

**s9.m1.p15** **Temperature dependent study of copper(II) carboxylates with 2-aminopyridine.** N. Lah<sup>1</sup>, G. Giester<sup>2</sup>, C. Lengauer<sup>2</sup>, P. Šegedin<sup>1</sup> and I. Leban<sup>1</sup>, <sup>1</sup>*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerceva 5, POB 537, SI-1001 Ljubljana, Slovenia,* <sup>2</sup>*Institute for Mineralogy and Crystallography, University of Vienna, Althanstr. 14, A-1090 Vienna, Austria. e-mail: ivan.leban@uni-lj.si*

Keywords: copper(II) compounds, phase transition, crystal structure.

In continuation of our research on copper(II) carboxylates four dimeric copper carboxylates with 2-aminopyridine as the axial ligand were prepared. For the same type of complexes containing higher carboxylic parts with six C atoms or more disorder has already been observed at room temperature. A distinct picture of atomic motion, however, has not yet been obtained due to the lack of information on crystal structures at different temperatures.

In order to examine and characterize the nature of this disorder a non-ambient X-ray study below 290K was carried out. The results were completed with low temperature DSC measurements.

For the copper(II) hexanoate with 2-aminopyridine (R3) five data sets from 290 to 100K were collected. The results of the X-ray analysis show that the disorder could be ascribed only to higher displacements of the C-atoms at 290K. No thermal anomaly can be observed in the DSC measurements.

In the case of the other three compounds, i.e. the copper(II) heptanoate (P2<sub>1</sub>/a), octanoate (P2<sub>1</sub>/a), and nonanoate (P2<sub>1</sub>/a) with 2-aminopyridine, the disorder at room temperature cannot be simply explained in terms of higher atomic displacements. Additionally the DSC measurements revealed that these carboxylates undergo phase transitions at 236K plus 286K (heptanoate), at 250K (nonanoate), and at 268K (octanoate). The detailed analysis will be presented.

**s9.m1.p16** **Implications of charge transfer in molecular organic crystals.** V. Oison, C. Koenig and C. Katan, *GMCM, UMR-CNRS 6626 - Univ. Rennes 1, France*  
Keywords: charge transfer, molecular, hydrogen bonds.

Molecular organic charge transfer crystals exhibit a dazzling variety of phase transitions which can be driven by temperature, pressure, photoirradiation,... They are composed of two types of molecules: electron donors (D) and acceptors (A) and exhibit features ranging from zero to three dimensions. As charge transfer plays a leading part in these compounds, the modeling of their properties is usually based on the character and population of the highest occupied molecular orbital (HOMO) of D and lowest unoccupied molecular orbital (LUMO) of A.

Our aim here is to analyse in more details the implications of charge transfer between D and A using ab-initio electronic structure calculations. We first focus on the electronic redistribution which appears in isolated molecules upon ionization. We select tetrathiafulvalene which is a well known electron donor and a benzoquinone derivative for the acceptor. Both are planar molecules with frontier orbitals of  $\pi$  character. We show that adding electrons to the LUMO of A (removing from the HOMO of D) affects a few lower lying  $\sigma$  molecular orbitals and thus increases the reactivity of these molecules in their planes. This effect leads to additional inter-molecular interactions in the crystalline states which can in no way be accounted for by the frontier orbitals. In an atomic point charge model this is related to the fact that the charge variation upon ionization can also be large for atoms on which frontier orbitals have no or very little weight (for example hydrogen in D and chlorine in A).

Some of these crystals present hydrogen bonds which we believe to be crucial for the understanding of the different types of phase transitions observed in families of compounds. Calculations on a A-D-A complex show that the hydrogen bond involves the same lower lying  $\sigma$  orbitals as mentioned above. Moreover, a charge transfer between A and D increases significantly the strength of hydrogen bonding. The consequences of both effects are discussed in more details for charge transfer complexes presenting a *neutral to ionic* phase transition.