Poster

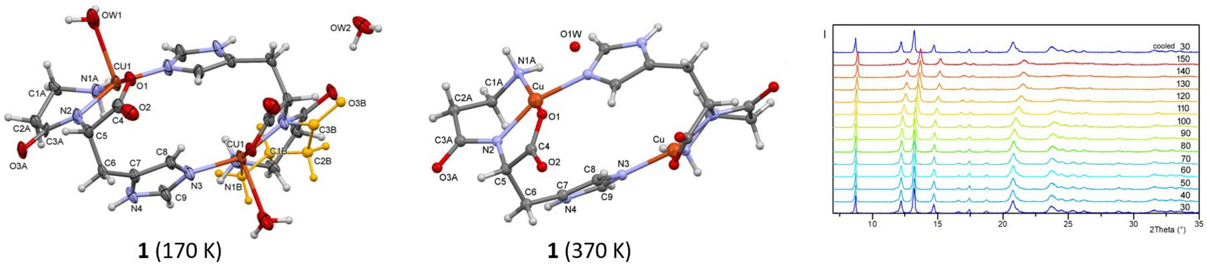
Robustness and stability of the L-carnosine copper(II) dimer. Coordinatively unsaturated sites of the high-temperature structure

I. Đilović, D. Mrvoš-Sermek, M. Tašner, D. Matković-Čalogović

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, Zagreb, Croatia

dubravka@chem.pmf.hr

Coordination compounds of L-carnosine, (β-alanyl-L-histidine) (H_2**car**) have been the subject of much research, as they have potential therapeutic applications due to their antioxidant and anti-inflammatory properties. We are interested in the coordination possibilities of L-carnosine in reaction with copper(II) under different conditions. Freeman and Szymanski [1] published the structure of the dimeric complex in which two deprotonated carnosine molecules bridge two Cu(II) ions by N imidazole atoms, $[Cu_2(car)_2(H_2O)_2]\cdot 2H_2O$ (**1**). We have prepared the same compound by liquid-assisted (water) mechanochemical synthesis. By solution based synthesis in methanol we have prepared $[Cu_2(\mathbf{car})_2(MeOH)_{2x}(H_2O)_{2(1-x)}]\cdot mH_2O\cdot nMeOH$ (**2**), and $[Cu_2(\mathbf{car})_2(MeOH)_2]\cdot 5.5MeOH$ (**3**). Both of these compounds are unstable and readily convert to **1** on exposure to moist air. These three crystal structures comprise almost the same building blocks – isoskeletal dimers that differ in the apical ligand coordinated to Cu(II) ions (water or methanol molecule). These can be removed by heating, altering the Cu(II) ion coordination sphere from square-pyramidal to square-planar. Temperature-dependent structural analysis of **1** indicated the robustness of the Cu(car) dimers (Fig. 1).



1 (170 K)

1 (370 K)

Figure 1. Structure of **1** at 170 K. The major disordered part is colored according to the atom coloring scheme, while the minor part is colored in orange (left). Structure of **1** at 370 K. Only the major disordered part is shown (middle). Variable-temperature PXRD study of the as-synthesized **1**.
Powder patterns were collected from 30 to 150 °C in intervals of 10 degrees, and the last one (top) was collected after cooling to 30 °C. The temperatures are in °C (right).

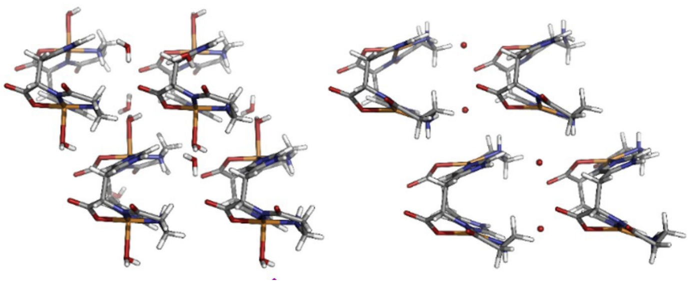


Figure 2. Comparison of the crystal structures **1** at 170 K (left) and at 370 K (right).

During the transformation of **1** from 270 to 370 K (Fig. 2), the distance $Cu(II)\cdots OH_2$ changes from 2.4 Å to 3.2 Å resulting in the loss of the apical water molecule, and the only solvent water molecule has an occupancy of 50%. Upon cooling the original structure is restored. The high-temperature structure has CUS (coordinatively unsaturated sites). Possible coordination of other apical ligands will be also discussed.

[1] Freeman H. C., Szymanski, J. T., (1965) *Chem. Commun.*, **23**, 598–599.