JOURNAL OF
Materials
CHEMISTRY

A new layered aluminophosphate $[C_4H_{12}N_2][Al_2P_2O_8(OH)_2]$ templated by piperazine

Kaixue Wang, Jihong Yu, Peng Miao, Yu Song, Jiyang Li, Zhan Shi and Ruren Xu*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130023, P. R. China. E-mail: rrxu@mail.jlu.edu.cn; Fax: INT +86-431-5671974

Received 20th December 2000, Accepted 30th April 2001
First published as an Advance Article on the web 24th May 2001

A new layered aluminophosphate with an Al/P ratio of unity, designated AlPO-CJ9 (CJ9: China, Jilin University, number 9), has been synthesized hydrothermally. The crystalline product is characterized by powder and single-crystal X-ray diffraction (XRD), FT-IR and thermogravimetric analyses. The structure of AlPO-CJ9 contains $[Al_2P_2O_8(OH)_2]^{2-}$ macroanionic sheets stacked in an AAAA sequence. The inorganic layer based on a 3 × 4 × 6 net is featured by a type of chain built up by corner-sharing three-membered rings. The nonbonding interaction energies (E_{inter}), including H-bonding, van der Waals and Coulombic interactions between the inorganic layer and several organic amines are studied, which are valuable in evaluating the templating abilities of the organic templates.

Introduction

Since the discovery of microporous aluminophosphates by Wilson *et al.*,[1] great interest has been aroused in the synthesis of new aluminophosphate materials. These materials have potential applications in the fields of catalysis, ion-exchange, adsorption and host–guest assembly.[2–8] Because of the utilization of new synthesis methods and the employment of various organic templates, a large number of new aluminophosphate compounds have been prepared, which exhibit rich diversity in both structure and composition.[9] Notable examples are various two-dimensional anionic aluminophosphate layers including $[Al_2P_2O_9]^{2-}$,[10–15] $[AlP_2O_8]^{3-}$,[16–18] $[Al_2P_3O_{12}]^{3-}$,[19–24] $[Al_3P_4O_{16}]^{3-}$,[25–35] and $[Al_4P_5O_{20}H]^{2-}$.[36] These materials are all templated by organic amines, which reside within the interlayer region, playing a structure-directing, space-filling and charge-balancing role. It is noted that one template can lead to different inorganic sheet structures, and that the same inorganic sheet structure can be directed by different templates. In order to realize the goal of rational synthesis of target materials, it is important to understand the templating ability of various organic amines in the formation of the inorganic layers. Molecular dynamics simulation approaches have been proven to be efficient in elucidating the structure-directing abilities of organic amines. Catlow and co-workers[37–40] considered that the nonbonding interactions between the organic guest and inorganic host could be used to select suitable templating candidates in forming a specific framework. Recently, we have considered the nonbonding interaction energies between the inorganic layers and the templates, which are dominated by H-bond and van der Waals interactions, to evaluate the templating ability of various organic amines in the formation of layered aluminophosphates with $Al_3P_4O_{16}^{3-}$ stoichiometry.[41] Suitable template molecules can be predicted that have lower interaction energies with the host network.

In this work, using piperazine as a template, we have prepared a two-dimensional aluminophosphate compound, denoted AlPO-CJ9, which possesses a type of 3 × 4 × 6 net analogous to those of $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$,[10] $[C_2H_{10}N_2][Al_2P_2O_8(OH)_2]$ (UiO-15-125),[11] and $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$ (UiO-18-100).[12] These 3 × 4 × 6 nets are templated by piperazine, 1,2-diaminopropane, ethylenediamine and 1,3-diaminopropane, respectively. The templating ability of these organic amines can be understood by calculation of the nonbonding interaction energies between the inorganic layer and the organic templates. This will further assist in the rational synthesis of target materials with specific structures.

Experimental section

AlPO-CJ9 was prepared under hydrothermal conditions with molar composition $2.0Al(^iPrO)_3 : 4.0H_3PO_4 : 4.5$piperazine : $227H_2O$. Aluminium triisopropoxide (1.00 g) was first dispersed in distilled water (10 mL) by stirring, followed by the addition of piperazine (0.95 g) as a structure-directing agent. Finally, H_3PO_4 (85 wt %, 0.67 mL) was added dropwise to the above reaction mixture. The mixture was stirred until it was homogeneous and gave a pH value of about 8.5. Then, the resulting gel was loaded in a Teflon-lined stainless steel autoclave and heated at 180 °C for 4 days. The resulting crystalline product was filtered off, washed with distilled water, and dried at 60 °C overnight.

The X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with CuKα ($\lambda = 1.5418$ Å) radiation. Thermogravimetric analysis was performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of 10 °C min^{-1}. The elemental analysis was carried out on a Perkin-Elmer 2400 Series II CHNS/O analyzer. Inductively coupled plasma (ICP) analysis was conducted on a Perkin-Elmer Optima 3300 DV spectrometer.

Energy calculations were accomplished using the Burchart1.01–Dreding2.21 force field with the Cerius^2 software package,[42] and the processing procedure was according to ref. 41. We assume $E_{inter} = E - E_f - E_R$, where E is the total energy of the whole structure, E_f is the energy of the framework, and E_R is the energy of the encapsulated organic template.

Structure determination: a suitable single crystal with size dimensions 0.32 × 0.08 × 0.08 mm was selected. The intensity data were collected on a Siemens SMART diffractometer equipped with a CCD bidimensional detector using graphite-monochromatic MoKα radiation ($\lambda = 0.71073$ Å) at a temperature of 20 ± 2 °C. Data processing was accomplished with

DOI: 10.1039/b010206g

Table 1 Crystal data and structure refinement for AlPO-CJ9

Empirical formula	$AlPO_5C_2H_7N$
Formula weight	183.04
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 8.884(2)$ Å, $\alpha = 90°$
	$b = 6.874(2)$ Å, $\beta = 93.820(5)°$
	$c = 9.553(2)$ Å, $\gamma = 90°$
Volume/Å^3	582.1(2)
Z, calculated density/Mg m^{-3}	4, 2.089
Absorption coefficient/mm^{-1}	0.583
$F(000)$	376
Crystal size/mm	0.320 × 0.080 × 0.080
Theta range for data collection/°	2.30–23.23
Limiting indices	$-9 \leqslant h \leqslant 9$, $-7 \leqslant k \leqslant 0$, $-8 \leqslant l \leqslant 9$
Reflections collected/unique	1310/692 [R(int) = 0.0302]
Completeness to theta = 23.36 (%)	83.1
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	692/1/119
Goodness-of-fit on F^2	1.096
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0277$, w$R_2 = 0.0689$
R indices (all data)	$R_1 = 0.0384$, w$R_2 = 0.0729$
Largest diff. peak and hole/e Å^{-3}	0.322 and –0.270

$^a R_1 = \sum(\Delta F/\sum(F_o))$; w$R_2 = (\sum[w(F_o{}^2 - F_c{}^2)])/\sum[w(F_o{}^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o{}^2)$.

the SAINT processing program.[43] The structure was solved by the direct methods with SHELXTL software package,[44] and the heaviest atoms (Al and P) were easily located. Oxygen, carbon, nitrogen, and framework hydrogen atoms were subsequently located in the difference Fourier maps, and the hydrogen atoms of the piperazine molecule were placed geometrically. Diprotonation of the piperazine molecules were suggested on the basis of charge balance. Crystal data and details of the data collection are given in Table 1. The atomic coordinates, the selected bond distances and angles are presented in Tables 2 and 3, respectively.

CCDC reference number 163034. See http://www.rsc.org/suppdata/jm/b0/b010206g/ for crystallographic data in CIF or other electronic format.

Results and discussion

ICP analysis for AlPO-CJ9 gives the contents of Al and P as 13.9 and 15.8 wt%, respectively, indicating an Al/P ratio of 1/1 for the product. Elemental analysis gives that the contents of C, H and N as 12.04, 3.75 and 7.12 wt%, respectively, consistent with the expected values of 13.12, 3.86 and 7.65 wt% on the basis of the empirical formula given by single-crystal structural analysis.

Table 2 Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for AlPO-CJ9

	x	y	z	U(eq)
P(1)	7972(1)	−3966(1)	9310(1)	16(1)
Al(1)	9643(1)	−1398(1)	7195(1)	16(1)
O(1)	8797(3)	−2160(3)	8796(3)	21(1)
O(2)	6317(3)	−3899(3)	8815(3)	22(1)
O(3)	8104(3)	−3961(3)	10920(3)	18(1)
O(4)	8697(3)	−5813(3)	8763(3)	20(1)
O(5)	10155(3)	−3992(3)	6913(4)	22(1)
N(1)	5154(4)	−5468(5)	6451(4)	21(1)
C(1)	4242(5)	−3763(6)	5939(5)	26(1)
C(2)	6393(4)	−5915(6)	5542(4)	25(1)
H(1)	4600(50)	−6560(60)	6500(40)	34(12)
H(2)	5410(40)	−5250(60)	7300(30)	24(13)
H(3)	3430(50)	−3590(50)	6500(40)	29(12)
H(4)	4950(40)	−2600(60)	5930(40)	29(10)
H(5)	7090(40)	−4770(50)	5530(30)	18(9)
H(6)	6860(40)	−7160(50)	5870(30)	16(9)
H(7)	10460(50)	−3990(60)	6120(50)	39(18)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond lengths [Å] and angles [°] for AlPO-CJ9

P(1)–O(2)	1.514(3)	P(1)–O(4)	1.531(2)
P(1)–O(3)	1.535(3)	P(1)–O(1)	1.539(3)
Al(1)–O(3)#1	1.787(2)	Al(1)–O(1)	1.825(3)
Al(1)–O(4)#2	1.831(3)	Al(1)–O(5)#2	1.863(3)
Al(1)–O(5)	1.864(2)	O(3)–Al(1)#3	1.787(2)
O(4)–Al(1)#4	1.831(3)	O(5)–Al(1)#4	1.863(3)
O(5)–H(7)	0.82(5)	N(1)–C(2)	1.479(5)
N(1)–C(1)	1.489(5)	C(1)–C(2)#5	1.504(6)
C(2)–C(1)#5	1.504(6)		
O(2)–P(1)–O(3)	108.68(15)	O(2)–P(1)–O(4)	109.90(13)
O(2)–P(1)–O(1)	110.41(14)	O(4)–P(1)–O(3)	109.79(14)
O(3)–P(1)–O(1)	108.15(13)	O(4)–P(1)–O(1)	109.87(15)
O(3)#1–Al(1)–O(4)#2	103.54(13)	O(3)#1–Al(1)–O(1)	105.77(12)
O(3)#1–Al(1)–O(5)#2	103.59(12)	O(1)–Al(1)–O(4)#2	150.69(12)
O(4)#2–Al(1)–O(5)#2	88.69(13)	O(1)–Al(1)–O(5)#2	84.51(14)
O(1)–Al(1)–O(5)	87.98(14)	O(3)#1–Al(1)–O(5)	102.51(12)
O(5)#2–Al(1)–O(5)	153.89(7)	O(4)#2–Al(1)–O(5)	85.72(13)
P(1)–O(3)–Al(1)#3	133.42(16)	P(1)–O(1)–Al(1)	136.91(16)
Al(1)#4–O(5)–Al(1)	143.1(2)	P(1)–O(4)–Al(1)#4	136.38(15)
Al(1)–O(5)–H(7)	103(3)	Al(1)#4–O(5)–H(7)	113(3)

The experimental and simulated XRD patterns of AlPO-CJ9 are shown in Fig. 1. Their peak positions are in good agreement with each other, suggesting the phase purity of the as-synthesized product. The differences in intensity may be due to the preferred orientation of the powder sample.

The TG profile of AlPO-CJ9 shows an obvious weight loss *ca.* 24.3% around 350 °C (Fig. 2), which is attributed to the decomposition of the piperazinium cations in the product (calc. 24.6 wt%). An XRD study shows that the structure of AlPO-CJ9 is retained on calcination at 250 °C, and that it becomes an amorphous phase at above 350 °C. The weight loss of *ca.* 8.2% at temperatures higher than 530 °C is probably a result of the cleavage of bridging OH groups.

AlPO-CJ9 contains anionic sheets built up from alternating vertex sharing $AlO_3(OH)_2$ and PO_4 polyhedra. There is one crystallographically distinguishable P atom and one crystallographically distinguishable Al atom in the asymmetric unit (Fig. 3). Each P atom is tetrahedrally coordinated to four oxygen atoms, with three oxygen atoms being shared by adjacent Al units. The P–O$_{\text{bridging}}$ distances range from 1.531(2) to 1.539(3) Å (P–O$_{\text{av}}$ = 1.535 Å). There is a terminal P–O group for each PO_4 tetrahedron with a shorter distance of 1.514(3) Å. Each Al atom shares three O atoms with adjacent P atoms, and connects two adjacent Al atoms through a bridging OH group.

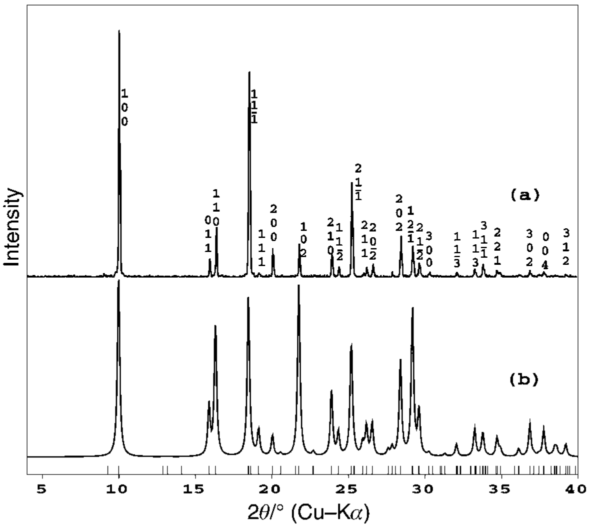


Fig. 1 (a) Experimental and (b) simulated X-ray powder diffraction patterns of AlPO-CJ9.

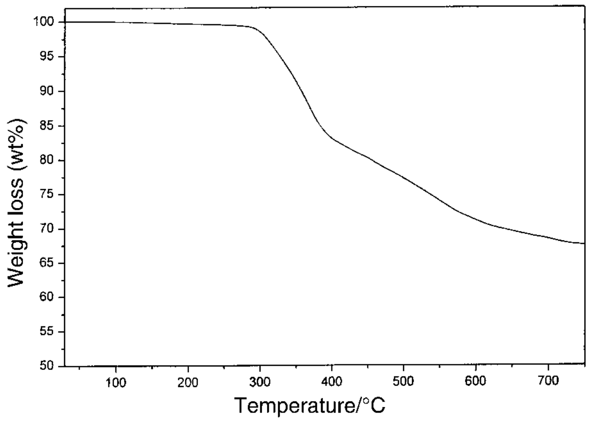


Fig. 2 TG profile of AlPO-CJ9.

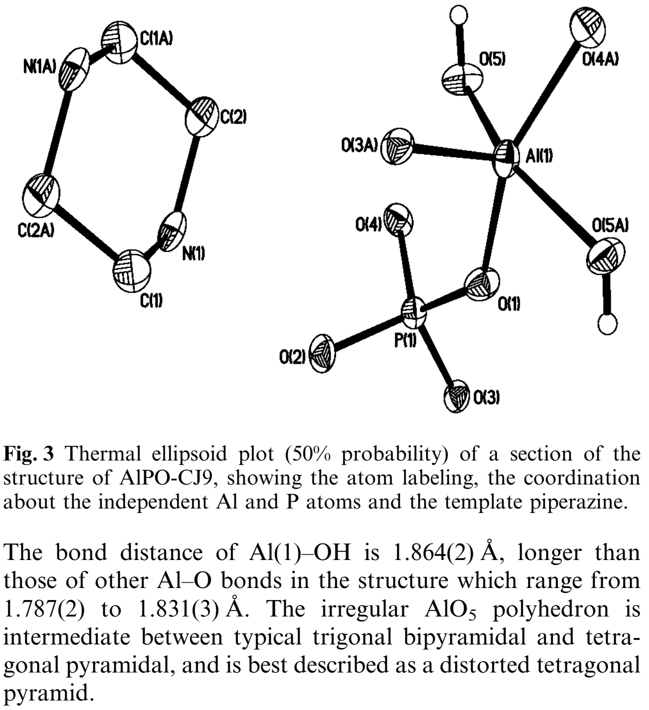


Fig. 3 Thermal ellipsoid plot (50% probability) of a section of the structure of AlPO-CJ9, showing the atom labeling, the coordination about the independent Al and P atoms and the template piperazine.

The bond distance of Al(1)–OH is 1.864(2) Å, longer than those of other Al–O bonds in the structure which range from 1.787(2) to 1.831(3) Å. The irregular AlO_5 polyhedron is intermediate between typical trigonal bipyramidal and tetragonal pyramidal, and is best described as a distorted tetragonal pyramid.

AlPO-CJ9 features a chain formed by a corner-sharing linkage of three-membered rings (Fig. 4a). The chain parallel to the [010] direction consists of $AlO_3(OH)_2$ tetragonal pyramids sharing three O atoms with adjacent PO_4 tetrahedra. Adjacent $AlO_3(OH)_2$ tetragonal pyramids are bridged by two hydroxyl groups. This type of chain has never been found in previously reported aluminophosphates. Connection of these chains *via* Al–O–P linkages leads to the anionic $[Al_2P_2O_8(OH)_2]^{2-}$ layer, parallel to the *bc* plane (Fig. 4b), with three-, four- and six-membered rings. Interestingly, if bridging OH groups between two adjacent Al atoms are removed, the 3 × 4 × 6 network becomes a 2-D 4 × 8 × 8 net, which is very common in the structure of 3-D open-framework aluminophosphates.[45–47]

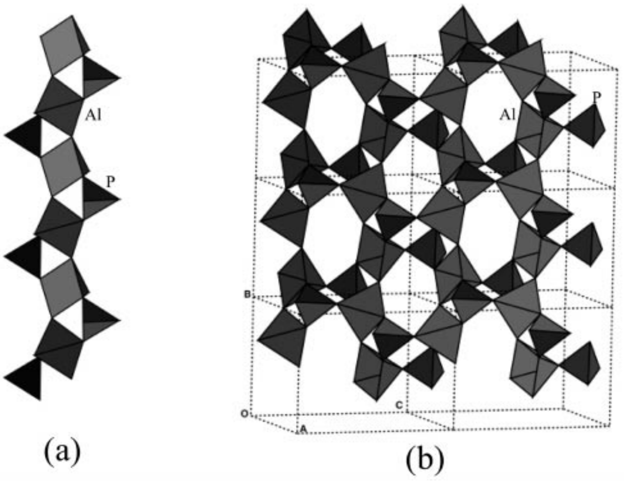


Fig. 4 (a) The chain composed of corner-sharing three-membered rings running parallel to the [010] direction, and (b) the inorganic sheet built up by the linkages of the adjacent chains *via* Al–O–P linkages.

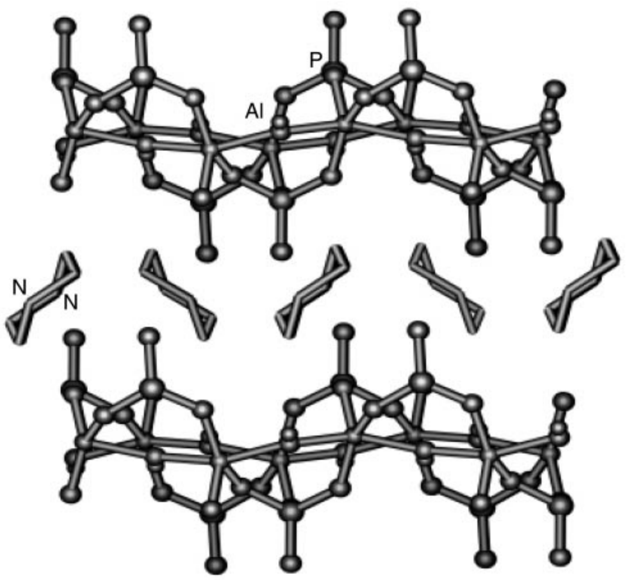


Fig. 5 View of the structure of AlPO-CJ9 along the [001] direction, showing the inorganic layers intercalated by the diprotonated piperazine cations.

Diprotonated piperazine molecules, neutralizing the negative charges of the anionic layers, are located in the interlayer region (Fig. 5). The inorganic layers are held together *via* hydrogen bonds between the terminal phosphonyl oxygen atoms O(2) and the nitrogen atoms of the piperazine cations. A summary of the H-bond interactions is presented in Table 4. Each nitrogen atom of the piperazine molecule forms two H-bonds, one of which is formed to the terminal P–O(2) group of the upper layer, and the other to that of the lower layer. The H-bonding interactions are strong ($(d(\mathrm{D{-}H\cdots A}))_{\mathrm{av}} = 2.675$ Å), which renders the inorganic layers stacked closely.

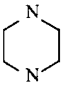
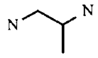
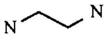
The inorganic sheet structure of AlPO-CJ9 is closely related to those of $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$, $[C_2H_{10}N_2][Al_2P_2O_8(OH)_2]$ (UiO-15-125), and $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$ (UiO-18-100), all of which contain an anionic $[Al_2P_2O_8(OH)_2]$ layer with 3 × 4 × 6 nets. UiO-15-125 and UiO-18-100 are the high temperature forms of UiO-15 and UiO-18, respectively. The differences among them are the stacking sequences of the inorganic layers. The layers of $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$ and UiO-18-100 are stacked in an ABAB sequence, whilst those of AlPO-CJ9 and UiO-15-125 are stacked in an AAAA sequence. The inorganic layer of UiO-18-100 distorts more greatly than those of AlPO-CJ9, $[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$ and UiO-15-125. This makes the terminal P–O bonds not parallel in one direction.

Interestingly, four different organic amines including piperazine, 1,2-diaminopropane, ethylenediamine, and 1,3-diaminopropane, can all direct the formation of a similar

Table 4 Hydrogen bonds for AlPO-CJ9

D–H···A	*d*(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	∠(DHA)/°
N(1)–H(1)···O(2)#6	0.90(4)	1.82(4)	2.700(4)	166(4)
N(1)–H(2)···O(2)	0.84(3)	1.86(3)	2.650(4)	156(4)

Table 5 Interaction energies of host–guest systems, including VDW and H-bond energies per unit of $Al_4P_4O_{16}(OH)_4^{4-}$ and the interlayer spacing *D* based on the experimental structural data

No.	Formula	Organic amine	*D*/Å	VDW/kcal mol^{-1}	H-bond/kcal mol^{-1}	Stacking sequence
1	$[C_4H_{12}N_2][Al_2P_2O_8(OH)_2]$ (AlPO-CJ9)		8.884	−0.33	−23.91	AAAA
2	$[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$		9.316	10.99	−31.93	ABAB
3	$[C_2H_{10}N_2][Al_2P_2O_8(OH)_2]$ (UiO-15-125)		10.289	70.62	−23.49	AAAA
4[a]	$[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$ (UiO-18-100)		10.776	16.59	−22.95	ABAB

[a] The hydrogen atoms of 1,3-diaminopropane are added theoretically through the H-adjust procedure.

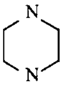
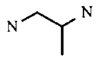
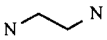
layered structure. These diprotonated template cations not only balance the negative charge of the macroanionic layers, but also interact with the host layers through H-bonds to terminal P–O groups. The H-bond interaction energies between the inorganic layers and the organic templates, including piperazine, 1,2-diaminopropane, ethylenediamine and 1,3-diaminopropane, are −23.91, −31.93, −23.49 and −22.95 kcal mol^{-1} per unit of $Al_4P_4O_{16}(OH)_4^{4-}$, respectively (Table 5). It is of note that the *d*-spacings of these inorganic layers are similar, which range from 8.88 to 10.78 Å. It is believed that the manner of H-bond interactions are important in stabilizing the layered structures, even though the size and shape of the organic amines are different from each other.

To understand the templating ability of these organic amines, we calculate the nonbonding interaction energies (E_{inter}), including H-bond, van der Waals and Coulombic interactions between the host inorganic layers and the guest organic amines based on the experimental structural data. The results are listed in Table 6. The H-bond interaction between the inorganic sheets and the templates can stabilize the 2D layered structures. In order to favor the formation of H-bonds to the inorganic sheets, the template molecules always need to exist in a special geometrical configuration. Thus, the van der Waals interaction is often an energetically unfavorable factor in the layered structures, as can be noted in Table 6. The values of E_{inter} between the inorganic framework and the organic amines are similar to each other (−151.36 to −156.63 kcal mol^{-1} per unit of $Al_4P_4O_{16}(OH)_4^{4-}$), which implies that these four organic amines have a similar structure-directing ability in the formation of this 3×4×6 net layer. The interaction energy E_{inter} of UiO-18-100 (−151.36 kcal mol^{-1}) is a bit higher, which may be due to that the hydrogen atoms of 1,3-diaminopropane are added theoretically through the H-adjust procedure by us. Although the sizes and shapes of these four templating molecules are different, the optimized interlayer spacing is very similar (11.89–12.97 Å). This suggests that the sizes and shapes of the template molecules do not affect the interlayer space very much. The results illustrate that the nonbonding interaction energy can be used to evaluate the structure-directing ability of the organic amines in the formation of some layered structure.

Conclusion

A new two-dimensional aluminophosphate compound AlPO-CJ9 has been synthesized from a hydrothermal system using piperazine as a structure-directing agent. The structure is

Table 6 Optimized interaction energies of host–guest (E_{inter}) including VDW, H-bond and Coulombic energies per unit of $Al_4P_4O_{16}(OH)_4^{4-}$ and the optimized interlayer spacing *D*

No.	Formula	Organic amine	*D*/Å	VDW/ kcal mol^{-1}	H-bond/ kcal mol^{-1}	Coulombic interaction/kcal mol^{-1}	E_{inter}/ kcal mol^{-1}
1	$[C_4H_{12}N_2][Al_2P_2O_8(OH)_2]$ (AlPO-CJ9)		12.675	−14.47	−15.57	−123.13	−153.27
2	$[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$		11.490	−12.12	−17.57	−124.39	−153.98
3	$[C_2H_{10}N_2][Al_2P_2O_8(OH)_2]$ (UiO-15-125)		11.576	−10.38	−22.07	−124.18	−156.63
4[a]	$[C_3H_{12}N_2][Al_2P_2O_8(OH)_2]$ (UiO-18-100)		12.572	−12.69	−18.67	−120.00	−151.36

[a] The hydrogen atoms of 1,3-diaminopropane are added theoretically through the H-adjust procedure.

featured by a type of chain built up by corner-sharing three-membered rings. The nonbonding interaction energies between the inorganic layers and the organic amines, including piperazine, 1,2-diaminopropane, ethylenediamine and 1,3-diaminopropane are studied. That four different types of amines can lead to a similar layered aluminophosphate demonstrates that the nonbonding interaction energy is valuable in providing an insight of the structure-directing abilities of organic amines in the formation of host inorganic structures.

Acknowledgements

We are grateful to the State Basic Research Project (G2000077507) and the National Natural Science Foundation of China for financial support. J. Y. is thankful for the support by TRAPOYT of MOE, P. R. C.

References

1. S. T. Wilson, B. M. Lok, C. A. Messian, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146; S. T. Wilson, B. M. Lok and E. M. Flanigen, *US Pat.*, 4 310 440, 1982.
2. J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1994, **106**, 963.
3. M. E. Davis, *Chem. Eur. J.*, 1997, **3**, 1745.
4. G. A. Ozin and C. Gil, *Chem. Rev.*, 1989, **89**, 1749.
5. T. Bein, *Chem. Mater.*, 1996, **8**, 1636.
6. G. A. Ozin, A. Kuperman and A. Stein, *Angew. Chem., Int. Ed. Engl.*, 1989, **101**, 373.
7. G. A. Ozin, *Adv. Mater.*, 1992, **4**, 612.
8. M. Hartmann and L. Kevan, *Chem. Mater.*, 1999, **99**, 635.
9. J. Yu, R. Xu and J. Li, *Solid State Sci.*, 2000, **2**, 181.
10. H. Yuan, J. Chen, Z. Shi, W. Chen, Y. Wang, P. Zhang, J. Yu and R. Xu, *J. Chem. Soc., Dalton. Trans.*, 2000, 1981.
11. K. O. Kongshaug, H. Fjellvag and K. P. Lillerud, *J. Mater. Chem.*, 1999, **9**, 1591.
12. K. O. Kongshaug, H. Fjellvag and K. P. Lillerud, *Microporous Mesoporous Mater.*, 2000, **38**, 311.
13. K. O. Kongshaug, H. Fjellvag and K. P. Lillerud, *Microporous Mesoporous Mater.*, 1999, **32**, 17.
14. S. Cheng, J. N. Tzeng and B. Y. Hsu, *Chem. Mater.*, 1997, **9**, 1788.
15. K. Maeda, A. Tuel and C. Baerlocher, *J. Chem. Soc., Dalton Trans.*, 2000, 2457.
16. J. Yu and I. D. Williams, *J. Solid State Chem.*, 1998, **136**, 141.
17. K. R. Morgan, G. J. Gainsford and N. B. Milestone, *Chem. Commun.*, 1997, 61.
18. M. A. Leech, A. R. Cowley, K. Prout and A. M. Chippindale, *Chem. Mater.*, 1998, **10**, 451.
19. A. M. Chippindale, A. V. Powell, L. M. Bull, R. H. Jones, A. K. Cheetham, J. M. Thomas and R. Xu, *J. Solid, State Chem.*, 1992, **96**, 199.
20. S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Mater.*, 1996, **8**, 2391.
21. S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Commun.*, 1996, 1761.
22. J. Yu, K. Sugiyama, K. Hiraga, N. Togashi, O. Terasaki, Y. Tanaka, S. Nakata, S. Qiu and R. Xu, *Chem. Mater.*, 1998, **10**, 3636.
23. P. Lightfoot, Z. A. D. Lethbridge, R. E. Morris, D. S. Wragg, P. A. Wright, Å. Kvick and G. B. M. Vaughan, *J. Solid State Chem.*, 1999, **143**, 74.
24. A. M. Chippindale and R. I. Walton, *J. Solid State Chem.*, 1999, **145**, 731.
25. R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, A. K. Cheetham and A. V. Powell, *J. Chem. Soc., Chem. Commun.*, 1991, 1266.
26. J. M. Thomas, R. H. Jones, R. Xu, J. Chen, A. M. Chippindale, S. Natarajan and A. K. Cheetham, *J. Chem. Soc., Chem. Commun.*, 1992, 929.
27. R. H. Jones, A. M. Chippindale, S. Natarajan and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1994, 565.
28. K. Morgan, G. Gainsford and N. Millestone, *J. Chem. Soc., Chem. Commun.*, 1995, 425.
29. P. A. Barrett and R. H. Jones, *J. Chem. Soc., Chem. Commun.*, 1995, 1979.
30. I. D. Williams, Q. Gao, J. Chen, L. Ngai, Z. Lin and R. Xu, *Chem. Commun.*, 1996, 1781.
31. S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Inorg. Chem.*, 1996, **35**, 6373.
32. Q. Gao, B. Li, J. Chen, S. Li and R. Xu, *J. Solid State Chem.*, 1997, **129**, 37.
33. A. M. Chippindale, A. R. Cowley, Q. Huo, R. H. Jones and A. D. Law, *J. Chem. Soc., Dalton Trans.*, 1997, 2639.
34. D. J. Williams, J. S. Kruger, A. F. McLeroy, A. P. Wilkinson and J. C. Hanson, *Chem. Mater.*, 1999, **11**, 2241.
35. J. Yu, J. Li, K. Sugiyama, N. Togashi, O. Terasaki, K. Hiraga, B. Zhou, S. Qiu and R. Xu, *Chem. Mater.*, 1999, **11**, 1727.
36. L. Vidal, V. Gramlich, J. Patarin and Z. Gabelica, *Eur. J. Solid State Inorg. Chem.*, 1998, **35**, 545.
37. D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas and G. J. Hutchings, *Nature*, 1996, **382**, 604.
38. D. W. Lewis, G. Sankar, J. K. Wyles, J. M. Thomas, C. R. A. Catlow and D. J. Willock, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2675.
39. D. W. Lewis, C. M. Freeman and C. R. A. Catlow, *J. Phys. Chem.*, 1995, **99**, 11194.
40. C. R. A. Catlow, D. S. Coombes, D. W. Lewis, J. Pereira and G. Carlos, *Chem. Mater.*, 1998, **10**, 3249.
41. J. Li, J. Yu, W. Yan, Y. Xu, W. Xu, S. Qiu and R. Xu, *Chem. Mater.*, 1999, **11**, 2600.
42. Cerius^2; Molecular Simulation/Biosystems Corporation, San Diego, CA, 1995.
43. SMART and SAINT (software package), Siemens analytical X-ray Instruments, Inc., Madison, WI, 1996.
44. SHELXTL version 5.1, Siemens Industrial Automation Inc., 1997.
45. J. M. Bennett, W. J. Dytrych, J. J. Pluth, J. W. Richardson Jr. and J. V. Smith, *Zeolites*, 1986, **6**, 349.
46. K. Wang, J. Yu, G. Zhu, Y. Zou and R. Xu, *Microporous Mesoporous Mater.*, 2000, **39**, 281.
47. B. Wei, G. Zhu, J. Yu, S. Qiu and O. Terasaki, *Chem. Mater.*, 1999, **11**, 3417.