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Crystal structure of bis[2-(benzothiazol-2-yl)phenolato-κ^2N,O]copper(II)

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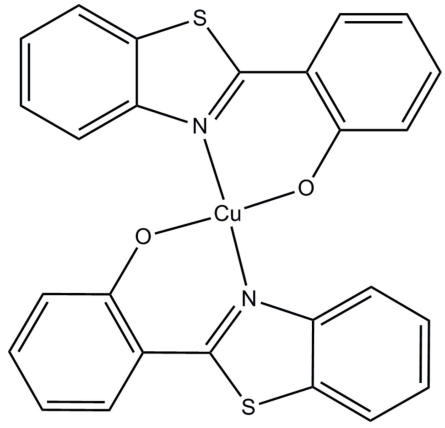
In the title complex, $[Cu(C_{13}H_8NOS)_2]$, the Cu^{II} atom is coordinated by two N atoms and two O atoms from two bidentate benzothiazolphenolate ligands, forming a distorted tetrahedral geometry [dihedral angle between two N—Cu—O planes: 45.1 (2)°]. The dihedral angles between the benzothiazole ring systems and the phenol rings are 4.1 (4) and 5.8 (4)°, indicating an almost planar geometry. Weak intra- and intermolecular C—H···O hydrogen bonds are observed. In the crystal, weak π–π interactions between aromatic and thiazole rings [centroid–centroid distances = 3.626 (3) and 3.873 (3) Å] link the molecules into a two-dimensional supramolecular network along the *bc* plane.

Keywords: crystal structure; Cu(II) complex; benzothiazolphenol; hydrogen bonding; π–π interactions.

CCDC reference: 1419096

1. Related literature

For background to benzothiazole complexes and their applications, see: López-Banet *et al.* (2014); Liu *et al.* (2011); Booysen *et al.* (2010); Henary & Fahrni (2002). For the structures and luminescent properties of metal complexes, see: Yu *et al.* (2003); Katkova *et al.* (2011); Balashova *et al.* (2013); Wang *et al.* (2002).



2. Experimental

2.1. Crystal data

$[Cu(C_{13}H_8NOS)_2]$
M_r = 516.07
Monoclinic, $P2_1/n$
a = 7.8177 (17) Å
b = 21.195 (5) Å
c = 12.495 (3) Å
β = 91.077 (2)°
V = 2070.1 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.29 mm^{-1}
T = 296 K
0.08 × 0.06 × 0.05 mm

2.2. Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.902, T_{max} = 0.925
21140 measured reflections
3855 independent reflections
2045 reflections with $I > 2\sigma(I)$
R_{int} = 0.149

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.086
$wR(F^2)$ = 0.224
S = 1.08
3855 reflections
298 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −1.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O33	0.93	2.41	2.997 (12)	121
C7—H7···O17^{i}	0.93	2.59	3.305 (13)	134
C20—H20···O17	0.93	2.42	3.000 (13)	121
C23—H23···O33^{ii}	0.93	2.61	3.303 (13)	132

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: BQ2400).

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supporting information

Acta Cryst. (2015). E**71**, m173–m174 [https://doi.org/10.1107/S2056989015015303]

Crystal structure of bis[2-(benzothiazol-2-yl)phenolato-κ^2N,O]copper(II)

Namhun Kim and Sung Kwon Kang

S1. Experimental

S1.1. Synthesis and crystallization

To a solution of 2-(2-hydroxyphenyl)benzothiazole (0.227 g, 1.0 mmol) in EtOH (15 ml) was added a 1N NaOH solution slowly until pH = 8 at room temperature. After 6 h of stirring, a solution of $Cu(NO_3)_2.3H_2O$ (0.121g, 0.50 mmol) in EtOH (15 ml) was added. After 24 h of stirring at room temperature, the product was isolated as a dark green powder by removing the solvent. Green single crystals of the title complex were obtained by slow evaporation of its concentrated solution in dichloromethane at room temperature.

S1.2. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

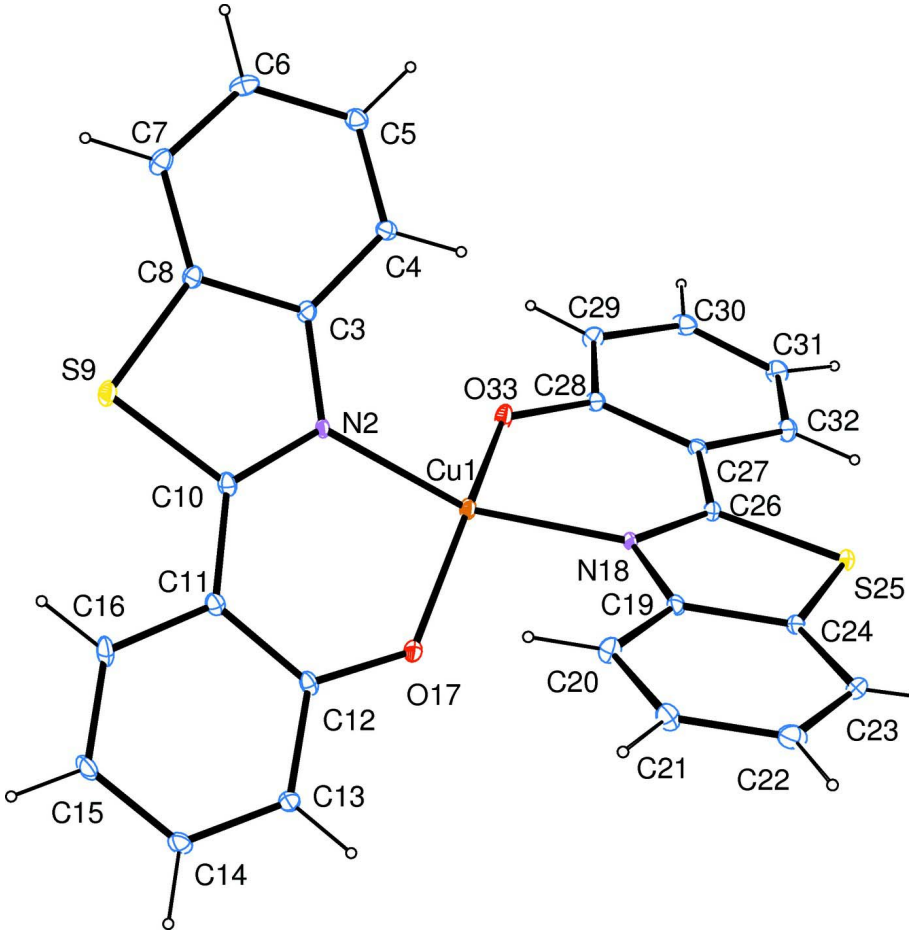

Figure 1

Molecular structure of the title complex, showing the atom-numbering scheme and 30% probability ellipsoids.

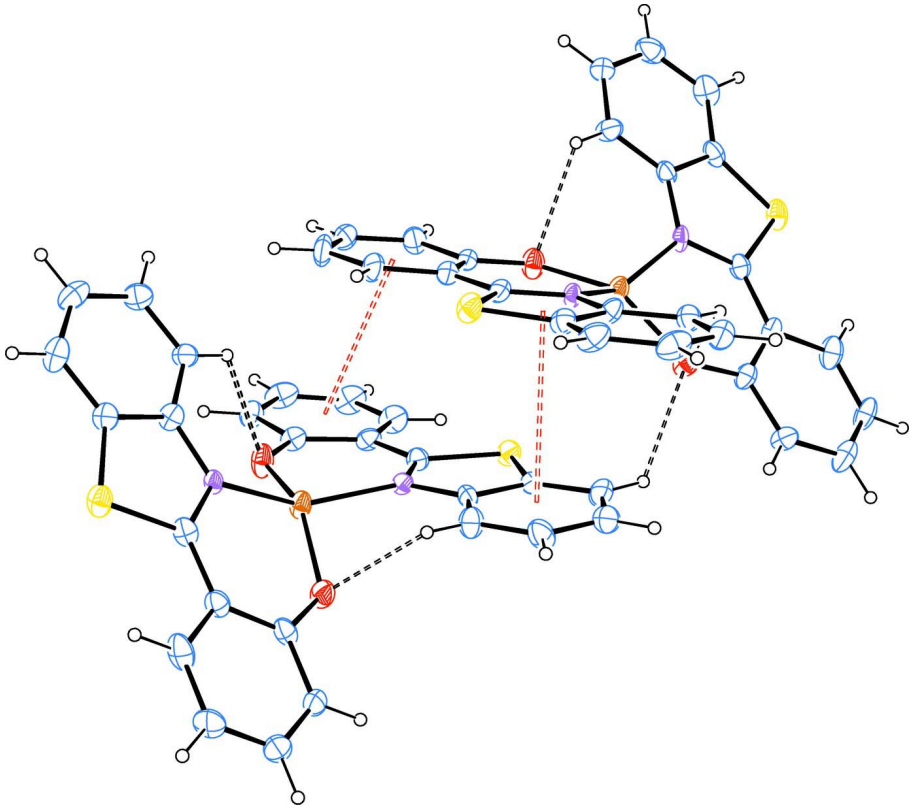

Figure 2

Dimeric formation *via* C—H···O (black dashed lines) and π-π (red) interactions.

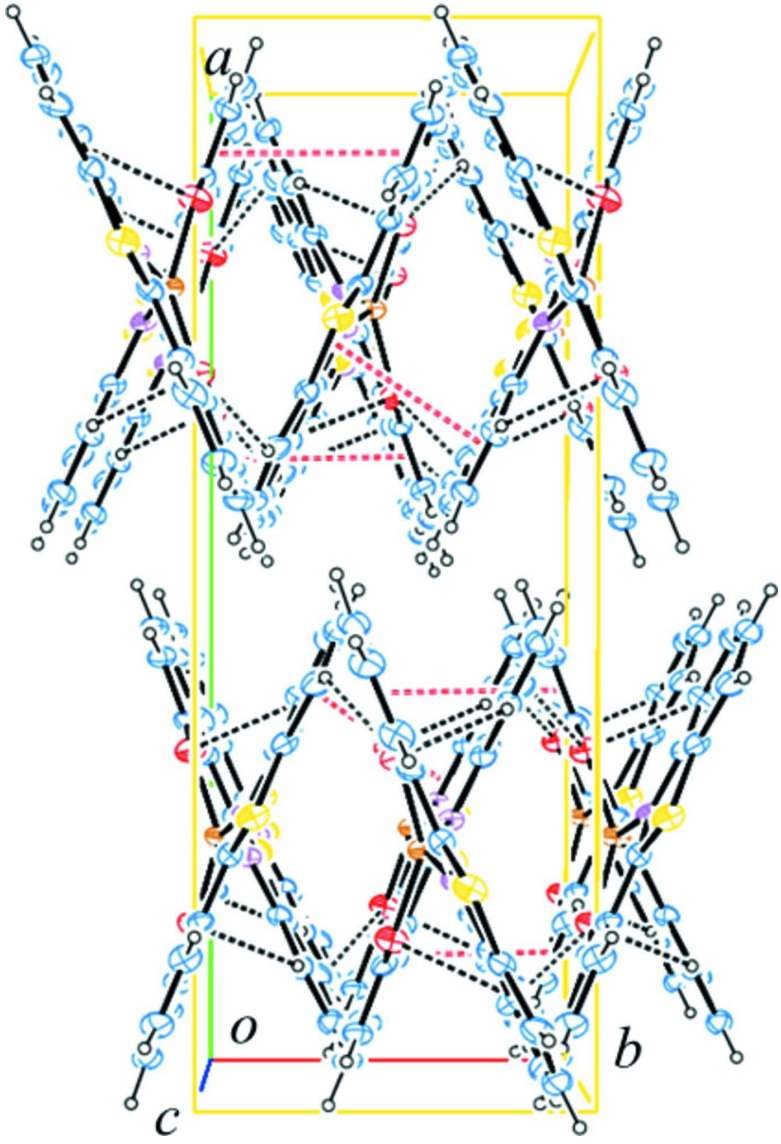

Figure 3

Part of the crystal structure of the title complex, showing the 2-D network of molecules linked by intermolecular C—H···O hydrogen bonds (black dashed lines) and π-π interactions (red).

bis[2-(benzothiazol-2-yl)phenolato-κ^2N,O]copper(II)

Crystal data

$[Cu(C_{13}H_8NOS)_2]$
$M_r = 516.07$
Monoclinic, $P2_1/n$
$a = 7.8177$ (17) Å
$b = 21.195$ (5) Å
$c = 12.495$ (3) Å
$\beta = 91.077$ (2)°
$V = 2070.1$ (8) Å^3
$Z = 4$
$F(000) = 1052$
$D_x = 1.656$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1300 reflections
$\theta = 3.1$–18.7°
$\mu = 1.29$ mm^{-1}
$T = 296$ K
Block, green
0.08 × 0.06 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.902, T_{max} = 0.925
21140 measured reflections
3855 independent reflections
2045 reflections with $I > 2\sigma(I)$
R_{int} = 0.149
θ_{max} = 25.5°, θ_{min} = 1.9°
h = −9→9
k = −25→25
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.086
$wR(F^2)$ = 0.224
S = 1.08
3855 reflections
298 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 14.3316P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −1.21 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.

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

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.05754 (17)	0.25058 (6)	0.87875 (8)	0.0412 (4)
N2	0.1275 (10)	0.2275 (3)	0.7303 (5)	0.0320 (18)
C3	0.2057 (13)	0.1712 (4)	0.7036 (7)	0.040 (2)
C4	0.2656 (13)	0.1241 (5)	0.7711 (8)	0.042 (2)
H4	0.2553	0.1287	0.8447	0.050*
C5	0.3393 (14)	0.0711 (5)	0.7315 (9)	0.050 (3)
H5	0.3784	0.0397	0.7778	0.060*
C6	0.3563 (15)	0.0639 (5)	0.6218 (10)	0.057 (3)
H6	0.4056	0.0272	0.5955	0.069*
C7	0.3018 (16)	0.1096 (5)	0.5514 (9)	0.056 (3)
H7	0.3172	0.1052	0.4782	0.068*
C8	0.2228 (13)	0.1630 (5)	0.5931 (7)	0.042 (3)
S9	0.1445 (4)	0.22811 (13)	0.52567 (19)	0.0492 (7)
C10	0.0888 (13)	0.2633 (4)	0.6462 (7)	0.041 (3)
C11	0.0162 (13)	0.3243 (5)	0.6463 (7)	0.042 (2)
C12	−0.0326 (13)	0.3561 (4)	0.7415 (7)	0.041 (2)
C13	−0.0964 (14)	0.4177 (5)	0.7335 (8)	0.048 (3)
H13	−0.1232	0.4395	0.7955	0.058*
C14	−0.1203 (15)	0.4465 (5)	0.6363 (9)	0.051 (3)
H14	−0.1662	0.4870	0.6329	0.062*
C15	−0.0770 (16)	0.4161 (5)	0.5440 (9)	0.058 (3)
H15	−0.0936	0.4357	0.4780	0.070*

C16	−0.0096 (16)	0.3572 (5)	0.5493 (8)	0.057 (3)
H16	0.0210	0.3376	0.4860	0.069*
O17	−0.0164 (10)	0.3307 (3)	0.8372 (5)	0.0496 (19)
N18	0.1264 (10)	0.2750 (3)	1.0266 (5)	0.0340 (19)
C19	0.2058 (13)	0.3322 (4)	1.0571 (7)	0.040 (2)
C20	0.2587 (14)	0.3789 (5)	0.9866 (8)	0.048 (3)
H20	0.2450	0.3738	0.9131	0.057*
C21	0.3307 (15)	0.4321 (5)	1.0281 (9)	0.054 (3)
H21	0.3648	0.4640	0.9819	0.064*
C22	0.3545 (15)	0.4401 (6)	1.1372 (11)	0.066 (4)
H22	0.4041	0.4771	1.1631	0.079*
C23	0.3056 (16)	0.3940 (5)	1.2079 (9)	0.056 (3)
H23	0.3249	0.3988	1.2811	0.068*
C24	0.2262 (13)	0.3397 (5)	1.1673 (7)	0.044 (3)
S25	0.1515 (4)	0.27492 (13)	1.23252 (18)	0.0478 (7)
C26	0.0923 (12)	0.2389 (4)	1.1125 (7)	0.038 (2)
C27	0.0203 (13)	0.1783 (4)	1.1113 (7)	0.039 (2)
C28	−0.0212 (13)	0.1443 (5)	1.0149 (7)	0.039 (2)
C29	−0.0817 (13)	0.0823 (5)	1.0220 (8)	0.047 (3)
H29	−0.1032	0.0591	0.9600	0.056*
C30	−0.1096 (16)	0.0555 (5)	1.1211 (9)	0.059 (3)
H30	−0.1487	0.0142	1.1251	0.071*
C31	−0.0805 (16)	0.0889 (5)	1.2129 (9)	0.059 (3)
H31	−0.1069	0.0712	1.2786	0.070*
C32	−0.0128 (15)	0.1482 (5)	1.2087 (8)	0.057 (3)
H32	0.0121	0.1692	1.2724	0.068*
O33	−0.0039 (10)	0.1691 (3)	0.9204 (5)	0.053 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0658 (9)	0.0340 (6)	0.0238 (5)	−0.0022 (7)	0.0006 (5)	0.0018 (5)
N2	0.049 (5)	0.028 (4)	0.019 (3)	0.000 (4)	−0.005 (3)	0.003 (3)
C3	0.049 (7)	0.038 (6)	0.032 (5)	−0.004 (5)	0.009 (5)	0.006 (4)
C4	0.039 (6)	0.043 (6)	0.043 (6)	0.005 (5)	−0.001 (5)	0.001 (5)
C5	0.052 (8)	0.047 (7)	0.051 (7)	0.002 (6)	0.004 (6)	0.008 (5)
C6	0.057 (9)	0.037 (6)	0.078 (9)	−0.001 (5)	0.019 (7)	−0.010 (6)
C7	0.075 (9)	0.045 (7)	0.049 (7)	−0.013 (6)	0.011 (6)	−0.008 (5)
C8	0.045 (7)	0.044 (6)	0.038 (5)	−0.005 (5)	0.006 (5)	0.001 (4)
S9	0.069 (2)	0.0508 (16)	0.0282 (12)	−0.0052 (14)	0.0067 (12)	0.0016 (11)
C10	0.049 (6)	0.039 (7)	0.034 (5)	−0.011 (5)	−0.001 (4)	0.008 (4)
C11	0.047 (7)	0.040 (6)	0.038 (5)	−0.007 (5)	−0.005 (5)	0.006 (4)
C12	0.049 (7)	0.036 (6)	0.037 (5)	−0.012 (5)	−0.013 (5)	0.010 (4)
C13	0.064 (8)	0.034 (6)	0.045 (6)	0.004 (5)	−0.012 (5)	−0.005 (5)
C14	0.064 (8)	0.030 (6)	0.059 (7)	−0.002 (5)	−0.010 (6)	0.005 (5)
C15	0.079 (9)	0.046 (7)	0.049 (7)	0.005 (6)	−0.010 (6)	0.020 (5)
C16	0.081 (9)	0.061 (8)	0.030 (5)	−0.019 (7)	−0.007 (5)	0.012 (5)
O17	0.073 (5)	0.045 (4)	0.030 (4)	0.007 (4)	−0.001 (3)	−0.001 (3)

N18	0.054 (5)	0.029 (4)	0.019 (3)	0.009 (4)	−0.003 (3)	0.004 (3)
C19	0.048 (7)	0.033 (5)	0.037 (5)	0.003 (5)	−0.018 (5)	−0.003 (4)
C20	0.054 (7)	0.045 (6)	0.044 (6)	−0.015 (5)	0.004 (5)	−0.002 (5)
C21	0.055 (8)	0.049 (7)	0.057 (7)	−0.013 (6)	−0.014 (6)	0.007 (5)
C22	0.059 (9)	0.045 (7)	0.093 (10)	0.001 (6)	−0.025 (8)	−0.014 (7)
C23	0.075 (9)	0.051 (7)	0.043 (6)	0.015 (6)	−0.007 (6)	−0.015 (5)
C24	0.051 (7)	0.039 (6)	0.041 (6)	0.011 (5)	−0.016 (5)	−0.010 (4)
S25	0.070 (2)	0.0490 (15)	0.0244 (12)	0.0134 (14)	−0.0030 (12)	−0.0009 (11)
C26	0.042 (6)	0.044 (7)	0.027 (5)	0.006 (5)	0.001 (4)	0.000 (4)
C27	0.049 (7)	0.031 (5)	0.038 (5)	0.004 (5)	0.005 (5)	0.010 (4)
C28	0.044 (7)	0.039 (6)	0.034 (5)	0.002 (5)	0.010 (5)	0.007 (4)
C29	0.051 (7)	0.040 (6)	0.050 (6)	−0.009 (5)	0.004 (5)	−0.002 (5)
C30	0.069 (9)	0.044 (7)	0.065 (8)	0.007 (6)	0.021 (7)	0.022 (6)
C31	0.081 (10)	0.051 (7)	0.044 (7)	0.003 (6)	0.020 (6)	0.024 (5)
C32	0.078 (9)	0.060 (8)	0.034 (6)	0.011 (7)	0.012 (6)	0.011 (5)
O33	0.084 (6)	0.048 (4)	0.028 (4)	−0.016 (4)	0.003 (4)	−0.001 (3)

Geometric parameters (Å, º)

Cu1—O17	1.864 (7)	C15—H15	0.9300
Cu1—O33	1.869 (7)	C16—H16	0.9300
Cu1—N18	1.983 (7)	N18—C26	1.347 (11)
Cu1—N2	2.004 (7)	N18—C19	1.412 (11)
N2—C10	1.326 (11)	C19—C24	1.392 (12)
N2—C3	1.385 (11)	C19—C20	1.393 (13)
C3—C4	1.383 (13)	C20—C21	1.359 (14)
C3—C8	1.401 (12)	C20—H20	0.9300
C4—C5	1.359 (14)	C21—C22	1.383 (15)
C4—H4	0.9300	C21—H21	0.9300
C5—C6	1.388 (14)	C22—C23	1.377 (16)
C5—H5	0.9300	C22—H22	0.9300
C6—C7	1.372 (15)	C23—C24	1.397 (14)
C6—H6	0.9300	C23—H23	0.9300
C7—C8	1.395 (14)	C24—S25	1.706 (11)
C7—H7	0.9300	S25—C26	1.738 (9)
C8—S9	1.723 (10)	C26—C27	1.404 (13)
S9—C10	1.743 (10)	C27—C32	1.403 (12)
C10—C11	1.413 (13)	C27—C28	1.434 (13)
C11—C16	1.409 (13)	C28—O33	1.301 (10)
C11—C12	1.425 (13)	C28—C29	1.401 (13)
C12—O17	1.316 (10)	C29—C30	1.383 (14)
C12—C13	1.402 (13)	C29—H29	0.9300
C13—C14	1.369 (13)	C30—C31	1.363 (15)
C13—H13	0.9300	C30—H30	0.9300
C14—C15	1.370 (15)	C31—C32	1.365 (15)
C14—H14	0.9300	C31—H31	0.9300
C15—C16	1.355 (15)	C32—H32	0.9300

O17—Cu1—O33	147.0 (3)	C15—C16—H16	118.4
O17—Cu1—N18	95.7 (3)	C11—C16—H16	118.4
O33—Cu1—N18	92.7 (3)	C12—O17—Cu1	130.5 (6)
O17—Cu1—N2	93.1 (3)	C26—N18—C19	111.3 (7)
O33—Cu1—N2	96.2 (3)	C26—N18—Cu1	122.7 (6)
N18—Cu1—N2	148.4 (3)	C19—N18—Cu1	125.9 (6)
C10—N2—C3	113.4 (8)	C24—C19—C20	120.9 (9)
C10—N2—Cu1	122.1 (6)	C24—C19—N18	114.1 (8)
C3—N2—Cu1	124.2 (6)	C20—C19—N18	125.0 (8)
C4—C3—N2	128.5 (8)	C21—C20—C19	118.4 (10)
C4—C3—C8	118.3 (9)	C21—C20—H20	120.8
N2—C3—C8	113.3 (8)	C19—C20—H20	120.8
C5—C4—C3	121.1 (9)	C20—C21—C22	121.6 (11)
C5—C4—H4	119.5	C20—C21—H21	119.2
C3—C4—H4	119.5	C22—C21—H21	119.2
C4—C5—C6	120.0 (10)	C23—C22—C21	120.8 (11)
C4—C5—H5	120.0	C23—C22—H22	119.6
C6—C5—H5	120.0	C21—C22—H22	119.6
C7—C6—C5	121.4 (10)	C22—C23—C24	118.6 (10)
C7—C6—H6	119.3	C22—C23—H23	120.7
C5—C6—H6	119.3	C24—C23—H23	120.7
C6—C7—C8	118.0 (10)	C19—C24—C23	119.7 (10)
C6—C7—H7	121.0	C19—C24—S25	110.2 (7)
C8—C7—H7	121.0	C23—C24—S25	130.0 (8)
C7—C8—C3	121.3 (9)	C24—S25—C26	91.7 (4)
C7—C8—S9	128.5 (8)	N18—C26—C27	126.6 (8)
C3—C8—S9	110.1 (7)	N18—C26—S25	112.7 (7)
C8—S9—C10	90.7 (5)	C27—C26—S25	120.8 (7)
N2—C10—C11	127.5 (9)	C32—C27—C26	119.2 (9)
N2—C10—S9	112.6 (7)	C32—C27—C28	117.3 (9)
C11—C10—S9	119.9 (7)	C26—C27—C28	123.5 (8)
C16—C11—C10	120.3 (9)	O33—C28—C29	118.5 (9)
C16—C11—C12	116.6 (10)	O33—C28—C27	122.2 (9)
C10—C11—C12	123.2 (8)	C29—C28—C27	119.3 (8)
O17—C12—C13	118.3 (9)	C30—C29—C28	120.0 (10)
O17—C12—C11	122.9 (9)	C30—C29—H29	120.0
C13—C12—C11	118.8 (9)	C28—C29—H29	120.0
C14—C13—C12	121.4 (10)	C31—C30—C29	120.9 (11)
C14—C13—H13	119.3	C31—C30—H30	119.5
C12—C13—H13	119.3	C29—C30—H30	119.5
C13—C14—C15	120.3 (10)	C30—C31—C32	120.3 (10)
C13—C14—H14	119.8	C30—C31—H31	119.9
C15—C14—H14	119.8	C32—C31—H31	119.9
C16—C15—C14	119.6 (10)	C31—C32—C27	122.0 (10)
C16—C15—H15	120.2	C31—C32—H32	119.0
C14—C15—H15	120.2	C27—C32—H32	119.0
C15—C16—C11	123.2 (11)	C28—O33—Cu1	131.1 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O33	0.93	2.41	2.997 (12)	121
C7—H7···O17^{i}	0.93	2.59	3.305 (13)	134
C20—H20···O17	0.93	2.42	3.000 (13)	121
C23—H23···O33^{ii}	0.93	2.61	3.303 (13)	132

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