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$|(C_4NH_{12})_4|[M_4Al_{12}P_{16}O_{64}]$ (M = Co, Zn): New Heteroatom-Containing Aluminophosphate Molecular Sieves with Two Intersecting 8-Ring Channels

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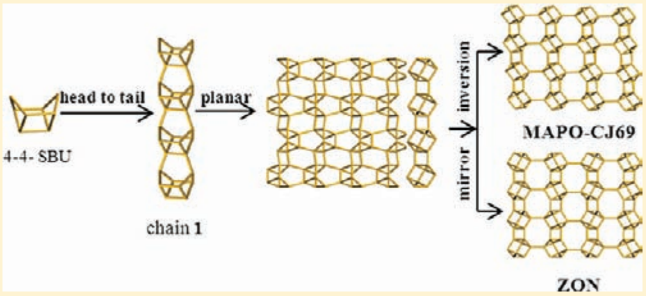
Supporting Information

ABSTRACT: Two novel heteroatom-containing aluminophosphate molecular sieves, $|(C_4NH_{12})_4|[M_4Al_{12}P_{16}O_{64}]$ (denoted MAPO-CJ69, M = Co and Zn), have been solvothermally synthesized using diethylamine as the structure-directing agent. The framework of MAPO-CJ69 exhibits a new zeolite topology which is constructed by strict alternation of metal-centered $(Al/M)O_4$ tetrahedra and PO_4 tetrahedra to form a three-dimensional anionic $[M_4Al_{12}(PO_4)_{16}]^{4-}$ framework. The structure contains two intersecting 8-ring channels along the [010] and [001] directions, and the protonated diethylamine cations reside in the 8-ring channels to achieve charge neutrality. The structure of MAPO-CJ69 is composed of the 4-4- secondary building unit (SBU), which has been found in some known zeolites, such as AFR, SFO, ZON, OWE, etc. The structural relationships between these zeolites have been discussed.



INTRODUCTION

In 1982, Wilson et al. first discovered aluminophosphate molecular sieves, designated $AlPO_4$-*n* (*n* denotes a structure type), as a new class of microporous crystalline materials.[1] Since then, aluminophosphate molecular sieves have been extensively studied due to their rich structural diversity[2] as well as important applications in catalysis, adsorption, and separation.[3] A large number of aluminophosphates with various frameworks have been synthesized using organic amine or ammonium cations as templates or structure-directing agents. To date, among the 201 identified zeolite topological structures,[4] 60 are based on aluminophosphates.

Different from traditional aluminosilicate zeolites which have an anionic framework, the structures of $AlPO_4$-*n* are based on the strict alternation of AlO_4 and PO_4 tetrahedra forming a neutral framework. The lattice Al and/or P atoms can be partially replaced by other metal or Si atoms to form heteroatom-containing aluminophosphate molecular sieves with Brönsted acid sites. Particularly, transition-metal-substituted aluminophosphate molecular sieves, as one important member of the aluminophosphate family, attract much attention because of their unique catalytic properties associated with the acidic sites and redox centers.[5] These excellent properties promise their application as potential single-site solid catalysts whose active centers at a solid surface are spatially well separated.[6] For examples, CoAPO-18 and MnAPO-18 exhibit outstanding catalysis activity and product selectivity in the oxidation of *n*-alkanes in air,[3a] and FeAlPO-5 is found as a powerful redox molecular sieve catalyst for selective oxidation of cyclohexane in air.[7] In addition, introduction of heteroatoms into aluminophosphate frameworks has generated some novel zeotype structures without AlPO-*n* molecular sieve counterparts. Notable examples are Co-, Mg-, Mn-, or Zn-containing aluminophosphates UCSB-6 (zeotype SBS), Co-, Mg-, Mn-, or Zn-containing aluminophosphates UCSB-8 (SBE), Co-, Mg-, or Zn-containing aluminophosphates UCSB-10 (SBT),[8] and CoAPO-CJ40 (JRY).[9]

Herein, we report two heteroatom-containing aluminophosphate molecular sieves, $|(C_4NH_{12})_4|[M_4Al_{12}P_{16}O_{64}]$ (denoted MAPO-CJ69, M = Co, Zn), synthesized using diethylamine as the structure-directing agent in a solvothermal system. Their structures exhibit a novel zeolite topology that possesses two intersecting 8-ring channels extending along the [010] and [001] directions. This framework is featured by the 4-4- secondary building unit (SBU). Its structure has been discussed compared with some known zeolites including AFR, SFO, OWE, and ZON, all of which are built up by the 4-4- SBU. Furthermore, a hypothetical structure has been proposed using the 4-4- SBU.

EXPERIMENTAL SECTION

Syntheses of MAPO-CJ69 (M = Co, Zn). The compounds were prepared under solvothermal conditions. In a typical synthesis of MAPO-CJ69 (M = Co, Zn), 1.90 mL of H_3PO_4 (85 wt % in water) was first dispersed in the mixture of 8 mL of tetraethylene glycol and

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2 mL of H_2O, and then 0.227 g of $Co(NO_3)_2{\cdot}6H_2O$ (or 0.232 g of $Zn(NO_3)_2{\cdot}6H_2O$) and 0.750 g of $Al(^iPrO)_3$ were added with stirring for 2 h. Afterward, 2.90 mL of diethylamine (99 wt % aqueous solution) was dispersed into the above mixture with stirring for 2 h to give rise to a homogeneous gel with an overall molar composition of $0.21MO{:}Al(^iPrO)_3$:7.54diethylamine:$7.56H_3PO_4$:12.49tetraethylene glycol:$40.47H_2O$. The gel was sealed in a 23-mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 days under static conditions. The final products containing single crystals of MAPO-CJ69 as the main phase and several byproducts were washed with distilled water by sonication and then dried in air at room temperature.

Structure Determination. Two suitable single crystals with dimensions of 0.12 × 0.12 × 0.08 mm and 0.13 × 0.11 × 0.08 mm for CoAPO-CJ69 and ZnAPO-CJ69, respectively, were selected for single-crystal X-ray diffraction analysis at 298 ± 2 K. Data were collected on a Bruker AXS SMART APEX II diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the SAINT processing program.[10] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 crystallographic software package.[11] All framework atoms Co/Zn, Al, P, and O atoms were accurately located. The transition metal M (Co or Zn) and aluminum occupy the same site, and the M/Al ratio is 1/3 in the framework as suggested by inductively coupled plasma (ICP) analysis. The occupancies of M atoms at sites 1, 2, 3, and 4 were 0.494(3), 0.211(3), 0.151(4), and 0.142(3) for Co atoms and 0.437(4), 0.256(4), 0.177(4), and 0.130(4) for Zn atoms, respectively, which were refined using SHELXTL-97 according to the different bond lengths of M−O. The longer bond length of M1−O indicates that heavier Co or Zn atoms were located in site 1. The C and N atoms were subsequently located from the difference Fourier map. On the basis of the charge balance, protonation of the diethylamine molecules was introduced. Each of the C(2), C(3), and N(1) atoms of diethylamine was disordered over two positions with 50% occupancy. All non-hydrogen atoms were refined anisotropically. Crystallographic data of MAPO-CJ69 (M = Co, Zn) are listed in Table 1.

Characterization. Powder X-ray diffraction (PXRD) data for MAPO-CJ69 (M = Co, Zn) were collected on a Rigaku D-Max 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). ICP analysis was carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Crystal morphology was studied by field emission scanning electron microscopy (XL30ESEM-FEG, Holand FEL Co.). Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TGA7 unit in the air with a heating rate of 10 K min^{-1}.

Table 1. Crystal Data and Structural Refinement for MAPO-CJ69 (M = Co, Zn)[a]

compounds	CoAPO-CJ69	ZnAPO-CJ69
empirical formula	$C_4H_{12}NCoAl_3P_4O_{16}$	$C_4H_{12}NZnAl_3P_4O_{16}$
fw	593.90	600.34
temp.	296(2) K	296(2) K
wavelength (Å)	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a (Å)	8.9024(7)	8.885(7)
b (Å)	14.2796(11)	14.231(11)
c (Å)	15.0637(11)	15.049(11)
α (deg)	90	90
β (deg)	95.0680(10)	94.957(12)
γ (deg)	90	90
vol. (Å^3)	1907.5(3)	1895.7(2)
Z, calcd density (Mg m^{-3})	4, 2.068	4, 2.104
abs coeff (mm^{-1})	1.453	1.853
F(000)	1188	1200
cryst size (mm^3)	0.12 × 0.12 × 0.08	0.13 × 0.11 × 0.08
θ range (deg) for data collection	1.97−28.37	1.97−27.88
limiting indices	$-11 \le h \le 6$	$-8 \le h \le 11$
	$-19 \le k \le 17$	$-18 \le k \le 17$
	$-20 \le l \le 18$	$-19 \le l \le 19$
no. of reflns collected/unique	13 790/4772 [R(int) = 0.0281]	13 185/4509 [R(int) = 0.0439]
completeness to θ	28.37, 99.8%	27.88, 99.8%
abs corr	semiempirical from equivalents	semiempirical from equivalents
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	4772/1/293	4509/1/253
GOF on F^2	1.107	1.045
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0478, wR_2 = 0.1235	R_1 = 0.0562, wR_2 = 0.1494
R indices (all data)	R_1 = 0.0682, wR_2 = 0.1335	R_1 = 0.0854, wR_2 = 0.1642
largest diff. peak and hole (e Å^{-3})	0.731 and −0.449	1.164 and −0.548

[a] $R_1 = \Sigma(\Delta F/\Sigma(F_o))$; $wR_2 = (\Sigma[w(F_o^{\,2} - F_c^{\,2})])/\Sigma[w(F_o^{\,2})^2]^{1/2}$, $w = 1/[\sigma^2(F_o^{\,2}) + (0.0484P)^2 + 4.5089P]$ for CoAPO-CJ69, $w = 1/[\sigma^2(F_o^{\,2}) + (0.0615P)^2 + 7.0407P]$ for ZnAPO-CJ69, where $P = (F_o^{\,2} + 2F_c^{\,2})/3$.

RESULTS AND DISCUSSION

Synthesis and Characterization of MAPO-CJ69 (M = Co, Zn). MAPO-CJ69 (M = Co, Zn) can be synthesized as a main phase from a reaction mixture with a molar ratio of $0.21MO{:}Al(^iPrO)_3$:7.54diethylamine:$7.56H_3PO_4$:12.49tetraethylene glycol:$40.47H_2O$ at 180 °C for 8 days. Unfortunately, we were unable to obtain the pure phase in the above reaction system. Since the morphology of MAPO-CJ69 crystals is different from those of the byproducts, pure MAPO-CJ69 crystals can be easily picked up manually for further characterization. Figure 1 shows the scanning electronic micrograph of the selected CoAPO-CJ69 single crystals, which exhibits a platelike morphology.

The influence of some experimental factors on the synthesis of MAPO-CJ69, such as the type of transition-metal atom and the amount of H_3PO_4 and diethylamine, has been studied (Table 2). It was found that only layered aluminophosphate Mu-4[12] was obtained in the absence of transition-metal ions in the above synthetic system, implying that the existence of transition-metal atoms, such as Co and Zn, might be necessary for formation of MAPO-CJ69. Incorporation of Co or Zn atoms resulted in different byproducts. Introduction of Co atoms led to formation of CoAPO-34,[13] CoAPO-CJ40,[9] Mu-4,[12] and LMU-3[14] as byproducts, while addition of Zn atoms tended to generate byproducts ZnAPO-34[13] and ZnAPO-CJ40.[9] The amounts of H_3PO_4 and diethylamine were important for the synthesis of MAPO-CJ69. For MAPO-CJ69 (M = Co, Zn), the optimal amount of H_3PO_4 and diethylamine in the reaction mixture was 7.56 and 7.54 mol, respectively, while MAPO-CJ40 (M = Co, Zn)[9] tended to be formed when a larger amount of H_3PO_4 was used. However, on decreasing the amount of H_3PO_4 to 7.03 mol MAPO-34 (M = Co, Zn)[13] was preferred to be crystallized. On the other hand, increasing or decreasing the amount of diethylamine also produced MAPO-34,[13] MAPO-CJ40,[9] and other byproducts.

The type of solvent also imparts a strong influence on the crystallization of MAPO-CJ69. The target product MAPO-CJ69 (M = Co, Zn) could only be obtained when a mixture of tetraethylene glycol and water was used. When triglycol or ethylene glycol was used to replace tetraethylene glycol with

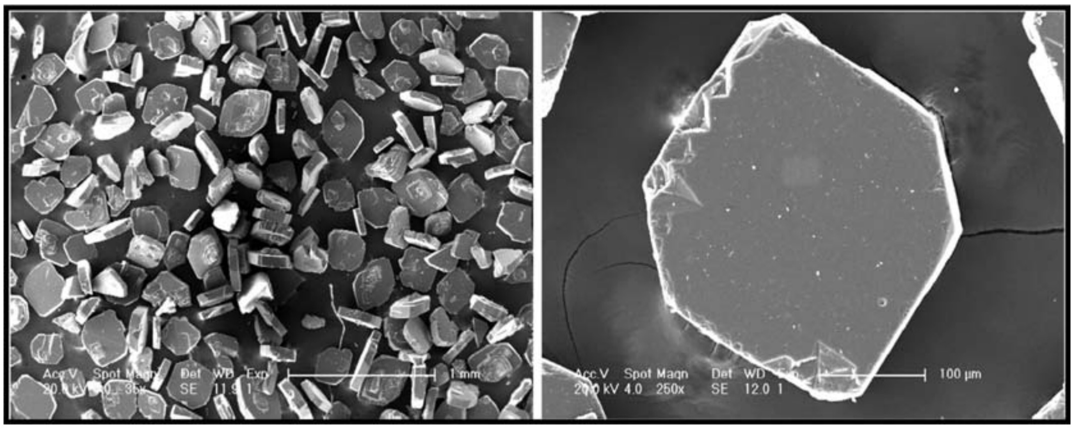

Figure 1. Scanning electronic micrograph of the selected CoAPO-CJ69 single crystals.

Table 2. Synthesis Conditions and Resulting Products[a]

no.	$M(NO_3)_2{\cdot}6H_2O$/mol		H_3PO_4/mol	Diethylamine/mol	Products
1	M = Zn	0	7.56	7.54	Mu-4
2		0.21	7.03	7.54	ZnAPO-34
3		0.21	7.56	7.54	ZnAPO-CJ69 + ZnAPO-34
4		0.21	8.38	7.54	ZnAPO-34 + ZnAPO-CJ40
5		0.21	8.92	7.54	ZnAPO-CJ40
6		0.21	7.56	7.27	ZnAPO-34
7		0.21	7.56	7.81	ZnAPO-34
8	M = Co	0	7.56	7.54	Mu-4
9		0.21	7.03	7.54	CoAPO-34 + Mu-4 + LMU-3
10		0.21	7.56	7.54	CoAPO-CJ69 + CoAPO-CJ40 + Mu-4 + LMU-3
11		0.21	8.38	7.54	CoAPO-CJ40 + CoAPO-34 + Mu-4 + LMU-3
12		0.21	8.92	7.54	CoAPO-CJ40 + Mu-4 + LMU-3
13		0.21	7.56	7.27	CoAPO-34 + Mu-4 + LMU-3
14		0.21	7.56	7.81	CoAPO-CJ40 + CoAPO-34 + Mu-4 + LMU-3

[a] Al source, Al(*i*PrO)$_3$ (1 mol); solvent, tetraethylene glycol (12.49 mol) + H_2O (30.26 mol); reaction temperature, 180 °C; reaction time, 8 days.

other conditions unchanged, MAPO-34, MAPO-CJ40, and Mu-4 were formed.

Figure 2 shows that the experimental powder X-ray diffraction (PXRD) patterns of MAPO-CJ69 (M = Co, Zn) are in agreement with the simulated one based on the crystal structure of CoAPO-CJ69, which suggests that the samples of the manually selected single crystals are pure.

Compositional analysis results for MAPO-CJ69 (M = Co, Zn) are presented in Table 3. It gives the ratio of (M + Al)/P of 1 and the ratio of M/Al of 1/3. These analysis results are in agreement with the empirical formula $|(C_4NH_{12})_4|[M_4Al_{12}P_{16}O_{64}]$ (M = Co, Zn) given by single-crystal structure analyses.

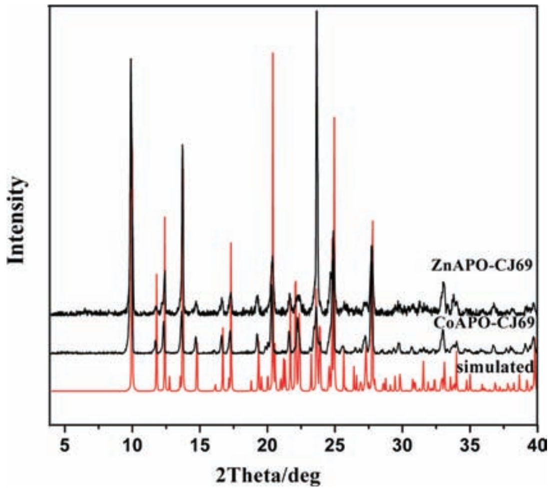

Figure 2. Experimental powder X-ray diffraction patterns of MAPO-CJ69 (M = Co, Zn) and the simulated one based on the crystal structure of CoAPO-CJ69.

Table 3. Compositional Analysis Results for MAPO-CJ69 (M = Co, Zn)

compds	contents (wt %) M	Al	P	C	H	N
CoAPO-CJ69 obsd	9.12	14.36	20.95	8.43	2.11	2.23
CoAPO-CJ69 calcd	9.92	13.63	20.86	8.09	2.04	2.36
ZnAPO-CJ69 obsd	11.45	12.67	21.27	8.13	2.16	2.30
ZnAPO-CJ69 calcd	10.89	13.48	20.64	8.00	2.01	2.33

TG analysis, as shown in Figure 3, shows a total weight loss of 11.42 and 12.54 wt % from 100 to 800 °C for CoAPO-CJ69 and ZnAPO-CJ69, respectively, which corresponds to decomposition of the occluded template diethylamine (calcd 12.49 wt % for CoAPO-CJ69 and 12.34 wt % for ZnAPO-CJ69, respectively). PXRD studies implied that their structures collapsed with decomposition of the diethylamine template upon calcination at 550 °C.

Crystal Structures of MAPO-CJ69 (M = Co, Zn). Single-crystal X-ray diffraction analyses show that MAPO-CJ69 (M = Co, Zn) exhibits a novel zeotype framework, which crystallizes in the monoclinic space group $P2_1/c$ (No. 14). Figure 4 shows the thermal ellipsoids of CoAPO-CJ69. In each asymmetric unit of CoAPO-CJ69 there are eight crystallographically independent positions: four crystallographically unique P atoms and four

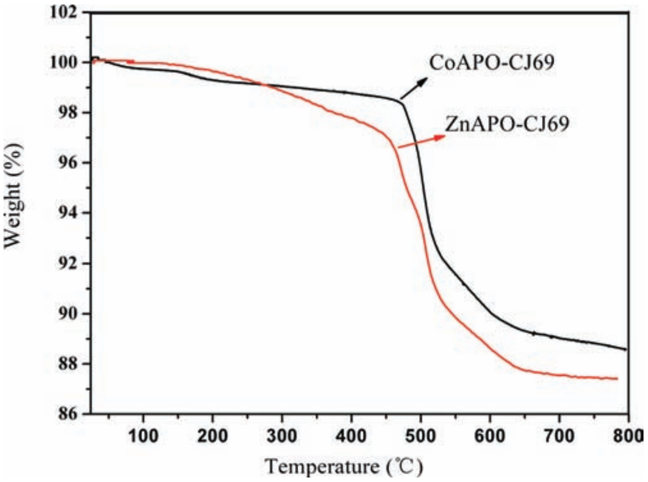

Figure 3. TG curves of MAPO-CJ69 (M = Co, Zn).

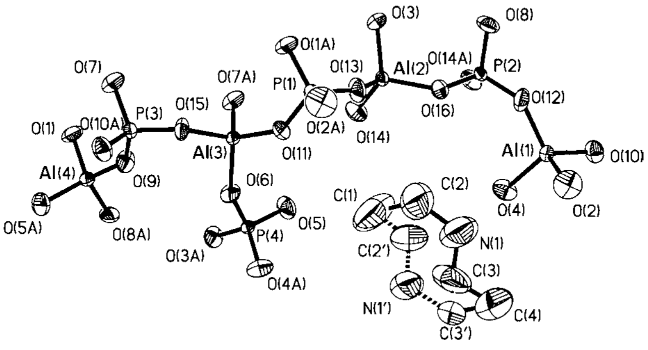

Figure 4. Thermal ellipsoids given at 50% probability, showing the atomic labeling scheme of CoAPO-CJ69.

crystallographically distinct metal sites that are shared by the Al and Co atoms with occupancies of 0.75 and 0.25 based on ICP analysis. All Co/Al and P atoms are tetrahedrally coordinated by oxygen atoms to form Al(Co)−O−P bonds. The average bond length of P−O_{av} is 1.513(7) Å, which is in good agreement with those observed in other aluminophosphate molecular sieves. The average Co/Al−O_{av} bond length of 1.773(2) Å lies between the range of typical Al−O (1.73 Å) and Co−O (1.96 Å) bond lengths, which is reasonable for cobalt aluminophosphates.[14]

The asymmetric unit of ZnAPO-CJ69 is similar to that of CoAPO-CJ69, in which the Co atom is replaced by Zn atom. The average bond distances of P−O_{av} and M−O_{av} are 1.512(8) and 1.763(1) Å, respectively. The selected bond lengths and angles of MAPO-CJ69 (M = Co, Zn) are listed in Tables S1 and S2 in the Supporting Information.

The structures of MAPO-CJ69 (M = Co, Zn) are based on the strict alternation of metal-centered $(Al/M)O_4$ tetrahedra and PO_4 tetrahedra to form a three-dimensional anionic $[M_4Al_{12}(PO_4)_{16}]^{4-}$ framework. It possesses two intersecting channels running along the [010] and [001] directions, both of which have an 8-ring opening with pore sizes of 5.2 × 3.9 (O···O distance) and 4.6 × 3.5 Å (O···O distance), respectively (Figure 5). The disordered protonated diethylamine cations are located in the intersections of the 8-ring channels and balance the negative charge of the framework.

At present, 201 zeolite framework types have been reported.[4] MAPO-CJ69 (M = Co, Zn) exhibits a new zeotype framework. It has a framework density of 16.78 T/1000 $Å^3$, which is comparable to those of zeolites with 8-ring channels. The framework of MAPO-CJ69 (M = Co, Zn) can also be described as a three-periodic net with higher symmetry. The intrinsic symmetry of this underlying net, as determined by Systre software,[15] is $P2/c$ with four different T sites. The vertex symbols for four T sites in the net of MAPO-CJ69 are $4.6.4.6.6.8$, $4.6.4.6_2.4.8$, $4.8.4.8_2.6_3.8$, and $4.4.4.8.6.6_3$. This three-periodic net is carried by a unique natural tiling with the transitivity of (4 9 7 2).[16] There are two different tiles in this tiling with the face symbols $[4^4.6^2]$ and $[4^6.6^4.8^4]$ (Figure 6). The signature of this tiling is $[4^4.6^2] + [4^6.6^4.8^4]$. As shown in Figure 6, the 2-D 8-ring intersecting channels running along the [010] and [001] directions are clearly defined by the alternating arrangement of tiles of $[4^4.6^2]$ and $[4^6.6^4.8^4]$.

The framework of MAPO-CJ69 (M = Co, Zn) is composed of the characteristic 4-4- secondary building unit (SBU). Such SBU has also been found in some known zeolite frameworks. The different connections of 4-4- SBUs can generate various known zeolite topologies,[4] such as AFR with 12-ring and 8-ring intersecting channels (denoted as 2-D 12 × 8), SFO (2-D 12 × 8), ZON (2-D 8 × 8), OWE (2-D 8 × 8) and MAPO-CJ69 (2-D 8 × 8). In addition, the zeotypes DFO[17] and SAO[18] which are both prepared as metalloaluminophosphates also contain 4-4- units as well as other SBUs.

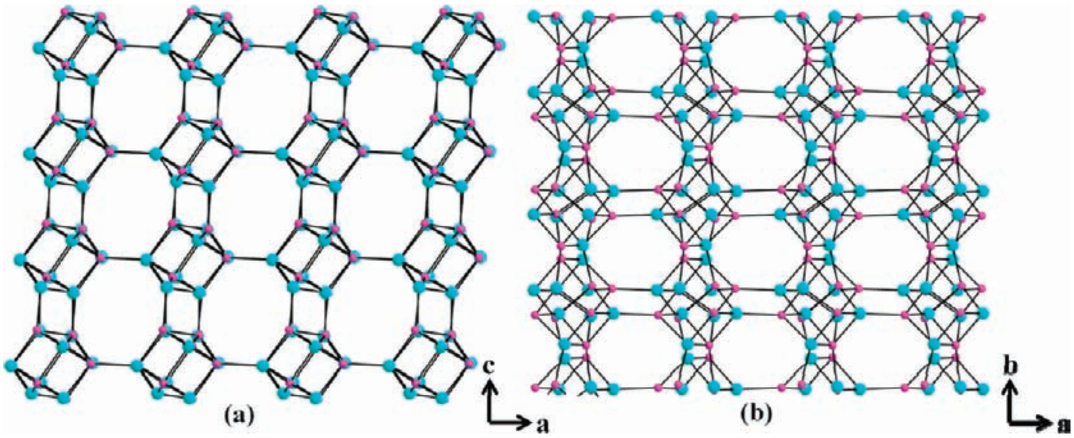

Figure 5. Framework of CoAPO-CJ69 viewed along (a) the [010] direction and (b) the [001] direction (color code: Al and Co, cyan; P, pink).

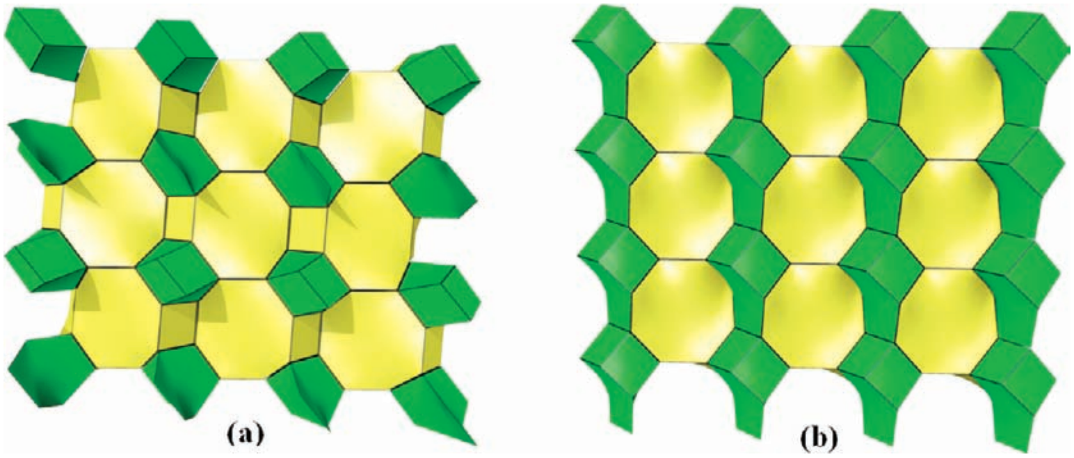

Figure 6. Structural features of MAPO-CJ69 displayed by tiles: (a) viewed along the [010] direction and (b) viewed along the [001] direction. Face symbols for green and yellow are [$4^4.6^2$] and [$4^6.6^4.8^4$], respectively.

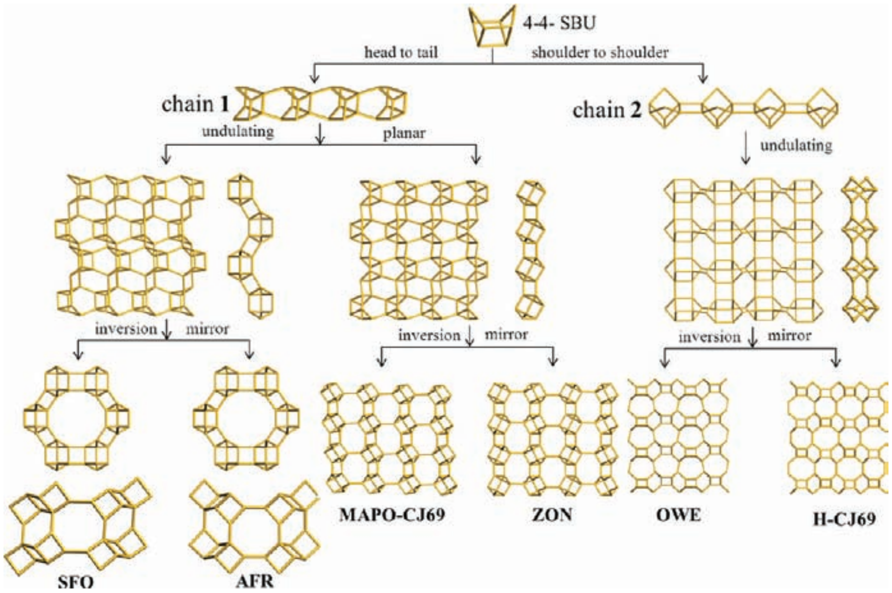

Figure 7. Scheme showing the whole building process from 4-4- SBUs to three couples of structurally closely related structures: SFO and AFR, MAPO-CJ69 and ZON, OWE and a hypothetical structure H-CJ69.

As described by Morris et al.,[19] the “head to tail” connection of the 4-4- SBUs can form chain 1 and chains 1 are further linked to form an undulating layer. Such layers can be linked in two different ways, i.e., via “inversion symmetry” and “mirror symmetry” to generate SFO and AFR structures, respectively. It is noted that MAPO-CJ69 is composed of the planar layer formed by the “head to tail” connection of the 4-4- SBUs. The linkage of the planar layers via “inversion symmetry” results in MAPO-CJ69, while the connection of the planar layers via “mirror symmetry” gives rise to ZON.

Except the “head to tail” connection mode of the 4-4- SBUs which can generate chain 1, the “shoulder to shoulder” connection of 4-4- SBUs can form chain 2. These chains are linked to form undulating layers, which are further linked via “inversion symmetry” to form zeotype OWE, or via “mirror symmetry” to form a hypothetical structure, denoted as H-CJ69. H-CJ69 has the orthorhombic space group *Cmmm*, a = 14.1634 Å, b = 17.9672 Å, c = 7.11390 Å, which possesses 2-D intersecting 8-ring channels along the [100] and [001] directions. Figure 7 illustrates the whole building process from 4-4- SBUs to the three couples of structurally closely related zeolites, SFO and AFR, MAPO-CJ69 and ZON, OWE and a hypothetical structure H-CJ69. This building process provides insight into the design of new zeolite structures.

■ CONCLUSIONS

Two novel heteroatom-containing aluminophosphate molecular sieves, MAPO-CJ69 (M = Co, Zn) with a new zeolite topology, have been successfully prepared in the solvothermal system. The strict alternating connection of MO_4/AlO_4 and PO_4 terahedra forms the 3-D open framework of MAPO-CJ69 (M = Co, Zn), in which the M/Al ratio is 1/3. The framework of MAPO-CJ69 (M = Co, Zn) contains 2-D intersecting 8-ring channels running along the [010] and [001] directions. The protonated diethylamine cations, as the structure-directing agent, reside in the intersection of the channels. The structure of MAPO-CJ69 is built up exclusively by 4-4- SBUs, which has been found in some known zeolites such as SFO, AFR, and OWE. Such 4-4- SBUs can be linked through the “head to tail” as well as “shoulder to shoulder” modes. The “head to tail” connection of the 4-4- SBUs forms both the undulating layer and the planar layer. The structures of SFO and AFR can be described by linkage of the undulating layers via "inversion symmetry" and "mirror symmetry", respectively, while the structures of MAPO-CJ69 and ZON can be viewed as connection of the planar layers via "inversion symmetry" and "mirror symmetry", respectively. Furthermore, layers formed by the "shoulder to shoulder" connection of the 4-4- SBUs can generate OWE as well as a hypothetical zeolite H-CJ69 via "inversion symmetry" and "mirror symmetry", respectively. This work not only demonstrates a new zeolite topology but also provides insight into construction of zeolite frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data (CIF), bond lengths (Angstroms), and angles (degees) for MAPO-CJ69 (M = Co, Zn). This material is available free of charge via the Internet at http://pubs.acs.org.

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