

Tetra- μ -acetato-bis[(1,3-benzothiazole)-copper(II)]($Cu-Cu$)

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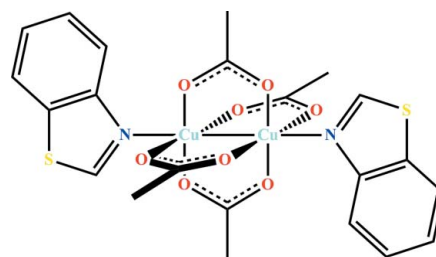
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.032; wR factor = 0.075; data-to-parameter ratio = 16.9.

The title compound, $[Cu_2(CH_3CO_2)_4(C_7H_5NS)_2]$ or $[(C_7H_5NS)Cu]_2(\mu-O_2CCH_3)_4$, crystallizes with one molecule per unit cell. The coordination number of copper is six with four basal O atoms, one axial N atom and one axial Cu atom. Four acetate ligands act as bidentate linker and connect two Cu atoms, with a crystallographic inversion center located at the mid-point of the Cu—Cu bond. The acetate ligands form slightly distorted square planes around each metal ion, while the copper ions are displaced by 0.2089 (4) Å from these planes towards the N atoms. Thus, the Cu—Cu distance is elongated to 2.6378 (7) Å, compared with the 2.2180 (7) Å distance between the two basal planes. The angle between the basal plane and the Cu—N bond is 4.84 (6)°.

Related literature

The structural prototype of $(LCu)_2(\mu-O_2CCH_3)_4$ complexes is the crystal structure of cupric acetate monohydrate ($L =$ water), see: Van Niekerk & Schoening (1953); Ferguson & Glidewell (2003). For similar structures with $L =$ benzimidazole, see: Bukowska-Strzyżewska *et al.* (1982) and $L =$ 2-amino-benzothiazole, see: Sun *et al.* (2007). For theoretical studies see: Rodríguez-Forteza *et al.* (2001) and for magnetic properties of dinuclear copper complexes, see: Tokii & Muto (1983). For FIR spectroscopic data and the magnetic moment of the complex with $L =$ benzothiazole, see: Ford *et al.* (1968).



Experimental

Crystal data

 $[Cu_2(C_2H_3O_2)_4(C_7H_5NS)_2]$
 $M_r = 633.66$

 Triclinic, $P\bar{1}$
 $a = 7.185$ (1) Å

 $b = 8.1918$ (12) Å

 $c = 11.8265$ (16) Å

 $\alpha = 106.516$ (16)°

 $\beta = 106.429$ (16)°

 $\gamma = 97.344$ (17)°

 $V = 623.49$ (18) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 1.92$ mm⁻¹
 $T = 293$ K

 $0.3 \times 0.2 \times 0.1$ mm

Data collection

Stoe IPDS I diffractometer

Absorption correction: numerical

 (*X-SHAPE*; Stoe & Cie, 1999)

 $T_{\min} = 0.575$, $T_{\max} = 0.840$

7525 measured reflections

2784 independent reflections

 2092 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.075$
 $S = 0.97$

2784 reflections

165 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.45$ e Å⁻³

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2011); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5042).

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supporting information

Acta Cryst. (2011). E67, m1089 [doi:10.1107/S1600536811027140]

Tetra- μ -acetato-bis[(1,3-benzothiazole)copper(II)](Cu—Cu)

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S1. Comment

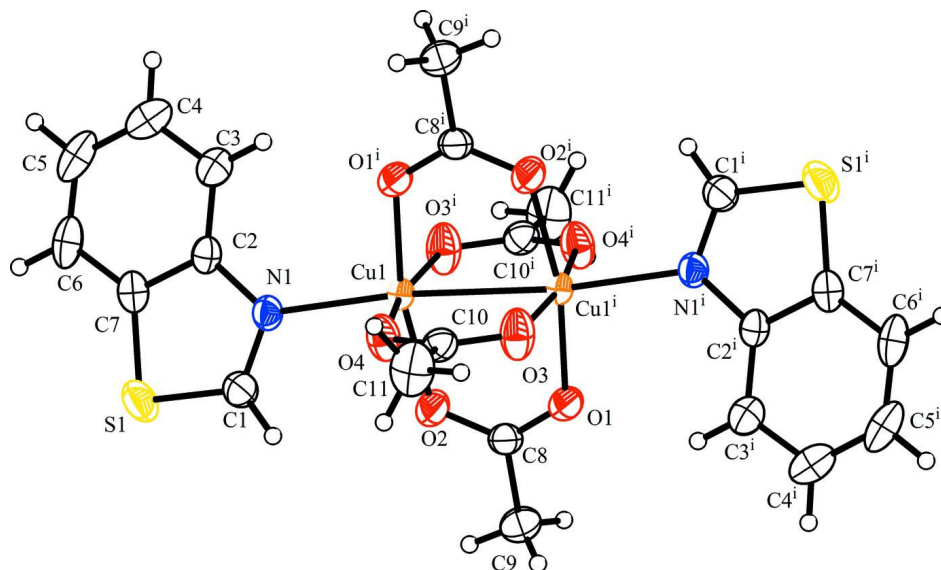
Copper(II) acetate complexes of the general formula $[LCu]_2(\mu^2-OAc)_4$, where L is a ligand with an oxygen or nitrogen ligand atom have been well explored. The structural evidence of a copper-copper bond was given by van Niekerk & Schoening in 1953. The title compound is a dinuclear complex disposed around an inversion center located at the midpoint of the Cu—Cu bond. The coordination environment of Cu(II) ions can be described as a slightly distorted octahedron, with each copper atom being surrounded by four μ^2 -bridging bidentate acetate ligands in the basal plane and one benzothiazole ligand in one axial position (Fig. 1). The sixth coordination site is occupied by the neighbouring copper(II) atom. The Cu—Cu distance is about 0.02 Å longer as in Cu(II) acetate monohydrate $[(H_2O)Cu]_2(\mu^2-OAc)_4$ with 2.6157 (8) Å (Ferguson & Glidewell 2003) and 0.03 Å shorter than in the benzimidazole complex 2.663 (1) Å (Bukowska-Strzyzewska *et al.* 1982). To our knowledge there is only one more dinuclear complex with acetate ligands and a benzothiazole derivative known (Sun *et al.* 2007). The magnetic moment of $[(C_7H_5NS)Cu]_2(\mu^2-OAc)_4$ of $\mu = 1.42 \mu_B$ at room temperature is an evidence for Cu—Cu interactions with coupling of the electron spins, Ford *et al.* 1968. Magnetic susceptibilities of benzothiazole, thiazole and thiazole derivatives have been measured by Tokii & Muto 1983. Theoretical studies on intramolecular antiferromagnetic coupling in carboxylato-bridged dinuclear copper(II) complexes have been performed by Rodríguez-Fortea *et al.* 2001.

S2. Experimental

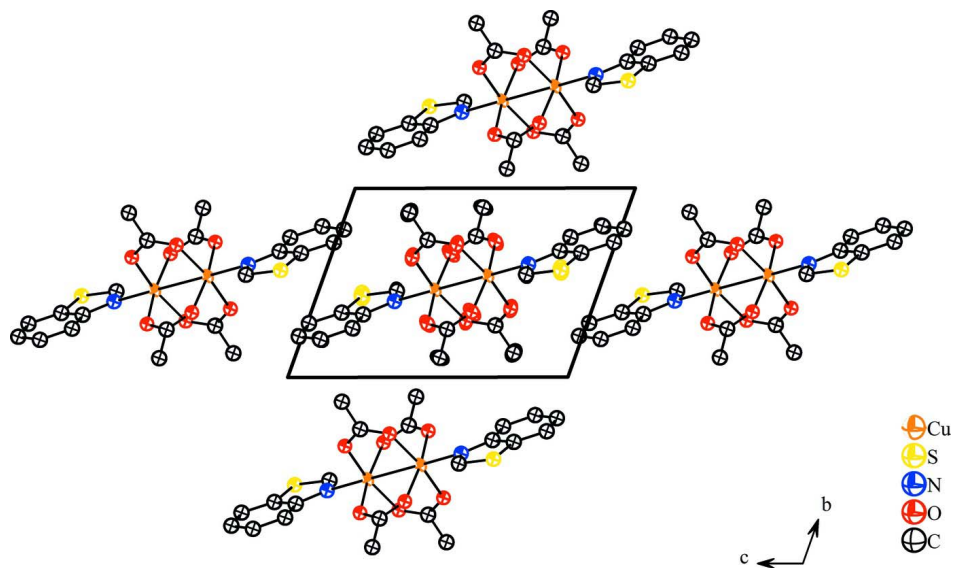
Green platelets of $[(C_7H_5NS)Cu]_2(\mu^2-OAc)_4$ were obtained by the reaction of 0.20 g cupric acetate monohydrate (1 mmol, Merck) with 0.22 ml benzothiazole (0.27 g, 2 mmol, Acros) in 20 ml of ethanol at ambient temperature by slow evaporation of the solvent within two weeks. **Yield:** 0.59 g (93%). **Mp:** 206 °C (Decomp.). **UV/VIS:** (chloroform) λ_{max} 358, 690 nm. **IR:** 3080(w), 3057(w), 2995(w), 2927(w), 1612(s), 1562(m), 1468(m), 1454(m), 1431(s), 1348(m), 1321(w), 1304(m), 1273(w), 1205(w), 1155(w), 1066(w), 1049(w), 1030(w), 1016(w), 949(w), 897(m), 870(w), 856(w), 810(w), 762(m), 733(m), 681(m), 627(m), 534(w), 507(w), 424(w) cm^{-1} . **Elem. Anal. calcd for** $C_{22}H_{22}Cu_2N_2O_8S_2$: C, 41.70; H, 3.50; N, 4.42; S, 10.12; found: C, 41.30; H, 3.30; N, 4.17; S, 10.14.

S3. Refinement

Hydrogen atoms were placed in idealized positions and constrained riding on their parent atoms [C—H = 0.93–0.96 Å with $U_{iso}(H) = 1.2 U_{eq}(C)$]. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

**Figure 1**

The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.
[Symmetry code: (i) $-x + 1, -y + 1, -z + 1$]

**Figure 2**

The packing of (I), viewed along the *b* axis, H atoms have been omitted for clarity.

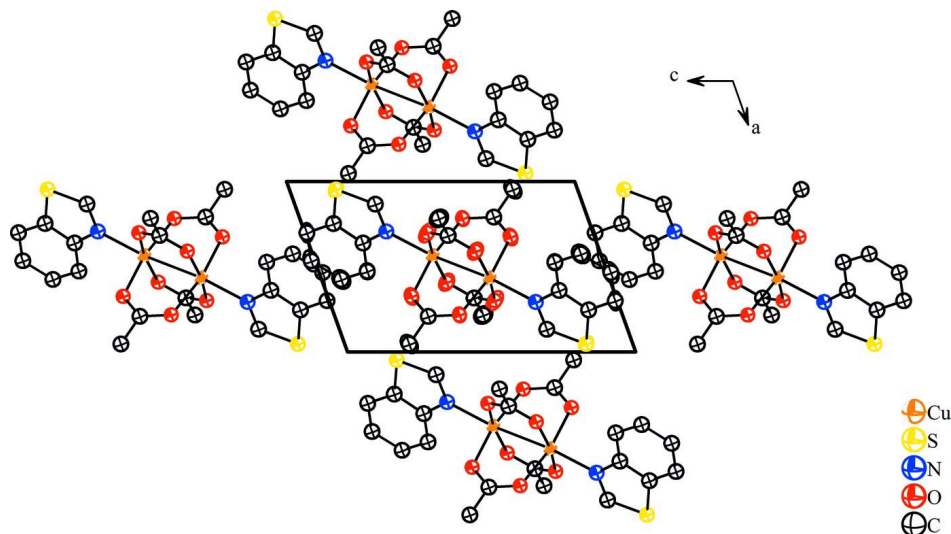


Figure 3

The packing of (I), viewed along the *a* axis, H atoms have been omitted for clarity.

Tetra- μ -acetato-bis[(1,3-benzothiazole)copper(II)](Cu—Cu)

Crystal data

$[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_7\text{H}_5\text{NS})_2]$

$M_r = 633.66$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.185$ (1) Å

$b = 8.1918$ (12) Å

$c = 11.8265$ (16) Å

$\alpha = 106.516$ (16)°

$\beta = 106.429$ (16)°

$\gamma = 97.344$ (17)°

$V = 623.49$ (18) Å³

$Z = 1$

$F(000) = 322$

$D_x = 1.688$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1512 reflections

$\theta = 3.8$ – 56.3 °

$\mu = 1.92$ mm⁻¹

$T = 293$ K

Plate, green

$0.3 \times 0.2 \times 0.1$ mm

Data collection

Stoe IPDS I

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 0 pixels mm⁻¹

Oscillation scans

Absorption correction: numerical

(*X-SHAPE*; Stoe & Cie, 1999)

$T_{\min} = 0.575$, $T_{\max} = 0.840$

7525 measured reflections

2784 independent reflections

2092 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 28.1$ °, $\theta_{\min} = 2.7$ °

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.075$

$S = 0.97$

2784 reflections

165 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
 $w = 1/[\sigma^2(F_o^2) + (0.0379P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.013$
 $\Delta\rho_{\max} = 0.45 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{Å}^{-3}$

Special details

Experimental. A single crystal suitable for X-ray diffraction was selected under a polarization microscope and sealed in a capillary tube. Complete scattering intensities data sets were collected with an imaging plate diffractometer (IPDS I, Stoe & Cie). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data.

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. Hydrogen atoms were placed in idealized positions and constrained riding on their parent atoms [C–H = 0.93–0.96 Å with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$]. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.43471 (5)	0.46234 (4)	0.58527 (3)	0.02316 (11)
S1	0.04719 (13)	0.43274 (11)	0.83857 (7)	0.0430 (2)
N1	0.2932 (4)	0.4019 (3)	0.71570 (19)	0.0265 (5)
O3	0.6747 (3)	0.6371 (3)	0.70893 (18)	0.0428 (5)
O4	0.7826 (3)	0.7015 (3)	0.56499 (17)	0.0390 (5)
O1	0.5911 (3)	0.2831 (3)	0.56937 (19)	0.0374 (5)
C2	0.3612 (4)	0.3329 (3)	0.8112 (2)	0.0259 (6)
O2	0.6990 (4)	0.3443 (3)	0.4247 (2)	0.0427 (6)
C6	0.3008 (5)	0.2858 (4)	0.9930 (3)	0.0411 (8)
H6	0.2271	0.2953	1.0468	0.049*
C4	0.5758 (5)	0.2012 (4)	0.9319 (3)	0.0458 (8)
H4	0.6848	0.1503	0.9462	0.055*
C5	0.4659 (6)	0.2169 (4)	1.0127 (3)	0.0462 (9)
H5	0.5055	0.1798	1.0813	0.055*
C11	0.9534 (6)	0.8715 (4)	0.7759 (3)	0.0542 (10)
H11A	0.9499	0.8716	0.8564	0.081*
H11B	0.9337	0.9812	0.7663	0.081*
H11C	1.0803	0.8550	0.7693	0.081*
C9	0.7821 (5)	0.1025 (4)	0.4827 (3)	0.0415 (7)
H9A	0.9197	0.1415	0.4931	0.062*
H9C	0.7166	0.0146	0.4018	0.062*
H9B	0.7733	0.0542	0.5466	0.062*
C1	0.1335 (5)	0.4564 (4)	0.7205 (3)	0.0344 (7)
H1	0.0685	0.5058	0.6633	0.041*
C3	0.5264 (5)	0.2595 (4)	0.8310 (3)	0.0359 (7)
H3	0.6015	0.2501	0.7780	0.043*

C7	0.2462 (5)	0.3417 (3)	0.8892 (2)	0.0307 (6)
C10	0.7917 (4)	0.7261 (3)	0.6755 (2)	0.0288 (6)
C8	0.6835 (4)	0.2542 (3)	0.4930 (2)	0.0278 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0256 (2)	0.02769 (17)	0.02156 (16)	0.00738 (12)	0.01074 (12)	0.01282 (12)
S1	0.0358 (5)	0.0654 (5)	0.0383 (4)	0.0139 (4)	0.0222 (4)	0.0223 (4)
N1	0.0267 (14)	0.0329 (12)	0.0228 (11)	0.0055 (9)	0.0097 (9)	0.0127 (9)
O3	0.0453 (15)	0.0499 (12)	0.0239 (10)	-0.0096 (10)	0.0076 (9)	0.0115 (9)
O4	0.0353 (13)	0.0522 (13)	0.0247 (10)	-0.0037 (10)	0.0095 (9)	0.0124 (9)
O1	0.0467 (14)	0.0429 (11)	0.0437 (12)	0.0252 (10)	0.0268 (10)	0.0275 (10)
C2	0.0283 (16)	0.0263 (12)	0.0203 (12)	-0.0001 (10)	0.0065 (10)	0.0082 (10)
O2	0.0588 (16)	0.0442 (12)	0.0552 (13)	0.0307 (11)	0.0389 (12)	0.0338 (11)
C6	0.061 (2)	0.0362 (16)	0.0259 (14)	-0.0033 (14)	0.0177 (14)	0.0124 (13)
C4	0.056 (2)	0.0381 (16)	0.0425 (18)	0.0160 (15)	0.0071 (16)	0.0191 (15)
C5	0.073 (3)	0.0337 (16)	0.0285 (15)	0.0051 (15)	0.0081 (15)	0.0182 (13)
C11	0.055 (2)	0.050 (2)	0.0364 (18)	-0.0127 (16)	0.0009 (16)	0.0081 (15)
C9	0.045 (2)	0.0338 (15)	0.056 (2)	0.0195 (14)	0.0224 (16)	0.0201 (15)
C1	0.0300 (18)	0.0488 (17)	0.0292 (14)	0.0109 (13)	0.0104 (12)	0.0188 (13)
C3	0.040 (2)	0.0374 (15)	0.0337 (15)	0.0099 (13)	0.0121 (13)	0.0175 (13)
C7	0.0354 (18)	0.0305 (14)	0.0236 (13)	-0.0010 (11)	0.0114 (11)	0.0074 (11)
C10	0.0269 (17)	0.0295 (14)	0.0261 (13)	0.0053 (11)	0.0031 (11)	0.0102 (11)
C8	0.0253 (16)	0.0263 (13)	0.0327 (14)	0.0073 (11)	0.0087 (11)	0.0115 (11)

Geometric parameters (Å, °)

Cu1—O1	1.9589 (19)	C6—C5	1.367 (5)
Cu1—O2 ⁱ	1.9689 (19)	C6—C7	1.401 (3)
Cu1—O3	1.978 (2)	C6—H6	0.9300
Cu1—O4 ⁱ	1.984 (2)	C4—C3	1.381 (4)
Cu1—N1	2.203 (2)	C4—C5	1.391 (5)
Cu1—Cu1 ⁱ	2.6378 (7)	C4—H4	0.9300
S1—C1	1.727 (3)	C5—H5	0.9300
S1—C7	1.732 (3)	C11—C10	1.497 (4)
N1—C1	1.293 (4)	C11—H11A	0.9600
N1—C2	1.398 (3)	C11—H11B	0.9600
O3—C10	1.261 (3)	C11—H11C	0.9600
O4—C10	1.246 (3)	C9—C8	1.500 (4)
O4—Cu1 ⁱ	1.984 (2)	C9—H9A	0.9600
O1—C8	1.253 (3)	C9—H9C	0.9600
C2—C3	1.390 (4)	C9—H9B	0.9600
C2—C7	1.396 (4)	C1—H1	0.9300
O2—C8	1.256 (3)	C3—H3	0.9300
O2—Cu1 ⁱ	1.9689 (19)		
O1—Cu1—O2 ⁱ	167.71 (7)	C5—C4—H4	119.3

O1—Cu1—O3	90.12 (10)	C6—C5—C4	121.3 (2)
O2 ⁱ —Cu1—O3	88.37 (10)	C6—C5—H5	119.4
O1—Cu1—O4 ⁱ	88.25 (10)	C4—C5—H5	119.4
O2 ⁱ —Cu1—O4 ⁱ	90.67 (10)	C10—C11—H11A	109.5
O3—Cu1—O4 ⁱ	167.89 (8)	C10—C11—H11B	109.5
O1—Cu1—N1	100.05 (8)	H11A—C11—H11B	109.5
O2 ⁱ —Cu1—N1	92.24 (8)	C10—C11—H11C	109.5
O3—Cu1—N1	98.77 (8)	H11A—C11—H11C	109.5
O4 ⁱ —Cu1—N1	93.33 (8)	H11B—C11—H11C	109.5
O1—Cu1—Cu1 ⁱ	84.48 (6)	C8—C9—H9A	109.5
O2 ⁱ —Cu1—Cu1 ⁱ	83.24 (6)	C8—C9—H9C	109.5
O3—Cu1—Cu1 ⁱ	85.57 (6)	H9A—C9—H9C	109.5
O4 ⁱ —Cu1—Cu1 ⁱ	82.33 (6)	C8—C9—H9B	109.5
N1—Cu1—Cu1 ⁱ	173.67 (6)	H9A—C9—H9B	109.5
C1—S1—C7	88.85 (13)	H9C—C9—H9B	109.5
C1—N1—C2	110.6 (2)	N1—C1—S1	116.61 (19)
C1—N1—Cu1	118.25 (16)	N1—C1—H1	121.7
C2—N1—Cu1	130.51 (18)	S1—C1—H1	121.7
C10—O3—Cu1	121.50 (17)	C4—C3—C2	118.0 (3)
C10—O4—Cu1 ⁱ	125.44 (19)	C4—C3—H3	121.0
C8—O1—Cu1	123.50 (15)	C2—C3—H3	121.0
C3—C2—C7	120.5 (2)	C2—C7—C6	120.8 (3)
C3—C2—N1	125.5 (2)	C2—C7—S1	109.93 (18)
C7—C2—N1	114.0 (2)	C6—C7—S1	129.2 (2)
C8—O2—Cu1 ⁱ	124.42 (18)	O4—C10—O3	124.7 (3)
C5—C6—C7	117.9 (3)	O4—C10—C11	117.7 (3)
C5—C6—H6	121.0	O3—C10—C11	117.6 (2)
C7—C6—H6	121.0	O1—C8—O2	124.2 (2)
C3—C4—C5	121.4 (3)	O1—C8—C9	117.9 (2)
C3—C4—H4	119.3	O2—C8—C9	118.0 (3)

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