ESRF	Experiment title: Microcrystal diffraction on microporous solids	Experiment number: CH-115
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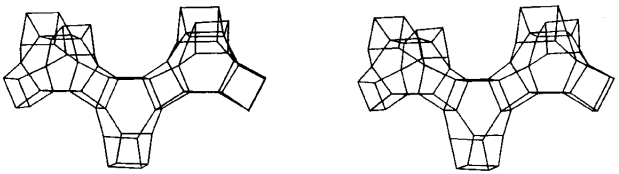
Report: **The structure of STA-1 by microcrystal diffraction [1]**

The synthesis of novel microporous materials has usually depended on the use of commercially-available alkylammonium ions as templates. It has more recently become clear that customised laboratory synthesis of templates offers an alternative approach. Desired pore sizes and connectivity may be targeted and molecules designed that, if incorporated must give the required features. Typically, structure solution of new microporous solids has proceeded via single crystal X-ray crystallography or, for materials available only as powders, by model building. The recent development of microcrystal diffraction at highly intense synchrotrons X-ray sources redefines the size boundary between these two categories. Among the products of our own syntheses, the magnesium aluminophosphate STA-1 forms in the presence of diquinuclidinium cationic templates of the formula $[C_7H_7N\text{-}(CH_2)_n\text{-}NC_7H_7]^{2+}$ as tetragonal bipyramids truncated on (001) with equatorial base dimensions varying from a few microns (for n = 9) to 30-40 microns (for n = 7). We report here its structure solution by microcrystal diffraction using synchrotrons radiation at the ESRF, to our knowledge the first unknown microporous framework structure to be solved this way.

1 G.W.Noble, P. A.Wright, P. Lightfoot, R. E. Morris, A. Kvick, H. Graafsma (subm. Angew. Chem.)

Powder diffraction on STA-1 gives a tetragonal cell with symmetry close to body-centred but violated by weak reflections. Attempts to solve the structure by model building were unsuccessful. Microcrystal diffraction data were therefore collected on the Materials Science Beamline. Several shifts were taken obtaining perfect centring and alignment of the beam. A crystal of STA-1 ca. 30 x 30 x 30 μm was glued to a fine glass fibre and mounted on the 3 circle fixed kappa Siemens diffractometer fitted with a SMART CCD detector. The wavelength was calibrated as 0.484 Å and 1250 frames were collected at ω intervals of 0.1°, the detector covering $80 < 2\theta < 280$, (d-spacing $1.00 < d < 3.47$Å), at 200K. Normalisation and integration of the data were carried out using the Siemens SAINT software, giving refined lattice parameters of a = 13.620(4)Å, c = 21 .649(5)Å. The space group was identified as P $\bar{4}n2$ from the systematic absences and intensity statistics. The framework structure was solved using SIR92 and refined (R = 0.059, Rw = 0.076).



STA-1 is made up of two different structural building units, each of $\bar{4}m$ symmetry, linked via a shared face, or four membered ring, as illustrated in stereo (Fig.1). The building units are arranged in a body-centred array, and it is the strict alternation of aluminium with phosphorus in the tetrahedral cation sites that lowers the symmetry to primitive. The pore structure consists of two sets of large pore channels, bounded by 12-membered rings, that run parallel to [100] and [010] at different heights. A projection along [100] is shown in Figure 2. These channel systems are linked in the z-direction by large pores, so that connectivity is three dimensional, although the channel pathway in this direction is not straight.