

Synthesis and crystal structure of a new layered aluminophosphate [Al₃P₄O₁₆][C₆N₃H₁₇][H₃O]

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Received 19 December 2003; received in revised form 22 March 2004; accepted 30 March 2004

Abstract

A new layered aluminophosphate denoted AIPO-AEPP has been synthesized under hydrothermal conditions using *N*-(2-aminoethyl)-piperazine (AEPP) as structure directing molecule. The compound, with the empirical formula [Al₃P₄O₁₆][C₆N₃H₁₇][H₃O] crystallizes in the orthorhombic space group *P*2₁2₁ (No. 19) with *a* = 14.550(8) Å, *b* = 16.163(8) Å, *c* = 18.677(9) Å, *Z* = 4, *R*₁ = 0.0253 and *wR*₂ = 0.0644. Inorganic sheets contain a 4 × 6 network previously found in a layered compound synthesized with 1,2-dimethylimidazole molecules. Layers stack in the ABAB sequence and are held together by doubly protonated organic molecules and H₃O⁺ cations. AIPO-AEPP represents the second example of layered aluminophosphate for which protonated water acts as a co-temple along with organic molecules.

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Keywords: Layered; Aluminophosphate; Structure; Synthesis; Template

1. Introduction

The discovery of microporous aluminophosphate molecular sieves AIPO_{4-n} by scientists at Union Carbide Corp. [1] was the starting point for the development of materials with a rich diversity of compositions and architectures. Over the last two decades, a variety of crystalline aluminophosphates with anionic chains (one-dimensional (1D)) [2–7], layers (2D) [8–45] and open-frameworks (3D) [46–53] have been obtained by hydrothermal or solvothermal methods. The family of 2D compounds is particularly rich in terms of composition and network topologies [54]. Up to six different stoichiometries have been reported, with the P/Al ratio of 1 [22,32,33,36,37], 5:4 [25], 4:3 [8–14,16–18,20,21,27,28,31,38–45], 18:13 [35,42], 2:3 [9,15,26,29,30] and 2 [19,23,24]. In these compounds, aluminum atoms can be 4-, 5- or 6-coordinated and can form Al–O–Al pairs or infinite chains of polyhedra [33,37,39]. In the particular case of aluminophosphates with Al₃P₄O₁₆³⁻ stoichiometry, inorganic layers generally consist of AlO₄ and

PO₃(=O) tetrahedra. These layers are separated by protonated templating molecules that balance the charge and form H-bonds with terminal PO₃(=O) units. For inorganic sheets with Al₃P₄O₁₆³⁻ stoichiometry, three different 2D networks have been reported and designated as 4 × 6, 4 × 6 × 8 and 4 × 6 × 12 nets, depending on the number of P or Al atoms in each ring [55]. The specific role of the templating molecule in the formation of a given 2D network is still poorly understood. In particular, one molecule can lead to different sheet structures whereas the same sheet structure can be obtained using several structure directing agents. As an example, the same 4 × 6 × 12 net has been obtained using 1,4-diaminobutane [10], 1,4-diaminocyclohexane [13], 1,5-diaminopropane [21], butylamine [21] and 2-methylpiperazine [44]. Layers stack in the AAAA sequence with butylamine and 2-methylpiperazine and in the ABAB sequence with other organic molecules.

Organic molecules can also be fragmented during synthesis and the obtained fragments can play a structure-directing role. The *N,N,N',N'*-tetramethyl-1,3-propanediamine molecule used in the preparation of AIPO₄₋₂₁ is split into three triatomic species, i.e. two

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dimethylammonium and one propyl species, which are encapsulated in the aluminophosphate framework [56]. Other examples of fragmentation of the organic amine have been observed during the crystallization of AlPO_4 -15 [57], of a 1D aluminophosphate [7] and of a 2D-layered compound prepared with 1,2-dimethylimidazole [31] and further denoted AlPO-DMI . The latter compound consists of layers with $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$ stoichiometry, separated by and hydrogen-bonded to 1,2-dimethylimidazole molecules and ammonium cations NH_4^+ .

In the present work, a new 2D-layered aluminophosphate material has been prepared using *N*-(2-aminoethyl)-piperazine (AEPP). AlO_4 and $\text{PO}_3(=\text{O})$ tetrahedra in the sheets form a $4 \times 6 \times 8$ net similar to that found in AlPO-DMI prepared with 1,2-dimethylimidazole [31]. By contrast to this compound, though AEPP molecules undergo thermal degradation under synthesis conditions, NH_4^+ ions are not present in the interlayer space. Actually, these cations are replaced by H_3O^+ species that adopt a tetrahedral geometry. $[\text{Al}_3\text{P}_4\text{O}_{16}][\text{C}_6\text{N}_3\text{H}_{17}][\text{H}_3\text{O}]$ is the second reported 2D-layered aluminophosphate for which protonated water acts as a co-template along with an organic molecule.

2. Experimental section

2.1. Synthesis

The new layered aluminophosphate was synthesized under hydrothermal conditions using *N*-(2-aminoethyl)-piperazine (AEPP) molecules as a structure directing agent. Pseudo-boehmite (CATAPAL B, Vista, 74 wt% Al_2O_3) and phosphoric acid (85 wt% in water) were used as aluminum and phosphorus species, respectively. Typically, 5 g pseudo-boehmite was first dispersed in a solution containing 4.94 mL phosphoric acid and 26 mL water, and the mixture was stirred for about 2 h at room temperature. Then, 4.72 mL *N*-(2-aminoethyl)-piperazine was added dropwise and stirring was maintained for two additional hours. The thick gel, with the composition $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-1AEPP-50H}_2\text{O}$ was then transferred into a 100 mL capacity Teflon-lined stainless steel autoclave and heated under static conditions at 220°C for 36 h. After crystallization, the solid was rapidly cooled, recovered by filtration, washed with distilled water and air-dried at room temperature. A white powder was obtained in high yield (>98%) and consisted in elongated, doubly terminated prisms of ca. 100–300 μm length (Fig. 1).

2.2. X-ray data collection and structure determination

A single crystal data set was collected at room temperature on a Picker 4-circle diffractometer with $\text{CuK}\alpha$ radiation. The structure was solved using

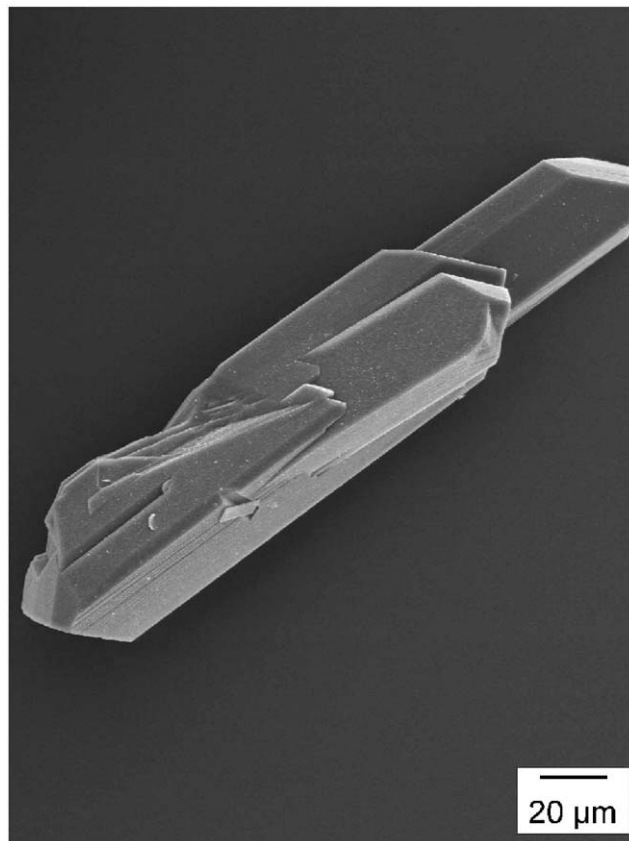


Fig. 1. Typical morphology of AlPO-AEPP crystals.

SHELX-97 [58] and refined with SHELX-93 [59]. Further details on crystallographic data and the structure refinement are given in Table 1. Atomic parameters and interatomic distances and bond angles are listed in Tables 2–5. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 227139. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44)-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

2.3. Characterization

The amount of water and organic template in the as-made solid was evaluated from thermal analysis data recorded on a Setaram TG DTA 92 apparatus. Approximately 25 mg of the compound was heated in air from 25°C to 750°C at a heating rate of 5°C/min. The P and Al contents were obtained by ICP (Spectro-flame, SPECTRO) after dissolution of the solid in HF:HCl solutions. The amounts of C and N were determined at the Centre d'Analyses du CNRS, Solaize, France, using coulometry and catharometry after calcination of the sample.

Table 1
Crystal data and structure refinement for AIPO-AEPP

Empirical formula	C ₁₂ H ₄₀ Al ₆ N ₆ O ₃₄ P ₈
Formula weight	1222.14
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	<i>a</i> = 14.550(8) Å α = 90° <i>b</i> = 16.163(8) Å β = 90° <i>c</i> = 18.677(9) Å γ = 90°
Volume	4392(4) Å ³
<i>Z</i>	4
Density (calculated)	1.848 Mg/m ³
Absorption coefficient	5.176 mm ⁻¹
<i>F</i> (000)	2496
Crystal size	0.1 × 0.1 × 0.06 mm
Theta range for data collection	3.62°–49.97°
Index ranges	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 16, 0 ≤ <i>l</i> ≤ 18
Reflections collected	2557
Completeness to theta = 49.97°	99.8%
Reflections < 2σ	2313
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2557/108/621
Goodness-of-fit on <i>F</i> ²	1.060
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0253, <i>wR</i> ₂ = 0.0645
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0324, <i>wR</i> ₂ = 0.0673
Absolute structure parameter	−0.03(3)
Largest diff. peak and hole	0.261 and −0.328 e.Å ³

SEM pictures were obtained on a Hitachi S800 microscope.

Solid-state NMR spectra were recorded on a Bruker DSX 400 spectrometer equipped with a standard 4 mm probe head. Samples were spun at the magic angle in zirconia rotors with a spinning speed of ca. 12 kHz. The pulse lengths were 2 μs ($\pi/4$) and 0.7 μs ($\pi/6$) and the recycle delays were 60 and 1 s for ³¹P and ²⁷Al nuclei, respectively. ³¹P and ²⁷Al chemical shifts were referenced to Al(H₂O)₆³⁺ and H₃PO₄ (85 wt%), respectively.

¹H–¹³C CP/MAS spectra were obtained using a conventional cross-polarization sequence with a contact time of 1.5 ms and a recycle delay of 5 s. ¹³C chemical shifts were referenced to tetramethylsilane (TMS). The spectrum of AIPO-AEPP has been submitted as supplementary material.

3. Results and discussion

The Al₂O₃–P₂O₅–AEPP–H₂O system is very complex and leads to a variety of compounds, depending on the gel composition, the crystallization temperature and the crystallization time. AIPO-AEPP is only obtained at temperatures higher than 180°C. At 180°C, a gel with composition Al₂O₃–P₂O₅–AEPP–50H₂O leads to a series of solids, mostly 2D-layered compounds, as evidenced by X-ray diffraction and SEM pictures. A

Table 2
Atomic coordinates^a and equivalent isotropic displacement parameters (*U*(eq)^b) for AIPO-AEPP

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^b	pp
P1	0.75965(10)	0.66400(9)	0.95136(8)	0.0140(4)	1
P2	0.92707(10)	0.78229(9)	1.11338(8)	0.0129(4)	1
P3	1.05030(10)	0.23951(9)	0.87877(8)	0.0130(4)	1
P4	0.55478(11)	0.43928(9)	0.93197(8)	0.0160(4)	1
P5	0.89014(10)	0.42117(9)	1.08706(8)	0.0126(4)	1
P6	0.92378(10)	0.93170(9)	0.90011(8)	0.0158(4)	1
P7	0.72944(10)	1.18698(10)	0.93469(8)	0.0158(4)	1
P8	1.08672(10)	0.58045(9)	0.95899(8)	0.0137(4)	1
Al1	0.55931(12)	0.62230(10)	0.98668(9)	0.0129(4)	1
Al2	0.91706(11)	0.60590(10)	1.05750(9)	0.0132(4)	1
Al3	0.70155(12)	0.34759(11)	1.02810(9)	0.0145(4)	1
Al4	0.92000(11)	1.11198(11)	0.95145(10)	0.0162(4)	1
Al5	0.78575(12)	0.84551(11)	1.00302(9)	0.0148(4)	1
Al6	1.06073(11)	0.39161(10)	0.98444(9)	0.0132(4)	1
O1	0.8411(3)	0.6210(3)	0.9881(2)	0.0237(11)	1
O2	0.6739(3)	0.6482(3)	0.9968(2)	0.0207(10)	1
O3	0.5658(3)	0.4159(2)	0.8554(2)	0.0278(11)	1
O4	0.5437(3)	0.5332(2)	0.9373(2)	0.0224(10)	1
O5	0.8919(3)	0.5147(2)	1.1030(2)	0.0188(10)	1
O6	0.9536(3)	0.4037(2)	1.0232(2)	0.0190(10)	1
O7	0.7781(3)	0.7574(3)	0.9505(2)	0.0273(11)	1
O8	1.0277(3)	0.5975(3)	1.0249(2)	0.0221(10)	1
O9	0.9427(3)	1.0251(2)	0.8995(2)	0.0214(10)	1
O10	0.7329(3)	1.2014(3)	0.8553(2)	0.0266(11)	1
O11	0.8500(3)	0.9182(2)	0.9579(2)	0.0271(11)	1
O12	0.9192(3)	0.3738(2)	1.1518(2)	0.0286(11)	1
O13	0.7923(3)	0.4006(3)	1.0635(2)	0.0273(11)	1
O14	0.8994(3)	0.8991(3)	0.8290(2)	0.0315(12)	1
O15	1.1815(3)	0.6156(3)	0.9734(2)	0.0288(11)	1
O16	0.5131(3)	0.6106(3)	1.0721(2)	0.0231(11)	1
O17	0.8383(3)	0.8195(3)	1.0842(2)	0.0252(11)	1
O18	0.7495(3)	0.6340(2)	0.8753(2)	0.0202(10)	1
O19	0.6370(3)	0.4162(3)	0.9782(2)	0.0392(13)	1
O20	1.0044(3)	0.7987(2)	1.0598(2)	0.0226(10)	1
O21	0.8030(3)	1.1274(3)	0.9607(2)	0.0305(12)	1
O22	0.7400(3)	1.2677(3)	0.9754(2)	0.0382(13)	1
O23	0.9463(3)	0.8182(2)	1.1859(2)	0.0242(10)	1
O24	0.4688(3)	0.3984(3)	0.9639(2)	0.0283(11)	1
O25	1.0562(3)	0.3261(2)	0.9116(2)	0.0220(10)	1
O26	0.9147(3)	0.6882(2)	1.1183(2)	0.0193(10)	1
O27	1.0966(3)	0.4868(2)	0.9516(2)	0.0255(11)	1
O28	1.0459(3)	0.6165(3)	0.8921(2)	0.0283(11)	1
O29	0.6350(3)	1.1485(3)	0.9528(2)	0.0257(11)	1
O30	0.9648(3)	0.1982(3)	0.9087(2)	0.0301(12)	1
O31	1.1358(3)	0.1901(3)	0.9018(2)	0.0255(11)	1
O32	1.0470(3)	0.2443(3)	0.79861(19)	0.0257(11)	1
N1	0.7083(4)	0.9131(3)	0.7231(3)	0.0301(14)	1
C2	0.6237(5)	0.9434(5)	0.7550(5)	0.045(2)	1
H2A	0.5960	0.9000	0.7837	0.054	1
H2B	0.5807	0.9585	0.7176	0.054	1
C3	0.6434(5)	1.0176(5)	0.8015(4)	0.040(2)	1
H3A	0.5859	1.0404	0.8189	0.048	1
H3B	0.6795	1.0006	0.8425	0.048	1
N4	0.6941(4)	1.0825(4)	0.7613(3)	0.0363(16)	1
H4A	0.6568	1.1048	0.7280	0.044	1
H4B	0.7111	1.1230	0.7916	0.044	1
C5	0.7762(6)	1.0481(5)	0.7262(4)	0.048(2)	1
H5A	0.8201	1.0308	0.7622	0.057	1
H5B	0.8049	1.0905	0.6970	0.057	1
C6	0.7509(6)	0.9754(4)	0.6799(4)	0.050(2)	1
H6A	0.7089	0.9929	0.6425	0.060	1

Table 2 (continued)

Atom	x	y	z	$U(\text{eq})^b$	pp
H6B	0.8056	0.9531	0.6574	0.060	1
C7	0.6990(5)	0.8340(4)	0.6850(4)	0.0366(19)	1
H7A	0.7463	0.8297	0.6486	0.044	1
H7B	0.6396	0.8315	0.6615	0.044	1
C8	0.7079(5)	0.7639(4)	0.7368(4)	0.0362(19)	1
H8A	0.6563	0.7646	0.7696	0.043	1
H8B	0.7068	0.7119	0.7109	0.043	1
N9	0.7944(4)	0.7708(3)	0.7773(3)	0.0266(13)	1
H9A	0.7936	0.7351	0.8136	0.040	1
H9B	0.8002	0.8220	0.7942	0.040	1
H9C	0.8415	0.7593	0.7486	0.040	1
N1'	0.8487(3)	0.4107(3)	0.7352(2)	0.0187(12)	1
C2'	0.8218(5)	0.4085(4)	0.8105(3)	0.0304(18)	1
H2A'	0.8174	0.3516	0.8265	0.037	1
H2B'	0.7619	0.4341	0.8163	0.037	1
C3'	0.8907(5)	0.4534(4)	0.8548(4)	0.0332(19)	1
H3A'	0.9494	0.4250	0.8520	0.040	1
H3B'	0.8711	0.4534	0.9045	0.040	1
N4'	0.9017(4)	0.5406(3)	0.8294(3)	0.0265(14)	1
H4A'	0.8499	0.5691	0.8386	0.032	1
H4B'	0.9481	0.5649	0.8535	0.032	1
C5'	0.9215(5)	0.5434(4)	0.7510(4)	0.0341(18)	1
H5A'	0.9222	0.6004	0.7349	0.041	1
H5B'	0.9817	0.5198	0.7419	0.041	1
C6'	0.8508(5)	0.4964(4)	0.7103(4)	0.0320(18)	1
H6A'	0.7910	0.5216	0.7172	0.038	1
H6B'	0.8651	0.4978	0.6596	0.038	1
C7'	0.7938(5)	0.3561(4)	0.6901(4)	0.0310(18)	1
H7A'	0.7965	0.3748	0.6408	0.037	1
H7B'	0.7302	0.3574	0.7055	0.037	1
C8'	0.8307(4)	0.2692(4)	0.6956(4)	0.0291(17)	1
H8A'	0.8179	0.2477	0.7431	0.035	1
H8B'	0.7992	0.2344	0.6612	0.035	1
N9'	0.9312(4)	0.2650(3)	0.6821(3)	0.0244(13)	1
H9A'	0.9445	0.2178	0.6599	0.037	1
H9B'	0.9612	0.2672	0.7236	0.037	1
H9C'	0.9481	0.3075	0.6548	0.037	1
O1W	0.9499(4)	0.7471(3)	1.3195(3)	0.0473(14)	1
O2W	0.9032(4)	0.4261(3)	1.2916(3)	0.0434(13)	1
H11W	0.960(7)	0.679(7)	1.330(5)	0.060	0.75 ^c
H12W	1.021(7)	0.788(6)	1.339(5)	0.060	0.75
H13W	0.957(6)	0.767(6)	1.260(6)	0.060	0.75
H14W	0.867(7)	0.755(6)	1.338(5)	0.060	0.75
H21W	0.904(7)	0.412(6)	1.234(6)	0.060	0.75
H22W	0.973(7)	0.385(6)	1.308(5)	0.060	0.75
H23W	0.918(7)	0.494(7)	1.305(5)	0.060	0.75
H24W	0.839(7)	0.409(6)	1.320(5)	0.060	0.75

^aThe positions of the protons belonging to the template molecule are calculated.

^b $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^cThe population parameters of the water protons have been fixed to 0.75.

crystalline material is first formed after 24 h. Then, the solid gradually changes with time as evidenced by X-ray diffraction, showing the appearance and disappearance of phases with low stability. After 1 week, the powder pattern is typical of $\text{AlPO}_4\cdot 15\text{H}_2\text{O}$, formed in the presence of NH_4^+ ions resulting from the degradation of templating

Table 3
Selected bond lengths (Å)

P(1)–O(18)	1.508(4)	P(7)–O(10)	1.502(4)
P(1)–O(2)	1.531(4)	P(7)–O(22)	1.518(5)
P(1)–O(7)	1.533(4)	P(7)–O(21)	1.519(4)
P(1)–O(1)	1.535(4)	P(7)–O(29)	1.546(4)
P(2)–O(23)	1.500(4)	P(8)–O(28)	1.500(4)
P(2)–O(17)	1.525(4)	P(8)–O(15)	1.515(5)
P(2)–O(20)	1.529(4)	P(8)–O(8)	1.526(4)
P(2)–O(26)	1.535(4)	P(8)–O(27)	1.526(4)
Al(1)–O(4)	1.726(4)	Al(3)–O(13)	1.707(4)
Al(1)–O(2)	1.729(4)	Al(3)–O(22)#3	1.717(4)
Al(1)–O(20)#1	1.738(4)	Al(3)–O(19)	1.727(5)
Al(1)–O(16)	1.742(4)	Al(3)–O(31)#4	1.732(4)
P(3)–O(32)	1.500(4)	Al(4)–O(21)	1.730(4)
P(3)–O(30)	1.518(4)	Al(4)–O(30)#5	1.733(4)
P(3)–O(25)	1.531(4)	Al(4)–O(9)	1.738(4)
P(3)–O(31)	1.540(4)	Al(4)–O(24)#2	1.741(5)
P(4)–O(3)	1.488(4)	Al(5)–O(15)#1	1.700(5)
P(4)–O(19)	1.522(5)	Al(5)–O(11)	1.722(4)
P(4)–O(4)	1.529(4)	Al(5)–O(7)	1.733(4)
P(4)–O(24)	1.536(5)	Al(5)–O(17)	1.749(4)
Al(2)–O(1)	1.721(4)	Al(6)–O(29)#2	1.721(4)
Al(2)–O(8)	1.726(4)	Al(6)–O(25)	1.725(4)
Al(2)–O(5)	1.741(4)	Al(6)–O(6)	1.729(4)
Al(2)–O(26)	1.749(4)	Al(6)–O(27)	1.737(4)
P(5)–O(12)	1.491(4)	O(15)–Al(5)#2	1.700(5)
P(5)–O(13)	1.527(4)	O(16)–P(6)#1	1.556(4)
P(5)–O(6)	1.535(4)	O(20)–Al(1)#2	1.738(4)
P(5)–O(5)	1.541(4)	O(22)–Al(3)#5	1.717(4)
P(6)–O(14)	1.472(4)	O(24)–Al(4)#1	1.741(5)
P(6)–O(9)	1.535(4)	O(29)–Al(6)#1	1.721(4)
P(6)–O(11)	1.538(4)	O(30)–Al(4)#3	1.733(4)
P(6)–O(16)#2	1.557(4)	O(31)–Al(3)#6	1.732(4)

Symmetry transformations used to generate equivalent atoms: #1 $x - 1/2, -y + 3/2, -z + 2$; #2 $x + 1/2, -y + 3/2, -z + 2$; #3 $x, y - 1, z$; #4 $x - 1/2, -y + 1/2, -z + 2$; #5 $x, y + 1, z$; #6 $x + 1/2, -y + 1/2, -z + 2$.

molecules. The various phases formed during the crystallization process could not be obtained pure. Moreover, crystals were often small and of low quality and a structure determination has not been possible.

For a composition $\text{Al}_2\text{O}_3\text{--}2\text{P}_2\text{O}_5\text{--}1.4\text{AEPP--}50\text{H}_2\text{O}$, a crystalline material was obtained after 2 days at 180°C. The powder pattern was very similar to that reported for AlPO-HDA , a 3D open-framework compound with $\text{Al/P} = 4/5$ and containing hexanediamine molecules [47]. The similarity between the two compounds was further supported by solid-state NMR and chemical analysis ($\text{Al/P} = 0.82$). Xu and coworkers have reported that the above framework type could also be obtained using templating molecules like 1,5-pentanediamine and diethylenetriamine [60]. In both cases, the N–N distance between the two amino groups is approximately the same as that existing in AEPP molecules.

Between 180°C and 220°C, gels with the composition $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--AEPP--}50\text{H}_2\text{O}$ give a mixture of compounds, including AlPO-AEPP . The percentage of the latter increases with the crystallization temperature. At

Table 4
Selected bond angles (deg)

O(18)–P(1)–O(2)	112.9(2)	O(28)–P(8)–O(15)	111.2(3)
O(18)–P(1)–O(7)	108.9(2)	O(28)–P(8)–O(8)	112.2(2)
O(2)–P(1)–O(7)	108.3(2)	O(15)–P(8)–O(8)	107.5(2)
O(18)–P(1)–O(1)	110.6(2)	O(28)–P(8)–O(27)	110.3(3)
O(2)–P(1)–O(1)	107.8(2)	O(15)–P(8)–O(27)	107.6(3)
O(7)–P(1)–O(1)	108.4(3)	O(8)–P(8)–O(27)	107.8(2)
O(23)–P(2)–O(17)	109.2(2)	O(13)–Al(3)–O(22)#3	110.3(2)
O(23)–P(2)–O(20)	112.7(3)	O(13)–Al(3)–O(19)	107.9(2)
O(17)–P(2)–O(20)	108.7(2)	O(22)#3–Al(3)–O(19)	110.5(2)
O(23)–P(2)–O(26)	110.6(2)	O(13)–Al(3)–O(31)#4	108.1(2)
O(17)–P(2)–O(26)	108.2(2)	O(22)#3–Al(3)–O(31)#4	110.4(2)
O(20)–P(2)–O(26)	107.3(2)	O(19)–Al(3)–O(31)#4	109.5(2)
O(4)–Al(1)–O(2)	112.8(2)	O(21)–Al(4)–O(30)#5	107.5(2)
O(4)–Al(1)–O(20)#1	106.6(2)	O(21)–Al(4)–O(9)	111.1(2)
O(2)–Al(1)–O(20)#1	108.7(2)	O(30)#5–Al(4)–O(9)	108.7(2)
O(4)–Al(1)–O(16)	110.4(2)	O(21)–Al(4)–O(24)#2	108.9(2)
O(2)–Al(1)–O(16)	107.3(2)	O(30)#5–Al(4)–O(24)#2	110.0(2)
O(20)#1–Al(1)–O(16)	111.1(2)	O(9)–Al(4)–O(24)#2	110.6(2)
O(32)–P(3)–O(30)	111.4(3)	O(15)#1–Al(5)–O(11)	111.0(2)
O(32)–P(3)–O(25)	110.8(2)	O(15)#1–Al(5)–O(7)	113.2(2)
O(30)–P(3)–O(25)	107.5(2)	O(11)–Al(5)–O(7)	108.6(2)
O(32)–P(3)–O(31)	109.4(2)	O(15)#1–Al(5)–O(17)	104.7(2)
O(30)–P(3)–O(31)	109.3(2)	O(11)–Al(5)–O(17)	110.5(2)
O(25)–P(3)–O(31)	108.5(2)	O(7)–Al(5)–O(17)	108.7(2)
O(3)–P(4)–O(19)	113.4(3)	O(29)#2–Al(6)–O(25)	109.3(2)
O(3)–P(4)–O(4)	109.0(2)	O(29)#2–Al(6)–O(6)	108.9(2)
O(19)–P(4)–O(4)	106.8(3)	O(25)–Al(6)–O(6)	111.4(2)
O(3)–P(4)–O(24)	110.6(3)	O(29)#2–Al(6)–O(27)	112.7(2)
O(19)–P(4)–O(24)	108.4(3)	O(25)–Al(6)–O(27)	106.1(2)
O(4)–P(4)–O(24)	108.4(3)	O(6)–Al(6)–O(27)	108.6(2)
O(1)–Al(2)–O(8)	110.1(2)	P(1)–O(1)–Al(2)	153.7(3)
O(1)–Al(2)–O(5)	110.7(2)	P(1)–O(2)–Al(1)	139.9(3)
O(8)–Al(2)–O(5)	107.6(2)	P(4)–O(4)–Al(1)	148.1(3)
O(1)–Al(2)–O(26)	111.6(2)	P(5)–O(5)–Al(2)	137.7(3)
O(8)–Al(2)–O(26)	107.9(2)	P(5)–O(6)–Al(6)	152.7(3)
O(5)–Al(2)–O(26)	108.8(2)	P(1)–O(7)–Al(5)	144.5(3)
O(12)–P(5)–O(13)	112.7(3)	P(8)–O(8)–Al(2)	145.4(3)
O(12)–P(5)–O(6)	111.4(2)	P(6)–O(9)–Al(4)	139.2(3)
O(13)–P(5)–O(6)	107.3(2)	P(6)–O(11)–Al(5)	145.0(3)
O(12)–P(5)–O(5)	110.0(2)	P(5)–O(13)–Al(3)	160.4(3)
O(13)–P(5)–O(5)	106.6(2)	P(8)–O(15)–Al(5)#2	175.2(3)
O(6)–P(5)–O(5)	108.7(2)	P(6)#1–O(16)–Al(1)	132.5(3)
O(14)–P(6)–O(9)	112.9(2)	P(2)–O(17)–Al(5)	140.8(3)
O(14)–P(6)–O(11)	114.5(3)	P(4)–O(19)–Al(3)	153.0(3)
O(9)–P(6)–O(11)	105.6(2)	P(2)–O(20)–Al(1)#2	142.5(3)
O(14)–P(6)–O(16)#2	110.2(3)	P(7)–O(21)–Al(4)	138.8(3)
O(9)–P(6)–O(16)#2	106.5(2)	P(7)–O(22)–Al(3)#5	154.2(3)
O(11)–P(6)–O(16)#2	106.6(2)	P(4)–O(24)–Al(4)#1	136.6(3)
O(10)–P(7)–O(22)	111.0(3)	P(3)–O(25)–Al(6)	151.6(3)
(10)–P(7)–O(21)	113.0(3)	P(2)–O(26)–Al(2)	135.4(3)
O(22)–P(7)–O(21)	108.2(3)	P(8)–O(27)–Al(6)	144.9(3)
O(10)–P(7)–O(29)	108.0(2)	P(7)–O(29)–Al(6)#1	149.2(3)
O(22)–P(7)–O(29)	109.0(3)	P(3)–O(30)–Al(4)#3	146.3(3)
O(21)–P(7)–O(29)	107.5(2)	P(3)–O(31)–Al(3)#6	147.2(3)

Symmetry transformations used to generate equivalent atoms: #1 $x - 1/2, -y + 3/2, -z + 2$; #2 $x + 1/2, -y + 3/2, -z + 2$; #3 $x, y - 1, z$; #4 $x - 1/2, -y + 1/2, -z + 2$; #5 $x, y + 1, z$; #6 $x + 1/2, -y + 1/2, -z + 2$.

220°C, AIPO-AEPP is obtained as a pure phase after 24 h (Fig. 1). Due to the high crystallization temperature, the solid almost completely disappears after 72 h and AIPO₄-15 is formed through the rapid decomposi-

Table 5
Selected bond lengths (Å) and bond angles (deg) for hydrogen bonds in AIPO-AEPP

N'(9)–O(28)	2.793	N'(9)–H(9B')–O(32)	161.9
N'(9)–O(32)	2.772	N'(9)–H(9C')–O(16)	167.7
N'(9)–O(16)	2.987	N'(9)–H(9A')–O(28)	171.4
N'(4)–O(18)	2.815	N'(4)–H(4A')–O(18)	169.3
N'(4)–O(28)	2.696	N'(4)–H(4B')–O(28)	173.3
N(9)–O(32)	2.742	N(9)–H(9C)–O(32)	169.7
N(9)–O(18)	2.943	N(9)–H(9A)–O(18)	157.8
N(9)–O(14)	2.752	N(9)–H(9B)–O(14)	139.3
N(4)–O(23)	2.955	N(4)–H(4A)–O(23)	157.7
N(4)–O(10)	2.663	N(4)–H(4B)–O(10)	174.0
O(33)–O(10)	2.864	O(33)–H(11W)–O(3)	157.8
O(33)–O(3)	2.731	O(33)–H(12W)–O(12)	152.0
O(33)–O(23)	2.746	O(33)–H(13W)–O(23)	162.6
O(33)–O(12)	2.848	O(33)–H(14W)–O(10)	161.3
O(34)–O(3)	2.854	O(34)–H(21W)–O(12)	168.2
O(34)–O(18)	2.882	O(34)–H(22W)–O(23)	166.8
O(34)–O(23)	2.834	O(34)–H(23W)–O(3)	161.1
O(34)–O(12)	2.756	O(34)–H(24W)–O(18)	168.6

tion of the template. The C/N ratio in the solid determined by bulk analysis is 2.01, and corresponds exactly to the C/N ratio of the organic molecule. Moreover, the framework IR spectrum of AIPO-AEPP does not show any absorption between 1400 and 1500 cm⁻¹, characteristics of ammonium ions. This suggests that AIPO-AEPP does not contain NH₄⁺ cations, as it is the case for AIPO-DMI prepared with 1,2-dimethylimidazole [31]. ¹H-¹³C CP/MAS NMR has confirmed that AEPP molecules are intact in the solid. The spectrum (see supplementary material) is composed of four main signals at ca. 37, 45, 48 and 55 ppm. Chemical shifts are close to those of the molecule in solution (38.6, 46.1, 54.7 and 61.9 ppm, respectively). The signal around 37 ppm, which corresponds to one of the carbon atoms of the alkyl chain, clearly appears as a doublet. As discussed below, this doublet results from the two non-equivalent positions for AEPP molecules between the sheets. Even though AEPP molecules undergo thermal degradation during synthesis, NH₄⁺ ions do not play a templating role in the formation of AIPO-AEPP. As far as ammonium ions are formed, they direct the crystallization of AIPO₄-15.

The structure of AIPO-AEPP contains anionic sheets with Al₃P₄O₁₆³⁻ stoichiometry. The asymmetric unit cell contains six crystallographically non-equivalent Al sites. All aluminum atoms are tetrahedrally coordinated to framework oxygens with Al–O bond lengths and O–Al–O bond angles in the range of 1.700(5)–1.749(4) Å and 106.1(2)–113.2(2)°, respectively (Tables 3 and 4). These values are in agreement with those previously found for aluminum tetrahedra in crystalline aluminophosphates. The eight crystallographically distinct phosphorus atoms share three oxygens with neighboring Al atoms,

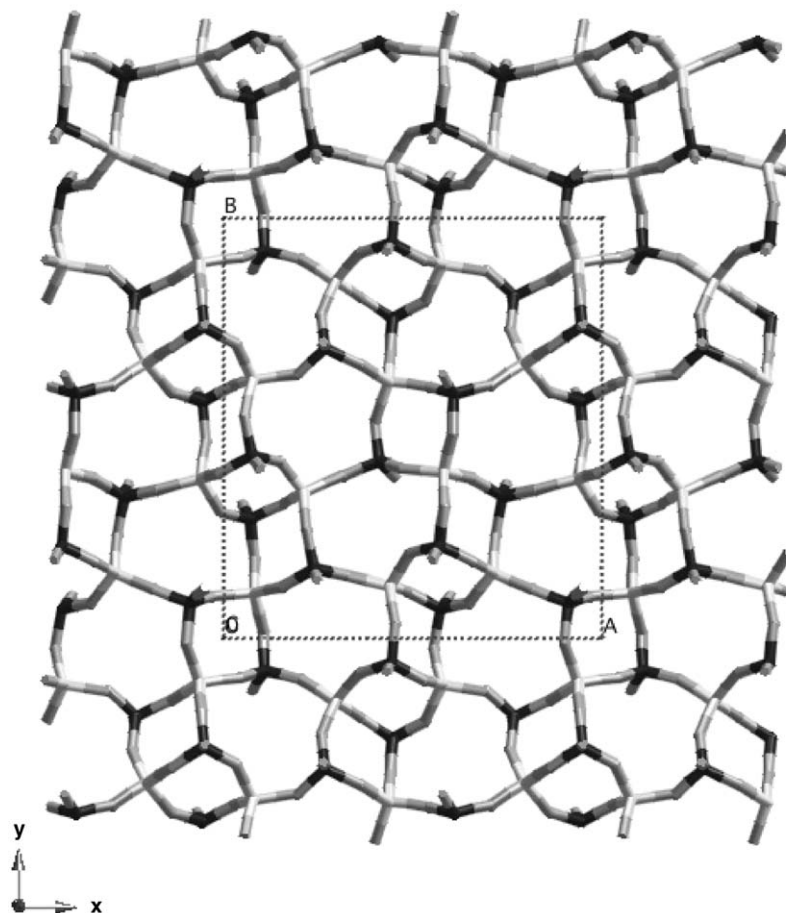


Fig. 2. $[\text{Al}_3\text{P}_4\text{O}_{16}]^{3-}$ layer, viewed along $[001]$, shown as skeletal drawing (light gray: Al tetrahedra, dark gray: P tetrahedra).

with P–O distances in the range of 1.515(5)–1.557(4) Å. The fourth P–O bond length is shorter, typical of P=O groups (1.472(4)–1.508(4) Å). AlO_4 and $\text{PO}_3(=\text{O})$ units alternate within the inorganic sheets to form a 2D network with a 4×6 net parallel to the ab plane (Fig. 2). This 4×6 net was previously found in a layered compound prepared using 1,2-dimethylimidazole as structure directing molecule [31]. However, in addition to the nature of interlayer organic molecules, this compound differs from AIPO-AEPP by the stacking sequence of the layers. In the compound containing dimethylimidazolium cations, inorganic sheets stack in an $AAAA$ sequence, with an interlayer spacing of 10.4 Å. The structure of AIPO-AEPP consists of the same layers stacking in an ABAB sequence and separated by a distance of ca. 9.3 Å.

The inorganic sheets in AIPO-AEPP are charge balanced by doubly protonated AEPP molecules and H_3O^+ cations located in the interlayer space. As already discussed, the presence of H_3O^+ instead of NH_4^+ was confirmed by elemental analysis, solid state NMR and IR spectroscopy. As seen in Fig. 3(a), AEPP molecules and H_3O^+ cations form infinite chains running parallel to the b -axis. Chains of protonated water molecules are

separated from each other by two chains of organic molecules. In the similar structure obtained using 1,2-dimethylimidazole, NH_4^+ ions and organic molecules also form infinite chains, but in a perpendicular direction (Fig. 3(b)). There are two different positions for AEPP molecules between the layers. They essentially differ by the orientation of the ring with respect to the sheets. In each chain, molecules with the ring perpendicular to the layers alternate with molecules that have the ring approximately parallel to the layers. Interlayer species not only play a charge balance role but they also act as H-bonding donors to terminal oxygens of phosphate groups. The complexity of the hydrogen-bond network is illustrated in Fig. 4. Each organic molecule participates in five hydrogen bonds with framework oxygen atoms: three through the nitrogen atom of the alkyl chain and two through the nitrogen atom of the ring (Table 5). The hydrogen-bonding scheme between AEPP molecules and inorganic sheets depends on the orientation of the ring (Fig. 5(a)). For molecules with the parallel orientation, the N atom in the ring (N4) is bonded to two terminal oxygens of two different layers. The NH_3^+ end group of the chain (N9) is bonded to two terminal oxygens on one side and one

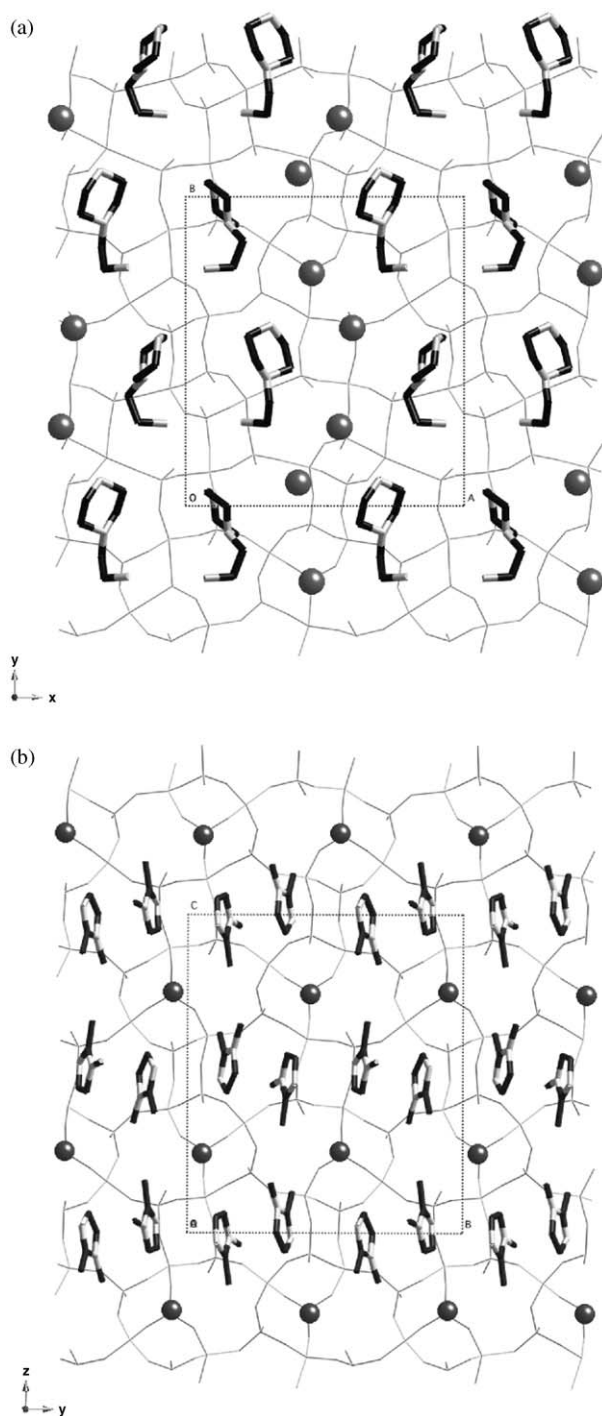


Fig. 3. Arrangement of organic molecules and tetrahedral species (shown as gray spheres) between the same aluminophosphate layers. (a) AEPP molecules and H_3O^+ cations in AlPO-AEPP, (b) 1,2-dimethylimidazole and NH_4^+ cations.

terminal oxygen on the other side. For the other orientation, the N atom in the ring ($\text{N}4'$) is bonded to two terminal oxygens of the same side. The nitrogen atom of the chain ($\text{N}9'$) participates in one bond to an oxygen atom of the same sheet and two bonds to oxygen atoms on the other side of the interlayer space. One of

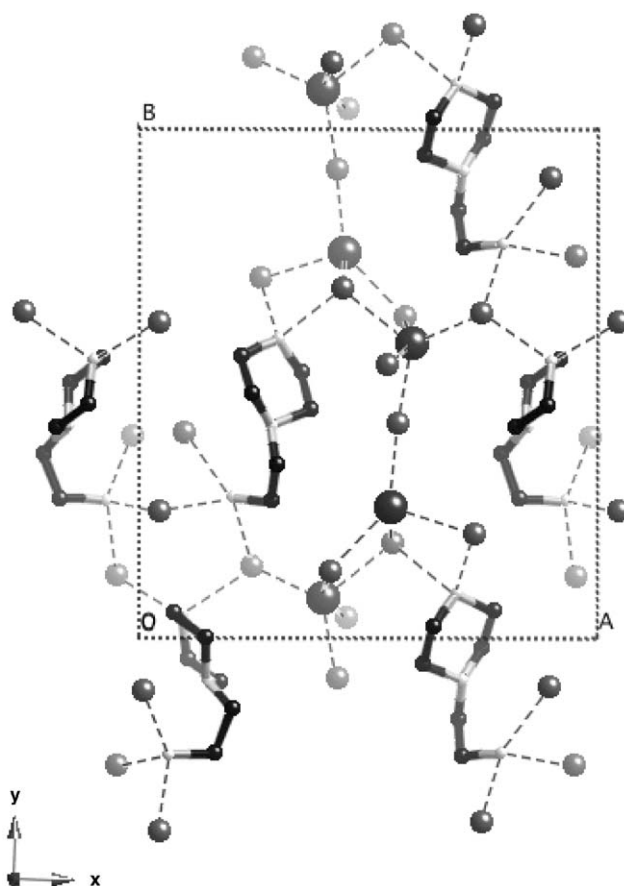


Fig. 4. Hydrogen bonding network between interlayer molecules and framework oxygen atoms. Large spheres: oxygen atoms from water molecules; small spheres: framework oxygen atoms (gray scale reflects height in z).

these two bonds involves a terminal $\text{P}=\text{O}$ group and the other a bridging oxygen between AlO_4 and PO_4 tetrahedra.

Aluminophosphate layers are also held together by hydrogen bonds between H_3O^+ cations and framework oxygen atoms (Table 5). Each protonated water molecule forms three hydrogen bonds to terminal $\text{P}=\text{O}$ groups on one side and one H-bond to one $\text{P}=\text{O}$ group on the opposite sheet (Figs. 4 and 5(b)). All hydrogen positions are partially occupied, with a population parameter of 3/4. Water tetrahedra are linked to each other via framework oxygen atoms and form infinite chains parallel to the $[010]$ direction. The orientation of tetrahedra within a chain follows the sequence UUDDUUDD (U = upward, D = downward). As seen in Fig. 5(b), water chains can also be considered as a succession of 4-membered-rings units, formed by two oxygen atoms of water molecules and two oxygen atoms of phosphate groups. The hydrogen-bonding network is completely different from that of AlPO-DMI prepared with 1,2-dimethylimidazole [31]. In the latter, NH_4^+ tetrahedra are isolated with all proton positions fully occupied (Fig. 6). The number of H bonds per

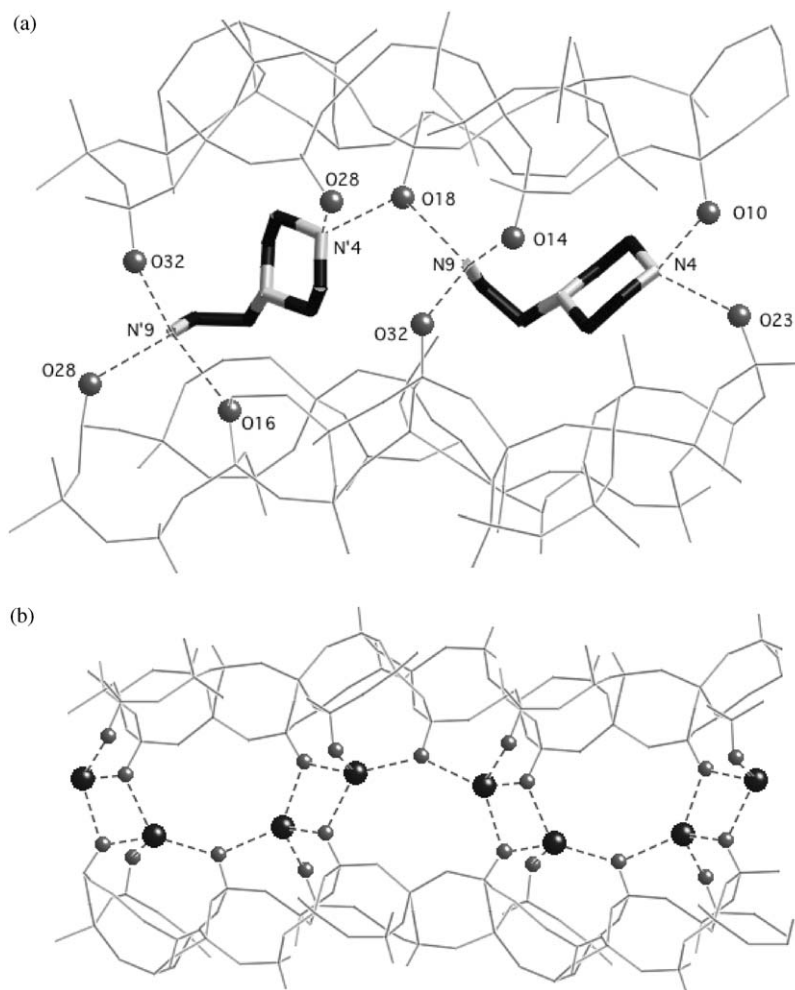
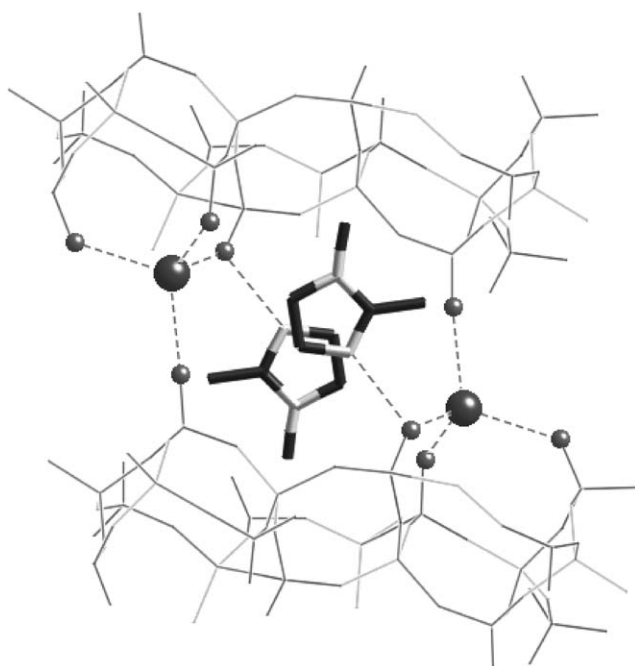


Fig. 5. Hydrogen bonding schemes between oxygen atoms of aluminophosphate layers and AEPP molecules (a) or H₃O⁺ tetrahedra (b).



tetrahedron is equal to four while, obviously, it is only three for H₃O⁺ cations. By contrast to the title compound, organic molecules are weakly bound to inorganic layers by only one hydrogen bond. As a consequence, they do not connect sheets to one another and the structure is thus essentially maintained by ammonium cations NH₄⁺.

The nature of organic molecules and the way they interact with framework oxygen atoms have a great influence on the structure, particularly the distance between inorganic sheets. For molecules like AEPP that possess several atoms forming multiple H-bonds with opposite aluminophosphate layers, the organic–inorganic interactions are strong. During crystallization, sheets tend to get closer to optimize the contact between protons of the molecule and oxygen atoms of the framework. The interlayer distance is small and the space is almost fully occupied by AEPP molecules

Fig. 6. Hydrogen bonding schemes between 1,2-dimethylimidazole molecules and aluminophosphate layers. Large dark spheres represent NH₄⁺ ions.

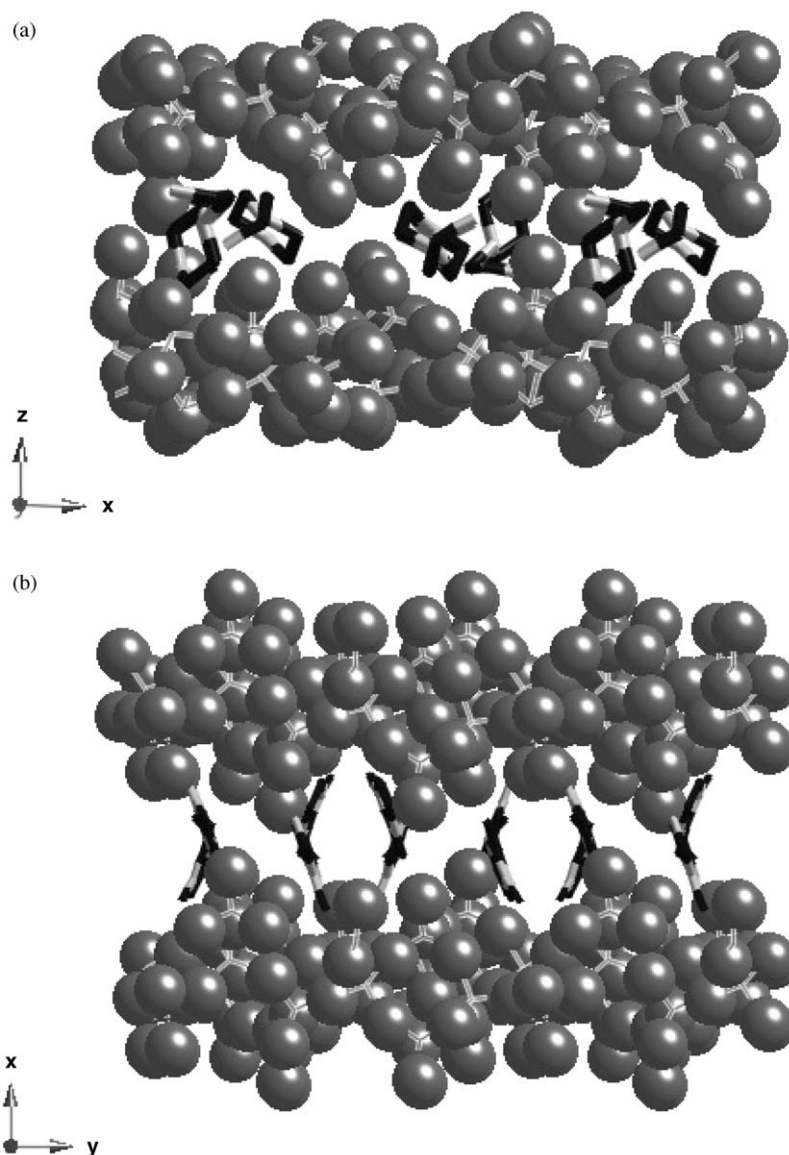


Fig. 7. View parallel to the layers of AIPO-AEPP (a) and AIPO-DMI (b). Gray spheres represent framework oxygen atoms.

(Fig. 7(a)). By contrast to AEPP, 1,2-dimethylimidazole molecules can only offer one H-bond to inorganic sheets. The presence of methyl groups moves layers from each other along the [100] direction. Moreover, molecules stand approximately perpendicular to the layers and occupy only a fraction of the interlayer space (Fig. 7(b)).

Yan et al. [45] attribute the presence of water molecules as co-templates in AIPO-CJ12, a layered aluminophosphate prepared using *N,N,N',N'*-tetramethylethylenediamine, to the weak H-bonding interaction between organic molecules and inorganic sheets. Indeed, the tertiary amine can only offer one hydrogen atom per N atom to form a H-bond to the inorganic sheet. Thus, H_3O^+ species serve as extra H-bond donors and stabilize the structure. This is also the case in the layered compound prepared using 1,2-dimethylimida-

zole. Organic molecules form only one H-bond to inorganic sheets, and NH_4^+ cations are necessary to enhance the hydrogen bonding interaction between the sheets. In AIPO-AEPP, the presence of H_3O^+ cations cannot be attributed to a weak hydrogen bond network between organic and inorganic species. Indeed, each *N*-(2-aminoethyl)-piperazine molecule forms five hydrogen bonds to oxygen atoms in the aluminophosphate sheets. Nonetheless, it seems that the 4×6 network found in AIPO-AEPP and AIPO-DMI cannot be obtained without co-templating molecules like H_3O^+ or NH_4^+ .

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