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Synthesis of a novel microporous magnesioaluminophosphate, STA-6, containing an unbound azamacrocycle†

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The azamacrocycle 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane has been found to template a tetrahedrally-connected aluminophosphate-based framework solid containing a novel high symmetry cage.

Innovative synthetic work continues to yield novel microporous solids with a wide range of pore geometries and chemical compositions.[1] The most fruitful route to such solids uses organic molecules as structure-directing agents around which the inorganic frameworks crystallise. In many cases there is a close match between the pore structure of the inorganic solid and the shape of the organic template, typically an amine or a quaternary ammonium salt. As a continuation of our own studies into template control of aluminophosphate synthesis[2,3] we have investigated the magnesioaluminophosphate products obtained by using macrocyclic polyamines. Previous work has shown that the known aluminophosphate AlPO-42 (with the same framework topology as zeolite A) may be prepared using the cryptand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane ('Kryptofix 222'),[4] and that a novel gallophosphate is prepared using 1,4,8,11-tetraazacyclotetradecane ('cyclam') as a template,[5] although in this case the macrocycle is bound to the framework. We report here the first use of the macrocycle 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane as a template, which directs the crystallisation of a novel tetrahedrally-connected framework structure in which the macrocycle is incorporated unbound within a previously unobserved cage of remarkably high symmetry.

The title compound, STA-6 (St. Andrews-6), was discovered during hydrothermal synthesis at 190 °C for 48 h from gels of starting composition; 0–0.20 $Mg(OAc)_2:1.0–0.80\ Al(OH)_3:1.0\ H_3PO_4:0.4R:400H_2O$, where R is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.‡ Without magnesium, the aluminophosphate AlPO-21[6] is produced, but when magnesium is introduced a second phase (STA-6) co-crystallises. At Mg/P values of 0.15–0.20:1 STA-6 is the dominant phase. Single crystals of STA-6 are readily separated from the rest of the solid product and scanning electron microscopy of this fraction shows elongated tetragonal prisms around 25 μm wide and 100 μm long. Energy dispersive analysis of emitted X-rays (EDX) indicates that 15–20% of the 'aluminium' site is substituted by magnesium. ^{27}Al MASNMR indicates that all the aluminium in STA-6 is tetrahedral (δ 35.1) and ^{31}P MASNMR of STA-6 shows a main resonance at δ −26.2 with shoulders to low and high field, consistent with tetrahedral phosphorus surrounded by different numbers of Mg and Al in second nearest neighbour coordination spheres.[7] There are also two sharp resonances at δ 0 and −2, which make up less than 2% of the total ^{31}P signal, which may be attributed to magnesium phosphate impurity. ^{13}C MASNMR of STA-6 gives four sharp resonances, (δ 21.0, 43.5, 54.5 and 62.8), suggesting that the template is included intact. To confirm this, the inorganic framework was dissolved in 6 N HCl to liberate the organic contents and the ^{13}C solution NMR found to be identical (δ 14.9, 40.7, 42.4, 47.3) to that observed from an aqueous solution of the starting ligand at a similar pH. The chemical shifts of the macrocycle in solution vary with the degree of protonation and the configuration of the molecule,[8] so it is not surprising that the observed shifts from the constrained molecule in STA-6 are not identical to those measured in solution (at pH 8, δ values are 19.1, 39.1 51.1, 52.0, at pH 12 δ values are 17.9, 41.0, 47.0, 50.3). The chemical shifts in solution can be attributed to molecules that are not protonated (pH 12), diprotonated (pH 8) or tetraprotonated (pH 1), and so have different geometries.

The structure of STA-6 was solved using microcrystal diffraction employing synchrotron X-radiation.§ To confirm that this crystal was representative of STA-6, the X-ray powder diffraction pattern of STA-6 was compared with the pattern simulated from the single crystal structure and gave good agreement when the simulated template position (see later) was included. The structure is novel, and yet remarkably simple (Fig. 1a–c). It can be considered to be built up from chains of face-sharing double six-membered rings (D6R's), where each double six-membered ring is rotated by 90° around the direction of the chain (the *c*-axis of STA-6) with respect to the adjacent D6R's. Each chain is linked to four other chains *via* Al–O–P bonds perpendicular to the *c*-axis. This results in the formation of large cages, the pores of which are connected in one dimension (parallel to *c*) through eight-membered ring openings with free diameters of 4.2 Å, but which are separated from adjacent cages in the *ab*-plane by six-membered rings. One such cage is shown in Fig. 1c. The longest axis of each cage (along the *c*-axis) is around 10.0 Å, whereas the free diameter in the *ab*-plane is around 9.0 Å. The cage is a little smaller than the α-cages observed in the zeolites A, Rho and ZK-5, and is only connected to the other cages along one axis, rather than three, as is the case with the cubic zeolites mentioned above.

Combining structural data with inorganic and organic analysis indicates a unit cell composition of *ca.* $Mg_3Al_{13}P_{16}O_{64}\cdot 1.5R\cdot 2.5H_2O$, so that 75% of the cages contain azamacrocycles, which are likely to be diprotonated to maintain electroneutrality (Found: C, 10.6; H, 2.1; N, 3.7%. $Mg_3Al_{13}P_{16}O_{64}\cdot 1.5(C_{14}H_{34}N_4)\cdot 2.5H_2O$ requires: C, 10.6; H, 2.4; N, 3.5%). Although it is not possible to determine the precise template location from the X-ray data, computer simulations of its position were performed by a combination of Monte Carlo generation of different conformations and docking of these into the $AlPO_4$ framework. Subsequently, the energy of the template molecules inside the pore structure was minimised using the CVFF forcefield within the program Discover[9] using simulated annealing. This indicates that the macrocycle can

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3909/

Also available: a full description of the crystallography and powder diffraction profiles of STA-6. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3909/, otherwise available from BLDSC (No. SUP 57669, 4 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

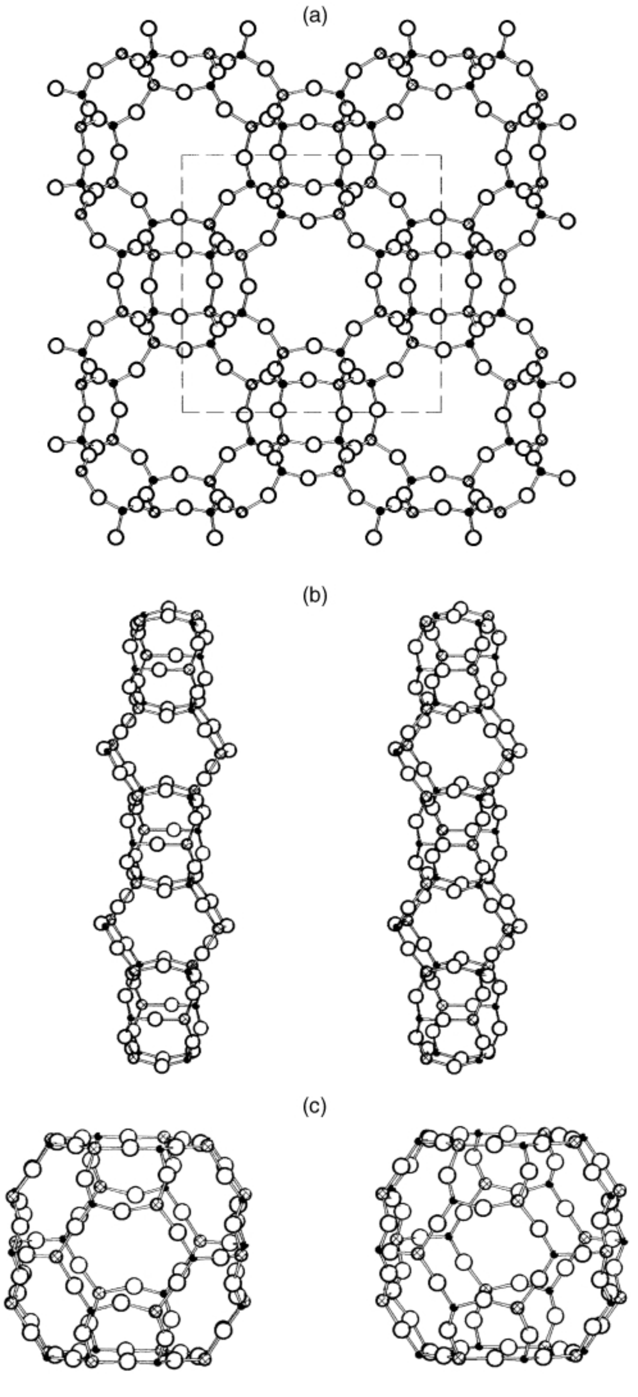

Fig. 1 Representations of the structure of STA-6. (a) A projection down the *c*-axis (unit cell outlined), (b) a stereoview showing the chains of double six-membered rings that run parallel to the *c*-axis and (c) a stereoview of the novel kind of high symmetry cage found in STA-6. Aluminium (and magnesium) atoms are represented by hatched spheres, phosphorus atoms by dark spheres and oxygen atoms as white spheres. Aluminium atoms (and magnesium) are strictly ordered with phosphorus in the framework.

indeed fit within the cage and suggests an energy-minimised location and configuration of the tetra-*N*-methylcyclam as shown in Fig. 2. Further computation and NMR studies are in progress to characterise the configuration and state of protonation of the included macrocycle more completely.

Calcination of STA-6 in flowing oxygen at 550 °C for 12 h removes the template completely. To confirm that the framework connectivity of STA-6 is retained, powder diffraction was performed on a calcined sample that had carefully been protected from exposure to moisture. The experimental profile was matched closely by that calculated from the framework alone (Fig. 3) indicating the framework is retained intact. In addition, N_2 adsorption at 77 K on a calcined sample revealed a 'Type I' adsorption isotherm typical of microporous solids, with a pore volume of 0.13 cm^3 g^{-1}, which represents the accessible pore volume left after minor loss of structural integrity and blockage of the channels.

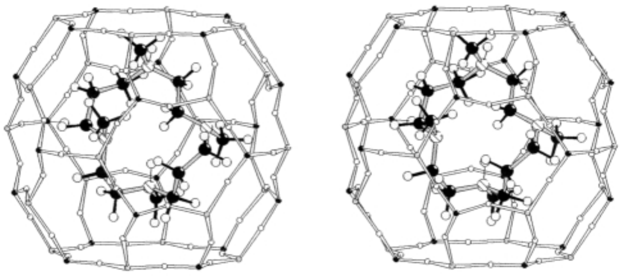

Fig. 2 Stereoview of the computer-simulated minimum energy configuration of diprotonated 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane within the cage of STA-6. Note that the macrocycle is in the *trans*-III configuration.

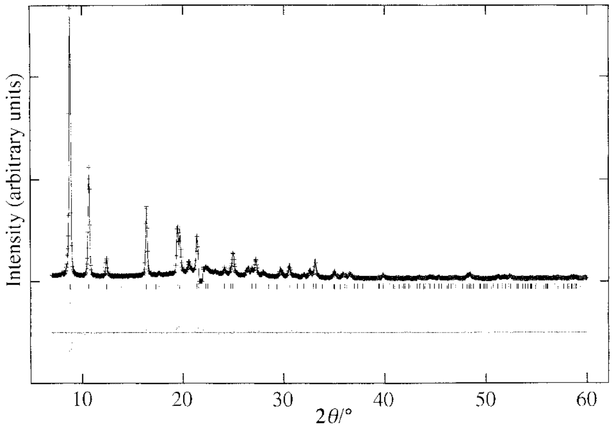

Fig. 3 Experimental (crosses), simulated (full line) and difference profiles for calcined, dry STA-6, obtained by the Rietveld refinement of powder X-ray data using Cu-Kα_1 radiation (R_{wp} = 13.7%, R_p = 10.8%). The structure has symmetry *P*4/*mnc*, with unit cell parameters *a* = 14.282(1), *c* = 10.249(1) Å.

This is the first reported use of an azamacrocycle to give a novel tetrahedrally-connected framework structure type. Use of related crown ether and oxaazamacrocycles and cryptands in zeolite and aluminophosphate synthesis has been shown to result in supercage structures such as those of zeolites Y, hexagonal Y and Rho, and the aluminophosphate AlPO-42. The discovery of STA-6 underlines the tendency of macrocycles to template cage structures, as well as revealing a very simple, novel framework topology.

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Notes and references

‡ Synthesis: although 1,4,8,11-tetramethyl-1,4,8,11-tetraazatetradecane is available commercially, we chose to prepare it more economically by *N*-methylation of cyclam.[10] In a typical inorganic synthesis, 0.166 g of magnesium acetate tetrahydrate was dissolved in a solution of 0.38 g phosphoric acid in 20 cm^3 distilled water. To this 0.288 g of hydrated aluminium hydroxide (Aldrich) and 0.4 g of the template were added and stirred until homogeneous, before being heated in a Teflon-lined stainless steel autoclave. This gives phase pure STA-6 with a yield of 75% calculated on phosphorus.

§ Crystallography: a single microcrystal of STA-6, an elongated tetragonal prism 25 µm wide and 80 µm long, was examined at the microcrystal diffraction station 9.8 at the synchrotron source at the Daresbury Laboratory. Crystal data: formula $Mg_3Al_{13}P_{16}O_{64}\cdot 1.5R\cdot 2.5H_2O$, *formula weight* = 2376, $Z = 1$, tetragonal, $P4/mnc$, $a = 14.322(2)$, $c = 10.424(1)$ Å, $V = 2138.2(5)$ Å^3, $T = 295(1)$ K, $R_1 = 0.094$, $wR_2(F^2) = 0.313$ for 1097 unique data ($F > 4\sigma(F)$), 15082 data collected ($R_{int} = 0.058$). A three-circle (fixed kappa) Siemens diffractometer fitted with a Siemens SMART CCD detector was used. The wavelength was calibrated prior to the experiment as 0.6885 Å. A hemisphere of data were collected in ω steps of 0.4° at two different φ values. Data were integrated for d-spacings less than 8.4 Å and the resolution limit was 0.7 Å. Data reduction was carried out using the Bruker AXS SAINT and SADABS packages.[11] The basic framework structure was solved using the SHELXS package and refined using SHELXL.[12] It was not possible to identify complete template molecules unambiguously from the difference Fourier synthesis, because there will necessarily be disorder as the symmetry of the template is lower than that of the framework. However, if the template positions suggested by molecular modelling are included, allowing for statistical disorder, the residuals are reduced to $R_1 = 0.084$ and $wR_2(F^2) = 29.4$. No attempt was made to locate water molecules. Aluminium and phosphorus are strictly ordered within this space group, with Al–O bond lengths between 1.756(5) and 1.777(5) Å and P–O bond lengths between 1.491(4) and 1.521(4) Å. CCDC reference number 186/1693. See http:/www.rsc.org/suppdata/dt/1999/3909/ for crystallographic files in .cif format.

Powder diffraction experiments on STA-6 were performed on a STOE STADIP diffractometer using Cu-Kα_1 monochromated radiation. Both as-made and calcined (550 °C, kept dry) samples were studied. Rietveld refinement of the data was performed using as a starting model atomic coordinates of the STA-6 framework derived from single crystal diffraction and of the template obtained from modelling studies, and permitting restrained refinement of the framework atom positions. Final lattice parameters for the two runs were $a = 14.339(1)$, $c = 10.443(1)$ Å and $a = 14.282(1)$, $c = 10.249(1)$ Å for the as-made and calcined samples, respectively. Both Rietveld fits gave good agreement ($R_{wp} = 12.8\%$ (as-made) and 13.7% (calcined)).

Solid State NMR: MASNMR spectra were obtained on a Varian 300 MHz spectrometer. The following typical conditions were employed: for ^{27}Al, acquisition time 20.2 ms, relaxation delay 0.5 s, spinning rate 8 kHz, for ^{31}P CP MAS, contact time 3 ms, acquisition time 15 ms, recycle delay 1 s, spinning rate 9.1 kHz, for ^{13}C CP MAS, contact time 1 ms, recycle delay 1 s, spinning speed 4.5 kHz; ^{31}P and ^{27}Al chemical shifts were referenced to a 85 wt% solution of H_3PO_4 and to $[Al(H_2O)_6]^{3+}$ respectively.

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