research communications

Crystal structure of bis[*μ-N*-(*η²*-prop-2-en-1-yl)-piperidine-1-carbothioamide-*κ²S:S*]bis[(thiocyanato-*κN*)copper(I)]

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The title crystalline compound, $[Cu_2(NCS)_2(C_9H_{16}N_2)_2]$, was obtained from the reaction of copper(I) thiocyanate (CuSCN) with (*N*-prop-2-en-1-yl)piperidine-1-carbothioamide as a chelating and bridging thiourea ligand in chlorobenzene. The Cu_2S_2 core of the dimeric molecule is situated on a crystallographic inversion centre. The copper atom is coordinated by a thiocyanate nitrogen atom, each sulfur atom of the two thiourea ligands, and the C≡C double bond of the ligand in a distorted tetrahedral geometry. The dimers are linked by N—H···S hydrogen bonds, forming a network extending in two dimensions parallel to (100).

1. Chemical context

Thiourea and its derivatives, *N*-substituted thiourea and *N*, *N'*-disubstituted thiourea, are well-known ligands to copper ions, such as for their structural relatedness of proteins in bioinorganic chemistry and controlling redox potentials of copper ions in electrochemistry. Recently, copper–thiourea complexes [Cu(tu)s] have been investigated as electronic materials, for precursors of copper sulfide to be applied as semiconductors (Shamraiz *et al.*, 2017; Sarma *et al.*, 2019; Patel *et al.*, 2019), photocatalysts (Tran *et al.*, 2012; Pal *et al.*, 2015), and sensors (Liu & Xue, 2011; Sabah *et al.*, 2016; Sagade & Sharma, 2008). Cu(tu)s have also been used as a component of the precursor ink for forming CuIn(S, Se) as photo-absorbing layers in solar cells (Uhl *et al.*, 2016). The solubility of Cu(tu)s in non-polar solvents is a potentially important property for their application as electronic materials. In order to synthesize a hydrophobic Cu(tu)s, we developed an allyl and a piperidinyl group bearing thiourea, (*N*-prop-2-en-1-yl)piperidine-1-carbothioamide, as a hydrophobic bidentate ligand and report here the crystal structure of the title non-ionic Cu[I] complex containing thiocyanates as coordinating anions.
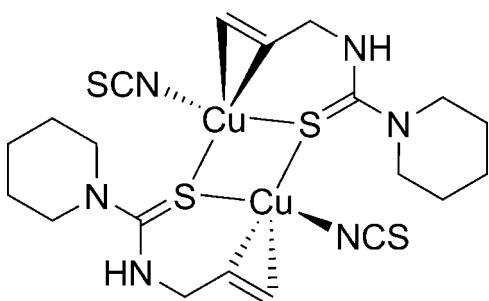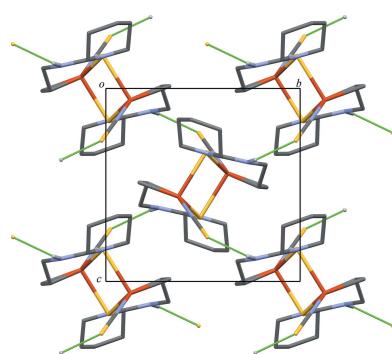
Table 1
Selected geometric parameters (Å, °).

Cu1—S2	2.2835 (8)	Cu1—C15	2.095 (3)
Cu1—S2^i	2.6491 (8)	Cu1—Cg1	1.969
Cu1—N6	1.924 (3)	N5—H5	0.856 (10)
Cu1—C14	2.068 (3)	C14—C15	1.351 (5)
S2—Cu1—S2^i	101.98 (3)	C14—Cu1—C15	37.86 (13)
N6—Cu1—S2	107.15 (8)	C15—Cu1—S2	130.85 (10)
N6—Cu1—S2^i	97.44 (8)	C15—Cu1—S2^i	101.56 (10)
N6—Cu1—C14	147.71 (13)	Cu1—S2—Cu1^i	78.02 (3)
N6—Cu1—C15	111.75 (13)	Cg1—Cu1—S2	113.57
C14—Cu1—S2	95.68 (9)	Cg1—Cu1—S2^i	101.31
C14—Cu1—S2^i	99.83 (9)	Cg1—Cu1—N6	129.88

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$\cdots A$
N5—H5$\cdots$S3^{ii}	0.86 (2)	2.60 (3)	3.375 (3)	151 (3)
C7—H7$B\cdots$S2	0.99	2.48	3.028 (3)	114

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

N-allylthiourea)dicopper(I) dinitrate [Cu$_2$(atu)$_2$(CH$_3$CN)$_2$]-(NO$_3$)$_2$, a cationic analogue of the title compound with acetonitrile instead of thiocyanate and without the piperidine ring, shows a similar geometry around copper but has no crystallographic inversion centre because of the asymmetric packing of the nitrate anions [Cambridge Structural Database (CSD) refcode RENNON; Filinchuk *et al.*, 1996].

2. Structural commentary

The molecular structure of the title compound possessing a Cu$_2$S$_2$ central core is shown in Fig. 1. The dimeric molecule is situated on a crystallographic inversion centre. Selected geometric parameters are shown in Table 1. The coordination about the Cu atom can be described as distorted tetrahedral containing N6, S2, S2^i, and Cg1 [Cg1 is the mid-point of C14 and C15; symmetry code: (i) $-x + 1, -y + 1, -z + 1$]. The four-coordinate geometry index, $\tau_4 = [360° - (\alpha + \beta)] / 141°$, evaluated from the two largest angles ($\alpha < \beta$), which has ideal values of 1 for a tetrahedral and 0 for a square-planar geometry (Yang *et al.*, 2007), is equal to 0.83. The Cu$\cdots$Cu^i separation in the dimer is 3.1180 (6) Å. The C14=C15 double bond is η^2-π-coordinated to Cu, the bond being elongated to 1.351 (5) Å. The N atom of the piperidine ring (N4) shows no pyramidalization, with a displacement of 0.041 (3) Å from the plane of the bonded C atoms (C7, C11 and C12). The piperidine ring adopts a chair conformation with puckering parameters: $Q = 0.573$ (4), $\theta = 176.3$ (4), and $\varphi = 153$ (6) (Cremer & Pople, 1975). There is one intramolecular interaction, C7—H7$B\cdots$S2, generating an $S(5)$ ring motif (Fig. 1 and Table 2). In comparison, the crystal structure of bis(acetonitrile)bis(η^2-

3. Supramolecular features

In the crystal, the dimers are linked by N—H$\cdots$S hydrogen bonds [N5—H5$\cdots$S3^{ii}; symmetry code: (ii) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$], forming a network extending in two dimensions parallel to (100) (Fig. 2, Fig. 3, and Table 2). There is no significant interaction between two-dimensional networks. In contrast, the crystal structure of [Cu$_2$(atu)$_2$(CH$_3$CN)$_2$](NO$_3$)$_2$ exhibits a complementary C—H$\cdots$S interaction between discrete copper dimers forming a dimer of dimeric structures (RENNON; Filinchuk *et al.*, 1996). The discrete copper dimer exhibits six N—H$\cdots$O interactions to the surrounding six nitrate anions.


Figure 1
The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radius. The hydrogen bonds are shown as green dashed lines. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$].
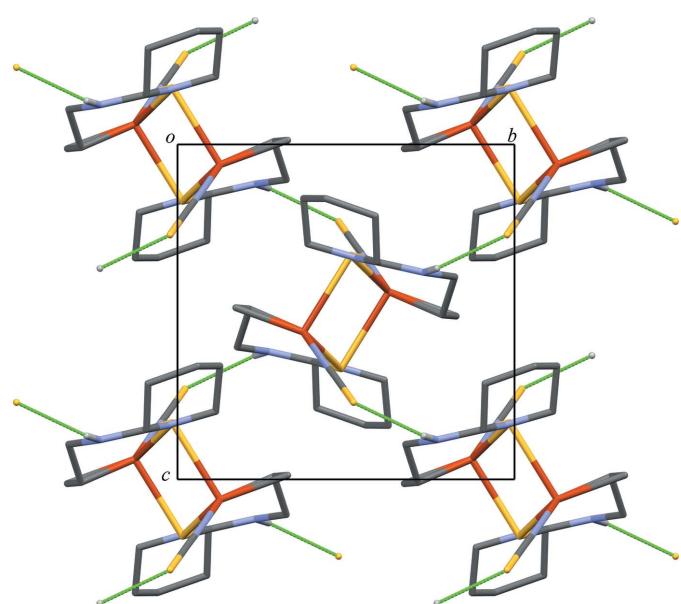

Figure 2
A packing diagram of the title compound viewed along the *a* axis, *i.e.* a top view of the two-dimensional network. The N—H$\cdots$S hydrogen bonds are shown as green dashed lines. H atoms not involved in the interactions were omitted for clarity.
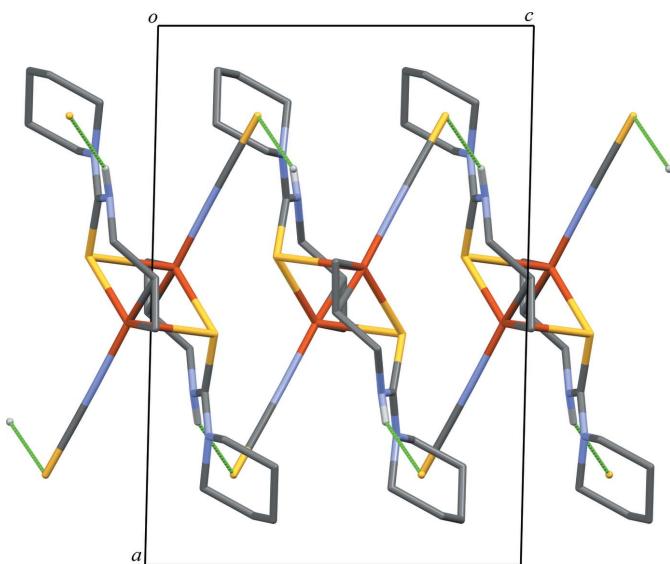
Figure 3
A packing diagram of the title compound viewed along the *b* axis, *i.e.* a side view of the two-dimensional network. The N—H⋯S hydrogen bonds are shown as green dashed lines. H atoms not involved in the interactions were omitted for clarity.

4. Database survey

A search of the CSD (Version 5.41, update of August 2020; Groom *et al.*, 2016) using *ConQuest* (Bruno *et al.*, 2002) for compounds containing the 1-allylthiourea skeleton gave 892 hits, and for those containing the thiourea derivatives as ligands gave 945 hits of Cu complexes. The crystal structures of the ligand of the title compound, (*N*-prop-2-en-1-yl)piperidine-1-carbothioamide, itself and its metal complexes have not been reported. A survey for a Cu complex containing the 1-allylthiourea fragment as a κS-coordination ligand reveals 53 examples, which includes six examples of η²-π-coordination of an allyl group to Cu. All of these six examples are Cu^I complexes, which comprise four coordination polymers of 4-allyl-semicarbazide as ligands (Mel'nyk *et al.*, 2001, 2011; Olijnik *et al.*, 2011), one coordination polymer of 1,3-diallyl-thiourea as ligand (BOGNUH; Vakulka *et al.*, 2007), and one discrete centrosymmetric dimer of 1-allylthiourea as ligand (RENNON; Filinchuk *et al.*, 1996).

5. Synthesis and crystallization

To a chlorobenzene solution (2.5 mL) containing copper(I) thiocyanate (CuSCN, 122 mg, 1.0 mmol) and allyl isothiocyanate (298 mg, 3.0 mmol) in a 20 mL capped screw-tube bottle was slowly added piperidine (171 mg, 2.0 mmol) at 373 K under air and the mixture was stirred for 5 minutes. After that, it was left at room temperature. The pale-white precipitate formed in the bottle, and gradually changed to a pale-white solid containing single crystals. The mixture was filtered after 5 days to give a pale-white solid containing single crystals (267 mg, 0.87 mmol, 87%). Single crystals suitable for X-ray crystallographic analysis were selected in the product.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu_2(NCS)_2(C_9H_{16}N_2S)_2]$
M_r	611.83
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	13.9881 (5), 9.8220 (4), 9.7446 (4)
β (°)	91.391 (6)
V (Å³)	1338.43 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	1.92
Crystal size (mm)	$0.15 \times 0.15 \times 0.1$
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.747, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	12737, 3071, 2516
R_{int}	0.041
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.045, 0.098, 1.08
No. of reflections	3071
No. of parameters	168
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.61, −0.40

Computer programs: *RAPID-AUTO* (Rigaku, 2006), *SHELXT* 2018/2 (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *PLATON* (Spek, 2020), *Mercury* (Macrae *et al.*, 2020), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

Analysis calculated for $(C_{10}H_{16}CuN_3S_2)_2$: C, 39.26; H, 5.27; N, 13.74; S, 20.96. Found: C, 38.72; H, 4.78; N, 13.59; S, 20.28.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Atoms H14, H15*A*, and H15*B* were located in a difference-Fourier map and refined freely, considering the influence of the coordination of the ethenyl group to Cu^I. H11*A* and H11*B* were also located in the difference-Fourier map and refined freely, because the distance between intramolecular H11*B* and H5 in the neighbouring molecule was abnormally short in the riding model. Other C-bound H atoms were placed in geometrically calculated positions (C—H = 0.99 Å) and refined as part of a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H5 atom was located in the difference-Fourier map but was refined with a distance restraint of N—H = 0.86±0.01 Å, and with $U_{iso}(H)$ set to $1.2U_{eq}(N)$.

Acknowledgements

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supporting information

Crystal structure of bis[*μ*-*N*-(*η*²-prop-2-en-1-yl)piperidine-1-carbothioamide-*κ²S*:*S*]bis[(thiocyanato-*κN*)copper(I)]

Takeshi Tanaka, Yukiyasu Kashiwagi and Masami Nakagawa

Computing details

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO* (Rigaku, 2006); data reduction: *RAPID-AUTO* (Rigaku, 2006); program(s) used to solve structure: *SHELXT* 2018/2 (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015*b*); molecular graphics: *PLATON* (Spek, 2020), *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).
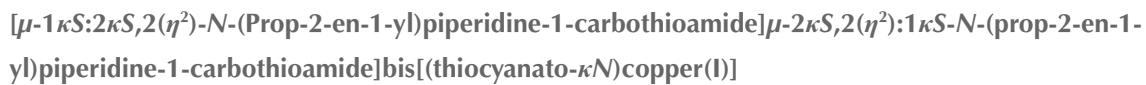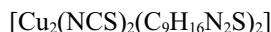
[*μ*-1*κS*:2*κS*,2(*η*²)-*N*-(Prop-2-en-1-yl)piperidine-1-carbothioamide]*μ*-2*κS*,2(*η*²):1*κS*-*N*-(prop-2-en-1-yl)piperidine-1-carbothioamide]bis[(thiocyanato-*κN*)copper(I)]

Crystal data

[Cu₂(NCS)₂(C₉H₁₆N₂S)₂]	$F(000) = 632$
$M_r = 611.83$	$D_x = 1.518$ Mg m⁻³
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
$a = 13.9881$ (5) Å	Cell parameters from 9884 reflections
$b = 9.8220$ (4) Å	$\theta = 5.0$–55.0°
$c = 9.7446$ (4) Å	$\mu = 1.92$ mm⁻¹
$\beta = 91.391$ (6)°	$T = 173$ K
$V = 1338.43$ (9) Å³	Block, clear colourless
$Z = 2$	0.15 × 0.15 × 0.1 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	12737 measured reflections
Radiation source: sealed X-ray tube	3071 independent reflections
Graphite monochromator	2516 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.041$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.5°$
	$h = -18 \rightarrow 17$
	$k = -12 \rightarrow 12$
$T_{min} = 0.747$, $T_{max} = 1.000$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.045$	and constrained refinement
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 1.6287P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
3071 reflections	$(\Delta/\sigma)_{max} = 0.001$
168 parameters	$\Delta\rho_{max} = 0.61$ e Å⁻³
1 restraint	$\Delta\rho_{min} = -0.40$ e Å⁻³
Primary atom site location: dual	

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	0.55125 (3)	0.62670 (4)	0.43953 (4)	0.03267 (13)
S2	0.42819 (5)	0.51488 (7)	0.33025 (7)	0.02780 (17)
S3	0.83263 (6)	0.47774 (11)	0.22981 (13)	0.0594 (3)
N4	0.23866 (19)	0.5307 (3)	0.3387 (3)	0.0402 (6)
N6	0.66753 (18)	0.5688 (3)	0.3556 (3)	0.0353 (6)
N5	0.31829 (18)	0.7313 (3)	0.3819 (3)	0.0376 (6)
H5	0.2655 (15)	0.774 (3)	0.369 (4)	0.045*
C14	0.4691 (2)	0.7864 (3)	0.5090 (3)	0.0346 (7)
C16	0.7358 (2)	0.5304 (3)	0.3044 (3)	0.0331 (7)
C12	0.3206 (2)	0.5985 (3)	0.3524 (3)	0.0301 (6)
C15	0.5614 (2)	0.8269 (3)	0.5125 (4)	0.0342 (7)
C13	0.4006 (2)	0.8228 (3)	0.3952 (3)	0.0367 (7)
H13A	0.377117	0.916542	0.410448	0.044*
H13B	0.435145	0.822461	0.307731	0.044*
C7	0.2322 (2)	0.3865 (3)	0.2969 (4)	0.0448 (9)
H7A	0.197211	0.334276	0.366632	0.054*
H7B	0.297289	0.347654	0.291007	0.054*
C8	0.1816 (3)	0.3743 (4)	0.1611 (4)	0.0510 (9)
H8A	0.174400	0.276834	0.137225	0.061*
H8B	0.220513	0.417941	0.089947	0.061*
C11	0.1427 (3)	0.5915 (4)	0.3497 (5)	0.0548 (11)
C10	0.0912 (3)	0.5872 (4)	0.2135 (5)	0.0608 (12)
H10A	0.126101	0.642923	0.146529	0.073*
H10B	0.026342	0.626044	0.222292	0.073*
C9	0.0836 (3)	0.4406 (4)	0.1618 (5)	0.0625 (12)
H9A	0.041038	0.388028	0.221843	0.075*
H9B	0.055244	0.439964	0.067737	0.075*
H15A	0.600 (2)	0.820 (3)	0.596 (3)	0.026 (8)*
H15B	0.591 (3)	0.872 (4)	0.437 (4)	0.048 (11)*
H14	0.439 (2)	0.754 (4)	0.592 (4)	0.048 (10)*
H11A	0.096 (3)	0.536 (4)	0.409 (4)	0.046 (10)*
H11B	0.148 (3)	0.677 (5)	0.384 (4)	0.065 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0320 (2)	0.0261 (2)	0.0401 (2)	−0.00062 (15)	0.00349 (16)	−0.00623 (16)
S2	0.0315 (4)	0.0221 (3)	0.0298 (4)	0.0011 (3)	0.0010 (3)	−0.0023 (3)
S3	0.0348 (5)	0.0492 (6)	0.0952 (8)	−0.0068 (4)	0.0218 (5)	−0.0268 (5)

N4	0.0328 (13)	0.0283 (13)	0.0595 (18)	−0.0020 (11)	−0.0021 (13)	−0.0037 (13)
N6	0.0344 (14)	0.0333 (14)	0.0383 (15)	−0.0027 (11)	0.0053 (12)	−0.0028 (11)
N5	0.0318 (13)	0.0241 (13)	0.0568 (17)	0.0039 (11)	−0.0007 (13)	−0.0033 (12)
C14	0.0492 (18)	0.0220 (14)	0.0329 (16)	0.0044 (13)	0.0047 (15)	−0.0025 (12)
C16	0.0319 (15)	0.0270 (15)	0.0404 (17)	−0.0057 (12)	−0.0011 (14)	−0.0036 (13)
C12	0.0343 (15)	0.0246 (15)	0.0313 (15)	0.0017 (12)	0.0002 (13)	0.0021 (12)
C15	0.0475 (18)	0.0212 (14)	0.0335 (16)	−0.0015 (13)	−0.0060 (16)	−0.0024 (12)
C13	0.0436 (17)	0.0219 (14)	0.0444 (18)	0.0004 (13)	−0.0016 (15)	−0.0017 (13)
C7	0.0388 (17)	0.0244 (16)	0.071 (2)	−0.0027 (13)	−0.0087 (17)	0.0017 (16)
C8	0.045 (2)	0.0370 (19)	0.071 (3)	0.0051 (16)	−0.0147 (19)	−0.0061 (18)
C11	0.0334 (18)	0.041 (2)	0.091 (3)	−0.0019 (16)	0.010 (2)	−0.012 (2)
C10	0.0366 (18)	0.042 (2)	0.103 (4)	0.0095 (16)	−0.015 (2)	0.003 (2)
C9	0.046 (2)	0.047 (2)	0.093 (3)	0.0064 (18)	−0.028 (2)	−0.007 (2)

Geometric parameters (Å, º)

Cu1—S2	2.2835 (8)	C15—H15A	0.96 (3)
Cu1—S2[i]	2.6491 (8)	C15—H15B	0.96 (4)
Cu1—N6	1.924 (3)	C13—H13A	0.9900
Cu1—C14	2.068 (3)	C13—H13B	0.9900
Cu1—C15	2.095 (3)	C7—H7A	0.9900
S2—C12	1.733 (3)	C7—H7B	0.9900
S3—C16	1.636 (3)	C7—C8	1.490 (5)
N4—C12	1.329 (4)	C8—H8A	0.9900
N4—C7	1.476 (4)	C8—H8B	0.9900
N4—C11	1.476 (4)	C8—C9	1.517 (5)
N6—C16	1.151 (4)	C11—C10	1.494 (6)
Cu1—*Cg*1	1.969	C11—H11A	1.04 (4)
N5—H5	0.856 (10)	C11—H11B	0.91 (5)
N5—C12	1.336 (4)	C10—H10A	0.9900
N5—C13	1.464 (4)	C10—H10B	0.9900
C14—C15	1.351 (5)	C10—C9	1.528 (6)
C14—C13	1.492 (5)	C9—H9A	0.9900
C14—H14	0.98 (4)	C9—H9B	0.9900
S2—Cu1—S2[i]	101.98 (3)	H15A—C15—H15B	115 (3)
N6—Cu1—S2	107.15 (8)	N5—C13—C14	114.1 (3)
N6—Cu1—S2[i]	97.44 (8)	N5—C13—H13A	108.7
N6—Cu1—C14	147.71 (13)	N5—C13—H13B	108.7
N6—Cu1—C15	111.75 (13)	C14—C13—H13A	108.7
C14—Cu1—S2	95.68 (9)	C14—C13—H13B	108.7
C14—Cu1—S2[i]	99.83 (9)	H13A—C13—H13B	107.6
C14—Cu1—C15	37.86 (13)	N4—C7—H7A	109.6
C15—Cu1—S2	130.85 (10)	N4—C7—H7B	109.6
C15—Cu1—S2[i]	101.56 (10)	N4—C7—C8	110.3 (3)
Cu1—S2—Cu1[i]	78.02 (3)	H7A—C7—H7B	108.1
C12—S2—Cu1[i]	102.73 (10)	C8—C7—H7A	109.6
*Cg*1—Cu1—S2	113.57	C8—C7—H7B	109.6

$Cg1$—Cu1—S2^i	101.31	C7—C8—H8A	109.3
$Cg1$—Cu1—N6	129.88	C7—C8—H8B	109.3
C12—S2—Cu1	111.18 (10)	C7—C8—C9	111.8 (4)
C12—N4—C7	123.7 (3)	H8A—C8—H8B	107.9
C12—N4—C11	125.0 (3)	C9—C8—H8A	109.3
C7—N4—C11	111.0 (3)	C9—C8—H8B	109.3
C16—N6—Cu1	177.9 (3)	N4—C11—C10	110.1 (4)
C12—N5—H5	118 (3)	N4—C11—H11A	114 (2)
C12—N5—C13	126.5 (3)	N4—C11—H11B	109 (3)
C13—N5—H5	113 (3)	C10—C11—H11A	101 (2)
Cu1—C14—H14	106 (2)	C10—C11—H11B	113 (3)
C15—C14—Cu1	72.15 (19)	H11A—C11—H11B	109 (3)
C15—C14—C13	123.0 (3)	C11—C10—H10A	109.6
C15—C14—H14	120 (2)	C11—C10—H10B	109.6
C13—C14—Cu1	106.9 (2)	C11—C10—C9	110.4 (3)
C13—C14—H14	115 (2)	H10A—C10—H10B	108.1
N6—C16—S3	179.1 (3)	C9—C10—H10A	109.6
N4—C12—S2	119.9 (2)	C9—C10—H10B	109.6
N4—C12—N5	119.1 (3)	C8—C9—C10	110.5 (3)
N5—C12—S2	121.0 (2)	C8—C9—H9A	109.6
Cu1—C15—H15A	104.7 (19)	C8—C9—H9B	109.6
Cu1—C15—H15B	102 (2)	C10—C9—H9A	109.6
C14—C15—Cu1	69.98 (18)	C10—C9—H9B	109.6
C14—C15—H15A	121.1 (18)	H9A—C9—H9B	108.1
C14—C15—H15B	123 (2)		
Cu1—S2—C12—N4	−157.3 (2)	C13—N5—C12—S2	2.0 (5)
Cu1^i—S2—C12—N4	−75.4 (3)	C13—N5—C12—N4	−177.4 (3)
Cu1^i—S2—C12—N5	105.2 (3)	C13—C14—C15—Cu1	−98.9 (3)
Cu1—S2—C12—N5	23.3 (3)	C7—N4—C12—S2	−3.8 (5)
Cu1—C14—C13—N5	78.7 (3)	C7—N4—C12—N5	175.6 (3)
N4—C7—C8—C9	−55.6 (4)	C7—N4—C11—C10	−61.3 (4)
N4—C11—C10—C9	57.8 (5)	C7—C8—C9—C10	52.8 (5)
C12—N4—C7—C8	−114.7 (4)	C11—N4—C12—S2	−177.5 (3)
C12—N4—C11—C10	113.1 (4)	C11—N4—C12—N5	1.9 (5)
C12—N5—C13—C14	−62.8 (4)	C11—N4—C7—C8	59.7 (4)
C15—C14—C13—N5	158.0 (3)	C11—C10—C9—C8	−53.6 (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
N5—H5⋯S3^{ii}	0.86 (2)	2.60 (3)	3.375 (3)	151 (3)
C7—H7*B*⋯S2	0.99	2.48	3.028 (3)	114

Symmetry code: (ii) −x+1, y+1/2, −z+1/2.