

**MS35-O4** Structural behavior of highly hydrated cyclodextrin complexesJanusz Lipkowski<sup>1</sup>, Iwona Justyniak<sup>2</sup>

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Cyclodextrins are commonly known as materials having intra-molecular cavity able to accommodate guest species. This property, when combined with sorption in the inter-molecular space in the solid state structures of CDs leads to the very interesting structures and properties. When combined with complexation of metal ions by CDs, this area links to the very important, so-called- MOFs.

Cyclodextrins are hydrophilic in their outer part while more hydrophobic in the intramolecular space. Typical structural behavior is thus hydration in the outer sphere, or solvation, if water is mixed with other solvents, like alcohols. However, as we have recently discovered, hydration of the crystals while in mother solution may, in some cases, significantly differ quantitatively from the crystals picked-out in a drop of solution ! Two novel crystal structures were found for such highly hydrated CDs and will be discussed in this paper. The structures can convert in a single crystal to single crystal transformation when partially dehydrated.

In general, such behavior may be observed only when CD moieties are at equilibrium with a solution of the respective guest and solvent species. The equilibria are quite sensitive to minor changes of solution chemical composition what may be observed microscopically as morphology changes of the crystalline phases. This phenomenon will be illustrated with short movies demonstrating crystal behavior on change of its environment

Additional information concerns the supramolecular aggregation of water in the samples. This will be discussed based on temperature dependence of lattice parameters of one of the highly hydrated structures. It shows a mixed hydrophilic/hydrophobic behavior. Hydrophobic hydration produces a reduction in density and an increase in the heat capacity. The expanded network causes the density decrease whereas the ordered bonds must be bent on increasing the temperature, so affecting the heat capacity. Thus, hydrophobic hydration behaves in an opposite manner to polar hydration, which increases the density and decreases heat capacity due to their associated disorganized hydrogen bonds being already bent or broken [1]. Experimental x-ray data will be presented to illustrate such a behaviour on CD complex structure

Reference:

Martin Chaplin, "Water – structure and science", [www.lsbu.ac.uk/water](http://www.lsbu.ac.uk/water)

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**Keywords:** cyclodextrin, organic zeolite, porous molecular structure, hydration, polymorphism

**MS35-O5** Single-crystal-to-single-crystal transformations and porosity studies of mixed-ligand metal-organic frameworksClive L. Oliver<sup>1</sup>

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Metal-organic frameworks (MOFs), infinite systems built up of metal ions and organic ligands, have been extensively studied in materials and supramolecular chemistry due their structural diversity and application as porous materials, in catalysis, ion exchange, gas storage and purification. [1] We have investigated the construction of MOFs using transition metals (e.g., cadmium, copper, zinc) and mixed ligands (e.g., trimesic acid, 5-nitroisophthalic acid, 1,2-bis(4-pyridyl), 4,4'-bipyridine-N,N'-dioxide) with a view of producing porous materials which may be used for the sorption of gases or liquids. Several MOFs were produced which were characterized by single crystal X-ray diffraction, powder X-ray diffraction (PXRD), thermal analysis and sorption studies. At least three of these MOFs retained their crystallinity upon heating as indicated by variable-temperature PXRD. One of the MOFs is a 2-fold interpenetrated, pillared, cadmium metal-organic framework consisting of trimesic acid and 1,2-bis(4-pyridyl)ethane.[2] This compound exhibits a temperature-induced single-to-crystal-single-crystal (SC-SC) transformation upon the release of N,N'-dimethylformamide (stable up to 300 °C). SC-SC transformation was also observed when the desolvated form absorbed selected polar and non-polar organic solvents. In addition, gas (N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O) sorption experiments were performed showing 2.5% N<sub>2</sub>, 4.5% CO<sub>2</sub> and 3.4% N<sub>2</sub>O absorption by mass at room temperature and moderate gas pressures (~10 bar). A second 2D network consisting of zinc, trimesate and 4,4'-bipyridine-N,N'-dioxide also remarkably showed a SC-SC transformation upon desolvation. In both structures no clear channels are present in the structure which indicate the occurrence of cooperative structural changes upon desolvation in order to retain their monocrySTALLINITY.

**Keywords:** single-crystal-to-single-crystal transformation, porosity