COPPER(I) HALIDE COORDINATION COMPOUNDS WITH N-PHENYLUREA ALLYL DERIVATIVES

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It has been demonstrated earlier that allyl derivatives of urea successfully form crystalline coordination compounds with Cu(I) and Ag(I) in which olefin fragments are bound to metal atoms. In search for materials with prominent NLO properties two new ligands of this type (Fig. 1) – 3-phenyl-1,1-diallylurea (**dapu**) and 1-phenyl-3-allylurea (**mapu**) – were prepared via condensation of phenyl isocyanate with respective amines.

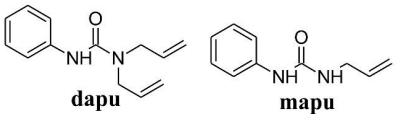

Fig. 1. Studied ligands

Copper(I) coordination compounds **2**–**5** were obtained in form of well-shaped single crystals from solutions of reagents in alcohols by means of comproportionation of copper(II) halides and metallic copper in presence of aforementioned ligands assisted by alternating current. The crystals of **dapu** (**1**) and **2**–**5** were studied by X-ray diffraction (Table 1). For **1**, **2**, and **3** nonlinear optical properties, namely second harmonic generation (SHG), were measured.

Compounds **2** and **3** formed simultaneously from the same starting solution and **3** demonstrated tendency to recrystallize into **2** over time. Crystals of **2** and **3** were easily separated in carbon tetrachloride as a floatation medium relying on their different density.

2 crystallizes in form of layered 2*D* coordination polymer. In its structure copper(I) halide exists as tricyclic $\{Cu_4Cl_4\}$ unit with two crystallographically independent metal atoms. Cu1 atoms form chelate cycles with **dapu** molecules that involve σ- and π-coordination whereas more sterically hindered Cu2 atoms are solely π-coordinated. Neighboring $\{Cu_4Cl_4\}$ units are linked by bridging ligand molecules.

Structure of **3** is composed of isolated molecules in which cyclic symmetrical $\{Cu_2Cl_2\}$ fragments are present. Each copper atom coordinates both of allyl groups of the single **dapu** molecule resulting into exclusive π-coordination

Compounds **4** and **5** are isostructural and share some structural similarity with **3**. In their molecules $\{Cu_2Hal_2\}$ (Hal ≡ Cl, Br) cycles are also present but fragments of **mapu** are σ- and π-coordinated with formation of chelate cycles.

Table 1. Selected crystal data for the discussed compounds

	Composition	Crystal system and space group	Cu(I) halide fragment	Coordination types
1	**dapu** ($C_{13}H_{16}N_2O$)	Monoclinic, $P2_1$	—	—
2	(**dapu**)$_2Cu_4Cl_4$	Monoclinic, $P2_1/n$	$\{Cu_4Cl_4\}$	σ,π & π
3	(**dapu**)$_2Cu_2Cl_2$	Monoclinic, $P2_1/c$	$\{Cu_2Cl_2\}$	π
4	(**mapu**)$_2Cu_2Cl_2$	Monoclinic, $P2_1/c$	$\{Cu_2Cl_2\}$	σ,π
5	(**mapu**)$_2Cu_2Br_2$	Monoclinic, $P2_1/c$	$\{Cu_2Br_2\}$	σ,π