

## A Novel Porous Sheet Aluminophosphate: $\text{Al}_3\text{P}_4\text{O}_{16}^{3-} \cdot 1.5[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$

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The synthesis, characterization and properties of the title compound are described; the structure is unique, consisting of macroionic sheets with large pores (ca. 7 Å diameter) in the sheets and intergrown organic cations between the layers.

In the course of devising new microporous, microcrystalline solids potentially capable of exhibiting (Brønsted) catalytic activity,<sup>1–3</sup> we have prepared and characterized an inorganic–organic molecular composite with unusual structural and adsorptive properties. It consists of puckered continuous sheets of anionic aluminium phosphate, interspersed in a regular fashion with a monolayer of closely-packed diprotonated 1,4-diaminobutane.

The most remarkable feature of the structure (Fig. 1) is that within each inorganic sheet there is a supermesh of apertures of ca. 7 Å free diameter. Such is the disposition of the molecules in the interlamellar organic layers that pores of this diameter penetrate the entire structure in a direction perpendicular to the sheets, thus yielding a solid having unidimensional pores like those of zeolites such as Theta-1<sup>4</sup> and ZSM-23,<sup>5</sup> certain detemplated microporous ALPOs (aluminophosphates) such as ALPO-5,<sup>6</sup> and the channel complexes of urea and thiourea.<sup>7,8</sup>

Upon shaking the dry solid with water, the resulting dispersed state displays colloidal properties reminiscent of montmorillonite clays. We are currently exploring ways of replacing the organic cationic sheets with inorganic ones with the aim of producing an inorganic solid that may then be converted<sup>9–11</sup> into a pillared, open structure in which two-dimensional porosity in the planes of the sheets is added to the existing porosity perpendicular to them.

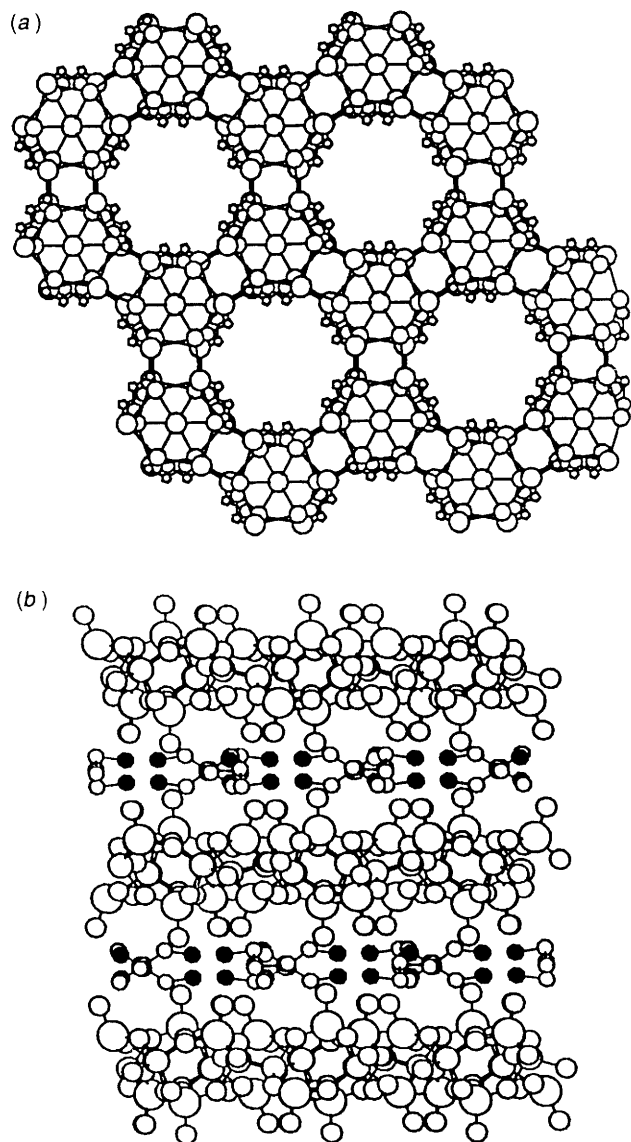
The title compound was synthesized under hydrothermal conditions. Typically the starting material consisted of a mixture of phosphoric acid (2.88 g; 85 wt%) with water (10 ml), hydrated aluminium oxide (2.31 g; 55 wt%  $\text{Al}_2\text{O}_3$ , 45 wt%  $\text{H}_2\text{O}$ ) and Cab-o-Sil (0.45 g; Fluka, UK). The mixture was stirred until homogeneous followed by the addition of 1,4-diaminobutane (0.82 g) and water (5 ml). The final reaction mixture, with a composition  $0.6\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0.7\text{NH}_2(\text{CH}_2)_4\text{NH}_2 : 35\text{H}_2\text{O}$ , was stirred again to homogeneity, sealed in a Teflon-lined stainless steel autoclave and heated at 190 °C for 4 days under autogeneous pressure. The resulting product, consisting of large single crystals

(suitable for 4-circle diffractometry†) and some amorphous material (consisting of unreacted  $\text{SiO}_2$ ) was filtered and dried in air at ambient temperature. A powder pattern of the material showed it to be unique. No silicon was detectable in the crystalline product by energy dispersive X-ray analysis.

The thermogravimetric–differential thermal (TG–DT) analysis showed that the compound loses about 5% of its weight at around 100 °C, a loss accompanied by an endothermic change associated with the removal of occluded water. The organic template decomposes at about 400 °C, and thereafter the crystal structure collapses into an amorphous phase. An *in situ* X-ray diffraction experiment carried out under an inert atmosphere showed that dehydration and re-adsorption of the sample were accompanied by no significant changes in the structure.

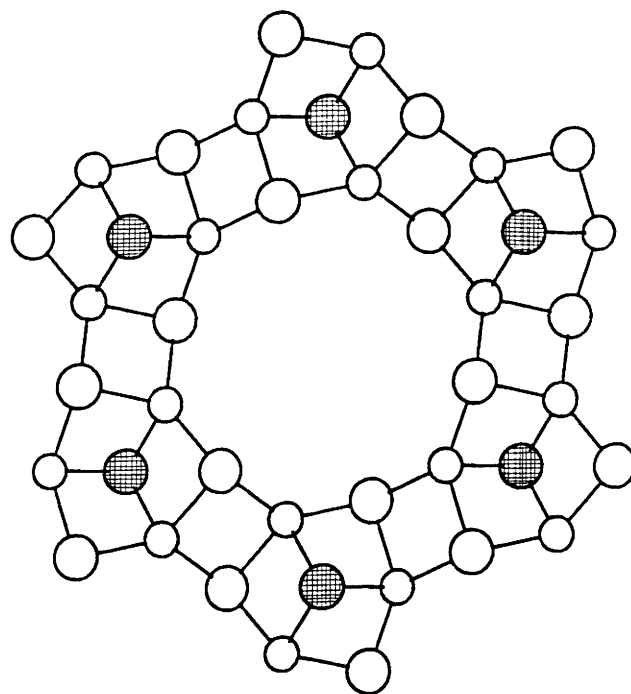
The structure consists of macroanionic layers of formula  $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$  with interlamellar  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$  ions. The individual layers consist of a network of  $\text{AlO}_4$  and  $\text{PO}_4$  tetrahedra, all the  $\text{AlO}_4$  vertices being shared (av. Al–O 1.737 Å) but only three-quarters of the  $\text{PO}_4$  (av. P–O 1.531 Å), the

† A suitable crystal for X-ray analysis was obtained from the synthesized material. *Crystal data* for  $\text{Al}_3\text{P}_4\text{O}_{16}\text{C}_6\text{H}_{21}\text{N}_3 \cdot 1.176\text{H}_2\text{O}$ , trigonal,  $P\bar{3}c1$ ,  $a = 12.957(5)$ ,  $c = 18.413(3)$  Å;  $V = 2676.86$  Å<sup>3</sup>;  $Z = 4$ ,  $M = 617.34$ ,  $\mu(\text{Mo-K}\alpha) = 4.415$  cm<sup>-1</sup>,  $D_c = 1.532$  g cm<sup>-3</sup>. Data were collected on an Enraf-Nonius CAD4 diffractometer using the  $\omega$ – $2\theta$  scan technique, for the range  $0 < 2\theta < 50^\circ$ . The total number of reflections measured was 6288, of which 1546 were unique and 846 were with  $I > 2.5\sigma(I)$ . Structure was solved by direct methods.<sup>12</sup> Hydrogen atoms were geometrically placed. Refinement of 106 variables was by full-matrix least-squares.<sup>13</sup> The water molecules located in channels included in refinement with fixed thermal parameter ( $U_{\text{iso}} = 0.125$ ) gave refined occupancies 0.172 (17) and 0.220 (19). Final residuals  $R = 0.065$ ,  $R_w = 0.057$ . Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

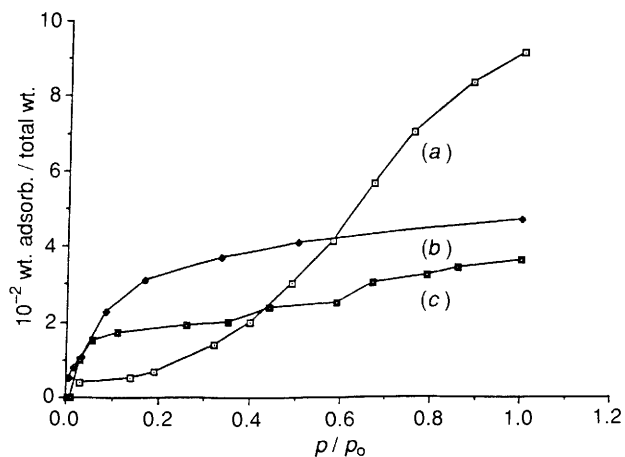


**Fig. 1** (a) Plan view of the structure, showing two ionic sheets defining an array of large (12-membered) apertures of diameter ca. 7 Å. In decreasing sizes the circles correspond to P, Al, N, C. The oxygen atoms are approximated by the mid-points of the P–Al contacts. (b) Elevation view of portion of stacked, intergrown inorganic anions and organic cations  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$ . In decreasing sizes the circles represent P, Al, O, N and C (N atoms are shaded for clarity).

remaining vertex being a P=O group (av. P=O 1.507 Å). This two-dimensional network consists of a central circular 12-membered ring, surrounded by a series of 4-membered ones of which there are two distinct types. One set of these rings consists of phosphorus atoms which constitute part of the wall of a 12-ring, whilst in the other a phosphoryl group 'caps' a 6-membered ring and alternates above and below the plane of the 12-ring (Fig. 2). Thus, although the macroanion has the same formula as in previously observed anions, the topology is different; cf. our previously determined<sup>14,15</sup> structures where 4-membered rings surround an 8-membered one. Similarly we have previously reported different structures with the same  $\text{Al}_2\text{P}_3\text{O}_{12}^{3-}$  layer composition.<sup>16</sup> An alternative way to regard the topology of the 2-D net is systematically to remove the capping  $\text{PO}_4$  group shown in Fig. 2. It is therefore clear that we have a 4.6.12 net (*viz.* 82a in the nomenclature of Smith



**Fig. 2** Plan view of a 12-membered ring and its connectivity. (Large circles denote P atoms, small ones Al). Removal of the hatched P atoms leads to a 4.6.12 net.



**Fig. 3** Sorption isotherms (at 294 K) for (a) water, (b) methanol and (c) benzene ( $p/p_0$  ratio of partial pressure of sorbate to its saturated vapour pressure)

*et al.*<sup>17,18</sup>). Such is the architecture of the structure that there are alternating pockets with hydrophilic and hydrophobic linings along the channel.

Adsorption studies on the dehydrated material were carried out, gravimetrically, with  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ , and  $\text{C}_6\text{H}_6$  as the probe molecules (see Fig. 3). Both the methanol and benzene display Langmuir type I isotherms with final weight changes at ambient temperature corresponding to 3.4 and 1.0 molecules per unit cell respectively. Water, however, displays a type V isotherm. This is not unknown for a microporous solid and has been reported for some ALPOs.<sup>19</sup> An *in situ* IR study using deuterated water confirmed the reversible nature of the uptake of this sorbate.

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