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Synthesis and structure of a 2-D aluminophosphate $Al_3P_4O_{16}\cdot 3CH_3CH_2CH_2NH_3$

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Using *n*-propylamine as a template, a new two-dimensional aluminophosphate $Al_3P_4O_{16}\cdot 3CH_3CH_2CH_2NH_3$, **1** [space group $P2_1/n$ (no. 14), $a = 11.310(1)$ Å, $b = 14.854(1)$ Å, $c = 14.796(1)$ Å, $\beta = 93.64(1)^\circ$, $Z = 4$] is synthesised in an alcoholic system and the structure is solved using single-crystal X-ray diffraction data. The structure consists of tetrahedral AlO_4 and $PO_3(=O)$ which are linked alternatively to form macroanionic layers parallel to the $(10\bar{1})$ plane. The organic cations ($C_3H_7NH_3^+$) are located in the interlayer regions and are connected to the oxgens of the layers by hydrogen bonding.The 2-D nets of compound **1** are constructed from 4.6.8-nets which resemble the 2-D nets $(4.6.8)_1(6.8.8)_1$ in microporous $AlPO_4$-21.

Introduction

Following the discovery of microporous aluminophosphates ($AlPO_4$-*n*) whose formation is promoted by the presence of organic templates,[1–3] a number of low-dimensional materials, *i.e.*, one-dimensional (1-D) chains and 2-D layers, have been successfully synthesized in non-aqueous systems.[4] These materials exhibit diverse stoichiometries with Al/P ratios lower than unity, in contrast to 3-D aluminophosphates with an Al/P ratio of 1/1 (except for JDF-20: $[Al_5P_6O_{24}H]^{2-}$ [5] and AlPO-HDA: $[Al_4P_5O_{20}H]^{2-}$ [6]). Among the 2-D layer compounds, three different stoichiometries have been observed, *i.e.*, $Al_3P_4O_{16}^{3-}$,[7–14] $Al_2P_3O_{12}^{3-}$,[15,16] and $AlP_2O_8^{3-}$.[14,17,18] In the case of $Al_3P_4O_{16}^{3-}$ compounds, except for $Al_3P_4O_{16}$-$2C_3N_2H_5$,[14] all the anionic inorganic layers are constructed from tetrahedral AlO_4 and $PO_3(=O)$ alternately linked to form 4.6-,[7,8] 4.6.8-,[9–11] and 4.6.12-nets.[12,13] The topologies of these 2-D nets show a resemblance to some of the three-connected 2-D nets in 3-D microporous compounds. For example, the 4.6.12-nets resemble the 2-D nets in $AlPO_4$-5.[19] Here we report a new 2-D aluminophosphate with 4.6.8-nets. The 4.6.8-nets resemble the 2-D nets in 3-D $AlPO_4$-21[19,20] that can be structurally directed by the same template, *n*-propylamine, as for the title compound.

Synthesis

Compound **1** was synthesised solvothermally in a reaction mixture of 1.0 $Al(OPr^i)_3$: 2.4 H_3PO_4 : 5.0 $CH_3CH_2CH_2NH_2$: 50 butan-2-ol at 180 °C for 9 days. $AlPO_4$-21 was prepared hydrothermally in a reaction mixture of 1.0 $Al(OPr^i)_3$: 1.0 H_3PO_4 : (0.5–1.0) $CH_3CH_2CH_2NH_2$: 100 H_2O at 180–220 °C for 9–12 days.[2,21] The synthesis procedure is identical for both compounds, except for the solvent. Aluminium triisopropoxide was first dispersed into weighed amounts of butan-2-ol or H_2O. Phosphoric acid (85%) was then added dropwise and the mixture was stirred continuously. Finally, *n*-propylamine was added to the mixture with further stirring to form a homogeneous gel. The reaction mixture was placed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 9 days under autogeneous pressure. The resulting product was filtered off and dried in air at 70 °C.

Powder X-ray diffraction (XRD) patterns were obtained on a Philips PW3050 X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å). The powder X-ray diffraction pattern of compound **1** shows good agreement with the simulated one based on single-crystal XRD structure analysis, establishing that the product is a single phase.

Single-crystal X-ray diffraction analysis

A colourless plate-like crystal of dimensions 0.16 × 0.80 × 0.03 mm was selected and mounted on a thin glass capillary using cyanoacrylate adhesive. The intensity data were measured on a Rigaku R-AXIS IV imaging-plate detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å) generated by a rotating anode X-ray tube. Details of data collection are listed in Table 1. The lattice constants were determined by a least-squares procedure applied to the measurement of 25 well centered reflections (2θ range 24.2–31.8°, Mo-Kα) on a Rigaku AFC7R diffractometer.

The structure was solved by direct methods using the program SIR92[22] and refined by the least-squares program SHELXL97.[23] In the final cycles of each refinement, non-hydrogen atoms except for C atoms were refined with anisotropic thermal parameters. Some C atoms have large thermal motions because the organic cations are located in large spaces

Table 1 Summary of data collection details for $Al_3P_4O_{16}\cdot 3CH_3CH_2CH_2NH_3$

Resolution range/Å	14.80–0.76
Total measured reflections	19 097
Unique reflections	5228
Possible reflections	6053
Completeness(%)	86.3
$R_{merge} = \sum \lvert \langle I \rangle - I_i \rvert / \sum I_i$ (%)	6.22
Oscillation angle per exposure	4.8
Total oscillation range	144.3
Camera length/mm	100
Exposure time per frame/min	30
Overlapped angle/°	0.3

Table 2 Crystal data and structure refinement for $Al_3P_4O_{16}\cdot 3CH_3CH_2CH_2NH_3$

Compound	$Al_3P_4O_{16}\cdot 3CH_3CH_2CH_2NH_3$
Empirical formula	$C_9H_{30}Al_3N_3O_{16}P_4$
Formula weight	641.18
Temperature/K	293(2)
Wavelength/Å	0.71069
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a/Å	11.310(1)
b/Å	14.854(1)
c/Å	14.796(1)
β/°	93.64(1)
Volume/Å^3	2480.7(4)
Z	4
D_c/g cm^{-3}	1.717
Absorption coefficient/mm^{-1}	0.488
F(000)	1328
Crystal size/mm	$0.160 \times 0.080 \times 0.030$
θ range for data collection/°	2.20–27.44
Index ranges	$0 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 17$, $-19 \leqslant l \leqslant 18$
Independent reflections ($I > 0$)	2620
No. obs. data [$I > 2\sigma(I)$]	1948
Adsorption correction	—
Refinement method	Full-matrix least-squares on F^2
No. of parameters refined	263
Goodness-of-fit on F^2	0.934
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0668$, $wR2 = 0.1146$
R indices (all data)	$R1 = 0.1111$, $wR2 = 0.1266$
Largest diff. peak and hole/e Å^{-3}	0.655, -0.467

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of compound **1**

Atom	x	y	z	U_{eq}[a]
P(1)	9162(2)	−2406(2)	4392(2)	12(1)
P(2)	8774(2)	−2608(2)	1286(2)	12(1)
P(3)	5862(3)	−923(1)	2402(2)	12(1)
P(4)	5867(3)	−4068(1)	2643(2)	13(1)
Al(1)	8668(3)	−1113(2)	2742(2)	12(1)
Al(2)	5963(2)	−2578(2)	1122(2)	10(1)
Al(3)	8662(3)	−3897(2)	2955(2)	11(1)
O(1)	10252(5)	−2327(3)	5057(4)	18(2)
O(2)	9231(7)	−1612(4)	3740(5)	18(2)
O(3)	8025(5)	−2393(4)	4853(5)	26(2)
O(4)	9317(7)	−3276(4)	3844(5)	22(2)
O(5)	4555(5)	−2315(4)	5514(4)	21(2)
O(6)	8964(7)	−3402(4)	1928(5)	22(2)
O(7)	9072(7)	−1738(4)	1812(5)	22(2)
O(8)	7470(5)	−2567(4)	955(4)	23(2)
O(9)	9223(7)	−4979(4)	3004(5)	23(2)
O(10)	5550(7)	−1584(4)	1623(5)	23(2)
O(11)	5069(8)	−1021(4)	3160(5)	29(2)
O(12)	7144(7)	−1088(4)	2754(5)	24(2)
O(13)	7155(7)	−3907(4)	3013(5)	25(2)
O(14)	5617(7)	−3476(4)	1813(5)	20(2)
O(15)	5028(7)	−3884(4)	3362(5)	26(2)
O(16)	9237(7)	−44(3)	2679(5)	21(2)
N(11)	6318(8)	−1079(4)	4822(6)	30(2)
C(12)	6479(13)	−104(8)	5088(11)	68(4)
C(13)	7722(15)	215(9)	4953(11)	75(5)
C(14)	8457(16)	−118(9)	5699(12)	89(6)
N(21)	6232(8)	−3625(4)	5093(6)	24(2)
C(22)	6347(12)	−4429(6)	5686(9)	50(3)
C(23)	7080(15)	−5193(9)	5186(12)	80(5)
C(24)	8339(18)	−4990(11)	5361(15)	117(7)
N(31)	3674(6)	−2415(5)	3694(5)	27(2)
C(32)	2351(11)	−2337(8)	3488(9)	61(4)
C(33)	2098(16)	−2536(12)	2448(13)	120(6)
C(34)	2160(3)	−3517(14)	2280(2)	275(18)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

between the layers and while one end of the cation is connected by hydrogen bonds to the oxygens of the layers (as will be discussed in the next section) the other end is free. The hydrogen atoms were geometrically placed. The isotropic thermal parameters of all the hydrogen atoms were constrained to be equal. A summary of the crystallographic data is given in Table 2.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/126.

Results and discussion

The atomic coordinates, and selected bond lengths and bond angles of compound **1** are given in Table 3 and 4, respectively.

The $Al_3P_4O_{16}{}^{3-}$ anionic layers are constructed from alternating tetrahedral Al and P units [Fig. 1(a)] and the labeling scheme is shown in Fig. 1(b). There are three crystallographically distinct Al sites. Each aluminium atom is coordinated to four phosphate groups. The Al–O bond lengths and O–Al–O bond angles are in the range 1.711(9)–1.746(7) Å and 106.0(3)–111.3(3)°, which are typical for aluminophosphates.[7–18] All the four crystallographically distinct P atoms share three oxygens with adjacent Al atoms and the P–O bond lengths are in the range 1.522 (6)–1.543(8) Å. The fourth P–O bond lengths for each P atom are P(1)–O(3) 1.493(6) Å, P(2)–O(5) 1.492(6) Å, P(3)–O(11) 1.488(8) Å and P(4)–O(15) 1.496(8) Å, which are the shortest among the others. These distances suggest that each crystallographically distinct P atom possesses one P=O group.[7–18]

The inorganic layer consists of a series of capped six-membered-rings (capped-6-MRs)† [Fig. 1(a)]. All the tetrahedral P(2) atoms cap the 6-MRs with the terminal oxygens protruding into the interlayer region above or below the sheet. The layer is constructed from corner sharing and edge sharing of these capped-6-MRs along [101] and [010], respectively, to form the 4.6.8-nets. It should be noted that the eight-membered-rings (8-MRs) possess both circular and elliptical shapes, as is the case in $[Al_3P_4O_{16}]^{3-}[NH_3(CH_2)_5NH_3]^{2+}$-$[C_5H_{10}NH_2]^+$,[10] in which the distortion of the 8-MRs was thought to be due to the differential templating effect of the two organic cations in the structure. However, in compound **1**, only one template species exists in the structure. The factors causing the distortion of 8-MRs are worth considering.

The organic ammonium cations ($CH_3CH_2CH_2NH_3{}^+$) reside in the interlayer regions between the inorganic layers, and the layers are stacked in AAAA sequence along the *c*-axis (Fig. 2). There are extensive H-bonding networks between the organic ammonium cations and the framework oxygens. The H-bonding information is summarised in Table 5. Each $RNH_3{}^+$ supplies three H atoms to form H-bonds with three different terminal oxygens attached to the phosphate groups. The O(5) atom attached to the capped phosphate P(2) group accepts three H atoms from three crystallographically distinct organic ammonium cations, whereas other terminal oxygens accept two H atoms from two crystallographically distinct templates to form H-bonds.

4.6.8-nets have been observed in several 2-D aluminophosphates, such as $[Al_3P_4O_{16}]^{3-}[NH_3(CH_2)_5NH_3]^{2+}$-$[C_5H_{10}NH_2]^+$ **2**,[10] $[Al_3P_4O_{16}]^{3-}[NH_3(CH_2)_2NH_3]^{2+}$-$[OH(CH_2)_2OH_2]^+[OH(CH_2)_2(OH)]$ **3**[9] and $[Al_3P_4O_{16}]^{3-}\cdot 3[CH_3CH_2NH_3]^{2+}$.[23] However, all 2-D structures with 4.6.8-nets possess the same topology, which is schematically shown in Fig. 3(a). The direction of the P=O in the capped phosphate groups is opposite to that of the other three P=O in the 6-MR. It is found that there are two typical stacking sequences of the inorganic layers, *i.e.*, AAAA (*e.g.* compound **2**[10]) and

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†*n*-MR represents a loop, where *n* is the number of T(Al or P)-atoms or O-atoms forming the loop.

Table 4 Selected bond lengths (Å) and angles (°) of compound **1**

P(1)–O(3)	1.493(6)	P(1)–O(2)	1.530(6)
P(1)–O(1)	1.532(6)	P(1)–O(4)	1.542(6)
P(2)–O(5)[a]	1.492(6)	P(2)–O(6)	1.521(6)
P(2)–O(8)	1.525(6)	P(2)–O(7)	1.534(6)
P(3)–O(11)	1.487(8)	P(3)–O(9)[b]	1.527(6)
P(3)–O(12)	1.528(8)	P(3)–O(10)	1.538(7)
P(4)–O(15)	1.496(8)	P(4)–O(14)	1.522(7)
P(4)–O(16)[c]	1.528(6)	P(4)–O(13)	1.541(8)
Al(1)–O(16)	1.718(6)	Al(1)–O(12)	1.725(9)
Al(1)–O(2)	1.736(7)	Al(1)–O(7)	1.745(7)
Al(2)–O(10)	1.728(6)	Al(2)–O(1)[d]	1.728(6)
Al(2)–O(8)	1.738(6)	Al(2)–O(14)	1.740(7)
Al(3)–O(13)	1.713(9)	Al(3)–O(9)	1.727(6)
Al(3)–O(4)	1.734(7)	Al(3)–O(6)	1.742(7)
N(11)–C(12)	1.51(1)	C(12)–C(13)	1.51(2)
C(13)–C(14)	1.43(2)	N(21)–C(22)	1.48(1)
C(22)–C(23)	1.61(2)	C(23)–C(24)	1.46(2)
N(31)–C(32)	1.51(1)	C(32)–C(33)	1.57(2)
C(33)–C(34)	1.48(2)		
O(3)–P(1)–O(2)	111.0(4)	O(3)–P(1)–O(1)	112.8(4)
O(2)–P(1)–O(1)	106.0(4)	O(3)–P(1)–O(4)	112.4(4)
O(2)–P(1)–O(4)	107.6(3)	O(1)–P(1)–O(4)	106.7(4)
O(5)[a]–P(2)–O(6)	110.5(4)	O(5)[a]–P(2)–O(8)	111.4(4)
O(6)–P(2)–O(8)	109.1(4)	O(5)[a]–P(2)–O(7)	109.3(4)
O(6)–P(2)–O(7)	108.6(3)	O(8)–P(2)–O(7)	107.9(4)
O(11)–P(3)–O(9)[b]	111.1(4)	O(11)–P(3)–O(12)	109.4(5)
O(9)[b]–P(3)–O(12)	108.4(4)	O(11)–P(3)–O(10)	112.5(4)
O(9)[b]–P(3)–O(10)	106.6(4)	O(12)–P(3)–O(10)	108.7(4)
O(15)–P(4)–O(14)	112.0(4)	O(15)–P(4)–O(16)[c]	110.8(4)
O(14)–P(4)–O(16)[c]	106.9(4)	O(15)–P(4)–O(13)	110.2(4)
O(14)–P(4)–O(13)	108.7(4)	O(16)[c]–P(4)–O(13)	108.1(4)
O(16)–Al(1)–O(12)	111.0(4)	O(16)–Al(1)–O(2)	108.8(4)
O(12)–Al(1)–O(2)	108.3(4)	O(16)–Al(1)–O(7)	109.4(4)
O(12)–Al(1)–O(7)	109.4(4)	O(2)–Al(1)–O(7)	110.1(4)
O(10)–Al(2)–O(1)[d]	109.7(3)	O(10)–Al(2)–O(8)	110.3(4)
O(1)[d]–Al(2)–O(8)	105.9(3)	O(10)–Al(2)–O(14)	109.0(3)
O(1)[d]–Al(2)–O(14)	111.3(3)	O(8)–Al(2)–O(14)	110.5(4)
O(13)–Al(3)–O(9)	110.7(4)	O(13)–Al(3)–O(4)	110.2(4)
O(9)–Al(3)–O(4)	109.0(3)	O(13)–Al(3)–O(6)	107.3(4)
O(9)–Al(3)–O(6)	109.8(4)	O(4)–Al(3)–O(6)	109.8(4)
P(1)–O(1)–Al(2)[e]	152.6(4)	P(1)–O(2)–Al(1)	146.6(5)
P(1)–O(4)–Al(3)	142.0(5)	P(2)–O(6)–Al(3)	147.6(5)
P(2)–O(7)–Al(1)	141.9(5)	P(2)–O(8)–Al(2)	153.0(4)
P(3)[c]–O(9)–Al(3)	145.5(5)	P(3)–O(10)–Al(2)	144.2(5)
P(3)–O(12)–Al(1)	157.9(5)	P(4)–O(13)–Al(3)	154.7(5)
P(4)–O(14)–Al(2)	151.6(5)	P(4)[b]–O(16)–Al(1)	150.7(5)
C(13)–C(12)–N(11)	111.(1)	C(14)–C(13)–C(12)	107.(1)
N(21)–C(22)–C(23)	109.(1)	C(24)–C(23)–C(22)	107.(1)
N(31)–C(32)–C(33)	107.(1)	C(34)–C(33)–C(32)	110.(2)

Symmetry transformations used to generate equivalent atoms: [a] $x+1/2, -y-1/2, z-1/2$ [b] $-x+3/2, y+1/2, -z+1/2$; [c] $-x+3/2, y-1/2, -z+1/2$; [d] $x-1/2, -y-1/2, z-1/2$; [e] $x+1/2, -y-1/2, z+1/2$; [f] $x-1/2, -y-1/2, z+1/2$.

ABAB (*e.g.* compound **3**[9]). Taking account of the 8-MR shape, two types of configurations are observed. In the case of compound **1** and **2** mentioned above, the inorganic layers contain two types of 8-MR systems with both circular and elliptical shape, whereas all the other layers contain regular elliptical 8-MRs.

It is worth mentioning that the 4.6.8-nets in the 2-D aluminophosphates resemble the $(4.6.8)_1(6.8.8)_1$ 2-D net (node 401) in 3-D microporous $AlPO_4$-21 as shown in Fig. 3(b) (its 3-D structure can be represented by the addition of up–down linkages to the 2-D nets).[19] An obvious difference of the 2-D nets in 2-D layer compounds from that in 3-D $AlPO_4$-21 lies in the presence of capped phosphate groups in the 6-MRs . It can be seen that if the capped phosphate groups are removed from the 6-MRs in the 2-D layer network, all the tetrahedral Al and P become three-connected, like the 2-D net in $AlPO_4$-21.

Interestingly, the 3-D microporous $AlPO_4$-21 can be synthesized in an aqueous system using the same template, *n*-propylamine, as for compound **1**. However, compound **1** can only be prepared in non-aqueous systems. It is known that non-aqueous systems favour the formation of low-dimensional materials. It should be noted that most of the low-dimensional materials were synthesized in non-aqueous systems. The existence of triply, doubly, or singly-bridging phosphate groups with terminal oxygens (P=O /or P–OH) in the low-dimensional

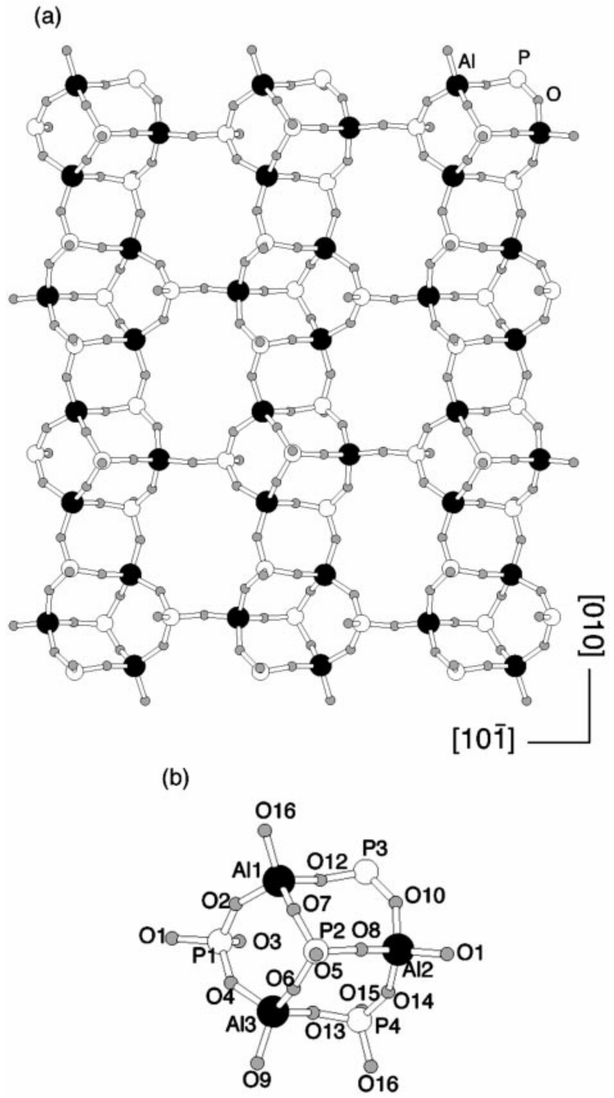

Fig. 1 (a) The inorganic sheet parallel to the (10$\bar{1}$) plane and (b) capped-6-MR showing the labeling scheme.

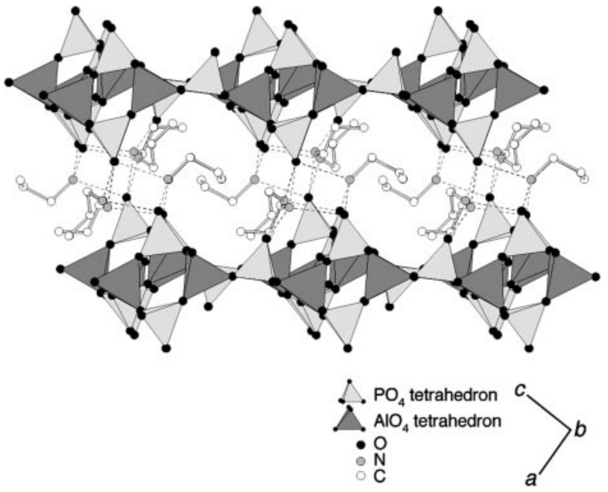

Fig. 2 View of the stacking of the layers with the interlamellar organic cations; H-bondings are indicated by dashed lines.

Table 5 Hydrogen-bonding distances (Å) present in $Al_3P_4O_{16}\cdot 3CH_3CH_2CH_2NH_3$

	Distance N–H···O
N11–H113···O3	2.74 (1)
N11–H111···O11	2.76 (1)
N11–H112···O5	2.94 (1)
N21–H212···O5	2.81 (1)
N21–H213···O15	2.85 (1)
N21–H211···O3	2.77 (1)
N31–H312···O5	2.82 (1)
N31–H313···O11	2.75 (1)
N31–H311···O15	2.73 (1)

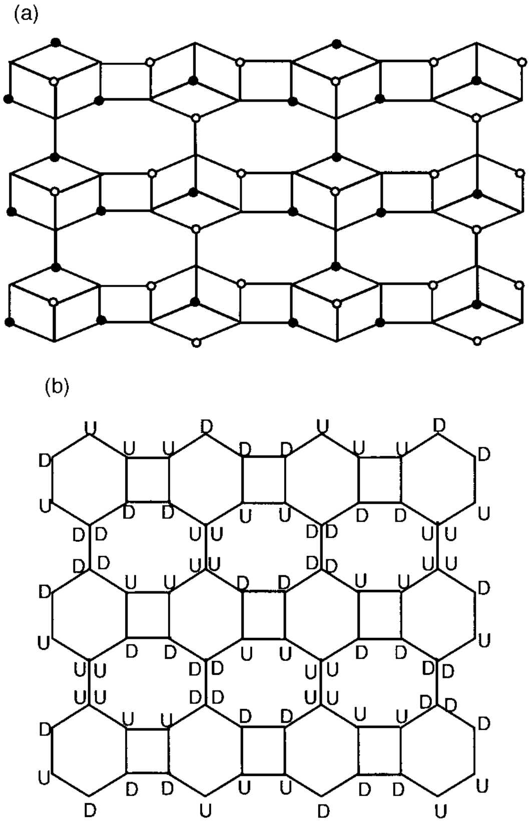

Fig. 3 (a) Topology of 4.6.8-nets in aluminophosphate with $Al_3P_4O_{16}{}^{3-}$ stoichiometry. The open and filled circles represent the positions of P atoms and correspond to the different directions of P=O bonds relative to the inorganic sheet, that is, face up and down, respectively. The nodes without circles represent those of Al atoms. Oxygen positions are not shown but are located about half-way between P and Al atoms. (b) $(4.6.8)_1(6.8.8)_1$ 2-D net in $AlPO_4$-21[19].

materials impedes the formation of a 3-D structure. Therefore, such terminal oxygen groups are suggested to be more stabilized in non-aqueous systems compared to aqueous systems.

Conclusion

The utilization of a non-aqueous synthesis technique has greatly extended the aluminophosphate family upon continuing synthesis of a number of low-dimensional materials. A new compound $Al_3P_4O_{16}\cdot 3CH_3CH_2CH_2NH_3$ was prepared in an alcoholic system in the presence of *n*-propylamine. Its structure consists of alternately linked tetrahedral AlO_4 and $PO_3(=O)$ to give $Al_3P_4O_{16}{}^{3-}$ stoichiometry. The 2-D inorganic nets are constructed from 4.6.8-nets which resemble the $(4.6.8)_1(6.8.8)_1$ 2-D nets in 3-D microporous $AlPO_4$-21, which can be also synthesized using the same template (*n*-propylamine) but in aqueous systems. Further investigation of the formation mechanism in different solvent systems might prove to be a valuable contribution towards achieving a rational design of target materials.

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