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Crystal structures of $[(\mu_2\text{-L1})\text{dibromido-dicopper(II)}]$ dibromide and poly $[(\mu_2\text{-L1})\text{diiodido-dicopper(I)}]$ -di- μ -iodido-dicopper(I), where L1 is 2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane

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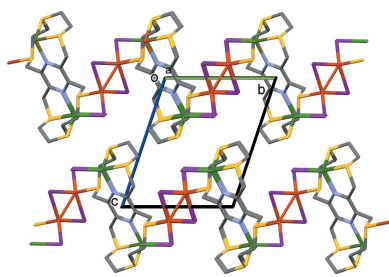
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The reaction of the hexathiapyrazinophane ligand, 2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane (**L1**), with copper(II) dibromide led to the formation of a binuclear complex, $[\mu_2\text{-2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane}]_2[\text{bromidocopper(II)}]_2$ dibromide, $[\text{Cu}_2\text{Br}_2(\text{C}_{16}\text{H}_{24}\text{N}_2\text{S}_6)]\text{Br}_2$, (**I**). The complex possesses inversion symmetry with the pyrazine ring being situated about a center of symmetry. The ligand coordinates to the copper(II) atom in a bis-tetradentate manner and the copper atom has a fivefold NS_3Br coordination environment with a distorted shape. The reaction of ligand **L1** with copper(I) iodide also gave a binuclear complex, which is bridged by a Cu_2I_2 unit to form a two-dimensional coordination polymer, poly $[(\mu_2\text{-2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane})\text{tetra-}\mu\text{-iodido-tetracopper(I)}]$, $[\text{Cu}_4\text{I}_4(\text{C}_{16}\text{H}_{24}\text{N}_2\text{S}_6)]_n$, (**II**). The binuclear unit possesses inversion symmetry with the pyrazine ring being located about a center of symmetry. The Cu_2I_2 unit is also located about an inversion center. The two independent copper(I) atoms are both fourfold coordinate. That coordinating to the ligand **L1** in a bis-tridentate manner has an NS_2I coordination environment and an irregular shape, while the second copper(I) atom, where **L1** coordinates in a bis-monodentate manner, has an SI_3 coordination environment with an almost perfect tetrahedral geometry. In the crystal of **I**, the cations and Br^- anions are linked by a number of $\text{C-H}\cdots\text{S}$ and $\text{C-H}\cdots\text{Br}$ hydrogen bonds, forming a supramolecular network. In the crystal of **II**, the two-dimensional coordination polymers lie parallel to the *ab* plane and there are no significant inter-layer contacts present.

1. Chemical context

Tetrasubstituted pyrazines are interesting ligands for the formation of multi-dimensional coordination polymers and metal-organic frameworks: for example, tetra-2-pyridylpyrazine (Ouellette *et al.*, 2004; Nawrot *et al.*, 2015) and pyrazinetetracarboxylic acid (Masci & Thuéry, 2008; Zhang *et al.*, 2014). In recent years a new ligand, 2,3,5,6-(4-carboxyl-tetraphenyl)pyrazine, has been used successfully to form a number of metal-organic frameworks (Wang *et al.*, 2019).

A number of such ligands involving $\text{N}_{\text{pyrazine}}$ and S coordination sites have been synthesized and their coordination behaviour with transition metals investigated (Assoumatine, 1999). The title ligand, **L1** (Assoumatine & Stoeckli-



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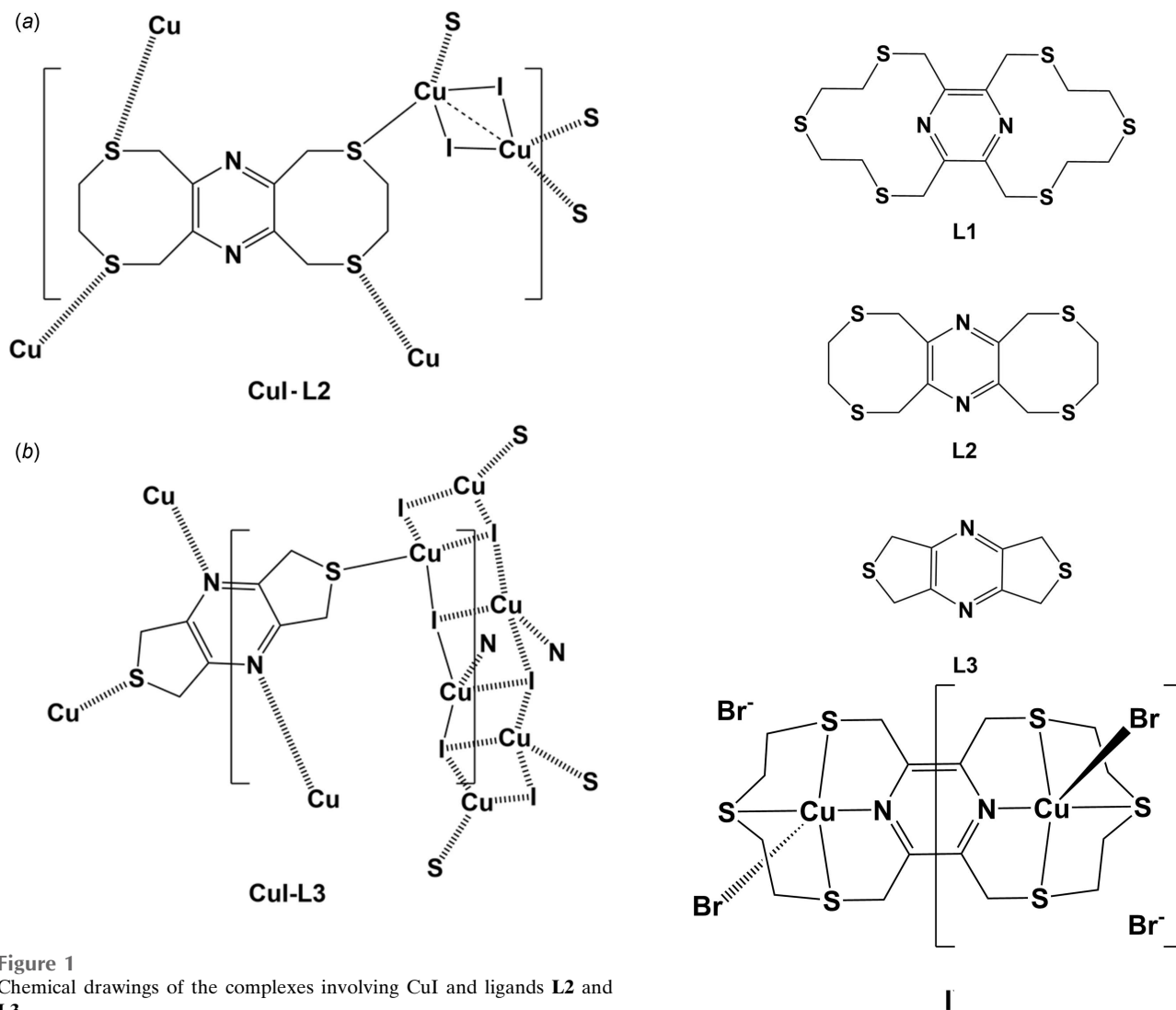


Figure 1
Chemical drawings of the complexes involving CuI and ligands **L2** and **L3**.

Evans, 2020*a*), is the third in a series of pyrazinethiophane ligands that have been shown to form chains, networks and frameworks with copper halides (Assoumatine, 1999), especially with CuI. For example, ligand **L2**, 3,4,8,10,11,13-hexahydro-1*H*,6*H*-bis([1,4]dithiincino)[6,7-*b*:6',7'-*e*]pyrazine, when reacted with CuI formed a two-dimensional coordination polymer, poly[[μ_4 -3,4,8,10,11,13-hexahydro-1*H*,6*H*-bis([1,4]dithiincino)[6,7-*b*:6',7'-*e*]pyrazine]di-iodido-dicopper(I)] (Fig. 1*a*; Assoumatine & Stoeckli-Evans, 2020*b*). Ligand **L3**, 5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine, when reacted with CuI formed a three-dimensional coordination polymer, poly[[μ_4 -5,7-dihydro-1*H*,3*H*-dithieno[3,4-*b*:3',4'-*e*]pyrazine- κ^4 N:N':S:S']tetra- μ_3 -iodidotetracopper] (Fig. 1*b*; Assoumatine & Stoeckli-Evans, 2020*c*). Interestingly, in compound **CuI-L2** the copper atom does not coordinate to the pyrazine N atom, whereas in compound **CuI-L3** one of the two independent copper atoms does coordinate to the pyrazine N atom. Herein, we report on the results of the reactions of ligand **L1** with CuBr₂ and CuI, where in both cases the pyrazine N atom is involved in coordination to the copper(II) and copper(I) atoms, respectively.

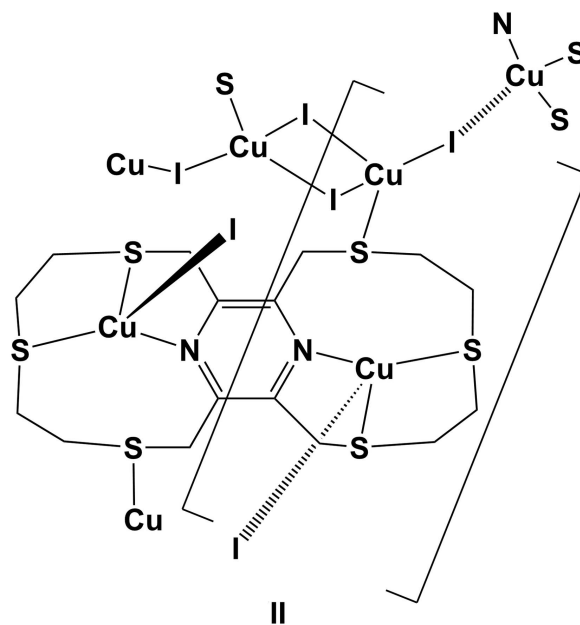


Table 1
Selected geometric parameters (Å, °) for **I**.

Cu1—N1	2.046 (6)	Cu1—S3	2.333 (2)
Cu1—S1	2.346 (2)	Cu1—Br1	2.3672 (11)
Cu1—S2	2.4549 (18)		
N1—Cu1—S1	85.26 (18)	S3—Cu1—Br1	94.97 (6)
N1—Cu1—S3	85.38 (18)	N1—Cu1—S2	104.48 (15)
S3—Cu1—S1	168.54 (7)	S1—Cu1—S2	88.79 (7)
N1—Cu1—Br1	145.45 (15)	S3—Cu1—S2	87.17 (7)
S1—Cu1—Br1	96.48 (6)	Br1—Cu1—S2	110.05 (6)

2. Structural commentary

The reaction of the hexathiapyrazinophane ligand, 2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane (**L1**), with copper(II) dibromide led to the formation of a binuclear complex, $[(\mu_2\text{-L1})\text{dibromodicooper(II)}]\text{dibromide}$, (**I**); see Fig. 2. The complex possesses inversion symmetry with the pyrazine ring being situated about a center of symmetry. Selected bond distances and angles are given in Table 1. The ligand coordinates to the copper(II) atoms in a bis-tetra-dentate manner. The symmetry related Cu atoms have a fivefold NS_3Br coordination environment with a distorted shape, as indicated by the fivefold index parameter τ_5 of 0.38 ($\tau_5 = 0$ for an ideal square-pyramidal coordination sphere, and $= 1$ for an ideal trigonal-pyramidal coordination sphere; Addison *et al.*, 1984). There are four five-membered chelate rings; Cu1/N1/C2/C3/S1 and Cu1/N1/C1/C8/S3 which are inclined by *ca* 90° to chelate rings Cu1/S1/C4/C5/S2 and Cu1/S2/C6/C7/S3 (Fig. 2).

Reaction of **L1** with copper(I) iodide also gave a binuclear complex, which is bridged by a Cu_2I_2 unit to form a two-dimensional coordination polymer, poly- $[(\mu_2\text{-L1})\text{diiodido}]\text{diiodidodicopper(I)}\text{di}(\mu\text{-iodido})\text{dicopper(I)}$, (**II**); see Fig. 3. The binuclear complex possesses inversion symmetry with the pyrazine ring being located about a center of symmetry. The

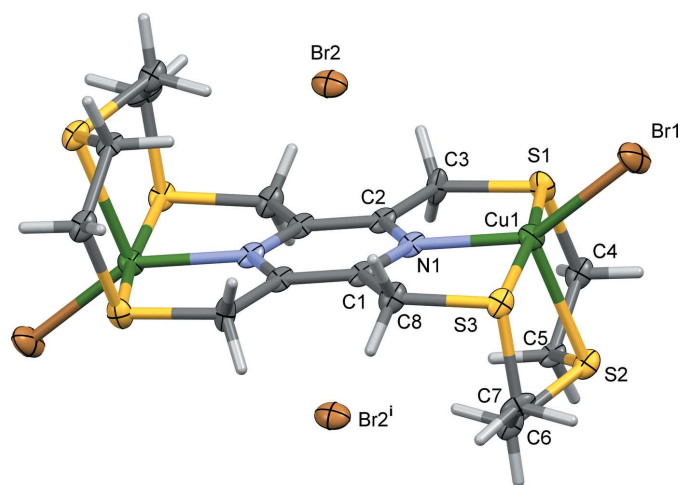


Figure 2
A view of the molecular structure of complex **I**, with atom labelling for the asymmetric unit; symmetry code: (i) $-x + 1, -y + 1, -z$. Displacement ellipsoids are drawn at the 50% probability level.

Table 2
Selected geometric parameters (Å, °) for **II**.

Cu1—N1	2.095 (10)	Cu2—I1	2.665 (2)
Cu1—S1	2.342 (4)	Cu2—I2	2.6166 (19)
Cu1—S2	2.331 (4)	I1—Cu2 ⁱⁱ	2.675 (2)
Cu1—I2 ⁱ	2.5193 (18)	Cu2—Cu2 ⁱⁱ	2.663 (4)
Cu2—S3	2.359 (4)		
N1—Cu1—S2	110.2 (3)	S3—Cu2—I1 ⁱⁱ	99.22 (11)
N1—Cu1—S1	85.3 (3)	I2—Cu2—I1 ⁱⁱ	112.01 (7)
S2—Cu1—S1	91.74 (14)	I1—Cu2—I1 ⁱⁱ	120.18 (7)
N1—Cu1—I2 ⁱ	121.1 (3)	Cu2—I1—Cu2 ⁱⁱ	59.82 (7)
S2—Cu1—I2 ⁱ	112.48 (12)	Cu1 ⁱⁱⁱ —I2—Cu2	94.93 (7)
S1—Cu1—I2 ⁱ	130.61 (10)	Cu2 ⁱⁱ —Cu2—I1	60.27 (7)
S3—Cu2—I2	109.54 (11)	Cu2 ⁱⁱ —Cu2—I1 ⁱⁱ	59.91 (7)
S3—Cu2—I1	105.86 (10)	S3—Cu2—Cu2 ⁱⁱ	115.75 (13)
I2—Cu2—I1	109.04 (8)	I2—Cu2—Cu2 ⁱⁱ	134.68 (11)

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

Cu_2I_2 unit is also located about an inversion center. Selected bond distances and angles are given in Table 2. The two independent copper(I) atoms, Cu1 and Cu2, are both fourfold coordinate. Atom Cu1 coordinates to the ligand **L1** in a tridentate fashion and has an NS_2I coordination environment. The fourfold index parameter τ_4 is 0.77 indicating a very irregular shape ($\tau_4 = 1$ for a perfect tetrahedral environment, 0 for a perfect square-planar environment and 0.85 for a perfect trigonal-pyramidal environment; Yang *et al.*, 2007). There are three chelate rings, two of which are five-membered (Cu1/N1/C2/C3/S1 and Cu1/S1/C4/C5/S2) and one eight-membered (Cu1/N1/C1/C8/S3/C7/C6/S2). The second copper(I) atom, Cu2, coordinates to **L1** in a monodentate fashion and has an SI_3 environment with an almost perfect tetrahedral geometry; here the fourfold index parameter τ_4 is 0.91.

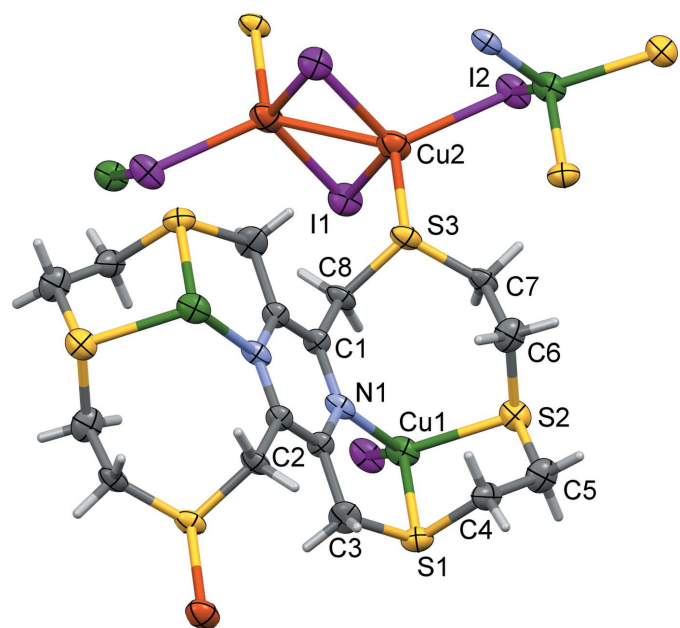


Figure 3
A view of the molecular structure of complex **II**, with atom labelling for the asymmetric unit; symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z$; (iii) $x - 1, y, z$. Displacement ellipsoids are drawn at the 50% probability level. (Atom Cu1 is green, while atom Cu2 is orange.)

Table 3
Hydrogen-bond geometry (Å, °) for **I**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6B \cdots S1 ⁱ	0.98	2.85	3.753 (9)	154
C5—H5A \cdots S3 ⁱⁱ	0.98	2.81	3.634 (8)	143
C3—H3A \cdots Br2 ⁱⁱⁱ	0.98	2.86	3.814 (8)	165
C3—H3B \cdots Br2 ⁱⁱ	0.98	2.83	3.770 (7)	160
C5—H5B \cdots Br2 ^{iv}	0.98	2.87	3.821 (7)	164
C7—H7B \cdots Br2 ⁱ	0.98	2.82	3.646 (8)	142
C8—H8A \cdots Br2 ^l	0.98	2.84	3.769 (9)	159
C8—H8B \cdots Br2 ^v	0.98	2.89	3.713 (7)	142

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

The Cu1—N1 bond lengths in the two complexes, 2.046 (6) Å in **I** and 2.095 (10) Å in **II**, are significantly different (Linden, 2020). They have a difference of 0.049 (12) Å so differ by 4.1σ (*i.e.*, $0.049 \text{ Å} = 0.012 \text{ Å} \times 4.1$). In **I**, the bond length Cu1—S2 of 2.455 (2) Å is significantly longer than bond lengths Cu1—S1 [2.346 (2) Å] and Cu1—S3 [2.333 (2) Å]. In **II**, bond lengths Cu1—S1 and Cu1—S2, involving the five-membered chelate rings, *viz.* 2.342 (4) and 2.331 (4) Å, respectively, are similar to those in **I**, while bond length Cu2—S3 [2.359 (4) Å] is only slightly longer. The bridging Cu2—Cu2ⁱ distance in the Cu₂I₂ unit in **II** is 2.663 (4) Å (Table 2), considerably shorter than the same distance observed in complex **CuI-L2** [2.776 (1) Å] [Fig. 1a; Assoumatine & Stoeckli-Evans, 2020b].

3. Supramolecular features

In the crystal of **I**, the cations are linked by pairs of C6—H6B \cdots S1ⁱ hydrogen bonds to form chains along the *a*-axis direction. Chains are also formed along the *b*-axis direction *via* C5—H5A \cdots S3ⁱⁱ hydrogen bonds (Table 3). These interactions result in the formation of a supramolecular network that lies parallel to the *ab* plane (Fig. 4). There are also a large number of C—H \cdots Br contacts present involving the anion, Br2[−],

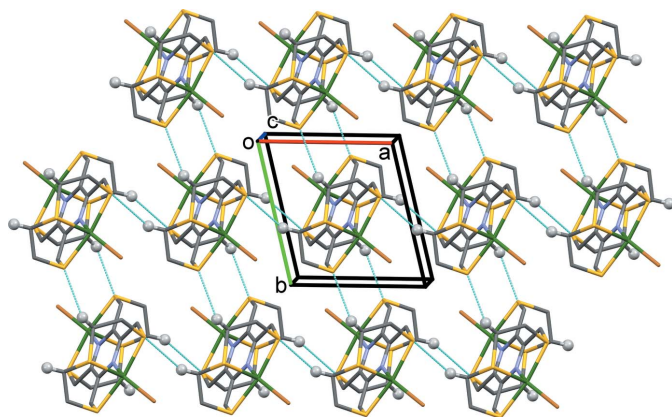


Figure 4
A view along the *c* axis of the crystal packing of **I**. The C—H \cdots S hydrogen bonds are shown as dashed lines (see Table 3). For clarity, the Br[−] anion and the H atoms not involved in these intermolecular interactions have been omitted.

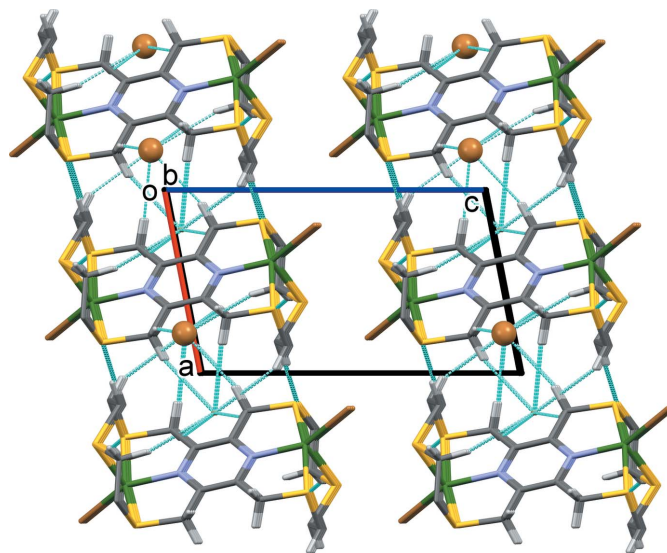


Figure 5
A view along the *b* axis of the crystal packing of **I**. The C—H \cdots S and C—H \cdots Br[−] hydrogen bonds (Table 3) are shown as dashed lines (see Table 3). For clarity, only the H atoms involved in these intermolecular interactions have been included.

strengthening the supramolecular network (Fig. 5 and Table 3). There are no significant inter-layer contacts present in the crystal.

In the crystal of **II**, the two-dimensional coordination polymers lie parallel to the (001) plane, as shown in Fig. 6. There are no significant inter-layer contacts present in the crystal (Fig. 7).

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.41, last update March 2020; Groom *et al.*, 2016) for

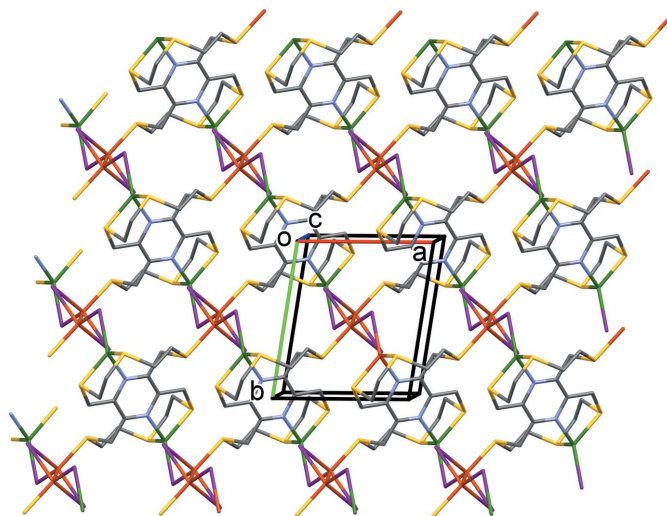


Figure 6
A view along the *c* axis of the two-dimensional structure of complex **II**. For clarity, H atoms have been omitted.

Table 4
Experimental details.

	I	II
Crystal data		
Chemical formula	[Cu ₂ Br ₂ (C ₁₆ H ₂₄ N ₂ S ₆)]Br ₂	[Cu ₄ I ₄ (C ₁₆ H ₂₄ N ₂ S ₆)]
<i>M_r</i>	883.45	1198.49
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	223	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.2090 (7), 8.1422 (8), 12.3904 (14)	7.7713 (8), 8.9456 (9), 11.2464 (14)
α , β , γ (°)	71.842 (12), 74.702 (12), 72.694 (12)	106.839 (13), 104.644 (13), 93.412 (12)
<i>V</i> (Å ³)	647.93 (13)	716.53 (15)
<i>Z</i>	1	1
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	8.30	7.69
Crystal size (mm)	0.20 × 0.20 × 0.03	0.30 × 0.20 × 0.05
Data collection		
Diffractometer	Stoe IPDS 1	Stoe IPDS 1
Absorption correction	Multi-scan (<i>MULABS</i> ; Spek, 2020)	Multi-scan (<i>MULABS</i> ; Spek, 2020)
<i>T</i> _{min} , <i>T</i> _{max}	0.421, 1.000	0.435, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	5057, 2320, 1843	5260, 2505, 1698
<i>R</i> _{int}	0.076	0.100
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.613	0.606
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.060, 0.153, 1.01	0.070, 0.183, 0.95
No. of reflections	2320	2505
No. of parameters	106	127
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	1.65, -1.67	2.25, -2.58

Computer programs: *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS-1* (Stoe & Cie, 1997), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020), *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *pubCIF* (Westrip, 2010).

tri- or hexa-thiabenzophane ligands gave only three hits. They include the trithiabenzophane ligand, 2,5,8-trithia(9)-*m*-benzophane (CSD refcode VEYNES; Groot & Loeb, 1990), and a palladium and a silver complex of the same ligand, *viz.* dichloro[2,5,8-trithia(9)-*m*-benzophane]palladium(II) (KOMNOP; Groot *et al.*, 1991), a mononuclear complex, and poly[[2,5,8-trithia(9)-*m*-cyclophane-*S,S',S''*]-silver(I) trifluoromethylsulfonate acetonitrile solvate] (ZIDPEH; Casabo *et al.*, 1995), a two-dimensional coordination polymer. In KOMNOP, the ligand coordinates in a

bidentate manner. The palladium(II) atom is fourfold S₂Cl₂ coordinate with a square-planar environment (index parameter τ_4 is 0.04). In ZIDPEH, the ligand coordinates in a bridging μ_3 -monodentate manner. The silver(I) atom is fivefold NOS₃ coordinate with an irregular shape (index parameter τ_5 is 0.56).

A search for benzophane ligands similar to **L2** and **L3** gave zero hits for **L2** and ten hits for **L3**. The latter compounds have been compared in a recent article (Assoumatine & Stoeckli-Evans, 2020*d*), which also describes the syntheses and crystal structures of both **L2** and **L3**.

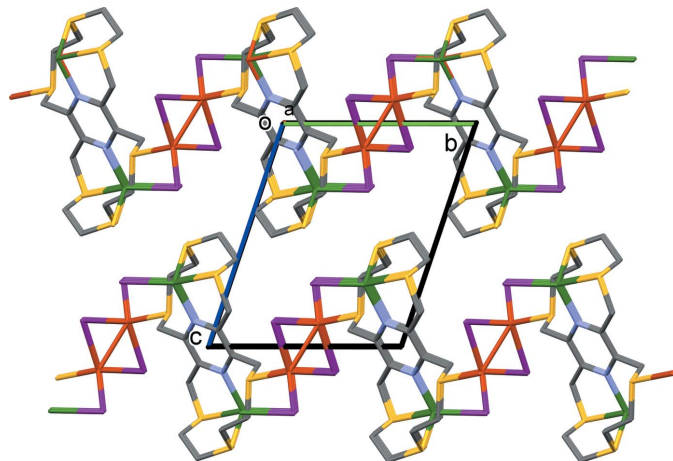


Figure 7
A view along the *a* axis of the crystal packing of complex **II**. For clarity, H atoms have been omitted.

5. Synthesis and crystallization

The synthesis and crystal structure of the ligand 2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane (**L1**), have been reported (Assoumatine & Stoeckli-Evans, 2020*a*).

Synthesis of complex [(μ_2 -L1)dibromido dicopper(II)] dibromide (I): A solution of **L1** (15 mg, 0.03 mmol) in CHCl₃ (10 ml) was introduced into a 16 mm diameter glass tube and layered with MeCN (2 ml) as a buffer zone. Then a solution of CuBr₂ (7 mg, 0.03 mmol) in MeCN (5 ml) was added gently to avoid possible mixing. The glass tube was sealed and left in the dark at room temperature for at least 3 weeks, whereupon brown crystals of complex **I** were isolated in the buffer zone.

Synthesis of complex poly-[(μ_2 -L1)diiodido-dicopper(I)-di(μ -iodido)-dicopper(I)] (II): A solution of **L1** (15 mg, 0.03 mmol) in CH₂Cl₂ (5 ml) was introduced into a 16 mm

diameter glass tube and layered with MeCN (2 ml) as a buffer zone. A solution of CuI (6 mg, 0.03 mmol) in MeCN (5 ml) was added gently to avoid possible mixing. The glass tube was sealed under an atmosphere of nitrogen and left in the dark at room temperature for at least 3 weeks, whereupon small orange crystals of complex **II** were isolated in the buffer zone.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The C-bound H atoms were included in calculated positions and treated as riding on their parent atoms: C–H = 0.98 Å for **I** and 0.97 Å for **II**, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Intensity data were measured using a STOE IPDS-1 one-circle diffractometer. For the triclinic system often only 93% of the Ewald sphere is accessible, which explains why the alerts `diffn_reflns_laue_measured_fraction_full` value (0.94) below minimum (0.95) for both compounds **I** and **II** are given. This involves 145 random reflections out of the expected 2336 for the IUCr cutoff limit of $\sin \theta/\lambda = 0.60$ for **I**, and 155 random reflections out of the expected 2600 reflections for **II**. The residual electron-density peaks are approximately 1 Å from the halogen atoms in both structures.

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supporting information

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Crystal structures of [$(\mu_2$ -L1)dibromidodicopper(II)] dibromide and poly[[$(\mu_2$ -L1)diiodidodicopper(I)]-di- μ -iodido-dicopper(I)], where L1 is 2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane

Tokouré Assoumatine and Helen Stoeckli-Evans

Computing details

For both structures, data collection: *EXPOSE* in *IPDS-I* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS-I* (Stoe & Cie, 1997); data reduction: *INTEGRATE* in *IPDS-I* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *pubCIF* (Westrip, 2010).

$[\mu_2$ -2,5,8,11,14,17-Hexathia-[9.9](2,6,3,5)-pyrazinophane]bis[bromidodicopper(II)] dibromide (I)

Crystal data

$[\text{Cu}_2\text{Br}_2(\text{C}_{16}\text{H}_{24}\text{N}_2\text{S}_6)]\text{Br}_2$

$M_r = 883.45$

Triclinic, $P\bar{1}$

$a = 7.2090$ (7) Å

$b = 8.1422$ (8) Å

$c = 12.3904$ (14) Å

$\alpha = 71.842$ (12)°

$\beta = 74.702$ (12)°

$\gamma = 72.694$ (12)°

$V = 647.93$ (13) Å³

$Z = 1$

$F(000) = 428$

$D_x = 2.264$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5000 reflections

$\theta = 2.7$ – 25.8 °

$\mu = 8.30$ mm⁻¹

$T = 223$ K

Plate, brown

$0.20 \times 0.20 \times 0.03$ mm

Data collection

STOE IPDS 1

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

φ rotation scans

Absorption correction: multi-scan

(MULABS; Spek, 2020)

$T_{\min} = 0.421$, $T_{\max} = 1.000$

5057 measured reflections

2320 independent reflections

1843 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.076$

$\theta_{\text{max}} = 25.8$ °, $\theta_{\text{min}} = 2.7$ °

$h = -8 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.153$

$S = 1.01$

2320 reflections

106 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

$$w = 1/[\sigma^2(F_o^2) + (0.1019P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.65 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.67 \text{ e } \text{\AA}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.19307 (12)	0.19827 (12)	0.45400 (7)	0.0328 (3)
Cu1	0.38840 (13)	0.35871 (11)	0.29477 (7)	0.0163 (3)
S1	0.1670 (3)	0.6379 (2)	0.28528 (15)	0.0215 (4)
S2	0.6115 (3)	0.4639 (2)	0.36310 (15)	0.0197 (4)
S3	0.6481 (3)	0.1120 (2)	0.27313 (15)	0.0175 (4)
N1	0.4546 (9)	0.4439 (7)	0.1184 (5)	0.0156 (7)
C1	0.5922 (11)	0.3381 (9)	0.0573 (6)	0.0156 (7)
C2	0.3618 (10)	0.6046 (9)	0.0628 (6)	0.0156 (7)
C3	0.2054 (11)	0.7229 (9)	0.1295 (6)	0.0202 (16)
H3A	0.080095	0.744824	0.104611	0.024*
H3B	0.240502	0.837592	0.109580	0.024*
C4	0.3042 (11)	0.7561 (10)	0.3270 (6)	0.0213 (9)
H4A	0.262709	0.883424	0.290981	0.026*
H4B	0.267942	0.739951	0.411020	0.026*
C5	0.5303 (11)	0.6978 (9)	0.2940 (6)	0.0156 (7)
H5A	0.592228	0.768345	0.318918	0.019*
H5B	0.570091	0.717761	0.209820	0.019*
C6	0.8280 (12)	0.3836 (9)	0.2624 (6)	0.0213 (9)
H6A	0.808898	0.438922	0.182395	0.026*
H6B	0.945536	0.410333	0.272072	0.026*
C7	0.8506 (11)	0.1809 (9)	0.2918 (7)	0.0223 (16)
H7A	0.867485	0.130400	0.372431	0.027*
H7B	0.971846	0.130109	0.243159	0.027*
C8	0.6904 (12)	0.1574 (9)	0.1173 (6)	0.0213 (9)
H8A	0.833237	0.139237	0.087755	0.026*
H8B	0.644904	0.070380	0.097392	0.026*
Br2	0.21653 (11)	0.20772 (10)	0.02398 (7)	0.0267 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0270 (5)	0.0335 (5)	0.0267 (5)	-0.0116 (4)	-0.0043 (3)	0.0114 (3)
Cu1	0.0194 (5)	0.0085 (5)	0.0194 (5)	-0.0036 (4)	-0.0032 (4)	-0.0013 (3)
S1	0.0215 (10)	0.0172 (10)	0.0201 (9)	0.0018 (8)	-0.0013 (7)	-0.0053 (7)

S2	0.0281 (10)	0.0115 (9)	0.0223 (9)	-0.0028 (8)	-0.0095 (8)	-0.0060 (7)
S3	0.0270 (10)	0.0051 (8)	0.0195 (8)	-0.0025 (8)	-0.0085 (7)	0.0005 (6)
N1	0.0223 (18)	0.0065 (15)	0.0219 (16)	-0.0034 (14)	-0.0088 (13)	-0.0053 (12)
C1	0.0223 (18)	0.0065 (15)	0.0219 (16)	-0.0034 (14)	-0.0088 (13)	-0.0053 (12)
C2	0.0223 (18)	0.0065 (15)	0.0219 (16)	-0.0034 (14)	-0.0088 (13)	-0.0053 (12)
C3	0.029 (4)	0.012 (4)	0.014 (3)	0.008 (3)	-0.007 (3)	-0.006 (3)
C4	0.031 (3)	0.011 (2)	0.022 (2)	-0.002 (2)	-0.0101 (19)	-0.0047 (17)
C5	0.0223 (18)	0.0065 (15)	0.0219 (16)	-0.0034 (14)	-0.0088 (13)	-0.0053 (12)
C6	0.031 (3)	0.011 (2)	0.022 (2)	-0.002 (2)	-0.0101 (19)	-0.0047 (17)
C7	0.024 (4)	0.011 (4)	0.035 (4)	0.002 (3)	-0.020 (3)	-0.004 (3)
C8	0.031 (3)	0.011 (2)	0.022 (2)	-0.002 (2)	-0.0101 (19)	-0.0047 (17)
Br2	0.0247 (4)	0.0210 (4)	0.0385 (5)	-0.0073 (4)	-0.0041 (3)	-0.0127 (3)

Geometric parameters (Å, °)

Cu1—N1	2.046 (6)	C2—C3	1.497 (9)
Cu1—S1	2.346 (2)	C3—H3A	0.9800
Cu1—S2	2.4549 (18)	C3—H3B	0.9800
Cu1—S3	2.333 (2)	C4—C5	1.536 (10)
Cu1—Br1	2.3672 (11)	C4—H4A	0.9800
S1—C3	1.811 (7)	C4—H4B	0.9800
S1—C4	1.822 (7)	C5—H5A	0.9800
S2—C6	1.815 (8)	C5—H5B	0.9800
S2—C5	1.814 (7)	C6—C7	1.542 (9)
S3—C7	1.802 (7)	C6—H6A	0.9800
S3—C8	1.808 (7)	C6—H6B	0.9800
N1—C1	1.342 (9)	C7—H7A	0.9800
N1—C2	1.340 (9)	C7—H7B	0.9800
C1—C2 ⁱ	1.394 (10)	C8—H8A	0.9800
C1—C8	1.482 (11)	C8—H8B	0.9800
N1—Cu1—S1	85.26 (18)	S1—C3—H3B	108.4
N1—Cu1—S3	85.38 (18)	H3A—C3—H3B	107.5
S3—Cu1—S1	168.54 (7)	C5—C4—S1	115.1 (5)
N1—Cu1—Br1	145.45 (15)	C5—C4—H4A	108.5
S1—Cu1—Br1	96.48 (6)	S1—C4—H4A	108.5
S3—Cu1—Br1	94.97 (6)	C5—C4—H4B	108.5
N1—Cu1—S2	104.48 (15)	S1—C4—H4B	108.5
S1—Cu1—S2	88.79 (7)	H4A—C4—H4B	107.5
S3—Cu1—S2	87.17 (7)	C4—C5—S2	109.4 (4)
Br1—Cu1—S2	110.05 (6)	C4—C5—H5A	109.8
C3—S1—C4	102.4 (3)	S2—C5—H5A	109.8
C3—S1—Cu1	98.5 (2)	C4—C5—H5B	109.8
C4—S1—Cu1	101.4 (3)	S2—C5—H5B	109.8
C6—S2—C5	104.4 (3)	H5A—C5—H5B	108.3
C6—S2—Cu1	93.8 (2)	C7—C6—S2	105.4 (5)
C5—S2—Cu1	96.5 (2)	C7—C6—H6A	110.7
C7—S3—C8	100.9 (4)	S2—C6—H6A	110.7

C7—S3—Cu1	101.0 (2)	C7—C6—H6B	110.7
C8—S3—Cu1	97.8 (3)	S2—C6—H6B	110.7
C1—N1—C2	119.4 (6)	H6A—C6—H6B	108.8
C1—N1—Cu1	119.9 (5)	C6—C7—S3	115.5 (5)
C2—N1—Cu1	120.7 (5)	C6—C7—H7A	108.4
N1—C1—C2 ⁱ	120.2 (7)	S3—C7—H7A	108.4
N1—C1—C8	119.9 (6)	C6—C7—H7B	108.4
C2 ⁱ —C1—C8	119.9 (6)	S3—C7—H7B	108.4
N1—C2—C1 ⁱ	120.4 (6)	H7A—C7—H7B	107.5
N1—C2—C3	120.1 (6)	C1—C8—S3	115.4 (5)
C1 ⁱ —C2—C3	119.5 (7)	C1—C8—H8A	108.4
C2—C3—S1	115.3 (5)	S3—C8—H8A	108.4
C2—C3—H3A	108.4	C1—C8—H8B	108.4
S1—C3—H3A	108.4	S3—C8—H8B	108.4
C2—C3—H3B	108.4	H8A—C8—H8B	107.5
C2—N1—C1—C2 ⁱ	0.2 (10)	Cu1—S1—C4—C5	30.4 (6)
Cu1—N1—C1—C2 ⁱ	-179.9 (4)	S1—C4—C5—S2	-59.9 (6)
C2—N1—C1—C8	-177.6 (5)	C6—S2—C5—C4	148.0 (5)
Cu1—N1—C1—C8	2.3 (8)	Cu1—S2—C5—C4	52.4 (4)
C1—N1—C2—C1 ⁱ	-0.2 (10)	C5—S2—C6—C7	-158.1 (5)
Cu1—N1—C2—C1 ⁱ	179.9 (4)	Cu1—S2—C6—C7	-60.3 (5)
C1—N1—C2—C3	178.9 (6)	S2—C6—C7—S3	62.3 (6)
Cu1—N1—C2—C3	-1.0 (8)	C8—S3—C7—C6	74.9 (6)
N1—C2—C3—S1	3.6 (8)	Cu1—S3—C7—C6	-25.4 (6)
C1 ⁱ —C2—C3—S1	-177.3 (5)	N1—C1—C8—S3	-11.6 (8)
C4—S1—C3—C2	99.9 (5)	C2 ⁱ —C1—C8—S3	170.6 (5)
Cu1—S1—C3—C2	-3.8 (5)	C7—S3—C8—C1	-89.9 (6)
C3—S1—C4—C5	-71.0 (6)	Cu1—S3—C8—C1	13.0 (5)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6B \cdots S1 ⁱⁱ	0.98	2.85	3.753 (9)	154
C5—H5A \cdots S3 ⁱⁱⁱ	0.98	2.81	3.634 (8)	143
C3—H3A \cdots Br2 ^{iv}	0.98	2.86	3.814 (8)	165
C3—H3B \cdots Br2 ⁱⁱⁱ	0.98	2.83	3.770 (7)	160
C5—H5B \cdots Br2 ⁱ	0.98	2.87	3.821 (7)	164
C7—H7B \cdots Br2 ⁱⁱ	0.98	2.82	3.646 (8)	142
C8—H8A \cdots Br2 ⁱⁱ	0.98	2.84	3.769 (9)	159
C8—H8B \cdots Br2 ^v	0.98	2.89	3.713 (7)	142

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

Poly[[μ_2 -2,5,8,11,14,17-hexathia-[9.9](2,6,3,5)-pyrazinophane]tetra- μ -iodido-tetracopper(I)] (II)

Crystal data

[Cu₄I₄(C₁₆H₂₄N₂S₆)]
 $M_r = 1198.49$
 Triclinic, $P\bar{1}$
 $a = 7.7713$ (8) Å
 $b = 8.9456$ (9) Å
 $c = 11.2464$ (14) Å
 $\alpha = 106.839$ (13)°
 $\beta = 104.644$ (13)°
 $\gamma = 93.412$ (12)°
 $V = 716.53$ (15) Å³

$Z = 1$
 $F(000) = 558$
 $D_x = 2.777$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 4652 reflections
 $\theta = 2.0$ – 25.8 °
 $\mu = 7.69$ mm⁻¹
 $T = 293$ K
 Plate, orange
 $0.30 \times 0.20 \times 0.05$ mm

Data collection

STOE IPDS 1
 diffractometer
 Radiation source: fine-focus sealed tube
 Plane graphite monochromator
 φ rotation scans
 Absorption correction: multi-scan
 (MULABS; Spek, 2020)
 $T_{\min} = 0.435$, $T_{\max} = 1.000$

5260 measured reflections
 2505 independent reflections
 1698 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.100$
 $\theta_{\max} = 25.5$ °, $\theta_{\min} = 2.4$ °
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.183$
 $S = 0.95$
 2505 reflections
 127 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
 $w = 1/[\sigma^2(F_o^2) + (0.110P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.25$ e Å⁻³
 $\Delta\rho_{\min} = -2.58$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.73534 (12)	0.70224 (11)	0.11663 (9)	0.0396 (3)
I2	0.34990 (12)	0.56223 (11)	0.29340 (9)	0.0370 (3)
Cu1	1.2404 (2)	0.2890 (2)	0.28830 (16)	0.0332 (4)
Cu2	0.5027 (2)	0.4653 (2)	0.10778 (18)	0.0415 (5)
S1	1.3999 (4)	0.0851 (4)	0.3255 (3)	0.0326 (8)
S2	1.1079 (5)	0.2923 (4)	0.4531 (3)	0.0349 (8)
S3	0.6749 (4)	0.2663 (4)	0.1450 (3)	0.0296 (7)
N1	1.0914 (12)	0.1189 (12)	0.1149 (10)	0.025 (2)

C1	0.9371 (16)	0.1373 (15)	0.0368 (12)	0.0238 (18)
C2	1.1538 (15)	-0.0213 (15)	0.0762 (11)	0.0238 (18)
C3	1.3271 (19)	-0.0448 (18)	0.1606 (13)	0.038 (3)
H3A	1.421167	-0.033142	0.120089	0.046*
H3B	1.314897	-0.152610	0.162526	0.046*
C4	1.2385 (17)	0.0077 (18)	0.3947 (13)	0.035 (3)
H4A	1.126049	-0.037376	0.327911	0.042*
H4B	1.284935	-0.075140	0.427765	0.042*
C5	1.206 (2)	0.1374 (18)	0.5023 (14)	0.039 (2)
H5A	1.319763	0.181893	0.567821	0.047*
H5B	1.127970	0.092387	0.541897	0.047*
C6	0.8751 (19)	0.2106 (18)	0.3709 (14)	0.039 (2)
H6A	0.868179	0.113955	0.301594	0.047*
H6B	0.817806	0.185297	0.431304	0.047*
C7	0.7789 (16)	0.3263 (16)	0.3162 (12)	0.030 (2)
H7A	0.864140	0.420800	0.338968	0.036*
H7B	0.686666	0.355435	0.359299	0.036*
C8	0.8623 (16)	0.2892 (16)	0.0814 (13)	0.030 (2)
H8A	0.824277	0.329504	0.008985	0.036*
H8B	0.956964	0.366690	0.147795	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0407 (5)	0.0292 (6)	0.0494 (6)	0.0003 (4)	0.0136 (4)	0.0134 (4)
I2	0.0437 (5)	0.0156 (5)	0.0585 (6)	0.0031 (4)	0.0271 (4)	0.0110 (4)
Cu1	0.0348 (8)	0.0176 (10)	0.0487 (10)	0.0019 (7)	0.0144 (7)	0.0110 (7)
Cu2	0.0424 (10)	0.0387 (12)	0.0546 (12)	0.0177 (8)	0.0220 (8)	0.0219 (9)
S1	0.0277 (15)	0.030 (2)	0.0386 (18)	0.0065 (13)	0.0051 (13)	0.0109 (15)
S2	0.0374 (17)	0.025 (2)	0.042 (2)	0.0028 (14)	0.0146 (14)	0.0084 (15)
S3	0.0284 (15)	0.0216 (19)	0.045 (2)	0.0109 (13)	0.0161 (14)	0.0138 (14)
N1	0.025 (5)	0.013 (6)	0.042 (6)	0.005 (4)	0.017 (5)	0.009 (4)
C1	0.029 (4)	0.014 (5)	0.031 (5)	0.007 (3)	0.011 (4)	0.009 (3)
C2	0.029 (4)	0.014 (5)	0.031 (5)	0.007 (3)	0.011 (4)	0.009 (3)
C3	0.052 (8)	0.022 (8)	0.038 (8)	0.021 (6)	0.014 (6)	0.002 (6)
C4	0.030 (6)	0.038 (9)	0.046 (8)	0.005 (6)	0.012 (6)	0.028 (7)
C5	0.050 (6)	0.027 (6)	0.044 (6)	0.005 (5)	0.012 (5)	0.018 (5)
C6	0.050 (6)	0.027 (6)	0.044 (6)	0.005 (5)	0.012 (5)	0.018 (5)
C7	0.029 (5)	0.024 (6)	0.042 (5)	0.013 (4)	0.018 (4)	0.011 (4)
C8	0.029 (5)	0.024 (6)	0.042 (5)	0.013 (4)	0.018 (4)	0.011 (4)

Geometric parameters (Å, °)

Cu1—N1	2.095 (10)	C1—C2 ⁱⁱⁱ	1.373 (17)
Cu1—S1	2.342 (4)	C1—C8	1.511 (18)
Cu1—S2	2.331 (4)	C2—C3	1.504 (19)
Cu1—I2 ⁱ	2.5193 (18)	C3—H3A	0.9700
Cu2—S3	2.359 (4)	C3—H3B	0.9700

Cu2—I1	2.665 (2)	C4—C5	1.50 (2)
Cu2—I2	2.6166 (19)	C4—H4A	0.9700
I1—Cu2 ⁱⁱ	2.675 (2)	C4—H4B	0.9700
Cu2—Cu2 ⁱⁱ	2.663 (4)	C5—H5A	0.9700
S1—C3	1.803 (13)	C5—H5B	0.9700
S1—C4	1.834 (13)	C6—C7	1.50 (2)
S2—C5	1.779 (16)	C6—H6A	0.9700
S2—C6	1.808 (14)	C6—H6B	0.9700
S3—C7	1.793 (13)	C7—H7A	0.9700
S3—C8	1.803 (12)	C7—H7B	0.9700
N1—C1	1.346 (16)	C8—H8A	0.9700
N1—C2	1.364 (16)	C8—H8B	0.9700
N1—Cu1—S2	110.2 (3)	C2—C3—S1	116.7 (10)
N1—Cu1—S1	85.3 (3)	C2—C3—H3A	108.1
S2—Cu1—S1	91.74 (14)	S1—C3—H3A	108.1
N1—Cu1—I2 ⁱ	121.1 (3)	C2—C3—H3B	108.1
S2—Cu1—I2 ⁱ	112.48 (12)	S1—C3—H3B	108.1
S1—Cu1—I2 ⁱ	130.61 (10)	H3A—C3—H3B	107.3
S3—Cu2—I2	109.54 (11)	C5—C4—S1	110.1 (10)
S3—Cu2—I1	105.86 (10)	C5—C4—H4A	109.6
I2—Cu2—I1	109.04 (8)	S1—C4—H4A	109.6
S3—Cu2—I1 ⁱⁱ	99.22 (11)	C5—C4—H4B	109.6
I2—Cu2—I1 ⁱⁱ	112.01 (7)	S1—C4—H4B	109.6
I1—Cu2—I1 ⁱⁱ	120.18 (7)	H4A—C4—H4B	108.2
Cu2—I1—Cu2 ⁱⁱ	59.82 (7)	C4—C5—S2	114.4 (10)
Cu1 ^{iv} —I2—Cu2	94.93 (7)	C4—C5—H5A	108.7
Cu2 ⁱⁱ —Cu2—I1	60.27 (7)	S2—C5—H5A	108.7
Cu2 ⁱⁱ —Cu2—I1 ⁱⁱ	59.91 (7)	C4—C5—H5B	108.7
S3—Cu2—Cu2 ⁱⁱ	115.75 (13)	S2—C5—H5B	108.7
I2—Cu2—Cu2 ⁱⁱ	134.68 (11)	H5A—C5—H5B	107.6
C3—S1—C4	100.9 (7)	C7—C6—S2	110.2 (10)
C3—S1—Cu1	96.4 (5)	C7—C6—H6A	109.6
C4—S1—Cu1	94.5 (5)	S2—C6—H6A	109.6
C5—S2—C6	104.7 (7)	C7—C6—H6B	109.6
C5—S2—Cu1	98.8 (5)	S2—C6—H6B	109.6
C6—S2—Cu1	105.0 (5)	H6A—C6—H6B	108.1
C7—S3—C8	102.8 (6)	C6—C7—S3	117.8 (10)
C7—S3—Cu2	106.0 (4)	C6—C7—H7A	107.9
C8—S3—Cu2	105.2 (5)	S3—C7—H7A	107.9
C1—N1—C2	116.6 (10)	C6—C7—H7B	107.9
C1—N1—Cu1	124.9 (9)	S3—C7—H7B	107.9
C2—N1—Cu1	118.5 (8)	H7A—C7—H7B	107.2
N1—C1—C2 ⁱⁱⁱ	122.1 (12)	C1—C8—S3	113.2 (9)
N1—C1—C8	117.1 (11)	C1—C8—H8A	108.9
C2 ⁱⁱⁱ —C1—C8	120.8 (11)	S3—C8—H8A	108.9
N1—C2—C1 ⁱⁱⁱ	121.3 (11)	C1—C8—H8B	108.9
N1—C2—C3	117.9 (11)	S3—C8—H8B	108.9

C1 ⁱⁱⁱ —C2—C3	120.7 (12)	H8A—C8—H8B	107.7
C2—N1—C1—C2 ⁱⁱⁱ	0.0 (19)	Cu1—S1—C4—C5	-52.9 (10)
Cu1—N1—C1—C2 ⁱⁱⁱ	179.6 (9)	S1—C4—C5—S2	62.8 (12)
C2—N1—C1—C8	177.4 (10)	C6—S2—C5—C4	74.9 (11)
Cu1—N1—C1—C8	-3.0 (15)	Cu1—S2—C5—C4	-33.3 (10)
C1—N1—C2—C1 ⁱⁱⁱ	0.0 (19)	C5—S2—C6—C7	-176.2 (10)
Cu1—N1—C2—C1 ⁱⁱⁱ	-179.6 (9)	Cu1—S2—C6—C7	-72.6 (10)
C1—N1—C2—C3	179.3 (11)	S2—C6—C7—S3	121.3 (9)
Cu1—N1—C2—C3	-0.3 (15)	C8—S3—C7—C6	-78.8 (11)
N1—C2—C3—S1	18.3 (17)	Cu2—S3—C7—C6	171.0 (9)
C1 ⁱⁱⁱ —C2—C3—S1	-162.3 (10)	N1—C1—C8—S3	-103.2 (11)
C4—S1—C3—C2	72.6 (13)	C2 ⁱⁱⁱ —C1—C8—S3	74.2 (14)
Cu1—S1—C3—C2	-23.2 (12)	C7—S3—C8—C1	96.8 (10)
C3—S1—C4—C5	-150.3 (10)	Cu2—S3—C8—C1	-152.4 (8)

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