

catena-Poly[copper(I)-di- μ -bromido-copper(I)-bis[μ -4-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione- κ^2 S:S]]

Saowanit Saithong,^a Jonathan Charmant^b and Chaveng Pakawatchai^{a*}

^aDepartment of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand, and

^bSchool of Chemistry, University of Bristol, Bristol BS8 1TS, England

Correspondence e-mail: chavengp@gmail.com

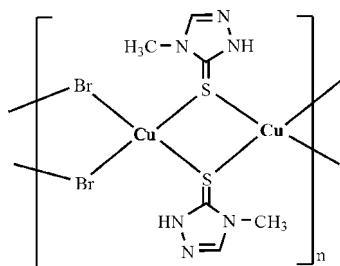
Received 29 March 2012; accepted 3 April 2012

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{N-N}) = 0.004$ Å; R factor = 0.027; wR factor = 0.056; data-to-parameter ratio = 18.7.

In the title coordination polymer, $[\text{CuBr}(\text{C}_3\text{H}_5\text{N}_3\text{S})]_n$, the Cu^{I} atom adopts a tetrahedral CuS_2Br_2 coordination geometry arising from two S -bonded 4-methyl-1*H*-1,2,4-triazole-3(4*H*)-thione ligands and two bromide ions. Both the S and Br atoms act as bridging ligands, connecting pairs of Cu^{I} atoms and generating chains propagating in $[100]$. Inter-chain $\text{N-H}\cdots\text{N}$ hydrogen bonds generate layers in the ac plane. Weak intra-chain $\text{N-H}\cdots\text{Br}$ interactions also occur.

Related literature

For related structures of metals coordinated by 1,2,4-triazole derivatives, see: Cingi *et al.* (1996); Haasnoot (2000); Kajdan *et al.* (2000); Menzies & Squattrito (2001); Klingele & Brooker (2003).



Experimental

Crystal data

$[\text{CuBr}(\text{C}_3\text{H}_5\text{N}_3\text{S})]$

$M_r = 258.62$

Monoclinic, $P2_1/n$

$a = 5.5781$ (11) Å

$b = 12.931$ (3) Å

$c = 9.810$ (2) Å

$\beta = 97.69$ (3)°

$V = 701.2$ (2) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 9.02$ mm⁻¹

$T = 100$ K

$0.28 \times 0.12 \times 0.06$ mm

Data collection

Bruker D8 CCD diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 1998)
 $T_{\text{min}} = 0.284$, $T_{\text{max}} = 0.582$

7830 measured reflections
1610 independent reflections
1513 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.056$

$S = 1.16$

1610 reflections

86 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.64$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—S1	2.3124 (9)	Cu1—Br1	2.4638 (7)
Cu1—S1 ⁱ	2.4012 (9)	Cu1—Br1 ⁱⁱ	2.5085 (8)
Cu1—Br1—Cu1 ⁱⁱ	67.81 (2)	Cu1—S1—Cu1 ⁱ	73.60 (3)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1-H1}\cdots\text{N2}^{\text{iii}}$	0.86 (2)	2.35 (3)	2.890 (4)	121 (3)
$\text{N1-H1}\cdots\text{Br1}$	0.86 (2)	2.78 (2)	3.566 (3)	153 (3)

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

We gratefully acknowledge financial support from the Center for Innovation in Chemistry (PERCH-CIC) Commission on Higher Education, Ministry of Education, and the Department of Chemistry, Faculty of Science, Prince of Songkla University. We also thank the School of Chemistry, University of Bristol, for the single crystal X-ray diffraction instrument service.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6718).

References

- Bruker (2003). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cingi, M. B., Bigoli, F., Lanfranchi, M., Leporati, E., Pellinghelli, M. A. & Foglia, C. (1996). *Inorg. Chem.* **95**, 37–43.
- Haasnoot, J. G. (2000). *Coord. Chem. Rev.* **200–202**, 131–185.
- Kajdan, T. W., Squattrito, P. J. & Dubey, S. N. (2000). *Inorg. Chim. Acta*, **300–302**, 1082–1089.
- Klingele, M. H. & Brooker, S. (2003). *Coord. Chem. Rev.* **241**, 119–132.

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.

Menzies, C. M. & Squattrito, P. J. (2001). *Inorg. Chim. Acta*, **314**, 194–200.
Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supplementary materials

Acta Cryst. (2012). E68, m565–m566 [doi:10.1107/S1600536812014444]

catena-Poly[copper(I)-di- μ -bromido-copper(I)-bis[μ -4-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione- κ^2 S:S]]**Saowanit Saithong, Jonathan Charmant and Chaveng Pakawatchai****Comment**

1,2,4-Triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. The interest in unsubstituted and substituted 1,2,4-triazole derivatives arise from their ability to bond metal ions in a various forms. A large number of mononuclear, oligonuclear and polynuclear metal coordination compounds with 1,2,4-triazole derivatives as ligands including the coordination chemistry have been described (Cingi *et al.*, 1996; Haasnoot, 2000; Kajdan *et al.*, 2000; Menzies & Squattrito, 2001; Klingele & Brooker, 2003).

Herein, we report the crystal structure of the title compound. The polymeric complex of $[\text{Cu}(\mu_2\text{-Hmptrz})(\mu_2\text{-Br})]_n$ is isomorphous with those complex that has been report $[\text{Cu}(\mu_2\text{-Hmptrz})(\mu_2\text{-I})]_n$ (Wang *et al.*, 2011). The chemical structure of this complex is shown in Scheme 1. Each Cu atom is a distorted tetrahedral geometry with the angles around Cu centre atom ranging from 104.74 (3)° to 117.72 (3)° and it is coordinated by two μ_2 -S donating Hmptrz molecules and two μ_2 -Br atoms. The one-dimensional chain built from two type of $\text{Cu}(\mu_2\text{-S})_2$ and $\text{Cu}(\mu_2\text{-Br})_2$ unit sharing the Cu centre atoms. Each pair of μ_2 -S and of μ_2 -Br bridges alternate to link between two Cu centre atoms giving the linked rhomboid of Cu_2S_2 and Cu_2Br_2 core forming a 1-D chain running along *a*-axis. Each Cu_2S_2 rhomboid is located at nearly perpendicular position to adjacent Cu_2Br_2 rhomboid with a dihedral angle of 86.90 (4)° between these planes. A view of the one-dimensional polymeric chain is shown in Figure 1.

The Cu...Cu distances of of $\text{Cu}(\mu_2\text{-S})_2$ and $\text{Cu}(\mu_2\text{-Br})_2$ unit are 2.8246 (9) and 2.7740 (9) Å. The latter distance is slightly shorter than the sum of van der Waals radii of Cu atoms (2.80 Å). The inter-molecular hydrogen bonds N(1)—H(1)...N(2)ⁱⁱⁱ [N(1)...N(2)ⁱⁱⁱ = 2.890 (4) Å, iii: -*x* + 1, -*y* + 2, -*z* + 2] between the adjacent 1-D polymeric chains are observed generating the two-dimensional sheets of supramolecular interactions running in *ac*-plane. The arrangement of the polymeric chains and the inter-molecular hydrogen bonds in crystal packing of this complex are shown in Figures 2 and 3, respectively.

Experimental

The mixture of Hmptrz ligand (0.28 g, 2.43 mmol) and copper (I) iodide (0.15 g, 1.05 mmol) in acetonitrile solution was refluxed N_2 gas. The yellow filtrate was allowed to stand at room temperature for 2 days. The block colorless crystals of $[\text{Cu}(\mu_2\text{-Hmptrz})(\mu_2\text{-Br})]_n$ were isolated. This complex melts and decomposes at 234–235 °C.

Refinement

All hydrogen atoms on carbon atoms were constrained, C—H = 0.95 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for C-*sp*² atoms of pyridine and phenyl rings and C—H = 0.98 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for C-*sp*³ atoms of the methyl group, respectively. The hydrogen atom on N atom is located in a difference Fourier map and restrained, N—H = 0.86 Å with $U_{\text{iso}}(\text{H}) =$

$1.2U_{eq}(N)$.

Computing details

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* (Bruker, 2003) and *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

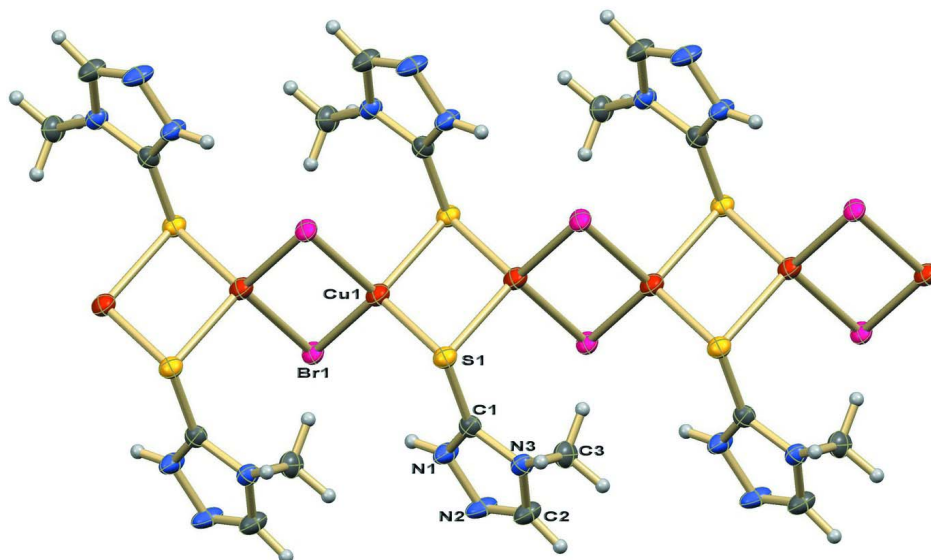
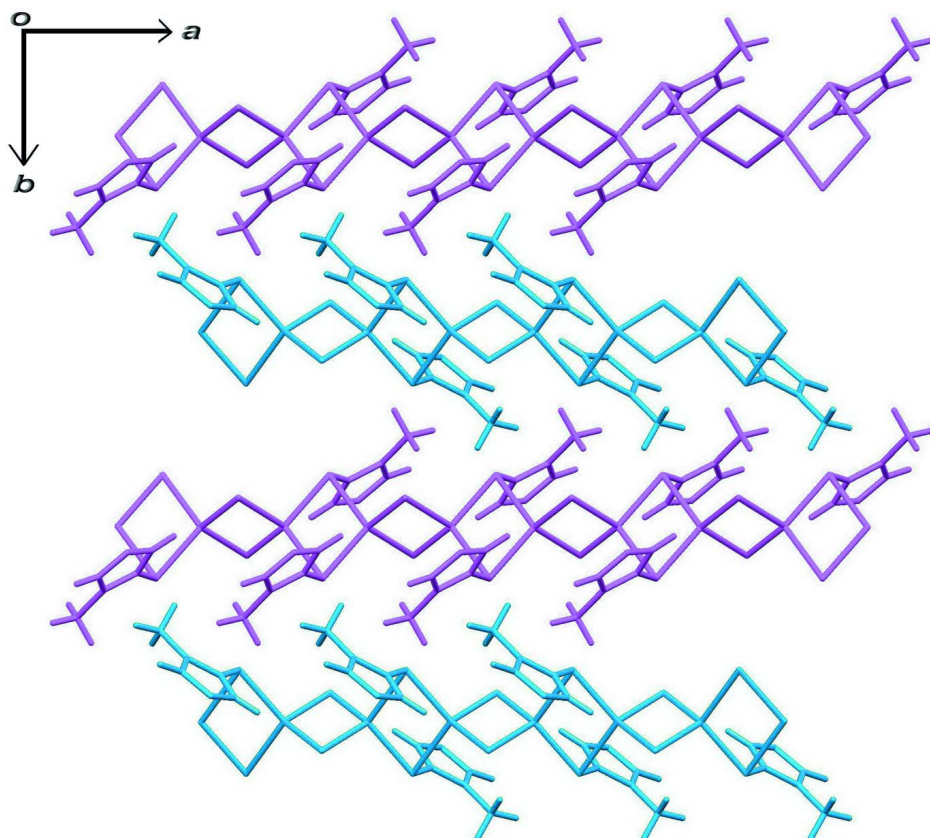
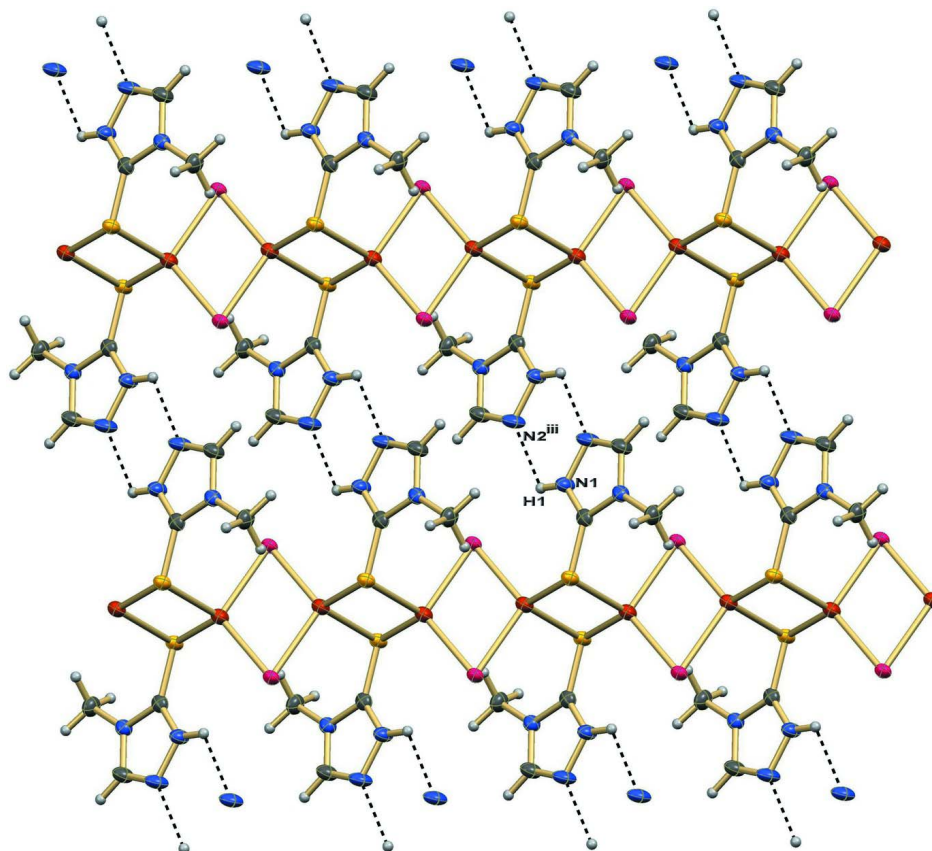


Figure 1

A view of the 1-D polymeric chain of $[\text{Cu}(\mu_2\text{-Hmptrz})(\mu_2\text{-Br})]_n$ with displacement ellipsoids plotted at the 50% probability level.

**Figure 2**

The arrangement of the polymeric chains in packing of $[\text{Cu}(\mu_2\text{-Hmptrz})(\mu_2\text{-Br})]_n$.


Figure 3

The inter-molecular hydrogen bonds generating 2-D sheet of $[\text{Cu}(\mu_2\text{-Hmptrz})(\mu_2\text{-Br})]_n$.

catena-Poly[copper(I)-di- μ -bromido-copper(I)-bis[μ -4-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione- κ^2 S:S]]

Crystal data

$[\text{CuBr}(\text{C}_3\text{H}_5\text{N}_3\text{S})]$

$M_r = 258.62$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 5.5781(11)\ \text{\AA}$

$b = 12.931(3)\ \text{\AA}$

$c = 9.810(2)\ \text{\AA}$

$\beta = 97.69(3)^\circ$

$V = 701.2(2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 496$

$D_x = 2.450\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71074\ \text{\AA}$

Cell parameters from 2999 reflections

$\theta = 2.6\text{--}27.5^\circ$

$\mu = 9.02\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Prism, colorless

$0.28 \times 0.12 \times 0.06\ \text{mm}$

Data collection

Bruker D8 CCD
diffractometer

Radiation source: sealed X-ray tube

Graphite monochromator

Detector resolution: $8.366\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 1998)

$T_{\min} = 0.284$, $T_{\max} = 0.582$

7830 measured reflections

1610 independent reflections

1513 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -7 \rightarrow 7$

$k = -16 \rightarrow 16$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 1.2302P]$
$S = 1.16$	where $P = (F_o^2 + 2F_c^2)/3$
1610 reflections	$(\Delta/\sigma)_{\max} = 0.001$
86 parameters	$\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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.

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 $F^2 > 2\sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.25060 (7)	0.99881 (3)	0.51220 (4)	0.01363 (11)
Br1	0.02520 (5)	1.07438 (2)	0.68746 (3)	0.01177 (9)
S1	0.52061 (14)	0.86702 (6)	0.58000 (7)	0.01143 (16)
N1	0.5464 (5)	0.9389 (2)	0.8453 (3)	0.0139 (5)
H1	0.417 (5)	0.976 (2)	0.838 (4)	0.017*
N2	0.6910 (5)	0.9341 (2)	0.9706 (3)	0.0164 (6)
N3	0.8341 (4)	0.83717 (19)	0.8149 (3)	0.0113 (5)
C1	0.6309 (5)	0.8819 (2)	0.7499 (3)	0.0115 (6)
C2	0.8636 (6)	0.8719 (2)	0.9480 (3)	0.0150 (6)
H2	0.9944	0.8528	1.0154	0.018*
C3	0.9938 (6)	0.7674 (2)	0.7517 (3)	0.0154 (6)
H3A	0.9086	0.7025	0.7263	0.023*
H3B	1.1385	0.7530	0.8173	0.023*
H3C	1.0414	0.7999	0.6692	0.023*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01225 (19)	0.0179 (2)	0.01017 (19)	0.00017 (15)	-0.00072 (14)	-0.00002 (15)
Br1	0.01057 (15)	0.01533 (16)	0.00898 (15)	-0.00146 (11)	-0.00027 (10)	-0.00234 (11)
S1	0.0127 (4)	0.0118 (4)	0.0094 (3)	-0.0004 (3)	0.0001 (3)	-0.0016 (3)
N1	0.0140 (13)	0.0179 (14)	0.0093 (12)	0.0056 (11)	-0.0001 (10)	0.0004 (10)
N2	0.0215 (14)	0.0184 (14)	0.0081 (12)	0.0047 (12)	-0.0024 (10)	0.0004 (11)
N3	0.0116 (12)	0.0102 (12)	0.0118 (12)	0.0013 (10)	0.0005 (10)	0.0013 (10)
C1	0.0116 (14)	0.0094 (14)	0.0134 (15)	-0.0018 (11)	0.0008 (11)	0.0017 (11)

C2	0.0167 (15)	0.0165 (16)	0.0107 (14)	0.0034 (13)	-0.0020 (12)	0.0005 (12)
C3	0.0132 (15)	0.0172 (16)	0.0163 (16)	0.0052 (12)	0.0042 (12)	0.0005 (13)

Geometric parameters (Å, °)

Cu1—S1	2.3124 (9)	N1—N2	1.378 (4)
Cu1—S1 ⁱ	2.4012 (9)	N1—H1	0.862 (18)
Cu1—Br1	2.4638 (7)	N2—C2	1.296 (4)
Cu1—Br1 ⁱⁱ	2.5085 (8)	N3—C1	1.354 (4)
Cu1—Cu1 ⁱⁱⁱ	2.7740 (9)	N3—C2	1.370 (4)
Cu1—Cu1 ⁱ	2.8246 (9)	N3—C3	1.463 (4)
Br1—Cu1 ⁱⁱ	2.5085 (8)	C2—H2	0.9500
S1—C1	1.708 (3)	C3—H3A	0.9800
S1—Cu1 ⁱ	2.4012 (9)	C3—H3B	0.9800
N1—C1	1.327 (4)	C3—H3C	0.9800
S1—Cu1—S1 ⁱ	106.40 (3)	C2—N3—C3	127.2 (3)
S1—Cu1—Br1	117.72 (3)	N1—C1—N3	105.0 (3)
S1 ⁱ —Cu1—Br1	108.84 (3)	N1—C1—S1	129.5 (2)
S1—Cu1—Br1 ⁱⁱ	104.74 (3)	N3—C1—S1	125.5 (2)
S1 ⁱ —Cu1—Br1 ⁱⁱ	106.25 (3)	N2—C2—N3	111.7 (3)
Br1—Cu1—Br1 ⁱⁱ	112.19 (2)	N2—C2—H2	124.1
Cu1—Br1—Cu1 ⁱⁱⁱ	67.81 (2)	N3—C2—H2	124.1
Cu1—S1—Cu1 ⁱ	73.60 (3)	N3—C3—H3A	109.5
C1—N1—N2	112.6 (3)	N3—C3—H3B	109.5
C1—N1—H1	129 (3)	H3A—C3—H3B	109.5
N2—N1—H1	119 (3)	N3—C3—H3C	109.5
C2—N2—N1	103.6 (3)	H3A—C3—H3C	109.5
C1—N3—C2	107.1 (3)	H3B—C3—H3C	109.5
C1—N3—C3	125.7 (3)		
S1—Cu1—Br1—Cu1 ⁱⁱⁱ	-121.64 (4)	N2—N1—C1—N3	1.1 (3)
S1 ⁱ —Cu1—Br1—Cu1 ⁱⁱⁱ	117.29 (3)	N2—N1—C1—S1	-177.6 (2)
Br1 ⁱⁱ —Cu1—Br1—Cu1 ⁱⁱⁱ	0.0	C2—N3—C1—N1	-1.1 (3)
Cu1 ⁱ —Cu1—Br1—Cu1 ⁱⁱⁱ	172.54 (4)	C3—N3—C1—N1	-179.4 (3)
S1 ⁱ —Cu1—S1—C1	93.28 (12)	C2—N3—C1—S1	177.7 (2)
Br1—Cu1—S1—C1	-29.05 (12)	C3—N3—C1—S1	-0.6 (4)
Br1 ⁱⁱ —Cu1—S1—C1	-154.45 (11)	Cu1—S1—C1—N1	16.7 (3)
Cu1 ⁱⁱⁱ —Cu1—S1—C1	-97.63 (12)	Cu1 ⁱ —S1—C1—N1	92.2 (3)
Cu1 ⁱ —Cu1—S1—C1	93.28 (12)	Cu1—S1—C1—N3	-161.8 (2)
S1 ⁱ —Cu1—S1—Cu1 ⁱ	0.0	Cu1 ⁱ —S1—C1—N3	-86.3 (3)
Br1—Cu1—S1—Cu1 ⁱ	-122.33 (3)	N1—N2—C2—N3	-0.2 (4)
Br1 ⁱⁱ —Cu1—S1—Cu1 ⁱ	112.27 (3)	C1—N3—C2—N2	0.8 (4)
Cu1 ⁱⁱⁱ —Cu1—S1—Cu1 ⁱ	169.09 (4)	C3—N3—C2—N2	179.1 (3)
C1—N1—N2—C2	-0.5 (4)		

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots N2 ⁱⁱⁱ	0.86 (2)	2.35 (3)	2.890 (4)	121 (3)
N1—H1 \cdots Br1	0.86 (2)	2.78 (2)	3.566 (3)	153 (3)

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