MS15-P3 Hydrogen bonds in supramolecular crystals of carboxylic acid salts with aliphatic amines

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Design of new materials with interesting structure and properties is a very important area of research in materials science. This strategy is based on the formation of hydrogen bonds between molecules and/or ions in the crystal.[1-3] The salts composed of carboxylic acids and amines serve as a perfect example of compounds which crystal structures are stabilized by ionic interactions along with strong N-H…O hydrogen bonds.[4] In the salts of oxalic acid with amines there are many characteristic structural motifs i.e.: isolated oxalate monoanions or dianion units, linear chains of carboxylate monoanions formed by strong O-H…O hydrogen bonds or dimers of carboxylate monoanions.[5,6] In present study we have analyzed supramolecular structures of four salts: allylammonium hydrogen oxalate hemihydrates[7] (I), allylammonium hydrogen succinate[8] (II), bis(allylammonium) oxalate[9] (III) and isobutylammonium hydrogen oxalate hemihydrates[10] (IV) (Fig. 1). In the crystal structures of (I), (II) and (IV) the anionic sublattices are stabilized by strong O-H…O hydrogen bonds, while in (III) where anions are unprotonated only N-H…O hydrogen bonds are observed. The anionic and cationic substructures are linked to each other by N-H…O bonds accompanied by electrostatic interactions. The molecules form different structural patterns i.e.: chains (I), helical-like chains (II), layers (II) (III) or channels (IV), depending on the hydrogen bonds arrangement. References: [1] G. R. Desiraju, *Acc. Chem. Res*., 37 (2002) 565-573. [2] G. R. Desiraju, J. Chem. Sci., 122, (2010) 667-675. [3] G. R. Desiraju, J. Am. Chem. Soc., 135, (2013) 9952-9967. [4] K. Ejsmont, J. Zaleski, Acta. Cryst. E62 (2006) o2512-o2513. [5] R. Vaidhyanathan, S. Natarajan, C. N. R. Rao, J. Chem. Soc. Dalton Trans., (2001) 699-706. [6] J. C. MacDonald, C. P. Doeewstein, M.M. Pilley, Cryst. Growth Des. 1, (2001) 29-38. [7] B. Dziuk, B. Zarychta, K. Ejsmont, Acta Cryst. E70, (2014) o852. [8] B. Dziuk, B. Zarychta, K. Ejsmont, Acta Cryst. E70, (2014), o917-o918. [9] B. Dziuk, B. Zarychta, K. Ejsmont, Acta Cryst. E70, (2014), o1229-o1230. [10] B. Dziuk, B. Zarychta, K. Ejsmont, Acta Cryst. E70, (2014), o1175.

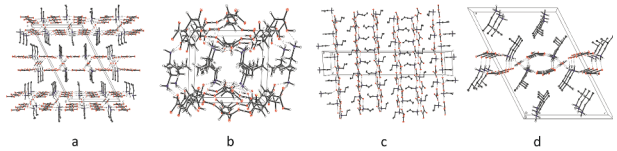

Figure 1. Crystal structure of (a) allylammonium hydrogen oxalate hemihydrate, (b) allylammonium hydrogen succinate, (c) bis(allylammonium) oxalate and (d) isobutylammonium hydrogen oxalate hemihydrate

Keywords: carboxylic acid salts, hydrogen bonds, supramolecules

MS15-P4 Atomic nature of the high anisotropy of borate thermal expansion

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The oxygen compounds are the excellent objects for thermal studies due to their wide occurrence. The actual data were taken preferably from the crystal chemistry of borates as one of the most representative class of oxygen compounds: in borates the boron atom could be located in BO_4 tetrahedra same as Si in SiO_4 tetrahedra as well as in BO_3 triangles like the carbon in carbonate ion CO_3. The borates are the champions in strongly anisotropic thermal deformations due to presence of the rigid B–O groups, BO3 triangles and symmetrically non-fixed angles in the unit cells. A question can arise, why such anisotropy of thermal deformations characteristic for borates is not characteristic to the same extent, for example, for silicates? Answer is simple – there are no unalterable atomic groups in silicates, such as rigid boron-oxygen groups, and there are no TO_3 triangles. In their turn, these planar anionic groups, like TO_3 triangles, form the basis of crystal structures of carbonates and nitrates, thereby compounds of these classes exhibit a strong anisotropy of thermal vibrations of oxygen atoms O and central atoms *T* (C, N) and, as a consequence, a strong anisotropy of thermal deformations of a compound in general is characteristic for them. Thus, mass manifestation of strong anisotropy of thermal deformation of crystals has at least three main reasons: (1) shears which are characterised by changes of angular lattice parameters; (2) strong anisotropy of atomic thermal vibrations in planar anionic groups (TO_3 triangles); (3) hinges, or deformations of an assembly of corner-sharing rigid groups, having no own (internal) degrees of freedom to adjust themselves to varying thermodynamic conditions (*T*, *p*, *X*). The first of the listed reasons can be realized in silicates and their structural analogues, the first and the second in carbonates, and all the three reasons are realized in borates. That is why borates demonstrate strongly anisotropic thermal expansion most often. It can be assumed that this is characteristic not only for thermal deformations, but also for pressure, compositional and other types of crystal structure deformations.

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[1] Bubnova R. S. & Filatov, S. K. Z. Kristallogr., 2013, 228 (9), 395–428. [2] Filatov, S. K. & Bubnova, R. S. Phys. Chem. Glasses: Eur. J. Sci. Technol. B, 2015, 56 (1), 24–35.

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