Structure of templated microcrystalline DAF-5† ($Co_{0.28}Al_{0.72}PO_4C_{10}H_{20}N_2$) determined by synchrotron-based diffraction methods

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Micro-single crystal diffraction techniques employing synchrotron radiation are used to determine the structures of the disordered template (4-piperidinopiperidine) within the recently synthesised, chabazite-related cobalt aluminium phosphate known as DAF-5; the structural details revealed are inaccessible by high-resolution powder diffraction.

In the search for microporous solids possessing unusual catalytic and other properties[1] accurate knowledge of template–host interaction is of crucial importance. Computational techniques[2,3] are indeed able to design templates for the synthesis of specific microporous architectures. Experimental determination of the location, orientation and disorder of templates within the microporous host is however, necessary for improving our ability to predict and optimise the appropriate templates. Recently[4] the *de novo* design code ZEBEDEE led to the choice of 4-piperidinopiperidine ($C_{10}H_{20}N_2$) as the template for producing a chabazitic cavity which is more symmetrical than that achieved in the open-structured cobalt phosphate known as DAF-4, a solid-acid catalyst (closely related in structure to the zeolitic mineral levyne) that shape-selectively converts methanol preferentially to ethene and propene.[5] Here, microcrystalline diffraction techniques, feasible only with synchrotron radiation, are used to establish the structural properties of the template within this new chabazitic aluminophosphate.

DAF-5 was crystallised from a gel of composition 0.4 $CoO:0.8\ Al_2O_3:1.5\ P_2O_5:30\ H_2O:2.5\ C_{10}H_{20}N_2$ which was heated under hydrothermal pressure at 160 °C for 3–6 h. A phase-pure material was produced which gave a unique X-ray powder diffractogram collected on station 2.3 of the Daresbury Synchrotron radiation source (which operates at 2 GeV with a typical current between 120 and 250 mA) in capillary mode using a wavelength of 1.399 94 Å. Unit cell parameters were obtained using the auto-indexing program TREOR.[6] Structure factor amplitudes were extracted using a Le Bail decomposition.[7] These data were used to solve the structure by direct methods using the program SIRPOW,[8] the starting model so obtained being utilized for subsequent Rietveld refinement.[9,10] This clearly established the nature of the framework [the best fit is shown in Fig. 1 and the framework structure, as subsequently determined together with the template, in Fig. 2(*a*)]. Difference Fourier maps indicated that the organic molecule experiences extensive disorder; but detailed structural information could not be derived from the powder diffraction data.

To determine the nature of the disorder of this template and find its possible orientations we employed single-crystal diffraction methods on a microcrystal of DAF-5 having dimensions close to 30 × 30 × 30 μm.‡ Collection of accurate data on such small crystals can be best performed using synchrotron sources,[11–13] such as the facility recently commissioned at station 9.8 of the Daresbury SRS,[14] where focusing optics ensures high photon flux on the sample. Data were collected on a Siemens SMART CCD Area detector at a wavelength of 0.6889 Å. The structure was again solved by direct methods.[15] The location of the template molecule could

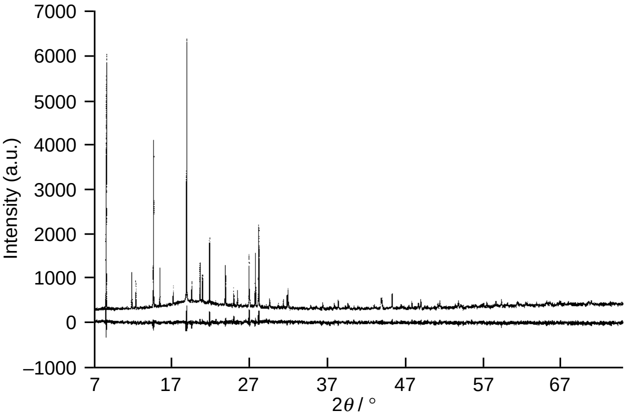

Fig. 1 High-resolution X-ray powder diffraction pattern (solid line) recorded at station 2.3 of the Daresbury Synchrotron radiation source employing a wavelength of 1.3999 Å. The dashed curve shows the best fit to the experimental data generated using the Rietveld analysis program GSAS. The difference profile is shown in the bottom of the figure.

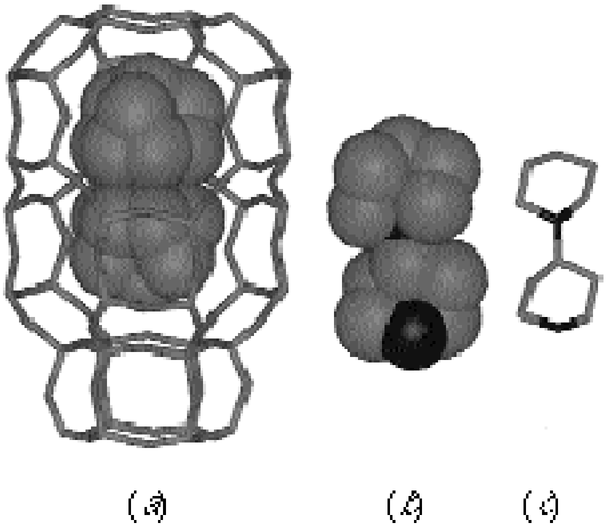

Fig. 2 Graphical representation of the structures of DAF-5 derived from the single crystal experiment is shown in (*a*). For clarity only one of the cages is given which contains all possible conformations of the occluded template molecule 4-piperidinopiperidine. One of the possible conformations of the template molecule is also shown using ball (*b*) and stick (*c*) representations where carbon atoms are shown in grey and nitrogen in black.

be ascertained from a careful interpretation of the difference Fourier map in terms of the possible conformers. This approach yielded plausible template orientations shown in the location inside the cage in Fig. 2, which also depicts one of the orientations of the single template molecule. The calculated position of the template[5] has six equivalent, statically disordered positions. Furthermore, molecular dynamics simulations (using Discover[16]) indicate independent rotation around the C–N bridge in the molecule as well as a precessional motion. However, the symmetry of the molecule is such that the extremes of the molecule and bridging atoms show small amplitudes of thermal motion. These findings are consistent with the atomic positions found in the diffraction study.

Our study demonstrates the power of microcrystalline diffraction techniques together with computer modelling in revealing complex structural features of templated microporous solids.

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Footnotes and References

† Davy Faraday Number 5. For DAF-4 see ref. 5.

‡ *Crystal data*: $Co_{0.28}Al_{0.72}PO_4C_{1.67}N_{0.33}H_{3.33}$, M_r = 158.96, trigonal space group $R3$, a = 13.537(5), c = 15.480(6) Å, U = 2457 Å^3, Z = 18, D_c = 1.934 g cm^{-3}, μ = 1.361 mm^{-1}, $F(000)$ = 1433. Crystal of size 0.03 × 0.03 × 0.03 mm. Data were collected at 295 K employing a wavelength of 0.6889 Å, on a Siemens SMART CCD area detector diffractometer, equipped with a silicon (111) crystal monochromator and a palladium coated focusing mirror on the single crystal diffraction station (no. 9.8) at the Daresbury Laboratory Synchrotron Radiation Source. Coverage of a hemisphere of reciprocal space was achieved by 0.2° frame increments in ω, with θ_{min} = 2.11° and θ_{max} = 26.47° (index ranges $-5 \leqslant h \leqslant 16$, $-16 \leqslant k \leqslant 4$, $-15 \leqslant l \leqslant 19$). Corrections were applied to account for incident beam decay and absorption effects. A solution was provided *via* direct methods and refined by full-matrix least-squares on F^2. 2188 reflections were measured, producing 969 unique data with R_{int} = 0.0455. 100 parameters and 264 restraints (imposed in order to model the disordered template molecule; these consisted of restraints on geometry, to impose approximate non-crystallographic molecular symmetry and similarity of groups of bond lengths and angles as well as equivalence of crystallographically independent disorder components, and on atomic displacement parameters, to approximate a rigid bond model and similarity of displacements for disorder sites) refined to R_1 = 0.0633 and wR_2 = 0.1785 [$I > 2\sigma(I)$] with s = 0.971 and a residual electron density of 0.58, −0.71 e Å^{-3}.

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