An Open Framework Aluminophosphate with Unique 12-Membered Ring Channels: $Al_9(PO_4)_{12}(C_{24}H_{91}N_{16}) \cdot 17H_2O$

Yao-Hua Xu,[1] Bing-Guang Zhang,[2] Xiao-Feng Chen, Shu-Hua Liu, Chun-Ying Duan, and Xiao-Zeng You[1]

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China

By using the hydrothermal method, a new large-pore three dimensional aluminophosphate $Al_9(PO)_{12}(C_{24}H_{81}N_{16}) \cdot 17H_2O$ has been synthesized. The compound crystallizes in the cubic space group *I-43m* with $a = 16.7963(13)$ Å, $V = 4738.5(6)$ Å^3, and $Z = 2$. The P/Al ratio of this compound is 4:3 and the structure consists of Al-centered and P-centered tetrahedra in which all the AlO_4 tetrahedra vertices and three of PO_4 tetrahedra corners are shared. The framework contains unique 12-membered ring channels, which intersect each other with 12-membered ring windows in three dimensions, and almost spherical cavities, in which water and amine ions are located. The window containing three P=O groups selectively interacts with 4-(2-aminoethyl)diethylenetriamine by the effect of recognition in the hydrothermal condition. The compound could exist up to 260°C. At higher temperature, the amine was decomposed and released, and the compound was transferred into amorphous phase. The component Al of the compound can be partly substituted with other elements, such as Sn, Zn, Mg, Co, Mn, and Cd, by which the charge of the framework can be adjusted. © 1999 Academic Press

Key Words: **Aluminium; microporous; phosphate; TREN**

INTRODUCTION

Zeolites and microporous compounds are interesting not only due to their great surface/volume ratio, which may be useful in the field of gas absorption, but also due to their special channel or cavity structures, which may be applied in the fields of catalysis, ion exchange, molecular recognition, optics, electronics and so forth (1–7). Since the discovery of microporous aluminophosphates in 1982 (8, 9), the elements consisting of the microporous materials are not limited in Si, Al, and O, but include many other elements, such as most transition metal elements and main group elements (10, 11). Some interesting compounds with special structures, such as five-coordinated Ti (12), chiral 3D phase

(13), 20, 18, 14, and 12-membered ring channels (14–18), and mesoporous structure (19, 20), have been found. These compounds have been synthesized with special structure-direction agents or under special conditions. The relationship between the structures and the structure-direction agents for these compounds is not very clear. In fact, the compounds with different structures can be synthesized with the same structure-direction agent and the same compound can be synthesized with different structure-direction agents, which indicates a complication in hydrothermal synthesis. Here we report an open framework aluminophosphate with unique 12-membered ring channels intersecting each other with 12-membered ring windows in three dimensions, and this compound selectively contains 4-(2-aminoethyl) diethylenetriamine (TREN) as a guest by the interaction of molecular recognition in the hydrothermal condition.

EXPERIMENTAL

Hydrothermal Synthesis and Analysis Methods

All starting materials were reagent grade purchased. The compound was prepared by hydrothermal synthesis from a mixture of aluminum phosphate gel containing TREN as a structure-directing template and charge balance ions. The empirical aluminum phosphate gel was prepared by mixing $NaAlO_2$, H_3PO_4 (85%), TREN:HCl, and water in a mole ratio as $Al_2O_3:4P_2O_5:6(TREN):200H_2O$ with pH = 6–7 which was adjusted by adding dropwise 6 mol/l NaOH solution. The mixture was sealed in a stainless autoclave with Teflon-liner and heated at 140°C for 5 days. The product was filtered, washed with distilled water, and dried at ambient temperature.

The elemental analysis was performed on a PE 240C elemental analyzer. The infrared spectrum (IR) was recorded on a Fourier Nicolet FT-170 SX spectrophotometer with pressed KBr pellets. Simultaneous differential thermal analysis and thermogravimetric analysis (DTA-TG) were performed on a SDT 2960 simultaneous DTA-TGA thermal analyst instrument in flowing air at a heating rate of 10°C/min.

220

Structure Determination and Refinement

A football-like colorless crystal with dimensions $0.2 \times 0.2 \times 0.2$ mm was selected from the product for indexing and intensity data collection at 293(2) K on a Siemens P4 four-circle diffractometer using monochromated MoKα ($\lambda = 0.71073$ Å) radiation from a rotating-anode generator operating on 50 kV and 90 mA. As a check on crystal and instrument stability, three representative reflections were measured every 100 points. Intensity data were collected using the θ–2θ scan mode with a variable scan speed 5.0–50.0/min in ω. The data were corrected for Lorentz polarization effects during data reduction using XSCANS (21). An empirical absorption correction based on ψ-scan measurements was applied.

The structure was solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL (22). All computations were carried out on a PC-586 computer using the SHELXTL package. Analytical expressions of neutral-atom scattering factors and anomalous dispersion corrections were incorporated (23). All the nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the water were not found from the fourier-difference map due to the larger isotropic U of the oxygen atoms. The hydrogen atoms of the amine were placed in calculated positions (C–H 0.96 Å) and allowed to ride on their respective parent atoms and the hydrogen atoms were assigned by fixing isotropic thermal parameters of 1.2 times the equivalent isotropic U of the atoms to which they were attached. The contributions of these hydrogen atoms were included in the structure-factor calculations except the hydrogen atoms of the water which were not considered. Details of the data collection and structure refinement can be found in Table 1. Atom positions are listed in Table 2 and some selected distances and angles are given in Table 3.

RESULTS AND DISCUSSION

Composition and Structure

Elemental analysis found: 12.38 wt% C, 4.89 wt% H, and 9.44 wt% N. Calculation for $Al_9(PO_4)_{12}(C_{24}H_{91}N_{16}) \cdot 17H_2O$: 12.6 wt% C, 5.0 wt% H, and 9.8 wt% N. The single crystal X-ray diffraction study demonstrates that the colorless football-like crystal has a novel open framework consisting of corner sharing TO_4 tetrahedra with unique 12-membered ring channels in three dimensions.

In this compound, there are two crystallographic independent aluminum atoms and three independent oxygen atoms which are combining with one phosphorous atom. Two different Al sites in the independent unit are in special positions. The phosphorous atom and three oxygen atoms are in general positions (Table 2). In the unit, there are also two different N sites as well as two different C sites, which are bonding together and belonging to amine. All of the

N and C sites are in general position. There are also three independent oxygen atoms in the unit. One is located in a special position and two are located in general positions, all of which belong to the water in the compound.

TABLE 1
Crystal Data and Structure Refinement for 1

Identification code	$x3$
Empirical formula	$C_{24}H_{115}Al_9N_{16}O_{65}P_{12}$
Formula weight	2282.78
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	$I\bar{4}3m$
Unit cell dimensions	$a = 16.7963(13)$ Å alpha $= 90°$
	$b = 16.7963(13)$ Å beta $= 90°$
	$c = 16.7963(13)$ Å gamma $= 90°$
Volume, z	4739.5(6) Å^3, 2
Density (calculated)	1.600 Mg/m^3
Absorption coefficient	0.412 mm^{-1}
F (000)	2376
Crystal size	$0.20 \times 0.20 \times 0.20$ mm
θ range for data collection	2.43 to 24.97°
Limiting indices	$-1 \le h \le 16,\ -1 \le k \le 19,$
	$-1 \le l \le 19$
Reflections collected	2696
Independent reflections	523 ($R_{int} = 0.0471$)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	523/0/62
Goodness-of-fit on F^2	1.122
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0627$, w$R2 = 0.1476$
R indices (all data)	$R1 = 0.0627$, w$R2 = 0.1555$
Absolute structure parameter	0.9(6)
Largest diff. peak and hole	0.582 and -0.426 eÅ^{-3}

$R1 = \sum||F_0| - |F_c||/\sum|F_0|$
$wR2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)]]^{1/2}$

TABLE 2
Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [Å$^2 \times 10^3$] for 1. U(eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	y	z	U(eq)
Al(1)	0	5000	0	24(1)
P(2)	−1222(1)	4336(1)	1222(1)	30(1)
Al(2)	0	5000	2500	29(1)
O(1)	−1410(2)	3471(3)	1410(2)	51(1)
O(2)	−904(3)	4800(2)	1941(2)	63(1)
O(3)	−575(2)	4374(3)	575(2)	41(1)
N(1)	−2000(3)	2000(3)	−2000(3)	30(2)
C(1)	−1795(5)	2447(5)	−1275(6)	40(2)
C(2)	−1449(3)	3290(4)	−1449(3)	39(2)
N(2)	−1968(2)	3759(3)	−1968(2)	37(1)
O(1W)	0	0	0	97(8)
O(2W)	−935(4)	935(4)	935(4)	96(4)
O(3W)	−495(6)	2421(8)	495(6)	198(6)
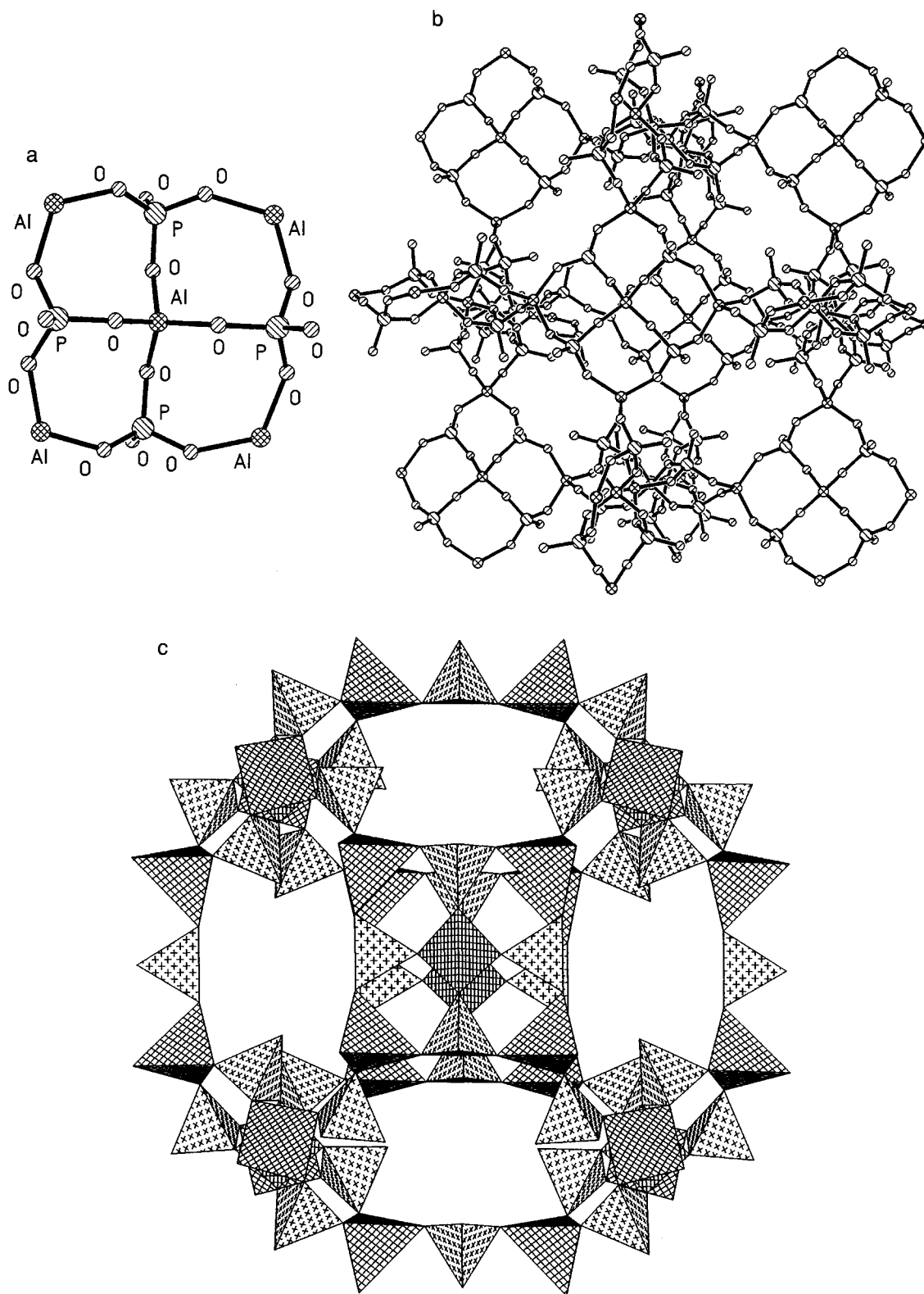
FIG. 1. The bigger building unit and the network structure and cage of the compound. (a) The bigger building sheet; (b) the unit cell (without amine ions and water); (c) the spherical cage.

TABLE 3
Selected Bond Lengths [Å] and Angles [°] for 1

$Al(1)-O(3)^a$	1.724(4)	$Al(1)-O(3)^b$	1.724(4)
$Al(1)-O(3)^c$	1.724(4)	$Al(1)-O(3)$	1.724(4)
$P(2)-O(1)$	1.520(5)	$P(2)-P(2)$	1.534(3)
$P(2)-O(2)^d$	1.534(3)	$P(2)-O(3)$	1.537(4)
$Al(2)-O(2)^e$	1.816(4)	$Al(2)-O(2)$	1.816(4)
$Al(2)-O(2)^a$	1.816(4)	$Al(2)-O(2)^f$	1.816(4)
$N(1)-C(1)$	1.471(10)	$C(1)-C(2)$	1.559(9)
$C(2)-N(2)$	1.462(8)		
$O(3)^a-Al(1)-O(3)^b$	104.9(3)	$O(3)^a-Al(1)-O(3)^c$	111.8(2)
$O(3)-Al(1)-O(3)^c$	111.8(2)	$O(3)-Al(1)-O(3)$	111.8(2)
$O(3)-Al(1)-O(3)$	111.8(2)	$O(3)^c-Al(1)-O(3)$	104.9(2)
$O(1)-P(2)-O(2)$	113.2(2)	$O(1)-P(2)-O(2)^d$	113.2(2)
$O(2)-P(2)-O(2)^d$	107.0(3)	$O(1)-P(2)-O(3)$	109.4(3)
$O(2)-P(2)-O(3)$	106.8(2)	$O(2)^d-P(2)-O(3)$	106.8(2)
$O(2)^d-Al(2)-O(2)$	105.49(10)	$O(2)^e-Al(2)-O(2)^a$	105.49(10)
$O(2)-Al(2)-O(2)^a$	117.8(2)	$O(2)^e-Al(2)-O(2)^e$	117.8(2)
$O(2)-Al(2)-O(2)^f$	105.49(10)	$O(2)^a-Al(2)-O(2)^f$	105.49(10)
$P(2)-O(2)-Al(2)$	142.4(3)	$P(2)-O(3)-Al(1)$	144.8(3)
$C(1)^g-N(1)-C(1)^h$	110.3(4)	$C(1)^g-N(1)-C(1)^i$	142.1(9)
$C(1)-N(1)-C(1)^i$	110.3(4)	$C(1)-N(1)-C(1)^j$	110.3(4)
$C(1)^i-N(1)-C(1)^j$	110.3(4)	$C(1)^g-N(1)-C(1)^k$	110.3(4)
$C(1)^h-N(1)-C(1)^k$	110.3(4)	$C(1)^g-C(1)-C(1)^k$	120.000(2)
$N(1)-C(1)-C(2)$	113.3(7)	$N(2)-C(2)-C(1)^g$	112.3(5)
$N(2)-C(2)-C(1)$	112.3(5)		

Note. Symmetry transformations used to generate equivalent atoms: $^a-x, -y+1, z;$ $^b-x, -y+1, -z;$ $^c-x, y, -z;$ $^d-z, y, -x;$ $^e-y-1/2, -x+1/2, -z+1/2;$ $^f-y+1/2, x+1/2, -z+1/2;$ $^gz, y, x;$ $^hx, -z, -y;$ $^i-y, -z, x;$ $^jz, -x, -y;$ $^k-y, -x, z.$

Four units of Al_2PO_3 are joining together by sharing the same Al(1) atom to form a bigger building unit Al_5P_4 (Fig. 1a). To the Al_5P_4 building unit, the five aluminum atoms are in one plane, two P atoms are located below the plane, and two are above the plane with the same distance of 1.1175 Å. So the Al_5P_4 building unit is a square building sheet. The Al_5P_4 building sheets are vertically linked together by sharing corner aluminum atoms to form an open framework structure (Fig. 1b). Eighteen building sheets of Al_5P_4 are linking together to form a cubic cell, among which six sheets are lying in the cubic faces and 12 sheets are vertically connecting with them, and a big cage is formed inside. In the cubic cell corner, six buildings sheets of Al_5P_4 are linking together and form a 12-membered ring window; these windows are connecting together to form a 12-membered ring channel in the $\langle 111 \rangle$ direction. These channels intersect each other with 12-membered ring windows, in which a great spherical cavity is formed (Fig. 1c), and form an opening framework in three dimensions with unique 12-membered ring channels. The channels are filled with water and amine ions. Water is lying inside the cavities, and amine ions are located around the windows.

Figure 2 shows the 12-membered ring window with amine ions and water, which are hydrogen-bonding with the
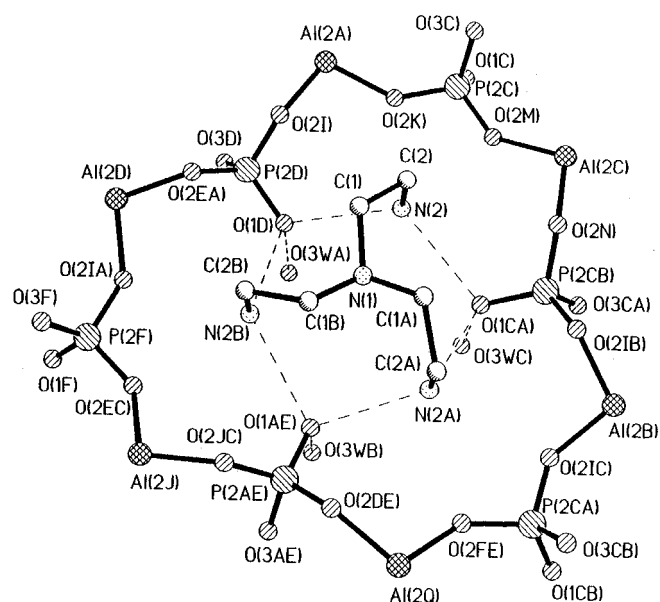

FIG. 2. The 12-membered ring window with amine and water. The hydrogen bonds are shown as dashed lines.

free oxygen O(1) atom of the PO_4 group. Each free oxygen atom O(1) of the PO_4 groups is hydrogen-bonding with two terminal N(2) atoms of amine with the distance of $O(1) \cdots H—N(2)$ 2.837 Å and one water with $O(1) \cdots H—O(3w)$ 2.799 Å. So the amine ions are stably anchored in the windows. The windows have special form with C_3 symmetry with three free oxygen atoms of PO_4 groups portruding into the channel, which are hydrogen-bonding with terminal N atoms of amine. This may be the reason why it selectively included TREN by molecular recognition in the hydrothermal condition. The size of the window is gauged by O(1AE)-O(1D) of 4.899 Å and O(1AE)-P(2C) of 8.942 Å. Based on the charge balance criterion of the compound, it is clear that there are two kinds of amine ions, $(C_6H_{20}N_4)^{2+}$ and $(C_6H_{21}N_4)^{3+}$. They are disordered in the compound in the ratio of 3:1. The water inside the cages is also hydrogen-bonding each other with the distance of $O(1w) \cdots H—O(2w)$ 2.720 Å, $O(2w) \cdots H—O(3w)$ 2.707 Å, and $O(3w) \cdots H—O(3wA)$ 2.351 Å. The latter is shorter than the others and this may be attributed to the influence of the special position in the channel. These water and amines as well as the free oxygen atoms of PO_4 groups together form a net structure by hydrogen-bonding each other (Fig. 3). The mount of H^+ ions in the cage can also be changed by substituting the Al atom with other elements, such as Mg, Co, Zn, Cd, Sn, and Mn. For example, the crystals of $Mn_4Al_5(PO_4)_{12}$ $(C_{24}H_{91}N_{18}) \cdot 14H_2O$, $Co_4Al_5(PO_4)_{12}$ $(C_{24}H_{97}N_{20}) \cdot 13H_2O$, $Mg_5Al_4(PO_4)_{12}R$ (R = TREN, water, etc.), $Zn_4Al_5(PO_4)_{12}$ $(C_{24}H_{109}N_{24}) \cdot 9H_2O$, which had the same structure as that of the title compound, had been prepared.
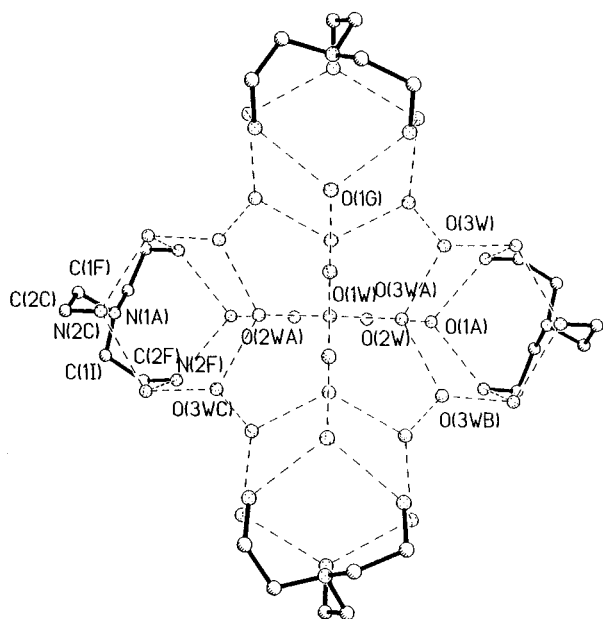
FIG. 3. The amine ions and water located in the channel. The hydrogen bonds are shown as dashed lines.

However, the compound has no the second harmonic generation (SHG) property, although it is crystallized in the space group of $I\text{-}43m$, which has noncentric symmetry.

IR Spectrum

The IR spectrum of the compound showed the characteristics of amine and phosphate. The broadened absorption band with several peaks between 2300–3800 cm^{-1} is attributed to the stretching vibration of water and amine. The two absorption bands at 1647 and 1627 cm^{-1} are ascribed

TABLE 4
Anisotropic Displacement Parameters [Å$^2\times10^3$] for 1. The Anisotropic Displacement Factor Exponent Takes the Form:
$-2\pi^2\,[(ha^*)^2 U_{11}+\cdots+2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al(1)	24(1)	24(2)	24(1)	0	0	0
P(2)	29(1)	31(1)	29(1)	4(1)	3(1)	−4(1)
Al(2)	32(1)	32(1)	22(1)	0	0	0
O(1)	58(2)	39(2)	58(2)	10(2)	21(2)	−10(2)
O(2)	96(3)	60(2)	33(2)	−6(2)	−4(2)	5(2)
O(3)	40(1)	41(2)	40(1)	7(1)	18(2)	−7(1)
N(1)	30(2)	30(2)	3(2)	−1(2)	1(2)	−1(2)
C(1)	37(4)	36(4)	48(5)	2(5)	20(4)	3(4)
C(2)	39(2)	38(3)	39(2)	−13(2)	−3(3)	−13(2)
N(2)	42(2)	27(2)	42(2)	−7(2)	1(2)	−7(2)

TABLE 5
Hydrogen Coordinates ($\times10^4$) and Isotropic Displacement Parameters (Å$^2\times10^3$) for 1

	x	y	z	U (eq)
H(1A)	−1403(5)	2146(5)	−988(6)	48
H(1B)	−2260(5)	2496(5)	−947(6)	48
H(2D)	−938(3)	3234(4)	−1701(3)	47
H(2E)	−1375(3)	3583(4)	−966(3)	47
H(2A)	−1753(2)	4239(3)	−2062(2)	56
H(2B)	−2031(2)	3492(3)	−2422(2)	56
H(2C)	−2445(2)	3823(3)	−1726(2)	56

to the bending vibration of water. The absorption bands at 1549 and 1475 cm^{-1} are assigned to the bending vibration of the N–H group of amine. The weak absorption bands between 1310–1400 cm^{-1} are referred to the bending vibration of C–H group of amine. The weak absorption band at 1293 cm^{-1} is ascribed to the stretching vibration of HPO$_4$ group, indicating that the free oxygen of the PO$_4$ group is partly protonated caused by hydrogen bonding with amine, which is confirmed by the result of crystal structure analysis. The strong absorption bands between 900–1200 cm^{-1} are referred to the stretching vibration of PO$_4$ tetrahedra. The two weak absorption bands at 848 and 870 cm^{-1} are assigned to the wagging vibration of the NH group of amine. The medium strong absorption bands between 400–800 cm^{-1} are attributed to the bending vibration of PO$_4$ tetrahedra. The more complex absorption bands between 2500–3000 cm^{-1} indicate that TREN in this compound is protonated and located in a certain position.

Thermal Property

The DTA-TG curves of the compound (Fig. 4) showed that there were two steps of weight loss. There are three endothermic peaks in the DTA curve at 107, 216, and 252°C, respectively, and about 12.65 wt% weight loss in the TG curve between 50–273°C, which are attributed to the water of the compound. Between 280–754°C, there is about 24.16 wt% weight loss and several exothermic peaks and endothermic peaks, which are ascribed to the amine. In this process, amine was oxided by oxygen and decomposed into smaller molecules. It was also found that carbon was formed in this process and partly left in the bulk which appeared black in color. Between 754–1000°C, there are some exothermic peaks, endothermic peaks, and weight loss. This is referred to the left carbon oxidation and losing and the aluminophosphate decomposition with loss of P$_2$O$_5$ and water. Powder X-ray diffraction analysis shows that the titled compound was transferred into an amorphous phase when it was heated at 550°C for 5 h.
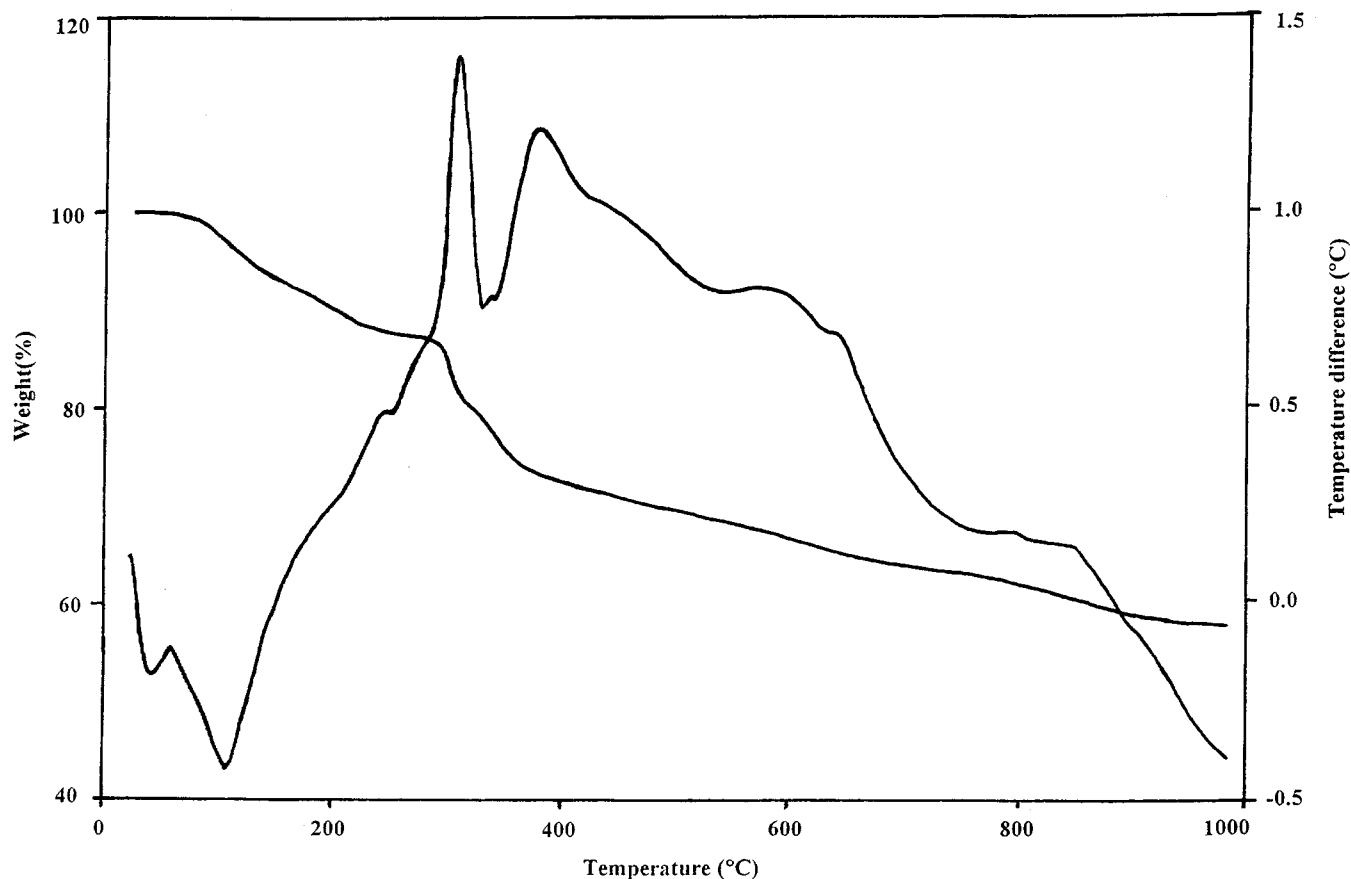
FIG. 4. The DTA-TG curves of the compound.

CONCLUSIONS

A novel opening framework aluminophosphate with unique 12-membered ring channels in three dimensions has been hydrothermally synthesized using TREN as a structure-directing template. It shows the selective inclusion of TREN by molecular recognition in hydrothermal condition. The compound, $Al_9(PO_4)_{12}(C_{24}H_{91}N_{16}) \cdot 17H_2O$, which has unique intersecting 12-membered ring channels in three dimensions with great spherical cages, can be stably existing up to 260°C. The content of Al in this compound can be partly substituted with other elements such as Mg, Cd, Mn, Co, and Zn, by which the charge of the framework can be adjusted.

ACKNOWLEDGMENTS

REFERENCES

1. C. M. Lopez, F. J. Machado, J. Goldwasser, B. Mendez, K. Rodriguez and M. M. Ramirez-Agudelo, *Zeolites* **19,** 133 (1997).
2. Q. Gao, Y. Huang, and R. Xu, *J. Chem. Soc. Chem. Commun.* 1905 (1996).
3. G. A. Ozin, *Adv. Mater.* **4,** 612 (1992).
4. D. E. De Vos, T. Frederic, and P. A. Jacobs, *Angew. Chem. Int. Ed. Engl.* **33,** 431 (1994); *Angew. Chem.* **106,** 447 (1994).
5. G. D. Stucky and J. E. Mac Dougall, *Science* **247,** 669 (1990).
6. G. D. Stucky, M. L. F. Phillips, and T. E. Gier, *Chem. Mater.* **1,** 492 (1989).
7. G. D. Stucky, *Proc. Inorg. Chem.* **40,** 99 (1992).
8. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannon, and E. M. Flanigen, *J. Am. Chem. Soc.* **104,** 1146 (1982).
9. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannon, and E. M. Flanigen, *ACS Symp. Ser.* **218,** 799 (1983).
10. Q. Kan, F. P. Glasser, and R. Xu, *J. Mater. Chem.* **3,** 983 (1993).
11. J. Chen, R. H. Jones, S. Natarajan, M. B. Hursthouse, and J. M. Thomas, *Angew. Chem. Int. Ed. Engl.* **33,** 639 (1994); *Angew. Chem.* **106,** 667 (1994).
12. M. A. Roberts, G. Sankar, J. M. Thomas, R. H. Jones, H. Du, J. Chen, W. Pang, and R. Xu, *Nature* **381,** 401 (1996).
13. S. M. Stalder and A. P. Wilkinson, *Chem. Mater.* **9,** 2168 (1997).

14. M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, and H. Kessler, *Nature* **352,** 320 (1991).

15. R. H. Jones, J. M. Thomas, J. Chen, R. Xu, Q. Huo, S. Li, Z. Ma, and A. M. Chippindale, *J. Solid State Chem.* **102,** 204 (1993).

16. M. E. Davis, C. Saldarriaga, C. Montes, J. Gorces, and C. Crowder, *Nature* **331,** 698 (1988).

17. R. M. Dessau, J. L. Schlenker, and J. B. Higgins, *Zeolites* **10,** 522 (1990).

18. S. T. Wilson, B. M. Lok, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.* **104,** 1146 (1982).

19. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* **359,** 710 (1992).

20. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCulen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.* **114,** 10834 (1992).

21. "XSCANS (Version 2.1)," Siemens Analytical X-Ray Instruments, Madison, WI, 1994.

22. "SHELXTL (Version 5.0) Reference Manual," Siemens Industrial Automation, Analytical Instrumentation, Madison, WI, 1995.

23. "International Tables for X-Ray Crystallography" (A. J. C. Wilson, Ed.), Vol. C. Kluwer, Dordrecht, 1992.