Syntheses, crystal structures and Hirshfeld surface analyses of bis(2-mercaptobenzimidazole)bromo- and iodocopper(I) complexes

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The title complexes, bromidobis(2,3-dihydro-1H-1,3-benzodiazone-2-thione)copper(I), \([\text{CuBr}(\text{C}_7\text{H}_6\text{N}_2\text{S})_2]\) (1), and bis(2,3-dihydro-1H-1,3-benzodiazone-2-thione)iodidocopper(I) acetone monosolvate, \([\text{CuI}(\text{C}_7\text{H}_6\text{N}_2\text{S})_2]\)·CH₃COCH₃ (2), were prepared by the reaction of copper(I) bromide/iodide with 2-mercaptobenzimidazole. Both complexes have mononuclear structures with the copper atom coordinated by two 2-mercaptobenzimidazole molecules via their S atoms and one halide atom in an approximate trigonal–planar arrangement. In their extended structures, N—H/C1/C1/C1S hydrogen bonds and C1/C25–C25 contacts are found in both complexes; as a result of the acetone solvent molecule in (2), N—H/C1/C1/C1O contacts are also observed. Hirshfeld surface analyses were carried out to aid in the visualization of these interactions, which showed that H/C1/C1/C1H contacts contribute 34.6% for (1) and 34.1% for (2) to the overall surface, followed by contributions from H/C1/C1/S/S/C1/C1/C1H and C/C/C contacts, respectively. As expected, H/C1/C1/O/OH contacts are observed only in (2). The IR and ¹H and ¹³C NMR spectra of (1) and (2) are described.

1. Chemical context

2-Mercaptobenzimidazole (C₇H₆N₂S; bimztH₂) has many uses including as an antioxidant to prevent rubber deterioration (Moldovan & Alexandrescu, 2002), an absorbant of mercury from industrial waste water in the form of 2-mercaptobenzimidazole-clay (Manohar et al., 2002), as a modifier of electrode surfaces to increase the efficiency of electrochemical analysis (Berchmans et al., 2000), as an intermediate in the production of the anti-inflammatory drug lanzoprazole (Wongwattana, 2004) and as a Cu corrosion inhibitor (Finsgar, 2013).

The preparation of bimztH₂ involves the reaction between o-phenylenediamine and potassium ethyl xanthate in an ethanol–water mixture followed by reaction with acetic acid and water at 333–343 K (Vanallan & Deacon, 1971). The structure of bimztH₂ exhibits tautomerism between its thione and thiol forms (Rout et al., 1984) as shown in the scheme below.
We now describe the syntheses and crystal structures of bimztH₂ complexes with copper(I) halides, CuX (X = Br, I). It may be noted that the S atom of the ligand is a soft base and therefore favoured to form a coordinate bond with a soft acid such as copper(I). Hirshfeld surface analyses were performed to gain further insight into the intermolecular interactions in these structures.

### 2. Structural commentary

The mononuclear structures of [Cu(bimztH₂)₂Br] (1) and [Cu(bimztH₂)₂I]CH₂COCH₃ (2) are depicted in Fig. 1. Both complexes crystallize in the monoclinic system, space group P₂₁/c. The copper ions adopt distorted trigonal–planar coordination geometries with one Cu—X bond (X = Br, I) and two Cu—S bonds, the lengths of which lie between 2.2189 (15) and 2.5479 (7) Å, being close to those found in complexes with a trigonal–planar geometry such as [Cu₂(mimtH)₅]²⁺ (Atkinson et al., 1985) and [Cu(SC₆H₅)₃]²⁻ (Coucouvanis et al., 1980). When comparing (1) and (2), the bond angles are distorted from the ideal values of 120° with greater distortion in (2) resulting from the presence of the acetone solvent molecule and an N₄—H₄A O₁ hydrogen bond. The acetone molecules in (2) result in weaker C=S bonds as supported by IR and ¹³C NMR data (vide infra). Both complexes feature a pair of intramolecular N—H···X hydrogen bonds as listed in Tables 1 and 2 for (1) and (2), respectively.

### 3. Supramolecular features

The supramolecular assemblies in (1) and (2) (Tables 1 and 2) feature pairwise N—H···S hydrogen bonds, generating a graph-set R₂⁺(8) pattern with N₁···S₁’ = 3.384 (4) Å for (1) and N₂···S₁’ = 3.331 (4) Å for (2) [symmetry code: (i) −x + 1, −y + 1, −z + 1 for (1) and −x − 1, −y + 1, −z + 1 for (2)]. The acetone solvent molecule in (2) leads to the formation of an N₄—H₄A···O₁ hydrogen bond with N₄···O₁ = 2.840 (5) Å. The intra- and intermolecular hydrogen-bond contacts of (1) and (2) are listed in Tables 1 and 2, respectively.

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**Table 1**

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|-----|------|-------|---------|
| N₁—H₁A···S₁’  | 0.70 (4) | 2.69 (4) | 3.384 (4) | 170 (5) |
| N₂—H₂A···Br₁ | 0.82 (4) | 2.65 (4) | 3.361 (4) | 146 (4) |
| N₄—H₄A···Br₁ | 0.84 (4) | 2.54 (4) | 3.364 (4) | 166 (4) |

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

**Table 2**

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|-----|------|-------|---------|
| N₁—H₁A···I | 0.86 (2) | 2.81 (2) | 3.649 (4) | 167 (6) |
| N₂—H₂A···S₁’ | 0.86 (2) | 2.47 (2) | 3.331 (4) | 176 (6) |
| N₃—H₃A···I | 0.85 (2) | 2.91 (4) | 3.666 (3) | 148 (5) |
| N₄—H₄A···O₁ | 0.85 (2) | 2.02 (3) | 2.840 (5) | 161 (6) |

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

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**Figure 1**

The molecular structures of (1) and (2) showing xx% [please supply] displacement ellipsoids.

**Figure 2**

The intra- and intermolecular hydrogen-bonding interactions of (1).
and (2) are shown in Figs. 2 and 3, respectively. In addition, aromatic π–π stacking contacts are observed between adjacent imidazole rings (Cg1: N1/C1/N2/C7/C2 and Cg2: N3/C8/N4/C14/C9) and phenyl rings (Cg3: C2–C7 and Cg4: C9–C14) of neighbouring complex molecules. The π–π interactions in the packing of (1) occur between Cg1–Cg3 (set 1) and Cg2–Cg4 (set 2) as inter-digitated [100] stacks with a minimum centroid–centroid separation of 3.566 (3) Å (Fig. 4), while in the packing of (2) (Fig. 5), corresponding Cg2–Cg4 interactions occur, which also leads to [100] stacks [minimum centroid–centroid separation = 3.608 (3) Å].

4. Hirshfeld surface analysis

The Hirshfeld surface (HS) analyses (HS mapped over \( d_{\text{norm}} \) are shown in Fig. 6) and \( d_1 \) and \( d_2 \) fingerprint plots (Figs. 7 and 8) were generated using Crystal Explorer 17.5 (Turner et al., 2017). The red spots indicate the donors and acceptors of the hydrogen bonds, appearing close to H1A and S1 of the N1—H1A•••S1 bond for (1) and close to H2A•••S1 of the N2A—H2A•••S1 bond for (2). In addition, a red spot is found between H4A and O1 of the acetone solvent molecule for (2). The fingerprint plots for (1) show that the principal intermolecular contacts are H•••H at 34.6% (Fig. 7b), H•••S/S•••H
with a square-planar geometry [Cambridge Structural Data-Base (Groom et al., 2016) refcode GURMOV; Jolley et al., 2001]. In the case of the Co\textsuperscript{II} complex, two sulfur atoms are bonded with the metal atom in a tetrahedral coordination geometry (refcode ZOKYAZ; Ravikumar et al., 1995). Cu\textsuperscript{I} complexes with 2-mercaptobenzimidazole derivatives have been investigated as a model of copper proteins (refcodes QORGUZ, QORHAG and QORHEK; Balamurugan et al., 2001). A series of polynuclear clusters containing Ni\textsuperscript{II} and Co\textsuperscript{II} (refcodes FOPVEN, FOPVIR and FOPXOZ; Han et al., 2015) of this ligand have been synthesized and the magnetic susceptibility of an Ni\textsuperscript{II} complex (FOPVEN) has been reported. The photophysical properties of the rigid structure of a hexanuclear Cu\textsuperscript{II} complex of 2-mercaptobenzimidazole constructed by S bridges has been studied (refcode COPNUT; Singh et al., 2017).

5. Database survey

2-Mercaptobenzimidazole has been found to form a complex with Pt, the bond formation being via the sulfur atom only

6. Synthesis, crystallization and characterization

**[Cu(bimztH\textsubscript{2})\textsubscript{2}Br]** (1)

A mass of 0.19 g (1.2 mmol) of bimztH\textsubscript{2} was placed in 30 ml of acetone at 318 K and stirred until completely dissolved to form a colourless solution. CuBr (0.09 g; 0.6 mmol) was added followed by further stirring for about 15 min to obtain a yellow solution, which was refluxed for 120 min at 353 K to become turbid with a light-yellow colour and then filtered. The colourless filtrate was left at room temperature for 3 days to form transparent needles and then filtered by vacuum suction to obtain 0.16 g of (1) (58% yield, m.p. 518–523 K). Elemental analysis (%): found (calculated); C = 38.32 (37.86), H = 2.78 (2.73), N = 12.17 (12.62), S = 14.71 (14.45).

**[Cu(bimztH\textsubscript{2})\textsubscript{2}I]** CH\textsubscript{3}COCH\textsubscript{3} (2)

The same procedure for (1) was followed except that 0.060 g of CuI (1.6 mmol) replaced the CuBr and 0.21 g of colourless needles of (2) were recovered (73%, yield, m.p. 518–523 K). Elemental analysis (%); found (calculated); C = 38.32 (37.86), H = 2.78 (2.73), N = 12.17 (12.62), S = 14.71 (14.45).

**FT–IR spectra**

Suzuki (1962) proposed that features in thioamide IR spectra could be assigned to band I at 1395–1570 cm\textsuperscript{-1} arising from the N—H deformation and C—N stretching; band II at 1270–1420 cm\textsuperscript{-1} from C—N stretching, N—H deformation and C—H bending, band III at 940–1140 cm\textsuperscript{-1} from C—N and C=S stretching and band IV at 680–860 cm\textsuperscript{-1} due to C=S stretching (compare Jolley et al., 2001). Additionally, Raper et al. (1988) studied absorption bands of thioamide in the complex prepared from bimzH\textsubscript{2} and copper(II) perchlorate and found them at 1470 cm\textsuperscript{-1} (band I), 1360 cm\textsuperscript{-1} (band II), 1180 cm\textsuperscript{-1} (band III) and 740 cm\textsuperscript{-1} (band IV) compared with those of the free ligand at 1468 cm\textsuperscript{-1}, 1357 cm\textsuperscript{-1}, 1181 cm\textsuperscript{-1} and 744 + 713 cm\textsuperscript{-1}, respectively. The broad absorption band at 3155 cm\textsuperscript{-1} is due to N—H stretching, which moves to a higher wavenumber and splits into two upon complexation.

For all our complexes, the FT–IR spectrum indicates the shift of bands I and II to a higher wavenumber, similar to the behaviour of N—H stretching due to the coordination through the sulfur atom and resulting charge transfer from N to S.
which makes the N−H and C−N bonds stronger (Aslanidis et al., 2002). Band III of thioamide for all complexes shifts to a lower wavenumber but this is hard to quantify because this area also covers C−N stretching. Band IV for C=S stretching changes significantly from 744 and 713 cm⁻¹ in the free ligand to 734 cm⁻¹ in the complex, reflecting copper–sulfur coordination. A change also occurs for the C−S bending mode at 602 cm⁻¹ of C−S bending to lower wavenumber, corresponding with previous work (Raper et al., 1988). In the case of [Cu(bimztH₂)₂I]CH₃COCH₃, the absorption bands at 1688 cm⁻¹ in the free ligand

### Table 3
IR peak assignments (cm⁻¹) for the bimztH₂ ligand and (1) and (2).

| Compound   | v(N−H) | Thioamide band I | Thioamide band II | Thioamide band III | Thioamide band IV | δ (C=S) |
|------------|--------|------------------|------------------|--------------------|-------------------|---------|
| bimztH₂    | 3155   | 1468             | 1357             | 1180               | 744, 713          | 602     |
| (1)        | 3201, 3383 | 1470           | 1360             | 1180               | 734               | 598     |
| (2)        | 3202, 3385 | 1470           | 1361             | 1175               | 734               | 598     |

### Table 4
¹H NMR chemical shifts (p.p.m.) of the bimztH₂ ligand, (1) and (2).

| Compound   | H₄, H₇ | H₅, H₆ | N−H   |
|------------|--------|--------|-------|
| bimztH₂    | 7.49 (4H, m) | 7.49 (4H, m) | 13.28 (br, s) |
| (1)        | 7.26 (2H, dd, J = 6.3 Hz) | 7.19 (2H, dd, J = 5.5 Hz) | 12.87 (br, s) |
| (2)        | 7.58 (2H, s)       | 7.58 (2H, s)       | 13.57 (br, s) |

### Table 5
¹³C NMR chemical shifts (p.p.m.) of the bimztH₂ ligand and (1) and (2).

| Compound   | C₂ (C=S) | C₄,7 (CH) | C₅,6 (CH) | C₈,9 (C) |
|------------|----------|----------|----------|---------|
| bimztH₂    | 168.34   | 109.75   | 122.59   | 132.48  |
| (1)        | 165.11   | 110.35   | 123.06   | 132.06  |
| (2)        | 164.10   | 110.65   | 123.29   | 131.96  |

Experimental details.

| Crystal data | Chemical formula | Mᵣ | Crystal system, space group | β (°) | V (Å³) | Z | Radiation type | µ (mm⁻¹) | Crystal size (mm) |
|--------------|------------------|-----|----------------------------|-------|--------|---|----------------|----------|------------------|
|              | [CuBr(C₂H₂N₂S)₂] | 443.85 | Monoclinic, P2₁/c         | 95.564 (2) | 1575.8 (3) | 44 | Mo Ka           | 4.19     | 0.46 x 0.05 x 0.04 |

### Data collection

| | Bruker CCD area detector | Bruker CCD area detector |
|---|--------------------------|--------------------------|
| Tmin, Tmax | 0.713, 1.000 | 0.749, 1.000 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 11218, 2200 | 14555, 3200 |
| Rint | 0.039 | 0.021 |
| (sin θ/λ)max (Å⁻¹) | 0.595 | 0.595 |

Computer programs: SMART and SAINT (Bruker, 2003), SHELXT (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), Mercury (Macrae et al., 2020), WinGX publication routines (Farrugia, 2012) and pubCIF (Westrip, 2010).
and 1384 cm⁻¹ were found (figure not shown). After heating at 383 K for 10 minutes, these bands disappeared. Therefore these are due to C=O stretching and C—H bending, respectively, indicating the presence of acetone in the compound. IR data are summarized in Table 3.

1H NMR and 13C NMR spectra

1H NMR data for the ligand and (1) and (2) are listed in Table 4. The chemical shift at 13.28 ppm (br, s) belongs to two groups of N—H protons. The ratio of integration reveals that the two protons have the same environment. The ratio of N—H and aromatic protons is 1:2 without the signal of the S—H proton, indicating that both ligand and complex contain thione groups of N—H protons. The ratio of integration reveals that these are due to C8,9, corresponding with the work of Isab et al. (2003). Furthermore, the ligand exhibits chemical shifts around 7.49 ppm due to four methane protons on an aromatic benzene ring at positions H4, H7, H5, and H6, which change upon complex formation. The 13CNMR spectra of the ligand and complexes (Table 5) reveal seven carbon signals, including that of the thiocarbonyl group at 168.34 ppm, four carbon atoms in the aromatic ring at 132.48 ppm. In the complex, C2 and C5,6 have downfield chemical shifts due to electron density on nitrogen and 122.59 ppm for C4,7 and C5,6, respectively, and two quaternary carbon atoms at 109.75 ppm, four carbon atoms in the aromatic ring at 109.75 ppm, four carbon atoms in the aromatic ring at 109.75 ppm. In the complex, C2 and C5,6 have downfield chemical shifts due to the electron transfer to C8,9, corresponding with the work of Isab et al. (2003). For (2), the carbonyl signal at 206.64 ppm and methane carbon at 30.86 ppm indicate the presence of acetone in the compound.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. All H atoms of (1) were clearly resolved in difference-density maps and all H-atom parameters were freely refined. For (2), the carbon-bound H atoms were placed in calculated locations with C—H = 0.93–0.96 Å and refined as riding atoms with Ueq(H) = 1.2Ueq(C) or 1.5Ueq(methyl C). The H-atom positions of the amide groups of (2) were found in difference maps and refined with N—H distances restrained to 0.85 (2) and 0.86 (2) Å.

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Computing details

For both structures, data collection: *SMART* (Bruker, 2003); cell refinement: *SMART* (Bruker, 2003); data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae et al., 2020); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012) and pubICIF (Westrip, 2010).

Bromidobis(2,3-dihydro-1H-1,3-benzodiazole-2-thione)copper(I) (1)

**Crystal data**

\[\text{[CuBr(C}_7\text{H}_5\text{N}_2\text{S})_2]\]

\[M_r = 443.85\]

Monoclinic, \(P2_1/c\)

\(a = 4.1549 (4) \text{ Å}\)

\(b = 28.708 (3) \text{ Å}\)

\(c = 13.2735 (13) \text{ Å}\)

\(\beta = 95.564 (2)^\circ\)

\(V = 1575.8 (3) \text{ Å}^3\)

\(Z = 4\)

**Data collection**

Bruker CCD area detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Frames, each covering 0.3° in \(\omega\) scans

Absorption correction: multi-scan

(SADABS; Bruker, 2003)

\(T_{\text{min}} = 0.713, T_{\text{max}} = 1.000\)

**Refinement**

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.041\)

\(wR(F^2) = 0.093\)

\(S = 1.08\)

2750 reflections

247 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

\(w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.5475P]\)

where \(P = (F_o^2 + 2F_c^2)/3\)
\((\Delta/\sigma)_{\text{max}} < 0.001\)
\(\Delta \rho_{\text{max}} = 0.66 \text{ e Å}^{-3}\)

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

|        | x       | y       | z       | Uiso*/Ueq |
|--------|---------|---------|---------|-----------|
| Br1    | 0.35082 | 0.31949 | 0.29213 | 0.04740   |
| Cu1    | 0.35888 | 0.34728 | 0.46565 | 0.0570    |
| S1     | 0.5237  | 0.42049 | 0.50112 | 0.0489    |
| N1     | 0.7906  | 0.48624 | 0.3871  | 0.0439    |
| C1     | 0.7004  | 0.44151 | 0.4012  | 0.0399    |
| S2     | 0.1419  | 0.30563 | 0.58260 | 0.0688    |
| N2     | 0.7887  | 0.41786 | 0.3211  | 0.0414    |
| C2     | 0.9318  | 0.49139 | 0.2975  | 0.0407    |
| N3     | -0.1802 | 0.22338 | 0.5747  | 0.0527    |
| C3     | 1.0529  | 0.52902 | 0.2500  | 0.0545    |
| N4     | -0.0687 | 0.24669 | 0.4289  | 0.0444    |
| C4     | 1.1761  | 0.52084 | 0.1592  | 0.0595    |
| C5     | 1.1740  | 0.47661 | 0.1173  | 0.0572    |
| C6     | 1.0519  | 0.43907 | 0.1639  | 0.0528    |
| C7     | 0.9299  | 0.44709 | 0.2558  | 0.0395    |
| C8     | -0.0348 | 0.25789 | 0.5269  | 0.0463    |
| C9     | -0.3156 | 0.19077 | 0.5067  | 0.0393    |
| C10    | -0.4919 | 0.15060 | 0.5169  | 0.0530    |
| C11    | -0.5958 | 0.12685 | 0.4308  | 0.0560    |
| C12    | -0.5244 | 0.14225 | 0.3371  | 0.0623    |
| C13    | -0.3471 | 0.18181 | 0.3265  | 0.0610    |
| C14    | -0.2427 | 0.20588 | 0.4124  | 0.0411    |
| H1A    | 0.734   | 0.5041  | 0.417   | 0.032     |
| H2A    | 0.764   | 0.3900  | 0.310   | 0.049     |
| H3     | 1.054   | 0.5568  | 0.282   | 0.045     |
| H3A    | -0.203  | 0.2208  | 0.631   | 0.038     |
| H4     | 1.259   | 0.5470  | 0.126   | 0.069     |
| H4A    | 0.008   | 0.2643  | 0.387   | 0.033     |
| H5     | 1.263   | 0.4737  | 0.057   | 0.062     |
| H6     | 1.045   | 0.4107  | 0.139   | 0.073     |
| H10    | -0.542  | 0.1438  | 0.573   | 0.051     |
| H11    | -0.727  | 0.0991  | 0.436   | 0.082     |
| H12    | -0.591  | 0.1243  | 0.284   | 0.065     |
| H13    | -0.285  | 0.1901  | 0.269   | 0.052     |
**Atomic displacement parameters (Å²)**

|   | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U²³  |
|---|------|------|------|------|------|------|
| Br1 | 0.0583 (3) | 0.0418 (3) | 0.0432 (3) | −0.0072 (2) | 0.0106 (2) | −0.0012 (2) |
| Cu1 | 0.0745 (5) | 0.0403 (3) | 0.0586 (4) | −0.0038 (3) | 0.0192 (3) | −0.0036 (3) |
| S1 | 0.0628 (8) | 0.0383 (6) | 0.0469 (7) | 0.0016 (5) | 0.0115 (6) | −0.0075 (5) |
| N1 | 0.050 (2) | 0.030 (2) | 0.051 (3) | 0.0076 (18) | 0.0024 (19) | −0.0082 (19) |
| C1 | 0.035 (2) | 0.033 (2) | 0.049 (3) | 0.0086 (19) | −0.0047 (19) | −0.006 (2) |
| S2 | 0.1016 (11) | 0.0582 (8) | 0.0498 (8) | −0.0207 (8) | 0.0242 (7) | −0.0117 (6) |
| N2 | 0.050 (2) | 0.028 (2) | 0.047 (2) | 0.0024 (17) | 0.0089 (17) | −0.0078 (17) |
| C2 | 0.039 (2) | 0.037 (2) | 0.045 (3) | 0.0032 (19) | −0.002 (2) | −0.001 (2) |
| N3 | 0.077 (3) | 0.046 (2) | 0.037 (3) | −0.001 (2) | 0.022 (2) | 0.006 (2) |
| C3 | 0.062 (3) | 0.035 (3) | 0.064 (3) | −0.002 (2) | −0.005 (3) | 0.001 (2) |
| N4 | 0.055 (2) | 0.044 (2) | 0.035 (2) | −0.0042 (19) | 0.0065 (18) | 0.0093 (18) |
| C4 | 0.058 (3) | 0.058 (3) | 0.063 (4) | −0.009 (3) | 0.003 (3) | 0.015 (3) |
| C5 | 0.049 (3) | 0.069 (4) | 0.055 (3) | 0.002 (3) | 0.011 (3) | 0.001 (3) |
| C6 | 0.053 (3) | 0.048 (3) | 0.058 (3) | 0.003 (2) | 0.008 (2) | −0.005 (3) |
| C7 | 0.035 (2) | 0.038 (2) | 0.045 (3) | 0.0021 (18) | 0.0008 (19) | −0.003 (2) |
| C8 | 0.053 (3) | 0.042 (3) | 0.046 (3) | 0.009 (2) | 0.012 (2) | 0.007 (2) |
| C9 | 0.042 (2) | 0.038 (2) | 0.039 (2) | 0.0065 (19) | 0.0125 (19) | 0.0053 (19) |
| C10 | 0.062 (3) | 0.049 (3) | 0.052 (3) | 0.001 (2) | 0.028 (3) | 0.012 (3) |
| C11 | 0.060 (3) | 0.040 (3) | 0.068 (4) | −0.002 (2) | 0.012 (3) | 0.004 (3) |
| C12 | 0.075 (4) | 0.053 (3) | 0.057 (4) | −0.011 (3) | −0.003 (3) | −0.001 (3) |
| C13 | 0.079 (4) | 0.063 (4) | 0.041 (3) | −0.010 (3) | 0.003 (3) | 0.009 (3) |
| C14 | 0.043 (3) | 0.042 (3) | 0.038 (3) | 0.004 (2) | 0.004 (2) | 0.004 (2) |

**Geometric parameters (Å, °)**

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| Br1—Cu1 | 2.4346 (8) | N4—C14 | 1.383 (6) |
| Cu1—S2 | 2.2189 (15) | N4—H4A | 0.84 (4) |
| Cu1—S1 | 2.2464 (13) | C4—C5 | 1.386 (7) |
| S1—C1 | 1.688 (5) | C4—H4 | 0.95 (5) |
| N1—C1 | 1.356 (6) | C5—C6 | 1.364 (7) |
| N1—C2 | 1.384 (6) | C5—H5 | 0.92 (5) |
| N1—H1A | 0.70 (4) | C6—C7 | 1.386 (6) |
| C1—N2 | 1.342 (5) | C6—H6 | 0.88 (5) |
| S2—C8 | 1.691 (5) | C9—C10 | 1.380 (6) |
| N2—C7 | 1.378 (5) | C9—C14 | 1.386 (6) |
| N2—H2A | 0.82 (4) | C10—C11 | 1.365 (7) |
| C2—C3 | 1.371 (6) | C10—H10 | 0.82 (5) |
| C2—C7 | 1.387 (6) | C11—C12 | 1.378 (7) |
| C3—C8 | 1.350 (6) | C11—H11 | 0.97 (5) |
| N3—C9 | 1.381 (6) | C12—C13 | 1.368 (7) |
| N3—H3A | 0.76 (4) | C12—H12 | 0.90 (5) |
| C3—C4 | 1.374 (7) | C13—C14 | 1.367 (7) |
| C3—H3 | 0.90 (4) | C13—H13 | 0.86 (4) |
| N4—C8 | 1.334 (6) |   |   |   |   |   |

*Acta Cryst. (2022). E78, 519-524*
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| S2—Cu1—S1    | 119.59 (5)   | C6—C5—H5     | 121 (3)      |
| S2—Cu1—Br1   | 121.07 (4)   | C4—C5—H5     | 117 (3)      |
| S1—Cu1—Br1   | 118.74 (4)   | C5—C6—C7     | 116.8 (5)    |
| C1—N1—C2     | 108.47 (15)  | C5—C6—H6     | 124 (3)      |
| C1—N1—H1A    | 111.5 (4)    | C7—C6—H6     | 119 (3)      |
| C1—N1—H1A    | 120 (4)      | N2—C7—C6     | 131.9 (4)    |
| C2—N1—H1A    | 127 (4)      | N2—C7—C2     | 107.1 (4)    |
| N2—C1—N1     | 105.6 (4)    | C6—C7—C2     | 121.0 (4)    |
| N2—C1—S1     | 127.9 (3)    | N4—C8—N3     | 105.8 (4)    |
| N1—C1—S1     | 126.5 (3)    | N4—C8—S2     | 128.4 (3)    |
| C8—S2—Cu1    | 108.64 (16)  | N3—C8—S2     | 125.8 (4)    |
| C1—N2—C7     | 110.9 (4)    | C10—C9—N3    | 133.5 (4)    |
| C1—N2—H2A    | 127 (3)      | C10—C9—C14   | 121.0 (4)    |
| C7—N2—H2A    | 122 (3)      | N3—C9—C14    | 105.5 (4)    |
| C3—C2—N1     | 133.2 (4)    | C11—C10—C9   | 117.6 (5)    |
| C3—C2—C7     | 121.8 (4)    | C11—C10—H10  | 124 (3)      |
| N1—C2—C7     | 105.0 (4)    | C9—C10—H10   | 118 (3)      |
| C8—N3—C9     | 111.3 (4)    | C10—C11—C12  | 121.1 (5)    |
| C8—N3—H3A    | 129 (3)      | C10—C11—H11  | 119 (3)      |
| C9—N3—H3A    | 119 (3)      | C12—C11—H11  | 120 (3)      |
| C2—C3—C4     | 117.0 (5)    | C13—C12—C11  | 121.6 (6)    |
| C2—C3—H3     | 118 (3)      | C13—C12—H12  | 121 (3)      |
| C4—C3—H3     | 125 (3)      | C11—C12—H12  | 117 (3)      |
| C8—N4—C14    | 111.2 (4)    | C14—C13—C12  | 117.7 (5)    |
| C8—N4—H4A    | 120 (3)      | C14—C13—H13  | 120 (3)      |
| C14—N4—H4A   | 129 (3)      | C12—C13—H13  | 122 (3)      |
| C3—C4—C5     | 121.3 (5)    | C13—C14—N4   | 132.8 (4)    |
| C3—C4—H4     | 117 (3)      | C13—C14—C9   | 121.0 (4)    |
| C5—C4—H4     | 122 (3)      | N4—C14—C9    | 106.2 (4)    |
| C6—C5—C4     | 122.0 (5)    |                |              |
| C2—N1—C1     | 0.9 (5)      | C14—N4—C8—N3 | 1.7 (5)      |
| C2—N1—C1—S1  | 179.3 (3)    | C14—N4—C8—S2 | −176.8 (3)   |
| Cu1—S1—C1—N2 | −11.7 (4)    | C9—N3—C8—N4  | −1.8 (5)     |
| Cu1—S1—C1—N1 | 170.2 (3)    | C9—N3—C8—S2  | 176.7 (3)    |
| N1—C1—N2—C7  | −0.8 (5)     | Cu1—S2—C8—N4 | −4.7 (5)     |
| S1—C1—N2—C7  | −179.2 (3)   | Cu1—S2—C8—N3 | 177.1 (4)    |
| C1—N1—C2—C3  | 178.4 (5)    | C8—N3—C9—C10 | −178.4 (5)   |
| C1—N1—C2—C7  | −0.7 (5)     | C8—N3—C9—C14 | 1.2 (5)      |
| N1—C2—C3—C4  | −179.6 (5)   | N3—C9—C10—C11 | 178.5 (5)   |
| C7—C2—C3—C4  | −0.7 (7)     | C14—C9—C10—C11 | −1.1 (7)   |
| C2—C3—C4—C5  | 0.7 (8)      | C9—C10—C11—C12 | 0.6 (8)    |
| C3—C4—C5—C6  | −0.3 (8)     | C10—C11—C12—C13 | 0.0 (9)   |
| C4—C5—C6—C7  | −0.2 (8)     | C11—C12—C13—C14 | −0.2 (9)   |
| C1—N2—C7—C6  | −178.7 (5)   | C12—C13—C14—N4 | −178.5 (5) |
| C1—N2—C7—C2  | 0.4 (5)      | C12—C13—C14—C9 | −0.3 (7)   |
| C5—C6—C7—N2  | 179.3 (5)    | C8—N4—C14—C13 | 177.4 (5)   |
| C5—C6—C7—C2  | 0.3 (7)      | C8—N4—C14—C9  | −1.0 (5)    |
Bis(2,3-dihydro-1H-1,3-benzodiazole-2-thione)iodidocopper(I) acetone solvate (2)

Crystal data

\[\text{[CuI(C}_7\text{H}_6\text{N}_2\text{S})_2]\cdot\text{C}_3\text{H}_6\text{O}\]  

\(M_r = 548.91\)  

Monoclinic, \(P\overline{2}_1/c\)  

Cell parameters from 5872 reflections  
\(a = 4.5154\) (3) Å  
\(b = 22.2157\) (15) Å  
\(c = 20.4062\) (14) Å  
\(\beta = 94.818\) (1)°  
\(V = 2039.8\) (2) Å³  
\(Z = 4\)  

\(\mu = 2.80\) mm⁻¹  

\(T = 293\) K  

Needle, colourless  

0.38 × 0.14 × 0.08 mm

Data collection

Bruker CCD area detector  

14555 measured reflections  

3597 independent reflections  

3200 reflections with \(I > 2\sigma(I)\)  

\(\theta_{\text{min}} = 2.2\)–\(26.6\)°  

\(\theta_{\text{max}} = 25.0\)°  

\(h = -5\)–\(5\)  

\(k = -26\)–\(26\)  

\(l = -24\)–\(24\)

Refinement

Refinement on \(F^2\)  
Least-squares matrix: full  
\(R[F^2 > 2\sigma(F^2)] = 0.039\)  
\(wR(F^2) = 0.089\)  
\(S = 1.08\)  
3597 reflections  
247 parameters  
4 restraints  
Primary atom site location: structure-invariant direct methods  
Secondary atom site location: difference Fourier map  
Hydrogen site location: mixed  
\(H\) atoms treated by a mixture of independent and constrained refinement  
\(\Delta \rho_{\text{max}} = 1.14\) e Å⁻³  
\(\Delta \rho_{\text{min}} = -0.90\) e Å⁻³

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1A···S1i | 0.70 (4) | 2.69 (4) | 3.384 (4) | 170 (5) |
| N2—H2A···Br1 | 0.82 (4) | 2.65 (4) | 3.361 (4) | 146 (4) |
| N4—H4A···Br1 | 0.84 (4) | 2.54 (4) | 3.364 (4) | 166 (4) |

Symmetry code: (i) \(-x + 1, -y + 1, -z + 1\).
Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

| Atom | x    | y    | z    | Uiso* / Ueq |
|------|------|------|------|-------------|
| Cu1  | 0.2323 (2) | 0.42788 (3) | 0.63559 (3) | 0.0789 (2) |
| I1   | 0.34973 (7) | 0.31632 (2) | 0.65076 (2) | 0.06112 (13) |
| S1   | −0.1755 (4) | 0.45699 (6) | 0.57174 (7) | 0.0838 (5) |
| S2   | 0.3444 (3) | 0.50247 (5) | 0.70750 (6) | 0.0518 (3) |
| N1   | −0.1238 (9) | 0.35326 (17) | 0.50250 (18) | 0.0544 (9) |
| N2   | −0.4365 (10) | 0.41666 (16) | 0.45551 (19) | 0.0555 (10) |
| N3   | 0.7524 (8) | 0.42258 (15) | 0.76321 (17) | 0.0454 (8) |
| N4   | 0.6946 (8) | 0.50239 (16) | 0.82129 (18) | 0.0483 (8) |
| C1   | −0.2443 (12) | 0.4079 (2) | 0.5087 (2) | 0.0548 (11) |
| C2   | −0.2433 (10) | 0.32568 (19) | 0.4450 (2) | 0.0476 (10) |
| C3   | −0.1898 (11) | 0.2710 (2) | 0.4161 (2) | 0.0557 (11) |
| H3   | −0.054352 | 0.243569 | 0.435797 | 0.067* |
| C4   | −0.3470 (11) | 0.2590 (2) | 0.3568 (2) | 0.0592 (12) |
| H4   | −0.316081 | 0.222687 | 0.335867 | 0.071* |
| C5   | −0.5483 (12) | 0.2993 (2) | 0.3277 (2) | 0.0610 (13) |
| H5   | −0.561343 | 0.289205 | 0.287859 | 0.073* |
| C6   | −0.6020 (12) | 0.3539 (2) | 0.3555 (2) | 0.0579 (12) |
| C7   | −0.4427 (10) | 0.36649 (18) | 0.4150 (2) | 0.0479 (10) |
| C8   | 0.6017 (9) | 0.47473 (18) | 0.7644 (2) | 0.0442 (10) |
| C9   | 0.9438 (9) | 0.41641 (18) | 0.8198 (2) | 0.0438 (9) |
| C10  | 1.1416 (10) | 0.3719 (2) | 0.8413 (2) | 0.0541 (11) |
| C11  | 1.170348 | 0.337767 | 0.816134 | 0.065* |
| C12  | 1.2591 (11) | 0.3804 (2) | 0.9021 (3) | 0.0619 (13) |
| C13  | 1.328668 | 0.351140 | 0.918471 | 0.074* |
| C14  | 1.2554 (11) | 0.4315 (2) | 0.9394 (2) | 0.0620 (13) |
| C15  | 1.362526 | 0.435638 | 0.980133 | 0.074* |
| C16  | 1.0610 (10) | 0.4761 (2) | 0.9175 (2) | 0.0550 (11) |
| C17  | 1.035593 | 0.510598 | 0.942271 | 0.066* |
| C18  | 0.9046 (9) | 0.46766 (19) | 0.8569 (2) | 0.0458 (10) |
| C19  | 0.1969 (15) | 0.6773 (3) | 0.9353 (3) | 0.0795 (17) |
| H15A | 0.041024 | 0.704543 | 0.919993 | 0.119* |
| H15B | 0.126452 | 0.650874 | 0.967768 | 0.119* |
| H15C | 0.363937 | 0.699853 | 0.954390 | 0.119* |
| C16  | 0.2888 (11) | 0.6414 (2) | 0.8792 (2) | 0.0553 (11) |
| C17  | 0.1359 (14) | 0.6534 (3) | 0.8138 (3) | 0.0797 (16) |
| H17A | −0.010436 | 0.684287 | 0.817434 | 0.120* |
| H17B | 0.278159 | 0.666406 | 0.784409 | 0.120* |
| H17C | 0.040343 | 0.617277 | 0.797060 | 0.120* |
|     | U^11   | U^22   | U^33   | U^12   | U^13   | U^23   |
|-----|--------|--------|--------|--------|--------|--------|
| Cu1 | 0.1375 (7) | 0.0464 (4) | 0.0480 (3) | 0.0166 (4) | -0.0207 (4) | -0.0050 (3) |
| I1  | 0.0590 (2)  | 0.03985 (18) | 0.0816 (3) | 0.00121 (13) | -0.01114 (16) | -0.00181 (14) |
| S1  | 0.1445 (14) | 0.0479 (7)   | 0.0528 (7)  | 0.0360 (8)   | -0.0277 (8)  | -0.0143 (6)   |
| S2  | 0.0627 (7)  | 0.0405 (6)   | 0.0517 (6)  | 0.0037 (5)   | 0.0028 (5)   | -0.0012 (5)   |
| N1  | 0.077 (3)   | 0.040 (2)    | 0.045 (2)   | 0.0109 (19)  | -0.0036 (19) | -0.0014 (16)  |
| N2  | 0.078 (3)   | 0.039 (2)    | 0.049 (2)   | 0.0103 (19)  | -0.0031 (19) | -0.0006 (17)  |
| N3  | 0.049 (2)   | 0.0382 (19) | 0.050 (2)   | 0.0005 (16)  | 0.0054 (16)  | -0.0060 (15)  |
| N4  | 0.057 (2)   | 0.039 (2)    | 0.049 (2)   | 0.0016 (17)  | 0.0095 (17)  | -0.0059 (17)  |
| C1  | 0.083 (3)   | 0.039 (2)    | 0.042 (2)   | 0.009 (2)    | 0.001 (2)    | -0.0012 (19)  |
| C2  | 0.061 (3)   | 0.040 (2)    | 0.043 (2)   | -0.003 (2)   | 0.012 (2)    | 0.0001 (18)   |
| C3  | 0.066 (3)   | 0.041 (2)    | 0.062 (3)   | 0.004 (2)    | 0.014 (2)    | -0.005 (2)    |
| C4  | 0.077 (3)   | 0.044 (3)    | 0.059 (3)   | -0.011 (2)   | 0.018 (3)    | -0.014 (2)    |
| C5  | 0.078 (3)   | 0.055 (3)    | 0.050 (3)   | -0.018 (3)   | 0.006 (2)    | -0.007 (2)    |
| C6  | 0.072 (3)   | 0.049 (3)    | 0.051 (3)   | -0.008 (2)   | -0.002 (2)   | 0.004 (2)     |
| C7  | 0.064 (3)   | 0.037 (2)    | 0.043 (2)   | -0.004 (2)   | 0.010 (2)    | 0.0021 (18)   |
| C8  | 0.045 (2)   | 0.040 (2)    | 0.049 (2)   | -0.0065 (18) | 0.0120 (19)  | -0.0023 (18)  |
| C9  | 0.043 (2)   | 0.042 (2)    | 0.047 (2)   | -0.0049 (18) | 0.0097 (18)  | -0.0012 (18)  |
| C10 | 0.055 (3)   | 0.049 (3)    | 0.060 (3)   | 0.002 (2)    | 0.010 (2)    | -0.004 (2)    |
| C11 | 0.058 (3)   | 0.063 (3)    | 0.065 (3)   | 0.009 (2)    | 0.005 (2)    | 0.007 (2)     |
| C12 | 0.060 (3)   | 0.077 (3)    | 0.049 (3)   | -0.002 (3)   | 0.003 (2)    | -0.001 (2)    |
| C13 | 0.060 (3)   | 0.057 (3)    | 0.048 (3)   | -0.003 (2)   | 0.009 (2)    | -0.008 (2)    |
| C14 | 0.045 (2)   | 0.043 (2)    | 0.051 (2)   | -0.0016 (19) | 0.0104 (19)  | -0.0014 (19)  |
| C15 | 0.100 (4)   | 0.072 (4)    | 0.067 (3)   | 0.025 (3)    | 0.007 (3)    | -0.006 (3)    |
| C16 | 0.063 (3)   | 0.046 (3)    | 0.057 (3)   | 0.001 (2)    | 0.007 (2)    | -0.004 (2)    |
| C17 | 0.088 (4)   | 0.088 (4)    | 0.064 (3)   | 0.006 (3)    | 0.006 (3)    | 0.001 (3)     |
| O1  | 0.094 (3)   | 0.065 (2)    | 0.077 (2)   | 0.029 (2)    | -0.002 (2)   | -0.0166 (19)  |

**Geometric parameters (Å, °)**

| Bond          | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| Cu1—S2       | 2.2430 (13) | C5—C6     | 1.369 (7) |
| Cu1—S1       | 2.2594 (17) | C5—H5     | 0.9300    |
| Cu1—I1       | 2.5479 (7)  | C6—C7     | 1.386 (6) |
| S1—C1        | 1.696 (4)   | C6—H6     | 0.9300    |
| S2—C8        | 1.689 (4)   | C9—C10    | 1.380 (6) |
| N1—C1        | 1.341 (6)   | C9—C14    | 1.387 (6) |
| N1—C2        | 1.391 (6)   | C10—C11   | 1.383 (7) |
| N1—H1A       | 0.86 (2)    | C10—H10   | 0.9300    |
| N2—C1        | 1.345 (6)   | C11—C12   | 1.386 (7) |
| N2—C7        | 1.387 (5)   | C11—H11   | 0.9300    |

*Acta Cryst. (2022). E78, 519-524 sup-7*
N2—H2A 0.86 (2) C12—C13 1.374 (7)
N3—C8 1.345 (5) C12—H12 0.9300
N3—C9 1.390 (5) C13—C14 1.384 (6)
N3—H3A 0.85 (2) C13—H13 0.9300
N4—C8 1.348 (5) C15—C16 1.484 (7)
N4—C14 1.381 (6) C15—H15A 0.9600
N4—H4A 0.85 (2) C15—H15B 0.9600
C2—C3 1.381 (6) C15—H15C 0.9600
C2—C7 1.384 (6) C16—O1 1.209 (6)
C3—C4 1.376 (7) C16—C17 1.474 (7)
C3—H3 0.9300 C17—H17A 0.9600
C4—C5 1.375 (7) C17—H17B 0.9600
C4—H4 0.9300 C17—H17C 0.9600

S2—Cu1—S1 107.10 (5) N2—C7—C6 131.8 (4)
S2—Cu1—I1 127.30 (4) N3—C8—N4 128.4 (3)
S1—Cu1—I1 119.98 (5) N3—C8—S2 124.9 (3)
C1—Cu1—S1 110.01 (18) N4—C8—S2 108.7 (3)
C8—S2—Cu1 106.54 (15) N4—C14—C9 121.6 (4)
C1—N1—C2 110.3 (4) N4—C14—C13 121.4 (4)
C1—N1—H1A 120 (4) C14—C13—C9 121.4 (4)
C2—N1—H1A 129 (4) C13—C12—C11 121.8 (5)
C1—N2—C7 110.1 (4) C12—C13—H13 121.8 (5)
C1—N2—H2A 124 (4) C12—C13—H13 121.8 (5)
C7—N2—H2A 126 (4) C12—C13—H13 121.8 (5)
C8—N3—C9 110.5 (3) C14—C13—H14 121.4 (4)
C8—N3—H3A 123 (4) C10—C11—C12 121.6 (4)
C9—N3—H3A 126 (4) C10—C11—C12 121.6 (4)
C8—N4—C14 110.4 (4) C10—C11—H10 121.6 (4)
C8—N4—H4A 121 (4) C10—C11—H10 121.6 (4)
C14—N4—H4A 128 (4) C9—C10—C11 121.8 (5)
N1—C1—C2 107.1 (4) C9—C10—C11 121.8 (5)
N1—C1—H1 127.1 (4) C9—C10—H10 121.8 (5)
N1—C1—S1 125.7 (3) C9—C10—H10 121.8 (5)
C3—C2—C7 121.2 (4) C1—C2—C7 121.2 (4)
C3—C2—N1 132.7 (4) C1—C2—N1 132.7 (4)
C7—C2—N1 106.1 (4) C1—C2—C7 121.2 (4)
C4—C3—C2 116.7 (5) C1—C2—C7 121.2 (4)
C4—C3—H3 121.7 H15A—C15—H15B 109.5
C2—C3—H3 121.7 C16—C15—H15B 109.5
C5—C4—C3 121.9 (4) H15A—C15—H15C 109.5
C5—C4—H4 119.1 H15B—C15—H15C 109.5
C3—C4—H4 119.1 O1—C16—C17 122.2 (5)
C6—C5—C4 122.1 (5) O1—C16—C15 120.4 (5)
C6—C5—H5 119.0 C17—C16—C15 117.4 (5)
C4—C5—H5 119.0 C16—C17—H17A 109.5
C5—C6—C7 116.4 (5) C16—C17—H17B 109.5
C5—C6—H6 121.8 H17A—C17—H17B 109.5

Acta Cryst. (2022). E78, 519-524
| Angle (°) | C7—C6—H6 | 121.8 | C16—C17—H17C | 109.5 |
|-----------|-----------|-------|----------------|-------|
| C2—C7—N2 | 106.4 (4) | H17A—C17—H17C | 109.5 |
| C2—C7—C6 | 121.7 (4) | H17B—C17—H17C | 109.5 |

| Angle (°) | C2—N1—C1—N2 | −1.0 (6) | C9—N3—C8—N4 | 0.1 (5) |
|-----------|-------------|---------|--------------|-------|
| C2—N1—C1—S1 | 178.0 (4) | C9—N3—S8—S2 | −179.9 (3) |
| C7—N2—C1—N1 | 0.9 (6) | C14—N4—C8—N3 | −0.3 (5) |
| C7—N2—C1—S1 | −178.2 (4) | C14—N4—C8—S2 | 179.6 (3) |
| Cu1—S1—C1—N1 | 13.2 (5) | Cu1—S2—C8—N3 | 10.3 (4) |
| Cu1—S1—C1—N2 | −168.0 (4) | Cu1—S2—C8—N4 | −169.7 (3) |
| C1—N1—C2—C3 | 178.4 (5) | C8—N3—C9—C10 | −180.0 (5) |
| C1—N1—C2—C7 | 0.8 (5) | C8—N3—C9—C14 | 0.2 (5) |
| C7—C2—C3—C4 | −0.8 (7) | C14—C9—C10—C11 | 1.0 (7) |
| N1—C2—C3—C4 | −178.1 (5) | N3—C9—C10—C11 | −178.8 (4) |
| C2—C3—C4—C5 | −0.2 (7) | C9—C10—C11—C12 | −0.7 (7) |
| C3—C4—C5—C6 | 0.8 (8) | C10—C11—C12—C13 | −0.1 (8) |
| C4—C5—C6—C7 | −0.2 (7) | C11—C12—C13—C14 | 0.6 (7) |
| C3—C2—C7—N2 | −178.2 (4) | C8—N4—C14—C13 | −179.3 (5) |
| N1—C2—C7—N2 | −0.3 (5) | C8—N4—C14—C9 | 0.4 (5) |
| C3—C2—C7—C6 | 1.4 (7) | C12—C13—C14—N4 | 179.3 (5) |
| N1—C2—C7—C6 | 179.3 (4) | C12—C13—C14—C9 | −0.3 (7) |
| C1—N2—C7—C2 | −0.4 (5) | C10—C9—C14—N4 | 179.8 (4) |
| C1—N2—C7—C6 | −179.9 (5) | N3—C9—C14—N4 | −0.4 (4) |
| C5—C6—C7—C2 | −0.8 (7) | C10—C9—C14—C13 | −0.5 (7) |
| C5—C6—C7—N2 | 178.6 (5) | N3—C9—C14—C13 | 179.4 (4) |

**Hydrogen-bond geometry (Å, †)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|----------|------|-------|-------|---------|
| N1—H1A···I1 | 0.86 (2) | 2.81 (2) | 3.649 (4) | 167 (6) |
| N2—H2A···S1i | 0.86 (2) | 2.47 (2) | 3.331 (4) | 176 (6) |
| N3—H3A···I1 | 0.85 (2) | 2.91 (4) | 3.666 (3) | 148 (5) |
| N4—H4A···O1 | 0.85 (2) | 2.02 (3) | 2.840 (5) | 161 (6) |
| C15—H15A···I1ii | 0.96 | 3.31 | 4.240 (6) | 165 |

Symmetry codes: (i) −x, −y+1, −z+1; (ii) −x, y+1/2, −z+3/2.