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## Structure of Bis[(4,5- $\eta$ )-3,3,6,6-tetramethyl-1-thiacyclohept-4-yne]-bis( $\mu$ -thiophenolato)-dicopper(I)

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**Abstract.**  $[\text{Cu}_2(\text{C}_6\text{H}_5\text{S})_2(\text{C}_{10}\text{H}_{16}\text{S})_2]$ ,  $M_r = 682.04$ , monoclinic,  $P2_1/n$ ,  $a = 11.644$  (2),  $b = 12.138$  (1),  $c = 24.124$  (2) Å,  $\beta = 102.31$  (1)°,  $V = 3331.2$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.36$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54051$  Å,  $\mu = 3.85$  mm<sup>-1</sup>,  $F(000) = 1424$ ,  $T = 298$  K,  $R = 0.053$  for 6140 observed reflexions. The molecule is a cyclic dimer containing two Cu atoms and two bridging thiophenolato ligands in its center. In addition each Cu atom is  $\eta^2$ -coordinated via the C $\equiv$ C group of the thiacycloheptyne ligands. The high stability of the Cu<sup>I</sup> complex is a consequence of the large strain energy in 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne, which is significantly reduced during the process of complex formation.

**Introduction.** The study of the title compound was undertaken as part of an investigation of Cu<sup>I</sup> compounds with different anionic and neutral ligands. The alkyne 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne represents a highly strained cycloalkyne with a low-lying LUMO (lowest unoccupied molecular orbital) and is, therefore, an interesting ligand for Cu<sup>I</sup> (Bennet & Schwemlein, 1989).

**Experimental.** The complex was prepared from equimolar amounts of copper(I) thiophenolate and 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne in tetrahydrofuran at 195 K. After hydrolysis and extraction

with *n*-hexane the product was recrystallized from *n*-hexane. Light-green crystals were obtained, stable to air and X-rays. A crystal of size 0.7 × 0.3 × 0.1 mm was used for all measurements. An Enraf-Nonius CAD-4 diffractometer was used with graphite-monochromated Cu  $K\alpha$  radiation. The cell parameters were determined by least-squares refinement of the setting angles of 25 reflexions with  $2\theta$  from 76.6 to 97.0°. Intensity data were measured by  $\theta/2\theta$  scans ( $4.5 \leq 2\theta \leq 153^\circ$ ,  $0 \leq h \leq 14$ ,  $0 \leq k \leq 15$ ,  $-30 \leq l \leq 30$ ). There was no significant decay for three standard reflexions monitored after every 2 h. 7836 data were measured of which 6715 were symmetry independent ( $R_{\text{int}} = 0.0283$ ). 6140 reflexions with  $|F_o| > 3\sigma(F_o)$  were considered observed and were used in all calculations. The data were corrected for Lorentz and polarization but not for absorption effects.

The structure was solved by the heavy-atom method. All H atoms were localized in theoretical positions ( $sp^2$  hybridization for benzene-type C atoms and  $sp^3$  hybridization and 'staggered' conformation for all other C atoms). The structure was refined by full-matrix least-squares procedures on  $F$  assigning anisotropic thermal displacement parameters to Cu, S and C, and one common isotropic thermal parameter for all H atoms. The refinement converged at  $R = 0.053$  and  $wR = 0.055$  with  $w = 1/[\sigma^2(F_o) + 0.0009F_o^2]$ . 411 parameters were refined and the ratio of reflexions to the number of variables

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Table 1. *Positional and thermal parameters*

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
Cu(1)	0.70975 (5)	0.46591 (4)	0.06097 (2)	0.0456 (3)
Cu(2)	0.82526 (5)	0.60738 (4)	0.15318 (2)	0.0454 (3)
S(1)	0.72793 (9)	0.44405 (8)	0.15685 (3)	0.0486 (5)
S(2)	0.70533 (9)	0.65336 (8)	0.06859 (4)	0.0502 (5)
S(11)	0.6658 (1)	0.1961 (1)	-0.0894 (1)	0.0826 (8)
S(31)	1.1476 (1)	0.8005 (1)	0.2736 (1)	0.0745 (8)
C(10)	0.6930 (3)	0.4000 (3)	-0.0150 (1)	0.050 (2)
C(11)	0.6858 (3)	0.3264 (3)	0.0191 (1)	0.049 (2)
C(12)	0.6611 (4)	0.2090 (3)	0.0285 (2)	0.056 (2)
C(13)	0.5815 (4)	0.1949 (4)	0.0703 (2)	0.084 (3)
C(14)	0.7743 (4)	0.1441 (3)	0.0480 (2)	0.076 (3)
C(15)	0.5950 (4)	0.1670 (4)	-0.0309 (2)	0.068 (3)
C(16)	0.6136 (4)	0.3334 (4)	-0.1093 (2)	0.078 (3)
C(17)	0.6827 (4)	0.4318 (4)	-0.0759 (2)	0.061 (3)
C(18)	0.8044 (4)	0.4414 (4)	-0.0891 (2)	0.082 (3)
C(19)	0.6134 (5)	0.5374 (4)	-0.0907 (2)	0.084 (3)
C(20)	0.8373 (3)	0.3428 (3)	0.1793 (1)	0.046 (2)
C(21)	0.9411 (4)	0.3408 (3)	0.1604 (2)	0.063 (3)
C(22)	1.0278 (4)	0.2649 (4)	0.1816 (2)	0.079 (3)
C(23)	1.0119 (6)	0.1906 (4)	0.2203 (2)	0.088 (4)
C(24)	0.9107 (6)	0.1882 (4)	0.2391 (2)	0.086 (4)
C(25)	0.8208 (4)	0.2655 (3)	0.2188 (2)	0.064 (3)
C(30)	0.9363 (3)	0.7232 (3)	0.1865 (1)	0.050 (2)
C(31)	0.9573 (3)	0.6416 (3)	0.2167 (1)	0.049 (2)
C(32)	1.0295 (4)	0.5943 (3)	0.2710 (2)	0.057 (2)
C(33)	1.1324 (4)	0.5287 (4)	0.2583 (2)	0.082 (3)
C(34)	0.9543 (5)	0.5235 (4)	0.3021 (2)	0.077 (3)
C(35)	1.0744 (4)	0.6974 (3)	0.3071 (2)	0.064 (3)
C(36)	1.0264 (4)	0.8825 (3)	0.2370 (2)	0.068 (3)
C(37)	0.9605 (4)	0.8407 (3)	0.1778 (2)	0.061 (2)
C(38)	1.0382 (5)	0.8533 (4)	0.1346 (2)	0.101 (4)
C(39)	0.8479 (5)	0.9067 (3)	0.1598 (2)	0.084 (4)
C(40)	0.7859 (3)	0.7209 (3)	0.0244 (2)	0.052 (2)
C(41)	0.8889 (4)	0.6760 (4)	0.0124 (2)	0.069 (3)
C(42)	0.9482 (5)	0.7301 (4)	-0.0234 (2)	0.086 (4)
C(43)	0.9069 (5)	0.8309 (4)	-0.0458 (2)	0.090 (4)
C(44)	0.8086 (5)	0.8762 (4)	-0.0354 (2)	0.078 (3)
C(45)	0.7468 (4)	0.8225 (3)	0.0001 (2)	0.064 (3)

Table 2. *Selected bond lengths (Å) and angles (°)*

Cu(1)—Cu(2)	2.904 (1)	S(1)—C(20)	1.769 (4)
Cu(1)—S(1)	2.293 (1)	S(2)—C(40)	1.766 (4)
Cu(1)—S(2)	2.284 (1)	S(11)—C(15)	1.813 (4)
Cu(1)—C(10)	1.970 (3)	S(11)—C(16)	1.803 (5)
Cu(1)—C(11)	1.962 (3)	S(31)—C(35)	1.799 (4)
Cu(2)—S(1)	2.295 (1)	S(31)—C(36)	1.797 (4)
Cu(2)—S(2)	2.283 (1)	C(10)—C(11)	1.230 (5)
Cu(2)—C(30)	1.962 (3)	C(30)—C(31)	1.223 (4)
Cu(2)—C(31)	1.969 (3)		
Cu(2)—Cu(1)—S(1)	50.76 (3)	Cu(2)—Cu(1)—S(2)	50.50 (3)
Cu(2)—Cu(1)—C(10)	152.92 (11)	Cu(2)—Cu(1)—C(11)	153.80 (10)
Cu(1)—Cu(2)—S(1)	50.70 (2)	Cu(1)—Cu(2)—S(2)	50.54 (3)
Cu(1)—Cu(2)—C(30)	153.40 (10)	Cu(1)—Cu(2)—C(31)	151.40 (10)
Cu(1)—S(1)—Cu(2)	78.53 (3)	Cu(1)—S(2)—Cu(2)	78.95 (4)
S(1)—Cu(1)—S(2)	91.89 (4)	S(1)—Cu(2)—S(2)	91.87 (4)
C(10)—C(11)—C(12)	147.8 (4)	C(11)—C(10)—C(17)	147.1 (4)
C(30)—C(31)—C(32)	145.9 (4)	C(31)—C(30)—C(37)	147.7 (4)

is greater than 14.9. The ratio of maximum least-squares shift to e.s.d. in the last refinement cycle was -0.013; maximum and minimum heights in final  $\Delta\rho$  map were 0.65 and -0.84 e Å<sup>-3</sup>. The atomic scattering factors and correction for anomalous dispersion for the Cu atom were taken from *International Tables for X-ray Crystallography* (1974). The complex neutral-atom scattering factors for S and C were taken from *SHELX76*. Programs used were *SHELXS86* (Sheldrick, 1986), *SHELX76* (Sheldrick, 1976) and *PLATON88* (Spek, 1982) on MicroVAX II and VAX3200 computers.

**Discussion.** Final atomic parameters are given in Table 1, selected bond distances and angles are reported in Table 2.\* Fig. 1 shows the structural formula and a view of the molecule, and illustrates the atom-numbering scheme chosen.

\* Tables of structure factors, anisotropic thermal parameters, and H-atom positional and isotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52935 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

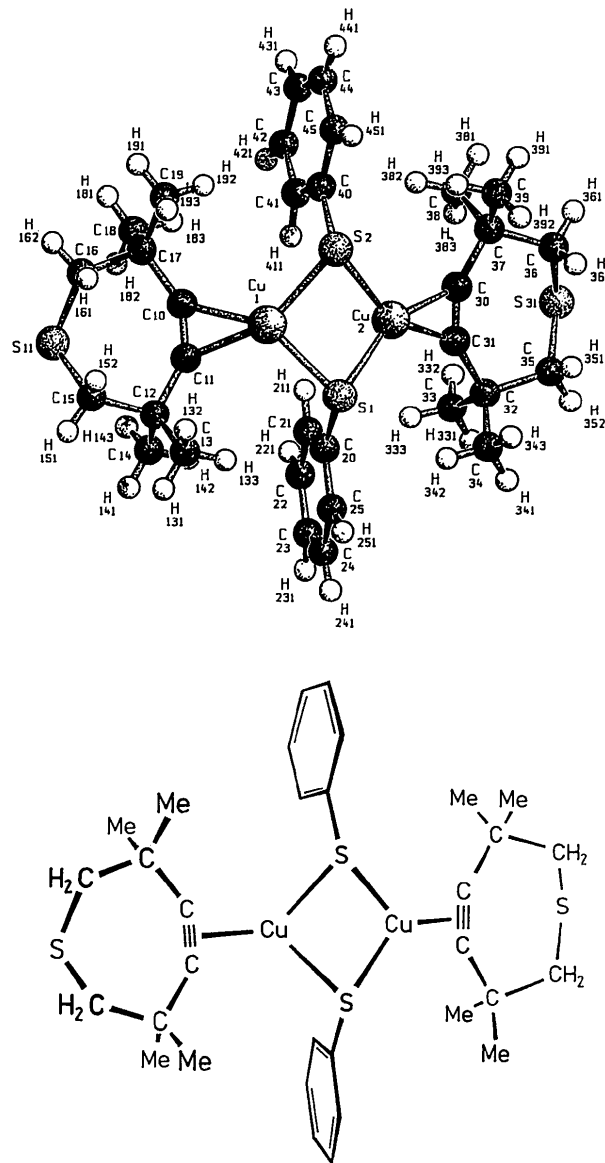


Fig. 1. *SCHAKAL88* (Keller, 1986) drawing and formula scheme of  $[\text{Cu}_2(\text{C}_6\text{H}_5\text{S})_2(\text{C}_{10}\text{H}_{16}\text{S})_2]$ .

The structure is built up by a dimeric molecule. Both Cu atoms are bridged by the S atoms of the thiophenolato anions forming a non-planar Cu<sub>2</sub>S<sub>2</sub> ring. Although sulfur has a high affinity to copper, the thiocycloheptyne ligands are  $\eta^2$ -bonded via the alkyne groups. Interestingly, the angles C(10)—C(11)—C(12) of 147.8 (4), C(11)—C(10)—C(17) of 147.1 (4), C(30)—C(31)—C(32) of 145.9 (4) and C(31)—C(30)—C(37) of 147.7 (4)° are not changed much compared to the corresponding angles in the uncomplexed thiacycloheptyne of 145.8° (Krebs & Wilke, 1983). However, the shift of the C≡C stretching frequencies from 2200 and 2170 cm<sup>-1</sup> in the uncomplexed alkyne to 1970 and 1950 cm<sup>-1</sup> in the Cu—thiophenolate complex shows that a significant interaction between the alkyne and the Cu ligand has taken place.

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### Structure of the Organic Superconductor (DMET)<sub>2</sub>AuCl<sub>2</sub>

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**Abstract.** 2-(4,5-Dimethyldiselenol-2-ylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin dichloroaurate(I) (2/1), (C<sub>10</sub>H<sub>10</sub>S<sub>4</sub>Se<sub>2</sub>)<sub>2</sub>[AuCl<sub>2</sub>], *M<sub>r</sub>* = 1100.58, triclinic, *P* $\bar{1}$ , *a* = 7.021 (3), *b* = 7.742 (3), *c* = 15.622 (6) Å,  $\alpha$  = 108.60 (3),  $\beta$  = 98.27 (3),  $\gamma$  = 70.82 (3)°, *V* = 759.5 (4) Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 2.41 Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71068 Å,  $\mu$  = 10.30 mm<sup>-1</sup>, *F*(000) = 517, *T* = 297 K, *R* = 0.062 for 2345 reflections. The structure consists of sheets of C<sub>10</sub>H<sub>10</sub>S<sub>4</sub>Se<sub>2</sub> (DMET) and of AuCl<sub>2</sub>. The ordered DMET molecules are stacked in a columnar structure. Some short intermolecular contacts lie not only within a column, but also between columns. The contact mode is similar to that of (DMET)<sub>2</sub>Au(CN)<sub>2</sub> and (DMET)<sub>2</sub>AuI<sub>2</sub> within a column, but is different between columns.

**Introduction.** All previously discovered superconductors based on an unsymmetrical donor DMET have

a linear anion as counter anion: Au(CN)<sub>2</sub><sup>-</sup>, AuCl<sub>2</sub><sup>-</sup>, AuBr<sub>2</sub><sup>-</sup>, AuI<sub>2</sub><sup>-</sup>, I<sub>3</sub><sup>-</sup> and IBR<sub>2</sub><sup>-</sup> (Kikuchi, Kikuchi, Namiki, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Anzai, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Honda, Ishikawa, Saito, Ikemoto, Murata, Anzai, Ishiguro & Kobayashi, 1988; Kikuchi, Murata, Honda, Namiki, Saito, Ishiguro, Kobayashi & Ikemoto, 1987). These compounds belong to groups 3, 4 and 5 in the classification according to the low-temperature behavior of conductivity (Murata, Kikuchi, Takahashi, Kobayashi, Honda, Saito, Kanoda, Tokiwa, Anzai, Ishiguro & Ikemoto, 1988; Kikuchi, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1988; Kanoda, Takahashi, Kikuchi, Saito, Ikemoto & Kobayashi, 1988). Room-