

# COORDINATION BEHAVIOUR OF 1,2,3-TRIALLYLGUANIDINIUM AND 1,3-DIALLYLBENZIMIDAZOLIUM CATIONS IN ZWITTER-IONIC COPPER(I) HALIDE $\pi$ -COMPLEXES

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Previous investigations on zwitter-ionic copper (I) halide  $\pi$ -complexes with allyl- and diallylammonium salts revealed different behaviour of the ligand, which depends on stoichiometry of the complex and the character of the halide atom [1]. It would be interesting to clear up the stabilization of positive charge and to study the influence of organic cations containing more than one nitrogen atom on the structure formation of copper (I)  $\pi$ -complexes. To solve this problem we have used 1,2,3-triallylguanidinium ( $H^+TAG$ ) and 1,3-diallylbenzimidazolium ( $DABI^+$ ) halides as representatives of alicyclic and heterocyclic compounds. The  $H^+TAG$  cation is also of major importance in the study of not numerous ionic  $\pi$ -complexes with unsaturated derivatives of azomethyins [2,3]. In addition, we have kept on our research into the behaviour of halide atoms depending on their character and its influence on the structure formation.

Thus, the following copper (I)  $\pi$ -complexes  $[H^+TAG]Cu_3Cl_{2.77}Br_{1.23}$  (I),  $[H^+TAG]Cu_3Br_4$  (II),  $[DABI^+]Cu_2Cl_3$  (III),  $[DABI^+]Cu_2Cl_{1.30}Br_{1.70}$  (IV) and  $[DABI^+]Cu_2Br_3$  (V) have been prepared. These hitherto unknown compounds were prepared by the original alternating-current electrochemical method (using copper electrodes) from copper (II) halides  $CuX_2$  ( $X = Cl, Br$ ) and  $H^+TAG$  or  $DABI^+$  halides correspondingly. The

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synthesis of the complexes, which form at the electrodes as well-faceted colorless crystals, can be described by the following schemes:



As an intermediate product in synthesis of III, yellowish crystals of copper (II) complex of  $[\text{H}^+\text{DABI}]_2\text{CuCl}_4$  composition (VI) have been obtained:



Structures of the compounds were x-ray crystallographically characterized on single crystals [4,5]. Table 1 lists crystallographic data for complexes I-VI.

Table 1. Crystal data for compounds I-VI.

No.	Formula	Space group	Z	a [Å] α, [deg]	b [Å] β, [deg]	c [Å] γ, [deg]
I	$[(\text{C}_3\text{H}_5\text{NH}-)_3\text{C}]\text{Cu}_3\text{Cl}_{2.77}\text{Br}_{1.2}$	<i>R</i> 3	3	10.332(3)		13.990(3)
II	$[(\text{C}_3\text{H}_5\text{NH}-)_3\text{C}]\text{Cu}_3\text{Br}_4$	<i>R</i> 3	3	10.542(3)		14.326(3)
III	$[\text{C}_6\text{H}_4\text{CHN}_2(\text{C}_3\text{H}_5)_2]\text{Cu}_2\text{Cl}_3$	<i>C</i> 2/c	4	12.197(9)	17.105(9) 109.89(8)	7.793(6)
IV	$[\text{C}_6\text{H}_4\text{CHN}_2(\text{C}_3\text{H}_5)_2]\text{Cu}_2\text{Cl}_{1.30}\text{Br}_{1.70}$	<i>P</i> 2 <sub>1</sub> /c	4	9.22(1)	22.094(6) 118.26(4)	9.272(8)
V	$[\text{C}_6\text{H}_4\text{CHN}_2(\text{C}_3\text{H}_5)_2]\text{Cu}_2\text{Br}_3$	<i>P</i> 2 <sub>1</sub> /c	4	9.263(2)	22.267(5) 117.51(2)	9.263(2)
VI	$[\text{C}_6\text{H}_4\text{CHN}_2(\text{C}_3\text{H}_5)_2]_2\text{CuCl}_4$	<i>F</i> ddd	8	7.714(2)	26.220(5)	28.405(6)

Captions to the figures of the article "Coordination behaviour of 1,2,3-trialkylguanidinium and 1,3-dialkylbenzimidazolium cations in zwitter-ionic copper(I) halide  $\pi$ -complexes" by Ya.E. Filinchuk, E.A. Goreshnik and M.G. Mys'kiv.

$\pi$ -complexes I and II appear to be isostructural. The copper (I) atom has trigonal pyramidal coordination, formed by three halide atoms and the C=C bond. The inorganic fragment is  $\text{Cu}_3\text{X}_4^-$  anion lying on axis 3. One of the halide atoms of  $\text{Cu}_3\text{X}_4^-$  anion is in the partial position and serves as an apical ligand for the three Cu(I) atoms (Cu-X(1) 2.759(3) Å in I and 2.721(4) Å in II). This enables practically ordered occupation of the respective positions by Cl and Br atoms: axial position by the larger Br (Cl:Br ratio 0.04:0.96) and equatorial position by the smaller Cl atom (Cl:Br ratio 0.91:0.09). Thus, strong ordering in copper (I)  $\pi$ -complexes is observed for the first time.  $\text{H}^+\text{TAG}$  cations and  $\text{Cu}_3\text{X}_4^-$  anions occupying partial positions on axis 3 owing to  $\pi$ -bonding combine into sheets (Fig. 1). The coordinated C=C bond is slightly lengthened to 1.35(1) Å in I and 1.34(1) Å in II.

In contrast to I and II, partial substitution of Cl by Br atoms in complexes with  $\text{DABl}^+$  leads to different structures: compound III crystallizes in sp. gr.  $C2/c$ , compounds IV and V crystallize in sp. gr.  $P2_1/c$  (isostructural). In III  $\text{Cu}_2\text{Cl}_3^-$  moieties are connected through bridging  $\text{DABl}^+$  cations by Cu-(C=C) contacts, forming organometallic chain in the [101] direction (Fig. 2). Both  $\text{Cu}_2\text{Cl}_3^-$  anions and  $\text{DABl}^+$  cations occupies partial positions on the axis 2. In consequence of bridging function of Cl(1) atom shortened Cu...Cu distance is observed (2.889(6) Å). Probably this peculiarity in the structure of trigonal planar coordination sphere of copper atom explains the absence of elongation of C=C bond (1.32(2) Å), involved in the effective Cu-(C=C) interaction (the distance Cu-mid-point of C=C group is equal to 1.89(2) Å).

As one can see on the Fig. 3, the structure of IV and V has condensed inorganic fragment with respect to III: instead of separate  $\text{Cu}_2\text{Cl}_3^-$  anions  $(\text{Cu}_2\text{X}_3)_n^{n-}$  chains are formed. Therefore a half of copper atoms are coordinated by X only. Consequently, the fairly different  $\text{DABl}^+$  coordination behaviour is observed: only one of the two C=C bonds of



DABI<sup>+</sup> cation is coordinated with copper (I) atom. In the structure of IV the Cl,Br ordering is also noticeable: X(1) and X(2) positions linked with  $\pi$ -coordinated Cu atoms have Cl:Br ratio about 0.55:0.45, but X(3) position, linked with  $\sigma$ -coordinated Cu atom only, is occupied by the Cl,Br mixture with a 0.20:0.80 ratio. It may be caused by  $\pi \rightarrow 4s^0$  electron donation from C=C bond to  $\pi$ -coordinated copper atom and as a result of the tendency of Cu(I) to be bonded with more electronegative halide atom. In the case of I, not electronic, but steric factors are dominant. Thus in I and IV the uncommon for copper (I) halide  $\pi$ -complexes Cl,Br ordering is observed.

Using ZINDO/1 calculations of the effective atomic charges [6] we have revealed how the positive charge of the ligand cations is dispersed in I, III and IV. Due to N-H...X bonding, the positive charge is mainly located on the H(N)-atoms and on the carbon atom of the guanidinium group in I, and is used for suppression of  $\sigma$ -donor abilities of N-atoms in III and IV.

Formation of copper (II) complex of [DABI<sup>+</sup>]<sub>2</sub>CuCl<sub>4</sub> composition (VI) as intermediate in the synthesis of IV also deserves attention. In this case copper (II) atom in partial position (222 crossing) has unusual tetrahedral coordination (Fig. 4). Complexes IV and V may serve as a useful model for comprehension of some bioorganic processes involving Cu(I)  $\leftrightarrow$  Cu(II) oxidation-reduction.

Basing on the structure data of I-VI, it can be concluded that symmetries of H<sup>+</sup>TAG and DABI<sup>+</sup> cations play a significant role in structure formation. Thus, trigonal symmetry of H<sup>+</sup>TAG cation and the possibility of its achievement by the Cu<sub>3</sub>X<sub>4</sub><sup>-</sup> anion leads to formation of rhombohedral cell of I and II. The symmetry of DABI<sup>+</sup> cation facilitates the formation of unusual for Cu(I) and Cu(II) inorganic fragments in III and VI.

## REFERENCES

1. V.V. Olijnyk, Zh. Struct. Khimii., V. 39. No. 1. 98 (1998)
2. Ya.E. Filinchuk, Mys'kiv M.G. Koord. Khim., V. 25. No. 1. 55 (1999)
3. V.V. Olijnyk, Schollmeyer D., Filinchuk Ya.E., Mys'kiv M.G. Koord. Khim., V. 24. No. 1., 52 (1998)
4. Ya.E. Filinchuk, Koord. Khim., in press (1999)
5. E.A. Goreschnik, V.N. Davidov, O.V. Pavlyuk, M.G. Mys'kiv, Koord. Khim., n press (1999)
6. D.W. Bearden, Computer Software Reviews, V. 33 (3), 525 (1993)