Thiourea *N*- and *S*-Derivatives as Ligands: Synthesis and Crystal Structure of $4CuCl \cdot 6All–NHCSNH_2$ and $[(All–NH)_2C–SC_2H_5]Cu_2Cl_xBr_{3-x}$ (*x* = 0.765, All is Allyl)

Ya. E. Filinchuk, V. V. Oliinik, T. Glovyak, and M. G. Mys'kiv

Franko State University, ul. Lomonosova 8, Lviv, 290005 Ukraine
Ukrainian State Forestry University, Lviv, Ukraine
Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland
Received August 1, 2000

Abstract—Crystals of the compounds $4CuCl \cdot 6CH_2=CH–CH_2–NHCSNH_2$ (**I**) and $[(CH_2=CH–CH_2–NH)_2C–SC_2H_5]Cu_2Cl_xBr_{3-x}$ (*x* = 0.765) (**II**) were synthesized by the ac electrochemical method, and their crystal structures were determined (CuK_α and MoK_α radiation, 2575 and 1090 unique reflections with $F \geq 4\sigma(F)$, $R = 0.050$ and 0.028 for **I** and **II**, respectively). Complex **I** crystallizes in space group $C2/c$, $a = 17.230(7)$ Å, $b = 12.258(5)$ Å, $c = 42.95(2)$ Å, $\beta = 97.48(4)°$, $V = 8994(7)$ Å^3, $Z = 8$. The structure of π-complex **II** is described by space group $P2_1/n$, $a = 10.633(5)$ Å, $b = 9.280(5)$ Å, $c = 16.024(4)$ Å, $\gamma = 102.16(3)°$, $V = 1546(1)$ Å^3, $Z = 4$. Complex **I** is built from isolated units of the aforementioned composition; every allylthiourea molecule coordinates two metal atoms through the sulfur atom. The distorted tetrahedral surrounding of every Cu(I) atom involves three S atoms and one Cl atom. The *N,N'*-diallyl-*S*-ethylisotiouronium cation coordinates two copper atoms through the C=C bonds, 1.32(1) and 1.35(1)Å, uniting the cuprohalide chains in layers. The structure of complex **II** is very close to the structure of the previously studied π-complex of diallylammonium $[H^+L]Cu_2Cl_3$.

In our previous work [1], using analysis of the crystal structures of the copper(I) nitrate complexes with functional derivatives of olefins, we established the order of the increasing ability of ligands to coordinate copper(I): $NO_3^- < C=C \leq N(H) \leq N(\equiv C) < Cl^- \approx S(=C)$. The thiourea sulfur atom having a unique affinity to Cu(I), is coordinated to two copper(I) atoms in an usual manner [1–3] and effectively competes even with chlorine atoms for the site in the coordination sphere of the metal [4, 5]. Only one case of coordination of the C=C double bond to Cu(I) in the presence of the S(=C) group is known in the π-complex of copper(I) nitrate with allylthiourea (ATU) $[Cu(ATU)(CH_3CN)]NO_3$ [3] as a result of competition between the C=C bond and labile NO_3^- group for the remaining site in the coordination sphere of the copper(I) atom.

The *S*-allyl derivatives of thiourea, by contrast, have the properties of solely π-ligands, since the sulfur atom is deactivated due to the cationic nature of the species. In the copper(I) halide complexes with *S*-allylisothiouronium, $[CH_2=CH–CH_2–SC(NH_2)_2]CuX_2$ (X = Cl or Br), the metal atom coordinates three halogen atoms and the C=C bond [6].

As a continuation of our studies into the stereochemistry of the copper(I) complexes and the competition of ligands in the Cu(I) coordination sphere, we synthesized and structurally characterized the complexes of *N*- and *S*-allyl derivatives of thiourea $4CuCl \cdot 6CH_2=CH–CH_2–NHCSNH_2$ (**I**) and $[(CH_2=CH–CH_2–NH)_2C–SC_2H_5]Cu_2Cl_xBr_{3-x}$ (*x* = 0.765) (**II**).

EXPERIMENTAL

N-Allylthiourea and *N,N'*-diallylthiourea (DATU) were prepared by treating a water–alcohol mixture of allyl isothiocianate with an aqueous solution of ammonia or an ethanol solution of allylamine, respectively [7]. Complex **I** (as edged colorless monoclinic prisms) was synthesized by the ac electrochemical method on copper electrodes ($U = 0.20$ V, $I = 0.13$ mA) in an ethanol solution (6 ml) of $CuCl_2 \cdot 2H_2O$ (2 mmol), 1 ml of 36% HCl, and ATU (4 mmol). The relatively stable crystals of **I** were grown over the course of 40 h. A strongly acidic medium was necessary to prevent the reaction of Cu(II) with ATU followed by the formation of a powdered complex.

N,N'-Diallyl-*S*-ethylisothiouronium (DAEITU) bromide was synthesized from DATU and ethyl bromide as in [7, p. 580]. Complex **II** (as well edged plates) was prepared by the ac electrochemical reduction of Cu(II) to Cu(I) on copper electrodes ($U = 0.30$ V, $I = 0.23$ mA) in an ethanol solution (6 ml) of $CuCl_2 \cdot 2H_2O$ (3 mmol) and DAEITU bromide (1.5 mmol). The crystals of **II**, relatively stable in air, were grown over a week; they were stable during the X-ray diffraction experiment. The yield was almost quantitative. The density of the

Table 1. Crystallographic and intensity collection data for complexes **I** and **II**

Parameter	I	II
Empirical formula	$C_{24}H_{48}N_{12}S_6Cl_4Cu_4$	$C_9H_{17}N_2SBr_{2.235}Cl_{0.765}Cu_2$
M	1093.1	452.8
Crystal size, mm	$0.4 \times 0.3 \times 0.15$	$0.35 \times 0.3 \times 0.2$
$F(000)$	4448	895
Space group	$C2/c$	$P2_1/n$
a, Å	17.230(7)	10.633(5)
b, Å	12.258(5)	9.280(5)
c, Å	42.95(2)	16.024(4)
β, deg	97.48(4)	
γ, deg		102.16(3)
V, Å^3	8994(7)	1546(1)
Z	8	4
ρ(exp), g/cm^3	1.61	1.94
ρ(calcd), g/cm^3	1.614(2)	1.946(3)
Radiation	CuK_α	MoK_α
Diffractometer	KM-4	DARCh-1
Monochromator	Graphite	Zr filter
Scan mode	$\omega/2\theta$	$\theta/2\theta$
$2\theta_{max}$, deg	130.3	49.82
μ, mm^{-1}	8.45 (CuK_α)	5.23 (MoK_α)
Number of reflections:		
measured	7248	1279
unique	6849	1107
unique with $F \geq 4\sigma(F)$	2575	1090
Number of parameters/restrictions	451/90	158/0
$R(F)$ c $F \geq 4\sigma(F)/R_w(F^2)$	0.0499/0.1943	0.0280/0.0696
Weight scheme*: A, B	0.1026, 0	0.0456, 1.1276
GOOF in F^2	0.973	1.070
$\Delta\delta$ max/min, e/Å^3	0.65/–0.66	0.35/–0.31

* $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, $P = [F_o^2 + 2F_c^2]/3$.

crystals was measured by the flotation method in a bromoform–chloroform mixture.

After the preliminary photographic study, the structures were solved using diffraction arrays collected on KM-4 and DARCh-1 single-crystal diffractometers. Intensities of reflections were corrected for the Lorentz and polarization effects. The structures were solved by direct methods; light and H atoms were located from difference Fourier syntheses. Absorption correction was applied with the DIFABS program. The solution of the structures and the absorption correction were performed using the CSD program package [8]. All non-hydrogen atoms were refined for F^2 in the full-matrix anisotropic variant with the use of the SHELXL97 program [9]. The hydrogen atoms were refined in the rider

model with isotropic thermal parameters equal to $1.2U$ of the neighboring non-hydrogen atom. While refining structure **I**, mild restrictions were applied: the gradual increase of anisotropic thermal parameters for the carbon atoms of the allyl group and geometric restrictions of the C–C distances (the SIMU, DFIX, and DANG instructions). In structure **II**, the parameters of occupation of the halogen X positions with the Cl and Br atoms were refined. Extinction was not corrected. The peaks of the residual electronic density were localized near the copper, sulfur, and halogen atoms.

Crystallographic data, a summary of the X-ray diffraction experiment and refinement parameters are presented in Table 1. Atomic coordinates and thermal

Table 2. Atomic coordinates and thermal parameters* in structures **I** and **II**

Atom	x	y	z	U, Å^2	Atom	x	y	z	U, Å^2
		I					**I**		
Cu(1)	0.63629(9)	0.2313(1)	0.66647(4)	0.0556(5)	C(11)	0.424(2)	0.455(2)	0.7076(8)	0.30(2)
Cu(2)	0.50995(9)	0.3252(1)	0.59566(3)	0.0510(4)	C(21)	0.4742(9)	0.919(1)	0.6719(4)	0.121(6)
Cu(3)	0.72413(9)	0.2661(1)	0.59368(4)	0.0527(4)	C(31)	0.546(1)	−0.084(2)	0.5882(5)	0.168(9)
Cu(4)	0.66752(8)	0.5091(1)	0.64139(3)	0.0475(4)	C(41)	0.372(1)	0.414(3)	0.4760(8)	0.31(2)
Cl(1)	0.6388(2)	0.1087(2)	0.71540(6)	0.0587(8)	C(51)	0.895(1)	0.159(2)	0.7657(5)	0.20(1)
Cl(2)	0.3792(1)	0.3383(2)	0.56938(6)	0.0518(7)	C(61)	0.900(2)	0.505(2)	0.4956(6)	0.37(2)
Cl(3)	0.8100(2)	0.2089(3)	0.55742(6)	0.0687(9)	H(11)	0.499	0.192	0.699	0.09
Cl(4)	0.7006(1)	0.6933(2)	0.65909(6)	0.0490(7)	H(21)	0.552	0.669	0.648	0.09
S(1)	0.5160(1)	0.2046(2)	0.63766(6)	0.0452(7)	H(31)	0.721	0.037	0.588	0.06
S(2)	0.5526(1)	0.5027(2)	0.60809(6)	0.0468(7)	H(41)	0.480	0.323	0.527	0.09
S(3)	0.7327(1)	0.1622(2)	0.63944(6)	0.0400(6)	H(51)	0.730	0.268	0.726	0.10
S(4)	0.5979(2)	0.2423(2)	0.56806(6)	0.0508(7)	H(61)	0.830	0.411	0.564	0.08
S(5)	0.6493(1)	0.4039(2)	0.68479(6)	0.0440(6)	H(12A)	0.351	0.316	0.660	0.10
S(6)	0.7639(1)	0.4288(2)	0.61686(6)	0.0475(7)	H(12B)	0.380	0.312	0.629	0.10
N(11)	0.4581(6)	0.2278(8)	0.6909(2)	0.071(3)	H(22A)	0.372	0.601	0.620	0.09
N(21)	0.5027(5)	0.6601(8)	0.6419(2)	0.071(3)	H(22B)	0.394	0.506	0.602	0.09
N(31)	0.7058(5)	−0.0065(7)	0.6015(2)	0.048(2)	H(32A)	0.668	−0.099	0.647	0.08
N(41)	0.5185(6)	0.3202(9)	0.5160(2)	0.074(3)	H(32B)	0.679	−0.007	0.670	0.08
N(51)	0.7569(7)	0.3274(7)	0.7287(2)	0.086(4)	H(42A)	0.641	0.302	0.495	0.11
N(61)	0.8296(6)	0.4803(7)	0.5670(2)	0.063(3)	H(42B)	0.693	0.265	0.523	0.11
N(12)	0.3861(6)	0.2981(9)	0.6483(2)	0.084(4)	H(52A)	0.808	0.513	0.730	0.11
N(22)	0.4079(5)	0.5599(8)	0.6140(2)	0.075(3)	H(52B)	0.751	0.563	0.705	0.11
N(32)	0.6810(6)	−0.0319(7)	0.6513(2)	0.068(3)	H(62A)	0.818	0.668	0.585	0.09
N(42)	0.6477(6)	0.2849(9)	0.5142(2)	0.091(4)	H(62B)	0.777	0.646	0.613	0.09
N(52)	0.7678(6)	0.5073(8)	0.7161(2)	0.088(4)	H(13A)	0.351	0.234	0.704	0.15
N(62)	0.7977(6)	0.6227(8)	0.5967(2)	0.077(3)	H(13B)	0.417	0.229	0.733	0.15
C(1)	0.4495(6)	0.249(1)	0.6609(2)	0.053(3)	H(23A)	0.415	0.769	0.634	0.12
C(2)	0.4821(6)	0.5791(9)	0.6231(2)	0.046(3)	H(23B)	0.413	0.699	0.665	0.12
C(3)	0.7034(5)	0.0323(8)	0.6296(2)	0.039(2)	H(33A)	0.711	−0.167	0.606	0.09
C(4)	0.5882(7)	0.2890(9)	0.5307(3)	0.054(3)	H(33B)	0.705	−0.127	0.571	0.09
C(5)	0.7313(7)	0.412(1)	0.7119(2)	0.060(3)	H(43A)	0.526	0.420	0.480	0.14
C(6)	0.7989(6)	0.5164(8)	0.5908(2)	0.045(3)	H(43B)	0.523	0.296	0.470	0.14
C(13)	0.402(1)	0.263(2)	0.7124(4)	0.125(7)	H(53A)	0.860	0.386	0.749	0.15
C(23)	0.4472(7)	0.737(1)	0.6525(4)	0.096(5)	H(53B)	0.812	0.329	0.773	0.15
C(33)	0.6850(7)	−0.115(1)	0.5908(3)	0.076(4)	H(63A)	0.835	0.617	0.543	0.13
C(43)	0.5015(8)	0.350(1)	0.4832(3)	0.116(6)	H(63B)	0.917	0.563	0.553	0.13
C(53)	0.827(1)	0.324(1)	0.7517(4)	0.132(7)	H(12)	0.357	0.400	0.731	0.23
C(63)	0.863(1)	0.548(1)	0.5447(3)	0.104(5)	H(22)	0.529	0.801	0.685	0.11
C(12)	0.393(2)	0.381(2)	0.7173(6)	0.19(1)	H(32)	0.588	−0.210	0.581	0.14
C(22)	0.4869(8)	0.824(1)	0.6713(4)	0.095(5)	H(42)	0.400	0.298	0.462	0.22
C(32)	0.600(1)	−0.138(2)	0.5863(4)	0.118(6)	H(52)	0.875	0.214	0.728	0.21
C(42)	0.418(1)	0.359(2)	0.4737(4)	0.179(9)	H(62)	0.817	0.456	0.509	0.23
C(52)	0.868(1)	0.227(2)	0.7485(5)	0.18(1)	H(11A)	0.462	0.444	0.694	0.36
C(62)	0.860(1)	0.500(2)	0.5147(5)	0.19(1)	H(11B)	0.412	0.525	0.713	0.36

Table 2. (Contd.)

Atom	x	y	z	U, Å^2	Atom	x	y	z	U, Å^2
	I					**II**			
H(21A)	0.433	0.949	0.659	0.15	C(5)	−0.3381(6)	0.2498(7)	0.5004(4)	0.035(2)
H(21B)	0.505	0.964	0.685	0.15	C(6)	−0.2448(6)	0.3952(7)	0.5120(5)	0.037(2)
H(31A)	0.552	−0.011	0.594	0.20	C(7)	−0.1922(7)	0.4889(8)	0.4508(6)	0.046(2)
H(31B)	0.496	−0.114	0.584	0.20	C(8)	−0.5284(7)	0.1455(9)	0.2596(5)	0.059(3)
H(41A)	0.381	0.478	0.487	0.37	C(9)	−0.6041(9)	0.006(1)	0.2973(7)	0.094(4)
H(41B)	0.321	0.397	0.467	0.37	H(1)	−0.159	0.178	0.421	0.05
H(51A)	0.890	0.164	0.787	0.24	H(2)	−0.450	0.233	0.399	0.05
H(51B)	0.920	0.100	0.758	0.24	H(1A)	0.037	0.330	0.379	0.07
H(61A)	0.945	0.547	0.499	0.44	H(1B)	0.174	0.298	0.351	0.07
H(61B)	0.888	0.466	0.477	0.44	H(2A)	0.080	0.086	0.298	0.06
	II				H(3A)	−0.143	0.078	0.262	0.07
Cu(1)	0.10827(9)	0.1062(1)	0.44009(7)	0.0498(3)	H(3B)	−0.125	−0.028	0.336	0.07
Cu(2)	0.34422(9)	0.4287(1)	0.49731(7)	0.0476(3)	H(5A)	−0.299	0.171	0.521	0.04
X(1)**	0.3067(1)	0.1697(1)	0.51419(9)	0.0533(6)	H(5B)	−0.415	0.250	0.533	0.04
X(2)	−0.0494(1)	0.1506(2)	0.5570(1)	0.0444(7)	H(6)	−0.221	0.423	0.567	0.04
X(3)	0.5202(1)	0.5098(2)	0.61754(9)	0.0465(7)	H(7A)	−0.213	0.465	0.395	0.05
S	−0.3575(2)	0.1523(3)	0.2528(1)	0.0592(6)	H(7B)	−0.135	0.577	0.464	0.05
N(1)	−0.1911(5)	0.1491(6)	0.3733(4)	0.039(1)	H(8A)	−0.542	0.229	0.293	0.07
N(2)	−0.3748(5)	0.2200(6)	0.4137(4)	0.039(2)	H(8B)	−0.561	0.156	0.204	0.07
C(1)	0.0847(8)	0.269(1)	0.3540(5)	0.059(2)	H(9A)	−0.591	−0.077	0.265	0.11
C(2)	0.0262(8)	0.1414(9)	0.3218(5)	0.051(2)	H(9B)	−0.694	0.009	0.297	0.11
C(3)	−0.1131(7)	0.0749(9)	0.3191(5)	0.055(2)	H(9C)	−0.576	−0.002	0.354	0.11
C(4)	−0.3040(6)	0.1755(8)	0.3556(5)	0.035(2)					

* For non-hydrogen atoms, $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j)$.

** The values of the factor of occupation of the X(1–3) positions with the Cl and Br atoms:
    X(1) = 0.535(5)Cl + 0.465(5)Br;
    X(2) = 0.897(5)Cl + 0.103(5)Br;
    X(3) = 0.802(5)Cl + 0.198(5)Br.

parameters are given in Table 2, and bond lengths, angles, and torsion angles are listed in Table 3.

RESULTS AND DISCUSSION

In structure **I**, the olefin bond of the allyl group is not involved in the interaction with the copper(I) atom. Every ATU molecule coordinates two metal atoms through the sulfur atom in such a manner that the distorted tetrahedral environment of every Cu(I) atom includes three S atoms and one Cl atom. Thus, in this structure, a Cu$_4$S$_6$Cl$_4$ core is formed in which the copper and sulfur atoms form the tetrahedral and octahedral voids, respectively (Fig. 1a). In the case of Cu(I), the coordination polyhedron is most distorted toward

the trigonal pyramid; the Cu–Cl bond is elongated to 2.579(3) Å. The extension of the Cu(1)–Cu(4) atoms from the plane of the coordinated sulfur atoms is 0.614, 0.826, 0.798, or 0.831 Å, respectively. The powerful coordination activity of the thiol groups is of interest; they displace the chlorine atoms from the Cu(I) coordination sphere, allowing them to form only isolated Cu–Cl units that are not characteristic for structures of cuprohalide complexes. The chlorine atoms occupy the distant axial positions, Cu–Cl 2.828(5) and 3.164(6) Å [4], in the copper(I) chloride complex with thiourea of 1 : 2 composition and are entirely removed from the Cu(I) coordination sphere in the 1 : 3 complex [5].

Since the metal atoms are not coordinated by the C=C bonds of the ATU molecules, these molecules are

Table 3. Selected bond lengths (*d*), bond angles (ω), and torsion angles (φ) in structures **I** and **II**

Bond	*d*, Å	Angle[1]	ω, deg	Bond	*d*, Å	Angle	ω, deg
		I				**II**	
Cu(1)–S(5)	2.258(3)	S(5)Cu(1)S(1)	111.3(1)	Cu(1)–X(1)[1]	2.385(2)	X(1)Cu(1)X(2)	99.70(7)
Cu(1)–S(1)	2.295(3)	S(5)Cu(1)S(3)	118.3(1)	Cu(1)–X(2)	2.604(2)	X(1)Cu(1)X(2)'	105.97(6)
Cu(1)–S(3)	2.308(3)	S(5)Cu(1)Cl(1)	105.8(1)	Cu(1)–X(2)'	2.333(2)	X(1)Cu(1)*m*(1,2)	127.5(2)
Cu(1)–Cl(1)	2.579(3)	S(1)Cu(1)S(3)	109.6(1)	Cu(1)–C(1)	2.100(8)	X(2)Cu(1)X(2)'	95.96(6)
		S(1)Cu(1)Cl(1)	105.9(1)	Cu(1)–C(2)	2.141(8)	X(2)Cu(1)*m*(1,2)	105.2(2)
		S(3)Cu(1)Cl(1)	105.0(1)	Cu(1)–*m*(1,2)[2]	2.015(8)	X(2)'Cu(1)*m*(1,2)	116.2(2)
Cu(2)–S(4)	2.280(3)	S(4)Cu(2)S(1)	98.9(1)			C(1)Cu(1)C(2)	36.3(3)
Cu(2)–S(1)	2.324(3)	S(4)Cu(2)S(2)	108.9(1)	Cu(2)–X(1)	2.368(2)	X(1)Cu(2)X(3)	99.27(6)
Cu(2)–S(2)	2.337(3)	S(4)Cu(2)Cl(2)	115.7(1)	Cu(2)–X(3)	2.681(2)	X(1)Cu(2)X(3)'	107.55(6)
Cu(2)–Cl(2)	2.390(3)	S(1)Cu(2)S(2)	115.7(1)	Cu(2)–X(3)'	2.333(2)	X(1)Cu(2)*m*(6,7)	126.7(2)
		S(1)Cu(2)Cl(2)	110.7(1)	Cu(2)–C(6)	2.130(6)	X(3)Cu(2)X(3)'	98.02(7)
		S(2)Cu(2)Cl(2)	107.1(1)	Cu(2)–C(7)	2.099(7)	X(3)Cu(2)*m*(6,7)	103.0(2)
Cu(3)–S(6)	2.294(3)	S(6)Cu(3)S(4)	121.5(1)	Cu(2)–*m*(6,7)[2]	2.004(6)	X(3)'Cu(2)*m*(6,7)	116.3(2)
Cu(3)–S(4)	2.325(3)	S(6)Cu(3)S(3)	97.3(1)			C(6)Cu(2)C(7)	37.3(3)
Cu(3)–S(3)	2.330(3)	S(6)Cu(3)Cl(3)	111.3(1)			Cu(1)X(1)Cu(2)	98.33(6)
Cu(3)–Cl(3)	2.388(3)	S(4)Cu(3)S(3)	106.5(1)			Cu(1)X(2)Cu(1)'	84.04(6)
		S(4)Cu(3)Cl(3)	106.0(1)			Cu(2)X(3)Cu(2)'	81.98(7)
		S(3)Cu(3)Cl(3)	114.4(1)	C(1)–C(2)	1.32(1)	C(1)C(2)C(3)	128.8(8)
Cu(4)–S(2)	2.288(3)	S(2)Cu(4)S(6)	108.5(1)	C(2)–C(3)	1.48(1)	C(2)C(3)N(1)	113.7(7)
Cu(4)–S(6)	2.301(3)	S(2)Cu(4)S(5)	106.6(1)	C(3)–N(1)	1.468(9)	C(3)N(1)C(4)	126.3(6)
Cu(4)–S(5)	2.322(3)	S(2)Cu(4)Cl(4)	112.1(1)	N(1)–C(4)	1.306(8)	N(1)C(4)N(2)	121.0(7)
Cu(4)–Cl(4)	2.426(3)	S(6)Cu(4)S(5)	108.1(1)	C(4)–N(2)	1.317(8)	N(1)C(4)S	118.1(6)
		S(6)Cu(4)Cl(4)	112.8(1)	C(4)–S	1.742(8)	N(2)C(4)S	120.9(5)
		S(5)Cu(4)Cl(4)	108.4(1)	S–C(8)	1.808(8)	C(4)SC(8)	104.4(4)
C(1)–S(1)	1.70(1)	Cu(1)S(1)Cu(2)	105.9(1)	C(8)–C(9)	1.50(1)	SC(8)C(9)	114.1(7)
C(1)–N(11)	1.30(1)	C(1)S(1)Cu(1)	105.6(4)	N(2)–C(5)	1.453(9)	C(4)N(2)C(5)	125.9(6)
C(1)–N(12)	1.30(1)	C(1)S(1)Cu(2)	106.7(4)	C(5)–C(6)	1.509(9)	N(2)C(5)C(6)	112.9(6)
C(2)–S(2)	1.72(1)	Cu(4)S(2)Cu(2)	113.3(1)	C(6)–C(7)	1.35(1)	C(5)C(6)C(7)	126.2(7)
C(2)–N(21)	1.30(1)	C(2)S(2)Cu(4)	110.0(4)				
C(2)–N(22)	1.31(1)	C(2)S(2)Cu(2)	112.1(4)				
C(3)–S(3)	1.71(1)	Cu(1)S(3)Cu(3)	104.7(1)				
C(3)–N(31)	1.31(1)	C(3)S(3)Cu(1)	104.9(3)				
C(3)–N(32)	1.31(1)	C(3)S(3)Cu(3)	108.5(4)				
C(4)–S(4)	1.69(1)	Cu(2)S(4)Cu(3)	110.0(1)				
C(4)–N(41)	1.34(1)	C(4)S(4)Cu(2)	110.6(4)				
C(4)–N(42)	1.32(1)	C(4)S(4)Cu(3)	112.2(4)				
C(5)–S(5)	1.71(1)	Cu(1)S(5)Cu(4)	105.0(1)				
C(5)–N(51)	1.31(1)	C(5)S(5)Cu(1)	109.2(4)				
C(5)–N(52)	1.32(1)	C(5)S(5)Cu(4)	109.0(4)				
C(6)–S(6)	1.72(1)	Cu(3)S(6)Cu(4)	112.2(1)				
C(6)–N(61)	1.29(1)	C(6)S(6)Cu(3)	111.8(4)				
C(6)–N(62)	1.33(1)	C(6)S(6)Cu(4)	111.5(4)				

Table 3. (Contd.)

Angle	φ	$\bar{\varphi}\,(s)^3$	φ	$\bar{\varphi}\,(s)^3$	φ_{stand}^{4}
	I (X = Cl)		**III** (X = I)		
X–Cu–S–Cu'	164.7(1)–176.3(1)	171.1(3.5)	173.7(1)–179.42(9)	177.2(2.0)	180
S–Cu–S'–Cu'	38.9(2)–75.5(1)	59.8(11.3)	40.6(2)–72.5(2)	59.4(8.6)	60
X–Cu–S–C	38.6(4)–64.1(4)	51.4(8.6)	8.7(6)–70.2(4)	48.4(24.3)	60
S–Cu–S'–C	51.2(4)–87.3(4)	69.3(12.6)	37.8(4)–113.2(5)	72.7(30.0)	60
S"–Cu–S'–C	158.3(4)–179.8(3)	170.9(6.7)	137.8(5)–180.0(4)	162.5(16.9)	180
Cu–S–C–N	23.1(9)–48.5(8)	32.5(7.0)	6(1)–40(1)	26.4(13.1)	
Cu'–S–C–N	134.5(7)–159.9(7)	151.6(7.4)	143(1)–176.3(8)	156.1(13.0)	

Angle	φ	Angle	φ
X(3)–Cu(2)–X(1)–Cu(1)	−95.65(7)	N(1)–C(4)–N(2)–C(5)	2(1)
X(3)'–Cu(2)–X(1)–Cu(1)	162.82(5)	C(4)–N(2)–C(5)–C(6)	76.7(9)
X(2)–Cu(1)–X(1)–Cu(2)	178.32(7)	N(2)–C(5)–C(6)–C(7)	−3(1)
X(2)'–Cu(1)–X(1)–Cu(2)	−82.55(7)	C(5)–C(6)–C(7)–Cu(2)	100.5(6)
X(1)–Cu(1)–X(2)–Cu(1)'	−107.37(7)	C(3)–N(1)–C(4)–S	−12(1)
X(1)–Cu(2)–X(3)–Cu(2)'	109.36(6)	N(1)–C(4)–S–C(8)	163.8(6)
Cu(1)–C(1)–C(2)–C(3)	102.1(9)	C(5)–N(2)–C(4)–S	−176.9(5)
C(1)–C(2)–C(3)–N(1)	−13(1)	N(2)–C(4)–S–C(8)	−16.9(7)
C(2)–C(3)–N(1)–C(4)	140.4(8)	C(4)–S–C(8)–C(9)	−71.9(7)
C(3)–N(1)–C(4)–N(2)	168.4(7)		

Note: [1] The Br : Cl ratio is given in Table 2.

[2] $m(1,2)$ or $m(6,7)$ is the midst of the C(1)=C(2) or C(6)=C(7) bond, respectively.

[3] $\bar{\varphi}$, s is the mean value and root mean square for the angles.

[4] The φ_{stand} angles characterize the standard fragment (the adamantane molecule).

not fixed in the structure, as a result of which a significant increase in the thermal parameters of the carbon atoms (Table 2), an apparent distortion of the geometry of the allyl groups, and a higher divergence factor are observed. The conjunction of the lone electron pairs of the nitrogen atoms with the double bond of the neighboring thiourea group of the ATU molecule makes the amide group planar. The copper atoms are coordinated by the >C=S group at one side of the plane of the thiourea group; the thiourea group forms a significant angle with the corresponding CuSCu' plane (47.7°–62.6°). This evidences the transfer of the electronic density from the nitrogen atoms to the sulfur atom with a partial transformation of the >C=S double bond into the >C–S⁻ ordinary bond permitting coordination to Cu(I) through the sp^3 hybrid electronic pairs (coordination of the sulfur atom to even three metal atoms can be expected); this is evidenced also by the tetrahedral CSCu and CuSCu' angles (Table 3). The plane of the thiourea group is fixed by hydrogen bonds of the N–H⋯Cl type formed within the cluster (Table 4). The tet-

ranuclear fragments in structure **I** are jointed by van der Waals forces and several intermolecular H bonds.

A fragment of similar structure was found earlier in the copper(I) iodide complex with *N*-ethylthiourea of the 4CuI · 6C₂H₅–NHCSNH₂ · H₂O (**III**) composition [10]. For comparing the geometry of **I** and **III**, torsion angles containing copper atoms are given in Table 3. The values of the X–Cu–S–Cu' (X = Cl, I) angles are close to 180° in the case of **III** due to less influence of weak N–H⋯I hydrogen bonds on the geometry of the coordination cores. The only significant distinction in structures **I** and **III** is the less rigid orientation of the thiourea group relative to the CuSCu' **III** plane in **III** (the corresponding dihedral angles are 23.9° and 9.1° for two ethylthiourea molecules and 52.2°–64.7° for the other four), which is responsible for the wide scattering in the values of the torsion angles in structure **III**.

In contrast to the neutral ATU molecule, the sulfur atom of the isothiouronium cation shows no donor properties toward copper(I). Hence, the coordination activity of the halide ligands in structure **II** is restored and π-coordination Cu–(C=C) is realized. The trigonal-
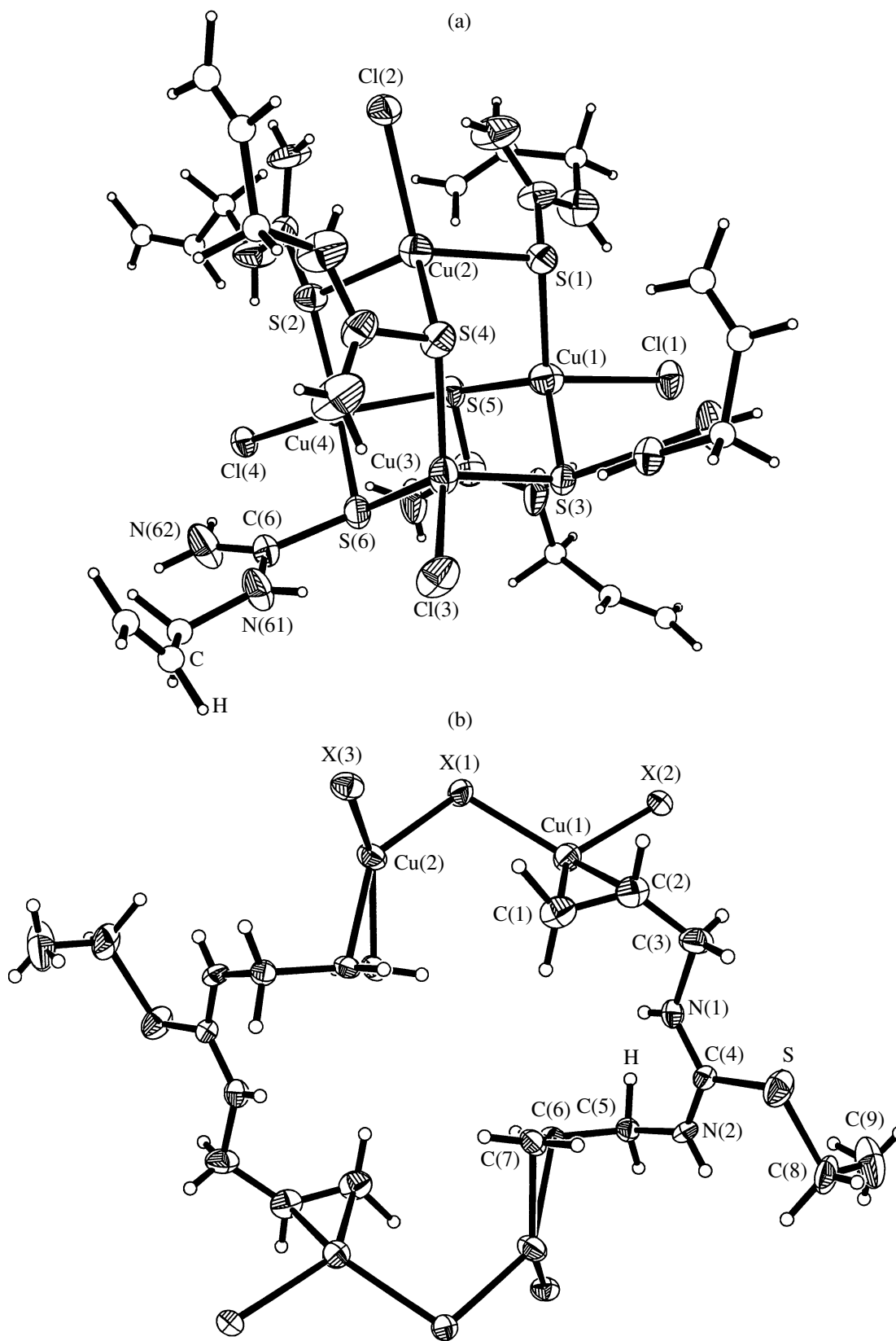
(a)

(b)

Fig. 1. (a) Asymmetric unit in structure **I** and (b) fragment of structure **II**. Schemes of numbering and ellipsoids of 30% probability are shown.

Table 4. Geometry of hydrogen bonds in structures **I** and **II**

N–H⋯B bond	Distance, Å			NHB angle, deg
	H⋯B	N⋯B	N–H	
I				
N(11)–H(11)⋯Cl(1)	2.63	3.48(1)	0.86	168
N(21)–H(21)⋯Cl(4)	2.57	3.419(9)	0.86	172
N(41)–H(41)⋯Cl(2)	2.68	3.54(1)	0.86	171
N(51)–H(51)⋯Cl(1)	2.51	3.37(1)	0.86	174
N(61)–H(61)⋯Cl(3)	2.51	3.36(1)	0.86	171
N(12)–H(12B)⋯Cl(2)	2.56	3.41(1)	0.86	171
N(22)–H(22A)⋯S(3)[a]	2.75	3.569(9)	0.86	160
N(22)–H(22B)⋯Cl(2)	2.47	3.32(1)	0.86	170
N(32)–H(32A)⋯Cl(4)[b]	2.65	3.397(9)	0.86	146
N(32)–H(32B)⋯Cl(1)	2.58	3.407(9)	0.86	161
N(42)–H(42A)⋯Cl(3)[c]	2.49	3.25(1)	0.86	148
N(42)–H(42B)⋯Cl(3)	2.44	3.28(1)	0.86	169
N(52)–H(52A)⋯Cl(1)[d]	2.68	3.40(1)	0.86	143
N(52)–H(52B)⋯Cl(4)	2.60	3.43(1)	0.86	164
N(62)–H(62A)⋯Cl(2)[e]	2.47	3.281(9)	0.86	158
N(62)–H(62B)⋯Cl(4)	2.59	3.45(1)	0.86	172
II				
N(1)–H(1)⋯X(2)	2.51	3.305(6)	0.86	155
N(2)–H(2)⋯X(3)[f]	2.67	3.250(6)	0.86	126

Note: Symmetry operations: [a] $x - 1/2, y + 1/2, z$; [b] $x, y - 1, z$; [c] $-x + 3/2, -y + 1/2, -z + 1$; [d] $-x + 3/2, y + 1/2, -z + 3/2$; [e] $x + 1/2, y + 1/2, z$; [f] $-x, -y + 1, -z + 1$.

pyramidal environment of both copper atoms is formed by two halogen atoms and the C=C bond in the equatorial plane and one halogen atom in the apical position (Fig. 1b). The extension of the metal atom from the equatorial plane correlates with the removal of the axial ligand; its value is 0.158 Å for Cu(1) and 0.323 Å for Cu(2). It is noteworthy that the τ angle formed by the plane of the equatorial ligands and the C=C bond also decreases from 18.3° for Cu(1) to 12.5° for Cu(2). The C=C bond lengths are 1.32(1) and 1.35(1) Å, respectively.

The $Cu_2X_3^-$ anions in structure **II** play the role of inorganic fragments; through the pairs of elongated Cu–X contacts, they are united in chains oriented along the [110] direction. These chains are jointed by bridging (through the C=C bonds) DAEITU species, showing high conformational flexibility, into the (001) layers (Fig. 2). In three-dimensional structure **II**, the individual [(DAEITU)Cu₂X₃]ₙ chains are linked by hydrogen bonds of the N–H⋯X type (Table 4). Interestingly, the random occupation of the X positions with Cl and Br atoms (see the note to Table 2) depends on their struc-

tural functions. The X(2) and X(3) halogen atoms forming dimeric Cu₂X₂ fragments undergo electrostatic repulsion from the nearby X' atom fixed by the center of symmetry. This seems to be responsible for the smaller number of larger Br atoms in these positions. Similar behavior is found in the structure of the copper(I) π-complex with *N*,*N*'-diallylguanidine ligand [(CH₂=CH–CH₂–NH)₂CNH₂]Cu₂Cl₃₋ₓBrₓ ($x = 1.36$) [11] built from the $(Cu_2X_3)_2^{2-}$ centrosymmetric dimers; the fraction of the bromine atoms in the position of a halogen atom forming the Cu₂X₂ fragment is twice as small as in the two other positions. Structure **II** is quite similar to the structure of the previously studied π-complex of diallylammonium [H⁺L]Cu₂Cl₃ [12]. However, the bridging cations of the π-ligand in the latter complex unite similar inorganic fragments in a somewhat different manner than in **II**, but still show a noticeable conformational flexibility.

Structures **I** and **II** demonstrate coordination capacities of the allyl derivatives of thiourea and isothiouronium salts that agree well with the aforementioned series of ligand capacity to coordinate copper(I) [1].
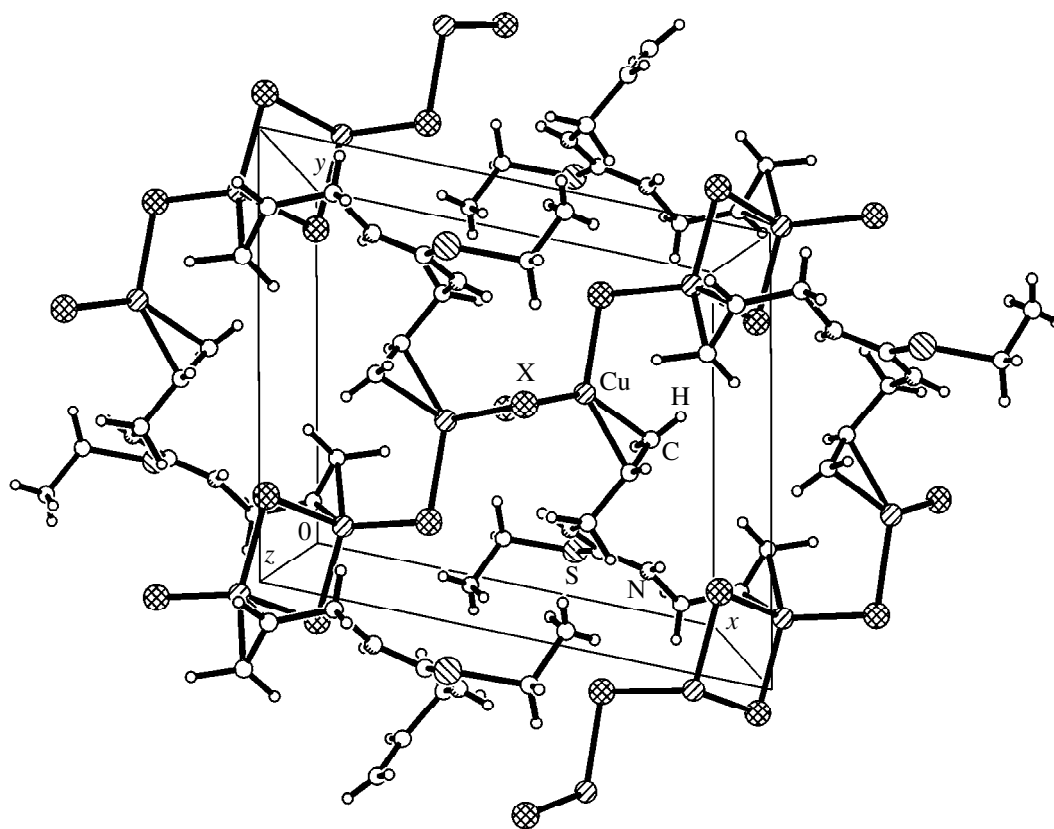
Fig. 2. Organometallic layers in the (001) plane in structure **II**.

REFERENCES

1. Filinchuk, Ya.E., Oliinik, V.V., and Schollmeier, D., *Koord. Khim.*, 1999, vol. 25, no. 3, p. 226.

2. Oliinik, V.V., Goreshnik, E.A., Schollmeier, D., and Mys'kiv, M.G., *Koord. Khim.*, 1997, vol. 23, no. 7, p. 548.

3. Filinchuk, Ya.E., Schollmeier, D., Oliinik, V.V., *et al.*, *Koord. Khim.*, 1996, vol. 22, no. 11, p. 870.

4. Spofford, W.A. and Amma, E.L., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1970, vol. 26, no. 10, p. 1474.

5. Okaya, Y. and Knobler, C.B., *Acta Crystallogr.*, 1964, vol. 17, no. 7, p. 928.

6. Oliinik, V.V., Schollmeier, D., Filinchuk, Ya.E., and Mys'kiv, M.G., *Koord. Khim.,* 1998, vol. 24, no. 1, p. 52.

7. Weygand, C. and Hilgetag, G., *Organische-chemische Experimentierkunst*, Leipzig: J. A. Barth, 1970, 4th ed.

Translated under the title *Metody eksperimenta v organicheskoi khimii*, Moscow: Khimiya, 1968.

8. Aksel'rud, L.G., Grin', Yu.N., Zavalii, P.Yu., *et al.*, *Paket programm dlya strukturnogo analiza kristallov CSD. Obshchee opisanie* (Program Package for Structural Analysis of CSD Crystals. General Account), Lvov: Lvov. Gos. Univ., 1990.

9. Sheldrick, G.M., *SHELXL97: Program for the Refinement of Crystal Structures*, Germany: Univ. of Göttingen, 1997.

10. Pakawatchai, C., Thanyasirikul, Y., Saepae, T., *et al.*, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, vol. 54, no. 12, p. 1750.

11. Filinchuk, Ya.E. and Mys'kiv, M.G., *Koord. Khim.*, 1999, vol. 25, no. 5, p. 376.

12. Oliinik, V.V., Glovyak, T., and Mys'kiv, M.G., *Koord. Khim.*, 1999, vol. 25, no. 10, p. 790.