New chain architecture for a one-dimensional aluminophosphate, $[H_3NCH_2CH_2NH_3][AlP_2O_8H]$

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A new type of one-dimensional aluminophosphate polymer chain is found for $[H_3NCH_2CH_2NH_3][AlP_2O_8H]$ containing fused Al_2P_2 four-membered rings, with terminal PO_4H side-groups.

The chemistry of aluminophosphates templated by organic amines continues to yield unexpected results, with the recent report of a new stoichiometry (Al_3P_5) from an alcoholic system,[1] and that through use of basic conditions, the known $[AlP_2O_8]^{3-}$ formulation can exist as a two-dimensional sheet with large 20-membered rings.[2] Previously aluminophosphates based on $[AlP_2O_8]^{3-}$ were only found as variably protonated one-dimensional polymer chains consisting of Al_2P_2 rings corner shared at Al [Fig. 1(*a*)].[3–5] We now report a new type of chain architecture for the one-dimensional ALPO $[H_3NCH_2CH_2NH_3][AlP_2O_8H]$ **1** which has a linear arrangement of fused (edge-shared) Al_2P_2 four-membered rings, and (PO_4H) side groups [Fig. 1(*b*)].

Compound **1** was synthesised from a predominantly alcoholic solvent system, utilising a gel composition of 1.0 $Al(OPr^i)_3$: 12.5 H_3PO_4 : 5.0 en : 80 EG : 12.5 H_2O. Crystals of **1** suitable for a single-crystal X-ray structure determination† were obtained after heating this mixture for 14 days at 180 °C under autogeneous pressure in a Teflon-lined autoclave. The compound formed is essentially phase-pure, based on powder X-ray diffraction.

The structure of **1** is shown in polyhedral representation in Fig. 2. It consists of one-dimensional $[AlP_2O_8H]^{2-}$ polymeric anions, made up of tetrahedral AlO_4 and PO_4 units. These are connected in a zigzag ladder arrangement of fused Al_2P_2 four-membered rings, with pendant PO_4H side groups. Thus there are both terminal and triply bridging phosphate groups, with connectivities to Al of one and three. This is different from the previously published structures of $[AlP_2O_8]^{3-}$ type anions in which both phosphates are chemically similar simple bridges linked to two Al. The Al_2P_2 rings in **1** have all four Al and P coplanar with two bridging oxygens (adjacent) above and two below the ring plane. The ring has dihedral angles of 75.4° to its adjoining neighbours, to create the zigzag effect.

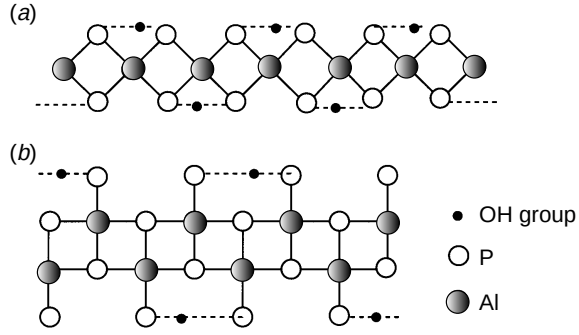

Fig. 1 Schematic representation of $[AlP_2O_8H]^{2-}$ polymers; (*a*) corner- and (*b*) edge-shared four-membered ring chain

The metric parameters for this compound are well determined (data : parameter ratio *ca.* 20 : 1) and allow reasonably detailed analysis of the aluminophosphate bonding. Fig. 3 shows a fragment of the chain with atom labelling scheme. The aluminate group has one short Al–O distance [Al(1)–O(4) 1.685(1) Å] associated with an almost linear bridge to the terminal phosphate [Al(1)–O(4)–P(1) 171.8(1)°]. The other three Al–O bonds are in the range 1.741–1.746(1) Å and have angles at oxygen of 137.5–139.7(1)°. The shortening implies stronger p–d π bonding between Al and O for the sp hybridised oxygen bridge; interestingly no shortening is observed for P(1)–O(4) compared to the other P–O_{bridge} bonds [P–O 1.535–1.544(1) Å]. There are four oxygens terminal to the phosphorus atoms, three on the PO_4H side group. One of these has a longer bond [P(1)–O(1) 1.578(1) Å], and an associated hydrogen atom, so is assigned as P–OH. The other three P–$O_{terminal}$ bonds, which involve the oxygen atoms O(2), O(3) and O(8), are shorter [1.499–1.509(2) Å] and can be thought of as a mixture of P=O and P–O^- canonical forms.

The one-dimensional chains are hydrogen-bonded to and separated by ethylene diammonium ions, with all six NH_3 protons acting as simple hydrogen-bond donors to the O(2), O(3) and O(8) terminal oxygens which carry substantial negative charge. The chains are also in van der Waals contact with two neighbours through the terminal phosphates, but there are no intermolecular P–OH···O=P (or P–OH···$^-$O–P) hydrogen bonds. Rather these are intramolecular [O(1)–H(1)···O(2) 2.641 Å] along the individual one-dimensional strand, as indicated in the Figures.

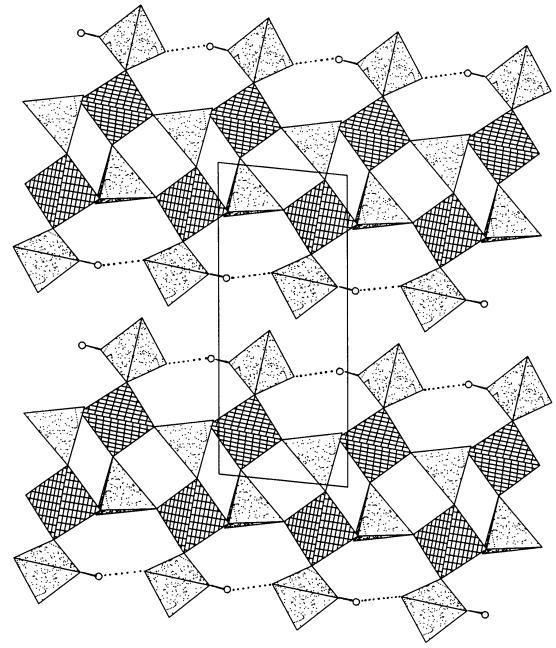

Fig. 2 Polyhedral view of $[H_3NCH_2CH_2NH_3][AlP_2O_8H]$ **1** along the *b*-axis showing neighbouring anion chains

Isomerism within ALPO systems is a well known phenomenon, with a wealth of structures known for the neutral three-dimensional $AlPO_4$-*n*,[6] and the two-dimensional $[Al_2P_3O_{12}]^{3-}$ [7,8] and $[Al_3P_4O_{16}]^{3-}$ systems.[9] The isomer types are affected by the organo-templates which are usually amines, as well as the reaction conditions. Variables such as temperature, pressure, time and solvent system, as well as gel composition and concentration have profound effects, even for the same organic template. Thus, in addition to compound **1**, a number of other low-dimensional ALPOs have been formed using ethylenediamine (en), including a $[Al_3P_4O_{16}]^{3-}$ phase,[10] the isostructural one-dimensional polymers of the classical type [Fig.1(*a*)] $[H_3NCH_2CH_2NH_3][AlP_2O_8H]\cdot H_2O$[11] and $[NH_4][H_3NCH_2CH_2NH_3][AlP_2O_8]$,[5] as well as the salt $[NH_4][H_3NCH_2CH_2NH_3]_4[Al(PO_4)_4]$.[11] These last two also require the decomposition of en to form ammonia.

The promotion of low dimensionality in aluminophosphate materials by use of non-aqueous solvent systems has been discussed by Ozin and coworkers,[1] who also demonstrated that the one-dimensional polymer $[H_3NC_5H_9]_5[Al_3P_5O_{20}H]$ can be transformed in the solid state to the two-dimensional compound $[H_3NC_5H_9]_2[Al_2P_3O_{12}H]$. In the present case, the solvent system is predominantly ethylene glycol and a large excess of phosphoric acid is used, which may account for the low Al : P ratio of 1 : 2, compared to the other phases templated by ethylenediamine.

The existence of the PO_4H side-groups in **1** indicates a low level of polyhedral condensation, which may have implications for the mechanism of build-up of ALPO polymers with higher levels of complexity. It should be noted that ribbons of fused four-membered rings, topologically equivalent to the 'ladder' structure of **1**, may be found in various higher dimensional ALPOs, for example in many of the $[Al_3P_4O_{16}]^{3-}$ and $AlPO_4$-*n* phases. The current structure would seem to be ideally set up for condensation of AlO_4 units across the P′–OH···O–P hydrogen bonded bridges (Fig. 3) to form new Al_3P_3 six-membered rings, another commonly featured ALPO structural sub-unit.

To our knowledge, however, terminal phosphate groups have not been seen previously for polymeric ALPO systems, although they exist in the molecular ion $[Al(PO_4)_4]^{9-}$.[11] We predict the recent findings of novel stoichiometries and dimensionalities in ALPO materials is likely to continue, if the phosphate components may also exist in this terminal mode, connected to a single aluminate, rather than as two-, three- or four-connected tetrahedral building blocks.

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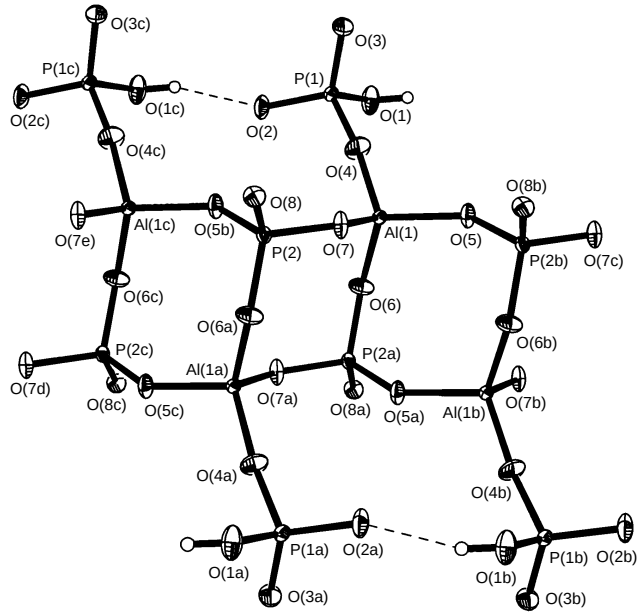

Fig. 3 Thermal ellipsoid (40%) plot of **1** with labelling scheme for the anion

Footnotes

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† A colourless bar of dimensions 300 × 120 × 80 μm was selected. Structure carried out using a Siemens P4-RA diffractometer and solution and refinement by SHELXTL-PLUS; *Crystal data*: $C_2H_{11}AlN_2O_8P_2$, M_w = 280.0, triclinic, $P\bar{1}$, a = 4.901(1), b = 9.032(1), c = 11.691(1) Å, α = 81.38, β = 82.27(1), γ = 75.83(1)°, U = 493.5(1) Å^3, Z = 2, D_c = 1.89 Mg m^{-3}, R = 0.034, R_w = 0.042 for 3486 data with $F \geqslant 4\sigma(F)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/442.

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