Chem. Mater. **2008,** *20,* 4179–4181

Cotemplating Ionothermal Synthesis of a New Open-Framework Aluminophosphate with Unique Al/P Ratio of 6/7

Hongzhu Xing,[†] Jiyang Li,[†] Wenfu Yan,[†] Peng Chen,[†]
Zhao Jin,[†] Jihong Yu,[*,†] Sheng Dai,[‡] and Ruren Xu[†]

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China, and Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Received March 10, 2008
Revised Manuscript Received May 8, 2008

Many efforts are being dedicated to synthesize microporous materials with novel structures, new compositions, and unique morphologies because of their widespread applications in catalysis, sorption, and ion exchange.[1] Such materials are typically prepared by hydrothermal or solvothermal methods in aqueous or nonaqueous conditions by using organic amines or quaternary ammonium ions as the templates or structure-directing agents (SDAs).[2] In 2004, Morris and co-workers developed a novel ionothermal synthesis method for preparing molecular sieves, which is based on the use of ionic liquid as both the solvent and the structure-directing agent.[3] This new method has interesting features and potential advantages over the traditional methods of molecular sieve synthesis.[3,4] For example, because of the vanishingly low vapor pressure of ionic liquids, synthesis can take place at ambient pressure, thus eliminating safety concerns associated with high hydrothermal pressures. In addition, altering the chemistry of the solvent system away from a molecular solvent (e.g., water/alcohol) to an ionic liquid also changes the chemistry of the synthesis system. Several microporous aluminophosphates have been synthesized by using this method.[4,5] Most of these structures are known frameworks except SIZ-1[3] with a new interrupted aluminophosphate structure and SIZ-7[4a] with a new zeotype cobalt aluminophosphate framework. To explore new microporous materials by using ionothermal method is of great interest.

Templating or structure directing effect is an important issue for the synthesis of molecular sieves.[6] The choice of appropriate SDA is crucial in the synthesis of microporous compounds with a specific structure. In some cases, two types of templates cooperatively play the structure-directing role in the hydrothermal/solvothermal system. The cotemplating synthesis has been proven to be an effective route to microporous materials. Notably, zeolites SSZ-25 (MWW),[7] SSZ-32X (MTT),[8] SSZ-47B,[9] ferrierite (FER),[10] aluminophosphate AFI,[11] and silicoaluminophosphates SAV and KFI[12] have been successfully prepared in the presence of two templates. Recently, Wang et al. studied the structure directing role of amines for the formation of aluminophosphate molecular sieve AFI in ionothermal synthesis.[13] Because the ionic liquid acts as both solvent and structure-directing agent, introducing an additional amine that cooperatively acts as a co-template along with ionic liquid will open a new route to the synthesis of microporous materials.

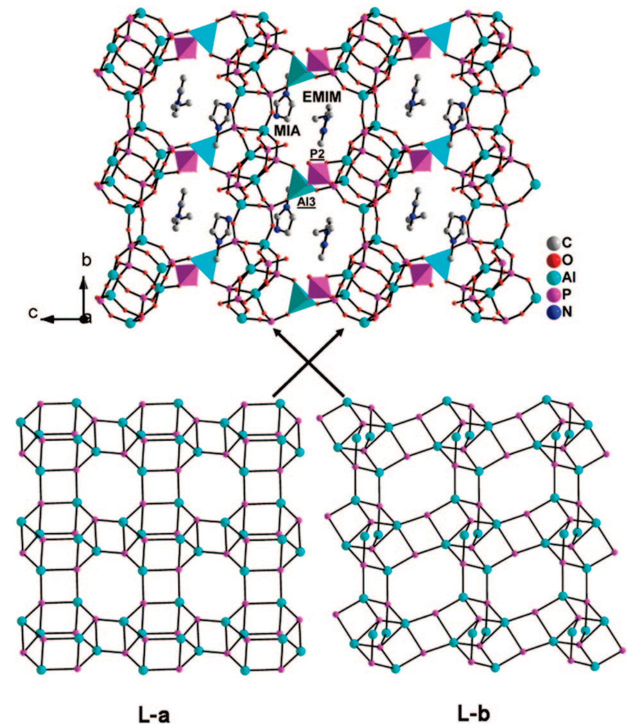

Figure 1. View of JIS-1 structure along [100] direction with co-templates of the MIAH$^+$ and EMIM$^+$ cations located in the channels (top) and the two component layers (bottom), L-a and L-b (oxygen atoms are omitted for clarity).

Among various microporous materials, aluminophosphates display rich variety of structures including neutral zeolite-like open frameworks with Al/P ratio of unity and a range of anionic frameworks with diverse Al/P ratios.[14] Up to now,

---

[*] Corresponding author. E-mail: jihong@jlu.edu.cn.
[†] Jilin University.
[‡] Oak Ridge National Laboratory.

(1) Čejka, J.; Van Bekkum, H.; Corma, A.; Schüth, F. *Introduction to zeolite science and practice*; Elsevier: New York, 2007.
(2) (a) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663. (b) Morris, R. E.; Weigel, S. J. *Chem. Soc. Rev.* **1997**, *26*, 309.
(3) Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. *Nature* **2004**, *430*, 1012.
(4) (a) Parnham, E. R.; Morris, R. E. *J. Am. Chem. Soc.* **2006**, *128*, 2204. (b) Parnham, E. R.; Morris, R. E. *Chem. Commun.* **2006**, 380. (c) Parnham, E. R.; Morris, R. E. *Acc. Chem. Res.* **2007**, *40*, 1005.
(5) Xu, Y. P.; Tian, Z. J.; Wang, S. J.; Hu, Y.; Wang, L.; Wang, B. C.; Ma, Y. C.; Hou, L.; Yu, J. Y.; Lin, L. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 3965.
(6) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.
(7) Zones, S. I.; Hwang, S. J.; Davis, M. E. *Chem. Eur. J.* **2001**, *7*, 1990.
(8) Zones, S. I.; Zhang, G.; Krishna, K. R.; Biscardi, J. A.; Marcantonio, P.; Vittoratos, E. US Patent Appl. No. 2005/092651A1, 2005.
(9) Burton, A. W.; Zones, S. I. US Patent No. 7,063,828, 2006.
(10) Pinar, A. B.; Gomez- Hortigüela, L.; Perez-Pariente, J. *Chem. Mater.* **2007**, *19*, 5617.
(11) Gómez-Hortigüela, L.; Márquez-Álvarez, C.; Corà, F.; López-Arbeloa, F.; Pérez-Pariente, J. *Chem. Mater.* **2008**, *20*, 987.
(12) Castro, M.; Garcia, R.; Warrender, S. J.; Slawin, A. M. Z.; Wright, P. A.; Cox, P. A.; Fecant, A.; Bats, N. *Chem. Commun.* **2007**, 3470.
(13) Wang, L.; Xu, Y.; Wei, Y.; Duan, J.; Chen, B.; Wang, B.; Ma, H.; Tian, Z.; Lin, L. *J. Am. Chem. Soc.* **2006**, *128*, 7432.
(14) (a) Yu, J.; Xu, R. *Acc. Chem. Res.* **2003**, *36*, 481. (b) Yu, J.; Xu, R. *Chem. Soc. Rev.* **2006**, *35*, 593.

10.1021/cm800701x CCC: $40.75

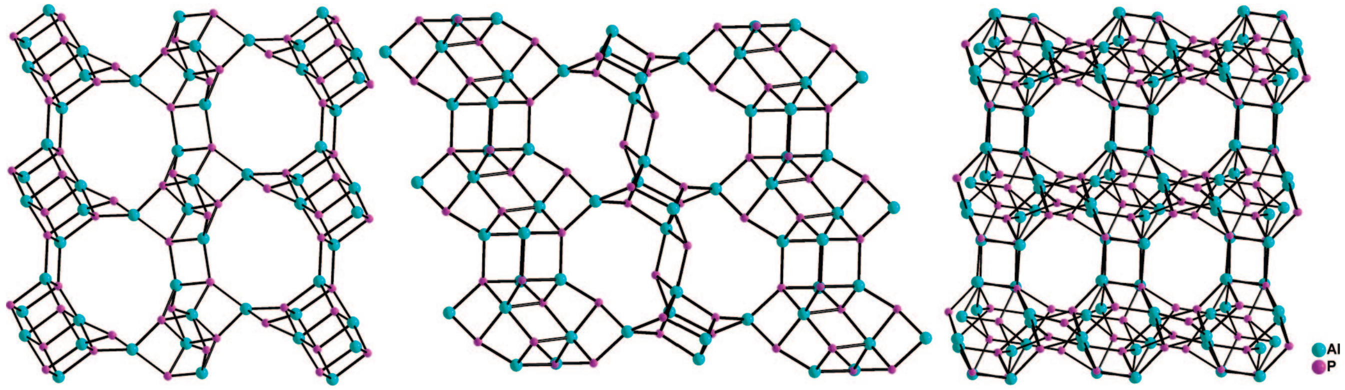

Figure 2. Channel structures of JIS-1 along *a*, *b*, and *c* axes, respectively (left to right).

the known Al/P ratios are found as 1/2, 2/3, 3/4, 3/5, 4/5, 5/6, 11/12, 12/13, and 13/18. Hypothetical structures with the Al/P ratios of 6/7, 7/8, 8/9, 9/10, and so forth can be generated based on a combination of different Al and P coordination states.[15] However, aluminophosphates with these Al/P ratios are not yet observed.

In this communication, we demonstrate the first example of cotemplating ionothermal synthesis of new open-framework compound. By using aromatic amine 1-methylimidazole (MIA) and ionic liquid 1-methyl-3-ethylimidazolium bromide (EMIMBr) as the co-templates, a new aluminophosphate $[\mathrm{EMIM}]^+[\mathrm{MIAH}]^+[\mathrm{Al_6P_7O_{27}(OH)}]^{2-}$, denoted JIS-1 (Jilin Ionothermal Synthesis-1), with a not yet observed Al/P ratio of 6/7 has been successfully synthesized.

Typically, a Teflon lined autoclave (volume 21 mL) was charged with H_3PO_4 (0.342 g, 85 wt % in H_2O), aluminum isopropoxide (0.107 g), MIA (0.120 g), and EMIMBr (1.030 g). After 8 days of crystallization at 180 °C, the crystalline colorless cuboid solid was obtained, further washed thoroughly with acetone and water several times, and then dried in the air. Suitable single crystal with dimensions of $0.15 \times 0.12 \times 0.12$ mm^3 of JIS-1 was selected for single-crystal X-ray diffraction analysis. X-ray powder diffraction pattern was recorded on a Rigaku D/Max 2550 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The experimental XRD pattern agreed well with the simulated one generated on the basis of the single-crystal structure analysis (Supporting Information, Figure S1), proving the phase purity of the as-synthesized product. Thermogravimetric analysis (TGA) was accomplished on a Perkin-Elmer thermal analyzer at a rate of 10 °C min^{-1} under flowing air. It showed a total weight loss of about 21.5% (calcd, 22.3%) in the region 400−1000 °C, corresponding to the decomposition of the occluded templates and dehydration of P-OH terminal groups (Supporting Information, Figure S2). XRD analysis indicated that the structure of JIS-1 was stable at 400 °C and collapsed after removal of the templates. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer (calcd (wt %) Al, 15.84; P, 21.30; found Al, 15.91; P, 21.25). The elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer (calcd (wt %) C, 11.7; H, 1.9; N, 5.5; found C, 10.4; H, 1.6; N, 5.3).

Single-crystal structural analysis[16,17] reveals that the structure of JIS-1 consists of an anionic open framework $[\mathrm{Al_6P_7O_{28}H}]^{2-}$. Protonated MIAH$^+$ cations along with EMIM$^+$ cations act as the templates to compensate the negative charges of the inorganic framework. Each asymmetric unit of JIS-1 (Supporting Information, Figure S3) contains six crystallographically distinct Al atoms and seven crystallographically distinct P atoms. Al(4) and Al(6) are pentacoordinated to five bridging oxygen atoms that form distorted trigonal bipyramids. The other four Al atoms are tetrahedrally coordinated to four oxygens shared by adjacent P atoms. The Al−O bond lengths (1.721(19)−1.875(2) Å) are within the typical ranges reported for aluminophosphate materials. Of the seven crystallographically distinct P atoms, P(3)−P(7) each connect four bridging oxygens to adjacent Al atoms. However, P(1) and P(2) share three oxygens with adjacent Al atoms, leaving a terminal P−OH and P═O group, respectively. The P−O bond lengths are in the range of 1.4818(9)−1.546(2) Å. An H-bond exsits between the P−OH and P═O groups with the O···O distance of 2.4959(17) Å.

The alternating connection of Al-centered polyhedra and P-centered tetrahedra constructs the open-framework structure of JIS-1. It is featured by two layers, L-a and L-b, as seen in Figure 1. L-a consists of double 6-ring (D6R) units. The connection of D6R forms a 4.6.8-net sheet perpendicular to the [001] direction. Such a 4.6.8-net has been found in zeolite CHA[18] and aluminophosphate SIZ-1.[3] L-b is built up from the connection of "double intergrown-capped 6-rings" to form a 4.6.8-net sheet perpendicular to the [001] direction. This 4.6.8-net sheet has been observed in the

---

(15) Zhou, D.; Chen, L.; Yu, J.; Li, Y.; Yan, W.; Deng, F.; Xu, R. *Inorg. Chem.* **2005**, *44*, 4391.

(16) Single crystal X-ray structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 20 ± 2 °C. Data were processed with the SAINT program. The structure of JIS-1 was solved in triclinic space group $P\bar{1}$ by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL97. All Al, P, O, C, and N atoms were easily located. The H atom of P-OH group and the proton of the protonated MIAH$^+$ cation that was suggested by charge balance were found in the difference Fourier maps, and the others were placed geometrically and refined in a riding model.

(17) Crystal data for JIS-1, $\mathrm{Al_6P_7O_{28}H{\cdot}C_{10}N_4H_{18}}$: $M_r = 1021.96$, triclinic space group $P\bar{1}$ (no. 2), $a = 9.0150(5)$ Å, $b = 9.4739(6)$ Å, $c = 19.7373(11)$ Å, $\alpha = 88.9640(10)°$, $\beta = 78.9380(10)°$, $\gamma = 85.4890(10)°$, $V = 1649.26(17)$ Å^3, $Z = 2$. Refinement of 471 parameters against 10464 reflections ($R_{\mathrm{int}} = 0.0256$, 7174 reflections with $I > 2(\sigma)$) led to R_1 (observed data) $= 0.0572$, $wR_2 = 0.1592$, and $s = 1.072$.

(18) Baerlocher, C. L.; McCusker, B. D.; Olson, H. *Atlas of Zeolite Framework Types*; Elsevier: New York, 2007.

known layered compound $(PyH)H_2Al_2P_3O_{12}$.[19] L-a and L-b are further connected by P(2) and Al(3) atoms to build up the three-dimensional channel system with intersecting 10-, 10-, and 8-ring channels along the [100], [010], and [001] directions, respectively (Figure 2).

Both the $EMIM^+$ cation and the protonated $MIAH^+$ cation are found to coexist in the intersection of the tridirectional channels in the structure of JIS-1 (Figure 1). There is a H-bond between the amino group of $MIAH^+$ and the framework oxygen atom with the N(4)···O(26) distance of 2.938(6) Å. It is noted that JIS-1 could not be prepared in the absence of MIA in ionothermal system. This indicates the cotemplating role of both aromatic amine MIA and ionic liquid EMIMBr in the formation of JIS-1 in the ionothermal system. Theoretically, if using solely $EMIM^+$ cations instead of $MIAH^+/EMIM^+$ cations as the templates, the framework is energetically unfavorable, and the calculated host−guest non-bonding interaction energy including van der Waals force and H-bonding is 56.64 kcal/mol per unit cell higher than that of the optimized experimental model of JIS-1.[20]

JIS-1 is the first compound with Al/P ratio of 6/7 in the family of aluminophosphates. Its framework is constructed from AlO_{4b}, AlO_{5b}, PO_{4b}, and PO_{3b} (b: bridging) via Al−O−P linkages. We have found the relationship between the Al/P ratio and the Al and P coordination states[14] which satisfies the following equation:

$$\sum_i m_{\mathrm{AlO}_{ib}} \times i_{\mathrm{AlO}_{ib}} = \sum_j n_{\mathrm{PO}_{jb}} \times j_{\mathrm{PO}_{jb}} \tag{1}$$

where i (j) is the number of bridging oxygens coordinated to Al (P), m (n) is the number of AlO_{ib} (PO_{jb}) coordination, $m\mathrm{AlO}_{ib}/n\mathrm{PO}_{jb}$ = Al/P, and $i = 3, 4, 5$, and 6, corresponding to 3-, 4-, 5-, and 6-connected Al atoms, respectively, and $j = 1, 2, 3$, and 4, corresponding to PO_4 tetrahedra with one, two, three, and four bridging oxygens, respectively. Table 1 lists 16 possible combinations of different Al and P coordinations that give rise to the $[Al_6P_7O_{28}]^{3-}$ stoichiometry.

Table 1. All Possible Coordinations of Al and P Atoms in Aluminophosphates with an Al/P Ratio of 6/7

	Al coordination			P coordination				
no.	AlO_4	AlO_5	AlO_6	PO_{4b}	$PO_{3b}O_t$	$PO_{2b}O_{2t}$	PO_bO_{3t}	structure
1	6	0	0	5	0	2	0	
2	6	0	0	4	2	1	0	
3	6	0	0	3	4	0	0	
4	6	0	0	5	1	0	1	
5	5	1	0	5	1	1	0	
6	5	1	0	4	3	0	0	
7	5	0	1	6	0	1	0	
8	5	0	1	5	2	0	0	
9	5	1	0	6	0	0	1	
10	4	2	0	6	0	1	0	
11	4	2	0	5	2	0	0	JIS-1
12	4	1	1	6	1	0	0	
13	4	0	2	7	0	0	0	
14	3	3	0	6	1	0	0	
15	3	2	1	7	0	0	0	
16	2	4	0	7	0	0	0	

In conclusion, a cotemplating synthetic method has been used in the ionothermal synthesis of a new open-framework aluminophosphate with a not yet observed Al/P ratio of 6/7. The structure of JIS-1 possesses tridirectional intersecting 10-ring, 10-ring, and 8-ring channels along the three crystallographic axes. Both ionic liquid EMIMBr and aromatic amine MIA act as templates in the formation of JIS-1. The cotemplating ionothermal synthesis will be a feasible approach for the discovery of new microporous open-framework materials.

Acknowledgment. The authors thank the National Natural Science Foundation of China, the State Basic Research Project of China (2006CB806103 and 2007CB936402), the "III" Research Project of China, and the Major International Joint Research Project of China for financial support.

Supporting Information Available: Experimental and simulated powder XRD patterns, thermogravimetric curve, and thermal ellipsoid plots (PDF) and X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM800701X

---

(19) Chippindale, A. M.; Powell, A. V.; Bull, L. M.; Jones, R. H.; Cheetham, A. K.; Thomas, J. M.; Xu, R. *J. Solid State Chem.* **1992**, *96*, 199.

(20) $Cerius^2$ package (Materials Studio software 4.0 and $Cerius^2$ program 3.8, Accelrys Inc.) was used to calculate the non-bonding interactions between the host framework and the guest molecules by using Burchart 01-Dreiding2.21 force field. Four $EMIM^+$ molecules were loaded into the framework by the Monte Carlo sorption method instead of two pairs of $EMIM^+/MIAH^+$ cations. Energy optimization was performed by using energy minimization, where the framework and unit cell were fixed. The host−guest interaction energy was calculated based on the energy optimization.