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Synthesis and structure of a new layered aluminium phosphate: $[BuNH_3]_3[Al_3P_4O_{16}]$

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A new two-dimensional aluminium phosphate, $[BuNH_3]_3[Al_3P_4O_{16}]$, has been synthesized under solvothermal conditions at 453 K using butylamine as template. The structure, solved using single-crystal X-ray diffraction data measured at 200 K [trigonal, space group $P\bar{3}$, $a = 13.158(2)$, $c = 9.633(2)$ Å, $U = 1444.4$ Å^3, $Z = 2$], consists of *AAAA*-stacked $[Al_3P_4O_{16}]^{3-}$ layers containing 12-membered rings of alternating AlO_4 and PO_4 tetrahedra. Disordered butylammonium cations lie between the layers with their hydrophobic tails pointing into the channels bounded by the 12-membered rings.

Microporous solids find widespread application in a variety of important technological processes including heterogeneous catalysis, molecular sieving and ion exchange.[1,2] Recently, the scope has been extended to include their use as ceramic precursors[3,4] and as hosts for quantum wires[5] and quantum dots.[6] Traditionally research in this area has concentrated on aluminosilicate zeolites but many open-framework organically templated phosphates, containing a variety of metals including Al, Be, Ga, In, Zn and transition metals such as V, Fe, Co and Mo, are now known. These examples all have three-dimensional network structures. In addition, there exist a number of layered phosphate materials which can be thought of as analogues of clays. Two series of layered aluminium phosphates with P : Al ratios of 4 : 3[7–18] and 3 : 2,[19–21] in which the interlamellar spaces are occupied by either organic amine cations or metal complexes such as $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine), have been characterised to date. For the compounds with P : Al ratio of 4 : 3, which are pertinent to this paper, three distinct two-dimensional networks have been identified which contain alternating AlO_4 and PO_4 tetrahedra in four- and six-,[12,17,18] four- and eight-[8–11] or four- and 12-membered rings.[7,13–15] By controlling the structural nature and stacking sequence of the aluminium phosphate layers, it has been possible to produce materials which are inherently microporous.[7] Here we report the synthesis and characterisation of a new layered aluminium phosphate with P : Al ratio of 4 : 3. The topology of an individual layer is the same as that previously observed in three other aluminium phosphates containing intercalated diammonium cations.[7,14,15] However, here we demonstrate that the replacement of these diammonium-intercalated species by an alkyl monoammonium intercalate produces changes in the hydrogen-bonding pattern between the layers, and hence a different layer stacking sequence.

Experimental

Synthesis and initial characterisation

The compound $[BuNH_3]_3[Al_3P_4O_{16}]$ **A** was synthesized from a gel of composition $Al(OPr^i)_3$: 2.4 H_3PO_4 (aq) : 17.4 BuOH : 5.1 $NBuH_2$. Typically, aluminium isopropoxide (1 g) and phosphoric acid (85% w/w, 0.63 cm^3) were added to butan-1-ol (7.86 cm^3). The mixture was stirred until homogeneous and the butylamine (2.47 cm^3) added. The gel was heated at 453 K in a Teflon-lined autoclave under autogenous pressure for 10 d. Several crystals were retained in the mother-liquor but the bulk solid product was collected by filtration, washed with distilled water and briefly dried in air at 353 K. It consisted entirely of colourless hexagonal prismatic crystals which readily cleaved into hexagonal plates.

There was good agreement between the measured powder X-ray diffraction pattern and the one calculated using the single-crystal data results below with the exception of one unidentifiable peak of low intensity at $d = 9.87$ Å. Energy-dispersive X-ray emission analysis of a finely ground sample of the crystals, determined using a JEOL 2000FX analytical electron microscope, showed that the product was essentially monophasic with a constant phosphorus : aluminium ratio [for 17 crystallites examined P : Al = 0.75(3)] {Combustion analysis, Found: C, 20.92; H, 5.34; N, 6.29. Calc. for $[CH_3(CH_2)_3NH_3]_3[Al_3P_4O_{16}]$: C, 21.09; H, 5.31; N, 6.15%}, confirming that butylamine was present in the product.

Crystallography

Single-crystal X-ray diffraction data were collected using an Enraf-Nonius MACH 3 (CAD4) diffractometer (graphite-monochromated Cu-Kα radiation, $\lambda = 1.5418$ Å) fitted with an Oxford Cryosystems Cryostream cooler. The selected crystals were removed from the mother-liquor without washing and sealed into capillaries as prolonged exposure to air caused the crystals to fragment normal to the three-fold axis.

The unit-cell dimensions were determined from 25 well centred reflections at 293 and 200 K and found to be trigonal at both temperatures [293 K: $a = 13.173(2)$ and $c = 9.647(2)$ Å. 200 K: $a = 13.158(2)$ and $c = 9.633(2)$ Å].

Intensity data were collected at 200 K using the ω–2θ scan technique over the range $2 \leqslant \theta \leqslant 72°$. The crystal was supported in a fibre loop containing perfluoropolyether oil during the data collection. There were no clear systematic absences so the correct choice of Laue group was made by comparing possible equivalent reflections. The space group chosen was $P\bar{3}$ (no. 147)[22] which was confirmed by successful refinement of the structure. X-Ray absorption was measured using ψ scans. Data reduction was performed using the program RC 93.[23] The structure was solved by direct methods using the program SHELXS

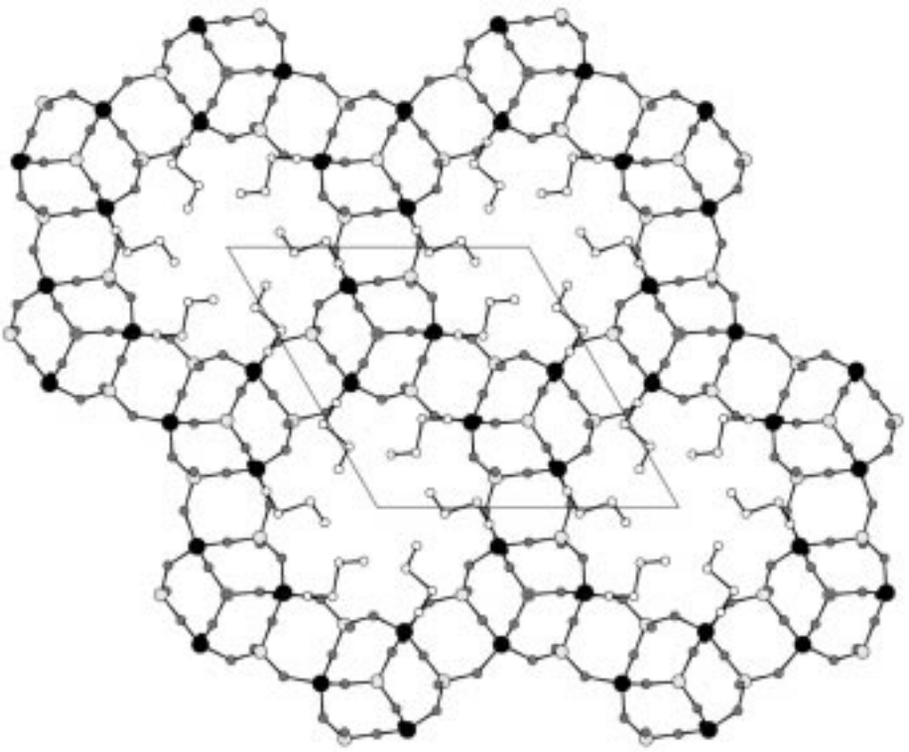

Fig. 1 View of compound **A** along the *c* axis showing the predominant conformer of the butylammonium cation located in 12-membered rings. Key: large black circle, Al; large light grey circle, P; small dark grey circle, O; small black circle, N; open circle, C; hydrogen atoms have been omitted. Drawing package CAMERON [31]

86 [24] and the framework atoms located. All subsequent Fourier calculations and full-matrix least-squares refinements were carried out using the program CRYSTALS.[25] Peaks in the observed Fourier map were interpreted as being due to template carbon and nitrogen atoms. However, it became clear during the course of the refinement that the butylammonium cation was conformationally disordered. A second site for each of the nitrogen and carbon atoms was located in a Fourier-difference map. As a consequence of the disorder it was necessary to apply restraints to the bond lengths and angles of the template cations.[26,27] Thus, the N(1)–C(2) and N(11)–C(12) bond lengths were restrained to be 1.48(1) Å, C(2)–C(3) and C(12)–C(13) to be 1.52(1) Å and the remaining C–C bond lengths to be 1.54(1) Å. All N–C–C and C–C–C bond angles were restrained to be 108(2)°. A single isotropic thermal parameter was refined for each pair of equivalent atoms in the two template fragments and the hydrogen atoms were placed geometrically after each cycle of refinement. A total of 106 parameters was included in the final stages of refinement based on *F* and a weighting scheme based on a three-term modified Chebyshev polynomial [28] applied. The final cycle of refinement converged at $R = 0.065$ and $R' = 0.072$. Crystal and experimental data for compound **A** at 200 K are given in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/563.

Results and Discussion

Atomic parameters, bond lengths and angles for compound **A** are given in Tables 2 and 3.

The structure consists of macroanionic layers of empirical formula $[Al_3P_4O_{16}]^{3-}$ with charge balancing $[BuNH_3]^+$ cations located between the layers. The inorganic framework is formed

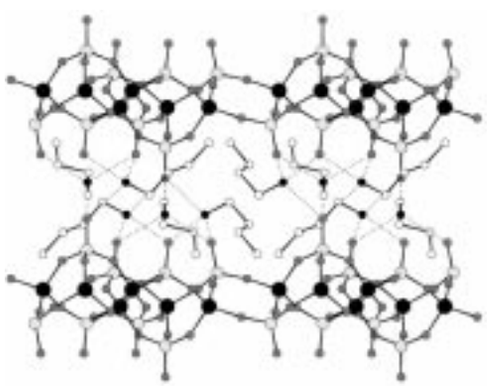

Fig. 2 View of compound **A** parallel to the aluminium phosphate layers. Hydrogen bonds, represented by dotted lines, are shown between the predominant conformer of the butylammonium cation and the aluminium phosphate layers (key as for Fig. 1)

from a network of alternately linked corner-sharing AlO_4 and PO_4 tetrahedra with all the vertices of the aluminium-centred tetrahedra, but only three-quarters of the phosphorus-centred tetrahedra, being shared. This results formally in a phosphoryl (P=O) group on each of the two distinct phosphorus atoms. The average bridging Al–O and P–O distances [1.732(3) and 1.530(6) Å respectively] compare well with those seen in berlinite (1.739 and 1.516 Å respectively) [29] and the P(1)=O(2) and P(2)=O(5) bond lengths of 1.498(6) and 1.488(4) Å respectively are in good agreement with those found for terminal phosphoryl groups in $H_3PO_4 \cdot 0.5H_2O$ (1.497 and 1.485 Å).[30]

The layers contain approximately circular 12-membered rings (average O · · · O diameter ≈9.56 Å) which are surrounded by a series of four-membered rings (Fig. 1). The P(1)=O(2) and P(2)=O(5) groups alternate above and below the plane of the 12-membered rings. Two distinct template sites, of occupancies 0.83(1) and 0.17(1), have been located in the interlayer space and both have essentially the same conformation. The C_4H_9 fragments are approximately planar and have the *anti* conform-

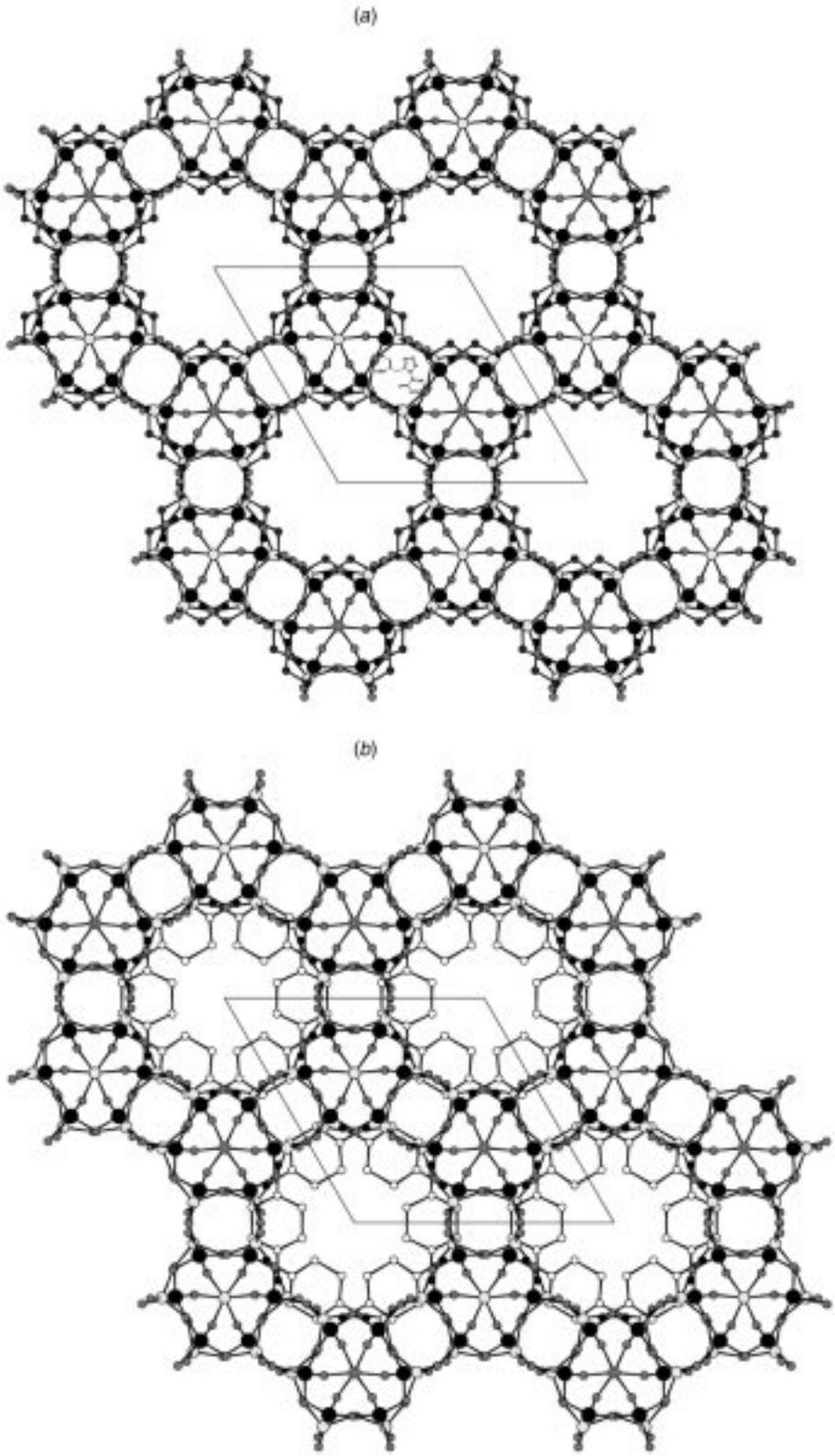

Fig. 3 View of compounds (*a*) $[NH_3(CH_2)_4NH_3]_{1.5}[Al_3P_4O_{16}]\cdot 1.8H_2O$ **B** and (*b*) $[C_6H_{16}N_2]_{1.5}[Al_3P_4O_{16}]\cdot 2H_2O$ **C** along their respective *c* axes showing the effect of the different diamine templates on pore size. Water molecules located in the centres of the pores are not shown. Key as for Fig. 1

ation expected on steric grounds. The NH_3 groups are not, however, coplanar with the alkyl groups. The more occupied template site is located such that the NH_3 group forms three moderately short hydrogen bonds, two of which are to phosphoryl groups in one adjacent aluminophosphate layer [N(1)···O(5) 2.73(1) and N(1)···O(5′) 2.88(1) Å] while the third is to a phosphoryl group in the other adjacent layer [N(1)···O(2) 2.81(1) Å] (Fig. 2). The NH_3 group of the second, lower-occupancy, template site forms only two hydrogen bonds of length under 3 Å, both of which are to phosphoryl groups of the same layer [N(11)···O(5) 2.92(2) and N(11)···O(5′) 2.82(2) Å]. The alkyl group of this site projects further into the 12-membered ring than that of the higher-occupancy case. When viewed along the *c* axis (Fig. 1) it can be seen that the hydrophobic alkyl groups point towards the centre of and block the channels generated by alignment of the 12-membered rings. There are no direct hydrogen bonds between adjacent aluminophosphate layers and the resulting weakness

of the intralayer forces is reflected in the ease of cleavage of the crystals parallel to the layers.

Layers with the same connectivity have been observed previously in compounds $[NH_3(CH_2)_4NH_3]_{1.5}[Al_3P_4O_{16}]\cdot 1.8H_2O$ **B**,[7] $[C_6H_{16}N_2]_{1.5}[Al_3P_4O_{16}]\cdot 2H_2O$ **C**,[14] and $[NH_3(CH_2)_5NH_3]_{1.5}[Al_3P_4O_{16}]\cdot 2H_2O$ **D**[15] which contain the diamine templates 1,4-diaminobutane, 1,4-diaminocyclohexane and 1,4-diaminopentane respectively. In all cases, the alignment of the 12-membered rings to create channels parallel to the *c* axis is preserved. However the stacking of the layers in these compounds is different to that found for compound **A**. In **A** the layers stack in an *AAAA* sequence whereas in **B**, **C** and **D** an *ABAB* sequence is observed with accompanying doubling of the *c*-axis lattice parameter (Table 4).

The interchain N · · · N separations in the diamine cations in **B**, **C** and **D** are similar (5.82–6.12 Å) as are the hydrogen-bonding schemes. In these cases, as for **A**, the nitrogen atoms of the template ions are hydrogen bonded to the terminal phosphoryl oxygens of the layers. At one end of the dication the nitrogen forms two hydrogen bonds to oxygen atoms of two P=O groups in the layer above and a third to a P=O group in the layer below, whereas the second nitrogen of the chain forms two hydrogen bonds to the layer below and one to the layer above. Both ends of the template are now involved in hydrogen bonding and the template does not block the channels to the same extent as the C_4H_9 groups do in **A**.

Thus the layered materials **B**, **C** and **D** can now possess inherent microporosity perpendicular to the *c* axis (Fig. 3). In **B** the resulting channel size is ≈6.6 Å and adsorption of species such as benzene has been demonstrated experimentally.[7] In **C** the channel size is reduced to ≈3.3 Å by the pore-blocking action of the cyclic template dication, thus limiting the size of the sorbates which can be adsorbed through the 12-membered rings.[14] In **D**, however, the severe disorder of the carbon chain of the template cation, which is to be expected given that for the observed constant N · · · N separation in the diamine compounds and the chain of five carbon atoms must have the same overall length as the four-carbon chains in **B** and **C**, makes it

Table 1 Crystallographic data for compound **A**, $[BuNH_3]_3[Al_3P_4O_{16}]$

Formula	$C_{12}H_{36}Al_3N_3O_{16}P_4$
M	683.27
Crystal system	Trigonal
Space group	*P*$\bar{3}$ (no. 147)
a/Å	13.158(3)
c/Å	9.633(2)
U/Å^3	1444.4
Z	2
D_c/g cm^{-3}	1.572
T/K	200
F(000)	717.5
Crystal size/mm	0.21 × 0.06 × 0.06
μ(Cu-Kα)/cm^{-1}	39.98
2θ Range/°	2–144
Transmission coefficients (maximum, minimum)	1.00, 0.90
Unique data	1888
Observed data [$I > 3\sigma(I)$]	1332
R_{merge}	0.063
Number of parameters	106
Goodness of fit	1.12
R	0.065[a]
R′	0.072[b]
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e Å^{-3}	−0.62, 1.01

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 3 Selected interatomic contacts (Å) and angles (°) with e.s.d.s in parentheses for compound **A**

Al(1)–O(1)	1.740(3)	Al(1)–O(4)	1.736(3)
Al(1)–O(3)	1.736(3)	Al(1)–O(6)	1.718(3)
P(1)–O(1) × 3	1.530(3)	P(2)–O(4)	1.529(3)
P(1)–O(2)	1.498(6)	P(2)–O(5)	1.488(4)
P(2)–O(3)	1.527(3)	P(2)–O(6)	1.531(3)
N(1)–C(2)*	1.476(7)	N(11)–C(12)*	1.47(1)
C(2)–C(3)*	1.539(8)	C(12)–C(13)*	1.51(1)
C(3)–C(4)*	1.545(9)	C(13)–C(14)*	1.54(1)
C(4)–C(5)*	1.525(8)	C(14)–C(15)*	1.54(1)
O(1)–Al(1)–O(3)	109.0(2)	O(1)–Al(1)–O(6)	109.7(2)
O(1)–Al(1)–O(4)	110.3(1)	O(3)–Al(1)–O(6)	110.0(1)
O(3)–Al(1)–O(4)	109.9(1)	O(4)–Al(1)–O(6)	108.0(2)
O(1)–P(1)–O(1) × 3	108.7(1)	O(4)–P(2)–O(5)	112.4(2)
O(1)–P(1)–O(2) × 3	110.2(1)	O(3)–P(2)–O(6)	108.7(1)
O(3)–P(2)–O(4)	106.7(2)	O(4)–P(2)–O(6)	108.1(2)
O(3)–P(2)–O(5)	111.0(2)	O(5)–P(2)–O(6)	109.7(2)
Al(1)–O(1)–P(1)	146.8(2)	Al(1)–O(4)–P(2)	142.8(2)
Al(1)–O(3)–P(2)	144.0(2)	Al(1)–O(6)–P(2)	162.5(2)
N(1)–C(2)–C(3)*	110.1(6)	N(11)–C(12)–C(13)*	100.4(16)
C(2)–C(3)–C(4)*	106.2(7)	C(12)–C(13)–C(14)*	110.4(17)
C(3)–C(4)–C(5)*	110.7(8)	C(13)–C(14)–C(15)*	104.4(18)

* Formed part of a chemical restraint in the refinement.

Table 2 Atomic parameters with estimated standard deviations (e.s.d.s) in parentheses for non-hydrogen atoms in compound **A** at 200 K

Atom	*x*	*y*	*z*	U_{iso}	Occupancy*
Al(1)	0.673 57(8)	0.148 68(8)	0.457 7(1)	0.012 0	
P(1)	2/3	1/3	0.258 3(2)	0.017 7	
P(2)	0.552 11(7)	−0.114 02(1)	0.373 5(1)	0.013 3	
O(1)	0.676 2(2)	0.229 3(2)	0.313 2(4)	0.028 0	
O(2)	2/3	1/3	0.102 8(6)	0.038 4	
O(3)	0.647 9(2)	0.012 0(2)	0.403 6(3)	0.017 8	
O(4)	0.806 1(2)	0.221 5(2)	0.546 1(3)	0.020 1	
O(5)	0.541 0(3)	−0.138 4(3)	0.221 8(4)	0.035 8	
O(6)	0.564 5(2)	0.132 5(2)	0.569 2(4)	0.024 2	
N(1)	0.165 8(4)	0.501 4(6)	0.081 2(5)	0.036 0	0.827(6)
C(2)	0.062 6(6)	0.400 8(6)	0.017 1(8)	0.055 3	0.827(6)
C(3)	−0.021 2(8)	0.319 7(8)	0.130(1)	0.086 5	0.827(6)
C(4)	0.022 1(7)	0.233 8(8)	0.169(1)	0.075 7	0.827(6)
C(5)	−0.056(1)	0.147(1)	0.280(1)	0.099 0	0.827(6)
N(11)	0.108(2)	0.450(2)	0.151(2)	0.036 0	0.173(6)
C(12)	−0.007(3)	0.341(2)	0.101(3)	0.055 3	0.173(6)
C(13)	−0.027(3)	0.268(3)	0.232(4)	0.086 5	0.173(6)
C(14)	0.011(4)	0.174(3)	0.224(4)	0.075 7	0.173(6)
C(15)	−0.020(5)	0.115(5)	0.367(5)	0.099 0	0.173(6)

* 1.00 unless otherwise stated.

Table 4 Lattice parameters (293 K) and stacking sequences of layered aluminium phosphates with the same framework connectivity

Compound	*a*/Å	*c*/Å	Space group	Stacking sequence	Ref.
A $[BuNH_3]_3[Al_3P_4O_{16}]$	13.173(2)	9.647(2)	$P\bar{3}$	*AAAA*	This work
B $[NH_3(CH_2)_4NH_3]_{1.5}[Al_3P_4O_{16}]\cdot 1.8H_2O$	12.957(5)	18.413(3)	$P\bar{3}c1$	*ABAB*	7
C $[C_6H_{16}N_2]_{1.5}[Al_3P_4O_{16}]\cdot 2H_2O$	12.923 5(2)	18.237 3(3)	$P\bar{3}c1$	*ABAB*	14
D $[NH_3(CH_2)_5NH_3]_{1.5}[Al_3P_4O_{16}]\cdot 2H_2O$	13.007(2)	18.553(4)	$P\bar{3}c1$	*ABAB*	15

difficult to estimate the effective channel size in this case.[15] However, all three compounds containing diamines also contain water molecules clustered in the centres of the channels, whereas there is insufficient space for water molecules to reside in the same positions in **A**.

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