

# The First Complex of Diallylpolysulfide: Synthesis and Crystal Structure of [Cu<sub>3</sub>Br<sub>3</sub>(CH<sub>2</sub>=CH-CH<sub>2</sub>-(S)<sub>4</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>)]

N. F. Salivon<sup>a</sup>, Y. E. Filinchuk<sup>b,1</sup>, and V. V. Olijnyk<sup>a,\*</sup><sup>a</sup> Lviv/Ukraine, National University of Forestry and Wood Technology of Ukraine<sup>b</sup> Geneva/Switzerland, Laboratory of Crystallography, University of Geneva

Received January 20th, 2006.

**Abstract.** A crystalline  $\pi$ -complex [Cu<sub>3</sub>Br<sub>3</sub>(CH<sub>2</sub>=CH-CH<sub>2</sub>-(S)<sub>4</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>)] has been obtained by an alternating-current electrochemical synthesis starting from CuBr<sub>2</sub> and diallyltetrasulfide (DATS). Its structure is orthorhombic, space group *Pbca*,  $a = 9.9911(6)$ ,  $b = 23.2792(16)$ ,  $c = 12.8005(9)$  Å,  $V = 2977.2(3)$  Å<sup>3</sup> (at 293 K),  $Z = 8$ ;  $R_1 = 0.0377$ ,  $wR_2 = 0.0760$ . The DATS molecule behaves as a bichelate pentadentate ligand: Cu1 atom is chelated by one of the two olefin groups and a weakly bonded sulfur atom,

Cu3 atoms is chelated by two sulfur atoms and Cu2 is coordinated to the second olefin group. Centrosymmetric and pseudo-centrosymmetric Cu<sub>2</sub>Br<sub>2</sub> units are associated into a finite Cu<sub>6</sub>Br<sub>6</sub> fragment by Cu...Br contacts of 3.116(1) Å.

**Keywords:** Copper;  $\pi$ -Complex; Diallyltetrasulfide; Crystal structure

## 1 Introduction

Organic polysulfides are known for their pronounced physiological activity (antibacterial, cancer preventive etc.) [1, 2], but their complexes with metals became a subject of the systematic research only recently. Here we report on a synthesis and crystal structure of the first complex of diallylpolysulfide, containing a chain of four sulfur atoms, with copper(I) bromide. It will be shown that two types of sulfur atoms, one bridging a carbon and a sulfur atom and the other bridging two sulfur atoms, interact with metal atoms. In two earlier reported closely related groups of copper(I) halide complexes, with diallylsulfide (2CuCl·DAS [3] and 5CuBr·2DAS [4]) and with diallyldisulfide (2CuX·DADS, X = Cl, Br [5]), the organic molecules also exhibit two types of S-ligands: in the sulfide the S-atom is bridging two carbon atoms, while in the disulfide it is bonded both to carbon and sulfur. It is remarkable that in the presence of the most donor diallyl-substituted S-ligand only half of the olefin groups are involved into the Cu-(C=C)  $\pi$ -interaction [3, 4], while in the complexes of diallyldisulfide all the C=C groups are coordinated to the metallic centers [5]. In will be shown here that the Cu-(C=C) interaction can be even more competitive than Cu-S, provided that the sulfur atoms have no alkyl substituents.

\* Prof. V. V. Olijnyk  
National University of Forestry and Wood Technology  
Lviv, Gen. Chuprynyk str., 103, 79057/Ukraine  
E-mail: vv\_olijnyk@mail.ru; oljnyk@forest.lviv.ua

<sup>1</sup> Current address: SNBL at ESRF, BP-220, 38043 Grenoble, France.

**Table 1** Crystal data and details of data collection and structure refinement for 3CuBr-DATS.

Compound	[Cu <sub>3</sub> Br <sub>3</sub> {C <sub>3</sub> H <sub>5</sub> (S) <sub>4</sub> C <sub>3</sub> H <sub>5</sub> }]
Empirical formula	C <sub>6</sub> H <sub>10</sub> Br <sub>3</sub> Cu <sub>3</sub> S <sub>4</sub>
Formula weight	640.73
Space group	<i>Pbca</i>
$a$ / Å	9.9911(6)
$b$ / Å	23.279(1)
$c$ / Å	12.8005(9)
$V$ / Å <sup>3</sup>	2977.2(3)
$Z$ , $D_c$ / g·cm <sup>-3</sup>	8, 2.859
$F(000)$	2416
$2\theta_{\max}$ / °	53.7
Refl. collected/unique	17918/3126
Data/restraints/parameters	3126/0/145
$R_{\text{int}}$ , $R_{\sigma}$	0.0807, 0.0842
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0377$ $wR_2 = 0.0668$
$R$ indices (all data)	$R_1 = 0.0882$ , $wR_2 = 0.0760$
Goodness-of-fit on $F^2$	0.784
$(\Delta/\sigma)_{\max}$	0.000
Largest diff. peak and hole / e·Å <sup>-3</sup>	0.99 and -0.56

## 2 Experimental Section

**Synthesis of diallyltetrasulfide (DATS).** The known experimental procedure for preparation of the diallyldisulfide [6] has been modified to produce DATS with 30 % yield. For this, allyl chloride, Na<sub>2</sub>S and S were used in 1.5:2:3.5 molar ratios and a fraction boiling at 65–80 °C/12 torr has been collected,  $n_D^{25} = 1.5727$ .

**Preparation of the 3CuBr-DATS complex.** The complex has been obtained by an alternating-current electrochemical technique. 2 mmol of DATS were added to a solution of CuBr<sub>2</sub>·2H<sub>2</sub>O (6 mmol) in ethanol (6 ml). The mixture was placed into a glass reservoir and copper electrodes were mounted via an air-tight rubber cork. Under an applied tension of alternating current (50 Hz, 0.2 V, 0.1 mA) good quality colorless crystals of the complex appeared on the electrodes in 20 hours.

**Table 2** Selected bond distances /Å, interbond and torsion angles /° in the structure of 3CuBr·DATS.

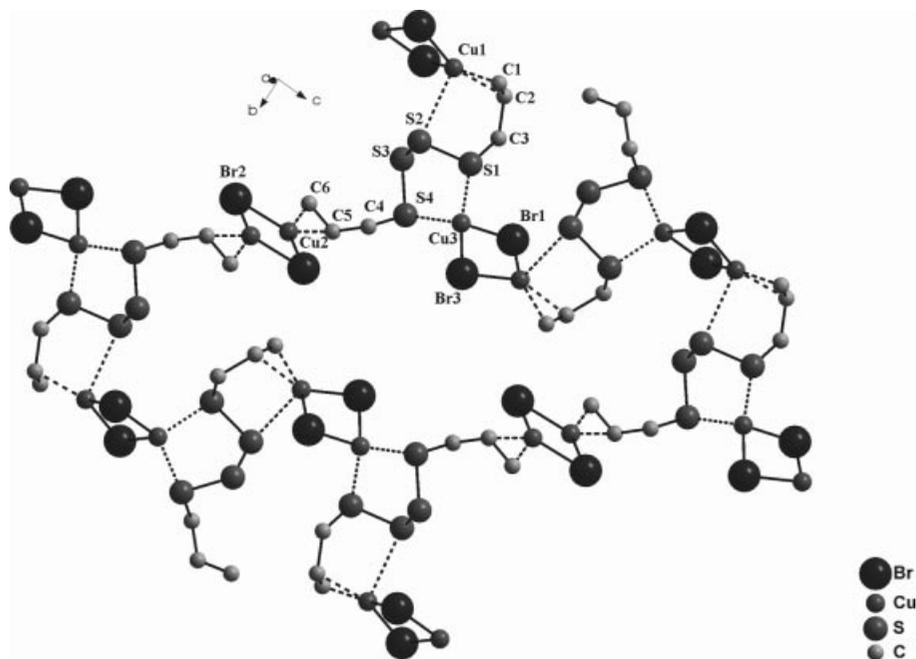
Cu1–Br1'	2.4044(14)	Br1'–Cu1–Br3'	103.40(4)
Cu1–Br3'	2.4266(14)	Br1'–Cu1–S2	93.20(5)
Cu1–S2	2.988(2)	Br3'–Cu1–S2	104.04(5)
Cu1–C1	2.074(7)	C1–Cu1–C2	37.4(3)
Cu1–C2	2.118(6)		
Cu2–Br2	2.4282(13)	Br2–Cu2–Br2'	99.23(5)
Cu2–Br2'	2.4033(14)	Br2–Cu2–Br3'	99.33(4)
Cu2–Br3'	3.1160(14)	Br2'–Cu2–Br3'	102.11(4)
Cu2–C6	2.048(7)	C5–Cu2–C6	38.0(3)
Cu2–C5	2.119(8)		
Cu3–Br1	2.4383(14)	Br1–Cu3–Br3	101.24(4)
Cu3–Br3	2.4665(13)	Br1–Cu3–S4	116.08(8)
Cu3–S1	2.352(2)	Br1–Cu3–S1	109.83(7)
Cu3–S4	2.304(2)	Br3–Cu3–S1	114.97(8)
		Br3–Cu3–S4	114.44(7)
		S1–Cu3–S4	100.83(7)
C1–C2	1.345(11)	C3–S1–S2	103.2(3)
C2–C3	1.569(10)	S1–S2–S3	104.96(12)
C3–S1	1.818(8)	S2–S3–S4	103.13(12)
S1–S2	2.042(2)	S3–S4–C4	103.1(3)
S2–S3	2.068(3)	C1–C2–C3–S1	–19.7(10)
S3–S4	2.047(3)	C2–C3–S1–S2	67.0(6)
S4–C4	1.831(8)	C3–S1–S2–S3	70.4(3)
C4–C5	1.503(10)	S1–S2–S3–S4	56.39(14)
C5–C6	1.357(10)	S2–S3–S4–C4	69.3(3)
		S3–S4–C4–C5	87.2(6)
		S4–C4–C5–C6	–89.8(9)

**Single-crystal X-ray diffraction.** The crystal was mounted on a Stoe IPDS II diffractometer equipped with an image plate detector and Mo X-ray tube. 180°  $\omega$  oscillation images with an increment of 0.9° were collected at 20 °C with 10 min exposure, crystal-to-detector distance 120 mm. All diffraction intensities could be indexed [7] by assuming two randomly intergrown domains, each possessing a primitive orthorhombic lattice. These two domains were accounted for during the intensity integration. Although overlapping intensities

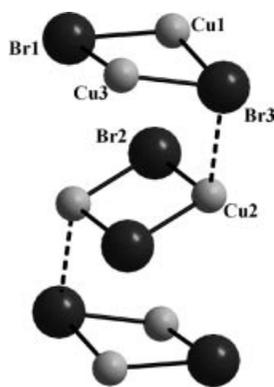
were omitted (~20 % of all reflections), highly redundant data set (~98 % completeness, in average 5 equivalents per unique reflection) was obtained for a larger domain. The data were corrected for Lorentz factor and polarization effects, and numerically for absorption (10 faces for a needle-like crystal,  $\mu = 12.8 \text{ mm}^{-1}$ ,  $T_{\text{min,max}} = 0.269, 0.641$ ). Cell parameters were obtained by a least-squares refinement based on reflection angles in the range  $3.5 < 2\theta < 54.3^\circ$ . No significant variation of average intensity during the measurement was observed. Systematic absences suggested space group *Pbca* (No. 61). The structure was solved by direct methods [8] with subsequent difference Fourier syntheses. Hydrogen atoms were placed in geometrically calculated positions and refined in a riding model with isotropic temperature factors equal to 1.2U of the neighbouring atom. A full least-squares refinement on  $F^2$  was performed on positional and thermal parameters for all atoms (anisotropically for all non-H atoms) by using SHELXL-97 [8]. Reduced cell calculations and a non-crystallographic symmetry check (PLATON2003) [9] did not indicate higher lattice symmetry or missed symmetry elements. No warnings for twinning or superstructure were observed. Crystal data and details of data collection and structure refinement are given in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 608647. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax, +44-(1223)336-033; E-mail, deposit@ccdc.cam.ac.uk). Lists of structure factors can be obtained from the authors.

### 3 Results and Discussions

A fragment of the  $[\text{Cu}_3\text{Br}_3\{\text{C}_3\text{H}_5(\text{S})_4\text{C}_3\text{H}_5\}]$  complex is shown on the Figure 1. Three crystallographically independent copper(I) atoms have a different coordination environment (see Table 2). The Cu1 atom has a trigonal pyramidal coordination formed by two Br atoms and one C=C bond



**Figure 1** A fragment of the 3CuBr·DATS complex, showing the coordination environment for the copper(I) atoms and coordination behaviour of the diallyltetrasulfide ligand.



**Figure 2** Centrosymmetric and pseudo-centrosymmetric  $\text{Cu}_2\text{Br}_2$  units associated into the finite  $\text{Cu}_6\text{Br}_6$  fragment by the elongated  $\text{Cu}\cdots\text{Br}$  contacts.

in the equatorial position, and a polysulfide S atom (bridging two other sulfur atoms within the  $-\text{S}_4-$  chain) in the apical position at 2.988(2) Å. A deviation of the Cu1 atom from the plane of equatorial ligands towards the apical position equals 0.341(4) Å. Coordination sphere of the Cu2 atom differs only by an atom occupying the apical position: instead of the weakly bonded sulfur atom, there is a bromine atom at  $\text{Cu2}\cdots\text{Br3}'$  distance of 3.1160(14) Å. The corresponding deviation of the Cu2 atom toward the apical position is smaller than for the Cu1 and equals 0.258(3) Å. The Cu3 atom has a slightly distorted tetrahedral coordination, formed by two Br and two S atoms, see Table 2. The DATS molecule behaves as a bichelate pentadentate ligand and bridges three metal atoms. The chelating function of DATS is manifested by two different 5-membered chelate cycles: one involves the Cu1 atom, the C1=C2 group and a polysulfide S2 atom, while the other is made by the  $\text{S}_4$ -chain coordinated to the Cu3 atom with two outer sulfur atoms S1 and S4. It is remarkable that the  $\text{CuS}_4$  heterocycle is practically identical to the  $\text{LiS}_4$  cycle, recently predicted for the most stable form of the dimethyltetrafulfide complex with  $\text{Li}^+$  [10].

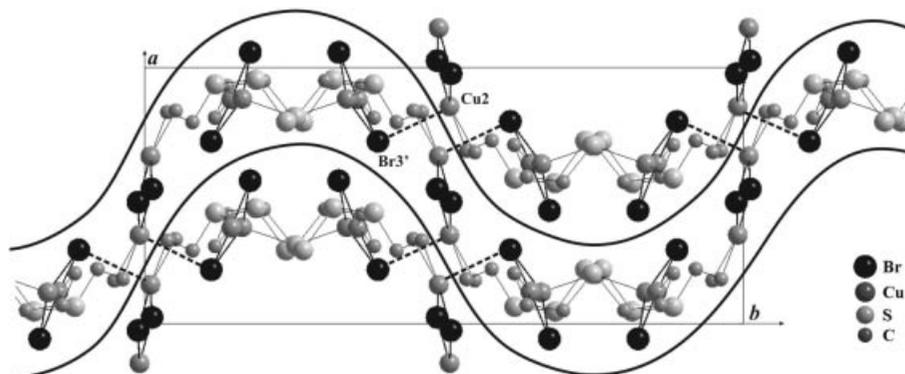
The basic inorganic fragments in the structure are the rhomb-like  $\text{Cu}_2\text{Br}_2$  units. There are two types of the  $\text{Cu}_2\text{Br}_2$  units in the structure: flat centrosymmetric and slightly

non-planar pseudo-centrosymmetric ones. They are associated by the elongated  $\text{Cu2}\cdots\text{Br3}'$  contacts into a finite  $\text{Cu}_6\text{Br}_6$  fragment, see Figure 2. The  $\text{Cu}_2\text{Br}_2$  units are also linked by the organic molecules into an infinite metal-organic layer extended in the (100) plane. A fragment of the layer is shown on the Figure 1 on the  $bc$ -projection. As can be seen from a different projection, on the  $ab$ -plane (Figure 3), the two-dimensional metal-organic layer is highly undulated and sine-shaped. Its periodic displacement along [100] has an amplitude of  $a/2$  ( $\sim 5$  Å), and the propagation direction [010]. The undulated layers are stacked in-phase along [100] and connected into the three-dimensional structure by the weak  $\text{Cu2}\cdots\text{Br3}'$  contacts. The structure is also stabilized by weak  $\text{C-H}\cdots\text{Br}$  and  $\text{C-H}\cdots\text{S}$  hydrogen bonds at  $\text{C}\cdots\text{Br}$  and  $\text{C}\cdots\text{S}$  distances above 3.5 Å.

It is remarkable, that one of the sulfur atoms (S3) does not interact with the metal atoms, despite a usually high affinity of sulfur to  $\text{Cu}^+$  ions. Indeed, the Cu-S bonding usually suppresses the  $\text{Cu}-(\text{C}=\text{C})$   $\pi$ -interaction. This has been observed in the diallylsulfide complexes [3–4], where only a part of olefin groups is  $\pi$ -coordinated by copper atoms, and in the complexes with allylsubstituted thioureas, where the  $\text{Cu}-(\text{C}=\text{C})$  interaction is completely eliminated [11–13], while sulfur atoms satisfy their coordination abilities. In this regard, it is interesting to compare affinity of sulfur atoms to  $\text{Cu}^I$  in complexes with mono-, di- and tetrasulfides.

The sulfur atom in the monosulfide is bridging two carbon atoms and is subjected to an inductive electron donating effect of the two allyl groups. Therefore, in complexes of copper(I) halides with diallylsulfide the Cu-S bonding prevails over the  $\text{Cu}-(\text{C}=\text{C})$  interaction. For instance, in  $2\text{CuCl}\cdot\text{DAS}$  [3] each S atom of the two independent DAS molecules is coordinated to two metal centers at 2.263(4)–2.365(4) Å. At the same time, only one DAS molecule is coordinated to the metal atom through the  $\text{C}=\text{C}$  bonds of both allyl groups. In the  $5\text{CuBr}\cdot 2\text{DAS}$  [4] complex, the S atom is also bridging two  $\text{Cu}^I$  atoms at 2.290(3) Å, while only one allyl group of the DAS molecule is coordinated to the metal atom.

The sulfur atom in the disulfide is bridging one carbon atoms and one sulfur atom, therefore it is subjected to an



**Figure 3** Sine-shaped two-dimensional metal-organic layers in the structure of  $3\text{CuBr}\cdot\text{DATS}$ . Hydrogen atoms are omitted for clarity.

inductive electron donating effect of a single allyl group. Indeed, in  $2\text{CuX}\cdot\text{DADS}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [5], the Cu-S and Cu-(C=C) interactions are equally competitive: each of the two sulfur atoms is coordinated to only one copper atom at 2.315(1)-2.381(1) Å, while each of the two C=C bonds is involved into a weak Cu-(C=C)  $\pi$ -interaction.

There are two types of sulfur atoms in the tetrasulfide, atoms of one type bridge carbon and sulfur and of the other – bridge two sulfur atoms. The donor properties of the S atoms appear to be even lower than in diallyldisulfide and the Cu-(C=C) interaction becomes yet more competitive: both allyl groups are coordinated to copper at the usual Cu-C distances (see Table 2). Moreover, two carbon-bonded sulfur atoms S1 and S4 are coordinated to the same Cu atom at 2.304(2)-2.352(2) Å, and the polysulfide atoms are either moved to a distant apical position at 2.988(2) Å (S2) or do not interact with the metal centers (S3).

The above comparisons show that the affinity of sulfur atoms to Cu(I) decreases as the number of sulfur atoms in the diallyl(poly)sulfide is increased. The coordination activity of the labile olefin  $\pi$ -ligands is adjusted to the donor properties of the S ligands. Variation of the length of the polysulfide chain and selection of the alkyl substituents opens up a way to construction of dialkylpolysulfide ligands with predefined coordination properties.

## References

- [1] E. Block, *Angew. Chem.* **1992**, *104*, 1158; *Angew. Chem. Int. Engl.* **1992**, *31*, 1135.
- [2] A. K. Fazlur-Rahman, J. G. Verkade, *Inorg. Chem.* **1992**, *31*, 2064.
- [3] E. A. Goreschnik, M. G. Mys'kiv, *Russ. J. Coord. Chem.* **1997**, *23*, 595.
- [4] V. V. Olijnyk, E. A. Goreschnik, Z. Zhonchin'ska, T. Glowiak, *Russ. J. Coord. Chem.* **1999**, *25*, 137.
- [5] N. F. Salivon, V. V. Olijnyk, *Russ. J. Coord. Chem.* **2006**, in press.
- [6] V. V. Nosyreva, S. V. Amosova, *Z. Org. Khim.* **1990**, *26*, 1412 (in Russian).
- [7] Stoe & Cie, *X-RED and X-Area Software*. Stoe & Cie, Darmstadt, Germany, 2003.
- [8] G. M. Sheldrick, *SHELXS97 and SHELXL97. Programs for the solution and refinement of crystal structures*, University of Göttingen, Germany, 1997.
- [9] A. L. Spek, *PLATON. A Multipurpose Crystallographic Tool*, University of Utrecht, Netherlands, 2003.
- [10] Y. Steudel, M. W. Wong, R. Steudel, *Chem. Eur. J.* **2005**, *11*, 1281.
- [11] V. V. Olijnyk, E. A. Goreschnik, D. Schollmeyer, M. G. Mys'kiv, *Russ. J. Coord. Chem.* **1997**, *23*, 511.
- [12] Ya. E. Filinchuk, V. V. Olijnyk, D. Schollmeyer, *Russ. J. Coord. Chem.* **1999**, *25*, 209.
- [13] V. V. Olijnyk, Ya. E. Filinchuk, N. L. Pandiak, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1904.