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LETTER TO THE EDITOR

Two Unusual Layer Aluminophosphates Templated by Imidazolium Ions; $[N_2C_3H_5][AlP_2O_8H_2 \cdot 2H_2O]$ and $2[N_2C_3H_5][Al_3P_4O_{16}H]$

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Two new aluminophosphates $[ImH][AlP_2O_8H_2 \cdot 2H_2O]$ 1 and $2[ImH][Al_3P_4O_{16}H]$ 2 have been synthesized solvothermally at 160°C. Both compounds represent totally new structure types for the already extensive $[AlP_2O_8]$ and $[Al_3P_4O_{16}]$ families. Compound 1 has a simple, puckered 2-D sheet structure containing Al_4P_4 8-membered rings and octahedral Al centers which are hydrated by *trans* aqua ligands. It is monoclinic, space group $C2/c$, $a = 21.854(4)$, $b = 7.188(2)$, $c = 6.990(2)$ Å, $\beta = 103.77(2)°$, $V = 1063.5(5)$ Å. Single crystal structure analysis gave $R = 0.038$, $R_w = 0.040$ for 943 reflection intensities. Compound 2 has a complex layer structure which contains double 6MR subunits, the building blocks of many 3-D ALPOs, and has 5-coordinate as well as 4-coordinate aluminum. Single crystal structure analysis of 2 indicated the triclinic system, space group P-1, $a = 8.940(2)$, $b = 9.360(2)$, $c = 11.721(2)$ Å, $\alpha = 97.10(2)°$, $\beta = 95.10(2)°$, $\gamma = 91.91(2)°$, $V = 968.4(3)$ Å. Refinement gave $R = 0.044$, $R_w = 0.040$ for 1613 unique observed reflections.

INTRODUCTION

Aluminophosphates continue to be synthesized in a variety of stoichiometries and architectures, showing a more diverse chemistry than their analogues the aluminosilicates. In particular a number of phosphate-rich ionic ALPOs, $[AlP_2O_8]^{3-}$, $[Al_2P_3O_{12}]^{3-}$, and $[Al_3P_4O_{16}]^{3-}$ have been formed. These can be viewed as combinations of phosphate ion $[PO_4]^{3-}$ and $[AlPO_4]$ in 1:1, 1:2 and 1:3 ratios, respectively. Recently a 2-D form of $[AlP_2O_8]^{3-}$ was found from basic solution (1), which contrasts the several known protonated 1-D analogues (2–4). For $[Al_2P_3O_{12}]^{3-}$ a wide range of stable isomers (5, 6), including chiral forms (7), are possible. The stoichiometry $[Al_3P_4O_{16}]^{3-}$ has also been found in a number of compounds. These show interesting 2-D isomeric forms typically with tetrahedral AlO_4 and PO_4 units and one terminal $[P{=}O/P{-}O^-]$ for each phosphorus (8–12). The organic counterions in these compounds usually possess terminal ammonium groups NH_3R^+, which offer extensive H-bonding possibilities to the terminal oxygens of the ALPO net.

Herein we report the synthesis and structures of two new aluminophosphates $[ImH][AlP_2O_8H_2 \cdot 2H_2O]$ **1** and $2[ImH][Al_3P_4O_{16}H]$ **2**, $[ImH]$ = imidazolium, $[N_2C_3H_5]$, which have entirely different architectures than previous anionic ALPO isomers. Compound **1** is an unusual hydrated ALPO, which has octahedral Al centers and 8-membered Al_4P_4 rings arranged in a 2-D sheet. Compound **2** is best described as a double-layer sheet structure composed of double 6-membered ring building blocks (hexagonal prisms of Al_6P_6). This has several different types of Al and P centers including 5-coordinate AlO_5 units.

EXPERIMENTAL

Synthesis of **1** was carried out using solvothermal methods, from a gel composition of 1.0 $Al(OPr^i)_3$: 3.5 H_3PO_4 : 2 Im : 25 butan-2-ol. Crystals were formed after heating at 160°C for 6 days, with the product essentially phase pure by powder X-ray diffraction. The yield for **1** was 60% based on Al. Use of a higher temperature (180°C) for the synthesis conditions resulted in excessive decomposition of the organic components. Compound **2** was made similarly at 160°C, but using 4.1 mol. equiv. H_3PO_4 and 5 mol. equivalents of imidazole. The yield for **2** was 65% based on Al. The *iso*-butanol was not distilled prior to use and the phosphoric acid is an 85% aqueous solution, so that ca. 5 mol equivalents of H_2O are also present under the reaction conditions.

For the structure determinations, data were collected using a Siemens P4-RA diffractometer and structures solved

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and refined using the SHELXTL suite of programs (G. W. Sheldrick, Siemens Analytical Instruments, 1993). All hydrogen atoms were located for inorganic components. Crystal Data for **1**: $C_3H_{11}AlN_2O_{10}P_2$, Monoclinic, $C2/c$, $a = 21.854(4)$, $b = 7.188(2)$, $c = 6.990(2)$ Å, $\beta = 103.77(2)^\circ$, $V = 1063.5(5)$ Å^3, $Z = 4$, $D_c = 2.02$ M gm^{-3}, $\mu_{(\text{Mo-}K\alpha)} = 0.55$ mm^{-1}; 946 reflections ($F > 4\sigma(F)$ and 94 l.s. parameters gave $R = 0.038$, $R_w = 0.040$, GOOF = 1.40. Crystal Data for **2**: $C_6H_{11}Al_3N_4O_{16}P_4$, Triclinic, P-1, $a = 8.940(2)$, $b = 9.360(2)$, $c = 11.721(2)$ Å, $\alpha = 97.10(2)^\circ$, $\beta = 95.10(2)$, $\gamma = 91.91(2)^\circ$, $V = 968.4(3)$ Å^3, $Z = 2$, $D_c = 2.06$ M gm^{-3}, $\mu_{(\text{Mo-}K\alpha)} = 0.62$ mm^{-1}; 1613 reflections ($F > 4\sigma(F)$ and 294 l.s. parameters gave $R = 0.044$, $R_w = 0.040$, GOOF = 1.11.

RESULTS AND DISCUSSION

The single crystal X-ray structure determinations showed that the compounds fitted previously seen stoichiometries but with novel structural arrangements. In the case of **1**, a highly puckered sheet structure is found, a polyhedral representation of which is shown in Fig. 1. All Al centers are octahedrally coordinated with two terminal aqua ligands in a *trans* arrangement. Each Al is connected in a planar arrangement to four hydrogen phosphate groups via Al–O–P bridges. The Al sits on a crystallographic inversion center, with Al–O bond lengths of 1.855(2) and 1.913(2) Å to the phosphates and 1.923(2) Å to the aqua ligands.

The $[HPO_4]$ groups in turn act as simple bridges between two Al centers and have terminal P=O (1.510(2) Å) and P–OH (P–O length = 1.583(2) Å) functionalities. The topology of the aluminate–phosphate connectivity pattern is shown in Fig. 2. It consists of a series of interconnected Al_4P_4 8-membered rings, four-connected at each Al, which we believe to be the first example of its type.

Compound **2** has an unusual double layer arrangement for the inorganic component. The connectivity of the Al and P atoms within the sheet is shown in Fig. 3, and double 6-membered rings can be seen. These are common building blocks of a number of 3-D ALPO-n structures, for example, Chabazite (13), ALPO-18 (14), and SAPO-37 (15). Their involvement in this structure can be attributed to the fact that in **2** two Al and two P have the tetrahedral connectivity with four bridging oxygens as found for the ALPO-*n*.

The overall network does not become 3-D since each double 6MR unit contains phosphate groups (one per asymmetric unit) with a terminal $[P = O/P\text{–}O^-]$ functionality (1.483(5) Å) and which connect to only 3 Al. However, each double 6MR is connected to four others within the sheet, via bridges involving the third Al center, which is 5-coordinate, and a hydrogen phosphate functionality, (P=O = 1.492, P–OH = 1.566(5) Å) which forms simple bridges between two aluminum centers.

The Al–O bond lengths for the tetrahedral aluminums vary from 1.708–1.760(5) Å, whereas for the penta coordinate Al they are longer 1.779–1.892(5) Å. The presence of AlO_6 and AlO_5 units in aluminophosphates is uncommon but well precedented. For example, octahedral, hydrated Al centers are found in the mineral Variscite $[AlPO_4 \cdot 2H_2O]$ and a number of aluminophosphates such as VPI-5 (16). Penta-coordinate aluminate centers are known in the 3-D ALPOs with formula $[Al_3P_3O_{13}]^{2-}$ (17), as well as in the 2-D ALPO $[pyH][Al_2P_3O_{12}H]$ (5).

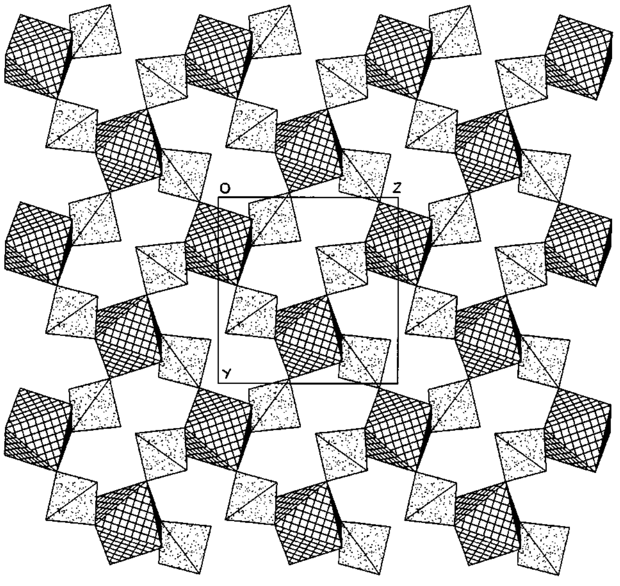

FIG. 1. Polyhedral representation of **1** looking down the *a*-axis (AlO_6 units cross-hatched; PO_4 units random dot pattern).

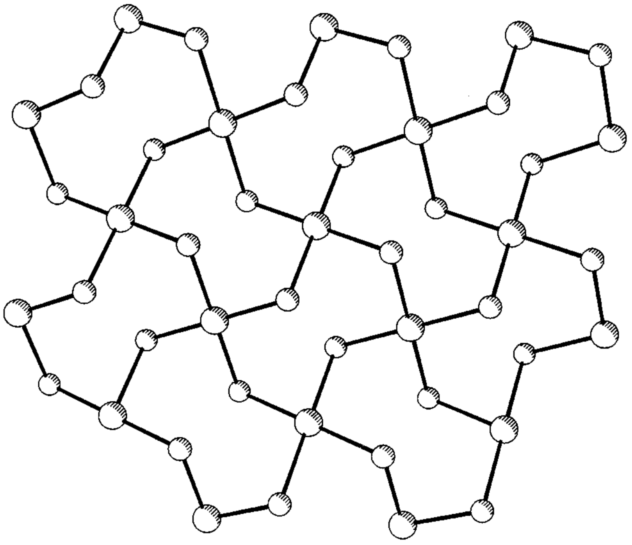

FIG. 2. Topological connectivity of AlO_6 and PO_4 units in **1**, showing only Al and P atoms (Al are larger spheres).

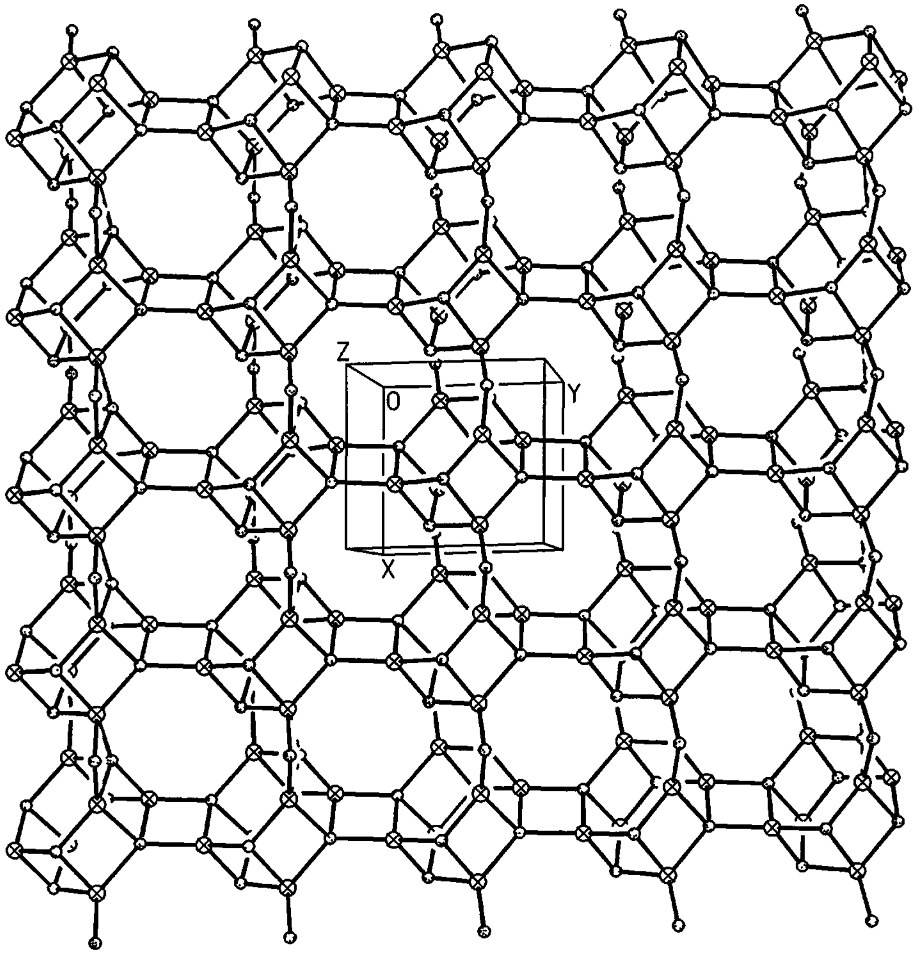

FIG. 3. Plan view of **2**, along the *c*-axis showing connectivity of Al and P atoms and double 6MR subunits (Al cross-hatched).

The role of the organic template as a structure directing agent in these systems is not always clear, although we and others have found that small changes can result in different network isomers (8). A strong network of hydrogen bonds between the organic cations and the inorganic component is invariably found for anionic ALPOs such as $[Al_3P_4O_{16}]^{3-}$ which typically have terminal $[P{=}O/P{-}O^-]$ groups with 2 or 3 hydrogen-bonds formed to each phosphate terminal oxygen.

The use of imidazole (18), which upon protonation forms the imidazolium ion $[N_2C_3H_5]^+$ was made in order to investigate the templating effect of organoamines which do not form terminal NH_3R^+ ammonium ions and offer more limited H-bond forming capability. In addition to the formation of hydrogen bonds to available acceptors, the overall crystal structure must also be compatible with steric packing requirements of the organic group. In this respect as well the planar imidazolium ion is quite different from straight chain aliphatic ammonium ions.

The structure of the inorganic components and the overall packing arrangements in both **1** and **2** reflect these two needs. The reduced hydrogen bonding capacity of imidazolium apparently results in inorganic structures which have lower H-bond requirements from the organic counter-ions. The presence of hydrogen phosphate $[PO_4H]$ groups in both compounds can be seen as a way to reduce the required degree of H-bonding from organic cations, since the inorganic network then has fewer $[P{=}O/P{-}O^-]$ H-bond acceptor groups, whilst providing (P–OH) hydrogen-bond donors itself.

Additionally the packing constraints that would be required of three planar $[ImH]^+$ ions per formula unit is also a major consideration, which would tend to preclude unprotonated inorganic nets for $[AlP_2O_8]^{3-}$ and $[Al_3P_4O_{16}]^{3-}$. The packing in the structure of **2** is shown in Fig. 4. The two crystallographically independent imidazolium ions are able to fit in a cavity within the double sheet as well as in between the inorganic layers. The

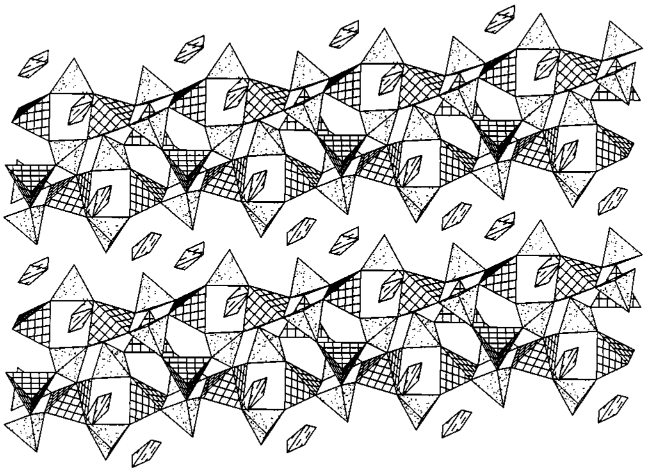

FIG. 4. Polyhedral view of **2** along the *b*-axis showing packing of imidazolium ions (Al units cross-hatched; PO_4 units random dot pattern).

imidazolium ions also group pairwise in parallel alignment and have favorable graphitic-type van der Waals contact with one neighboring ion (planar separation = 3.1 Å).

The $[ImH]^+$ ions are capable of forming two hydrogen bonds at an angle of ca. 140°. In the structure of **2**, one $[ImH]^+$ of the asymmetric unit forms two strong H-bonds, whilst the other suffers from some degree of rotational disorder (57:43%). In **1** the $[ImH]^+$ ion sits on a two-fold axis but is again rotationally disordered, with only the major component making good H-bond contacts. The presence of the aqua ligands in **1** also provides additional H-bond donors.

Formation of hydrated aluminophosphates such as **1** with octahedrally coordinated Al may be expected at temperatures of 160°C and lower. Other hydrated phases with octahedral Al can be formed in this lower temperature regime of solvothermal synthesis, which has been examined in some detail for the large pore VPI-5 3-D ALPO system (16). Studies on the dehydration of **2** are currently under investigation.

The ability of different organic counterions to serve as structure directing agents for aluminophosphates is of great interest in rational building of inorganic networks. The use of different classes of organotemplate, such as the imidazolium planar aromatic type, will undoubtedly allow continued progress in uncovering the full range of structural isomerism for aluminophosphates and related inorganic materials.

CONCLUSIONS

The use of imidazole in the templating of aluminophosphates has resulted in two new structural types for the $[AlP_2O_8]$ and $[Al_3P_4O_{16}]$ families. The moderate solvothermal temperature of 160°C may assist formation of the hydrated phase $[ImH][AlP_2O_8H_2 \cdot 2H_2O]$ **1**. Increase of the imidazole concentration allows formation of $2[ImH][Al_3P_4O_{16}H]$ **2**. The crystal structures of both **1** and **2** are affected not only by the planar spatial nature of [ImH] cations, but also their reduced hydrogen-bonding capacity compared to terminal organoammonium ions.

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Note added in proof. Compound **1** also has been recently reported in *Chem. Mater.* **1** (1998).

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