

# STRUCTURAL CHEMISTRY OF COPPER(I) $\pi$ -COMPLEXES WITH ALLYL ESTERS OF SOME HETEROCYCLIC SUBSTITUTED ACETIC ACIDS

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Copper(I)  $\pi$ -complexes with alkenes have received considerable theoretical and practical interest because of their remarkable catalytic, luminescent activities and of other useful properties. Among them, a key role of heterocyclic allyl derivatives in crystal engineering of copper compounds with extremely rare occurred inorganic fragments were found in recent years. The synergy of a flexible allyl group and a conformationally rigid heterocyclic core plays an exceptionally crucial role in a stabilization of the unique fragments, resulting in compounds with enhanced nonlinear optical susceptibilities and a range of useful properties. In our work we firstly explored  $\pi$ -coordination activity of allyl esters of heterocyclic substituted acetic acids regarding copper(I) salts. For these purpose, two heterocyclic ligands have been prepared: allyl 1*H*-benzotriazol-1-ylacetate (Lig1) and diallyl 2,2'-(1,3,4-thiadiazole-2,5-diyl)disulfanediyl)diacetate (Lig2) (Fig.).

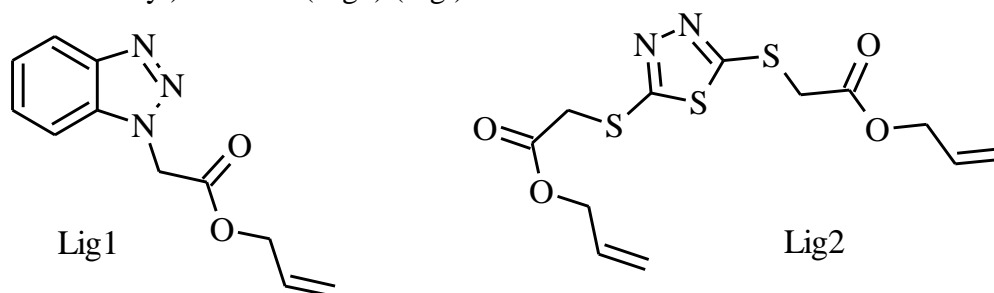


Fig. Ligands used for the complexes preparation

Crystalline copper  $\pi$ -compounds **1-4** (Table) were obtained under *ac* electrochemical conditions from alcohol solution of Lig1 or Lig2 and the corresponding copper(II) salts.

Table. Selected crystal data for copper(I)  $\pi$ -complexes with Lig1 and Lig2

|          | Composition                                    | Space group | $V, \text{\AA}^3$ | $Z$ | Density, $\text{g/cm}^3$ | Coordination           |
|----------|--|-------------|-------------------|-----|--------------------------|------------------------|
| <b>1</b> | $[\text{Cu}_2(\text{Lig1})_4(\text{BF}_4)_2]$  | $P-1$       | 1222.76(7)        | 1   | 1.59                     | $\sigma / \pi, \sigma$ |
| <b>2</b> | $[\text{Cu}_2(\text{Lig1})_4(\text{ClO}_4)_2]$ | $P-1$       | 1241.09(12)       | 1   | 1.60                     | $\sigma / \pi, \sigma$ |
| <b>3</b> | $[\text{Cu}_2(\text{Lig2})\text{Cl}_2]$        | $P-1$       | 906.62(7)         | 2   | 1.99                     | $\pi, \sigma$          |
| <b>4</b> | $[\text{Cu}_2(\text{Lig2})\text{Br}_2]$        | $P-1$       | 940.23(3)         | 2   | 2.23                     | $\pi, \sigma$          |

Complexes **1** and **2** are isostructural and crystallize in centrosymmetric  $P \bar{1}$  space group with two Lig1 molecules and one Cu(I) atom in the asymmetric unit. One independent Lig1 molecule is coordinated to the metal ions in a  $\pi, \sigma$ -bridging mode, being attached to copper by means of allylic C=C bond and one triazole N atom. Second Lig1 molecule (is  $\sigma$ -bonded only) together with F or O anion atoms completes coordination environment of Cu(I). Complexes **3** and **4** are also isostructural but their asymmetric units contain one organic ligand and two crystallographically independent copper(I). Molecule Lig2 is  $\pi, \sigma$ -bonded to copper atoms via allylic C=C bond and two thiadiazole N atoms. Different coordination environment of Cu1 and Cu2 in the structures **3** and **4** leads to a formation of stepped cubane  $\{\text{Cu}_4\text{Hal}_4\}$  fragments.