

[H₃N(CH₂)₅NH₃] \cdot AlP₂O₈H, a one-dimensional aluminophosphateS. Phan Thanh,^a J. Marrot,^b J. Renaudin^a and V. Maisonneuve^{a*}

^aLaboratoire des Fluorures – UPRES-A 6010 Faculté des Sciences, Université du Maine, Avenue Olivier-Messiaen, 72085 Le Mans CEDEX 9, France, and ^bInstitut Lavoisier, IREM, UMR CNRS C 8637, Université de Versailles Saint-Quentin-en-Yvelines, 45 Avenue des Etats Unis, 75035 Versailles CEDEX, France
Correspondence e-mail: vincent.maisonneuve@univ-lemans.fr

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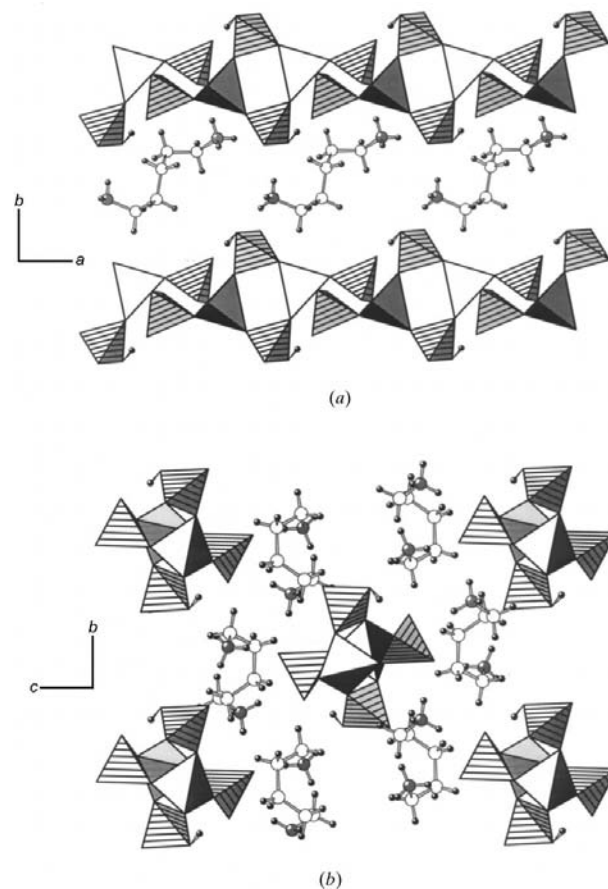
The structure of the title compound, pentane-1,5-diammonium aluminium(III) hydrogen bis(phosphate), (C₅H₁₆N₂)[AlP₂O₈H], obtained solvothermally at 473 K, has been determined by single-crystal X-ray diffraction. It consists of one-dimensional [AlP₂O₈H]²⁻ macroanions, connected to each other by pentanediammonium cations. Contrary to similar compounds with P/Al = 2, the three-dimensional structure is mainly obtained *via* a network of hydrogen bonds.

Comment

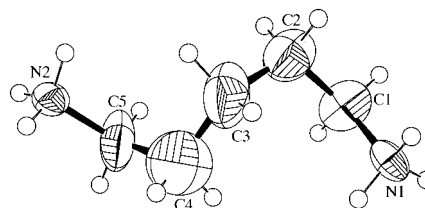
The investigation of the Al₂O₃–H₃PO₄–aliphatic diamine–EtOH system led to a new one-dimensional aluminophosphate templated by pentane-1,5-diamine. The structure of [H₃N(CH₂)₅NH₃] \cdot AlP₂O₈H, (I), consists of inorganic chains, formulated as [AlP₂O₈H]²⁻, separated by organic molecules (Fig. 1*a*). The inorganic part is built up from tetrahedral AlO₄ and PO₄ units, in which all AlO₄ vertices are connected. This arrangement forms a corner-shared Al₂P₂ four-membered ring with PO₄H groups. The Al–O distances, ranging from 1.727 (3) to 1.731 (3) Å, and the O–Al–O angles, lying between 106.4 (2) and 111.3 (2)°, are consistent with those found in the mineral berlinite. In contrast, the P–O distances vary from 1.490 (3) to 1.539 (3) Å and from 1.499 (3) to 1.546 (3) Å for the P1 and P2 phosphate groups, respectively. This dispersion is attributable to multiple-bond character. Pentane-1,5-diamine molecules, which must be protonated to balance the negative charges, ensure the cohesion between inorganic chains *via* hydrogen bonds. All the protons of the ammonium cations are linked to terminal O atoms of the PO₄H group. According to N–H \cdots O hydrogen-bond lengths for the two amine functions, the N1 terminal group is more strongly connected to the inorganic chains. Details of the hydrogen bonding are given in Table 2. [H₃N(CH₂)₅NH₃]²⁺ cations present a bent conformation because of their size. In this case, the atomic displacement parameters of the C atoms are rather large, especially in the central part (atoms C3 and C4) of the

molecule (Fig. 2). This situation is the complete opposite of that observed in [H₃N(CH₂)₆NH₃] \cdot AlF₅ (Phan Thanh *et al.*, 2000), where the diammonium cation exhibits a stretched conformation between the AlF₅ inorganic chains. In addition, in the compound called ULM13, both the bent and stretched conformations for the 1,6-diaminohexane molecules can be observed (Renaudin & Férey, 1995).

Up to now, two types of chain architecture for the one-dimensional aluminophosphates, with a P/Al ratio of 2 in the formulation, have been reported in the literature: [H₃NCH₂CH₂NH₃] \cdot AlP₂O₈H (Williams *et al.*, 1997) shows a one-dimensional polymer chain consisting of edge-shared Al₂P₂ four-membered rings, with pendant PO₄H side groups, whereas [H₃NCH₂CH₂NH₃] \cdot AlP₂O₈ \cdot H₂O (Wang *et al.*, 1990),

**Figure 1**

The projection of the title compound along (a) the *c* axis, showing its one-dimensional character and the bent conformation of the diammonium cation, and (b) the *a* axis. PO₄ tetrahedra are hatched.

**Figure 2**

An ORTEP-3 view (Farrugia, 1997) of the pentanediammonium cation in the title compound. Displacement ellipsoids are shown at the 50% probability level.

[Et₃NH]·AlP₂O₈H₂ (Jones *et al.*, 1990) and [NH₄][H₃NCH₂-CH₂NH₃]·AlP₂O₈ (Gao *et al.*, 1996) present a linear arrangement of corner-shared Al₂P₂ four-membered rings similar to that in (I). However, the greater size of the diammonium cation in (I) leads to a distorted inorganic chain. On one hand, the small size of the organic molecule in these four compounds leads to a three-dimensional organization ensured by a combination of van der Waals forces and hydrogen bonds. On the other hand, in the title compound, the structure accommodates the more significant length of the organic chain by a distortion of both the organic part and the inorganic chain. Consequently, the three-dimensional character is then obtained mainly by the set of hydrogen bonds (Fig. 1*b*). It was also noticed that this involves a shortening of the O—H···O distance, from 2.641 (2) Å in [H₃NCH₂CH₂NH₃]·AlP₂O₈H to 2.457 (4) Å in (I).

Experimental

The title compound was prepared from a starting mixture of aluminium isopropoxide [(CH₃)₂CHO]₃Al—H₃PO₄—pentane-1,5-diamine—EtOH with the molar ratio 1:2.5:100 under solvothermal conditions (473 K, 7 d, autogenous pressure) in a Teflon-lined autoclave. The resulting product was filtered and dried in air at 353 K for 1 h. A suitable single crystal was isolated by optical microscopy. The crystal cell of (I) was obtained from long-exposure rotation photographs. Systematic extinction conditions led to the *P*₂₁/*n* space group.

Crystal data

(C ₅ H ₁₆ N ₂)[AlP ₂ O ₈ H]	<i>D</i> _x = 1.621 Mg m ⁻³
<i>M</i> _r = 322.13	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Cell parameters from 5007 reflections
<i>a</i> = 7.8783 (2) Å	<i>θ</i> = 2.32–29.83°
<i>b</i> = 10.46890 (10) Å	<i>μ</i> = 0.429 mm ⁻¹
<i>c</i> = 16.0680 (4) Å	<i>T</i> = 296 (2) K
<i>β</i> = 95.1470 (10)°	Parallelepiped, colorless
<i>V</i> = 1319.90 (5) Å ³	0.12 × 0.06 × 0.05 mm
<i>Z</i> = 4	

Data collection

Siemens SMART diffractometer	3421 independent reflections
<i>ω</i> scans	1901 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: semi-empirical (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.038
<i>T</i> _{min} = 0.844, <i>T</i> _{max} = 0.978	<i>θ</i> _{max} = 29.83°
8939 measured reflections	<i>h</i> = -10 → 10
	<i>k</i> = -14 → 13
	<i>l</i> = -21 → 9

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0573 <i>P</i>) ² + 3.0698 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.058	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.136	(Δ/ <i>σ</i>) _{max} < 0.001
<i>S</i> = 1.080	Δ <i>ρ</i> _{max} = 1.36 e Å ⁻³
2521 reflections	Δ <i>ρ</i> _{min} = -0.60 e Å ⁻³
167 parameters	Extinction correction: <i>SHELXL93</i> (Sheldrick, 1993)
H-atom parameters constrained	Extinction coefficient: 0.0130 (77)

For the refinement of the H atoms of the CH₂ and NH₃ groups, geometrical restraints were used that implied equal distances (N—H = 0.89 Å and C—H = 0.97 Å) and angles to the central atom (*AFIX* option). H atoms of the CH₂ and NH₃ groups were refined with a common isotropic displacement parameter. The Fourier map showed a relatively large electron-density peak of 1.36 e Å⁻³ at distances of 0.94 and 1.28 Å from H5A and C5, respectively.

Table 1

Selected geometric parameters (Å, °).

P1—O6	1.490 (3)	Al1—O1	1.729 (3)
P1—O8	1.533 (3)	Al1—O8 ⁱⁱ	1.731 (3)
P1—O5	1.537 (3)	Al1—O3	1.731 (3)
P1—O2	1.539 (3)	N1—C1	1.483 (8)
P2—O7	1.499 (3)	C1—C2	1.512 (8)
P2—O4	1.525 (3)	C2—C3	1.509 (9)
P2—O3 ⁱ	1.530 (3)	C3—C4	1.503 (9)
P2—O1	1.546 (3)	C4—C5	1.484 (9)
Al1—O5	1.727 (3)	C5—N2	1.459 (8)
N1—C1—C2	114.5 (5)	C5—C4—C3	114.4 (9)
C3—C2—C1	116.8 (7)	N2—C5—C4	117.0 (9)
C4—C3—C2	127.0 (9)		

Symmetry codes: (i) $-x, 2 - y, -z$; (ii) $1 - x, 2 - y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2···O4 ⁱ	0.82	1.67	2.457 (4)	160
N1—H1A···O2 ⁱⁱ	0.89	2.00	2.885 (5)	177
N1—H1B···O6	0.89	1.89	2.745 (5)	162
N1—H1C···O7 ⁱⁱⁱ	0.89	1.86	2.727 (5)	163
N2—H2C···O6 ^{iv}	0.89	1.88	2.750 (5)	165
N2—H2D···O4 ^v	0.89	2.05	2.869 (5)	153
N2—H2E···O7 ^{iv}	0.89	1.98	2.861 (6)	171

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $1 - x, 1 - y, -z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $1 + x, y, z$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SHELXTL96* (Siemens, 1996); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *DIAMOND* (Bergerhoff, 1996) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL96*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1096). Services for accessing these data are described at the back of the journal.

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