

Synthesis, crystal structure and Hirshfeld surface analysis of *catena*-poly[[bis(semicarbazide- κ^2 N,O)-copper(II)]- μ -sulfato- κ^2 O:O']

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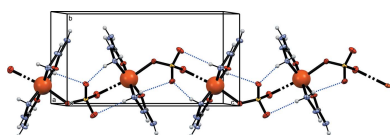
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The title polymer, $[\text{Cu}(\text{SO}_4)(\text{CH}_5\text{N}_3\text{O})_2]_n$, has been synthesized from aqueous solutions of CuSO_4 and semicarbazide. In the crystal structure, the Cu^{II} atoms are chelated by two neutral semicarbazide molecules through the oxygen atom and a nitrogen atom of the amino group. The remaining two positions of the Jahn–Teller-distorted octahedral coordination sphere are occupied by oxygen atoms of two sulfate anions in the axial positions. The coordination bonds of the latter associate the polyhedra into polymeric chains running parallel to the *c* axis. There is a weak intramolecular hydrogen bond between the N–H group and an oxygen atom of the SO_4^{2-} anion. Thirteen relatively weak intermolecular hydrogen-bonding interactions link the chains into a three-dimensional network. Hirshfeld surface analysis revealed that 64.7% of the intermolecular interactions are from $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts and 20.1% from $\text{H}\cdots\text{H}$ contacts. Other interactions such as $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ or $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ contribute less to the crystal packing.

1. Chemical context

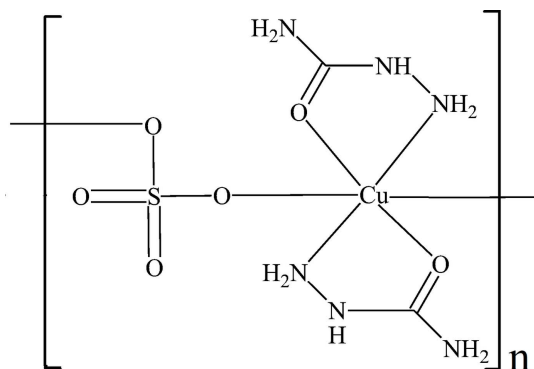
Semicarbazide (SEC), a water-soluble white solid, is a derivative of urea with formula $\text{O}=\text{C}(\text{NH}_2)(\text{N}_2\text{H}_3)$. It is used in the preparation of pharmaceuticals including nitrofurantoin antibacterials (furazolidone, nitrofurazone, nitrofurantoin) and related compounds (Vass *et al.*, 2008). Originally, SEC was primarily detected as a nitrofurazone veterinary metabolite, but over time it was found that azodicarbonamide and flour stored in sealed cans could lead to the formation of SEC as well (Tian *et al.*, 2014). Therefore, the toxicity of SEC as a food contaminant is of crucial interest. SEC hydrochloride has an oral LD_{50} of 225 mg kg^{-1} in mice and 123 mg kg^{-1} in the rat. Some studies suggest that SEC hydrochloride is a mutagen, an animal carcinogen and a teratogen. As a result of the lack of data in humans and an overall limited evidence of carcinogenicity in animals, SEC was classified by the International Agency for Research on Cancer as a Group 3 agent, *i.e.* not classifiable as to its carcinogenicity to humans (Takahashi *et al.*, 2014). However, SEC products (semicarbazones and thiosemicarbazones) are known to have antiviral, anti-infective and antineoplastic activities through binding to copper or iron in cells (Becalski *et al.*, 2004; Tian *et al.*, 2014). It is well known that the biopharmaceutical properties of active pharmaceutical ingredients may be improved by metal complex formation (Khudoyberganov *et al.*, 2022; Ruzmetov *et al.*, 2022a,b). In turn, this phenomenon may lead to a reduction in the



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toxicity of hazardous organic substances in coordination compounds (Egorova & Ananikov, 2017; Flora & Pachauri *et al.*, 2010; Ahmed *et al.*, 2020). Therefore, it is of great interest to study the metal complex formation of SEC. In this context, we report here the synthesis, crystal structure and Hirshfeld surface analysis of a new copper complex of SEC with sulfate anions as co-ligands, $[\text{Cu}(\text{CH}_5\text{N}_3\text{O})_2(\text{SO}_4)]_n$.



2. Structural commentary

The expanded asymmetric unit of the title polymer is shown in Fig. 1. The Cu^{II} atom is chelated by two SEC molecules through the oxygen atoms (O1 and O2) and the nitrogen atoms (N1 and N4) of NH_2 groups, leading to a slightly distorted square-planar coordination environment with bond lengths in the range between 1.9218 (17) and 2.015 (2) Å and bond angles between 81.50 (7) and 101.89 (8)°. Two remote oxygen atoms, O6 and O3ⁱ, of two SO_4^{2-} anions augment the coordination sphere (Table 1). As a result of the Jahn–Teller

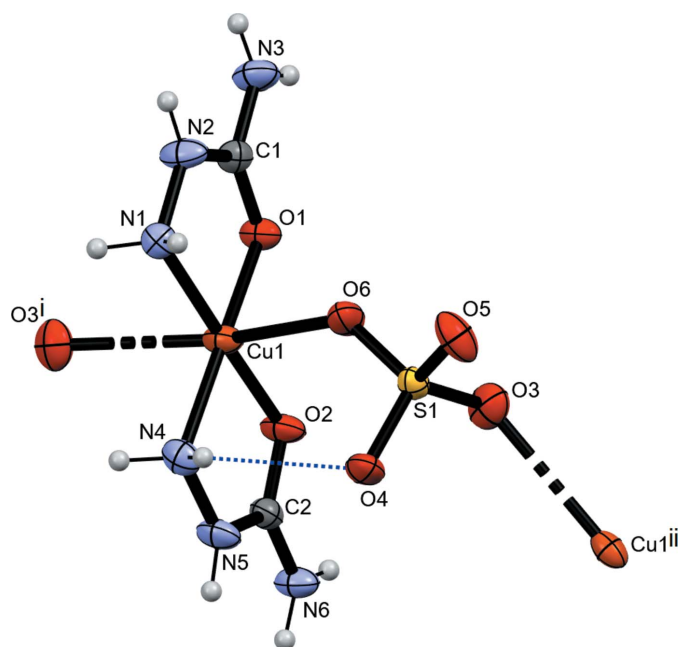


Figure 1
The expanded asymmetric part of the title compound $[\text{Cu}(\text{SEC})_2(\text{SO}_4)]_n$, with the atom-numbering scheme. The intramolecular hydrogen bond is indicated by a dashed line. Displacement ellipsoids are plotted at the 50% probability level. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z - 1/2$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$].

Table 1
Selected bond lengths (Å).

Cu1—O1	1.9549 (17)	Cu1—N4	2.015 (2)
Cu1—O2	1.9218 (17)	Cu1—O6	2.3776 (18)
Cu1—N1	1.9769 (19)	Cu1—O3 ⁱ	2.6947 (19)

Symmetry code: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1A···O4 ⁱ	0.89	2.06	2.928 (3)	164
N1—H1B···O4 ⁱⁱ	0.89	2.43	3.302 (3)	167
N1—H1B···O5 ⁱⁱ	0.89	2.24	2.871 (3)	128
N2—H2···O5 ⁱⁱⁱ	0.86	1.97	2.751 (3)	151
N3—H3A···O3 ^{iv}	0.86	2.20	2.985 (3)	152
N3—H3B···O1 ^v	0.86	2.59	3.036 (3)	113
N4—H4A···O4	0.89	2.47	3.125 (3)	131
N4—H4A···O5 ⁱⁱ	0.89	2.57	3.097 (3)	119
N4—H4B···O5 ⁱ	0.89	2.49	3.309 (3)	152
N5—H5···O6 ^{vi}	0.86	2.59	3.228 (3)	132
N5—H5···O4 ^{vii}	0.86	2.39	2.954 (3)	123
N6—H6A···O1 ^{viii}	0.86	2.51	3.123 (3)	129
N6—H6A···O2 ^{viii}	0.86	2.17	2.971 (3)	154
N6—H6A···O6 ^{vi}	0.86	2.03	2.845 (3)	157

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

effect, a substantial elongation of the two axial Cu—O bonds is observed and the coordination sphere around Cu^{II} becomes a distinctly distorted octahedron.

Coordination bonds involving the SO_4^{2-} ligands associate individual polyhedra into polymeric chains running parallel to the *c* axis (Fig. 2). A weak intramolecular hydrogen bond between N4—H4 and oxygen atom O4 of the SO_4 anion (Table 2), enclosing a six-membered ring with graph-set notation $S_1^1(6)$ (Etter, 1990), consolidates the conformation (Fig. 1). The lengths of the S—O bonds are very similar, showing a distribution between 1.4702 (17) and 1.4769 (17) Å, in very good agreement with the mean value of 1.473 Å for S—O bonds (Gagné & Hawthorne, 2018).

3. Supramolecular features

For hydrogen-bonding interactions, there are six proton acceptor and ten proton donor functionalities, forming a complex system of 13 intermolecular hydrogen bonds (Table 2). Within this network, bifurcated hydrogen bonds

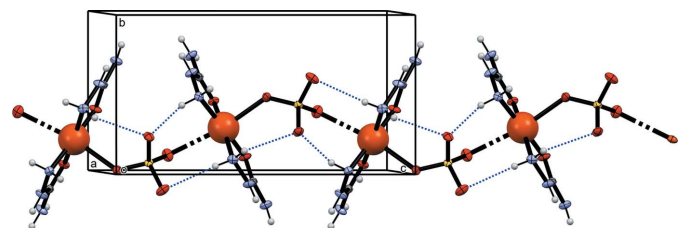


Figure 2
The formation of polymeric chains. Intramolecular hydrogen bonds are indicated by dotted lines.

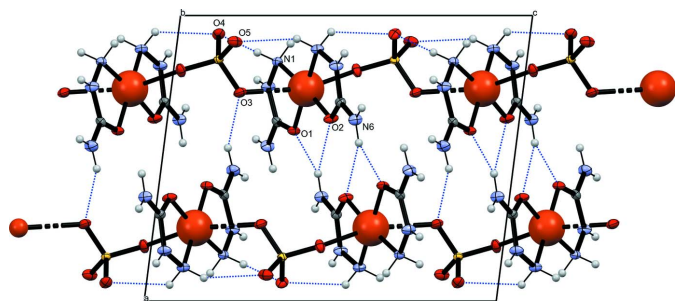


Figure 3
The crystal structure of the title compound. Intermolecular hydrogen bonds are indicated by dashed lines.

involving hydrogen atoms H4A, H5 and H6A are noted. Each of the atoms O4 and O5 is an acceptor for four hydrogen bonds whereas atoms O1 and O6 are hydrogen-bonded to two hydrogen atoms, and O2 and O3 to one hydrogen atom each. The hydrogen bonds form numerous different associates with various dimensions, *e.g.* there are many rings with graph-set notations ranging from $R_1^1(n)$ to $R_6^6(n)$. The hydrogen bonds indicated in Table 2 link the polymeric chains into a three-dimensional network (Fig. 3).

4. Hirshfeld surface analysis

Hirshfeld surfaces were calculated and two-dimensional fingerprints generated using *CrystalExplorer2021* (Spackman *et al.*, 2021). Fig. 4 shows the Hirshfeld surface of the title compound with d_{norm} (normalized contact distance) plotted over the range -0.5974 to 1.0842 a.u. The interactions given in Table 2 play a key role in the molecular packing of the complex, and nearly two thirds (or 64.7%) of intermolecular interactions correspond to $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts. The overall two-dimensional fingerprint plot and those delineated into $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$, $\text{H}\cdots\text{H}$, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ and

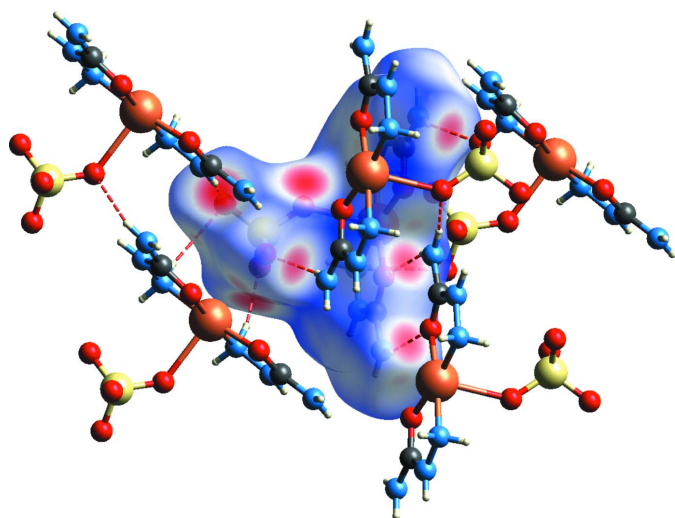


Figure 4
View of the Hirshfeld surface plotted over d_{norm} .

$\text{Cu}\cdots\text{O}/\text{O}\cdots\text{C}$ interactions are shown in Fig. 5. The 2.5% contribution of the $\text{Cu}\cdots\text{O}/\text{O}\cdots\text{Cu}$ contact is explained by the existence of the very long $\text{Cu}-\text{O}3$ bond, which is considered by *CrystalExplorer* to be an intermolecular contact.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, update of November 2021; Groom *et al.*, 2016) for semicarbazide metal complexes gave 45 hits. In all entries, neutral semicarbazide molecules coordinate in a chelating fashion enclosing five-membered rings with exception of the Pd complex NAZYES (Bergs *et al.*, 1997) where a single semicarbazide molecule coordinates monodentately through an NH_2 group. In 21 mixed-ligand complexes, chloride ions serve as co-ligands except in the structure with refcode SEGWAC (Chuklanova *et al.*, 1988) where all four ligand positions of the Zn^{II} atom are occupied by Cl^- ligands and protonated semicarbazide molecules present as non-coordinating molecules. Chloride anions likewise are non-coordinating in four cases, and NO_3^- anions in five structures. Water molecules of crystallization are encountered in 13 complexes. There is only one coordination polymer among the identified compounds, SCACCU10 (Chiesi Villa *et al.*, 1971). The coordination polyhedron of most of the metal complexes is an octahedron while a tetrahedron is revealed in six cases and penta-coordination is found in three structures. Inclusion of the SO_4^{2-} anion into the coordination sphere of the central metal cation is reported only for the title compound.

6. Synthesis and crystallization

0.02 g (0.2 mol) of semicarbazide hydrochloride, 0.022 g (0.09 mol) of copper sulfate and 0.0054 g (0.09 mol) of monoethanolamine were dissolved separately in 1 ml of water

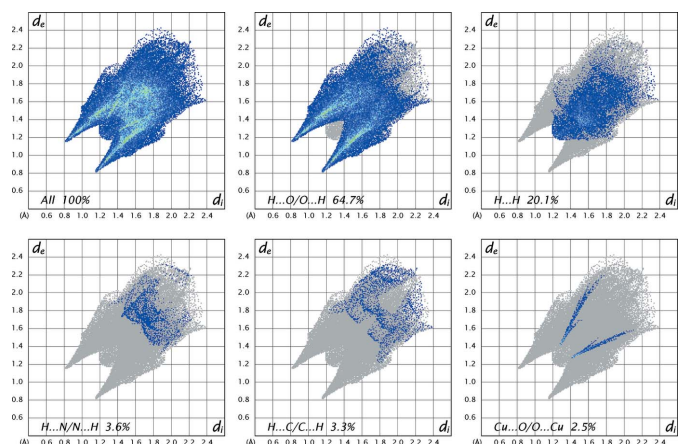


Figure 5
The full two-dimensional fingerprint plot of $[\text{Cu}(\text{SEC})_2(\text{SO}_4)]_n$ showing all interactions and those delineated into $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$, $\text{H}\cdots\text{H}$, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ and $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$ interactions. The d_i and d_e values are the closest internal and external distances (\AA) from given points on the Hirshfeld surface.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Cu(SO ₄)(CH ₅ N ₃ O) ₂]
<i>M_r</i>	309.76
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.5555 (2), 6.8624 (1), 12.9061 (2)
β (°)	97.265 (2)
<i>V</i> (Å ³)	927.36 (3)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	5.82
Crystal size (mm)	0.18 × 0.16 × 0.14
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix3000
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku, 2020)
<i>T</i> _{min} , <i>T</i> _{max}	0.084, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	8102, 1785, 1656
<i>R</i> _{int}	0.037
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.613
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.080, 1.07
No. of reflections	1785
No. of parameters	146
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.32, -0.42

Computer programs: *CrysAlis PRO* (Rigaku, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

at room temperature. The three solutions were mixed and left in a thermostat at 298 K. After two days, blue crystals started to precipitate. The crystals were filtered off, washed with ethanol and dried.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. N-bound hydrogen atoms were placed in calculated positions and refined in the riding-model approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$, N–H = 0.89 Å for the N1 and N4 nitrogen atoms and N–H = 0.86 for the remaining nitrogen atoms.

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Computing details

Data collection: *CrysAlis PRO* (Rigaku, 2020); cell refinement: *CrysAlis PRO* (Rigaku, 2020); data reduction: *CrysAlis PRO* (Rigaku, 2020); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

catena-Poly[[bis(semicarbazide- κ^2N,O)copper(II)]- μ -sulfato- $\kappa^2O:O'$]

Crystal data

[Cu(SO₄)(CH₅N₃O)₂]

$M_r = 309.76$

Monoclinic, $P2_1/c$

$a = 10.5555$ (2) Å

$b = 6.8624$ (1) Å

$c = 12.9061$ (2) Å

$\beta = 97.265$ (2)°

$V = 927.36$ (3) Å³

$Z = 4$

$F(000) = 628$

$D_x = 2.219$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 4840 reflections

$\theta = 3.5$ – 70.8°

$\mu = 5.82$ mm⁻¹

$T = 293$ K

Block, light blue

$0.18 \times 0.16 \times 0.14$ mm

Data collection

XtaLAB Synergy, Single source at home/near,

HyPix3000

diffractometer

Radiation source: micro-focus sealed X-ray

tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku, 2020)

$T_{\min} = 0.084$, $T_{\max} = 1.000$

8102 measured reflections

1785 independent reflections

1656 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 71.1^\circ$, $\theta_{\min} = 4.2^\circ$

$h = -12 \rightarrow 12$

$k = -8 \rightarrow 6$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.080$

$S = 1.07$

1785 reflections

146 parameters

0 restraints

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.5652P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.32 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{Å}^{-3}$$

Extinction correction: SHELXL-2018/3

(Sheldrick, 2015b),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0019 (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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.25619 (3)	0.28648 (5)	0.38274 (3)	0.02624 (15)
S1	0.15524 (5)	0.43123 (8)	0.62353 (4)	0.02198 (17)
O1	0.40378 (15)	0.4485 (2)	0.36355 (13)	0.0265 (4)
O2	0.36126 (16)	0.0997 (2)	0.46464 (15)	0.0320 (4)
O4	0.06548 (18)	0.2652 (3)	0.61509 (14)	0.0327 (4)
O3	0.26979 (17)	0.3862 (3)	0.69698 (15)	0.0390 (5)
N1	0.16194 (18)	0.4839 (3)	0.29178 (15)	0.0240 (4)
H1A	0.129486	0.430444	0.231376	0.029*
H1B	0.098181	0.533034	0.322557	0.029*
N4	0.11789 (19)	0.0915 (3)	0.40077 (17)	0.0284 (4)
H4A	0.057785	0.146007	0.433787	0.034*
H4B	0.081860	0.049058	0.338815	0.034*
N5	0.1763 (2)	-0.0647 (3)	0.46025 (18)	0.0311 (5)
H5	0.132873	-0.161448	0.479156	0.037*
N2	0.2496 (2)	0.6315 (3)	0.27463 (18)	0.0333 (5)
H2	0.225589	0.736581	0.241505	0.040*
N6	0.3650 (2)	-0.2015 (3)	0.53428 (18)	0.0318 (5)
H6A	0.446089	-0.194830	0.552441	0.038*
H6B	0.323773	-0.304631	0.547814	0.038*
N3	0.4573 (2)	0.7341 (3)	0.29420 (19)	0.0369 (5)
H3A	0.536565	0.718013	0.317642	0.044*
H3B	0.433312	0.836957	0.258968	0.044*
C1	0.3723 (2)	0.6007 (3)	0.31234 (18)	0.0238 (5)
C2	0.3037 (2)	-0.0535 (3)	0.48563 (18)	0.0240 (5)
O5	0.09208 (18)	0.6011 (3)	0.66402 (17)	0.0407 (5)
O6	0.19228 (18)	0.4786 (3)	0.52040 (13)	0.0333 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0189 (2)	0.0213 (2)	0.0375 (2)	-0.00162 (12)	-0.00018 (15)	0.00774 (14)
S1	0.0190 (3)	0.0238 (3)	0.0234 (3)	-0.0045 (2)	0.0034 (2)	-0.0019 (2)
O1	0.0184 (8)	0.0231 (8)	0.0378 (9)	0.0007 (6)	0.0025 (7)	0.0065 (7)
O2	0.0225 (9)	0.0225 (8)	0.0491 (11)	-0.0053 (7)	-0.0035 (8)	0.0109 (8)

O4	0.0322 (10)	0.0292 (9)	0.0356 (10)	-0.0134 (7)	0.0001 (8)	0.0053 (7)
O3	0.0233 (9)	0.0524 (12)	0.0391 (10)	-0.0035 (8)	-0.0043 (8)	0.0060 (9)
N1	0.0187 (10)	0.0263 (10)	0.0271 (10)	0.0015 (8)	0.0036 (8)	-0.0003 (8)
N4	0.0196 (10)	0.0276 (10)	0.0374 (11)	-0.0021 (8)	0.0007 (8)	-0.0011 (9)
N5	0.0251 (11)	0.0225 (9)	0.0453 (12)	-0.0067 (8)	0.0030 (9)	0.0045 (9)
N2	0.0246 (11)	0.0277 (11)	0.0468 (13)	0.0013 (8)	0.0014 (9)	0.0164 (10)
N6	0.0282 (12)	0.0234 (10)	0.0432 (13)	-0.0014 (8)	0.0016 (9)	0.0102 (9)
N3	0.0319 (13)	0.0342 (12)	0.0446 (13)	-0.0088 (9)	0.0050 (10)	0.0145 (10)
C1	0.0240 (12)	0.0231 (11)	0.0256 (11)	0.0011 (9)	0.0086 (9)	0.0000 (9)
C2	0.0250 (12)	0.0212 (11)	0.0262 (11)	-0.0032 (9)	0.0040 (9)	-0.0011 (9)
O5	0.0284 (10)	0.0392 (10)	0.0548 (12)	-0.0009 (8)	0.0065 (9)	-0.0220 (9)
O6	0.0425 (11)	0.0316 (9)	0.0276 (9)	-0.0112 (8)	0.0115 (8)	-0.0017 (7)

Geometric parameters (Å, °)

Cu1—O1	1.9549 (17)	N1—N2	1.408 (3)
Cu1—O2	1.9218 (17)	N4—H4A	0.8900
Cu1—N1	1.9769 (19)	N4—H4B	0.8900
Cu1—N4	2.015 (2)	N4—N5	1.414 (3)
Cu1—O6	2.3776 (18)	N5—H5	0.8600
Cu1—O3 ⁱ	2.6947 (19)	N5—C2	1.345 (3)
S1—O4	1.4769 (17)	N2—H2	0.8600
S1—O3	1.4719 (18)	N2—C1	1.341 (3)
S1—O5	1.4714 (19)	N6—H6A	0.8600
S1—O6	1.4702 (17)	N6—H6B	0.8600
O1—C1	1.258 (3)	N6—C2	1.320 (3)
O2—C2	1.261 (3)	N3—H3A	0.8600
N1—H1A	0.8900	N3—H3B	0.8600
N1—H1B	0.8900	N3—C1	1.324 (3)
O1—Cu1—N1	83.36 (7)	N2—N1—H1A	110.3
O1—Cu1—N4	173.06 (8)	N2—N1—H1B	110.3
O1—Cu1—O6	94.90 (7)	Cu1—N4—H4A	110.3
O2—Cu1—O1	92.02 (7)	Cu1—N4—H4B	110.3
O2—Cu1—N1	174.70 (8)	H4A—N4—H4B	108.6
O2—Cu1—N4	82.52 (8)	N5—N4—Cu1	107.04 (14)
O2—Cu1—O6	99.05 (7)	N5—N4—H4A	110.3
N1—Cu1—N4	101.89 (8)	N5—N4—H4B	110.3
N1—Cu1—O6	83.95 (7)	N4—N5—H5	121.8
N4—Cu1—O6	90.21 (8)	C2—N5—N4	116.32 (19)
O2—Cu1—O3 ⁱ	96.00 (7)	C2—N5—H5	121.8
O1—Cu1—O3 ⁱ	90.24 (7)	N1—N2—H2	121.5
N1—Cu1—O3 ⁱ	81.50 (7)	C1—N2—N1	116.94 (19)
N4—Cu1—O3 ⁱ	86.13 (9)	C1—N2—H2	121.5
O6—Cu1—O3 ⁱ	163.90 (6)	H6A—N6—H6B	120.0
O3—S1—O4	110.64 (11)	C2—N6—H6A	120.0
O5—S1—O4	108.79 (11)	C2—N6—H6B	120.0
O5—S1—O3	108.05 (12)	H3A—N3—H3B	120.0

O6—S1—O4	110.20 (10)	C1—N3—H3A	120.0
O6—S1—O3	109.80 (11)	C1—N3—H3B	120.0
O6—S1—O5	109.31 (12)	O1—C1—N2	120.0 (2)
C1—O1—Cu1	112.13 (15)	O1—C1—N3	121.8 (2)
C2—O2—Cu1	114.46 (15)	N3—C1—N2	118.2 (2)
Cu1—N1—H1A	110.3	O2—C2—N5	119.3 (2)
Cu1—N1—H1B	110.3	O2—C2—N6	121.6 (2)
H1A—N1—H1B	108.5	N6—C2—N5	119.1 (2)
N2—N1—Cu1	107.15 (14)	S1—O6—Cu1	133.39 (11)
Cu1—O1—C1—N2	-2.6 (3)	O3—S1—O6—Cu1	76.86 (17)
Cu1—O1—C1—N3	177.26 (19)	N1—N2—C1—O1	-2.4 (3)
Cu1—O2—C2—N5	-7.0 (3)	N1—N2—C1—N3	177.7 (2)
Cu1—O2—C2—N6	174.70 (19)	N4—N5—C2—O2	6.7 (3)
Cu1—N1—N2—C1	5.9 (3)	N4—N5—C2—N6	-175.0 (2)
Cu1—N4—N5—C2	-2.9 (2)	O5—S1—O6—Cu1	-164.78 (14)
O4—S1—O6—Cu1	-45.26 (18)		

Symmetry code: (i) $x, -y+1/2, z-1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O4 ⁱ	0.89	2.06	2.928 (3)	164
N1—H1B \cdots O4 ⁱⁱ	0.89	2.43	3.302 (3)	167
N1—H1B \cdots O5 ⁱⁱ	0.89	2.24	2.871 (3)	128
N2—H2 \cdots O5 ⁱⁱⁱ	0.86	1.97	2.751 (3)	151
N3—H3A \cdots O3 ^{iv}	0.86	2.20	2.985 (3)	152
N3—H3B \cdots O1 ^v	0.86	2.59	3.036 (3)	113
N4—H4A \cdots O4	0.89	2.47	3.125 (3)	131
N4—H4A \cdots O5 ⁱⁱ	0.89	2.57	3.097 (3)	119
N4—H4B \cdots O5 ⁱ	0.89	2.49	3.309 (3)	152
N5—H5 \cdots O6 ^{vi}	0.86	2.59	3.228 (3)	132
N5—H5 \cdots O4 ^{vii}	0.86	2.39	2.954 (3)	123
N6—H6A \cdots O1 ^{viii}	0.86	2.51	3.123 (3)	129
N6—H6A \cdots O2 ^{viii}	0.86	2.17	2.971 (3)	154
N6—H6A \cdots O6 ^{vi}	0.86	2.03	2.845 (3)	157

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $-x, -y+1, -z+1$; (iii) $x, -y+3/2, z-1/2$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+1, y+1/2, -z+1/2$; (vi) $x, y-1, z$; (vii) $-x, -y, -z+1$; (viii) $-x+1, -y, -z+1$.