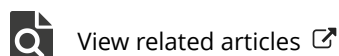
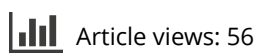
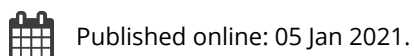
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# Zwitterionic $\pi$ -coordination compounds of copper(I) with monosubstituted alkynes: synthesis, crystal and electronic structure of two copper(I) halide $\pi$ -complexes with 4-amino-1-propargylpyridinium

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## Zwitterionic $\pi$ -coordination compounds of copper(I) with monosubstituted alkynes: synthesis, crystal and electronic structure of two copper(I) halide $\pi$ -complexes with 4-amino-1-propargylpyridinium

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### ABSTRACT

Crystals of two mononuclear  $\pi$ -coordination compounds of copper(I) halide with 4-amino-1-propargylpyridinium cation – [(HC≡CCH<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)CuBr<sub>2</sub>] (**1**) and [(HC≡CCH<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)CuCl<sub>1.61</sub>Br<sub>0.39</sub>] (**2**) – were obtained in the CuX–H<sub>2</sub>O–(HC≡CCH<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)Br system (HC≡CCH<sub>2</sub>N<sup>+</sup>C<sub>5</sub>H<sub>4</sub>NH<sub>2</sub> is 4-amino-1-propargylpyridinium cation (*app*<sup>+</sup>), X=Cl or Br). The purity and identity of the synthesized compounds were verified by elemental analysis and IR spectroscopy. The compounds were structurally characterized using X-ray single crystal method and are isostructural. Both crystals are built of zwitterionic *app*CuX<sub>2</sub> units, in which triple C≡C bond is coordinated to only one copper(I) ion. The Cu–*m* distance (*m* is the middle of the C≡C bond) is 1.933(5) and 1.917(3) Å for **1** and **2**, respectively. The predisposition of copper(I) halides to coordination polymer self-assembly through Cu–X...Cu bridge formation is not realized in **1** and **2**. However, the ≡C–H...X and N–H...X hydrogen bonds along with  $\pi$ – $\pi$  stacking of 4-aminopyridinium groups compensate an absence of the structure-forming interaction Cu–X...Cu. DFT calculations of an electron structure of [(*app*)CuCl<sub>2</sub>] were carried out (the restricted Hartree–Fock (RHF) method with a 6–31 G\* orbital basis set). Calculated values of the charge density distribution on atoms as well as the constructed molecular orbitals (MOs) are in agreement with stereochemical parameters of the (Cu(I)–(C≡C))–core of both coordination compounds.


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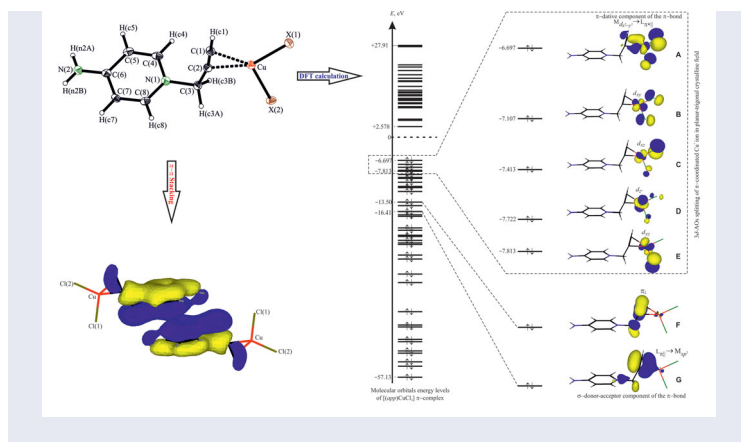
### KEYWORDS

Synthesis; alkyne copper(I)  $\pi$ -coordination compounds; XRD analysis; DFT studies;  $\pi$ – $\pi$  stacking; hydrogen bonds

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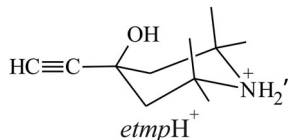
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## 1. Introduction

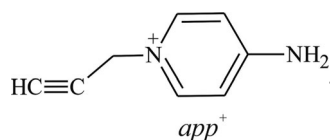
Copper(I) salts are efficient catalysts for many chemical conversions of acetylene and its derivatives [1–6]. For example, the catalytic activity of copper(I) chloride is due to an ability of copper(I) complexes formed in the  $\text{CuCl-MCl-H}_2\text{O-HC}\equiv\text{CR}$  system (MCl is alkali metal or ammonium chloride or amine hydrochloride;  $\text{R} = \text{H}, \text{CH}_2\text{OH}, \text{CH}=\text{CH}_2$ , etc.) to significantly affect the reactivity of the  $\text{C}\equiv\text{C}$  and  $\equiv\text{C-H}$  bonds due to  $\pi$ - and  $\pi, \sigma$ -interactions with alkynes [7–9]. In addition, coordination compounds synthesized in the *Nieuwland's* catalytic system can be considered as precursors to obtain polyacetylene materials for light-emitting diodes, solar cells, biosensors and other devices which require electrically conductive conjugate polyelectrolytes [10]. Reliable information on the crystal structures of intermediate  $\pi$ -coordination compounds of *Nieuwland's* system along with the ascertained electron-stereochemical interdependencies are so important to understanding the role of the copper(I) halide  $\pi$ -coordination compounds in catalytic conversions of alkynes [11,12].

A majority of structurally studied  $\pi$ -coordination compounds of copper(I) halides with monosubstituted alkynes is represented by polymeric complexes, whereas the structure of analogous  $\pi$ -complexes with disubstituted alkynes is mainly mononuclear [13–18]. However, it was shown [19] that it is possible to synthesize mononuclear complexes of copper(I) halides with monosubstituted alkyne ligand, especially if the ligand contains a bulky ring substituent attached to the  $\text{C}\equiv\text{C}$  bond. In particular, the direct interaction of CuCl with 4-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidinium chloride,



results in formation of the  $[(\text{etmpH})\text{CuCl}_2]$  zwitterionic  $\pi$ -complex. Proceeding with further study of the crystal structures of the zwitterionic  $\pi$ -complexes of copper(I) halides

with monosubstituted alkynes, we have replaced the *etmpH*<sup>+</sup> by 4-amino-1-propargylpyridinium cation,



In addition, *app*<sup>+</sup> was used like a model ligand to confirm the assumption of influence of the steric factor on nuclearity of the formed monosubstituted alkyne  $\pi$ -complexes. The *app*<sup>+</sup> species, in a similar way to *etmpH*<sup>+</sup>, have larger size than propargyl chloride, propargyl alcohol, phenylacetylene, propargylamine, vinylacetylene, octa-1,7-diyne and 2-methylbut-3-yn-2-ol, which were used to obtain [CuCl(HC≡CCH<sub>2</sub>Cl)], [CuCl(HC≡CCH<sub>2</sub>OH)], [CuCl(HC≡CC<sub>6</sub>H<sub>5</sub>)] [20], [(HC≡CCH<sub>2</sub>NH<sub>3</sub>)CuCl<sub>2</sub>], [(HC≡CCH<sub>2</sub>NH<sub>3</sub>)CuBr<sub>2</sub>] [21], [(HC≡CCH<sub>2</sub>NH<sub>3</sub>)CuCl<sub>1.13</sub>Br<sub>0.87</sub>] [22], [(HC≡CCH<sub>2</sub>NH<sub>3</sub>)Cu<sub>2</sub>Br<sub>3</sub>] [23], [Cu<sub>7</sub>Cl<sub>7</sub>(HC≡CCH=CH<sub>2</sub>)<sub>3</sub>] [24], [Cu<sub>2</sub>Cl<sub>2</sub>(HC≡C(CH<sub>2</sub>)<sub>4</sub>C≡CH)] [25] and [{CuCl((CH<sub>3</sub>)<sub>2</sub>C(OH)C≡CH)}<sub>4</sub>] [26]  $\pi$ -coordination compounds.

Taking into account the information given above, we undertook an attempt to synthesize and study crystal and electronic structures of two isostructural copper(I) halide  $\pi$ -coordination compounds with monosubstituted alkynes – [(*app*)CuBr<sub>2</sub>] (**1**) and [(*app*)CuCl<sub>1.61</sub>Br<sub>0.39</sub>] (**2**) – which form in the CuX–H<sub>2</sub>O–(HC≡CCH<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)Br system (HC≡CCH<sub>2</sub>N<sup>+</sup>C<sub>5</sub>H<sub>4</sub>NH<sub>2</sub> is 4-amino-1-propargylpyridinium cation (*app*<sup>+</sup>), X=Cl, Br). The electronic structure of these mononuclear compounds was calculated based on the geometrical parameters of the [(*app*)CuCl<sub>2</sub>] model complex. The relationship between geometrical parameters of **1** and **2** and the charge density distribution on atoms was also considered.

## 2. Experimental

### 2.1. Materials

To synthesize the alkyne ligand (*app*Br) and zwitterionic  $\pi$ -complexes ((*app*)CuX<sub>2</sub>), the following chemicals were used: freshly precipitated [27] copper(I) chloride–CuCl (white powder,  $M = 98.99 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 4.14 \text{ g}\cdot\text{cm}^{-3}$ ,  $K_s = 1.72 \cdot 10^{-7}$ ,  $t_{\text{melting}} = 426 \text{ }^\circ\text{C}$  [28]) and copper(I) bromide–CuBr (white powder,  $M = 143.45 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 4.72 \text{ g}\cdot\text{cm}^{-3}$ ,  $K_s = 5.25 \cdot 10^{-9}$ ,  $t_{\text{melting}} = 492 \text{ }^\circ\text{C}$  [29]); propargyl bromide–HC≡CCH<sub>2</sub>Br (colorless liquid,  $M = 118.96 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 1.57 \text{ g}\cdot\text{cm}^{-3}$ ,  $t_{\text{boiling}} = 89 \text{ }^\circ\text{C}$ ); 4-aminopyridine–H<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>N (colorless solid,  $M = 94.11 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 1.26 \text{ g}\cdot\text{cm}^{-3}$ ,  $t_{\text{melting}} = 159 \text{ }^\circ\text{C}$ ,  $\text{p}K_a = 9.17$ ), acetonitrile–CH<sub>3</sub>CN (colorless liquid,  $M = 41.05 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 0.786 \text{ g}\cdot\text{cm}^{-3}$ ,  $t_{\text{boiling}} = 81 \text{ }^\circ\text{C}$ ), toluene–C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (colorless liquid,  $M = 92.14 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 0.865 \text{ g}\cdot\text{cm}^{-3}$ ,  $t_{\text{boiling}} = 110 \text{ }^\circ\text{C}$ ). All reagents were purchased from commercial sources.

### 2.2. Synthesis of *app*Br

4-Amino-1-propargylpyridinium bromide was prepared by alkylation of propargyl bromide with 4-aminopyridine, analogously to the synthesis of 1-propargylpyridinium

**Table 1.** Crystal data and experimental details for the single crystals of **1** and **2**.

Compound	1	2
Empirical formula	Br <sub>2</sub> CuN <sub>2</sub> C <sub>8</sub> H <sub>9</sub>	Br <sub>0.39</sub> Cl <sub>1.61</sub> CuN <sub>2</sub> C <sub>8</sub> H <sub>9</sub>
Formula weight (g·mol <sup>-1</sup> )	356.53	284.95
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
Unit cell dimensions (Å, °)		
<i>a</i>	7.018(3)	6.878(3)
<i>b</i>	7.390(3)	7.243(3)
<i>c</i>	10.743(4)	10.614(4)
$\alpha$	82.42(3)	83.32(3)
$\beta$	80.61(3)	80.75(3)
$\gamma$	73.66(3)	73.32(3)
<i>V</i> (Å <sup>3</sup> ), <i>Z</i>	525.3(4), 2	498.5(4), 2
Calculated density (g·cm <sup>-3</sup> )	2.254	1.898
Absorption coefficient (mm <sup>-1</sup> )	9.639	4.135
<i>F</i> (000)	340	282
Crystal size (mm <sup>3</sup> )	0.09 × 0.06 × 0.01	0.18 × 0.11 × 0.03
Crystal description	Colorless prism	Colorless prism
Temperature (K)	85(2)	100(2)
Wavelength (Å)	0.71073	0.71073
2 $\theta$ range for data collection (°)	9.19–56.00	8.87–64.00
Limiting indices	–9 ≤ <i>h</i> ≤ 8; –9 ≤ <i>k</i> ≤ 9; –14 ≤ <i>l</i> ≤ 13	–10 ≤ <i>h</i> ≤ 10; –7 ≤ <i>k</i> ≤ 10; –15 ≤ <i>l</i> ≤ 15
Reflection collected	8348	7743
Independent reflections	2531 [ <i>R</i> <sub>int</sub> =0.0517]	3336 [ <i>R</i> <sub>int</sub> =0.0452]
Parameters / restraints	122/0	120/0
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.119	1.103
Final <i>R</i> indices [ <i>F</i> ≥ 4σ( <i>F</i> )]	<i>R</i> <sub>1</sub> =0.0423, <i>wR</i> <sub>2</sub> =0.1049	<i>R</i> <sub>1</sub> =0.0412, <i>wR</i> <sub>2</sub> =0.10290
<i>R</i> indices (all data)	0.0501	0.0508
Weighing scheme [ <i>w</i> ]	[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> )+(0.0554 <i>P</i> ) <sup>2</sup> +0.8947 <i>P</i> ] <sup>-1</sup> where <i>P</i> =( <i>F</i> <sub>o</sub> <sup>2</sup> +2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3	[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> )+(0.0559 <i>P</i> ) <sup>2</sup> +0.3133 <i>P</i> ] <sup>-1</sup> where <i>P</i> =( <i>F</i> <sub>o</sub> <sup>2</sup> +2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3

bromide [30]. The solution of HC≡CCH<sub>2</sub>Br (21.4 g, 0.18 mol) in toluene (6.8 mL) was added dropwise to the solution of H<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>N (5.6 g, 0.06 mol) in absolute acetonitrile (16 mL) with stirring. The resulting mixture was stirred at 20 °C for 4 h. The precipitate formed was filtered off, washed on a filter with cold acetonitrile, and dried under vacuum to obtain crystalline *app*Br. The product yield was 9.6 g (75%).

(HC≡CCH<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)Br: IR (UR-20 spectrometer, 3800–400 cm<sup>-1</sup>, KBr pellet) – 3253 (H–C≡), 2132 (C≡C), 1589 (N–H). Anal. Calc. –C (45.07), H (4.23), N (13.15), Br (37.55); Found –C (45.15), H (4.28), N (12.98), Br (37.59).

### 2.3. Synthesis of crystalline $\pi$ -coordination compounds **1** and **2**

The crystalline zwitterionic  $\pi$ -coordination compounds [(*app*)CuBr<sub>2</sub>] (**1**) and [(*app*)CuCl<sub>1.61</sub>Br<sub>0.39</sub>] (**2**) were synthesized by direct reaction of 4-amino-1-propargylpyridinium bromide (*app*Br) with copper(I) bromide and copper(I) chloride, respectively. For **1**: *app*Br (0.01 mol, 2.1 g) was placed into a flask containing 12 mL of 40% aqueous solution of HBr. The contents of the flask were heated to the boiling point, then 1.4 g of CuBr (0.01 mol) was added. To prevent oxidation of Cu(I) with atmospheric oxygen, a few crystals of SnCl<sub>2</sub>·2H<sub>2</sub>O were added to the reaction mixture. The solution prepared was slowly cooled to room temperature. For **2**: this zwitterionic  $\pi$ -complex was prepared in the same way as **1**, viz., the preheated solution containing 25 mL of 36% HCl aqueous solution, *app*Br (4.3 g, 0.02 mol), CuCl (2.0 g, 0.02 mol) and a few crystals

**Table 2.** Selected bond lengths (*d*, Å) and angles ( $\omega$ , °) in **1** and **2**.

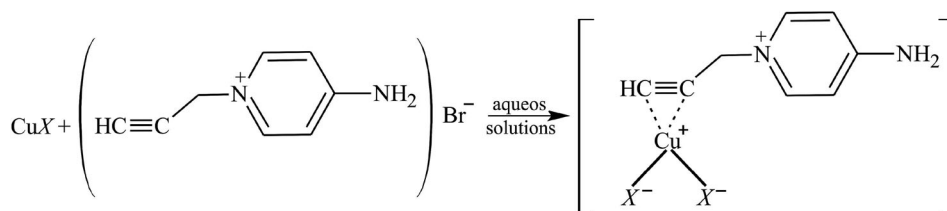
<i>D</i>	<b>1</b>	<b>2</b>	$\omega$	<b>1</b>	<b>2</b>
Cu–X(1)*	2.350(1)	2.257(1)	X(1)–Cu–X(2)	107.38(4)	106.80(4)
Cu–X(2)**	2.383(1)	2.291(1)	X(1)–Cu– <i>m</i>	131.2(1)	131.8(1)
Cu–C(1)	2.048(5)	2.027(3)	<i>m</i> –Cu–X(2)	121.3(1)	121.3(1)
Cu–C(2)	2.003(5)	1.997(3)	C(1)–Cu–C(2)	34.6(2)	35.2(1)
Cu– <i>m</i> ***	1.933(5)	1.917(3)	C(1)≡C(2)–C(3)	166.0(5)	167.3(3)
C(1)≡C(2)	1.206(7)	1.218(4)	C(2)–C(3)–N(1)	111.8(4)	112.1(2)
C(2)–C(3)	1.477(7)	1.480(4)			
C(3)–N(1)	1.487(6)	1.478(4)			

\*X(1)=100% Br (for **1**) and 81.5(3)% Cl + 18.5(3)% Br (for **2**).

\*\*X(2)=100% Br (for **1**) and 79.5(3)% Cl + 20.5(3)% Br (for **2**).

\*\*\**m* – the middle of the C≡C bond.

of SnCl<sub>2</sub>·2H<sub>2</sub>O was slowly cooled. Both solutions were left for a few days at room temperature for crystallization. Prismatic colorless crystals of **1** and **2** were formed according to the following reaction:



The specific densities of both synthesized crystals were measured with a flotation method in the chloroform–bromoform mixture ( $d^{20}$  values were 2.3(1) and 1.9(1) g·cm<sup>-3</sup> for **1** and **2**, respectively).

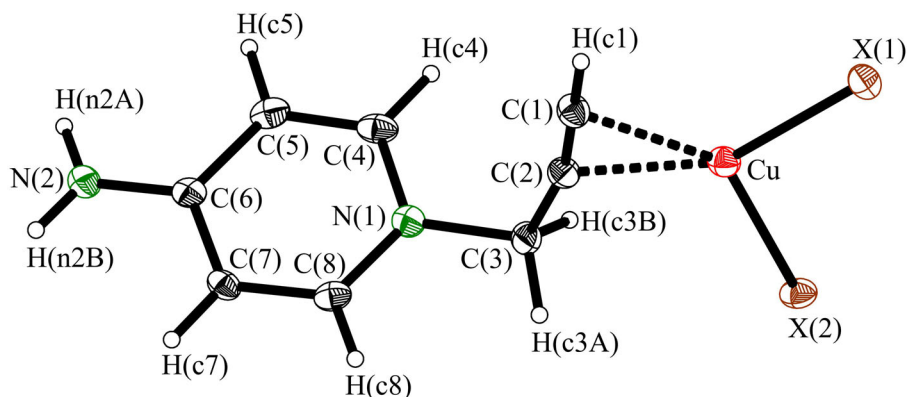
[(HC≡CCH<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)CuBr<sub>2</sub>] (**1**): IR (UR-20 spectrometer, 3800–400 cm<sup>-1</sup>, KBr pellet) – 3167 (H–C≡), 1992 (C≡C), 1554 (N–H), 516 (Cu–C). Anal. Calc. – C (26.93), H (2.52), N (7.85), Cu (17.82), Br (44.88); Found – C (27.01), H (2.59), N (7.79), Cu (17.71), Br (44.90).

[(HC≡CCH<sub>2</sub>NC<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)CuCl<sub>1.61</sub>Br<sub>0.39</sub>] (**2**): IR (UR-20 spectrometer, 3800–400 cm<sup>-1</sup>, KBr pellet) – 3163 (H–C≡), 1978 (C≡C), 1560 (N–H), 518 (Cu–C). Anal. Calc. – C (33.71), H (3.16), N (9.83), Cu (22.30), Cl (20.07), Br (10.95); Found: C (34.01), H (3.20), N (9.75) Cu (22.40), Cl (21.49), Br (9.15) (The KFK-2 colorimeter was used to determine the Cu contents in **1** and **2**).

#### 2.4. X-ray crystal structure determination

X-ray diffraction data for the zwitterionic  $\pi$ -coordination compounds **1** and **2** were collected on the Xcalibur Onyx diffractometer with Mo  $K_{\alpha}$  radiation. The collected diffraction data were processed with the CrysAlis program [31]. Both structures were solved with direct methods, applying ShelXS software package [32]; all localized atoms were refined by least squares method on  $F^2$  by ShelXL [33] with the graphical user interface of OLEX<sup>2</sup> [34].

Displacement parameters for non-hydrogen atoms were refined using an anisotropic model. Hydrogens (except  $\equiv$ C-bonded H1 in **2**) were placed in ideal positions and refined as riding with relative isotropic displacement parameters. The



**Figure 1.** The atom numbering scheme for the asymmetric part of **1** (X(1) and X(2) positions are occupied by 100% Br and **2** (X(1) and X(2) positions are occupied by mixture of 81.5(3)% Cl + 18.5(3)% Br and 79.5(3)% Cl + 20.5(3)% Br, respectively). Thermal ellipsoids are displayed at the 50% probability level for non-hydrogen atoms.

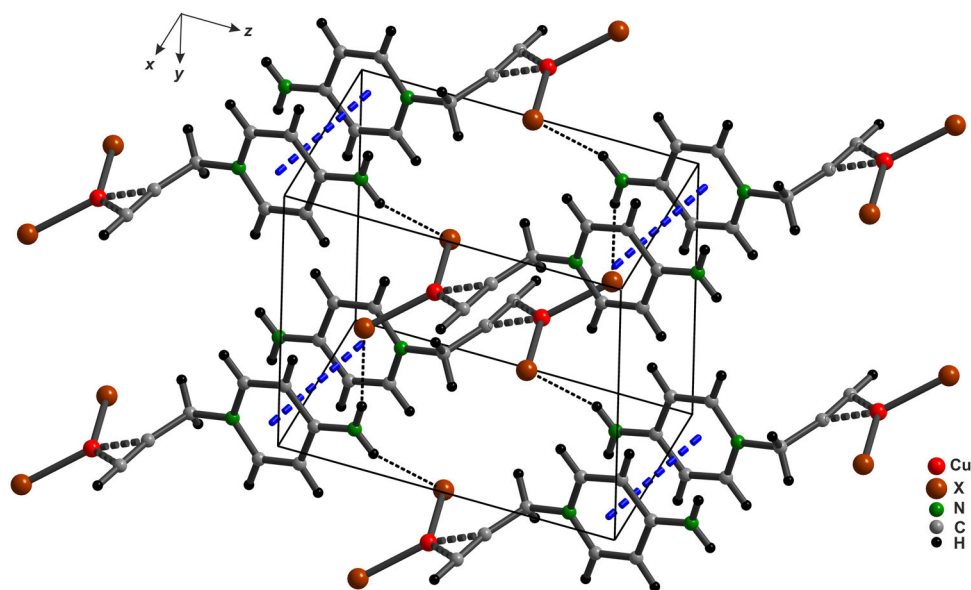
**Table 3.** DFT calculated energies for  $[(app)CuCl_2]$  and its separate parts.

Structural moiety	Total energy, $\text{kJ}\cdot\text{mol}^{-1}$	Binding energy, $\text{kJ}\cdot\text{mol}^{-1}$	Sum energy of all bonds, $\text{kJ}\cdot\text{mol}^{-1}$
$[(H_2NC_5H_4NCH_2C\equiv CH)CuCl_2]$	-436880	-35549	9244.2
$H_2NC_5H_4N^+CH_2C\equiv CH$	-216477	-32353	8619.2
$CuCl_2^-$	-219182	-1805	576.0

crystallographic parameters and details of X-ray data collection for **1** and **2** are presented in Table 1. The position parameters of atoms and their thermal parameters for **1** and **2** are given in Tables S1 and S2, respectively. Selected bond lengths and angles for both compounds are presented in Table 2. Figures of the structures were drawn using DIAMOND 3.1 software [35]. The structural unit and crystal packing of the zwitterionic  $\pi$ -coordination compounds are presented in Figures 1 and 2, respectively.

## 2.5. DFT studies

Considering that concentrated aqueous solutions of  $NH_4Cl$  (or salts of organic amines) and  $CuCl$ , in comparison with solutions of other copper(I) halides, are able to more efficiently catalyze the conversion of  $C_2H_2$  and its terminal derivatives [1,2,7], it was important to know how the electron density is distributed in coordination compounds of copper(I) chloride with monosubstituted acetylene homologues, which are formed as intermediates in such catalytic systems. In this regard, a quantum chemical calculation of the electronic structure of **1** and **2** was carried out using the model  $\pi$ -complex  $[(app)CuCl_2]$  as an example. DFT calculations (the restricted Hartree–Fock (RHF) method with a 6-31G\* orbital basis set) were performed at the B3LYP level using the HyperChem program version 8.0.6 [36]. The crystal structure parameters of **2** were used as starting data to construct both the  $[(app)CuCl_2]$  complex and 4-amino-1-propargylpyridinium cation. A charge density distribution on atoms was calculated without a geometrical optimization of the structural fragments of  $[(app)CuCl_2]$  and  $app^+$ . All calculations were based on the assumption that  $[(app)CuCl_2]$  and  $app^+$  are in vacuum



**Figure 2.**  $\pi$ - $\pi$  Stacking and hydrogen bonds in **1** and **2**.

as isolated species. DFT calculated values of energies for the model complex and its separate species are given in Table 3.

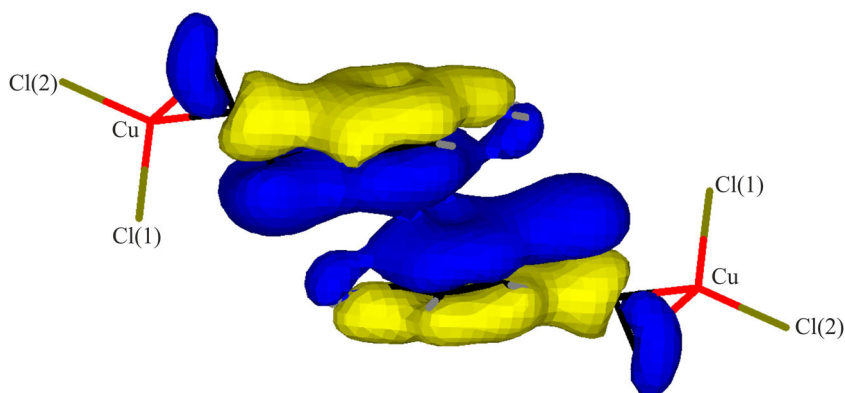
### 3. Results and discussion

#### 3.1. Structure-forming role of 4-aminopyridinium monosubstituted alkynes

Copper(I) halides are known to be practically insoluble in water and alcohols, but soluble in concentrated aqueous or aqueous-alcohol solutions of ammonium halides, alkali metal halides or organic amine halides. The characteristic feature of these concentrated solutions is the formation of a large variety of polynuclear  $[\text{Cu}_m\text{Cl}_n]^{(n-m)-}$  complexes [37]. In the course of the interaction of alkynes with the concentrated solutions (e.g. under conditions of the *Nieuwland's* oligomerization of acetylene), alkyne molecules form  $\pi$ -metalorganic compounds with these  $[\text{Cu}_m\text{Cl}_n]^{(n-m)-}$  anions. In our case, the *appBr* compound plays the role of both an ammonium halide (to increase the solubility of  $\text{CuX}$ ) and an alkyne (to  $\pi$ -coordinate to a metal center of  $[\text{Cu}_m\text{Cl}_n]^{(n-m)-}$ ).

Both crystal structures (**1** and **2**) consist of mononuclear discrete units –  $[(\text{app})\text{CuX}_2]$  (see Figure 1) that is similar to the previously studied  $[(\text{etmpH})\text{CuX}_2]$   $\pi$ -coordination compound [19]. Their formation is predetermined by mode of coordination ( $\eta^2$ -mode) of the potentially  $\pi$ -bidentate  $\text{C}\equiv\text{C}$  group of  $\text{app}^+$  with copper(I). The coordination polyhedron of Cu(I) in the  $[(\text{app})\text{CuX}_2]$  discrete unit has a trigonal planar form consisting of the  $\pi$ -coordinated  $\text{C}\equiv\text{C}$  bond and two halide ions. Such a trigonal planar environment of Cu(I) favors the efficient Cu(I)–( $\text{C}\equiv\text{C}$ ) bonding that is confirmed by fairly short Cu–*m* distances (*m* is the middle of the  $\text{C}\equiv\text{C}$  bond) which are 1.933(5) and 1.917(3) Å for **1** and **2**, respectively. For comparison, the Cu–*m* distances are 1.960(6) Å ( $\text{X}=\text{Br}$ ) and 1.923(9) Å ( $\text{X}=\text{Cl}$ ) in polynuclear zwitterionic  $\pi$ -complexes of





**Figure 3.**  $\pi$ - $\pi$  Interaction of the delocalized  $\pi$ -bonds of the 4-aminopyridinium rings in pair of neighboring  $[(\text{app})\text{CuCl}_2]$  units.

propargylammonium ( $[(\text{HC}\equiv\text{CCH}_2\text{NH}_3)\text{CuX}_2]$ ) [21], with Cu(I) ions in the trigonal-pyramidal environment.

Because of the  $\eta^2$ -coordination, the basic geometrical parameters of  $\text{app}^+$  propargyl group undergo certain changes (Table 2). The  $\text{C}\equiv\text{C}$  bond lengthens to 1.206(7) and 1.218(4) Å for **1** and **2**, respectively (for comparison, the lengths of the non-coordinated  $\text{C}\equiv\text{C}$  bonds in structures of propargylammonium bromide, propargylammonium chloride and propargylammonium hexafluorosilicate are 1.194, 1.166 [38] and 1.161 Å [39], respectively). The values of the  $\text{C}(1)\equiv\text{C}(2)-\text{C}(3)$  angles in **1** and **2** are 166.0(5) and 167.3(3)°, respectively, which is different from expected in free alkynes (180° value).

It is interesting to discuss here the superposition of forces which result in the supramolecular organization of **1** and **2**. First of all, it is important to note that in the case of a zwitterionic structure (that is, when a positive charge of such a complex is formally located on the N atom of the pyridine ring, and a negative charge is on the halide ions), the ionic interaction determines relative orientations of the discrete fragments in crystal structures of these coordination compounds. In most cases, the formation of polynuclear  $\pi$ -complexes of copper(I) halides often is as a result of the implementation of the  $\mu$ -X bridge function, *i.e.*, through formation of weak contacts  $\text{Cu}-\text{X}\cdots\text{Cu}$  [7]. Cu(I) ions in such polynuclear complexes mostly possess trigonal-pyramidal coordination consisting of two halide ions and the  $\text{C}\equiv\text{C}$ -group of alkyne in the base of the pyramid and another halide ion in the apical position ( $X_{\text{ap}}$ ). However, the mononuclear units with the trigonal planar coordination of Cu(I) are realized in **1**, **2** and  $[(\text{etmpH})\text{CuX}_2]$ . Among the  $\pi$ -complexes of  $\text{CuX}$  with monosubstituted alkynes, such a type of coordination occurs rarely. The  $\text{Cu}\cdots X_{\text{ap}}$  distances that appear between Cu(I) and halide ions of two closest neighboring discrete  $[(\text{app})\text{CuX}_2]$  units are 3.608(2) and 3.560(2) Å for **1** and **2**, respectively. Each of the values exceeds the respective sum of the van der Waals atomic radii ( $r_{\text{v}}(\text{Cl})+r_{\text{v}}(\text{Cu})=3.15$  Å,  $r_{\text{v}}(\text{Br})+r_{\text{v}}(\text{Cu})=3.25$  Å) [40]. But even such long and consequently weak  $\text{Cu}\cdots X_{\text{ap}}$  interactions lower the energy of the system. In turn, the trigonal planar coordination of Cu(I) is accompanied by a subtle displacement of the copper ion from the plane of the equatorial ligands ( $\Delta$ ) to the remote  $X_{\text{ap}}$  ligand ( $\Delta=0.024$  and 0.027 Å for **1** and **2**, respectively). Unlike **1** and **2**,

**Table 4.** Hydrogen bonding parameters (Å and °) in **1** and **2**.

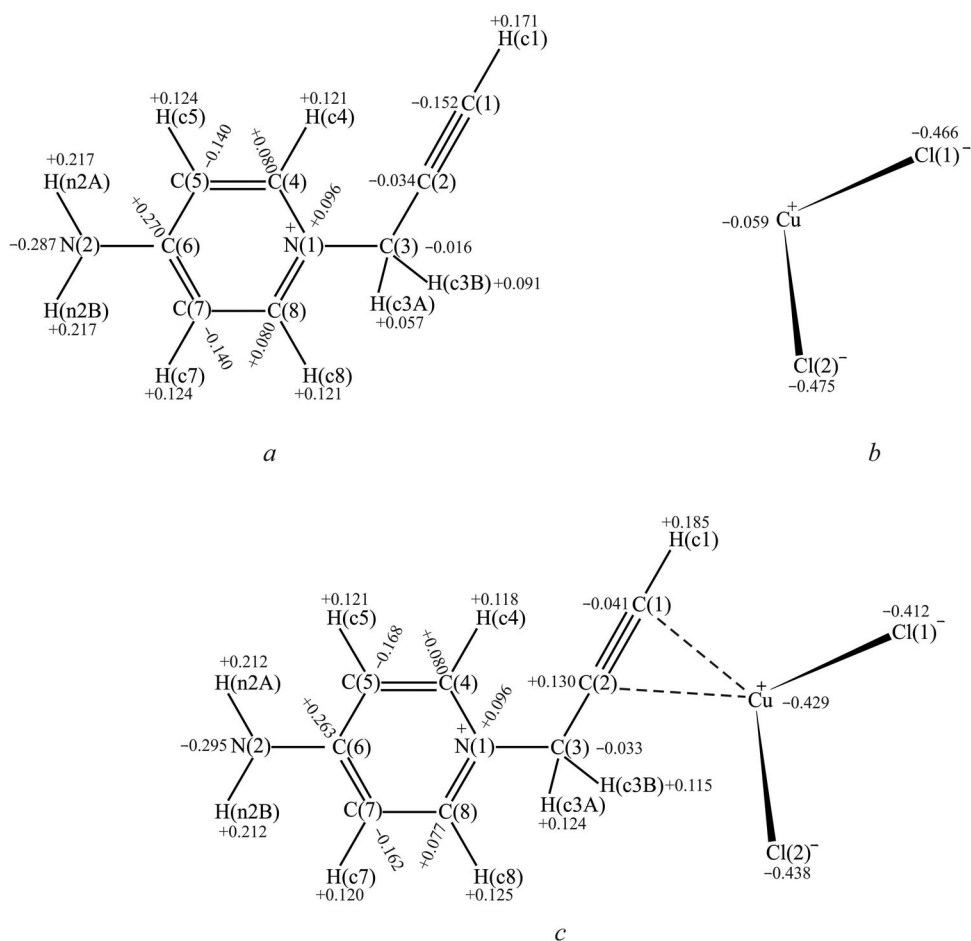
H-bond <sup>a</sup>	D–H	H...A	D...A	D–H...A
<b>1</b>				
N(2)–H(n2A)···Br(1) <sup>i</sup>	0.88(6)	2.59(6)	3.440(4)	162(5)
N(2)–H(n2B)···Br(2) <sup>ii</sup>	0.88(6)	2.78(6)	3.477(4)	138(5)
≡C(1)–H(c1)···Br(2) <sup>iii</sup>	0.90(6)	2.85(6)	3.674(5)	154(5)
<b>2</b>				
N(2)–H(n2A)···X(1) <sup>i</sup>	0.88(2)	2.44(1)	3.294(3)	163(1)
N(2)–H(n2B)···X(2) <sup>ii</sup>	0.88(2)	2.62(1)	3.352(3)	141(1)
≡C(1)–H(c1)···X(2) <sup>iii</sup>	0.95(2)	2.64(1)	3.571(3)	167(1)

<sup>a</sup>Symmetry codes: (i)  $x, -1+y, 1+z$ ; (ii)  $x, y, 1+z$ ; (iii)  $1+x, y, z$ .

the Cu···Cl<sub>ap</sub> distance in the [(*etmp*H)CuCl<sub>2</sub>] structure exceeds 6 Å and the  $\Delta$  value is smaller, 0.004 Å.

The *app*<sup>+</sup> demonstrates special structural-organization possibilities; this cation is able to form the zwitterionic mononuclear  $\pi$ -complexes with CuX. On the other hand, the steric factor of the bulky organic ligand, seemingly, plays an important role in formation of the mononuclear structures, but it is unlikely that it is decisive. There are many examples of the zwitterionic  $\pi$ -complexes of copper(I) halides with bulky ligands which nevertheless do not impede formation of binuclear structural units [41]. For example, 1-allyl-4-aminopyridinium cation being the close analog of *app*<sup>+</sup> forms the binuclear complex with CuX, whereas cations of 1-allyl-2-aminopyridinium and 1-allyl-3-aminopyridinium yield the polynuclear  $\pi$ -coordination compound [42]. In such compounds, 4-amino derivatives of pyridine have higher symmetry in comparison with 2-amino or 3-amino pyridine derivatives and their alternatively charged poles are on the opposite sides of the pyridine ring. In the final analysis it provides efficient  $\pi$ - $\pi$  stacking of the aromatic rings of 4-aminopyridinium cations in the crystal packing. When stacking the  $-N^+C_5H_4-NH_2$  groups in the crystal lattices of **1** and **2**, the nitrogen of the amino group bearing a partial negative charge orients to a positively charged nitrogen of the adjacent pyridinium ring, and *vice versa*. In this manner, the  $\{[(app)CuX_2]\}_2$  centrosymmetric pairs pack into peculiar one-dimensional columns oriented along the [100] direction (see Figure 2). The distances between planes of pyridinium rings within the  $\{[(app)CuX_2]\}_2$  pair are 3.426(7) and 3.370(4) Å for **1** and **2**, respectively, and the distances between their centroids are 4.237(7) Å (for **1**) and 4.147(4) Å (for **2**). However, the distances between planes of pyridinium rings of adjacent pairs are 3.600(7) Å (for **1**) and 3.521(4) Å (for **2**) and the distances between their centroids are 3.686(7) and 3.674(4) Å for **1** and **2**, respectively. The interaction of 4-aminopyridinium groups in copper(I) halide coordination compounds with 1-allyl-4-aminopyridinium [41], that have the same stoichiometry as **1** and **2**, results in similar geometric parameters. The analogous distances between planes of the pyridinium rings in [(1-allyl-4-aminopyridinium)CuX<sub>2</sub>] are bigger by 5–6%, and the distances between their centroids are shorter by 1–5% as compared to **1** and **2**. Partial overlap of the delocalized  $p_z$ -orbitals of aromatic rings in [(*app*)CuCl<sub>2</sub>] favors efficient  $\pi$ - $\pi$  stacking. The  $\pi$ - $\pi$  interaction between delocalized  $\pi$ -bonds of the pair of 4-aminopyridinium rings calculated for the zwitterionic  $\pi$ -complex of [(*app*)CuCl<sub>2</sub>] is represented in Figure 3.

Like most structurally studied alkyne  $\pi$ -complexes with copper(I) halides, the crystal structures of **1** and **2** are also stabilized by strong hydrogen bonds of the type

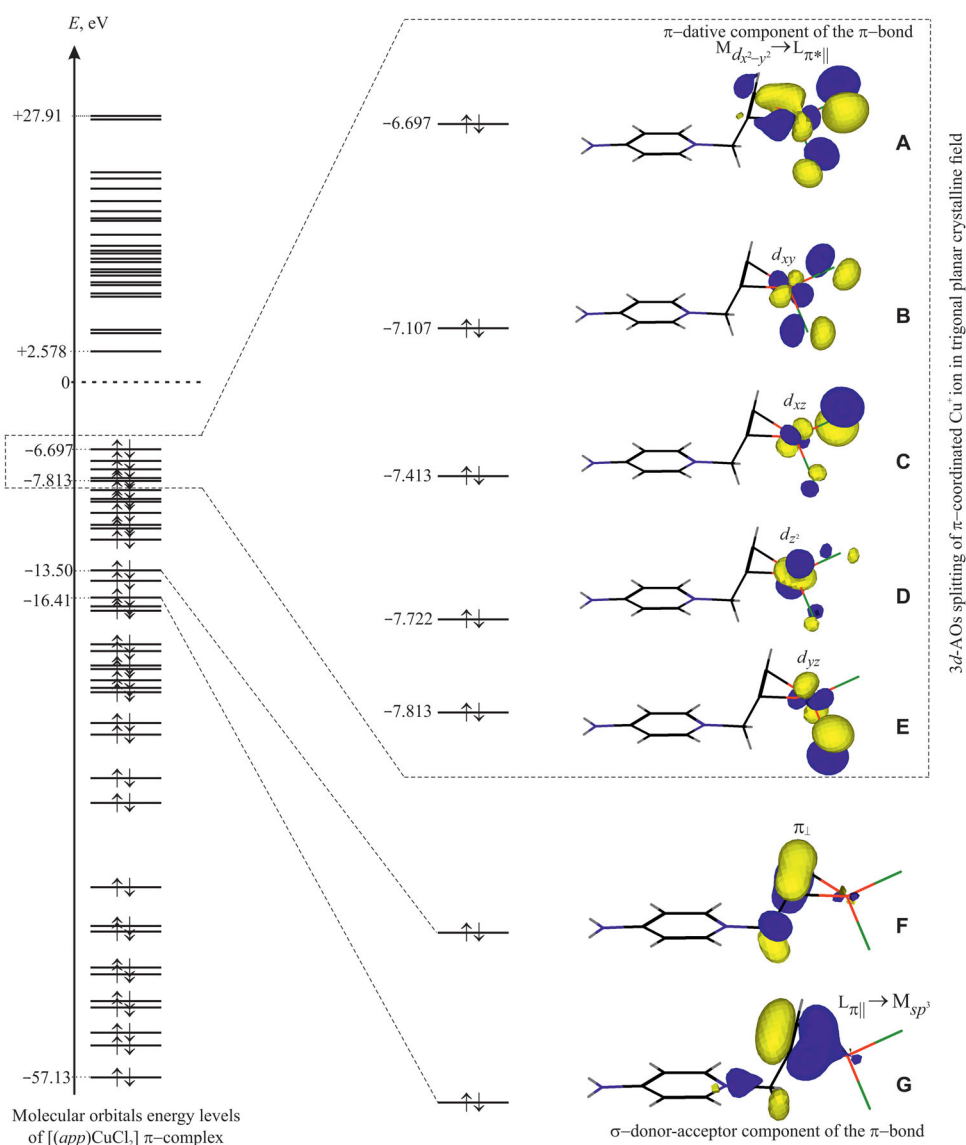


**Figure 4.** Charge density ( $\pm\delta, \bar{e}$ ) distribution on atoms in  $app^+$  (a),  $CuCl_2^-$  (b) and  $[(app)CuCl_2]$  (c).

$\equiv C-H \cdots X^-$  (Table 4). Furthermore, the structural units in **1** and **2** are cross-linked by hydrogen bridges of the  $N-H \cdots X^-$  type [43,44]. But, in spite of the fact that in **1** and **2** the  $-NH_2$  group of  $app^+$  is non-protonated, the  $NH \cdots X^-$  hydrogen bonds are efficient. With regards to the geometric parameters of hydrogen bonds in **1** and **2**, these are almost the same as  $N-H^+ \cdots X^-$  interactions, which are observed in the structures of copper(I) halide  $\pi$ -complexes with propargylammonium, whose amino groups are protonated [21,22]. This can be explained by redistribution of the electron density within the  $app^+$  species owing to the conjugation of the delocalized  $\pi$ -bonds of the aromatic ring with the non-hybrid  $p$ -orbital on the N atom of the amino group. This explains why the H–N–H fragment and the ring of the pyridinium cation are coplanar.

### 3.2. Electron preconditions for zwitterionic $\pi$ -complexes formation

$Cu(I)-(C \equiv C)$   $\pi$ -bonding alters electronic parameters of the  $\pi$ -coordinated  $app^+$  ion as compared with a free (non-coordinated)  $app^+$  ion. The DFT calculations performed for  $[(app)CuCl_2]$  reveal that the electron density of carbons of the  $C \equiv C$  bond within the



**Figure 5.** The diagram of MOs, constructed for the  $[(app)CuCl_2]$  (left) and the  $3d$ -AOs splitting of the  $\pi$ -coordinated  $Cu^+$  ion in trigonal planar crystalline field (right).

$\pi$ -coordinated core efficiently shifts to  $Cu(I)$ . So, the charge density values ( $\delta$ ) on C(1) and C(2) for a non-coordinated  $app^+$  are  $-0.152$  and  $-0.034 \bar{e}$ , respectively, and the  $\delta$  value for  $Cu^+$  of  $CuCl_2^-$  is  $-0.059 \bar{e}$  (Figure 4a,b). However, the charge density on the carbon atoms of the  $\pi$ -coordinated  $C\equiv C$  bond of  $[(app)CuCl_2]$  is decreased whereas the electron density on the  $\pi$ -coordinated  $Cu^+$  ion is increased; the  $\delta$  values for the C(1) and C(2) atoms are  $-0.041$  and  $+0.130 \bar{e}$ , respectively, and  $\delta = -0.429 \bar{e}$  for Cu ion (Figure 4c).

According to the Dewar–Chatt–Duncanson concept [2,45,46], the formation of alkyne  $\pi$ -complexes with  $Cu(I)$  (having the  $3d^{10}4s^04p^0$  valence state) salts is

accompanied by interaction of the frontier MOs of alkyne with MOs of metal complexes (e.g.  $\text{CuCl}_2^-$ ), resulting in two three-center MOs (Figure 5). One of them is formed by overlap of the unoccupied  $sp^3$ -hybridized orbital of the M with the bonding  $\pi_{||}$ -MO of alkyne (the donor-acceptor component of the  $L\pi_{||} \rightarrow Msp^3$  bond (Figure 5, fragment **G**), where M is Cu(I) and L is alkyne ( $app^+$ ), whereas the other MO is formed owing to an overlap of the symmetrical occupied  $d_{x^2-y^2}$ -orbital of Cu(I) and the antibonding  $\pi_{||}^*$ -MO of alkyne (the dative component of the  $Md_{x^2-y^2} \rightarrow L\pi_{||}^*$  bond (Figure 5, fragment **A**)). Both three-center bonds promote the Cu(I)-(C≡C) bond strengthening (the  $E_{\text{Cu(I)-(C}\equiv\text{C})}$  calculated for the  $[(app)\text{CuCl}_2]$   $\pi$ -complex is  $49.2 \text{ kJ}\cdot\text{mol}^{-1}$ ). However, these two three-center bonds influence the properties of the  $\pi$ -coordinated ligand differently. Even a negligible shift of the electron density from the occupied 3d atomic orbitals (AOs) of Cu(I) to the antibonding  $\pi_{||}^*$ -MO of alkyne results in C≡C-R bond angle distortion (*cis*-distortion) and minor C≡C bond lengthening that is seen in **1** and **2** (see Table 2). Electron donation from  $\pi_{||}$ -MO of alkyne to one of the unoccupied  $sp^3$ -hybrid orbitals of Cu(I) decreases the electron density of the C≡C bond and each carbon acquires a certain positive charge ( $\delta^+$ ) (see Figure 4). In this case the  $\pi$ -coordinated C≡C group acts like a soft electrophilic agent. The C≡C group compared with the C=C group exhibits both weaker electron-donor and electron-acceptor properties in the ground state; the two highest occupied molecular orbitals (HOMOs) of the C≡C group are degenerate and have lower level energy than the only HOMO of the C=C group and the two lowest unoccupied molecular orbitals (LUMOs) of the C≡C group have higher energy than the only LUMO of the C=C group [2,7]. When deforming the C≡C-R, resulting from Cu(I)-(C≡C) coordination, the electron-donor and electron-acceptor properties of the C≡C group increase causing a split of *d*-orbitals of  $\pi$ -coordinated Cu(I). In addition, the Cu(I)-(C≡C)  $\pi$ -interaction results in a split of the two degenerate  $\pi$ -MOs of the C≡C bond onto  $\pi_{||}$ -MO and  $\pi_{\perp}$ -MO having different energies (see Figure 5, fragments **F** and **G**).

In turn, the Cu(I)-(C≡C) bonding taking place in the  $\pi$ -complexes **1** and **2** causes deformation of the initial tetrahedral coordination of Cu(I), peculiar to copper(I)  $\sigma$ -compounds (for example, in the structure of CuCl), towards trigonal planar [7,47]. The deformation of the coordination polyhedron entails an electron density deficiency on the  $d_{x^2-y^2}$  orbital of Cu(I) due to its interaction with the antibonding  $\pi_{||}^*$ -MO of the C≡C group. On the contrary, the antinode of another  $d_{z^2}$ -orbital is directed towards the remote axial ligand (e.g.  $\text{Cl}_{\text{ax}}$ ) (Figure 5, fragment **D**), thus the  $d_{z^2}$ -orbital acquires the residual electron density. Hence, the Cu(I)-(C≡C) interaction is accompanied by shortening of the distances from copper(I) to the ligands located in the base of the pyramid and by lengthening of the Cu(I)- $X_{\text{ax}}$  bond, i.e. Cu(I) is shifted towards the ligands being in the base of the coordination polyhedron. The more efficient the dative component of the  $\pi$ -bond, the more substantial is the deformation of polyhedron. The Cu-*m* distance is also shortened due to the synergism of the  $[L \rightarrow \text{Cu(I)}]_{\sigma}$  and  $[\text{Cu(I)} \rightarrow L]_{\pi}$  components of the  $\pi$ -bond.

Thus, the coordination polyhedron of Cu(I) produces the trigonal planar crystalline field of the ligands removing the degeneracy of the 3d AOs of Cu(I). The MO diagram of the  $[(app)\text{CuCl}_2]$  zwitterionic  $\pi$ -complex as well as the split of 3d-AOs by trigonal planar crystalline field are presented in Figure 5. According to crystal field theory [48],

the degenerate  $d$ -AOs in tetrahedral crystal field are split into two sets of AOs with different energy levels. There are such splitting parameters in the tetrahedral crystal field: the doubly degenerated  $d_{z^2}$ ,  $d_{x^2-y^2}$  AOs are characterized by lower level energy, whereas the triply degenerate  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  AOs have higher energy. In  $[(app)CuCl_2]$  owing to the  $\pi$ -coordination, the split parameters in the trigonal planar crystal field acquire somewhat different sequence of the split  $3d$ -AOs. The sequence of the levels is the following:  $d_{yz} < d_{z^2} < d_{xz} < d_{xy} < d_{x^2-y^2}$  (see Figure 5, fragments **A**, **B**, **C**, **D** and **E**).

#### 4. Conclusion

The experimental data analysis obtained in crystal structures of two zwitterionic mononuclear  $\pi$ -coordination compounds of copper(I) halides with the 4-amino-1-propargylpyridinium cation –  $[(app)CuBr_2]$  (**1**) and  $[(app)CuCl_{1.61}Br_{0.39}]$  (**2**) – along with the quantum-chemical calculations of the electronic structure of the model  $[(app)CuCl_2]$   $\pi$ -complex have indicated specific features of the coordination chemistry of copper(I) halide  $\pi$ -complexes with monosubstituted alkynes. The influence of  $\pi$ - $\pi$  stacking of 4-aminopyridinium rings and the  $\equiv C-H \cdots X^-$  or  $N-H \cdots X^-$  hydrogen bridges on crystal structures of the zwitterionic  $\pi$ -complexes is considered.

The Cu(I) polyhedron geometric parameters in **1** and **2** determined by the efficient Cu(I)–(C $\equiv$ C) interaction are in agreement with the hypothesis that during  $\pi$ -coordination two degenerate  $\pi$ -MOs of the C $\equiv$ C of alkyne are split into two MOs ( $\pi_{||}$  and  $\pi_{\perp}$ ) with different energy levels. Owing to the C $\equiv$ C bond activation, the alkyne becomes more reactive. The synergism of the  $[(C\equiv C) \rightarrow Cu(I)]_{\sigma}$  and  $[Cu(I) \rightarrow (C\equiv C)]_{\pi}$  components of the Cu(I)–(C $\equiv$ C) bond results in split of the  $3d$ -AOs of the  $\pi$ -coordinated Cu ion onto five energy levels ( $d_{yz} < d_{z^2} < d_{xz} < d_{xy} < d_{x^2-y^2}$ ).

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#### Disclosure statement

No potential conflict of interest was reported by the authors.

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