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BRIEF COMMUNICATION

The Synthesis and Characterization of a One-Dimensional Aluminophosphate: $[C_{10}N_2H_9][Al(PO_4)(PO_2(OH)_2)]$

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A new one-dimensional aluminum phosphate has been synthesized under solvothermal conditions at 180°C in the presence of 4,4′-dipyridine and the structure solved using room-temperature single-crystal X-ray diffraction data. ($[C_{10}N_2H_9]^+[H_2AlP_2O_8]^-$, $M_r = 376.13$, triclinic, space group $P\bar{1}$, $a = 4.9169(9)$ Å, $b = 10.696(3)$ Å, $\gamma = 14.660(8)$ Å, $\alpha = 107.84(3)°$, $\beta = 95.68(3)°$, $\gamma = 99.91(2)°$, $V = 713.8(1)$ Å^3, $Z = 2$, 1626 observed data measured with ($I > 3(\sigma(I))$, $R = 4.56\%$ and $R_w = 5.42\%$). The structure consists of chains containing 4-membered rings of AlO_4 and PO_4 tetrahedra constituting a backbone from which hang "pendant" $PO_2(OH)_2$ groups. The chains are held together by hydrogen bonding via the dipyridyl cations.

INTRODUCTION

Since 1982, there has been much study of microporous aluminum phosphates (AlPOs) because of their potentially exploitable sorption and catalytic properties (1, 2). Some of these materials, e.g., $AlPO_4$-34 (chabazite) (3) and $AlPO_4$-37 (faujasite) (3) adopt the same three-dimensional structures as those of known zeolites, but others e.g., JDF-20 (4) and VPI-5 (5), appear to have unique frameworks. More recently, a number of AlPOs with two-dimensional structures and properties akin to clays and the zirconium phosphates have been synthesized. Examples include $(NH_3(CH_2)_5NH_3)(C_5H_{10}NH_2)Al_3P_4O_{16}$ (6) and $(PyH)H_2Al_2P_3O_{12}$ (7). One-dimensional structures are also known, including a number of minerals (8). One example, tancoite, $LiNa_3HAl(PO_4)_2(OH)$ (9), has a structurally related synthetic analogue, $Na_4Al(PO_4)_2(OH)$ (10), containing octahedrally coordinated aluminum. $(Et_3NH)H_2AlP_2O_8$ (11) and $(NH_3CH_2CH_2NH_3)HAlP_2O_8$ (12) are the only examples to date of synthetic AlPO chain structures with organic amine cations as the charge-compensating ions and these contain tetrahedrally coordinated aluminum.

In this work, we describe the synthesis and crystal structure of a new one-dimensional AlPO based on AlO_4 and PO_4 tetrahedra which has no synthetic or naturally occurring analogue.

EXPERIMENTAL

The title compound was synthesized under hydrothermal conditions from a predominantly nonaqueous system. Aluminum isopropoxide (1 g) was dispersed in butan-2-ol (7.86 cm^3) by stirring for about 10 min. 4,4′-dipyridine (1.84 g) was then added together with a small amount of $Si(OEt)_4$ (0.1 cm^3) which can act as a mineralizer (13) and the mixture stirred for a further 10 min. Finally, orthophosphoric acid (0.9 cm^3, 85% by weight) was added with further stirring to give a gel of overall composition.

$Al(OPr)_3$: 2.7 H_3PO_4: 17.5 2-BuOH: 0.1 $Si(OEt)_4$: 2.4 4,4′-dipyridine. The gel was sealed in a Teflon-lined stainless-steel autoclave and heated at 180°C for 10 days. The solid product was collected by filtration, washed with distilled water, and dried in air at 80°C. The product contained white polycrystalline material and single crystals, which were in the form of colorless rectangular blocks. The powder X-ray diffraction pattern showed that the product was almost pure although a small amount of a dense phase, the cristobalite form of $AlPO_4$, was present as an impurity. Energy-dispersive X-ray analysis, performed using a JEOL 2000FX analytical electron microscope, confirmed that the crystallites examined had Al : P ratios of *ca* 1 : 2 and 1 : 1, the former being the majority phase. There was no detectable amount of silicon present in any of the crystallites studied.

Room-temperature diffraction data were collected from a suitable single crystal using an Enraf–Nonius CAD4 diffractometer (graphite-monochromated CuKα radiation, $\lambda = 1.5418$ Å) in the ω–2θ scanning mode. Full experimental

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information is given in Table 1. The unit cell was determined as triclinic from the measurement of 25 centered reflections and cell parameters optimized by least-squares refinement. The structure was solved in the space group *P*-1 using the direct methods program SHELX-86 (15) and the nonhydrogen atoms of the framework and template located. All Fourier calculations and subsequent full-matrix least-squares refinements were carried out using the program CRYSTALS (16). Three hydrogen atoms were found in difference Fourier maps, two of which were associated with phosphate oxygen atoms (O(7) and O(8)) while the third was bonded to one of the dipyridyl nitrogen atoms (N(1)). It was assumed that, in order for the structure to be charge balanced, the dipyridyl cation is only singly protonated and so hydrogen was not placed on N(2) but all other hydrogen atoms of the amine, including that of N(1), were placed geometrically after each cycle of refinement. 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 isotropic thermal parameters fixed at 0.05 $Å^2$. A correction for secondary extinction was applied (17). In the final cycle, 215 parameters were refined including anisotropic thermal parameters for all nonhydrogen atoms to give residuals of $R = 4.56$ and $R_w = 5.42\%$. Atomic coordinates and thermal parameters are given in Table 2 and selected interatomic distances and bond angles in Table 3.

TABLE 1
Crystal Data for $[C_{10}N_2H_9][Al(PO_4)(PO_2(OH)_2)]$

Molecular formula	$AlP_2O_8C_{10}N_2H_{11}$
Formula weight	376.13
Crystal system	Triclinic
a (Å)	4.9169(9)
b (Å)	10.696(3)
c (Å)	14.660(8)
α (°)	107.84(3)
β (°)	95.68(3)
γ (°)	99.91(2)
Unit-cell volume ($Å^3$)	713.83
Space group	*P*-1
Z	2
ρ_{calc} (gcm^{-3})	1.75
Linear absorption coefficient (cm^{-1})	38.45
Crystal size (mm)	$0.35 \times 0.05 \times 0.1$
Radiation	Cu*K*α ($\lambda = 1.5418$ Å)
θ_{max} (°)	72
Scan type	ω–2θ
Total data collected	2875
Unique data	2574
Observed data ($I > 3\sigma(I)$)	1626
Merging *R*	0.0225
Weighting scheme	Chebyshev 3 term (14)
Residual electron density (min, max) ($eÅ^{-3}$)	−0.46, 0.37
No. of parameters refined	215
R	0.0456
R_w	0.0542

TABLE 2
Atomic Coordinates and Isotropic Thermal Parameters for $[C_{10}N_2H_9][Al(PO_4)(PO_2(OH)_2)]$ (with e.s.d.s in parentheses)

Atom	*x*	*y*	*z*	*U*(iso)
P(1)	0.2643(2)	0.6624(1)	0.98188(7)	0.0183
P(2)	0.4755(2)	0.6544(1)	1.33324(7)	0.0214
Al(1)	0.3214(2)	0.4969(1)	1.11780(8)	0.0177
O(1)	0.4038(6)	0.8035(3)	0.9947(2)	0.0276
O(2)	−0.0512(6)	0.6396(3)	0.9459(2)	0.0235
O(3)	0.3727(6)	0.5566(3)	0.9063(2)	0.0284
O(4)	0.3011(6)	0.6334(3)	1.0783(2)	0.0277
O(5)	0.3180(6)	0.5418(3)	1.2414(2)	0.0271
O(6)	0.7494(6)	0.7270(4)	1.3224(3)	0.0321
O(7)	0.2849(7)	0.7578(3)	1.3629(3)	0.0345
O(8)	0.4972(7)	0.5858(3)	1.4108(2)	0.0309
N(1)	1.1443(7)	1.0612(4)	1.8857(3)	0.0296
N(2)	−0.0802(8)	0.7104(4)	1.5534(3)	0.0335
C(1)	0.6604(9)	0.9232(4)	1.7584(3)	0.0247
C(2)	0.784(1)	1.0535(5)	1.7650(4)	0.0372
C(3)	1.028(1)	1.1211(5)	1.8303(4)	0.0326
C(4)	1.034(1)	0.9374(5)	1.8821(4)	0.0355
C(5)	0.784(1)	0.8663(5)	1.8187(4)	0.0321
C(6)	0.4035(9)	0.8504(4)	1.6879(3)	0.0266
C(7)	0.271(1)	0.9102(5)	1.6297(4)	0.0354
C(8)	0.033(1)	0.8364(5)	1.5633(4)	0.0396
C(9)	0.044(1)	0.6513(5)	1.6079(4)	0.0393
C(10)	0.284(1)	0.7183(5)	1.6752(4)	0.0385
H(711)	0.102(9)	0.710(6)	1.348(4)	0.0500
H(811)	0.670(9)	0.604(6)	1.449(4)	0.0500

DISCUSSION

The structure consists of infinite aluminophosphate chains of formula $[Al(PO_4)(PO_2(OH)_2)^-]_n$ running parallel to the *a* axis and linked by monoprotonated 4,4′-dipyridyl cations. Within the chains both the aluminum and phosphorus atoms are tetrahedrally coordinated to oxygen atoms and show ranges of bond lengths and angles similar to those found in other AlPOs (6, 7).

There are two crystallographically distinct PO_4 units. P(1) is attached to a terminal oxygen atom; the P(1)–O(1) bond length of 1.492(3) Å indicates that it possesses some multiple-bond character. The remaining three oxygens bridge to three adjacent aluminum atoms to form 4-membered rings. The rings are joined along opposite edges to form a zigzag chain "backbone" (Fig. 1). The second phosphorus unit, $P(2)O_4$, has only one oxygen bridging to Al and extends away from the chain as a "pendant" group. Of the three remaining P(2)–O bonds, one has partial double-bond character (P(2)–O(6), 1.484(3) Å), whilst the other two, rather longer bonds (P(2)–O(7), 1.560(3) Å and P(2)–O(8), 1.535(3) Å), constitute P–OH groups. This is confirmed by the location of the hydrogen atoms in the difference Fourier maps. The separation of oxygen atoms of adjacent pendant

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for $[C_{10}N_2H_9][Al(PO_4)(PO_2(OH)_2)]$

P(1)–O(1)	1.492(3)	O(1)–P(1)–O(2)	109.8(2)
P(1)–O(2)	1.541(3)	O(1)–P(1)–O(3)	113.5(2)
P(1)–O(3)	1.533(3)	O(2)–P(1)–O(3)	106.1(2)
P(1)–O(4)	1.538(3)	O(1)–P(1)–O(4)	111.0(2)
		O(2)–P(1)–O(4)	108.3(2)
P(2)–O(5)	1.530(3)	O(3)–P(1)–O(4)	107.9(2)
P(2)–O(6)	1.484(3)		
P(2)–O(7)	1.560(3)	O(5)–P(2)–O(6)	114.8(2)
P(2)–O(8)	1.535(3)	O(5)–P(2)–O(7)	107.3(2)
		O(6)–P(2)–O(7)	108.3(2)
Al(1)–O(2)[a]	1.738(3)	O(5)–P(2)–O(8)	104.4(2)
Al(1)–O(3)[b]	1.731(3)	O(6)–P(2)–O(8)	113.5(2)
Al(1)–O(4)	1.741(3)	O(7)–P(2)–O(8)	108.1(2)
Al(1)–O(5)	1.729(3)		
		O(2)–Al(1)–O(3)	105.8(1)
O(7)–H(711)	0.93(4)	O(2)–Al(1)–O(4)	110.8(1)
O(8)–H(811)	0.94(4)	O(3)–Al(1)–O(4)	110.0(2)
		O(2)–Al(1)–O(5)	111.1(2)
N(1)–C(3)	1.323(6)	O(3)–Al(1)–O(5)	108.9(1)
N(1)–C(4)	1.325(6)	O(4)–Al(1)–O(5)	110.2(2)
N(2)–C(8)	1.324(7)		
N(2)–C(9)	1.327(7)	P(1)–O(2)–Al(1)[c]	136.6(2)
C(1)–C(2)	1.391(6)	P(1)–O(3)–Al(1)[d]	140.8(2)
C(1)–C(5)	1.377(6)	P(1)–O(4)–Al(1)	138.4(2)
C(1)–C(6)	1.477(6)	P(2)–O(5)–Al(1)	137.2(2)
C(2)–C(3)	1.388(6)		
C(4)–C(5)	1.392(6)		
C(6)–C(7)	1.390(7)		
C(6)–C(10)	1.381(7)		
C(7)–C(8)	1.386(6)		
C(9)–C(10)	1.386(7)		

Note. Symmetry operations needed to produce equivalent atoms: (*a*) $-x, 1-y, 2-z$; (*b*) $1-x, 1-y, 2-z$; (*c*) $-x, 1-y, 2-z$; (*d*) $1-x, 1-y, 2-z$.

$PO_2(OH)_2$ groups is sufficiently short to suggest the presence of intrachain hydrogen bonding (O(6) … O(7)′, 2.58 Å).

The 4,4-dipyridyl template groups lie in between the chains and are stacked on top of each other at a separation of ~ 4.92 Å (Fig. 2). The short N(1) … O(1) and N(2) … O(8) distances, 2.584 and 2.636 Å, respectively, indicate that adjacent AlPO chains are linked by hydrogen bonding through the organic cations to form layers. The O(4) … O(4)′ and O(6) … O(7)′ separations between adjacent chains are 12.19 and 6.04 Å, respectively.

The title compound has a unique structure although the one-dimensional nature of the framework is common to two other amine containing AlPOs with an Al:P ratio of 1:2; namely, $Et_3NH(H_2AlP_2O_8)$ (11) and $(NH_3CH_2CH_2NH_3)HAlP_2O_8$ (12). The structures of the latter two compounds are also constructed from chains of four-membered rings, but, in contrast to the compound described here, the rings are joined together by corner sharing rather than edge sharing and both the phosphorus atoms participate in ring formation. Pendant dihydrogen phosphate groups are not found in either of the two previously reported structures. In both the title compound and $(NH_3CH_2CH_2NH_3)HAlP_2O_8$ (12), the AlPO chains are not directly linked but are connected via hydrogen bonding to protonated amine molecules to generate a two-dimensional array. In $Et_3NH(H_2AlP_2O_8)$ (11), however, direct hydrogen bonding between AlPO chains generates a rigid three-dimensional array, and the amine cation is only loosely associated with the inorganic framework.

APPENDIX

Supplementary Information: Anisotropic Thermal Parameters for $[C_{10}N_2H_9][Al(PO_4)(PO_2(OH)_2)]$ (with e.s.d.s in parentheses)

Atom	$U(11)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
P(1)	0.0157(5)	0.0196(5)	0.0194(5)	0.0055(4)	−0.0039(4)	0.0011(4)
P(2)	0.0202(5)	0.0263(6)	0.0172(5)	0.0063(4)	−0.0007(4)	0.0005(4)
Al(1)	0.0163(6)	0.0223(6)	0.0143(5)	0.0038(5)	−0.0016(4)	0.0035(4)
O(1)	0.025(2)	0.027(2)	0.040(2)	0.016(1)	−0.011(1)	−0.004(1)
O(2)	0.015(1)	0.026(1)	0.029(2)	0.002(1)	−0.003(1)	0.001(1)
O(3)	0.021(2)	0.040(2)	0.026(2)	−0.002(1)	−0.003(1)	0.008(1)
O(4)	0.038(2)	0.026(2)	0.022(1)	0.007(1)	−0.005(1)	0.006(1)
O(5)	0.029(2)	0.039(2)	0.016(1)	0.004(1)	−0.001(1)	−0.002(1)
O(6)	0.017(1)	0.045(2)	0.046(2)	0.019(2)	0.003(1)	−0.004(1)
O(7)	0.026(2)	0.030(2)	0.047(2)	0.003(2)	0.004(1)	0.005(1)
O(8)	0.039(2)	0.042(2)	0.023(2)	0.014(1)	−0.012(1)	−0.004(2)
N(1)	0.023(2)	0.034(2)	0.029(2)	0.002(2)	−0.004(2)	0.000(2)
N(2)	0.032(2)	0.048(2)	0.024(2)	0.008(2)	−0.008(2)	−0.000(2)
C(1)	0.024(2)	0.025(2)	0.022(2)	0.004(2)	−0.002(2)	0.000(2)
C(2)	0.040(3)	0.034(3)	0.042(3)	0.010(2)	−0.017(2)	−0.001(2)
C(3)	0.032(2)	0.025(2)	0.041(3)	0.008(2)	−0.009(2)	−0.004(2)
C(4)	0.036(3)	0.036(3)	0.041(3)	0.017(2)	−0.012(2)	−0.002(2)
C(5)	0.036(3)	0.031(2)	0.035(2)	0.011(2)	−0.014(2)	−0.005(2)
C(6)	0.026(2)	0.030(2)	0.021(2)	0.002(2)	−0.002(2)	0.003(2)
C(7)	0.038(3)	0.036(3)	0.040(3)	0.018(2)	−0.015(2)	−0.005(2)
C(8)	0.044(3)	0.043(3)	0.037(3)	0.012(2)	−0.015(2)	0.003(2)
C(9)	0.042(3)	0.037(3)	0.045(3)	0.011(2)	−0.014(2)	−0.016(2)
C(10)	0.044(3)	0.032(3)	0.046(3)	0.013(2)	−0.019(2)	−0.003(2)

Supplementary Information: Atomic Coordinates and Isotropic Thermal Parameters for Hydrogen Atoms of $[C_{10}N_2H_9][Al(PO_4)(PO_2(OH)_2)]$ (with e.s.d.s in parentheses)

Atom	x	y	z	U(iso)
H(111)	1.3202	1.1116	1.9322	0.0250
H(21)	0.6974	1.0987	1.7228	0.0383
H(31)	1.1156	1.2152	1.8356	0.0317
H(41)	1.1271	0.8950	1.9251	0.0375
H(51)	0.7021	0.7735	1.8170	0.0334
H(71)	0.3460	1.0057	1.6358	0.0379
H(81)	−0.0563	0.8803	1.5207	0.0407
H(91)	−0.0370	0.5556	1.6002	0.0405
H(101)	0.3712	0.6704	1.7153	0.0400
H(711)	0.102(9)	0.710(6)	1.348(4)	0.0500
H(811)	0.670(9)	0.604(6)	1.449(4)	0.0500

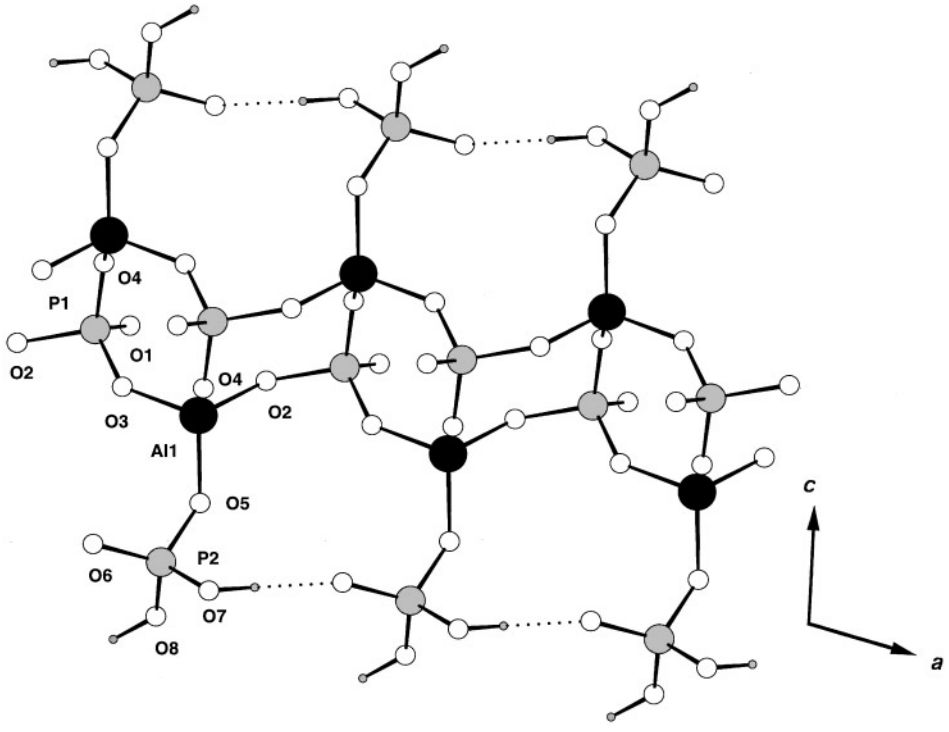

FIG. 1. View of the $[Al(PO_4)(PO_2(OH)_2)^-]_n$ unit along the *b* axis showing the zigzag chains of 4-membered rings built from $Al(1)O_4$ and $P(1)O_4$ tetrahedra and the pendant $P(2)O_2(OH)_2$ groups. Intrachain hydrogen bonds are represented by dotted lines. (Drawing package, CAMERON (18)).

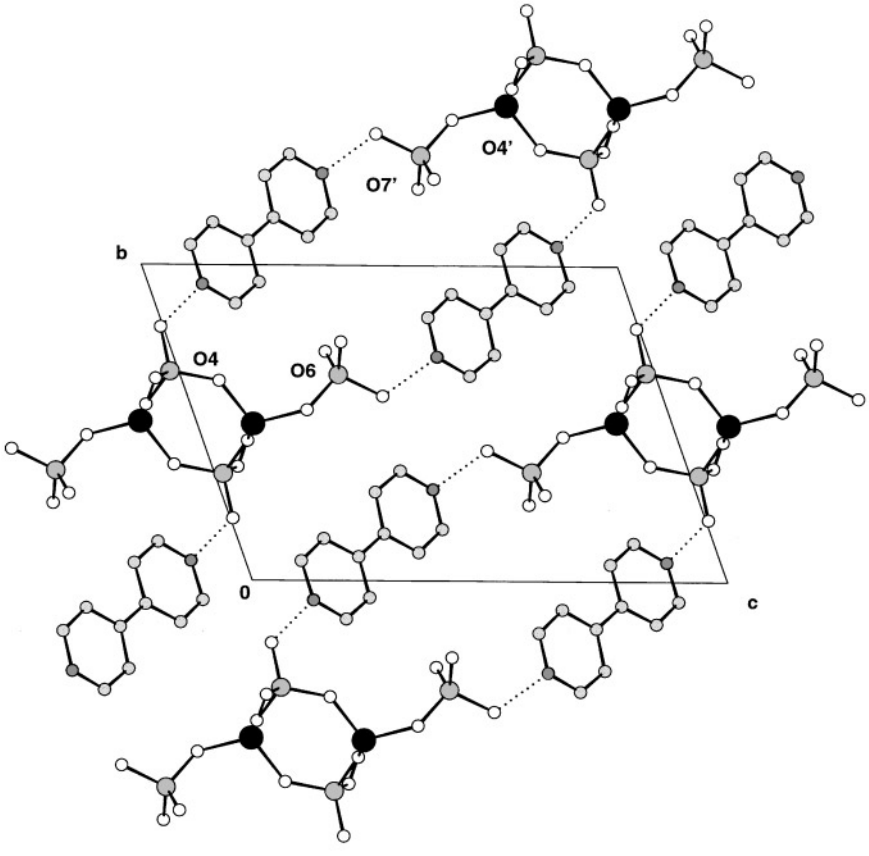

FIG. 2. View along the *a* axis showing hydrogen bonding of the 4,4′-dipyridyl cations to the AlPO chains to generate a layered structure. Hydrogen atoms have been omitted for clarity. Distances O(4) … O(4)′ and O(6) … O(7)′ are 12.19 and 6.04 Å.

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