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Articles

Template Cooperation Effect Leading to the New Layered Aluminophosphate $CN_3H_6\cdot Al(HPO_4)_2\cdot 2H_2O$

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$CN_3H_6\cdot Al(HPO_4)_2\cdot 2H_2O$, prepared by hydrothermal methods at 120 °C, contains infinite stacks of guanidinium cations (intermolecule C···C separation ∼3.5 Å) interleaving a distinctive anionic aluminophosphate layer topology based on polyhedral eight-rings of vertex-sharing $AlO_4(OH_2)_2$ octahedra and HPO_4 tetrahedra. Crystal data: $CN_3H_6\cdot Al(HPO_4)_2\cdot 2H_2O$, $M_r = 315.05$, orthorhombic, *Pnma* (No. 62), $a = 6.965(2)$ Å, $b = 20.624(4)$ Å, $c = 7.168(2)$ Å, $V = 1029.7(5)$ Å^3, $Z = 4$, $R = 3.42\%$, $R_w = 3.40\%$ [85 parameters, 829 observed reflections with $I > 3\sigma(I)$].

Introduction

Over the past few years, synthetic methodologies have been developed[1−15] to prepare numerous two-dimensional (layered) and one-dimensional (chainlike) aluminophosphates (AlPOs), to complement the family of three-dimensional, zeolitic AlPOs.[16] Ozin et al.[17] have reviewed these structures as part of their effort to develop a general model for AlPO synthesis. Interesting experimental aspects of AlPO syntheses procedures include the use of nonaqueous solvents[15] and unusual templating species such as $[Co(en)]^{3+}$ (en = ethylenediamine).[12] Very recently, Leech et al.[18] have described the preparation of single crystals of a new type of layered AlPO denoted $M\cdot Al(HPO_4)_2\cdot 2H_2O$ (M = pyridine $[C_5NH_6{}^+]$ or imidazole $[C_3N_2H_5{}^+]$) by room temperature crystallizations from silica gels. These are the first reported layered AlPOs templated by organic species which contain a 1:2 Al:P atomic ratio. Isostructural gallophosphates $M\cdot Ga(HPO_4)_2\cdot 2H_2O$ (M = pyridine or imidazole) were prepared by the same workers.[18]

In this paper we describe the hydrothermal synthesis and structure of $CN_3H_6\cdot Al(HPO_4)_2\cdot 2H_2O$. This new guanidinium AlPO shares the $M\cdot Al(HPO_4)_2\cdot 2H_2O$-type layer topology.[17] We suggest that template−template interactions might be significant in assisting in the formation of this particular modification of the $M\cdot Al(HPO_4)_2\cdot 2H_2O$ family.

Experimental Section

Synthesis and Initial Characterization. $CN_3H_6\cdot Al(HPO_4)_2\cdot 2H_2O$ was prepared by mixing 1.80 g of guanidinium carbonate $[(CN_3H_6)_2CO_3]$, 1.02 g of Al_2O_3 (Aldrich activated alumina), 4.61 g of 85% H_3PO_4, and 7 mL of deionized water (starting guanidinium:Al:P:water ratio ≈ 2:1:4:40) in a 23-mL Teflon-lined hydrothermal bomb. A white slurry resulted from the room temperature mixing of these reagents. The bomb was sealed and heated to 120 °C for 24 h. Upon cooling, the solid products were recovered by vacuum filtration. These consisted of rectangular plates (to 0.5 mm maximum linear dimension) of the title compound accompanied by white powder. Powder X-ray diffraction indicated that the white powder consisted largely of poorly crystalline $CN_3H_6\cdot Al(HPO_4)_2\cdot 2H_2O$, accompanied by a small amount of $AlPO_4$.[19]

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Table 1. Crystallographic Parameters for $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$

empirical formula	$P_2AlO_{10}CN_3H_{12}$
formula weight	315.05
crystal system	orthorhombic
a (Å)	6.965(2)
b (Å)	20.624(4)
c (Å)	7.168(2)
V (Å^3)	1029.7(5)
Z	4
space group	*Pnma* (No. 62)
T (°C)	25(2)
λ (Mo Kα) (Å)	0.71073
ρ_{calc} (g/cm^3)	2.03
μ (cm^{-1})	5.6
total data	6123
obsd data[a]	829
parameters	85
min, max $\Delta\rho(e/\text{Å}^3)$	−0.38, +0.59
$R(F)$[b]	3.42
$R_w(F)$[c]	3.40

[a] $I > 3\sigma(I)$ after data merging to 1533 reflections. [b] $R = 100 \times \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = 100 \times [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w_i = 1/\sigma^2(F)$.

Preparations starting from the stoichiometry of the target compound resulted in negligible yields of $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$.

Structure Determination. The crystal structure of $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$ was established from single-crystal X-ray diffraction data using a Siemens P4 diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å, room temperature [25(2) °C]). A clear plate, dimensions ~0.05 × 0.3 × 0.4 mm, was mounted on a thin glass fiber. The application of peak search, centering, indexing and least-squares routines resulted in a primitive orthorhombic cell [25 peaks ($4° < 2\theta < 24°$)]. Intensity data were collected for $2° < 2\theta < 60°$. An empirical absorption correction from ψ scans (min, max equivalent transmission factors = 0.520, 0.592) was applied during data reduction. The systematic absences ($0kl$, $k + l \neq 2n$; $hk0$, $h \neq 2n$) indicated space groups $Pn2_1a$ (No. 33) or *Pnma* (No. 62). Starting coordinates for the Al, P, and O atoms were elucidated by direct methods (program SHELXS86[20]) in space group *Pnma*, and the centrosymmetric space group was assumed for the remainder of the crystallographic analysis. The remaining non-hydrogen atoms were located from difference maps. The O(H) and N(1)(H) protons were located from difference maps and the N(2) protons were placed geometrically [d(N−H) = 0.95 Å]. All the H atoms were refined by riding on their respective O or N atoms; an atom-type isotropic thermal factor was refined to account for their thermal motion. A Larson-type secondary extinction correction[21] was optimized. Refinement with CRYSTALS[22] proceeded to convergence (Table 1).

Results

Final atomic positional and thermal parameters for $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$ are listed in Table 2, with selected geometrical data in Table 3. $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$ is a new layered phase built up from anionic sheets of strictly alternating, vertex sharing $AlO_4(H_2O)_2$ octahedra and HPO_4 tetrahedra, fused together via Al−O−P bonds. Interlayer guanidinium cations complete the crystal structure (Figures 1 and 2).

Table 2. Atomic Coordinates/Thermal Factors for $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$

atom	x	y	z	U_{eq}[a]
Al(1)	0	0	1/2	0.0101
P(1)	0.3673(1)	0.08396(5)	0.6238(1)	0.0100
O(1)	0.2767(4)	0.1463(1)	0.7200(4)	0.0188
O(2)	0.4243(3)	0.0363(1)	0.7746(3)	0.0139
O(3)	0.5371(3)	0.1110(1)	0.5164(4)	0.0132
O(4)	0.2219(3)	0.0543(1)	0.4882(3)	0.0129
O(5)	0.1432(4)	−0.0640(1)	0.6324(4)	0.0144
C(1)	0.5329(9)	1/4	0.217(1)	0.0267
N(1)	0.5088(9)	1/4	0.4014(7)	0.0393
N(2)	0.5470(6)	0.1943(2)	0.1307(6)	0.0422

[a] U_{eq} (Å^2) = $^1/_3[U_1 + U_2 + U_3]$.

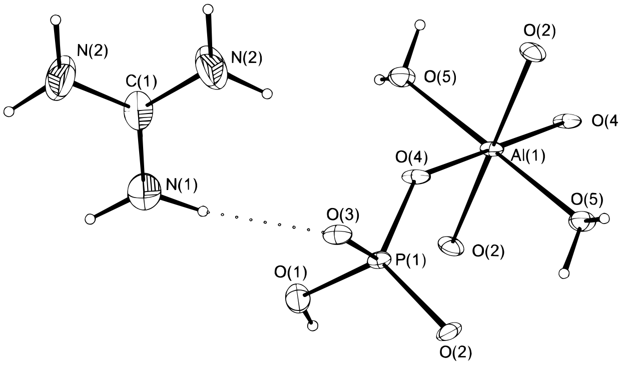

Figure 1. View of the bonding unit in $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$ showing atom labeling scheme (50% thermal ellipsoids; spheres of arbitrary radius for H atoms).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$

Al(1)−O(2) × 2	1.857(2)	Al(1)−O(4) × 2	1.911(2)
Al(1)−O(5) × 2	1.907(2)	P(1)−O(1)	1.589(3)
P(1)−O(2)	1.514(3)	P(1)−O(3)	1.518(3)
P(1)−O(4)	1.531(3)	C(1)−N(1)	1.330(8)
C(1)−N(2) × 2	1.310(5)		
O(2)−Al(1)−O(2)	180	O(2)−Al(1)−O(4)	88.2(1)
O(2)−Al(1)−O(4)	91.8(1)	O(4)−Al(1)−O(4)	180
O(2)−Al(1)−O(5)	90.3(1)	O(2)−Al(1)−O(5)	89.7(1)
O(4)−Al(1)−O(5)	90.3(1)	O(4)−Al(1)−O(5)	89.7(1)
O(5)−Al(1)−O(5)	180	O(1)−P(1)−O(2)	108.7(2)
O(1)−P(1)−O(3)	103.4(1)	O(2)−P(1)−O(3)	113.4(1)
O(1)−P(1)−O(4)	109.6(1)	O(2)−P(1)−O(4)	111.5(1)
O(3)−P(1)−O(4)	109.9(1)	Al(1)−O(2)−P(1)	163.1(2)
Al(1)−O(4)−P(1)	137.8(2)	N(1)−C(1)−N(2)	118.7(3)
N(2)−C(1)−N(2)	122.6(6)		

The aluminum species [d_{av}(Al−O) = 1.928(9) Å] occupies an inversion center, makes four Al−O bonds to adjacent phosphorus atoms, and is also coordinated to two water molecules in trans configuration. The single distinct phosphorus center makes two P−O−Al bonds to two different adjacent aluminum atoms with a d_{av}(P−O) value of 1.531(9) Å. There are two terminal P−O vertexes, one of which is short, indicating a degree of multiple bond character as also seen in $C_5NH_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$[18] and one of which is protonated, showing its characteristic lengthening.[23] Bond valence sum (BVS) calculations[24] for Al (2.89) and P (4.97) yielded typical values.

The polyhedral connectivity in $CN_3H_6{\cdot}Al(HPO_4)_2{\cdot}2H_2O$ leads to infinite anionic layers of stoichiometry $[Al(HPO_4)_2{\cdot}2H_2O]^-$, arrayed normal to [010]. Elliptical polyhedral eight-rings (four Al and four P nodes) are formed by the strictly alternating AlO_6/PO_4 connectivity

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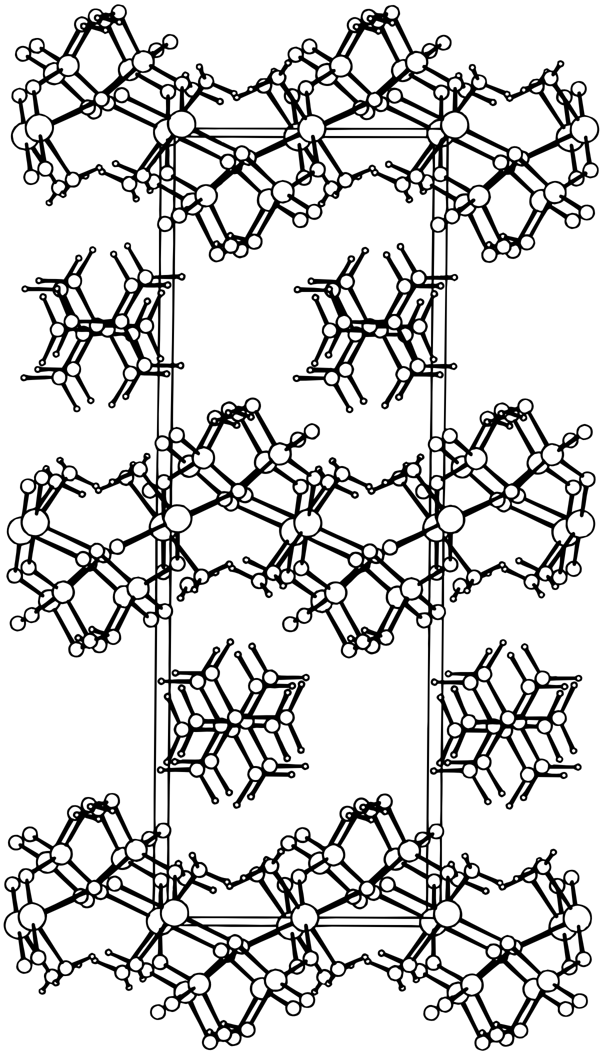

Figure 2. View down [100] of the unit cell packing for CN_3H_6·$Al(HPO_4)_2$·$2H_2O$ showing the infinite stacks of guanidinium cations interleaving $[Al(HPO_4)_2·2H_2O]^-$ layers.

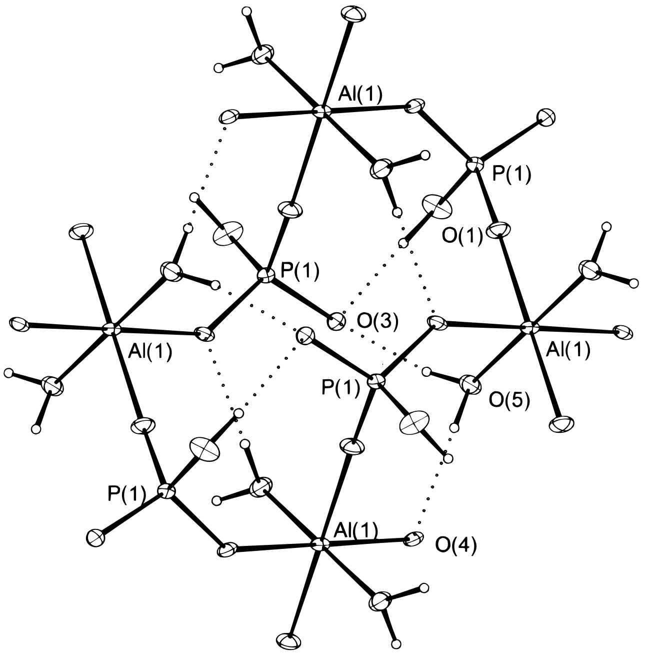

Figure 3. View down [010] of an AlPO layer in CN_3H_6·$Al(HPO_4)_2$·$2H_2O$ showing the eight-ring building block, with H bonds indicated by dotted lines.

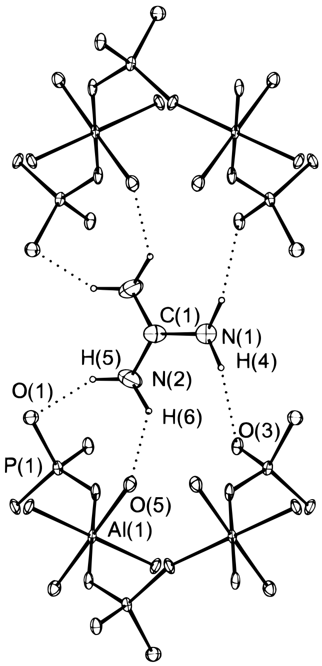

Figure 4. Detail of the CN_3H_6·$Al(HPO_4)_2$·$2H_2O$ structure, showing template to AlPO layer H bonding interactions.

(Figure 3). An intraring P−OH···O hydrogen bonding link is present as P−O(1)H(1)···O(3) (Table 4). Both the water molecule hydrogen atoms also participate in intrasheet hydrogen bonding, as Al−O(5)H(2)···O(3) and Al−O(5)H(3)···O(4) links. These interactions may be responsible for the corrugated nature of the AlPO layers (Figure 2). There are no interlayer H bonding interactions involving P−OH or $Al-OH_2$ donor groups.

The guanidinium cation, with molecular symmetry .*m*. [d_{av}(C−N) = 1.317 (5) Å], makes H-bonding interactions to O atoms of the AlPO layers from each of its six N−H groups (Table 4), although those involving the $N(2)H_2$ groups are very long [d(H···O) > 2.3 Å] (Figure 4). The acceptor O atoms form parts of P−OH, P−O, and $Al-OH_2$ groupings. A striking feature of the resulting structure is the infinite columns of guanidinium cations (Figure 2) which stack normal to [100]. Within a column, the guanidinium cations stack such that the planes of pairs of molecules are essentially parallel and separated by ~3.5 Å, which is similar to the characteristic stacking separation of this cation in various molecular crystals.[25]

Discussion

CN_3H_6·$Al(HPO_4)_2$·$2H_2O$ is closely related to C_5NH_6·$Al(HPO_4)_2$·$2H_2O$ and $C_3N_2H_5$·$Al(HPO_4)_2$·$2H_2O$,[18] both of which contain $[Al(HPO_4)_2·2H_2O]^-$ layers similar to those seen in the title compound. Although these phases crystallize in different space groups, it is notable that the $AlO_4(H_2O)_2$ species occupies an inversion center in each case. The octahedral/tetrahedral polyhedral connectivity in these phases is quite distinct from the all-

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Table 4. Hydrogen Bonding in $CN_3H_6 \cdot Al(HPO_4)_2 \cdot 2H_2O$[a]

O(1)−H(1)···O(3)	0.84	1.79	2.624(4)
O(5)−H(2)···O(3)	0.84	1.83	2.652(4)
O(5)−H(3)···O(4)	0.83	1.96	2.725(4)
N(1)−H(4)···O(3)	0.95	2.07	2.989(3)
N(2)−H(5)···O(1)	0.95	2.37	3.140(5)
N(2)−H(6)···O(5)	0.95	2.31	2.996(5)

[a] The three distances (Å) refer to the *X*−H, H···*Y*, and *X*···*Y* separations, respectively.

tetrahedral topologies of the earlier layered/chainlike AlPOs,[17] although an octahedral Al-centered building unit with trans water molecules has been observed in the hydrated modification of the three-dimensional phase VPI-5.[26] The condensed phase $AlPO_4 \cdot H_2O$, known as AlPO−H4, contains $AlO_4(H_2O)_2$ octahedra (trans water molecules) and AlO_4 tetrahedra.[27]

These $R \cdot Al(HPO_4)_2 \cdot 2H_2O$ phases were prepared by significantly different procedures. $CN_3H_6 \cdot Al(HPO_4)_2 \cdot 2H_2O$ was prepared by a hydrothermal reaction, with sparingly soluble activated Al_2O_3 providing the source of aluminum. Its partner compounds[18] were prepared by a novel silica gel route at ambient conditions, with the highly soluble $Al(NO_3)_3 \cdot 9H_2O$ supplying the Al^{3+} to the reaction. Although the overall eight-ring-AlPO/organic layering pattern is common to all three structures, the template−layer interactions are specific to each phase. In $CN_3H_6 \cdot Al(HPO_4)_2 \cdot 2H_2O$, each guanidinium cation makes six N−H···O bonding interactions and serves to bridge adjacent AlPO sheets by means of these ionic interactions. However, in $C_5NH_6 \cdot Al(HPO_4)_2 \cdot 2H_2O$,[18] only one such bond is formed per pyridine molecule (i.e., there are no "bridging" interlayer ionic interactions at all), while in $C_3N_2H_5 \cdot Al(HPO_4)_2 \cdot 2H_2O$,[17] two N−H···O bonds occur. In very crude terms, these three template molecules are about the same size and shape, suggesting that steric factors[28] play a significant role in the template-assisted formation of these layered phases.

The stacked array of guanidinium cations in $CN_3H_6 \cdot Al(HPO_4)_2 \cdot 2H_2O$ is distinctive. Molecular dynamic studies[29] of the guanidinium cation in aqueous solution have shown that an energy minimum occurs when roughly parallel pairs of $[CN_3H_6]^+$ cations are separated by ∼3.3 Å—i.e., electrostatic cation−cation repulsion is presumably overcome by favorable solvation effects. It is tempting to speculate that such associations of guanidinium cations are occurring in solution and exerting a cooperative templating effect in the formation of $CN_3H_6 \cdot Al(HPO_4)_2 \cdot 2H_2O$.

The templating behavior of the guanidinium cation in $CN_3H_6 \cdot Al(HPO_4)_2 \cdot 2H_2O$ is quite different from its behavior with respect to zincophosphate frameworks,[30] where three-dimensional ZnPO networks have been observed, stabilized by N−H···O interactions. Conversely, in combination with vanadium(V) and phosphate progenitors, the novel layered phase $(CN_3H_6)_2 \cdot (VO_2)_3(PO_4)(HPO_4)$[31] results, in which closely associated parallel *pairs* of guanidinium cations cooperate to template the $[(VO_2)_3(PO_4)(HPO_4)]^-$ layers, rather than the infinite stacks of the same species in the title compound.

Acknowledgment. This work is supported by the Australian Research Council.

Note added in press: The solvothermal synthesis (in butan-2-ol at 160 °C) and single crystal structure of $C_3N_2H_5 \cdot Al(HPO_4)_2 \cdot 2H_2O$[18] have also been reported by Yu and Williams.[32]

Supporting Information Available: Tables of anisotropic thermal factors and H atom positions (1 page); tables of observed and calculated structure factors (5 pages). See any current masthead page for ordering and Internet access information.

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