

MS41-04 Entropies from Diffraction Experiments: Towards Polymorph Prediction, Anders Ø. Madsen^a, Nanna Wahlberg^a, Hlkon Hope^b, Sine Larsen^{a,c}, *Department of Chemistry, University of Copenhagen, Denmark.* ^bUC Davis, California, USA.
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A central part of crystal structure prediction is to assess the relative stabilities of proposed structures. This is normally done by calculation of crystal energies or enthalpies (H). However it is well known that differences in entropies (S) can be sufficiently large to alter the order of stability of polymorphs with temperature (T), as expressed by the Gibbs equation $G = H - TS$. Indeed, in spite of recent success in prediction of crystal structures, polymorphs remain elusive [1].

We demonstrate how differences in solid state entropies of polymorphic compounds can be obtained by analysis of the anisotropic displacement parameters derived from X-ray or neutron diffraction experiments [2-4]. This approach paves the way for understanding how molecular vibrations contribute to the stabilities of crystals. The results may thus provide guidance for the development of computational approaches to entropy estimation. We provide examples where the approach has been applied to the polymorphs of pyrazinamide, paracetamol [5], famotidine [6] and the epimeric xylitol and ribitol crystals [4,7], compare the experimental results to periodic DFT calculations [8,9] and discuss the merits and limitations of the approach as a tool for crystal structure prediction and crystal engineering.

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MS41-05 X-ray diffraction and spectroscopic study of selected complexes of amino acids with carboxylic acids at high pressures and low temperatures. Boris Zakharov,^{ab} Boris Kolesov,^{bc} Evgeniy Losev,^{ab} Elena Boldyreva,^{ab} *Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia,* ^bREC-008, *Novosibirsk State University, Novosibirsk, Russia,* ^c*Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia*
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Multicomponent crystals with components present in a well-defined stoichiometric ratio (salts and co-crystals) attract much attention. Crystals of amino acids and their derivatives are of special interest for studies at non-ambient conditions due to the following reasons. First of all, studies of such compounds are interesting for improving our understanding of factors determining the formation of a crystal structure and its variations vs. temperature and pressure. Also they are promising as new materials, and the structure-forming units in these crystals are similar to those in the biopolymers and can be used as biomimetics.

The main aim of this study was to compare the effect of increasing pressure and decreasing temperature on crystal structures of some selected derivatives of amino acids, that are bis(DL-serinium) oxalate dihydrate, DL-alaninium semi-oxalate monohydrate, and co-crystal of glycine with glutaric acid. A remarkable feature of these compounds is that very short O-H...O hydrogen bonds are present in the crystal structures.

The properties of several types of H-bonds in bis(DL-serinium) oxalate dihydrate and DL-alaninium semi-oxalate monohydrate have been studied on cooling, and it was possible to correlate donor-acceptor distances with frequencies of OH stretching vibrations. The present study is a rare example when correlations between geometry and energy parameters have been found for selected individual H-bonds in the same crystalline compound at multiple temperatures. Originally, we supposed that a co-crystal - salt transition may be possible for co-crystal of glycine with glutaric acid, similarly to what has been observed for some other compounds, but real behavior of the system turned out to be quite unexpected and more complex. The molecules of glutaric acid remained non-ionized in all the temperature range from ambient down to 100 K, but conformational polymorphic transformation with a change in the space symmetry group and doubling of Z' has been observed at 220-230 K.

Bis(DL-serinium) oxalate dihydrate and co-crystal of glycine with glutaric acid were studied at high pressures. Pressure-induced phase transitions related to lowering symmetry in both objects were detected and studied. It is interesting to note that high-pressure and low-temperature phases of glycine with glutaric acid co-crystal have the same structures.

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