Synthesis, crystal structure and Hirshfeld surface analysis of \textit{catena-poly[[bis(semicolonbaze-κ²N,O)-copper(II)]-μ-sulfato-κ²O:O']

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The title polymer, [Cu(SO\textsubscript{4})(CH\textsubscript{5}N\textsubscript{3}O\textsubscript{2})\textsubscript{n}], has been synthesized from aqueous solutions of CuSO\textsubscript{4} and semicarbazide. In the crystal structure, the Cu\textsuperscript{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\textsubscript{4}\textsuperscript{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 O/C1/C1/C1H/H/C1/C1/C1O contacts and 20.1\% from H/C1/C1/C1H contacts. Other interactions such as N/C1/C1/C1H/H/C1/C1/C1No or C/C1/C1/C1H/H/C1/C1/C1C contribute less to the crystal packing.

1. Chemical context

Semicarbazide (SEC), a water-soluble white solid, is a derivative of urea with formula O═C(NH\textsubscript{2})(N\textsubscript{2}H\textsubscript{3}). It is used in the preparation of pharmaceuticals including nitrofuran antibacterials (furazolidone, nitrofurazone, nitrofurantoin) and related compounds (Vass \textit{et al.}, 2008). Originally, SEC was primarily detected as a nitrofuran 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 \textit{et al.}, 2014). Therefore, the toxicity of SEC as a food contaminant is of crucial interest. SEC hydrochloride has an oral LD\textsubscript{50} of 225 mg kg\textsuperscript{−1} in mice and 123 mg kg\textsuperscript{−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, \textit{i.e.} not classifiable as to its carcinogenicity to humans (Takahashi \textit{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 \textit{et al.}, 2004; Tian \textit{et al.}, 2014). It is well known that the biopharmaceutical properties of active pharmaceutical ingredients may be improved by metal complex formation (Khudoybergenov \textit{et al.}, 2022; Ruzmetov \textit{et al.}, 2022a,b). In turn, this phenomenon may lead to a reduction in the
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, [Cu(CH₃N₃O)₂(SO₄)]ₙ.

2. Structural commentary

The expanded asymmetric unit of the title polymer is shown in Fig. 1. The CuII atom is chelated by two SEC molecules through the oxygen atoms (O1 and O2) and the nitrogen atoms (N1 and N4) of NH₂ 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). Atoms (N1 and N4) of NH₂ 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 O3, of two SO₄²⁻ anions augment the coordination sphere (Table 1). As a result of the Jahn–Teller effect, a substantial elongation of the two axial Cu—O bonds is observed and the coordination sphere around CuII becomes a distinctly distorted octahedron.

Coordination bonds involving the SO₄²⁻ 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 SO₄ anion (Table 2), enclosing a six-membered ring with graph-set notation S(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 1

The expanded asymmetric part of the title compound [Cu(SEC)₂(SO₄)]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 + 1/2, z − 1/2; (ii) x, −y + 1/2, z + 1/2].

Figure 2

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

| Table 1 | Selected bond lengths (Å). |
|---------|---------------------------|
| Cu1—O1 | 1.9549 (17)               |
| Cu1—O2 | 1.9218 (17)               |
| Cu1—N1 | 1.9769 (19)               |
| Cu1—N4 | 2.015 (2)                 |

Table 2

Hydrogen-bond geometry (Å, °).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|------|---------|
| N1—H1A···O4vii | 0.89 | 2.06 | 2.928 (3) | 164 |
| N1—H1B···O4vi | 0.89 | 2.43 | 3.302 (3) | 167 |
| N1—H1B···O5ui | 0.89 | 2.24 | 2.871 (3) | 128 |
| N2—H2···O5ii | 0.86 | 1.97 | 2.751 (3) | 151 |
| N3—H3A···O3vi | 0.86 | 2.20 | 2.985 (3) | 152 |
| N3—H3B···O1v | 0.86 | 2.59 | 3.036 (3) | 113 |
| N4—H4A···O4 | 0.89 | 2.47 | 3.125 (3) | 131 |
| N4—H4A···O5vii | 0.89 | 2.57 | 3.097 (3) | 119 |
| N4—H4B···O5v | 0.89 | 2.49 | 3.309 (3) | 152 |
| N5—H5···O6vi | 0.86 | 2.59 | 3.228 (3) | 132 |
| N5—H5···O4vii | 0.86 | 2.39 | 2.954 (3) | 123 |
| N6—H6A···O1iii | 0.86 | 2.51 | 3.123 (3) | 129 |
| N6—H6A···O2vii | 0.86 | 2.17 | 2.971 (3) | 154 |
| N6—H6A···O6vi | 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 + 1/2, 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.
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 $d_{\text{norm}}$ (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 O···H/H···O contacts. The overall two-dimensional fingerprint plot and those delineated into O···H/H···O, H···H, N···H/H···N, C···H/H···C and Cu···O/O···C interactions are shown in Fig. 5. The 2.5% contribution of the Cu···O/O···Cu contact is explained by the existence of the very long Cu—O3 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.
Table 3
Experimental details.

Crystal data
Chemical formula [Cu(SO$_4$)(CH$_5$N$_3$O)$_2$]
$M_r$ 309.76
Crystal system, space group Monoclinic, $P2_1/c$
Temperature (K) 293
$α$, $β$, $γ$ (Å)
$eta$ (°) 97.265 (2)
$V$ (Å$^3$) 927.36 (3)
$Z$ 4
Radiation type Cu $Kα$
Absorption correction Multi-scan (CrysAlis PRO; Rigaku, 2020)
No. of measured, independent and observed $|F > 2σ(F)|$ reflections 8102, 1785, 1656
$R_{int}$ 0.037
$R_{max}$ (Å$^{-1}$) 0.613
$〈\sin θ/λ〉_{max}$ (Å$^{-1}$) 0.613

Refinement
$R(F^2 > 2σ(F^2))$, $wR(F^2)$, $S$ 0.029, 0.080, 1.07
No. of reflections 1785
No. of parameters 146
H-atom treatment H-atom parameters constrained
$Δρ_{max}$, $Δρ_{min}$ (e Å$^{-3}$) 0.32, −0.42

Data collection
Diffractometer XtaLAB Synergy, Single source at home/near, HyPix3000
Absorption correction Multi-scan (CrysAlis PRO; Rigaku, 2020)
$T_{min}$, $T_{max}$ 0.084, 1.00

| Parameter | Value |
|-----------|-------|
| $M_r$ | 309.76 |
| Crystal system | Monoclinic, $P2_1/c$ |
| Temperature | 293 K |
| $α$, $β$, $γ$ | (Å) |
| $β$ | 97.265 (2) |
| $V$ | 927.36 (3) Å$^3$ |
| $Z$ | 4 |
| Radiation type | Cu $Kα$ |
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku, 2020) |
| $T_{min}$, $T_{max}$ | 0.084, 1.00 |

8. 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 $U_{iso}(H) = 1.2U_{eq}(N)$, $N—H = 0.89$ Å for the N1 and N4 nitrogen atoms and $N—H = 0.86$ for the remaining nitrogen atoms.

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Chemical formula $[\text{Cu(SO}_4\text{(CH}_5\text{N}_3\text{O)}_2\text{]}$
Supporting information

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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-κ²N,O)copper(II)]-µ-sulfato-κ²O₂O']**

**Crystal data**

\[\text{[Cu(SO}_4\text{)(CH}_3\text{N}_3\text{O}_2\text{)]} \]

\(M_r = 309.76\)

Monoclinic, \(P2_1/c\)

\(a = 10.5555 (2) \text{ Å}\)

\(b = 6.8624 (1) \text{ Å}\)

\(c = 12.9061 (2) \text{ Å}\)

\(\beta = 97.265 (2)^\circ\)

\(V = 927.36 (3) \text{ Å}^3\)

\(Z = 4\)

\(F(000) = 628\)

\(D_x = 2.219 \text{ Mg m}^{-3}\)

\(\text{Cu }K\alpha \text{ radiation, } \lambda = 1.54184 \text{ Å}\)

Cell parameters from 4840 reflections

\(\theta = 3.5\text{–}70.8^\circ\)

\(\mu = 5.82 \text{ mm}^{-1}\)

\(T = 293 \text{ K}\)

Block, light blue

0.18 × 0.16 × 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\(^{-1}\)

\(\omega\) 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

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*Acta Cryst.* (2022). E78, 1131-1134
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.5652P]$  
where $P = (F_o^2 + 2F_c^2)/3$

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

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

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

**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 | 0.25619 (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) | 0.2652 (3)  | 0.61509 (14) | 0.0327 (4)  |
| O4  | 0.06548 (18) | 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 | 0.536656      | 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 (Å²)**

|   | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---------|---------|---------|---------|---------|---------|
| 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—O3i | 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—O3i | 96.00 (7) | C2—N5—H5 | 121.8  |
| O1—Cu1—O3i | 90.24 (7) | N1—N2—H2 | 121.5  |
| N1—Cu1—O3i | 81.50 (7) | C1—N2—N1 | 116.94 (19) |
| N4—Cu1—O3i | 86.13 (9) | C1—N2—H2 | 121.5  |
| O6—Cu1—O3i | 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 (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|-------|-------|---------|
| N1—H1A···O4i | 0.89 | 2.06 | 2.928 (3) | 164 |
| N1—H1B···O4ii | 0.89 | 2.43 | 3.302 (3) | 167 |
| N1—H1B···O5ii | 0.89 | 2.24 | 2.871 (3) | 128 |
| N2—H2···O5iii | 0.86 | 1.97 | 2.751 (3) | 151 |
| N3—H3A···O3iv | 0.86 | 2.20 | 2.985 (3) | 152 |
| N3—H3B···O1v | 0.86 | 2.59 | 3.036 (3) | 113 |
| N4—H4A···O4 | 0.89 | 2.47 | 3.125 (3) | 131 |
| N4—H4A···O5ii | 0.89 | 2.57 | 3.097 (3) | 119 |
| N4—H4B···O5i | 0.89 | 2.49 | 3.309 (3) | 152 |
| N5—H5···O6vi | 0.86 | 2.59 | 3.228 (3) | 132 |
| N5—H5···O4viii | 0.86 | 2.39 | 2.954 (3) | 123 |
| N6—H6A···O1viii | 0.86 | 2.51 | 3.123 (3) | 129 |
| N6—H6A···O2viii | 0.86 | 2.17 | 2.971 (3) | 154 |
| N6—H6A···O6vi | 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.