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Crystal structure of tetra-μ-acetato-bis[(5-amino-2-methylsulfanyl-1,3,4-thiadiazole-κN^1)copper(II)]

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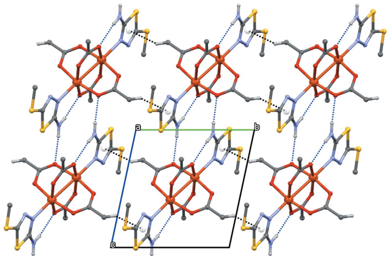
The reaction of 2-methylthio-5-amino-1,3,4-thiadiazole (Me-SNTD; $C_3H_5N_3S_2$) with copper(II) acetate monohydrate [$Cu(OAc)_2 \cdot H_2O$; $C_4H_8CuO_5$] resulted in the formation of the title binuclear compound, [$Cu_2(C_2H_3O_2)_4(C_3H_5N_3S_2)_2$] or [$Cu_2(OAc)_4$(Me-SNTD)$_2$]. The structure has triclinic ($P\,\overline{1}$) symmetry with a crystallographic inversion centre located at the midpoint of the line connecting the Cu atoms in the dimer. These two Cu atoms of the dimer [$Cu\cdots Cu$ = 2.6727 (6) Å] are held together by four carboxylate groups. Each Cu atom is further coordinated to the N atom of an Me-SNTD molecule and exhibits a Jahn–Teller-distorted octahedral geometry. The dimers are connected into infinite chains by hydrogen bonds between the NH (Me-SNTD) and the carboxylate groups of neighbouring molecules, generating an $R_2^2(12)$ ring motif. The molecules are further linked by $C—H\cdots\pi$ interactions between the thiadiazole rings and the methyl groups of the acetate units.



1. Chemical context

1,3,4-Thiadazoles are an important class of heterocycles and are of great interest because of their broad spectrum of biological activity. 1,3,4-Thiadiazole derivatives and their metal complexes have been shown to display antimicrobial (Önkol *et al.*, 2008; Abdel-Wahab *et al.*, 2009; Kadi *et al.*, 2010), antituberculosis (Karakuşş *et al.*, 2002; Foroumadi *et al.*, 2004), antioxidant (Chitale *et al.*, 2011; Sunil *et al.*, 2010; Khan *et al.*, 2010), anticancer (Padmavathi *et al.*, 2009; Kumar *et al.*, 2010;) and antifungal (Matysiak *et al.*, 2007; Klip *et al.*, 2010; Verma *et al.*, 2011; Zoumpoulakis *et al.*, 2012) activities. In addition, some of the 1,3,4-thiadiazole-ring-containing ligands can be efficient uptake agents of toxic metal ions (Mincione *et al.*, 1997). 1,3,4-Thiadiazoles also exhibit great potential as pesticides in the fields of herbicides, fungicides, insecticides and even as plant-growth regulators. Their diverse biological activity possibly arises from the presence of the =NCS moiety in the molecule (Oruç *et al.*, 2004). An interesting feature of the metal–ligand chemistry of these compounds is that the complexes can be either mononuclear (Tzeng *et al.*, 2004; Varna *et al.*, 2018; Qiu *et al.*, 2014) or binuclear (Deckert *et al.*, 2016; Ardan *et al.*, 2017). A search of the Cambridge Structural Database (CSD Version 5.4, update of February 2019; Groom *et al.*, 2016) revealed that although crystal structures have been reported for complexes of either 1,3,4-thiadiazole derivatives or OAc with a number of metal ions, including

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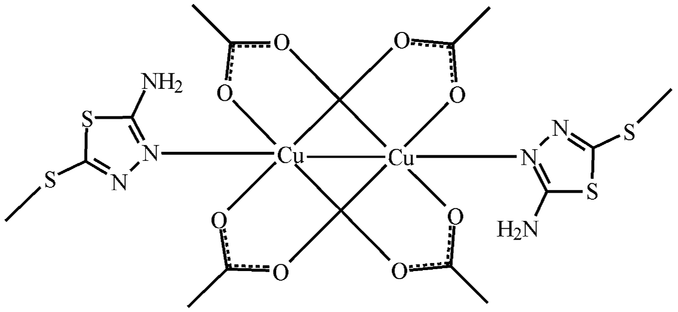
zinc, copper, nickel, manganese, cadmium, cobalt and palladium, no examples are known of mixed-ligand metal complexes containing both 1,3,4-thiadiazole derivatives and OAc. Herein, we report on the synthesis and crystal structure of a new binuclear complex, $[Cu_2(OAc)_4L_2]$, with L = 2-methylthio-5-amino-1,3,4-thiadiazole (Me-SNTD).



2. Structural commentary

The title binuclear Cu^{II} complex, (I) (Fig. 1), is arranged about a crystallographic inversion centre located at the midpoint of the Cu$\cdots$Cu-connecting line. The asymmetric unit comprises one half of the complex molecule, namely, one Cu atom, two acetate groups and one 2-methylthio-5-amino-1,3,4-thiadiazole molecule. The two Cu atoms in the dimer are held together by the four carboxylate groups. Each Cu atom is bound in a square-pyramidal configuration to four carboxylate O atoms and to the N atom of an Me-SNTD molecule.

Each copper atom is displaced by 0.754 (3) Å from the plane defined by basal-plane atoms O1, O2, O3 and O4 towards the nitrogen atom, N2. The Cu1A —Cu1—N2 angle is 177.95 (7)° [symmetry code: (A) $2 - x, 1 - y, 1 - z$]. The Cu—O bond lengths range from 1.962 (2) to 2.001 (2) Å and the Cu—N distance is 2.180 (3) Å. The Cu$\cdots$Cu distance is 2.6727 (6) Å and each metal atom exhibits a Jahn–Teller-distorted octahedral geometry. The observed Cu—O2 bond length of 1.983 (2) Å is longer than the Cu—O1 distance of 1.962 (2) Å. The elongation of this Cu—O distance may be due to the intramolecular N3—H$\cdots$O2 hydrogen bond (Table 1). The conformation of the ligand is approximately planar, with a maximum deviation from the least-squares plane of 0.066 (2) Å for atom N3. The thiadiazole ring is planar (r.m.s. deviation 0.0063 Å). The dihedral angle between the planes of the two independent acetate groups is 82.646 (14)°. The thiadiazole ring is twisted by 18.37 (2)° with respect to the acetate (C4/C5/O1/O2) ligand mean plane.

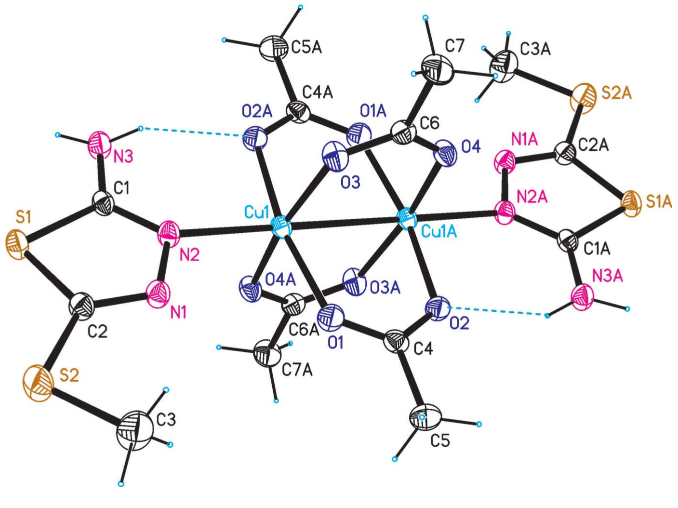


Figure 1
The molecular structure of $[Cu_2(OAc)_4(Me\text{-}SNTD)_2]$ with the atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level. Intramolecular hydrogen bonds are shown as dashed lines. Atoms labelled with the suffix A are generated by the symmetry operation $2 - x, 1 - y, 1 - z$.

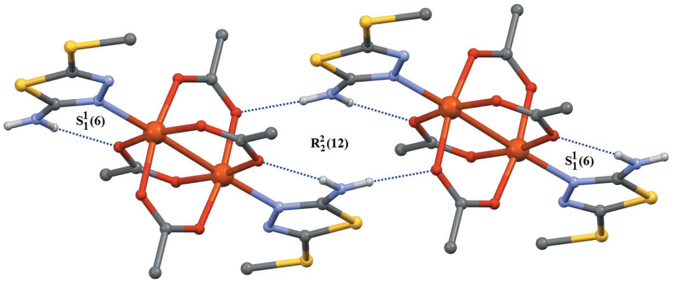


Figure 2
Part of the crystal structure with hydrogen bonds shown as dashed lines. For clarity, H atoms not involved in hydrogen bonding are omitted.

3. Supramolecular features

The packing of (I) is shown in Fig. 2. The acetate group containing oxygen atoms O1 and O3 does not form any hydrogen bonds. However, the acetate group containing oxygen atoms O2 and O4 forms both intra- and intermolecular hydrogen bonds. Each binuclear complex molecule exhibits one intramolecular N3—H3$\cdots$O2^{i} hydrogen bond, forming a six-membered ring. The dimers are connected through an intermolecular N3—H3$\cdots$O4^{ii} hydrogen bond between the

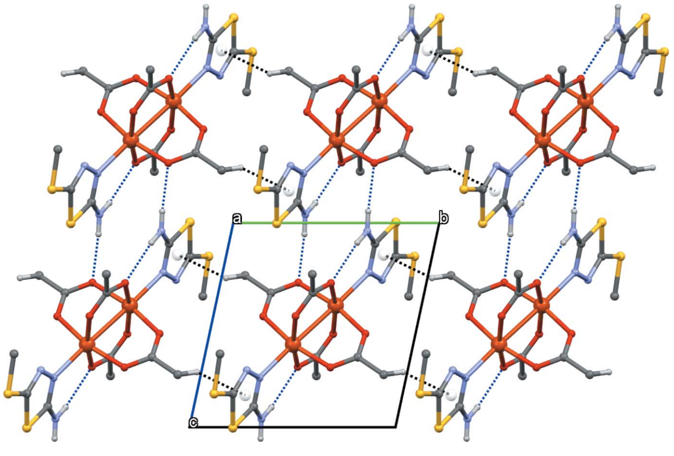


Figure 3
Packing of the structural units in (I). Hydrogen bonds are indicated by blue dashed lines and C—H$\cdots\pi$ interactions by black dashed lines.

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

Cg is the centroid of the S1/N1/N2/C1/C2 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$A\cdots$O4$^{\rm i}$	0.86 (1)	2.16 (2)	2.963 (4)	156 (4)
N3—H3$B\cdots$O2$^{\rm ii}$	0.86 (1)	2.11 (3)	2.884 (4)	150 (4)

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

NH (Me-SNTD) and the carboxylate groups, forming chains propagating parallel to [001]. The above-mentioned hydrogen bonds give rise to $R_2^2(12)$, $C_2^2(14)$ and $S_1^1(6)$ graph-set motifs (Table 1 and Fig. 2). Additional C—H$\cdots\pi$ interactions between the thiadiazole rings and the acetate methyl groups generate a three-dimensional supramolecular framework (Fig. 3).

4. Database survey

A survey of the Cambridge Structural Database (CSD Version 5.4, update of February 2019; Groom *et al.*, 2016) revealed that crystal structures have been reported for complexes of 1,3,4-thiadiazole derivatives and OAc with a number of metal ions, including zinc, copper, nickel, manganese, cadmium, cobalt and palladium. Copper(II) acetate complexes of the general formula [$Cu_2(OAc)_4L_2$], where L is a ligand with an oxygen or nitrogen ligator atom, have been well explored. The structures of 2-methylthio-5-amino-1,3,4-thiadiazole and a complex of this molecule with cadmium have been deposited in the CSD [XUVPEK (Lynch, 2010) and JIZKEK (Soudani *et al.*, 2014), respectively]. However, no mixed-ligand metal complexes containing both 1,3,4-thiadiazole derivatives and OAc have been documented in the CSD.

5. Synthesis and crystallization

$Cu(OAc)_2 \cdot H_2O$ (0.218 g, 1 mmol) and 2-methylthio-5-amino-1,3,4-thiadiazole (0.147 g, 1 mmol) were dissolved separately in a mixture of methanol-dichloromethane (10 mL, 1:1 *v*/*v*), mixed together and stirred for 1.5 h. The green solid that precipitated was dissolved in methanol to form a green solution. Single crystals of the complex suitable for X-ray analysis were obtained by slow evaporation of the solution over a period of 10 d.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The restraint N—H = 0.86 ± (1) Å was applied. Methyl H atoms were positioned geometrically C—H = 0.96) and refined as riding with $U_{\rm iso}({\rm H}) = 1.5U{\rm eq}({\rm C})$.

Funding information

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Table 2
Experimental details.

Crystal data	
Chemical formula	[$Cu_2(C_2H_3O_2)_4(C_3H_5N_3S_2)_2$]
$M_{\rm r}$	657.69
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	571
a, b, c (Å)	8.1069 (4), 8.8955 (4), 9.0421 (5)
α, β, γ (°)	100.656 (4), 98.966 (4), 97.643 (4)
V (Å^3)	624.14 (5)
Z	1
Radiation type	Cu $K\alpha$
μ (mm^{-1})	5.70
Crystal size (mm)	0.44 × 0.38 × 0.28
Data collection	
Diffractometer	Rigaku Oxford Diffraction Xcalibur, Ruby
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
$T_{\rm min}$, $T_{\rm max}$	0.083, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11239, 2582, 2244
$R_{\rm int}$	0.052
(sin $\theta/\lambda)_{\rm max}$ (Å^{-1})	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.118, 1.07
No. of reflections	2582
No. of parameters	165
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.47, −0.44

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Crystal structure of tetra-μ-acetato-bis[(5-amino-2-methylsulfanyl-1,3,4-thiadiazole-κN^1)copper(II)]

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Tetra-μ-acetato-bis[(5-amino-2-methylsulfanyl-1,3,4-thiadiazole-κN^1)copper(II)]

Crystal data

$[Cu_2(C_2H_3O_2)_4(C_3H_5N_3S_2)_2]$
M_r = 657.69
Triclinic, $P\overline{1}$
a = 8.1069 (4) Å
b = 8.8955 (4) Å
c = 9.0421 (5) Å
α = 100.656 (4)°
β = 98.966 (4)°
γ = 97.643 (4)°
V = 624.14 (5) Å^3
Z = 1
F(000) = 334
D_x = 1.750 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 5762 reflections
θ = 5.0–75.8°
μ = 5.70 mm^{-1}
T = 571 K
Block, blue
0.44 × 0.38 × 0.28 mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Ruby diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 10.2576 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
T_{min} = 0.083, T_{max} = 1.000
11239 measured reflections
2582 independent reflections
2244 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 76.2°, θ_{min} = 5.1°
h = −10→10
k = −11→11
l = −10→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.118
S = 1.07
2582 reflections
165 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 0.1915P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 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	0.94133 (5)	0.41682 (4)	0.59528 (5)	0.03080 (16)
S1	0.77895 (10)	0.21114 (9)	1.00281 (9)	0.0416 (2)
S2	0.42143 (12)	0.08505 (14)	0.83586 (12)	0.0659 (3)
O4	1.0956 (3)	0.3780 (2)	0.2926 (2)	0.0403 (5)
O2	0.8200 (3)	0.5370 (3)	0.2953 (3)	0.0409 (5)
O1	0.7249 (3)	0.3994 (3)	0.4563 (3)	0.0458 (5)
O3	1.0032 (3)	0.2430 (2)	0.4575 (3)	0.0438 (5)
N3	1.0840 (4)	0.3406 (3)	0.9585 (3)	0.0442 (6)
N2	0.8489 (3)	0.2883 (3)	0.7575 (3)	0.0354 (5)
N1	0.6790 (3)	0.2193 (3)	0.7215 (3)	0.0385 (6)
C1	0.9196 (4)	0.2903 (3)	0.8988 (3)	0.0327 (6)
C6	1.0679 (4)	0.2556 (3)	0.3428 (3)	0.0363 (6)
C4	0.7032 (4)	0.4586 (3)	0.3410 (4)	0.0367 (6)
C2	0.6271 (4)	0.1756 (3)	0.8362 (4)	0.0383 (6)
C7	1.1194 (5)	0.1119 (4)	0.2574 (5)	0.0567 (9)
H7A	1.106850	0.114281	0.150585	0.085*
H7B	1.048657	0.021473	0.270116	0.085*
H7C	1.235495	0.108716	0.297339	0.085*
C5	0.5263 (4)	0.4374 (5)	0.2518 (5)	0.0565 (9)
H5A	0.459075	0.495634	0.311649	0.085*
H5B	0.477358	0.329410	0.228270	0.085*
H5C	0.529261	0.473477	0.158389	0.085*
C3	0.3241 (6)	0.0719 (6)	0.6412 (5)	0.0740 (13)
H3C	0.373741	0.001172	0.574724	0.111*
H3D	0.341504	0.172515	0.616365	0.111*
H3E	0.204871	0.034989	0.627943	0.111*
H3A	1.119 (5)	0.357 (4)	1.0554 (14)	0.048 (10)*
H3B	1.149 (5)	0.377 (5)	0.903 (5)	0.070 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0315 (2)	0.0301 (2)	0.0309 (3)	0.00161 (15)	0.00874 (17)	0.00645 (16)
S1	0.0421 (4)	0.0494 (4)	0.0336 (4)	−0.0010 (3)	0.0112 (3)	0.0114 (3)
S2	0.0408 (5)	0.0941 (7)	0.0623 (6)	−0.0141 (5)	0.0082 (4)	0.0347 (6)
O4	0.0516 (13)	0.0353 (10)	0.0367 (12)	0.0105 (9)	0.0164 (10)	0.0054 (9)
O2	0.0312 (10)	0.0497 (11)	0.0409 (12)	0.0015 (9)	0.0043 (9)	0.0130 (10)
O1	0.0333 (11)	0.0572 (13)	0.0450 (13)	−0.0018 (9)	0.0039 (9)	0.0154 (11)
O3	0.0599 (14)	0.0309 (9)	0.0423 (13)	0.0072 (9)	0.0171 (11)	0.0056 (9)

N3	0.0374 (14)	0.0580 (16)	0.0353 (16)	−0.0021 (11)	0.0051 (12)	0.0132 (13)
N2	0.0371 (13)	0.0357 (11)	0.0334 (13)	−0.0002 (9)	0.0077 (10)	0.0106 (10)
N1	0.0375 (13)	0.0409 (12)	0.0373 (14)	−0.0007 (10)	0.0072 (11)	0.0138 (10)
C1	0.0377 (14)	0.0286 (11)	0.0339 (15)	0.0037 (10)	0.0127 (12)	0.0081 (11)
C6	0.0389 (15)	0.0318 (13)	0.0352 (16)	0.0085 (11)	0.0027 (12)	0.0006 (11)
C4	0.0294 (13)	0.0399 (14)	0.0369 (17)	0.0024 (11)	0.0060 (12)	0.0004 (12)
C2	0.0365 (15)	0.0382 (14)	0.0408 (17)	0.0001 (11)	0.0084 (13)	0.0130 (12)
C7	0.077 (3)	0.0424 (17)	0.056 (2)	0.0278 (17)	0.0212 (19)	0.0030 (15)
C5	0.0329 (16)	0.075 (2)	0.059 (2)	0.0039 (15)	0.0028 (16)	0.0144 (19)
C3	0.053 (2)	0.093 (3)	0.067 (3)	−0.015 (2)	−0.004 (2)	0.024 (2)

Geometric parameters (Å, º)

Cu1—Cu1^{i}	2.6728 (8)	N3—H3B	0.856 (10)
Cu1—O4^{i}	2.0007 (19)	N2—N1	1.394 (3)
Cu1—O2^{i}	1.983 (2)	N2—C1	1.313 (4)
Cu1—O1	1.962 (2)	N1—C2	1.282 (4)
Cu1—O3	1.970 (2)	C6—C7	1.510 (4)
Cu1—N2	2.180 (2)	C4—C5	1.502 (4)
S1—C1	1.745 (3)	C7—H7A	0.9600
S1—C2	1.740 (3)	C7—H7B	0.9600
S2—C2	1.752 (3)	C7—H7C	0.9600
S2—C3	1.789 (5)	C5—H5A	0.9600
O4—C6	1.262 (4)	C5—H5B	0.9600
O2—C4	1.267 (4)	C5—H5C	0.9600
O1—C4	1.251 (4)	C3—H3C	0.9600
O3—C6	1.249 (4)	C3—H3D	0.9600
N3—C1	1.339 (4)	C3—H3E	0.9600
N3—H3A	0.857 (10)		
O4^{i}—Cu1—Cu1^{i}	83.88 (6)	N2—C1—S1	113.1 (2)
O4^{i}—Cu1—N2	94.39 (9)	N2—C1—N3	124.8 (3)
O2^{i}—Cu1—Cu1^{i}	84.10 (7)	O4—C6—C7	117.0 (3)
O2^{i}—Cu1—O4^{i}	89.30 (9)	O3—C6—O4	125.8 (3)
O2^{i}—Cu1—N2	94.80 (9)	O3—C6—C7	117.2 (3)
O1—Cu1—Cu1^{i}	82.97 (7)	O2—C4—C5	117.6 (3)
O1—Cu1—O4^{i}	89.12 (10)	O1—C4—O2	124.5 (3)
O1—Cu1—O2^{i}	167.07 (9)	O1—C4—C5	117.8 (3)
O1—Cu1—O3	90.92 (10)	S1—C2—S2	119.34 (18)
O1—Cu1—N2	98.11 (10)	N1—C2—S1	115.2 (2)
O3—Cu1—Cu1^{i}	83.44 (7)	N1—C2—S2	125.5 (3)
O3—Cu1—O4^{i}	167.22 (9)	C6—C7—H7A	109.5
O3—Cu1—O2^{i}	87.81 (10)	C6—C7—H7B	109.5
O3—Cu1—N2	98.26 (9)	C6—C7—H7C	109.5
N2—Cu1—Cu1^{i}	177.95 (7)	H7A—C7—H7B	109.5
C2—S1—C1	86.58 (14)	H7A—C7—H7C	109.5
C2—S2—C3	100.75 (18)	H7B—C7—H7C	109.5
C6—O4—Cu1^{i}	122.12 (19)	C4—C5—H5A	109.5

C4—O2—Cu1^{i}	122.8 (2)	C4—C5—H5B	109.5
C4—O1—Cu1	125.6 (2)	C4—C5—H5C	109.5
C6—O3—Cu1	124.56 (19)	H5A—C5—H5B	109.5
C1—N3—H3A	121 (3)	H5A—C5—H5C	109.5
C1—N3—H3B	119 (3)	H5B—C5—H5C	109.5
H3A—N3—H3B	119 (4)	S2—C3—H3C	109.5
N1—N2—Cu1	116.61 (18)	S2—C3—H3D	109.5
C1—N2—Cu1	128.89 (19)	S2—C3—H3E	109.5
C1—N2—N1	113.1 (2)	H3C—C3—H3D	109.5
C2—N1—N2	112.1 (3)	H3C—C3—H3E	109.5
N3—C1—S1	122.1 (2)	H3D—C3—H3E	109.5

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the S1/N1/N2/C1/C2 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O4^{ii}	0.86 (1)	2.16 (2)	2.963 (4)	156 (4)
N3—H3*B*···O2^{i}	0.86 (1)	2.11 (3)	2.884 (4)	150 (4)
C7—H7*B*···*Cg*^{iii}	0.96	3.00	3.346 (4)	103

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