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Keywords: natural quantum wires, inorganic-organic hybrids, photoluminescence

MS24.P19

Acta Cryst. (2011) A**67,** C363

Structural diversity in layered organic materials through templating Co-crystallisation

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Layered materials are desirable targets in designing crystalline architectures, due to their many distinct, favourable physical properties. For example, in the pharmaceutical manufacturing industry, layered materials are more compactable into tablets, especially where the interactions between layers are much weaker than those within the layers, while in the design of porous materials, layered materials are much more likely to lead to channel structures and therefore provide an easy route to solvent or gas exchange. Crystal engineering is a well-developed approach for generating supramolecular constructs, mainly using hydrogen bonding as its structure-directing tool. However, it is often the presence of weaker interactions which lead to the formation of a truly layered structure - this is inevitably more difficult to control and can also often lead to the presence of significant structural defects, some of them beneficial to function.

We have developed a wide range of approaches for generating layered materials from multi-component crystallisations. This has not only involved conventional co-crystallisation of more than one molecule into the crystalline lattice, but also utilising co-molecules in a templating role, guiding the assembly of molecules towards a layered crystalline form. Amongst the significant findings in engineering and controlling the assembly of materials whose functionality is based on a layered architecture, the following will be discussed:

- a simple and reliable route to the formation of paracetamol Form II, a layered metastable polymorph with favourable compaction properties, produced through templating multi-component crystallisation [1];
- the porous, layered molecular material 4-phenoxyphenol, which is based on a dominant hexagonal hydrogen bonded motif, with *breathable* channels that are robust when both solvent-filled and empty;
- layered, channel-containing molecular complexes of nucleic acid bases, that show promise for the possibility of solvent or gas exchange, where C-H···F hydrogen bonds are integral to the formation of channels;
- multi-component systems including hydrates of both phloroglucinol and gallic acid in which solvent molecules play a crucial role in constructing and connecting the layers, and whose disposition can be elucidated by a combination of diffraction and quantum chemical calculations. The significant functional features of these structures are both layered and porous channel architectures, and the locally ordered defect structure is also vital to their function.

These functional molecular materials have as a common theme, a strongly hydrogen bonded motif, assembled into layers by weaker or stronger interlayer interactions, together with the possibility of local ordering, all of which can be vital in lending these materials their particular potential functional capabilities.

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Keywords: layered, porous, templating

MS24.P20

Acta Cryst. (2011) A**67,** C363

Ionic co-crystals of active pharmaceutical ingredients and their applications in the pharmaceutical industry

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The use of electrostatic interactions such as those present in ionic co-crystals (ICCs) containing alkali metals and alkaline earth metals compounds has never been systematically explored in the field of molecular Crystal Engineering. In this type of structures the interaction between inorganic ions and organic molecules must be seen as a special case of solvation, with the organic molecules acting as a solvent molecules (in competition with water if present) towards metal ions [1]. In the case of primary and secondary amides, N-H and C=O dipoles act respectively as donor and acceptor for hydrogen bonds, thus with the possibility of "solvating" inorganic salts.

We present here our results, from the serendipitous co-crystallizaton of barbituric acid with alkali halides, to the exploitation of the phenomenon and its application to crystal engineering issues. In particular we have investigated: the thermal behaviour of barbituric acid ICCs with alkali bromide and the associated dehydration processes; the "solvating properties" of a number of molecules, some of which are active pharmaceutical ingredients (APIs): diacetamide, malonamide, oxamide, urea, cyanuric acid, uric acid, carbamazepine, nicotinamide and piracetam. As for the inorganic counterpart, the $CaCl_2$ salt was chosen because of its non-toxicity and potential applications in the Pharmaceutical field. Synthetic methods for this study vary from classical crystallization from solution, to slurry and mechanochemical solid state techniques (grinding and kneading).

ICCs were obtained for most of the organic molecules. Crystal structures were solved from single crystal data, or by powder diffraction using simulated annealing (SA) procedures when no single crystal was available. Due to the high number of degrees of freedom in the SA algorithm, an alternative approach was adopted: $Ca\cdots O_{water}$ fragments extracted from the Cambridge Structural Database were inserted as rigid bodies in the algorithm to minimize calculation time and bias solutions towards chemically reasonable coordination patterns. All crystalline compounds were analyzed with DSC, TGA and variable temperature XRD. Dissolution rate measurements were performed on ICCs of APIs. The new phases differ from the starting components for physical properties such as melting point and solubility rate.

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Keywords: solvent_free_reaction, pharmaceutical, powder_diffraction