Copper(I) π-Complexes with Allyl Derivatives of Guanidine: Synthesis and Crystal Structure of the $[(CH_2=CH-CH_2-NH=)_3C]Cu_3Cl_{4-x}Br_x$ ($x = 1.23$) and $[(CH_2=CH-CH_2-NH=)_3C]Cu_3Br_4$ Compounds

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Abstract—Crystal compounds $[(CH_2=CH-CH_2-NH=)_3C]Cu_3Cl_{4-x}Br_x$ ($x = 1.23$) (**I**) and $[(CH_2=CH-CH_2-NH=)_3C]Cu_3Br_4$ (**II**) were prepared by ac electrochemical synthesis and structurally characterized [DARCh diffractometer, MoK_α radiation, 1258 (**I**) and 1488 (**II**) reflections with $F \geq 4\sigma(F)$, $R = 0.031$ and 0.037 for **I** and **II**, respectively]. The crystals of the isostructural compounds are trigonal, space group $R3$, $Z = 3$. Unit cell parameters are $a = 10.332(3)$, $c = 13.990(3)$ Å, $V = 1294(1)$ Å^3 for **I** and $a = 10.542(3)$, $c = 14.326(3)$ Å, $V = 1379(1)$ Å^3 for **II**. The trigonal-pyramidal coordination sphere of the copper atom involves three halogen atoms and a C=C bond in the equatorial plane. The inorganic $Cu_3X_4^-$ anions are positioned in axes 3 and combined with triallylguanidinium cations into layers by the Cu–(C=C) interactions. The length of the coordinated C=C bond is 1.35(1) Å in **I** and 1.34(1) Å in **II**. Net atomic charges are calculated for structure **I**.

Previous studies of the zwitterionic π-complexes of copper(I) halides with allyl- and diallylammonium salts have revealed that the behavior of a ligand depends on both the stoichiometry of the complex and the nature of halogen [1]. A variable number of allyl substituents in the protonated azomethine ligands (guanidinium and isothiouronium salts) allows the realization of different stoichiometries for zwitterionic π-complexes, thus enlarging the group of compounds of this type [2–4]. The guanidinium cation contains three nitrogen atoms and, hence, is of interest in the context of the stabilization of positive charge in the ionic copper(I) π-complexes, the more so as the azomethine derivatives are poorly studied as π-ligands [5]. For this purpose, the copper(I) halide π-complexes with a *sym*-triallylguanidinium ligand, $[(CH_2=CH-CH_2-NH=)_3C]Cu_3Cl_{4-x}Br_x$ ($x = 1.23$) (**I**) and $[(CH_2=CH-CH_2-NH=)_3C]Cu_3Br_4$ (**II**), were synthesized and their crystal structures were studied.

EXPERIMENTAL

sym-Triallylguanidinium bromide was synthesized from *N,N'*-diallyl-*S*-ehtylisothiouronium (preliminary prepared from *N,N'*-diallylthiourea and ethyl bromide according to [6]) and allylamine by the modified method [7]. High-quality single crystals of **I** and **II** were synthesized by ac ($U = 0.3$ V) electrochemical reduction of Cu(II) to Cu(I) on copper electrodes in ethanol solutions containing triallylguanidine and CuCl$_2 \cdot$ 2H$_2$O or CuBr$_2$, respectively. Air-stable crystals of compounds **I** and **II** grew as distorted planar ditrigonal prisms in a week.

After the preliminary photographic study, the structures were solved using the arrays of diffraction data collected on a DARCh single-crystal diffractometer (MoK_α radiation); intensities of reflections were corrected for the Lorentz and polarization effects.

Crystallographic data and data collection parameters are given in Table 1.

The structures were solved by direct methods; light and H atoms were located from difference Fourier syntheses. The non-hydrogen atoms were refined by the full-matrix anisotropic method (isotropic for hydrogen atoms) for all measured reflections (including nonunique) with $F \geq 4\sigma(F)$. All calculations and absorption correction (DIFABS program) were performed using the CSD program package [8].

Atomic coordinates and thermal parameters for structures **I** and **II** are given in Table 2, and bond lengths, bond angles, and torsion angles are listed in Table 3.

RESULTS AND DISCUSSION

Compounds **I** and **II** are isostructural. The nitrogen atoms in the triallylguanidinium (TAGUH$^+$) cation do not exhibit σ-donating properties. Consequently, the trigonal-pyramidal coordination sphere of copper is formed from three halogen atoms and the C=C bond in

Table 1. Crystal data and data collection parameters for **I** and **II**

Parameter	**I**	**II**
M	567.4	690.5
Crystal size, mm	$0.4 \times 0.3 \times 0.25$	$0.5 \times 0.4 \times 0.2$
$F(000)$	828	978
Space group	$R3$	$R3$
a, Å	10.332(3)	10.542(3)
c, Å	13.990(3)	14.326(3)
V, Å^3	1294(1)	1379(1)
Z	3	3
ρ(exp), g/cm^3	2.15	2.45
ρ(calcd), g/cm^3	2.185(2)	2.495(2)
μ_{Mo}, cm^{-1}	72.27	127.64
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Number of reflections:		
measured	1324	1567
used with $F \geq 4\sigma(F)$	1258	1488
unique with $F \geq 4\sigma(F)$	486	512
$2\theta_{max}$, deg	55	55
Number of refined parameters	87	85
R/R_w	0.031/0.031	0.037/0.038
R/R_w^*	0.030/0.031	0.033/0.033
Weight scheme	$[\sigma(F_o)^2 + 0.0005 F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0011 F_o^2]^{-1}$
GOOF	1.09	1.01

* From unique reflections.

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

Atom	x	y	z	B, Å^2
Cu	0.19806(9)	0.04001(9)	0.1447(1)	3.50(3)
	0.1903(1)	0.0299(1)	0.1381(1)	4.35(4)
X(1)***	0	0	0.00	3.54(4)
Br(1)	0	0	0.00	4.32(4)
X(2)***	0.1811(2)	0.2237(1)	0.2292(1)	3.07(6)
Br(2)	0.19234(9)	0.22693(9)	0.2274(1)	3.51(3)
N	0.3133(6)	−0.2161(6)	0.1494(5)	3.2(2)
	0.3105(7)	−0.2198(7)	0.1418(6)	4.0(3)
C(1)	0.4074(9)	0.1616(9)	0.0833(7)	4.0(3)
	0.400(1)	0.149(1)	0.0770(6)	4.6(4)
C(2)	0.3648(7)	0.0157(7)	0.0730(5)	2.9(2)
	0.357(1)	0.007(1)	0.0687(6)	4.0(3)
C(3)	0.4257(7)	−0.0622(7)	0.1313(6)	3.0(2)
	0.4183(9)	−0.0681(9)	0.1263(5)	3.4(3)
C(4)	1/3	−1/3	0.1512(8)	2.8(2)
	1/3	−1/3	0.143(1)	3.5(3)
H(1.1)	0.463(6)	0.207(6)	0.119(4)	1(1)
	0.464(9)	0.22(1)	0.126(6)	3(2)
H(1.2)	0.38(1)	0.21(1)	0.034(6)	5(2)
	0.387(9)	0.21(1)	0.037(6)	5(2)
H(2.1)	0.319(6)	−0.027(7)	0.030(4)	2(1)
	0.32(1)	−0.03(1)	0.025(8)	3(3)
H(3.1)	0.467(8)	−0.016(9)	0.192(6)	5(2)
	0.472(9)	−0.021(9)	0.185(7)	3(2)
H(3.2)	0.475(7)	−0.070(7)	0.092(5)	3(2)
	0.47(1)	−0.08(1)	0.092(6)	2(2)
H(N)	0.246(8)	−0.234(8)	0.166(5)	2(2)
	0.24(1)	−0.23(1)	0.151(6)	2(2)

* Atomic coordinates and thermal parameters in the upper row correspond to **I** and in the lower row, to **II**.

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

*** Occupancy factors $G(X_i)$ for the X(1,2) positions of Cl and Br atoms: X(1) = 0.04(1)Cl + 0.96(1)Br, X(2) = 0.910(7)Cl + 0.090(7)Br.

equatorial plane. The inorganic fragment is represented by the $Cu_3X_4^-$ anion positioned in axis 3. The X(1) atom occupies a special position and functions as an axial ligand common to three copper atoms, whereas the X(2) atom is coordinated to two copper atoms and is an equatorial ligand. Owing to steric factors, chlorine and bromine atoms in structure **I** are virtually orderly distributed over the corresponding positions: the larger-sized Br occupies an apical position, while Cl is positioned in the equatorial plane of the pyramid (cf. footnote to Table 2).

The displacement Δ of the copper atom from the plane of equatorial ligands (0.38 Å for **I** and 0.46 Å for **II**) correlates with the Cu–(axial ligand) distance [Cu–X(1) 2.759(3) Å in **I** and 2.721(4) Å in **II**] [9]. Despite the tangible Δ values, the angle τ the C=C bond forms with the plane of equatorial ligands is small (3.2° in **I**

and 0.7° in **II**). The shortening of the Cu–X(1) distance upon the substitution of bromine atoms for the equatorial chlorine atoms (structure **II**) is also noteworthy. The Cu(I) coordination core in **II** is closer to tetrahedron than in **I**, and the π-interaction is less effective [C(1)CuC(2) angle decreases from 37.6(3)° (**I**) to 36.8(4)° (**II**)]. The C=C bond is slightly elongated [to 1.35(1) Å in **I** and 1.34(1) Å in **II**].

Earlier, the analogous $Cu_3Cl_4^-$ anion was found in the monoclinic crystals of the copper(I) chloride π-complex with p-benzoquinone, $NH_4Cu_3Cl_4(C_6H_4O_2)_{1.5} \cdot$

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

Bond	d, Å		Angle	ω, deg	
	I	**II**		**I**	**II**
Cu–X(1)	2.759(3)	2.721(4)	X(1)CuX(2)	98.2(1)	99.9(1)
Cu–X(2)	2.316(4)	2.431(3)	X(1)CuX(2)'	97.4(1)	99.6(1)
Cu–X(2)'	2.352(3)	2.445(3)	X(1)Cu*m*(1,2)	104.7(3)	105.6(3)
Cu–C(1)	2.07(1)	2.11(1)	X(2)CuX(2)'	104.2(1)	104.9(1)
Cu–C(2)	2.115(9)	2.14(1)	X(2)Cu*m*(1,2)	119.9(3)	116.3(3)
Cu–*m*(1,2)**	1.98(1)	2.02(1)	X(2)'Cu*m*(1,2)	126.2(3)	126.1(3)
			C(1)CuC(2)	37.6(3)	36.8(4)
X(1)–Cu'	2.759(3)	2.721(3)	CuX(1)Cu'	72.09(8)	73.00(9)
X(1)–Cu"	2.759(3)	2.721(3)	CuX(1)Cu"	72.09(8)	73.00(9)
			Cu'X(1)Cu"	72.09(8)	73.00(9)
			CuX(2)Cu'	88.1(1)	83.2(1)
C(1)–C(2)	1.35(1)	1.34(1)	C(2)C(1)H(1.1)	120(5)	127(6)
C(1)–H(1.1)	0.73(6)	1.0(1)	C(2)C(1)H(1.2)	120(6)	128(6)
C(1)–H(1.2)	1.0(1)	0.9(1)	H(1.1)C(1)H(1.2)	119(8)	105(9)
C(2)–C(3)	1.49(1)	1.49(1)	C(1)C(2)C(3)	123.7(8)	123.4(9)
C(2)–H(2.1)	0.76(6)	0.7(1)	C(1)C(2)H(2.1)	119(5)	117(9)
			C(3)C(2)H(2.1)	116(5)	118(9)
C(3)–N	1.447(9)	1.44(1)	C(2)C(3)N	111.5(7)	111.2(8)
C(3)–H(3.1)	0.97(8)	1.00(9)	C(2)C(3)H(3.1)	114(5)	120(6)
C(3)–H(3.2)	0.78(8)	0.8(1)	C(2)C(3)H(3.2)	99(5)	104(7)
			NC(3)H(3.1)	108(5)	111(6)
			NC(3)H(3.2)	102(6)	100(7)
			H(3.1)C(3)H(3.2)	122(8)	110(9)
N–C(4)	1.327(7)	1.334(8)	C(3)NC(4)	126.9(7)	126.9(8)
N–H(N)	0.66(9)	0.7(1)	C(3)NH(N)	122(7)	116(9)
			C(4)NH(N)	111(7)	118(9)
C(4)–N'	1.327(7)	1.334(8)	NC(4)N'	120	120
C(4)–N"	1.327(7)	1.334(8)	NC(4)N"	120	120
			N'C(4)N"	120	120
			Hydrogen bonds		
H(3.2)···X(2)	2.83(7)	2.94(9)	C(3)H(3.2)···X(2)	147(7)	144(9)
C(3)···X(2)	3.768(9)	3.86(1)			
H(N)···X(2)	2.58(9)	2.7(1)	NH(N)···X(2)	155(8)	158(10)
N···X(2)	3.196(8)	3.300(9)			

Torsion angles

Angle	φ, deg		Angle	φ, deg	
	I	**II**		**I**	**II**
X(2)CuX(1)Cu'	−14.6	−15.2	CuC(1)C(2)C(3)	−104.7	−105.9
X(2)'CuX(1)Cu'	91.0	92.0	C(1)C(2)C(3)N	−145.7	−148.9
X(1)CuX(2)Cu'	16.5	16.3	C(2)C(3)NC(4)	141.8	141.4
X(2)'CuX(2)Cu'	−83.5	−86.6	C(3)NC(4)N'	166.3	168.2

 * In structure **I**, the X atom corresponds to the ratios of Cl and Br given in Table 2; in structure **II**, it corresponds to the Br atom.
** *m*(1,2) is the midpoint of the multiple C(1)=C(2) bond.
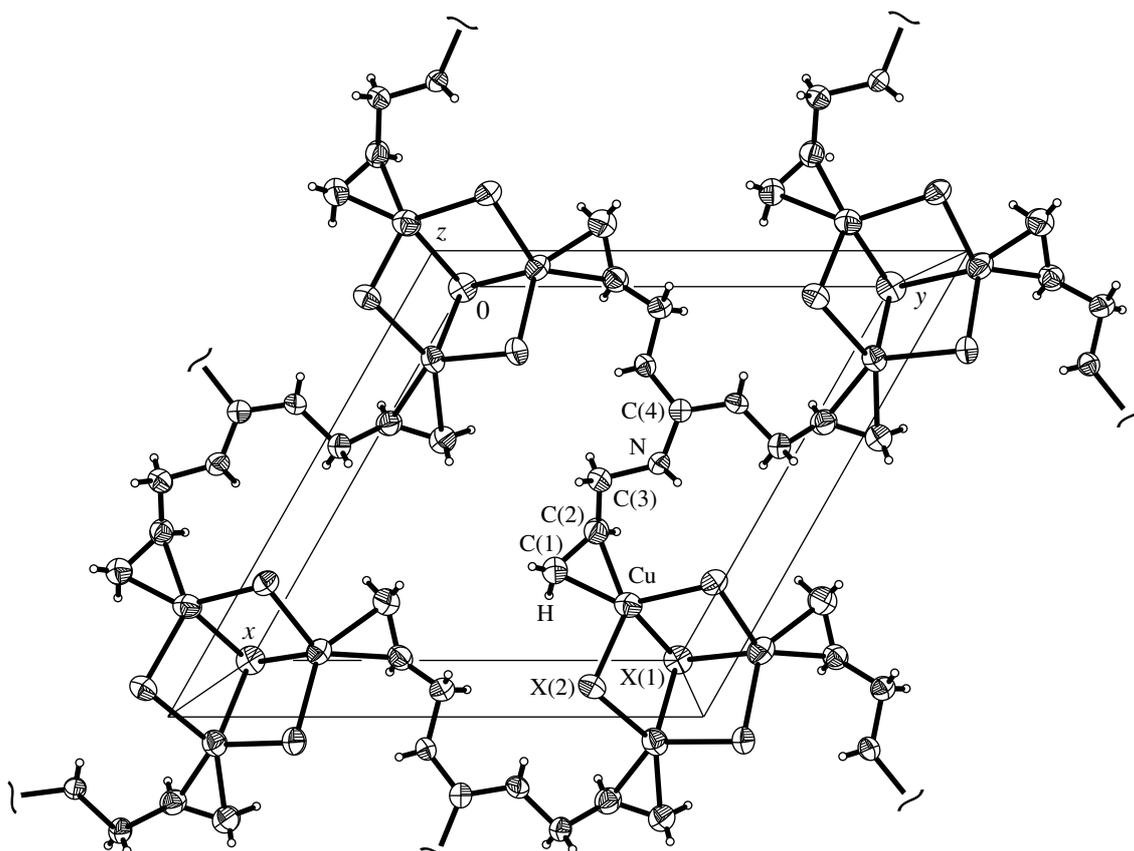
The fragment of structure **I** (one layer is shown).

H_2O [Cu–(axial ligand) distances range from 2.491(1) to 2.520(1) Å] [10].

The TAGUH$^+$ cation is positioned in axis 3. It functions as a tridentate π-ligand and combines the inorganic cations into layers arranged in the (001) plane (figure). The cations, multiplied along the c period by axis 3_1 (3_2), are joined together by the C(3)–H(3.2)···X(2) hydrogen bonds (Table 3) and van der Waals forces.

To reveal how the positive charge is stabilized at the TAGUH$^+$ cation, atomic charges were calculated for π-complex **I** by the modified iterative SCF LCAO MO method in the INDO approximation (ZINDO/1) using the HYPERCHEM program [11]. In the calculations, the fraction of Br in $G(X_i)$ (Table 2) was ignored. Structure **I** was represented by a cluster composed of 304 atoms (904 initial AOs were used). The results of calculations are presented in Table 4. The net charge of $+0.03\bar{e}$ found for the copper atom is typical of the copper chloride π-complexes (because of the Cl–Cu p–d_π interaction) [12]. The significant negative charges on the nitrogen ($-0.26\bar{e}$) and chlorine X(2) ($-0.42\bar{e}$) atoms are due to polarization induced by the N–H(N)···X(2) hydrogen bond (Table 3). A somewhat overstated negative charge was obtained for the X(1)

atom ($-0.58\bar{e}$), because a significant fraction of Br in $G(X(1))$ was ignored, while the Cu–X(1) bond length was not varied. The positive charge of the TAGUH$^+$ cation is distributed over the three H(N) atoms ($+0.24\bar{e}$) and the C(4) atom ($+0.47\bar{e}$).

Let us briefly discuss the structure-forming role of the TAGUH$^+$ cation in **I** and **II**. The hitherto studied structures of the copper(I) halide π-complexes with *N*-allylguanidinium, *N,N'*-diallylguanidinium, and *S*-allylisothiouronium salts are, as a rule, low-symmetry compounds [2–4]. Since the stoichiometry of these complexes is determined by the number of allyl groups in the ligand, the metal : ligand ratio in the case of the TAGUH$^+$ cation is 3 : 1. The trigonal symmetry of the

Table 4. Atomic charges in structure **I**

Atom	$q, \bar{e}$	Atom	$q, \bar{e}$	Atom	$q, \bar{e}$
Cu	+0.03	C(2)	+0.04	H(2.1)	+0.10
X(1)	−0.58	C(3)	+0.01	H(3.1)	+0.08
X(2)	−0.42	C(4)	+0.47	H(3.2)	+0.11
N	−0.26	H(1.1)	+0.11	H(N)	+0.24
C(1)	−0.10	H(1.2)	+0.10		

ligand and the possibility of the same symmetry being realized for the inorganic $Cu_3X_4^-$ anion favor the formation of the trigonal unit cells in **I** and **II**.

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