A Reactive Template in the Synthesis of a Novel Layered Aluminium Phosphate $(Al_3P_4O_{16})^{3-}[NH_3(CH_2)_5NH_3]^{2+}(C_5H_{10}NH_2)^+$

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Starting from 1,5-diaminopentane as template it is possible to produce a novel microporous layered aluminophosphate (Al:P = 0.75) in which there are two distinct kinds of eight-membered rings within the layers: those that are approximately circular (diameter 7.0 Å) accommodate piperidinium ions, while the elliptical ones (*ca.* 5.9–8.0 Å) contain 1,5-diammoniumpentane ions.

The synthesis of three-dimensional microporous aluminium phosphates (AlPOs) in 1982[1,2] initiated intense activity in this area of chemistry. Some of these new materials and their hetero-atom substituted analogues have the same structures as those of naturally occurring aluminosilicate zeolites, *e.g.* SAPO-37 has the same structure as the naturally occurring mineral faujasite.[3] However, many of these compounds have structures which have no counterpart in nature.[4–7] We have recently synthesised and solved the structures of several layered AlPOs,[8,9] including those where the layers are themselves porous.[10] Here, we report the structure of a new layered AlPO possessing two distinct eight-membered windows within the sheets, which accommodate two different organic cations, one of them generated during the course of synthesis.

The title compound **1** was synthesised under hydrothermal conditions. Typically, the starting material consisted of a mixture of phosphoric acid (1.28 g; 85% by mass) with triethylene glycol (20 ml), hydrated aluminium oxide (1.03 g, 55% Al_2O_3, 45% H_2O by mass). The mixture was stirred until homogeneous, then 1,5-diaminopentane (0.681 g) was added. A small quantity of HF (40% solution) was added as mineraliser (0.07 ml). The final reaction mixture, with a composition $Al_2O_3:P_2O_5:1.2NH_2(CH_2)_5NH_2:40(Et)_3(OH)_2:0.3HF$, was stirred again to achieve homogeneity, sealed in a Teflon-lined stainless steel autoclave and heated to 190 °C for 6 d under autogeneous pressure. The resulting product (**1**) consisting of large single crystals suitable for four-circle diffractrometry,† was filtered and dried in air at ambient temperature. A powder diffraction pattern of the material showed it to be new. The same material has also been synthesised in ethylene glycol as well as by changing the Al/P ratio to 0.75. The differential thermal and thermogravimetric analysis indicate only one mass loss at 400 °C, which corresponds to the removal of template ions. The product of calcination showed only one crystalline phase, which was identified from its powder pattern to be a dense $AlPO_4$ phase.

The structure of **1** consists of macroanionic $Al_3P_4O_{16}{}^{3-}$ sheets separated by organic cations. The basic structural units of the anionic layers are Al and P centred tetrahedra (Fig. 1). All the vertices of the AlO_4 units are shared with an average Al–O bond length of 1.729 Å. Only three quarters of the PO_4 vertices are shared (P–O_{av} 1.534 Å), formally resulting in the presence of phosphoryl P=O groups (P=O_{av} 1.495 Å). These values are in good agreement with those seen in earlier sheet structures *e.g.* Al–O 1.727, P–O 1.537, P=O 1.490[9] and Al–O 1.737, P–O 1.531, P=O 1.507 Å.[10] The bridging distances are comparable with those seen in berlinite (which is the AlPO analogue of quartz[11]) which has Al–O 1.739 and P–O 1.516 Å. The Al and P containing tetrahedra, which are linked in a strictly alternating manner, give rise to a puckered sheet structure in the *bc* plane and is similar to those determined previously.[9,12] The layers in **1** stack in an AAAA sequence (Fig. 1), which have been previously observed,[10,12] but it is in contrast to that observed in $[Al_3P_4O_{16}]^{3-}$ $[NH_3(CH_2)_2NH_3]^{2+}$ $[OH(CH_2)_2OH_2]^+$ $[OH(CH_2)_2OH]$ where ABAB stacking is observed.[9]

In the synthesis of three-dimensional $AlPO_4$ structures fragmentation of the amine template has been previously seen *e.g.* in the case of $AlPO_4$-15.[13] However, cyclization is new. The mechanism for the formation of piperidine probably entails initial monoprotonation of one of the amino groups, an internal S_N2 attack by the unprotonated amine group followed by elimination of ammonia leading to formation of the piperidinium ion.[14] The organo ammonium cations are found in the interlamellar region of the structure, and occupy positions which lie close to the voids formed by the eight-membered rings, there being two cations between the layers for each window (Fig. 1). The sheets are held together by hydrogen bonds involving only the 1,5-diammonium cations. The hydrogen bonds involving the piperidinium cation do not

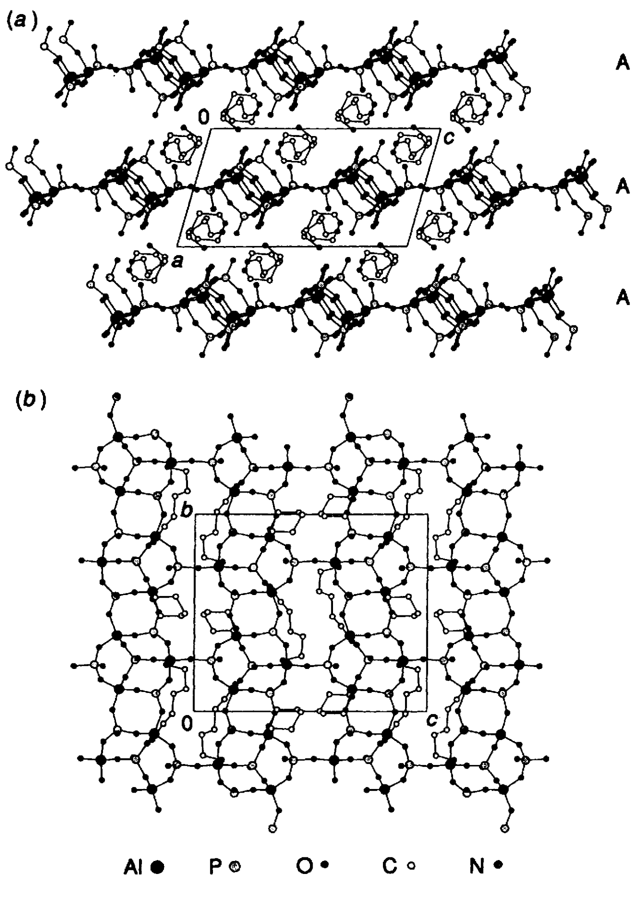

Fig. 1 (*a*) View of **1** showing the interlamellar organic cations (*b*) View normal to a sheet, showing the different cations residing in the differently shaped rings

serve to hold the sheets together; these are directed to only one face of a sheet.

There are two types of crystallographic eight-membered rings in **1**. The first ring is approximately circular in shape with O–O contacts which range between 6.22 and 7.02 Å; the piperidinium cations are situated in the windows of these rings. The other rings have an elliptical shape with O–O distances varying between 5.88 and 7.99 Å. The 1,5-diammonium pentane cations are situated in the windows of these rings with the chain axis of the carbon backbone having the same orientation as the longest axis of the window. This may indicate a differential templating effect of the two organic cations in causing distortions of the structure.

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Footnote

† *Crystal data* for **1**, $Al_3P_4O_{16}C_{10}H_{28}N_3$: M = 650.18, monoclinic, space group $P2_1/c$, a = 9.801(2), b = 14.837(2), c = 17.815(3) Å, β = 105.65(1)°, U = 2494.7 Å^3, Z = 4, D_c = 1.731 g cm^{-3}, λ = 1.5418 Å, μ(Cu-Kα) = 45.09 cm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer for the range $0 < 2\theta < 145°$. A total of 6531 reflections gave 4867 unique data of which 3356 were considered to be observed $I > 3\sigma(I)$, and used in the refinement of the structure. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares (CRYSTALS) to R = 0.035, R_w = 0.058. A total of 358 parameters were used in the refinement Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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