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ACO-Zeotype Iron Aluminum Phosphates with Variable Al/Fe Ratios Controlled by F^- Ions

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Three new iron aluminum phosphates $[(C_2H_{10}N_2)_4][Fe_{8-x}Al_xF_x(H_2O)_{2-x}(PO_4)_8]\cdot 2H_2O$ (χ = 1.64, 1.33, 0.80) with ACO-zeotype structures denoted as FeAPO-CJ66(**a**), FeAPO-CJ66(**b**), and FeAPO-CJ66(**c**), respectively, have been synthesized in the fluoride ion system. Their framework structures are made of double 4-ring (D4R) building units formed by the alternating connection of $Fe(Al)O_4F(O)$ trigonal bipyramids and PO_4 tetrahedra, which possess 3D intersecting 8-ring channels running along the [001], [010], and [100] directions. Fluoride ions or water molecules reside in the center of D4Rs, and diprotonated ethylenediamine cations and water molecules are occluded in the free space of channels to stabilize the whole structure. Notably, the Al/Fe ratios in the frameworks can be effectively controlled from 1/3.9 to 1/5.0 to 1/9.0 by adjusting the amounts of phosphoric acid and hydrofluoric acid added to the initial reaction mixture. Mössbauer and magnetic measurements show that the Fe ions in the compounds are bivalent and undergo antiferromagnetic ordering at room temperature.

Introduction

Zeolites with regular nanoporous void spaces have shown widespread applications in catalysis, ion exchange, and separation.[1−4] Since the first discovery of aluminophosphate molecular sieves ($AlPO_4$-*n*) by Wilson et al. in 1982,[5] various aluminophosphate molecular sieves have been synthesized in hydrothermal or solvothermal systems by using organic amines or quaternary ammonium cations as templates or structure-directing agents (SDAs). The structures of $AlPO_4$-*n* are composed of the strict alternation of AlO_4 and PO_4 tetrahedra forming a neutral framework with an Al/P ratio of 1. The partial substitution of the Al atoms in the framework by silicon or other metal elements results in the heteroatom containing aluminophosphate molecular sieves with special properties in catalysis, photoluminescence, magnetism, and so forth.[6−9] For example, MAPO-18 (M = Mg, Zn, Co, ...) has catalytic activity in the shape-selective conversion of methanol to light olefins,[8] a family of metal-substituted zeotype materials UCSB-*n* exhibit strong room-temperature luminescence upon excitation by long-wavelength UV radiation,[9] and a novel chiral heteroatom containing aluminophosphate molecular sieve MAPO-CJ40 (M = Co, Zn) possesses optical activity.[10]

Moreover, the introduction of heteroatoms into the frameworks of aluminophsophates has the advantage of enabling some novel zeotype structures without AlPO-*n* molecular sieve counterparts. Such unique zeolite structures can not be prepared in the pure aluminophosphate synthetic system. One of the known examples is zeotype ACO featured by double 4-rings (D4Rs) and 3D intersecting 8-ring channels. In 1997, a cobalt aluminophosphate $(R_2)(Al_{0.22}Co_{1.78}P_2O_8)(H_2O)_{1/2}$ (R = $H_3NCH_2CH_2NH_3$, denoted as ACP-1) with ACO-zeotype topology was first synthesized by using ethylenediamine (en) as the template.[11] In the same year, an iron phosphate $[H_3NCH_2CH_2NH_3]_2[Fe_4O(PO_4)_4]\cdot H_2O$[12] with

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the same zeotype structure was also reported. Mixed Fe^{2+} and Fe^{3+} ions were found in this compound, which exhibits long-range magnetic ordering at approximately 12 K. Furthermore, a cobalt phosphate, $CoPO_4 \cdot 0.5C_2H_{10}N_2 \cdot 0.25H_2O$,[13] and a fluorinated cobalt phosphate, $(H_2en)_{0.5}[F_{0.17}(H_2O)_{0.08}Co(HPO_3)_{0.17}(PO_4)_{0.83}] \cdot 0.25H_2O$,[14] were prepared, and both of them have the ACO topological structure. Notably, these ACO-zeotype structures with different framework compositions are all synthesized by using ethylenediamine as templates.

It is well known that the amount and distribution of heteroatoms in the framework are closely related to the special properties of metal-substituted aluminophosphates (MAPOs). However, how to control the content and location of heteroatoms in the frameworks of MAPOs remains a significant challenge. Different from neutral frameworks of $AlPO_4$-*n* molecular sieves, most heteroatom-containing aluminophosphates possess anionic frameworks that need extraframework cations (i.e., protonated organic template and water) to balance the negative charges of the frameworks. The number and distribution of the negative charges in the host inorganic framework vary with the framework structure and the content of heteroatoms in the framework, which can be adjusted by the guest templates through the host−guest charge-density matching principle proposed by Stucky et al.[15] Besides organic amines as the templates, the F^- ions can also be employed in the synthesis to direct the formation of some special cage structures, such as double 4-rings (D4Rs) and to compensate for changes in the inorganic framework.[16,17] Thus, the cotemplating role of organic amines and F^- ions will facilitate the preparation of heteroatom-containing aluminophosphates with unique zeolite structures and novel framework compositions.

In this work, by introducing fluorine ions in the synthetic system together with ethylenediamine decomposed from diethylenetriamine (DETA) as cotemplates, three new iron aluminophosphates $|(C_2H_{10}N_2)_4|[Fe_{8-x}Al_xF_x(H_2O)_{2-x}(PO_4)_8] \cdot 2H_2O$ (χ = 1.64, 1.33, 0.80) have been synthesized. All of them have the ACO-zeotype structure and exhibit a new framework composition for such zeolite topology. Interestingly, the Al/Fe ratios in the frameworks can be effectively controlled by varying the amounts of hydrofluoric acid and phosphoric acid in the initial reaction mixture. Their syntheses, structures, and magnetic properties have been discussed.

Experimental Section

Materials and Methods. The reagents and solvents employed were commercially available and used as received without further purification. Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The crystal morphology was studied by field-emission scanning electron microscopy (JEOL JSM-6700F) using conventional sample preparation and imaging techniques. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a TA Q500 analyzer in air at a heating rate of 10 °C min^{-1}. The F elemental analysis was implemented on a Mettler Toledo instrument.

Syntheses of FeAPO-CJ66(a−c). These three compounds have been synthesized in the similar reaction system of Fe_2O_3-Al_2O_3-P_2O_5-DETA-HF-H_2O at 433 K for 6 days except that the amounts of orthophosphoric acid and hydrofluoric acid are different. Typically, aluminum triisopropoxide and the ferric oxalate were directly added to a 9 mL Teflon-lined stainless steel autoclave, followed by the addition of diethylenetriamine (DETA), orthophosphoric acid (85 wt %), and hydrofluoric acid (40 wt %) successively without stirring. The reaction was carried out at 433 K under autogenous pressure for 6 days. After being filtered off, washed with deionized water, and dried at room temperature, the pure phases of these products were obtained. The yields of FeAPO-CJ66(**a**−**c**) are 39, 28, and 32%, respectively.

Mössbauer Spectroscopy and Magnetic Measurements. The ^{57}Fe Mössbauer measurement was made on an Oxford MS-500 instrument at room temperature. The spectra were recorded using a ^{57}Co/Pd source. α-Iron foil was employed as a standard. Temperature-dependent magnetic susceptibility data were recorded on a Quantum-Design MPMS-XL SQUID magnetometer under an applied field of 5000 Oe over the temperature range of 2−300 K.

Structural Determination. Suitable single crystals of FeAPO-CJ66(**a**−**c**) with dimensions of 0.10 × 0.10 × 0.15 mm^3, 0.10 × 0.10 × 0.13 mm^3, and 0.08 × 0.07 × 0.11 mm^3, respectively, were selected for single-crystal X-ray diffraction analyses. The intensity data were collected on a Bruker Smart Apex II CCD diffractometer by oscillation scans using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at temperatures of 20 ± 2, 23 ± 2, and 23 ± 2 °C, respectively. Cell refinement and data reduction were accomplished with the SAINT processing program.[18] The structures of FeAPO-CJ66(**a**−**c**) were all solved in the $I\bar{4}2m$ space group by direct methods and refined by a full matrix least-squares technique with the SHELXTL crystallographic software package.[19] The heaviest atoms of Al/Fe, O/F, and P could be unambiguously located. Iron and aluminum occupy the same site, and their occupancies were determined by inductively coupled plasma (ICP) analyses. Fluorine and oxygen occupy the same site, and the fluorine content was confirmed by F elemental analyses. The C and N atoms were subsequently located in the difference Fourier maps. Because of the positional disorder of the C atoms, the H atoms in the structure were not added. All non-hydrogen atoms were refined anisotropically. Crystal data and refinement parameters for the structure determination are presented in Table 1. The selected bond distances and bond angles are listed in Table 1s of the Supporting Information.

CCDC 795214 (FeAPO-CJ66(**c**)), 795215 (FeAPO-CJ66(**b**)), and 795216 (FeAPO-CJ66(**a**)) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis. FeAPO-CJ66(**a**−**c**) were synthesized in F^- media by using ethylenediamine decomposed from DETA and F^- ions as the cotemplates. The gel compositions for the syntheses of pure phases of FeAPO-CJ66(**a**−**c**) are listed in

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Table 1. Crystal Data and Structure Refinement for FeAPO-CJ66(**a**−**c**)[a]

compounds	FeAPO-CJ66(**a**)	FeAPO-CJ66(**b**)	FeAPO-CJ66(**c**)
empirical formula	$C_8H_{44.72}Al_{1.64}F_{1.64}Fe_{6.36}N_8O_{34.36}P_8$	$C_8H_{45.34}Al_{1.33}F_{1.33}Fe_{6.67}N_8O_{34.67}P_8$	$C_8H_{46.4}Al_{0.8}F_{0.8}Fe_{7.2}N_8O_{35.2}P_8$
formula weight (g/mol)	1481.37	1490.02	1504.80
temperature (K)	293(2)	296(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073 Å
crystal system, space group	tetragonal, $I\bar{4}2m$	tetragonal, $I\bar{4}2m$	tetragonal, $I\bar{4}2m$
unit cell dimensions			
a (Å)	10.2660(2)	10.2941(7)	10.292(2)
b (Å)	10.2260(2)	10.2941(7)	10.292(2)
c (Å)	9.6311(3)	9.6484(12)	9.629(3)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
volume ($Å^3$)	1015.03(19)	1022.43(16)	1020.0(5)
Z, calculated density (mg/m^3)	1, 2.423	1, 2.420	1, 2.450
absorption coefficient (mm^{-1})	2.693	2.771	2.947
F(000)	745	749	757
crystal size (mm^3)	0.15 × 0.10 × 0.10	0.13 × 0.10 × 0.10	0.11 × 0.08 × 0.07
θ range (deg) for data collection	2.81−28.30	2.80−28.27	2.80−27.54
limiting indices	$-13 \le h \le 12$ $-13 \le k \le 13$ $-12 \le l \le 8$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-7 \le l \le 12$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-7 \le l \le 12$
reflections collected/unique	3746/687 [R(int) = 0.0280]	3767/692 [R(int) = 0.0272]	3536/642 [R(int) = 0.0379]
completeness to θ (%)	28.30, 99.8	28.27, 100.0	27.54, 99.7
absorption correction	empirical	empirical	empirical
max and min transmission	0.7745 and 0.6882	0.7691 and 0.7146	0.8203 and 0.7376
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	687/0/52	692/6/52	642/6/52
goodness-of-fit on F^2	0.913	1.003	1.019
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0429$, $wR_2 = 0.1135$	$R_1 = 0.0549$, $wR_2 = 0.1357$	$R_1 = 0.0668$, $wR_2 = 0.1842$
R indices (all data)	$R_1 = 0.0456$, $wR_2 = 0.1165$	$R_1 = 0.0617$, $wR_2 = 0.1417$	$R_1 = 0.0875$, $wR_2 = 0.2032$
absolute structure parameter	0.05(7)	0.03(8)	0.00(11)
largest diff. peak and hole ($eÅ^{-3}$)	0.576 and −0.572	0.551 and −0.831	0.641 and −0.767

[a] $R_1 = \Sigma(\Delta F/\Sigma(F_o))$, $wR_2 = (\Sigma[w(F_o^2 - F_c^2)])/\Sigma[w(F_o^2)^2]^{1/2}$, and $w = 1/\sigma^2(F_o^2)$.

Table 2. Gel Compositions (Molar Ratio) for the Syntheses of FeAPO-CJ66(**a**−**c**)

samples	H_3PO_4	HF	$C_6Fe_2O_{12} \cdot 5H_2O$	$Al(OPr^i)_3$	DETA[a]	H_2O[b]
FeAPO-CJ66(**a**)	21.7	1.8	2.0	1.0	27.4	24.8
FeAPO-CJ66(**b**)	21.7	4.1	2.0	1.0	27.4	28.7
FeAPO-CJ66(**c**)	5.2	5.9	2.0	1.0	27.4	14.8

[a] Diethylenetriamine. [b] The water brought from the phosphoric acid and hydrofluoric acid.

Table 2. Many synthesis parameters were found to affect the formation of FeAPO-CJ66(**a**−**c**). First, Fe ions as heteroatoms were critical to the synthesis of FeAPO-CJ66(**a**−**c**). If the reaction was performed in the pure aluminophosphate system, then only 1D aluminophosphate $(C_4H_{15}N_3)[AlPO_4F_2]$ (denoted AlPO-CJ28)[20] was formed. When $FeCl_2 \cdot 4H_2O$ or $FeCl_3 \cdot 6H_2O$ was used as the iron source in the reaction instead of ferric oxalate, the product was an unknown phase of iron aluminum phosphate but not the FeAPO-CJ66. However, when 2−10 mmol of oxalic acid (molar ratio of oxalic acid/$Al(OPr^i)_3$ of about 6−30) was added to the above-mentioned reaction system, the target compound could be synthesized. This indicates that the oxalic anion plays a significant role in the synthesis of FeAPO-CJ66, although the final products do not contain oxalic anion. As with phosphoric and hydrofluoric acid, the oxalic anion may play the role of adjusting the pH value of the reaction mixture. However, the pH value of the reaction mixture is difficult to measure because all reactants are directly added to the Teflon-lined stainless steel autoclave without stirring. Further study of the role of the oxalic anion in the synthesis is ongoing. Second, the introduction of hydrofluoric acid was also a vital factor in the synthesis of FeAPO-CJ66(**a**−**c**). The absence of hydrofluoric acid or an amount of hydrofluoric acid in the reaction mixture of less than 0.6 mmol or more than 2 mmol would lead to no crystallinity in the product. Interestingly, by adjusting the amounts of phosphoric acid and hydrofluoric acid in the reactant mixture (Table 2), three different products of FeAPO-CJ66(**a**−**c**) with the crystal colors changing from light gray to gray to brown were obtained. This suggests that the contents of Fe ions in these products are gradually increased. SEM images show that the crystal morphologies of FeAPO-CJ66(**a**−**c**) are also different, they become more and more regular and perfect with the increase in Fe content (Figure 1s in the Supporting Information).

Formula Determination. Three compounds with the same structures have been synthesized by varying the amounts of phosphoric acid and hydrofluoric acid in

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[20] Liu, Y.; Han, Y. D.; Li, Y.; Song, X. W.; Li, J. Y.; Yu, J. H.; Xu, R. R. *Chem. Res. Chin. Univ.* **2010**, 26.

Table 3. Compositional Analyses and TG Analyses for the Resulting Products of FeAPO-CJ66(**a**−**c**)

			contents (wt %)								
samples	formula		Al	Fe	P	Al/Fe/P	F	C	H	N	TG
a	$\|(C_2H_{10}N_2)_4\|[Fe_{6.36}Al_{1.64}F_{1.64}(H_2O)_{0.36}(PO_4)_8]\cdot 2H_2O$	exp	2.98	24.3	17.1	1/3.9/5.0	2.18	7.419	3.209	7.640	21.64
		calc	2.98	24.0	16.7	1/3.9/4.9	2.28	6.477	3.018	7.556	21.77
b	$\|(C_2H_{10}N_2)_4\|[Fe_{6.67}Al_{1.33}F_{1.33}(H_2O)_{0.67}(PO_4)_8]\cdot 2H_2O$	exp	2.39	25.0	17.1	1/5.0/6.2	1.48	7.341	3.362	7.522	21.41
		calc	2.41	25.1	16.6	1/5.0/6.0	1.55	6.440	3.041	7.513	21.56
c	$\|(C_2H_{10}N_2)_4\|[Fe_{7.20}Al_{0.80}F_{0.80}(H_2O)_{1.20}(PO_4)_8]\cdot 2H_2O$	exp	1.41	26.3	16.8	1/9.0/10.4	1.08	7.145	3.151	7.430	21.42
		calc	1.43	26.8	16.5	1/9.0/10.0	1.03	6.372	3.084	7.434	21.29

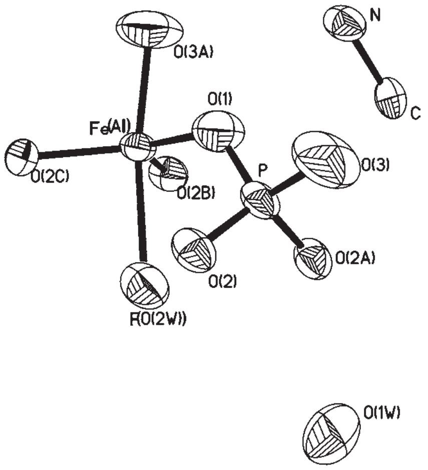

Figure 1. Thermal ellipsoids given at 30% probability, showing the atomic labeling scheme of FeAPO-CJ66(**c**).

the experiments. The powder X-ray diffraction patterns of FeAPO-CJ66(**a**−**c**) correspond well to the simulated XRD based on the single-crystal structure of FeAPO-CJ66(**c**), indicating the pure phases of the as-synthesized samples (Figure 2s in the Supporting Information). The framework compositions of these compounds are determined according to the ICP, CHN, and F elemental analyses (Table 3). The ICP analyses give rise to the following Al/Fe ratios in these compounds: 1/3.9, 1/5.0, and 1/9.0. The F elemental analyses indicate that the content of F^- ions is close with that of Al atoms in the frameworks, which become smaller and smaller with the increase in the Fe contents in the frameworks. This reveals that the F^- ions can dramatically control the number of heteroatoms incoporated into the framework. The CHN analyses show that the contents of C, H, and N in FeAPO-CJ66(**a**−**c**) are in good agreement with the single-crystal structure analyses (Table 3), which also indicates that DETA molecules decompose to en in the reaction.

TG analyses show that two continuous weight loss steps are observed from 300 to 640 °C (Figure 3s in the Supporting Information), which are attributed to the removal of F^- ions, water molecules, and organic ethylenediamine in the structure. The total observed weight loss is consistent with the calculated values based on the compositional analyses (Table 3). The XRD study indicates that the structures of FeAPO-CJ66(**a**−**c**) can be stable up to 280 °C but collapse after the removal of the organic amines and F^- ions.

Structures of FeAPO-CJ66(a−c). The structures of FeAPO-CJ66(**a**−**c**) are all crystallized in body-centered tetragonal space group $I\bar{4}2m$, and their structures are analogous to zeotype ACO. Here, we choose FeAPO-CJ66(**c**) as an example to describe their structures. The structure of FeAPO-CJ66(**c**) is composed of anionic framework $|(C_2H_{10}N_2)_4|[Fe_{7.20}Al_{0.80}F_{0.80}(H_2O)_{1.20}(PO_4)_8]\cdot 2H_2O$ containing an interconnecting 3D channel system defined by 8-rings and diprotonated ethylenediamine and water molecules in the channels to balance the negative charges of the framework. One asymmetrical unit of FeAPO-CJ66(**c**) contains one crystallographically unique metal (M) site that is occupied by the Al and Fe atoms and one crystallographically unique P site (Figure 1). The M atom is trigonal bipyramidally coordinated to four oxygen atoms and one fluorine atom (or water molecule). The P atom is tetrahedrally coordinated to oxygen atoms with nearby metal atoms. The M−O bond distances vary from 1.922(5) to 2.003(15) Å, which are between the values of the Al−O and the Fe−O bond lengths. The O−M−O bond angles vary from 80.4(8) to 124.31(17)°. M−F(O_w) bond lengths change from 2.3046(10) to 2.3481(19) Å and are longer than the M−O bond lengths, leading to the irregular trigonal bypyramid. The P−O bond lengths are in the range of 1.477(17)−1.520(8) Å, and the O−P−O bond angles vary from 104.5(5) to 112.8(5)°, which is reasonable for aluminophsophates. As seen in Table 1s in the Supporting Information, the M−O and M−F(O_w) bond distances increase from FeAPO-CJ66(**a**) to FeAPO-CJ66(**b**) and to FeAPO-CJ66 (**c**), indicating the gradual increase in Fe content in the frameworks of FeAPO-CJ66(**a**−**c**). This is consistent with the observed color change of the as-synthesized products and the ICP analyses.

The framework of FeAPO-CJ66(**c**) is build up from the alternating connection of trigonal bipyramidal Fe(Al) atoms and tetrahedral P atoms through bridging oxygen atoms. The framework is featured by the $Fe(Al)_4P_4$ double 4-ring (D4R) unit as the building blocks. One D4R unit is made of four (Al/Fe)-centered trigonal bipyramids and four PO_4 tetrahedra connected through bridging oxygen atoms, and a μ_4-F/O atom resides in the center of the unit to stabilize D4R. The 3D framework structure can be viewed as being constructed by the crossing linkage of one $Fe(Al)_4P_4$ D4R unit to eight neighboring D4Rs via the Fe(Al)−O−P bonds. It contains 3D intersecting 8-ring channels along the [001], [010], and [100] directions, respectively. Diprotonated en cations decomposed from DETA and water molecules are locate in the channels (Figure 2). The free aperture of the 8-ring window in FeAPO-CJ66(**c**) along the [001] direction is 6.3 × 7.3 Å^2 (Figure 2c). The framework density is 16.5 T/1000 Å^3, which is close to those of known aluminophosphate molecular sieves with 8-ring channels, such as GIS and MER.[21]

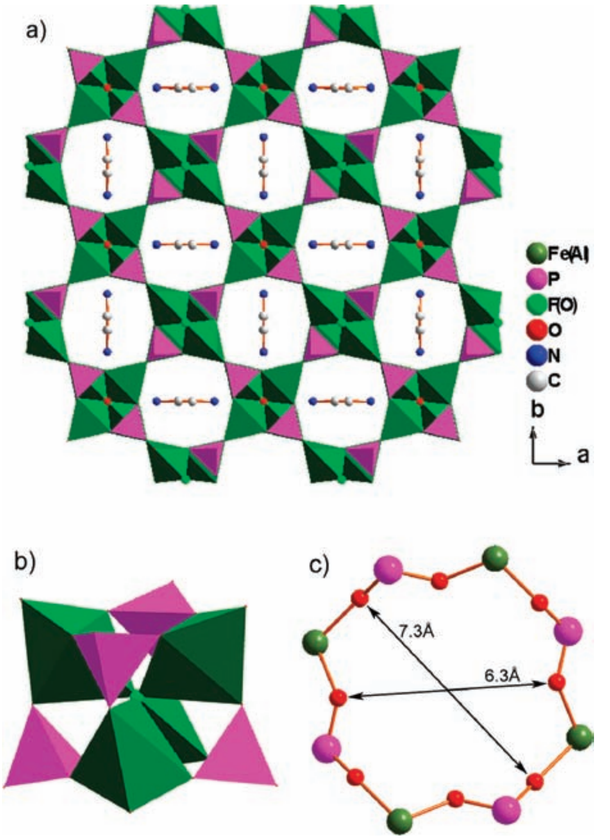

Figure 2. (a) Structure of FeAPO-CJ66(**c**) viewed along the [001] direction showing the 8-ring channels. (b) Fe(Al)$_4$P$_4$ D4R unit. (c) Size of the 8-ring window along the [001] direction.

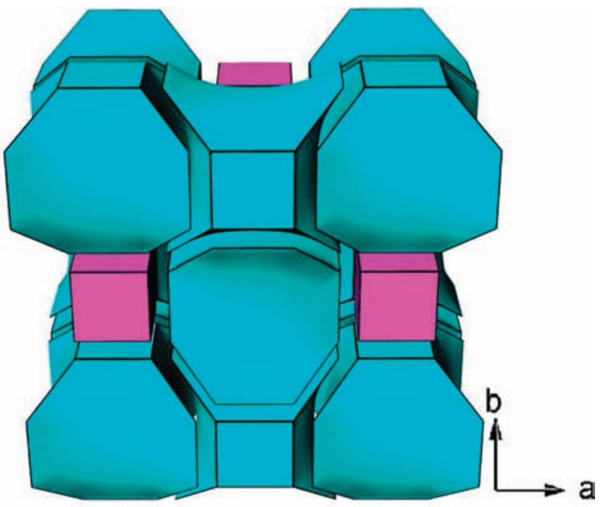

Figure 3. Structural features of FeAPO-CJ66(**c**) displayed by tiles: the face symbols for blue and pink tiles are [$4^2.8^4$] and [4^6], respectively.

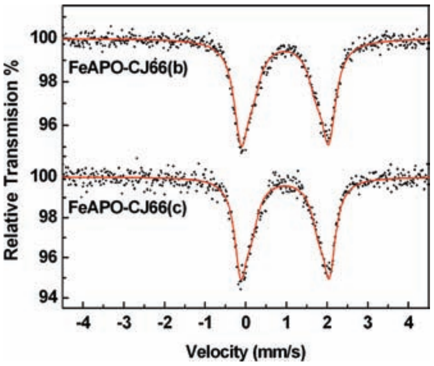

Figure 4. ^{57}Fe Mössbauer spectra of FeAPO-CJ66(**b**, **c**) observed at room temperature.

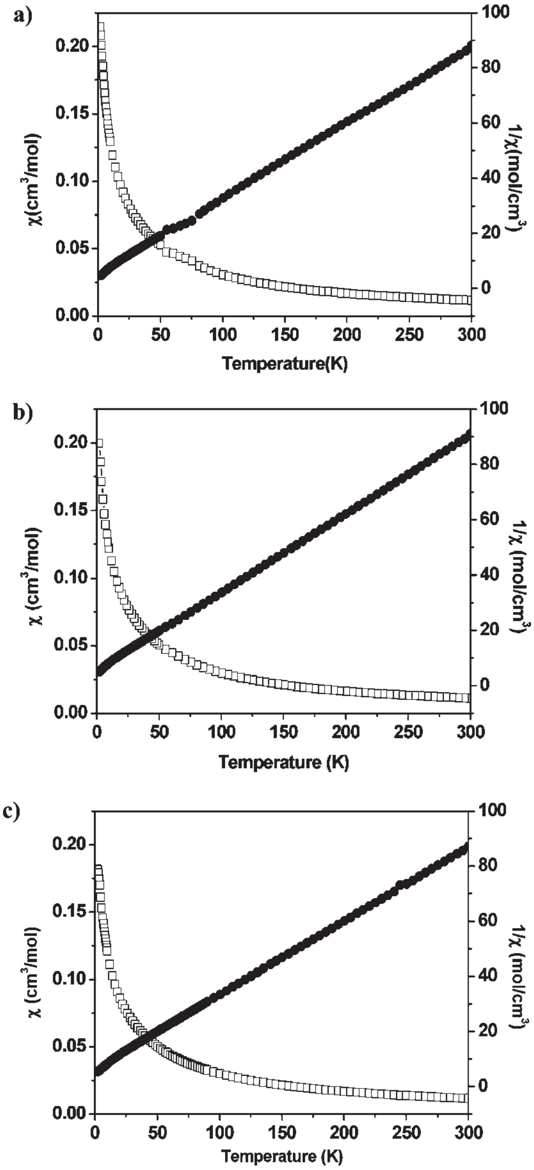

Figure 5. Variable-temperature magnetic susceptibilities of (a) FeAPO-CJ66(**a**), (b) FeAPO-CJ66(**b**), and (c) FeAPO-CJ66(**c**).

The framework of FeAPO-CJ66 (c) can also be described as a three-period net with the highest symmetry of Im-3m containing only one type of T site as determined by the Systre software.[22] The vertex symbol for the T site in the net is $4_3 \cdot 8_3$. This three-period net is carried by a unique natural tiling with a transitivity of (1 2 2 2). There are two different tiles in this tiling with face symbols of [4^6]

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(21) (a) Fischer, K.; Schramm, V. *Adv. Chem. Ser.* **1971**, *101*, 250–258. (b) Solov'eva, L. P.; Borisov, S. V.; Bakakin, V. V. *Sov. Phys. Crystallogr.* **1972**, *16*, 1035–1038.

(22) Delgado-Friedrichs, O.; O'Keeffe, M. *Acta Crystallogr., Sect. A* **2003**, *59*, 351.

and [$4^2.8^4$] (Figure 3). The signature of this tiling is [4^6] + 3[$4^2.8^4$].

To date, four members of the zeolite ACO family with three different types of framework compositions (i.e., cobalt aluminophosphate, iron phosphate, and cobalt phosphate) have been reported.[11−14] FeAPO-CJ66(**a**−**c**) are new members of the ACO family, which exhibit a novel framework composition. Besides cobalt aluminophosphate ACP-1 with an Al/Co ratio of about 1/8, FeAPO-CJ66 is the second heteroatom containing aluminophosphate with the ACO zeotype structure. Remarkably, the Al/Fe ratios in the frameworks can be controlled by the number of F^- ions in the synthesis, which can be availably adjusted from 1/9 to 1/5 to 1/3.9. This phenomenon is rarely observed in the heteratom-containing aluminophosphates. Compounds with ACO-type structures all crystallize in the $I\bar{4}2m$ space group except $(H_2en)^{2-}[Co_4(PO_4)_4]\cdot H_2O$[13] crystallized in the $P2_12_12_1$ space group because of the empty center of the D4Rs. Wang et al. speculated that the D4R units demanded the occupation of small molecules inside to support their high symmetry.[14] It reveals the prominent roles of F^- ions in the structural construction of compounds with D4Rs.

Mössbauer Spectroscopy and Magnetic Properties. Bond valence calculations[23] clearly indicate that Fe ions in the frameworks of FeAPO-CJ66(**a**−**c**) are divalent. To confirm the divalent nature of Fe ions in these compounds, the powder ^{57}Fe room-temperature Mössbauer spectra of FeAPO-CJ66(**b**, **c**) have been studied as shown in Figure 4. The best fit leads to the single contribution from Fe^{2+} ions in trigonal bipyramidal coordinations of FeAPO-CJ66(**b**, **c**).[24,25]

The variable-temperature magnetic susceptibility of powder samples of FeAPO-CJ66(**a**−**c**) measured on a field of 5000 Oe over the temperature range of 2−300 K is shown in Figure 5. The molar magnetic susceptibility per Fe obeys the Curie−Weiss law ($\chi_m = C/(T - \theta)$) with a Weiss constant of $\theta = -18.1$ K and a Curie constant of $C = 3.630$ cm^3 mol^{-1} K for FeAPO-CJ66(**a**), $\theta = -18.9$ K and $C = 3.577$ cm^3 mol^{-1} K for FeAPO-CJ66(**b**), and $\theta = -22.0$ K and $C = 3.705$ cm^3 mol^{-1} K for FeAPO-CJ66(**c**). The high negative value of the Weiss constant indicates antiferromagnetic nearest-neighbor superexchange between the Fe ions in FeAPO-CJ66(**a**−**c**). The effective magnetic moments per Fe ion calculated from the Curie constant are $5.37\mu_B$ for FeAPO-CJ66(**a**), $5.35\mu_B$ for FeAPO-CJ66(**b**), and $5.44\mu_B$ for FeAPO-CJ66(**c**), which are larger than the typical value of spin-only for the high-spin Fe(II) ($\mu_{\text{spin-only}} = 4.90\mu_B$). This high value is attributed to the orbital contribution of high-spin Fe(II) ions. Similar phenomena have been reported in some metal phosphates.[26]

Conclusions

Three new members of the zeolite ACO family, iron aluminophosphates FeAPO-CJ66(**a**−**c**), have been successfully synthesized in the fluoride ion system by using F^- ions and ethylenediamine as the cotemplates. They exhibit a new framework composition for ACO-zeotype topology. Their structures have double 4-rings (D4Rs) and 3D intersecting channel systems defined by 8-rings. The iron is divalent in the frameworks and undergoes antiferromagnetic ordering at room temperature. The Al/Fe ratios in the frameworks can be effectively controlled by F^- ions residing in the center of the D4Rs of the frameworks, which can be adjusted from 1/9 to 1/5 to 1/3.9 through increasing the content of F^- ions in the synthesis. This work provides a feasible synthesis strategy to prepare heteroatom-containing aluminophsophates with variable compositions.

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Supporting Information Available: Crystallographic data (CIF), bond lengths (Å), and angles (deg) for FeAPO-CJ66-(**a**−**c**) and SEM, XRD, and TGA of FeAPO-CJ66(**a**−**c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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