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Synthesis and Structure of an Unusual New Layered Aluminophosphate Containing Oxalate Groups, $[NH_3CH_2CH_2NH_3]_{2.5}[Al_4H(HPO_4)_4(H_2PO_4)_2(C_2O_4)_4]$

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The first example of an aluminophosphate containing organic anions covalently bonded to the framework of the structure is reported; $[NH_3CH_2CH_2NH_3]_{2.5}[Al_4H(HPO_4)_4(H_2PO_4)_2(C_2O_4)_4]$ was prepared hydrothermally and adopts a layered structure. The oxalate groups act as bidentate ligands to Al^{3+} and hold the structure together by strong interlayer P-O-H–oxalate hydrogen bonds. The structure was solved from synchrotron X-ray diffraction data collected on a very small single crystal, space group *C2/m*, $a = 19.683(4)$ Å, $b = 12.360(3)$ Å, $c = 16.734(3)$ Å, $\beta = 110.51(3)°$. © 1999 Academic Press

INTRODUCTION

Since the first publication of the aluminophosphate family of microporous solids in 1982 (1), interest in the templated hydrothermal synthesis of further examples of these and related metal phosphates has escalated. Recent examples cover one-dimensional (2), two-dimensional (3), and three-dimensional materials (4), exhibiting a variety of structural building units and containing Al^{3+} in four-, five-, and six-coordinate environments. Although many metals have been substituted for Al^{3+} in these systems, many different organic templates have been utilized and several different nonaqueous solvent systems have also been employed (5), there has been a notable absence of attempts to introduce alternative species onto the *anion* sublattice, i.e., inclusion of both PO_4^{3-} and other (nontetrahedral) anions in the same structure. Changing the chemical and topological properties of the anion can be expected to open up a further wide array of interesting structural host–guest chemistry. So far anionic substitutions have been confined to fluoride (6) and arsenate (7), substitutions which also readily occur in phosphates of other metals. In our recent hydrothermal work we have been interested in incorporating organic anions into metal phosphate systems, in order to produce mixed anion framework or layered materials. The simplest organic anion to be considered is oxalate, $C_2O_4^{2-}$. The first example of a three-dimensional metal–phosphate–oxalate, *viz.* $Fe_4(PO_4)_2(C_2O_4) \cdot 2H_2O$ (8) has recently been reported. We note that a one-dimensional tin phosphato-oxalate has also been recently reported (9). This paper describes the result of our first exploratory study in the Al–PO_4–C_2O_4 system and reports a new layered structure, $[NH_3CH_2CH_2NH_3]_{2.5}[Al_4H(HPO_4)_4(H_2PO_4)_2(C_2O_4)_4]$ (**1**).

EXPERIMENTAL

Compound (**1**) was synthesised hydrothermally from a mixture of $Al(OH)_3$, H_3PO_4 (85% aq.), $H_2C_2O_4 \cdot 2H_2O$, and en (en, ethylenediammine) in H_2O in a molar ratio 1 : 1 : 2 : 1 : 90. The reactants were placed in a Teflon-lined steel autoclave and heated at 160°C for 90 h. The structure was solved by single crystal diffraction at a synchrotron source. Data were collected at beam-line ID11 at the European Synchrotron Radiation Facility (ESRF), Grenoble (10). A thin plate crystal (100 × 50 × 10 μm) was mounted on a fine glass fibre and data were collected on a three-circle (fixed kappa) Siemens diffractometer fitted with a SMART CCD detector, at room temperature. The wavelength was calibrated prior to the experiment as 0.4435 Å. Data were collected in ω intervals of 0.1° over 140°, with the detector covering a fixed 2θ range. The resolution limit was 0.50 Å. Crystal data for (**1**) $[NH_3CH_2CH_2NH_3]_{2.5}$ $[Al_4H(HPO_4)_4$

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$(H_2PO_4)_2(C_2O_4)_4]$, monoclinic, space group $C2/m$, $a = 19.683(4)$ Å, $b = 12.360(3)$ Å, $c = 16.734(3)$ Å, $\beta = 110.51(3)°$, $V = 3813(1)$ Å^3, $Z = 4$, $D_C = 2.02$ g cm^{-3}, $R = 0.116$, $R_W = 0.146$ based on F, for 3076 unique reflections ($I > 3\sigma(I)$). The structure was solved using SHELXS97 (11) and refined using teXsan (12). Due to the weakly diffracting nature, only isotropic refinement of all atoms was possible. Disorder was observed around one PO_4^{3-} site and two of the en sites, which were modeled as two discrete sites of 50% occupancy. Bond valence-sum analysis (13) was used to infer the locations of H atoms, though these were not located from the diffraction data. For charge balance all the en groups are required to be doubly protonated, and one extra H^+ is required, in addition to those suggested on the P-O-H groups, which is presumed to be disordered. X-ray powder diffraction showed the bulk material to be almost phase pure, with a small amount of unidentified impurity (strongest peak at $d = 4.60$ Å). The identity of this minor phase is unclear, but may be $Al_2P_6O_{18} \cdot 9.5H_2O$ (ICDD PDF No. 37-210). Further work is ongoing in order to prepare a phase-pure sample.

RESULTS AND DISCUSSION

The structure can be described as two-dimensional (Fig. 1), with anionic $[Al_4H(HPO_4)_4(H_2PO_4)_2(C_2O_4)_4]^{5-}$ layers separated by $[NH_3CH_2CH_2NH_3]^{2+}$ templating cations. Strong interlayer links are also made via P-O-H–oxalate hydrogen bonds. Due to the complexity of the structure (3 independent A1, 5 independent P, and a total of 50 independent non-H atoms in the asymmetric unit), it is instructive to consider it in terms of simpler building units.

The basic unit is a double chain of linked HPO_4 and AlO_6 polyhedra running parallel to the **b** axis (Fig. 2). Each double chain contains three chemically similar but crystallographically distinct HPO_4 and AlO_6 polyhedra, each of which share three vertices with intrachain neighbors. Of the remaining AlO_6 vertices, one is used to link neighboring chains in the **c** direction, via the H_2PO_4 groups, to form layers (Fig. 3). The other vertices are coordinated by bidentate terminal oxalate groups which, in turn, act as H-bond acceptors from the terminal P-O-H groups of the intrachain HPO_4 groups (Fig. 2). Each layer contains eight-membered rings of alternating AlO_6 and HPO_4/H_2PO_4 polyhedra. The central H_2PO_4 unit, P(5), is found to be disordered and has two equally occupied orientations pointing "in" or

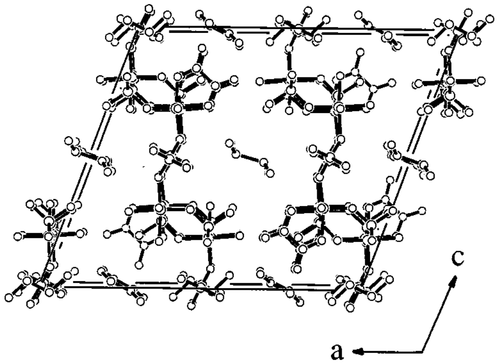

FIG. 1. View of the structure of (1) down the **b**-axis, showing en templates between aluminium–phosphate–oxalate layers.

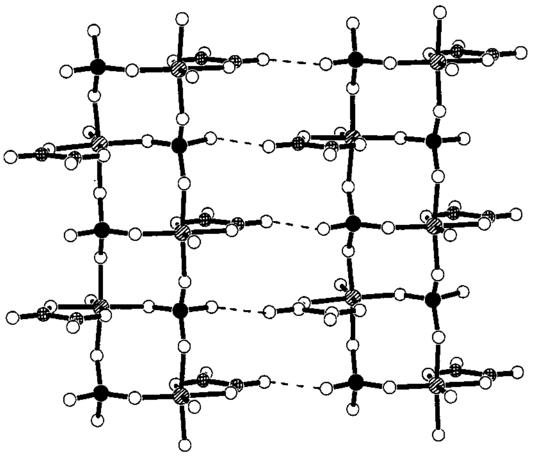

FIG. 2. Two double chains composed of vertex-sharing AlO_6 and HPO_4 polyhedra. Chains are linked covalently above and below into sheets (Fig. 3) and by P-O-H–ox H bonds as shown (donor–acceptor H-bond distances 2.53–2.70 Å). Al, P, and C atoms are shown with diagonal, filled, and hatched shading, respectively.

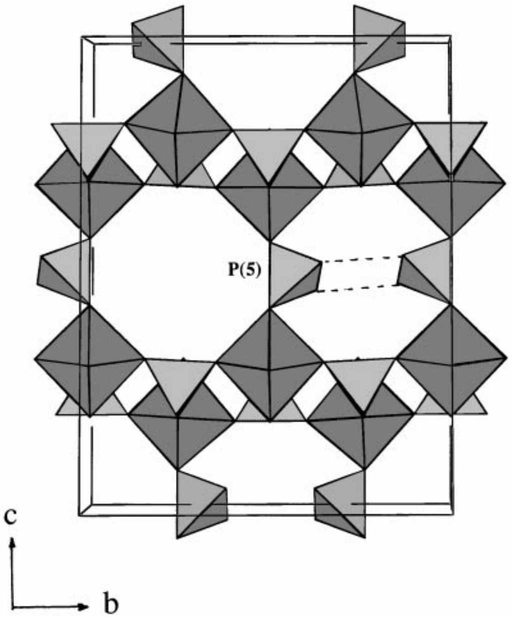

FIG. 3. Projection down the **a**-axis showing interchain, intralayer links via H_2PO_4 polyhedra. Note that the central H_2PO_4 groups are statistically disordered over two orientations; one possible orientation is shown.

"out", respectively; this is shown in Fig. 3. It is likely that there is order within each individual set of interchain links, dictated by strong H bonding between neighboring H_2PO_4 groups (as shown).

This material presents several new structural features in aluminophosphate chemistry. The double AlO_6/PO_4 chain motif is unique. Analogous double AlO_4/PO_4 chains have been observed (2); in that case the single available AlO_4 vertex is coordinated to a terminal HPO_4 group, thus retaining overall one-dimensional character. The same type of double MO_6/PO_4 chain, however, has been reported in $Mo(OH)_3PO_4$ (14). Also interesting is the observation of the "termination" or "capping" of the Al–O network in the third direction, by oxalate groups which coordinate in only a bidentate rather than a *bis*-bidentate manner; *bis*-bidentate coordination of oxalate to octahedral metals is well known in many framework and layered metal oxalates (15) and is observed in our own new phosphate–oxalate (8). The only previous example in aluminophosphate chemistry of an "organic" species being involved in the Al^{3+} coordination sphere occurs in the structure of $AlF(HPO_4)$.en (6), where the en acts as a monodentate ligand to Al^{3+}.

"Capping" behaviour comparable to that observed in (**1**) has been seen very recently in the iron molybdate phase MoO_4FeCl(2,2′-bipy) (16) [bipy, bipyridine], which exhibits analogous FeO_6/MoO_4 double chains, with the oxalate position being taken by the topologically-related 2,2-bipy ligand (i.e., 2,2′-bipy acts as a *mono*-bidentate ligand—a "one-sided" oxalate). Conversely, 2,2′-bpm [bpm, bipyrimidine] has been shown to substitute directly for oxalate in framework topologies where the ligand acts in a *bis*-bidentate manner (17) (i.e., 2,2′-bpm acts as a "two-sided" oxalate). From these results, it can be seen that judicious choice of multidentate organic ligands provides a mechanism for selectively truncating or extending the coordination sphere of the metal–oxide sublattice in these systems, and a means of tailoring dimensionality and architecture of inorganic–organic hybrid solids, with consequent design and control of chemical or physical properties.

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