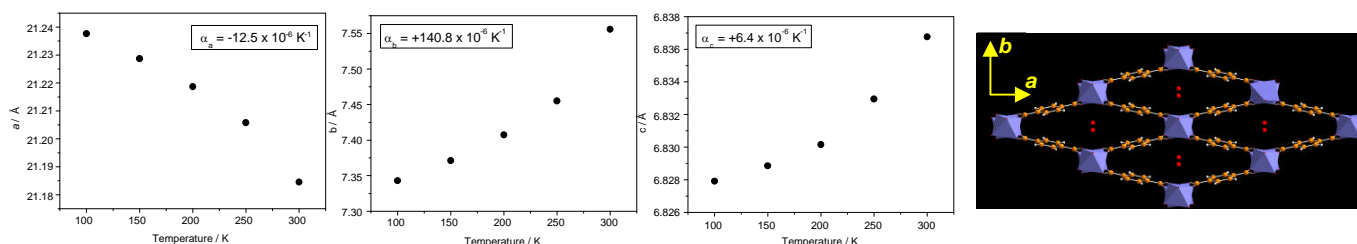
	<b>Experiment title:</b> Unusual Thermal Expansivity Behaviour of Metal-Organic Frameworks	<b>Experiment number:</b> CH-2713
<b>Beamline:</b> ID31	<b>Date of experiment: -</b> from: 06 May 2009 to: 11 May 2009	<b>Date of report:</b> February 2010
<b>Shifts:</b> 15	<b>Local contact(s):</b> A. Fitch	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Richard I. Walton, Franck Millange*, Manuela E. Medina*, Nathalie Guillou* Department of Chemistry, University of Warwick, UK Institut Lavoisier, Université de Versailles		

## Report:

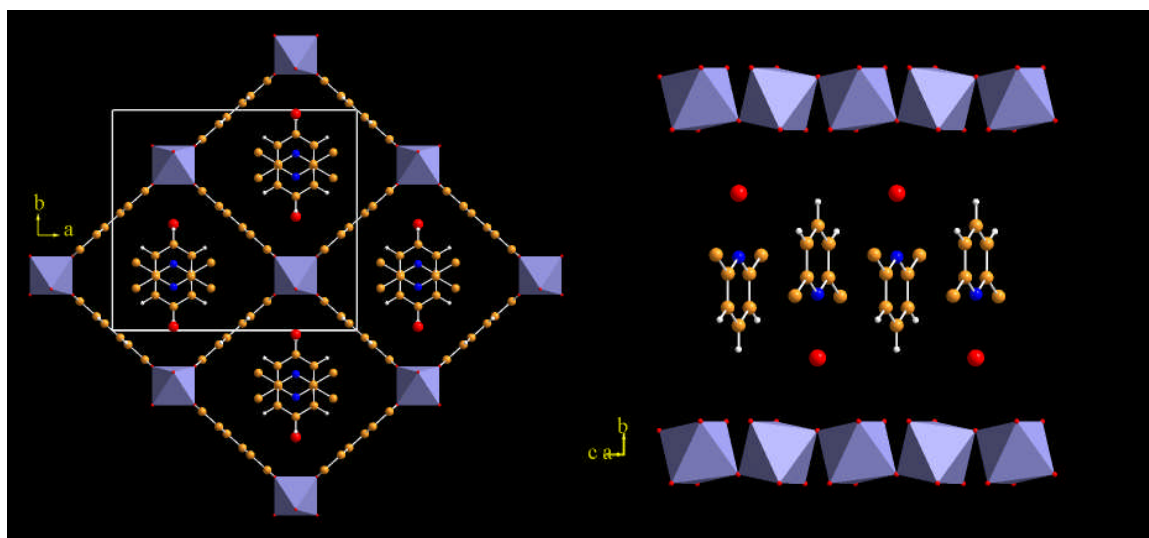
Nanoporous materials continue to attract much attention because of their applications in separation, ion-exchange and shape-selective catalysis that provide many technological and commercial uses. Inorganic zeolite-materials have been well-studied for these uses for a good many years, but attention has recently focussed upon a new family of nanoporous materials: metal-organic frameworks (MOFs).<sup>1</sup> MOFs have structures constructed from clusters of metal polyhedra linked by polydentate organic ligands to yield three-dimensional extended networks with porosity on the nanoscale. One attraction in studying these materials lies in the possibility of design in their synthesis: by selecting metals with desired coordination number and geometry preferences and choosing ligands of certain size and shape, it is conceivable that an extended network may be constructed with desired connectivity, porosity and chemical functionality.<sup>2</sup> A second remarkable feature of many metal-organic frameworks is their structural flexibility: many materials show a massive volume change upon uptake of guest molecules with crystallinity maintained.<sup>3, 4</sup>

The aim of this work was to study the flexibility of MOFs, including a study of their thermal expansivity and also the effect of the presence of guest molecules. The solid MIL-53, a metal carboxylate containing Fe(III) and benzene-dicarboxylate linkers,<sup>5</sup> was studied, as shown in Figure 1, the material shows highly anisotropic thermal expansivity with positive thermal expansion in two directions and negative in others. We are currently refining the structures of the material at each temperature in order to understand the origin of this anisotropy.



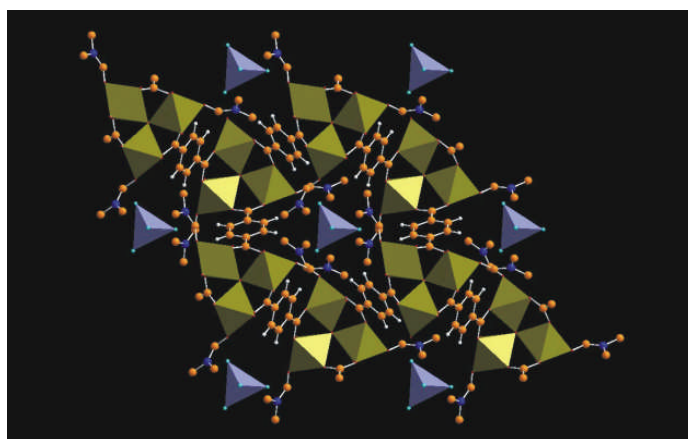
**Figure 1: Thermal variation of cell parameters for MIL-53-Fe(H<sub>2</sub>O). The structure is shown viewed along c**

During our allocation of beamtime we have also studied the structures of the same MOF, MIL-53, in which various guest molecules have been introduced into the porous structure, replacing the water initially present. In the case of the organic lutidine (dimethylpyridine) we previously had used time-resolved diffraction at the Daresbury SRS to show its rapid sorption by the solid.<sup>6</sup> We have now solved the structure of the final product by examining a sample of the material immersed in the organic liquid within a capillary that has been centrifuged to concentrate the solid and proved that the material actually contains lutidine co-sorbed with water (Figure 2). The water forms a bridge between the lutidine molecule and framework OH by doubly hydrogen bonding and this gives a fully expanded form of the MIL-53 structure. The results of this structural study are currently being prepared for publication.<sup>7</sup>



**Figure 2:** Two views of the expanded form of MIL-53 that is formed when lutidine is introduced. Left: a view along the channels running parallel to *c*, and right showing the relative positions of lutidine molecules and co-sorbed water (red circles).

Using this allocation of beamtime we also took the opportunity to examine the structures of some other related MOF materials. In one case we were able to isolate an intermediate phase seen during the crystallisation of MIL-53. The high quality data obtained on ID31 allowed full structure solution and refinement to prove that the intermediate is related to a known MOF, MOF-235, that is built from trimeric Fe clusters but also contains extra-framework  $[\text{FeCl}_4]^-$  that balance the negative charge of the framework. This is an important result since it shows that the transient kinetic product during crystallisation does not contain the same iron connectivity seen in the final product, suggesting that redissolution of the intermediate must occur before nucleation of the product. These results have just been published in *Angew. Chem.*<sup>8</sup>



**Figure 3 :** Polyhedral view of the refined structure of the intermediate phase seen during the crystallisation of MIL-53 showing trimeric building units.

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