	<b>Experiment title:</b> Analysis of complex structures using high-resolution powder diffraction data	<b>Experiment number:</b> 01-01-716
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## Report:

High-resolution powder diffraction data were collected on nine samples during the two experimental sessions. Two of these were metal-peptide framework (MPF) materials, one a metal-organic framework (MOF) material, three non-zeolite microporous silicates, one a germanosilicate zeolite, one a zirconium phosphate layered material, and one an organic semiconductor with a phase transition at 136°C. None of the structures were known.

A basic structure for the MPF-9 material ( $\text{Cu}(\text{NH}_3)_2(\text{C}_{23}\text{N}_3\text{O}_8)\cdot\text{H}_2\text{O}$ ;  $C2$ ;  $a=19.266\text{\AA}$ ,  $b=4.885\text{\AA}$ ,  $c=30.514\text{\AA}$ ,  $\beta=92.5^\circ$ ) was found using the direct-space global optimization program *Fox* [1]. The structure was then completed using difference Fourier techniques and refined using the Rietveld method [2]. The final structure is shown in Figure 1 and the profile fit in Figure 2.

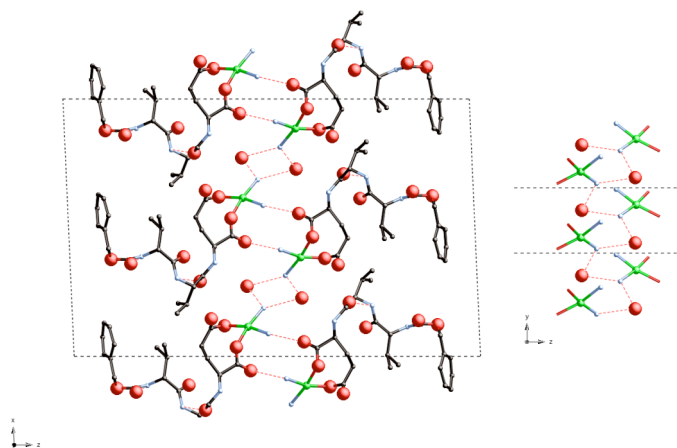


Figure 1. Structure of MPF-9 showing the H-bonding scheme

Unfortunately, the quality of the MPF-2 sample ( $\text{Ca}(\text{C}_{23}\text{N}_3\text{O}_8)\cdot 4\text{H}_2\text{O}$ ; monoclinic;  $a=113.7\text{\AA}$ ,  $b=9.7\text{\AA}$ ,  $c=29.9\text{\AA}$ ,  $\beta=94.8^\circ$ ) was insufficient for detailed structure analysis, but its pattern does indicate that the material has a lamellar structure.

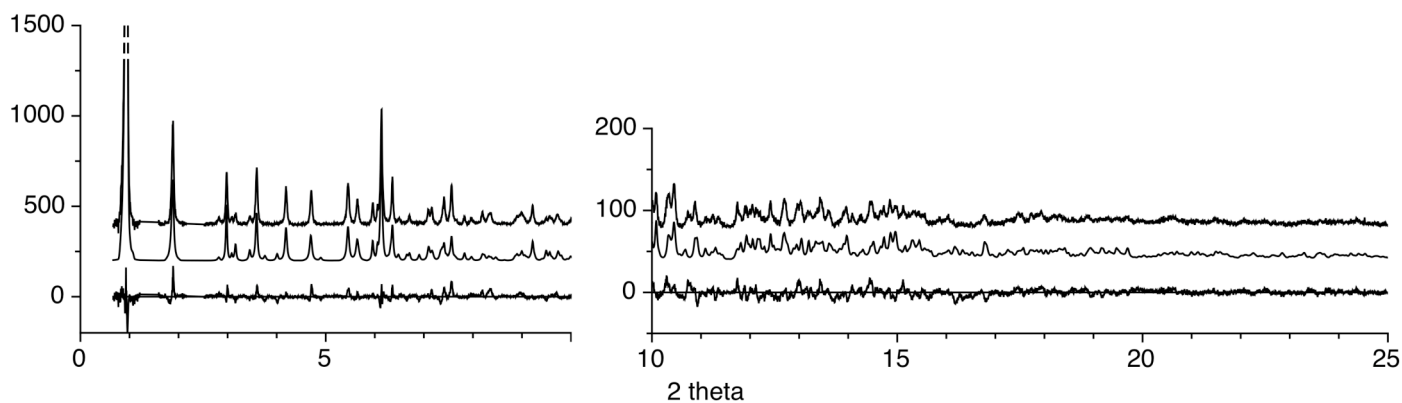


Figure 2. Observed (top), calculated (middle) and difference (bottom) profiles for the Rietveld refinement of MPF-9 ( $\lambda = 0.50007 \text{ \AA}$ ). The first peak has been cut at  $3/8$  of its maximum and the  $10\text{-}25^\circ 2\theta$  region has been scaled up by a factor of 5 to show more detail.

Initial attempts to solve the structure of the scandium silicate sample (orthorhombic;  $a=28.510\text{\AA}$ ,  $b=7.084\text{\AA}$ ,  $c=13.462\text{\AA}$ ) yielded some promising (incomplete) models, but subsequent difference Fourier maps could not be interpreted satisfactorily. High-resolution transmission electron microscopy images have now shown that the material is highly faulted, so no further structural analysis has been undertaken.

The data collected on the two niobium silicate samples (one as synthesized and one calcined) are being used in conjunction with data collected on a textured sample. The patterns can be indexed equally well on a hexagonal ( $a=27.2\text{\AA}$ ,  $c=7.5\text{\AA}$ ), an orthorhombic ( $a=23.5\text{\AA}$ ,  $b=13.6\text{\AA}$ ,  $c=7.5\text{\AA}$ ) or a monoclinic ( $a=12.4$ ,  $b=13.6\text{\AA}$ ,  $c=7.5 \text{ \AA}$ ,  $\beta=107^\circ$ ) unit cell, so to begin with, the highest symmetry (hexagonal) cell was assumed. This did not succeed, and the texture measurements have now shown that the symmetry cannot be hexagonal, and is probably orthorhombic. We are currently collecting precession electron diffraction data on these samples to determine the correct orthorhombic space group.

Despite the fact that the diffraction pattern of the  $\text{ZrPO}_4$ -quinoline sample is of high quality with extremely sharp peaks ( $\text{FWHM} \sim 0.013^\circ 2\theta$ ), we have not yet been able to index it. The material was synthesized in a way analogous to that used for  $\text{ZrPO}_4$ -pyridine, whose structure we solved recently [3], and its structure should help elucidate the synthesis process. SEM experiments are underway to establish whether or not there is a second phase present, and electron diffraction will be used to facilitate the indexing.

The organic semiconductor sample was measured at room temperature, and then heated up to  $145^\circ$  and measured again. Unfortunately, the sample did not undergo the expected phase transition. We must assume that the oven was not properly calibrated.

A structure proposal has been made for the germanosilicate zeolite ITQ-33 [4], but the calculated pattern does not fit the measured one very well. We are currently investigating the reason for the discrepancy.

## References

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