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Crystal structure of bis{μ-4-methyl-N'-[3-(oxidoimino)butan-2-ylidene]benzenesulfonohydrazidato}bis[(dimethyl sulfoxide-κO)copper(II)]

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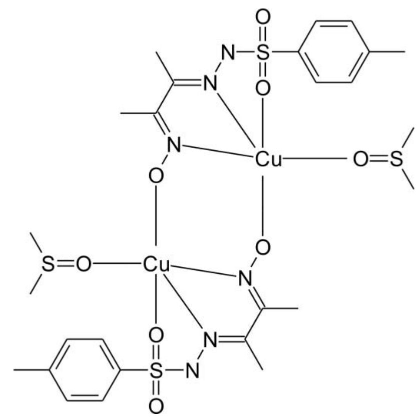
In the title compound, $[Cu_2(C_{11}H_{13}N_3O_3S)_2(C_2H_6OS)_2]$, the Cu^{II} cation is N,N',O-chelated by a deprotonated hydroxyimino-tosylhydrazone ligand and coordinated by a dimethyl sulfoxide molecule. One O atom from the adjacent hydroxyimino-tosylhydrazone ligand bridges the Cu^{II} cation, forming the centrosymmetric dimeric complex. The cation is in an overall distorted N_2O_3 square-pyramidal coordination environment. The methylbenzene ring is twisted with respect to the hydrazine fragment, with a dihedral angle of 89.54 (9)° between the planes. An intramolecular C—H$\cdots$O hydrogen bond occurs. In the crystal, molecules are linked by weak C—H$\cdots$O and C—H$\cdots$S interactions. Weak π–π stacking is also observed between parallel benzene rings of adjacent molecules, the centroid–centroid distance being 3.9592 (17) Å.

Keywords: crystal structure; hydroxyimino-tosylhydrazone derivative; Cu^{II} dimer; π–π stacking.

CCDC reference: 1014769

1. Related literature

For the synthesis and applications of hydroxyimino-tosylhydrazones as complexing agents, see: Beger *et al.* (1991). For the crystal structure of the 4-methyl-N'-[3-(hydroxyimino)-butan-2-ylidene]benzenesulfonohydrazide ligand, see: Bulhosa *et al.* (2012).



2. Experimental

2.1. Crystal data

$[Cu_2(C_{11}H_{13}N_3O_3S)_2(C_2H_6OS)_2]$
M_r = 817.95
Triclinic, $P\bar{1}$
a = 7.8097 (3) Å
b = 8.4670 (3) Å
c = 15.1586 (6) Å
α = 74.656 (2)°
β = 75.955 (2)°
γ = 65.042 (2)°
V = 866.47 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.52 mm^{-1}
T = 293 K
0.61 × 0.28 × 0.07 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.457, T_{max} = 0.901
5765 measured reflections
4054 independent reflections
3366 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.091
S = 1.04
4054 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N2	1.9580 (19)	Cu1—O3^i	1.8798 (16)
Cu1—N3	1.9728 (18)	Cu1—O4	2.2517 (17)
Cu1—O2	2.0970 (16)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$\cdots$O4	0.93	2.39	3.299 (3)	166
C2—H2$\cdots$O1^{ii}	0.93	2.57	3.430 (4)	154
C9—H9$A\cdots$S2^{iii}	0.96	2.75	3.693 (3)	166
C10—H10$C\cdots$O1^{iv}	0.96	2.47	3.415 (4)	166

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Acknowledgements

We gratefully acknowledge Professor Dr Manfredo Hörner (Federal University of Santa Maria, Brazil) for his help and support with the X-ray measurements. DPS and MCBS thank CNPq, CAPES and FAPERGS for the award of scholarships.

Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5805).

References

Beger, J., Siedler, F., Mühl, P. & Gloe, K. (1991). German Patent DD287027A5.
Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bulhosa, M. C. S., Gervini, V. C., Bresolin, L., Locatelli, A. & Oliveira, A. B. de (2012). *Acta Cryst.* E**68**, o592.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2014). E**70**, m316–m317 [doi:10.1107/S1600536814016651]

Crystal structure of bis{*μ*-4-methyl-*N*′-[3-(oxidoimino)butan-2-ylidene]benzene-sulfonohydrazidato}bis[(dimethyl sulfoxide-*κO*)copper(II)]

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S1. Chemical context

S2. Structural commentary

Hydroxyimino-tosylhydrazone derivatives are N,O-donors that show an application as complexing agents (Beger *et al.*, 1991). In the crystal structure of the title compound the Cu^{II} cations are five-coordinated by one crystallographically independent deprotonated hydroxyimino-tosylhydrazone derivative, one DMSO molecule and one O-atom from a second, symmetry generated, hydroxyimino-tosylhydrazone derivative into dimers (Fig. 1). The metal centres are in a slightly distorted pyramidal environment. The aromatic ring and the N1/N2/C7/C8/N3/O3-fragment angle amount to 89,54 (09)°. In this complex molecule significant structural changes of the N–O and N–N bonds. For the uncoordinated ligand the N–O and N–N bonds distances amount to 1.4084 (16) Å and 1.3807 (16) Å. These distances indicate the double bond character for the N–N and the single bond character for the N–O bond (Bulhosa *et al.*, 2012). In contrast, in the title compound, the acidic hydrogen of the hydrazine fragment is removed and the negative charge is delocalized over the N–N–C–C–N–O fragment. Therefore, N–N and N–O distances amount to 1.367 (3) Å and 1.343 (2) Å. Additionally, the complexes are linked by N–O bridges into dimers (Fig. 2). Finally, the dimers are arranged along the *b*-axis with very weak *π*–*π* interactions.

S3. Supramolecular features

S4. Database survey

S5. Synthesis and crystallization

Starting materials were commercially available and were used without further purification. The ligand synthesis was adapted from a procedure reported previously and its structure is already published (Bulhosa *et al.*, 2012). *N*′-[3-(Hydroxyimino)butan- 2-ylidene]-4-methylbenzene-1-sulfonohydrazide was dissolved in methanol (2 mmol/40 mL) with stirring maintained for 30 min and deprotonated with sodium, while the solution turns yellow. At the same time, a solution of copper(II) acetate monohydrate (1 mmol/40 mL) in methanol was prepared under continuous stirring. A mixture of both solutions was maintained with stirring at room temperature for 6 h. The methanol was removed by evaporation and crystals suitable for X-ray diffraction were obtained in DMSO by the slow evaporation of the solvent.

S6. Refinement

H atoms attached to C atoms were positioned with idealized geometry and were refined isotropically with U_{iso}(H) set to 1.2 times U_{eq}(C) for the aromatic and 1.5 times U_{eq}(C) for methyl H atoms using a riding model with C—H = 0.93 Å and

C—H = 0.96 Å, respectively.

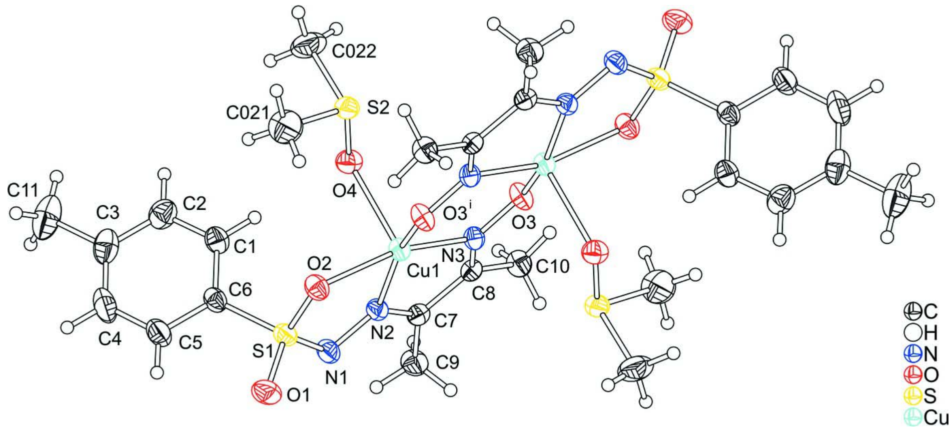

Figure 1

The molecular structure of the title compound with labeling and displacement ellipsoids drawn at the 40% probability level showing the dimeric structure. Symmetry code: (i)-*x* + 1,-*y* + 1,-*z* + 1

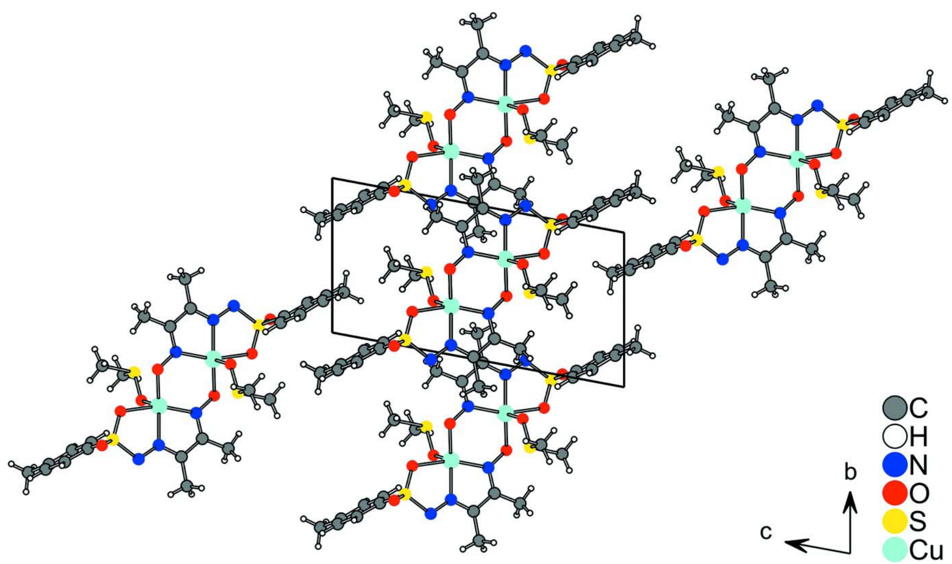

Figure 2

Molecules of the title compound arranged along *b*-axis showing the column of the aromatic rings with very weak *π*–*π* interactions.

Bis{*μ*-4-methyl-*N′*-[3-(oxidoimino)butan-2-ylidene]benzenesulfonohydrazidato}-*κ*[4]*O*,*N*,*N′*:*O′*;*κ*[4]*O′*:*O*,*N*,*N′*-bis[(dimethyl sulfoxide-*κO*)copper(II)]

Crystal data

$[Cu_2(C_{11}H_{13}N_3O_3S)_2(C_2H_6OS)_2]$
M_r = 817.95
Triclinic, $P\overline{1}$
Hall symbol: -P 1
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c = 15.1586 (6) Å
α = 74.656 (2)°
β = 75.955 (2)°
γ = 65.042 (2)°
V = 866.47 (6) Å^3
Z = 1
F(000) = 422
D_x = 1.568 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7693 reflections
θ = 2.8–28.1°
μ = 1.52 mm^{-1}
T = 293 K
Block, black
0.61 × 0.28 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube, Bruker Kappa CCD
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.457, T_{max} = 0.901
5765 measured reflections
4054 independent reflections
3366 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 28.4°, θ_{min} = 2.7°
h = −10→10
k = −11→7
l = −20→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.091
S = 1.04
4054 reflections
208 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.3887P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.58200 (4)	0.31552 (3)	0.593265 (18)	0.02826 (9)
S1	0.77302 (8)	0.04077 (8)	0.74973 (4)	0.03261 (14)
S2	0.14080 (8)	0.50296 (8)	0.67789 (4)	0.03775 (15)
O2	0.6646 (2)	0.2330 (2)	0.72499 (11)	0.0355 (4)
N2	0.7236 (3)	0.0618 (2)	0.59334 (13)	0.0287 (4)
C10	0.6295 (4)	0.1222 (3)	0.35609 (16)	0.0370 (5)
H10A	0.5581	0.2316	0.3194	0.056*
H10B	0.5663	0.0413	0.3685	0.056*
H10C	0.7556	0.0715	0.3231	0.056*
C7	0.7440 (3)	0.0142 (3)	0.51572 (15)	0.0293 (4)
O4	0.2837 (2)	0.3281 (2)	0.65248 (12)	0.0386 (4)
O1	0.9442 (3)	−0.0107 (3)	0.78807 (13)	0.0480 (5)

N1	0.8225 (3)	−0.0535 (3)	0.66265 (13)	0.0361 (4)
O3	0.4716 (2)	0.4478 (2)	0.40297 (11)	0.0346 (4)
N3	0.5685 (3)	0.3140 (2)	0.46524 (12)	0.0281 (4)
C8	0.6430 (3)	0.1565 (3)	0.44490 (15)	0.0271 (4)
C2	0.3225 (4)	−0.0775 (4)	0.88982 (19)	0.0486 (7)
H2	0.1983	−0.0485	0.8810	0.058*
C1	0.4370 (4)	−0.0029 (4)	0.82421 (17)	0.0400 (6)
H1	0.3897	0.0761	0.7719	0.048*
C6	0.6226 (3)	−0.0460 (3)	0.83647 (15)	0.0332 (5)
C9	0.8650 (4)	−0.1691 (3)	0.49726 (19)	0.0417 (6)
H9A	0.9189	−0.2428	0.5517	0.062*
H9B	0.9659	−0.1646	0.4470	0.062*
H9C	0.7878	−0.2174	0.4813	0.062*
C3	0.3885 (5)	−0.1948 (4)	0.96864 (19)	0.0526 (7)
C5	0.6905 (4)	−0.1601 (4)	0.91562 (18)	0.0471 (6)
H5	0.8141	−0.1876	0.9251	0.057*
C4	0.5723 (5)	−0.2326 (4)	0.9805 (2)	0.0583 (8)
H4	0.6181	−0.3091	1.0337	0.070*
C021	0.1846 (5)	0.5082 (5)	0.7870 (2)	0.0674 (9)
H02A	0.3027	0.5237	0.7789	0.101*
H02B	0.1927	0.3987	0.8286	0.101*
H02C	0.0821	0.6049	0.8122	0.101*
C022	−0.0802 (4)	0.4738 (5)	0.7154 (3)	0.0650 (9)
H02D	−0.1256	0.4685	0.6633	0.097*
H02E	−0.1723	0.5718	0.7436	0.097*
H02F	−0.0618	0.3656	0.7597	0.097*
C11	0.2614 (6)	−0.2742 (5)	1.0403 (3)	0.0812 (12)
H11A	0.1395	−0.2329	1.0205	0.122*
H11B	0.2444	−0.2393	1.0982	0.122*
H11C	0.3194	−0.4011	1.0480	0.122*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03260 (15)	0.02483 (15)	0.02657 (15)	−0.00907 (11)	−0.00598 (10)	−0.00532 (10)
S1	0.0312 (3)	0.0331 (3)	0.0312 (3)	−0.0074 (2)	−0.0101 (2)	−0.0054 (2)
S2	0.0296 (3)	0.0328 (3)	0.0422 (3)	−0.0086 (2)	−0.0041 (2)	0.0001 (2)
O2	0.0420 (9)	0.0315 (9)	0.0331 (8)	−0.0111 (7)	−0.0110 (7)	−0.0062 (7)
N2	0.0290 (9)	0.0258 (9)	0.0288 (9)	−0.0084 (7)	−0.0051 (7)	−0.0038 (7)
C10	0.0443 (13)	0.0342 (13)	0.0342 (12)	−0.0130 (10)	−0.0068 (10)	−0.0115 (10)
C7	0.0272 (10)	0.0285 (11)	0.0315 (11)	−0.0107 (9)	−0.0015 (8)	−0.0071 (9)
O4	0.0341 (9)	0.0360 (9)	0.0434 (10)	−0.0108 (7)	−0.0056 (7)	−0.0080 (7)
O1	0.0360 (9)	0.0588 (12)	0.0493 (11)	−0.0131 (9)	−0.0180 (8)	−0.0081 (9)
N1	0.0388 (11)	0.0311 (10)	0.0289 (9)	−0.0027 (8)	−0.0078 (8)	−0.0057 (8)
O3	0.0486 (10)	0.0259 (8)	0.0310 (8)	−0.0119 (7)	−0.0166 (7)	−0.0023 (6)
N3	0.0315 (9)	0.0268 (9)	0.0270 (9)	−0.0129 (7)	−0.0048 (7)	−0.0034 (7)
C8	0.0265 (10)	0.0282 (11)	0.0277 (10)	−0.0122 (8)	−0.0009 (8)	−0.0071 (8)
C2	0.0486 (15)	0.0597 (18)	0.0432 (15)	−0.0256 (14)	−0.0016 (12)	−0.0154 (13)

C1	0.0441 (14)	0.0450 (14)	0.0322 (12)	−0.0163 (11)	−0.0121 (10)	−0.0049 (11)
C6	0.0394 (12)	0.0306 (12)	0.0276 (11)	−0.0080 (9)	−0.0097 (9)	−0.0069 (9)
C9	0.0451 (14)	0.0316 (12)	0.0417 (14)	−0.0051 (10)	−0.0072 (11)	−0.0117 (11)
C3	0.073 (2)	0.0493 (17)	0.0369 (14)	−0.0293 (15)	0.0038 (13)	−0.0115 (12)
C5	0.0512 (16)	0.0452 (15)	0.0355 (13)	−0.0083 (12)	−0.0157 (11)	−0.0011 (11)
C4	0.081 (2)	0.0475 (17)	0.0336 (14)	−0.0170 (16)	−0.0146 (14)	0.0048 (12)
C021	0.071 (2)	0.070 (2)	0.057 (2)	−0.0141 (18)	−0.0073 (16)	−0.0295 (17)
C022	0.0335 (14)	0.060 (2)	0.091 (3)	−0.0199 (14)	0.0026 (15)	−0.0057 (18)
C11	0.111 (3)	0.077 (3)	0.057 (2)	−0.055 (2)	0.020 (2)	−0.0123 (19)

Geometric parameters (Å, º)

Cu1—N2	1.9580 (19)	C2—C1	1.378 (4)
Cu1—N3	1.9728 (18)	C2—C3	1.385 (4)
Cu1—O2	2.0970 (16)	C2—H2	0.9300
Cu1—O3^{i}	1.8798 (16)	C1—C6	1.385 (3)
Cu1—O4	2.2517 (17)	C1—H1	0.9300
S1—O1	1.4376 (18)	C6—C5	1.385 (3)
S1—O2	1.4745 (17)	C9—H9A	0.9600
S1—N1	1.606 (2)	C9—H9B	0.9600
S1—C6	1.765 (2)	C9—H9C	0.9600
S2—O4	1.5114 (18)	C3—C4	1.379 (5)
S2—C022	1.781 (3)	C3—C11	1.507 (4)
S2—C021	1.783 (3)	C5—C4	1.384 (4)
N2—C7	1.295 (3)	C5—H5	0.9300
N2—N1	1.367 (3)	C4—H4	0.9300
C10—C8	1.486 (3)	C021—H02A	0.9600
C10—H10A	0.9600	C021—H02B	0.9600
C10—H10B	0.9600	C021—H02C	0.9600
C10—H10C	0.9600	C022—H02D	0.9600
C7—C8	1.467 (3)	C022—H02E	0.9600
C7—C9	1.498 (3)	C022—H02F	0.9600
O3—N3	1.343 (2)	C11—H11A	0.9600
O3—Cu1^{i}	1.8798 (16)	C11—H11B	0.9600
N3—C8	1.299 (3)	C11—H11C	0.9600
O3^{i}—Cu1—N2	160.52 (8)	C1—C2—H2	119.3
O3^{i}—Cu1—N3	105.85 (7)	C3—C2—H2	119.3
N2—Cu1—N3	81.34 (8)	C2—C1—C6	119.7 (2)
O3^{i}—Cu1—O2	90.50 (6)	C2—C1—H1	120.1
N2—Cu1—O2	80.08 (7)	C6—C1—H1	120.1
N3—Cu1—O2	160.90 (7)	C1—C6—C5	119.9 (2)
O3^{i}—Cu1—O4	95.33 (7)	C1—C6—S1	119.73 (18)
N2—Cu1—O4	101.95 (7)	C5—C6—S1	120.4 (2)
N3—Cu1—O4	96.11 (7)	C7—C9—H9A	109.5
O2—Cu1—O4	92.01 (7)	C7—C9—H9B	109.5
O1—S1—O2	116.12 (11)	H9A—C9—H9B	109.5
O1—S1—N1	109.45 (11)	C7—C9—H9C	109.5

O2—S1—N1	110.60 (10)	H9A—C9—H9C	109.5
O1—S1—C6	105.75 (11)	H9B—C9—H9C	109.5
O2—S1—C6	107.02 (11)	C4—C3—C2	117.8 (3)
N1—S1—C6	107.42 (11)	C4—C3—C11	121.2 (3)
O4—S2—C022	105.09 (14)	C2—C3—C11	121.0 (3)
O4—S2—C021	106.15 (14)	C4—C5—C6	119.1 (3)
C022—S2—C021	98.59 (18)	C4—C5—H5	120.4
S1—O2—Cu1	114.45 (9)	C6—C5—H5	120.4
C7—N2—N1	120.75 (19)	C3—C4—C5	121.9 (3)
C7—N2—Cu1	114.72 (15)	C3—C4—H4	119.0
N1—N2—Cu1	123.60 (15)	C5—C4—H4	119.0
C8—C10—H10A	109.5	S2—C021—H02A	109.5
C8—C10—H10B	109.5	S2—C021—H02B	109.5
H10A—C10—H10B	109.5	H02A—C021—H02B	109.5
C8—C10—H10C	109.5	S2—C021—H02C	109.5
H10A—C10—H10C	109.5	H02A—C021—H02C	109.5
H10B—C10—H10C	109.5	H02B—C021—H02C	109.5
N2—C7—C8	114.58 (19)	S2—C022—H02D	109.5
N2—C7—C9	123.5 (2)	S2—C022—H02E	109.5
C8—C7—C9	121.8 (2)	H02D—C022—H02E	109.5
S2—O4—Cu1	116.15 (10)	S2—C022—H02F	109.5
N2—N1—S1	110.24 (15)	H02D—C022—H02F	109.5
N3—O3—Cu1^{i}	120.90 (13)	H02E—C022—H02F	109.5
C8—N3—O3	117.04 (18)	C3—C11—H11A	109.5
C8—N3—Cu1	113.71 (15)	C3—C11—H11B	109.5
O3—N3—Cu1	128.55 (14)	H11A—C11—H11B	109.5
N3—C8—C7	115.07 (19)	C3—C11—H11C	109.5
N3—C8—C10	122.8 (2)	H11A—C11—H11C	109.5
C7—C8—C10	122.1 (2)	H11B—C11—H11C	109.5
C1—C2—C3	121.5 (3)		

O1—S1—O2—Cu1	132.54 (11)	O3^{i}—Cu1—N3—C8	165.37 (15)
N1—S1—O2—Cu1	7.05 (14)	N2—Cu1—N3—C8	3.91 (15)
C6—S1—O2—Cu1	−109.67 (11)	O2—Cu1—N3—C8	17.4 (3)
O3^{i}—Cu1—O2—S1	−164.58 (11)	O4—Cu1—N3—C8	−97.30 (15)
N2—Cu1—O2—S1	−1.72 (10)	O3^{i}—Cu1—N3—O3	−24.6 (2)
N3—Cu1—O2—S1	−15.2 (3)	N2—Cu1—N3—O3	173.91 (18)
O4—Cu1—O2—S1	100.06 (11)	O2—Cu1—N3—O3	−172.62 (17)
O3^{i}—Cu1—N2—C7	−112.5 (2)	O4—Cu1—N3—O3	72.70 (17)
N3—Cu1—N2—C7	0.93 (15)	O3—N3—C8—C7	−178.83 (17)
O2—Cu1—N2—C7	−174.63 (16)	Cu1—N3—C8—C7	−7.6 (2)
O4—Cu1—N2—C7	95.40 (16)	O3—N3—C8—C10	1.8 (3)
O3^{i}—Cu1—N2—N1	56.5 (3)	Cu1—N3—C8—C10	173.05 (16)
N3—Cu1—N2—N1	170.01 (18)	N2—C7—C8—N3	8.5 (3)
O2—Cu1—N2—N1	−5.55 (17)	C9—C7—C8—N3	−169.7 (2)
O4—Cu1—N2—N1	−95.52 (17)	N2—C7—C8—C10	−172.10 (19)
N1—N2—C7—C8	−174.51 (18)	C9—C7—C8—C10	9.6 (3)
Cu1—N2—C7—C8	−5.1 (2)	C3—C2—C1—C6	0.4 (4)

N1—N2—C7—C9	3.7 (3)	C2—C1—C6—C5	−1.7 (4)
Cu1—N2—C7—C9	173.13 (18)	C2—C1—C6—S1	176.8 (2)
C022—S2—O4—Cu1	176.67 (15)	O1—S1—C6—C1	173.2 (2)
C021—S2—O4—Cu1	−79.50 (17)	O2—S1—C6—C1	48.8 (2)
O3^{i}—Cu1—O4—S2	−1.22 (11)	N1—S1—C6—C1	−70.0 (2)
N2—Cu1—O4—S2	169.76 (11)	O1—S1—C6—C5	−8.3 (2)
N3—Cu1—O4—S2	−107.83 (11)	O2—S1—C6—C5	−132.7 (2)
O2—Cu1—O4—S2	89.47 (11)	N1—S1—C6—C5	108.5 (2)
C7—N2—N1—S1	179.00 (16)	C1—C2—C3—C4	1.1 (4)
Cu1—N2—N1—S1	10.5 (2)	C1—C2—C3—C11	179.4 (3)
O1—S1—N1—N2	−139.82 (16)	C1—C6—C5—C4	1.5 (4)
O2—S1—N1—N2	−10.66 (19)	S1—C6—C5—C4	−177.0 (2)
C6—S1—N1—N2	105.82 (17)	C2—C3—C4—C5	−1.4 (5)
Cu1^{i}—O3—N3—C8	−162.43 (15)	C11—C3—C4—C5	−179.6 (3)
Cu1^{i}—O3—N3—Cu1	27.9 (2)	C6—C5—C4—C3	0.1 (5)

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*
C1—H1···O4	0.93	2.39	3.299 (3)	166
C2—H2···O1^{ii}	0.93	2.57	3.430 (4)	154
C9—H9*A*···S2^{iii}	0.96	2.75	3.693 (3)	166
C10—H10*C*···O1^{iv}	0.96	2.47	3.415 (4)	166

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