

Hexabromidotetrakis(μ_3 -4-pyridinium-thiolato- κ^3 S:S:S)hexacopper(I)

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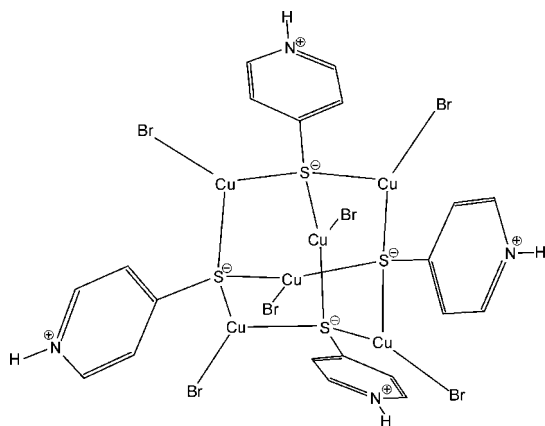
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Key indicators: single-crystal X-ray study; $T = 170$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in main residue; R factor = 0.032; wR factor = 0.076; data-to-parameter ratio = 17.5.

The crystal structure of the title compound, $[\text{Cu}_6\text{Br}_6(\text{C}_5\text{H}_5\text{NS})_4]$, consists of a hexanuclear $\text{Cu}_6\text{Br}_6\text{S}_4$ cluster in which each copper atom is connected to one bromine atom. The sulfur atoms are each connected to three copper atoms *via* μ_3 coordination. Two of the bromine atoms are located on a twofold axis and the clusters are located on a fourfold rotoinversion axis. One unique Cu atom is disordered over two positions; site occupancy factors are 0.6 and 0.4. The other Cu atom is disordered about a twofold rotation axis.

Related literature

For the isotopic chlorido compound, see: Cheng *et al.* (2004). For related literature, see: Jess *et al.* (2007); Näther & Jess (2006); Näther *et al.* (2003).



Experimental

Crystal data

$[\text{Cu}_6\text{Br}_6(\text{C}_5\text{H}_5\text{NS})_4]$
 $M_r = 1305.34$
 Tetragonal, $I4_1/a$
 $a = 15.3161$ (9) Å

$c = 13.2602$ (8) Å
 $V = 3110.6$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 12.03$ mm⁻¹
 $T = 170$ (2) K

0.11 × 0.10 × 0.09 mm

Data collection

Stoe IPDS-1 diffractometer
 Absorption correction: numerical
 (*X-SHAPE*; Stoe & Cie, 1998a)
 $T_{\min} = 0.231$, $T_{\max} = 0.349$

13166 measured reflections
 1853 independent reflections
 1566 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.076$
 $S = 1.03$
 1853 reflections

106 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.76$ e Å⁻³
 $\Delta\rho_{\min} = -1.01$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—S1	2.249 (5)	Cu2—S1	2.278 (2)
Cu1—S1 ⁱ	2.253 (5)	Cu2—Br2	2.3718 (13)
Cu1—Br1	2.377 (4)	Cu2—Cu1 ⁱⁱⁱ	2.689 (6)
Cu1—Cu2 ⁱⁱ	2.924 (4)	Cu2—Br1 ^{iv}	2.9058 (18)
Cu1 ⁱ —S1	2.319 (6)	Cu2—Cu1 ⁱⁱ	2.924 (4)
Cu1 ⁱ —S1 ⁱ	2.324 (7)	Br1—Cu1 ⁱⁱⁱ	2.666 (3)
Cu1 ⁱ —Br1	2.477 (6)	Br1—Cu2 ^v	2.9058 (18)
Cu1 ⁱ —Br1 ⁱⁱⁱ	2.666 (3)	Br2—Cu2 ⁱⁱ	2.3718 (13)
Cu1 ⁱ —Cu2 ⁱⁱ	2.689 (6)	S1—Cu1 ^{vi}	2.253 (5)
Cu2—Cu2 ⁱⁱ	0.884 (3)	S1—Cu2 ⁱⁱ	2.256 (2)
Cu2—S1 ⁱⁱ	2.256 (2)	S1—Cu1 ^{vi}	2.324 (7)

Symmetry codes: (i) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{5}{4}$; (ii) $-x + 1, -y + \frac{3}{2}, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x, y + \frac{1}{2}, -z + 1$; (v) $x, y - \frac{1}{2}, -z + 1$; (vi) $y - \frac{1}{4}, -x + \frac{5}{4}, -z + \frac{5}{4}$.

Data collection: *IPDS* (Stoe & Cie, 1998b); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2621).

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Hexabromidotetrakis(μ_3 -4-pyridiniumthiolato- κ^3 S:S:S)hexacopper(I)

M. Wriedt, I. Jess and C. Näther

Comment

Recently, we are interested in the synthesis, structures and thermal properties of coordination polymers based on copper(I) halides and N-donor ligands (Jeß *et al.*, 2007; Näther & Jeß, 2006 and Näther *et al.*, 2003). We have found for example that most of the ligand rich compounds can be transformed into ligand deficient compounds on heating. Starting from these findings we have initiated systematic investigations on this topic. In these investigations we have reacted copper(I) bromide with 4,4'-bipyridyldisulfide. In this reaction, a cleavage of the S—S bond takes place leading to the formation of the title compound (I). To identify this product in further reaction by X-ray powder diffraction, a structure determination was performed.

The title compound is isotopic to that of the corresponding chlorine compound reported by Cheng *et al.* (2004). In this compound unusual large anisotropic displacement parameters were found, which are indicative for disordering. In the present structure determination similar observations were made but in contrast to the previous work a reasonable split model was used in the structure refinement.

The asymmetric unit of the title compound consists of two copper atoms, one bromine atom and one 4-pyridiniumthiolate ligand in general positions as well as one bromine atom which is located on a 2-fold axis. One copper atom is located near the 2-fold axis and therefore, disordered due to symmetry (see experimental part). The second copper atom shows also disorder and was refined using a split model, with both split positions located in general positions.

The crystal structure consists of a hexanuclear $\text{Cu}_6\text{Cl}_6\text{S}_4$ cluster, which are located on 4-fold rotoinversion axis (Fig. 1). The copper atoms forms strongly distorted octahedra (Fig. 2). Each of the copper atoms is connected to one bromine atom. Two of these bromine atoms act as terminal ligands, whereas the others bridge the clusters *via* μ_2 coordination. The Cu_2Br_2 units are located on centres of inversion. The sulfur atoms are each connected to three copper atoms *via* μ_3 coordination. The CuBr distances are in the range of 2.377 (4)–2.9058 (18) Å, and the CuS distances are in the range of 2.249 (5)–2.324 (7) Å. These values are comparable to the corresponding chlorine compound reported by Cheng *et al.* (2004).

Experimental

CuBr and 4,4'-bipyridyldisulfide was obtained from Alfa Aesar and ethanol was obtained from Fluka. 0.125 mmol (17.0 mg) copper(I) bromide, 0.125 mmol (27.5 mg) 4,4'-bipyridyldisulfide and 1.0 ml of ethanol were transferred in test-tube, which were closed and heated to 120 °C for three days. On cooling red block-shaped single crystals of (I) are obtained.

Refinement

All H atoms were located in difference map but were positioned with idealized geometry and were refined isotropic with $U_{\text{eq}} = 1.2 U_{\text{eq}}$ of the parent atom using a riding model with C—H = 0.95 Å and N—H = 0.88 Å. Cu1 is disordered in two positions

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and was refined using a split model. Cu2 is also disordered around a 2-fold-axis. Therefore, structure refinement was also performed in space groups $I4_1$ and $I2/a$ but the disordering remains constant. From the inspection of the reciprocal space there are no hints for super structure reflections or satellites.

Figures

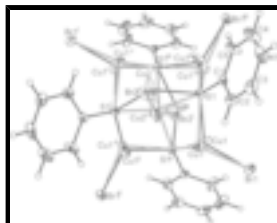


Fig. 1. Crystal structure of compound I with labelling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: i = $1 - x, 1, 5 - y, z$; ii = $1.25 - y, 1/4 + x, 1.25 - z$; iii = $-1/4 + y, 1.25 - x, 1.25 - z$.

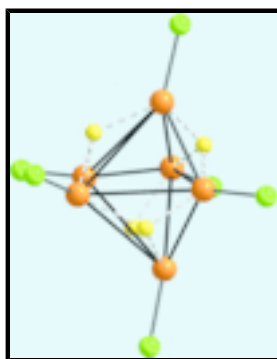


Fig. 2. View of the $\text{Cu}_6\text{Br}_6\text{S}_4$ cluster. The strongly distorted Cu_6 octahedra are indicated by black lines. The Cu—S bonds are shown as dashed lines.

#di-bromo-tetrakis(μ_2 -bromo)-tetrakis(μ_3 -4-pyridiniumthiolato-S)- #hexa-copper(I) Hexabromido-tetrakis(μ_3 -4-pyridiniumthiolato- κ^3 S)hexacopper(I)

Crystal data

$[\text{Cu}_6\text{Br}_6(\text{C}_5\text{H}_5\text{NS})_4]$

$M_r = 1305.34$

Tetragonal, $I4_1/a$

$a = 15.3161(9) \text{ \AA}$

$b = 15.3161(9) \text{ \AA}$

$c = 13.2602(8) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 3110.6(3) \text{ \AA}^3$

$Z = 4$

$F_{000} = 2464$

$D_x = 2.787 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8000 reflections

$\theta = 10.2\text{--}27.4^\circ$

$\mu = 12.03 \text{ mm}^{-1}$

$T = 170(2) \text{ K}$

Block, red

$0.11 \times 0.10 \times 0.09 \text{ mm}$

Data collection

Stoe IPDS-1
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

1853 independent reflections

1566 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$T = 170(2)$ K $\theta_{\max} = 28.0^\circ$
 φ scans $\theta_{\min} = 2.7^\circ$
 Absorption correction: numerical
 (X-SHAPE; Stoe & Cie, 1998a) $h = -20 \rightarrow 20$
 $T_{\min} = 0.231$, $T_{\max} = 0.349$ $k = -20 \rightarrow 20$
 13166 measured reflections $l = -16 \rightarrow 16$

Refinement

Refinement on F^2 Hydrogen site location: inferred from neighbouring sites
 Least-squares matrix: full H-atom parameters constrained
 $R[F^2 > 2\sigma(F^2)] = 0.032$ $w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 16.8187P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.076$ $(\Delta/\sigma)_{\max} < 0.001$
 $S = 1.03$ $\Delta\rho_{\max} = 0.76 \text{ e } \text{Å}^{-3}$
 1853 reflections $\Delta\rho_{\min} = -1.01 \text{ e } \text{Å}^{-3}$
 106 parameters Extinction correction: SHELXL,
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.00071 (9)
 Secondary atom site location: difference Fourier map

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.4617 (3)	0.5805 (3)	0.5937 (3)	0.0423 (8)	0.60
Cu1'	0.4786 (3)	0.5808 (4)	0.5715 (4)	0.0194 (6)	0.40
Cu2	0.48859 (13)	0.77650 (11)	0.45951 (9)	0.0490 (7)	0.50
Br1	0.39720 (3)	0.44117 (3)	0.56699 (3)	0.02079 (14)	
Br2	0.5000	0.7500	0.28378 (4)	0.01889 (15)	
S1	0.38433 (6)	0.69606 (6)	0.53945 (7)	0.0143 (2)	
C1	0.3113 (2)	0.6747 (2)	0.4421 (3)	0.0142 (7)	
C2	0.3238 (3)	0.6077 (3)	0.3712 (3)	0.0217 (8)	
H2	0.3740	0.5714	0.3750	0.026*	
N1	0.1928 (2)	0.6479 (3)	0.2893 (3)	0.0310 (9)	

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H1	0.1554	0.6397	0.2399	0.037*
C3	0.2632 (3)	0.5951 (3)	0.2966 (3)	0.0265 (9)
H3	0.2706	0.5488	0.2497	0.032*
C4	0.1787 (3)	0.7131 (4)	0.3560 (4)	0.0377 (12)
H4	0.1286	0.7492	0.3494	0.045*
C5	0.2365 (3)	0.7272 (3)	0.4331 (4)	0.0291 (10)
H5	0.2260	0.7725	0.4805	0.035*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.061 (2)	0.0210 (8)	0.045 (2)	-0.0072 (12)	-0.0381 (13)	0.0073 (12)
Cu1'	0.0236 (11)	0.0183 (10)	0.0164 (14)	0.0035 (7)	-0.0060 (7)	-0.0003 (9)
Cu2	0.0315 (11)	0.1027 (19)	0.0126 (5)	-0.0408 (12)	0.0046 (5)	-0.0101 (6)
Br1	0.0270 (2)	0.0170 (2)	0.0184 (2)	-0.00091 (14)	0.00016 (15)	-0.00071 (14)
Br2	0.0169 (3)	0.0285 (3)	0.0112 (3)	0.0030 (2)	0.000	0.000
S1	0.0128 (4)	0.0197 (4)	0.0102 (4)	0.0017 (3)	-0.0010 (3)	-0.0028 (3)
C1	0.0132 (16)	0.0196 (18)	0.0098 (18)	-0.0018 (14)	0.0028 (13)	0.0014 (13)
C2	0.026 (2)	0.024 (2)	0.015 (2)	0.0031 (16)	-0.0010 (15)	-0.0053 (15)
N1	0.0221 (19)	0.054 (3)	0.017 (2)	-0.0103 (17)	-0.0069 (14)	-0.0011 (17)
C3	0.033 (2)	0.032 (2)	0.015 (2)	-0.0063 (18)	-0.0014 (17)	-0.0063 (17)
C4	0.025 (2)	0.061 (3)	0.026 (3)	0.012 (2)	-0.0053 (19)	-0.011 (2)
C5	0.022 (2)	0.045 (3)	0.020 (2)	0.0159 (19)	-0.0050 (16)	-0.0080 (19)

Geometric parameters (\AA , $^\circ$)

Cu1—S1	2.249 (5)	Br1—Cu2 ^v	2.9058 (18)
Cu1—S1 ⁱ	2.253 (5)	Br2—Cu2 ⁱⁱ	2.3718 (13)
Cu1—Br1	2.377 (4)	S1—C1	1.739 (4)
Cu1—Cu2 ⁱⁱ	2.924 (4)	S1—Cu1 ^{vi}	2.253 (5)
Cu1'—S1	2.319 (6)	S1—Cu2 ⁱⁱ	2.256 (2)
Cu1'—S1 ⁱ	2.324 (7)	S1—Cu1 ^{vi}	2.324 (7)
Cu1'—Br1	2.477 (6)	C1—C2	1.405 (5)
Cu1'—Br1 ⁱⁱⁱ	2.666 (3)	C1—C5	1.405 (6)
Cu1'—Cu2 ⁱⁱ	2.689 (6)	C2—C3	1.370 (6)
Cu2—Cu2 ⁱⁱ	0.884 (3)	C2—H2	0.9500
Cu2—S1 ⁱⁱ	2.256 (2)	N1—C3	1.351 (7)
Cu2—S1	2.278 (2)	N1—C4	1.351 (7)
Cu2—Br2	2.3718 (13)	N1—H1	0.8800
Cu2—Cu1 ⁱⁱⁱ	2.689 (6)	C3—H3	0.9500
Cu2—Br1 ^{iv}	2.9058 (18)	C4—C5	1.369 (7)
Cu2—Cu1 ⁱⁱ	2.924 (4)	C4—H4	0.9500
Br1—Cu1 ⁱⁱⁱ	2.666 (3)	C5—H5	0.9500
S1—Cu1—S1 ⁱ	105.20 (17)	Cu1 ⁱⁱⁱ —Br1—Cu2 ^v	57.53 (13)
S1—Cu1—Br1	116.11 (19)	Cu2—Br2—Cu2 ⁱⁱ	21.47 (8)

S1 ⁱ —Cu1—Br1	133.8 (2)	C1—S1—Cu1	115.35 (17)
S1—Cu1—Cu2 ⁱⁱ	49.64 (9)	C1—S1—Cu1 ^{vi}	113.14 (17)
S1 ⁱ —Cu1—Cu2 ⁱⁱ	88.90 (13)	Cu1—S1—Cu1 ^{vi}	117.82 (10)
Br1—Cu1—Cu2 ⁱⁱ	133.62 (17)	C1—S1—Cu2 ⁱⁱ	103.96 (13)
S1—Cu1'—S1 ⁱ	100.7 (2)	Cu1—S1—Cu2 ⁱⁱ	80.94 (10)
S1—Cu1'—Br1	109.9 (2)	Cu1 ^{vi} —S1—Cu2 ⁱⁱ	121.47 (12)
S1 ⁱ —Cu1'—Br1	125.0 (2)	C1—S1—Cu2	101.96 (13)
S1—Cu1'—Br1 ⁱⁱⁱ	114.5 (2)	Cu1—S1—Cu2	101.85 (10)
S1 ⁱ —Cu1'—Br1 ⁱⁱⁱ	103.7 (2)	Cu1 ^{vi} —S1—Cu2	103.73 (11)
Br1—Cu1'—Br1 ⁱⁱⁱ	103.49 (18)	Cu2 ⁱⁱ —S1—Cu2	22.47 (8)
S1—Cu1'—Cu2 ⁱⁱ	52.91 (13)	C1—S1—Cu1'	113.1 (2)
S1 ⁱ —Cu1'—Cu2 ⁱⁱ	93.4 (2)	Cu1—S1—Cu1'	9.69 (15)
Br1—Cu1'—Cu2 ⁱⁱ	141.5 (3)	Cu1 ^{vi} —S1—Cu1'	125.38 (18)
Br1 ⁱⁱⁱ —Cu1'—Cu2 ⁱⁱ	65.72 (11)	Cu2 ⁱⁱ —S1—Cu1'	71.99 (12)
Cu2 ⁱⁱ —Cu2—S1 ⁱⁱ	80.2 (2)	Cu2—S1—Cu1'	93.47 (13)
Cu2 ⁱⁱ —Cu2—S1	77.3 (2)	C1—S1—Cu1 ^{vi}	117.1 (2)
S1 ⁱⁱ —Cu2—S1	119.14 (7)	Cu1—S1—Cu1 ^{vi}	108.83 (14)
Cu2 ⁱⁱ —Cu2—Br2	79.26 (4)	Cu1 ^{vi} —S1—Cu1 ^{vi}	9.67 (14)
S1 ⁱⁱ —Cu2—Br2	115.46 (8)	Cu2 ⁱⁱ —S1—Cu1 ^{vi}	125.75 (15)
S1—Cu2—Br2	114.60 (8)	Cu2—S1—Cu1 ^{vi}	110.33 (13)
Cu2 ⁱⁱ —Cu2—Cu1 ⁱⁱⁱ	132.2 (2)	Cu1'—S1—Cu1 ^{vi}	116.86 (16)
S1 ⁱⁱ —Cu2—Cu1 ⁱⁱⁱ	55.10 (11)	C2—C1—C5	118.2 (4)
S1—Cu2—Cu1 ⁱⁱⁱ	108.27 (15)	C2—C1—S1	123.2 (3)
Br2—Cu2—Cu1 ⁱⁱⁱ	131.90 (15)	C5—C1—S1	118.7 (3)
Cu2 ⁱⁱ —Cu2—Br1 ^{iv}	171.01 (19)	C3—C2—C1	119.6 (4)
S1 ⁱⁱ —Cu2—Br1 ^{iv}	108.10 (7)	C3—C2—H2	120.2
S1—Cu2—Br1 ^{iv}	100.83 (7)	C1—C2—H2	120.2
Br2—Cu2—Br1 ^{iv}	93.74 (5)	C3—N1—C4	121.5 (4)
Cu1 ⁱⁱⁱ —Cu2—Br1 ^{iv}	56.75 (9)	C3—N1—H1	119.2
Cu2 ⁱⁱ —Cu2—Cu1 ⁱⁱ	125.8 (2)	C4—N1—H1	119.2
S1 ⁱⁱ —Cu2—Cu1 ⁱⁱ	49.42 (9)	N1—C3—C2	120.5 (4)
S1—Cu2—Cu1 ⁱⁱ	107.74 (10)	N1—C3—H3	119.7
Br2—Cu2—Cu1 ⁱⁱ	135.00 (11)	C2—C3—H3	119.7
Cu1 ⁱⁱⁱ —Cu2—Cu1 ⁱⁱ	6.43 (14)	N1—C4—C5	120.1 (4)
Br1 ^{iv} —Cu2—Cu1 ⁱⁱ	63.17 (8)	N1—C4—H4	119.9
Cu1—Br1—Cu1'	8.97 (13)	C5—C4—H4	119.9
Cu1—Br1—Cu1 ⁱⁱⁱ	85.40 (14)	C4—C5—C1	120.0 (4)
Cu1'—Br1—Cu1 ⁱⁱⁱ	76.51 (18)	C4—C5—H5	120.0
Cu1—Br1—Cu2 ^v	126.65 (10)	C1—C5—H5	120.0
Cu1'—Br1—Cu2 ^v	120.68 (12)		

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Symmetry codes: (i) $-y+5/4, x+1/4, -z+5/4$; (ii) $-x+1, -y+3/2, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y+1/2, -z+1$; (v) $x, y-1/2, -z+1$; (vi) $y-1/4, -x+5/4, -z+5/4$.

Fig. 1

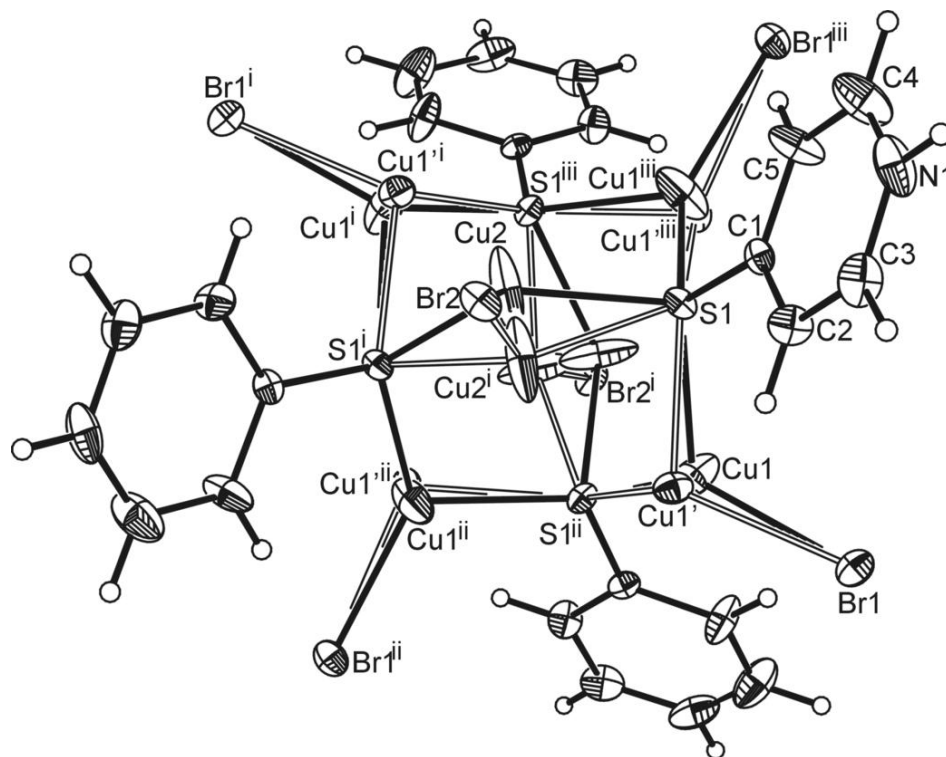


Fig. 2

