



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

Yurii Slyvka,^a Nazariy T. Pokhodylo,^{b*} Evgeny Goreschnik,^c Olexii Pavlyuk^a and Marian Mys'kiv^a

Received 12 October 2021

Accepted 21 October 2021

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: copper(I); η^2 -interaction; pyridine-2-thiol; allyl derivative; crystal structure.

CCDC references: 2116969; 2116968

Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya, 6, Lviv, 79005, Ukraine,

^bDepartment of Organic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya, 6, Lviv, 79005, Ukraine, and ^cDepartment of Inorganic Chemistry and Technology, Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia.

*Correspondence e-mail: pokhodylo@gmail.com

The title compounds, di- μ -chlorido-bis({2-[(η -2,3)-(prop-2-en-1-yl)sulfanyl]pyridine- κ N}copper(I)), [Cu₂Cl₂(C₈H₉NS)₂], and di- μ -bromido-bis({2-[(η -2,3)-(prop-2-en-1-yl)sulfanyl]pyridine- κ N}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 three-dimensional network.

1. Chemical context

Cu-containing complexes have been found very promising regarding their catalytic activities in organic syntheses, non-linear 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 (Goreschnik *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 Cu^I salts that are unknown (or less stable) in the free state. For instance, the first examples of

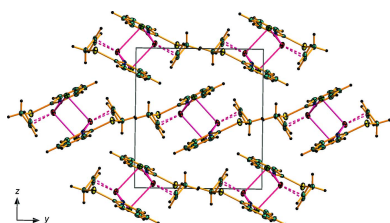
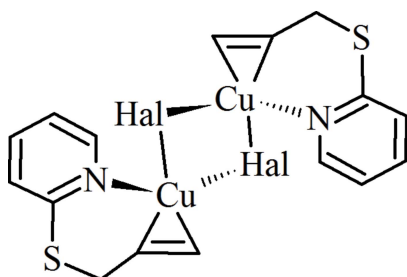


Table 1
Selected bond lengths (Å) for **I**.

Cu1—Cl1	2.2691 (9)	Cu1—C8	2.037 (3)
Cu1—Cl1 ⁱ	2.6186 (9)	Cu1—C9	2.052 (3)
Cu1—N1	2.026 (2)		

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

Cu(C₆H₅SO₃), Cu(*p*-CH₃C₆H₄SO₃) or CuHSO₄ π -complexes as well as the direct Cu^I···F(SiF₆²⁻) interaction have been observed in copper(I) π -compounds with allyl derivatives of triazole and thiadiazole (Goresnik *et al.*, 2016; Ardan *et al.*, 2017; Slyvka *et al.*, 2018b; Fedorchuk *et al.*, 2020). *N*-Allyl derivatives of pyridine were found to be suitable ligands for the crystal engineering of Cu^I coordination compounds with inorganic fragments of different complexity and related to the *pK_a* values of the initial pyridine bases (Goresnik *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 π -coordination compounds [Cu₂Cl₂(*Psup*)₂] (**I**) & [Cu₂Br₂(*Psup*)₂] (**II**) with 2-[(prop-2-en-1-yl)sulfanyl]pyridine (*Psup*), C₈H₉NS.



2. Structural commentary

The title compounds are isostructural and crystallize in the centrosymmetric space group *P2₁/c* with one *Psup* organic molecule, one copper(I) ion and one halide ion in the asym-

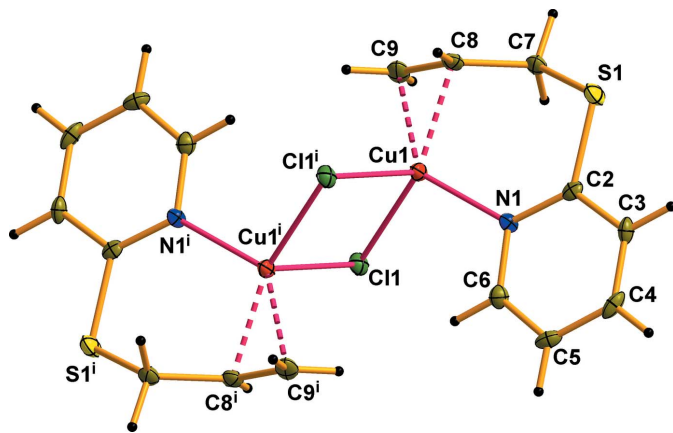


Figure 1
The molecular structure of **I** with displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2
Selected bond lengths (Å) for **II**.

Cu1—Br1	2.4097 (6)	Cu1—C8	2.048 (4)
Cu1—Br1 ⁱ	2.7113 (6)	Cu1—C9	2.065 (4)
Cu1—N1	2.025 (3)		

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

metric unit. As shown in Figs. 1 and 2, these structures are constructed from centrosymmetric [Cu₂Hal₂(*Psup*)₂] [*Hal* = Cl (**I**) 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^I cation includes the η^2 allylic C=C bond, the pyridine N atom and a *Hal*1 ion in the basal plane (Tables 1 and 2). The apical position of the Cu^I polyhedron is occupied by the *Hal*1ⁱ [symmetry code: (i) $-x + 1, -y + 1, -z + 1$] ion at 2.6186 (9) Å in **I** and at 2.7113 (6) Å in **II**. The corresponding four-coordinate geometry indices τ_4 (Yang *et al.*, 2007) are 0.81 (**I**) and 0.83 (**II**). For comparison, in the structures of previously studied CuCl and CuBr π,σ -complexes with allylacetoneoxime, the Cu—*Hal*_{ap} distances are slightly higher at 2.719 (5) and 2.778 (4) Å (Filinchuk *et al.*, 1998).

Being π -connected to the metal center, the C8=C9 bond of the ligand is elongated due to back-donation from an occupied 3*d* metal orbital to a low-lying empty π^* -orbital of the olefin to 1.364 (4) Å (**I**) and to 1.354 (6) Å (**II**) in comparison with an uncoordinated allylic C=C bond (Slyvka *et al.*, 2021). The allylsulfanyl group in (**I**) and (**II**) has synclinal conformation relative to the S1—C7 bond and an antiperiplanar conformation relative to the C7—C8 bond [the corresponding torsion angles C2—S1—C7—C8 and S1—C7—C8—C9 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

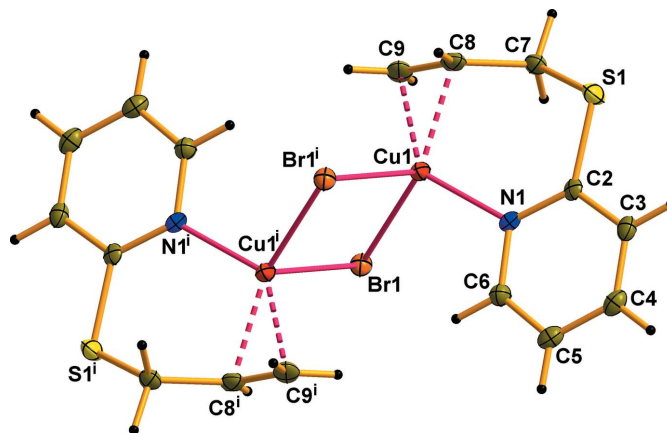


Figure 2
The molecular structure of **II** with displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C3—H3···Cl1 ⁱⁱ	0.95	2.91	3.581 (3)	129
C6—H6···Cl1	0.95	2.80	3.447 (3)	126
C7—H7B···Cl1 ⁱⁱⁱ	0.99	2.89	3.676 (3)	137

Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

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 H7B 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 closest related compounds to the title compounds, containing a similar {Cu₂Hal₂} 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(μ_2 -chloro)-bis(η^2 -allylacetoneoxime-*N*)dicopper(I) (**IV**) (GOKYAG; Filinchuk *et al.*, 1998), bis(μ_2 -bromo)-bis(η^2 -allylacetoneoxime-*N*)dicopper(I) (**V**) (GOKYEK; Filinchuk *et al.*, 1998), bis[(μ_2 -bromo)(η^2 -2-(allylthio)benzimidazole-*N*)copper(I)] (**VI**) (WUCRAN; Goreshnik *et al.*, 2002) and bis{[(μ_2 -iodo){(η^2 -allyl)(2-pyridyl)dimethylsilane}copper]} (**VII**) (XAZGIP; Kamei *et al.*, 2005).

Compounds (**III**) and (**VII**) crystallize in the triclinic crystal system in space group $P\bar{1}$. Compounds (**IV**), (**V**) and (**VI**) crystallize in the monoclinic crystal system in space group $P2_1/c$ (settings $P2_1/a$, $P2_1/c$ and $P2_1/n$, respectively). Structures

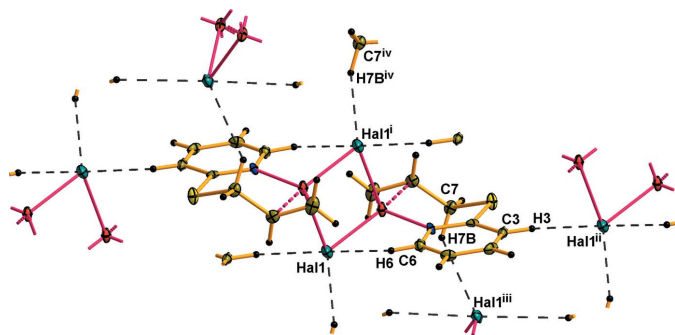


Figure 3
Fragment of the extended structure of **I** with hydrogen bonds shown as dashed lines. Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, -y + \frac{3}{2}, -z + \frac{1}{2}$. The packing for **II** is essentially identical.

Table 4
Hydrogen-bond geometry (Å, °) for **II**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C3—H3···Br1 ⁱⁱ	0.95	3.02	3.696 (4)	129
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) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

(**III**), (**IV**), (**V**) and (**VI**) are built up from centrosymmetric [Cu₂Hal₂(Ligand)₂] dimers. In the compounds bis[(μ_2 -chloro)chloro(η^2 -1-allyl-2-aminopyridinium)copper(I)] (**XIII**) (BEBFOE) and bis[(μ_2 -chloro)bromo(η^2 -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(μ_3 -chloro)bis(μ_2 -chloro)bis(η^2 -1-allylpyridinium)dichlorotetracopper(I)] (**X**) (YAPQIQ; Pavlyuk *et al.*, 2005) forces the realization of an infinite {Cu₄Cl₄}_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)sulfanyl]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.

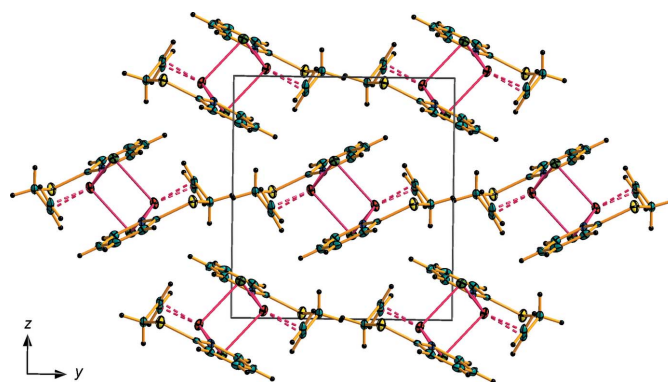


Figure 4
A view along the *a*-axis direction of the crystal packing of **I**.

Table 5
Experimental details.

	I	II
Crystal data		
Chemical formula	[Cu ₂ Cl ₂ (C ₈ H ₉ NS) ₂]	[Cu ₂ Br ₂ (C ₈ H ₉ NS) ₂]
<i>M_r</i>	500.42	589.34
Crystal system, space group	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	150	150
<i>a</i> , <i>b</i> , <i>c</i> (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)
<i>V</i> (Å ³)	929.1 (3)	966.50 (11)
<i>Z</i>	2	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
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 (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)
<i>T</i> _{min} , <i>T</i> _{max}	0.546, 0.693	0.191, 0.368
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	8088, 2161, 1730	6837, 2162, 1854
<i>R</i> _{int}	0.058	0.044
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.686	0.682
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 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
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ was applied in all cases.

Funding information

This work was supported by the Ministry of Education and Science of Ukraine (Grant Nos. 0120U101622 and 0120U102028) and the Slovenian Research Agency (ARRS) within the research program P1–0045 Inorganic Chemistry and Technology.

References

- Arđan, B., Kinzhybalov, V., Slyvka, Y., Shyyka, O., Luk'yanov, M., Lis, T. & Mys'kiv, M. (2017). *Acta Cryst.* **C73**, 36–46.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Fedorchuk, A. A., Slyvka, Yu. I., Goreschnik, E. A., Kityk, I. V., Czaja, P. & Mys'kiv, M. G. (2018). *J. Mol. Struct.* **1171**, 644–649.
- Fedorchuk, A., Goreschnik, E., Slyvka, Yu. & Mys'kiv, M. (2020). *Acta Chim. Slov.* **67**, 1148–1154.
- Filinchuk, Ya. E., Mys'kiv, M. G. & Davydov, V. N. (1998). *Koord. Khim. (Russ.) (Coord. Chem.)*, **24**, 771–775.
- Fukushima, K., Kobayashi, A., Miyamoto, T. & Sasaki, Y. (1976). *Bull. Chem. Soc. Jpn*, **49**, 143–146.
- Goreschnik, E. A., Schollmeyer, D. & Mys'kiv, M. G. (2002). *ZAAC*, **628**, 2118–2122.
- Goreschnik, E. A., Slyvka, Yu. I. & Mys'kiv, M. G. (2011). *Inorg. Chim. Acta*, **377**, 177–180.
- Goreschnik, E. A., Veryasov, G., Morozov, D., Slyvka, Yu., Arđan, B. & Mys'kiv, M. G. (2016). *J. Organomet. Chem.* **810**, 1–11.
- Goreschnik, E., Schollmeier, D. & Mys'kiv, M. (2003). *Acta Cryst.* **C59**, m478–m481.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hordiichuk, O. R., Slyvka, Yu. I., Kinzhybalov, V. V., Goreschnik, E. A., Bednarchuk, T. J., Bednarchuk, O., Jedryka, J., Kityk, I. & Mys'kiv, M. G. (2019). *Inorg. Chim. Acta*, **495**, 119012.
- Iakovidis, I., Delimaris, I. & Piperakis, S. M. (2011). *Mol. Biol. Int.* **2011**, 1–13.
- Kamei, T., Fujita, K., Itami, K. & Yoshida, J. (2005). *Org. Lett.* **7**, 4725–4728.
- Kowalska, D. A., Kinzhybalov, V., Slyvka, Y. I. & Wołczyr, M. (2021). *Acta Cryst.* **B77**, 241–248.
- Marzano, C., Pellei, M., Alidori, S., Brossa, A., Lobbia, G. G., Tisato, F. & Santini, C. (2006). *J. Inorg. Biochem.* **100**, 299–304.
- Pavlyuk, O. V., Goreschnik, E. A., Ciunik, Z. & Mys'kiv, M. G. (2005). *ZAAC*, **631**, 793–797.
- Rigaku OD (2021). *CrysAlis PRO*. Rigaku Oxford Diffraction, Tokyo, Japan.
- Rourke, J. (2006). *Appl. Organomet. Chem.* **20**, 811–811.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Slyvka, Yu., Fedorchuk, A. A., Goreschnik, E., Lakshminarayana, G., Kityk, I. V., Czaja, P. & Mys'kiv, M. (2018b). *Chem. Phys. Lett.* **694**, 112–119.
- Slyvka, Yu., Goreschnik, E., Pavlyuk, O. & Mys'kiv, M. (2013). *Open Chem.* **11**, 1875–1901.

- Slyvka, Y., Kinzhybalov, V., Shyyka, O. & Mys'kiv, M. (2021). *Acta Cryst. C* **77**, 249–256.
- Slyvka, Yu. I., Fedorchuk, A. A., Pokhodylo, N. T., Lis, T., Kityk, I. V. & Mys'kiv, M. G. (2018a). *Polyhedron*, **147**, 86–93.
- Tisato, F., Marzano, C., Porchia, M., Pellei, M. & Santini, C. (2010). *Med. Res. Rev.* **30**, 708–749.
- Wang, X.-S., Zhao, H., Li, Y.-H., Xiong, R.-G. & You, X.-Z. (2005). *Top. Catal.* **35**, 43–61.
- Yang, L., Powell, D. R. & Houser, R. P. (2007). *Dalton Trans.* pp. 955–964.
- Yoshikai, N. & Nakamura, E. (2012). *Chem. Rev.* **112**, 2339–2372.

supporting information

Acta Cryst. (2021). E77, 1180-1184 [https://doi.org/10.1107/S2056989021011002]

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

Yurii Slyvka, Nazariy T. Pokhodylo, Evgeny Goreshnik, Olexii Pavlyuk and Marian Mys'kiv

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- κ N}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)°
 $V = 929.1$ (3) Å³
 $Z = 2$

$F(000) = 504$
 $D_x = 1.789$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3255 reflections
 $\theta = 3.8$ – 28.9 °
 $\mu = 2.80$ mm⁻¹
 $T = 150$ K
 Irregular, yellowish
 0.33 × 0.28 × 0.19 mm

Data collection

New Gemini, Dual, Cu at home/near, Atlas diffractometer
 Detector resolution: 10.6426 pixels mm⁻¹
 ω scans
 Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2021)
 $T_{\min} = 0.546$, $T_{\max} = 0.693$
 8088 measured reflections

2161 independent reflections
 1730 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 29.2$ °, $\theta_{\min} = 2.9$ °
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 11$
 $l = -15 \rightarrow 15$

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
 $w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 0.6316P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.51$ e Å⁻³
 $\Delta\rho_{\min} = -0.64$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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	0.0130 (4)	0.0140 (4)	0.0249 (5)	-0.0034 (3)	0.0076 (4)	-0.0022 (3)
N1	0.0066 (12)	0.0092 (12)	0.0125 (13)	0.0009 (10)	0.0013 (11)	0.0005 (11)
C2	0.0131 (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, °)

Cu1—C11	2.2691 (9)	C4—H4	0.9500
Cu1—C11 ⁱ	2.6186 (9)	C4—C5	1.383 (4)
Cu1—N1	2.026 (2)	C5—H5	0.9500
Cu1—C8	2.037 (3)	C5—C6	1.375 (4)
Cu1—C9	2.052 (3)	C6—H6	0.9500
S1—C2	1.766 (3)	C7—H7A	0.9900
S1—C7	1.804 (3)	C7—H7B	0.9900
N1—C2	1.340 (4)	C7—C8	1.503 (4)
N1—C6	1.349 (4)	C8—H8	0.9500
C2—C3	1.397 (4)	C8—C9	1.364 (4)
C3—H3	0.9500	C9—H9A	0.9500
C3—C4	1.366 (4)	C9—H9B	0.9500
C11—Cu1—C11 ⁱ	95.20 (3)	C4—C5—H5	120.9
N1—Cu1—C11 ⁱ	97.91 (7)	C6—C5—C4	118.1 (3)
N1—Cu1—C11	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—C11 ⁱ	103.19 (9)	C5—C6—H6	117.9
C8—Cu1—C11	144.63 (9)	S1—C7—H7A	108.7
C8—Cu1—C9	38.96 (12)	S1—C7—H7B	108.7
C9—Cu1—C11 ⁱ	106.96 (10)	H7A—C7—H7B	107.6
C9—Cu1—C11	106.81 (10)	C8—C7—S1	114.4 (2)
Cu1—C11—Cu1 ⁱ	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
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—C9	-152.1 (3)	C7—S1—C2—N1	-19.4 (3)
N1—C2—C3—C4	-0.6 (5)	C7—S1—C2—C3	161.8 (2)

C2—S1—C7—C8	68.1 (3)	C7—C8—C9—Cu1	96.2 (3)
C2—N1—C6—C5	2.3 (4)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots Cl1 ⁱⁱ	0.95	2.91	3.581 (3)	129
C6—H6 \cdots Cl1	0.95	2.80	3.447 (3)	126
C7—H7B \cdots Cl1 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- μ -bromido-bis({2-[(η -2,3)-(prop-2-en-1-yl)sulfanyl]pyridine- κ N}copper(I)) (II)

Crystal data

[Cu₂Br₂(C₈H₉NS)₂]
 $M_r = 589.34$
 Monoclinic, $P2_1/c$
 $a = 9.5009$ (6) \AA
 $b = 9.6022$ (5) \AA
 $c = 11.0936$ (8) \AA
 $\beta = 107.257$ (7) $^\circ$
 $V = 966.50$ (11) \AA^3
 $Z = 2$

$F(000) = 576$
 $D_x = 2.025$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA
 Cell parameters from 3535 reflections
 $\theta = 3.1\text{--}29.0^\circ$
 $\mu = 6.55$ 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
 ω scans
 Absorption correction: analytical (CrysalisPro; Rigaku OD, 2021)
 $T_{\min} = 0.191$, $T_{\max} = 0.368$
 6837 measured reflections

2162 independent reflections
 1854 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 29.0^\circ$, $\theta_{\min} = 2.9^\circ$
 $h = -12 \rightarrow 12$
 $k = -10 \rightarrow 12$
 $l = -12 \rightarrow 13$

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
 $w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 1.3651P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.82$ e \AA^{-3}
 $\Delta\rho_{\min} = -0.74$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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 (\AA , $^\circ$)

Cu1—Br1	2.4097 (6)	C4—H4	0.9500
Cu1—Br1 ⁱ	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

S1—C2	1.765 (4)	C7—H7A	0.9900
S1—C7	1.793 (4)	C7—H7B	0.9900
N1—C2	1.338 (5)	C7—C8	1.505 (5)
N1—C6	1.357 (5)	C8—H8	0.9500
C2—C3	1.397 (5)	C8—C9	1.354 (6)
C3—H3	0.9500	C9—H9A	0.9500
C3—C4	1.375 (5)	C9—H9B	0.9500
Cu1—Br1—Cu1 ⁱ	82.521 (18)	C4—C5—H5	120.9
Br1—Cu1—Br1 ⁱ	97.479 (19)	C6—C5—C4	118.1 (4)
N1—Cu1—Br1 ⁱ	98.64 (8)	C6—C5—H5	120.9
N1—Cu1—Br1	106.43 (9)	N1—C6—C5	123.9 (4)
N1—Cu1—C8	101.60 (14)	N1—C6—H6	118.1
N1—Cu1—C9	136.30 (14)	C5—C6—H6	118.1
C8—Cu1—Br1 ⁱ	104.22 (11)	S1—C7—H7A	108.5
C8—Cu1—Br1	141.26 (11)	S1—C7—H7B	108.5
C8—Cu1—C9	38.43 (15)	H7A—C7—H7B	107.5
C9—Cu1—Br1	104.57 (12)	C8—C7—S1	115.0 (3)
C9—Cu1—Br1 ⁱ	107.05 (12)	C8—C7—H7A	108.5
C2—S1—C7	106.04 (17)	C8—C7—H7B	108.5
C2—N1—Cu1	128.0 (2)	Cu1—C8—H8	93.7
C2—N1—C6	117.2 (3)	C7—C8—Cu1	104.9 (2)
C6—N1—Cu1	114.5 (2)	C7—C8—H8	118.0
N1—C2—S1	122.9 (3)	C9—C8—Cu1	71.5 (2)
N1—C2—C3	122.3 (3)	C9—C8—C7	123.9 (4)
C3—C2—S1	114.7 (3)	C9—C8—H8	118.0
C2—C3—H3	120.3	Cu1—C9—H9A	104.7
C4—C3—C2	119.3 (4)	Cu1—C9—H9B	95.0
C4—C3—H3	120.3	C8—C9—Cu1	70.1 (2)
C3—C4—H4	120.4	C8—C9—H9A	120.0
C3—C4—C5	119.1 (4)	C8—C9—H9B	120.0
C5—C4—H4	120.4	H9A—C9—H9B	120.0
Cu1—N1—C2—S1	-6.5 (4)	C2—C3—C4—C5	1.2 (5)
Cu1—N1—C2—C3	171.5 (3)	C3—C4—C5—C6	-1.3 (6)
Cu1—N1—C6—C5	-172.5 (3)	C4—C5—C6—N1	0.1 (6)
S1—C2—C3—C4	178.3 (3)	C6—N1—C2—S1	-179.3 (3)
S1—C7—C8—Cu1	-74.2 (3)	C6—N1—C2—C3	-1.4 (5)
S1—C7—C8—C9	-151.7 (3)	C7—S1—C2—N1	-20.3 (3)
N1—C2—C3—C4	0.2 (5)	C7—S1—C2—C3	161.7 (3)
C2—S1—C7—C8	68.3 (3)	C7—C8—C9—Cu1	95.9 (3)
C2—N1—C6—C5	1.3 (5)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots Br1 ⁱⁱ	0.95	3.02	3.696 (4)	129

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) $-x+1, y+1/2, -z+1/2$.