JOURNAL OF SOLID STATE CHEMISTRY 111, 18–25 (1994)

An Example of a Reactive Template in the Synthesis of a Novel Layered Aluminum Phosphate, $(Al_3P_4O_{16})^{3-}(NH_3(CH_2)_5NH_3)^{2+}(C_5H_{10}NH_2)^+$

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Received November 1, 1993; accepted January 20, 1994

IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

It is a pleasure to have the opportunity of contributing to a special issue of this journal honoring the sixtieth birthday of an old friend. It was in the early 1960s that I first began to notice the work of Ram Rao, who was then at Kanpur. Before long we entered into active correspondence since so many of his papers overlapped strongly with those of my group in the University of Wales. I then heard the late Professor Stuart Anderson describe him as a "ball of fire." In due course, while he held a visiting appointment at the University of Oxford, he came and visited me in Aberystwyth. Since that time we have been in constant touch, published frequently together, and attempted to undertake other activities pertaining to chemistry in a broader perspective. It was during his tenure of the Presidency of the International Union of Pure and Applied Chemistry that I became Chairman of one of its committees (CHEMRAWN, chemical research applied to world needs).

Ram Rao is a man of numerous interests and wide tastes in solid-state and structural chemistry. He is also a great mover and inspirer of people. He has, from the outset of his career, been keenly interested in preparative solid-state chemistry and savors, as many of us do, the joy accompanying the emergence of a hitherto unknown structure as a result of the application of novel preparative techniques. It gives me personally especial pleasure to offer this paper to the "Rao issue," especially when one of my co-authors is Indian, and the other two were former associates of a friend (Tony Cheetham), whose work was first drawn to my attention by Ram Rao.

J. M. Thomas

A new layered aluminum phosphate with P:Al ratio 4:3 has been prepared under nonaqueous conditions in the presence of 1,5-diaminopentane and the structure has been determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$), with lattice parameters $a = 9.801(2)$, $b = 14.837(2)$, $c = 17.815(3)$ Å, $\beta = 105.65(1)°$, and $V = 2494.7$ Å^3 ($R = 0.042$ and $R_w = 0.058$). The structure consists of AlO_4 and PO_4 tetrahedra linked to form layers. Two organic cations, diprotonated 1,5-diaminopentane and protonated piperidine derived from cyclization of the starting amine, lie between the inorganic layers and are hydrogen bonded to the layers through NH_3^+ and NH_2^+ groups, respectively. The two organic cations are located in two crystallographically distinct eight-membered win-

0022-4596/94 $6.00

dows within the layers, the piperidinium cations being associated with circular cavities of ~6.9 Å in diameter, and the 1,5-diaminopentane cations with elliptical cavities (of axes ~5.9 and 8.0 Å).

INTRODUCTION

Since the discovery in 1982 of three-dimensional aluminum phosphates (1, 2), there has been intense activity in this area of research (3, 4). Some of these materials adopt the same framework structures as those of known zeolites, e.g., $AlPO_4$-17 has the erionite structure (5), but others, e.g., VPI-5 (6) and JDF-20 (7), appear to be unique. While there has been much activity directed towards synthesizing and characterizing such three-dimensional materials, relatively little work has been done on lower dimensional aluminum phosphates, some of which are analogues of the naturally occurring aluminosilicate clay minerals (8). Recently, we have synthesised both chain (9) and layered aluminum phosphates (10–12) with a variety of P : Al ratios. For example, in the case of the two-dimensional materials, we have observed P : Al ratios of 3 : 2 (10) and 4 : 3 (11, 12) with a range of ring sizes within the layers. The size of the rings and their stacking sequences can result in microporosity in some of these materials (12). In the present work, we report the synthesis and characterization of a layered aluminum phosphate in which half the templating agent has undergone a cyclization reaction leading to two types of organic cation between the inorganic AlPO sheets.

SYNTHESIS

The title compound was synthesized from a reaction mixture of composition $Al_2O_3 : P_2O_5 : 1.2\ NH_2(CH_2)_5NH_2$: 40 triethylene glycol: 0.3 HF. Phosphoric acid (1.28 g, 85 wt%) and triethylene glycol (20 ml) were added to hydrated aluminum oxide (1.03 g, 55 wt% Al_2O_3, 45 wt% H_2O) and the mixture was stirred until homogeneous. The templating agent 1,5-diaminopentane and a small quantity of HF were added and the gel was sealed in a Teflon-lined stainless steel autoclave and heated under autogenous pressure at 190°C for 6 days. The crystalline product was filtered, washed with distilled water, and dried in air at 90°C. Single crystals suitable for structural analysis were in the form of colorless transparent tiles of approximate dimensions $0.15 \times 0.15 \times 0.5\ mm^3$. Thermogravimetric analysis of a bulk sample of the product showed a weight loss over the temperature range 390–450°C corresponding to the removal of template. A powder X-ray diffraction pattern of the heated product indicated the presence of one crystalline phase, berlinite, $AlPO_4$ (13).

STRUCTURE DETERMINATION

Data were collected using an Enraf–Nonius CAD4 diffractometer with graphite monochromated Cu$K\alpha$ radiation (λ = 1.5418 Å). The unit cell was determined from the setting angles of 25 well-centered reflections over the range $(10 < 2\theta < 31)^\circ$. The space group $P2_1/c$ was determined from the systematic absence conditions ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) (14). Three standard reflections were measured every hour and showed no appreciable variation during the course of the data collection. Data were corrected for Lorenz and polarization effects and for absorption using azimuthal scans (15). Crystal data for the compound are given in Table 1. The structure was solved by direct methods using the program SHELX-86 (16). Observed and difference Fourier maps were used to locate the nonhydrogen and hydrogen atoms of the organic templates, respectively, although subsequently the hydrogen atoms were placed geometrically and allowed to "ride" on the atoms to which they were bonded. Full-matrix least-squares refinement, with anisotropic thermal parameters for the nonhydrogen atoms, was carried out

TABLE 1

Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $(Al_3P_4O_{16})^{3-}(NH_3(CH_2)_5NH_3)^{2+}(C_5H_{10}NH_2)^+$

Crystal system	Monoclinic
Space group	$P2_1/c$
Formula	$Al_3P_4O_{16}C_{10}H_{28}N_3$
Formula mass	650.18
a (Å)	9.801(2)
b (Å)	14.837(2)
c (Å)	17.815(3)
β (°)	105.65(1)
Volume (Å^3)	2494.7
Z	4
ρ_{calc} (g cm^{-3})	1.731
Crystal size (mm)	$0.15 \times 0.15 \times 0.5$
μ (cm^{-1})	45.09
Transmission factors	1.52–1.99
Scan type	$\omega - 2\theta$
Scan angle ($\omega + 0.15 \tan \theta$)	1.20
$2\theta_{max}$ (°)	145
Total data collected	6531
Unique data	4867
Observed data ($I > 3\sigma(I)$)	3356
R_{merg}	0.035
R	0.042
R_w	0.058
No. of variables	358
Highest residual peak in Δ Fourier map (e Å^{-3})	0.45

TABLE 2

Atomic Parameters with E. S. D.'s in Parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
P(1)	0.52373(8)	0.26091(5)	0.07345(4)	0.0161
P(2)	0.68183(8)	0.09167(5)	0.32672(4)	0.0162
P(3)	0.25937(8)	0.26411(5)	−0.25203(4)	0.0167
P(4)	0.34858(8)	−0.09066(5)	0.16247(4)	0.0160
Al(1)	0.4021(1)	0.38714(6)	0.17949(5)	0.0152
Al(2)	0.5296(1)	0.26041(6)	−0.10243(5)	0.0147
Al(3)	0.4305(1)	0.11042(6)	0.16904(5)	0.0156
O(1)	0.6792(3)	0.2677(2)	0.1095(2)	0.0325
O(2)	0.4625(3)	0.1716(2)	0.0926(1)	0.0243
O(3)	0.4437(3)	0.3381(2)	0.1005(1)	0.0248
O(4)	0.4858(3)	0.2685(2)	−0.0155(1)	0.0229
O(5)	0.5824(3)	0.1104(2)	0.2457(1)	0.0280
O(6)	0.3390(3)	0.4933(1)	0.1518(1)	0.0255
O(7)	0.8318(3)	0.1091(2)	0.3269(1)	0.0289
O(8)	0.6363(3)	0.3501(2)	−0.1134(1)	0.0270
O(9)	0.3718(3)	0.2655(2)	−0.1737(1)	0.0292
O(10)	0.2728(3)	0.3247(2)	0.2064(1)	0.0273
O(11)	0.1135(2)	0.2733(2)	−0.2413(1)	0.0253
O(12)	0.2908(3)	0.1574(2)	0.1982(1)	0.0277
O(13)	0.3846(3)	0.0022(1)	0.1351(1)	0.0251
O(14)	0.5539(3)	0.3917(2)	0.2560(1)	0.0267
O(15)	0.1973(2)	−0.0957(2)	0.1652(1)	0.0276
O(16)	0.6176(3)	0.1600(1)	−0.1058(1)	0.0253
N(1)	0.0092(3)	0.7625(2)	0.1190(2)	0.0300
N(2)	−0.1259(3)	1.1394(2)	0.1776(2)	0.0292
N(3)	0.8010(3)	0.4255(2)	0.1787(2)	0.0284
C(1)	0.7300(5)	0.5100(2)	0.1435(2)	0.0377
C(2)	0.7156(4)	0.5095(3)	0.0558(2)	0.0433
C(3)	0.8610(4)	0.4973(3)	0.0406(2)	0.0422
C(4)	0.9340(5)	0.4122(3)	0.0807(2)	0.0411
C(5)	0.9465(4)	0.4164(3)	0.1678(2)	0.0366
C(6)	−0.0836(5)	0.7844(2)	0.0398(2)	0.0383
C(7)	−0.1211(4)	0.8852(2)	0.0343(2)	0.0396
C(8)	−0.2150(5)	0.9103(3)	0.0873(3)	0.0468
C(9)	−0.2401(4)	1.0120(3)	0.0923(3)	0.0493
C(10)	−0.1025(4)	1.0616(3)	0.1301(3)	0.0464
H(11)	0.7891(5)	0.5628(2)	0.1675(2)	0.0412
H(12)	0.6343(5)	0.5147(2)	0.1530(2)	0.0412
H(21)	0.6718(4)	0.5672(3)	0.0321(2)	0.0464
H(22)	0.6538(4)	0.4578(3)	0.0315(2)	0.0464
H(31)	0.9211(4)	0.5505(3)	0.0629(2)	0.0445
H(32)	0.8504(4)	0.4940(3)	−0.0168(2)	0.0445
H(41)	1.0304(5)	0.4068(3)	0.0722(2)	0.0464
H(42)	0.8755(5)	0.3588(3)	0.0576(2)	0.0464
H(51)	1.0056(4)	0.4695(3)	0.1912(2)	0.0383
H(52)	0.9917(4)	0.3599(3)	0.1935(2)	0.0383
H(61)	−0.0335(5)	0.7689(2)	−0.0005(2)	0.0379
H(62)	−0.1731(5)	0.7485(2)	0.0303(2)	0.0379
H(71)	−0.0312(4)	0.9207(2)	0.0506(2)	0.0387
H(72)	−0.1721(4)	0.9006(2)	−0.0208(2)	0.0387
H(81)	−0.1684(5)	0.8879(3)	0.1410(3)	0.0484
H(82)	−0.3087(5)	0.8797(3)	0.0670(3)	0.0484
H(91)	−0.3078(4)	1.0226(3)	0.1244(3)	0.0507
H(92)	−0.2814(4)	1.0361(3)	0.0385(3)	0.0507
H(101)	−0.0608(4)	1.0838(3)	0.0881(3)	0.0521
H(102)	−0.0350(4)	1.0186(3)	0.1644(3)	0.0521
H(111)	0.059(6)	0.704(4)	0.120(3)	0.07(2)
H(112)	0.090(6)	0.811(4)	0.136(3)	0.06(2)
H(113)	−0.042(5)	0.768(3)	0.155(2)	0.03(1)
H(221)	−0.030(6)	1.172(4)	0.202(3)	0.07(2)

TABLE 2—*Continued*

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
H(222)	−0.162(6)	1.121(3)	0.223(3)	0.06(1)
H(223)	−0.184(7)	1.170(4)	0.146(4)	0.08(2)
H(331)	0.807(5)	0.419(3)	0.231(3)	0.04(1)
H(332)	0.744(5)	0.375(4)	0.154(3)	0.05(1)

using the CRYSTALS suite of programs (17). The applied weighting scheme was that of Tukey and Prince based on a three-term modified Chebyshev polynomial (18) and the final residuals were $R = 0.042$ and $R_w = 0.058$.

TABLE 3

Selected Interatomic Contacts (Å)

P(1) –O(1)	1.489(3)
P(1) –O(2)	1.531(2)
P(1) –O(3)	1.537(2)
P(1) –O(4)	1.531(2)
P(2) –O(5)	1.534(2)
P(2) –O(6)	1.536(2)
P(2) –O(7)	1.492(2)
P(2) –O(8)	1.529(2)
P(3) –O(9)	1.528(2)
P(3) –O(10)	1.534(2)
P(3) –O(11)	1.499(2)
P(3) –O(12)	1.543(2)
P(4) –O(13)	1.534(2)
P(4) –O(14)	1.530(2)
P(4) –O(15)	1.498(2)
P(4) –O(16)	1.538(2)
Al(1)–O(3)	1.728(2)
Al(1)–O(6)	1.715(2)
Al(1)–O(10)	1.739(2)
Al(1)–O(14)	1.727(2)
Al(2)–O(4)	1.719(2)
Al(2)–O(8)	1.736(2)
Al(2)–O(9)	1.717(3)
Al(2)–O(16)	1.731(2)
Al(3)–O(2)	1.734(2)
Al(3)–O(5)	1.728(3)
Al(3)–O(12)	1.737(2)
Al(3)–O(13)	1.732(2)
N(1) –C(6)	1.494(4)
N(2) –C(10)	1.486(5)
N(3) –C(1)	1.487(4)
N(3) –C(5)	1.497(4)
C(1) –C(2)	1.530(4)
C(2) –C(3)	1.531(4)
C(3) –C(4)	1.530(4)
C(4) –C(5)	1.523(4)
C(6) –C(7)	1.537(4)
C(7) –C(8)	1.532(4)
C(8) –C(9)	1.535(4)
C(9) –C(10)	1.524(4)

TABLE 4

Selected Interatomic Angles (°)

O(2) –P(1) –O(1)	112.3(1)
O(3) –P(1) –O(1)	111.3(1)
O(3) –P(1) –O(2)	108.1(1)
O(4) –P(1) –O(1)	112.1(1)
O(4) –P(1) –O(2)	107.1(1)
O(4) –P(1) –O(3)	105.5(1)
O(6) –P(2) –O(5)	108.2(1)
O(7) –P(2) –O(5)	110.2(1)
O(7) –P(2) –O(6)	111.2(1)
O(8) –P(2) –O(5)	108.9(1)
O(8) –P(2) –O(6)	106.3(1)
O(8) –P(2) –O(7)	111.9(1)
O(10)–P(3) –O(9)	108.5(1)
O(11)–P(3) –O(9)	111.1(1)
O(11)–P(3) –O(10)	110.4(1)
O(12)–P(3) –O(9)	108.0(1)
O(12)–P(3) –O(10)	108.3(1)
O(12)–P(3) –O(11)	110.5(1)
O(14)–P(4) –O(13)	108.5(1)
O(15)–P(4) –O(13)	111.7(1)
O(15)–P(4) –O(14)	109.3(1)
O(16)–P(4) –O(13)	106.4(1)
O(16)–P(4) –O(14)	108.6(1)
O(16)–P(4) –O(15)	112.2(1)
O(6) –Al(1)–O(3)	107.4(1)
O(10)–Al(1)–O(3)	110.5(1)
O(10)–Al(1)–O(6)	109.6(1)
O(14)–Al(1)–O(3)	108.5(1)
O(14)–Al(1)–O(6)	111.0(1)
O(14)–Al(1)–O(10)	109.9(1)
O(8) –Al(2)–O(4)	110.7(1)
O(9) –Al(2)–O(4)	105.6(1)
O(9) –Al(2)–O(8)	109.5(1)
O(16)–Al(2)–O(4)	109.8(1)
O(16)–Al(2)–O(8)	109.6(1)
O(16)–Al(2)–O(9)	111.7(1)
O(5) –Al(3)–O(2)	108.7(1)
O(12)–Al(3)–O(2)	110.4(1)
O(12)–Al(3)–O(5)	110.2(1)
O(13)–Al(3)–O(2)	107.2(1)
O(13)–Al(3)–O(5)	111.3(1)
O(13)–Al(3)–O(12)	109.0(1)
Al(3) –O(2) –P(1)	142.5(2)
Al(1) –O(3) –P(1)	145.2(2)
Al(2) –O(4) –P(1)	151.3(2)
Al(3) –O(5) –P(2)	159.6(2)
Al(1) –O(6) –P(2)	149.7(2)
Al(2) –O(8) –P(2)	144.1(2)

TABLE 4—*Continued*

Al(2) -O(9) -P(3)	163.4(2)
Al(1) -O(10)-P(3)	139.0(2)
Al(3) -O(12)-P(3)	140.4(2)
Al(3) -O(13)-P(4)	141.4(1)
Al(1) -O(14)-P(4)	160.1(2)
Al(2) -O(16)-P(4)	142.7(2)
C(5) -N(3) -C(1)	112.0(3)
C(2) -C(1) -N(3)	109.3(3)
C(3) -C(2) -C(1)	110.3(3)
C(4) -C(3) -C(2)	110.7(3)
C(5) -C(4) -C(3)	110.0(3)
C(4) -C(5) -N(3)	108.5(3)
C(7) -C(6) -N(1)	110.3(3)
C(8) -C(7) -C(6)	111.7(3)
C(9) -C(8) -C(7)	114.0(3)
C(10)-C(9) -C(8)	111.3(4)
C(9) -C(10)-N(2)	111.8(3)

STRUCTURE DESCRIPTION AND DISCUSSION

The nonhydrogen atomic coordinates and isotropic thermal parameters, interatomic distances, and interatomic angles are listed in Tables 2, 3, and 4, respectively. The structure of the compound, drawn using the program CAMERON (19), is shown in Figs. 1–3.

The structure consists of macroanionic $Al_3P_4O_{16}^{3-}$ sheets separated by diprotonated 1,5-diaminopentane and piperidinium cations. The basic structural units of the anionic layers are Al- and P-centered tetrahedra (Fig. 1). All the vertices of the AlO_4 units are shared and have an average Al–O bond length of 1.729 Å. Only 3/4 of the PO_4 vertices are shared, however ($P–O_{av}$ = 1.534 Å), formally resulting in the presence of phosphoryl P═O groups ($P═O_{av}$ = 1.495 Å). These values are in good agreement with those seen previously in other layered aluminum phosphates. For example, in $[Al_3P_4O_{16}]^{3-}(NH_3(CH_2)_2NH_3)^{2+}(OH(CH_2)_2OH_2)^{+}(OH(CH_2)_2OH)$ (11), the corresponding

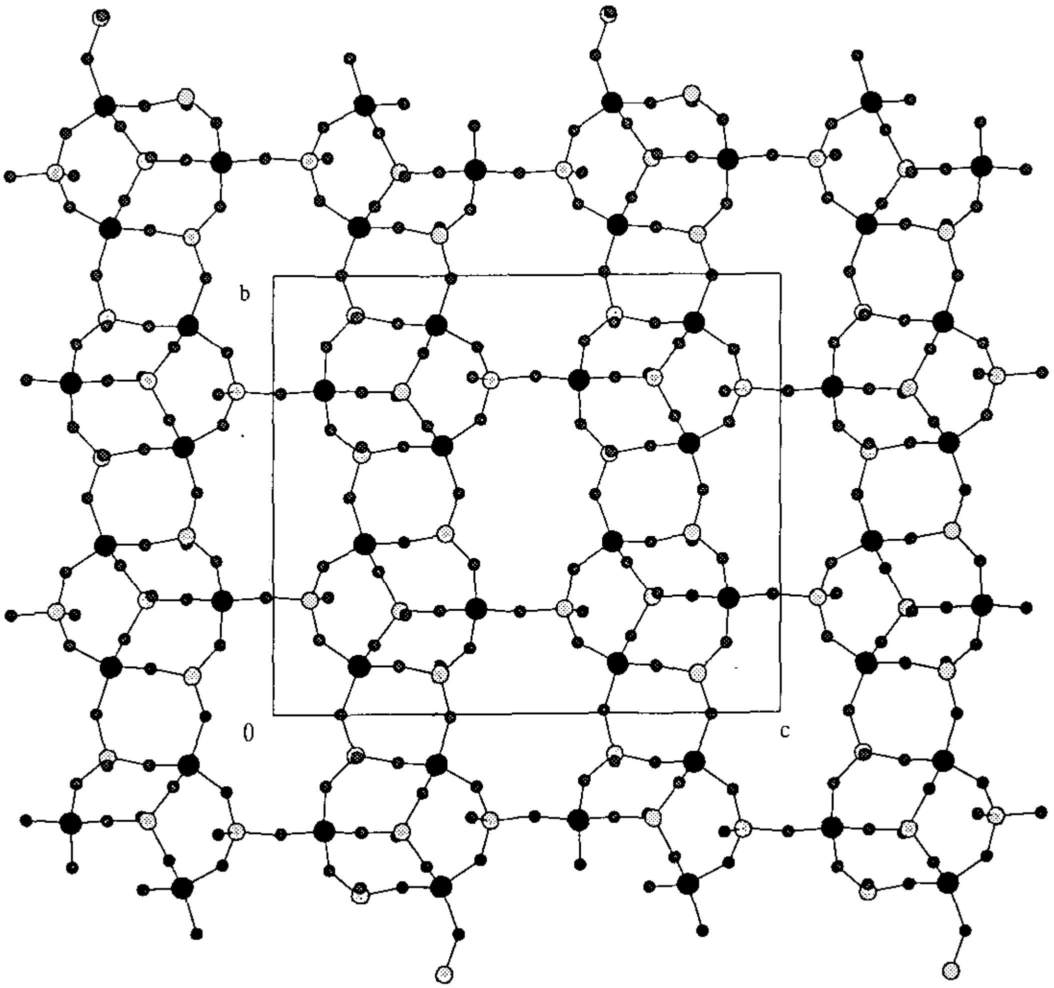

FIG. 1. View of AlPO framework normal to the plane of the layer (along *a*-axis). Elements: ● P, ◎ Al, ◉ O.

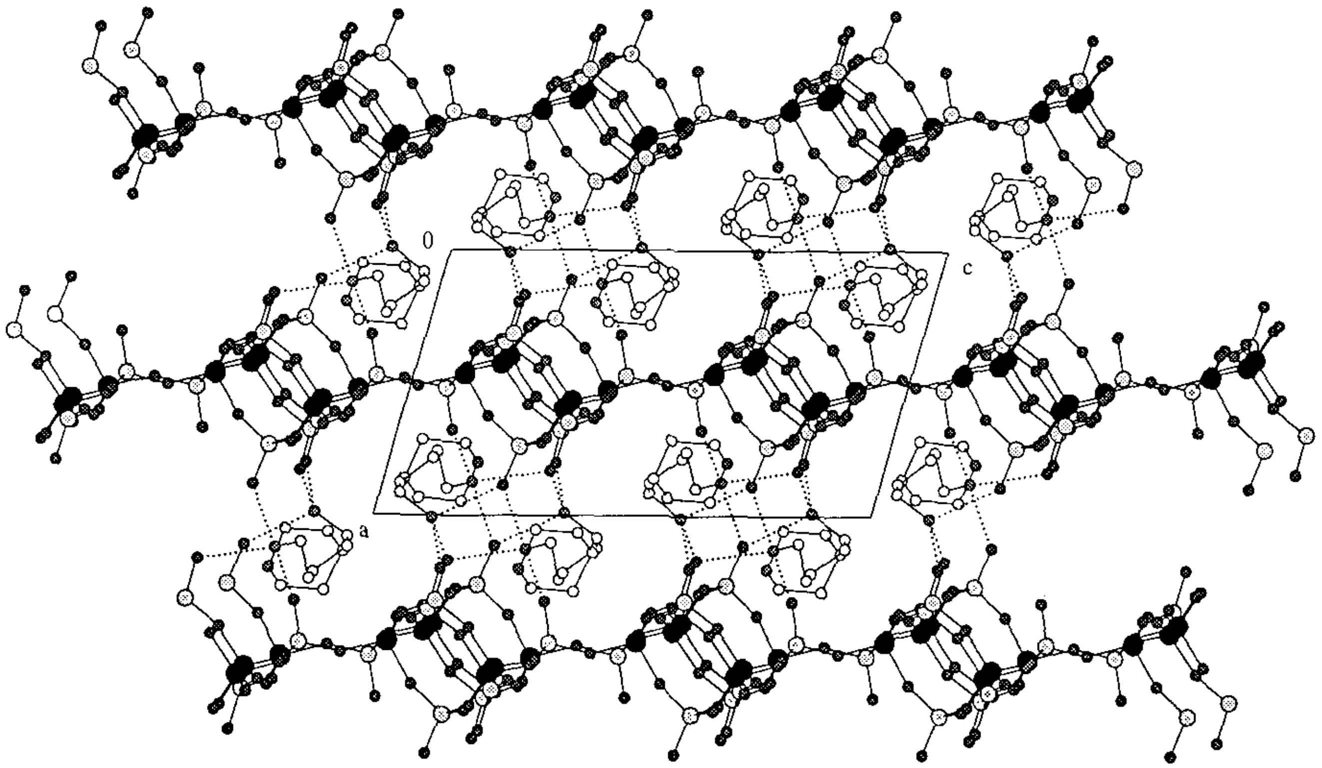

FIG. 2. View parallel to plane of layer showing interlayer hydrogen bonding (hydrogen bonding involving the piperidinium cations has been omitted).

average values are Al–O 1.727, P–O 1.537, and P=O 1.490 Å, and in $[Al_3P_4O_{16}]^{3-} \cdot 1.5(NH_3(CH_2)_4NH_3]^{2+}$ (12), Al–O 1.737, P–O 1.531, and P=O 1.507 Å. The bridging distances are also comparable with those in berlinite, the $AlPO_4$ analogue of quartz, which has average Al–O and P–O bond lengths of 1.737 and 1.516 Å, respectively (13).

The Al- and P-containing tetrahedra, which are linked in a strictly alternating manner, give rise to a puckered sheet structure in the *bc* plane (Fig. 2). The structure consists of eight- and four-membered rings; however, by systematically removing 1/4 of the phosphate groups, it can be seen that the structure is based on a 4 : 6 : 8 net. There are two crystallographically distinct eight-membered rings within these sheets; one elliptical with O···O distances varying between 5.85 and 7.99 Å and the other more circular in shape with O···O contacts in the range 6.88–6.90 Å. The organoamine cations are located in the interlamellar region of the structure, occupying positions

TABLE 5

Interlayer Spacing of $[Al_3P_4O_{16}]^{3-}$ Sheets in Aluminum Phosphates

	Cell constants (Å, °)				Interlayer spacing (Å)	Stacking sequence	Plane of sheet	Ref.
	a	*b*	*c*	*β*				
I	9.801(2)	14.837(2)	17.815(3)	105.65(1)	9.44	AAAA	*bc*	this work
II	9.014(1)	14.771(2)	17.704(2)	90.0	8.85	ABAB	*ab*	(11)
III	9.021(1)	14.845(2)	9.592(2)	105.23(1)	9.26	AAAA	*ab*	(20)

I $[Al_3P_4O_{16}]^{3-}(NH_3(CH_2)_5NH_3)^{2+}(C_5H_{10}NH_2)^+$
II $[Al_3P_4O_{16}]^{3-}(NH_3(CH_2)_2NH_3)^{2+}(OH(CH_2)_2OH_2)^+(OH(CH_2)_2OH)$
III $[Al_3P_4O_{16}]^{3-}(CH_3CH_2CH_2NH_3)_3^+$

Note. The interlayer spacings are given by *a* sin *β*, *c*/2, and *c* sin *β* for **I**, **II**, and **III**, respectively.

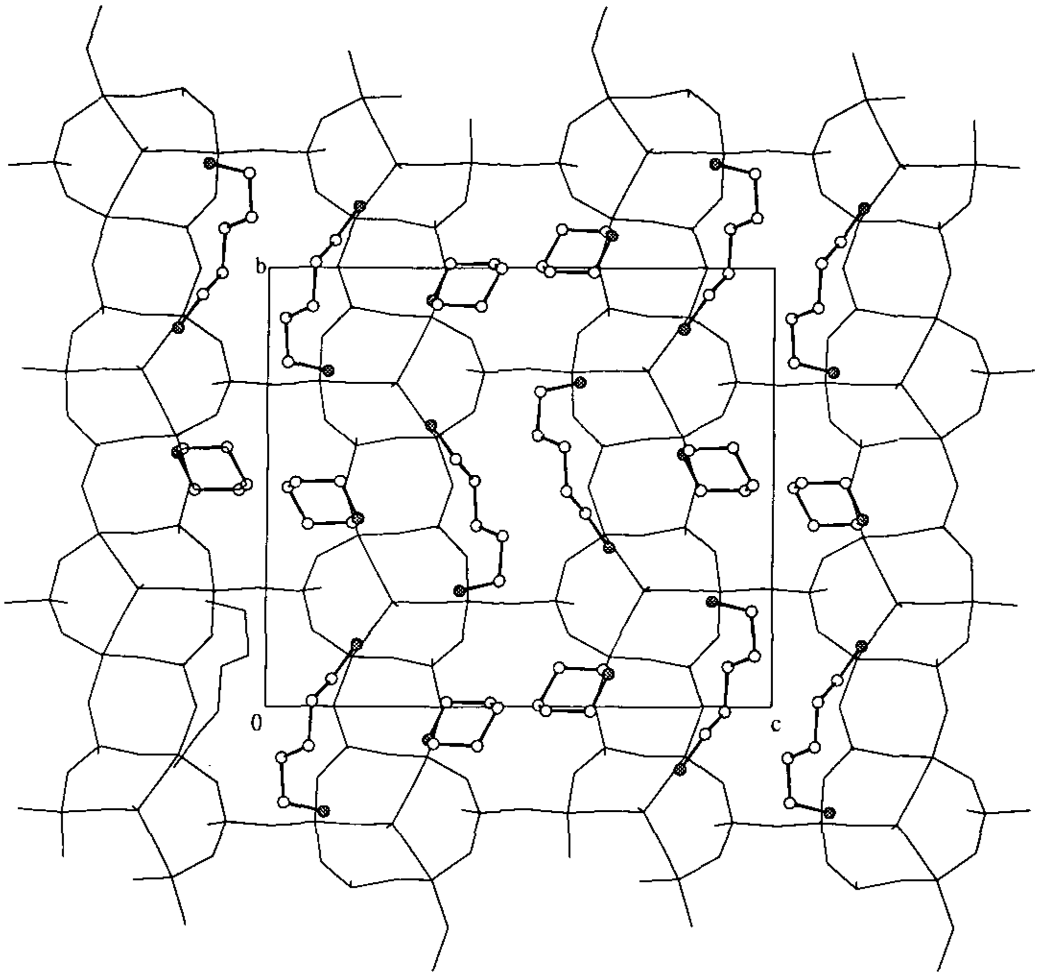

FIG. 3. View normal to the plane of layer showing location of template molecules; 1,5-diaminopentane cations reside in elliptical channels and piperidinium cations in circular channels. Elements: ○ C, ⊜ N.

which lie close to the voids formed by the eight-membered rings, there being two cations between each two layers for each window (Fig. 3). The diprotonated 1,5-diaminopentane cations are situated in the elliptical windows with the chain axis of the carbon backbone having the same orientation as the longer axis of the window, while the piperidinium cations are only associated with the circular windows. These distortions of the structure may be indicative of a differential templating effect of the two organic cations.

The $[Al_3P_4O_{16}]^{3-}$ sheets are held together by a network of hydrogen bonding involving the 1,5-diaminopentane cations (Fig. 2). At one end of the dication, the nitrogen forms two hydrogen bonds to O atoms of the 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 (N(1)···O and N(2)···O distances in the range 2.73–2.81 Å). The two hydrogen bonds from the nitrogen of each piperidinium cation are not involved in holding the layers together, as both are directed toward only one face of a sheet (N(3)···O distances of 2.76 and 2.80 Å). The layers stack in an AAAA sequence.

Two other layered AlPOs with P : Al ratio 4 : 3 have been characterized previously which have similar layer topology (based on a 4 : 6 : 8 net) with four-membered rings surrounding the eight-membered rings. The structural similarity of the layers in the three compounds is reflected by the similarity of the in-layer lattice parameters (Table 5). In the case of compound **I**, however, one of these cell parameters (*c*) is doubled as a result of there being the two crystallographically distinct eight-membered rings within the layers. The layers can then stack in either an AAAA sequence, as is observed in the present work and in **III** (19), or an ABAB sequence, as is observed for **II** (11). The stacking order, as well as the organic template chain length, appears to influence the magnitude of the interlayer separation.

CONCLUSION

Although fragmentation of the amine template has been noted previously in the synthesis of three-dimensional AlPO structures, e.g., in the case of $AlPO_4$-15 (21), the present study is the first reported example of template cyclization and the incorporation of two different organic cations between aluminum phosphate layers. Presumably the production of the piperidinium cation involves protonation of one of the amino groups in 1,5-diaminopentane, followed by internal SN_2 attack by the unprotonated amine group leading to ring closure and the elimination of ammonia.

ACKNOWLEDGMENTS

We thank the SERC for general financial support and provision of the CSSR Database at the Daresbury Laboratory, and Ms. Lisa Pearce and Dr. A. D. M. Curtis for valuable discussions. One of us (A.M.C.) also thanks the University of Oxford for a Glasstone Research Fellowship.

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