Syntheses and crystal structures of two copper(I)–halide π,σ-coordination compounds based on 2-[(prop-2-en-1-yl)sulfanyl]pyridine

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The title compounds, di-μ-chlorido-bis([2-[(η-2,3)-(prop-2-en-1-yl)sulfanyl]pyridine-κN]copper(I)), [Cu2Cl2(C8H9NS)2], and di-μ-bromido-bis([2-[(η-2,3)-(prop-2-en-1-yl)sulfanyl]pyridine-κN]copper(I)), [Cu2Br2(C8H9NS)2], were obtained by alternating-current electrochemical synthesis starting from an ethanolic solution of 2-[(prop-2-en-1-yl)sulfanyl]pyridine (Psup) and the copper(II) halide. The isostructural crystals are built up from centrosymmetric [Cu2Hal₂(Psup)₂] dimers, which are formed due to the π,σ-chelating behavior of the organic ligand. In the crystals, the dimers are linked by C—H···Hal hydrogen bonds as well as by aromatic π—π stacking interactions into a threedimensional network.

1. Chemical context

Cu-containing complexes have been found very promising regarding their catalytic activities in organic syntheses, nonlinear optical properties and fluorescent activity (Wang et al., 2005; Yoshikai & Nakamura, 2012; Slyvka et al., 2018a; Fedorchuk et al., 2020). Copper complexes also exhibit considerable biochemical activities, ranging from antibacterial and anti-inflammatory properties to cytostatic and enzyme inhibitory (Iakovidis et al., 2011; Tisato et al., 2010). Some of these compounds have been tested in vitro as potential anticancer drugs and found to be effective against A549 adenocarcinoma cells that are resistant to the widely used anticancer drug cisplatin (Marzano et al., 2006). It is worth noting that copper is an essential trace element with vital roles in many metalloenzymes participating in intracellular processes under normal and pathological conditions (Iakovidis et al., 2011).

Over the last two decades, increased interest has also been devoted to the crystal engineering of copper(I)–olefin complexes with allyl derivatives of heterocyclic compounds (Goreshnik et al., 2011; Slyvka et al., 2013; Hordiichuk et al., 2019). The presence of a C=C olefin bond in a substituent attached to the heterocyclic ring may serve as a key feature for the selective coordination of transition-metal ions due to metal–olefin π-bonding (Rourke, 2006; Slyvka et al., 2013; Kowalska et al., 2021). Allyl derivatives of some heterocyclic compounds were found to be suitable for the preparation of π-coordination compounds with CuI salts that are unknown (or less stable) in the free state. For instance, the first examples of
Cu(C₅H₅SO₃), Cu(p-CH₃C₆H₅SO₃) or CuHSO₄ \(\pi\)-complexes as well as the direct Cu\(^{\text{I}}\) \(\pi\)-compounds with allyl derivatives of triazole and thiadiazole (Goreshnik et al., 2016; Ardan et al., 2017; Slyvka et al., 2018b; Fedorchuk et al., 2020). \(\pi\)-Allyl derivatives of pyridine were found to be suitable ligands for the crystal engineering of Cu\(^{\text{I}}\) coordination compounds with inorganic fragments of different complexibility and related to the \(pK_a\) values of the initial pyridine bases (Goreshnik et al., 2003; Pavlyuk et al., 2005). Taking into account the fact that allylsulfanyl derivatives of pyridine have not been investigated for their coordination behavior regarding copper(I), in this work we present the synthesis and structural characterization of two novel copper(I) halide \(\pi\)-coordination compounds \([\text{Cu}_2\text{Cl}_2\text{(Psup)}_2]\) (I) & \([\text{Cu}_2\text{Br}_2\text{(Psup)}_2]\) (II) with 2-[(prop-2-en-1-yl)sulfanyl]pyridine (Psup), C₅H₅NS.

2. Structural commentary

The title compounds are isostructural and crystallize in the centrosymmetric space group \(P2_1/c\) with one Psup organic molecule, one copper(I) ion and one halide ion in the asymmetric unit. As shown in Figs. 1 and 2, these structures are constructed from centrosymmetric \([\text{Cu}_2\text{Hal}_2\text{(Psup)}_2]\) \([\text{Hal} = \text{Cl (I)} \text{ or Br (II)}]\) dimers, which are formed due to the chelating behavior of the organic ligand. A close to trigonal–pyramidal coordination environment of the Cu\(^{\text{I}}\) cation includes the \(\eta^2\) allyl \(\text{C}=\text{C}\) bond, the pyridine N atom and a \(\text{Hal}\) ion in the basal plane (Tables 1 and 2). The apical position of the Cu\(^{\text{I}}\) polyhedron is occupied by the \(\text{Hal}^1\) [symmetry code: (i) \(-x+1, -y+1, -z+1\)] dimers, which are formed due to the chelating behavior of the organic ligand. A close to trigonal–pyramidal coordination environment of the Cu\(^{\text{I}}\) cation includes the \(\eta^2\) allyl \(\text{C}=\text{C}\) bond, the pyridine N atom and a \(\text{Hal}\) ion in the basal plane (Tables 1 and 2). The corresponding four-coordinate geometry indices \(\tau_4\) (Yang et al., 2007) are 0.81 (I) and 0.83 (II). For comparison, in the structures of previously studied CuCl and CuBr \(\pi\)-complexes with allylacetonoxime, the Cu–\(\text{Hal}^\text{ap}\) distances are slightly higher at 2.719 (5) and 2.778 (4) Å (Filinchuk et al., 1998).

Being \(\pi\)-connected to the metal center, the C\(8\)=C\(9\) bond of the ligand is elongated due to back-donation from an occupied 3d metal orbital to a low-lying empty \(\pi^*\)-orbital of the olefin to 1.364 (4) Å (I) and to 1.354 (6) Å (II) in comparison with an uncoordinated allyl C\(=\text{C}\) bond (Slyvka et al., 2021). The allylsulfanyl group in (I) and (II) has synclinal conformation relative to the S\(1\)–C\(7\) bond and an antiperiplanar conformation relative to the C\(7\)–C\(8\) bond [the corresponding torsion angles C\(2\)–S\(1\)–C\(7\)–C\(8\) and S\(1\)–C\(7\)–C\(8\)–C\(9\) are 68.1 (3) and \(-152.1\) (3)°, respectively, in I and 68.3 (3) and \(-151.7\) (3)° (II)].

3. Supramolecular features

As shown in Fig. 3 and listed in Tables 3 and 4, the crystal structures of (I) and (II) features several weak intermolecular...
interactions. The hydrogen atom H6 of the pyridine ring participates in an intramolecular C—H···Hal bond with the Hal ion of the inorganic subunit. The other hydrogen atom H6 of the pyridine ring and the methylene hydrogen atom H7 of the allylsulfanyl substituent are involved in intermolecular C—H···Hal bonding, linking the dimeric moieties into a three-dimensional network. The pyridine rings of adjacent dimers are also involved in face-to-face π·π stacking interactions with a centroid–centroid separation of 3.680 (4) Å in I and 3.693 (4) Å in II. The unit-cell packing for I is shown in Fig. 4.

4. Database survey

The most closely related compounds to the title compounds, containing a similar [Cu2Hal4] dimer in which a π,σ-chelating ligand is bound to copper(I) are: di-μ-chlorobis[(1-allyl-3,5-dimethylpyrazole)copper(I)] (III) [Cambridge Structural Database (Version 2021.1; Groom et al., 2016) refcode ALMPCU; Fukushima et al., 1976], bis(μ2-chloro)biso(η2-allylacetonetoxime-N)copper(I) (IV) (GOKYAG; Filinchuk et al., 1998), bis(μ2-bromo)biso(η2-allylacetonetoxime-N)copper(I) (V) (GOKYEC; Filinchuk et al., 1998), bis(μ2-bromo)(η2-2-(allylthio)benzimidazolone-N)copper(I) (VI) (WUCRAN; Goreshnik et al., 2002) and bis[(μ2-iodo)](η2-allyl)(2-pyridyl)dimethylsilanecopper (VII) (XAZGIP; Kamei et al., 2005).

Compounds (III) and (VII) crystallize in the triclinic crystal system in space group P1. Compounds (IV), (V) and (VI) crystallize in the monoclinic crystal system in space group P21/c (settings P21/a, P21/c and P21/n, respectively). Structures (III), (IV), (V) and (VI) are built up from centrosymmetric [Cu2Hal4(Ligand)]2- dimers. In the compounds bis[(μ2-chloro)chloro(η2-1-allyl-2-aminopyridinium)copper(I)] (XIII) (BEBOFOE) and bis[(μ2-chloro)bromo(η2-1-allyl-2-aminopyridinium)copper(I)] (IX) (BEBGAR; Goreshnik et al., 2003), the 1-allyl-2-aminopyridinium cation acts as a monodentate π-ligand, being attached to the centrosymmetric anionic [Cu2Hal4]2- part through the allylic C=C bond. An analogous monodentate 1-allylpyridinium cation in the structure of catena-[bis(μ2-chloro)bis(μ2-chloro)bis(η2-1-allylpyridinium)dichlorotetracopper(I)] (X) (YAPQIQ; Pavlyuk et al., 2005) forces the realization of an infinite [Cu2Cl4]n inorganic chain.

5. Synthesis and crystallization

Crystals of the title compounds were obtained under conditions of alternating-current electrochemical synthesis (Slyvka et al., 2018a) starting from an ethanolic solution of 2-[(prop-2-en-1-yl)sulfonyl]pyridine (Psup) and the copper(II) halide. For this, a solution of Psup (1.5 mmol, 0.227 g) in 2.0 ml of 96% ethanol was added to a solution of CuCl2·2H2O (1.6 mmol, 0.273 g) or CuBr2 (1.6 mmol, 0.357 g) in 3.0 ml of 96% ethanol. The mixture was carefully stirred and then was placed into a small 5.5 ml test tube. A copper wire was wrapped into a spiral of 1 cm diameter. A straight copper wire was placed inside the spiral. These copper electrodes were inserted in a cork and immersed in the aforementioned mixture. The mixture was subjected to alternating current reduction (frequency 50 Hz, voltage 0.45 V) and after 3–4 days, good-quality slightly yellowish crystals of the title compounds appeared on the copper wire electrodes.
Table 5
Experimental details.

| Crystal data | | Crystal data |
|--------------|--------------|
| Chemical formula | [Cu2Cl2(C8H9NS)2] | [Cu2Br2(C8H9NS)2] |
| Crystal system, space group | Monoclinic, P21/c | Monoclinic, P21/c |
| Temperature (K) | 150 | 150 |
| a, b, c (Å) | 9.2729 (16), 9.5740 (13), 11.037 (2) | 9.5009 (6), 9.6022 (5), 11.0936 (8) |
| β (°) | 108.52 (2) | 107.257 (7) |
| V (Å³) | 929.1 (3) | 966.50 (11) |
| Z | 2 | 2 |
| Radiation type | Mo Kα | Mo Kα |
| μ (mm⁻¹) | 2.80 | 6.55 |
| Crystal size (mm) | 0.33 × 0.28 × 0.19 | 0.44 × 0.35 × 0.22 |

Data collection

| Diffractometer | Rigaku New Gemini, Dual Atlas | Rigaku New Gemini, Dual Atlas |
|----------------|-----------------------------|-----------------------------|
| Absorption correction | Analytical (CrysAlis PRO; Rigaku OD, 2021) | Analytical (CrysAlis PRO; Rigaku OD, 2021) |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 8088, 2161, 1730 | 6837, 2162, 1854 |
| Rmin, Rmax | 0.058, 0.686 | 0.044, 0.682 |
| (sin θ/λ)max (Å⁻¹) | | |

Refinement

| R[F² > 2σ(F²)], wR(F²), S | 0.036, 0.077, 1.08 | 0.034, 0.079, 1.08 |
| No. of reflections | 2161 | 2162 |
| No. of parameters | 109 | 109 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.51, -0.64 | 0.82, -0.75 |

Computer programs: CrysAlis PRO (Rigaku OD, 2021), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).

Compound I: yield 12%, m.p. 413 K; compound II: yield 8%, m.p. 407 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. All H atoms were positioned geometrically with C–H = 0.95–0.99 Å and refined as riding atoms. The constraint Uiso(H) = 1.2Ueq(C) was applied in all cases.

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Syntheses and crystal structures of two copper(I)–halide π,σ-coordination compounds based on 2-[(prop-2-en-1-yl)sulfanyl]pyridine

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Computing details
For both structures, data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); 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-µ-chlorido-bis((2-[η-2,3)-(prop-2-en-1-yl)sulfanyl]pyridine-κN)copper(I) (I)

Crystal data
[Cu₂Cl₂(C₈H₉NS)₂]  
\( M_r = 500.42 \)  
Monoclinic, \( P2_1/c \)  
\( a = 9.2729 \, (16) \, Å \)  
\( b = 9.5740 \, (13) \, Å \)  
\( c = 11.037 \, (2) \, Å \)  
\( \beta = 108.52 \, (2)^\circ \)  
\( V = 929.1 \, (3) \, Å³ \)  
\( Z = 2 \)  

Data collection
New Gemini, Dual, Cu at home/near, Atlas diffractometer  
Detector resolution: 10.6426 pixels mm⁻¹  
\( \omega \) scans  
Absorption correction: analytical  
(CrysAlisPro; Rigaku OD, 2021)  
\( T_{\text{min}} = 0.546, T_{\text{max}} = 0.693 \)  
8088 measured reflections  
2161 independent reflections  
1730 reflections with \( I > 2\sigma(I) \)  
\( R_{\text{int}} = 0.058 \)  
\( \theta_{\text{max}} = 29.2^\circ, \theta_{\text{min}} = 2.9^\circ \)  
\( h = -12 \rightarrow 12, k = -12 \rightarrow 11, l = -15 \rightarrow 15 \)  

Refinement
Refinement on \( F^2 \)  
Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.036 \)  
\( wR(F^2) = 0.077 \)  
\( S = 1.08 \)  
2161 reflections  
109 parameters  
0 restraints  
Primary atom site location: dual  

Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
\( w = 1/[\sigma(F_c^2) + (0.0228P)^2 + 0.6316P] \)  
where \( P = (F_c^2 + 2F_e^2)/3 \)  
\( \Delta/\sigma \) max = 0.001  
\( \Delta \rho_{\text{max}} = 0.51 \, e \, Å^{-3} \)  
\( \Delta \rho_{\text{min}} = -0.64 \, e \, Å^{-3} \)
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/A² |
|----|-------|-------|-------|---------|
| Cu1| 0.57740 (4) | 0.64590 (4) | 0.46958 (4) | 0.01225 (12) |
| Cl1| 0.36070 (8)  | 0.54060 (8)   | 0.34752 (7)  | 0.01340 (18)  |
| S1 | 0.91865 (9)  | 0.82046 (8)   | 0.47781 (8)  | 0.01693 (19)  |
| N1 | 0.7401 (3)   | 0.5908 (2)    | 0.3922 (2)   | 0.0098 (5)    |
| C2 | 0.8718 (3)   | 0.6558 (3)    | 0.4035 (3)   | 0.0113 (6)    |
| C3 | 0.9837 (3)   | 0.5968 (3)    | 0.3594 (3)   | 0.0142 (7)    |
| H3 | 1.075431     | 0.645998      | 0.368256     | 0.017*       |
| C4 | 0.9603 (4)   | 0.4679 (3)    | 0.3036 (3)   | 0.0175 (7)    |
| H4 | 1.036450     | 0.425281      | 0.275400     | 0.021*       |
| C5 | 0.8239 (4)   | 0.4003 (3)    | 0.2888 (3)   | 0.0158 (7)    |
| H5 | 0.803694     | 0.311139      | 0.249195     | 0.019*       |
| C6 | 0.7184 (3)   | 0.4656 (3)    | 0.3331 (3)   | 0.0145 (7)    |
| H6 | 0.624182     | 0.419633      | 0.321361     | 0.017*       |
| C7 | 0.7410 (4)   | 0.8972 (3)    | 0.4778 (3)   | 0.0145 (7)    |
| H7A| 0.759319     | 0.996020      | 0.504812     | 0.017*       |
| H7B| 0.669754     | 0.896375      | 0.389294     | 0.017*       |
| C8 | 0.6665 (4)   | 0.8249 (3)    | 0.5633 (3)   | 0.0137 (7)    |
| H8 | 0.729407     | 0.776905      | 0.636305     | 0.016*       |
| C9 | 0.5133 (4)   | 0.8248 (3)    | 0.5412 (3)   | 0.0198 (8)    |
| H9A| 0.447951     | 0.872113      | 0.468765     | 0.024*       |
| H9B| 0.471792     | 0.777530      | 0.598143     | 0.024*       |

Atomic displacement parameters (Å²)

|    | U¹¹ | U¹₂ | U¹₃ | U₂₂ | U₂₃ | U₃₃ |
|----|-----|-----|-----|-----|-----|-----|
| Cu1| 0.0103 (2) | 0.0106 (2) | 0.0177 (2) | −0.00093 (15) | 0.00702 (17) | −0.00293 (16) |
| Cl1| 0.0082 (4)  | 0.0164 (4)  | 0.0146 (4)  | −0.0007 (3)   | 0.0022 (3)   | 0.0002 (3)    |
| S1 | 0.0066 (12) | 0.0092 (12) | 0.0125 (13) | 0.0009 (10)   | 0.0013 (11)  | 0.0005 (11)   |
| N1 | 0.0130 (4)  | 0.0140 (4)  | 0.0249 (5)  | −0.0034 (3)   | 0.0076 (4)   | −0.0022 (3)   |
| C2 | 0.0213 (15) | 0.0132 (15) | 0.0063 (14) | 0.0031 (13)   | 0.0013 (13)  | 0.0022 (12)   |
| C3 | 0.0097 (15) | 0.0187 (17) | 0.0160 (16) | 0.0024 (13)   | 0.0064 (13)  | 0.0057 (14)   |
| C4 | 0.0147 (16) | 0.0270 (19) | 0.0129 (16) | 0.0101 (14)   | 0.0073 (14)  | 0.0026 (15)   |
| C5 | 0.0192 (17) | 0.0145 (16) | 0.0128 (16) | 0.0050 (14)   | 0.0037 (14)  | −0.0029 (13)  |
| C6 | 0.0117 (15) | 0.0160 (16) | 0.0162 (16) | 0.0010 (13)   | 0.0049 (14)  | 0.0018 (13)   |
| C7 | 0.0176 (17) | 0.0091 (15) | 0.0184 (16) | −0.0004 (13)  | 0.0079 (14)  | −0.0004 (13)  |
| C8 | 0.0182 (17) | 0.0080 (15) | 0.0154 (16) | −0.0003 (13)  | 0.0059 (14)  | −0.0017 (13)  |
| C9 | 0.0245 (19) | 0.0091 (16) | 0.031 (2)   | 0.0003 (14)   | 0.0164 (16)  | −0.0026 (14)  |
### Geometric parameters (Å, °)

| Bond/Angle                              | Distance/Value | Error | Distance/Value | Error |
|----------------------------------------|----------------|-------|----------------|-------|
| Cu1—Cl1                                 | 2.2691 (9)     |       | Cl1—Cu1i      | 2.6186 (9) |       |
| Cu1—Cl1i                                | 2.6186 (9)     |       | Cl1—Cu1i      | 2.2691 (9) |       |
| Cu1—Ni                                 | 2.026 (2)      |       | C4—H4         | 0.9500  |       |
| Cu1—C8                                 | 2.037 (3)      |       | C4—C5         | 1.383 (4) |       |
| Cu1—C9                                 | 2.052 (3)      |       | C5—H5         | 0.9500  |       |
| S1—C2                                  | 1.766 (3)      |       | C5—C6         | 1.375 (4) |       |
| S1—C7                                  | 1.804 (3)      |       | H7A—C7        | 0.9900  |       |
| N1—C2                                  | 1.340 (4)      |       | C7—H7B        | 0.9900  |       |
| N1—C6                                  | 1.349 (4)      |       | C7—C8         | 1.503 (4) |       |
| C2—C3                                  | 1.397 (4)      |       | C8—H8         | 0.9500  |       |
| C3—H3                                  | 0.9500         |       | C8—C9         | 1.364 (4) |       |
| C3—C4                                  | 1.366 (4)      |       | C9—H9A        | 0.9500  |       |

| Bond/Angle                              | Distance/Value | Error | Distance/Value | Error |
|----------------------------------------|----------------|-------|----------------|-------|
| Cl1—Cu1—Cl1i                           | 95.20 (3)      |       | C4—C5—H5      | 120.9 |       |
| N1—Cu1—Cl1i                            | 97.91 (7)      |       | C6—C5—C4      | 118.1 (3) |       |
| N1—Cu1—Cl1                             | 105.77 (7)     |       | C6—C5—H5      | 120.9 |       |
| N1—Cu1—C8                              | 101.34 (11)    |       | N1—C6—C5      | 124.2 (3) |       |
| N1—Cu1—C9                              | 136.50 (12)    |       | N1—C6—H6      | 117.9 |       |
| C8—Cu1—Cl1i                            | 103.19 (9)     |       | C5—C6—H6      | 117.9 |       |
| C8—Cu1—Cl1                             | 144.63 (9)     |       | S1—C7—H7A     | 108.7 |       |
| C8—Cu1—C9                              | 38.96 (12)     |       | S1—C7—H7B     | 108.7 |       |
| C9—Cu1—Cl1i                            | 106.96 (10)    |       | H7A—C7—H7B    | 107.6 |       |
| C9—Cu1—Cl1                             | 106.81 (10)    |       | C8—C7—S1      | 114.4 (2) |       |
| Cu1—Cl1—Cu1                            | 84.80 (3)      |       | C8—C7—H7A     | 108.7 |       |
| C2—S1—C7                               | 105.89 (15)    |       | C8—C7—H7B     | 108.7 |       |
| C2—N1—Cu1                              | 128.2 (2)      |       | Cu1—C8—H8     | 93.7 |       |
| C2—N1—C6                               | 116.7 (3)      |       | C7—C8—Cu1     | 105.2 (2) |       |
| C6—N1—Cu1                              | 114.72 (19)    |       | C7—C8—H8      | 118.4 |       |
| N1—C2—S1                               | 122.7 (2)      |       | C9—C8—Cu1     | 71.15 (18) |       |
| N1—C2—C3                               | 122.3 (3)      |       | C9—C8—C7      | 123.2 (3) |       |
| C3—C2—S1                               | 115.0 (2)      |       | C9—C8—H8      | 118.4 |       |
| C2—C3—H3                               | 120.2          |       | Cu1—C9—H9A    | 105.0 |       |
| C4—C3—C2                               | 119.5 (3)      |       | Cu1—C9—H9B    | 94.9  |       |
| C4—C3—H3                               | 120.2          |       | C8—C9—Cu1     | 69.90 (18) |       |
| C3—C4—H4                               | 120.5          |       | C8—C9—H9A     | 120.0 |       |
| C3—C4—C5                               | 119.0 (3)      |       | C8—C9—H9B     | 120.0 |       |
| C5—C4—H4                               | 120.5          |       | H9A—C9—H9B    | 120.0 |       |

| Bond/Angle                              | Distance/Value | Error | Distance/Value | Error |
|----------------------------------------|----------------|-------|----------------|-------|
| Cu1—N1—C2—S1                          | −7.6 (4)       |       | C2—C3—C4—C5   | 1.8 (5) |       |
| Cu1—N1—C2—C3                          | 171.1 (2)      |       | C3—C4—C5—C6   | −1.0 (5) |       |
| Cu1—N1—C6—C5                          | −171.2 (2)     |       | C4—C5—C6—N1   | −1.1 (5) |       |
| S1—C2—C3—C4                           | 178.2 (2)      |       | C6—N1—C2—S1   | 179.9 (2) |       |
| S1—C7—C8—Cu1                          | −75.0 (2)      |       | C6—N1—C2—C3   | −1.4 (4) |       |
| S1—C7—C8—Cu1                          | −152.1 (3)     |       | C7—S1—C2—N1   | −19.4 (3) |       |
| N1—C2—C3—C4                           | −0.6 (5)       |       | C7—S1—C2—C3   | 161.8 (2) |       |

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

**Hydrogen-bond geometry ($\AA$, °)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|----------|------|-------|-------|---------|
| C3—H3···C11$^a$ | 0.95 | 2.91 | 3.581 (3) | 129 |
| C6—H6···C11 | 0.95 | 2.80 | 3.447 (3) | 126 |
| C7—H7B···C11$^{iii}$ | 0.99 | 2.89 | 3.676 (3) | 137 |

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

**Di-$\mu$-bromido-bis((2-[(η-2,3)-(prop-2-en-1-yl)sulfanyl]pyridine-κN)copper(I)) (II)**

**Crystal data**

$[\text{Cu}_2\text{Br}_2(\text{C}_8\text{H}_9\text{NS})_2]$  
$M_r = 589.34$  
Monoclinic, $P2_1/c$  
$a = 9.5009$ (6) Å  
$b = 9.6022$ (5) Å  
$c = 11.0936$ (8) Å  
$\beta = 107.257$ (7)°  
$V = 966.50$ (11) Å$^3$  
$Z = 2$

$F(000) = 576$  
$D_x = 2.025$ Mg m$^{-3}$  
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å  
Cell parameters from 3535 reflections  
$\theta = 3.1–29.0$°  
$\mu = 6.55$ mm$^{-1}$  
$T = 150$ K  
Irregular, yellowish  
$0.44 \times 0.35 \times 0.22$ mm

**Data collection**

New Gemini, Dual, Cu at home/near, Atlas diffractometer  
Detector resolution: 10.6426 pixels mm$^{-1}$  
$\omega$ scans  
Absorption correction: analytical  
(CrystalisPro; Rigaku OD, 2021)  
$T_{\text{min}} = 0.191$, $T_{\text{max}} = 0.368$  
6837 measured reflections

**Refinement**

Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.034$  
$wR(F^2) = 0.079$  
$S = 1.08$  
2162 reflections  
109 parameters  
0 restraints

Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
$\Delta\rho_{\text{max}} = 0.82$ e Å$^{-3}$  
$\Delta\rho_{\text{min}} = -0.74$ 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| 0.36045 (4) | 0.54960 (3) | 0.34080 (3) | 0.01538 (12) |
| Cu1| 0.58645 (5) | 0.64663 (4) | 0.47542 (4) | 0.01478 (13) |
| S1 | 0.91726 (10) | 0.82315 (9) | 0.48313 (10) | 0.0201 (2) |
| N1 | 0.7467 (3) | 0.5936 (3) | 0.3976 (3) | 0.0135 (6) |
| C2 | 0.8735 (4) | 0.6601 (3) | 0.4079 (3) | 0.0127 (7) |
| C3 | 0.9838 (4) | 0.6033 (4) | 0.3631 (3) | 0.0176 (8) |
| H3 | 1.072777 | 0.652922 | 0.372109 | 0.021* |
| C4 | 0.9622 (4) | 0.4747 (4) | 0.3060 (4) | 0.0191 (8) |
| H4 | 1.036808 | 0.433779 | 0.276414 | 0.023* |
| C5 | 0.8301 (4) | 0.4056 (4) | 0.2920 (3) | 0.0186 (8) |
| H5 | 0.811443 | 0.317584 | 0.251361 | 0.022* |
| C6 | 0.7270 (4) | 0.4681 (4) | 0.3387 (4) | 0.0168 (8) |
| H6 | 0.636629 | 0.420650 | 0.329185 | 0.020* |
| C7 | 0.7453 (4) | 0.8986 (4) | 0.4850 (4) | 0.0171 (8) |
| H7A| 0.762903 | 0.996856 | 0.512413 | 0.021* |
| H7B| 0.677805 | 0.898701 | 0.397736 | 0.021* |
| C8 | 0.6700 (4) | 0.8262 (4) | 0.5692 (4) | 0.0192 (8) |
| H8 | 0.729668 | 0.778274 | 0.641149 | 0.023* |
| C9 | 0.5222 (5) | 0.8253 (4) | 0.5484 (4) | 0.0247 (9) |
| H9A| 0.459626 | 0.872317 | 0.477213 | 0.030* |
| H9B| 0.481069 | 0.777660 | 0.605052 | 0.030* |

Atomic displacement parameters (Å²)

|    | U11  | U22  | U33  | U12  | U13  | U23  |
|----|------|------|------|------|------|------|
| Br1| 0.01321 (19) | 0.0189 (2) | 0.0130 (2) | −0.00013 (14) | 0.00236 (14) | 0.00135 (13) |
| Cu1| 0.0151 (2) | 0.0135 (2) | 0.0174 (3) | −0.00122 (17) | 0.00731 (19) | −0.00381 (16) |
| S1 | 0.0185 (5) | 0.0159 (5) | 0.0268 (5) | −0.0045 (4) | 0.0081 (4) | −0.0043 (4) |
| N1 | 0.0154 (15) | 0.0150 (14) | 0.0108 (15) | 0.0022 (12) | 0.0048 (12) | −0.0002 (11) |
| C2 | 0.0152 (18) | 0.0151 (17) | 0.0073 (17) | 0.0006 (14) | 0.0024 (14) | 0.0040 (13) |
| C3 | 0.0165 (19) | 0.0237 (19) | 0.0136 (19) | −0.0004 (15) | 0.0063 (15) | 0.0019 (14) |
| C4 | 0.0192 (19) | 0.023 (2) | 0.016 (2) | 0.0059 (16) | 0.0066 (16) | 0.0024 (15) |
| C5 | 0.021 (2) | 0.0209 (19) | 0.0142 (19) | 0.0041 (15) | 0.0054 (15) | −0.0011 (14) |
| C6 | 0.0167 (19) | 0.0165 (18) | 0.018 (2) | −0.0004 (15) | 0.0058 (15) | −0.0007 (14) |
| C7 | 0.022 (2) | 0.0116 (17) | 0.019 (2) | −0.0006 (15) | 0.0079 (16) | −0.0002 (14) |
| C8 | 0.030 (2) | 0.0103 (17) | 0.019 (2) | −0.0003 (15) | 0.0101 (17) | −0.0027 (14) |
| C9 | 0.033 (2) | 0.0115 (18) | 0.036 (2) | −0.0004 (16) | 0.020 (2) | −0.0065 (15) |

Geometric parameters (Å, °)

|   | Cu1—Br1 | 2.4097 (6) | C4—H4 | 0.9500 |
|---|---------|------------|-------|-------|
| Cu1—Br1' | 2.7113 (6) | C4—C5 | 1.387 (5) |
| Cu1—N1 | 2.025 (3) | C5—H5 | 0.9500 |
| Cu1—C8 | 2.048 (4) | C5—C6 | 1.374 (5) |
| Cu1—C9 | 2.065 (4) | C6—H6 | 0.9500 |
### Bond Lengths (Å)

| Bond                  | Length  | Symmetry Code |
|-----------------------|---------|----------------|
| S1—C2                 | 1.765 (4) |                |
| S1—C7                 | 1.793 (4) |                |
| N1—C2                 | 1.338 (5) |                |
| N1—C6                 | 1.357 (5) |                |
| C2—C3                 | 1.397 (5) |                |
| C3—H3                 | 0.9500   |                |
| C3—C4                 | 1.375 (5) |                |

### Bond Angles (°)

| Angle                  | Angle  | Symmetry Code |
|------------------------|--------|----------------|
| Cu1—Br1—Cu1i          | 82.521 (18) |                |
| Br1—Cu1—Br1i          | 97.479 (19) |                |
| N1—Cu1—Br1i           | 98.64 (8) |                |
| N1—Cu1—Br1            | 106.43 (9) |                |
| N1—Cu1—C8             | 101.60 (14) |               |
| N1—Cu1—C9             | 136.30 (14) |               |
| C8—Cu1—Br1            | 104.22 (11) |               |
| C8—Cu1—Br1i           | 141.26 (11) |               |
| C8—Cu1—C9             | 38.43 (15) |                |
| C9—Cu1—Br1            | 104.57 (12) |               |
| C9—Cu1—Br1i           | 107.05 (12) |               |
| C2—S1—C7              | 106.04 (17) |               |
| C2—N1—Cu1             | 128.0 (2) |                |
| C2—N1—C6              | 117.2 (3) |                |
| C6—N1—Cu1             | 114.5 (2) |                |
| N1—C2—S1              | 122.9 (3) |                |
| N1—C2—C3              | 122.3 (3) |                |
| C3—C2—S1              | 114.7 (3) |                |
| C2—C3—H3              | 120.3 |                |
| C4—C3—C2              | 119.3 (4) |                |
| C4—C3—H3              | 120.3 |                |
| C3—C4—H4              | 120.4 |                |
| C3—C4—C5              | 119.1 (4) |               |
| C5—C4—H4              | 120.4 |                |

### Hydrogen Bonds

| Hydrogen Bond          | D—H   | H···A     | D···A   | D—H···A  |
|------------------------|-------|----------|--------|----------|
| C3—H3···Br1          | 0.95  | 3.02     | 3.696 (4) | 129      |

Symmetry code: (i) −x+1, −y+1, −z+1.
|          |          |          |          |
|----------|----------|----------|----------|
| C6—H6···Br1 | 0.95     | 2.94     | 3.576 (4) | 126      |
| C7—H7B···Br1 iii | 0.99 | 2.94 | 3.744 (4) | 139      |

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