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$[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$: An Aluminium Phosphate with a New Layer Topology

Ann M. Chippindale[1] and Richard I. Walton

Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, United Kingdom

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A new two-dimensional aluminophosphate, $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$ has been synthesized under solvothermal conditions at 453 K in the presence of 2,2,6,6,- tetramethylpiperidine and the structure determined using room-temperature single-crystal X-ray diffraction data ($M_r = 483.16$, triclinic, space group P-1, $a = 8.541(3)$, $b = 9.298(1)$, $c = 12.660(5)$ Å, $\alpha = 73.26(2)$, $\beta = 89.58(4)$, and $\gamma = 87.70(2)°$; $V = 962.06$ Å^3, $Z = 2$, $R = 3.88\%$, and $R_w = 4.47\%$ for 2049 observed data ($I > 3(\sigma(I))$). The structure has a new framework topology and contains AlO_4 and PO_4 tetrahedra linked to generate layers containing 4- and 8-membered rings of alternating aluminium- and phosphorus-based polyhedra. The organic cations reside between the layers and are hydrogen bonded to the inorganic framework. The layer topology is closely related to that observed previously in the pyridine-containing AlPO, $[C_5H_6N][Al_2(HPO_4)_2(PO_4)]$. © 1999 Academic Press

INTRODUCTION

Solvothermal methods have now been used to prepare several low-dimensional aluminophosphates, in addition to numerous AlPOs with three-dimensional, zeolitic-type structures. The majority of the one- and two-dimensional materials have been synthesised under predominantly nonaqueous rather than aqueous conditions using alcoholic solvents such as butanol or ethylene glycol and they incorporate a range of organic-amine or complex-metal cations in the interlamellar or interchain voids. A second synthetic method has recently been developed involving crystallization of AlPOs from silica gels at room temperature (1) and it has produced additional new layered materials. For example, using pyridine as the structure-directing agent can give rise to either $(C_5H_6N)[Al_2(HPO_4)_2(PO_4)]$, in solvothermal synthesis in the presence of butan-2-ol (2), or $(C_5H_6N)[Al(HPO_4)_2(H_2O)_2]$, in aqueous silica gel (1).

Three series of layered AlPOs with P:Al ratios of 4:3 (3–15), 3:2 (2, 16–19) and 2:1 (1, 20, 21) and two chain series with P:Al 5:3 (8, 16) and 2:1 (15, 22–25) are now known. Although the stoichiometries of these compounds are somewhat limited in number, the materials show great structural diversity, as aluminium can adopt four, five or six coordination in oxygen-based polyhedra, giving rise to a variety of framework architectures. Pertinent to the present work are the layered AlPOs with P:A1 ratio 3:2 and framework composition $[Al_2(HPO_4)_x(PO_4)_{3-x}]^{(3-x)-}$ ($x = 1$ or 2). Table 1 summarizes the eight examples currently known, including the one described below, which can be assembled from combinations of AlO_5, AlO_4 and PO_4 polyhedra. Six distinct layer topologies have been identified, all of which contain 4-membered rings of alternating Al- and P-based polyhedra together with 6-rings and/or 8-rings.

In the present work we report the synthesis and characterisation of $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4]$, a new two-dimensional aluminium phosphate with P:A1 ratio 3:2 containing interlayer 2,2,6,6-tetramethylpiperidinium cations. The framework structure, which is the first with $x = 2$ to contain only AlO_4 and PO_4 polyhedra, has a new layer topology. The relationship between the new framework and that of $(C_5H_6N)[Al_2(HPO_4)_2(PO_4)]$ (Compound **V**) (2) is discussed.

EXPERIMENTAL

Single crystals of the title compound, $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$, were prepared under solvothermal conditions. Aluminium isopropoxide (1 g) was dispersed in butan-2-ol (7.76 cm^3) by stirring for about 10 min. 2,2,6,6-Tetramethylpiperidine (2 cm^3) was then added and the mixture stirred for a further 10 min. Finally, orthophosphoric acid (0.63 cm^3, 85% by weight) was added to give a gel of overall composition: $Al(OPr)_3$: 2.4 H_3PO_4(aq): 17.3 2-BuOH: 2.4 2,2,2.6,6,-tetramethylpiperidine. The gel was stirred until homogeneous, sealed in a Teflon-lined stainless-steel autoclave, and heated at 453 K for 8 days.

The solid product was collected by filtration, washed with deionized water, and left to dry in air at 343 K. The product contained white polycrystalline material and colorless

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[1] To whom correspondence should be addressed.

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TABLE 1
Summary of Layered AlPOs with P : Al Ratio 3 : 2

	Amine (T)	x^a	Polyhedral building units	Ring sizes^b	Ref.
I	2-Butylamine	1	AlO_4, PO_4	4, 6	2
II^c	Cyclopentylamine	1	AlO_4, PO_4	4, 6	16
III^c	Cyclohexylamine	1	AlO_4, PO_4	4, 6, 8	17
IV^c	Cyclohexylamine	1	AlO_4, PO_4	4, 6	17
V	Pyridine	2	AlO_4, AlO_5, PO_4	4, 8	2
VI	4-Methylpyridine	2	AlO_4, AlO_5, PO_4	4, 6	18
VII	1-Methylimidazole	2	AlO_4, AlO_5, PO_4	4, 6	19
VIII	2,2,6,6-Tetramethylpiperidine	2	AlO_4, PO_4	4, 8	This work

Note. Compounds **II** and **IV** have isostructural layers as do Compounds **VI** and **VII**.
^{a}x value in formula $(TH)_{3-x}[Al_2(HPO_4)_x(PO_4)_{3-x}]$.
^{b}Number of alternating Al- and P-based polyhedra enclosing ring.
^{c}Compounds **II**, **III**, and **IV** are also called UT3, UT4, and UT5, respectively.

rectangular plates of the title compound. The powder X-ray diffraction pattern of a bulk sample confirmed that the latter phase was the major component in the product, although a small amount of α-$AlPO_4$ (berlinite) was present as an impurity. Energy-dispersive X-ray emission analysis, performed using a JEOL 2000FX analytical electron microscope with α-$AlPO_4$ calibration standard, confirmed that the crystallites examined had P : Al ratios of ca. 3 : 2 and 1 : 1,

TABLE 2
Crystallographic Data for $[(C_9H_{20}N)][Al_2(HPO_4)_2(PO_4)]$

Formula	$C_9H_{22}NAl_2P_3O_{12}$
M_r	483.16
Crystal size (mm)	0.3 × 0.2 × 0.05
Crystal habit	Colourless plate
Crystal system	Triclinic
Space group	P-1
a (Å)	8.541 (3)
b (Å)	9.298(1)
c (Å)	12.660(5)
α (°)	73.26(2)
β (°)	89.58 (4)
γ (°)	87.70(2)
Cell volume (Å^3)	962.06
Z	2
Temperature (K)	295
ρ_{calc} (gcm^{-3})	1.668
$\mu_{CuK\alpha}$ (cm^{-1})	43.40
θ_{max}	72
Scan tye	$\omega - 2\theta$
Index ranges	$-10 \leq h \leq 10, -10 \leq k \leq 11, 0 \leq l \leq 15$
Unique data	3468
Observed data ($I > 3\sigma(I)$)	2049
R_{merge}	0.0261
Weighting scheme	Chebyshev 3 term
Residual electron density (min, max) (eÅ^{-3})	-0.31, 0.29
Number of parameters refined	251
R	0.0388
R_w	0.0447

TABLE 3
Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$

Atom	x	y	z	U_{eq}
Al(1)	0.6124(1)	0.3930(1)	0.3840(1)	0.0169
Al(2)	0.2195(1)	0.1120(1)	0.5100(1)	0.0165
P(1)	0.4516(1)	0.2718(1)	0.62119(8)	0.0160
P(2)	0.3805(1)	0.2203(1)	0.28289(9)	0.0183
P(3)	0.9083(1)	0.2052(1)	0.37859(9)	0.0176
O(1)	0.5397(4)	0.1627(3)	0.7142(3)	0.0244
O(2)	0.3005(4)	0.2089(4)	0.5922(3)	0.0251
O(3)	0.5532(4)	0.3178(4)	0.5181(3)	0.0289
O(4)	0.4061(4)	0.4130(3)	0.6547(3)	0.0254
O(5)	0.8086(3)	0.3471(3)	0.3703(3)	0.0251
O(6)	0.2415(4)	0.3085(5)	0.2220(3)	0.0365
O(7)	0.0360(3)	0.1931(3)	0.4642(3)	0.0250
O(8)	0.9797(4)	0.2098(3)	0.2666(3)	0.0281
O(9)	0.1977(3)	$-0.0728(3)$	0.5865(3)	0.0256
O(10)	0.5007(4)	0.3313(4)	0.2933(3)	0.0295
O(11)	0.3392(4)	0.1183(3)	0.3976(2)	0.0238
O(12)	0.4577(6)	0.1209(4)	0.2182(3)	0.0345
N(1)	$-0.2581(5)$	0.3142(4)	0.8188(3)	0.0274
C(1)	$-0.0911(6)$	0.2977(6)	0.7795(4)	0.0345
C(2)	0.0165(7)	0.3573(7)	0.8521(5)	0.0454
C(3)	$-0.0185(9)$	0.2969(7)	0.9760(6)	0.0506
C(4)	$-0.1841(9)$	0.3293(7)	1.0024(5)	0.0441
C(5)	$-0.3012(7)$	0.2632(5)	0.9416(4)	0.0315
C(6)	$-0.0514(7)$	0.1341(7)	0.7861(5)	0.0481
C(7)	$-0.0877(7)$	0.3913(7)	0.6606(5)	0.0414
C(8)	$-0.3032(7)$	0.0936(6)	0.9831(4)	0.0419
C(9)	$-0.4684(8)$	0.3276(7)	0.9462(5)	0.0503
H(8)	1.084(5)	0.249(6)	0.252(5)	0.05
H(12)	0.456(7)	0.013(4)	0.243(5)	0.05

Note. U_{eq} is defined as one-third the trace of the orthogonalised U_{ij} tensor.

the former being the majority phase. Repeating the synthesis using a gel containing stoichiometric amounts of phosphorus and aluminium in the ratio 3 : 2 did not improve the purity of the product.

Room-temperature X-ray diffraction data were collected from a crystal of the title compound using an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å)) (Table 2). The unit cell was determined as triclinic from the measurement of 25 well-centred reflections and the cell parameters optimized by least-squares refinement. Intensity data were then measured using the ω–2θ scan technique. Three standard reflections were measured every hour during the data collection and no significant intensity variations were observed. Data were corrected for absorption using ψ-scans and further corrected for Lorentz and polarization effects within the program RC93 (26). The structure was solved in the space group P-1 (No. 2 (27)) using the direct methods program SHELX-86 (28) and the framework aluminium, phosphorus and oxygen atoms located. All subsequent Fourier calculations and least-squares refinements were carried out using the CRYSTALS suite of programs (29). The carbon and nitrogen atoms of the template and the hydrogen atoms of the framework were then found in difference Fourier maps. Hydrogen atoms of the template were placed geometrically as it was not possible to locate their position in the Fourier maps. The positions of the hydrogen atoms of the framework hydroxyl groups were refined with O–H bond lengths restrained to be 1.00(5) Å and with isothermal parameters fixed at 0.05 Å^2. A correction for secondary extinction was applied (30). In the final cycle, 251 parameters, including anisotropic thermal parameters for all nonhydrogen framework and template atoms, were refined. A three-term Chebyshev polynomial was applied as the weighting scheme (31) and the refinement converged to give $R = 0.0388$ ($R_w = 0.0477$). Atomic coordinates and isotropic thermal

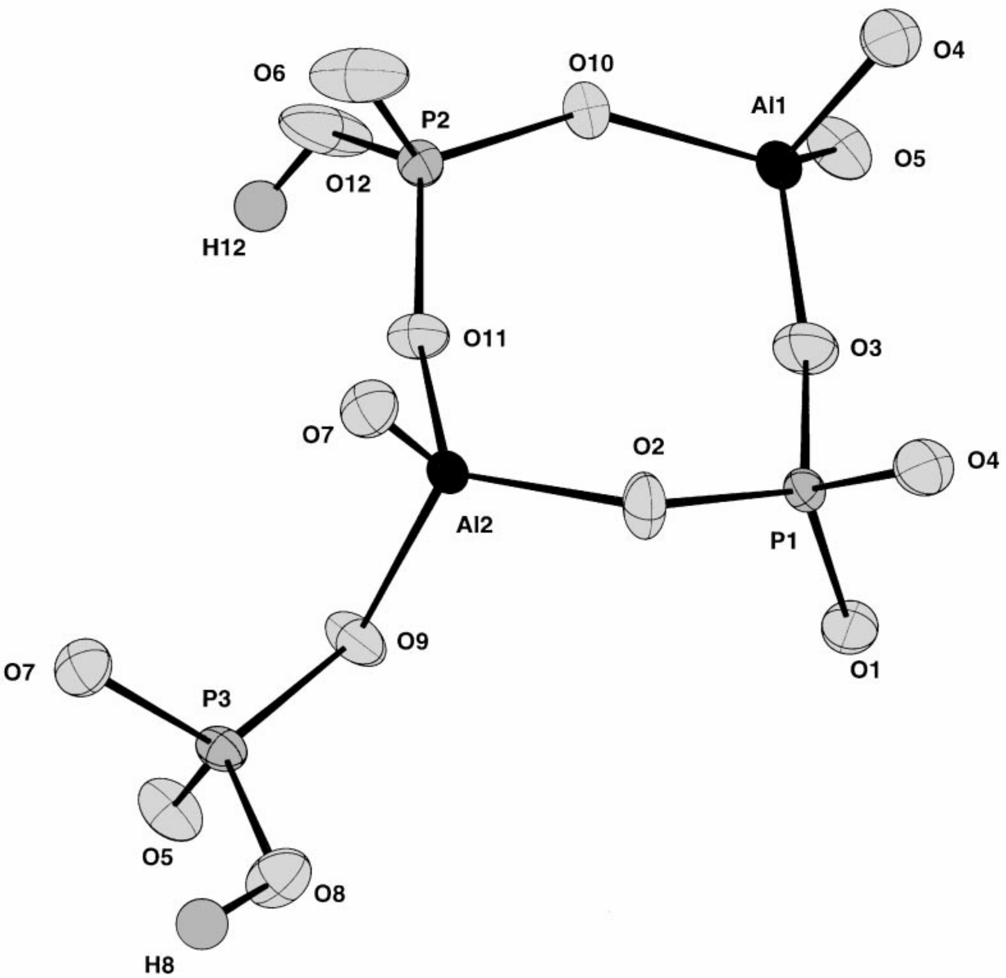

FIG. 1. The local coordination of the framework atoms in the title compound. Thermal ellipsoids at 50% probability. (Drawing package, CAMERON (32)).

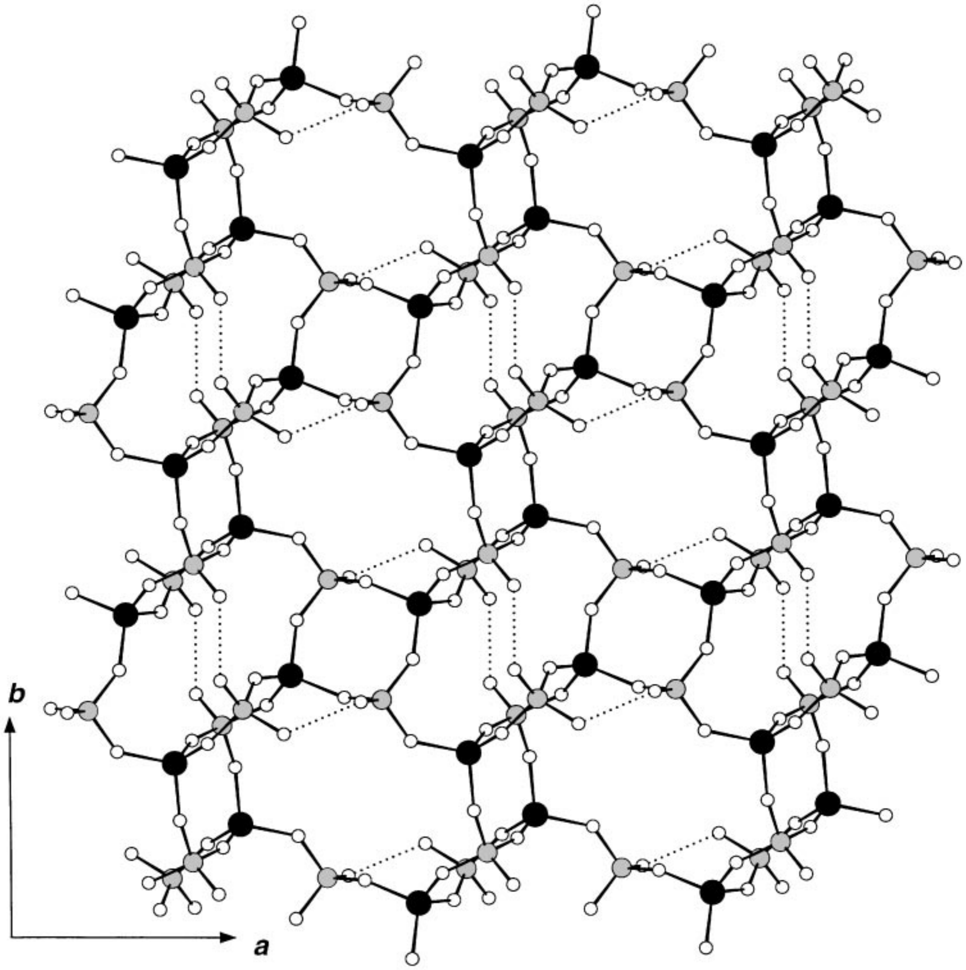

FIG. 2. View along the *c* axis of one $[Al_2(HPO_4)_2(PO_4)]^-$ layer showing the 4- and 8-membered rings of aluminium- and phosphorus-based tetrahedra. Hydrogen atoms have been omitted but intralayer hydrogen bonds are shown as dotted lines. Key: large black spheres = Al; large grey spheres = P; small white spheres = O.

parameters are given in Table 3 and selected interatomic distances and bond angles are given in Table 4.

DISCUSSION

The framework structure is assembled from a network of AlO_4 and PO_4 tetrahedra (Fig. 1). There are two crystallographically distinct AlO_4 units, both of which share all their vertices with phosphorus-based tetrahedra ($\text{Al–O}_{\text{av}} = 1.730$ Å $(\text{O–Al–O})_{\text{av}} = 109.5°$). Two of the three crystallographically distinct PO_4 units, $P(1)O_4$ and $P(3)O_4$, share three vertices with AlO_4 groups, whilst the third, $P(2)O_4$, shares only two vertices with AlO_4 groups. There are four terminal P–O bonds, two of which, P(2)–O(12) and P(3)–O(8), constitute P–OH groups, as confirmed by the location of the hydrogen atoms in Fourier maps. The remaining P–O bonds are slightly shorter than the average (P(1)–O(1) = 1.498(3) Å, P(2)–O(6) = 1.500(3) Å, $\text{P–O}_{\text{av}} = 1.521$ Å), suggesting they possess some degree of multiple bond character.

The aluminium- and phosphorus-based tetrahedra are linked to generate buckled anionic layers of formula $[Al_2(HPO_4)_2(PO_4)]^-$, which lie in the *ab* plane (Fig. 2) and stack in an *AAA* sequence (Figs. 3 and 4). The layers can be described as consisting of 4- and 8-membered rings of alternating AlO_4 and PO_4 polyhedra (Fig. 2). There are three crystallographically distinct 4-rings and two distinct 8-rings, both approximately elliptical in shape with cross-pore $O \cdots O$ distances in the ranges 3.929(6)–8.396(6) and 5.988(6)–7.871(6) Å, respectively. Strong hydrogen bonds exist within the layers between the P=O and P–OH groups. ($O(6) \cdots O(8)$, 2.451(5) Å and $O(1) \cdots O(12)$, 2.526(4) Å, but there are no interlayer hydrogen bonding interactions.

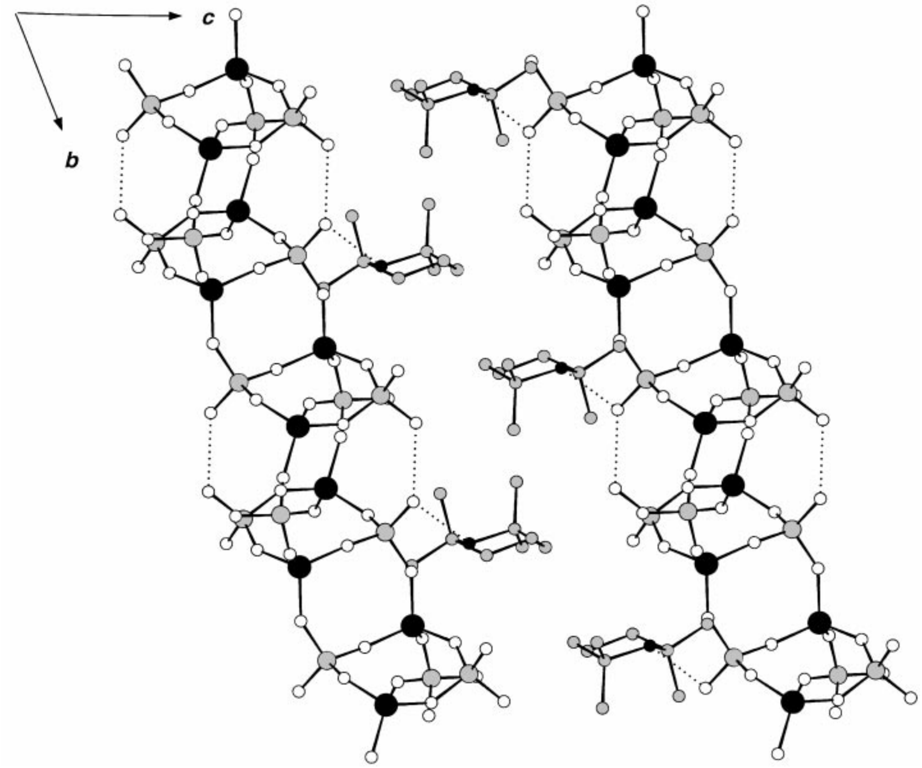

FIG. 3. View of the title compound along the *a* axis showing 2,2,6,6-tetramethylpiperidinium cations occupying sites between the AlPO layers. The intraframework and framework-amine hydrogen bonds are shown as dotted lines (intralayer distance O(1)···O(12), 2.526(4) Å; framework-amine distance, N(1)···O(1), 2.833(5) Å. Key: as for Fig. 2 with small black spheres = N; small grey spheres = C (hydrogen atoms are omitted).

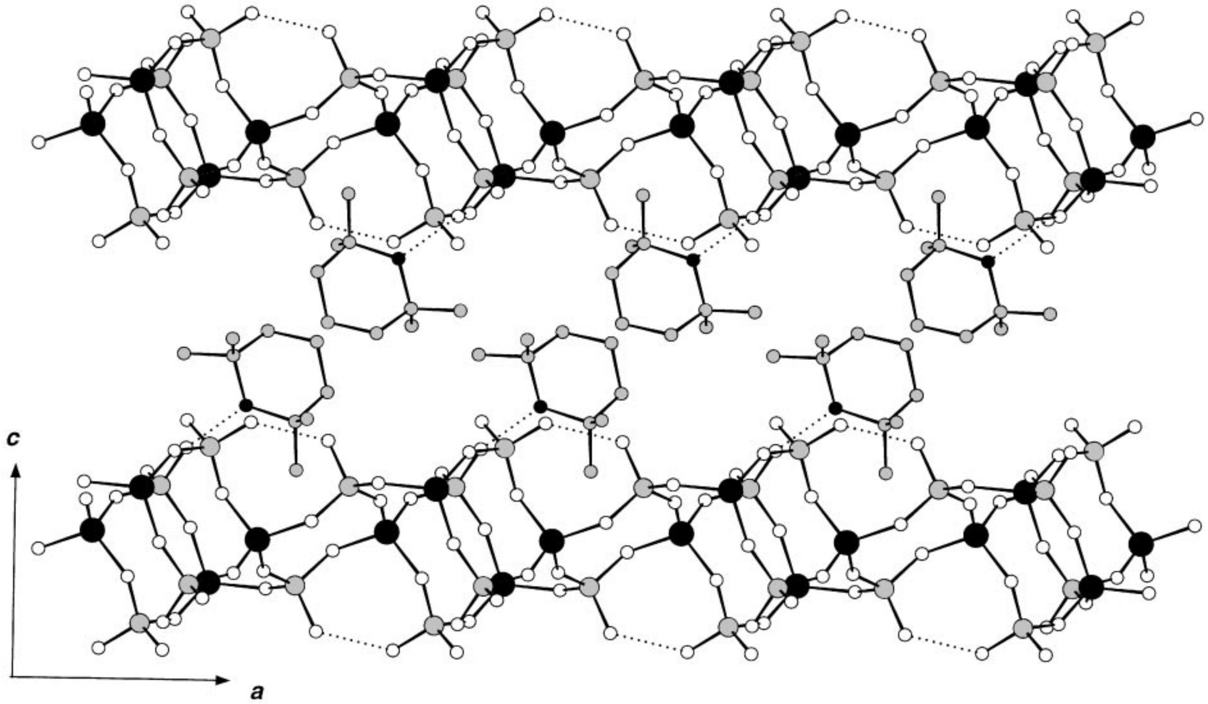

FIG. 4. View of title compound along *b* axis. The intraframework and framework-amine hydrogen bonds are shown as dotted lines (intralayer distance, O(6)···O(8), 2.451(5) Å; framework-amine distance, N(1)···O(1), 2.833(5) Å). Key: as for Fig. 2 with small black spheres = N; small grey spheres = C (hydrogen atoms are omitted).

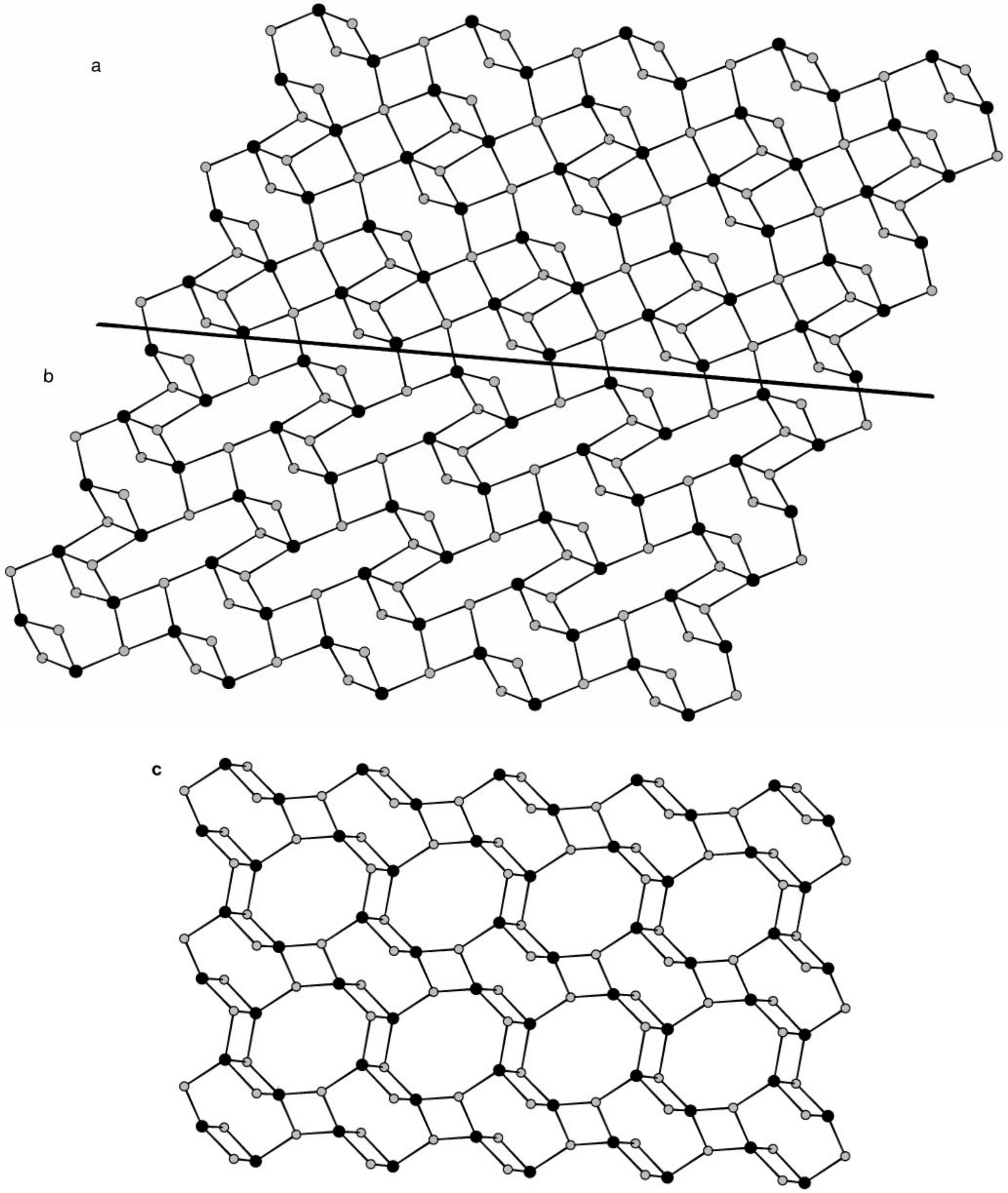

FIG. 5. The relationship between the aluminium-phosphorus layer networks (oxygen atoms omitted) of 4- and 8-membered rings in (a) $(C_5NH_6)[Al_2(HPO_4)_2(PO_4)]$ (Compound **V**) (2), (b) a theoretical form of $[Al_2(HPO_4)_2(PO_4)]^-$, and (c) the title compound, $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$. $(C_5NH_6)[Al_2(HPO_4)_2(PO_4)]$ shown in (a) contains both 4- and 5-connected Al atoms. Breaking the linkage between the pentacoordinated aluminium and one of the four-connected phosphorus atoms generates the layer topology shown in (b) which contains only 4-connected Al atoms and which is identical to that of the title compound in (c) Key: black spheres = Al; grey spheres = P.

TABLE 4
Selected Bond Distances (Å) and Angles (°) for $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$

Al(1)–O(3)	1.721(3)	P(1)–O(1)	1.498(3)
Al(1)–O(4)^{a}	1.729(3)	P(1)–O(2)	1.527(3)
Al(1)–O(5)	1.732(3)	P(1)–O(3)	1.527(3)
Al(1)–O(10)	1.731(3)	P(1)–O(4)	1.528(3)
Al(2)–O(2)	1.724(3)	P(2)–O(6)	1.500(3)
Al(2)–O(7)	1.740(3)	P(2)–O(10)	1.517(3)
Al(2)–O(9)	1.729(3)	P(2)–O(11)	1.536(3)
Al(2)–O(11)	1.735(3)	P(2)–O(12)	1.529(4)
		P(3)–O(5)	1.519(3)
N(1)–C(1)	1.524(7)	P(3)–O(7)^{b}	1.521(3)
N(1)–C(5)	1.535(6)	P(3)–O(8)	1.529(3)
C(1)–C(2)	1.530(8)	P(3)–O(9)^{c}	1.517(3)
C(1)–C(6)	1.524(8)		
C(1)–C(7)	1.507(7)	O(8)–H(8)	0.975(4)*
C(2)–C(3)	1.538(9)	O(12)–H(12)	0.961(4)*
C(3)–C(4)	1.49(1)		
C(4)–C(5)	1.518(8)		
C(5)–C(8)	1.512(7)		
C(5)–C(9)	1.534(8)		
A1(2)–O(2)–P(1)	144.5(2)	P(3)–O(8)–H(8)	116.82(6)
A1(1)–O(3)–P(1)	162.1(2)	P(2)–O(12)–H(12)	122.30(6)
A1(1)^{a}–O(4)–P(1)	147.3(2)		
A1(1)–O(5)–P(3)	136.9(2)		
Al(2)–O(7)–P(3)^{d}	144.2(2)		
A1(2)–O(9)–P(3)^{c}	147.6(2)		
A1(1)–O(10)–P(2)	145.3(2)		
A1(2)–O(11)–P(2)	141.8(2)		

Note. AlO_4 tetrahedra; O–Al–O angles in the range 106.8(2)–111.3(2)°. PO_4 tetrahedra; O–P–O angles in the range 107.1(2)–113.0(2)°. Amine template; N–C–C angles in the range 104.6(4)–110.6(4)°, C–C–C angles in the range 108.6(5)–113.(5)°.

*Chemical restraint applied.

Symmetry transformations used to generate equivalent atoms:

$^{a}1-x, 1-y, 1-z$.

$^{b}1+x, y, z$.

$^{c}1-x, -y, 1-z$.

$^{d}x-1, y, z$.

The negative charge on the AlPO layers is balanced by protonated 2,2,6,6-tetramethylpiperidine molecules, which stack in a zigzag arrangement parallel to the *b* axis (Fig. 3). The nitrogen atom of the template is hydrogen bonded to a single oxygen atom (N(1)–H ⋯ O(1), 2.833(5) Å) of the inorganic layer. Cohesion of the layers is due entirely to van der Waals interactions between corresponding methyl and methylene carbon atoms neighboring molecules and between methyl carbon atoms and oxygen atoms of the layers.

The title compound, $[C_9H_{20}N][Al_2(HPO_4)_2(PO_4)]$, has a new layered structure and is the eighth amine-containing A1PO to be prepared with a P:Al ratio of 3:2 (Table 1). The frameworks of the title compound and $(C_5NH_6)[Al_2(HPO_4)_2(PO_4)]$ (Compound **V**) (2) have closely related topologies; the former can be generated theoretically from the latter by breaking the linkage between the pentacoordinated aluminium and one of the four-connected phosphorus atoms (Fig. 5). Chemical ways of achieving this transformation are currently being investigated.

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