

Synthesis and Crystal Structure of Hexakis(N-allylthiourea)tetracopper(I) Tetratrifluoromethanesulfonate, $[\text{Cu}_4\{\text{CH}_2=\text{CHCH}_2\text{NHC}(\text{S})\text{NH}_2\}_6](\text{SO}_3\text{CF}_3)_4$

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Abstract. Hexakis(N-allylthiourea)tetracopper(I) Tetratrifluoromethanesulfonate, $[\text{Cu}_4\{\text{CH}_2=\text{CHCH}_2\text{NHC}(\text{S})\text{NH}_2\}_6](\text{CF}_3\text{SO}_3)_4$ (sp.gr. $P2_1/n$, $a = 13.5463(8)$, $b = 24.129(2)$, $c = 19.128(1)$ Å, $\beta = 108.053(6)^\circ$, $Z = 4$, $R = 0.0440$ for 13548 unique reflections) was obtained by reduction of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ with excess of N-allylthiocarbamide in benzene medium. Four crystallographical

independent Cu atoms possess trigonal environment of three S atoms of $\text{CH}_2=\text{CHCH}_2\text{NHC}(\text{S})\text{NH}_2$ moiety and form $\text{Cu}_4\text{S}_6^{4+}$ adamantane-like fragments. The latter are connected with CF_3SO_3^- anions via (C)–H···F hydrogen bonds.

Keywords: Copper(I) triflate; Thiourea; Crystal structure

Thiourea is used as an additive for copper electroplating and also employed as an inhibitor for copper corrosion in aqueous aggressive environments [1]. This gives rise to studies of complex formation in copper salts – thiourea solutions. N-alkylsubstituted thioureas reduce Cu^{II} salts, stabilizing the lower oxidation state Cu^{I} by strong binding with bridging or terminal S atoms, forming in particular an unordinary stable Cu_4S_6 adamantane core [2–7]. On the other hand, we have demonstrated that the olefine bonds of N-allyl substituted thiourea (ATU) and thiosemicarbazide (ATSC) are able in the presence of the S-donor to coordinate copper atom (in π, n -complexes $[\text{Cu}(\text{ATU})(\text{CH}_3\text{CN})]\text{NO}_3$ [8], $[\text{Cu}(\text{ATSC})-\text{NH}_2\text{SO}_3$ and $[\text{Cu}_2(\text{ATSC})_2]\text{SO}_4$ [9]) or even to compete with thioamide group for the coordination place, as in the case of $[\text{Cu}(\text{ATSC})(\text{H}^+\text{ATSC})]\text{SiF}_6$ [10]. In this paper we communicate the crystal structure of copper(I) triflate complex with ATU.

Experimental Part

Preparation of the complex. 0.5 mmol (0.20 g) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot x\text{H}_2\text{O}$ was mixed with 10 ml of 0.5 M allylthiourea solution (0.58 g) in benzene. As a heterogeneous redox reaction passed the copper(II) triflate dissolved during 20 min, forming colourless solution. Slow evaporation (over the period of one week) of the solvent at 40 °C yielded colourless plate-like crystals of $[\text{Cu}_4(\text{ATU})_6](\text{SO}_3\text{CF}_3)_4$ (**1**).

X-ray single crystal investigation. Preliminary room temperature study (DARCH diffractometer) revealed a trigonal coordination of metal centers by sulfur atoms and a substantial disorder of alkyl groups. Low temperature measurements on nearly 1 μm -thin plate crystal were carried out on the Stoe IPDS diffractometer equipped with an image plate detector and the Mo X-ray tube. Crystal data and details of data collection [11] and refinement [12] are given in Table 1.

180 ϕ oscillation images were collected at 180(1) K in the range of 0–180° with 10 min exposure per image. Crystal to detector dis-

Table 1 Crystal and structure refinement data for **1**.

Compound	$[\text{Cu}_4(\text{NH}_2\text{CSNHC}_3\text{H}_5)_6](\text{SO}_3\text{CF}_3)_4$
Empirical formula	$\text{C}_{28}\text{H}_{48}\text{N}_{12}\text{O}_{12}\text{F}_{12}\text{S}_{10}\text{Cu}_4$
Formula weight	1547.54
Crystal shape/color	elongated brick/colorless
Crystal system, space group	monoclinic, $P2_1/n$
$a/\text{Å}$	13.5463(8)
$b/\text{Å}$	24.129(2)
$c/\text{Å}$	19.128(1)
$\beta/^\circ$	108.053(6)
$V/\text{Å}^3$	5944.5(6)
$Z, D_c/(\text{g}\cdot\text{cm}^{-3})$	4, 1.729
$F(000)$	3120
$\theta_{\text{max}}/^\circ$	56.24
Index ranges	$-17 \leq h \leq 17$ $-31 \leq k \leq 31$ $-25 \leq l \leq 25$
Absorption coefficient/mm	1.860
Refl. collected/unique	51892/13548
Data/restraints/parameters	13548/0/703
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0440$, $wR_2 = 0.0635$
R indices (all data)	$R_1 = 0.1802$, $wR_2 = 0.0904$
Goof on F^2 , weighting scheme	0.617, $w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\text{max}}$	0.002
Largest diff. peak and hole/ $e\cdot\text{Å}^{-3}$	0.59 and -0.53

tance was 60 mm. Data were corrected for Lorenz and polarization effects, and numerically for absorption (13 faces, $T_{\text{min,max}} = 0.864, 0.930$). The cell parameters were obtained by the least-squares refinement with regards to the angle parameters of 8000 reflections in the range $4.7 < \theta < 55.1^\circ$. No variation of average intensity during the measurement was observed. Small crystal size diminishes absorption and provides a good crystal quality, however diffracted intensities are relatively low. This explains high R_1 index for all reflections and small Goof value. No warnings of twinning were observed.

Structures were solved from the Patterson synthesis and subsequent difference Fourier maps. 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 the positional and the thermal parameters for all atoms, anisotropically for all non H-atoms using SHELXL-97 program [12]. Neutral atom

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scattering factors and anomalous dispersion corrections were those incorporated in SHELXL-97.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 203546. Copies 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.

Results and Discussion

The structure **1** consists of $[\text{Cu}_4(\text{ATU})_6]^{4+}$ complex cations shown on Figure 1. Each copper atom forms three bonds with the sulfur atoms and one contact with an oxygen atom of the triflate anion, which complete the coordination polyhedron to trigonal pyramid. The copper-thiourea clusters are interlinked by triflate anions, which strongly interact with the thiourea ligands through (N)H...O hydrogen bonds. The adamantane-like Cu_4S_6 core exhibits substantial deformation from its ideal geometry: copper atoms are displaced towards the plane of sulfur ligands, forming short Cu-Cu distances (2.820(1)–3.021(1) Å); Cu-S-Cu angles ranging from 76.35(6) to 82.80(6)° are far from ideal 120°. Furthermore, the differences in pyramidal distortion of the coordination polyhedra do not correlate with deviations of Cu atoms (Δ , Tabl. 2) from the plane of equatorial ligands, i.e. S atoms. For instance, larger trigonal distortion of the Cu1 coordination polyhedron (Cu1-O11 3.052(5) Å) corresponds to even larger Δ (0.204 Å) than for the less deformed Cu2 polyhedron (Cu2-O21 2.814(6) Å, $\Delta = 0.156$ Å). This uncommon feature is a result of an interplay among packing restraint, hydrogen bonds and Cu-Cu interactions, while Cu_4S_6 core deformation is defined by the nature of an apical ligand. The latter relation is best illustrated by examples of different ligands occupying apical positions in irregularly deformed Cu_4S_6 core [6,

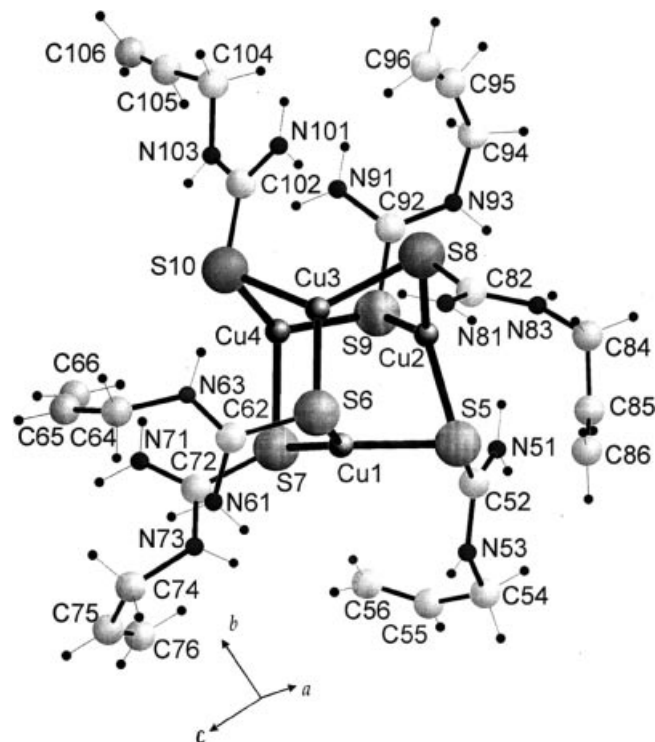


Fig. 1 Structure of $[\text{Cu}_4(\text{ATU})_6]^{4+}$ complex cation

Table 2 Selected distances ^{a)} / Å and angles /° for **1**.

Cu1-S7	2.269(2)	S7-Cu1-S6	132.07(7)
Cu1-S6	2.283(2)	S7-Cu1-S5	117.60(8)
Cu1-S5	2.287(2)	S6-Cu1-S5	107.88(7)
Cu1-O11	3.052(5)		
$\Delta(\text{Cu1})$	0.204		
Cu2-S8	2.267(2)	S8-Cu2-S5	118.81(7)
Cu2-S5	2.276(2)	S8-Cu2-S9	121.01(7)
Cu2-S9	2.277(2)	S5-Cu2-S9	118.78(7)
Cu2-O21	2.814(6)		
$\Delta(\text{Cu2})$	0.156		
Cu3-S10	2.252(2)	S10-Cu3-S6	121.48(7)
Cu3-S6	2.267(2)	S10-Cu3-S8	120.36(7)
Cu3-S8	2.294(2)	S6-Cu3-S8	117.08(7)
Cu3-O31	2.875(5)		
$\Delta(\text{Cu3})$	0.137		
Cu4-S10	2.248(2)	S10-Cu4-S7	127.09(8)
Cu4-S7	2.288(2)	S10-Cu4-S9	131.68(7)
Cu4-S9	2.292(2)	S7-Cu4-S9	96.01(7)
Cu4-O41	2.794(5)		
$\Delta(\text{Cu4})$	0.292		
Cu-Cu	2.820(1)–3.021(1)	Cu-S-Cu	76.35(6)–82.80(6)
S-C	1.717(7)–1.759(7)	Cu-S-C	103.7(2)–115.7(2)

^{a)} Δ – deviation of copper atom from the plane of S ligands.

7]. Regular and almost ideal adamantane-like geometry is observed for complexes with thioamide sulfur atoms occupying the fourth place of the coordination polyhedra [2, 4].

No Cu-(C=C) bonding is observed in the title structure. Allyl groups of the ATU ligands exhibit a noticeable thermal motion even at low temperature, but for all that, the following feature has been observed: the least disordered C76=C75-C74 allyl group form shortest hydrogen contacts (H74B...F42 2.65 Å, H75...F31 2.79 Å), while the most disordered C96=C95-C94 group shows no considerable (C)H...F(C) and (C)H...O(S) bonding.

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