	0.0486 (19)	0.0485 (17)	0.0389 (18)	−0.0005 (14)	0.0180 (15)	0.0016 (14)
C5	0.056 (2)	0.0391 (17)	0.0474 (19)	−0.0063 (14)	0.0138 (16)	−0.0014 (14)
C6	0.0431 (17)	0.0391 (16)	0.0348 (16)	0.0026 (13)	0.0126 (14)	0.0028 (13)
C7	0.072 (2)	0.0434 (17)	0.0413 (18)	0.0170 (16)	0.0155 (17)	−0.0081 (14)
C8	0.056 (2)	0.0445 (17)	0.0388 (18)	0.0079 (15)	0.0103 (15)	−0.0083 (14)
O4	0.154 (3)	0.082 (2)	0.0673 (19)	−0.0355 (19)	0.047 (2)	−0.0023 (15)

Geometric parameters (Å, º)

S1—O1	1.446 (2)	C2—H2B	0.9700
S1—O2	1.450 (2)	C3—H3A	0.9700
S1—O3	1.453 (2)	C3—H3B	0.9700
S1—C1	1.773 (3)	C4—C5	1.342 (4)
N1—C6	1.327 (3)	C4—H4	0.9300
N1—C4	1.374 (4)	C5—H5	0.9300
N1—C3	1.470 (3)	C6—H6	0.9300
N2—C6	1.320 (4)	C7—C8	1.499 (4)
N2—C5	1.368 (4)	C7—H7A	0.9700
N2—C7	1.482 (3)	C7—H7B	0.9700
C1—C2	1.517 (4)	C8—C8^{i}	1.528 (5)
C1—H1A	0.9700	C8—H8A	0.9700
C1—H1B	0.9700	C8—H8B	0.9700
C2—C3	1.520 (4)	O4—H4A	0.8500
C2—H2A	0.9700	O4—H4B	0.8499

O1—S1—O2	112.16 (14)	C2—C3—H3A	109.3
O1—S1—O3	112.80 (14)	N1—C3—H3B	109.3
O2—S1—O3	112.80 (15)	C2—C3—H3B	109.3
O1—S1—C1	106.52 (13)	H3A—C3—H3B	107.9
O2—S1—C1	106.97 (15)	C5—C4—N1	107.4 (2)
O3—S1—C1	104.93 (13)	C5—C4—H4	126.3
C6—N1—C4	108.0 (2)	N1—C4—H4	126.3
C6—N1—C3	126.0 (2)	C4—C5—N2	107.0 (3)
C4—N1—C3	126.1 (2)	C4—C5—H5	126.5
C6—N2—C5	108.7 (2)	N2—C5—H5	126.5
C6—N2—C7	124.9 (2)	N2—C6—N1	108.9 (2)
C5—N2—C7	126.4 (3)	N2—C6—H6	125.6
C2—C1—S1	113.08 (19)	N1—C6—H6	125.6
C2—C1—H1A	109.0	N2—C7—C8	112.6 (2)
S1—C1—H1A	109.0	N2—C7—H7A	109.1
C2—C1—H1B	109.0	C8—C7—H7A	109.1
S1—C1—H1B	109.0	N2—C7—H7B	109.1
H1A—C1—H1B	107.8	C8—C7—H7B	109.1
C1—C2—C3	113.0 (2)	H7A—C7—H7B	107.8

C1—C2—H2A	109.0	C7—C8—C8^{i}	111.0 (3)
C3—C2—H2A	109.0	C7—C8—H8A	109.5
C1—C2—H2B	109.0	C8^{i}—C8—H8A	109.5
C3—C2—H2B	109.0	C7—C8—H8B	109.2
H2A—C2—H2B	107.8	C8^{i}—C8—H8B	109.4
N1—C3—C2	111.7 (2)	H8A—C8—H8B	108.0
N1—C3—H3A	109.3	H4A—O4—H4B	104.5

O1—S1—C1—C2	173.2 (2)	C6—N2—C5—C4	−0.4 (4)
O2—S1—C1—C2	53.1 (2)	C7—N2—C5—C4	−179.5 (3)
O3—S1—C1—C2	−66.9 (2)	C5—N2—C6—N1	0.6 (3)
S1—C1—C2—C3	163.8 (2)	C7—N2—C6—N1	179.7 (2)
C6—N1—C3—C2	111.4 (3)	C4—N1—C6—N2	−0.6 (3)
C4—N1—C3—C2	−68.4 (4)	C3—N1—C6—N2	179.6 (2)
C1—C2—C3—N1	−71.0 (3)	C6—N2—C7—C8	−83.8 (4)
C6—N1—C4—C5	0.3 (3)	C5—N2—C7—C8	95.1 (4)
C3—N1—C4—C5	−179.9 (3)	N2—C7—C8—C8^{i}	176.4 (3)
N1—C4—C5—N2	0.1 (4)		

Symmetry code: (i) $-x+1, -y, -z$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O2^{ii}	0.85	1.97	2.818 (4)	180
O4—H4*B*···O3^{iii}	0.85	2.04	2.821 (4)	152
C4—H4···O1^{iv}	0.93	2.40	3.217 (4)	146
C5—H5···O1^{v}	0.93	2.40	3.321 (4)	170
C6—H6···O4	0.93	2.39	3.209 (4)	147

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