

Preliminary report: 1st June 2007

Experiment No. 01-02-769 Beamline: BM01A Dates: 07-MAR-07 to 09-MAR-2007

Title: *Exploring the structural transformations of metal-organic framework materials on adsorption and desorption of solvent molecules.*

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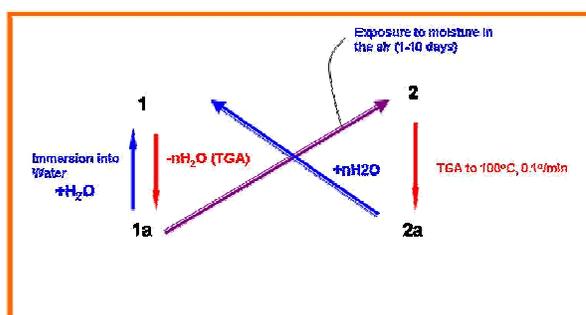
Summary of experiment/results obtained

This experiment was aimed at extracting information on the structural transformations involving the chiral three-dimensional systems

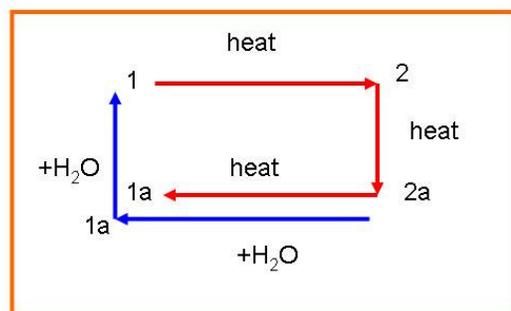
$\{[\text{Cu}((1R,2R\text{-diaminocyclohexane}))_2]_2[\text{Ru}(\text{CN})_6] \cdot 10\text{H}_2\text{O}\}_\infty$ (**1**): monoclinic, C2

and $\{[\text{Cu}((1R,2R\text{-diaminocyclohexane}))_2]_{12}[\text{Ru}(\text{CN})_6]_6 \cdot 24\text{H}_2\text{O}\}_\infty$ (**2**): triclinic, P1

and to correlate this information with the static adsorption/desorption isotherms and the immersion calorimetric results. In-house measurements had been carried out on the original systems, **1** & **2**, and on the dried samples, **1a** & **2a**. Samples **1a** & **2a** were then immersed in water and their diffractogram recorded. It was shown for both that the resulting diffractograms resembled that of crystalline **1**.



In-house results



In-situ SNBL measurements

For the in-situ experiments, carried out at the SNBL, only water vapour adsorption/desorption was studied. They showed that these transformations were more complex than first imagined. Heating **1** does give **1a**, but it was observed to first transform to **2**, then on continued heating to **2a**, and finally to **1a**. By passing nitrogen gas saturated with water vapour through the capillary it was possible to observe that **1a** does indeed revert to **1**. So the process is reversible but the pathway is not direct as was concluded from the in-house measurements. For system **2/2a** this transformation was not reversible. Heating **2** does indeed give **2a** but on passing a stream of nitrogen gas

saturated with water vapour it was seen that **2a** transforms to **1** passing through an intermediate stage, that is **1a**. This first transformation is very rapid and we need to perfect our experimental system to monitor this more accurately.

The in-house methanol adsorption isotherms indicated that the uptake of solvent by compound **2a** is a two step process. In view of the results noted above this seems reasonable and we propose that the first step involves the structural transformation of **2a** to **1a** followed by the uptake of the solvent molecules to form **1**. Water adsorption isotherms are particularly long and tedious to carry out but this is being done at the moment. The next step will be to repeat the above in-situ experiments using methanol, to show that the same complex transformation (**2** -heat- → **2a** -adding solvent- → **1a** -adding solvent- → **1**) is observed. The possibility of following this experiment by in-situ Raman spectroscopy would also be very interesting.