Synthesis and Structure of a One-dimensionally extended Aluminium Phosphate: $Et_3NH^+(H_2AlP_2O_8)^-$

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The preparation and characterization of a novel, chain aluminium phosphate macroanion, in which Al and P each have fourfold co-ordination, are described; its method of synthesis, using a predominantly non-aqueous environment with organic templates, gives rise to other crystalline solids with new structures.

In the mineral kingdom there are myriad examples of sets of structures and compositions in which members of a given set are related to others within it through the substitution of multiply charged ions by two others.[1] Well known examples are the network, three-dimensionally continuous silicates,[2] where Si^{4+} is substituted by Al^{3+} and an alkali metal cation, and in the sheet (alumino)silicates[3] where octahedrally co-ordinated Al^{3+} is substituted by Mg^{2+} and Li^+. Solid-state and inorganic chemists have long taken advantage of this simple fact, which has often led to the discovery and production of new structural types. The microporous pentasils, for instance, of which silicalite I and silicalite II are the

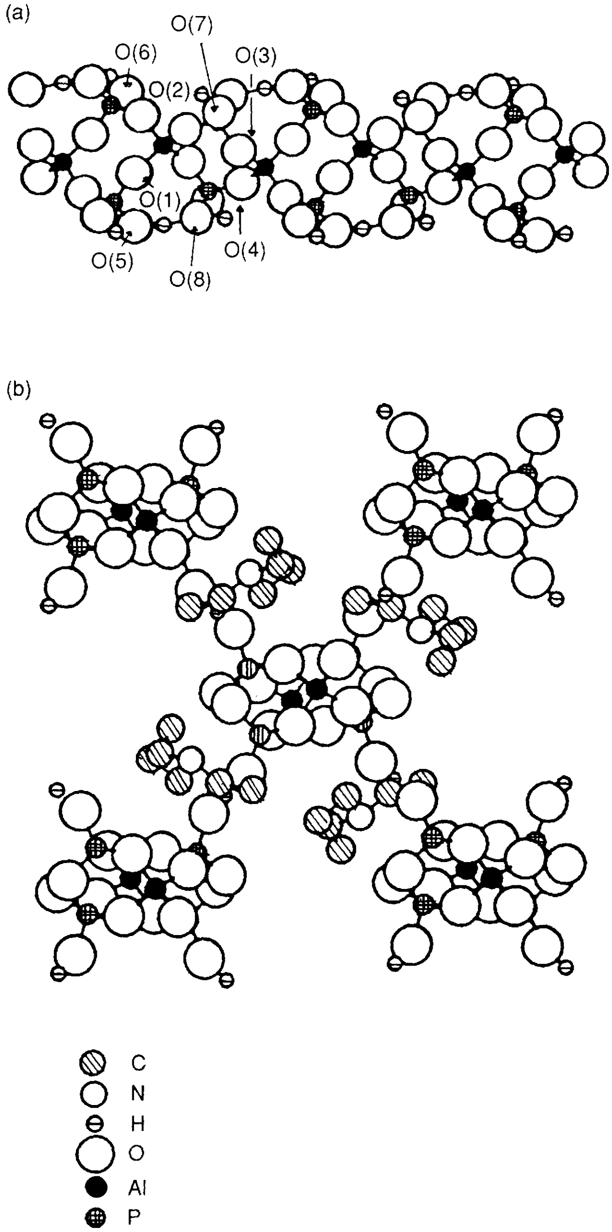

Figure 1. The newly discovered (title compound) chain structure along the backbone of which there is a recurrence of OH groups attached to phosphorus. (a) The view perpendicular to the chain axis. The sites of the protonated triethylamine are shown in the view along the chain in (b). Selected interatomic contacts: P(1)–O(5) 1.498(3), P(1)–O(6) 1.531(3), P(2)–O(7) 1.481(3), P(2)–O(8) 1.563(3), O(5)–O(8) 2.608(4), O(5)–N(1) 2.820(5), O(6)–O(7) 2.478(4) Å.

most prominent members (idealized formulae SiO_2) give rise to ZSM-5 and ZSM-11 [typical compositions $M^+{}_nSi_mO_{2m}Al_nO_{2n}$ (*m*/*n* 20—20 000; *m* >60)] and, of greater significance in present contexts, to a new family of microporous aluminium phosphates in which Si^{4+} is now replaced by Al^{3+} and P^{5+}. These so-called ALPOs constitute an extensive range of crystalline molecular sieves[4,5] (ALPO-5, -11, -17, *etc.*), many of which are exact structural analogues of, and others have no known structural counterparts with, naturally occurring and synthetic (alumino)silicate zeolites.

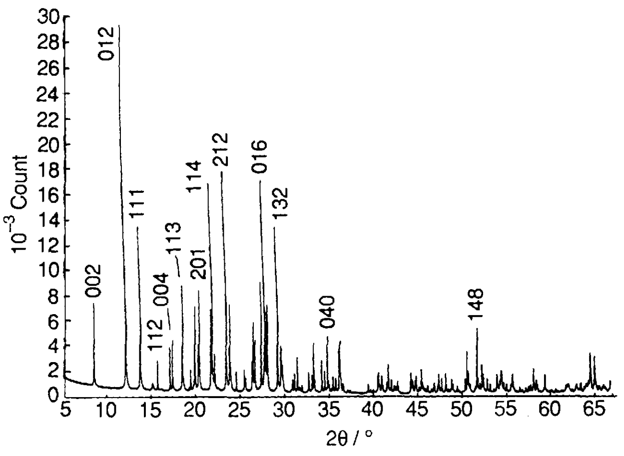

Figure 2. *X*-Ray diffractogram taken using synchrotron radiation (λ = 1.504 22 Å) of a biphasic mixture of ALPOs prepared under conditions similar to those employed for the title compound. One of the components is almost certainly the isostructural variant (in $AlPO_4$) of the newly discovered[9] $AlAsO_4$-1. The crystallographic characteristics of this new ALPO, which has both 4- and 6-co-ordinated Al ions are *a* = 8.629(1), *b* = 10.025(1), *c* = 19.711(1) Å, space group *Pcab*.

Here we describe a novel chain structure which, apart from being the first recorded example of a chain ALPO, is unusual also for other reasons. Thus, although it is not unrelated to the chain silicates inasmuch as both Al^{3+} and P^{5+} are (like Si^{4+} in diopside or nephrite) four-co-ordinated, it is neither pyroxenic (single chain) or amphibolean (double chain), but has its own unique structure (Figure 1) in which the Al to P ratio is 1 : 2 [contrast the 1 : 1 ratio in the two crystallographic forms (α and β) of the mineral berlinite $AlPO_4$]. The chain also bears a net negative charge, and has recurrently arranged along its backbone acidic OH groups attached to phosphorus.

The title compound was synthesized from a predominantly non-aqueous system in which s-butyl alcohol was used as solvent. A non-aqueous mixture of aluminium tri-isopropoxide, phosphoric acid (85% H_3PO_4), and triethylamine with the gel composition $6Et_3N\,Al_2O_3\,2.4P_2O_5\,35Bu^sOH$ was heated at 180 °C for 10 days under autogenous pressure. n-Butyl alcohol may be used in place of s-butyl alcohol. The crystalline product was filtered off, washed with water, and dried at ambient temperatures. Its crystal structure was determined by four-circle *X*-ray diffractometry.†

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† *Crystal data* for $C_6H_{18}AlNO_8P_2$, M = 321.14 monoclinic, space group $P2_1/n$, a = 12.073(2), b = 13.201(2), c = 8.522(1) Å, β = 97.2(1)°, U = 1346.9 Å^3, Z = 4, D_c = 1.584 g cm^{-3}, $F(000)$ = 672, λ = 1.5418 Å, μ (Cu-K_α) = 3.928 mm^{-1}. The aluminium and phosphorus atoms were found by direct methods and the remaining non-hydrogen atoms were located in Fourier maps. It was found during the course of the refinement that the template molecule NEt_3 was disordered. Aliphatic hydrogen atoms were geometrically placed. The remaining hydrogen atoms were located in difference Fourier maps. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Cu-K_α radiation in the range $0 < 2\theta \leqslant 150°$. The data were corrected for Lorentz-polarization and absorption effects. A total of 3635 reflections were measured of which 1862 unique reflections with $I \geqslant 3\sigma(I)$ were considered to be observed and used in a full-matrix least-squares refinement. Parameters varied in the refinement included positional ones for all non-hydrogen atoms, anisotropic thermal ones for the heavy atoms, and positional and isotropic thermal ones for the disordered atoms. Restraints were applied to the C–C and C–N bond lengths in the triethylamine moiety. The final crystallographic residuals were R 0.042 and R_w 0.049. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Within the chain both the aluminium and phosphorus atoms are tetrahedrally co-ordinated. The average Al–O distance (1.734 Å) and average P–O bonding distance (1.537 Å) are consistent with those found in α-berlinite (1.739 and 1.516 Å respectively).[6] The lengths of the terminal phosphorus–oxygen bonds are consistent with those found for P–OH and P=O groups,[7,8] and assignment to POH and P=O is borne out by the location of the hydrogen atoms. Strong hydrogen bonds which are parallel to the chain axis further enhance the rigidity of this group.

In situ (time-resolved) *X*-ray powder diffractometry on heated samples of the product showed it to undergo a phase transition and probably some decomposition in the range 80—100 °C, the resulting material being biphasic. One of these phases has been identified as β-berlinite. Thermogravimetry and Fourier transform IR spectroscopy indicate that there are mass losses at *ca.* 80, 200, and 380 °C of *ca.* 9.8, 18.8 and 18.2%, respectively. Loss of water is complete below 100 °C, and there is almost certainly dehydroxylation of the chains accompanying decomposition.

Preliminary examination of the catalytic performance of the as-prepared, and gently heated, new ALPO, using methanol conversion as a test reaction,[9] shows it to possess little or no activity. *X*-Ray emission analysis in an electron microscope has revealed that there are other phases (of the type described above) also present. We have prepared several new ALPO materials by a method similar to that for the title compound. Many of these yield bi- or even multi-phasic crystalline products. In one such mixture, see diffractogram shown in Figure 2, it proved possible to identify one of the phases. It is a new microporous ALPO but it is isomorphous with $AlAsO_4$ recently reported,[10] where the Al is in both four- and six-co-ordination. We designate this as ALPO-JDF‡ in line with current practice[11] for naming zeolite solids.

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‡ JDF for Jilin Davy Faraday.