

COORDINATION
COMPOUNDS

Synthesis and Structure of Ionic Copper(I) π -Complexes with Propargylammonium Chloride and Bromide $[\text{HC}\equiv\text{CCH}_2\text{NH}_3]\text{CuX}_2$

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Abstract—The crystals of $[\text{HC}\equiv\text{CCH}_2\text{NH}_3]\text{CuX}_2$ ($\text{X} = \text{Cl}$ (**I**), Br (**II**)) were prepared by alternating-current electrosynthesis and characterized by X-ray crystallography and IR spectroscopy. Complex **I** crystallizes in space group $Pcab$, $a = 19.010(6)$ Å, $b = 7.404(5)$ Å, $c = 8.690(3)$ Å, $V = 1223.1(10)$ Å³, $Z = 8$. The structure of **II** is described by space group $P2_1/b$, $a = 10.047(1)$ Å, $b = 7.673(1)$ Å, $c = 8.971(1)$ Å, $\gamma = 103.04(2)^\circ$, $V = 673.75(13)$ Å³, $Z = 4$. The structure of **I** consists of discrete units of the above-indicated composition, the copper atom forming a planar trigonal environment. In **II**, similar structural units are combined through the elongated Cu–Br distance (2.910(1) Å) to give chains along the [010] direction. The complexes differ in the efficiency of π -bonding; the Cu–(midpoint of the $\text{C}\equiv\text{C}$ bond) distance and the $\text{C}\equiv\text{C}$ bond length are 1.923(9), 1.23(1) Å and 1.960(6), 1.192(8) Å for **I** and **II**, respectively. The $\nu(\text{C}\equiv\text{C})$ frequencies in **I** and **II** are 157 and 137 cm^{-1} lower than the corresponding values for the free ligand. The decrease in the $\nu(\text{C}_{sp}\text{–H})$ values by 92 and 84 cm^{-1} attests to the activation of the $\equiv\text{C}\text{–H}$ bond.

Many alkyne reactions catalyzed by copper(I) salts afford intermediate cuprohalide π -complexes of acetylene terminal derivatives [1]. Systematic research into the structures of these intermediates is an important step on the path to understanding the mechanism of cuprocatalytic processes [1, 2].

A previous study of copper(I) chloride π -complexation with propargyl alcohol performed using molecular ($2\text{CuCl} \cdot \text{HC}\equiv\text{CCH}_2\text{OH}$ [3]) and anionic ($\text{HAN}[\text{Cu}_2\text{Cl}_3(\text{HC}\equiv\text{CCH}_2\text{OH})]$, HAN^+ is the anilinium cation [4]) π -complexes and the CuCl complex with vinylacetylene ($7\text{CuCl} \cdot 3\text{HC}\equiv\text{CCH}=\text{CH}_2$ [5]) as examples has shown that the terminal $\text{C}\equiv\text{C}$ group in organic molecules is capable of functioning as a bridge between two copper(I) atoms, similar to acetylene [6–9]. However, examples of a different behavior of the ethynyl group in acetylene monosubstituted derivatives are also known, namely, the acetylene bond functions in the structures of Cu(I) complexes ($\text{CuCl} \cdot \text{HC}\equiv\text{CC}_6\text{H}_5$, $\text{CuCl} \cdot \text{HC}\equiv\text{CCH}_2\text{Cl}$, and $\text{CuCl} \cdot \text{HC}\equiv\text{CCH}_2\text{OH}$ [10]) in the same way as the ethylene bond (for example, in the structures of CuX complexes ($\text{X} = \text{Cl}, \text{Br}$) with allylamine ($\text{CuX} \cdot \text{CH}_2=\text{CHCH}_2\text{NH}_2$ [12]) or allylammonium cation ($[\text{CH}_2=\text{CHCH}_2\text{NH}_3]\text{CuX}_2$ [13])), being π -coordinated to only one metal atom.

It was of interest to study the capacity of the $\text{C}\equiv\text{C}$ bond in monosubstituted acetylene derivatives containing an amino group for π -interaction with Cu(I) . To this end, the crystals of two zwitterion copper(I) π -complexes with propargylammonium chloride

and bromide, $[\text{HC}\equiv\text{CCH}_2\text{NH}_3]\text{CuCl}_2$ (**I**) and $[\text{HC}\equiv\text{CCH}_2\text{NH}_3]\text{CuBr}_2$ (**II**), were prepared and studied by X-ray crystallography and IR spectroscopy.

EXPERIMENTAL

Synthesis. Propargylamine (Aldrich) was titrated by concentrated solutions of HCl and HBr , respectively. Complexes **I** and **II** as well-faceted colorless thin plates were prepared by alternating-current electroreduction of Cu(II) as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or CuBr_2 (3 mmol) to Cu(I) at a copper electrode in the presence of the corresponding propargylammonium halide (4 mmol) in ethanol (4 ml) ($U = 0.30$ V, $I = 0.3\text{--}0.5$ mA). The crystals of **I** and **II** relatively stable in air grew over a period of 24 h. The yield was nearly quantitative.

X-ray crystallography. After preliminary study by the photo method, the structures were solved using the diffraction patterns obtained on a DARC-1 single-crystal diffractometer. The reflection intensities were corrected for Lorentz and polarization effects.

The structures were solved by direct methods; light atoms and hydrogen atoms were located from difference Fourier syntheses. The absorption correction was applied analytically with the ABSCOR program; the crystal dimensions and the indices of its six faces were employed in each case. The structures were solved and the absorption corrections were applied using the CSD program package [14]. The refinement on F^2 's of all non-hydrogen atoms was carried out in the full-matrix anisotropic approximation with the SHELXL97 pro-

Table 1. Crystallographic data, X-ray experiment details, and structure refinement characteristics for the structures of complexes **I** and **II**

Characteristics	I	II
FW	190.53	279.45
Crystal size, mm	0.02 × 0.36 × 0.14	0.026 × 0.32 × 0.12
$F(000)$	752	520
Space group	<i>Pcab</i>	<i>P2₁/b</i>
a , Å	19.010(6)	10.047(1)
b , Å	7.404(5)	7.673(1)
c , Å	8.690(3)	8.971(1)
γ , deg	90	103.04(2)
V , Å ³	1223.1(10)	673.75(13)
Z	8	4
$\rho_{\text{calcd.}}$, g/cm ³	2.069(3)	2.755(1)
μ_{Mo} , mm ⁻¹	4.313	14.984
$T_{\text{min}}/T_{\text{max}}$	0.570/0.915	0.209/0.666
Radiation/monochromator	MoK α /Zr filter	MoK α /Zr filter
$2\theta_{\text{max}}$, deg	45	50
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Range of hkl indices	$-3 \leq h \leq 30, -2 \leq k \leq 7, -2 \leq l \leq 9$	$-11 \leq h \leq 11, 0 \leq k \leq 9, -10 \leq l \leq 10$
Number of reflections		
measured	724	1425
unique	370	808
unique with $I \geq 2\sigma(I)$	349	756
Number of refined parameters	76	76
$R(F), I \geq 2\sigma(I)$	0.0269	0.0245
$wR(F^2)$ over all reflections	0.0624	0.0543
Extinction coefficient	0.0008(4)	0.0005(3)
Weighting scheme: * A, B	0.0453, 0	0.0283, 0.228
GOOF (F^2)	1.099	1.143
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e/Å ³	0.38/-0.31	0.60/-0.42

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

gram package [15]. The hydrogen atoms of the CH₂ and NH₃ groups were refined in the rider and rotating rigid body approximations (AFIX 24 and 135 instructions, respectively) with group isotropic temperature factors and refined X–H distances. The hydrogen atoms at the triple bonds were located from Fourier syntheses and refined in the isotropic approximation without restrictions. An extinction correction was applied. The relatively low residual electron density peaks were concentrated about the Cu and Br atoms.

The crystallographic data, X-ray experiment details, and the refinement characteristics for **I** and **II** are presented in Table 1, and the atomic coordinates and thermal factors are listed in Table 2; the interatomic dis-

tances, the bond angles, and some torsion angles are given in Table 3.

IR spectra. The compounds were washed with ethanol, dried, powdered with KBr, and pressed. A UR-20 spectrometer was used; the ν range was 3800–400 cm⁻¹.

[C₃H₅NH₃]Cl: 3252 s (H–C≡), 3120–2830, 2715, 2595, 2470 w, 2130 (C≡C), 2060, 2020 w, 1590 (^{as} $\delta_{\text{N-H}}$) s, 1490 s, 1452 s, 1395, 1376 s, 1315 w, 1137 s, 1121 s, 1010 s, 885 s, 723 s, 703 s, 535 s, 505 w.

[C₃H₅NH₃]CuCl₂: 3160 s (H–C≡), 3110 br, 2960 w, 1973 (C≡C), 1562 (^{as} $\delta_{\text{N-H}}$), 1492 s, 1483 s, 1433 w, 1370, 1345 w, 1307, 1117, 1097, 1010 w, 870 s, 750 w, 703, 520 (Cu–C).

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U \times 10^2, \text{\AA}^2$
I				
Cu	0.62528(6)	0.1593(2)	0.32602(13)	3.60(4)
Cl(1)	0.61572(13)	0.1566(4)	0.5814(2)	4.57(7)
Cl(2)	0.71749(10)	0.3331(3)	0.2520(3)	3.45(6)
N	0.6743(4)	0.0821(10)	-0.0518(9)	4.0(2)
C(1)	0.5372(5)	0.0549(13)	0.2333(13)	3.7(3)
C(2)	0.5740(5)	0.1090(11)	0.1264(11)	2.7(2)
C(3)	0.6033(5)	0.1597(15)	-0.0222(10)	4.0(3)
H(1)	0.501(4)	-0.018(13)	0.291(8)	5(3)
H(2)	0.6065	0.2979	-0.0279	7(2)
H(3)	0.5700	0.1177	-0.1073	7(2)
H(4)	0.7066	0.1022	0.0308	13(3)
H(5)	0.6928	0.1327	-0.1446	13(3)
H(6)	0.6673	-0.0450	-0.0652	13(3)
II				
Cu	0.75898(8)	0.22342(10)	0.18305(8)	4.21(3)
Br(1)	0.72423(8)	0.22408(9)	-0.07925(6)	4.44(2)
Br(2)	0.93451(7)	0.47500(7)	0.26600(7)	3.56(2)
N	0.8360(6)	0.1821(7)	0.5538(5)	4.50(15)
C(1)	0.5804(7)	0.0829(9)	0.2717(7)	4.3(2)
C(2)	0.6479(6)	0.1490(8)	0.3750(6)	3.37(15)
C(3)	0.6988(8)	0.2158(9)	0.5220(7)	4.5(2)
H(1)	0.485(5)	0.004(5)	0.191(4)	1(10)
H(2)	0.7037	0.3432	0.5269	10(2)
H(3)	0.6351	0.1581	0.5977	10(2)
H(4)	0.9026	0.2371	0.4886	8(2)
H(5)	0.8621	0.2160	0.6494	8(2)
H(6)	0.8234	0.0603	0.5451	8(2)

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

[C₃H₅NH₃]⁺CuBr₂: 3168 s (H–C≡), 3100 br, 2940 w, 1993 w (C≡C), 1570 w, 1555 (^{as}δ_{N–H}), 1480 s, 1465, 1430 w, 1368, 1307, 1110 s, 1005 w, 865 s, 695, 515 (Cu–C).

RESULTS AND DISCUSSION

The easy protonation of the amino group in an acid medium, as well as the similarity of the HC≡CCH₂NH₃⁺ and H₂C=CHCH₂NH₃⁺ cations, provided grounds to suggest that the role of the propargylammonium cation in the π -complexation with CuX (X = Cl, Br) would be similar to that of the allylammonium cation in two non-isostructural complexes,

[H₂C=CHCH₂NH₃]⁺CuCl₂ and [H₂C=CHCH₂NH₃]⁺CuBr₂ [13]. Meanwhile, the terminal position of the C≡C bond in HC≡CCH₂NH₃⁺ is favorable for the bridging function of the acetylene bond relative to Cu(I), as in the examples described in [3–5]. However, in the structures of [HC≡CCH₂NH₃]⁺CuCl₂ (**I**) and [HC≡CCH₂NH₃]⁺CuBr₂ (**II**) considered here, the terminal C≡C group of the organic compound is π -coordinated only to one Cu(I) atom (the amino-group N atom is shielded by the H⁺ cation and is not involved in the coordination to the metal atom); thus, the structures of **I** and **II** differ from those of the allylammonium analogues.

Table 3. Bond lengths (d) and bond (ω) and some torsion angles (ϕ) in the structures of **I** and **II***

Bond**	$d, \text{\AA}$		Angle**	ω, deg		Angle**	ϕ, deg	
	I	II		I	II		I	II
Cu–X(1)	2.227(2)	2.379(1)	X(1)CuX(2)	110.6(1)	112.55(4)	Br(1)CuBr(2)Cu'		89.56(4)
Cu–X(2)	2.268(2)	2.420(1)	$m(12)$ CuX(1)	126.8(1)	122.7(2)	Br(2')CuBr(2)Cu'		–162.74(3)
Cu–X(2')	3.060(2)	2.910(1)	$m(12)$ CuX(2)	121.0(1)	118.5(2)	CuC(1)C(2)C(3)	–177(4)	–176.7(8)
Cu–C(1)	2.012(9)	2.035(7)	Br(1)CuBr(2')		105.52(3)			
Cu–C(2)	2.024(9)	2.062(5)	Br(2)CuBr(2')		91.94(3)			
Cu– $m(12)$	1.923(9)	1.960(6)	$m(12)$ Br(2')		97.2(2)			
			C(1)CuC(2)	35.5(4)	33.8(2)			
			CuBr(2)Cu'		97.50(4)			
C(1)–C(2)	1.23(1)	1.192(8)	C(2)C(1)H(1)	160(5)	164(2)			
C(1)–H(1)	1.00(8)	1.25(4)	C(1)C(2)C(3)	166(1)	165.8(7)			
C(2)–C(3)	1.46(1)	1.464(8)	C(2)C(3)N	113.6(8)	112.1(5)			
C(3)–N	1.49(1)	1.486(9)	H(2)C(3)H(3)	107.7	107.9			
C(3)–H(2–3)	1.03	0.97	C(3)NH(4)	113.1	114.0			
N–H(4–6)	0.96	0.92	C(3)NH(5)	109.2	110.3			
			C(3)NH(6)	106.0	103.9			

* X is Cl in **I** and Br in **II**; $m(12)$ is the midpoint of the C(1)–C(2) multiple bond.

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

The A–H...B bond	Distance, \AA			The AHB angle, deg
	H...B	A...B	A–H	
I				
C(1)–H(1)...Cl(1)	2.69(8)	3.67(1)	1.00(8)	167(6)
C(3)–H(2)...Cl(1)	2.70	3.72(1)	1.03	173
N–H(4)...Cl(2)	2.58	3.331(9)	0.96	136
N–H(5)...Cl(2)	2.43	3.255(8)	0.96	144
N–H(6)...Cl(1)	2.42	3.351(9)	0.96	164
II				
C(1)–H(1)...Br(1)	2.61(5)	3.827(7)	1.25(4)	165(3)
C(3)–H(2)...Br(1)	2.92	3.885(7)	0.97	173
N–H(4)...Br(2)	2.68	3.420(5)	0.92	139
N–H(5)...Br(2)	2.86	3.481(5)	0.92	126
N–H(6)...Br(1)	2.57	3.447(5)	0.92	161

Despite the similarity, the zwitterion π -complexes **I** and **II** are not isostructural. The differences are due to the unequal efficiency of the Cu(I)–(C \equiv C) π -bonding, which dictates the geometry of the coordination core (the Cu– m distances (where m is the midpoint of the C \equiv C bond) and the π -coordinated C \equiv C bond lengths are 1.923(9), 1.23(1), and 1.960(6), 1.192(8) \AA for **I** and **II**, respectively). More efficient π -interaction in the case of **I** causes a more pronounced deformation of the

Cu(I) coordination sphere toward a planar trigonal one [16] (the apical Cl_{ap} atom in **I** is separated from the central copper atom by a distance of 3.060(2) \AA), whereas in the structure of **II**, the coordination polyhedron of the metal atom is a trigonal pyramid (two Br atoms and the C \equiv C bond are at the pyramid base, one more Br atom occupies the apical vertex, Cu–Br_{ap} = 2.910(1) \AA). The deflection of the metal atom from the equatorial plane

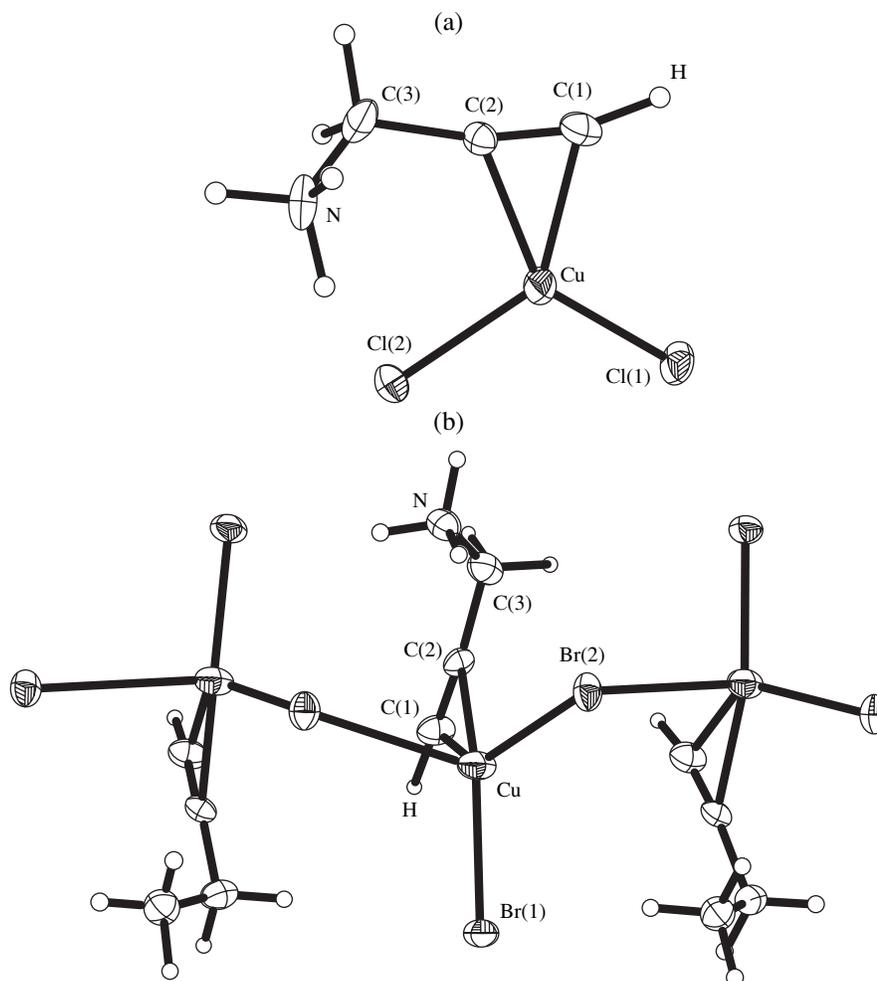


Fig. 1. Organometallic fragments in the structures of (a) **I** and (b) **II** (30% probability ellipsoids are shown).

correlates with the distance to the axial ligand and is equal to 0.158 and 0.323 Å for **I** and **II**, respectively. Notably, the τ angle formed by the plane of the equatorial ligands and the $\text{C}\equiv\text{C}$ bond increases from 3.1° in **I** to 5.2° in **II**. Thus, the structure of **I** consists of discrete $[\text{HC}\equiv\text{CCH}_2\text{NH}_3]\text{CuCl}_2$ fragments, while that of **II** is formed by $\{[\text{H}_2\text{C}=\text{CHCH}_2\text{NH}_3]\text{CuBr}_2\}_n$ polymer chains running along the [010] direction (Fig. 1). Similar inorganic anions $(\text{CuX}_2)_n^{n-}$ in copper(I) halide π -complexes have been encountered only in the structure with allylguanidine ligand, $[\text{CH}_2=\text{CH}-\text{CH}_2-\text{NHC}(\text{NH}_2)_2]\text{CuCl}_{2-x}\text{Br}_x$ ($x = 0.516$) [17]. Nevertheless, with allowance made for the $\text{Cu}\cdots\text{Cl}_{\text{ap}}$ contacts, the discrete fragments found in **I** can also be regarded as being associated to give $\{[\text{H}_2\text{C}=\text{CHCH}_2\text{NH}_3]\text{CuCl}_2\}_n$ chains, similar to those in **II** (Fig. 2). Differences, however, are not only in the degree of association of the inorganic fragments but in the way of their mutual arrangement, namely, in the structure of **I** the pseudo-chains are related by a 2_1 axis (Fig. 2a), while in **II**, individual chain fragments are symmetrically interre-

lated by an inversion center (Fig. 2b). In both cases, asymmetric units are combined in chains by the b plane.

The structural data on the π -interaction efficiency in **I** and **II** are consistent with the shift of the vibrational frequency of the triple bond in the IR spectra upon coordination to the metal atom. The $\text{C}(1)\text{CuC}(2)$ angles, which reflect both the approach of the carbon atoms to Cu(I) and the elongation of the triple bond, are $35.5(4)^\circ$ and $33.8(2)^\circ$; this is matched by $\Delta\nu(\text{C}\equiv\text{C})$ of 157 and 137 cm^{-1} in the IR spectra of **I** and **II**, respectively. The frequency shift from 130 to 200 cm^{-1} is typical of a $\text{C}\equiv\text{C}$ triple bond coordinated to one copper atom [10]. Although the deviation of the $\text{C}\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}-\text{R}$ angles from 180° is normally considered to reflect the degree of back donation (electron density transfer from the metal atom to the ligand π^* orbital), it has been noted [10] that this parameter does not reflect the degree of involvement of either σ or π component into the π -interaction with Cu(I). These angles in the complexes under discussion are $160(5)^\circ$ and $166(1)^\circ$ for **I** and $164(2)^\circ$ and $165.8(7)^\circ$ for **II**, which does not

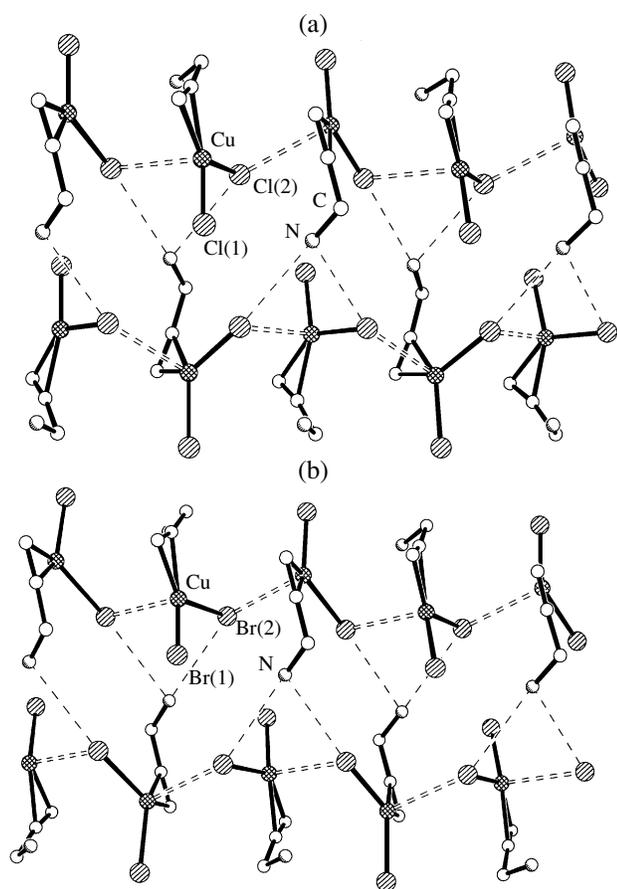


Fig. 2. Formation of layers in the (100) plane in the structures of (a) **I** and (b) **II** with participation of hydrogen bonds (the hydrogen atoms are omitted).

agree with the difference between the elongations of the $C\equiv C$ bond. Nevertheless, for acetylene π -complexes of various d metals, the shift of the triple bond frequency is proportional to the deviation of the above-mentioned angles from 180° over a broad range [18].

An important role in the stabilization of the structure of both complexes is played by the hydrogen bonds between the H atoms at the triple bond and the halogen atom (Table 4). Moreover, the strength of hydrogen bonds of this type has a certain influence on the π -interaction efficiency. Depending on the properties (electronegativity, polarizability) of the atom involved in the $\equiv C-H\cdots X$ interaction, the $C-H$ bond can be polarized to a higher or lower degree ($\equiv C^\delta-H^{\delta+}\cdots X^{\delta-}$); this, naturally, affects the strength of the $Cu(I)-(C\equiv C)$ π -bond. Although the structural data predict much higher stability for the $C(1)-H(1)\cdots Br(1)$ bond than for the $C(1)-H(1)\cdots Cl(1)$ bond, great deviations in the coordinates of the H atom preclude the possibility of reliable determination of the difference between the $C(1)-H(1)$ distances and, hence, strengthening of the $H(1)\cdots Br(1)$ bond. The elongation of the $C(1)\cdots Br(1)$ distance by exactly the difference between the Br and Cl atom radii

(0.15 Å) and nearly equal shifts of the $\equiv C-H$ stretching frequency for **I** and **II** (92 and 84 cm^{-1}) do not attest to the strengthening of the $H(1)\cdots Br(1)$ bond either. The decrease in the $\nu(C_{sp}-H)$ frequency points to activation of the acetylene $C-H$ bond upon coordination [11].

In addition to the $\equiv C-H\cdots X$ hydrogen bonds in **I** and **II**, the extended system of strong hydrogen bonds formed by NH_3^+ -group hydrogen atoms and the halogen atoms of the inorganic anion also has a pronounced influence on the structure formation in these complexes. This, apparently, accounts for the observed stability of the crystals of both compounds to decomposition in a dry atmosphere.

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