

The Pore Size Modification of a Layered Aluminophosphate [Al₃P₄O₁₆C₉H₂₄N₃] by Rational Selection of the Intercalated Template Cation

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The synthesis and structure of a novel layered aluminophosphate containing a twelve-membered ring using a cyclic organic diamine is described; the effective pore size of the ring is modified from 6.6 to 3.3 Å by the pore blocking action of the intercalated template ion.

The design of novel microporous materials that can function as new catalysts or molecular sieves is an active and wide-ranging field for both the academic and industrial communities. Materials which have been extensively studied include the naturally occurring aluminosilicate clays and zeolites.^{1,2} In an attempt to produce new materials with differing pore sizes much effort has been devoted to the structure directing effects of templating moieties.³ This has led to the synthesis of both naturally occurring and new materials with novel structures.⁴

Another profitable route to the alteration of shape selective properties is the post modification of materials. These include the use of pillaring reagents in clays to create new microporous solids.⁵ A further method for the restriction of pore sizes in zeolites involves the grafting of suitable organometallic reagents to the surface of zeolites.^{6,7} However, we show in this paper that by choice of a suitable templating ion that it is also possible to modify the effective pore size in a desired material at the synthesis stage.

A number of layered aluminophosphates have been previously synthesised which can be considered to be the analogues of aluminosilicate clays.^{8–11} To produce these materials acyclic diamines have been used as the templating reagents. In order to understand the structure-directing properties of these template molecules we have replaced a linear by a cyclic diamine, which restricts the possible conformations but maintains the same nitrogen–nitrogen separation as used previously. In practice this meant replacing 1,4-diaminobutane, which had produced a porous layered aluminophosphate containing a twelve-membered ring with 1,4-diaminocyclohexane as the templating reagent.

The title compound was synthesised hydrothermally from a nutrient gel containing in molar ratios 1.0 Al₂O₃ : 1.2 P₂O₅ : 1.5 C₆H₁₆N₂ : 25 H₂O with the sources of Al and P being aluminium isopropoxide and (85%) phosphoric acid with water which were all obtained from Aldrich. The resultant gel was stirred until homogeneous and sealed in a Teflon-lined stainless-steel autoclave at 190 °C for 15 days before the residual solid was collected, washed and dried.

The final product was a white microcrystalline powder from which it was possible to index the vast majority of the Bragg peaks in the diffraction pattern. The trigonal unit cell obtained (approximate dimensions $a = 12.937$, $c = 18.246$ Å) and the diffraction pattern itself bore a close resemblance to the target aluminophosphate synthesised earlier using 1,4-diaminobutane. High resolution powder diffraction with synchrotron radiation was used to locate the template ion and refine the structure. The high resolution afforded by synchrotron-based X-ray diffraction has been successfully used in the location of occluded species on a number of occasions^{12–14} and furthermore in this case enables us to exclude the small quantity of impurity phases from the refinement. The diffraction data were collected on station 2.3 of the Daresbury SRS. The step increment for the pattern was 0.01° and the time for each step was 2 s. The lower limit of d_{\min} was 0.934 Å the wavelength was 1.39942 Å. A starting model for the framework structure and terminal nitrogen atoms was taken from the previously characterised AlPO₄⁹ and the structure was analysed in the space group $P\bar{3}c1$ by Rietveld profile refinement¹⁵ using the GSAS suite of programs.¹⁶ The remaining non-hydrogen atoms of the template molecule were located in difference Fourier maps and the hydrogen atoms of

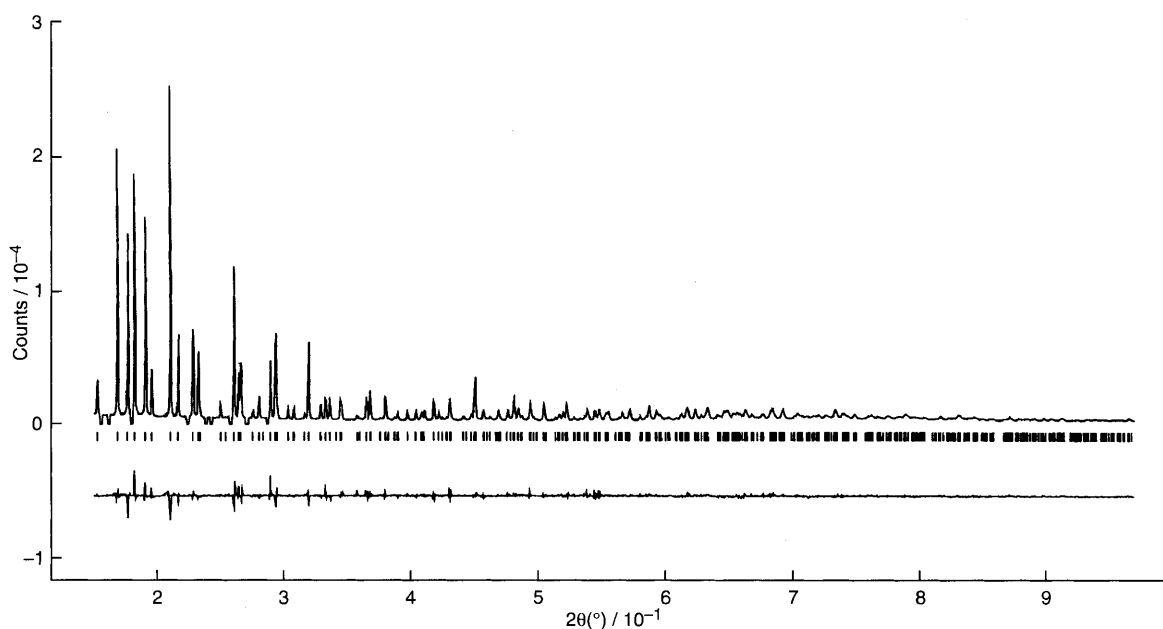


Fig. 1 Observed (·), calculated (—) and difference (lower trace) profiles for the title compound. The tick marks show the position of allowed reflections.

the template were geometrically placed. It proved necessary to apply restraints to the T–O bond lengths and the bond lengths and angles of the template ion. The model converged to¹⁶ $R_{wp} = 0.1193$, $R_p = 0.0890$ and $\chi^2 = 7.88$.

A Fourier map computed at this point revealed the location of two water molecules in the structure. These were included with fixed occupancy of 1/3 which is consistent with the maximum permitted occupancy for these sites which excludes unrealistic O...O symmetry related contacts. It proved possible to remove the constraints to the P–O and Al–O single bonds. The structural parameters which were allowed to vary in the final cycles of refinement included all atomic positions and isotropic thermal parameters (excluding the hydrogen atoms). The range of data used (d_{min} and d_{max}) was from 8.03 to 0.934 Å which led to final agreement factors¹⁶ of $R_{wp} = 0.1060$, $R_p = 0.0807$, $\chi^2 = 6.06$ and final unit-cell parameters of $a = 12.9235(2)$ and $c = 18.2373(3)$. Plots of observed calculated and difference profiles are given in Fig. 1.

Previously synthesised layered aluminophosphates have contained rings of varying sizes in which the maximum ring sizes have been six-¹⁷ eight-^{8,10} and twelve.^{9,11,18} These layered phosphates which have an Al:P ratio of 3:4 consist of vertex sharing AlO_4 and PO_4 tetrahedra with all of the vertices of the AlO_4 units being shared but only three-quarters of the PO_4 vertices shared thus leaving formally a P=O group. We have shown that these structure types can be related to two-dimensional nets with the inclusion of a capping PO_4^{3-} group. The structure here follows the pattern outlined above and possesses a twelve-membered ring with the capping PO_4^{3-} groups strictly alternating above and below the plane of the ring (Fig. 2(a) and (b)). Aligned twelve-membered channels have been obtained with both ABABAB⁹ and AAAAAA¹¹ stacking of the macroanionic layers. This has been attributed to the differing hydrogen-bonding abilities of monoamines as opposed to diamine templating ions. In the title compound, the individual layers stack in an ABABAB sequence which is dictated by the presence of the threefold inversion axis, but having the rings aligned directly above each other so as to produce a channel parallel to z .

The intercalated 1,4-diaminocyclohexane which possesses twofold symmetry lies between the layers with just under half of the molecule situated below one of the four-membered rings which surround the central twelve-membered ring, leaving the rest of the molecule extending into the central channel. This effectively decreases the pore size of the channel from 6.6 to 3.3 Å with the organic cation acting as a barrier to potential sorbates which would limit uptake of such species. This can be contrasted with our previous study where it was possible to absorb molecules as large as benzene. The two water molecules cluster together within the puckered aluminophosphate twelve-membered ring lying close to the centre of the effective channel with O...O distances ranging from 2.2–2.6 Å, which is indicative of strong O...O intramolecular hydrogen bonds within the cluster.

Thermogravimetric studies indicate that this water is lost between 130 and 210 °C. At temperatures > 250 °C decomposition of the organic template occurs with the production of a tridymitic dense phase. The dehydrated material underwent slow rehydration with complete rehydration taking place after two weeks exposure to the atmosphere.

It has proved possible to confer solid acidity upon microporous AIPOs by the substitution of either P^V by Si^{IV} or Al^{III} by divalent metal ions with the most common being Co, Zn, Mg and Mn.¹⁹ The combination of shape selectivity provided by the structure type and the solid acidity generated through heteroatom substitution has already been shown to have noteworthy catalytic potential.^{20,21} Whilst changes in shape selectivity are generally conferred by the synthesis of new materials, we have shown in this work another possible alternative route for controlling the effective pore size in a given material at the synthesis stage by manipulation of the structure-directing

template in a rational way. By maintaining the hydrogen-bonding network of the original material and by choice of a suitable new template we have preserved its ability to form the target structure type. The pore size is modified as a result of the change in steric nature of the new template ion. While the present material is unlikely to have significant catalytic potential the strategy we have outlined may prove useful in other materials.

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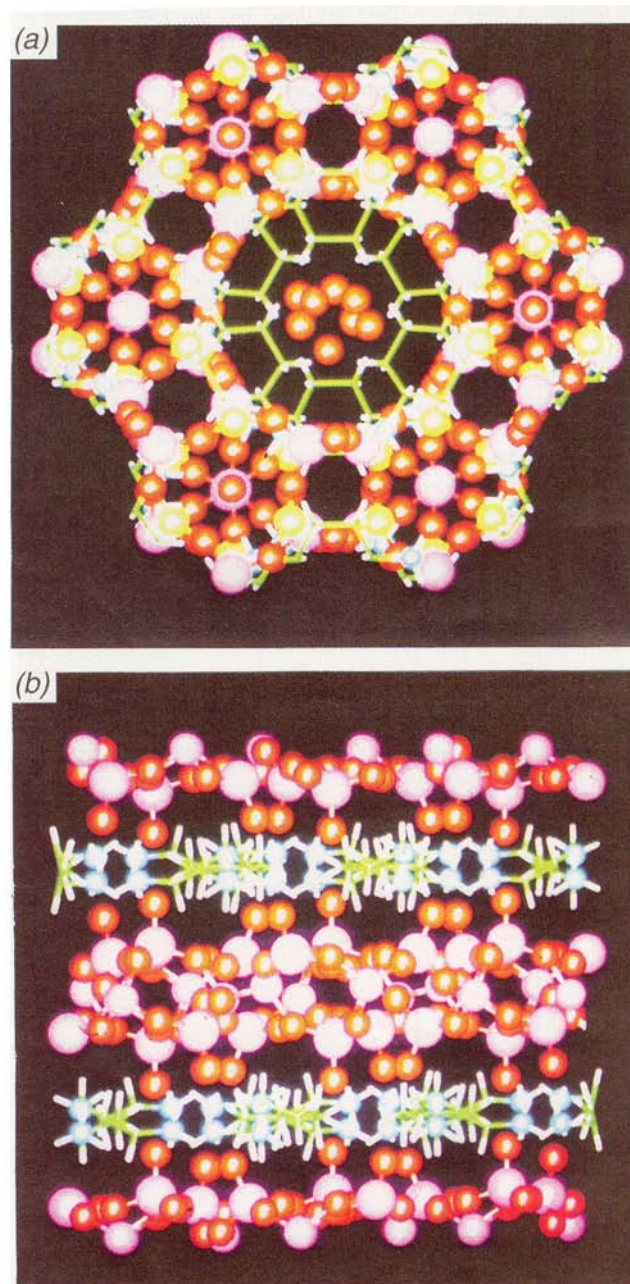


Fig. 2 (a) Plan view of the structure showing four ionic sheets and the reduction in pore size from 6.6 to 3.3 Å caused by the organic template. The atoms are depicted in the following colours; Al (yellow), P (purple), O (red), C (green) and N (blue). The two occluded water molecules (only oxygen positions shown) can be seen to cluster close to the mid-point of the puckered central channel. (b) Elevation view showing the intercalated organic cations $[C_6H_{16}N_2]^{2+}$ between the layers of inorganic anions. The colour scheme is as before except that Al and P are both purple to illustrate the contrast between the organic and inorganic layers (the nitrogen atoms are highlighted for clarity).

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