

# NOVEL COPPER(I) $\pi$ -COMPLEXES WITH ALLYL DERIVATIVES OF DISUBSTITUTED PSEUDOTHIOHYDANTOINS: SYNTHESIS, CRYSTAL STRUCTURE AND NLO PROPERTIES

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Using alternating current-electrochemical synthesis we have synthesized and studied by single crystal X-ray diffraction and IR-spectroscopy three novel Cu(I)  $\pi$ -complexes of the  $[\text{Cu}_4(\text{dapt})_2\text{Cl}_4] \cdot 0.375(\text{C}_2\text{H}_5\text{OH})$  (**1**),  $[\text{Cu}_2(\text{papt})_2\text{Cl}_2]$  (**2**) and  $[\text{Cu}(\text{papt})\text{NO}_3]$  (**3**) compositions (*dapt* – (2Z)-3-allyl-2-(allylimino)-1,3-thiazolidin-4-one, *papt* – (2Z)-2-(phenylimino)-3-allyl-1,3-thiazolidin-4-one).

The structure of compound **1** is built of dimeric tetranuclear  $[\text{Cu}_4(\text{dapt})_2\text{Cl}_4]$  fragments and ethanol molecules, which are located on the three-fold inversion axis and partially fill voids in the crystal structure. Central part of  $[\text{Cu}_4(\text{dapt})_2\text{Cl}_4]$  coordination dimer is formed by  $\{\text{Cu}_4\text{Cl}_4\}$  cluster, in which Cu atoms are bonded by bridging Cl atoms. Ligand molecule in **1** acts as tridentate chelating ligand and plays a bridged role being bonded simultaneously to the both crystallographically independent Cu atoms.

*Papt* molecule in **2** and **3** acts as bidentate chelate  $\pi, \sigma$ -ligand, being coordinated to the metal center through the imino N atom and C=C double bond of allyl group being located at the basal plane positions of the Cu atom's trigonal-pyramidal environment.  $\text{Cl}^-$  anions in **2** as well as O atoms of  $\text{NO}_3^-$  in **3** occupy two remaining positions (one basal and one apical) of the metal coordination polyhedron. Due to the anions ( $\text{Cl}^-$  and  $\text{NO}_3^-$ ) specificity, centrosymmetric dimeric  $[\text{Cu}_2(\text{papt})_2\text{Cl}_2]$  fragments with central planar  $\{\text{Cu}_2\text{Cl}_2\}$  moiety in **2** and polymeric structure **3**, built of the  $[\text{Cu}(\text{papt})\text{NO}_3]_n$  chains, are formed.

For all three compounds nonlinear-optical properties (NLO) were measured, namely – second harmonic generation (SHG) and third harmonic generation (THG), using 7 ns pulsed Nd: YAG laser (1064 nm), pulse reception 10 Hz. Interferometer filters for spectral selection at 355 nm and 532 nm were applied. All the samples have shown promising nonlinear optical efficiencies achieved up to about 3 pm/V.

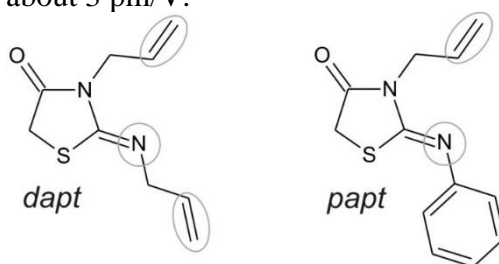


Fig. Ligand molecules with marked coordination sites

Table. Selected crystal data of **1–3**

№	Composition	Space group	Main Cu(I) fragment	Coordination type
1	$[\text{Cu}_4(\text{dapt})_2\text{Cl}_4] \cdot 0.375\text{EtOH}$	<i>R</i> -3	Tetranuclear dimer	$\sigma, \pi$
2	$[\text{Cu}_2(\text{papt})_2\text{Cl}_2]$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	Binuclear dimer	$\sigma, \pi$
3	$[\text{Cu}(\text{papt})\text{NO}_3]$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	Coordination chain	$\sigma, \pi$