

A Hybrid Open-Framework Aluminum Phosphate-Oxalate Possessing Large Circular 12-Membered Channels

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A new aluminum phosphate-oxalate, **I**, $[\text{N}_2\text{C}_4\text{H}_{12}]\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$, has been synthesized hydrothermally in the presence of structure-directing amines. The hybrid structure comprises a vertex-linkage of AlO_6 octahedra, PO_4 tetrahedra, and C_2O_4 units leading to three-dimensional connectivity. The connectivity between AlO_6 and PO_4 units are such that it forms double-six rings that are connected to each other via the oxalate units, thereby leading to the formation of a large circular 12-membered channel of width $\sim 9 \text{ \AA}$ along the c axis. The structure-directing amine along with one water molecule is situated within this channel. The connectivity also forms two different types of 8-membered channels along the a and b axes. The three-dimensional structure of **I**, is very similar to the naturally occurring aluminosilicate zeolite, gmelinite. Crystal data for **I** are: monoclinic, space group $Pccm$, $a = 9.992(1)$, $b = 11.644(1)$, $c = 12.231(1) \text{ \AA}$, $V = 1423.0(2)$, $M = 438.9$, $Z = 4$, $R_F = 0.07$.

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INTRODUCTION

The synthesis and structure of a variety of new open-framework metal phosphates have been described in recent literature (1). A variant of the metal phosphate family is that of the metal phosphate-oxalates. During the past few months, iron phosphate-oxalates with open architectures have been prepared and characterized (2–4). The iron phosphate-oxalates generally consist of layers of iron phosphates made by the vertex linkage between FeO_6 octahedra and PO_4 tetrahedra and are crosslinked by oxalate bridges completing the three-dimensional connectivity. Recently, the synthesis and structure of an aluminum phosphate-oxalate has been reported wherein the linkages between the AlO_6 , PO_4 , and oxalate moieties form layers that are held in position by hydrogen bond interactions with the amine molecules located in between the layers (5). In our continu-

ing research on framework materials, we have been exploring various families of oxalates (6, 7) and phosphate-oxalates with a view to obtain new architectures. Our efforts have enabled us to isolate a new aluminum phosphate-oxalate, **I**, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$, possessing one-dimensional 12-membered circular channels. The structure of **I** has many features that resemble the naturally occurring aluminosilicates (8). The amine and water molecules are located in the middle of these channels. The synthesis and structure of **I** are presented in this paper.

EXPERIMENTAL

Compound **I** was synthesized starting from a gel containing n -methyl piperazine (m-PIP) as the structure-directing agent. Aluminum hydroxide, phosphoric acid (85 wt%), oxalic acid, m-PIP, and water in the ratio $\text{Al}(\text{OH})_3 : \text{H}_3\text{PO}_4 : 2 \text{H}_2\text{C}_2\text{O}_4 : \text{m-PIP} : 200 \text{H}_2\text{O}$ were mixed and stirred until homogeneous. All the chemicals were obtained from Aldrich and used without further purification. The reaction mixture was sealed in a 23-ml capacity Teflon lined stainless steel autoclave (Moline, Parr, USA) and heated at 155°C for 92 h under autogeneous pressure. The fill factor was $\sim 40\%$ and the mixture had a pH of 2.0. The resulting mixture after the reaction did not show any appreciable change in the pH and remained at 2.0. The final product, after the above heat treatment, contained large quantities of rod-like single crystals admixed with a small quantity of white powder. The products were filtered and washed thoroughly with de-ionized water. The single crystals were easily separated under an optical microscope and used for all further characterization. The total yield of the product (single crystals) was about 20%. The powder X-ray diffraction pattern indicated that the product was a new material; the pattern is entirely consistent with the structure determined by single-crystal X-ray diffraction. A least-squares fit of the powder XRD ($\text{CuK}\alpha$) lines, using the hkl indices generated from the single-crystal X-ray data, gave the following cell: $a = 9.962(2)$, $b = 11.591(1)$, $c = 12.284(1) \text{ \AA}$, which is in agreement with

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that determined by single-crystal XRD. Powder data for **I**, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$, are listed in Table 1. Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere in the 30–700°C range using a heating rate of 10°C/min. EDAX analysis indicated a Al:P ratio 1:1, consistent with the stoichiometry determined by the single crystal studies.

A suitable single crystal of **I** was carefully selected under a polarizing microscope. Data collection was performed on a Siemens SMART diffractometer with a CCD detector in the θ 1.75–23.24° range. The structure was solved and refined using SHELXTL-PLUS (9) against $|F^2|$. The relevant details of the structure determination are presented in Table 2. The amine molecule, in **I**, was found to have decomposed during the hydrothermal reaction and was disordered. Instead of the starting *n*-methyl piperazine molecule, we found only a dimethylamine molecule from the difference Fourier maps, which sits in the special position to form a piperazine fragment. It is likely that there are other fragments of the amine molecules present within the channels. We, however, were not able to identify, unequivocally, any other fragments from the difference Fourier maps. Full-matrix least-squares refinement on $|F^2|$ (atomic coordinates, anisotropic thermal parameters for the nonhydrogen atoms of the framework, water and amine molecule) were carried out using the program SHELXTL-PLUS (9). The final atomic coordinates for **I** are presented in Table 3 and the bond distances and angles in Table 4 and 5.

TABLE 1
Powder X-Ray Data for **I**,
 $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}$	$\Delta(2\theta)^a$	d_{cal}	Δd^b	I_{rel}^c
0	1	0	7.62	−0.007	11.591	0.011	100
1	0	0	8.887	0.011	9.962	−0.012	91.38
1	1	1	13.750	−0.010	6.435	0.005	40.13
1	2	0	17.732	0.028	5.009	−0.007	26.24
1	1	2	18.639	0.022	4.766	−0.006	16.88
1	2	1	19.168	0.035	4.639	−0.009	11.51
2	1	0	19.418	0.023	4.576	−0.005	23.23
2	2	0	23.547	−0.004	3.778	0.000	33.65
1	1	3	24.736	0.006	3.600	−0.001	6.80
3	0	0	26.861	0.014	3.321	−0.002	4.46
1	2	3	28.173	0.027	3.170	−0.003	10.49
3	2	0	31.058	0.021	2.881	−0.002	10.65
3	1	2	31.536	−0.049	2.833	0.004	9.02
1	4	0	32.132	−0.037	2.782	0.004	18.14
0	3	4	37.440	0.035	2.404	−0.002	10.47
2	5	0	43.040	0.004	2.102	0.000	3.58
2	3	5	47.457	−0.045	1.914	0.002	2.43
4	4	0	48.171	−0.005	1.889	0.000	11.00

^a $2\theta_{\text{obs}} - 2\theta_{\text{calc}}$.

^b $d_{\text{obs}} - d_{\text{calc}}$.

^c $100 \times I/I_{\text{max}}$.

TABLE 2
Crystal Data and Structure Refinement Parameters for **I**,
 $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$

Empirical formula	$\text{Al}_2\text{P}_2\text{O}_{13}\text{N}_2\text{C}_6\text{H}_{15}$
Crystal system	Orthorhombic
Space group	<i>Pccm</i>
Crystal size (mm)	$0.20 \times 0.16 \times 0.16$
<i>a</i> (Å)	9.992(1)
<i>b</i> (Å)	11.644(1)
<i>c</i> (Å)	12.231(1)
Volume (Å ³)	1423.0(1)
<i>Z</i>	4
Formula mass	438.9
ρ_{calc} (gcm ^{−3})	1.39
λ (MoK α) Å	0.71073
μ (mm ^{−1})	3.74
θ range (°)	1.75–23.24
Total data collected	5520
Index ranges	$-11 \leq h \leq 11, -9 \leq k \leq 12,$ $-13 \leq l \leq 12$
Unique data	1074
Observed data ($\sigma > 2\sigma(I)$)	836
R_{merg}	0.07
Refinement method	Full-matrix least-squares on $ F^2 $
<i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.07; wR_2 = 0.18^a$
<i>R</i> indices (all data)	$R_1 = 0.09; wR_2 = 0.21$
Goodness-of-fit (<i>S</i>)	1.06
Number of variables	133
Largest difference map peak and hole eÅ ^{−3}	1.419 and −0.650

^a $w = 1/[\sigma^2(F_o)^2 + (0.1366P)^2 + 5.691P]$, where $P = [F_o^2 + 2F_c^2]/3$.

RESULTS AND DISCUSSION

The structure comprises a network of AlO_6 octahedra, PO_4 tetrahedra, and the oxalate units. The asymmetric unit contains two crystallographically distinct Al and P atoms, respectively, as shown in Fig. 1. AlO_6 octahedra and PO_4 tetrahedra link to form the basic building unit, a chain of double-six rings as shown in Fig. 2. These double-six rings are connected to each other via oxalate bridges forming the framework with the formula $[\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]^-$. Charge neutrality is achieved by the incorporation of the amine molecule in its protonated form; there are $[\text{C}_2\text{N}_1\text{H}_8]^+$ ions per framework formula unit. Bond valence sum calculations (10) were used to obtain the valence states of the various species present in the framework. The average bond valence sums for the various elements are as follows: Al = 3.03; P = 5.09; C = 3.7; O = 1.85, which agrees well with the usual valence states of the elements. One oxygen, O(9), with a bond valence sum value of 1.08 is assigned as a −OH group. The proton attached with O(9) was located in Fourier difference maps, in consistent with the above formalism.

The entire framework structure is built from the basic building unit (double six-ring) linking to each other via

TABLE 3
Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$\text{\AA}^2 \times 10^3$] for I, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$

Atom	x	y	z	$U(\text{eq})^a$
Al(1)	-453(3)	2751(2)	0	15(1)
Al(2)	-2309(3)	0	2500	14(1)
P(1)	2742(2)	881(2)	0	14(1)
P(2)	0	1977(2)	2500	12(1)
O(1)	2125(7)	2068(5)	0	22(2)
O(2)	308(4)	2751(3)	1521(4)	19(1)
O(3)	-704(7)	1470(6)	0	26(2)
O(4)	1466(7)	4216(5)	0	19(2)
O(5)	-1124(7)	3863(5)	0	21(2)
O(6)	-1200(4)	1220(4)	2223(4)	21(1)
O(7)	2385(5)	195(4)	1003(4)	21(1)
O(8)	-3880(4)	1123(4)	2416(4)	18(1)
O(9)	4313(7)	1093(6)	0	31(2)
C(1)	749(9)	5102(8)	0	16(2)
C(2)	-5000	659(7)	2500	12(2)
O(100)	738(24)	5000	2500	200(12)
N(11)	-3473(32)	3551(16)	2970(34)	279(19)
C(12)	-4815(61)	3778(39)	3546(45)	482(59)
C(10)	-3271(38)	3572(33)	1723(39)	755(79)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

oxalates. It is to be noted that the double six-rings are one of the commonly observed building units in aluminosilicate zeolites (8). Along the c axis, the linkages between the double six-rings and oxalates give rise to a uniform circular 12-membered one-dimensional channel of width $8.929 \times$

TABLE 4
Selected Bond Distances in I, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$

Moiety	Distance (\AA)	Moiety	Distance (\AA)
Al(1)–O(1)	1.850(7)	Al(2)–O(6) ⁱⁱ	1.834(4)
Al(1)–O(2)	1.866(5)	Al(2)–O(6)	1.834(4)
Al(1)–O(2) ⁱ	1.866(5)	Al(2)–O(7) ⁱⁱⁱ	1.847(4)
Al(1)–O(3)	1.888(7)	Al(2)–O(7) ^{iv}	1.847(4)
Al(1)–O(4)	1.983(7)	Al(2)–O(8) ⁱⁱ	2.046(5)
Al(1)–O(5)	2.039(7)	Al(2)–O(8)	2.046(5)
P(1)–O(7)	1.507(5)	P(2)–O(6)	1.526(4)
P(1)–O(7) ⁱ	1.507(5)	P(2)–O(6) ^{iv}	1.526(4)
P(1)–O(1)	1.513(7)	P(2)–O(2)	1.530(5)
P(1)–O(9)	1.588(7)	P(2)–O(2) ^v	1.530(5)
C(1)–O(4)	1.257(10)	C(2)–O(8)	1.247(6)
C(1) ^v –O(5)	1.262(11)	C(2)–O(8) ^{vi}	1.247(6)
C(1)–C(1) ^v	1.52(2)	C(2)–C(2) ^{viii}	1.53(2)

(i) $x, y, -z$; (ii) $x, -y, -z + 1/2$; (iii) $-x, -y, z$; (iv) $-x, y, -z + 1/2$; (v) $-x, -y + 1, -z$; (vi) $-x - 1, y, -z + 1/2$; (vii) $-x - 1, -y, z$

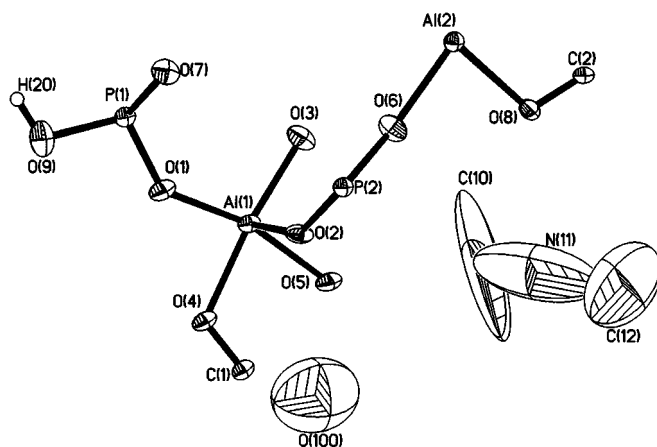


FIG. 1. ORTEP plot of I, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$. Thermal ellipsoids are given at 50% probability.

8.929 \AA (atom–atom contact distance not including the van der Waals radii) as shown in Fig. 3. The dimethylamine along with the water molecules are located in the middle of this channel. Similar structural features have been observed

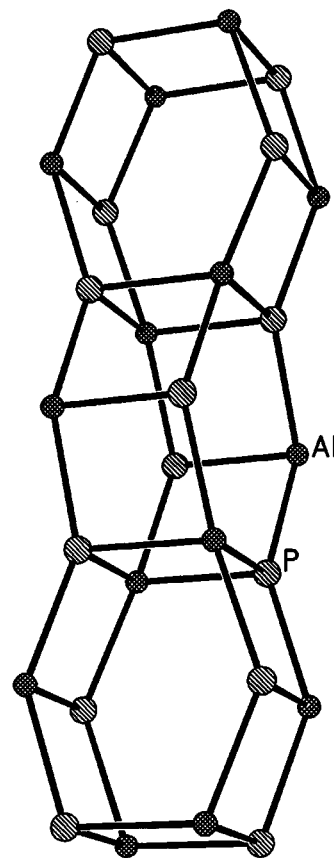


FIG. 2. The basic building unit present in I, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$. Oxygens atoms are omitted for clarity. Note that the linkages between the different polyhedral centers form double-six-rings, which are connected to form the cylinder-like arrangement.

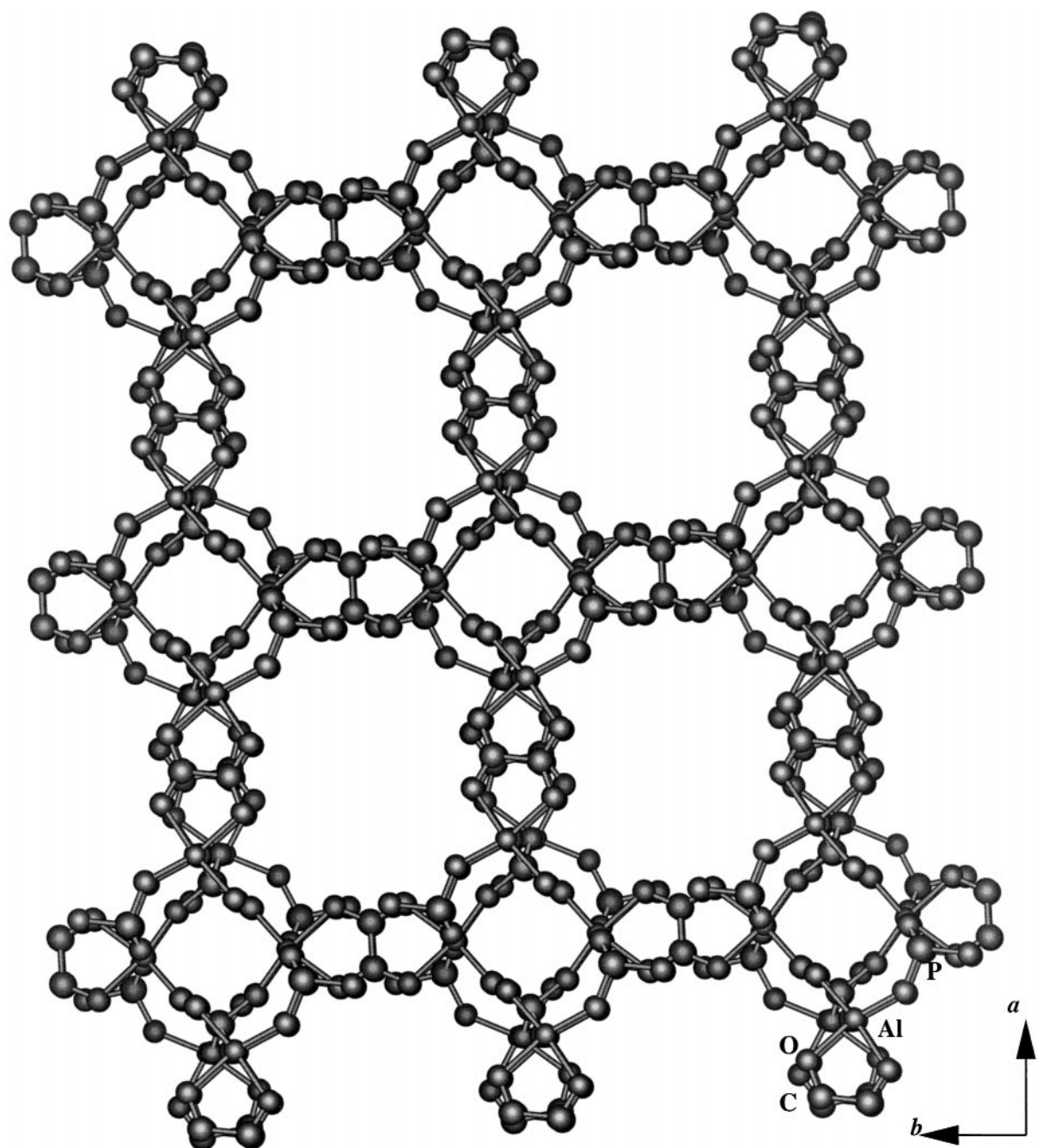


FIG. 3. The structure of **I**, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\cdot\text{H}_2\text{O}$ along the c axis showing the 12-membered channels. Note that the double six-rings are connected via the oxalate bridges. Amine and water molecules are omitted for clarity.

in the naturally occurring aluminosilicate, gmelinite. The structure of gmelinite is formed by similar double six-rings that are linked via four rings forming uniform circular 12-membered channels ($7.0 \times 7.0 \text{ \AA}$). In the present structure, the bidendate oxalate bridge performs a function similar to that of the 4-membered ring in gmelinite, both require two connections to complete the bridging role. Along the a axis, the double six-rings form a column (Fig. 1), which is

held in place by the oxalate links as shown in Fig. 4. This results in an 8-membered channel of $6.1 \times 5.3 \text{ \AA}$. Similar connectivity along the b axis results in yet another 8-membered channel of similar dimensions as shown in Fig. 5. The terminal $-\text{OH}$ group from the HPO_4 unit protrude into this channel (b axis). Similar channels have also been observed in gmelinite. Thus, the three-dimensional structure of **I** is closely related to gmelinite.

TABLE 5
Selected Bond Angles in I,
[N₂C₄H₁₂][Al₂(PO₄)(HPO₄)(C₂O₄)]H₂O

Moiety	Angle (°)	Moiety	Angle (°)
O(1)–Al(1)–O(2)	94.0(2)	O(6) ⁱⁱ –Al(2)–O(6)	105.6(3)
O(1)–Al(1)–O(2) ⁱ	94.0(2)	O(6) ⁱⁱ –Al(2)–O(7) ⁱⁱⁱ	96.5(2)
O(2)–Al(1)–O(2) ⁱ	171.1(3)	O(6)–Al(2)–O(7) ⁱⁱⁱ	86.4(2)
O(1)–Al(1)–O(3)	102.3(3)	O(6) ⁱⁱ –Al(2)–O(7) ^{iv}	86.4(2)
O(2)–Al(1)–O(3)	87.3(2)	O(6)–Al(2)–O(7) ^{iv}	96.5(2)
O(2) ⁱ –Al(1)–O(3)	87.3(2)	O(7) ⁱⁱⁱ –Al(2)–O(7) ^{iv}	175.3(3)
O(1)–Al(1)–O(4)	84.8(3)	O(6) ⁱⁱ –Al(2)–O(8) ⁱⁱ	87.7(2)
O(2)–Al(1)–O(4)	92.3(2)	O(6)–Al(2)–O(8) ⁱⁱ	165.6(2)
O(2) ⁱ –Al(1)–O(4)	92.3(2)	O(7) ⁱⁱⁱ –Al(2)–O(8) ⁱⁱ	86.5(2)
O(3)–Al(1)–O(4)	172.9(3)	O(7) ^{iv} –Al(2)–O(8) ⁱⁱ	89.8(2)
O(1)–Al(1)–O(5)	166.1(3)	O(6) ⁱⁱ –Al(2)–O(8)	165.6(2)
O(2)–Al(1)–O(5)	86.6(2)	O(6)–Al(2)–O(8)	87.7(2)
O(2) ⁱ –Al(1)–O(5)	86.6(2)	O(7) ⁱⁱⁱ –Al(2)–O(8)	89.8(2)
O(3)–Al(1)–O(5)	91.6(3)	O(7) ^{iv} –Al(2)–O(8)	86.5(2)
O(4)–Al(1)–O(5)	81.3(3)	O(8) ⁱⁱ –Al(2)–O(8)	79.8(2)
O(7)–P(1)–O(7) ⁱ	109.0(4)	O(6)–P(2)–O(6) ^{iv}	109.5(4)
O(7)–P(1)–O(1)	112.8(2)	O(6)–P(2)–O(2)	108.9(2)
O(7) ⁱ –P(1)–O(1)	112.8(2)	O(6) ^{iv} –P(2)–O(2)	110.8(2)
O(7)–P(1)–O(9)	108.4(2)	O(6)–P(2)–O(2) ^{iv}	110.8(2)
O(7) ⁱ –P(1)–O(9)	108.4(2)	O(6) ^{iv} –P(2)–O(2) ^{iv}	108.9(2)
O(1)–P(1)–O(9)	105.2(4)	O(2)–P(2)–O(2) ^{iv}	107.8(3)
O(4)–C(1)–O(5) ^v	127.9(9)	O(8)–C(2)–O(8) ^{vi}	128.6(8)

(i) $x, y, -z$; (ii) $x, -y, -z + 1/2$; (iii) $-x, -y, z$; (iv) $-x, y, -z + 1/2$; (v) $-x, -y + 1, -z$; (vi) $-x - 1, y, -z + 1/2$.

The environments of the two Al sites are chemically similar. Each Al is octahedrally coordinated by six oxygens with Al–O contacts varying between 1.834 and 2.046 Å (Al(1)_{av.} = 1.912 Å; Al(2)_{av.} = 1.909 Å) and O–Al–O angles lying between 79.8 and 175.3° (Al(1)_{av.} = 106.3; Al(2)_{av.} = 105.7°). The longest bond distances of Al(1)–O(4) = 1.983, Al(1)–O(5) = 2.039, Al(2)–O(8) = 2.046 Å are associated with bonding involving the oxalate units. The above values are in good agreement with those reported for the earlier aluminum phosphate-oxalate material (5). The two distinct phosphorus atoms are tetrahedrally coordinated with respect to their oxygen neighbors. The P–O distances are in the 1.507–1.588 Å range (av. 1.528 Å) and the O–P–O angles are in the 105.2–112.8 range (av. 109.5°), which is in good agreement with those previously observed (1–6). The P–O(9) bond distance of 1.588 Å is a P–OH bond and similar bond lengths have been found for P–OH groups in other structures. For example, in H₃PO₄·0.5H₂O and α -zirconium phosphate (11), the average P–OH bond lengths are 1.551 and 1.558 Å, respectively. The C–O bond distances and O–C–O bond angles are also as expected.

Thermogravimetric analysis (TGA) under an inert atmosphere in the range from room temperature to 700°C shows

three different regions of weight losses. The mass loss around 120°C corresponds to the loss of water, and the second mass loss at 250°C with a more or less continuous broad mass loss up to 600°C corresponds to the combined loss of the amine and the oxalate unit from the structure. The total observed mass loss of 41.9% corresponds well with the loss of water, amine, and the oxalate from the structure (calculated 42%). The powder XRD of the decomposed sample was found to be largely amorphous with broad XRD lines that matched with the condensed aluminum phosphate phase, berilinite.

It is instructive to compare the present structure with the only other known aluminum phosphate-oxalate (5). In the latter, the connectivity between the AlO₆ octahedra, PO₄ tetrahedra, and the oxalate units form layers. The structure-directing amine, ethylenediamine, is presumably located between these layers. In the present structure, however, the network between the various polyhedra forms a three-dimensional architecture that has close resemblance to the naturally occurring zeolites, gmelinite. The amine molecule, *n*-methyl piperazine, is decomposed during synthesis, forming piperazine, which is located in the 12-membered

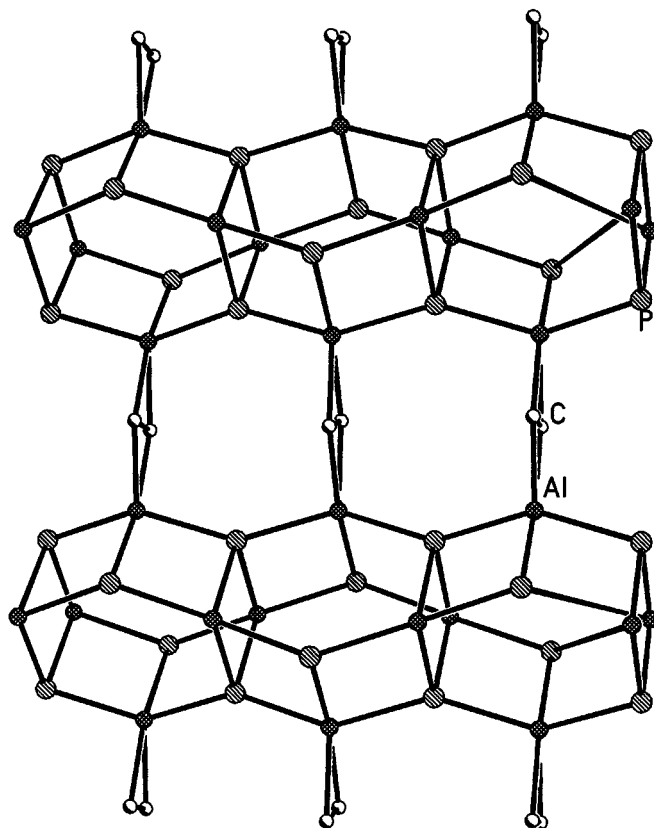


FIG. 4. Structure of I, [N₂C₄H₁₂][Al₂(PO₄)(HPO₄)(C₂O₄)]H₂O along the *a* axis showing the 8-membered channels. Oxygens, amine, and water molecules are omitted for clarity.

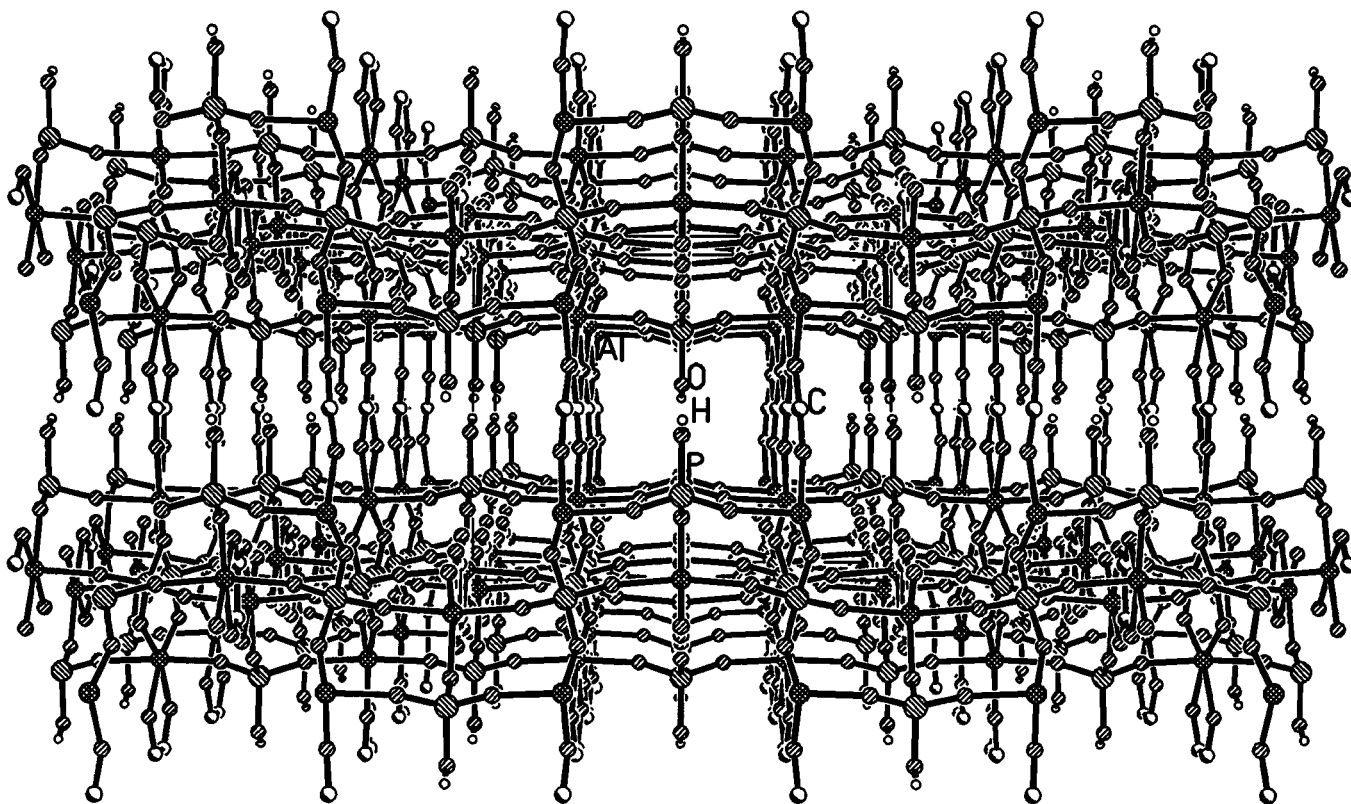


FIG. 5. Structure of I, $[\text{N}_2\text{C}_4\text{H}_{12}][\text{Al}_2(\text{PO}_4)(\text{HPO}_4)(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$ along the b axis showing the 8-membered channel. Note that the terminal $-\text{OH}$ group from the P atoms point into the 8-membered channels.

channels. The decomposition as well as reaction of the template molecules forming newer products during hydrothermal synthesis has been observed earlier (12, 13). The exact nature and role of these transformations are not yet clearly understood. One may, however, safely presume that amine molecules in these solids do have an important function of directing the formation of framework structure, as in the absence of it such structures are not formed. The synthesis of **I** possessing novel three-dimensional connectivity, underlines the need for further work in this area as newer structures are likely to be formed in the presence of other structure-directing agents.

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