

Copper(I) Halide π -Complexes with Diallylamine of the Extreme Stoichiometry. The Peculiarities of Synthesis and Crystal Structure of $3\text{CuX}\cdot(\text{C}_3\text{H}_5)_2\text{NH}$ ($\text{X} = \text{Cl}, \text{Br}$)

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By alternating current electrochemical synthesis, orthorhombic crystals of $3\text{CuCl}\cdot(\text{C}_3\text{H}_5)_2\text{NH}$ (I) and $3\text{CuBr}_{0.84}\text{Cl}_{0.16}\cdot(\text{C}_3\text{H}_5)_2\text{NH}$ (II) π -complexes with unusually high ratio CuX:diallylamine were obtained. The isostructural compounds were X-ray structurally characterized on single crystals. Molecule of diallylamine attaches to three copper(I) atoms of the same inorganic fragment. Copper atoms have different coordination spheres: Cu(1) possesses trigonal planar coordination formed by two halide atoms and C=C bond, the similar Cu(2) environment is completed by an additional halide atom to a trigonal pyramid, whereas Cu(3) is surrounded tetrahedrally by three halide atoms and one nitrogen atom. The effective atomic charges in I were calculated.

Key words: diallylamine copper(I) π -complex, synthesis, crystal structure

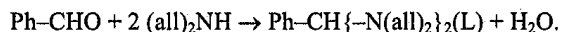
Diallylamine ($(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}$, DAA) is a tridentate π, σ -ligand, which demonstrates a bridging function in copper(I) chloride π -complex $2\text{CuCl}\cdot\text{DAA}$ [1], and the bridging-chelate function in π -complexes of copper(I) ionic salts, viz., $\text{CuBF}_4\cdot\text{DAA}$ [2], $\text{CuNO}_3\cdot\text{DAA}$ (A and B modifications) [3,4], $\text{CuClO}_4\cdot\text{DAA}$ [5]. As a part of studies on the π -complexation between copper(I) ionic salts and diallylamine, we have tried to obtain a π -complex of copper(I) trichloroacetate with DAA. Nevertheless, due to the known fact of Cl^- abstraction from trichloroacetic ion by Cu(I) [6], copper(I) chloride π -complex with an unusually high ratio CuCl:DAA (3:1) was obtained. Further attempt for obtaining a copper(I) bromide π -complex with Ph-CH[-N(-CH₂-CH=CH₂)₂]₂ (product of condensation of benzaldehyde with DAA), due to hydrolysis, yields the bromide analogue of the above complex. Thus, copper(I) π -complexes of $3\text{CuCl}\cdot\text{DAA}$ (I) and $3\text{CuBr}_{1-x}\text{Cl}_x\cdot\text{DAA}$ (II) ($x = 0.16$) compositions have been prepared and X-ray structurally characterized.

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EXPERIMENTAL

Preparation of complexes I and II. Good quality crystals of the complexes have been obtained by the alternating-current electrochemical technique [7]. To 4 ml of ethanolic solution of copper(II) trichloroacetate (2 mmol), 1.0 ml of diallyamine (8 mmol) was added. This solution was placed in a small 6-ml test-tube and copper-wire electrodes in cork (to protect against the oxidation by air) were inserted. With the alternating current (frequency 50 Hz) of 0.38 V crystals of the compound I appeared on the copper electrodes and on the glass of the inner side of the tube after 3 days. The formation of crystals of such composition in the presence of DAA in relatively high concentration may be caused by local excess of CuCl generated by unstable copper(I) trichloroacetate. This may occur near the electrodes, where Cu(II) \rightarrow Cu(I) reduction takes place. In a similar way trichloroacetate ion has been used to synthesize a new zwitterionic allylammonium π -complex of $[\text{Cu}_2\text{Cl}_3(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_3)_2]\text{CuCl}_2$ composition, starting from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and allylamine, previously titrated by trichloroacetic acid [8].

To synthesize the complex II, the condensation of benzaldehyde with DAA was carried out [9]:



1 ml of a 2 M water solution of CuBr_2 (2 mmol) in butanol-2 (3 ml) was mixed with 0.5 ml of L (1.5 mmol). By the same electrochemical Cu(II) + e \rightarrow Cu(I) reduction at the voltage of 0.40 V the crystals of compound II on the copper electrodes have grown during 4 months. Slow hydrolysis of L provided a constant low concentration of DAA in the reaction mixture, promoting the complex formation with unusually high ratio CuX:DAA (X denotes specified in Table 2 statistic of Cl and Br atoms). The admixture of Cl atoms in II is caused by impurity in L. An attempt to synthesize the complex I in this way resulted in obtaining the earlier investigated complex of $2\text{CuCl} \cdot \text{DAA}$ composition [1]. Moreover, we also failed to obtain I and II by varying the initial concentrations of copper(II) halide and DAA in the reaction mixture. The density of I and II was measured by flotation in the mixture of $\text{CHCl}_3/\text{CHBr}_3$.

Crystal structures of I and II. Approximate unit-cell dimensions and the space group were determined from rotation and Weissenberg photographs. The intensity data were measured on a KUMA KM4 diffractometer for I and a DARCH-2 diffractometer (an automated four-circle diffractometer of the former USSR production, the analogue of a Syntex P2₁) for II with the graphite monochromatized MoK_α radiation. The crystallographic data and data collection parameters for I and II are given in Table 1.

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

	I	II
Empirical formula	$\text{C}_6\text{H}_{11}\text{NCu}_3\text{Cl}_3$	$\text{C}_6\text{H}_{11}\text{NCu}_3\text{Cl}_{0.47}\text{Br}_{2.53}$
Color/shape	Colorless/brick	Yellowish/prism
Crystal size, [mm]	$0.3 \times 0.15 \times 0.4$	$0.25 \times 0.2 \times 0.35$
Formula weight	394.16	506.62
Temperature [K]	293	293
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pccn</i>	<i>Pccn</i>
Unit cell dimensions		
<i>a</i> [Å]	19.043(4)	19.280(4)
<i>b</i> [Å]	15.172(3)	15.419(4)
<i>c</i> [Å]	7.571(2)	7.859(2)
<i>V</i> [Å ³]	2187.4(9)	2336(1)
<i>Z</i>	8	8
<i>D_c</i> [g/cm ³]	2.393(2)	2.880(2)
<i>D_m</i> [g/cm ³]	2.35	2.83
Absorption coefficient, [cm ⁻¹]	66.66	164.29
Diffractometer/scan	KUMA KM/ω-2θ	DARCH/θ-2θ
λ [Å], graphite monochromator	0.71069	0.71069
<i>F</i> (000)	1536	1900

Table 1 (continuation)

	55	56
$2\theta_{\max}$, [°]		
Reflections measured	4449 (1/4 of r.l. sphere)	1268 (1/8 of r.l. sphere)
Unique reflections	837 [$F_o \geq 8\sigma(F_o)$]	849 [$F_o \geq 3\sigma(F_o)$]
Reflections used in refinement	1552 [$F_o \geq 8\sigma(F_o)$]	849 [$F_o \geq 3\sigma(F_o)$]
No. of parameters varied	162	165
Weighting scheme	$[\sigma(F_o)^2 + 0.0012F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0013F_o^2]^{-1}$
Goodness-of-fit on F	1.040	1.030
$R(F)$	0.0307	0.0422
$R_w(F)$	0.0327	0.0417
Max./min. $\Delta\rho$ [$e \text{ \AA}^{-3}$]	0.58 / -0.62	0.84 / -0.73

The cell parameters were obtained by the least-squares refinement with regards to the angle parameters of 25 reflections for I and of 24 reflections for II in the range $22.0 < 2\theta < 29.0^\circ$. Both structures were solved by the direct methods. All H atoms were found from difference Fourier syntheses for I and II. Absorption correction has been performed using program DIFABS. A full least-squares refinement on F was performed on the positional and the thermal parameters for all atoms, anisotropically for all non H-atoms. The neutral atom scattering factors were taken from [10]. The intensities were not corrected for extinction. All the calculations (including absorption corrections) were performed using the CSD program package (Crystal Structure Determination) [11]. The final atomic parameters are presented in Table 2. The anisotropic thermal parameters and the list of observed and calculated structure amplitudes for I and II are available on request.

Table 2. Positional coordinates and equivalent thermal parameters (with e.s.d's in parentheses) for I and II.

	x	y	z	$U_{eq} \cdot 10^2$ *
I				
Cu(1)	0.64879(4)	0.06440(5)	0.2003(1)	4.25(3)
Cu(2)	0.67306(5)	-0.02088(6)	0.5703(1)	4.30(3)
Cu(3)	0.49422(5)	-0.01505(6)	0.6978(1)	5.53(3)
Cl(1)	0.74764(9)	0.0411(1)	0.3645(2)	3.92(5)
Cl(2)	0.59460(9)	-0.0699(1)	0.1857(2)	3.73(5)
Cl(3)	0.58222(8)	0.0757(1)	0.5881(2)	3.30(5)
N	0.5269(3)	-0.1354(3)	0.7835(8)	3.1(2)
C(1)	0.6570(4)	0.1916(5)	0.113(1)	5.1(3)
C(2)	0.5911(3)	0.1659(4)	0.0848(9)	3.4(2)
C(3)	0.5320(3)	0.1965(4)	0.1982(9)	3.0(2)
C(4)	0.5838(4)	-0.1758(5)	0.682(1)	4.6(3)
C(5)	0.6533(4)	-0.1368(4)	0.7146(9)	3.8(2)
C(6)	0.7092(4)	-0.1468(5)	0.603(1)	4.6(3)
H(11)	0.696(4)	0.168(6)	0.03(1)	9(3)
H(12)	0.665(3)	0.210(4)	0.184(8)	3(2)
H(21)	0.574(2)	0.153(3)	-0.018(6)	1(1)
H(31)	0.547(4)	0.213(4)	0.32(1)	6(2)
H(32)	0.522(3)	0.247(4)	0.153(8)	4(2)
H(41)	0.562(3)	-0.175(4)	0.558(8)	4(2)
H(42)	0.585(4)	-0.232(6)	0.73(1)	9(3)
H(51)	0.665(3)	-0.123(4)	0.840(8)	5(2)
H(61)	0.757(4)	-0.138(4)	0.647(9)	5(2)
H(62)	0.703(3)	-0.167(4)	0.500(7)	1(1)
H(N)	0.540(3)	-0.120(3)	0.869(7)	1(1)
II				
Cu(1)	0.6463(1)	0.0671(1)	0.2101(3)	5.11(8)
Cu(2)	0.6750(1)	-0.0202(1)	0.5636(3)	5.58(8)

Table 2 (continuation)

Cu(3)	0.4904(1)	-0.0180(1)	0.6810(3)	5.87(9)
X(1) **	0.7519(1)	0.0458(2)	0.3614(2)	4.92(8)
X(2)	0.59504(9)	-0.0736(1)	0.1792(3)	4.61(7)
X(3)	0.58192(8)	0.0806(1)	0.5873(2)	3.90(6)
N	0.5275(6)	-0.1311(8)	0.778(2)	3.8(4)
C(1)	0.652(1)	0.192(1)	0.122(3)	6.9(8)
C(2)	0.5858(8)	0.166(1)	0.096(2)	4.5(6)
C(3)	0.5279(8)	0.1956(8)	0.204(2)	3.9(5)
C(4)	0.5830(9)	-0.175(1)	0.673(3)	6.1(8)
C(5)	0.6526(8)	-0.134(1)	0.701(3)	5.3(6)
C(6)	0.7079(8)	-0.148(1)	0.592(3)	5.7(7)
H(11)	0.692(8)	0.19(1)	0.03(2)	11(6)
H(12)	0.650(6)	0.218(8)	0.22(2)	4(4)
H(21)	0.575(6)	0.140(8)	-0.02(2)	4(4)
H(31)	0.549(9)	0.19(1)	0.33(3)	11(7)
H(32)	0.513(5)	0.238(8)	0.16(1)	2(3)
H(41)	0.566(5)	-0.172(7)	0.54(2)	1(3)
H(42)	0.599(7)	-0.22(1)	0.72(2)	7(5)
H(51)	0.669(8)	-0.09(1)	0.83(2)	7(5)
H(61)	0.767(8)	-0.121(9)	0.66(2)	6(4)
H(62)	0.699(8)	-0.20(1)	0.48(2)	8(6)
H(N)	0.536(4)	-0.122(5)	0.89(1)	1(2)

For non H-atoms $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^ a_j^* (a_i a_j)$. **Occupations: X(1) : 0.70(1) Br + 0.30(1) Cl;
X(2) : 0.88(1) Br + 0.12(1) Cl; X(3) : 0.95(1) Br + 0.05(1) Cl.

RESULTS AND DISCUSSION

π -Complexes **I** and **II** appear to be isostructural. The bond lengths, bond angles and the selected torsion angles in both crystals are listed in Table 3. Three copper(I) atoms have different coordination spheres. The Cu(1) atom possesses trigonal coordination, formed by two halide atoms and the C=C bond. The planar coordination corresponds to a slight deviation of Cu(1) atom from the plane through Cl(1), Cl(2) and midpoint of C(1)=C(2) (0.01 Å for **I** and 0.09 Å for **II**). The similar Cu(2) environment is completed by an additional halide atom to a trigonal pyramid at a distance Cu(2)-X(1)' of 2.851(3) Å for **I** and 2.915(4) Å for **II**. The corresponding deviation of Cu(2) atom from the plane of equatorial ligands equals 0.14 Å in both structures. The Cu(3) atom has the trigonal pyramidal coordination (X(2), X(3), N atoms and X(3)' atom at the apical position). In this case, copper atom is only σ -coordinated and the deviation of Cu(3) atom from the plane of equatorial ligands equals 0.82 Å for **I** and 0.78 Å for **II**. A considerably greater deviation in contrast to Cu(2) indicates that Cu(3) prefers a distorted tetrahedral coordination. In consequence of stereospecific $d \rightarrow \pi^*$ back donation, in the environment of π -coordinated Cu(2), the pyramidal distortion of the copper coordination sphere is shown to be influenced by steric factors to a lesser extent, since it is induced by the migration of Cu(I) towards the base plane of the tetrahedron rather than by the removal of the axial ligand.

Table 3. Bond lengths (Å), bond angles (°) (with e.s.d.'s in parentheses) and torsion angles (°) for I and II.

	I	II
Coordination spheres		
Cu(1)...Cu(3)	2.928(4)	2.873(5)
Cu(3)...Cu(3)	3.037(3)	2.922(4)
Cu(1)-X(1) *	2.283(4)	2.380(5)
Cu(1)-X(2)	2.287(4)	2.397(5)
Cu(1)-C(1)	2.046(8)	2.05(2)
Cu(1)-C(2)	2.084(7)	2.12(2)
Cu(1)- <i>m</i> (12) **	1.955(8)	1.98(2)
X(1)-Cu(1)-X(2)	105.1(1)	106.2(2)
X(1)-Cu(1)- <i>m</i> (12)	123.4(3)	123.6(6)
X(2)-Cu(1)- <i>m</i> (12)	131.5(3)	129.7(6)
C(1)-Cu(1)-C(2)	37.6(3)	37.6(7)
Cu(2)-X(1)	2.308(4)	2.401(5)
Cu(2)-X(1)'	2.851(3)	2.915(4)
Cu(2)-X(3)	2.271(4)	2.381(5)
Cu(2)-C(5)	2.104(7)	2.10(2)
Cu(2)-C(6)	2.045(8)	2.07(2)
Cu(2)- <i>m</i> (56) **	1.959(8)	1.97(2)
X(1)-Cu(2)-X(1)'	93.9(1)	94.9(2)
X(1)-Cu(2)-X(3)	104.2(1)	103.9(2)
X(1)-Cu(2)- <i>m</i> (56)	124.2(3)	125.9(6)
X(1)'-Cu(2)-X(3)	98.3(1)	94.2(1)
X(1)'-Cu(2)- <i>m</i> (56)	90.0(3)	92.2(6)
X(3)-Cu(2)- <i>m</i> (56)	130.1(3)	128.9(6)
C(5)-Cu(2)-C(6)	38.5(3)	38.8(7)
Cu(3)-X(2)	2.302(4)	2.432(5)
Cu(3)-X(3)	2.322(4)	2.442(5)
Cu(3)-X(3)'	2.765(3)	2.706(4)
Cu(3)-N	2.035(6)	2.03(1)
X(2)-Cu(3)-X(3)	109.6(1)	105.3(2)
X(2)-Cu(3)-X(3)'	95.7(1)	102.2(2)
X(2)-Cu(3)-N	127.2(2)	124.5(4)
X(3)-Cu(3)-X(3)'	107.3(1)	111.0(2)
X(3)-Cu(3)-N	115.2(2)	113.1(4)
X(3)'-Cu(3)-N	96.4(2)	99.7(4)
Molecule of ligand		
C(1)-C(2)	1.33(1)	1.34(3)
C(2)-C(3)	1.49(1)	1.48(2)
C(3)-N	1.461(9)	1.47(2)
N-C(4)	1.46(1)	1.51(2)
C(4)-C(5)	1.47(1)	1.50(3)
C(5)-C(6)	1.37(1)	1.39(3)
C(1)-C(2)-C(3)	121.9(7)	122(2)
C(2)-C(3)-N	115.9(6)	113(1)
C(3)-N-C(4)	110.6(6)	105(1)
N-C(4)-C(5)	114.2(6)	112(2)
C(4)-C(5)-C(6)	123.4(7)	122(2)
Cu(1)-C(1)-C(2)-C(3)	104.8	104.8
C(1)-C(2)-C(3)-N	150.2	149.0
C(2)-C(3)-N-C(4)	-175.2	-176.9
C(3)-N-C(4)-C(5)	-156.9	-157.1
N-C(4)-C(5)-C(6)	161.4	164.3
C(4)-C(5)-C(6)-Cu(2)	-105.1	-110.1

*X denotes Cl atom in I and specified in Table 2 statistic of Cl and Br atoms in II.

***m*(12) and *m*(56) – the mid-points of C(1)=C(2) and C(5)=C(6) distances, respectively.

The molecule of DAA, coordinating three copper(I) atoms, demonstrates bridging functions. The asymmetric units are combined into centrosymmetrical dimers (Fig. 1), which by the axial Cu(2)–X(1)' contacts form layer in the (010) plane (Fig. 2). The outside of this layer consists of the organic molecules. Thus, H-bonds of C–H...X type and the van der Waals interactions between related by a glide plane *c* layers complete the structure. Due to the twice-bridging function, the DAA molecule is considerably stretched, (C(1)...C(6) distance equals to 7.33(1) Å for **I** and 7.32(3) Å for **II**). Consequently, allylic groups lose their flexibility. As a result, C(1)=C(2) bond is not oriented exactly in the coordination plane of Cu(1) (the tilt is equal to 19° for **I** and 20° for **II**). Though strong C(1)–H(11)...X(1) contacts (see Table 4), stereospecific (Cu(I)→L)_π-dative component of the Cu(1)–(C=C) π-bonding is suppressed. Therefore, the C(1)=C(2) bond is not elongated (1.33(1) Å for **I** and 1.34(3) Å for **II**). In the case of Cu(2) coordination, the tilt of C(5)=C(6) bond from the plane of equatorial ligands equals to 10° for **I** and 11° for **II**. These values allow the Cu(2)–(C=C) π-bonding to be more effective: the C(5)=C(6) bond length is 1.37(1) Å for **I** and 1.39(3) Å for **II**.

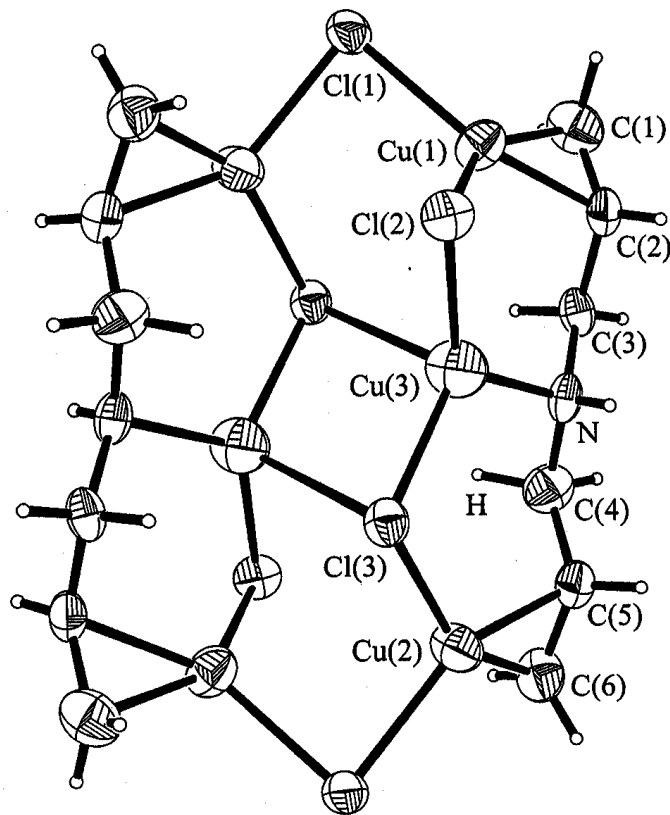


Figure 1. Centrosymmetrical fragment in **I**.

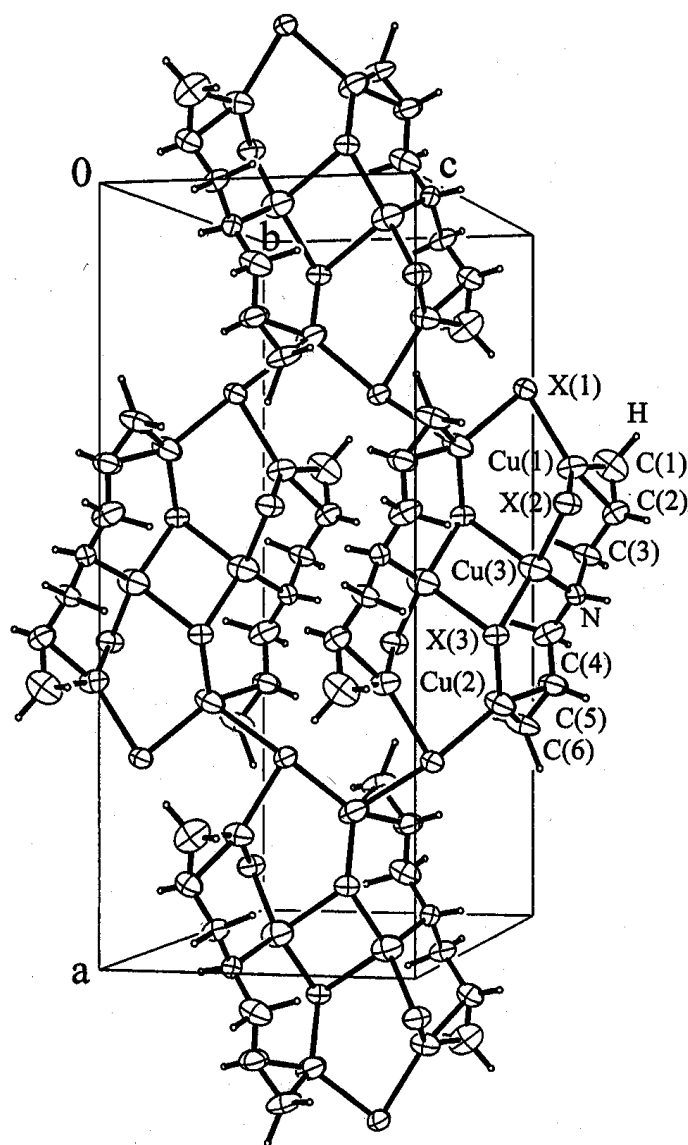


Figure 2. Layer in the (010) plane in the structure of II.

Table 4. Hydrogen bond lengths (Å) and bond angles (°) with e.s.d's (in parentheses) in the crystals of I and II.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
I				
C(1)-H(11)...Cl(1)	1.04(8)	2.54(8)	3.472(8)	149(6)
C(3)-H(32)...Cl(3)	0.86(6)	2.96(6)	3.682(7)	142(5)
C(4)-H(42)...Cl(2)	0.94(8)	3.03(8)	3.864(8)	148(6)
C(6)-H(61)...Cl(2)	0.98(7)	3.02(7)	3.965(9)	162(5)
N-H(N)...Cl(2)	0.73(5)	2.72(5)	3.453(7)	177(5)

Table 4 (continuation)

II				
C(1)–H(11)...X(1)	1.1(2)	2.8(2)	3.57(2)	128(9)
C(3)–H(31)...X(3)	1.0(2)	2.8(2)	3.65(2)	142(9)
C(5)–H(51)...X(1)	1.3(2)	2.6(2)	3.55(2)	133(9)
C(6)–H(61)...X(2)	1.3(2)	2.8(2)	4.03(2)	158(9)
N–H(N)...X(2)	0.89(8)	2.67(8)	3.52(1)	163(6)

In the structure of $2\text{CuCl}\cdot\text{DAA}$ [1], the DAA molecule is also twice-bridging, but not only within the same inorganic fragment: it binds together two fragments of Cu_4Cl_4 . Instead of a separate σ - and π -coordination, as it occurs in **I** and **II**, in the structure of $2\text{CuCl}\cdot\text{DAA}$ a half of copper(I) atoms has a combined environment (involving both σ - and π -ligands). In the π -complexes of copper(I) ionic salts, the Cu atom is chelately attached by the two olefin groups of a DAA ligand and by the nitrogen atom [2–5].

The crystals of **I** and **II** are stabilized by the hydrogen bonds of $\text{N–H}\dots\text{X}$ and $\text{C–H}\dots\text{X}$ types (Table 4). The strong $=\text{C–H}\dots\text{X}$ contacts are of particular interest. Owing to a polarity increase of the $\text{X}^{\delta-}\dots\text{H}^{\delta+}\text{–C}^{\delta-}(=\text{C})\dots\text{Cu}^{\delta+}$ chain, it may favour the stronger interaction of the $\text{C}=\text{C}$ bond with the copper atom. Taking into account the difference in Cl and Br radii, one can reveal that $\text{N–H(N)}\dots\text{X(2)}$ bond in **II** (2.67(8) Å) is much stronger than in **I** (2.72(5) Å). In contrast to **I**, in the structure **II** bromine and chlorine atoms statistically occupy positions with different (specified in Table 2) Br:Cl ratios. The X(2) and X(3) atoms of practically Br type interact effectively with copper atoms, drawing them together more tightly than in **I** (see Table 3).

A calculation of the effective atomic charges in **I** was performed, using the program package HYPERCHEM (ZINDO/1 semi-empirical method – a modified version, including the transition metal atoms of the iterative SCF method in the MNDO approximation) [12]. The greatest possible and the most closed cluster with the structure determined was selected (240 atoms, 780 orbitals). The calculation has revealed, that the atomic charges for Cu(1), Cu(2) and Cu(3) atoms are respectively equal to +0.05, +0.04 and +0.04 e and, owing to the π -back donation to the equatorial ligands (chlorine atoms), are close to the value found for the Cu_nCl_n cluster in the CuCl -sphalerite crystal structure (+0.075 e) [13]. The chlorine atoms possess a charge of –0.35, –0.39 and –0.30 e for Cl(1), Cl(2) and Cl(3), respectively. The total charge of the DAA molecule equals to +0.92 e. Thus, the negative charge in the structure **I** is mainly located on the chlorine atoms, whereas the positive charge is on the significantly polarized by H-bonds hydrogen atoms.

Acknowledgements

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