Crystal and molecular structure of tetranuclear copper(II)- and zinc(II)-containg complexes based on oxime-and-amide ligands

O. Kanderal[a], I. Fritsky[a], E. Prisyazhnaya[a], H. Kozłowski[b]
[a]*Department of Chemistry, National Taras Shevchenko University, Kiev 01033, Ukraine*
[b]*Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

Keywords: copper, zinc, polynuclear complexes

A series of copper(II) tetranuclear μ_3-(N,O,O)-oximato complexes have been obtained by interaction between mononuclear anionic complexes based on open-chain tetradentate ligands with the donor sets {2N(amide), 2N(oxime)} and {2N(hydrazide), 2N(oxime)} and copper(II) cationic complexes with bidentate amines: [{Cu(**L'**)Cu(**L**-4H)$(H_2O)_n$}$_2$]·xH_2O (**L** – oximate ligand, **L'** - bidentate amine ligand). They crystal and molecular structure was established by the X-ray analysis.

The primary square-planar coordination of copper ions involved in oxime ligands coordination in tetranuclear complexes remains unchangeable, moreover, they found themselves in a completely closed macrocyclic environment (Fig. 1). In the crystalline state, the dimeric fragments of the complexes with additional diamine ligands are united in tetranuclear dimers due to triple bridging function of one of the oxime group which is thus being involved both in in-plane and out-of-plane bridging. Comparison of the structures of tetranuclear aggregates reveals the reasons of different conformations of the binuclear fragments. In the complexes containing aromatic additional ligands, the planes of **dipy** or **phen** are nearly coplanar with the equatorial plane of Cu(1) atom of the second binuclear fragment, and there is a specific $\pi\cdots\pi$-interaction between the aromatic and the oxime groups which manifests in short intramolecular N···O and C···C contacts. These non-covalent interactions determine the conformation of the dimeric fragments.

In the binuclear fragments the distances between the oxime oxygen atoms are noticeably increased on bridging coordination: from 2.52(1) Å in the mononuclear Cu complexes 2.87 – 3.09 Å in the polynuclear. The binuclear fragments differ significantly by the angular conformation around the oximate bridges which results in different Cu···Cu separations observable in the complexes and different mutual disposition of the equatorial planes of the copper polyhedra. One of the most important consequence of this effect is that in the complexes with aliphatic amines the Cu···Cu separations allow two copper atoms to bridge one water molecule, while in the complexes with aromatic ligands the water molecule is monodentately coordinated to the Cu(2) atom.

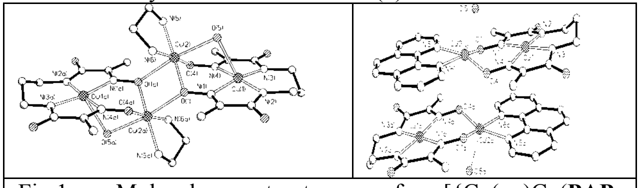

Fig.1. Molecular structure of [{Cu(**en**)Cu(**PAP**-4H)$(H_2O)_2$}$_2$]·2H_2O and [{Zn(**phen**)Cu(**PAP**-4H)$(H_2O)_2$}$_2$]·2H_2O