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Coordination behaviour of N,N′-diallylpiperazinium(2+) and N-allylhexamethylenetetraminium in their crystalline π-complexes with ionic copper(I) salts

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This brief review discusses the coordination behaviour of π-coordinated copper(I) in the structures of $[Cu_2(\mu\text{-}dapp)(NH_2SO_3)_4]\cdot 2H_2O$ (**1**), $[C_4H_{12}N_2][Cu_2(\mu\text{-}dapp)(NH_2SO_3)_6]\cdot 2H_2O$ (**2**), $[Cu_2(\mu\text{-}dapp)(H_2O)_6](SiF_6)_2\cdot 2H_2O$ (**3**), $[Cu_2(\mu\text{-}dapp)(NO_3)_4(H_2O)_2]\cdot 2H_2O$ (**4**), $[Cu(\mu\text{-}ahmta)(NO_3)(H_2O)](NO_3)\cdot H_2O$ (**5**), and $[Cu(\mu\text{-}ahmta)(H_2O)_2](BF_4)_2\cdot H_2O$ (**6**) complexes (*dapp* = N,N′-diallylpiperazinium(2+), ahmta = N-allyl-hexamethylenetetraminium), obtained as single crystals by means of an alternating current electrochemical technique. The above π-complexes are formed respectively by $CuSO_3NH_2$, Cu_2SiF_6, $CuNO_3$, and $CuBF_4$ salts, unknown in a free state.

Key words: *diallylpiperazinium(2+); N-allylhexamethylenetetraminium; copper(I) π-complexes*

1. Introduction

Crystal engineering is delineated by the nature and structural consequences of intermolecular forces and by the way in which such interactions are utilized for controlling the assembly of molecular building blocks into infinite architectures [1]. The most considerable recent advances in crystal engineering have been achieved within the framework design because it is possible to simplify complex crystalline structural features into easily identifiable network topologies based on the chemical and structural information of the constituent molecular tectons (building blocks) [2, 3]. Although significant progress has been made on the theoretical front of crystal engineering, structure prediction with theoretical tools has met with less success compared to network-based approaches [4, 5]. Since modelling intermolecular forces

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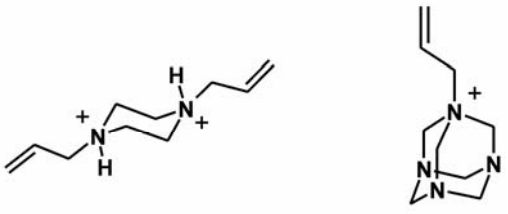
and cooperative effects in order to calculate crystalline lattice energies is a very difficult task, it is impossible to quantify intermolecular forces and atomic charges precisely. One can, however, estimate the directional preferences of molecules through electrostatic interactions [6]. It is obvious that crystal structure, which is not combined from simple tectons, is more difficult to predict and design, because it is still unkown which factors determine the structure formed. Only wider crystal chemistry investigations of organometallic architectures can help in this case.

Supramolecular motifs containing an olefin–copper(I) bond as a bridging spacer have recently attracted much attention [7]. Copper(I)–olefin π-complexes are involved in the preparation and reactions of olefin and alkyne complexes [8–10], as catalytically active species in copper-catalyzed reactions [11, 12], and as agents for selective olefin/paraffin separations [13, 14].

Our previous studies on copper(I) halide complexation with N,N′-diallylpiperazinium(2+) (*dapp*) [15] and N,N,N′,N′-tetraallylpiperazinium(2+) [16] cations revealed unusual coordination behaviour of the ligands: Cu(I)–(C=C) interaction does exist in the presence of Cl atoms and is absent in the case of Br. Such a dissimilarity is not displayed in copper(I) halide complexes with aliphatic olefin derivatives (e.g., copper(I) chloride and bromide form π-complexes with diallylammonium halide [17–20]) or with aromatic heterocyclic derivatives [21, 22].

On the other hand, the dimorphism of copper(I) chloride complexes with N-allylhexamethylenetetraminium (*ahmta*) chloride – $[(\mu_3\text{-}ahmta)Cu_2Cl_3]$ and $[(\mu\text{-}ahmta)Cu_2Cl_3]$ [23] – is a result of the different roles of the ligand: *ahmta* acts as a σ,σ,π- and σ,π-ligand, respectively.

In connection to this, we consider the coordination behaviour of *dapp* and *ahmta* moieties in $[Cu_2(\mu\text{-}dapp)(NH_2SO_3)_4]\cdot 2H_2O$ (**1**), $[C_4H_{12}N_2][Cu_2(\mu\text{-}dapp)(NH_2SO_3)_6]\cdot 2H_2O$ (**2**) [24], $[Cu_2(\mu\text{-}dapp)(H_2O)_6](SiF_6)_2\cdot 2H_2O$ (**3**), $[Cu_2(\mu\text{-}dapp)(NO_3)_4(H_2O)_2]\cdot 2H_2O$ (**4**), $[Cu(\mu\text{-}ahmta)(NO_3)(H_2O)]\cdot(NO_3)\cdot H_2O$ (**5**), and $[Cu(\mu\text{-}ahmta)(H_2O)_2](BF_4)_2\cdot H_2O$ (**6**) [25] π-complexes, which we have recently obtained and structurally investigated by X-ray diffraction. The ligand moieties are presented in Fig. 1.



a) b)

Fig. 1. Schematic view of the cations:
a) N,N′-diallylpiperazinium(2+) (*dapp*),
b) N-allylhexamethylenetetraminium (ahmta)

2. Results

Synthetic aspects. Crystalline π-complexes (**1**, **3–6**) were obtained by means of an alternating-current electrochemical technique [26]:

$$LX + CuX_2 \cdot nH_2O + Cu^0 \xrightarrow{C_2H_5OH,\ [\bar{e}]} L_aCu^I{}_bX_c \cdot dH_2O$$

L = *dapp*, *ahmta*; X = $1/2\,SiF_6^{2-}$, NO_3^-, $NH_2SO_3^-$ and BF_4^-. Compound **2** was formed under conditions described in [24].

One may note that although Cu_2SiF_6, $CuNO_3$, $CuNH_2SO_3$, and $CuBF_4$ are unknown in a free state, they can exist in the form of stable complexes due to relatively strong Cu(I)–(C=C) π-interactions. A brief structural survey of the compounds follows.

Structure of $[Cu_2(\mu\text{-}dapp)(NH_2SO_3)_4]\cdot H_2O$ (1). The centrosymmetric cation of diallylpiperazinium(2+) in this structure acts as a bridge (Fig. 2). The C=C bonds of allylic groups are coordinated by copper(I) atoms at a distance of 1.919(4) Å. It is interesting that the C=C bond successfully competes with the nitrogen atoms of two sulfamate anions. Moreover, this bond is elongated to 1.368(6) Å. The oxygen atom of the sulfamate anion is located in the axial position of the trigonal-pyramidal copper(I) coordination environment at a distance of 2.574(3) Å. The deviation of the Cu atom from the equatorial plane (*Δ*) is 0.12 Å. Such a geometry of the coordination centre should be attributed to the effective Cu(I)–(C=C) interaction. The presence of the water molecule, which forms a strong hydrogen bond with the oxygen atoms of sulfamate anions (2.39(4)–2.51(5) Å) and weaker ones with the nitrogen atom of the H–N-group of the piperazine ring (2.750(4) Å), promotes the stabilization of the crystal structure as well as weaker contacts such as N(H)…O(NH_2SO_2) (2.854(5) –2.936(5) Å, 145(4)–178(5)°).

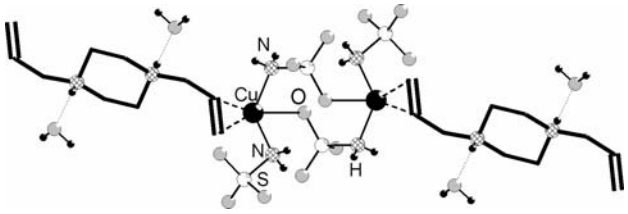


Fig. 2. A fragment of the infinite chain **1**

Structure of $[C_4H_{12}N_2][Cu_2(\mu\text{-}dapp)(NH_2SO_3)_6]\cdot 2H_2O$ (2). The structure of **2** contains centrosymmetric piperazinium(2+) and diallylpiperazinium(2+) cations. As before, the *dapp* cation plays a bridging function and forms dimers (Fig. 3). This is the first crystalline π-complex described where the coordination environment of copper(I) consists of three nitrogen atoms of $NH_2SO_3^-$ anions and a C=C bond. These nitrogen atoms in the tetrahedral coordination polyhedron of Cu(I), however, hinder

effective Cu(I)–(C=C) binding due to steric restrictions (Δ = 0.46 Å). An elongated distance *d*(Cu–*m*) 1.962(9) Å and imaginary abridgement of the coordinated C=C bond up to 1.29(2) Å are caused by a moderate disorder of this double bond.

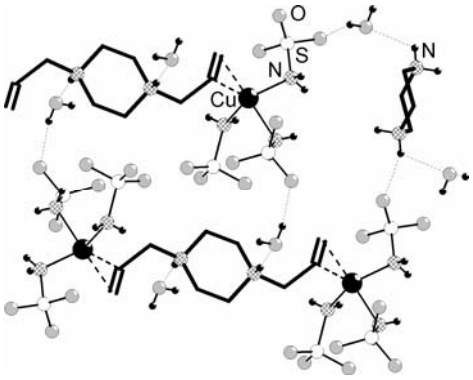


Fig. 3. The packing of $\{(O_3SH_2N)_3Cu(dapp)Cu(NH_2SO_3)_3\}$ dimers in structure **2** and the system of hydrogen bonds

The hydrogen bonds N–H…O (2.01(9)–2.36(7) Å, 140(8)–160(8)°) play a decisive role in the structure formation and withdraw electron density from the N atoms of sulfamat moieties. The latter circumstance allows Cu–(C=C) π-interactions to be realized even in the presence of three donor N atoms of sulfamate anions. The crystallization water molecule in this structure forms hydrogen bonds with both the oxygen atoms of sulfamate anions ((O_w)H...O 1.92(9)–2.12(6)Å, 155(8) –156(6)°) and with the H atoms of the piperazine(2+) core ((N)H...O_w 1.69(8) Å, 156(7)°).

Structure of $[Cu_2(\mu\text{-}dapp)(H_2O)_6](SiF_6)_2\cdot 2H_2O$ (3). The crystal structure of **3** contains only one independent Cu(I) atom. Its trigonal pyramidal coordination environment consists of three oxygen atoms (from H_2O molecules) and a double C=C bond of the ligand (see Table 1). The SiF_6^{2-} anion possesses an octahedral geometry (Si–F distances 1.652(9)–1.690(9) Å) and is involved only in the formation of hydrogen bonds. The small size of oxygen atoms as well as the stabilizing influence of strong H-bonds create conditions for very effective Cu–(C=C) π,σ-interaction. In reality, the Cu–*m* (*m* is the midpoint of a double C=C bond) distance is equal to 1.89(1) Å and the Cu atom is removed from the plane of equatorial ligands by only Δ = 0.17 Å. The length of the coordinated double bond equals 1.32(2) Å. Strong O–H...F hydrogen bonds (with distances *d*(H…F) 1.9(1)–2.3(1) Å and angles O–H...F 145(8)–162(9)°) withdraw excess electron density from the copper(I) atom and thus reduce a π-dative contribution. Due to the bridging function of the diallylpiperazinium(2+) cation (Fig. 4), the dimers $\{(H_2O)_3Cu(dapp)Cu(H_2O)_3\}$ are displayed in (3). They are combined into a three-dimensional framework by a branching network of

C–H...F and O–H...F hydrogen bonds. It is necessary to note that the molecule of crystallization water is held in the crystal structure by an effective N–H...O_{aq} hydrogen bond (the nitrogen atom belongs to the piperazine ring, *d*(H...O) is 1.8(2) Å, and the N–H...O_{aq} angle is 171(9)°).

Table 1. Selected distances and angles in the structures of **1–6** (*d*, Å and *ω*, °)

Structure	Parameter	Value	Structure	Parameter	Value
1	Cu–N2	2.030(4)	**4**	Cu–O_{aq}1	1.956(2)
	Cu–N3	2.040(3)		Cu–O2	1.991(1)
	Cu–O1	2.574(3)		Cu–O5	2.531(2)
	Cu–*m*1,2	1.919(4)		Cu–*m*4,5	1.884(2)
	C1–Cu–C2	39.2(1)		C4–Cu–C5	40.19(8)
	C1=C2	1.368(6)		C(4)=C(5)	1.379(3)
2	Cu–N3	2.101(6)	**5**	Cu–O11	2.033(2)
	Cu–N4	2.082(7)		Cu–N3	2.052(3)
	Cu–N5	2.295(6)		Cu–Ow1	2.241(3)
	Cu–*m*1,2	1.962(9)		Cu–*m*(1,2)	1.917(3)
	C1–Cu–C2	36.4(4)		C1–Cu–C2	39.7(1)
	C1=C2	1.29(2)		C1=C2	1.368(5)
3	Cu–O2	2.37(2)	**6**	Cu–O1	2.174(3)
	Cu–O3	1.989(9)		Cu–O2	2.032(2)
	Cu–O4	2.000(9)		Cu–N1	2.066(3)
	Cu–*m*1,5	1.89(1)		Cu–*m*1,2	1.921(4)
	C1–Cu–C5	38.5(5)		C1–Cu–C2	39.5(1)
	C1=C5	1.32(2)		C1=C2	1.374(5)

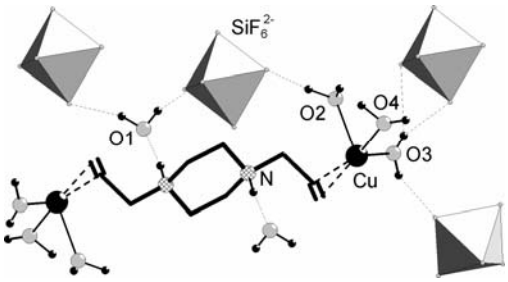


Fig. 4. {$(H_2O)_3$Cu(*dapp*)Cu$(H_2O)_3$} dimers and SiF_6^{2-} (octahedra) anions in the outer coordination sphere of crystal structure **3**

Structure of [Cu_2(μ-*dapp*)$(NO_3)_4(H_2O)_2$]·$2H_2O$ (4). The coordination polyhedron of the Cu(I) atom in π-complex **4** is a trigonal pyramid that contains a double C=C bond, a water molecule, an oxygen atom from a nitrate anion in the equatorial position, and one more oxygen atom of NO_3^- in the apical position (Table 1). Such ligands in the metal coordination environment promote an efficient Cu(I)–(C=C) interaction. A short copper–*m* distance of 1.884(4) Å is caused by the considerable axial

deformation of the coordination polyhedron (Cu–O5 2.531(2) Å), by the hard Lewis base in the apical position, and by the absence of steric restrictions. Although one of the hydrogen bonds (C5–H52...O3, 2.58(3) Å, 142(3)°) rotates the coordinated C=C group by an angle of 9.8°, this bond is elongated up to 1.379(3) Å nevertheless, which is evidence for significant π-dative interaction. The unusual small deviation of the Cu(I) atom from the plane of equatorial ligands (Δ = 0.05 Å) confirms a conclusion about the effective Cu(I)–(C=C) π-interaction, which one could explain by a specific unification of steric and electron factors in the formation of the copper(I) coordination sphere.

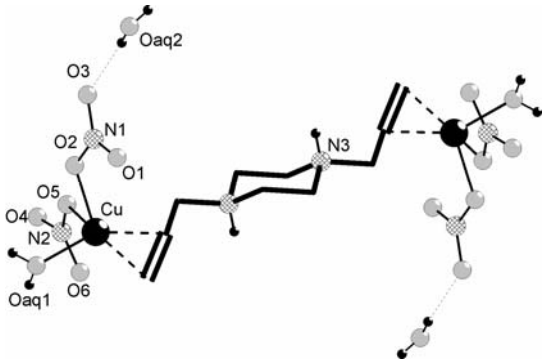


Fig. 5. The bridging function of *dapp* moiety in **4**

As a result of the bridging function of the diallylpiperazinium(2+) cation, structure **4** consists of {$(NO_3)_2(H_2O)Cu(\mu$-*dapp*$)Cu(H_2O)(NO_3)_2$} dimers (Fig. 5), which are integrated into a three-dimensional framework by a branching system of hydrogen bonds. In contrast to **1–3**, the crystallization water molecule here is held in the structure due to the hydrogen contacts of O_{aq}–H...O(–NO_2) and O_{aq}–H...O_{aq} (1.93(3) –2.22(3) Å, 154(3)–176(3)°). The H atom of the N–H-group takes part in a strong H-bond with the oxygen atom of the NO_3^- moiety (1.97(2) Å, 174(2)°). This hydrogen bond causes a lengthening of the N(2)–O(4) distance in the anion to 1.261(2) Å.

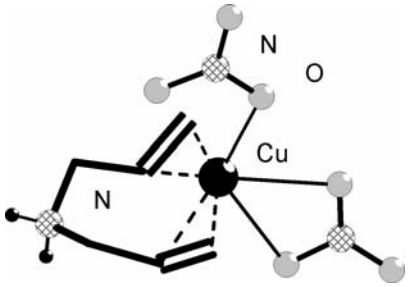


Fig. 6. The monodentate and bidentate functions of nitrate anions in the complex [Cu($(C_3H_5)_2NH_2$)$(NO_3)_2$]

Contrary to the above complex, in the case of dyallylammonium copper(I) dinitrate [27], NO_3^- moieties demonstrate a different coordination behaviour: one NO_3^- anion is monodentate, whereas the two oxygen atoms of the other nitrate anion are coordinated to the Cu(I) atom (Fig. 6).

Structure of [Cu(μ-ahtma)(NO_3)(H_2O)](NO_3)·H_2O (5). The Cu atom possesses a trigonal-pyramidal environment, formed by the oxygen atom of the nitrate anion, a nitrogen atom, and a C=C bond of adjacent *ahmta* cations in the equatorial plane. The apical position is occupied by the oxygen atom of the water moiety, so that *ahmta* acts as a bidentate bridging π,σ-ligand and connects Cu atoms into metal-organic chains lying along the [001] direction (Fig. 7). Water and nitrate moieties of the outer coordination sphere take part in the formation of a well-developed branched system of strong H-bonds (O_{aq}–H...O(–NO_2) 1.751(5)–2.051(5) Å, 157.3(1)–169.9(1)°; O_{aq}–H...O_{aq} 1.926(6) Å, 173.8(2)°). The latter unite metal-organic chains into a 3-D network. The pyramidal distortion of the coordination sphere, being rather moderate (Δ = 0.33 Å), corresponds to a slightly elongated Cu–Ow1 apical bond (2.241(3) Å) as compared to the ideal Cu^I–O distance of 1.99 Å [28].

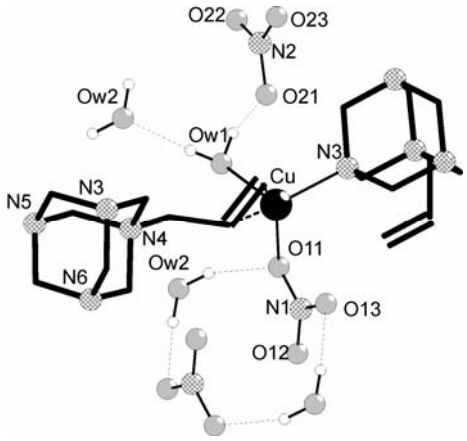


Fig. 7. The hydrogen bond system the structure **5**

It should be pointed out that one nitrate and one water moiety are situated in the inner coordination sphere and two others in the outer one.

Structure of [Cu(μ-ahtma)(H_2O)$_2$](BF_4)$_2$·H_2O (6). In this structure, one crystallographycally independent Cu atom possesses a reasonably deformed (Δ = 0.25Å) trigonal-pyramidal environment, formed by the oxygen atom of a water moiety, a nitrogen atom, and the C=C bond of adjacent *ahmta* cations in the equatorial plane. The apical position is occupied by the oxygen atom of another water moiety (Fig. 8). Similar to **5**, here *ahtma* also acts as a bidentate bridging π,σ-ligand that connects Cu atoms into metal-organic chains. Contrary to **5**, all anion moieties are in the outer coordination sphere, forming a branched network of strong H-bonds with

water molecules (O_{aq}–H...F 1.633(2)–2.026(4) Å, 142.3(2)–159.4(3)°). Tetrahedral BF_4^- are slightly disordered, because they are involved in weak interactions – van der Waals and F…H–O bonds.

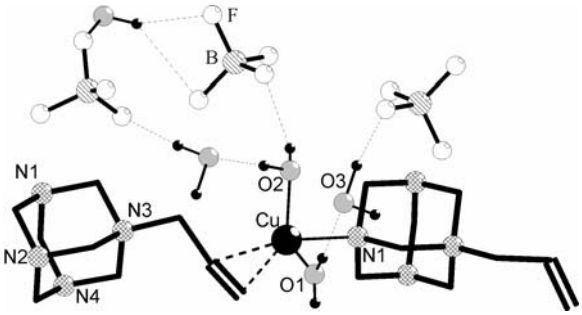


Fig. 8. The hydrogen bond system in structure **6**

3. Discussion

The diallylpiperazinium(2+) cation realizes all the coordination abilities in structures **1–4** as a bidentate π,π-ligand. This is not surprising, because the presence of two flexible allylic groups and the small size of the piperazine ring allow steric restrictions to be avoided at the stage when molecular building blocks assemble into

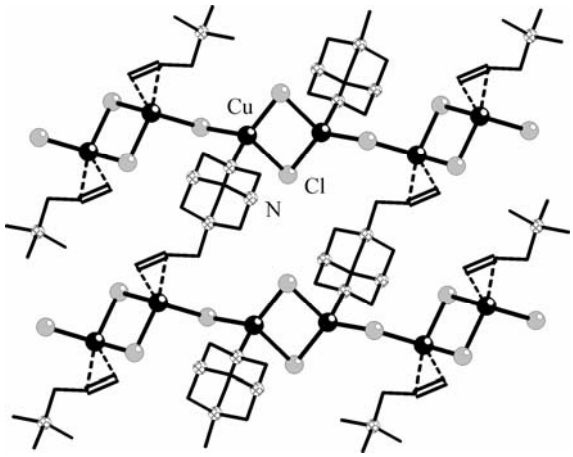


Fig. 9. A fragment of the structure of [(μ_3-*ahmta*)Cu_2Cl_3]

infinite architectures. Therefore, *dapp* plays a bridging role and forms either infinite chains (if some other ligands in the coordination environment are also bridging, as in complexes **1** and [Cu_2(μ-*dapp*)Cl_4] [15]) or X_3Cu–*dapp*–CuX_3 dimers (if X serves as a terminal ligand, as in structures **2–4**). In turn, the chloride anion acts as bridge

ligand and/or as a terminal one. Contrary to this, only two symmetrically related allylic groups of the N,N,N′,N′-tetraallylpiperazinium(2+) cation are coordinated to Cu atoms in the complex $[(C_3H_5)_2N(CH_2)_4N(C_3H_5)][Cu_2Cl_4]$ [16].

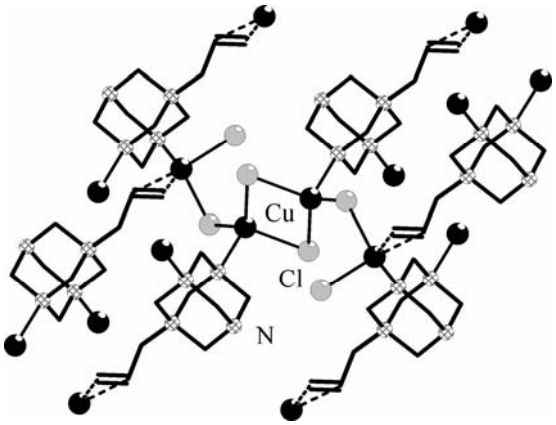


Fig. 10. Flattened layers in the crystal structure of $[(\mu\text{-}ahmta)Cu_2Cl_3]$

Concerning the coordination behaviour of N-allylhexamethylenetetraminium (*ahmta*), it should be emphasized that the presence of only one allylic group, free electron pairs of three nitrogen atoms, and the significant size and rigidity of the ligand all decide about its spatial properties in the structures. In copper(I) chloride complexes [23], *ahmta* connects CuCl fragments into different topologies depending on the role of the ligand. In the case of μ_3-*ahmta*, which acts as a π,σ,σ-ligand, the structure of a 3D-network is observed (Fig. 9). If its role changes to μ-*ahmta* (π,σ-ligand), infinite inorganic $[Cu_2Cl_3]_\infty$ chains, connected by bridging $[(CH_2)_6N_4(C_3H_5)]^+$ moieties into flattered layers, occur (Fig. 10). If *ahmta* dentation decreases up to one (σ-ligand), the structure consists of only isolated *ahmta*$CuCl_2$ fragments (Fig. 11).

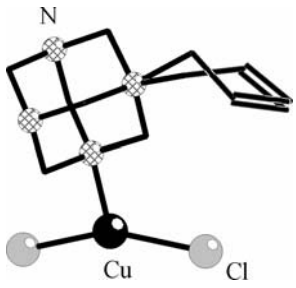


Fig. 11. An isolated *ahmta*$CuCl_2$ fragment
in the structure of $[(ahmta)CuCl_2]$

SiF_6^{2-} and BF_4^- anions are harder bases than the soft Lewis acid copper(I) atom. That is why these anions lie in the outer coordination sphere in structures **3** and **6**.

Due to significant "electron-withdrawing" ability, all fluorine atoms of the anions form a system of hydrogen bonds. The shortest contacts in **3** are caused by larger negative charge on the hexafluorosilicate anion as compared to the tetrafluoroborate moiety.

In **4** and **5**, some N–O bonds in NO_3^- anions differ in their lengths (1.233(4) –1.282(4) Å). An elongation of N–O2, N–O4, and N–O5 in **4**, and N–O11 and N–O21 bonds in **5** is caused by their role in the structure: O2, O5, and O11 are coordinated to Cu, whereas O4 and O21 take part in the formation of strong H-bonds; though the reason is different, the effect is nearly the same. The stereochemical peculiarities of the nitrate anion have been confirmed by earlier observations [27]. In structures **4** and **5**, Cu–O–N angles and Cu–O–N–O torsion angles are close to 120° and 0°, respectively, showing the directionality of copper(I)–ONO_2^- interactions via the free electron pairs of oxygen atoms.

The H(N)-atoms of the piperazine ring participate in strong hydrogen bonds. Crystallization water molecules are present in structures **1–3** due to these contacts, and are involved in structures **4–6** by H-bonds with anions and other water molecules.

Thus, the presence of strong (O–)H…O and O–H…F bonds in the construction of ionic copper(I) π-complexes creates additional possibilities in the structures of these ionic compounds as compared to copper(I) chloride complexes, in which only relatively weak (C–)H...Cl and sometimes (N–)H…Cl contacts are present.

Water moieties in the coordination sphere of Cu play an important role: they transfer some charge via H-bonds to the anion in the outer coordination sphere, providing an ionic character of the compounds.

Table 2. Geometric characteristics of the copper(I) coordination environment in the π-complexes under consideration

Compound	Cu–*m* [Å]	$l_{C=C}$ [Å]	Δ [Å]	Cu–L_{ap} [Å]	Angle C–Cu–C [deg]
1	1.919(4)	1.368(6)	0.12	2.574(3)	39.2(1)
2	1.962(9)	1.29(2)	0.46	2.295(6)	36.4(4)
3	1.89(1)	1.32(2)	0.17	2.37(2)	38.5(5)
4	1.884(2)	1.379(3)	0.05	2.531(2)	40.19(8)
5	1.917(3)	1.368(5)	0.33	2.241(3)	39.7(1)
6	1.921(4)	1.374(5)	0.25	2.174(3)	39.5(1)

It is possible to draw some conclusions about the contribution of both the σ-component, which depends on the magnitude of the Cu–*m* distance, and π-back donation component, which is connected with the elongation value of coordinated C=C bonds ($l_{C=C}$) (Table 2). This is not obligatory, hence strengthening of the σ–component (shortening Cu–*m*) intensifies the π-back donation component (increasing of $l_{C=C}$ value) of π-interactions. The magnitude C–Cu–C angle appears to be a convenient measure of Cu(I)–(C=C) interaction strength, because it depends on

either Cu–*m* distance or elongation of multiple C=C bond. Axial lengthening depends on the hybridization state of the copper atom, steric factors, and the basicity of the apical ligand. Therefore it cannot be a convenient parameter for our aim. The *Δ* value is the only evidence of copper(I) transfer from the sp^3- to the dsp^2-hybridization state (in the last case $\Delta = 0$) and, according to the oxidative addition concept [29], it is also a measure of the Cu(I)–(C=C) interaction effectiveness (see [29] for more details about the electron effects in copper(I) olefinic π-complexes). Figure 12 demonstrates the good convergence dependence of copper atom deviation from the *rms*-plane of equatorial ligands on the C–Cu–C angle for complexes **1–4**. Such linearity for complexes **1–4** is interpreted by the absence of any drastic effects in the Cu(I) coordination sphere, contrary to **5**, **6**, in which N donor atoms of the onium form of quasiaromatic hexamethylenetetramine are present in copper(I) surrounding of the complexes.

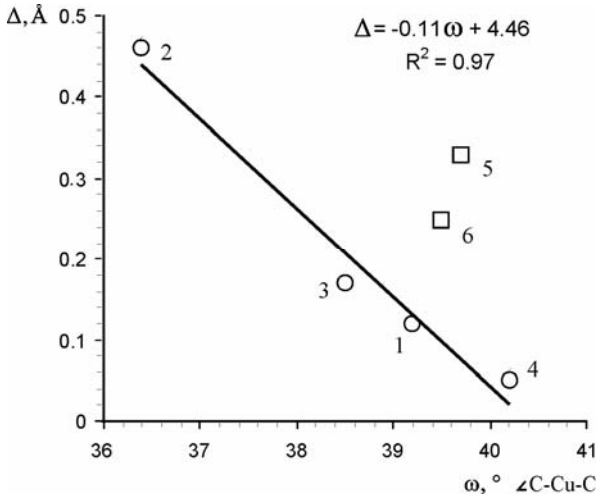


Fig. 12. The dependence of Cu atom deviation from the *rms*-plane of equatorial ligands on the C–Cu–C angle. The points for structures with *dapp* are depicted as ○ and for structures with *ahmta* as □. The trendline is calculated only for structures **1–4**

It should be noted that in comparison to recently obtained CuCl π-complexes with *ahmta* chloride [23], these structures show a stronger interaction of the ligand with Cu(I). The Cu–N3 distance in **5** is equal to 2.052(3) Å and Cu–N1 in **6** – 2.066(3) Å. They are shorter than the same contacts between the copper(I) and nitrogen atoms of the *ahtma* moiety (2.142(3)–2.241(3) Å) in the respective copper(I) chloride structures, which should be attributed to the ionic character of **5** and **6**. The existence of the [Cu(benzene)]$AlCl_4$ [30] π-complex confirms this conclusion. Thus, the ionic character of complexes **1–6** provides effective Cu(I)–(C=C) interactions and enables the sufficient stability of this type of the Cu(I) compound.

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