Synthesis and Structure of a Novel Aluminium Phosphate Anion: $(Al_3P_4O_{16})^{3-}$

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The preparation and characterization of the title macroanion in which both the Al and P are tetrahedrally coordinated is described; its synthesis from a predominantly non-aqueous medium containing organic templates yields other crystalline solids with the same macroanion but different structures.

New possibilities, both in designing novel structures and in modifying existing ones, were opened up by the work of Wilson *et al.*[1,2] who reported a large family of open three-dimensionally ordered, aluminium phosphates. These, and their derivatives, have already shown promise as microporous adsorbents and catalysts. Many of the newly prepared materials are structurally the same as naturally occurring or synthetic aluminosilicate zeolites (*e.g.* ALPO-34 has the same structure as that of chabazite: only the tenants of the tetrahedral sites are different). Several, however, are quite new, like ALPO-5 where both the Al and P atoms are tetahedrally coordinated to oxygen atoms, and some of the new structures, notably $AlAsO_4$-1[3] and $GaPO_4$-C3,[4] have the group III ion in more than one stereochemical environment. In the context of catalysis, the replacement of phosphorus by silicon, or a similar kind of substitution (*e.g.* Mg^{2+} or Ni^{2+} for Al^{3+}), leads to novel acidic solids that are effective in, for example, converting methanol to alkenes.[5] This is known to be the case for SAPO-34,[6] for example, and for Ni-SAPO-34.[7]

Bearing in mind the very large number of known silicate

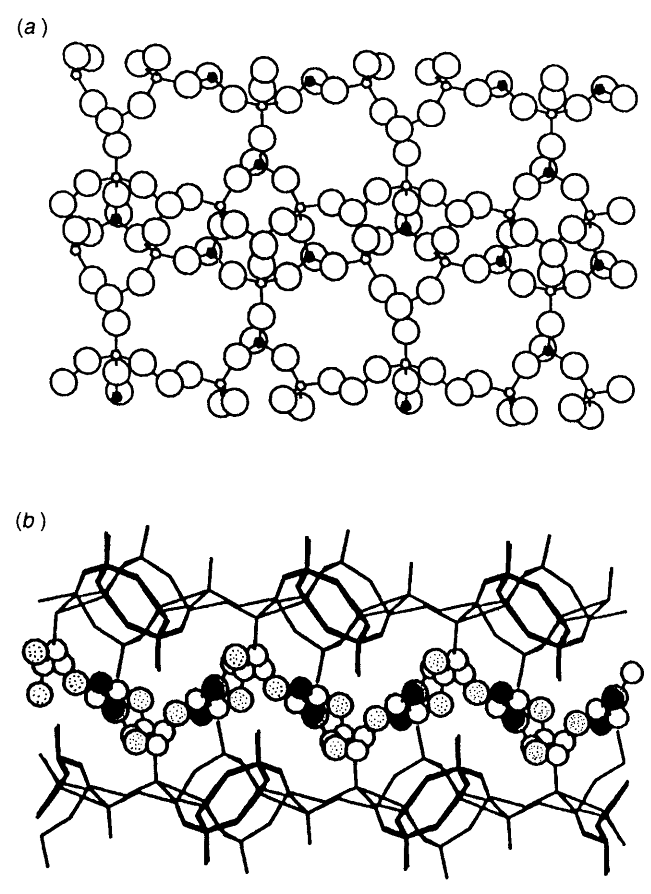

Fig. 1 The newly discovered (title compound) sheet structure: (*a*) the view normal to the plane of the sheet (● = P, ○ = Al, ◯ = O); (*b*) the view along the sheet plane (interlamellar layer retained). (◎ = O, ● = N, ◯ = C). Selected ranges (Å) and angles (°) of the metrical parameters in the title compounds. P–O 1.58–1.543; P=O 1.485–1.495; Al–O 1.712–.740; O–P–O 105.8–109.0; O–P=O 109.8–113.8; O–Al–O 105.1–112.7.

structures,[8] encompassing chain- and sheet- as well as three-dimensional-framework variants, one should expect that aluminium phosphates ($2Si^{IV} = Al^{III} + P^{V}$) could be capable of crystallizing in one- and two-dimensionally extended structures. Such low-dimensional structures would have many potential advantages as novel acid catalysts.[9] We have recently discovered that using a predominantly non-aqueous environment for synthesis, a chain aluminium phosphate $(H_2AlP_2O_8)^-$ bearing recurrent –P(O)(OH) acidic groups along the backbone does indeed exist.[10] We now report the preparation, under similar (non-aqueous) conditions, and the structural elucidation of the first example of a sheet aluminium phosphate anion, $(Al_3P_4O_{16})^{3-}$.

The title compound was synthesized from a predominantly non-aqueous system in which ethylene glycol was used as the solvent. A mixture of aluminium triisopropoxide, phosphoric acid (85% H_3PO_4) and ethylenediamine with the gel composition $12(CH_2NH_2)_2$ Al_2O_3 $1.8P_2O_5$ $60(CH_2OH)_2$ was heated under autogenous pressure for up to 7 days at 185 °C. The crystalline multiphasic product was filtered off, washed with water and dried at ambient temperatures. A suitable crystal was obtained and its structure was determined by four circle X-ray diffractometry.

The crystal structure of the sheet anion (designated A1 for convenience) is displayed in Fig. 1(*a*) and (*b*): it consists of macroanionic sheets [empirical formula $(Al_3P_4O_{16})^{3-}$] separated by organic moieties. The sheets are built up of vertex-sharing tetrahedral AlO_4 units [av. O–Al–O 109.5° (1.8)] and tetrahedral PO4 units. Whereas all of the AlO4 vertices are shared, only three-quarters of the PO4 vertices are, the remaining vertex being occupied by the P=O group. The tetrahedra are linked to give puckered strands of four-rings which are cross-linked to form eight-membered rings with an approximate diameter of 3.05 Å. These individual sheets then stack in an *ABAB* sequence to yield a structure that bears a resemblance to those of the acidic group IV phosphates.[11] In the ALPO structure the terminal P=O group is directed towards the interlamellar region whereas in the group IV phosphate a P–OH group is directed, in a similar manner.

During the course of the crystal structure† analysis it proved possible to locate most of the hydrogen atoms attached to the organic moieties. The location of the hydrogens, together with the metrical parameters of the molecules, suggested that the interlamellar region consisted of a diprotonated ethylenediammonium cation and two ethylene glycol moieties. The final difference Fourier map possessed several peaks of the order of 0.31 $eÅ^{-3}$ (max 0.35 $eÅ^{-3}$), none of which was in a chemically sensible position to account for the third proton that is required by the formula $(Al_3P_4O_{20}C_6N_2H_{23})$ for the purposes of charge balancing. Bond valence calculations[12] indicate a possible position for the 'missing' proton. The calculations show that bridging oxygen atoms are saturated (valence sums 2.02 to 2.08), but that the bonding requirements of the terminal oxygen atoms [valence sums for O(4), O(6), O(10), O(15) ~ 1.4] must be satisfied by hydrogen bonding to the interlamellar moieties. We have located the hydrogen atoms involved in these hydrogen atoms except for the one involved in a contact of 2.741(9) Å between O(15) and one of the oxygen atoms of an ethylene glycol moiety O(301). This evidence implies surprisingly that the oxygen labelled O(301) is protonated so as to produce a unipositive ethylene glycol cation.

The bond lengths within the sheet layers are unexceptional for an ALPO structure. The average Al–O contact of 1.727(9) Å is in good agreement with that found in the mineral berlinite[13] (which is the ALPO analogue of α-quartz). The key interatomic distances to note are those of the terminal P=O groups (which range between 1.485 Å and 1.495 Å) and are comparable to the terminal P=O groups in $H_3P_3O_4{\cdot}0.5H_2O$ (1.485 Å and 1.497 Å).[14] There is no evidence for any P–OH groups as the terminal P=O groups are much shorter than the P–OH groups found in $H_3P_3O_4{\cdot}0.5H_2O$ (av. 1.551 Å) and α-zirconiumphosphate (av. 1.558 Å).[15]

The organic interlamellar region is responsible for the integrity of the structure *via* a series of strong hydrogen bonds (*vide supra*) which are arranged in a complex network. This network dictates the *ABAB* stacking sequence which is reflected in the presence of a twofold screw axis normal to the

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† A suitable crystal for X-ray analysis was obtained from the synthesized material. *Crystal data* for $Al_3P_4O_{20}C_6N_2H_{23}$, orthorhombic, $P2_12_12_1$, a = 9.014(1), b = 14.771(2), c = 17.704(2) Å, V = 2357.27 Å^3, M_r = 648.09, μ(Cu-Kα) = 4.98 mm^{-1}, D_c = 1.826 g cm^{-3}. Data collected on an Enraf-Nonius CAD[4] diffractometer, using a ω-2θ scan technique, for a range $0 < 2\theta < 75°$. The total number of reflections measured was 3645 for which 2077 were unique and 1968 were considered to be observed $I > 3.5\sigma(I)$. The structure was solved by direct methods (SHELX86) analysis. All the non-hydrogen atoms which constituted the interlamellar organic layer were located easily in Fourier maps. Aliphatic hydrogen atoms were geometrically placed and all but one of the hydrogen atoms attached to the oxygen and nitrogen atoms of the ethylene glycol and ethylenediamine were located in different Fourier maps. Refinement (317 variables) was by full-matrix least-squares (CRYSTALS) analysis with anisotropic thermal parameters for the non-hydrogen atoms, and an overall thermal parameter for the aliphatic hydrogen atoms. Hydrogen atoms were allowed to ride on the atoms to which they were bonded. The final residuals were R = 0.039, R_w = 0.048. 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.

plane of the sheets. As evidence for the structure-influencing role of the organic cations we have also refined a low resolution structure of a second sheet aluminium phosphate (A2) based on the $Al_3P_4O_{16}^{3-}$ layers but in which the interlamellar region comprises only of the organic amine propylamine.[16] Now the layers stack in an *AAAA* sequence. In both structures the layers are situated approximately in the *ab* plane (A1 $a = 9.014$, $b = 14.771$ Å, $\alpha = 90°$; A2 space group $P2_1$ or $P2_1/m$, $a = 9.0210$, $b = 14.8450$ Å, $\alpha = 90°$).

Although this particular sheet ALPO bears no intrinsic P–OH groups, it ought to be possible by appropriate use of macrocations to render these materials acidic in a manner not dissimilar to the ways in which certain group IV metal phosphonates have also been made acidic and catalytically active.[17,18]

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