ESRF	**Experiment title:** Host-guest interactions in nanoporous Metal-Organic Frameworks	**Experiment number**: CH-3146
Beamline: ID31	**Date of experiment**: from: 14 May 2010 to: 17 May 2010	**Date of report**: *Received at ESRF:*
Shifts:	**Local contact(s)**: Adrian Hill	
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Report:

We have very sucessfully used ID31 in the past few years to study flexible metal organic framework materials in the presence of various guest molecules. These solids are able to respond to the presence of small molecules to undergo dramatic volume expansion or contraction involving atomic displacements of several Ångströms, giving them distinctive properties over conventional inorganic porous materials. By immersing a solid host in a liquid guest within a capillary followed by concentration of the solid using a centrifuge, we have been able to measure extremely high quality data from host:guest systems and then refine the location of the guest molecules. This has included a number of aromatic organic molecules[1] and aliphatic alcohols,[2] where we also able to isolate metastable, partially expanded forms of the solid.

During this allocation of beamtime we studied one of the simplest case: the hydration of the Cr(III) terephthalate, MIL-53. This material This material, $Cr(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$, was first described as a desolvated form: its structure consists of infinite chains of $\{CrO_4(OH)_2\}$ octahedra trans- linked by μ_2-bridging hydroxides and crosslinked by bis-bidentate terephthalate (1,4-benzenedicarboxylate) ligands whose oxygen donors complete the coordination about chromium.[3] Other analogues of the MIL-53 structure are known that contain the metals Fe, Al, Ga and In, all in the +3 oxidation state, [4] and this family of materials has been the focus of some considerable attention with respect to the sorption properties towards a variety of molecules from small gases such as CO_2, CH_4 and H_2S to a range of organic molecules, where it has been shown that considerable expansion of the structure may take place with insertion of guest molecules.[5] The hydrated form of MIL-53(Cr), $Cr(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)\cdot(H_2O)$ that is isolated as a green polycrystalline powder at room temperature contains one molecule of water per chromium. In the current work, high resolution powder X-ray diffraction has allowed accurate location of the guest water molecules in the solid, not previously described, Figure 1. The water molecules in hydrated MIL-53(Cr) reside in the one-dimensional channels and interact with hydrogen bonds to the hydroxide anions that form the backbone of the inorganic chain (closest O1--Ow1 distance of 2.800(6) Å), or to form a water dimer (Ow--Ow = 2.671(7) Å) (Figure 1b). It is established that dehydration occurs at 80 °C and this results in a dramatic unit cell volume expansion (from ~995 to ~1496 Å^3) involving displacement of the framework atoms of up to 5.2 Å.[5a] We have now found evidence for the expansion of MIL-53(Cr) in the presence of excess water. The final Rietveld plot following structure solution and refinement is shown in Figure 1. The structure solution reveals a fully expanded form of the solid that contains close to six water molecules per unit cell (one site Ow4 is partially occupied) in an ordered arrangement. The unit cell volume of the structure in this 'superhydrated' state

(~1550 Å^3) is larger than the dehydrated material previously reported (~1496 Å^3)[5a] but the symmetry (*Imcm*) is identical.

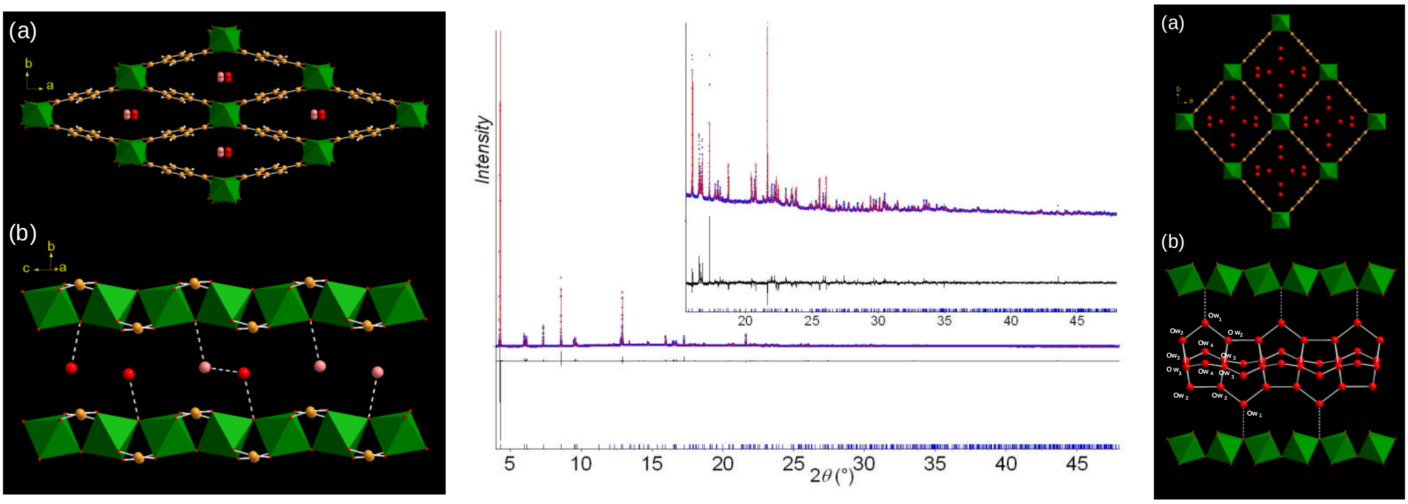

Fig. 1 (left) Two views of the structure of hydrated MIL-53(Cr)(H_2O) (a) parallel to the lozenge-shaped channels and (b) perpendicular view of a single channel. The green octahedra are Cr(III)-centred building units and the oxygen atoms of occluded water are shown as red or pink spheres. Although there is one crystallographic site for water, it is 50 % occupied and in (b) the scenarios of water hydrogen bonding are shown. (middle) Final Rietveld plot for superhydrated MIL-53(Cr)(6.2H_2O). (right) Two views of the structure of superhydrated MIL-53(Cr)(6.2H_2O) (a) parallel to the lozenge-shaped channels and (b) perpendicular view of a single channel. Legend as for Figure 2. Water-water hydrogen bonds are shown in white and the water-framework hydrogen bond as a dotted line.

The water molecules in the superhydrated form of MIL-53(Cr) are linked by inter-water hydrogen bonding (with closest oxygen-oxygen distances ranging from 2.627(5) to 2.769(4) Å) to form infinite tubes running parallel to the inorganic chain (Figure 3b). There are weaker hydrogen bonds between one of the water molecules and the framework hydroxide (3.069(8) Å). The tubular motif is constructed from four-, five- and six-rings of water molecules. A search of the Cambridge Crystal Structure Database reveals no other reported crystalline material with such a motif for hydrogen-bonded water in systems that encapsulate water. Although a variety of infinite tape (T) oligomers have been observed in organic molecular crystals, none reported so far has the tubular nature of the water in superhydrated MIL-53(Cr). The results of this study were complemented by time-resolved diffraction studies of the dehydration of the superhydrated and have been published in *Chemical Communications*.[6]

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