

Copper(I) π -Complexes with Allyl Derivatives of Guanidine. Synthesis and Crystal Structure of $[(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}=\text{C}=\text{NH}_2)_2\text{C}=\text{NH}_2]\text{Cu}_2\text{Cl}_{3-x}\text{Br}_x$ ($x = 1.36$)

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Abstract—Ac electrochemical synthesis was used to prepare crystals of the $[(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}=\text{C}=\text{NH}_2)_2\text{C}=\text{NH}_2]\text{Cu}_2\text{Cl}_{3-x}\text{Br}_x$ ($x = 1.36$) compound (**I**), and its structure was determined [a DARC_h diffractometer, MoK_α radiation, $a = 9.694(3)$, $b = 8.754(2)$, $c = 7.971(3)$ Å, $\alpha = 100.27(2)^\circ$, $\beta = 95.39(3)^\circ$, $\gamma = 100.74(2)^\circ$, $V = 648.3(7)$ Å³, space group $P\bar{1}$, $Z = 2$, $R = 0.050$ for 1175 independent reflections with $F \geq 4\sigma(F)$]. The coordination sphere of one of the copper atoms is a distorted tetrahedron formed from three halogen atoms and the C=C bond, and that of the other copper atom is planar-trigonal and consists of two halogen atoms and the C=C bond. The lengths of the coordinated double bonds of both allyl groups are equal to 1.34(2) Å. Complex **I** is structurally similar to the previously studied π -complex of diallylammonium $[(\text{C}_3\text{H}_5)_2\text{NH}_2]\text{Cu}_2\text{Br}_3$.

INTRODUCTION

Previous studies on the π -complexation of diallylammonium salts with copper(I) halides have demonstrated that this cation can be coordinated to a metal atom in different ways, depending on the stoichiometry of the compound [1–4]. Hydrogen atoms of the protonated amino group form strong hydrogen bonds that additionally stabilize the structure. It was of interest to examine behavior of a guanidine ligand, because it contains three nitrogen atoms and, hence, is a more basic derivative than ammonia. Besides, investigation of the

coordination of protonated allyl-substituted guanidines in the copper(I) π -complexes is of interest, because the ionic copper(I) π -complexes with unsaturated derivatives of azomethines are poorly studied [5, 6]. For this purpose, the copper(I) π -complex $[(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}=\text{C}=\text{NH}_2)_2\text{C}=\text{NH}_2]\text{Cu}_2\text{Cl}_{3-x}\text{Br}_x$ ($x = 1.36$) (**I**) was synthesized and its crystal structure was studied.

EXPERIMENTAL

N,N-Diallylguanidinium bromide (DAGUNBr) was synthesized from *N*-allyl-*S*-ethylisothiuronium bro-

Table 1. Crystallographic data and data collection parameters for complex **I**

Parameter	I	Parameter	I
<i>M</i>	434.3	Radiation	MoK_α
<i>F</i> (000)	421	Diffractometer	DARC _h
Space group	$P\bar{1}$	Scan technique	$\theta/2\theta$
<i>a</i> , Å	9.694(3)	Number of reflections:	
<i>b</i> , Å	8.754(2)	measured	1348
<i>c</i> , Å	7.971(3)	independent with $F \geq 4\sigma(F)$	1175
α , deg	100.27(2)	$2\theta_{\text{max}}$, deg	49
β , deg	95.39(3)	Number of refined parameters	203
γ , deg	100.74(2)	<i>R</i>	0.050
<i>V</i> , Å ³	648.3(7)	<i>R_w</i>	0.054
<i>Z</i>	2	Weighed scheme	$[\sigma(F_o)^2 + 0.0022F_o^2]^{-1}$
ρ (calcd), g/cm ³	2.226(2)	GOOF	1.16
μ_{Mo} , cm ⁻¹	81.57		

Table 2. Atomic coordinates and thermal parameters* for structure **I**

Atom**	x	y	z	B, Å ²
Cu(1)	0.8990(2)	0.4878(2)	-0.1748(2)	3.76(5)
Cu(2)	0.4137(2)	0.7639(2)	0.3775(2)	4.42(5)
X(1)	0.8221(2)	0.2002(2)	-0.3269(2)	3.52(5)
X(2)	0.1536(2)	0.5143(2)	-0.1100(2)	3.18(7)
X(3)	0.5311(2)	0.2109(3)	-0.6715(2)	6.14(8)
N(1)	0.808(1)	0.831(1)	0.012(1)	3.7(3)
N(2)	0.740(1)	0.951(1)	0.265(1)	3.4(3)
N(3)	0.765(1)	0.086(1)	0.046(1)	3.9(3)
C(1)	0.876(2)	0.598(2)	-0.385(2)	4.3(4)
C(2)	0.800(1)	0.656(1)	-0.266(1)	3.1(3)
C(3)	0.845(2)	0.823(2)	-0.156(2)	3.7(4)
C(4)	0.771(1)	0.954(1)	0.107(1)	2.9(3)
C(5)	0.727(1)	0.812(1)	0.343(1)	3.2(4)
C(6)	0.590(1)	0.691(1)	0.279(2)	3.8(4)
C(7)	0.494(2)	0.701(2)	0.150(2)	4.1(4)
H(1.1)	0.970(9)	0.660(9)	-0.40(1)	1(2)
H(1.2)	0.83(1)	0.50(2)	-0.48(2)	5(4)
H(2.1)	0.70(1)	0.61(1)	-0.28(1)	3(2)
H(3.1)	0.80(1)	0.88(1)	-0.20(1)	2(3)
H(3.2)	0.93(1)	0.85(1)	-0.16(1)	2(2)
H(5.1)	0.746(9)	0.85(1)	0.46(1)	2(2)
H(5.2)	0.81(1)	0.77(1)	0.32(1)	4(3)
H(6.1)	0.58(1)	0.59(1)	0.32(1)	3(2)
H(7.1)	0.44(1)	0.63(1)	0.13(2)	4(3)
H(7.2)	0.507(8)	0.78(1)	0.08(1)	1(2)
H(1)	0.821(7)	0.781(8)	0.058(8)	1(1)
H(2)	0.670(8)	0.024(9)	0.299(9)	1(2)
H(3)	0.71(1)	0.14(1)	0.11(2)	5(3)
H(4)	0.76(2)	0.08(2)	-0.03(2)	11(5)

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

** Site occupancy factors $G(X_i)$: X(1) = 0.474(9)Cl + 0.526(9)Br, X(2) = 0.732(8)Cl + 0.268(8)Br, and X(3) = 0.43(1)Cl + 0.57(1)Br.

amide (derived from allylthiourea and ethyl bromide according to [7]) and allylamine by the modified method [8]. Complex **I** in the form of well-edged colorless triclinic prisms was obtained by an electrochemical reduction of Cu(II) to Cu(I) ($U = 0.3$ V, $I = 0.21$ mA) on the copper electrodes in an ethanol solution containing CuCl_2 and DAGUNBr. Air-stable crystals of compound **I** grew during 20 h and did not decompose during the X-ray experiment.

After a preliminary study by photography, the structure was solved using the diffraction data measured on a DARC single crystal diffractometer; the intensities of reflections were corrected for the Lorentz and polarization effects. The structure was solved by the direct methods, all light and H atoms being determined from

the difference Fourier syntheses. Full-matrix anisotropic refinement of all the non-hydrogen atoms (isotropic for hydrogen atoms) and absorption correction (DIFABS program) were performed using the CSD program package [9].

Crystallographic data and data collection parameters for structure **I** are summarized in Table 1. Atomic coordinates and thermal parameters are presented in Table 2. Interatomic distances and bond and torsion angles are listed in Table 3.

RESULTS AND DISCUSSION

The presence of a positive charge delocalized over the conjugated guanidine group reduces the donating

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

Bond**	d , Å	Angle**	ω , deg	Bond**	d , Å	Angle**	ω , deg
Cu(1)–X(1)	2.531(3)	X(1)Cu(1)X(2)	101.8(1)	N(1)–C(4)	1.33(1)	C(3)N(1)C(4)	126(1)
Cu(1)–X(2)	2.433(4)	X(1)Cu(1)X(2)'	104.0(1)	N(1)–H(1)	0.65(7)	C(3)N(1)H(1)	122(6)
Cu(1)–X(2)'	2.376(4)	X(1)Cu(1) m (1,2)	109.9(4)			C(4)N(1)H(1)	110(6)
Cu(1)–C(1)	2.09(1)	X(2)Cu(1)X(2)'	96.5(1)	C(4)–N(2)	1.32(1)	N(1)C(4)N(2)	122(1)
Cu(1)–C(2)	2.10(1)	X(2)Cu(1) m (1,2)	115.7(4)	C(4)–N(3)	1.35(1)	N(1)C(4)N(3)	121(1)
Cu(1)– m (1,2)	1.99(1)	X(2)Cu(1) m (1,2)	125.9(4)			N(2)C(4)N(3)	118(1)
		C(1)Cu(1)C(2)	37.4(5)	N(2)–C(5)	1.45(1)	C(4)N(2)C(5)	124(1)
Cu(2)–X(1)	2.373(4)	X(1)Cu(2)X(3)	107.3(1)	N(2)–H(2)	1.04(8)	C(4)N(2)H(2)	112(4)
Cu(2)–X(3)	2.316(4)	X(1)Cu(2) m (6,7)	130.3(5)			C(5)N(2)H(2)	115(4)
Cu(2)–C(6)	2.10(1)	X(3)Cu(2) m (6,7)	121.9(5)	N(3)–H(3)	0.9(1)	C(4)N(3)H(3)	108(8)
Cu(2)–C(7)	2.07(1)	C(6)Cu(2)C(7)	37.7(6)	N(3)–H(4)	0.6(2)	C(4)N(3)H(4)	118(10)
Cu(2)– m (6,7)	1.97(2)					H(3)N(3)H(4)	120(10)
C(1)–C(2)	1.34(2)	C(2)C(1)H(1.1)	122(5)	C(5)–C(6)	1.52(2)	N(2)C(5)C(6)	114(1)
C(1)–H(1.1)	1.01(9)	C(2)C(1)H(1.2)	116(8)	C(5)–H(5.1)	0.96(9)	N(2)C(5)H(5.1)	106(5)
C(1)–H(1.2)	1.0(1)	H(1.1)C(1)H(1.2)	121(9)	C(5)–H(5.2)	1.0(1)	N(2)C(5)H(5.2)	104(7)
C(2)–C(3)	1.52(2)	C(1)C(2)C(3)	123(1)			C(6)C(5)H(5.1)	116(5)
C(2)–H(2,1)	0.9(1)	C(1)C(2)H(2.1)	120(6)			C(6)C(5)H(5.2)	115(7)
		C(3)C(2)H(2.1)	114(6)			H(5.1)C(5)H(5.2)	100(9)
C(3)–N(1)	1.41(2)	C(2)C(3)N(1)	113(1)	C(6)–C(7)	1.34(2)	C(5)C(6)C(7)	124(1)
C(3)–H(3.1)	0.8(1)	C(2)C(3)H(3.1)	107(8)	C(6)–H(6.1)	1.0(1)	C(5)C(6)H(6.1)	118(6)
C(3)–H(3.2)	0.8(1)	C(2)C(3)H(3.2)	104(7)			C(7)C(6)H(6.1)	117(6)
		N(1)C(3)H(3.1)	105(8)	C(7)–H(7.1)	0.7(1)	C(6)C(7)H(7.1)	108(10)
		N(1)C(3)H(3.2)	115(7)	C(7)–H(7.2)	0.96(8)	C(6)C(7)H(7.2)	124(5)
		H(3.1)C(3)H(3.2)	113(10)			H(7.1)C(7)H(7.2)	127(10)
Angle		φ , deg	Angle	φ , deg	Angle	φ , deg	
X(2)Cu(1)X(2)Cu(1)'		0	Cu(1)C(1)C(2)C(3)	–106.7	C(7)C(6)C(5)N(2)	–6.4	
X(1)Cu(1)X(2)Cu(1)'		105.8	C(1)C(2)C(3)N(1)	–145.3	C(6)C(5)N(2)C(4)	–75.8	
X(2)Cu(1)X(1)Cu(2)		83.7	C(2)C(3)N(1)C(4)	146.4	C(5)N(2)C(4)N(1)	–7.8	
X(3)Cu(2)X(1)Cu(1)		113.1	C(3)N(1)C(4)N(3)	0.6	C(5)N(2)C(4)N(3)	–172.7	
			Cu(2)C(7)C(6)C(5)	–104.5	N(2)C(4)N(1)C(3)	178.9	

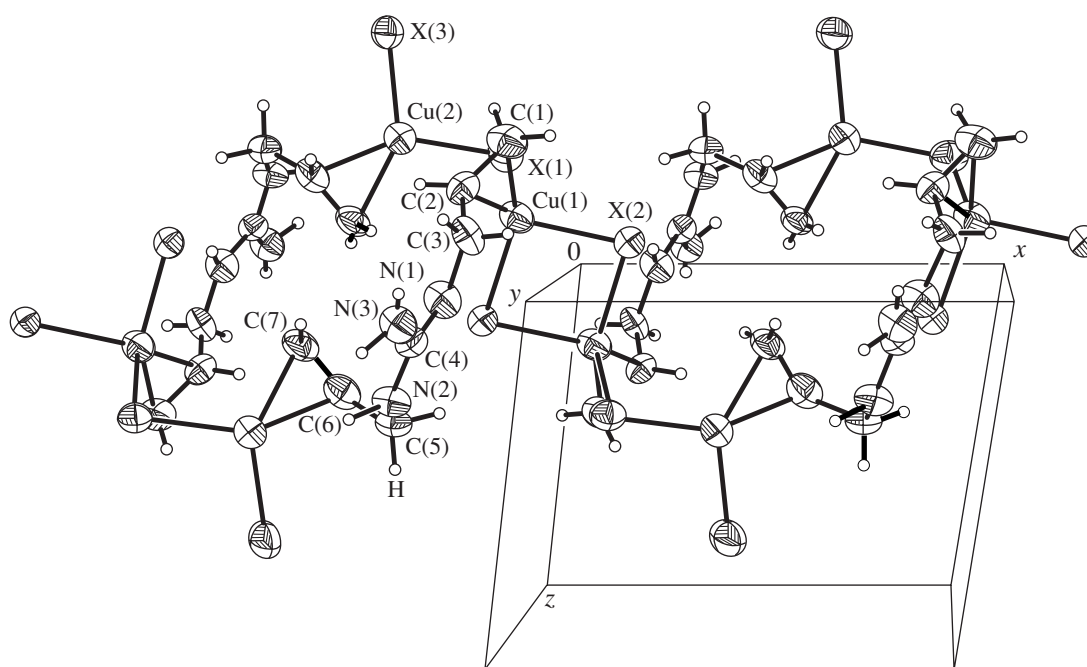
* The $G(X_i)$ values are presented in Table 2.

** $m(1,2)$ and $m(6,7)$ are midpoints of the multiple C(1)=C(2) and C(6)=C(7) bonds, respectively.

ability of the nitrogen atoms, thereby ruling out the Cu–N interaction. The coordination sphere of the copper atoms incorporates either three halogen (X) atoms and the C=C bond [distorted tetrahedral coordination of Cu(1)] or two halogen atoms and the C=C bond [planar-trigonal coordination of the Cu(2) atom]. The axially nearly undistorted coordination sphere of Cu(1) [Cu(1)–X(1) 2.531(3) Å] corresponds to a considerable displacement of the copper atom from the plane of equatorial ligands ($\Delta = 0.58$ Å) and a large angle between this plane and the C=C bond ($\tau = 31^\circ$). Complete removal of the axial ligand in the case of Cu(2) corresponds to the virtually planar coordination ($\Delta \approx 0$ Å) and equatorial orientation of the C=C bond ($\tau = 3.6^\circ$)

owing to the electronic factors. In both cases, the multiple C=C bond length is equal to 1.34(2) Å.

Structure **I** contains a centrosymmetric tetranuclear fragment $(\text{Cu}_2\text{X}_3)_2^{2-}$, in which the X(1) and X(2) atoms are bridging and the X(3) atom is terminal. Two independent Cu_2X_3^- parts of the adjacent dimers are linked together via the π -coordination of two DAGUN⁺ cations to form chains along [100] (see figure). Compound **I** is structurally similar to the complex of copper(I) bromide with diallylammonium (DAAH⁺) [(C₃H₅)₂NH₂]₂Cu₂Br₃ (**II**) [4], although certain distinctions occur in the structures of their inorganic anions.



Fragment of structure I.

The independent Cu_2Br_3^- fragments in **II** are linked together by the slightly elongated Cu–Br contacts to form chains oriented along [101]. As to the dimers similar to those in structure **I**, they can be distinguished only arbitrarily, with the Cu_2Br_3^- ions being linked together via the n plane.

The bidentate organic ligands in structures **I** and **II** play the same role, namely, they join together the inorganic fragments. The DAGUN⁺ cation in structure **I** exhibits a considerable conformational flexibility, resulting in its asymmetry (see torsion angles in Table 3), whereas the DAAH⁺ cation in structure **II** has pseudoaxis 2 passing through the nitrogen atom.

In the three-dimensional structure of **I**, the individual [100]-directed $[(\text{DAGUN})_2\text{Cu}_4\text{X}_6]_n$ chains are united by the branched system of hydrogen bonds of

the C–H...X and N–H...X types (more developed than in **II**). The geometries of the most important H bonds in structure **I** are presented in Table 4.

In the type of organic ligand, compound **I** is related to the complexes of copper(I) halides with the *S*-allyl-isothiuronium cation, $[\text{C}_3\text{H}_5\text{SC}(=\text{NH}_2)_2]\text{CuX}_2$ (X = Cl, Br) [5], and allylguanidinium cation, $[\text{C}_3\text{H}_5\text{NHC}(=\text{NH}_2)_2]\text{CuBr}_2$ and $[\text{C}_3\text{H}_5\text{NHC}(=\text{NH}_2)_2]\text{CuCl}_{2-x}\text{Br}_x$ ($x = 0.516$) [6]. In these complexes, the ligand is also coordinated via the C=C group, and the H atoms at the nitrogen atoms form a system of hydrogen bonds.

The isolated dimeric $\text{Cu}_4\text{Cl}_6^{2-}$ fragment also occurs in the polycation copper(I) complex with allylammonium (AAH⁺), $[\text{Cu}_4\text{Cl}_6(\text{AAH})_4]\text{SiF}_6$ [10]. Owing to the

Table 4. Geometry of hydrogen bonds in structure **I**

A–H...B bond*	Distance, Å			AHB angle, deg
	H...B	A...B	A–H	
C(2)–H(2.1)...X(3)	3.0(1)	3.63(1)	0.9(1)	126(8)
C(5)–H(5.2)...X(2)	2.9(1)	3.57(1)	1.0(1)	130(9)
N(1)–H(1)...X(2)	2.74(7)	3.33(1)	0.65(7)	154(7)
N(2)–H(2)...X(3)	2.30(8)	3.32(1)	1.04(8)	168(6)
N(3)–H(3)...X(3)	2.6(1)	3.52(1)	0.9(1)	162(10)
N(3)–H(4)...X(1)	2.8(2)	3.36(1)	0.6(2)	153(10)

* The $G(X_i)$ values are presented in Table 2.

predominant role of the outer-sphere SiF_6^{2-} anion in the formation of the structure, the $\text{Cu}_4\text{Cl}_6^{2-}$ fragment is composed in a manner different from that in **I** and consists of the Cu_4Cl_4 cycle and two terminal Cl atoms. In the $[\text{Cu}_2\text{Cl}_3(\text{AAH})_2]\text{CuCl}_2$ complex [11], the Cu_2Cl_3^- anion is monomeric and has the C_2 symmetry. Thus, the inorganic fragment $(\text{Cu}_2\text{X}_3)_n$ ($X = \text{Cl}, \text{Br}$) is present in both polycation and zwitterion [12] complexes (**I** and **II**).

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