



	<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: 4/3 2005 to: 8/3 2005	<b>Date of report:</b> 23/11 2005
<b>Shifts:</b> 12	<b>Local contact(s): Wouter van Beek</b>	<i>Received at ESRF:</i>
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## Report:

Coordination polymers 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.

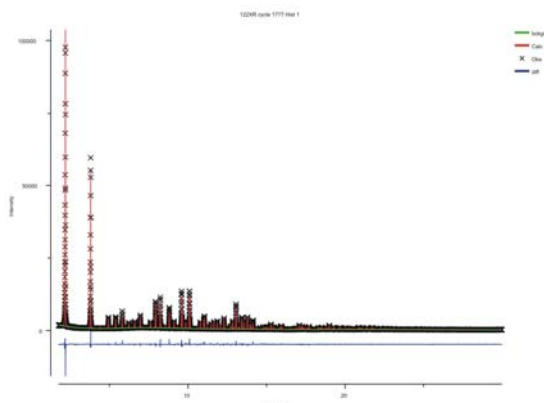
One of the most utilized methods of synthesis of MOF compounds is by solvothermal reaction of a metal compound and the organic linker. As a consequence of their extended structures, MOF compounds are commonly highly crystalline, but they also exhibit a fairly low solubility. This results in polycrystalline samples unsuitable for single-crystal diffraction experiments. Attempts to determine the crystal structure from these powder samples using common laboratory X-ray sources frequently meet with a number of problems. Because the MOFs are predominantly composed of light atoms with weak scattering power, the observed intensity rapidly declines with theta. Many MOFs also have quite large unit cells. This is in particular the case for the microporous framework compounds that we are predominantly interested in. As a result of these issues, one frequently observes many overlapping reflections with low intensity already at modestly low theta values. This often even prevents indexation of the sample. Synchrotron radiation with its superior brilliance and angular resolution is perfectly suited to circumvent these problems. Because of the former data with a sufficient signal to noise ratio even for the many weak reflections can be collected, while its resolution together with the high crystallinity of the samples allows for an easier discrimination of overlapping reflections. As an effect, indexation and structure solution are greatly facilitated.

In the present experiment, we have successfully collected powder diffraction data on several samples on the high resolution station of the Swiss-Norwegian beamline (SNBL). We will present the current status of the measurements from the beamtime below.

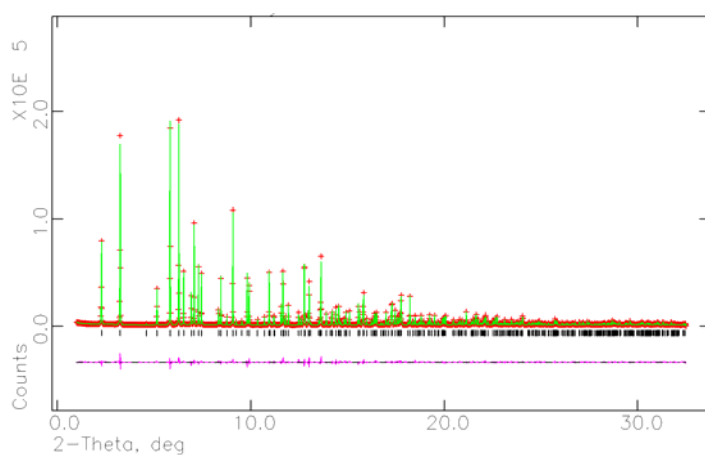
1. By reacting thiazolidine-2,4-dicarboxylic acid in mixtures of acetonitrile and water with zinc nitrate, cobalt nitrate and manganese nitrate, respectively, we were able to synthesize a series of isostructural compounds, denoted CPO-11. The structures were solved by direct methods from synchrotron powder x-ray data using EXPO2004. The refinement of CPO-1-Zn has been performed using GSAS (figure 1). The CPO-11 type of compounds is a 3D coordination polymer containing of two types of isolated, parallel channels (figure 2).

2. Figure 3 shows the status of refinement of a porous coordination polymer that is isostructural with a cobalt compound and a nickel compound we have previously reported (for the latter see the September report). The structural model was obtained from the single crystal structure determination of the cobalt compound. The refinement is currently stuck at acceptable residuals (R values below 10%,  $\chi^2 \sim 6$ ), however, the difference plot shows unacceptable large deviations which are caused in part by the strong asymmetry of the reflection shape at small angles and a problem of getting the best profile fit.

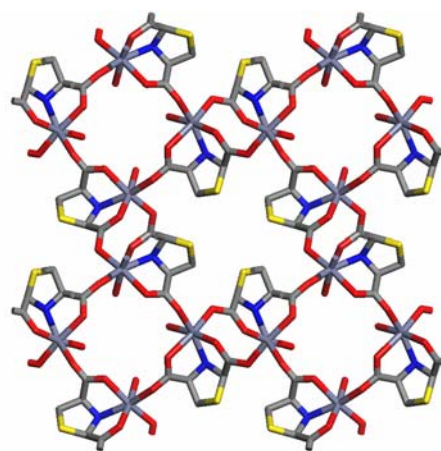
3. Interpenetration is frequently observed for frameworks with three-dimensional cavities that are large enough to allow a second network of the same type to occupy the space provided in the voids. We recently reported (*Dalton Trans.*, in press) such an interpenetrated structure formed by zinc, 2,2'-biphenyldicarboxylate, and 4,4'-bipyridine (orthorhombic,  $a = 23.270 \text{ \AA}$ ,  $b = 24.089 \text{ \AA}$ ,  $c = 29.240 \text{ \AA}$ ,  $V = 16391 \text{ \AA}^3$ ). There is the possibility that the structure will crystallize non-interpenetrated if the space requirements of the neutral bridging ligand change slightly. We, therefore, conducted analogous syntheses with similar bidentate nitrogen donor molecules. The results of the measurement for two such compounds are shown in figure 4. Both compounds crystallize in large unit cells as can be seen from the positions of the reflections. We have not been able to index the substance on the top successfully yet, unfortunately, even though the diffraction pattern is well resolved. Needless to say, it is a computationally daunting task to index unit cells of low symmetry and volumes in the range of 10000 to 20000 or possible more. The pattern on the bottom of figure 4 can be indexed as orthorhombic ( $a = 49.3617 \text{ \AA}$ ,  $b = 39.9208 \text{ \AA}$ ,  $c = 37.3629 \text{ \AA}$ ,  $V = 73626 \text{ \AA}^3$ !). At this point, we are unable to even compute a LeBail fit because of excessive peak overlap (in Fullprof, Jana2000 crashes on trying to fit the pattern).



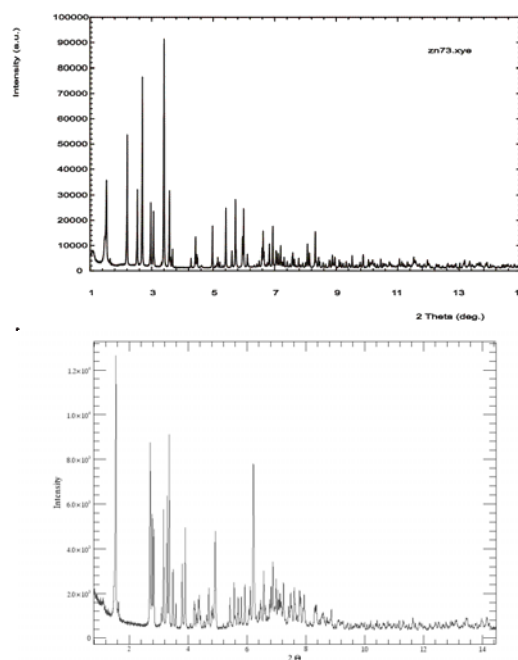
**Figure 3.** Rietveld refinement of a porous coordination polymer with honeycomb structure.



**Figure 1.** Observed, calculated and difference powder X-ray diffraction profiles for CPO-11-Zn.



**Figure 2.** The crystal structure of CPO-11-Zn seen along [001] showing the two types of isolated parallel channels



**Figure 4.** Synchrotron diffraction patterns of two large unit cell coordination polymers containing zinc, 2,2'-biphenyldicarboxylate and a bridging bidentate neutral ligand ( $\lambda \sim 0.5 \text{ \AA}$ ).