



# Structural diversity in copper(I) iodide complexes with 6-thioxopiperidin-2-one, piperidine-2,6-dithione and isoindoline-1,3-dithione ligands

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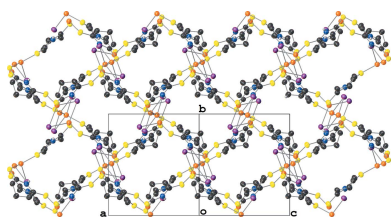
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Copper(I) iodide complexes are well known for displaying a diverse array of structural features even when only small changes in ligand design are made. This structural diversity is well displayed by five copper(I) iodide compounds reported here with closely related piperidine-2,6-dithione (SNS), isoindoline-1,3-dithione (SNS6), and 6-thioxopiperidin-2-one (SNO) ligands: di- $\mu$ -iodido-bis[(acetonitrile- $\kappa N$ )(6-sulfanylidene-piperidin-2-one- $\kappa S$ )copper(I)],  $[\text{Cu}_2\text{I}_2(\text{CH}_3\text{CN})_2(\text{C}_5\text{H}_7\text{NOS})_2]$  (**I**), bis(acetonitrile- $\kappa N$ )tetra- $\mu_3$ -iodido-bis(6-sulfanylidene-piperidin-2-one- $\kappa S$ )-tetrahydro-tetracopper(I),  $[\text{Cu}_4\text{I}_4(\text{CH}_3\text{CN})_4(\text{C}_5\text{H}_7\text{NOS})_4]$  (**II**), catena-poly[[ $(\mu$ -6-sulfanylidene-piperidin-2-one- $\kappa^2 O:S$ )copper(I)]- $\mu_3$ -iodido],  $[\text{CuI}(\text{C}_5\text{H}_7\text{NOS})]_n$  (**III**), poly[[ $(\text{piperidine-2,6-dithione-}\kappa S$ )copper(I)]- $\mu_3$ -iodido],  $[\text{CuI}(\text{C}_5\text{H}_7\text{NS}_2)]_n$  (**IV**), and poly[[ $(\mu$ -isoindoline-1,3-dithione- $\kappa^2 S:S$ )copper(I)]- $\mu_3$ -iodido],  $[\text{CuI}(\text{C}_8\text{H}_5\text{NS}_2)]_n$  (**V**). Compounds **I** and **II** crystallize as discrete dimeric and tetrameric complexes, whereas **III**, **IV**, and **V** crystallize as polymeric two-dimensional sheets. To the best of our knowledge, compound **III** is the first instance of an extended hexagonal  $[\text{Cu}_3\text{I}_3]$  structure that is not supported by bridging ligands. Structures **I**, **II**, and **IV** display weak to moderately strong  $\text{Cu}\cdots\text{Cu}$  cuprophilic interactions [ $\text{Cu}\cdots\text{Cu}$  internuclear distances range between 2.5803 (10) and 2.8485 (14) Å]. All structures except **III** display weak hydrogen-bonding interactions between the N—H of the ligand and the  $\mu_2$  and  $\mu_3\text{-I}^-$  atoms. Structure **III** contains classical N—H $\cdots$ O interactions between the SNO ligands that connect the molecules in a three-dimensional framework. Complex **V** features  $\pi$ – $\pi$  stacking interactions between the aryl rings of the SNS6 ligands within the same polymeric sheet. In structure **IV**, there were three partially occupied solvent molecules of dichloromethane and one partially occupied molecule of acetonitrile present in the asymmetric unit. The SQUEEZE routine [Spek (2015). *Acta Cryst. C* **71**, 9–18] was used to correct the diffraction data for diffuse scattering effects and to identify the solvent molecules. The given chemical formula and other crystal data do not take into account the solvent molecules.

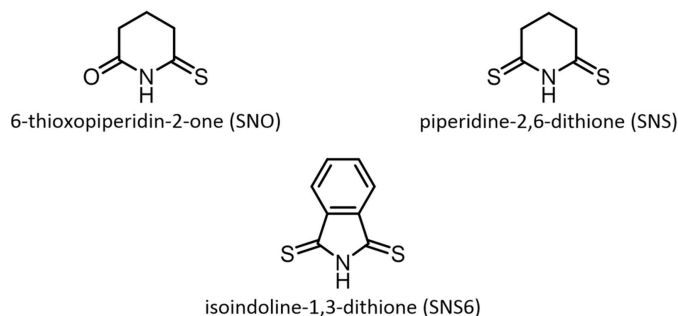


## 1. Chemical context

Copper (I) iodide compounds have been of interest for the past 50 years because of their diverse structural (Peng *et al.*, 2010) and spectroscopic properties (Ford *et al.*, 1999; Hardt & Pierre, 1973). In particular,  $\text{Cu}^{\text{I}}$  complexes range from simple  $\text{Cu}_2\text{I}_2L_2$  dimers ( $L$  = Lewis basic ligands) to complex three-dimensional coordination polymers (Peng *et al.*, 2010). Traditionally, soft Lewis basic donors such as thiols or phosphines have been used as ligands to the  $\text{Cu}^{\text{I}}$  centers. We were interested in exploring the structures of  $\text{Cu}^{\text{I}}$  coordination complexes with three ligands, piperidine-2,6-dithione (SNS), isoindoline-1,3-dithione (SNS6), and 6-thioxopiperidin-2-one

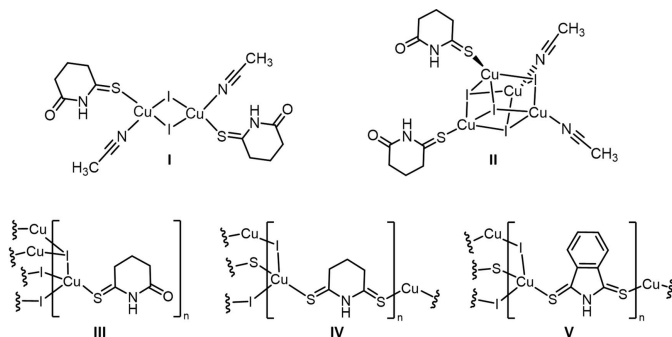


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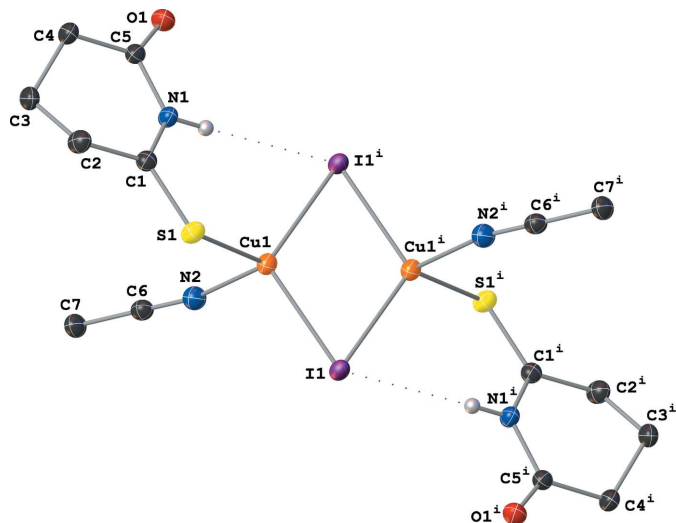
**Figure 1**  
Diagrams of the three ligands used in the preparation of structures I–V.

(SNO) (Fig. 1). These ligands have been previously utilized in our work due to their polydentate binding modes, which provide individual binding sites that display a range of ‘hard’ to ‘soft’ Lewis basic behavior (Dolinar & Berry, 2013, 2014). Herein we report the synthesis and structural characterization of a series of five copper(I) iodide complexes with piperidine-2,6-dithione (SNS), isindoline-1,3-dithione (SNS6), and 6-thioxopiperidin-2-one (SNO) ligands.



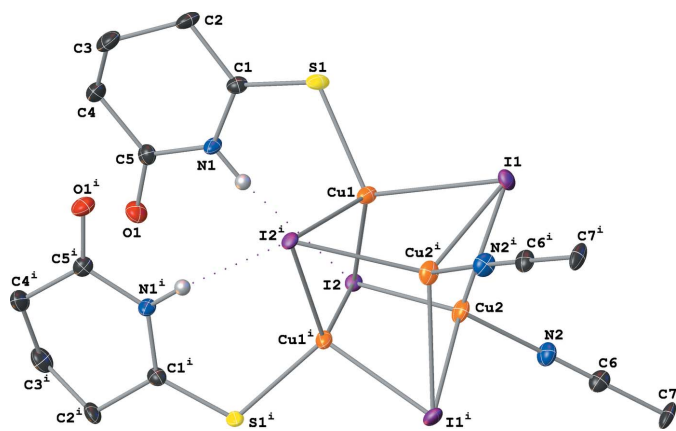
## 2. Structural commentary

Compound **I** crystallizes as a discrete dimer with a rhombic  $\text{Cu}_2(\mu_2\text{-I})_2$  core that resides on a crystallographic inversion center; thus, only one half of the dimer is symmetry-independent (Fig. 2). The rhombic core is close to having an ideal geometry with almost equal Cu–I distances (Table 1). Each Cu center is coordinated by two  $\mu_2\text{-I}^-$  atoms, one molecule of acetonitrile, and the thione moiety of the SNO ligand and has a slightly distorted tetrahedral geometry [I–Cu–I and I–Cu–L angles of  $100.19(3)$ – $118.719(16)^\circ$ ;  $L = \text{SNO}$  or acetonitrile]. The  $\text{Cu}\cdots\text{Cu}$  internuclear distance of  $2.7274(6)$  Å is slightly shorter than the sum of the covalent radii (*ca* 2.87 Å) and is consistent with a weak cuprophilic interaction. The Cu–N and Cu–S distances (Table 1) in **I** are similar to the Cu–N and Cu–S distances in other discrete  $\text{Cu}_2(\mu_2\text{-I})_2$  dimers reported to the Cambridge Structural Database (CSD) and selected with moderate search criteria (Groom *et al.* 2016; no errors, no polymers, single-crystal structures only). The SNO ligand adopts an envelope conformation, with a  $49.07(9)^\circ$  dihedral angle between the planes defined by atoms C2–C3–C4 and C2–C1–N1–C5–C4.



**Figure 2**  
A molecular drawing of **I** with 50% probability ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. All H atoms bound to C atoms are omitted. [Symmetry code: (i)  $-x + 1, -y + 1, -z$ .]

Complex **II** crystallizes with a  $\text{Cu}_4(\mu_3\text{-I})_4$  core; the four Cu atoms form a distorted tetrahedron with  $\mu_3\text{-I}^-$  atoms capping each of the tetrahedron faces (Fig. 3). The center of the tetrahedron resides on a crystallographic twofold axis and therefore only two of the Cu centers are symmetry-independent. These two Cu atoms have different first coordination spheres: Cu1 is coordinated by three  $\mu_3\text{-I}^-$  atoms and one thione-bound SNO ligand; Cu2 is coordinated by three  $\mu_3\text{-I}^-$  atoms and one acetonitrile ligand. Both Cu atoms have a distorted tetrahedral geometry [I–Cu–I and I–Cu–L angles between  $97.98(3)$  and  $118.71(2)^\circ$ ;  $L = \text{SNO}$  or acetonitrile]. The internuclear Cu $\cdots$ Cu distances vary between  $2.5803(10)$  and  $2.8150(11)$  Å (Table 1), which (similarly to **I**) are indicative of weak to moderately strong cuprophilic interactions between Cu atoms in the tetrahedron. The Cu1–S and Cu2–N distances in **II** (Table 1) are slightly shorter than the Cu–S and Cu–N distances in **I** as a result of the



**Figure 3**  
A molecular drawing of **II** shown with 50% probability ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. All H atoms bound to C atoms are omitted. [Symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$ .]

**Table 1**  
Selected bond lengths for structures **I–V**.

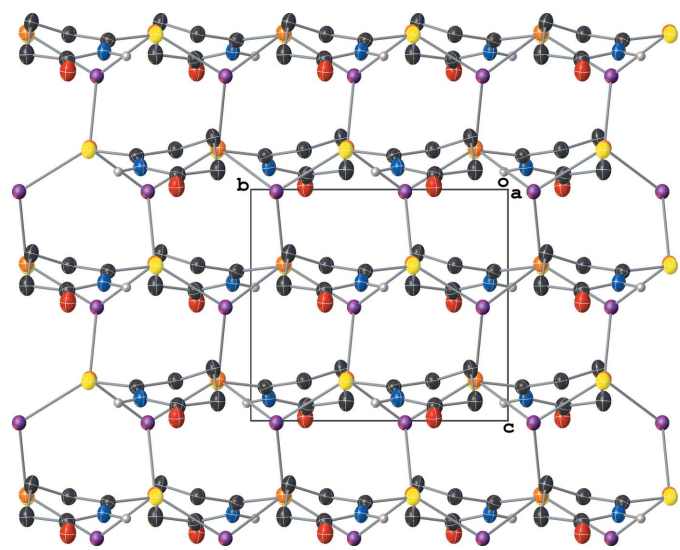
| <b>I<sup>a</sup></b> |                      |             | <b>II<sup>b</sup></b> |             | <b>III<sup>c</sup></b> |             | <b>IV<sup>d</sup></b> |             | <b>V<sup>e</sup></b> |             |
|----------------------|----------------------|-------------|-----------------------|-------------|------------------------|-------------|-----------------------|-------------|----------------------|-------------|
| Cu—I                 | I1—Cu1               | 2.6261 (6)  | I1—Cu1                | 2.6451 (6)  | I1—Cu1                 | 2.6264 (11) | I1—Cu1                | 2.6365 (8)  | I1—Cu1               | 2.6152 (13) |
|                      | I1—Cu1 <sup>i</sup>  | 2.6321 (7)  | I1—Cu2 <sup>i</sup>   | 2.7017 (7)  | I1—Cu1 <sup>i</sup>    | 2.6709 (12) | I1—Cu1 <sup>i</sup>   | 2.6687 (8)  | I1—Cu1 <sup>i</sup>  | 2.6798 (13) |
|                      |                      |             | I1—Cu2                | 2.7250 (6)  | I1—Cu1 <sup>ii</sup>   | 2.6342 (10) | I2—Cu2                | 2.6719 (8)  |                      |             |
|                      |                      |             | I2—Cu1                | 2.7796 (6)  |                        |             | I2—Cu2 <sup>ii</sup>  | 2.6724 (8)  |                      |             |
|                      |                      |             | I2—Cu1 <sup>i</sup>   | 2.6542 (6)  |                        |             |                       |             |                      |             |
| Cu···Cu              | Cu1—Cu1 <sup>i</sup> | 2.7274 (6)  | I2—Cu2                | 2.6456 (6)  |                        |             |                       |             |                      |             |
|                      |                      |             | Cu1—Cu1 <sup>i</sup>  | 2.8150 (11) |                        |             |                       |             |                      |             |
|                      |                      |             | Cu1—Cu2               | 2.7864 (8)  |                        |             |                       |             |                      |             |
|                      |                      |             | Cu1—Cu2 <sup>i</sup>  | 2.7106 (8)  |                        |             |                       |             |                      |             |
|                      |                      |             | Cu2—Cu2 <sup>i</sup>  | 2.5803 (10) |                        |             |                       |             |                      |             |
| Cu—S                 | Cu1—S1               | 2.3205 (6)  | Cu1—S1                | 2.2869 (10) | Cu1—S1                 | 2.2827 (15) | Cu1—S1                | 2.3086 (14) | Cu1—S1               | 2.269 (2)   |
|                      |                      |             |                       |             |                        |             | Cu1—S4 <sup>iii</sup> | 2.3075 (13) | Cu1—S2 <sup>ii</sup> | 2.273 (2)   |
|                      |                      |             |                       |             |                        |             | Cu2—S2                | 2.2802 (15) |                      |             |
|                      |                      |             |                       |             |                        |             | Cu2—S3                | 2.2933 (15) |                      |             |
| Cu—N                 | Cu1—N2               | 2.0225 (10) | Cu2—N2                | 1.974 (3)   |                        |             |                       |             |                      |             |

Symmetry codes: (a) (i)  $-x+1, -y+1, -z$  for **I**; (b) (i)  $-x+1, y, -z+\frac{1}{2}$  for **II**; (c) (i)  $-x+1/2, -y+\frac{3}{2}, z-\frac{1}{2}$  and (ii)  $x, -y+1, z-\frac{1}{2}$  for **III**; (d) (i)  $-x, -y, -z+1$ ; (ii)  $-x+1, -y+1, -z+1$  and (iii)  $-x+1, -y, -z+1$  for **IV**; (e) (i)  $x, y-1, z$  and (ii)  $x, -y+1, z+\frac{1}{2}$  for **V**.

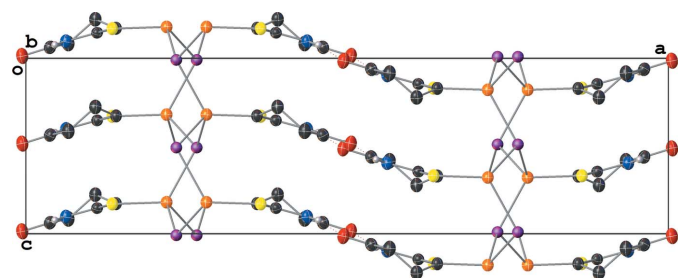
increase from two  $\mu_2\text{I}^-$  to three  $\mu_3\text{I}^-$  atoms coordinating to each Cu center. The SNO ligand adopts an envelope conformation with a  $47.5(2)^\circ$  dihedral angle between the planes defined by atoms C2–C3–C4 and C2–C1–N1–C5–C4.

Compound **III** crystallizes with layered two-dimensional polymeric sheets with a repeat (and symmetry-independent) unit formula of  $[\text{Cu}(\mu_3\text{I})(\text{SNO})]$ . The Cu atoms are coordinated by three  $\mu_3\text{I}^-$  atoms and one SNO ligand and have distorted tetrahedral geometries [I–Cu–I and I–Cu–S angles of  $97.12(4)$ – $120.62(4)^\circ$ ] (Fig. 4). The  $\text{I}^-$  ions have distorted trigonal pyramidal geometries [Cu–I–Cu angles of  $99.58(3)$ – $116.92(2)^\circ$ ] with two short and one long Cu–I bonds (Table 1). The polymeric sheet is based on fused  $\text{Cu}_3\text{I}_3$  six-membered rings with a screw-boat conformation ( $^3S_2$  with puckering amplitude  $Q = 1.3385 \text{ \AA}$ ; Cremer & Pople, 1975) that propagate parallel to and stack perpendicularly to the (100) crystallographic plane (Fig. 5). These fused six-membered rings are reminiscent of the zinc-blend structure present in crystalline  $\gamma\text{-CuI}$  (Gruzintsev & Zagorodnev, 2012) except that the anions are  $\mu_3$  rather than  $\mu_4$ . Each polymeric sheet is insulated by a sheath of SNO ligands, whose Cu–S bonds are perpendicular to the plane of propagation of the  $\text{Cu}_3\text{I}_3$  rings (Fig. 6). The Cu···Cu distances between neigh-

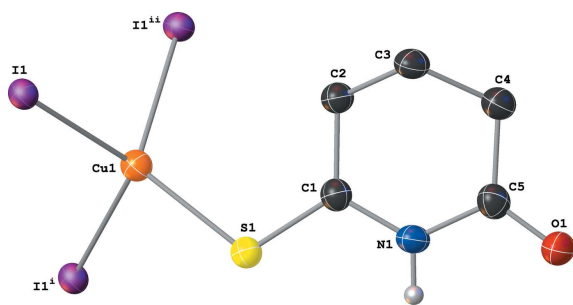
boring Cu atoms in the  $\text{Cu}_3\text{I}_3$  rings measure between  $4.2226(15)$  and  $4.5148(15) \text{ \AA}$ , which are outside the range of internuclear distances for cuprophilic interactions.



**Figure 5**  
A molecular drawing of **III**'s  $\text{Cu}_3\text{I}_3$  fused rings viewed along the crystallographic *a* axis with 50% probability ellipsoids. All H atoms bound to C atoms are omitted.



**Figure 6**  
A molecular drawing of **III** viewed along the crystallographic *b* axis with 50% probability ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. All H atoms bound to C atoms are omitted.



**Figure 4**  
A molecular drawing of the symmetry-independent portion of **III** with the full coordination sphere of the Cu center shown. All atoms are shown with 50% probability ellipsoids; all H atoms bound to C atoms are omitted. [Symmetry codes: (i)  $x, -y+1, z-\frac{1}{2}$ ; (ii)  $-x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$ .]

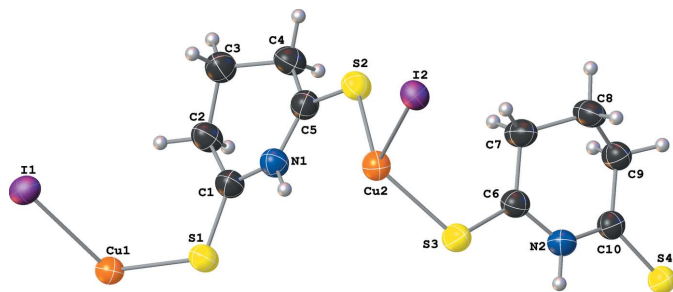


Figure 7

A molecular drawing of the repeat unit of **IV** shown with 50% probability ellipsoids.

Similarly to **III**, **IV** crystallizes with layered two-dimensional polymeric sheets with the symmetry-independent unit formula  $[\text{Cu}(\mu_2\text{-I})(\mu_2\text{-SNS})]_2$  (Fig. 7); the Cu and  $\mu_2\text{-I}^-$  atoms form  $\text{Cu}_2(\mu_2\text{-I})_2$  rhombi where the center of each rhombus resides on a crystallographic inversion center. Thus, the symmetry-independent unit is best described as containing two structurally distinct  $[\text{Cu}_2(\mu_2\text{-I})_2(\mu_2\text{-SNS})_2]$  half-dimers. The structures of the symmetry-independent  $\text{Cu}_2(\mu_2\text{-I})_2$  rhombi differ in two notable ways: first, while the  $\text{Cu}_2(\mu_2\text{-I})_2$  rhombus formed by Cu1, I1, and their symmetry-equivalents is slightly distorted, the rhombus formed by Cu2, I2, and their symmetry-equivalents is near ideal (Table 1). Secondly, the Cu...Cu distances in the rhombi differ by *ca* 0.07 Å [2.8485 (14) Å for the Cu1 rhombus; 2.7746 (15) Å for the Cu2 rhombus]. These values are consistent with little to no Cu...Cu cuprophilic interaction in the Cu1 dimer while also indicating that there is a weak Cu...Cu cuprophilic interaction in the Cu2 dimer. For both half dimers, the Cu atom's distorted tetrahedral [I—Cu—I angles between 115.06 (3) and 117.46 (3)° and S—Cu—I angles of 96.95 (4)–119.35 (6)°] coordination sphere is filled by two thione moieties from the  $\mu_2\text{-SNS}$  ligand; however, only one of these  $\mu_2\text{-SNS}$  ligands per Cu atom is symmetry-independent (Fig. 8).

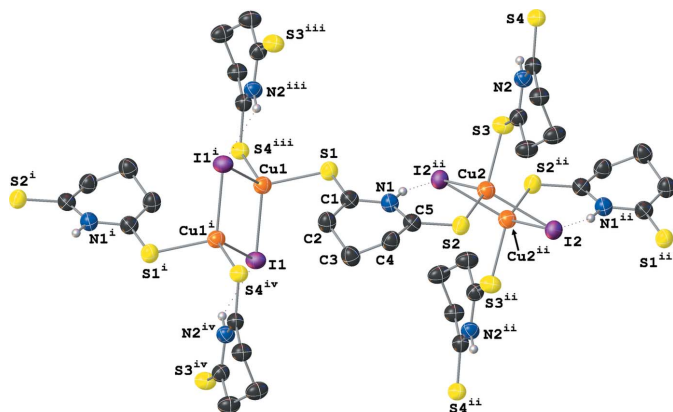


Figure 8

A molecular drawing of **IV** with the full coordination spheres of the Cu centers shown with selected atom labels. All atoms are shown with 50% probability ellipsoids; dotted lines are used to indicate hydrogen-bonding interactions. All H atoms bound to C atoms are omitted. [Symmetry codes: (i)  $-x, -y, 1 - z$ ; (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $-1 + x, y, z$ ]

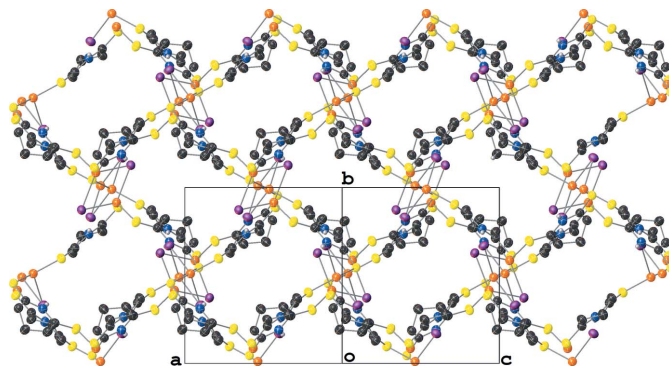


Figure 9

A molecular drawing of **IV** viewed along the [010] crystallographic direction with 50% probability ellipsoids. All H atoms bound to C atoms are omitted.

In contrast to the monodentate SNO ligands in **III**, which only permit polymer propagation in **III** through the  $\mu_3\text{-I}^-$  atoms, the bidentate SNS ligand facilitates polymer propagation in **IV**. This results in the formation of rings formed by four  $[\text{Cu}(\mu_2\text{-I})(\mu_2\text{-SNS})]$  units. The propagation of these rings in the (001) crystallographic plane results in a mesh-like sheet structure, and the layering of these sheets perpendicularly to the (001) plane results in the presence of sizable solvent-accessible voids (*ca* 200 Å<sup>3</sup>) in the structure (Fig. 9). These voids are filled with a combination of acetonitrile and dichloromethane in an approximately 2:1 ratio; however, these solvent species were positionally disordered and the *PLATON SQUEEZE* routine (Spek, 2015) was required to model the diffuse electron density from the solvent species in these voids (see *Refinement* section).

Complex **V** also crystallizes as two-dimensional polymeric sheets with the symmetry-independent unit formula  $[\text{Cu}(\mu_2\text{-I})(\mu_2\text{-SNS6})]$  (Fig. 10). The Cu center is coordinated by two  $\mu_2\text{-I}^-$  atoms and two thione moieties of the  $\mu_2\text{-SNS6}$  ligands and has a distorted tetrahedral geometry [I—Cu—I and I—

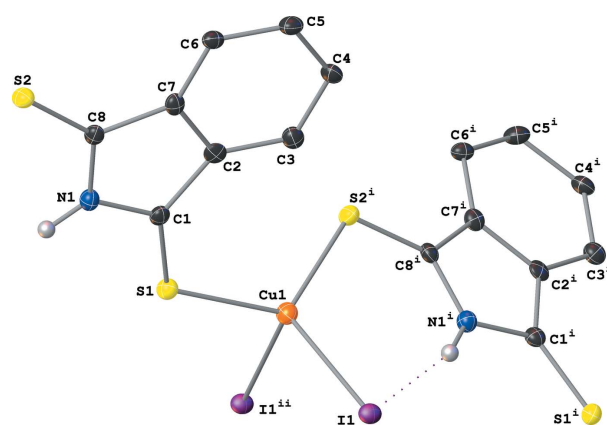
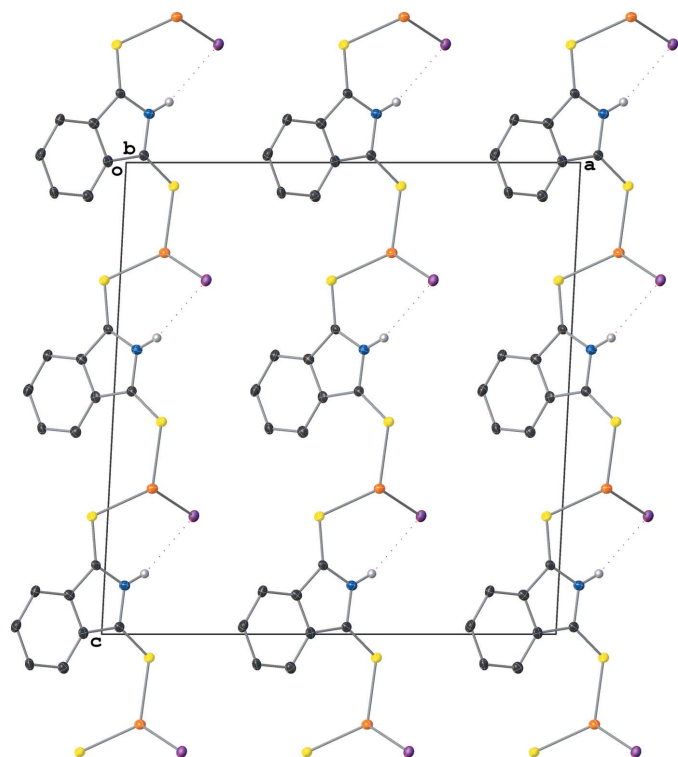


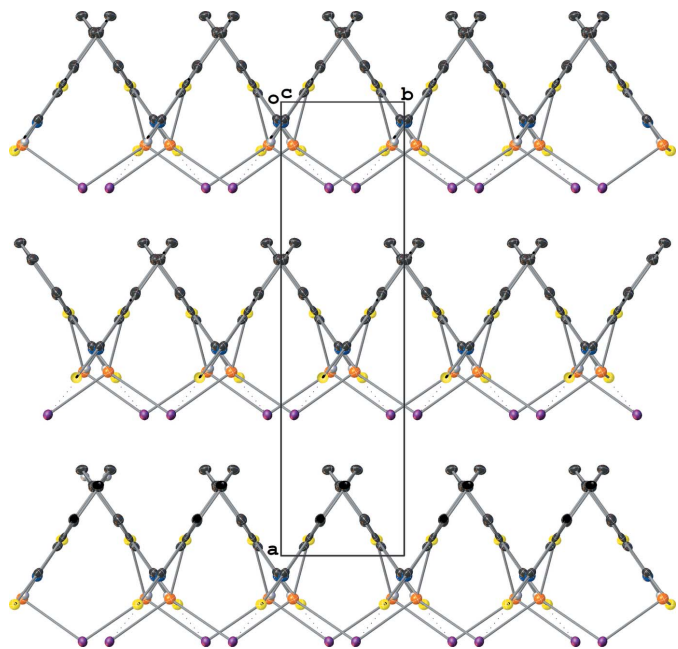
Figure 10

A molecular drawing of the symmetry-independent portion of **V** with the full coordination sphere of the Cu center shown. All atoms are shown with 50% probability ellipsoids; dotted lines are used to indicate hydrogen-bonding interactions. All H atoms bound to C atoms are omitted. [Symmetry codes: (i)  $x, 1 + y, z$ ; (ii)  $x, 1 - y, \frac{1}{2} + z$ .]



**Figure 11**  
A molecular drawing of **V** viewed along the crystallographic *b* axis with 50% probability ellipsoids with emphasis on the weak N—H...I interactions (dotted lines). All H atoms bound to C atoms are omitted.

Cu—S angles between 100.30 (6) and 120.16 (7)°]. Whereas the two S—Cu distances are almost identical, the two Cu—I distances are quite different (Table 1).



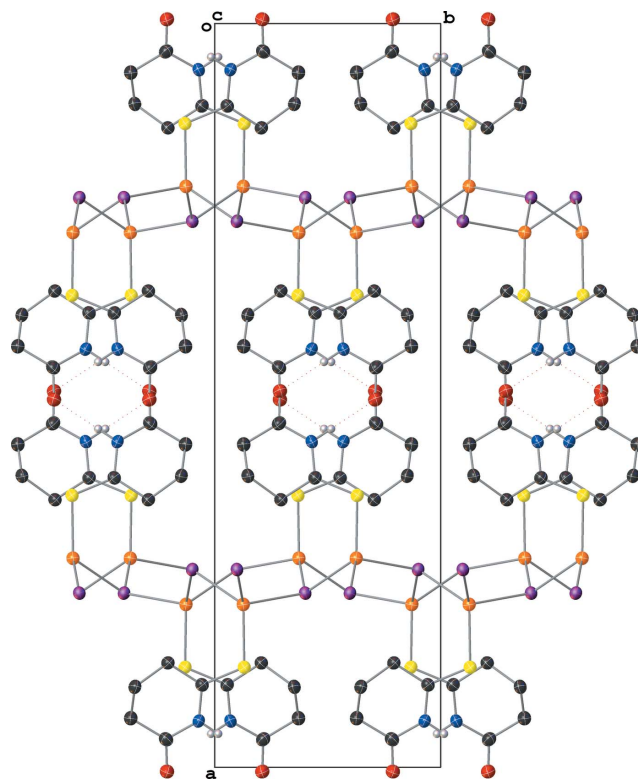
**Figure 12**  
A molecular drawing of **V** viewed along the crystallographic *c* axis with 50% probability ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. All H atoms bound to C atoms are omitted.

The polymeric sheet propagates parallel to the (100) crystallographic plane. The  $\mu_2$ -I<sup>−</sup> atoms bridge two Cu centers and form Cu—I zigzag chains that propagate parallel to the [010] crystallographic direction. Similarly to **IV**, the  $\mu_2$ -SNS6 ligands participate in the polymer propagation in **V** by bridging two Cu atoms and connecting the Cu—I chains and are generated by the *c* glide plane (Fig. 11). Among the five structures discussed, **V** is the only non-centrosymmetric structure. This results in a packing motif with a polar arrangement of SNS6 ligands on one side of the inorganic sheets, which results in a smaller spacing between the inorganic layers [7.598 (3) Å, see Fig. 12] in **V** than in **III** [14.134 (5) Å, see Fig. 13].

### 3. Supramolecular features

Among the five structures reported in this work, **III**, **IV**, and **V** crystallize as polymeric sheets; their extended structural characteristics are described above. In addition to the polymeric structural features in **III**, **IV**, and **V**, there are also several types of intermolecular interactions present in each of the five structures that are relevant to a description of their supramolecular architectures.

All structures except **III** display non-classical (*e.g.*, H-atom acceptors that are not N, O or Cl) hydrogen-bonding interactions between the N—H of the SNO/SNS/SNS6 ligands and the  $\mu_2$ -I<sup>−</sup>/ $\mu_3$ -I<sup>−</sup> atoms. According to our statistical analysis of 3396 N—H...I interactions observed in 2030 structures



**Figure 13**  
A molecular drawing of **III** viewed along the crystallographic *c* axis with 50% probability ellipsoids. Dotted lines are used to indicate hydrogen-bonding interactions. All H atoms bound to C atoms are omitted.

**Table 2**  
Hydrogen bonding geometries for **I–V**.

|                         | $D-H\cdots A$                    | $D-H$      | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|----------------------------------|------------|-------------|-------------|---------------|
| <b>I</b> <sup>a</sup>   | N1–H1 $\cdots$ I1 <sup>i</sup>   | 0.857 (12) | 2.845 (13)  | 3.6980 (12) | 173.8 (13)    |
| <b>II</b>               | N1–H1 $\cdots$ I2                | 0.870 (19) | 2.81 (2)    | 3.672 (3)   | 170 (4)       |
| <b>III</b> <sup>b</sup> | N1–H1 $\cdots$ O1 <sup>iii</sup> | 0.86 (2)   | 2.03 (2)    | 2.881 (5)   | 171 (5)       |
| <b>IV</b> <sup>c</sup>  | N1–H1 $\cdots$ I2 <sup>ii</sup>  | 0.88       | 2.79        | 3.628 (4)   | 160.9         |
|                         | N2–H2 $\cdots$ I1 <sup>iv</sup>  | 0.88       | 2.90        | 3.679 (4)   | 149.2         |
| <b>V</b> <sup>d</sup>   | N1–H1 $\cdots$ I1 <sup>iii</sup> | 0.88       | 2.84        | 3.692 (7)   | 163.2         |

Symmetry codes: (a) (i)  $-x+1, -y+1, -z$  for **I**; (b) (iii)  $-x+1, -y+1, -z+2$  for **III**; (c) (ii)  $-x+1, -y+1, -z+1$  and (iv)  $x+1, y, z$  for **IV**; (d) (iii)  $x, -y+1, z-\frac{1}{2}$  for **IV**.

reported to the CSD, their  $D\cdots A$  distances range from 3.15 to 4.12 Å with a mean  $D\cdots A$  distance of 3.69 (13) Å. The  $D\cdots A$  distances in structures **I**, **II**, **IV**, and **V** are typical for these types of interactions (Table 2). For structures **I** and **II**, the N–H $\cdots$ I interaction is intramolecular. For **IV**, there are two symmetry-independent hydrogen-bonding interactions, which is expected given that the structure contains two symmetry-independent SNS ligands. The first, between atoms N1–H1 $\cdots$ I1<sup>ii</sup> [symmetry code: (ii)  $-x+1, -y+1, -z+1$ ], is a stronger interaction; the second is between atoms N2<sup>iv</sup>–H2<sup>iv</sup> $\cdots$ I1 [symmetry code: (iv)  $x+1, y, z$ ] and is a weaker interaction (Table 2). Both interactions form  $S(6)$  hydrogen-bonding motifs (Etter *et al.* 1990), which provide some rigidity to the mesh-like sheet of the polymer.

Structure **III** is unique among all the structures discussed in this work as it is the only structure to exhibit classical hydrogen-bonding interactions. There are two identical hydrogen bonds per SNO ligand, with the N–H serving as an H-bond donor and the O atom serving as an H-bond acceptor [N1–H1 $\cdots$ O1<sup>iii</sup> and N1<sup>iii</sup>–H1<sup>iii</sup> $\cdots$ O1; symmetry code: (iii)  $-x+1, -y+1, -z+2$ ]. These hydrogen bonds are relatively strong (Table 2) and form  $R_2^2(8)$  motifs between the stacked  $[Cu_3I_3]_n$  polymeric layers. Their presence leads to an extended three-dimensional framework structure, where the propagation of the  $[Cu_3I_3]_n$  polymeric sheets accounts for two dimensions and the connection of those sheets through the hydrogen-bonding interactions provides the third (Fig. 13).

Structure **V** has two distinct types of intermolecular interactions. First, there is the non-classical hydrogen-bonding interaction between the N–H of the SNS6 ligand and the symmetry-equivalent  $\mu_2-I^-$  atoms [N1–H1 $\cdots$ I1<sup>iii</sup>; symmetry code: (ii)  $x, 1-y, -\frac{1}{2}+z$ ] within the same polymeric sheet. This interaction forms  $R_2^2(6)$  motifs that are of typical strength (see Figs. 10 and 11; Table 2). In addition to the non-classical hydrogen-bonding interactions, there are also  $\pi$ – $\pi$  stacking interactions between SNS6 ligands within the same polymeric sheet due to the presence of the extended  $\pi$  system in the SNS6 ligand backbone. These interactions, formed by the overlap between the five-membered rings with atoms C1–C2–C7–C8–N1 ( $R_5$ ) and the phenyl rings with atoms C2<sup>i</sup>–C3<sup>i</sup>–C4<sup>i</sup>–C5<sup>i</sup>–C6<sup>i</sup>–C7<sup>i</sup> ( $R_6$ ) [symmetry code: (i)  $x, 1+y, z$ ], is of moderate strength [plane  $R_5$  to  $R_6$  centroid distance: 3.369 (5) Å;  $R_5$  to  $R_6$  centroid offset distance: 1.165 (14) Å]. These  $\pi$ – $\pi$  stacking interactions, in tandem with the increased size of the SNS6 ligand relative to the SNS/SNO ligands,

results in a tightly packed two-dimensional sheet (packing coefficient: 71.8%), which prevents the formation of the more mesh-like structure seen in **IV** (packing coefficient: 54.1%) (Kitaigorodskii, 1973).

#### 4. Database survey

All searches in the Cambridge Structural Database (Version 5.41, latest update May 2020; Groom *et al.* 2016) were performed with moderate search criteria (for structures **I** and **II**: no errors or ions, not polymeric, only single crystal structures; for structures **III**, **IV**, and **V**: no errors or ions, only single crystal structures. The surveys of the database for each individual structure are described below.

**I**: A search for  $Cu_2(\mu_2-I)_2$  dimers with two neutral ligands binding with one nitrogen and one sulfur atom resulted in 17 matches. Only one had a homometallic  $[Cu(\mu_2-I)_2(S)(N)]_2$  type structure where the S and N donors were part of monodentate ligands, which indicates that the coordination environment in **I** is a relatively unusual one. This structure, bis[( $\mu_2$ -iodo)(acetonitrile)(triphenylthiophosphorane)copper(I)] (refcode: OCALOT; Lobana *et al.*, 2001), has similar Cu–S and Cu–N distances and a slightly longer Cu–I distance. However, OCALOT has a dramatically longer Cu $\cdots$ Cu distance [3.4141 (16) Å] than that in **I** (Table 1). This elongation is likely due to the larger steric requirements of the SPPH<sub>3</sub> sulfur donor ligand in OCALOT.

**II**: a survey of the Cambridge Structural Database for  $Cu_4(\mu_3-I)_4$  tetrahedrons with a mix of two Cu  $I_3N$  coordination spheres and two  $I_3S$  coordination spheres provided only one match, octakis( $\mu_3$ -iodo)bis[ $\mu_2$ -bis[(2,4-dimethylphenyl)thio]methane- $S,S'$ ]tetrakis(acetonitrile)octacopper(I) acetonitrile tetrahydrofuran solvate (refcode: ENAXAT; Martínez-Alanis *et al.*, 2011), which features two  $Cu_4(\mu_3-I)_4$  tetrahedrons. Two of the Cu centers in each tetrahedron have a ( $\mu_3$ -I)<sub>3</sub>(NCCH<sub>3</sub>) coordination sphere. The other two Cu centers have ( $\mu_3$ -I)<sub>3</sub>S coordination spheres with bridging bis[(3,5-dimethylphenyl)thio]methane ligands that tether the two tetrahedra together. The geometric parameters of this structure [Cu $\cdots$ Cu, Cu–I, Cu–S, and Cu–N distances: 2.69 (3), 2.68 (4), 2.315 (11), and Cu–N 1.979 (6) Å] are very similar to those in **II**.

An additional, broader search for all non-polymeric  $Cu_4(\mu_3-I)$  tetrahedra yielded 130 results for  $Cu_4(\mu_3-I)_4(L)_4$  ( $L = N, S, P, I, O, As$ ) tetrahedra with  $L$  as a neutral ligand. All of the resulting structures had identical first coordination spheres for each of the Cu centers [*e.g.*,  $Cu_4(\mu_3-I)_4(L)_4$ , rather than the  $Cu_4(\mu_3-I)_4(L)_2(L')_2$  in **II**]. To the best of our knowledge, **II** is the first reported instance of a non-polymeric  $Cu_4(\mu_3-I)_4$  tetrahedron with N and (non-bridging) S ligands.

**III**: A search for structures containing  $Cu_3(\mu_3-X)_3$  ring motifs that did not contain  $Cu_4(\mu_3-X)_4$  ( $X =$  any halogen) tetrahedral motifs yielded 60 structures. Four of them contained  $Cu_3(\mu_3-X)_3$  motifs and one of them (DENQEV; Liu *et al.*, 2018) contained a  $Cu_3(\mu_3-X)_3$  ring motif. This structure, catena-[bis[ $\mu$ -5-(1-aminoethyl)tetrazolato]tetrakis( $\mu$ -iodo)-copper(II)tetracopper(I)], contains four monovalent and one

divalent symmetry-independent Cu centers that form a one-dimensional ribbon. This ribbon, in combination with the bridging (1*S*)-1-(5-tetrazolyl) ethylamine ligands, forms a three-dimensional network. There are a few other examples of copper halide extended structures based on  $\text{Cu}_3(\mu_3\text{-}X)_3$  ring motifs that are both one-dimensional (Näther & Jess, 2003; Oliver *et al.*, 1977) and two-dimensional (Blake *et al.*, 1999; Haakansson *et al.*, 1991; Haakansson & Jagner, 1990). Among these, the  $[\text{Cu}_2\text{I}_2(\mu_3\text{-}1,3,5\text{-triazine})]_\infty$  structure reported by Blake *et al.* is the only two-dimensional sheet with hexagonal  $\text{Cu}_3\text{I}_3$  rings and  $\mu_3$ -triazine linkers. To the best of our knowledge, **III** is the first instance of this extended hexagonal  $\text{Cu}_3\text{I}_3$  structure that is not supported by bridging ligands.

**IV**: A search for polymeric structures containing  $\text{Cu}_2(\mu_2\text{-}X)_2(\mu_2\text{-}S)$  ( $X = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) rhombi afforded 91 matches that included 35 polymeric homometallic structures. Among the 35 structures, 23 were two-dimensional polymers. Whereas there were no closely related matches for **IV**, a similar structure (JIZPEQ; Raghuvanshi *et al.*, 2019) was found. This structure has the same chemical composition as **IV** except with  $\mu_2$ -1,3-dithiane ligands rather than  $\mu_2$ -SNS ligands. In contrast to the two-dimensional mesh-like structure of **IV**, JIZPEQ crystallizes with one-dimensional chains with links comprised of two  $\text{Cu}_2(\mu_2\text{-I})_2$  rhombi and two  $\mu_2$ -1,3-dithiane ligands. The geometric parameters of the  $\text{Cu}_2(\mu_2\text{-I})_2$  rhombi are in good agreement with those in **IV** [ $\text{Cu}\cdots\text{Cu}$ ,  $\text{Cu}-\text{I}$  (average), and  $\text{Cu}-\text{S}$  (average) distances: 2.8904 (6), 2.63 (2), and 2.329 (3) Å].

**V**: A search for structures with  $\text{Cu}-X$  zigzag chains that did not contain the  $\text{Cu}_2(\mu_2\text{-}X)_2$  rhombus afforded 112 matches. Among these, 56 were for polymeric homometallic structures and three of these [refcodes: AFUDUA (Caradoc-Davies *et al.*, 2002), CIQQOL (Musina *et al.*, 2017), and FIWWAK (Cingolani *et al.*, 2005)] contained one-dimensional  $\text{Cu}-\text{I}^-$  zigzag chains. All three structures contain tetrahedral  $\text{Cu}^{\text{I}}$  centers coordinated by the two  $\mu_2\text{-I}$  atoms and two neutral donor ligands (binding with sulfur and nitrogen for AFUNDA, arsenic for CIQQOL, and FIWWAK). These structures have similar geometries to that of **V** except for the  $\text{Cu}$ -ligand distances.

## 5. Synthesis and crystallization

The ligands piperidine-2,6-dithione (SNS) and 6-thioxopiperidin-2-one (SNO) were purchased from Sigma-Aldrich and used as received. Isoindoline-1,3-dithione (SNS6) was prepared in a similar manner to that previously described in the literature (Yde *et al.*, 1984).

Unless otherwise specified, all reactions were performed at room temperature under a dry  $\text{N}_2$  atmosphere using standard glovebox methods.

**I** was prepared by combining 10 ml of a clear yellow solution of 6-thioxopiperidin-2-one (0.500 mmol) in dichloromethane with 10 mL of a colorless solution of  $\text{CuI}$  (0.502 mmol) in acetonitrile. Upon combination, the solution turned a bright-orange color. Vapor diffusion of the orange

solution with diethyl ether afforded large, yellow, block-shaped crystals of **I** after three days.

Two by-products were also obtained from the reaction of 6-thioxopiperidin-2-one and  $\text{CuI}$ . The first (**II**) were small, yellow, plate-shaped crystals that co-crystallized with the larger yellow block-shaped crystals of **I**. The second by-product formed after exposing the initial orange solution from the reaction of 6-thioxopiperidin-2-one and  $\text{CuI}$  to air, and allowing that solution to slowly evaporate in air for approximately one week. After this time, small, red-orange crystals of **III** were obtained.

**IV** was prepared by layering 10 mL of a clear yellow solution of piperidine-2,6-dithione (1.01 mmol) in dichloromethane over 10 mL of a colorless solution of  $\text{CuI}$  (1.00 mmol) in acetonitrile. Dark-red crystals of **IV** were obtained after one week.

Black, needle-shaped crystals of **V** were obtained in a similar manner to **IV**, with the exception that 1.00 mmol of isoindoline-1,3-dithione was used instead of piperidine-2,6-dithione.

## 6. Refinement

For structure **I**, the diffraction data were consistent with the space groups  $P1$  and  $P\bar{1}$ ; the  $E$ -statistics were consistent for the centrosymmetric space group  $P\bar{1}$  and were used to make the final space-group determination. For structures **II-V**, a combination of the systematic absences in the diffraction data and the  $E$ -statistics were used to assign the centrosymmetric space groups  $C2/c$  (**II**),  $Pbcn$  (**III**),  $P2_1/c$  (**IV**) and the non-centrosymmetric space group  $Cc$  (**V**).

The structures were solved *via* intrinsic phasing and refined by least-squares refinement on  $F^2$  followed by difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic displacement parameters. Unless otherwise specified, all hydrogen atoms were included in the final structure-factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The coordinates of the H atoms bound to N atoms in structures **I**, **II**, and **III** were refined freely with a distance restraint for each N-H distance.

In structure **IV**, there were three partially occupied solvent molecules of dichloromethane and one partially occupied molecule of acetonitrile present in the asymmetric unit. A significant amount of time was invested in identifying and refining the disordered molecules. Bond-length restraints were applied to model the molecules, but the resulting isotropic displacement coefficients suggested the molecules were mobile. In addition, the refinement was computationally unstable. The SQUEEZE option (Spek, 2015) of the PLATON software suite (Spek, 2020) was used to correct the diffraction data for diffuse scattering effects and to identify the solvent molecule. PLATON calculated the upper limit of volume that can be occupied by the solvent in the unit cell to be 615 Å<sup>3</sup>. This solvent-accessible volume is comprised of two

**Table 3**  
Experimental details.

|                                                                                                                | I                                                                                                                                  | II                                                                                                                                 | III                                                                    | IV                                                                                              | V                                                                                                                                                                                               |
|----------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Crystal data                                                                                                   |                                                                                                                                    |                                                                                                                                    |                                                                        |                                                                                                 |                                                                                                                                                                                                 |
| Chemical formula                                                                                               | [Cu <sub>2</sub> I <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> N) <sub>2</sub> -(C <sub>5</sub> H <sub>7</sub> NOS) <sub>2</sub> ] | [Cu <sub>4</sub> I <sub>4</sub> (C <sub>2</sub> H <sub>3</sub> N) <sub>2</sub> -(C <sub>5</sub> H <sub>7</sub> NOS) <sub>2</sub> ] | [CuI(C <sub>5</sub> H <sub>7</sub> NOS)]                               | [Cu <sub>2</sub> I <sub>2</sub> (C <sub>5</sub> H <sub>7</sub> NS <sub>2</sub> ) <sub>2</sub> ] | [CuI(C <sub>8</sub> H <sub>5</sub> NS <sub>2</sub> )]                                                                                                                                           |
| <i>M<sub>r</sub></i>                                                                                           | 721.34                                                                                                                             | 1102.22                                                                                                                            | 319.62                                                                 | 671.35                                                                                          | 369.69                                                                                                                                                                                          |
| Crystal system, space group                                                                                    | Triclinic, <i>P</i> $\bar{1}$                                                                                                      | Monoclinic, <i>C</i> 2/ <i>c</i>                                                                                                   | Orthorhombic, <i>Pbcn</i>                                              | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                  | Monoclinic, <i>Cc</i>                                                                                                                                                                           |
| Temperature (K)                                                                                                | 100                                                                                                                                | 105                                                                                                                                | 100                                                                    | 100                                                                                             | 100                                                                                                                                                                                             |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)                                                                             | 8.121 (2), 8.433 (2), 9.154 (2)                                                                                                    | 14.4669 (8), 12.2157 (7), 16.9969 (11)                                                                                             | 26.982 (11), 8.195 (4), 7.351 (3)                                      | 13.2866 (9), 11.6974 (13), 14.8089 (9)                                                          | 15.174 (5), 4.1188 (16), 15.785 (6)                                                                                                                                                             |
| $\alpha$ , $\beta$ , $\gamma$ (°)                                                                              | 68.918 (12), 80.523 (12), 71.270 (9)                                                                                               | 90, 112.562 (5), 90                                                                                                                | 90, 90, 90                                                             | 90, 96.998 (6), 90                                                                              | 90, 92.98 (2), 90                                                                                                                                                                               |
| <i>V</i> (Å <sup>3</sup> )                                                                                     | 553.2 (2)                                                                                                                          | 2773.9 (3)                                                                                                                         | 1625.4 (13)                                                            | 2284.4 (3)                                                                                      | 985.2 (6)                                                                                                                                                                                       |
| <i>Z</i>                                                                                                       | 1                                                                                                                                  | 4                                                                                                                                  | 8                                                                      | 4                                                                                               | 4                                                                                                                                                                                               |
| Radiation type                                                                                                 | Mo <i>K</i> α                                                                                                                      | Cu <i>K</i> α                                                                                                                      | Cu <i>K</i> α                                                          | Cu <i>K</i> α                                                                                   | Mo <i>K</i> α                                                                                                                                                                                   |
| $\mu$ (mm <sup>-1</sup> )                                                                                      | 4.92                                                                                                                               | 39.97                                                                                                                              | 35.47                                                                  | 26.87                                                                                           | 5.72                                                                                                                                                                                            |
| Crystal size (mm)                                                                                              | 0.15 × 0.13 × 0.13                                                                                                                 | 0.1 × 0.08 × 0.04                                                                                                                  | 0.08 × 0.07 × 0.03                                                     | 0.22 × 0.13 × 0.09                                                                              | 0.30 × 0.02 × 0.01                                                                                                                                                                              |
| Data collection                                                                                                |                                                                                                                                    |                                                                                                                                    |                                                                        |                                                                                                 |                                                                                                                                                                                                 |
| Diffractometer                                                                                                 | Bruker APEXII Quazar                                                                                                               | Bruker SMART APEXII area detector                                                                                                  | Bruker SMART APEXII area detector                                      | Bruker SMART APEXII area detector                                                               | Bruker APEXII Quazar                                                                                                                                                                            |
| Absorption correction                                                                                          | Multi-scan ( <i>SADABS</i> ; Bruker, 2016)                                                                                         | Multi-scan ( <i>SADABS</i> ; Bruker, 2016)                                                                                         | Multi-scan <i>SADABS</i> ; Bruker, 2016)                               | Multi-scan ( <i>SADABS</i> ; Bruker, 2016)                                                      | Multi-scan ( <i>SADABS</i> ; Bruker, 2016)                                                                                                                                                      |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>                                                              | 0.079, 0.120                                                                                                                       | 0.042, 0.188                                                                                                                       | 0.030, 0.144                                                           | 0.009, 0.094                                                                                    | 0.322, 0.404                                                                                                                                                                                    |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 17922, 4099, 3988                                                                                                                  | 23553, 2753, 2669                                                                                                                  | 25274, 1631, 1467                                                      | 78133, 4597, 4236                                                                               | 11871, 3603, 3226                                                                                                                                                                               |
| <i>R</i> <sub>int</sub>                                                                                        | 0.021                                                                                                                              | 0.060                                                                                                                              | 0.051                                                                  | 0.063                                                                                           | 0.041                                                                                                                                                                                           |
| (sin $\theta$ /λ) <sub>max</sub> (Å <sup>-1</sup> )                                                            | 0.779                                                                                                                              | 0.622                                                                                                                              | 0.622                                                                  | 0.622                                                                                           | 0.770                                                                                                                                                                                           |
| Refinement                                                                                                     |                                                                                                                                    |                                                                                                                                    |                                                                        |                                                                                                 |                                                                                                                                                                                                 |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.012, 0.030, 1.07                                                                                                                 | 0.026, 0.063, 1.10                                                                                                                 | 0.032, 0.082, 1.07                                                     | 0.048, 0.126, 1.06                                                                              | 0.036, 0.089, 1.06                                                                                                                                                                              |
| No. of reflections                                                                                             | 4099                                                                                                                               | 2753                                                                                                                               | 1631                                                                   | 4597                                                                                            | 3603                                                                                                                                                                                            |
| No. of parameters                                                                                              | 122                                                                                                                                | 140                                                                                                                                | 94                                                                     | 181                                                                                             | 118                                                                                                                                                                                             |
| No. of restraints                                                                                              | 1                                                                                                                                  | 1                                                                                                                                  | 1                                                                      | 0                                                                                               | 2                                                                                                                                                                                               |
| H-atom treatment                                                                                               | H atoms treated by a mixture of independent and constrained refinement                                                             | H atoms treated by a mixture of independent and constrained refinement                                                             | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained                                                                   | H-atom parameters constrained                                                                                                                                                                   |
| $\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )                                                 | 0.43, -0.34                                                                                                                        | 0.84, -1.25                                                                                                                        | 1.31, -1.03                                                            | 1.58, -0.49                                                                                     | 3.17, -1.13                                                                                                                                                                                     |
| Absolute structure                                                                                             | —                                                                                                                                  | —                                                                                                                                  | —                                                                      | —                                                                                               | Flack <i>x</i> determined using 1438 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013) |
| Absolute structure parameter                                                                                   | —                                                                                                                                  | —                                                                                                                                  | —                                                                      | —                                                                                               | 0.034 (12)                                                                                                                                                                                      |

Computer programs: *APEX3* (Bruker, 2017), *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

accessible voids and is 27% of the unit-cell volume. The program calculated 155 electrons in the unit cell for the diffuse species. This corresponds to approximately one molecule of dichloromethane (42 electrons) that is 50% occupied and one molecule of acetonitrile (22 electrons) in the asymmetric unit. It is very likely that the solvent molecules are disordered over several positions. All derived results in Tables 1 and 2 are based on the known contents. No data are given for the diffusely scattering species.

Crystal data, data collection and structure refinement details are summarized in Table 3.

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## supporting information

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## Structural diversity in copper(I) iodide complexes with 6-thioxopiperidin-2-one, piperidine-2,6-dithione and isoindoline-1,3-dithione ligands

Amelia M. Wheaton, Ilia A. Guzei and John F. Berry

### Computing details

Data collection: *APEX3* (Bruker, 2017) for (I), (V); *APEX2* (Bruker, 2013) for (II), (III), (IV). Cell refinement: *APEX3* (Bruker, 2017) for (I), (V); *SAINT* (Bruker, 2013) for (II), (III), (IV). Data reduction: *APEX3* (Bruker, 2017) for (I), (V); *SAINT* (Bruker, 2013) for (II), (III), (IV). For all structures, program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### Di- $\mu$ -iodido-bis[(acetonitrile- $\kappa$ N)(6-sulfanylidene-piperidin-2-one- $\kappa$ S)copper(I)] (I)

#### Crystal data

$[\text{Cu}_2\text{I}_2(\text{C}_2\text{H}_3\text{N})_2(\text{C}_5\text{H}_7\text{NOS})_2]$

$M_r = 721.34$

Triclinic,  $P\bar{1}$

$a = 8.121$  (2) Å

$b = 8.433$  (2) Å

$c = 9.154$  (2) Å

$\alpha = 68.918$  (12)°

$\beta = 80.523$  (12)°

$\gamma = 71.270$  (9)°

$V = 553.2$  (2) Å<sup>3</sup>

$Z = 1$

$F(000) = 344$

$D_x = 2.165$  Mg m<sup>-3</sup>

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

Cell parameters from 9905 reflections

$\theta = 2.4\text{--}33.6^\circ$

$\mu = 4.92$  mm<sup>-1</sup>

$T = 100$  K

Block, yellow

$0.15 \times 0.13 \times 0.13$  mm

#### Data collection

Bruker APEXII Quazar

diffractometer

Radiation source: microfocus sealed X-ray tube,

Incoatec I $\mu$ s

Mirror optics monochromator

Detector resolution: 7.9 pixels mm<sup>-1</sup>

$0.5^\circ \omega$  and  $0.5^\circ \phi$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2016)

$T_{\min} = 0.079$ ,  $T_{\max} = 0.120$

17922 measured reflections

4099 independent reflections

3988 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 33.6^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 13$

$l = -14 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.012$

$wR(F^2) = 0.030$

$S = 1.07$

4099 reflections

122 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 0.2P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

|     | x            | y            | z            | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| I1  | 0.71563 (2)  | 0.27834 (2)  | −0.05209 (2) | 0.01894 (2)                      |
| Cu1 | 0.45123 (2)  | 0.38128 (2)  | 0.13294 (2)  | 0.01894 (3)                      |
| S1  | 0.56399 (3)  | 0.24010 (4)  | 0.37914 (3)  | 0.01986 (5)                      |
| O1  | 0.05297 (11) | 0.66482 (10) | 0.51701 (10) | 0.02183 (14)                     |
| N1  | 0.28752 (11) | 0.45357 (12) | 0.47278 (10) | 0.01722 (15)                     |
| H1  | 0.278 (2)    | 0.5149 (19)  | 0.3753 (15)  | 0.021*                           |
| N2  | 0.26648 (13) | 0.25871 (13) | 0.15713 (11) | 0.02214 (17)                     |
| C1  | 0.41889 (13) | 0.30218 (13) | 0.51318 (11) | 0.01629 (16)                     |
| C2  | 0.42947 (14) | 0.19443 (14) | 0.68381 (12) | 0.02105 (18)                     |
| H2A | 0.508966     | 0.227581     | 0.731337     | 0.025*                           |
| H2B | 0.479000     | 0.067327     | 0.694709     | 0.025*                           |
| C3  | 0.25216 (15) | 0.22197 (14) | 0.77191 (12) | 0.02196 (19)                     |
| H3A | 0.265859     | 0.157362     | 0.885379     | 0.026*                           |
| H3B | 0.176642     | 0.174405     | 0.734521     | 0.026*                           |
| C4  | 0.16790 (15) | 0.41932 (14) | 0.74515 (12) | 0.02137 (19)                     |
| H4A | 0.048628     | 0.437280     | 0.795116     | 0.026*                           |
| H4B | 0.235816     | 0.462532     | 0.795254     | 0.026*                           |
| C5  | 0.15956 (13) | 0.52448 (13) | 0.57383 (12) | 0.01738 (17)                     |
| C6  | 0.17193 (13) | 0.17425 (13) | 0.20890 (12) | 0.01823 (17)                     |
| C7  | 0.05487 (15) | 0.06411 (15) | 0.27580 (14) | 0.02279 (19)                     |
| H7A | 0.012545     | 0.043830     | 0.191652     | 0.034*                           |
| H7B | −0.044124    | 0.123970     | 0.332437     | 0.034*                           |
| H7C | 0.117167     | −0.049821    | 0.348452     | 0.034*                           |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|-----|--------------|--------------|--------------|--------------|-------------|--------------|
| I1  | 0.02097 (3)  | 0.01735 (3)  | 0.01597 (3)  | −0.00396 (2) | 0.00281 (2) | −0.00554 (2) |
| Cu1 | 0.02026 (6)  | 0.01995 (6)  | 0.01757 (6)  | −0.00817 (5) | 0.00300 (4) | −0.00688 (5) |
| S1  | 0.01667 (10) | 0.02251 (11) | 0.01925 (11) | −0.00292 (9) | 0.00063 (8) | −0.00856 (9) |
| O1  | 0.0229 (4)   | 0.0176 (3)   | 0.0234 (4)   | −0.0036 (3)  | 0.0001 (3)  | −0.0073 (3)  |
| N1  | 0.0191 (4)   | 0.0168 (4)   | 0.0141 (3)   | −0.0045 (3)  | 0.0007 (3)  | −0.0044 (3)  |
| N2  | 0.0219 (4)   | 0.0223 (4)   | 0.0229 (4)   | −0.0073 (3)  | 0.0004 (3)  | −0.0079 (3)  |
| C1  | 0.0164 (4)   | 0.0175 (4)   | 0.0165 (4)   | −0.0059 (3)  | −0.0013 (3) | −0.0062 (3)  |
| C2  | 0.0237 (5)   | 0.0204 (4)   | 0.0161 (4)   | −0.0028 (4)  | −0.0038 (3) | −0.0044 (3)  |
| C3  | 0.0292 (5)   | 0.0181 (4)   | 0.0165 (4)   | −0.0082 (4)  | 0.0017 (4)  | −0.0033 (3)  |
| C4  | 0.0270 (5)   | 0.0200 (4)   | 0.0159 (4)   | −0.0075 (4)  | 0.0037 (4)  | −0.0059 (3)  |

|    |            |            |            |             |             |             |
|----|------------|------------|------------|-------------|-------------|-------------|
| C5 | 0.0192 (4) | 0.0169 (4) | 0.0176 (4) | −0.0071 (3) | 0.0020 (3)  | −0.0071 (3) |
| C6 | 0.0180 (4) | 0.0177 (4) | 0.0183 (4) | −0.0029 (3) | −0.0013 (3) | −0.0069 (3) |
| C7 | 0.0233 (5) | 0.0219 (5) | 0.0254 (5) | −0.0108 (4) | 0.0042 (4)  | −0.0088 (4) |

*Geometric parameters (Å, °)*

|                                       |              |             |             |
|---------------------------------------|--------------|-------------|-------------|
| I1—Cu1                                | 2.6261 (6)   | C2—H2B      | 0.9900      |
| I1—Cu1 <sup>i</sup>                   | 2.6321 (7)   | C2—C3       | 1.5216 (16) |
| Cu1—Cu1 <sup>i</sup>                  | 2.7274 (6)   | C3—H3A      | 0.9900      |
| Cu1—S1                                | 2.3205 (6)   | C3—H3B      | 0.9900      |
| Cu1—N2                                | 2.0225 (10)  | C3—C4       | 1.5260 (16) |
| S1—C1                                 | 1.6607 (11)  | C4—H4A      | 0.9900      |
| O1—C5                                 | 1.2117 (13)  | C4—H4B      | 0.9900      |
| N1—H1                                 | 0.857 (12)   | C4—C5       | 1.4988 (15) |
| N1—C1                                 | 1.3493 (13)  | C6—C7       | 1.4518 (15) |
| N1—C5                                 | 1.4055 (13)  | C7—H7A      | 0.9800      |
| N2—C6                                 | 1.1446 (14)  | C7—H7B      | 0.9800      |
| C1—C2                                 | 1.4987 (15)  | C7—H7C      | 0.9800      |
| C2—H2A                                | 0.9900       |             |             |
| Cu1—I1—Cu1 <sup>i</sup>               | 62.489 (13)  | C3—C2—H2B   | 109.2       |
| I1—Cu1—I1 <sup>i</sup>                | 117.511 (13) | C2—C3—H3A   | 109.7       |
| I1 <sup>i</sup> —Cu1—Cu1 <sup>i</sup> | 58.647 (16)  | C2—C3—H3B   | 109.7       |
| I1—Cu1—Cu1 <sup>i</sup>               | 58.864 (17)  | C2—C3—C4    | 109.71 (9)  |
| S1—Cu1—I1                             | 102.61 (2)   | H3A—C3—H3B  | 108.2       |
| S1—Cu1—I1 <sup>i</sup>                | 118.719 (16) | C4—C3—H3A   | 109.7       |
| S1—Cu1—Cu1 <sup>i</sup>               | 132.375 (17) | C4—C3—H3B   | 109.7       |
| N2—Cu1—I1 <sup>i</sup>                | 105.18 (3)   | C3—C4—H4A   | 109.3       |
| N2—Cu1—I1                             | 111.38 (3)   | C3—C4—H4B   | 109.3       |
| N2—Cu1—Cu1 <sup>i</sup>               | 127.14 (3)   | H4A—C4—H4B  | 108.0       |
| N2—Cu1—S1                             | 100.19 (3)   | C5—C4—C3    | 111.49 (9)  |
| C1—S1—Cu1                             | 109.94 (4)   | C5—C4—H4A   | 109.3       |
| C1—N1—H1                              | 118.1 (10)   | C5—C4—H4B   | 109.3       |
| C1—N1—C5                              | 127.15 (9)   | O1—C5—N1    | 118.17 (9)  |
| C5—N1—H1                              | 114.7 (10)   | O1—C5—C4    | 125.23 (10) |
| C6—N2—Cu1                             | 162.96 (9)   | N1—C5—C4    | 116.60 (9)  |
| N1—C1—S1                              | 121.16 (8)   | N2—C6—C7    | 178.87 (12) |
| N1—C1—C2                              | 117.20 (9)   | C6—C7—H7A   | 109.5       |
| C2—C1—S1                              | 121.63 (8)   | C6—C7—H7B   | 109.5       |
| C1—C2—H2A                             | 109.2        | C6—C7—H7C   | 109.5       |
| C1—C2—H2B                             | 109.2        | H7A—C7—H7B  | 109.5       |
| C1—C2—C3                              | 112.14 (9)   | H7A—C7—H7C  | 109.5       |
| H2A—C2—H2B                            | 107.9        | H7B—C7—H7C  | 109.5       |
| C3—C2—H2A                             | 109.2        |             |             |
| Cu1—S1—C1—N1                          | −20.58 (9)   | C1—C2—C3—C4 | −54.31 (12) |
| Cu1—S1—C1—C2                          | 160.32 (7)   | C2—C3—C4—C5 | 54.18 (12)  |
| S1—C1—C2—C3                           | −153.63 (8)  | C3—C4—C5—O1 | 153.16 (10) |

|             |             |             |             |
|-------------|-------------|-------------|-------------|
| N1—C1—C2—C3 | 27.24 (13)  | C3—C4—C5—N1 | −27.45 (13) |
| C1—N1—C5—O1 | 178.41 (10) | C5—N1—C1—S1 | −177.90 (8) |
| C1—N1—C5—C4 | −1.02 (15)  | C5—N1—C1—C2 | 1.24 (15)   |

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

| $D-H\cdots A$                  | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------|----------|-------------|-------------|---------------|
| N1—H1 $\cdots$ I1 <sup>i</sup> | 0.86 (1) | 2.85 (1)    | 3.6980 (12) | 174 (1)       |

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

### Bis(acetonitrile- $\kappa N$ )tetra- $\mu_3$ -iodido-bis(6-sulfanylidene-piperidin-2-one- $\kappa S$ )-tetrahydro-tetracopper(I) (II)

#### Crystal data

$[\text{Cu}_4\text{I}_4(\text{C}_2\text{H}_3\text{N})_2(\text{C}_5\text{H}_7\text{NOS})_2]$

$M_r = 1102.22$

Monoclinic,  $C2/c$

$a = 14.4669$  (8)  $\text{\AA}$

$b = 12.2157$  (7)  $\text{\AA}$

$c = 16.9969$  (11)  $\text{\AA}$

$\beta = 112.562$  (5) $^\circ$

$V = 2773.9$  (3)  $\text{\AA}^3$

$Z = 4$

$F(000) = 2032$

$D_x = 2.639$   $\text{Mg m}^{-3}$

$\text{Cu K}\alpha$  radiation,  $\lambda = 1.54178$   $\text{\AA}$

Cell parameters from 9916 reflections

$\theta = 4.9\text{--}73.4^\circ$

$\mu = 39.97$   $\text{mm}^{-1}$

$T = 105$  K

Block, yellow

$0.1 \times 0.08 \times 0.04$  mm

#### Data collection

Bruker SMART APEXII area detector  
diffractometer

Radiation source: sealed X-ray tube, Siemens, K  
FFCU 2K 90

Equatorially mounted graphite monochromator

Detector resolution: 7.9 pixels  $\text{mm}^{-1}$

$0.60^\circ \omega$  and  $0.6^\circ \varphi$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2016)

$T_{\min} = 0.042$ ,  $T_{\max} = 0.188$

23553 measured reflections

2753 independent reflections

2669 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$

$\theta_{\max} = 73.4^\circ$ ,  $\theta_{\min} = 4.9^\circ$

$h = -17 \rightarrow 17$

$k = -15 \rightarrow 15$

$l = -19 \rightarrow 20$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.063$

$S = 1.10$

2753 reflections

140 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 8.1228P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.84$   $\text{e \AA}^{-3}$

$\Delta\rho_{\min} = -1.25$   $\text{e \AA}^{-3}$

#### 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 ( $\text{\AA}^2$ )*

|     | <i>x</i>    | <i>y</i>    | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| I1  | 0.60668 (2) | 0.86418 (2) | 0.17606 (2)  | 0.01452 (8)                      |
| I2  | 0.64470 (2) | 0.62302 (2) | 0.36802 (2)  | 0.01064 (8)                      |
| Cu1 | 0.56033 (4) | 0.66150 (4) | 0.20182 (3)  | 0.01367 (13)                     |
| Cu2 | 0.57587 (4) | 0.82337 (4) | 0.32174 (3)  | 0.01552 (13)                     |
| S1  | 0.60446 (7) | 0.54868 (7) | 0.11461 (5)  | 0.01569 (19)                     |
| O1  | 0.6145 (2)  | 0.2772 (2)  | 0.32682 (16) | 0.0174 (6)                       |
| N1  | 0.6055 (2)  | 0.3917 (3)  | 0.22074 (19) | 0.0126 (6)                       |
| H1  | 0.606 (4)   | 0.445 (3)   | 0.255 (2)    | 0.015*                           |
| N2  | 0.6525 (3)  | 0.9386 (3)  | 0.4015 (2)   | 0.0169 (7)                       |
| C1  | 0.6091 (3)  | 0.4194 (3)  | 0.1448 (2)   | 0.0123 (7)                       |
| C2  | 0.6188 (3)  | 0.3267 (3)  | 0.0903 (2)   | 0.0159 (8)                       |
| H2A | 0.690589    | 0.314522    | 0.102177     | 0.019*                           |
| H2B | 0.585384    | 0.347436    | 0.029590     | 0.019*                           |
| C3  | 0.5734 (3)  | 0.2208 (3)  | 0.1056 (2)   | 0.0202 (8)                       |
| H3A | 0.587416    | 0.160825    | 0.072514     | 0.024*                           |
| H3B | 0.499919    | 0.228893    | 0.086154     | 0.024*                           |
| C4  | 0.6177 (3)  | 0.1928 (3)  | 0.2001 (3)   | 0.0191 (8)                       |
| H4A | 0.581117    | 0.129536    | 0.210478     | 0.023*                           |
| H4B | 0.688502    | 0.170761    | 0.216276     | 0.023*                           |
| C5  | 0.6128 (3)  | 0.2859 (3)  | 0.2552 (2)   | 0.0132 (7)                       |
| C6  | 0.6848 (3)  | 1.0148 (3)  | 0.4409 (2)   | 0.0148 (7)                       |
| C7  | 0.7242 (3)  | 1.1137 (3)  | 0.4894 (2)   | 0.0180 (8)                       |
| H7A | 0.709649    | 1.176523    | 0.450663     | 0.027*                           |
| H7B | 0.796763    | 1.106656    | 0.519796     | 0.027*                           |
| H7C | 0.692732    | 1.124854    | 0.530632     | 0.027*                           |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$      |
|-----|--------------|--------------|--------------|--------------|--------------|---------------|
| I1  | 0.01753 (14) | 0.01161 (13) | 0.01566 (13) | −0.00092 (8) | 0.00776 (10) | 0.00418 (7)   |
| I2  | 0.01430 (13) | 0.01007 (13) | 0.00576 (12) | 0.00111 (7)  | 0.00185 (9)  | 0.00183 (7)   |
| Cu1 | 0.0197 (3)   | 0.0114 (3)   | 0.0103 (2)   | 0.0035 (2)   | 0.0062 (2)   | 0.00158 (19)  |
| Cu2 | 0.0167 (3)   | 0.0119 (3)   | 0.0134 (2)   | −0.0027 (2)  | 0.0007 (2)   | −0.00354 (19) |
| S1  | 0.0246 (5)   | 0.0150 (4)   | 0.0113 (4)   | 0.0070 (3)   | 0.0112 (4)   | 0.0050 (3)    |
| O1  | 0.0214 (14)  | 0.0183 (13)  | 0.0118 (11)  | −0.0011 (11) | 0.0056 (11)  | 0.0035 (10)   |
| N1  | 0.0198 (17)  | 0.0107 (14)  | 0.0071 (13)  | 0.0003 (12)  | 0.0049 (12)  | −0.0007 (11)  |
| N2  | 0.0173 (16)  | 0.0157 (16)  | 0.0139 (14)  | −0.0037 (13) | 0.0019 (12)  | −0.0027 (13)  |
| C1  | 0.0123 (17)  | 0.0152 (18)  | 0.0078 (14)  | 0.0021 (13)  | 0.0021 (13)  | 0.0000 (13)   |
| C2  | 0.0216 (19)  | 0.0150 (18)  | 0.0118 (15)  | 0.0062 (15)  | 0.0071 (15)  | −0.0020 (13)  |
| C3  | 0.023 (2)    | 0.019 (2)    | 0.0190 (18)  | −0.0007 (16) | 0.0083 (16)  | −0.0087 (15)  |
| C4  | 0.027 (2)    | 0.0127 (18)  | 0.0225 (18)  | −0.0004 (15) | 0.0145 (17)  | −0.0027 (15)  |
| C5  | 0.0111 (17)  | 0.0135 (17)  | 0.0132 (16)  | −0.0019 (13) | 0.0029 (14)  | −0.0001 (13)  |
| C6  | 0.0169 (18)  | 0.0143 (18)  | 0.0091 (14)  | 0.0025 (14)  | 0.0003 (14)  | 0.0011 (14)   |
| C7  | 0.029 (2)    | 0.0071 (17)  | 0.0103 (16)  | −0.0010 (15) | −0.0003 (15) | −0.0020 (13)  |

*Geometric parameters (Å, °)*

|                                        |              |                         |             |
|----------------------------------------|--------------|-------------------------|-------------|
| I1—Cu1                                 | 2.6451 (6)   | N1—C5                   | 1.405 (5)   |
| I1—Cu2 <sup>i</sup>                    | 2.7017 (7)   | N2—C6                   | 1.137 (5)   |
| I1—Cu2                                 | 2.7250 (6)   | C1—C2                   | 1.504 (5)   |
| I2—Cu1                                 | 2.6542 (6)   | C2—H2A                  | 0.9900      |
| I2—Cu1 <sup>i</sup>                    | 2.7796 (6)   | C2—H2B                  | 0.9900      |
| I2—Cu2                                 | 2.6456 (6)   | C2—C3                   | 1.518 (6)   |
| Cu1—Cu1 <sup>i</sup>                   | 2.8150 (11)  | C3—H3A                  | 0.9900      |
| Cu1—Cu2                                | 2.7864 (8)   | C3—H3B                  | 0.9900      |
| Cu1—Cu2 <sup>i</sup>                   | 2.7106 (8)   | C3—C4                   | 1.523 (5)   |
| Cu2—Cu2 <sup>i</sup>                   | 2.5803 (10)  | C4—H4A                  | 0.9900      |
| Cu1—S1                                 | 2.2869 (10)  | C4—H4B                  | 0.9900      |
| Cu2—N2                                 | 1.974 (3)    | C4—C5                   | 1.492 (5)   |
| S1—C1                                  | 1.654 (4)    | C6—C7                   | 1.451 (5)   |
| O1—C5                                  | 1.213 (5)    | C7—H7A                  | 0.9800      |
| N1—H1                                  | 0.870 (19)   | C7—H7B                  | 0.9800      |
| N1—C1                                  | 1.354 (5)    | C7—H7C                  | 0.9800      |
|                                        |              |                         |             |
| Cu1—I1—Cu2 <sup>i</sup>                | 60.911 (18)  | N2—Cu2—I1 <sup>i</sup>  | 98.80 (11)  |
| Cu1—I1—Cu2                             | 62.493 (17)  | N2—Cu2—I1               | 104.44 (10) |
| Cu2 <sup>i</sup> —I1—Cu2               | 56.78 (2)    | N2—Cu2—I2               | 114.05 (10) |
| Cu1—I2—Cu1 <sup>i</sup>                | 62.35 (2)    | N2—Cu2—Cu1              | 151.07 (11) |
| Cu2—I2—Cu1                             | 63.439 (17)  | N2—Cu2—Cu1 <sup>i</sup> | 143.75 (11) |
| Cu2—I2—Cu1 <sup>i</sup>                | 59.892 (17)  | N2—Cu2—Cu2 <sup>i</sup> | 134.36 (10) |
| I1—Cu1—I2                              | 107.43 (2)   | C1—S1—Cu1               | 111.24 (13) |
| I1—Cu1—I2 <sup>i</sup>                 | 112.60 (2)   | C1—N1—H1                | 117 (3)     |
| I1—Cu1—Cu1 <sup>i</sup>                | 110.454 (13) | C1—N1—C5                | 127.1 (3)   |
| I1—Cu1—Cu2 <sup>i</sup>                | 60.576 (18)  | C5—N1—H1                | 115 (3)     |
| I1—Cu1—Cu2                             | 60.157 (18)  | C6—N2—Cu2               | 169.7 (3)   |
| I2—Cu1—I2 <sup>i</sup>                 | 113.84 (2)   | N1—C1—S1                | 121.6 (3)   |
| I2—Cu1—Cu1 <sup>i</sup>                | 61.007 (19)  | N1—C1—C2                | 116.4 (3)   |
| I2 <sup>i</sup> —Cu1—Cu1 <sup>i</sup>  | 56.64 (2)    | C2—C1—S1                | 122.0 (3)   |
| I2 <sup>i</sup> —Cu1—Cu2               | 101.87 (2)   | C1—C2—H2A               | 109.0       |
| I2—Cu1—Cu2 <sup>i</sup>                | 107.32 (2)   | C1—C2—H2B               | 109.0       |
| I2—Cu1—Cu2                             | 58.129 (16)  | C1—C2—C3                | 112.8 (3)   |
| Cu2 <sup>i</sup> —Cu1—I2 <sup>i</sup>  | 57.602 (18)  | H2A—C2—H2B              | 107.8       |
| Cu2 <sup>i</sup> —Cu1—Cu1 <sup>i</sup> | 60.53 (2)    | C3—C2—H2A               | 109.0       |
| Cu2—Cu1—Cu1 <sup>i</sup>               | 57.881 (18)  | C3—C2—H2B               | 109.0       |
| Cu2 <sup>i</sup> —Cu1—Cu2              | 55.97 (2)    | C2—C3—H3A               | 109.7       |
| S1—Cu1—I1                              | 107.77 (3)   | C2—C3—H3B               | 109.7       |
| S1—Cu1—I2 <sup>i</sup>                 | 97.98 (3)    | C2—C3—C4                | 109.7 (3)   |
| S1—Cu1—I2                              | 117.03 (3)   | H3A—C3—H3B              | 108.2       |
| S1—Cu1—Cu1 <sup>i</sup>                | 140.07 (3)   | C4—C3—H3A               | 109.7       |
| S1—Cu1—Cu2                             | 159.65 (4)   | C4—C3—H3B               | 109.7       |
| S1—Cu1—Cu2 <sup>i</sup>                | 135.38 (3)   | C3—C4—H4A               | 109.0       |
| I1 <sup>i</sup> —Cu2—I1                | 118.71 (2)   | C3—C4—H4B               | 109.0       |
| I1 <sup>i</sup> —Cu2—Cu1 <sup>i</sup>  | 58.512 (18)  | H4A—C4—H4B              | 107.8       |

|                                        |              |             |            |
|----------------------------------------|--------------|-------------|------------|
| I1 <sup>i</sup> —Cu2—Cu1               | 109.64 (2)   | C5—C4—C3    | 112.9 (3)  |
| I1—Cu2—Cu1                             | 57.350 (16)  | C5—C4—H4A   | 109.0      |
| I2—Cu2—I1 <sup>i</sup>                 | 115.15 (2)   | C5—C4—H4B   | 109.0      |
| I2—Cu2—I1                              | 105.38 (2)   | O1—C5—N1    | 117.9 (3)  |
| I2—Cu2—Cu1 <sup>i</sup>                | 62.509 (18)  | O1—C5—C4    | 125.1 (3)  |
| I2—Cu2—Cu1                             | 58.432 (17)  | N1—C5—C4    | 117.0 (3)  |
| Cu1 <sup>i</sup> —Cu2—I1               | 111.24 (2)   | N2—C6—C7    | 178.5 (4)  |
| Cu1 <sup>i</sup> —Cu2—Cu1              | 61.59 (3)    | C6—C7—H7A   | 109.5      |
| Cu2 <sup>i</sup> —Cu2—I1               | 61.16 (2)    | C6—C7—H7B   | 109.5      |
| Cu2 <sup>i</sup> —Cu2—I1 <sup>i</sup>  | 62.06 (2)    | C6—C7—H7C   | 109.5      |
| Cu2 <sup>i</sup> —Cu2—I2               | 111.572 (12) | H7A—C7—H7B  | 109.5      |
| Cu2 <sup>i</sup> —Cu2—Cu1              | 60.528 (19)  | H7A—C7—H7C  | 109.5      |
| Cu2 <sup>i</sup> —Cu2—Cu1 <sup>i</sup> | 63.50 (2)    | H7B—C7—H7C  | 109.5      |
| <hr/>                                  |              |             |            |
| Cu1—S1—C1—N1                           | −11.4 (4)    | C1—C2—C3—C4 | −53.9 (4)  |
| Cu1—S1—C1—C2                           | 169.3 (3)    | C2—C3—C4—C5 | 51.0 (5)   |
| S1—C1—C2—C3                            | −152.4 (3)   | C3—C4—C5—O1 | 156.9 (4)  |
| N1—C1—C2—C3                            | 28.3 (5)     | C3—C4—C5—N1 | −22.9 (5)  |
| C1—N1—C5—O1                            | 175.3 (4)    | C5—N1—C1—S1 | −177.2 (3) |
| C1—N1—C5—C4                            | −4.9 (6)     | C5—N1—C1—C2 | 2.1 (6)    |

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

| $D-H\cdots A$     | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------|----------|-------------|-------------|---------------|
| N1—H1 $\cdots$ I2 | 0.87 (2) | 2.81 (2)    | 3.672 (3)   | 170 (4)       |

#### catena-Poly[[ $(\mu$ -6-sulfanylidene-piperidin-2-one- $\kappa^2 O:S$ )copper(I)]- $\mu_3$ -iodido] (III)

##### Crystal data

[CuI(C<sub>5</sub>H<sub>7</sub>NOS)]  
 $M_r = 319.62$   
 Orthorhombic, *Pbcn*  
 $a = 26.982$  (11)  $\text{\AA}$   
 $b = 8.195$  (4)  $\text{\AA}$   
 $c = 7.351$  (3)  $\text{\AA}$   
 $V = 1625.4$  (13)  $\text{\AA}^3$   
 $Z = 8$   
 $F(000) = 1200$

$D_x = 2.612$  Mg m<sup>−3</sup>  
 Cu  $K\alpha$  radiation,  $\lambda = 1.54178$   $\text{\AA}$   
 Cell parameters from 6676 reflections  
 $\theta = 3.3\text{--}73.1^\circ$   
 $\mu = 35.47$  mm<sup>−1</sup>  
 $T = 100$  K  
 Plate, orange  
 $0.08 \times 0.07 \times 0.03$  mm

##### Data collection

Bruker SMART APEXII area detector  
 diffractometer  
 Radiation source: sealed X-ray tube, Siemens, K  
 FFCU 2K 90  
 Equatorially mounted graphite monochromator  
 Detector resolution: 7.9 pixels mm<sup>−1</sup>  
 $0.60^\circ \omega$  and  $0.6^\circ \varphi$  scans  
 Absorption correction: multi-scan  
 SADABS; Bruker, 2016)

$T_{\min} = 0.030$ ,  $T_{\max} = 0.144$   
 25274 measured reflections  
 1631 independent reflections  
 1467 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$   
 $\theta_{\max} = 73.6^\circ$ ,  $\theta_{\min} = 3.3^\circ$   
 $h = -32 \rightarrow 33$   
 $k = -10 \rightarrow 9$   
 $l = -9 \rightarrow 9$

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$  $wR(F^2) = 0.082$  $S = 1.07$ 

1631 reflections

94 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 1.1889P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 1.31 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -1.03 \text{ e } \text{\AA}^{-3}$ *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 ( $\text{\AA}^2$ )*

|     | <i>x</i>     | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| I1  | 0.23415 (2)  | 0.59898 (3)  | 0.50901 (3)  | 0.02390 (13)                     |
| Cu1 | 0.28100 (2)  | 0.62683 (8)  | 0.82066 (9)  | 0.02635 (18)                     |
| S1  | 0.36555 (4)  | 0.63113 (12) | 0.83026 (14) | 0.0266 (2)                       |
| O1  | 0.50567 (13) | 0.2890 (4)   | 0.9865 (4)   | 0.0346 (8)                       |
| N1  | 0.43783 (13) | 0.4297 (5)   | 0.9030 (5)   | 0.0274 (8)                       |
| H1  | 0.4550 (18)  | 0.516 (4)    | 0.923 (7)    | 0.033*                           |
| C1  | 0.38916 (15) | 0.4443 (5)   | 0.8540 (6)   | 0.0253 (8)                       |
| C2  | 0.35970 (15) | 0.2932 (5)   | 0.8285 (6)   | 0.0269 (8)                       |
| H2A | 0.334849     | 0.311483     | 0.731519     | 0.032*                           |
| H2B | 0.341637     | 0.268491     | 0.942412     | 0.032*                           |
| C3  | 0.39185 (16) | 0.1470 (5)   | 0.7775 (7)   | 0.0303 (9)                       |
| H3A | 0.405740     | 0.162739     | 0.654072     | 0.036*                           |
| H3B | 0.371432     | 0.046611     | 0.776524     | 0.036*                           |
| C4  | 0.43403 (17) | 0.1289 (6)   | 0.9153 (7)   | 0.0333 (10)                      |
| H4A | 0.420142     | 0.095872     | 1.034455     | 0.040*                           |
| H4B | 0.456863     | 0.041794     | 0.874268     | 0.040*                           |
| C5  | 0.46238 (17) | 0.2851 (6)   | 0.9374 (6)   | 0.0299 (9)                       |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$     | $U^{22}$    | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|--------------|-------------|--------------|--------------|--------------|--------------|
| I1  | 0.02516 (19) | 0.0217 (2)  | 0.02479 (19) | 0.00135 (8)  | 0.00003 (9)  | −0.00010 (9) |
| Cu1 | 0.0258 (3)   | 0.0243 (3)  | 0.0290 (4)   | 0.0002 (2)   | −0.0002 (2)  | 0.0001 (3)   |
| S1  | 0.0245 (5)   | 0.0238 (5)  | 0.0315 (5)   | 0.0009 (4)   | −0.0001 (4)  | −0.0002 (4)  |
| O1  | 0.0273 (16)  | 0.0285 (16) | 0.048 (2)    | 0.0009 (14)  | −0.0039 (13) | −0.0007 (14) |
| N1  | 0.0253 (18)  | 0.0211 (17) | 0.036 (2)    | −0.0028 (13) | 0.0010 (15)  | −0.0012 (15) |
| C1  | 0.0257 (19)  | 0.025 (2)   | 0.0252 (19)  | 0.0017 (16)  | 0.0007 (16)  | −0.0006 (17) |
| C2  | 0.0245 (19)  | 0.025 (2)   | 0.031 (2)    | −0.0007 (16) | 0.0000 (17)  | −0.0015 (17) |
| C3  | 0.029 (2)    | 0.023 (2)   | 0.039 (2)    | −0.0018 (16) | 0.0003 (18)  | −0.0042 (19) |
| C4  | 0.029 (2)    | 0.025 (2)   | 0.046 (3)    | −0.0004 (18) | −0.001 (2)   | 0.001 (2)    |

|    |           |           |           |             |             |             |
|----|-----------|-----------|-----------|-------------|-------------|-------------|
| C5 | 0.028 (2) | 0.028 (2) | 0.034 (2) | 0.0032 (17) | 0.0023 (17) | 0.0001 (19) |
|----|-----------|-----------|-----------|-------------|-------------|-------------|

*Geometric parameters (Å, °)*

|                                         |             |             |            |
|-----------------------------------------|-------------|-------------|------------|
| I1—Cu1                                  | 2.6264 (11) | C2—H2A      | 0.9900     |
| I1—Cu1 <sup>i</sup>                     | 2.6709 (12) | C2—H2B      | 0.9900     |
| I1—Cu1 <sup>ii</sup>                    | 2.6342 (10) | C2—C3       | 1.526 (6)  |
| Cu1—S1                                  | 2.2827 (15) | C3—H3A      | 0.9900     |
| S1—C1                                   | 1.668 (4)   | C3—H3B      | 0.9900     |
| O1—C5                                   | 1.223 (6)   | C3—C4       | 1.531 (6)  |
| N1—H1                                   | 0.86 (2)    | C4—H4A      | 0.9900     |
| N1—C1                                   | 1.367 (6)   | C4—H4B      | 0.9900     |
| N1—C5                                   | 1.381 (6)   | C4—C5       | 1.500 (6)  |
| C1—C2                                   | 1.483 (6)   |             |            |
|                                         |             |             |            |
| Cu1—I1—Cu1 <sup>ii</sup>                | 106.77 (3)  | H2A—C2—H2B  | 107.8      |
| Cu1—I1—Cu1 <sup>i</sup>                 | 116.92 (2)  | C3—C2—H2A   | 109.1      |
| Cu1 <sup>ii</sup> —I1—Cu1 <sup>i</sup>  | 113.08 (4)  | C3—C2—H2B   | 109.1      |
| I1 <sup>iii</sup> —Cu1—I1 <sup>iv</sup> | 104.19 (4)  | C2—C3—H3A   | 109.7      |
| I1—Cu1—I1 <sup>iv</sup>                 | 116.85 (3)  | C2—C3—H3B   | 109.7      |
| I1—Cu1—I1 <sup>iii</sup>                | 99.58 (3)   | C2—C3—C4    | 109.6 (4)  |
| S1—Cu1—I1 <sup>iv</sup>                 | 97.12 (4)   | H3A—C3—H3B  | 108.2      |
| S1—Cu1—I1                               | 120.62 (4)  | C4—C3—H3A   | 109.7      |
| S1—Cu1—I1 <sup>iii</sup>                | 118.31 (4)  | C4—C3—H3B   | 109.7      |
| C1—S1—Cu1                               | 111.76 (15) | C3—C4—H4A   | 109.3      |
| C1—N1—H1                                | 120 (4)     | C3—C4—H4B   | 109.3      |
| C1—N1—C5                                | 125.7 (4)   | H4A—C4—H4B  | 108.0      |
| C5—N1—H1                                | 115 (4)     | C5—C4—C3    | 111.6 (4)  |
| N1—C1—S1                                | 118.4 (3)   | C5—C4—H4A   | 109.3      |
| N1—C1—C2                                | 118.3 (4)   | C5—C4—H4B   | 109.3      |
| C2—C1—S1                                | 123.3 (3)   | O1—C5—N1    | 119.3 (4)  |
| C1—C2—H2A                               | 109.1       | O1—C5—C4    | 122.8 (4)  |
| C1—C2—H2B                               | 109.1       | N1—C5—C4    | 117.9 (4)  |
| C1—C2—C3                                | 112.5 (3)   |             |            |
|                                         |             |             |            |
| Cu1—S1—C1—N1                            | −165.4 (3)  | C1—C2—C3—C4 | 52.5 (5)   |
| Cu1—S1—C1—C2                            | 13.3 (4)    | C2—C3—C4—C5 | −52.7 (5)  |
| S1—C1—C2—C3                             | 155.5 (3)   | C3—C4—C5—O1 | −154.2 (5) |
| N1—C1—C2—C3                             | −25.9 (5)   | C3—C4—C5—N1 | 26.9 (6)   |
| C1—N1—C5—O1                             | −177.4 (4)  | C5—N1—C1—S1 | 176.5 (4)  |
| C1—N1—C5—C4                             | 1.5 (7)     | C5—N1—C1—C2 | −2.2 (7)   |

Symmetry codes: (i)  $-x+1/2, -y+3/2, z-1/2$ ; (ii)  $x, -y+1, z-1/2$ ; (iii)  $x, -y+1, z+1/2$ ; (iv)  $-x+1/2, -y+3/2, z+1/2$ .*Hydrogen-bond geometry (Å, °)*

|               |       |             |             |               |
|---------------|-------|-------------|-------------|---------------|
| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------|-------|-------------|-------------|---------------|

|                         |          |          |           |         |
|-------------------------|----------|----------|-----------|---------|
| N1—H1...O1 <sup>v</sup> | 0.86 (2) | 2.03 (2) | 2.881 (5) | 171 (5) |
|-------------------------|----------|----------|-----------|---------|

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

### Poly[[[(piperidine-2,6-dithione- $\kappa$ S)copper(I)]- $\mu_3$ -iodido] (IV)

#### Crystal data

[Cu<sub>2</sub>I<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>NS<sub>2</sub>)<sub>2</sub>]

$M_r = 671.35$

Monoclinic,  $P2_1/c$

$a = 13.2866$  (9) Å

$b = 11.6974$  (13) Å

$c = 14.8089$  (9) Å

$\beta = 96.998$  (6)°

$V = 2284.4$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 1264$

$D_x = 1.952$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å

Cell parameters from 9761 reflections

$\theta = 3.4$ – $73.6^\circ$

$\mu = 26.87$  mm<sup>-1</sup>

$T = 100$  K

Block, red

$0.22 \times 0.13 \times 0.09$  mm

#### Data collection

Bruker SMART APEXII area detector  
diffractometer

Radiation source: sealed X-ray tube, Siemens, K  
FFCU 2K 90

Equatorially mounted graphite monochromator

Detector resolution: 7.9 pixels mm<sup>-1</sup>

$0.60^\circ$   $\omega$  and  $0.6^\circ$   $\varphi$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2016)

$T_{\min} = 0.009$ ,  $T_{\max} = 0.094$

78133 measured reflections

4597 independent reflections

4236 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$

$\theta_{\max} = 73.6^\circ$ ,  $\theta_{\min} = 3.4^\circ$

$h = -16 \rightarrow 16$

$k = -14 \rightarrow 14$

$l = -18 \rightarrow 18$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.126$

$S = 1.06$

4597 reflections

181 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 0.866P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.58$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.48$  e Å<sup>-3</sup>

#### 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 (Å<sup>2</sup>)

|     | <i>x</i>     | <i>y</i>     | <i>z</i>    | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| I2  | 0.55860 (2)  | 0.62760 (3)  | 0.40198 (2) | 0.04041 (13)                     |
| I1  | -0.04785 (2) | 0.16932 (3)  | 0.55075 (2) | 0.04179 (13)                     |
| Cu1 | 0.09352 (5)  | 0.01033 (6)  | 0.55762 (5) | 0.03868 (18)                     |
| Cu2 | 0.50067 (5)  | 0.41451 (7)  | 0.43516 (5) | 0.04040 (19)                     |
| S4  | 0.88076 (9)  | 0.04448 (10) | 0.29165 (8) | 0.0381 (3)                       |
| S2  | 0.38476 (10) | 0.38690 (11) | 0.31034 (9) | 0.0419 (3)                       |

|     |              |              |             |             |
|-----|--------------|--------------|-------------|-------------|
| S3  | 0.64474 (10) | 0.30477 (12) | 0.45389 (8) | 0.0444 (3)  |
| S1  | 0.24194 (9)  | 0.09681 (11) | 0.52729 (8) | 0.0410 (3)  |
| N1  | 0.2946 (3)   | 0.2359 (4)   | 0.4050 (3)  | 0.0400 (9)  |
| H1  | 0.341595     | 0.255812     | 0.449306    | 0.048*      |
| N2  | 0.7560 (3)   | 0.1895 (4)   | 0.3534 (3)  | 0.0393 (9)  |
| H2  | 0.784079     | 0.164625     | 0.406656    | 0.047*      |
| C6  | 0.6808 (4)   | 0.2704 (4)   | 0.3544 (3)  | 0.0392 (10) |
| C1  | 0.2258 (4)   | 0.1562 (5)   | 0.4253 (3)  | 0.0399 (10) |
| C10 | 0.7913 (4)   | 0.1441 (4)   | 0.2793 (4)  | 0.0373 (10) |
| C5  | 0.2980 (4)   | 0.2881 (4)   | 0.3228 (4)  | 0.0400 (10) |
| C2  | 0.1396 (4)   | 0.1307 (5)   | 0.3541 (4)  | 0.0451 (12) |
| H2A | 0.077033     | 0.121868     | 0.383553    | 0.054*      |
| H2B | 0.152702     | 0.056988     | 0.324839    | 0.054*      |
| C9  | 0.7453 (4)   | 0.1855 (5)   | 0.1882 (3)  | 0.0414 (11) |
| H9A | 0.687396     | 0.135704     | 0.165575    | 0.050*      |
| H9B | 0.796127     | 0.180538     | 0.144760    | 0.050*      |
| C7  | 0.6364 (5)   | 0.3190 (5)   | 0.2646 (4)  | 0.0473 (12) |
| H7A | 0.620041     | 0.400624     | 0.272580    | 0.057*      |
| H7B | 0.572524     | 0.278409     | 0.243395    | 0.057*      |
| C4  | 0.2216 (4)   | 0.2518 (5)   | 0.2464 (4)  | 0.0449 (11) |
| H4A | 0.247023     | 0.184112     | 0.216075    | 0.054*      |
| H4B | 0.211015     | 0.314198     | 0.200990    | 0.054*      |
| C8  | 0.7087 (5)   | 0.3083 (5)   | 0.1928 (4)  | 0.0480 (12) |
| H8A | 0.673595     | 0.331533     | 0.132807    | 0.058*      |
| H8B | 0.767460     | 0.359753     | 0.208203    | 0.058*      |
| C3  | 0.1218 (4)   | 0.2229 (5)   | 0.2805 (4)  | 0.0474 (12) |
| H3A | 0.072927     | 0.194853     | 0.229493    | 0.057*      |
| H3B | 0.092969     | 0.292195     | 0.305907    | 0.057*      |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$   | $U^{22}$   | $U^{33}$    | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|------------|------------|-------------|---------------|--------------|---------------|
| I2  | 0.0431 (2) | 0.0411 (2) | 0.0377 (2)  | −0.00315 (12) | 0.00764 (14) | 0.00019 (12)  |
| I1  | 0.0442 (2) | 0.0404 (2) | 0.0395 (2)  | 0.00544 (12)  | 0.00003 (14) | −0.00445 (12) |
| Cu1 | 0.0398 (4) | 0.0393 (4) | 0.0368 (4)  | 0.0010 (3)    | 0.0043 (3)   | 0.0020 (3)    |
| Cu2 | 0.0397 (4) | 0.0416 (4) | 0.0404 (4)  | 0.0001 (3)    | 0.0066 (3)   | −0.0006 (3)   |
| S4  | 0.0389 (6) | 0.0400 (6) | 0.0356 (5)  | 0.0026 (4)    | 0.0055 (4)   | 0.0004 (5)    |
| S2  | 0.0425 (6) | 0.0427 (6) | 0.0406 (6)  | −0.0043 (5)   | 0.0054 (5)   | 0.0042 (5)    |
| S3  | 0.0462 (7) | 0.0530 (7) | 0.0346 (6)  | 0.0106 (5)    | 0.0069 (5)   | 0.0011 (5)    |
| S1  | 0.0416 (6) | 0.0460 (7) | 0.0352 (6)  | −0.0036 (5)   | 0.0034 (5)   | 0.0044 (5)    |
| N1  | 0.039 (2)  | 0.044 (2)  | 0.0367 (19) | −0.0026 (17)  | 0.0041 (16)  | 0.0006 (18)   |
| N2  | 0.039 (2)  | 0.044 (2)  | 0.0346 (19) | 0.0019 (17)   | 0.0018 (16)  | 0.0039 (17)   |
| C6  | 0.041 (2)  | 0.038 (2)  | 0.038 (2)   | 0.0000 (19)   | 0.0046 (19)  | 0.003 (2)     |
| C1  | 0.041 (3)  | 0.044 (3)  | 0.035 (2)   | 0.000 (2)     | 0.004 (2)    | 0.001 (2)     |
| C10 | 0.036 (2)  | 0.037 (2)  | 0.039 (2)   | −0.0020 (18)  | 0.0048 (19)  | 0.001 (2)     |
| C5  | 0.038 (2)  | 0.042 (3)  | 0.040 (2)   | 0.001 (2)     | 0.0050 (19)  | −0.001 (2)    |
| C2  | 0.047 (3)  | 0.051 (3)  | 0.037 (3)   | −0.008 (2)    | 0.003 (2)    | 0.003 (2)     |
| C9  | 0.046 (3)  | 0.044 (3)  | 0.034 (2)   | 0.005 (2)     | 0.006 (2)    | −0.001 (2)    |

|    |           |           |           |            |           |           |
|----|-----------|-----------|-----------|------------|-----------|-----------|
| C7 | 0.055 (3) | 0.049 (3) | 0.037 (3) | 0.013 (2)  | 0.004 (2) | 0.002 (2) |
| C4 | 0.049 (3) | 0.045 (3) | 0.040 (3) | −0.005 (2) | 0.004 (2) | 0.006 (2) |
| C8 | 0.062 (3) | 0.047 (3) | 0.035 (2) | 0.012 (3)  | 0.010 (2) | 0.006 (2) |
| C3 | 0.042 (3) | 0.057 (3) | 0.042 (3) | −0.004 (2) | 0.001 (2) | 0.002 (2) |

*Geometric parameters (Å, °)*

|                                        |             |            |           |
|----------------------------------------|-------------|------------|-----------|
| I1—Cu1                                 | 2.6365 (8)  | C1—C2      | 1.490 (7) |
| I1—Cu1 <sup>i</sup>                    | 2.6687 (8)  | C10—C9     | 1.491 (7) |
| I2—Cu2                                 | 2.6719 (8)  | C5—C4      | 1.487 (7) |
| I2—Cu2 <sup>ii</sup>                   | 2.6724 (8)  | C2—H2A     | 0.9900    |
| Cu1—S4 <sup>iii</sup>                  | 2.3075 (13) | C2—H2B     | 0.9900    |
| Cu1—S1                                 | 2.3086 (14) | C2—C3      | 1.531 (8) |
| Cu2—S2                                 | 2.2802 (15) | C9—H9A     | 0.9900    |
| Cu2—S3                                 | 2.2933 (15) | C9—H9B     | 0.9900    |
| S4—C10                                 | 1.659 (5)   | C9—C8      | 1.521 (7) |
| S2—C5                                  | 1.659 (5)   | C7—H7A     | 0.9900    |
| S3—C6                                  | 1.654 (5)   | C7—H7B     | 0.9900    |
| S1—C1                                  | 1.652 (5)   | C7—C8      | 1.522 (8) |
| N1—H1                                  | 0.8800      | C4—H4A     | 0.9900    |
| N1—C1                                  | 1.365 (7)   | C4—H4B     | 0.9900    |
| N1—C5                                  | 1.367 (7)   | C4—C3      | 1.514 (8) |
| N2—H2                                  | 0.8800      | C8—H8A     | 0.9900    |
| N2—C6                                  | 1.378 (7)   | C8—H8B     | 0.9900    |
| N2—C10                                 | 1.354 (7)   | C3—H3A     | 0.9900    |
| C6—C7                                  | 1.498 (7)   | C3—H3B     | 0.9900    |
|                                        |             |            |           |
| Cu2—I2—Cu2 <sup>ii</sup>               | 62.54 (3)   | C1—C2—H2A  | 108.8     |
| Cu1—I1—Cu1 <sup>i</sup>                | 64.94 (3)   | C1—C2—H2B  | 108.8     |
| I1—Cu1—I1 <sup>i</sup>                 | 115.06 (3)  | C1—C2—C3   | 113.7 (5) |
| S4 <sup>iii</sup> —Cu1—I1              | 104.72 (4)  | H2A—C2—H2B | 107.7     |
| S4 <sup>iii</sup> —Cu1—I1 <sup>i</sup> | 111.04 (4)  | C3—C2—H2A  | 108.8     |
| S4 <sup>iii</sup> —Cu1—S1              | 106.30 (5)  | C3—C2—H2B  | 108.8     |
| S1—Cu1—I1 <sup>i</sup>                 | 111.41 (4)  | C10—C9—H9A | 109.4     |
| S1—Cu1—I1                              | 107.75 (4)  | C10—C9—H9B | 109.4     |
| I2—Cu2—I2 <sup>ii</sup>                | 117.46 (3)  | C10—C9—C8  | 111.3 (4) |
| S2—Cu2—I2 <sup>ii</sup>                | 117.47 (4)  | H9A—C9—H9B | 108.0     |
| S2—Cu2—I2                              | 99.46 (4)   | C8—C9—H9A  | 109.4     |
| S2—Cu2—S3                              | 119.35 (6)  | C8—C9—H9B  | 109.4     |
| S3—Cu2—I2 <sup>ii</sup>                | 96.95 (4)   | C6—C7—H7A  | 109.2     |
| S3—Cu2—I2                              | 106.83 (5)  | C6—C7—H7B  | 109.2     |
| C10—S4—Cu1 <sup>iii</sup>              | 108.78 (18) | C6—C7—C8   | 112.1 (5) |
| C5—S2—Cu2                              | 114.75 (19) | H7A—C7—H7B | 107.9     |
| C6—S3—Cu2                              | 110.88 (19) | C8—C7—H7A  | 109.2     |
| C1—S1—Cu1                              | 110.1 (2)   | C8—C7—H7B  | 109.2     |
| C1—N1—H1                               | 116.7       | C5—C4—H4A  | 109.5     |
| C1—N1—C5                               | 126.6 (5)   | C5—C4—H4B  | 109.5     |
| C5—N1—H1                               | 116.7       | C5—C4—C3   | 110.7 (5) |

|                               |            |              |            |
|-------------------------------|------------|--------------|------------|
| C6—N2—H2                      | 116.5      | H4A—C4—H4B   | 108.1      |
| C10—N2—H2                     | 116.5      | C3—C4—H4A    | 109.5      |
| C10—N2—C6                     | 127.0 (4)  | C3—C4—H4B    | 109.5      |
| N2—C6—S3                      | 117.7 (4)  | C9—C8—C7     | 109.9 (5)  |
| N2—C6—C7                      | 117.3 (4)  | C9—C8—H8A    | 109.7      |
| C7—C6—S3                      | 125.0 (4)  | C9—C8—H8B    | 109.7      |
| N1—C1—S1                      | 118.2 (4)  | C7—C8—H8A    | 109.7      |
| N1—C1—C2                      | 117.3 (5)  | C7—C8—H8B    | 109.7      |
| C2—C1—S1                      | 124.5 (4)  | H8A—C8—H8B   | 108.2      |
| N2—C10—S4                     | 120.0 (4)  | C2—C3—H3A    | 109.8      |
| N2—C10—C9                     | 117.5 (4)  | C2—C3—H3B    | 109.8      |
| C9—C10—S4                     | 122.5 (4)  | C4—C3—C2     | 109.2 (5)  |
| N1—C5—S2                      | 120.6 (4)  | C4—C3—H3A    | 109.8      |
| N1—C5—C4                      | 117.2 (4)  | C4—C3—H3B    | 109.8      |
| C4—C5—S2                      | 122.2 (4)  | H3A—C3—H3B   | 108.3      |
|                               |            |              |            |
| Cu1 <sup>iii</sup> —S4—C10—N2 | 8.2 (5)    | N2—C6—C7—C8  | −23.4 (7)  |
| Cu1 <sup>iii</sup> —S4—C10—C9 | −170.5 (4) | N2—C10—C9—C8 | 29.6 (7)   |
| Cu1—S1—C1—N1                  | 162.9 (4)  | C6—N2—C10—S4 | −178.4 (4) |
| Cu1—S1—C1—C2                  | −15.7 (5)  | C6—N2—C10—C9 | 0.4 (8)    |
| Cu2—S2—C5—N1                  | 4.8 (5)    | C6—C7—C8—C9  | 51.7 (7)   |
| Cu2—S2—C5—C4                  | −174.9 (4) | C1—N1—C5—S2  | 177.9 (4)  |
| Cu2—S3—C6—N2                  | −169.5 (3) | C1—N1—C5—C4  | −2.4 (8)   |
| Cu2—S3—C6—C7                  | 9.3 (5)    | C1—C2—C3—C4  | 48.8 (7)   |
| S4—C10—C9—C8                  | −151.7 (4) | C10—N2—C6—S3 | 175.3 (4)  |
| S2—C5—C4—C3                   | −145.6 (4) | C10—N2—C6—C7 | −3.7 (8)   |
| S3—C6—C7—C8                   | 157.7 (4)  | C10—C9—C8—C7 | −54.8 (6)  |
| S1—C1—C2—C3                   | 160.4 (4)  | C5—N1—C1—S1  | 175.1 (4)  |
| N1—C1—C2—C3                   | −18.2 (7)  | C5—N1—C1—C2  | −6.3 (8)   |
| N1—C5—C4—C3                   | 34.7 (7)   | C5—C4—C3—C2  | −56.3 (6)  |

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

| $D\cdots H\cdots A$             | $D\cdots H$ | $H\cdots A$ | $D\cdots A$ | $D\cdots H\cdots A$ |
|---------------------------------|-------------|-------------|-------------|---------------------|
| N1—H1 $\cdots$ I2 <sup>ii</sup> | 0.88        | 2.79        | 3.628 (4)   | 161                 |
| N2—H2 $\cdots$ I1 <sup>iv</sup> | 0.88        | 2.90        | 3.679 (4)   | 149                 |

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

#### Poly[[ $(\mu$ -isoindoline-1,3-dithione- $\kappa^2$ S:S)copper(I)]- $\mu_3$ -iodido] (V)

##### Crystal data

$[\text{CuI}(\text{C}_8\text{H}_5\text{NS}_2)]$

$M_r = 369.69$

Monoclinic,  $Cc$

$a = 15.174$  (5)  $\text{\AA}$

$b = 4.1188$  (16)  $\text{\AA}$

$c = 15.785$  (6)  $\text{\AA}$

$\beta = 92.98$  (2) $^\circ$

$V = 985.2$  (6)  $\text{\AA}^3$

$Z = 4$

$F(000) = 696$

$D_x = 2.492$   $\text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$

Cell parameters from 4507 reflections

$\theta = 2.6\text{--}31.9^\circ$

$\mu = 5.72 \text{ mm}^{-1}$   
 $T = 100 \text{ K}$

Block, black  
 $0.30 \times 0.02 \times 0.01 \text{ mm}$

#### Data collection

Bruker APEXII Quazar  
 diffractometer  
 Radiation source: microfocus sealed X-ray tube,  
 Incoatec I $\mu$ s  
 Mirror optics monochromator  
 Detector resolution:  $7.9 \text{ pixels mm}^{-1}$   
 $0.5^\circ \omega$  and  $0.5^\circ \varphi$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2016)

$T_{\min} = 0.322$ ,  $T_{\max} = 0.404$   
 11871 measured reflections  
 3603 independent reflections  
 3226 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$   
 $\theta_{\max} = 33.2^\circ$ ,  $\theta_{\min} = 2.6^\circ$   
 $h = -22 \rightarrow 22$   
 $k = -6 \rightarrow 6$   
 $l = -23 \rightarrow 23$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.089$   
 $S = 1.06$   
 3603 reflections  
 118 parameters  
 2 restraints  
 Primary atom site location: dual  
 Hydrogen site location: inferred from  
 neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 7.0163P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 3.17 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.13 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack  $x$  determined using  
 1438 quotients  $[(I^+)-(I^-)]/[(I^+)+(I^-)]$  (Parsons *et al.*, 2013)  
 Absolute structure parameter: 0.034 (12)

#### 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 ( $\text{\AA}^2$ )

|     | <i>x</i>     | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| II  | 0.68957 (2)  | 0.10931 (10) | 0.74974 (2)  | 0.01374 (11)                     |
| Cu1 | 0.59491 (6)  | 0.5992 (2)   | 0.69164 (6)  | 0.0146 (2)                       |
| S1  | 0.60747 (14) | 0.6607 (5)   | 0.54996 (12) | 0.0139 (3)                       |
| S2  | 0.46550 (14) | 0.2757 (5)   | 0.25028 (12) | 0.0146 (3)                       |
| N1  | 0.5450 (5)   | 0.4774 (16)  | 0.3969 (4)   | 0.0133 (12)                      |
| H1  | 0.587624     | 0.579000     | 0.371951     | 0.016*                           |
| C1  | 0.5382 (5)   | 0.4700 (18)  | 0.4850 (5)   | 0.0122 (13)                      |
| C2  | 0.4596 (5)   | 0.2691 (18)  | 0.4975 (5)   | 0.0124 (14)                      |
| C3  | 0.4197 (5)   | 0.1812 (19)  | 0.5712 (5)   | 0.0147 (14)                      |
| H3  | 0.442699     | 0.252848     | 0.625113     | 0.018*                           |
| C4  | 0.3448 (5)   | -0.015 (2)   | 0.5639 (5)   | 0.0148 (14)                      |
| H4  | 0.316667     | -0.082004    | 0.613403     | 0.018*                           |
| C5  | 0.3106 (5)   | -0.115 (2)   | 0.4828 (5)   | 0.0165 (15)                      |
| H5  | 0.259718     | -0.249734    | 0.478913     | 0.020*                           |
| C6  | 0.3493 (5)   | -0.0227 (18) | 0.4093 (5)   | 0.0128 (13)                      |
| H6  | 0.325668     | -0.090075    | 0.355269     | 0.015*                           |

|    |            |             |            |             |
|----|------------|-------------|------------|-------------|
| C7 | 0.4244 (5) | 0.1733 (18) | 0.4172 (5) | 0.0125 (13) |
| C8 | 0.4795 (5) | 0.3123 (19) | 0.3538 (5) | 0.0118 (13) |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$   | $U^{22}$     | $U^{33}$   | $U^{12}$    | $U^{13}$      | $U^{23}$    |
|-----|------------|--------------|------------|-------------|---------------|-------------|
| Il  | 0.0131 (2) | 0.01109 (17) | 0.0169 (2) | −0.0009 (2) | −0.00081 (15) | −0.0008 (2) |
| Cu1 | 0.0155 (5) | 0.0162 (5)   | 0.0122 (5) | −0.0008 (4) | 0.0004 (4)    | −0.0010 (4) |
| S1  | 0.0141 (9) | 0.0150 (8)   | 0.0124 (8) | 0.0001 (6)  | 0.0003 (7)    | −0.0011 (6) |
| S2  | 0.0132 (8) | 0.0185 (9)   | 0.0120 (8) | −0.0011 (7) | −0.0002 (7)   | −0.0017 (7) |
| N1  | 0.014 (3)  | 0.014 (3)    | 0.012 (3)  | 0.001 (2)   | 0.001 (2)     | 0.001 (2)   |
| C1  | 0.012 (3)  | 0.012 (3)    | 0.013 (3)  | 0.003 (2)   | 0.000 (3)     | 0.002 (3)   |
| C2  | 0.012 (4)  | 0.009 (3)    | 0.017 (3)  | 0.006 (3)   | 0.002 (3)     | 0.000 (2)   |
| C3  | 0.014 (3)  | 0.013 (3)    | 0.017 (3)  | 0.002 (3)   | 0.002 (3)     | 0.001 (3)   |
| C4  | 0.010 (3)  | 0.018 (3)    | 0.017 (4)  | 0.001 (3)   | 0.003 (3)     | 0.002 (3)   |
| C5  | 0.012 (3)  | 0.018 (4)    | 0.019 (4)  | −0.002 (3)  | −0.003 (3)    | 0.001 (3)   |
| C6  | 0.011 (3)  | 0.011 (3)    | 0.017 (3)  | 0.000 (2)   | −0.001 (3)    | 0.001 (3)   |
| C7  | 0.015 (3)  | 0.009 (3)    | 0.014 (3)  | 0.002 (2)   | 0.002 (3)     | 0.001 (2)   |
| C8  | 0.011 (3)  | 0.013 (3)    | 0.012 (3)  | 0.003 (2)   | 0.002 (3)     | 0.000 (2)   |

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

|                                         |             |          |            |
|-----------------------------------------|-------------|----------|------------|
| Il—Cu1                                  | 2.6152 (13) | C2—C7    | 1.405 (11) |
| Il—Cu1 <sup>i</sup>                     | 2.6798 (13) | C3—H3    | 0.9500     |
| Cu1—S1                                  | 2.269 (2)   | C3—C4    | 1.394 (12) |
| Cu1—S2 <sup>ii</sup>                    | 2.273 (2)   | C4—H4    | 0.9500     |
| S1—C1                                   | 1.632 (8)   | C4—C5    | 1.417 (12) |
| S2—C8                                   | 1.645 (7)   | C5—H5    | 0.9500     |
| N1—H1                                   | 0.8800      | C5—C6    | 1.380 (11) |
| N1—C1                                   | 1.400 (10)  | C6—H6    | 0.9500     |
| N1—C8                                   | 1.357 (10)  | C6—C7    | 1.396 (11) |
| C1—C2                                   | 1.473 (11)  | C7—C8    | 1.455 (11) |
| C2—C3                                   | 1.388 (11)  |          |            |
| Cu1—Il—Cu1 <sup>i</sup>                 | 102.12 (4)  | C2—C3—H3 | 120.9      |
| Il—Cu1—Il <sup>iii</sup>                | 102.12 (4)  | C2—C3—C4 | 118.1 (8)  |
| S1—Cu1—Il <sup>iii</sup>                | 100.30 (6)  | C4—C3—H3 | 120.9      |
| S1—Cu1—Il                               | 111.05 (6)  | C3—C4—H4 | 120.0      |
| S1—Cu1—S2 <sup>ii</sup>                 | 119.65 (8)  | C3—C4—C5 | 120.1 (8)  |
| S2 <sup>ii</sup> —Cu1—Il <sup>iii</sup> | 98.16 (7)   | C5—C4—H4 | 120.0      |
| S2 <sup>ii</sup> —Cu1—Il                | 120.16 (7)  | C4—C5—H5 | 119.1      |
| C1—S1—Cu1                               | 118.8 (3)   | C6—C5—C4 | 121.8 (8)  |
| C8—S2—Cu1 <sup>iv</sup>                 | 108.3 (3)   | C6—C5—H5 | 119.1      |
| C1—N1—H1                                | 123.3       | C5—C6—H6 | 121.1      |
| C8—N1—H1                                | 123.3       | C5—C6—C7 | 117.7 (7)  |
| C8—N1—C1                                | 113.3 (7)   | C7—C6—H6 | 121.1      |
| N1—C1—S1                                | 122.3 (6)   | C2—C7—C8 | 107.7 (7)  |
| N1—C1—C2                                | 104.3 (7)   | C6—C7—C2 | 120.9 (7)  |

|                             |            |             |            |
|-----------------------------|------------|-------------|------------|
| C2—C1—S1                    | 133.3 (6)  | C6—C7—C8    | 131.4 (7)  |
| C3—C2—C1                    | 130.6 (7)  | N1—C8—S2    | 126.7 (6)  |
| C3—C2—C7                    | 121.4 (7)  | N1—C8—C7    | 106.6 (6)  |
| C7—C2—C1                    | 108.0 (7)  | C7—C8—S2    | 126.7 (6)  |
| Cu1—S1—C1—N1                | −175.6 (5) | C2—C7—C8—S2 | −179.1 (6) |
| Cu1—S1—C1—C2                | 5.3 (9)    | C2—C7—C8—N1 | 1.0 (8)    |
| Cu1 <sup>iv</sup> —S2—C8—N1 | 18.3 (8)   | C3—C2—C7—C6 | −2.0 (11)  |
| Cu1 <sup>iv</sup> —S2—C8—C7 | −161.5 (6) | C3—C2—C7—C8 | 178.2 (7)  |
| S1—C1—C2—C3                 | 0.4 (13)   | C3—C4—C5—C6 | −0.2 (12)  |
| S1—C1—C2—C7                 | 178.6 (6)  | C4—C5—C6—C7 | 0.4 (12)   |
| N1—C1—C2—C3                 | −178.9 (8) | C5—C6—C7—C2 | 0.7 (11)   |
| N1—C1—C2—C7                 | −0.6 (8)   | C5—C6—C7—C8 | −179.6 (8) |
| C1—N1—C8—S2                 | 178.7 (6)  | C6—C7—C8—S2 | 1.1 (12)   |
| C1—N1—C8—C7                 | −1.5 (9)   | C6—C7—C8—N1 | −178.7 (8) |
| C1—C2—C3—C4                 | −179.8 (8) | C7—C2—C3—C4 | 2.1 (11)   |
| C1—C2—C7—C6                 | 179.5 (7)  | C8—N1—C1—S1 | −178.0 (6) |
| C1—C2—C7—C8                 | −0.2 (8)   | C8—N1—C1—C2 | 1.3 (8)    |
| C2—C3—C4—C5                 | −1.0 (12)  |             |            |

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

| $D-H\cdots A$                   | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|-------|-------------|-------------|---------------|
| N1—H1 $\cdots$ I1 <sup>iv</sup> | 0.88  | 2.84        | 3.692 (7)   | 163           |

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