SNBL	**Experiment title:** Analysis of complex structures using high-resolution powder diffraction data	**Experiment number**: 01-01-772
Beamline: BM01B	**Date of experiment**: from: 19-Nov-2008 to: 21-Nov-2008 29-Apr-2009 1-May-2009	**Date of report**: 25-Nov-2009
Shifts: 6+6	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

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Report:

Three of the high-resolution powder diffraction datasets collected during these two experimental sessions have now been fully analyzed. Two of the structures have already been published, and the manuscript describing the third will be submitted shortly. All three of these markedly different structures were solved using the powder charge flipping (*pCF*) algorithm [1] in the computer program *Superflip* [2].

MCM-70. The structure of the borosilicate zeolite MCM-70 was first published in 2005 [3], but there were some inconsistencies between the structure, the NMR data and the chemical analysis that needed to be resolved. To this end, the synthesis was optimized and high-resolution powder diffraction data collected. The pattern was indexed with an orthorhombic unit cell ($Pmn2_1$, a = 13.3167 Å, b = 4.6604 Å, c = 8.7000 Å), and the structure solved (Figure 1). Subsequent refinement showed that the proposed framework topology was indeed correct, but that a complete ordering of the B in the framework was present in this new sample. This new structure refinement, which is entirely consistent with the NMR data, has now been published [4].

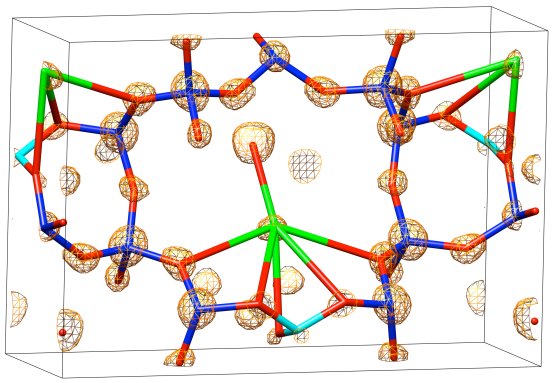

Figure 1. Electron density map for MCM-70 generated by powder charge-flipping. The final structure has been superimposed for comparison.

ZrPOF-Q2. In an attempt to repeat the synthesis of a photoluminescent zirconium phosphate-quinoline compound, a second phase with higher photoluminescence was obtained. Analysis of the high-resolution powder diffraction data of this phase ($P\bar{1}$, a = 7.706 Å, b = 12.355 Å, c = 6.585 Å, α = 97.0°, β = 89.7°, γ = 101.9°) showed that it consisted of zirconium phosphate chains interspersed with quinoline species. This is in contrast to the original compound (ZrPOF-Q1), which has zirconium phosphate layers separated by layers of quinoline. The quinoline:Zr ratio in ZrPOF-Q2 is twice that of ZrPO-Q1 and therefore a stronger photoluminescence is observed. The zirconium phosphate part of the structure was solved using the *pCF* algorithm [2], and then the quinoline species were located in a series of difference Fourier maps. Refinement of the full structure [5] converged with R_F = 0.056, R_{wp} = 0.149 (R_{exp} = 0.152) and the profile fit shown in Figure 2.

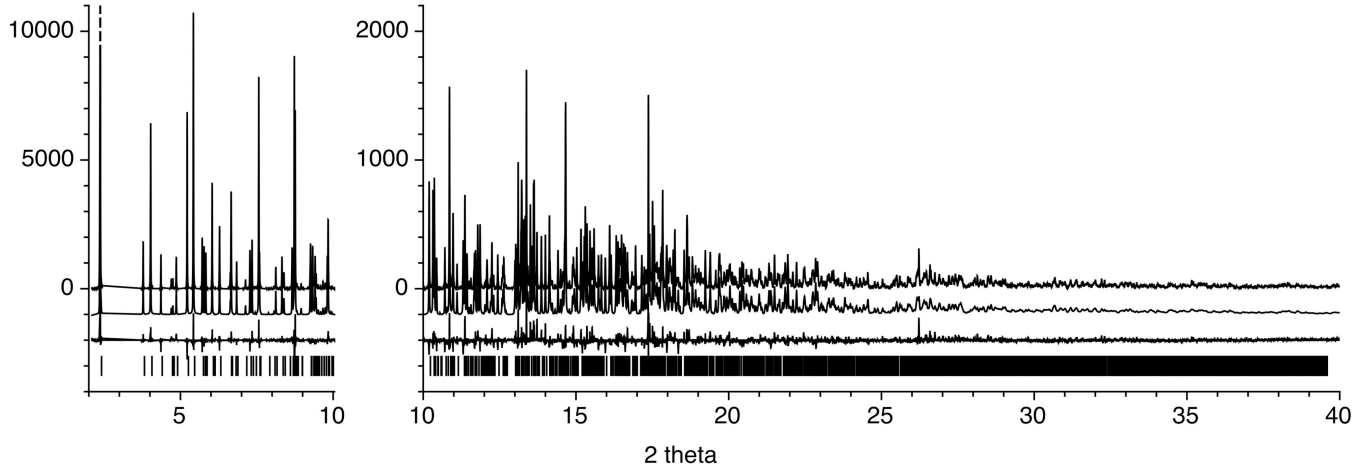

Figure 2. Observed (top), calculated (middle) and difference (bottom) profiles for the Rietveld refinement of ZrPOF-Q2. The first peak has been cut at approximately half height to show more detail.

$C_4H_7N_3O_6S$. Tricyanomethane ($HC(CN)_3$) is reported to be the strongest carbon acid known, but its crystal structure has never been reported. In one of many attempts to synthesize this elusive compound, the sodium salt was dissolved in sulfuric acid. The structure of the resulting polycrystalline precipitate revealed that not only had the tricyanomethanide been doubly hydrated, but H_2SO_4 had also been incorporated into the structure (Figure 3). Even though the chemical composition was quite different from the expected one, it was still possible to solve the structure ($P\bar{1}$, a = 8.459 Å, b = 9.858 Å, c = 5.319 Å, α = 95.9°, β = 94.8°, γ = 110.5°) using the *pCF* algorithm. Rietveld refinement converged with R_F = 0.060, R_{wp} = .148 (R_{exp} = 0.112).

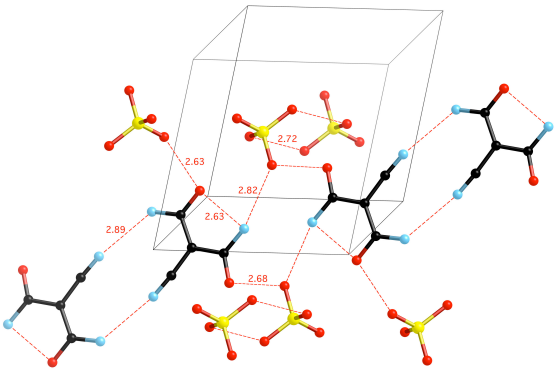

Figure 3. Structure of $C_3H_5N_3O_2{\cdot}H_2SO_4$ showing the hydrogen bonding network.

References

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