	Experiment title: High Resolution PXRD Studies of the Localisation of Guest Molecules Inside Nanoporous Metal-Organic Frameworks	**Experiment number**: **CH- 2624**
Beamline: ID31	**Date of experiment**: from: 14th March 2008 to: 18 March 2008	**Date of report**: January 2009
Shifts: 9	**Local contact(s)**: I. Margiolaki	*Received at ESRF:*

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Report:

Our objective was to use high resolution powder X-ray diffraction to investigate the localisation of guest molecules in nanoporous metal-organic framework materials. Some of these materials are already known to exhibit spectacular 'breathing' effect upon introduction of organic guest molecules into their porous structures, involving atomic displacements of several Ångströms. The full localisation of various guest molecules (polar, apolar, protic, aprotic) is important for the understanding of the sorption properties of this important family of materials (mainly the nature of the interaction between the host and the guest) for applications in separation and potentially catalysis. The materials are generally only formed as polycrystalline powders and hence the high resolution and fast count rate of ID31 is required to measure data of sufficiently quality for structrue refinement and also to permit large numbers of samples to be screened.

Our initial focus was to characterise properly the host material MIL-53, an iron (III) carboxylate $Fe^{III}(OH)\{O_2C\text{-}C_6H_4\text{-}CO_2\}H_2O$. In the presence of water this material exists in a closed form, rather like its known Cr(III) analogue. Careful TGA experiments in the laboratory revealed water loss to take place in one step in a small temperature range around 333 K. Our experiments on ID31, using samples careful dried within capillaries and heated *in situ*, revealed some striking results; in particular, and in stark contrast to its chromium and aluminium analogues which show a dramatic expansion of the cell during dehydration, with iron, reversible dehydration occurs via evolution of the structure through a highly distorted metastable anhydrous phase to a more regular phase above 423 K in which pore volume remains approximately constant.

This work has now been published in *Chemical Communications*,[1] and is illustrated in the figures below.

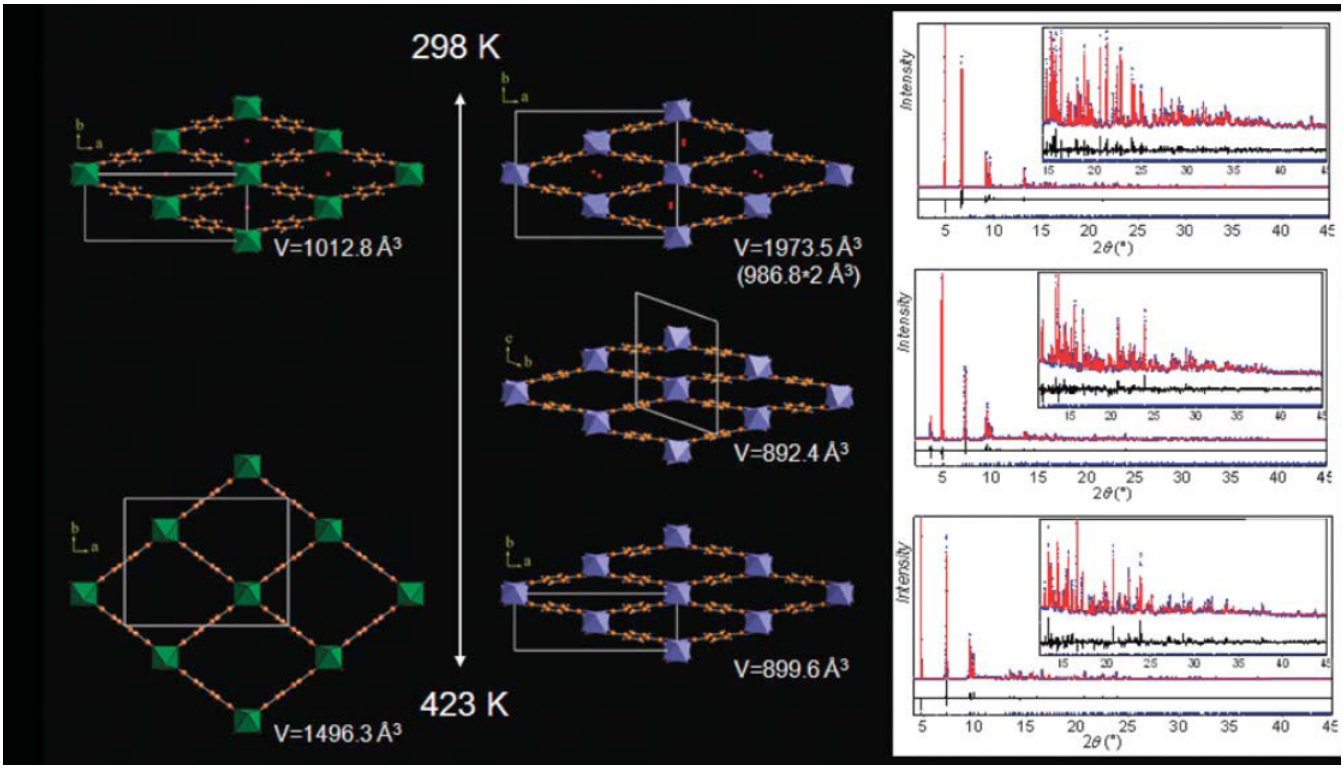

Figure 1: The structures of MIL-53(Cr), left, and its analogue MIL-53(Fe), middle, along with final Reitveld plots obtained form strcuture solution and refinement of the new Fe materials.

We also studied a number organic guests, such as lutidine (2,6, dimethyl pyridine) and isomers of xylene and for some of these materials we observe the unexpected co-sorption of water. Full structure refinement is now in progress for a number of these materials and we aim to publish a paper later this year describing the results of this detailed studied. These structures are also enabling us to understand our results of *in situ* EDXRD measurements (previously at the Daresbury SRS and now at HASYLAB) where we have monitored the sorption of the same guest molcules in real time.

1. "Effect of the Nature of the Metal on the Breathing Steps in MOFs with Dynamic Frameworks" F. Millange, N. Guillou, **R.I. Walton**, J. Grenèche, I. Margiolaki and G. Férey, *Chem. Commun.* (2008) 4732-4734