Copper(I) Chloride and Bromide π-Complexes with the *S*-Allylisothiouronium Ligand: Synthesis and Crystal Structure of $[CH_2{=}CH{-}CH_2{-}SC({=}NH_2)_2]^+CuX_2^-$

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Received January 15, 1997

Abstract—Crystals of compounds $[CH_2{=}CH{-}CH_2{-}SC({=}NH_2)_2]^+CuX_2^-$ [X = Cl⁻ (**I**), Br⁻ (**II**)] were prepared by ac electrochemical synthesis, and their crystal structure was determined. The crystals of isostructural compounds are triclinic, space group $P\bar{1}$, cell parameters: (**I**) $a = 6.6202(5)$, $b = 7.3399(7)$, $c = 9.1674(4)$ Å, $\alpha = 80.194(6)°$, $\beta = 80.999(5)°$, $\gamma = 89.722(7)°$, $V = 433.4(1)$ Å; (**II**) $a = 6.9425(9)$, $b = 7.528(3)$, $c = 9.281(2)$ Å, $\alpha = 79.24(2)°$, $\beta = 80.78(2)°$, $\gamma = 87.00(3)°$, $V = 470.2(1)$ Å³; $Z = 2$ for the indicated composition. In both structures, the *S*-allylisothiouronium (AITU) ligand is coordinated to the copper atom only through the C=C bond, whose length is 1.357(6) (**I**) and 1.362(9) Å (**II**). The behavior of AITU in structures (**I**) and (**II**) is quite similar to the behavior of the allylammonium cation in the previously studied π-complexes of $[C_3H_5NH_3]^+CuX_2^-$ (X = Cl⁻, Br⁻).

Our earlier investigation of the π-complexation of *N*-allylthiourea (ATU) with copper(I) showed that, being a strong σ-donor, the sulfur atom of the ATU molecule usually hinders the Cu(I)–(C=C) π-interaction. Because of this, $[Cu(ATU)(CH_3CN)]NO_3$ is so far the only synthesized ATU π,σ-complex with copper(I) salts [1]. To continue our investigation into the Cu(I) π-complexation with the sulfur-containing olefin ligands, we prepared derivatives of isothiourea, namely, *S*-allylisothiouronium salts $[CH_2{=}CH{-}CH_2{-}SC({=}NH_2)_2]^+X^-$ (X = Cl⁻ or Br⁻), synthesized π-complexes having the composition $[CH_2{=}CH{-}CH_2{-}SC({=}NH_2)_2]^+CuX_2^-$ [X = Cl (**I**)or Br (**II**)], and determined their crystal structure.

EXPERIMENTAL

S-allylisothiouronium (AITU) chloride and bromide were synthesized starting from thiourea and allyl chloride or bromide, as described in [2]. Crystals of the $[CH_2{=}CH{-}CH_2{-}SC({=}NH_2)_2]CuX_2$ complexes were prepared as well-edged colorless prisms by the ac electrochemical reduction Cu(II) ⟶ Cu(I) at copper electrodes in an ethanol solution of $CuCl_2 \cdot 2H_2O$ or $CuBr_2$ and corresponding AITU halide. Crystals of compounds **I** and **II**, which are rather stable in air, grew for 48 hours.

To solve the structure, the arrays of diffraction data were collected on a CAD-4 single-crystal diffractometer. The reflection intensities were corrected for Lorentz, polarization, and absorption effects.

The structures were solved by the direct methods using the CSD software package [3]. The parameters of non-hydrogen atoms were refined by the least-squares method in an anisotropic approximation, and the parameters of hydrogen atoms were found from the difference Fourier syntheses in an isotropic approximation.

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

Parameter	**I**	**II**
M, au.	251.5	340.4
$F(000)$	256	328
a, Å	6.6202(5)	6.9425(9)
b, Å	7.3399(7)	7.528(3)
c, Å	9.1674(4)	9.281(2)
α, deg	80.194(6)	79.24(2)
β, deg	80.999(5)	80.78(2)
γ, deg	89.722(7)	87.00(3)
V, Å³	433.4(1)	470.2(1)
Z	2	2
Space group	$P\bar{1}$	$P\bar{1}$
ρ(meas), g/cm³	1.92(2)	2.38(2)
ρ(calcd), g/cm³	1.926(1)	2.403(2)
μ_{Mo}, cm⁻¹	108.6	115.5
Scan type	ω/2θ	ω/2θ
Radiation	CuK_α	MoK_α
$2\theta_{max}$, deg	149.8	60
N_{hkl} ($F_o \geq 4\sigma F_o$)	1907	2001
R, R_w	0.044, 0.046	0.045, 0.037

Table 2. Coordinates of atoms and their thermal parameters* in structures **I** and **II****

Atom		x	y	z	B, Å^2
Cu		0.46370(8)	0.22376(8)	0.42148(6)	2.38(2)
		0.4584(1)	0.2238(1)	0.42584(8)	2.90(2)
X(1)		0.6737(1)	0.1074(1)	0.5942(1)	2.40(2)
		0.6809(1)	0.1015(1)	0.60139(7)	2.66(2)
X(2)		0.6354(1)	0.3015(1)	0.1830(1)	2.54(2)
		0.6294(1)	0.3149(1)	0.17787(7)	2.90(2)
S		0.0102(1)	0.2181(1)	0.8548(1)	2.36(2)
		0.0161(2)	0.2182(3)	0.8553(2)	2.80(5)
N(1)		0.3946(5)	0.2028(5)	0.9183(4)	2.65(9)
		0.3812(8)	0.1918(8)	0.9251(7)	3.1(2)
N(2)		0.1435(6)	0.2865(6)	0.0922(4)	3.24(9)
		0.1325(9)	0.2800(9)	0.0942(6)	3.6(2)
C(1)		0.1929(6)	0.3758(6)	0.4410(5)	2.76(9)
		0.1944(9)	0.3804(9)	0.4465(7)	3.1(2)
C(2)		0.2474(5)	0.3210(5)	0.5782(4)	2.03(8)
		0.2459(9)	0.3229(9)	0.5835(6)	2.3(2)
C(3)		0.1518(5)	0.1549(5)	0.6853(4)	1.89(8)
		0.1562(8)	0.1575(9)	0.6879(6)	2.4(2)
C(4)		0.2017(6)	0.2363(5)	0.9611(4)	2.25(9)
		0.1941(9)	0.2310(9)	0.9639(7)	2.7(2)
H(1)		0.443(7)	0.173(7)	0.839(6)	3(1)
		0.430(13)	0.181(12)	0.840(9)	6(3)
H(2)		0.453(8)	0.216(8)	0.980(7)	4(1)
		0.477(10)	0.219(9)	0.977(7)	4(2)
H(3)		0.032(7)	0.319(6)	0.110(5)	3(1)
		−0.016(10)	0.326(10)	0.132(7)	6(2)
H(4)		0.224(8)	0.268(7)	0.162(6)	4(1)
		0.201(9)	0.289(9)	0.146(6)	3(2)
H(1.1)		0.087(9)	0.304(8)	0.397(7)	6(2)
		0.105(7)	0.302(7)	0.422(5)	2(1)
H(1.2)		0.227(9)	0.490(8)	0.364(7)	5(1)
		0.236(8)	0.499(8)	0.395(5)	2(1)
H(2.1)		0.311(6)	0.386(6)	0.609(5)	2(1)
		0.328(7)	0.406(7)	0.618(5)	2(1)
H(3.1)		0.064(6)	0.101(6)	0.650(6)	2(1)
		0.044(8)	0.106(8)	0.627(6)	4(1)
H(3.2)		0.229(6)	0.056(5)	0.716(5)	2(1)
		0.252(7)	0.071(7)	0.708(5)	2(1)

* For non-hydrogen atoms $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$, for H atoms, B_{iso}.

** Parameters in the upper and lower rows correspond to complexes **I** and **II**, respectively.

The crystal data and details of data collection are presented in Table 1; the coordinates of atoms and their thermal parameters are presented in Table 2.

RESULTS AND DISCUSSION

Unlike the neutral ATU molecule, the sulfur atom in the AITU ligand [cationic form [CH$_2$=CH–CH$_2$–S–C$^+$(=NH$_2$)$_2$] should not exhibit tangible σ-donating properties with respect to Cu(I). Indeed, AITU in the structures of isomorphous compounds **I** and **II** is coordinated to the copper atom only through the C=C bond. The trigonal-pyramidal coordination of the metal atom is completed by the three halogen atoms (Fig. 1). The Cu(I)–(C=C) interaction contributes to the extension of the multiple C=C bond, whose length is 1.357(6) Å in **I** and 1.362(9) Å in **II** (Table 3).

Table 3. Bond lengths and angles and torsion angles in structures **I** and **II**

Bond*	d, Å		Angle*	ω, deg	
	I	**II**		**I**	**II**
Cu–X(1)	2.320(1)	2.447(2)	X(1)CuX(1)'	92.99(4)	96.99(8)
Cu–X(1)'	2.634(1)	2.748(3)	X(1)CuX(2)	113.28(5)	111.98(9)
Cu–X(2)	2.281(1)	2.408(2)	X(1)'CuX(2)	99.06(4)	99.61(8)
Cu–C(1)	2.107(4)	2.128(7)	X(1)Cum(12)	113.4(1)	114.2(2)
Cu–C(2)	2.078(4)	2.115(7)	X(1)'Cum(12)	104.4(1)	103.5(2)
Cu–m(12)	1.979(4)	2.009(7)	X(2)Cum(12)	125.8(1)	124.6(2)
			C(1)CuC(2)	37.8(2)	37.5(3)
C(1)–C(2)	1.357(6)	1.362(9)	C(2)C(1)H(1.1)	124(3)	113(3)
C(1)–H(1.1)	1.04(6)	0.96(5)	C(2)C(1)H(1.2)	132(3)	117(3)
C(1)–H(1.2)	1.00(6)	0.96(6)	H(1.1)C(1)H(1.2)	104(5)	129(4)
C(2)–C(3)	1.502(5)	1.521(9)	C(1)C(2)C(3)	122.6(4)	121.9(6)
C(2)–H(2.1)	0.75(4)	1.00(5)	C(1)C(2)H(2.1)	119(3)	116(3)
			C(3)C(2)H(2.1)	117(3)	121(3)
C(3)–H(3.1)	0.84(4)	1.15(6)	SC(3)C(2)	111.8(3)	111.3(5)
C(3)–H(3.2)	0.92(4)	0.92(5)	SC(3)H(3.1)	104(3)	106(3)
			SC(3)H(3.2)	106(3)	110(3)
			C(2)C(3)H(3.1)	112(3)	106(3)
			C(2)C(3)H(3.2)	121(3)	110(3)
			H(3.1)C(3)H(3.2)	100(4)	111(4)
S–C(3)	1.814(4)	1.818(7)	C(3)SC(4)	102.3(2)	102.8(3)
S–C(4)	1.735(4)	1.733(7)			
C(4)–N(1)	1.311(5)	1.324(9)	SC(4)N(1)	124.0(3)	123.8(5)
C(4)–N(2)	1.316(5)	1.328(9)	SC(4)N(2)	116.0(5)	116.0(5)
			N(1)C(4)N(2)	120.0(4)	120.2(6)
N(1)–H(1)	0.81(5)	0.82(8)	C(4)N(1)H(1)	126(4)	123(6)
N(1)–H(2)	0.75(6)	0.94(7)	C(4)N(1)H(2)	108(4)	122(4)
			H(1)N(1)H(2)	126(6)	111(8)
N(2)–H(3)	0.77(4)	1.09(7)	C(4)N(2)H(3)	118(3)	126(4)
N(2)–H(4)	0.89(5)	0.74(7)	C(4)N(2)H(4)	120(4)	122(5)
			H(3)N(2)H(4)	122(5)	113(6)

Torsion angles

Angle	φ, deg		Angle	φ, deg	
	I	**II**		**I**	**II**
X(1)'CuX(1)Cu'	0.0	0.0	C(1)C(2)C(3)S	115.7	116.0
X(2)CuX(1)Cu'	101.2	103.3	C(3)SC(4)N(1)	1.9	3.5
X(2)CuX(1)'Cu'	114.1	113.8	C(3)SC(4)N(2)	178.3	177.9
CuC(1)C(2)C(3)	99.1	98.2			

* m(12) is the middle of a multiple C(1)–C(2) bond.

The structure is composed of the centrosymmetric dimers Cu₂X₄(AITU)₂, which are formed owing to the elongated Cu···X contacts [2.634(1) in **I** and 2.748(3) Å in **II**]. The π-complex [C₃H₅NH₃]⁺CuCl₂⁻ of copper(I) chloride with allylammonium is constructed in a similar manner (Fig. 2). As in the case of allylammonium, the proton-blocked AITU⁺ cation is prevented from coordinating to Cu(I) through the sulfur atom. How-
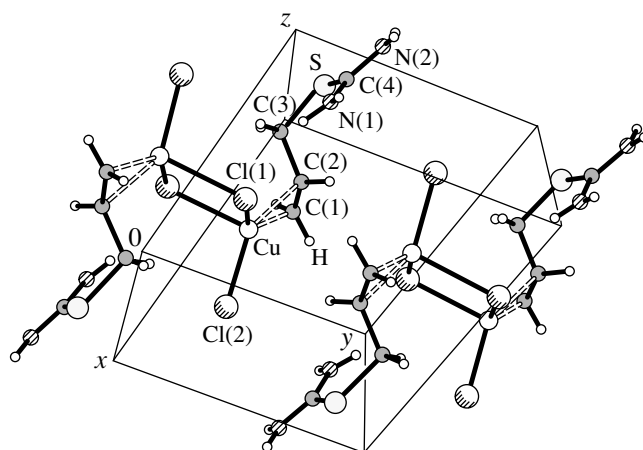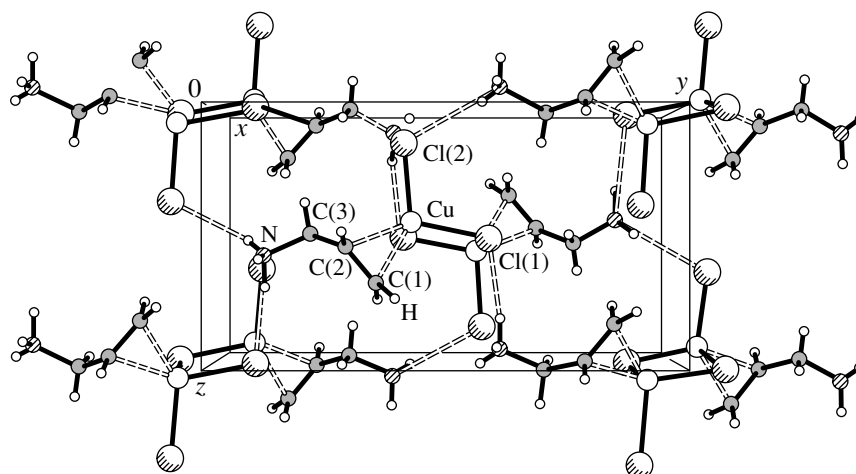
Fig. 1. Structure of complex **I**.

Fig. 2. Structure of the $[C_3H_5NH_3]^+CuCl_2^-$ complex.

ever, the H-bonds between the hydrogen atoms of the amido groups and the halogen atoms of the $Cu_2X_4^{2-}$ fragment stabilize the structure. The N–H...X contacts rather firmly fix the position of the terminal thiouronium group of the AITU ligand, as is also evidenced by the low values of thermal parameters of the light atoms. For this reason, the corresponding conformational parameters of the ligands in **I** and **II** virtually coincide. Weak C–H···X contacts also occur. Contrary to the compounds with ATU [1], sulfur almost does not contact hydrogen atoms in the structures under consideration.

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

A–H···B bond*	H···B, distance, Å		AHB angle, deg	
	I	**II**	**I**	**II**
N(1)–H(1)···X(1)	2.63(5)	2.73(8)	168(5)	163(8)
N(1)–H(2)···X(2)'	2.54(6)	2.51(7)	173(6)	160(6)
N(2)–H(3)···X(2)'	2.61(4)	2.43(7)	160(4)	157(5)
N(2)–H(4)···X(2)	2.78(5)	3.05(6)	140(4)	145(6)
C(3)–H(3.1)···X(1)	2.71(6)	2.58(6)	145(4)	145(4)
C(3)–H(3.2)···X(2)'	2.82(4)	3.02(5)	164(3)	150(4)

The geometry of the most important H-bonds is presented in Table 4.

Hence, the sulfur atom loses its σ-donating properties in the cationic form of the ATU isomer, i.e., S-allylthiourea, although the positive charge in AITU$^+$ is delocalized among the atoms of the thiouronium group. By contrast, diallyl sulfide (DAS), which is formally similar to AITU, is capable of forming π, σ-complexes with d^{10}-metals, e.g., $2AgNO_3 \cdot DAS$ [4]. The atomic charge calculations carried out with the HYPERCHEM program using a modified version of the SCF LCAO MO iteration method in the INDO approximation [5] have shown that the charge on the sulfur atom in ATU, DAS, and AITU is equal to –0.64, –0.42, and +0.01 $\bar{e}$, respectively. These data confirm the observed lowering of the σ-donating ability of sulfur with respect to copper(I) in the complexes studied.

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