π-Complexes of Copper(I) Ionic Salts: Synthesis and Crystal Structure of (4-Allylthiosemicarbazide)(sulfamato)copper(I) and Bis(4-allylthiosemicarbazide)(sulfato-O)dicopper(I)

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Abstract. Single crystals of $[Cu(ATSC)]NH_2SO_3$ (**1**) (ATSC –4-allylthiosemicarbazide) were obtained by electrochemical synthesis using alternating current. Compound (**1**) crystallizes in $P2_12_12_1$ sp. gr., $a = 6.8284(2)$, $b = 9.3054(3)$, $c = 16.1576(11)$ Å, $Z = 4$. ATSC moiety acts as tetradentate ligand, chelating two symmetrically related copper atoms. The Cu atom possesses trigonal pyramidal coordination, formed by two sulphur atoms (one of them at the apical position), nitrogen atom and C=C bond. Sulfamate anion is associated via hydrogen bonds. By slow hydrolysis of **1** crystals of $[Cu_2(ATSC)_2]SO_4$ (**2**) were obtained: $P\bar{1}$ sp. gr., $a = 9.526(2)$, $b = 12.687(2)$, $c = 14.7340(10)$ Å, $\alpha = 95.119(10)$, $\beta = 89.903(12)$, $\gamma = 109.113(14)°$, $Z = 4$. The asymmetric unit of **2** contains two formula units, which are related by pseudosymmetry via a glide plane *a*. One half of four ATSC molecules act as in **1**, the rest as tridentate ligands, which coordinate the two copper atoms in apical positions with sulfate anions. This Cu–S coordination was to date unknown. The structure of the ATSC ligands contributes to the unexpected competitiveness of C=bond in the coordination sphere of Cu^I inspite of strong donor atoms.

Keywords: Copper(I) sulfamate; Copper(I) sulfate; π-Complexes; Crystal structure

Die π-Komplexe von Kupfer(I)-ionischen Salzen: Die Darstellung und die Kristallstrukturen von (4-Allylthiosemicarbazid)(sulfamato)kupfer(I) und Bis(4-allylthiosemicarbazid)(sulfato-O)dikupfer(I)

Inhaltsübersicht. Einkristalle von $[Cu(ATSC)]NH_2SO_3$ (**1**) (ATSC–4-allylthiosemicarbazid) wurden durch die elektrochemische Synthese unter Anwendung von Wechselstrom erhalten. Die Verbindung kristallisiert in der Raumgruppe $P2_12_12_1$: $a = 6.8284(2)$, $b = 9.3054(3)$, $c = 16.1576(11)$ Å, $Z = 4$. Die ATSC-Einheit wirkt als vierzähniger Ligand, die mit den zwei symmetrisch verbundenen Kupferatomen verbrückt ist. Das Kupferatom hat trigonal-pyramidale Umgebung mit zwei Schwefelatomen (eines axial), ein Stickstoffatom und eine C=C-Bindung. Das Sulfamatanion ist über Wasserstoffbrückenbindungen assoziiert. Durch langsame Hydrolyse der Verbindung **1** wurden Einkristallen von $[Cu_2(ATSC)_2]SO_4$ (**2**) gewonnen: Raumgruppe $P\bar{1}$, $a = 9.526(2)$, $b = 12.687(2)$, $c = 14.7340(10)$ Å, $\alpha = 95.119(10)$, $\beta = 89.903(12)$, $\gamma = 109.113(14)°$, $Z = 4$. Die asymmetrische Einheit der Elementarzelle von **2** enthält zwei mit der Pseudosymmetrie über die Gleitspiegelebene *a* verbundene Formeleinheiten. Die Hälfte der vier ATSC-Moleküle wirkt wie in **1**, der andere Teil als dreizähniger Ligand, der die zwei Kupferatome in den Axialpositionen mit den Sulfatanionen koordiniert. Die Struktur der ATSC-Liganden trägt zu der unerwarteten Konkurrenzfähigkeit der C=C-Bindung in der Koordinationssphäre des Cu^I trotz starker Donoratome bei. Die stereochemische Besonderheit dieser Cu–S-Koordination war bisher nicht bekannt.

Introduction

As a ligand with potential S and N donors, thiosemicarbazide is interesting not only because of the structural chemistry of its multifunction coordination modes, but also because of the formation of complexes with antifungal, antimicrobal and antitumor properties. The biological activities of complexes with thiourea derivatives have been well documented [1]. So far, the coordination of thiosemicarbazides with transition metals has been explored more thoroughly than their coordination with non-transition metals. The most typical coordination mode of thiosemicarbazides is S,N^1-chelate: for Cu^{II} alone complexes with S,N^1-chelating thiosemicarbazide molecule or its monosubstituted N^4-derivatives, nine crystal structures are investigated [2, 3]. Rarer complexes with thiosemicarbazide (thiosemicarbazone) moiety functioning as

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S,S,N^1-bridging ligand, binding together two metal atoms, are investigated, partly because of the difficulty in obtaining single crystals. Thus, only a few such structures with transition metals are studied [4, 5], and only in case [5] polymeric chains $(\text{–metal–S–})_n$ are found. Among numerous crystal structures of complexes with thiosemicarbazide (thiosemicarbazone) moieties, bonded to transition metals via S atom, none of the metal atoms was found to be π-coordinated with double or triple C–C bond. It occurs only in case of simpler ligands – thiourea or its N,N′-derivatives, and noble metal ions in low oxidation states (Ru^I, Rh^I, Pt^{II}) [6], which effectively bind to two C=C bonds. d^{10}-Metal ions also turned out to be capable of π-coordination in the presence to metal thiocarbamide sulphur atoms possessing high affinity to metal centres. This only occurs in copper(I) nitrate π-complex with N-allylthiourea [7]. In this context and as a part of our program, the aim of the present work is to first obtain π-complexes with thiosemicarbazide derivative. As starting materials copper(I) ionic salts and sterically unhindered 4-allylthiosemicarbazide appeared to be appropriate. Alternating current synthesis [8] enabled to obtain single crystals suitable for structure determination. Thus, we have synthesized and investigated crystal structures of copper(I) sulfamate and copper(I) sulfate π-complexes with 4-allylthiosemicarbazide.

Experimental Part

IR spectra in KBr pellets (3800–400 cm^{-1}) were recorded on a UR-20 spectrophotometer.

Preparation of $[Cu(SO_3NH_2)_2] \cdot x H_2O$ salt. $(CuOH)_2CO_3$ was treated by 50% water solution of sulfamic acid. An excess of copper(II) hydroxocarbonate was filtered and a solution was evaporated in a water bath until blue crystals of the salt appeared. On cooling crystalline copper(II) sulfamate was isolated, washed with suction by cold ethanol and dried in air.

Synthesis of 4-allylthiosemicarbazide (ATSC). A solution of allylisothiocyanate (20.0 ml, 0.206 mol) in 20 mL of ethanol was slowly added via a backflow condenser to hydrazine hydrate efficiently cooled by running water, (10.0 ml, 0.206 mol) in 10 ml of ethanol. Obtained white dense suspension was stirred over 10 min., filtered with suction, washed by ethanol and dried in air. Recrystallization from acetonitrile yielded white needles of product. Yield: 17.3 g (64 %), m. p. 76 °C.

IR (KBr) ν(cm^{-1}): 3350 s, 3280 s, 3212 s, 3080 w, 3015 w, 2985 m, 2935 m, 1880 w, 1635 s, 1555 s, 1540 m, 1510 s, 1425 m, 1390 m, 1290 m, 1230 s, 1150 m, 1100 w, 1077 s, 990 w, 970 s, 940 s, 910 m, 780 m, 720 w, 625 s, 592 m, 415 m.

Preparation of $[Cu(ATSC)]NH_2SO_3$ (1) and $[Cu_2(ATSC)_2]SO_4$ (2). To 5 ml of a water-methanol (50 : 50) saturated solution of $[Cu(SO_3NH_2)_2] \cdot x H_2O$ 1 ml of acetonitrilic solution of ATSC (0.3 g, 2.3 mmol) was added. The blue suspension of Cu^{II} complex was placed in a small 6 ml test-tube and then copper-wire electrodes in cork were inserted. Under alternating current (frequency 50 Hz) of 0.40 V mazarine Cu^{II} complex dissolved slowly and colorless crystals of the complex **1** appeared on copper electrodes over 1 day. The density of **1** measured by flotation in $CHCl_3/CHBr_3$ mixture equals 1.88 $g \cdot cm^{-3}$. The yield was almost quantitative.

IR (KBr) ν(cm^{-1}): 3300–3170 s, 2425 w, 1642 m, 1630 m, 1580 m, 1570 m, 1555 m, 1500 w, 1385 s, 1320 w, 1250 w, 1155 w, 1120 w, 1040 m, 980 w, 945 m, 925 w, 895 w, 840 w, 825 w, 682 w.

During a long-term standing (3–5 months) of the hermetically sealed electrolyzer with reaction mixture at room temperature a light-brown crystals of **2** appeared on the copper electrodes and on the inner side of the tube (suitable for X-ray experiment). Crystals of **1** and **2** vanished by cyacryne and did not decompose during the X-ray experiment.

X-ray single crystal investigation of 1 and 2. Approximate unit-cell dimensions and the space group were determined from rotation and Weissenberg photographs. The intensity data were measured on an Enraf-Nonius CAD-4 diffractometer with the graphite-monochromated CuKα radiation. Crystal data and details of data collection and refinement are given in Table 1. The cell parameters were obtained by the least-squares refinement with regards to the angle parameters of 25 reflections in the range $36 < 2\theta < 53°$ for **1** and $31 < 2\theta < 43°$ for **2**. Reduced cell calculations [9] and non-

Table 1 Crystal and structure refinement data for compounds **1** and **2**

Compound	$[Cu(ATSC)]NH_2SO_3$	$[Cu_2(ATSC)_2]SO_4$
Empirical formula	$C_4H_{11}N_4O_3S_2Cu$	$C_8H_{18}N_6O_4S_3Cu_2$
Formula weight	290.83	485.54
Crystal shape/color	rhombic pyramid/ colorless	brick/brown
Crystal size/mm	$0.06 \times 0.10 \times 0.19$	$0.13 \times 0.13 \times 0.19$
Crystal system, space group	orthorhombic, $P2_12_12_1$	triclinic, $P\bar{1}$
a/Å	6.8284(2)	9.526(2)
b/Å	9.3054(3)	12.687(2)
c/Å	16.1576(11)	14.7340(10)
α/°		95.119(10)
β/°		89.903(12)
γ/°		109.113(14)
V/Å^3	1026.67(8)	1675.1(5)
Z, D_c/($g \cdot cm^{-3}$)	4, 1.8818(1)	4, 1.9255(6)
$F(000)$	592	984
2θ range for data collection/°	5.48–73.92	4.92–73.83
Temperature/K	293(2)	293(2)
Index ranges	$-8 \leq h \leq 8$ $-9 \leq k \leq 11$ $-19 \leq l \leq 20$	$0 \leq h \leq 11$ $-15 \leq k \leq 14$ $-18 \leq l \leq 18$
Absorption coefficient/mm^{-1}	6.772	6.886
Max./min. transmissions	0.356/0.671	0.352/0.473
Refl. collected/unique	1931/1931	6690/6322 ($R_{int} = 0.043$)
Data/restraints/parameters	1931/0/146	6322/0/440
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0378$, $wR_2 = 0.1009$	$R_1 = 0.0709$, $wR_2 = 0.1840$
R indices (all data)	$R_1 = 0.0403$, $wR_2 = 0.1024$	$R_1 = 0.0968$, $wR_2 = 0.2092$
Goof on F^2	1.099	1.047
$(\Delta/\sigma)_{max}$	0.000	0.001
Extinction coefficient	0.0013(4)	0.0013(3)
Largest diff. peak and hole/$e \cdot Å^{-3}$	0.593 and –0.499	0.954 and –0.856

Table 2 Selected bond distances (Å) and angles (°) for **1**

Cu–S1^{i}	2.2721(11)	M–Cu–N7^{i}	131.82(18)
Cu–S1	2.4608(10)	C1–Cu–C2	37.10(19)
Cu–N7^{i}	2.075(3)	M–Cu–S1^{i}	121.95(14)
Cu–C1	2.081(5)	N7^{i}–Cu–S1^{i}	86.83(10)
Cu–C2	2.130(4)	M–Cu–S1	103.20(14)
Cu–M$^{a)}$	1.996(4)	N7^{i}–Cu–S1	100.80(10)
		S1–Cu–S1^{i}	109.94(3)
		Cu–S1–Cu^{ii}	120.74(4)
		Cu–S1^{i}–C5^{i}	96.81(13)
		Cu–S1–C5	92.89(13)
		Cu–N7^{i}–N6^{i}	112.1(2)
C1–C2	1.340(7)	C1–C2–C3	123.9(4)
C2–C3	1.511(6)	C2–C3–N4	113.7(4)
C3–N4	1.461(6)	C3–N4–C5	122.6(3)
N4–C5	1.326(5)	N4–C5–N6	117.9(4)
C5–N6	1.326(5)	S1–C5–N4	120.2(3)
C5–S1	1.719(4)	S1–C5–N6	121.9(3)
N6–N7	1.415(5)	C5–N6–N7	121.7(3)
S2–N8	1.646(4)	O1–S2–O2	115.2(2)
S2–O1	1.450(3)	O1–S2–O3	110.5(2)
S2–O2	1.455(3)	O2–S2–O3	111.6(2)
S2–O3	1.462(3)	O1–S2–N8	105.0(2)
		O2–S2–N8	104.4(2)
		O3–S2–N8	109.7(2)

Symmetry transformations used to generate equivalent atoms:
i = *x – 1/2, –y + 3/2, –z + 1*; **ii** = *x + 1/2, –y + 3/2, –z + 1*
$^{a)}$ M – the mid-point of C(1) = C(2) distance.

Table 3 Selected bond distances (Å) and angles (°) for **2**

Cu1–S4	2.251(2)	M1–Cu1–N28	118.8(3)
Cu1–S1	2.515(2)	C1–Cu1–C2	37.8(3)
Cu1–N28	2.084(7)	M1–Cu1–S4	132.8(2)
Cu1–C1	2.105(8)	N28–Cu1–S4	87.61(18)
Cu1–C2	2.110(7)	M1–Cu1–S1	103.3(2)
Cu1–M1$^{a)}$	1.994(7)	N28–Cu1–S1	100.77(19)
C1–C2	1.366(13)	S1–Cu1–S4	109.49(8)
S4–C26	1.702(8)		
Cu2–S1	2.265(2)	M2^{i}–Cu2–N7	135.8(4)
Cu2–O4	2.295(5)	C8^{i}–Cu2–C9^{i}	38.8(4)
Cu2–N7	2.026(6)	M2^{i}–Cu2–S1	128.4(3)
Cu2–C8^{i}	2.042(8)	N7–Cu2–S1	89.47(18)
Cu2–C9^{i}	2.053(9)	M2^{i}–Cu2–O4	104.0(3)
Cu2–M2$^{i\ a)}$	1.931(8)	N7–Cu2–O4	90.5(2)
C8–C9	1.361(15)	S1–Cu2–O4	97.38(15)
S1–C5	1.733(7)	Cu1–S1–Cu2	121.09(8)
S5–O4	1.475(6)		
Cu3–S2	2.255(2)	M3–Cu3–N14	122.4(3)
Cu3–S3	2.548(2)	C15–Cu3–C16	37.6(4)
Cu3–N14	2.067(7)	M3–Cu3–S2	132.9(2)
Cu3–C15	2.080(8)	N14–Cu3–S2	87.8(2)
Cu3–C16	2.094(8)	M3–Cu3–S3	100.6(2)
Cu3–M3$^{a)}$	1.976(8)	N14–Cu3–S3	99.8(2)
C15–C16	1.344(13)	S2–Cu3–S3	109.30(9)
S2–C12	1.693(8)		
Cu4–S3	2.256(2)	M4–Cu4–N21	138.1(4)
Cu4–O8	2.359(5)	C22–Cu4–C23	39.1(4)
Cu4–N21	2.020(7)	M4–Cu4–S3	128.8(3)
Cu4–C22	2.031(9)	N21–Cu4–S3	88.82(19)
Cu4–C23	2.060(9)	M4–Cu4–O8	102.6(3)
Cu4–M4$^{a)}$	1.928(9)	N21–Cu4–O8	88.6(3)
C22–C23	1.370(16)	S3–Cu4–O	96.19(14)
S3–C19	1.703(7)	Cu3–S3–Cu4	121.90(8)
S6–O8	1.477(5)		

Symmetry transformation used to generate equivalent atoms:
i = *x – 1, y, z*

$^{a)}$ M1–M4 – the respective mid-points of C=C distances.

crystallographical symmetry check (PLATON99 [10]) did not indicate higher lattice symmetry or missed symmetry elements. Variations of intensity were corrected with cubic apline function. Absorption corrections have been performed with Psi-scans. Structures were solved by direct methods and subsequent difference Fourier techniques [11]. Hydrogen atoms of the sulfamate anion were located from the difference Fourier map and refined isotropically. The other H atoms were placed in structurally calculated positions and refined in a riding model with isotropic temperature factors. A full least-squares refinement on F^2 was performed on the positional and thermal parameters for all atoms, anisotropically for all non H-atoms using SHELXL-97 program [11]. Neutral atom scattering factors and anomalous dispersion corrections were those incorporated in SHELXL-97. The Flack parameter [12] for **1** refined to 0.02(4). Crystal of **2** was found to be non-merohedrally twinned. As a result, a part of collected reflections possessed excessive values of observed structure amplitudes. So, before final least-square cycles, 513 of 7203 total intensities with $(|F_{obs}| - |F_{calc}|)/\sigma(|F_{obs}|) > 8$ were removed (completeness diminished from 100% to 93.3%, s.u's of atomic coordinates – by a factor of 1.5). After correction, weighing and refinement the loss of linearity in δR-normal probability plot [13] had vanished. Selected bond lengths and bond angles in **1** and **2** are listed in Tables 2 and 3, respectively. Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-148034 and CCDC-148035. 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

In structure **1** ATSC moiety acts as tetradentate ligand, chelating two symmetrically related copper atoms: one in S,N^1-mode and by means of S atom and C=C bond for another Cu atom. In this way organic ligand entirely realizes its coordination abilities and occupies all coordination places of copper(I) polyhedron. Sulfamate anion takes part only in formation of hydrogen bonds in the outer coordination sphere. The Cu atom possesses tetrahedral coordination, slightly deformated to trigonal pyramid, formed by two sulphur atoms (one of them at the apical position), nitrogen atom and C=C bond. Due to the bridging function of ATSC moiety structure **1** consists of chains disposed in [100] direction (Fig. 1).

Structure **2** contains two formula units in asymmetric unit, though they are related by pseudosymmetry of glide plane *a* disposed in *xy* plane. Thus, there are pairs of chemically equivalent copper atoms (and ATSC moieties): Cu1 corresponds to Cu3 and Cu2 – to Cu4, respectively. Nevertheless, refinement with chemically equivalent bond length and angles constrained to be equal raised sharp discrepancy factors and s.u's of corresponding parameters. Two related

ATSC molecules act in the same way as in structure **1**, binding together two metal atoms in a twice chelating manner. ATSC moieties of the second pair are tridentate, since their sulphur atoms are not bridging (Fig. 2); the released coordination places in the environment of Cu2 and Cu4 are occupied by oxygen atoms of sulfate anions. So, structure **2** is built from the folded polymeric chains disposed in [100] direction (Fig. 3). All metal coordination spheres have strongly pronounced pyramidal distortion. Furthermore, small differences in pyramidal distortion for chemically equivalent atoms conform to changes in deviations (Δ) of copper atoms from the planes of equatorial ligands (through S and N atoms and mid-point of C=C bond). Thus, apical distance Cu1–S1 2.515(2) Å corresponds to $\Delta = 0.535$ Å, Cu3–S3 2.548(2) Å – to $\Delta = 0.478$ Å. For a more trigonally distorted environment of Cu2 and Cu4 (radius of O atom is 0.4 Å smaller than for S) the same conformity occurs: apical distance Cu1–O4 2.295(5) Å corresponds to $\Delta = 0.285$ Å, Cu4–O8 2.359(5) Å – to $\Delta = 0.230$ Å. Such accordance corroborates an actual crystallochemical distinction of chemically equivalent copper atoms. As Cu(I) coordination polyhedra become more pyramidal distorted, π-coordinated C=C bonds are oriented exactly in the planes of equatorial ligands: for nearly tetrahedral copper environment in the structure **1** (apical distance Cu–S1 2.461(1) Å, $\Delta = 0.514$ Å) tilt of C=C bond from the base plane (τ) equals 27.4°, for Cu1 and Cu3 atoms in **2** – 23.6 and 18.0°, for pyramidal environment of Cu2 and Cu4 atoms – 11.6 and 10.8°, respectively.

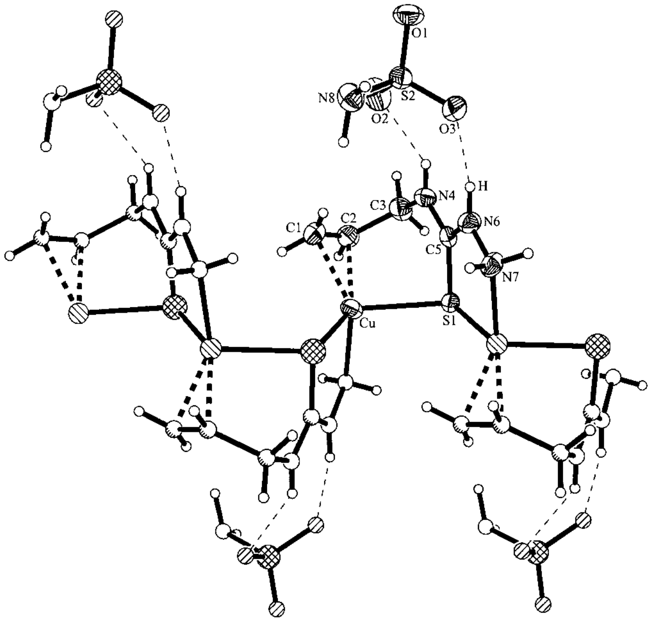

Fig. 1 Part of the polymeric structure of [Cu(ATSC)]NH_2SO_3 showing the numbering scheme, the N,S,S-bridging ATSC ligand and the coordination geometry about the copper atoms. Thermal ellipsoids are drawn for one asymmetric unit at 50% probability.

The most similar coordination of π-bonded Cu(I) atom was found in copper(I) nitrate π-complex (**3**) with N-allylthiourea (ATU) [7]. The lack of hydrazine

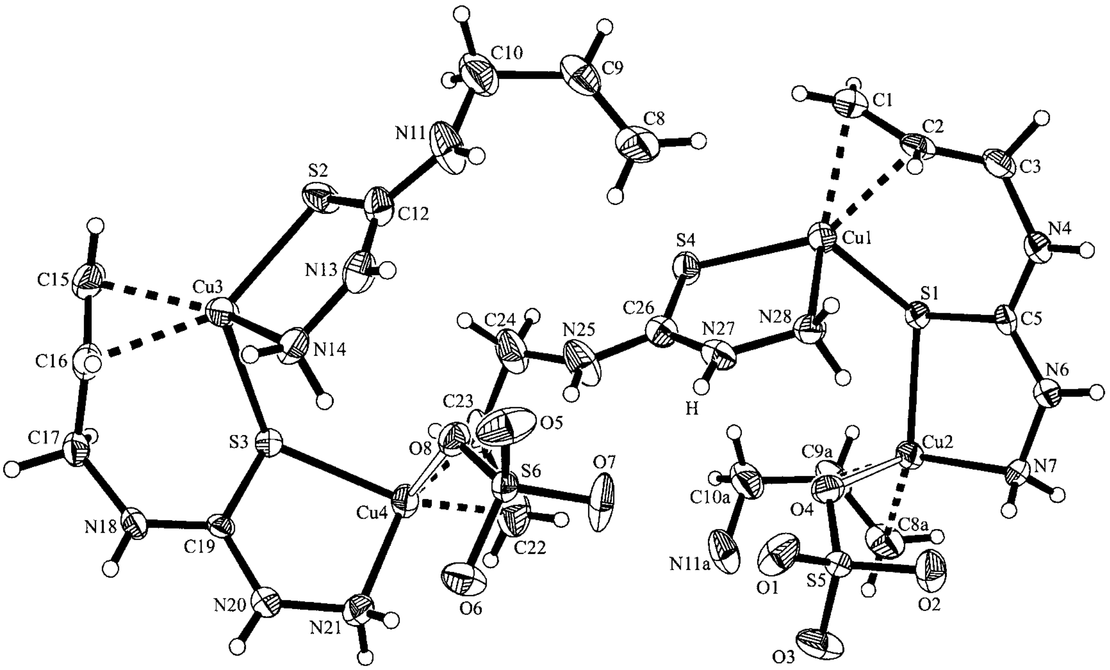

Fig. 2 Asymmetric unit of structure **2** showing the numbering scheme, the N,S,S-bridging and N,S-chelating ATSC moieties and the coordination geometry of the copper atoms. Thermal ellipsoids are drawn at 30% probability.

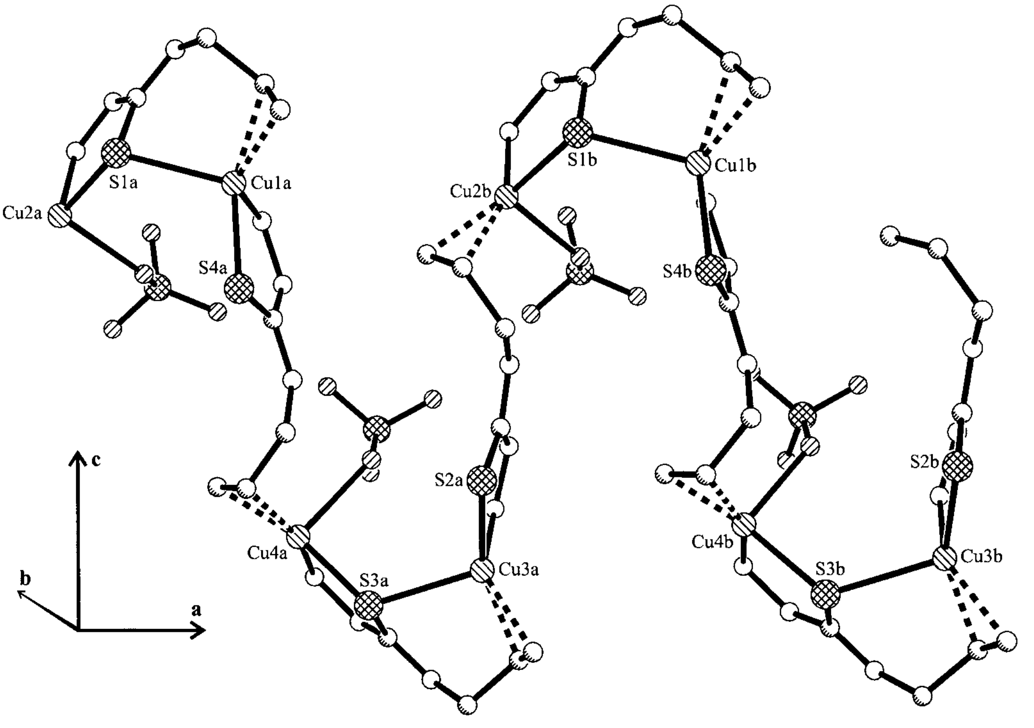

Fig. 3 Structure of the folded polymeric chain of $[Cu_2(ATSC)_2]SO_4$ along axis *a*. Hydrogen atoms are omitted. Two crystallographically independent formula units are related by pseudo glide plane *a*.

NH_2-group in ATU as against ATSC is compensated by nitrogen atoms of acetonitrile molecules at fairly short distances to copper atoms (1.944(7) and 1.949(8) Å for two independent metallic centres). The coordination spheres are strongly pronounced pyramids (apical distances Cu1–S2 2.750(3) Å and Cu2–S1 2.788(3) Å) with C=C bond, S and N atoms in equatorial planes. Deviations of copper atoms from the planes of equatorial ligands ($\Delta = 0.291$ and 0.272 Å) and tilts of C=C bonds from these planes ($\tau = 13.9$ and 7.4°) are appropriate to degree of pyramidal distortion.

It is possible to consider dependence of π-bonding effectiveness (C–Cu–C angle is the most convenient measure of both lengthening of C=C bond and shortening of Cu–(middle of C=C bond, M) distance) on geometry of coordination environment of Cu(I) and on the presence of donor atoms (S, N) in it. It is known [14] that distortion of tetrahedron to trigonal pyramid (expressed in terms of deviations of copper atom from the base plane of polyhedron) leads to π-bond strengthening. Actually, C–Cu–C angle increases from 37.8(3) and 37.6(4)° for Cu1 and Cu3 in **2** (37.1(2)° in **1**) to 38.8(4) and 39.1(4)° for Cu2 and Cu4; Cu–M distances change respectively (Table 2 and 3). However, considerable pyramidal distortions in **3** are not accompanied by large C–Cu–C angles, namely 37.2(4)° for both Cu atoms. This may be attributed partially to high donor abilities of nitrogen atoms of acetonitrile molecules, since donor ligands in copper(I) coordination sphere strongly suppress π-interaction [14]. Nevertheless, π-bonding efficiency for copper atoms, which are attached simultaneously to three (or two) strong donor atoms in **1** and **2**, appear to be fairly high.

According to the model of oxidative addition, orthogonality of L–Cu–L fragment in equatorial plane of coordination sphere stabilizes dsp^2-hybridization of atomic orbitals of the central atom [15], and in this way facilitates an effective π-bonding Cu–(C=C). Usually L–Cu–L angles in copper(I) π-complexes range from 100 to 120°. The values of N–Cu–N angles about 90° (accompanied by effective π-bonding) were achieved only with use of rigid chelating ligands, such as 2,2′-bipyridyl, 2,2′-bipyridylamine or 1,10-phenanthroline (see references cited in [15]). S,N^1-chelating ATSC turned out to be perfectly suited for this purpose, S–Cu–N angles formed by equatorial ligands in **1** and **2** range from 86.8(1) to 89.5(2)°, whereas for ATU π-complex **3** they are equal 112.3(2) and 109.7(2)°. Only the specificity of ATSC chelating favours unexpected competitiveness of C=C bond for a place in copper(I) coordination sphere, since affinity of different groups to Cu(I) increases in order [16]: $NO_3^- < C{=}C \le N(H) \le N({\equiv}C) < Cl^{\delta-} \approx S({=}C)$. Actually, the presence of thioamide sulphur atom practically always remove C=C bonds from environment of Cu(I), even in their excess, as it occurs in structure of copper(I) nitrate π-complex with N,N′-diallylthiourea [16]. In **2**, on the other hand, all double C–C bonds are coordinated, while S2 and S4 atoms have not exhausted their coordination abilities, since sulphur atom in copper(I) complexes usually acts as a bridging ligand.

One more feature of Cu–S bonding deserves attention. Each copper atom in **1** and **2** coordinates one sulphur atom of ATSC at a close distance and is situated exactly in the plane of the respective thioamide group. In the case of sulphur atom in structure **1** and S1 and S3 atoms in **2** the second copper atom forms lengthened contact Cu–S, which is rigorously directed relative to the plane of thioamide group and of the first Cu atom: dihedral angles between C–S–Cu planes range from 120 to 123°. Such spatial orientation arises from direction of electron pairs of sulphur atom, which exists mainly in sp^2, and owing to conjugation with electron pairs of nitrogen atoms, partially in sp^3 hybridization state. Double C=S bonds in **1** and **2** are elongated to 1.693(8)–1.733(7) Å, single C–N bonds of thioamide groups are lengthened to 1.316(10)–1.355(9) Å. Formation of strained dimeric Cu_2S_2 fragment with the participation of bridging S atoms of ATU molecules hindered by the exact implementation of this stereospecific behaviour of thioamide groups in **3**.

Although sulfamate anion in **1** does not coordinate copper atom, a configuration of N atom is tetrahedral and the conjugation of the electron pair with SO_3^--group is negligible. Furthermore, sulfamic nitrogen atom takes part in formation of the hydrogen bond by means of electron pair (Table 4). The S–N bond distance (1.646(4) Å) is shorter than such in the structure of sulfamic acid in its zwitterionic $NH_3^+SO_3^-$ form (1.772(1) Å) [17], and even shorter than that in potassium sulfamate (1.666(6) Å) [18]. Neutron diffraction study of the latter has also shown tetrahedral configuration of N atom for the sulfamate anion [18]. In structures of recently obtained first copper(I) sulfamate π-complexes the NH_2-group effectively binds with copper atom. This results in elongation of S–N bonds to 1.702(3) Å for molecular compound [19] and to 1.690(3) and 1.692(3) Å for zwitterionic π-complex [20], appropriate to nearly single bond order.

It is rather interesting that sulfate anions are coordinated by copper atoms in **2**, because SO_4^{2-} anion is much more harder base (by Pearsons concept) than the acid Cu^+. Actually, the compound discussed turned out to be the second π-complex where sulfate anion (and even any two-charge anion) is bonded to copper(I) atom, even at the apical position. The first one, with allylammonium cation as π-ligand, has been recently obtained [21]. Cu^{2+} (hard acid) complexes with sulfate anion bound to the Cu atom have been investigated, more e.g. with thiosemicarbazide [3]. The lengths of coordinated (on oxygen atoms) S–O bonds in **2** are more appropriate to double bond order, and are longer on average by 0.016 Å than those with none coordinated O atoms. This can be partially attributed to libration effects, since anisotropic thermal parameters point to noticeable libration of SO_3-groups about attached S–O bonds (Fig. 2). A well-developed systems of rather strong hydrogen bonds of the N(H)O types complete the structures. All H(N) atoms of both sulfamate anion and of ATSC moieties in **1** and **2** participate in a formation of hydrogen bonds, Table 4 contains their description for **1**.

Table 4 Hydrogen bonds in the compounds **1**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N7–H7A···N8^{i}	0.90	2.25	3.067(6)	150.7
N7–H7B···O1^{ii}	0.90	2.29	3.165(5)	164.3
N7–H7B···O3^{ii}	0.90	2.33	3.001(5)	131.0
N6–H6···O3^{iii}	0.86	1.91	2.757(5)	167.7
N4–H4···O2^{iii}	0.86	2.21	2.966(5)	146.3
N8–H8A···S1	0.75(6)	2.76(6)	3.489(4)	165(6)
N8–H8B···O1^{iv}	1.02(7)	1.97(7)	2.981(5)	171(6)

Symmetry transformations used to generate equivalent atoms: **i** = $x - 1/2, -y + 3/2, -z + 1$; **ii** = $x + 1/2, -y + 3/2, -z + 1$; **iii** = $-x + 3/2, -y + 2, z + 1/2$; **iv** = $-x + 2, y + 1/2, -z + 1/2$

Finally, useful method of obtaining of copper(I) sulfate complexes by slow hydrolysis of their sulfamate precursors should be emphasized.

References

[1] X. Shen, X.-F. Shi, B.-S. Kang, Y. Liu, Y.-X. Tong, H.-L. Jiang, K.-X. Chen, *Polyhedron* **1998**, *17*, 4049.

[2] a) D. Chattopadhyay, S. K. Majumdar, P. Lowe, C. H. Schwalbe, S. K. Chattopadhyay, S. Ghost, *J. Chem. Soc., Dalton Trans.* **1991**, 2121; b) F. Bigoli, M. A. Pellinghelli, A. Tiripicchio, *Cryst. Struct. Commun.* **1975**, *4*, 123; c) F. Bigoli, M. A. Pellinghelli, A. Tiripicchio, M. Tiripicchio Camellini, *Acta Crystallogr.* **1975**, *B 31*, 55; d) F. Bigoli, E. Leporati, M. A. Pellinghelli, *Cryst. Struct. Commun.* **1975**, *4*, 119; e) M. Lanfranchi, A. M. M. Lanfredi, A. Tiripicchio, M. Tiripicchio Camellini, *Acta Crystallogr.* **1978**, *B 34*, 95; f) A. M. M. Lanfredi, A. Tiripicchio, M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.* **1975**, 2168; g) A. Chiesi-Villa, A. G. Manfredotti, C. Guastini, *Cryst. Struct. Commun.* **1972**, *1*, 207; h) A. Chiesi Villa, A. G. Manfredotti, C. Guastini, *Cryst. Struct. Commun.* **1972**, *1*, 125.

[3] Chao Qirong, Li Cun, Zhou Jingyu, You Xiaozeng, Huang Jinshun, Wang Manfang, *Kexue Tongbao. (Chin. Sci. Bull., Engl.)* **1987**, *32*, 321.

[4] a) M. K. Woode, R. F. Bryan, B. A. Becoe, *Acta Crystallogr.* **1987**, *C 43*, 2324; b) M. B. Cingi, F. Bigoli, M. Lanfranchi, M. A. Pellinghelli, A. Vera, E. Buluggiu, *J. Chem. Soc., Dalton Trans.* **1992**, 3145; c) Chun-Ying Duan, Ze-Hua Liu, Xiao-Zeng You, Feng Xue, T. C. W. Mak, *J. Chem. Soc., Chem. Commun.* **1997**, 381.

[5] F. Nicolo, H. El Ghaziri, G. Chapuis, *Acta Crystallogr.* **1988**, *C 44*, 975.

[6] a) W. Simako, W. Tesch, V. M. Saponov, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics.* **1998**, *17*, 5674; b) D. Cauzzi, M. Costa, L. Gonsalvi, M. A. Pellin-

ghelli, G. Predieri, A. Tiripicchio, R. Zanoni, *J. Organomet. Chem.* **1997**, *541*, 377; c) D. Cauzzi, M. Lanfranchi, G. Marzolini, G. Predieri, A. Tiripicchio, M. Costa, R. Zanoni, *J. Organomet. Chem.* **1995**, *488*, 115.
[7] Ya. E. Filinchuk, D. Schollmeyer, V. V. Olijnyk, M. G. Mys'kiv, E. A. Goreshnik, *Russ. J. Coord. Chem.* **1996**, *22*, 815.
[8] B. M. Mykhalichko, M. G. Mys'kiv, UA-Pat. N 25459 A; B. N6, **1998**.
[9] A. L. Spek, *J. Appl. Crystallogr.* **1988**, *21*, 578.
[10] A. L. Spek, *PLATON99. Multipurpose Crystallographic Tool*, University of Utrecht, Netherlands, **1999**.
[11] G. M. Sheldrick, *SHELXS97 and SHELXL97. Programs for the solution and refinement of crystal structures*, University of Göttingen, Germany, **1997**.
[12] H. D. Flack, *Acta Crystallogr.* **1983**, *A 39*, 876.
[13] S. C. Abrahams, *Acta Crystallogr.* **1974**, *B 30*, 261.
[14] M. G. Mys'kiv, V. V. Olijnyk, *Russ. J. Coord. Chem.* **1995**, *21*, 275.
[15] V. V. Olijnyk, *Russ. J. Coord. Chem.* **1998**, *24*, 677.
[16] Ya. E. Filinchuk, V. V. Olijnyk, D. Schollmeyer, *Russ. J. Coord. Chem.* **1999**, *25*, 209.
[17] A. F. Cameron, F. D. Duncanson, *Acta Crystallogr.* **1976**, *B 32*, 1563.
[18] G. W. Cox, T. M. Sabine, V. M. Padmanabhan, N. T. Ban, M. K. Chung, A. J. Surjadi, *Acta Crystallogr.* **1967**, *23*, 578.
[19] Ya. E. Filinchuk, O. P. Mel'nyk, M. G. Mys'kiv, *Polish J. Chem.* **2000**, *74*, 385.
[20] O. P. Melnyk, D. Schollmeyer, V. V. Olijnyk, Ya. E. Filinchuk, *Acta Crystallogr. C.* **2000**. (in press).
[21] Ya. E. Filinchuk, V. N. Davydov, M. G. Mys'kiv, *Russ. J. Coord. Chem.* **2000**, *26*, 582.