



	<b>Experiment title:</b> <b>Crystal structure of metal-organic framework compounds from high resolution powder diffraction data</b>	<b>Experiment number:</b> 01-01-686
<b>Beamline:</b> BM01	<b>Date of experiment:</b> from: 15/9 2005 to: 20/9 2005	<b>Date of report:</b> 23/11 2005
<b>Shifts:</b> 15	<b>Local contact(s): Hermann Emerich, Wouter van Beek</b>	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  <b>*Pascal Dietzel, *Nicolas Creon, *Nataliya Sharova, Poul Norby, Helmer Fjellvåg,</b> <b>Department of Chemistry, University of Oslo, N-0315 Oslo, Norway</b>		

## Report:

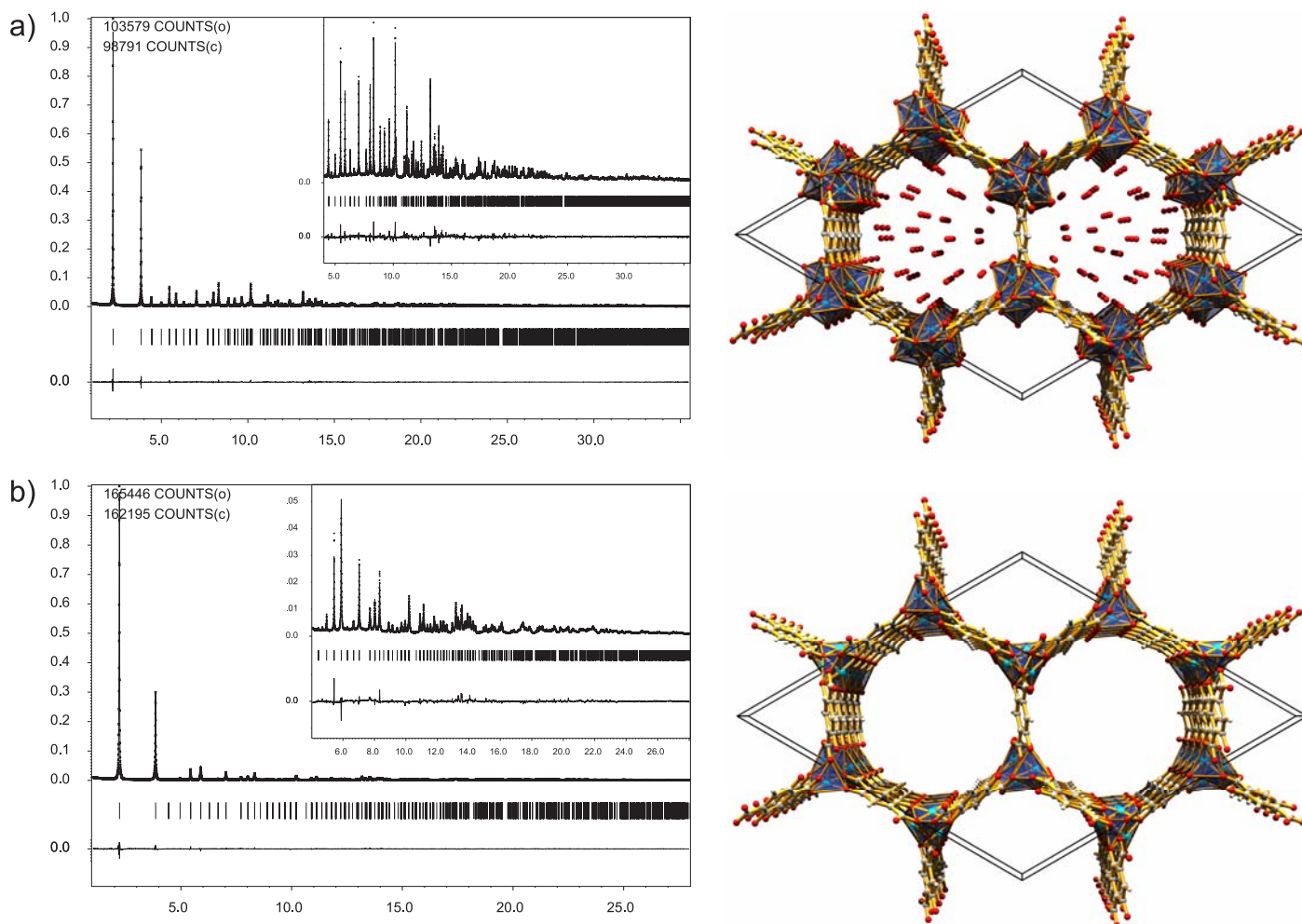
Coordination polymers (also known as metal-organic framework compounds) consist of metal or metal cluster centers that are linked by multidentate organic ligands. This interconnectivity can result in one-, two-, or three-dimensional networks. By an adept choice of components structures with large pore sizes can be achieved. The interest in this class of compounds stems not only from the structural diversity they display but moreover from their potential applicability in such areas as catalysis, gas adsorption and ion exchange.

The extended dimensionality of coordination polymers is naturally accompanied by a limited solubility which is exploited in their synthesis usually under solvothermal conditions. However, this also entails that the crystallites obtained in that way are often of a size that is not sufficient for structure determination by single crystal structure analysis. Structure determination from polycrystalline samples collected with conventional powder diffractometers in the home lab is usually not possible because the large unit cells of these supramolecular assemblies result in many overlapping reflections and the presence of many only weakly scattering light atoms of the organic moieties and of solvent filled cavities in the structure causes a rapid decrease in observed intensities with theta. The utilization of high resolution data collected at the high intensity synchrotron source is therefore vital for the structure determination of many metal-organic framework compounds.

In the present experiment, we have successfully collected high resolution powder diffraction data on about twenty coordination polymers synthesized in our lab for which we were unable to obtain large enough single crystals or good enough powder X-ray data.

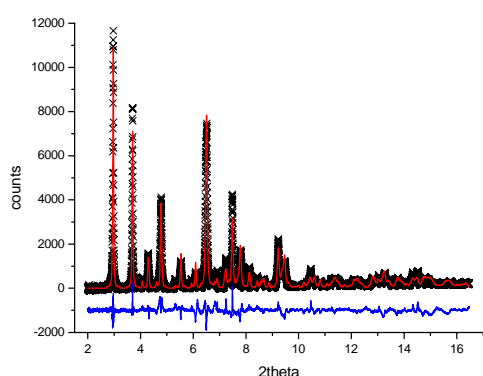
One of the substances we were particularly interested in this beamtime is formed as light green powder from nickel(II) acetate and 2,5-dihydroxyterephthalic acid. The powder pattern was virtually identical to the pattern of a cobalt(II) compound for which we recently reported the single crystal structure of its hydrated and dehydrated form (*Angew. Chem. Int. Ed.* **2005**, *44*, 6354). The crystallites of the nickel compound were too small, however, for single crystal work. The as-synthesized nickel compound was therefore measured to confirm that it is isostructural to the cobalt compound. Another sample of the substance was heated in a capillary a dynamic vacuum at 100°C and flame-sealed prior to the beamtime to try and refine the dehydrated structure. Refinements of both diffractograms confirm the honeycomb-like structure of the framework (figure 1). It contains one-dimensional channels of ~11 Å diameter which are filled with water in the hydrated state. In the dehydrated state, the metal has a vacant coordination site that is accessible from the cavity of the framework structure. Such open metal sites may enhance the strength of the interaction between framework

and adsorbed gas molecules, and the results of these refinements and hydrogen adsorption experiments have been submitted for publication.

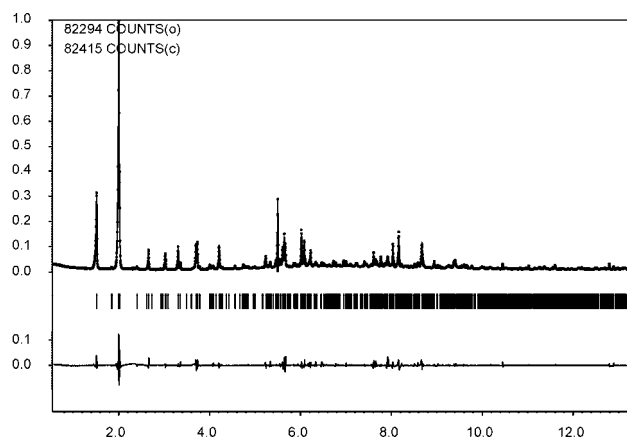


**Figure 1.** Rietveld refinement plots (insets: enlarged view of the high angle range) and structure drawings of the hydrated (a) and dehydrated (b) form of the nickel coordination polymer.

The majority of the remaining measurements have also been indexed successfully. Structure solution then is attempted by direct methods (using EXPO2004) or simulated or parallel annealing (with DASH or Fox) using the known organic fragments and metals as input. At this point of time, we have two structures that were successfully solved using rigid bodies and simulated annealing (the results for the simulated annealing of one of them are shown in figure 2). They were non-porous. Another sample where we have so far put a lot of effort into solving the structure is known to be permanently porous with a Langmuir surface area of  $\sim 1700 \text{ m}^2 \text{ g}^{-1}$ . The pattern is indexed in the orthorhombic crystal system ( $a = b = 21.9078 \text{ \AA}$ ,  $c = 37.1540 \text{ \AA}$ ,  $V = 17832 \text{ \AA}^3$ , figure 3). Structure solution is ongoing with the above mentioned methods.



**Figure 2.** Result of the simulated annealing using the rigid body of the large organic linker and zinc input.



**Figure 3.** Preliminary LeBail fit of a metal-organic framework compound with large permanent porosity.