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Synthesis and Characterization of Two Layered Aluminophosphates, $(T)_2HAl_2P_3O_{12}$ (T = 2-BuNH$_3^+$) and $(T)H_2Al_2P_3O_{12}$ (T = pyH$^+$)

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Two new aluminophosphates, $(T)_2HAl_2P_3O_{12}$ (T = 2-BuNH$_3^+$) **(I)** and $(T)H_2Al_2P_3O_{12}$ (T = pyH$^+$) **(II)**, with the same framework stoichiometry but different layer structures have been prepared under nonaqueous conditions and the structures determined by single-crystal X-ray diffraction. Compound **(I)** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$), with lattice parameters $a = 9.261(1)$, $b = 8.365(6)$, $c = 27.119(4)$ Å, $\beta = 91.50(1)°$, and $V = 2100.1$ Å^3 ($R = 0.072$ and $R_w = 0.090$). The structure consists of Al- and P-centered tetrahedra linked to form layers. Protonated 2-butylamine molecules are located in the interlayer spaces and hydrogen bonded to the layers through NH$_3^+$ groups. Weak hydrophobic van der Waals' interactions between alkyl groups of the 2-BuNH$_3^+$ cations hold the layers together. Compound **(II)** crystallizes in the triclinic space group P-1 ($Z = 2$), with $a = 8.574(2)$, $b = 8.631(3)$, $c = 10.371(2)$ Å, $\alpha = 81.84(3)$, $\beta = 87.53(2)$, $\gamma = 69.07(2)°$, and $V = 709.49$ Å^3 ($R = 0.039$ and $R_w = 0.052$). The structure contains tetrahedrally coordinated P atoms and both tetrahedral and trigonal pyramidal Al atoms linked to form layers which are held together through hydrogen bonding, creating cavities in which pyH$^+$ cations reside. © 1992 Academic Press, Inc.

Introduction

The existence of a large and diverse range of microporous aluminosilicates, including zeolites, clays, and pillared clays, is well established, but only recently has it become clear that similar versatility is exhibited by aluminophosphates. The first breakthrough in this area was the discovery of a group of three-dimensional $AlPO_4$ structures by Wilson *et al.* (*1, 2*) at Union Carbide in the early 1980s. Some of these materials, e.g., $AlPO_4$-37 (faujasite) and $AlPO_4$-34 (chabazite), adopt the same framework structures as those of known zeolites, but others, e.g. $AlPO_4$-5, appear to be unique. In most, but not all, cases, the aluminium and phosphorus atoms occupy sites with tetrahedral coordination. These materials have interesting sorption properties and can be rendered acidic for catalysis by the partial replacement of phosphorus by silicon, thereby forming the silicoaluminium phosphates (SAPOs) (*3*), or of aluminium by divalent metals (MeAPOs) (*4*). Several condensed aluminium phosphates find use in binders (*5*) and fertilizers (*6*).

It has now become clear, however, that

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aluminophosphate materials can also form one- and two-dimensional framework structures. For example, we have recently reported the synthesis and structures of both a one-dimensional framework with stoichiometry $(T)(H_2AlP_2O_8)$, $T = (C_2H_5)_3NH^+$, and a two-dimensional system, $(T)_3(Al_3P_4O_{16})$, $T = enH^+$, (*7*, *8*). The analogy between the latter material and the aluminosilicate clays is clear. The compound $(T)(AlP_2O_8)$ $(T = (CH_2NH_3^+)_2)$, which has been described as a two-dimensional AlPO structure (*9*), is more appropriately represented as a one-dimensional system with interchain hydrogen bonding. These novel materials, which were made in nonaqueous solvent media, suggest that the scope for discovering interesting and potentially useful materials in aluminophosphate systems is far from exhausted. Indeed, joint work involving teams in Jilin, London, and Oxford has revealed that aluminophosphate synthesis in nonaqueous solvents can to some extent be controlled by the choice of solvent and organic base. In the present work, we illustrate this control in the preparation and characterization of two novel layered AlPOs with the same framework stoichiometry of $(Al_2P_3O_{12})^{3-}$, but with quite distinct crystalline structures: $(T)_2HAl_2P_3O_{12}$ $(T = 2\text{-}BuNH_3^+)$ **(I)** and $(T)H_2Al_2P_3O_{12}$ $(T = pyH^+)$ **(II)**.

Experimental

Synthesis

Synthesis of **(I)** was effected by hydrothermal crystallization in a Teflon pressure vessel. A gel of composition $Al_2O_3 : P_2O_5 : 2\text{-}BuNH_2 : 2\text{-}BuOH$ in the molar ratios 1 : 2.4 : 9.8 : 35 was used. Aluminium isopropoxide (2 g) was added to 2-butanol with stirring. H_3PO_4 was then added and the mixture stirred for 40 min until a uniform consistency was obtained. The templating agent, $CH_3CH_2CH(NH_2)CH_3$, was pipetted into the gel, and the vessel was sealed and heated under autogenous pressure for 10 days at 180°C. After the vessel cooled, colorless, block-shaped crystals were filtered, washed with distilled water, and dried in air.

Crystals of **(II)** were prepared by an analogous reaction in which pyridine was substituted for the 2-$BuNH_2$. Here the gel composition was $Al_2O_3 : P_2O_5 : py : 2\text{-}BuOH$ in molar ratios 1 : 2.4 : 10 : 30, and the preparative regime was as above. The transparent plate-like crystals were washed in water and dried in air.

CHN analyses gave the following results: N, 4.86 : C, 17.33 : H, 4.91% for compound **(I)** and N, 2.93 : C, 12.86 : H, 2.12% for compound **(II)**.

Powder X-ray diffraction patterns and thermogravimetric analyses were recorded for bulk samples of **(I)** and **(II)** using a Philips PW 1050/81 vertical diffractometer and a Stanton Redcroft STA-780 thermal analyzer, respectively. A ^{15}N CP/MAS NMR spectrum was recorded for **(II)** using a Bruker MSL 200 spectrometer operating at a frequency of 20.3 MHz with a recycle delay of 5 sec for 7235 scans and a contact time of 1 msec. The ^{15}N chemical shift was externally referenced to liquid ammonia using ammonium sulphate as the secondary reference (24.5 ppm). Energy dispersive X-ray microanalysis for P : Al ratios was performed using a JEOL 2000FX electron microscope fitted with a Tracor Northern analysis system employing a solid-state detector with a beryllium window.

Determination of Crystal Structures

Suitable crystals of **(I)** and **(II)** were mounted on thin glass fibers using "Superglue" (cyanoacrylate). Data for each compound were collected on an Enraf-Nonius CAD4 diffractometer fitted with a graphite monochromator and using CuK_α radiation. Data were corrected for absorption using azimuthal scans (*10*). Pertinent experimental data are given in Table I. The structures were solved by Direct Methods using the program SHELX-86 (*11*). Nonhydrogen atoms were located in difference Fourier maps. Hydrogen atoms were then geometrically placed for the organic moieties.

Problems of disorder were encountered in both refinements. In the case of (**I**), one of the terminal methyl groups was rotationally disordered and both rotamers (C(231) and C(232)) were refined to give respective occupancies of 0.67(3) and 0.33(3). In addition, some of the temperature factors of the carbon atoms of the template methyl groups refined to extremely large values, but examination of difference Fourier maps did not reveal any further disorder. Thus it was decided to fix the values of *U*(iso) for the carbon atoms of the methyl groups at 0.25 Å^2. Restraints were applied to maintain the geometry of the 2-BuNH$_3^+$ cations (*12*).

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR CRYSTALS (I) AND (II)

	I	II
Crystal system	Monoclinic	Triclinic
Space group	$P\,2_1/c$	$P\ -1$
Formula	$Al_2P_3O_{12}C_8H_{25}N_2$	$Al_2P_3O_{12}C_5H_8N$
Formula mass	488.18	421.00
a (Å)	9.261(1)	8.574(2)
b (Å)	8.365(6)	8.631(3)
c (Å)	27.119(3)	10.371(2)
α (°)	90.0	81.84(3)
β (°)	91.50(1)	87.53(2)
γ (°)	90.0	69.07(2)
Volume (Å^3)	2100.10	709.49
Z	4	2
ρ_{calc} (gcm^{-3})	1.5440	1.9710
Crystal size (mm)	0.15 × 0.35 × 0.35	0.05 × 0.20 ×0.35
μ (mm^{-1})	3.992	5.790
Transmission factors	1.71–1.80	1.16–1.54
Scan type	ω–2θ	ω–2θ
Scan speed range (deg min^{-1})	1.8–6.7	1.3–6.7
Scan angle (ω + 0.15 tan θ)	1.20	0.80
$2\theta_{max}$ (°)	140	150
Total data collected	5922	3379
Unique data	3939	2839
Observed data ($I > 3\,\sigma\,(I)$)	2053	2269
R_{merg}	0.054	0.020
R	0.072	0.039
R_w	0.090	0.052
No. of variables	195	233

In the case of (**II**), the disorder of the pyridinium cation gives two orientations slightly tilted with respect to each other. These two orientations could be observed in difference Fourier maps and refined to occupancies of 0.69(2) and 0.31(2). For the major orientation, anisotropic thermal parameters were used with restraints applied to these parameters so that there was no residual motion along any chemical bonds. Restraints were also applied to the bond lengths within the pyridinium cation.

For (**I**) it was assumed that the 2-BuNH$_2$ molecules were protonated and hydrogen atoms were placed accordingly. We are unable to locate a proton attached to O(11) which, from bond valence calculations (*13*), we believe to be part of an hydroxyl group. In the case of (**II**), hydrogen atoms attached to O(4) and O(8) were located in difference Fourier maps and initially included in the refinement. We assume that the remaining hydrogen atom required for purposes of charge balancing is attached to the nitrogen atom of the pyridine ring, but we did not place this hydrogen atom. Supporting evidence for pyridine being present as a pyridinium cation is derived from ^{15}N MAS NMR, which is discussed below. During the final stages of refinement, hydrogen atoms were allowed to "ride" on the atoms to which they were bonded. A correction for secondary extinction was applied in the case of compound (**I**) (*14*). Full-matrix least-squares refinement was carried out using the CRYSTALS suite of programs (*15*) with weighting schemes based on 2- and 3-term Chebyshev series for (**I**) and (**II**), respectively (*16*). The largest residual peaks in the final difference maps were 1.49 e Å^{-3} (in the vicinity of one of the 2-BuNH$_2$ groups) for (**I**), and 0.41 e Å^{-3} for (**II**).

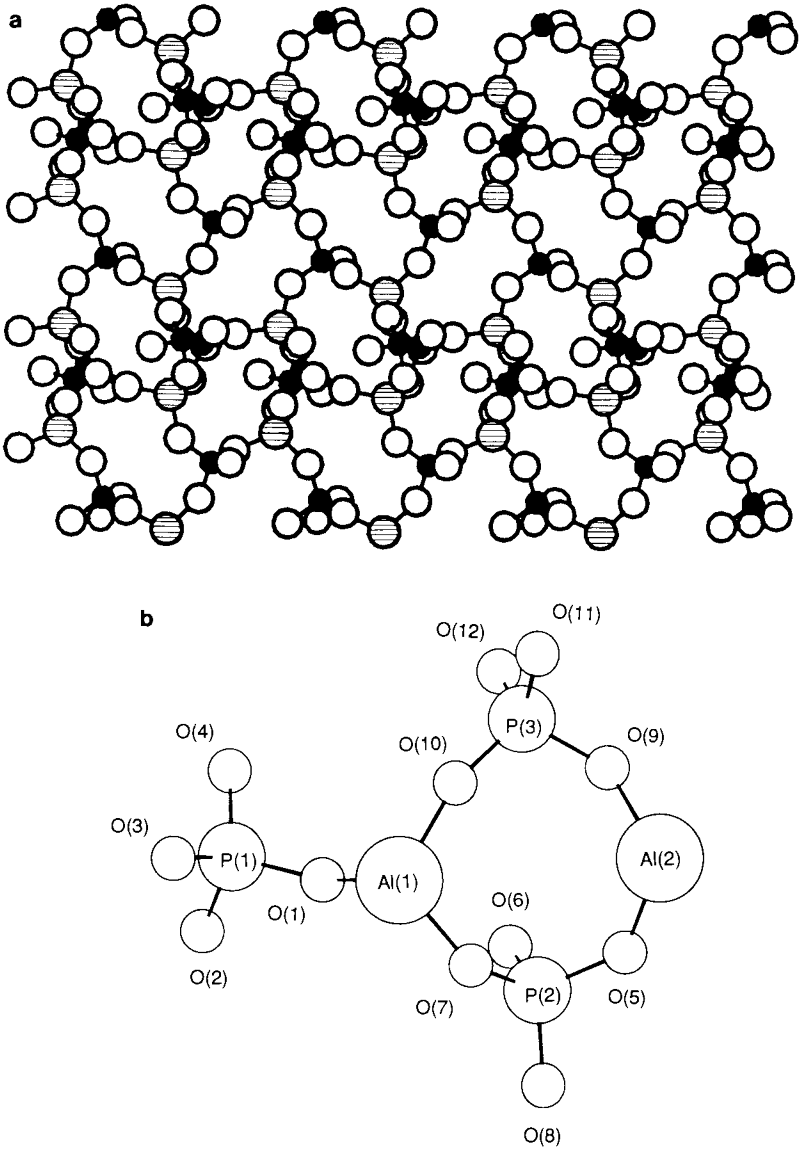

FIG. 1. (a) View normal to the plane of the layer, (b) the asymmetric unit, and (c) view along the layer plane for compound **(I)**, $(2\text{-BuNH}_3^+)_2(\text{HAl}_2\text{P}_3\text{O}_{12})$. Elements: ●, P; ⊜, Al; ▨, N; ⊖, C.

Results and Discussion

The crystal structures of **(I)** and **(II)** are shown in Figs. 1 and 2. Atomic coordinates and pertinent bond lengths and bond angles are given in Tables II–VII. Both **(I)** and **(II)** have the same framework stoichiometry $(\text{Al}_2\text{P}_3\text{O}_{12})^{3-}$ but have quite distinct layered structures.

The structure of **(I)** consists of mac-

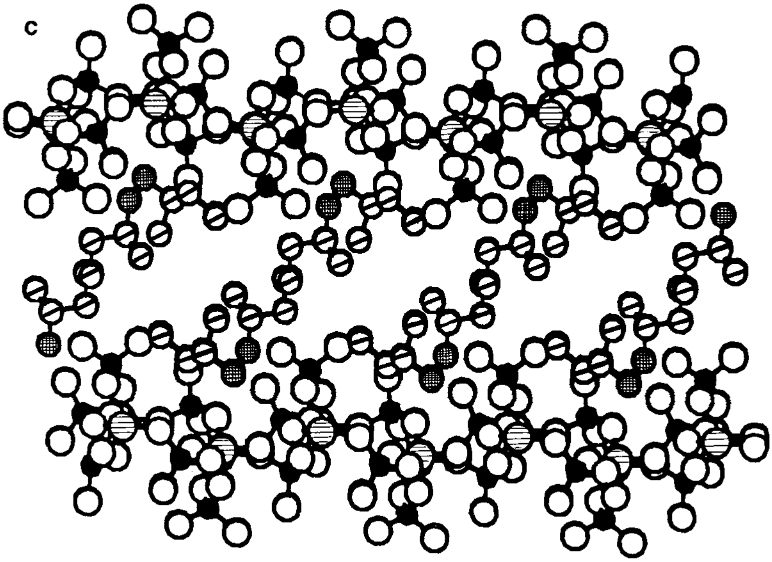

FIG. 1—*Continued.*

TABLE IIa

ATOMIC PARAMETERS WITH E.S.D.'S IN PARENTHESES FOR THE 2-BUTYL COMPOUND (**I**)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq/*U*(iso)
P(1)	0.4208(2)	0.4758(3)	0.21850(9)	0.0286
P(2)	−0.0630(2)	0.5235(3)	0.29751(9)	0.0276
P(3)	−0.0937(2)	0.6172(3)	0.1422(1)	0.0335
Al(1)	0.7027(2)	0.6793(3)	0.2331(1)	0.0253
Al(2)	0.1409(3)	0.6653(3)	0.2229(1)	0.0287
O(1)	0.5735(6)	0.5309(8)	0.2322(3)	0.0356
O(2)	0.3728(6)	0.3663(7)	0.2607(2)	0.0339
O(3)	0.3225(6)	0.6229(8)	0.2191(3)	0.0384
O(4)	0.4151(8)	0.390(1)	0.1698(3)	0.0468
O(5)	0.0835(6)	0.5739(8)	0.2765(3)	0.0325
O(6)	0.1102(7)	0.8678(8)	0.2281(3)	0.0362
O(7)	0.8242(6)	0.6499(8)	0.2825(3)	0.0330
O(8)	−0.0507(7)	0.5086(8)	0.3525(2)	0.0411
O(9)	0.0507(7)	0.5922(9)	0.1712(3)	0.0411
O(10)	0.7947(7)	0.6732(9)	0.1786(2)	0.0402
O(11)	−0.0686(7)	0.7579(9)	0.1052(2)	0.0440
O(12)	−0.1347(8)	0.470(1)	0.1149(3)	0.0492
N(1)	0.677(1)	0.231(2)	0.1484(4)	0.090(4)
N(2)	0.1611(9)	0.197(1)	0.6129(3)	0.045(2)
C(10)	0.654(3)	0.146(4)	0.0640(7)	0.2500
C(11)	0.651(2)	0.086(2)	0.1172(6)	0.138(8)
C(12)	0.507(2)	0.005(2)	0.1294(7)	0.143(8)
C(13)	0.491(3)	−0.133(3)	0.093(1)	0.2500
C(20)	0.086(2)	0.263(3)	0.5273(7)	0.1494
C(21)	0.204(1)	0.185(1)	0.5607(3)	0.067(4)
C(22)	0.239(2)	0.011(2)	0.5487(7)	0.133(8)
C(231)	0.313(5)	0.013(5)	0.499(1)	0.2500
C(232)	0.328(9)	−0.066(6)	0.591(2)	0.2500

TABLE IIb

HYDROGEN ATOMIC PARAMETERS WITH E.S.D.'S IN PARENTHESES FOR THE 2-BUTYL COMPOUND

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq/*U*(iso)
H(1)	0.769(1)	0.285(2)	0.1404(4)	0.2000
H(2)	0.680(1)	0.196(2)	0.1836(4)	0.2000
H(3)	0.595(1)	0.308(2)	0.1430(4)	0.2000
H(4)	0.1401(9)	0.311(1)	0.6214(3)	0.2000
H(5)	0.2400(9)	0.156(1)	0.6354(3)	0.2000
H(6)	0.0721(9)	0.131(1)	0.6170(3)	0.2000
H(8)	0.747(3)	0.201(4)	0.0565(7)	0.2000
H(9)	0.640(3)	0.053(4)	0.0414(7)	0.2000
H(10)	0.573(3)	0.223(4)	0.0592(7)	0.2000
H(11)	0.733(2)	0.010(2)	0.1232(6)	0.2000
H(12)	0.512(2)	−0.037(2)	0.1639(7)	0.2000
H(13)	0.425(2)	0.082(2)	0.1259(7)	0.2000
H(14)	0.399(3)	−0.189(3)	0.100(1)	0.2000
H(15)	0.574(3)	−0.210(3)	0.097(1)	0.2000
H(16)	0.487(3)	−0.091(3)	0.059(1)	0.2000
H(17)	0.068(2)	0.377(3)	0.5362(7)	0.2000
H(18)	−0.004(2)	0.199(3)	0.5314(7)	0.2000
H(19)	0.117(2)	0.256(3)	0.4923(7)	0.2000
H(20)	0.293(1)	0.250(1)	0.5570(3)	0.2000
H(21)	0.303(2)	−0.036(2)	0.5751(7)	0.2000
H(22)	0.146(2)	−0.051(2)	0.5467(7)	0.2000
H(23)	0.282(2)	0.004(2)	0.5154(7)	0.2000
H(231)	0.341(5)	−0.100(5)	0.492(1)	0.2000
H(232)	0.401(5)	0.082(5)	0.499(1)	0.2000
H(233)	0.243(5)	0.052(5)	0.473(1)	0.2000
H(234)	0.355(9)	−0.179(6)	0.584(2)	0.2000
H(235)	0.297(9)	−0.057(6)	0.626(2)	0.2000
H(236)	0.413(9)	0.005(6)	0.586(2)	0.2000

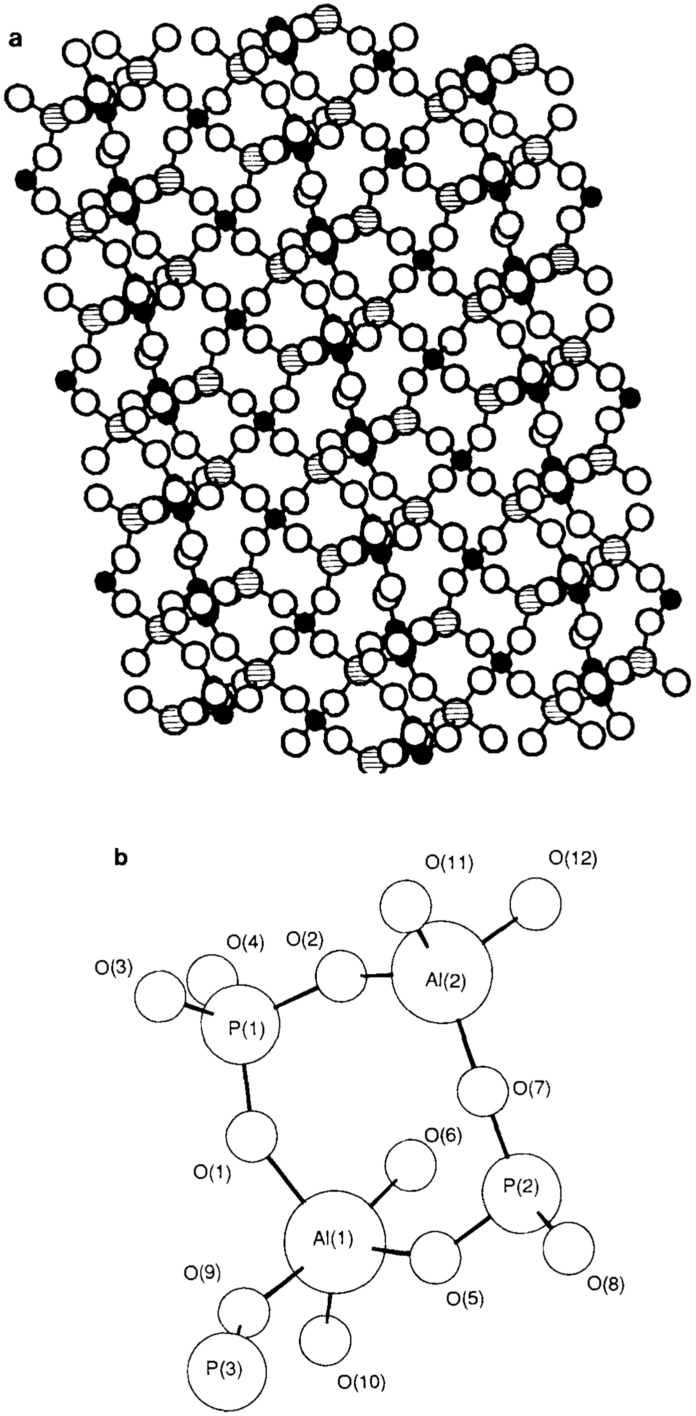

FIG. 2. (a) View normal to the plane of the layer, (b) the asymmetric unit, and (c) view along the layer plane for compound **(II)**, (pyH$^+$)(H$_2$Al$_2$P$_3$O$_{12}$). Elements are shown as in Fig. 1.

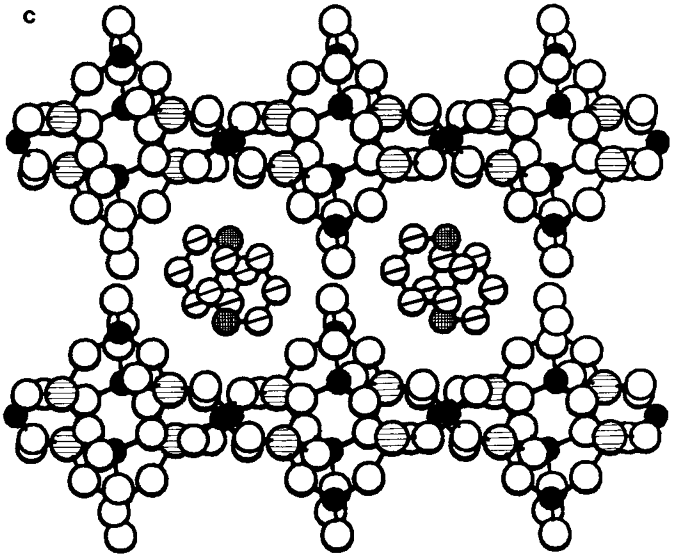

FIG. 2—*Continued.*

roanionic sheets (empirical formula $(HAl_2P_3O_{12})^{2-}$ intercalated by a template layer consisting of two crystallographically distinct 2-butylammonium cations (Fig. 1a). In the asymmetric unit of the $(HAl_2P_3O_{12})^{2-}$ ion, there are three crystallographically independent P atoms and two independent Al atoms (Fig. 1b). The environments of the two Al sites are chemically similar, each Al being tetrahedrally coordinated by four O atoms with Al–O contacts varying between 1.723 and 1.744 Å and Al–O–Al angles lying between 106.2° and 111.8°. These values are in good agreement with those found in the mineral berlinite (*17*). There are two chemically distinct sites for the three P atoms, but in each case, the P atom is tetrahedrally coordinated to four O atoms. For P(1) and P(2), three of the coordinating oxygen atoms are bonded to aluminium atoms and have P–O bond lengths ranging from 1.524–1.544 Å. The remaining P–O contacts (i.e. P(1)–O(4) and P(2)–O(8) of lengths 1.503 and 1.499 Å, respectively) are formally P=O double bonds. Terminal P=O groups in, for example $H_3PO_4 \cdot 0.5H_2O$, are 1.485 and 1.495 Å in length (*18*). The third P atom has two P–O bonds of 1.522 and 1.548 Å bridging to aluminium. The remaining P–O bonds around P(3) consist of a P(3)–O(11)H group of 1.568 Å and a P(3)=O(12) double bond of 1.479 Å. The P(3)–O(11) bond is of similar length to those found for P–OH groups in other structures. For example, in $H_3PO_4 \cdot 0.5H_2O$ and α-zirconium phosphate (*19*), the average P–OH bond lengths are 1.551 and 1.558 Å, respectively. The multiple-bond nature of all the P=O bonds is also reflected in the bond angles; all the O–P–O bond angles (106.3°–108.2°) are less than the O–P=O angles (110.2°–114.3°), as expected on the basis of elementary V.S.E.P.R. theory.

Hydrogen bonding plays an important role in linking the template ions to the individual $(HAl_2P_3O_{12})^{2-}$ layers (Fig. 1c). The nitrogen of each 2-butylammonium cation forms two hydrogen bonds to O atoms of P=O groups. Thus the N(1)–O(4), N(1)–O(12), N(2)–O(4), and N(2)–O(8) distances are 2.84, 2.82, 2.87, and 2.84 Å, respectively. There is also one intrasheet hydrogen bond of 2.62 Å between O(8) and O(11). It should be noted that none of these

TABLE III

Selected Interatomic Contacts in Angstrom with E.S.D.'s in Parentheses for the 2-Butyl Compound **(I)**

P(1)–O(1)	1.524(6)
P(1)–O(2)	1.540(7)
P(1)–O(3)	1.531(7)
P(1)–O(4)	1.503(7)
P(2)–O(5)	1.544(6)
P(2)–O(6)	1.533(7)
P(2)–O(7)	1.534(6)
P(2)–O(8)	1.499(7)
P(3)–O(9)	1.548(7)
P(3)–O(10)	1.522(6)
P(3)–O(11)	1.568(7)
P(3)–O(12)	1.479(7)
Al(1)–O(1)	1.724(7)
Al(1)–O(2)	1.723(7)
Al(1)–O(7)	1.744(7)
Al(1)–O(10)	1.725(7)
Al(2)–O(3)	1.725(7)
Al(2)–O(5)	1.738(7)
Al(2)–O(6)	1.724(7)
Al(2)–O(9)	1.725(7)
N(1)–C(11)	1.494*
N(2)–C(21)	1.483*
C(10)–C(11)	1.528*
C(11)–C(12)	1.541*
C(12)–C(13)	1.521*
C(20)–C(21)	1.540*
C(21)–C(22)	1.532*
C(22)–C(231)	1.539*
C(22)–C(232)	1.536*

Note. All interatomic contacts marked with an asterisk have formed part of a chemical restraint in the refinement.

TABLE IV

Selected Interatomic Angles in Degrees with E.S.D.'s in Parentheses for the 2-Butyl Compound **(I)**

O(2)–P(1)–O(1)	106.5(4)
O(3)–P(1)–O(1)	107.6(4)
O(3)–P(1)–O(2)	106.7(4)
O(4)–P(1)–O(1)	111.6(4)
O(4)–P(1)–O(2)	111.4(4)
O(4)–P(1)–O(3)	112.7(5)
O(6)–P(2)–O(5)	107.9(4)
O(7)–P(2)–O(5)	108.2(4)
O(7)–P(2)–O(6)	106.3(4)
O(8)–P(2)–O(5)	110.2(4)
O(8)–P(2)–O(6)	113.1(4)
O(8)–P(2)–O(7)	110.8(4)
O(10)–P(3)–O(9)	107.7(4)
O(11)–P(3)–O(9)	106.6(4)
O(11)–P(3)–O(10)	107.4(4)
O(12)–P(3)–O(9)	110.5(4)
O(12)–P(3)–O(10)	114.3(4)
O(12)–P(3)–O(11)	110.1(4)
O(2)–Al(1)–O(1)	111.8(3)
O(7)–Al(1)–O(1)	110.1(3)
O(7)–Al(1)–O(2)	107.9(3)
O(10)–Al(1)–O(1)	108.9(4)
O(10)–Al(1)–O(2)	108.8(4)
O(10)–Al(1)–O(7)	109.3(3)
O(5)–Al(2)–O(3)	106.2(3)
O(6)–Al(2)–O(3)	111.7(3)
O(6)–Al(2)–O(5)	108.0(4)
O(9)–Al(2)–O(3)	109.3(4)
O(9)–Al(2)–O(5)	111.8(4)
O(9)–Al(2)–O(6)	109.7(4)
Al(1)–O(1)–P(1)	149.4(5)
Al(1)–O(2)–P(1)	137.6(5)
Al(2)–O(3)–P(1)	138.3(5)
Al(2)–O(5)–P(2)	136.0(4)
Al(2)–O(6)–P(2)	147.5(4)
Al(1)–O(7)–P(2)	136.3(5)
Al(2)–O(9)–P(3)	139.3(5)
Al(1)–O(10)–P(3)	157.4(5)
C(10)–C(11)–N(1)	105.1*
C(12)–C(11)–N(1)	111.4*
C(12)–C(11)–C(10)	112.9*
C(13)–C(12)–C(11)	105.3*
C(20)–C(21)–N(2)	109.4*
C(22)–C(21)–N(2)	109.2*
C(22)–C(21)–C(20)	115.2*
C(231)–C(22)–C(21)	106.0*
C(232)–C(22)–C(21)	110.6*

Note. All interatomic parameters marked with an asterisk have formed part of a chemical restraint in the refinement.

hydrogen bonds cross-link the aluminophosphate sheets. Thus the only forces that hold the layers together are weak hydrophobic van der Waals' interactions between the alkyl groups of the 2-butylammonium cations. It is not therefore surprising to find that problems of template disorder were encountered and that the atoms in this region have large temperature factors.

The powder X-ray diffraction pattern of **(I)** was compared with a simulated pattern based upon the crystal structure determined in this work. Additional lines were ob-

TABLE Va

Atomic Parameters with E.S.D.'s in Parentheses for the Pyridine Compound **(II)**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq/*U*(iso)
P(1)	−0.0015(1)	0.13732(9)	0.80698(7)	0.0131
P(2)	0.01692(9)	0.34293(9)	0.37559(7)	0.0126
P(3)	−0.47695(9)	0.25225(9)	0.49201(8)	0.0130
Al(1)	−0.2347(1)	0.4214(1)	0.59819(9)	0.0127
Al(2)	0.2638(1)	0.0870(1)	0.58496(9)	0.0129
O(1)	−0.1536(3)	0.2598(3)	0.7318(2)	0.0210
O(2)	0.1569(3)	0.1260(3)	0.7287(2)	0.0239
O(3)	−0.0168(3)	−0.0310(3)	0.8454(2)	0.0205
O(4)	0.0141(4)	0.2125(3)	0.9321(2)	0.0230
O(5)	−0.1544(3)	0.3905(3)	0.4385(2)	0.0201
O(6)	−0.0808(3)	0.5149(3)	0.6402(2)	0.0210
O(7)	0.1356(3)	0.1813(3)	0.4506(2)	0.0222
O(8)	−0.0025(3)	0.3056(3)	0.2354(2)	0.0210
O(9)	−0.3952(3)	0.3268(3)	0.5799(2)	0.0200
O(10)	−0.4018(3)	0.6182(3)	0.6068(2)	0.0179
O(11)	0.3475(3)	−0.1276(3)	0.5853(2)	0.0185
O(12)	0.4276(3)	0.1597(3)	0.5832(2)	0.0216
N(1)	0.494(1)	0.724(1)	0.1492(7)	0.0387
C(2)	0.416(1)	0.812(1)	0.039(1)	0.0635
C(3)	0.489(2)	0.778(2)	−0.078(1)	0.0694
C(4)	0.647(2)	0.658(2)	−0.0809(9)	0.0641
C(5)	0.726(1)	0.572(1)	0.035(1)	0.0575
C(6)	0.644(1)	0.607(1)	0.1484(8)	0.0393
N(11)	0.721(3)	0.595(4)	−0.045(2)	0.092(9)
C(12)	0.598(3)	0.729(3)	−0.103(2)	0.054(7)
C(13)	0.469(3)	0.826(3)	−0.033(2)	0.044(6)
C(14)	0.453(3)	0.793(3)	0.102(2)	0.045(5)
C(15)	0.583(4)	0.655(3)	0.160(2)	0.041(5)
C(16)	0.715(3)	0.574(3)	0.084(2)	0.040(5)

served, pointing to the presence of a second, as yet unidentified, phase. As a consequence, the CHN analyses (N, 4.86 : C, 17.33 : H, 4.91%) are in poor agreement with expected values (N, 5.74 : C, 19.68 : H, 5.16%). Thermogravimetric analysis of a bulk sample revealed weight losses of 8.62% below 200°C and 24.9% at about 300°C. The heated product was amorphous.

TABLE Vb

Hydrogen Atomic Parameters with E.S.D.'s in Parentheses for the Pyridine Compound **(II)**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq/*U*(iso)
H(100)	0.0112	0.1445	0.9982	0.1000
H(101)	0.0196	0.1876	0.2138	0.1000
H(2)	0.307(1)	0.904(1)	0.047(1)	0.1000
H(3)	0.422(2)	0.837(2)	−0.158(1)	0.1000
H(4)	0.704(2)	0.647(2)	−0.1670(9)	0.1000
H(5)	0.840(1)	0.484(1)	0.032(1)	0.1000
H(6)	0.698(1)	0.536(1)	0.2304(8)	0.1000
H(12)	0.583(3)	0.748(3)	−0.200(2)	0.1000
H(13)	0.383(3)	0.932(3)	−0.074(2)	0.1000
H(14)	0.359(3)	0.851(3)	0.158(2)	0.1000
H(15)	0.597(4)	0.625(3)	0.257(2)	0.1000
H(16)	0.820(3)	0.485(3)	0.122(2)	0.1000

TABLE VI

Selected Interatomic Contacts in Angstrom with E.S.P.'s in Parenthesis for the Pyridine Compound **(II)**

P(1)–O(1)	1.515(2)
P(1)–O(2)	1.532(2)
P(1)–O(3)	1.501(2)
P(1)–O(4)	1.562(2)
P(2)–O(5)	1.521(2)
P(2)–O(6)	1.499(2)
P(2)–O(7)	1.527(2)
P(2)–O(8)	1.561(2)
P(3)–O(9)	1.510(2)
P(3)–O(10)	1.522(2)
P(3)–O(11)	1.532(2)
P(3)–O(12)	1.545(2)
Al(1)–O(1)	1.786(2)
Al(1)–O(5)	1.785(2)
Al(1)–O(6)	1.869(2)
Al(1)–O(9)	1.861(2)
Al(1)–O(10)	1.800(2)
Al(2)–O(2)	1.726(3)
Al(2)–O(7)	1.727(2)
Al(2)–O(11)	1.730(2)
Al(2)–O(12)	1.729(2)
N(1)–C(2)	1.334*
N(1)–C(6)	1.322*
C(2)–C(3)	1.364*
C(3)–C(4)	1.376*
C(4)–C(5)	1.389*
C(5)–C(6)	1.358*
N(11)–C(12)	1.337*
N(11)–C(16)	1.327*
C(12)–C(13)	1.381*
C(13)–C(14)	1.390*
C(14)–C(15)	1.387*
C(15)–C(16)	1.383*

Note. All interatomic parameters marked with an asterisk have formed part of a chemical restraint in the refinement.

Compound **(II)** is the first AlPO to be synthesised under nonaqueous conditions with an aromatic amine as template. The structure of **(II)** consists of macroanionic sheets of formula $(H_2Al_2P_3O_{12})^-$ with template pyridinium cations between the layers (Fig. 2a). In the asymmetric unit of the $(H_2Al_2P_3O_{12})^-$ ion, there are three types of P atom and two types of Al atom (Fig. 2b). Each P atom is tetrahedrally coordinated to four O atoms. The P–O distances are in the range 1.499–1.562 Å and O–P–O angles vary from 105.7–113.9°. The P(1)–O(4)H and P(2)–O(8)H groups have the longest P–O bond lengths at 1.562 and 1.561 Å, respectively. The P(1)–O(3) group with bond length 1.501 Å contains some multiple-bond character.

Of the two types of Al present, Al(2) shows almost regular tetrahedral coordination with Al(2)–O distances and O–Al(2)–O angles in the ranges 1.726–1.730 Å and 107.8°–111.7°, respectively. These values are again in good agreement with the corresponding ones for berlinite. Al(1) has oxygen coordination based on a distorted trigonal bipyramid with two axial Al(1)–O lengths of 1.869 and 1.861 Å and three shorter Al(1)–O lengths in the range 1.785–1.800 Å. The P–O bonds which share common oxygen atoms with the longer Al(1)–O bonds (i.e., P(2)–O(6) and P(3)–O(9)) are noticeably shorter than the other bridging P–O bond lengths. Pentacoordinate Al atoms showing similar distor-

TABLE VII

SELECTED INTERATOMIC ANGLES IN DEGREES WITH E.S.D.'S IN PARENTHESES FOR THE PYRIDINE COMPOUND (**II**)

O(2)–P(1)–O(1)	110.0(1)	O(7)–Al(2)–O(2)	111.7(1)
O(3)–P(1)–O(1)	111.8(1)	O(11)–Al(2)–O(2)	108.1(1)
O(3)–P(1)–O(2)	112.2(1)	O(11)–Al(2)–O(7)	110.4(1)
O(4)–P(1)–O(1)	107.4(2)	O(12)–Al(2)–O(2)	107.9(1)
O(4)–P(1)–O(2)	105.7(1)	O(12)–Al(2)–O(7)	110.7(1)
O(4)–P(1)–O(3)	109.4(1)	O(12)–Al(2)–O(11)	107.8(1)
O(6)–P(2)–O(5)	111.6(1)	Al(1)–O(1)–P(1)	147.7(2)
O(7)–P(2)–O(5)	109.7(1)	Al(2)–O(2)–P(1)	147.6(2)
O(7)–P(2)–O(6)	113.9(1)	Al(1)–O(5)–P(2)	136.2(1)
O(8)–P(2)–O(5)	107.6(1)	Al(1)–O(6)–P(2)	150.4(2)
O(8)–P(2)–O(6)	106.5(1)	Al(2)–O(7)–P(2)	147.6(2)
O(8)–P(2)–O(7)	107.2(1)	Al(1)–O(9)–P(3)	147.4(2)
O(10)–P(3)–O(9)	113.7(1)	Al(1)–O(10)–P(3)	134.5(2)
O(11)–P(3)–O(9)	111.6(1)	Al(2)–O(11)–P(3)	137.8(2)
O(11)–P(3)–O(10)	106.8(1)	Al(2)–O(12)–P(3)	142.1(2)
O(12)–P(3)–O(9)	105.8(1)	C(6)–N(1)–C(2)	121.7*
O(12)–P(3)–O(10)	109.4(1)	C(3)–C(2)–N(1)	119.6*
O(12)–P(3)–O(11)	109.5(1)	C(4)–C(3)–C(2)	119.6*
O(5)–Al(1)–O(1)	119.9(1)	C(5)–C(4)–C(3)	119.4*
O(6)–Al(1)–O(1)	88.2(1)	C(6)–C(5)–C(4)	118.2*
O(6)–Al(1)–O(5)	94.2(1)	C(5)–C(6)–N(1)	121.4*
O(9)–Al(1)–O(1)	86.7(1)	C(12)–N(11)–C(16)	114.5*
O(9)–Al(1)–O(5)	93.3(1)	C(13)–C(12)–N(11)	121.6*
O(9)–Al(1)–O(6)	172.3(1)	C(14)–C(13)–C(12)	123.6*
O(10)–Al(1)–O(1)	125.6(1)	C(15)–C(14)–C(13)	114.0*
O(10)–Al(1)–O(5)	114.5(1)	C(16)–C(15)–C(14)	118.6*
O(10)–Al(1)–O(6)	90.0(1)	C(15)–C(16)–N(11)	126.6*
O(10)–Al(1)–O(9)	88.3(1)		

Note. All interatomic parameters marked with an asterisk have formed part of a chemical restraint in the refinement.

tions have been reported previously in, for example, $Al_3As_3O_{12} \cdot C_4H_{12}N^+OH^-$ (*20*).

The $(H_2Al_2P_3O_{12})^-$ sheets are held together by hydrogen bonding between O(4)–H and O(3) groups of adjacent layers to create cavities in which the aromatic moieties reside. To achieve charge balance, a third proton is required, and it is proposed that pyridine is actually present in the cavities as the cation pyH^+. It was not possible to show this directly from the single-crystal data, but the ^{15}N CP/MAS spectrum showed a peak at 198 ppm (Fig. 3) identical to the one observed on a silica–alumina surface and previously ascribed by Maciel *et al.* to protonated pyridine [21].

Powder X-ray diffraction and analytical electron microscopy on bulk **(II)** suggested that the product was single phase with P : Al in the ratio 3 : 2, but CHN analysis gave N, 2.93 : C, 12.86 : H, 2.12%, rather lower than the calculated values of N, 3.33 : C, 14.27 : H, 1.92%. Thermogravimetric analysis showed two regions of weight loss below 500°C : one below 135°C (4.19%) and one over the range 135–220°C (13.05%). A powder X-ray diffraction pattern of the heated product showed that the structure had converted predominantly to the condensed phase berlinite and a phase identified by analytical electron microscopy as having a P : Al ratio of 2 : 1.

Conclusions

As a direct result of altering the identity of the amine used in the synthesis, we have prepared, under otherwise identical conditions, two AlPOs with the same framework composition but entirely different crystalline structures. While it cannot be stated unambiguously that the organic cations act as templates during crystal growth, the circumstantial evidence that this is the case is quite compelling for the pyridinium compound in the light of the structure shown in Fig. 2c. The present work thus shows that great scope exists for the preparation of new layered structures of aluminium phosphates by adroit choice of the organic template.

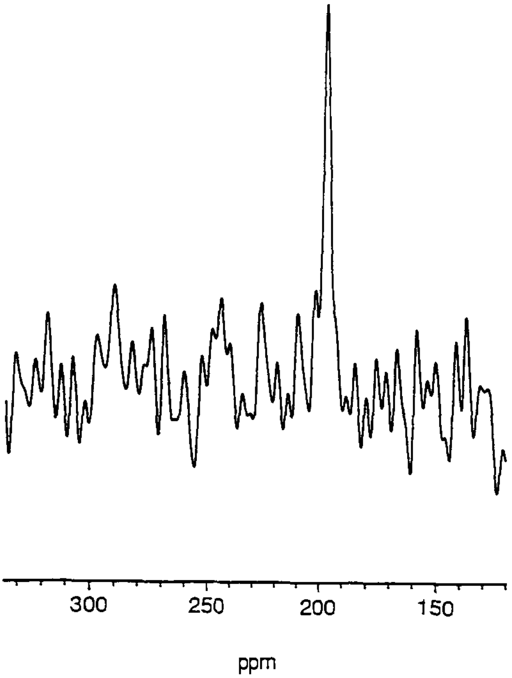

FIG. 3. 20.3 MHz ^{15}N CP/MAS spectrum of pyridine (natural abundance). Chemical shift referenced to liquid ammonia. Spinning speed of 4000 Hz, recycle delay 5 sec, 7235 scans, contact time 1 msec. No significant feature is observed in the chemical shift range expected for neutral pyridine (~317 ppm).

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