Acta Cryst
E
CRYSTALLOGRAPHIC
COMMUNICATIONS

ISSN 2056-9890

Crystal structure of bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole-κ^2N^2,N^3]bis(thiocyanato-κS)copper(II)

Abdelhakim Laachir,[a] Fouad Bentiss,[b] Salaheddine Guesmi,[a]* Mohamed Saadi[c] and Lahcen El Ammari[c]

[a]Laboratoire de Chimie de Coordination et d'Analytique (LCCA), Faculté des Sciences, Université Chouaib Doukkali, BP 20, M-24000 El Jadida, Morocco, [b]Laboratoire de Catalyse et de Corrosion de Matériaux (LCCM), Faculté des Sciences, Université Chouaib Doukkali, BP 20, M-24000 El Jadida, Morocco, and [c]Laboratoire de Chimie du Solide Appliquée, Faculty of Sciences, Mohammed V University in Rabat, Avenue Ibn Battouta, BP 1014, Rabat, Morocco.
*Correspondence e-mail: salaheddine_guesmi@yahoo.fr

Received 8 July 2016
Accepted 18 July 2016

Edited by C. Rizzoli, Universita degli Studi di Parma, Italy

Keywords: crystal structure; copper complex; 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole; thiocyanate ligand.

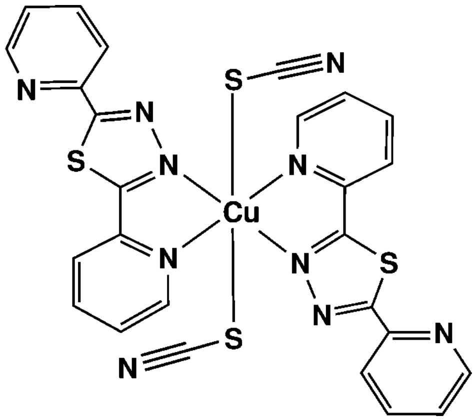
CCDC reference: 1494615

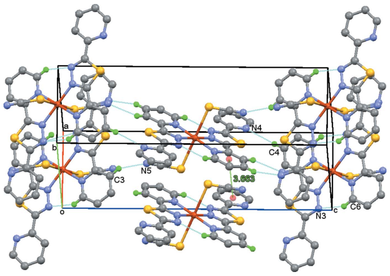
Supporting information: this article has supporting information at journals.iucr.org/e

The mononuclear title complex, [Cu(SCN)$_2$(C$_{12}$H$_8$N$_4$S)$_2$], was obtained by the reaction of 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole and potassium thiocyanate with copper(II) chloride dihydrate. The copper cation lies on an inversion centre and displays an elongated octahedral coordination geometry. The equatorial positions are occupied by the N atoms of two 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole ligands, whereas the axial positions are occupied by the S atoms of two thiocyanate anions. The thiadiazole and the pyridyl rings linked to the metal are approximately coplanar, with a maximum deviation from the mean plane of 0.190 (2) Å. The cohesion of the crystal structure is ensured by weak C—H$\cdots$N hydrogen bonds and π–π interactions between parallel pyridyl rings of neighbouring molecules [centroid-to-centroid distance = 3.663 (2) Å], leading to a three-dimensional network.

1. Chemical context

The use of compounds containing a 1,3,4-thiadiazole moiety as part of ligand systems has gained considerable attention in recent years (Kadam Sushama *et al.*, 2016). Indeed, a 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole (bptd) and its metal complexes have been extensively studied because of their potential applications in biology (Baghel *et al.*, 2014; Ahmed *et al.*, 2015; Zine *et al.*, 2016), magnetism (Bentiss *et al.*, 2004) and coordination chemistry (Bentiss *et al.*, 2002). An interesting feature of the metal-ligand chemistry of these compounds is that the complexes can be mononuclear (Bentiss *et al.*, 2011, 2012; Klingele *et al.*, 2010; Kaase & Klingele, 2014) or binuclear (Laachir *et al.*, 2013).





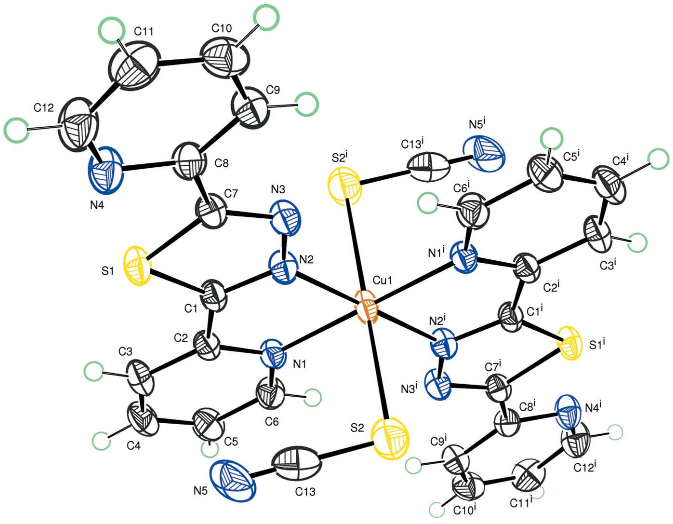


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are represented as small circles. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

We have recently reported the synthesis and characterization of monomeric complexes of Ni^{II} and Co^{II} with bptd in the presence of the pseudohalide azide (Laachir *et al.*, 2015*a*,*b*). In this context, we report here the synthesis and crystal structure of a new Cu^{II} complex with bptd and thiocyanate as co-ligands.

2. Structural commentary

The title complex has crystallographically imposed inversion symmetry, the copper atom lying on the Wyckoff special position *2b* of the space group $P2_1/c$. The elongated octahedral coordination polyhedron around the metal cation is provided by four nitrogen atoms of pyridine and thiadiazole rings occupying the equatorial plane and by the sulfur atoms of two thiocyanate anions at the apical positions (Fig. 1). The Cu—N distances are 2.0267 (16) and 2.0463 (15) Å, the Cu—S bond length is 2.8125 (7) Å. A bond-valence-sum calculation (Brown & Altermatt, 1985) for Cu gives the expected BVS value of 2.11 valence units. The conformation of the ligand is approximately planar, with a maximum deviation from the least-squares plane of 0.190 (2) Å for atom C12. The dihedral angles formed by the thiadiazole ring with the N1/C2–C6 and N4/C8–C12 pyridine rings are 1.94 (8) and 6.96 (5)°, respectively.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$N5^{i}	0.93	2.53	3.353 (3)	147
C6—H6$\cdots$N3^{ii}	0.93	2.35	3.143 (3)	142
C4—H4$\cdots$N4^{iii}	0.93	2.57	3.458 (3)	161

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

3. Supramolecular features

In the crystal, the molecules are linked by weak C—H$\cdots$N hydrogen bonds (Table 1) and by π–π stacking interactions between the pyridyl rings of adjacent complex molecules [intercentroid distance = 3.663 (2) Å], forming a three-dimensional network (Fig. 2).

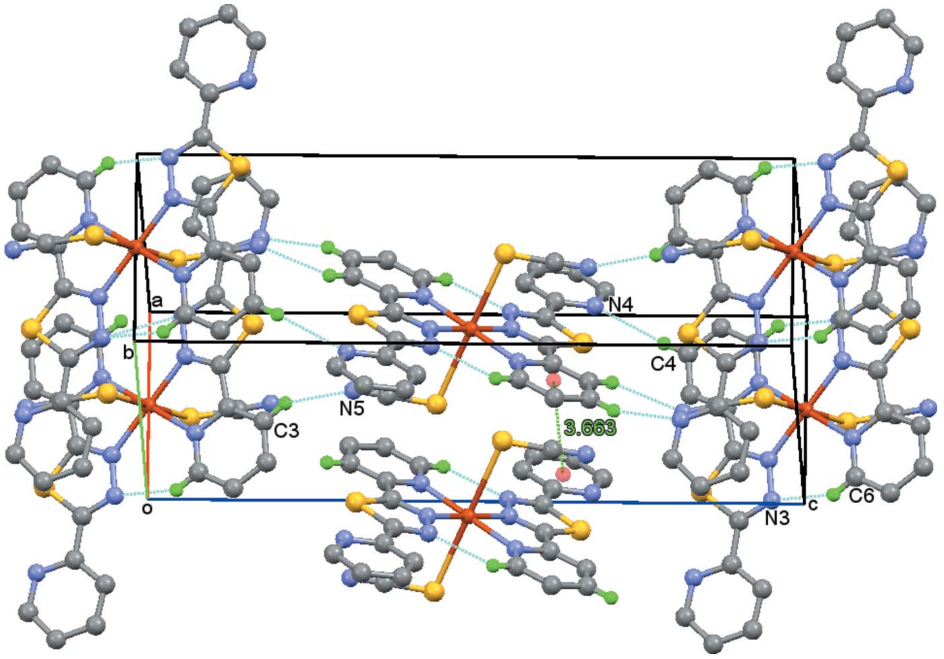


Figure 2
Crystal packing of the title compound, showing π–π interactions between pyridyl rings (green dashed lines) and intermolecular hydrogen bonds (blue dashed lines).

Acta Cryst. (2016). E**72**, 1176–1178 Laachir *et al.* • [Cu(SCN)$_2$(C$_{12}$H$_8$N$_4$S)$_2$] **1177**

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(SCN)_2(C_{12}H_8N_4S)_2]$
M_r	660.27
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	8.0205 (3), 7.8434 (3), 21.3454 (9)
β (°)	92.565 (2)
V (Å^3)	1341.45 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.17
Crystal size (mm)	0.35 × 0.32 × 0.26
Data collection	
Diffractometer	Bruker X8 APEX
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.604, 0.746
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	42199, 4089, 3155
R_{int}	0.060
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.097, 1.04
No. of reflections	4089
No. of parameters	187
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.51

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

4. Database survey

The structure of the title compound is similar to that of the related complexes $[Co(C_{12}H_8N_4S)_2(N_3)_2]$ (Laachir *et al.*, 2015*b*) and $[Ni(C_{12}H_8N_4S)_2(N_3)_2]$ (Laachir *et al.*, 2015*a*), in which the azide ion is substituted by the thiocyanate group. The CuN_4S_2 octahedron is more distorted than the NiN_6 and CoN_6 octahedra.

5. Synthesis and crystallization

2,5-Bis(pyridin-2-yl)-1,3,4-thiadiazole (bptd) was synthesized as described previously by Lebrini *et al.* (2005). A solution of bptd (24 mg, 0.1 mmol) in CH_3CN (10 mL) was layered onto a solution of $CuCl_2{\cdot}2H_2O$ (17 mg, 0.1 mmol) and KSCN (20 mg, 0.2 mmol) in CH_3CN/H_2O (1:1 *v*/*v*, 10 mL) in a test tube. The solution was left for two months at room temperature to give X-ray quality brown block-shaped crystals. After filtration, the product was washed with cold EtOH and dried under vacuum. Crystals were washed with water and dried under vacuum (yield 60%; m.p. 538 K). Analysis calculated for $C_{26}H_{16}N_{10}S_4Cu$: C, 47.30; H, 2.44; N, 21.21 S, 19.42. Found: C, 47.06; H, 2.43; N, 21.03; S, 19.56.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were located in a difference Fourier map and treated as riding, with C—H = 0.96 Å, and with $U_{iso}(H) = 1.2\,U_{eq}(C)$. One outlier (002) was omitted in the last cycles of refinement.

Acknowledgements

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray measurements and Chouaib Doukkali University, El Jadida, Morocco, for financial support.

References

Ahmed, Y. B., Merzouk, H., Harek, Y., Medjdoub, A., Cherrak, S., Larabi, L. & Narce, M. (2015). *Med. Chem. Res.* **24**, 764–772.
Baghel, U. S., Kaur, H., Chawla, A. & Dhawan, R. K. (2014). *Der Pharma Chem.* **6**, 66–69.
Bentiss, F., Capet, F., Lagrenée, M., Saadi, M. & El Ammari, L. (2011). *Acta Cryst.* E**67**, m834–m835.
Bentiss, F., Lagrenée, M., Vezin, H., Wignacourt, J. P. & Holt, E. M. (2004). *Polyhedron*, **23**, 1903–1907.
Bentiss, F., Lagrenée, M., Wignacourt, J. P. & Holt, E. M. (2002). *Polyhedron*, **21**, 403–408.
Bentiss, F., Outirite, M., Lagrenée, M., Saadi, M. & El Ammari, L. (2012). *Acta Cryst.* E**68**, m360–m361.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Kaase, D. & Klingele, J. (2014). *Acta Cryst.* E**70**, m252–m253.
Kadam Sushama, S., Nazeruddin, G. M., Rafique Sarkhwas, M. & Suryawanshi, S. B. (2016). *World J. Pharm. Res.* **5**, 1724–1737.
Klingele, J., Kaase, D., Klingele, M. H., Lach, J. & Demeshko, S. (2010). *Dalton Trans.* **39**, 1689–1691.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Laachir, A., Bentiss, F., Guesmi, S., Saadi, M. & El Ammari, L. (2013). *Acta Cryst.* E**69**, m351–m352.
Laachir, A., Bentiss, F., Guesmi, S., Saadi, M. & El Ammari, L. (2015*a*). *Acta Cryst.* E**71**, m24–m25.
Laachir, A., Bentiss, F., Guesmi, S., Saadi, M. & El Ammari, L. (2015*b*). *Acta Cryst.* E**71**, 452–454.
Lebrini, M., Bentiss, F. & Lagrenée, M. (2005). *J. Heterocycl. Chem.* **42**, 991–994.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zine, H., Rifai, L. A., Faize, M., Bentiss, F., Guesmi, S., Laachir, A., Smaili, A., Makroum, K., Sahibed-Dine, A. & Koussa, T. (2016). *J. Agric. Food Chem.* **64**, 2661–2667.

supporting information

Acta Cryst. (2016). E**72**, 1176-1178 [https://doi.org/10.1107/S2056989016011713]

Crystal structure of bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole-κ^2N^2,N^3]bis(thiocyanato-κS)copper(II)

Abdelhakim Laachir, Fouad Bentiss, Salaheddine Guesmi, Mohamed Saadi and Lahcen El Ammari

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

Bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole-κ^2N^2,N^3]bis(thiocyanato-κS)copper(II)

Crystal data

$[Cu(NCS)_2(C_{12}H_8N_4S)_2]$
$M_r = 660.27$
Monoclinic, $P2_1/c$
$a = 8.0205$ (3) Å
$b = 7.8434$ (3) Å
$c = 21.3454$ (9) Å
$\beta = 92.565$ (2)°
$V = 1341.45$ (9) Å^3
$Z = 2$
$F(000) = 670$
$D_x = 1.635$ Mg m^{-3}
Melting point: 538 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4089 reflections
$\theta = 2.5$–30.5°
$\mu = 1.17$ mm^{-1}
$T = 296$ K
Block, brown
0.35 × 0.32 × 0.26 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.604$, $T_{max} = 0.746$
42199 measured reflections
4089 independent reflections
3155 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 30.5$°, $\theta_{min} = 2.5$°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -27 \rightarrow 30$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.097$
$S = 1.04$
4089 reflections
187 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.834P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.4345 (2)	0.6803 (2)	0.38733 (8)	0.0240 (4)
C2	0.5958 (2)	0.6037 (2)	0.37724 (8)	0.0240 (4)
C3	0.6786 (3)	0.6181 (3)	0.32209 (9)	0.0327 (4)
H3	0.6314	0.6778	0.2881	0.039*
C4	0.8333 (3)	0.5416 (3)	0.31863 (10)	0.0372 (5)
H4	0.8909	0.5469	0.2818	0.045*
C5	0.9012 (3)	0.4572 (3)	0.37055 (11)	0.0366 (5)
H5	1.0065	0.4079	0.3696	0.044*
C6	0.8102 (3)	0.4473 (3)	0.42395 (10)	0.0320 (4)
H6	0.8563	0.3896	0.4586	0.038*
C7	0.1712 (2)	0.8133 (2)	0.39355 (9)	0.0251 (4)
C8	0.0124 (2)	0.9022 (3)	0.38144 (9)	0.0270 (4)
C9	−0.1027 (3)	0.9212 (3)	0.42773 (10)	0.0322 (4)
H9	−0.0804	0.8796	0.4680	0.039*
C10	−0.2511 (3)	1.0036 (3)	0.41222 (12)	0.0387 (5)
H10	−0.3306	1.0198	0.4421	0.046*
C11	−0.2792 (3)	1.0615 (3)	0.35150 (12)	0.0430 (5)
H11	−0.3782	1.1168	0.3396	0.052*
C12	−0.1570 (3)	1.0356 (3)	0.30870 (12)	0.0439 (6)
H12	−0.1772	1.0747	0.2679	0.053*
C13	0.3302 (3)	0.2765 (3)	0.36867 (13)	0.0423 (5)
N1	0.65894 (19)	0.5170 (2)	0.42789 (7)	0.0246 (3)
N2	0.36607 (19)	0.6566 (2)	0.44138 (7)	0.0258 (3)
N3	0.2129 (2)	0.7323 (2)	0.44510 (7)	0.0282 (3)
N4	−0.0124 (2)	0.9581 (2)	0.32252 (8)	0.0354 (4)
N5	0.3255 (3)	0.3117 (3)	0.31799 (10)	0.0568 (6)
Cu1	0.5000	0.5000	0.5000	0.02713 (10)
S1	0.31614 (6)	0.80256 (7)	0.33603 (2)	0.02941 (12)
S2	0.33021 (9)	0.22277 (9)	0.44310 (3)	0.04809 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0269 (9)	0.0275 (9)	0.0174 (8)	−0.0018 (7)	0.0005 (6)	0.0016 (7)
C2	0.0256 (8)	0.0274 (9)	0.0191 (8)	−0.0026 (7)	0.0017 (6)	−0.0008 (7)
C3	0.0359 (10)	0.0429 (12)	0.0196 (9)	−0.0034 (9)	0.0058 (7)	0.0018 (8)
C4	0.0368 (11)	0.0480 (13)	0.0278 (11)	−0.0035 (9)	0.0142 (8)	−0.0039 (9)
C5	0.0309 (10)	0.0421 (12)	0.0379 (12)	0.0034 (9)	0.0140 (9)	−0.0007 (9)
C6	0.0298 (10)	0.0346 (10)	0.0322 (11)	0.0052 (8)	0.0067 (8)	0.0050 (8)

C7	0.0244 (8)	0.0291 (9)	0.0219 (9)	−0.0009 (7)	0.0004 (6)	0.0005 (7)
C8	0.0257 (9)	0.0294 (9)	0.0256 (9)	−0.0003 (7)	−0.0006 (7)	0.0017 (7)
C9	0.0327 (10)	0.0371 (11)	0.0269 (10)	0.0007 (8)	0.0020 (8)	0.0004 (8)
C10	0.0318 (10)	0.0400 (12)	0.0449 (13)	0.0049 (9)	0.0081 (9)	−0.0054 (10)
C11	0.0314 (11)	0.0419 (12)	0.0554 (15)	0.0082 (9)	−0.0016 (10)	0.0047 (11)
C12	0.0414 (12)	0.0523 (14)	0.0376 (13)	0.0085 (11)	−0.0036 (10)	0.0139 (11)
C13	0.0331 (11)	0.0369 (12)	0.0568 (16)	0.0028 (9)	0.0003 (10)	−0.0137 (11)
N1	0.0247 (7)	0.0278 (8)	0.0217 (8)	0.0002 (6)	0.0047 (6)	0.0015 (6)
N2	0.0246 (7)	0.0311 (8)	0.0216 (8)	0.0017 (6)	0.0016 (6)	0.0026 (6)
N3	0.0267 (8)	0.0346 (9)	0.0236 (8)	0.0046 (7)	0.0035 (6)	0.0034 (7)
N4	0.0319 (9)	0.0440 (10)	0.0304 (9)	0.0065 (8)	0.0022 (7)	0.0108 (8)
N5	0.0803 (17)	0.0623 (15)	0.0260 (10)	0.0160 (13)	−0.0157 (10)	−0.0098 (10)
Cu1	0.02419 (16)	0.0377 (2)	0.02004 (17)	0.00875 (13)	0.00685 (11)	0.00895 (13)
S1	0.0304 (2)	0.0383 (3)	0.0196 (2)	0.0038 (2)	0.00108 (17)	0.00653 (19)
S2	0.0581 (4)	0.0487 (4)	0.0380 (3)	−0.0128 (3)	0.0077 (3)	−0.0015 (3)

Geometric parameters (Å, º)

C1—N2	1.313 (2)	C10—C11	1.382 (4)
C1—C2	1.452 (3)	C10—H10	0.9300
C1—S1	1.7106 (18)	C11—C12	1.384 (4)
C2—N1	1.356 (2)	C11—H11	0.9300
C2—C3	1.382 (3)	C12—N4	1.331 (3)
C2—S1	2.8397 (19)	C12—H12	0.9300
C3—C4	1.383 (3)	C13—N5	1.115 (3)
C3—H3	0.9300	C13—S2	1.644 (3)
C4—C5	1.382 (3)	N1—Cu1	2.0463 (15)
C4—H4	0.9300	N2—N3	1.370 (2)
C5—C6	1.383 (3)	N2—Cu1	2.0267 (16)
C5—H5	0.9300	N2—S1	2.5392 (16)
C6—N1	1.337 (2)	N3—S1	2.5657 (16)
C6—H6	0.9300	N4—S1	2.9062 (18)
C7—N3	1.301 (2)	N5—S2	2.759 (2)
C7—C8	1.465 (3)	Cu1—N2^{i}	2.0267 (16)
C7—S1	1.7300 (19)	Cu1—N1^{i}	2.0463 (15)
C8—N4	1.338 (3)	Cu1—S2^{i}	2.8124 (7)
C8—C9	1.390 (3)	Cu1—S2	2.8125 (7)
C8—S1	2.774 (2)	S1—S2^{ii}	4.0094 (9)
C9—C10	1.382 (3)	S2—S1^{iii}	4.0094 (9)
C9—H9	0.9300		
N2—C1—C2	118.82 (16)	N2—N3—S1	73.37 (9)
N2—C1—S1	113.60 (14)	C12—N4—C8	116.71 (19)
C2—C1—S1	127.58 (14)	C12—N4—S1	172.31 (16)
N1—C2—C3	122.97 (18)	C8—N4—S1	70.92 (11)
N1—C2—C1	113.12 (15)	C13—N5—S2	1.19 (15)
C3—C2—C1	123.91 (18)	N2—Cu1—N2^{i}	180.0
N1—C2—S1	141.62 (12)	N2—Cu1—N1^{i}	99.96 (6)

C3—C2—S1	95.40 (13)
C1—C2—S1	28.52 (8)
C2—C3—C4	118.45 (19)
C2—C3—H3	120.8
C4—C3—H3	120.8
C5—C4—C3	119.16 (19)
C5—C4—H4	120.4
C3—C4—H4	120.4
C4—C5—C6	119.0 (2)
C4—C5—H5	120.5
C6—C5—H5	120.5
N1—C6—C5	122.9 (2)
N1—C6—H6	118.6
C5—C6—H6	118.6
N3—C7—C8	124.76 (17)
N3—C7—S1	114.92 (14)
C8—C7—S1	120.27 (14)
N4—C8—C9	123.86 (18)
N4—C8—C7	114.43 (17)
C9—C8—C7	121.69 (18)
N4—C8—S1	81.95 (12)
C9—C8—S1	154.16 (14)
C7—C8—S1	32.59 (9)
C10—C9—C8	118.2 (2)
C10—C9—H9	120.9
C8—C9—H9	120.9
C9—C10—C11	118.7 (2)
C9—C10—H10	120.6
C11—C10—H10	120.6
C10—C11—C12	118.7 (2)
C10—C11—H11	120.6
C12—C11—H11	120.6
N4—C12—C11	123.8 (2)
N4—C12—H12	118.1
C11—C12—H12	118.1
N5—C13—S2	178.0 (3)
C6—N1—C2	117.53 (16)
C6—N1—Cu1	128.20 (13)
C2—N1—Cu1	114.18 (12)
C1—N2—N3	113.62 (15)
C1—N2—Cu1	113.43 (13)
N3—N2—Cu1	132.74 (12)
C1—N2—S1	38.12 (9)
N3—N2—S1	75.50 (9)
Cu1—N2—S1	151.43 (8)
N2^{i}—Cu1—N1^{i}	80.04 (6)
N2—Cu1—N1	80.04 (6)
N2^{i}—Cu1—N1	99.96 (6)
N1^{i}—Cu1—N1	180.0
N2—Cu1—S2^{i}	91.78 (5)
N2^{i}—Cu1—S2^{i}	88.22 (5)
N1^{i}—Cu1—S2^{i}	91.80 (5)
N1—Cu1—S2^{i}	88.20 (5)
N2—Cu1—S2	88.22 (5)
N2^{i}—Cu1—S2	91.78 (5)
N1^{i}—Cu1—S2	88.20 (5)
N1—Cu1—S2	91.80 (5)
S2^{i}—Cu1—S2	180.00 (2)
C1—S1—C7	86.79 (9)
C1—S1—N2	28.28 (7)
C7—S1—N2	58.51 (7)
C1—S1—N3	59.41 (7)
C7—S1—N3	27.38 (7)
N2—S1—N3	31.13 (5)
C1—S1—C8	113.89 (8)
C7—S1—C8	27.14 (7)
N2—S1—C8	85.63 (5)
N3—S1—C8	54.50 (5)
C1—S1—C2	23.90 (7)
C7—S1—C2	110.69 (7)
N2—S1—C2	52.18 (5)
N3—S1—C2	83.31 (5)
C8—S1—C2	137.77 (6)
C1—S1—N4	140.66 (7)
C7—S1—N4	54.21 (7)
N2—S1—N4	112.55 (5)
N3—S1—N4	81.50 (5)
C8—S1—N4	27.13 (5)
C2—S1—N4	164.06 (5)
C1—S1—S2^{ii}	95.46 (7)
C7—S1—S2^{ii}	63.79 (7)
N2—S1—S2^{ii}	82.33 (4)
N3—S1—S2^{ii}	70.21 (4)
C8—S1—S2^{ii}	64.66 (4)
C2—S1—S2^{ii}	105.86 (4)
N4—S1—S2^{ii}	73.36 (4)
C13—S2—N5	0.81 (10)
C13—S2—Cu1	101.44 (9)
N5—S2—Cu1	102.00 (6)
C13—S2—S1^{iii}	70.19 (8)

C7—N3—N2	111.07 (15)	N5—S2—S1^{iii}	69.96 (5)
C7—N3—S1	37.70 (9)	Cu1—S2—S1^{iii}	151.94 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···N5^{iv}	0.93	2.53	3.353 (3)	147
C6—H6···N3^{i}	0.93	2.35	3.143 (3)	142
C4—H4···N4^{v}	0.93	2.57	3.458 (3)	161

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+1, *y*+1/2, −*z*+1/2; (v) −*x*+1, *y*−1/2, −*z*+1/2.