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Diaquabis(2,5-di-4-pyridyl-1,3,4-thiadiazole- κN^2)bis(thiocyanato- κN)-copper(II) dihydrate

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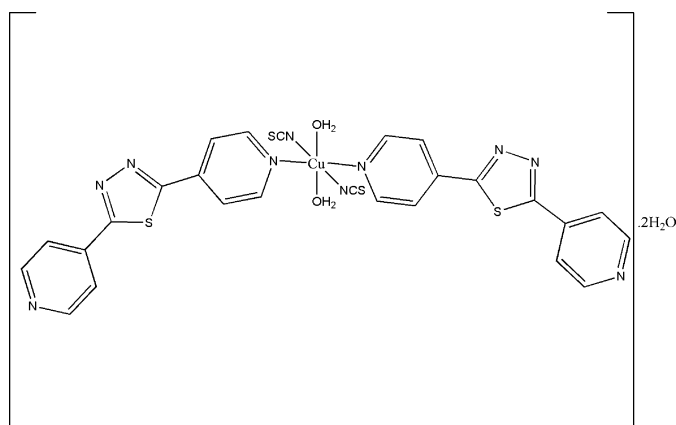
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.009$ Å; R factor = 0.061; wR factor = 0.170; data-to-parameter ratio = 13.1.

In the title compound, $[Cu(NCS)_2(C_{12}H_8N_4S)_2(H_2O)_2] \cdot 2H_2O$, the Cu atom is located on an inversion center and displays an octahedral geometry. Two N atoms of two different 2,5-di-4-pyridyl-1,3,4-thiadiazole ligands and two N atoms from two separate thiocyanate molecules form the equatorial plane, while two coordinated water molecules are in axial positions. The crystal structure is consolidated by extensive hydrogen bonding, forming a two-dimensional network.

Related literature

For related literature, see: Moulton & Zaworotko (2001); Su *et al.* (2003); Zhang *et al.* (2005); Zhou *et al.* (2006).



Experimental

Crystal data

 $[Cu(NCS)_2(C_{12}H_8N_4S)_2(H_2O)_2] \cdot 2H_2O$
 $M_r = 732.33$
Triclinic, $P\bar{1}$
 $a = 7.0555$ (11) Å
 $b = 8.3034$ (13) Å
 $c = 14.849$ (2) Å
 $\alpha = 104.629$ (2)°
 $\beta = 93.067$ (2)°
 $\gamma = 112.228$ (2)°

 $V = 768.3$ (2) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.03$ mm⁻¹
 $T = 298$ (2) K
 $0.28 \times 0.24 \times 0.19$ mm

Data collection

 Bruker APEXII area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{min} = 0.760$, $T_{max} = 0.828$

 3905 measured reflections
 2692 independent reflections
 1794 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.169$
 $S = 1.07$
 2692 reflections

 205 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.44$ e Å⁻³
 $\Delta\rho_{min} = -0.69$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2B \cdots N5$	0.82	2.03	2.835 (6)	169
$O2-H2C \cdots S2^i$	0.82	2.90	3.541 (4)	137
$O1-H1B \cdots S2^{ii}$	0.82	2.50	3.303 (4)	164
$O1-H1C \cdots O2^{iii}$	0.82	1.95	2.761 (6)	171

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP3 (Burnett & Johnson, 1996), ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2330).

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supporting information

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Diaquabis(2,5-di-4-pyridyl-1,3,4-thiadiazole- κN^2)bis(thiocyanato- κN)copper(II) dihydrate

Wei-Wu Ma and Ming-Hua Yang

S1. Comment

In recent years, the rational design and assembly of metal-organic frameworks (MOFs) with well regulated network structures have received remarkable attention in order to develop new functional materials with potential applications (Moulton & Zaworotko, 2001). Nevertheless, it is still a great challenge to predict the exact structures and compositions of polymeric compounds assembled in a motifs, although some structures with various architectures have been reported in MOFs. So far, much of the research has been concentrated on the exploitation of angular ligands with a molecular angle, such as ligands with a T-shape, V-shape *etc.*, in the construction of versatile coordination polymer architectures (Su *et al.*, 2003, Zhou *et al.*, 2006). However, the bent 2,5-di-4-pyridyl-1,3,4-thiadiazole (*L*), have been less studied as building blocks in the construction of metal-organic frameworks (Zhang *et al.*; 2005). The angular 2,5-di-4-pyridyl-1,3,4-thiadiazole has flexible coordination modes than general 4,4'-bipyridine-like ligands due to two more potential N-donors atoms. In this paper, we report the synthesis and crystal structure of the title complex with a multifunctional *L* ligand, (I).

The Cu atom is located on an inversion center and displays octahedral geometry (Fig. 1). Two nitrogen atoms of two different 2,5-di-4-pyridyl-1,3,4-thiadiazole ligands and two nitrogen atoms from two separated thiocyanate molecules form the basal plane, while two coordinated water molecules hold in axis position. The bond and angle are similar with others complexes with *L* ligand (Zhang *et al.*, 2005). These monuclear units are held together by means of H bonds involving the coordinated water molecules, sulfur atoms of thiocyanate, lattice water molecules and N atoms of pyridyl rings from *L* ligands, which further assemble into a 2-D supramolecular sheet (Fig.2, Table 1).

S2. Experimental

Cu(NCS)₂ (0.025 g, 0.13 mmol), *L* (0.031 g, 0.21 mmol), and NaOH (0.08 g, 0.2 mmol). were added in a solvent of methanol, the mixture was heated for ten hours under reflux. During the process stirring and influx were required. The resultant was then filtered to give a pure solution which was infiltrated by diethyl ether freely in a closed vessel, Four weeks later some single crystals of the size suitable for X-Ray diffraction analysis.

S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (methyl) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$. H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O—H = 0.82 (1)Å and H···H = 1.38 (2)Å) with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. In the last stage of refinement they were treated as riding on their parent O atoms.

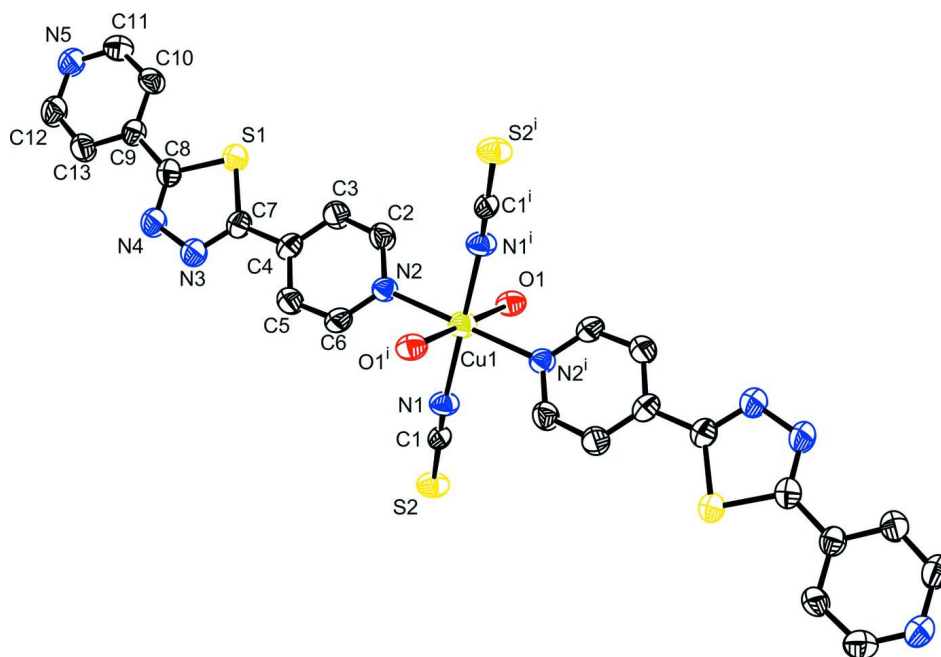


Figure 1

Molecular view of (I), with the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Water molecule and H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, 2 - y, -z$].

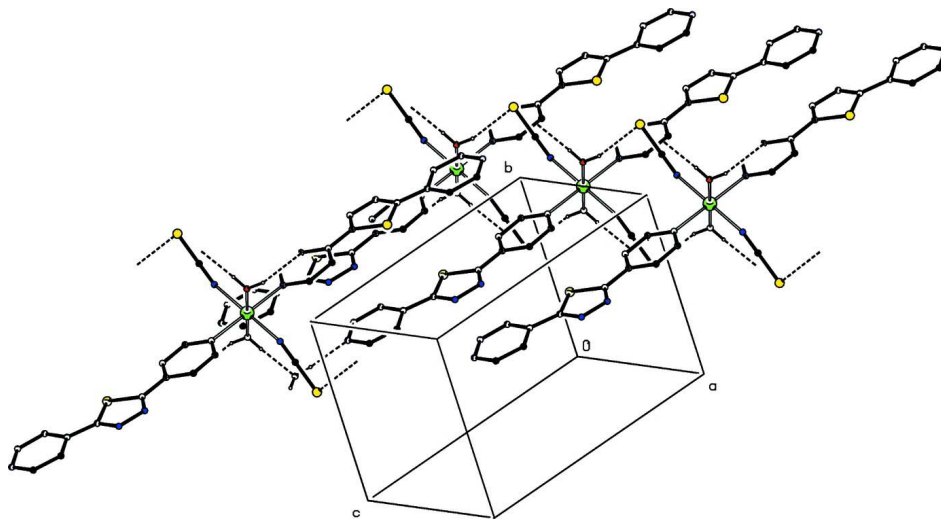


Figure 2

Partial packing view of (I), showing O—H...O, O—H...S and O—H...N hydrogen bonds leading to the formation of two-dimensional network. Hydrogen bonds are shown as dashed lines.

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Crystal data

$[\text{Cu}(\text{NCS})_2(\text{C}_{12}\text{H}_8\text{N}_4\text{S})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

$M_r = 732.33$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.0555(11)\ \text{\AA}$

$b = 8.3034(13)\ \text{\AA}$

$c = 14.849(2)\ \text{\AA}$

$\alpha = 104.629(2)^\circ$

$\beta = 93.067 (2)^\circ$
 $\gamma = 112.228 (2)^\circ$
 $V = 768.3 (2) \text{ \AA}^3$
 $Z = 1$
 $F(000) = 375$
 $D_x = 1.583 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2692 reflections
 $\theta = 1.4\text{--}25.1^\circ$
 $\mu = 1.03 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Block, blue
 $0.28 \times 0.24 \times 0.19 \text{ mm}$

Data collection

Bruker APEXII area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.761, T_{\max} = 0.828$

3905 measured reflections
 2692 independent reflections
 1794 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 25.1^\circ, \theta_{\min} = 1.4^\circ$
 $h = -8 \rightarrow 5$
 $k = -9 \rightarrow 9$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.169$
 $S = 1.07$
 2692 reflections
 205 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
 $w = 1/[\sigma^2(F_o^2) + (0.0774P)^2 + 0.6059P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e \AA}^{-3}$

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.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	1.0000	0.0000	0.0423 (3)
S1	-0.0367 (2)	0.7797 (2)	0.40422 (10)	0.0484 (4)
S2	0.7893 (2)	0.5558 (2)	-0.03644 (12)	0.0477 (4)
N1	0.6831 (7)	0.8539 (6)	-0.0062 (3)	0.0417 (11)
N2	0.4011 (6)	0.9385 (6)	0.1283 (3)	0.0349 (10)
N3	0.3261 (7)	0.7924 (7)	0.4413 (3)	0.0486 (13)
N4	0.2304 (8)	0.7563 (7)	0.5165 (3)	0.0489 (13)
N5	-0.3536 (8)	0.6276 (7)	0.7101 (3)	0.0511 (13)
O1	0.2491 (5)	0.7683 (5)	-0.0897 (3)	0.0434 (9)
H1B	0.1349	0.7366	-0.0728	0.065*

H1C	0.2596	0.6773	-0.1223	0.065*
O2	-0.6718 (6)	0.4775 (6)	0.8112 (3)	0.0586 (12)
H2B	-0.5687	0.5204	0.7880	0.088*
H2C	-0.6415	0.4525	0.8582	0.088*
C1	0.7271 (8)	0.7310 (8)	-0.0188 (4)	0.0347 (12)
C2	0.2117 (9)	0.9123 (8)	0.1465 (4)	0.0436 (14)
H2	0.1223	0.9275	0.1043	0.052*
C3	0.1394 (9)	0.8639 (8)	0.2240 (4)	0.0455 (14)
H3	0.0025	0.8407	0.2316	0.055*
C4	0.2713 (8)	0.8505 (7)	0.2895 (4)	0.0379 (13)
C5	0.4715 (9)	0.8795 (8)	0.2725 (4)	0.0475 (15)
H5	0.5660	0.8706	0.3150	0.057*
C6	0.5266 (9)	0.9218 (8)	0.1915 (4)	0.0432 (14)
H6	0.6604	0.9397	0.1802	0.052*
C7	0.2060 (8)	0.8066 (7)	0.3769 (4)	0.0395 (13)
C8	0.0424 (9)	0.7481 (8)	0.5080 (4)	0.0418 (13)
C9	-0.0929 (8)	0.7148 (7)	0.5800 (4)	0.0379 (13)
C10	-0.2927 (9)	0.7063 (8)	0.5682 (4)	0.0442 (14)
H10	-0.3440	0.7292	0.5160	0.053*
C11	-0.4144 (9)	0.6632 (8)	0.6357 (4)	0.0495 (15)
H11	-0.5479	0.6593	0.6276	0.059*
C12	-0.1584 (10)	0.6393 (9)	0.7221 (4)	0.0559 (17)
H12	-0.1112	0.6178	0.7757	0.067*
C13	-0.0248 (9)	0.6813 (8)	0.6596 (4)	0.0497 (15)
H13	0.1090	0.6871	0.6705	0.060*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0421 (6)	0.0432 (6)	0.0477 (6)	0.0197 (5)	0.0129 (4)	0.0186 (5)
S1	0.0490 (9)	0.0680 (11)	0.0412 (9)	0.0289 (8)	0.0147 (7)	0.0281 (8)
S2	0.0484 (9)	0.0420 (9)	0.0663 (11)	0.0258 (7)	0.0192 (8)	0.0252 (8)
N1	0.044 (3)	0.043 (3)	0.052 (3)	0.026 (2)	0.015 (2)	0.020 (2)
N2	0.032 (2)	0.037 (3)	0.038 (3)	0.014 (2)	0.009 (2)	0.015 (2)
N3	0.045 (3)	0.063 (3)	0.043 (3)	0.022 (3)	0.012 (2)	0.023 (3)
N4	0.048 (3)	0.064 (3)	0.041 (3)	0.021 (3)	0.014 (2)	0.027 (3)
N5	0.050 (3)	0.064 (4)	0.044 (3)	0.022 (3)	0.017 (2)	0.022 (3)
O1	0.035 (2)	0.043 (2)	0.051 (2)	0.0140 (17)	0.0117 (17)	0.0118 (18)
O2	0.055 (3)	0.059 (3)	0.051 (3)	0.013 (2)	0.018 (2)	0.011 (2)
C1	0.031 (3)	0.045 (3)	0.031 (3)	0.014 (2)	0.011 (2)	0.016 (3)
C2	0.041 (3)	0.052 (4)	0.043 (3)	0.018 (3)	0.007 (3)	0.023 (3)
C3	0.035 (3)	0.056 (4)	0.046 (3)	0.013 (3)	0.009 (3)	0.022 (3)
C4	0.040 (3)	0.034 (3)	0.036 (3)	0.011 (2)	0.012 (2)	0.009 (2)
C5	0.042 (3)	0.064 (4)	0.045 (4)	0.026 (3)	0.009 (3)	0.025 (3)
C6	0.040 (3)	0.054 (4)	0.043 (3)	0.022 (3)	0.017 (3)	0.020 (3)
C7	0.042 (3)	0.039 (3)	0.036 (3)	0.014 (3)	0.009 (3)	0.012 (3)
C8	0.047 (3)	0.043 (3)	0.037 (3)	0.017 (3)	0.006 (3)	0.014 (3)
C9	0.043 (3)	0.035 (3)	0.036 (3)	0.015 (2)	0.008 (2)	0.012 (3)

C10	0.046 (3)	0.053 (4)	0.047 (3)	0.026 (3)	0.009 (3)	0.026 (3)
C11	0.041 (3)	0.052 (4)	0.058 (4)	0.020 (3)	0.012 (3)	0.017 (3)
C12	0.054 (4)	0.075 (5)	0.042 (4)	0.023 (3)	0.014 (3)	0.026 (3)
C13	0.043 (3)	0.066 (4)	0.043 (4)	0.022 (3)	0.007 (3)	0.023 (3)

Geometric parameters (Å, °)

Cu1—N1	2.071 (4)	O2—H2C	0.8159
Cu1—N1 ⁱ	2.071 (4)	C2—C3	1.372 (8)
Cu1—O1 ⁱ	2.118 (4)	C2—H2	0.9300
Cu1—O1	2.118 (4)	C3—C4	1.365 (8)
Cu1—N2	2.178 (4)	C3—H3	0.9300
Cu1—N2 ⁱ	2.178 (4)	C4—C5	1.388 (8)
S1—C7	1.725 (6)	C4—C7	1.485 (7)
S1—C8	1.726 (5)	C5—C6	1.372 (7)
S2—C1	1.638 (6)	C5—H5	0.9300
N1—C1	1.150 (7)	C6—H6	0.9300
N2—C6	1.324 (7)	C8—C9	1.479 (7)
N2—C2	1.325 (7)	C9—C13	1.382 (7)
N3—C7	1.301 (7)	C9—C10	1.384 (7)
N3—N4	1.375 (6)	C10—C11	1.382 (8)
N4—C8	1.300 (7)	C10—H10	0.9300
N5—C11	1.305 (7)	C11—H11	0.9300
N5—C12	1.342 (8)	C12—C13	1.372 (8)
O1—H1B	0.8214	C12—H12	0.9300
O1—H1C	0.8200	C13—H13	0.9300
O2—H2B	0.8172		
N1—Cu1—N1 ⁱ	180.000 (1)	C4—C3—H3	120.5
N1—Cu1—O1 ⁱ	89.03 (16)	C2—C3—H3	120.5
N1 ⁱ —Cu1—O1 ⁱ	90.97 (16)	C3—C4—C5	118.0 (5)
N1—Cu1—O1	90.97 (16)	C3—C4—C7	121.8 (5)
N1 ⁱ —Cu1—O1	89.03 (17)	C5—C4—C7	120.2 (5)
O1 ⁱ —Cu1—O1	180.0	C6—C5—C4	118.4 (5)
N1—Cu1—N2	91.15 (17)	C6—C5—H5	120.8
N1 ⁱ —Cu1—N2	88.85 (17)	C4—C5—H5	120.8
O1 ⁱ —Cu1—N2	86.47 (15)	N2—C6—C5	124.1 (5)
O1—Cu1—N2	93.53 (15)	N2—C6—H6	118.0
N1—Cu1—N2 ⁱ	88.85 (17)	C5—C6—H6	118.0
N1 ⁱ —Cu1—N2 ⁱ	91.15 (17)	N3—C7—C4	124.0 (5)
O1 ⁱ —Cu1—N2 ⁱ	93.53 (15)	N3—C7—S1	113.8 (4)
O1—Cu1—N2 ⁱ	86.47 (14)	C4—C7—S1	122.1 (4)
N2—Cu1—N2 ⁱ	180.0 (2)	N4—C8—C9	123.7 (5)
C7—S1—C8	87.1 (3)	N4—C8—S1	113.7 (4)
C1—N1—Cu1	159.4 (4)	C9—C8—S1	122.6 (4)
C6—N2—C2	116.5 (5)	C13—C9—C10	118.0 (5)
C6—N2—Cu1	121.5 (4)	C13—C9—C8	119.9 (5)
C2—N2—Cu1	122.0 (3)	C10—C9—C8	122.0 (5)

C7—N3—N4	112.5 (5)	C11—C10—C9	118.6 (5)
C8—N4—N3	112.8 (4)	C11—C10—H10	120.7
C11—N5—C12	117.1 (5)	C9—C10—H10	120.7
Cu1—O1—H1B	118.7	N5—C11—C10	124.0 (6)
Cu1—O1—H1C	124.5	N5—C11—H11	118.0
H1B—O1—H1C	108.3	C10—C11—H11	118.0
H2B—O2—H2C	110.6	N5—C12—C13	123.5 (6)
N1—C1—S2	179.8 (5)	N5—C12—H12	118.2
N2—C2—C3	123.9 (5)	C13—C12—H12	118.2
N2—C2—H2	118.0	C12—C13—C9	118.7 (6)
C3—C2—H2	118.0	C12—C13—H13	120.6
C4—C3—C2	119.0 (5)	C9—C13—H13	120.6

Symmetry code: (i) $-x+1, -y+2, -z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H2B...N5	0.82	2.03	2.835 (6)	169
O2—H2C...S2 ⁱⁱ	0.82	2.90	3.541 (4)	137
O1—H1B...S2 ⁱⁱⁱ	0.82	2.50	3.303 (4)	164
O1—H1C...O2 ^{iv}	0.82	1.95	2.761 (6)	171

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