

THE NOVEL COPPER(I) π -COMPLEXES WITH DIALLYL DERIVATIVES OF UREA AND PARABANIC ACID

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1,3-Diallylurea (**dau**) has already been studied as a ligand for π -complexation of silver and has demonstrated its ability to be a linker in coordination polymers. Nevertheless, its behavior in presence of compounds that can catenate on their own such as copper(I) halides has never been studied prior. 1,3-Diallylparabanate (**dapa**) is structurally similar to 1,3-diallylurea. This compound has been researched in context of preparation of useful polymer materials, nevertheless, its usage as a ligand for copper(I) π -coordination is novel.

By means of alternating current electrochemical synthesis with wire copper electrodes in methanolic solutions of corresponding ligands and copper(II) halide salts the two novel copper(I) π -complexes [Cu2(**dau**)Cl1.58Br0.42] (**I**) and [Cu2(**dapa**)Cl1.74Br0.26] (**II**) were prepared in well-shaped crystalline form and studied with X-ray diffraction (Table).

Table. Selected crystal data of **I** and **II**

№	Composition	Space group	Cu(I) halide fragments	Coordination types
I	[Cu2(dau)Cl1.58Br0.42]	<i>P</i> 212121	Single-stranded chains	σ , π & π
II	[Cu2(dapa)Cl1.74Br0.26]	<i>I</i> 2/a	Single- and double-stranded chains	π

In the crystal of the complex **I** copper halide 1D-polymer chains stretch along [010] direction and adopt alternately two different orientations. The chains are linked by the bridging molecules of **dau** into 3D-polymer. Each **dau** molecule binds two copper atoms located in the neighboring chains: Cu1 acquires trigonal pyramidal coordination surrounding and is bonded via π - and σ -functions of ligand, whereas Cu2 is solely π -coordinated and has planar trigonal coordination environment (Fig. 1).

Within structure of compound **II** two different types of infinite copper(I) halide polymer chains ordered in a parallel manner are cross-linked by the **dapa** molecules into 2D-sheets where for every double-stranded chain (Cu1&Hal1) two single-stranded chains (Cu2&Hal2) are present (Fig. 2). The sheets are stacked on each other with protrusions of the sheet entering the depressions of the adjacent sheets and vice versa. Cu2 and Hal2 atoms in the adjacent sheets provide electrostatic attraction that holds the sheets together. In the structure of the compound **II** **dapa** is exclusively π -coordinated on both of the molecule's allyl groups. Atom Cu1 forms trigonal pyramidal coordination environment, whilst Cu2 atom is located in the planar trigonal surrounding.

Compounds **I** and **II** demonstrate the joint action of copper(I) halide catenation and cross-linkage by organic molecules resulting into formation of polymers of higher dimension than copper(I) halide chains on their own.

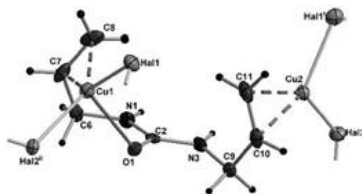


Fig. 1. Fragment of crystal structure **I**

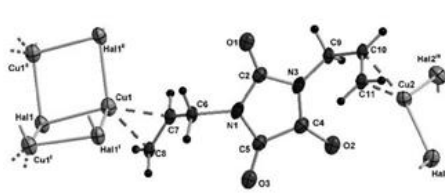


Fig. 2. Fragment of crystal structure **II**