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Crystal structure of new organically templated copper sulfate with 2-aminopyridinium

Tamara J. Lukianova,* Vasyl Kinzhybalo and Adam Pietraszko

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okolna str. 2, PO Box 1410, 50-950 Wroclaw, Poland. *Correspondence e-mail: T.Lukianova@int.pan.wroc.pl

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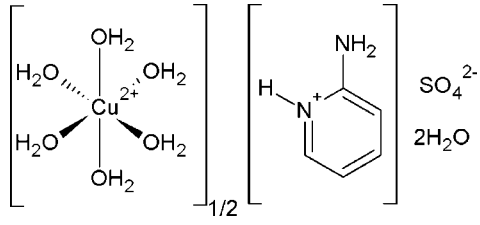
The title compound, $(C_5H_7N_2)_2[Cu(H_2O)_6](SO_4)_2\cdot4H_2O$ [systematic name: bis(2-aminopyridinium) hexaaquacopper(II) bis(sulfate) tetrahydrate], comprises axially elongated hexaaqua-coordinated octahedral Cu^{II} ions located on an inversion centre, non-coordinating sulfate anions, 2-aminopyridinium cations and lattice water molecules. The crystal structure is built of successive inorganic and organic layers extending parallel to (001) that are connected by an extensive three-dimensional hydrogen-bonded network of the type O—H···O and N—H···O, as well as π–π interactions [centroid–centroid distance 3.4140 (14) Å, offset 0.277 Å].

Keywords: crystal structure; organically templated materials; 2-aminopyridine; sulfates; hydrogen bonding; π–π interactions.

CCDC reference: 1429506

1. Related literature

For applications of 2-aminopyridine, see: Windholz (1976). For 2-aminopyridinium sulfate, see: Jebas *et al.* (2006). For other compounds with copper(II), see: Naïli *et al.* (2006); Rekik *et al.* (2006).



2. Experimental

2.1. Crystal data

$(C_5H_7N_2)_2[Cu(H_2O)_6](SO_4)_2\cdot4H_2O$
M_r = 626.07
Triclinic, $P\overline{1}$
a = 7.115 (3) Å
b = 8.211 (3) Å
c = 12.561 (4) Å
α = 91.83 (3)°
β = 104.59 (3)°
γ = 114.57 (3)°
V = 638.0 (4) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.10 mm^{-1}
T = 295 K
0.35 × 0.14 × 0.13 mm

2.2. Data collection

Rigaku Oxford Diffraction Xcalibur, Sapphire2 diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015)
T_{min} = 0.720, T_{max} = 1.000
7926 measured reflections
3173 independent reflections
2268 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.094
S = 1.03
3173 reflections
160 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O11W—H11A···O14W^{i}	0.84	2.00	2.821 (3)	167
O11W—H11B···O12^{ii}	0.84	2.22	3.032 (4)	162
O12W—H12A···O15W	0.84	1.88	2.719 (3)	172
O12W—H12B···O13	0.84	1.85	2.677 (3)	171
O13W—H13A···O14^{iii}	0.84	1.90	2.733 (3)	174
O13W—H13B···O14W	0.84	1.88	2.706 (3)	168
N1—H1···O13	0.86	2.03	2.855 (3)	160
N2—H2A···O11	0.86	2.01	2.869 (3)	176
N2—H2B···O12^{iv}	0.86	2.05	2.914 (3)	178
O14W—H14A···O15W^{ii}	0.84	1.92	2.758 (3)	174
O14W—H14B···O14^{ii}	0.84	1.90	2.738 (3)	176
O15W—H15A···O11^{v}	0.84	1.93	2.761 (3)	169
O15W—H15B···O12^{ii}	0.84	1.93	2.760 (3)	170

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

Data collection: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS2014/7* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg *et al.*, 1997); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HP2072).

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supporting information

Acta Cryst. (2015). E**71**, m191–m192 [https://doi.org/10.1107/S2056989015018629]

Crystal structure of new organically templated copper sulfate with 2-amino-pyridinium

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S1. Comment

Crystal structure of **I** is composed of 2-aminopyridinium (**2ap**) cations, isolated sulfate anions, metal cations octahedrally coordinated by six water molecules $[Cu(H_2O)_6]^{2+}$ and uncoordinated water molecules. The atom labeling scheme for compound **I** is shown in Fig. 1. The asymmetric unit contains one half of Cu atom (lies on a center of inversion) along with three water molecules coordinated to it, one sulfate group, one protonated amine and two solvation water molecules. The Cu ion environment shows considerable axial deformation to tetragonal bipyramidal due to Jahn-Teller effect. The Cu–O12W and Cu–O13W distances are equal to 1.935 (2) and 1.9790 (18) Å, respectively, and the Cu–O11W distance is strongly elongated to 2.398 (2) Å. The distances within the $[Cu(H_2O)_6]^{2+}$ octahedron are comparable to those observed in other compounds (Naïli *et al.*, 2006; Rekik *et al.*, 2006). The crystal packing consists of successive organic and inorganic layers parallel to 0*xy* plane. Inorganic layers are stabilized by a series of O–H···O hydrogen bonds (Table 1 and Fig. 2). Organic layers are built of π-π interacting stacks of **2ap** cations (Cg···Cg 3.4140 (14) Å, offset 0.277 Å) connected to inorganic layers through N–H···O hydrogen bonds (Table 1 and Fig. 3).

S2. Experimental

The title compound was synthesized by the following method. 2-aminopyridine (0.19g, 2 mmol) was dissolved in 4 ml double distilled water to obtain solution A. The pH of the solution was adjusted to 2.5, by the addition of 30% sulfuric acid. Copper sulfate (0.149 g, 6 mmol) was dissolved in 3ml double distilled water to obtain solution B. Solution A was added on solution B. The resulting solution was kept at room temperature. The green crystals of the title compound were obtained by slow evaporation during the period of several months.

S3. Refinement

The H atoms of water molecules were located from difference Fourier maps and were refined with O–H distances restrained to 0.840 (2) Å and Uiso(H) = 1.5 Ueq(O). In final refinement cycles H atoms of water were let to ride on parent O atom (AFIX 3).

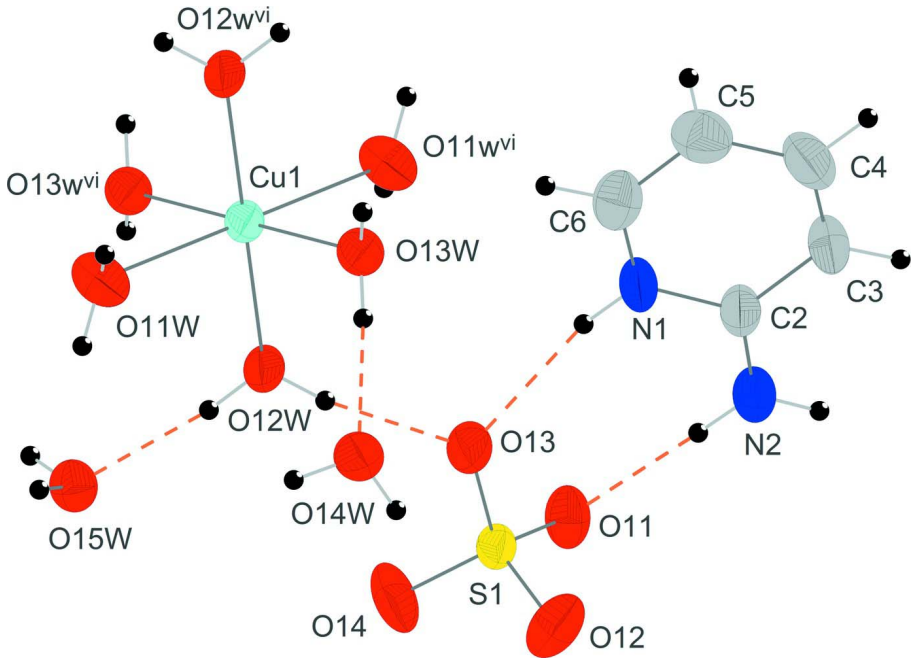

Figure 1

The asymmetric unit of the title compound, showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are denoted by orange dashed lines. [Symmetry codes: (*vi*) *-x + 1*, *-y + 1*, *-z + 1*].

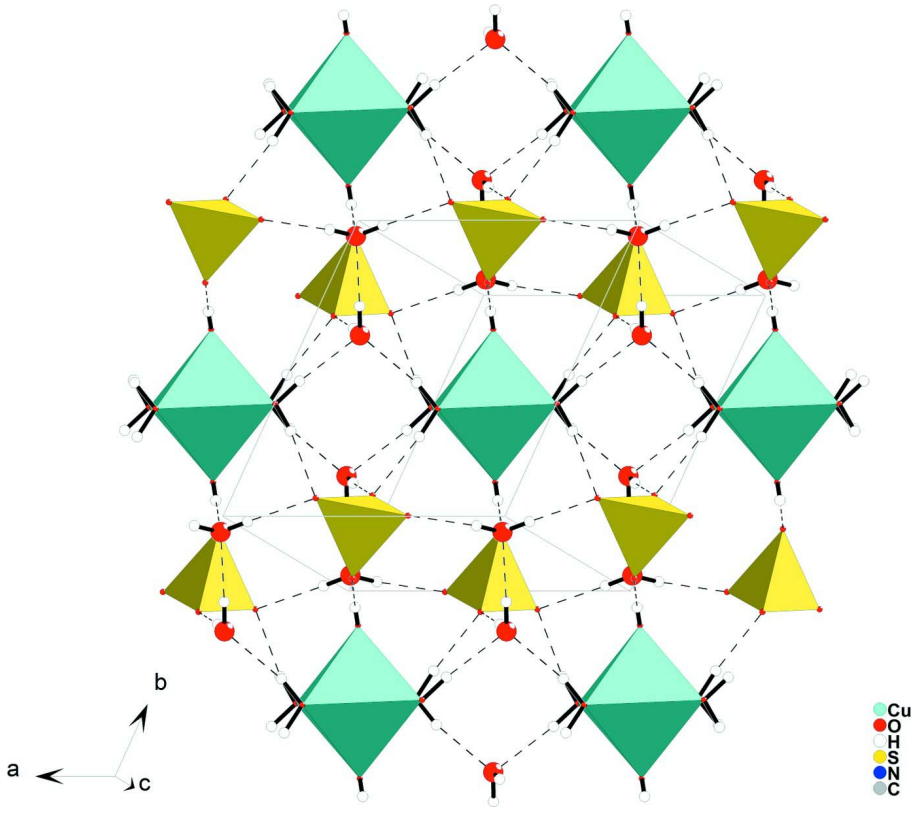

Figure 2

View of inorganic layers along perpendicular to this layer direction (c*). Dashed lines indicate the hydrogen bonds.

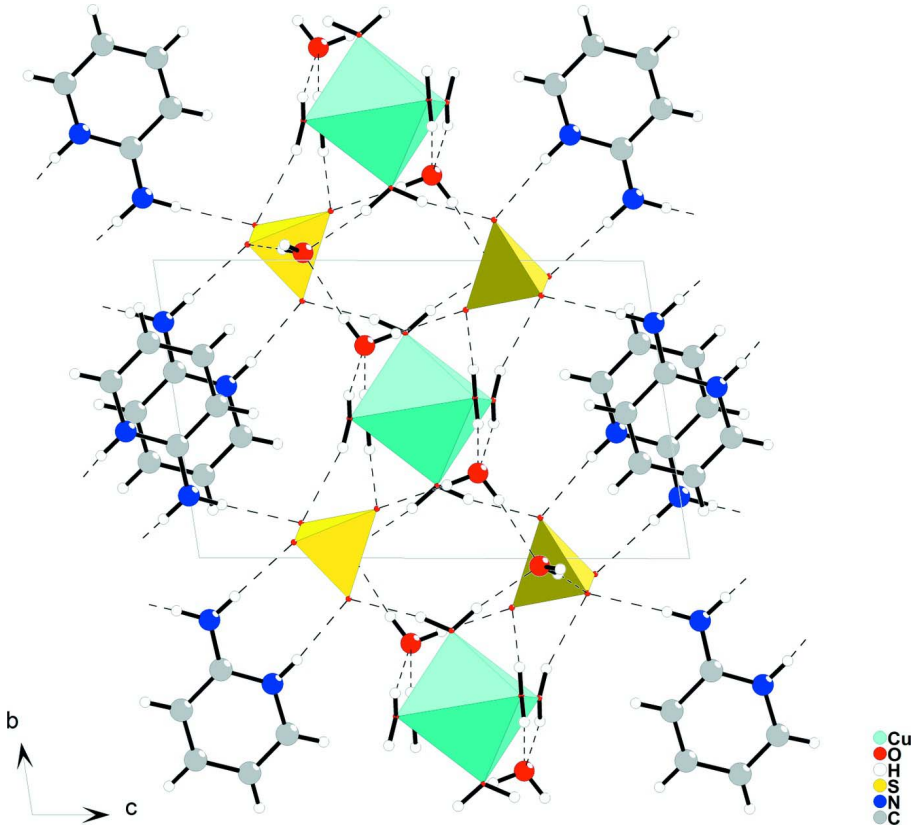

Figure 3

The molecular arrangement in $(C_5H_7N_2)_2[Cu^{II}(H_2O)_6](SO_4)_2{\cdot}4H_2O$ viewed along [100]. Dashed lines represent hydrogen bonds.

Bis(2-aminopyridinium) hexaaquacopper(II) bis(sulfate) tetrahydrate

Crystal data

$(C_5H_7N_2)_2[Cu(H_2O)_6](SO_4)_2{\cdot}4H_2O$
$M_r = 626.07$
Triclinic, $P\overline{1}$
$a = 7.115$ (3) Å
$b = 8.211$ (3) Å
$c = 12.561$ (4) Å
$\alpha = 91.83$ (3)°
$\beta = 104.59$ (3)°
$\gamma = 114.57$ (3)°
$V = 638.0$ (4) Å^3
$Z = 1$
$F(000) = 327$
$D_x = 1.629$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2602 reflections
$\theta = 3.3$–27.4°
$\mu = 1.10$ mm^{-1}
$T = 295$ K
Block, green
0.35 × 0.14 × 0.13 mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Sapphire2 diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 8.2214 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015)
$T_{min} = 0.720$, $T_{max} = 1.000$
7926 measured reflections
3173 independent reflections
2268 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$

θ_{max} = 29.4°, θ_{min} = 3.0°
h = −9→6
k = −10→11
l = −15→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.094
S = 1.03
3173 reflections
160 parameters
0 restraints

Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.2243P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 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}
Cu1	0.5000	0.5000	0.5000	0.03035 (15)
O11W	0.1945 (3)	0.4686 (3)	0.35088 (16)	0.0476 (5)
H11A	0.1489	0.5468	0.3566	0.071*
H11B	0.0825	0.3704	0.3272	0.071*
O12W	0.3772 (3)	0.2434 (2)	0.50851 (15)	0.0482 (6)
H12A	0.3051	0.1679	0.4500	0.072*
H12B	0.3718	0.1983	0.5673	0.072*
O13W	0.3680 (3)	0.5392 (2)	0.61353 (14)	0.0359 (4)
H13A	0.3521	0.6347	0.6187	0.054*
H13B	0.2510	0.4506	0.6110	0.054*
S1	0.34958 (11)	−0.04901 (9)	0.72795 (5)	0.03015 (17)
O11	0.5437 (3)	−0.0526 (3)	0.80214 (15)	0.0434 (5)
O12	0.1755 (3)	−0.1167 (3)	0.78078 (18)	0.0541 (6)
O13	0.3945 (4)	0.1366 (3)	0.70846 (16)	0.0493 (6)
O14	0.2833 (4)	−0.1658 (3)	0.62203 (16)	0.0566 (6)
N1	0.6656 (4)	0.4231 (3)	0.89059 (17)	0.0385 (6)
H1	0.6136	0.3421	0.8326	0.046*
N2	0.6983 (4)	0.2085 (3)	0.99866 (19)	0.0462 (6)
H2A	0.6458	0.1297	0.9395	0.055*
H2B	0.7349	0.1784	1.0629	0.055*
C2	0.7227 (4)	0.3756 (4)	0.9910 (2)	0.0364 (6)
C3	0.8066 (5)	0.5115 (4)	1.0846 (2)	0.0484 (8)
H3	0.8482	0.4852	1.1557	0.058*
C4	0.8263 (5)	0.6786 (4)	1.0711 (3)	0.0527 (8)
H4	0.8812	0.7670	1.1334	0.063*
C5	0.7659 (5)	0.7227 (4)	0.9654 (3)	0.0510 (8)
H5	0.7806	0.8391	0.9566	0.061*
C6	0.6855 (5)	0.5915 (4)	0.8760 (3)	0.0477 (8)

H6	0.6441	0.6171	0.8046	0.057*
O14W	−0.0364 (3)	0.2860 (3)	0.59552 (16)	0.0432 (5)
H14A	−0.0658	0.1958	0.6291	0.065*
H14B	−0.1086	0.2458	0.5285	0.065*
O15W	0.1567 (3)	0.0248 (2)	0.30825 (15)	0.0381 (5)
H15A	0.2371	0.0360	0.2675	0.057*
H15B	0.0585	0.0513	0.2734	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0418 (3)	0.0233 (2)	0.0246 (2)	0.0126 (2)	0.0103 (2)	0.00304 (17)
O11W	0.0435 (13)	0.0422 (12)	0.0502 (13)	0.0187 (10)	0.0034 (10)	−0.0031 (9)
O12W	0.0811 (16)	0.0242 (10)	0.0267 (10)	0.0126 (10)	0.0132 (10)	0.0046 (8)
O13W	0.0416 (11)	0.0323 (10)	0.0345 (10)	0.0166 (9)	0.0121 (9)	0.0024 (8)
S1	0.0370 (4)	0.0289 (4)	0.0247 (3)	0.0156 (3)	0.0071 (3)	0.0055 (3)
O11	0.0407 (12)	0.0640 (14)	0.0317 (10)	0.0304 (11)	0.0077 (9)	0.0081 (9)
O12	0.0433 (13)	0.0771 (16)	0.0562 (14)	0.0330 (12)	0.0231 (11)	0.0360 (12)
O13	0.0755 (16)	0.0315 (11)	0.0321 (11)	0.0188 (11)	0.0090 (10)	0.0076 (8)
O14	0.0838 (17)	0.0504 (13)	0.0325 (11)	0.0404 (13)	−0.0057 (11)	−0.0096 (9)
N1	0.0453 (15)	0.0451 (15)	0.0225 (11)	0.0202 (12)	0.0053 (10)	0.0028 (10)
N2	0.0582 (17)	0.0452 (15)	0.0291 (12)	0.0205 (13)	0.0062 (12)	0.0065 (10)
C2	0.0369 (17)	0.0448 (17)	0.0254 (14)	0.0166 (14)	0.0081 (12)	0.0043 (11)
C3	0.051 (2)	0.057 (2)	0.0256 (14)	0.0178 (17)	0.0040 (14)	0.0018 (13)
C4	0.052 (2)	0.050 (2)	0.0408 (18)	0.0150 (17)	0.0032 (15)	−0.0090 (15)
C5	0.049 (2)	0.0418 (18)	0.058 (2)	0.0192 (16)	0.0097 (17)	0.0062 (15)
C6	0.051 (2)	0.055 (2)	0.0384 (17)	0.0273 (17)	0.0093 (15)	0.0133 (14)
O14W	0.0480 (13)	0.0359 (11)	0.0390 (11)	0.0149 (10)	0.0075 (10)	0.0070 (8)
O15W	0.0356 (11)	0.0438 (12)	0.0357 (10)	0.0190 (9)	0.0090 (9)	0.0048 (8)

Geometric parameters (Å, º)

Cu1—O11W	2.398 (2)	N1—C2	1.347 (3)
Cu1—O11W^{i}	2.398 (2)	N1—C6	1.353 (4)
Cu1—O12W^{i}	1.935 (2)	N2—H2A	0.8600
Cu1—O12W	1.935 (2)	N2—H2B	0.8600
Cu1—O13W	1.9790 (18)	N2—C2	1.319 (4)
Cu1—O13W^{i}	1.9790 (18)	C2—C3	1.412 (4)
O11W—H11A	0.8397	C3—H3	0.9300
O11W—H11B	0.8396	C3—C4	1.341 (4)
O12W—H12A	0.8396	C4—H4	0.9300
O12W—H12B	0.8394	C4—C5	1.397 (4)
O13W—H13A	0.8398	C5—H5	0.9300
O13W—H13B	0.8398	C5—C6	1.355 (4)
S1—O11	1.471 (2)	C6—H6	0.9300
S1—O12	1.466 (2)	O14W—H14A	0.8397
S1—O13	1.464 (2)	O14W—H14B	0.8397
S1—O14	1.462 (2)	O15W—H15A	0.8399

N1—H1	0.8600	O15W—H15B	0.8401
O11W^{i}—Cu1—O11W	180.0	O14—S1—O11	109.47 (12)
O12W—Cu1—O11W	92.90 (9)	O14—S1—O12	109.29 (15)
O12W^{i}—Cu1—O11W^{i}	92.90 (9)	O14—S1—O13	109.78 (13)
O12W^{i}—Cu1—O11W	87.10 (9)	C2—N1—H1	118.2
O12W—Cu1—O11W^{i}	87.10 (9)	C2—N1—C6	123.6 (2)
O12W^{i}—Cu1—O12W	180.0	C6—N1—H1	118.2
O12W—Cu1—O13W	89.66 (8)	H2A—N2—H2B	120.0
O12W^{i}—Cu1—O13W^{i}	89.66 (9)	C2—N2—H2A	120.0
O12W^{i}—Cu1—O13W	90.34 (8)	C2—N2—H2B	120.0
O12W—Cu1—O13W^{i}	90.34 (8)	N1—C2—C3	116.8 (3)
O13W^{i}—Cu1—O11W	88.14 (8)	N2—C2—N1	120.1 (2)
O13W—Cu1—O11W^{i}	88.14 (8)	N2—C2—C3	123.1 (3)
O13W^{i}—Cu1—O11W^{i}	91.86 (8)	C2—C3—H3	119.9
O13W—Cu1—O11W	91.86 (8)	C4—C3—C2	120.1 (3)
O13W—Cu1—O13W^{i}	180.00 (11)	C4—C3—H3	119.9
Cu1—O11W—H11A	115.8	C3—C4—H4	119.3
Cu1—O11W—H11B	122.9	C3—C4—C5	121.3 (3)
H11A—O11W—H11B	104.7	C5—C4—H4	119.3
Cu1—O12W—H12A	119.8	C4—C5—H5	120.9
Cu1—O12W—H12B	125.3	C6—C5—C4	118.2 (3)
H12A—O12W—H12B	114.2	C6—C5—H5	120.9
Cu1—O13W—H13A	118.5	N1—C6—C5	119.9 (3)
Cu1—O13W—H13B	113.2	N1—C6—H6	120.0
H13A—O13W—H13B	108.7	C5—C6—H6	120.0
O12—S1—O11	108.78 (12)	H14A—O14W—H14B	106.1
O13—S1—O11	110.06 (13)	H15A—O15W—H15B	106.7
O13—S1—O12	109.43 (13)		
N1—C2—C3—C4	0.0 (4)	C3—C4—C5—C6	0.3 (5)
N2—C2—C3—C4	−179.7 (3)	C4—C5—C6—N1	0.0 (5)
C2—N1—C6—C5	−0.3 (5)	C6—N1—C2—N2	179.9 (3)
C2—C3—C4—C5	−0.2 (5)	C6—N1—C2—C3	0.3 (4)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11*W*—H11*A*···O14*W*^{ii}	0.84	2.00	2.821 (3)	167
O11*W*—H11*B*···O12^{iii}	0.84	2.22	3.032 (4)	162
O12*W*—H12*A*···O15*W*	0.84	1.88	2.719 (3)	172
O12*W*—H12*B*···O13	0.84	1.85	2.677 (3)	171
O13*W*—H13*A*···O14^{iv}	0.84	1.90	2.733 (3)	174
O13*W*—H13*B*···O14*W*	0.84	1.88	2.706 (3)	168
N1—H1···O13	0.86	2.03	2.855 (3)	160
N2—H2*A*···O11	0.86	2.01	2.869 (3)	176

N2—H2*B*···O12^{v}	0.86	2.05	2.914 (3)	178
O14*W*—H14*A*···O15*W*^{iii}	0.84	1.92	2.758 (3)	174
O14*W*—H14*B*···O14^{iii}	0.84	1.90	2.738 (3)	176
O15*W*—H15*A*···O11^{vi}	0.84	1.93	2.761 (3)	169
O15*W*—H15*B*···O12^{iii}	0.84	1.93	2.760 (3)	170

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