

STRUCTURAL CHEMISTRY OF Cu(I) π -COORDINATION COMPOUNDS WITH ALLYL DERIVATIVES OF HETEROCYCLES*Slyvka Yu. I.*

Department of Inorganic Chemistry, Ivan Franko National University of Lviv,
Kyryla i Mefodiya Str., 6, 79005, Lviv, Ukraine
yurii.slyvka@lnu.edu.ua

Copper(I) π -coordination compounds are quite appealing objects for interdisciplinary research in view of their catalytic, photoluminescent, ferroelectric, and nonlinear optical properties [1]. Cu(I)-olefin complexes based on allyl derivatives of organic heterocycles (ADH) dominate the crystal engineering of mentioned coordination compounds. That is defined by a specific concurrent coordination of heterocyclic donor atoms and “soft base” – allylic C=C bond to the central “soft acid” Cu⁺ ion. Crystalline compounds, self-assembled from the above organic ligands under the differently modified conditions of the alternating-current electrochemical technique, attract attention due to the presence of various Cu(I) salts (which are unstable or unknown in a free state): CuNO₃, CuHSO₄, Cu₂SO₄, Cu₂SiF₆, Cu(NH₂SO₃), *etc.* Usually, ADH in the structures of the obtained complexes performs a π, σ -bridging or π, σ -chelate-bridging function, linking the Cu(I) ions into island fragments or coordination polymers of different dimensions.

The design of compounds based on allyl derivatives of triazoles, tetrazoles, 1,3,4-oxadiazoles and 1,3,4-thiadiazoles predominantly is conditioned by the formation of stable building blocks – dimeric cationic {Cu₂(L)₂}²⁺ particles, in which both central ions are surrounded by two η^2 -allyl groups and by two [–N–N–] pairs of two heterocyclic rings. The apical position of the metal trigonal-pyramidal surrounding is occupied by a solvent molecule (usually H₂O) or anion donor atom. Isolated dimeric {Cu₂(L)₂(X)₂} fragment (X – anion or solvent molecule) is the most tolerant unit in the case of Cu(I) ionic salts. In the presence of halide-anion {Cu₂(L)₂(Hal)₂} units realize separately or act as secondary building blocks to form coordination polymers. Otherwise, copper(I) halide units combine into isolated Cu₂Hal₂ fragments, tetranuclear Cu₄Cl₄ fragments of “stepped-cubane” type or polymeric inorganic chains.

During electrochemically assisted preparation of π -complexes based on allyl derivatives of thiohydantoins Cu(I) coordination compounds with 5-alkoxy-3-allyl-2-thiohydantoins were formed *in situ* from corresponding alcohol solutions of FeCl₃ and 3-allyl-2-thiohydantoins. Allylthiohydantoins and allylpsedothiohydantoins molecules are mostly π, σ -chelating ligands. N-Allyl derivatives of piperazine being protonated tend to construct zwitterionic compounds with more complicated inorganic parts (for example, centrosymmetric {Cu₄Cl₈}²⁻), but increasing the number of allyl groups from 2 to 4 does not change the μ, μ -bridging character of the organic ligand.

Allylcytisine was used as an instrument to construct a novel π, σ -coordination compound with an acentric structure (Sp. gr. P1) and with the unusual anionic chain containing eight crystallographically independent copper(I) ions. The lasts form the specific {Cu₇{L(H⁺)Cl₁₀} subunits, linked by linearly-arranged Cu⁺ cations and bridging μ_3 -Cl anions into 1D-polymer.

Copper(I) π -complexes with ADH attract particular interest due to their high efficiency laser-stimulated second harmonic generation (SHG) and third harmonic generation (THG). The effect is almost independent of the polarization and is often higher than for the known nonlinear optical lead-containing glasses.

1. Yu. Slyvka, A.A. Fedorchuk, E. Goresnik, N. Pokhodylo, J. Jedryka, K. Ozga, M. Mys'kiv, *Polyhedron*. **2022**, *211*, 115545.