

**CRYSTAL ENGINEERING OF COPPER(I) AND SILVER(I) π -COMPLEXES
WITH 1,2,4-TRIAZOLES ALLYL DERIVATIVES**

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A great variety of Cu(I) and Ag(I) π -complexes with allyl-derivatives of numerous acyclic and heterocyclic ligands has been investigated over the last decades. As a result, many aspects of the influence of ligand structure, anion type and synthetic conditions on π -complexes crystal structure formation and on the effectiveness of the M(I)–(C=C) (M = Cu, Ag) interaction were studied. Nevertheless, much more still remains unexplored as it is evidenced by recent interesting results such as the discovery of new inorganic structural fragments, obtaining the first π -complexes with a number of anions, synthesis of the unique heterometallic complexes. This was made possible by the development of new synthetic approaches that allow the obtaining of Cu(I) and Ag(I) π -complexes in the form of high-quality single crystals by alternating-current electrochemical method or by direct interaction. This class of compounds is interesting because of their catalytic, biological, photoluminescent and optoelectronic properties.

Recently, the first π -complexes of Cu(I) with allyl derivatives of 1,2,4-triazole were investigated. The organic ligand acts as multidentate chelating π,σ -donor using triazole and η^2 -allyl moieties, resulting in a formation of the dimeric {Cu₂N₄} core with a trigonal-pyramidal

environment of the Cu cation. These dimers retain their stability even in the acetonitrile solution (which is known to be highly affined to Cu(I)), what was detected by means of ¹H and ¹³C NMR.

Herein, a series of first Cu(I) and Ag(I) π -complexes with new derivatives of 1,2,4-triazole with such anions as Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, SO₄²⁻, BF₄⁻, SiF₅⁻, CF₃COO⁻ and others are presented. A comparative analysis of the structures of new coordination compounds with already known is carried out and it is shown how changes in the ligand structure affect the crystalline organization of the complexes. Depending on the substituents in the 1,2,4-triazole core, as well as on the synthetic conditions, structures of varying dimensionality (0D, 1D, 2D) can be obtained. In addition to this, results of the study of nonlinear optical properties for the 1D copper(I) iodide complex with 2-allyl-3-

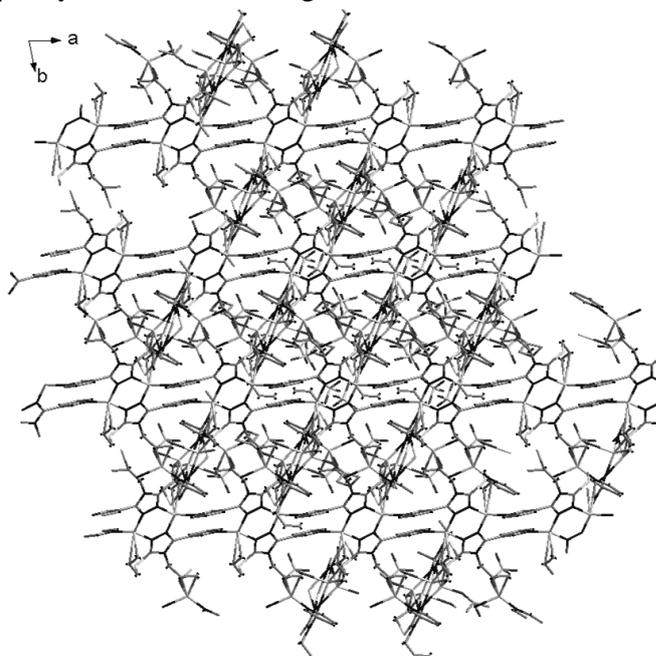


Fig. A part of the crystal structure of 2D AgClO₄ π -complex with 3-allylsulfanyl-4-allyl-5-*m*-pyridyl-4*H*-1,2,4-triazole

allylsulfanyl-2*H*-1,2,4-triazole are presented.

Particularly interesting is the structure of AgClO₄ π -complex with 3-allylsulfanyl-4-allyl-5-*m*-pyridyl-4*H*-1,2,4-triazole (**L**) (Fig.), in which dimeric cationic [Ag₂(**L**)₂]²⁺ fragments are linked into the 2D network by means of the N atom of the pyridine core, the bridging perchlorate anions and the 4-allyl group, which is η^2 -coordinated. It is worthy of note that this is the first complex with 1,2,4-triazoles in which the 4-allyl group is coordinated, despite the electron deficiency of the C=C bond.