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Investigation on the Chain-to-Chain and Chain-to-Open-Framework Transformations of Two One-Dimensional Aluminophosphate Chains

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Using ethylenediamine as a template, two one-dimensional (1-D) aluminophosphate compounds $[AlP_2O_8H][NH_3CH_2CH_2NH_3]$ (**1**) and $[AlP_2O_8][NH_3CH_2CH_2NH_3][NH_4]$ (**2**) have been prepared from a gel system: 1.0:*x*:*y*:44 $Al(i\text{-}PrO)_3$–H_3PO_4–en–EG ($x = 3.0$–9.0, $y = 1.0$–11.0). Compound **1** consists of edge-sharing four-membered ring (MR) chains, denoted as AlPO-ESC, and compound **2** consists of corner-sharing 4-MR chains, denoted as AlPO-CSC. The molar ratio of en:H_3PO_4 in the starting gel has an important influence on the final product. If en:$H_3PO_4 \geq 1$, AlPO-CSC is obtained, while if en:$H_3PO_4 < 1$, AlPO-ESC is formed. These two chains can transform to each other upon addition of some extra amount of en or H_3PO_4 to the reaction mixture in which AlPO-ESC or AlPO-CSC is crystallized. On the basis of XRD and ^{27}Al and ^{31}P MAS NMR analyses, a possible chain-to-chain transformation mechanism is proposed. The corner-sharing 4-MR chains of AlPO-CSC, as well as the edge-sharing 4-MR chains of AlPO-ESC can be assembled to 3-D open-framework compound $NiAlP_2O_8{\cdot}C_2N_2H_9$ through Ni^{2+} cations. It is noted that AlPO-CSC remains in the structure of $NiAlP_2O_8{\cdot}C_2N_2H_9$. It is believed that AlPO-ESC might be first transformed to AlPO-CSC followed by the assembly to 3-D open-framework of $NiAlP_2O_8{\cdot}C_2N_2H_9$ through Ni^{2+} cations.

Introduction

Microporous materials are of great interest for a range of molecular recognition applications, as well as for the widespread applications such as catalysts, absorption, and ion-exchange.[1,2] For these reasons, great efforts have been focused on the exploration of new microporous materials. Aluminophosphates are one of the important families of microporous materials. Recently, our laboratory and others have successfully synthesized a variety of organically templated aluminophosphates with 1-D chains, 2-D layers, and 3-D frameworks.[3] Their networks or frameworks are constructed from alternation of Al units (AlO_4, AlO_5, and AlO_6) and PO_4 units with one, two, three, or four oxygen atoms being shared by adjacent Al atoms. This leads to vast varieties in the stoichiometry of Al and P in the framework, such as $Al_2P_2O_8(OH)^-$,[4−7] $AlP_2O_8^{3-}$,[8−16] $Al_2P_3O_{12}^{3-}$,[17−20] $Al_3P_4O_{16}^{3-}$,[21−25] $Al_3P_5O_{20}H^{5-}$,[26] $Al_4P_5O_{20}^{3-}$,[27,28] $Al_5P_6O_{24}^{3-}$,[29] $Al_{11}P_{12}O_{48}^{3-}$,[30] $Al_{12}P_{13}O_{52}^{3-}$,[31] and $Al_{13}P_{18}O_{72}^{13-}$.[32,33]

Despite the great effort being made, the rational design

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and synthesis of microporous materials are still full of difficulties because of the unclear formation mechanism under hydrothermal or solvothermal conditions. The 1-D aluminophosphate chains built up by edge-sharing or corner-sharing of the Al_2P_2 4-MRs, denoted as AlPO-ESC and AlPO-CSC, respectively, are two types of fundamental chains[8−10] that can be found in a range of aluminophosphate frameworks. For example, the structure of AlPO-ESC can be seen in the framework of $Al_3P_3O_{12}(OH)^-$ ($AlPO_4$-21)[34] and AlPO-CSC in the structures of $Al_2P_3O_{10}(OH)_2{}^-$,[18] $Al_5P_6O_{24}{}^{3-}$ (JDF-20),[29] $Al_2(PO_4)_3H_2{}^-$,[35] etc. Ozin and coworkers proposed that further hydrolysis and condensation reaction of the linear corner-sharing 4-MR chain, the so-called parent chain, would lead to the formation of more complex structures such as 1-D chains, 2-D layers, and 3-D frameworks.[36] Recently, using the 1-D chains of AlPO-CSC as building units, we have successfully prepared the 3-D open-frameworks $MAlP_2O_8{\cdot}C_2N_2H_9$ through transition metal cations M^{2+} (M = Fe, Co, and Ni). This provides the experimental evidence that the 1-D AlPO-CSC chain is a parent chain for the formation of a range of aluminophosphates.[37,38] Because both AlPO-ESC and AlPO-CSC are built up from 4-MRs that are linked in a different manner, we believe that both of them are important structural building units (SBU) or precursors for open-framework aluminophosphates. Thus, further experimental study on the structural relationship of these two types of chains will be helpful in the understanding of the formation mechanism of microporous materials.

In this work, we report the synthesis and chain-to-chain transformation of two types of 1-D $AlP_2O_8{}^{3-}$ chains in the $Al(i\text{-}PrO)_3-H_3PO_4-en-EG$ system. Using the 1-D chains of AlPO-ESC as the building units, the 3D open-framework $NiAlP_2O_8{\cdot}C_2N_2H_9$ can also be assembled through Ni^{2+} cations.

Experimental Section

Synthesis of $[AlP_2O_8H][NH_3CH_2CH_2NH_3]$ (1) and $[AlP_2O_8]$-$[NH_3CH_2CH_2NH_3][NH_4]$ (2). Compounds **1** and **2** were prepared in a gel system $Al(i\text{-}PrO)_3-H_3PO_4-en-EG$. Typically, 0.40 g of finely ground aluminum triisopropoxide was first dispersed into 9.0 mL of ethylene glycol, followed by the addition of certain amount of ethylenediamine (en). Phosphoric acid (85 wt % in water) was added slowly to the above reaction mixture under continuous stirring. The reactant gel was transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 3 days under autogenous pressure. The crystalline product was filtered, washed with distilled water, and then dried at 70 °C overnight.

Study on the Chain-to-Chain Transformation. To the reaction system in which compound **1** or **2** was crystallized was added 1.0 mL of ethylendiamine or 0.13−0.50 mL of H_3PO_4 at room temperature, respectively. The reactant was further heated in the stainless autoclave at 180 °C for about 10 days.

Several such reactions were carried out parallely. At a certain time interval (2 days), an individual autoclave was taken out from the oven, followed by quenching in cold water immediately. The product was separated by centrifugation. The solid product was dried at ambient temperature.

Study on the Chain-to-Open-Framework Transformation. To the reaction systems in which compound **1** was crystallized, 1.96−5.88 mmol of $Ni(OAc)_2{\cdot}4H_2O$ was added, followed by further heating at 180 °C for about 10 days. The final product in light-green color was filtered out, washed, and dried at ambient temperature.

Characterization. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5148$ Å). Solid-state NMR experiments were performed with magic angle spinning (MAS) on an InfinityPlus-400 spectrometer operating at frequencies of 104.26 and 161.97 MHz for ^{27}Al and ^{31}P, respectively. Chemical shifts were referenced to an external standard of $Al(H_2O)_6{}^{3+}$ for ^{27}Al and 85% H_3PO_4 for ^{31}P. The sample was spun at 8.0 kHz for both ^{27}Al and ^{31}P.

Results and Discussion

Compounds **1** and **2** containing chains of AlPO-ESC and AlPO-CSC, respectively, are crystallized in the system with a gel composition of 1.0:x:y:82.4 $Al(i\text{-}PrO)_3-H_3PO_4-en-EG$. The synthesis conditions are listed in Table 1. It is noted that different H_3PO_4:en molar ratios in the starting gel can lead to different products. Figure 1 illustrates the products change with different en:H_3PO_4 ratios. Compound **1** is crystallized in the area with en:$H_3PO_4 < 1$. If en:$H_3PO_4 \geq 1$, compound **2** is crystallized. However, under the condition that the amount of en is too low, a dense aluminophosphate phase, cristobalite, is formed. In addition, no matter how much en is added to the starting gel, no crystalline phase can be obtained when the molar amount of H_3PO_4 is equal to 1.0. During the synthesis of AlPO-ESC and AlPO-CSC, the phosphoric acid not only supplies the source of phosphate but also affects the alkalinity and acidity of the starting gel

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Table 1. Synthesis Conditions for AlPO-ESC and AlPO-CSC

$\mathrm{Al}(i\text{-PrO})_3$	H_3PO_4	en	pH[a]	product
1.0	1.0	1.0−6.0	9.0−10.0	gel without crystal
1.0	3.0	1.0−2.0	5.0−8.0	AlPO-ESC
		3.0−8.0	9.0−10.0	AlPO-CSC
1.0	5.0	1.0	4.0−5.0	cristobalite
		2.0	5.0	AlPO-ESC + cristobalite
		3.0−4.0	6.0	AlPO-ESC
		5.0−8.0	9.0−10.0	AlPO-CSC
1.0	7.0	2.0−3.0	4.0−5.0	AlPO-ESC + cristobalite
		4.0−6.0	6.0	AlPO-ESC
		7.0−8.0	9.0−10.0	AlPO-CSC
1.0	9.0	6.0−8.0	5.0−6.0	AlPO-ESC
		9.0−11.0	9.0−10.0	AlPO-CSC

[a] Note: pH value was determined by pH test paper.

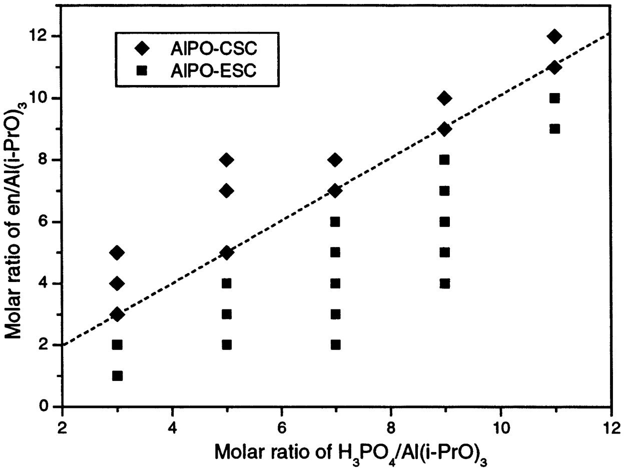

Figure 1. Diagram showing the influence of en:H_3PO_4 ratios on the final products.

together with ethylenediamine which acts as a structure-directing agent for the formation of AlPO-ESC and AlPO-CSC.

Both compounds **1** and **2** are prepared in a similar solvothermal system. The difference of their synthesis lies in the alkalinity and acidity of the starting gel that is affected by the en:H_3PO_4 ratio as presented in Table 1. It is noted that when certain amount of base such as ammonia, tripropanamine, or sodium hydroxide solution is added to the initial gel in which compound **1** should have been crystallized, the pH value of the gel is increased to 9.0−10.0 and the final product is compound **2**, whereas the addition of certain amount of acid to the starting gel of compound **2** to lower the pH value to 5.0−8.0 results in the formation of compound **1**. On the basis of the fact that the 1-D $AlP_2O_8^{3-}$ chains in compounds **1** and **2** are both built up by Al_2P_2 four-membered rings linked together in a different connection style, it is believed that there might be some intrinsic structural relationship between these two types of chains and that the structures of AlPO-ESC and AlPO-CSC might transform to each other under appropriate conditions. Therefore, we further investigate their chain-to-chain transformation under suitable synthesis conditions. It is found that upon addition of 0.5−1.0 mL of en or $NH_3{\cdot}H_2O$ to the reaction mixture in which compound **1** has already been crystallized, AlPO-ESC can transform to AlPO-CSC after further heating. On the other hand, the structural transformation from AlPO-CSC to AlPO-ESC can be achieved by addition of 0.13−0.50 mL of H_3PO_4 to the reaction mixture containing crystalline compound **2**.

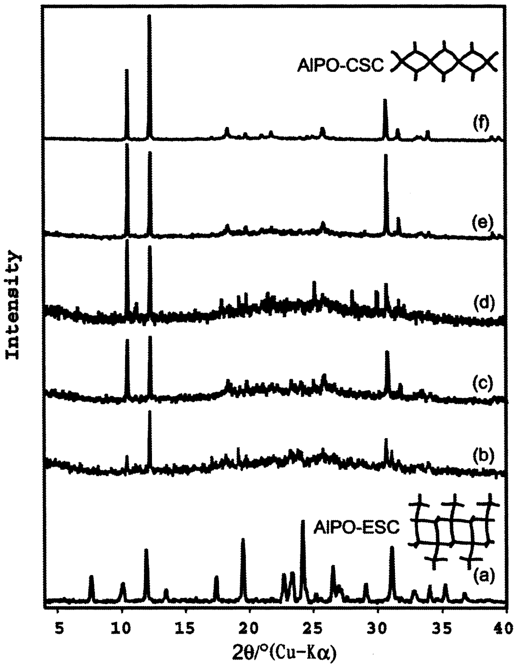

Figure 2. XRD studies on the phase transformation from AlPO-ESC to AlPO-CSC: (a) AlPO-ESC; samples heated for (b) 1, (c) 3, (d) 5, (e) 7, and (f) 9 days.

The chain-to-chain transformation from AlPO-ESC to AlPO-CSC is further investigated by XRD and ^{27}Al and ^{31}P MAS NMR analyses. XRD study on the transformation process from AlPO-ESC to AlPO-CSC is presented in Figure 2. Compound **1** with chains of AlPO-ESC is first crystallized in the reactant after heating for 3 days, to which 1.0 mL of en is added followed by further heating for 1−10 days. After 1 day, a little amount of compound **2** is crystallized and no compound **1** exists any longer. With the increase of the reaction time, the crystallinity of compound **2** increases evidently.

^{27}Al MAS NMR spectra of the samples obtained at different reaction time are shown in Figure 3. The chemical shifts at 30.9 and 39.0 ppm are attributed to the tetrahedrally coordinated Al atoms in AlPO-ESC. The peak at 30.9 ppm is caused by second-order quadrupolar interactions. ^{27}Al has a nuclear quadrupolar moment ($I = 5/2$) which interacts with the electric field gradient caused by the nonspherically symmetric charge distribution around ^{27}Al nucleus. Line broadening and chemical shift changes may arise from those quadrupolar interactions.[39] When the reactant is heated for about 1 day after the addition of extra en, the resonance at 30.9 ppm disappears and a small peak at −6.8 ppm emerges. The disappearance of the peak at 30.9 ppm implies that the charge distribution around ^{27}Al nucleus becomes spherically symmetric. The signal at −6.8 ppm corresponds to the chemical shift introduced by the six-coordinated Al atoms. With the increase of reaction time, the peak at −6.8 ppm becomes smaller and smaller, while the signal at 39.0 ppm

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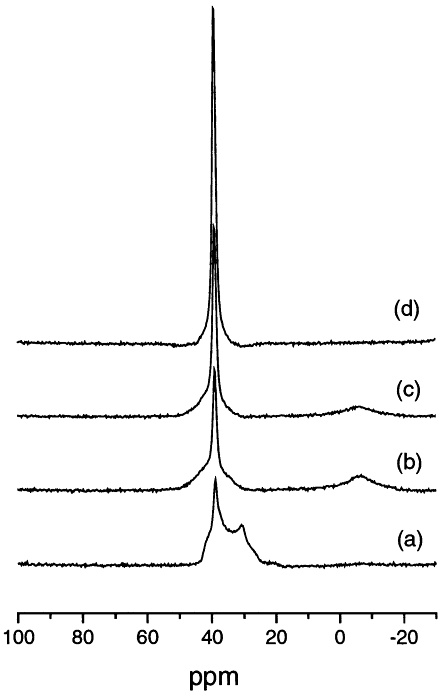

Figure 3. ^{27}Al MAS NMR spectra of (a) AlPO-ESC and samples heated for (b) 1, (c) 3, and (d) 9 days.

becomes sharper and sharper. At last, only one sharp peak at 39.0 ppm can be observed, which is due to the four-coordinated Al atoms in AlPO-CSC. The emergence and weakness of the signal at −6.8 ppm indicates the change of the environment of Al atoms during the chain-to-chain transformation. The six-coordinated Al atoms might be a transition state during the transformation. ^{31}P MAS NMR spectra are presented in Figure 4. The peaks at −11.9 and −10.3 ppm are ascribed to two crystallographically distinct P atoms in AlPO-ESC. The former is attributed to the four-coordinated P atoms within the backbone of AlPO-ESC, while the latter to the pendant HPO_4 groups. When the reactant is further heated for about 9 days after the addition of extra en, the signal at −10.3 ppm disappears, indicating that the pendant HPO_4 groups are transformed to the backbone PO_4 groups. The broad peaks around 0 ppm might be assigned to the transition states of P species. The disappearance of these peaks implies that all the P species have changed to four-coordinated ones. The sharp peak at −12.7 ppm is assigned to the unique tetrahedral environment of P atoms in the backbone of AlPO-CSC.

On the basis of the ^{27}Al and ^{31}P MAS NMR analyses, a possible scheme for the chain-to-chain transformation from AlPO-ESC to AlPO-CSC is proposed (Figure 5). Because of the addition of extra base to the reaction mixture, some of the Al−O−P bonds are cleaved through hydrolysis and transitional Al−OH and P−OH terminal groups are thus formed. This is consistent with the ^{27}Al and ^{31}P MAS NMR spectra discussed above. Under solvothermal conditions, rapid rotation and bending motions are expected to the unhydrolyzed Al−O−P linkages. Rotations will bring the Al−OH and P−OH groups close together, and further intrachain condensations will occur with the release of H_2O. In this way, two edge-sharing 4-MRs transform to two

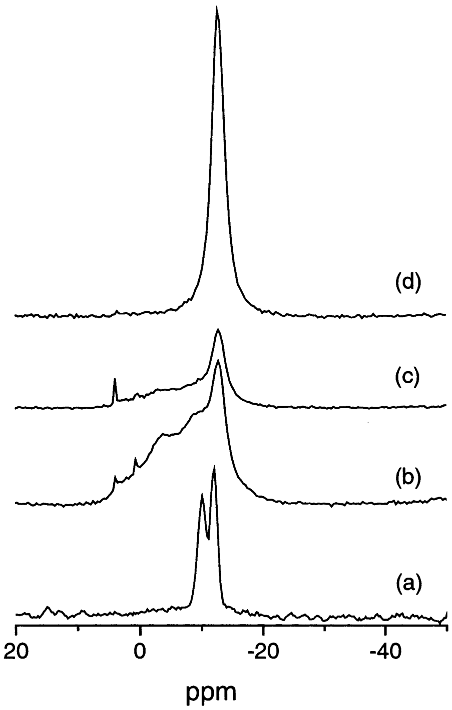

Figure 4. ^{31}P MAS NMR spectra of (a) AlPO-ESC and samples heated for (b) 1, (c) 3, and (d) 9 days.

corner-sharing 4-MRs. If this process proceeds simultaneously or in the forward direction, the corner-sharing 4-MR chains of AlPO-ESC will be finally transformed into edge-sharing 4-MR chains of AlPO-CSC. Similarly, if extra acid is added to the reactant containing compound **2** with the chains of AlPO-CSC, this process is expected to proceed in the reversed direction. Through a similar hydrolysis−condensation self-assembly pathway, AlPO-CSC will finally transform into AlPO-ESC. It is believed that the acidic and basic media play a key role in this hydrolysis−condensation self-assembly.

The 1-D $AlP_2O_8^{3-}$ chains, AlPO-ESC and AlPO-CSC, both contain terminal P=O and/or P−OH groups. This indicates their potential ability in condensing to 3-D open frameworks. In our recent work, 3-D open frameworks $MAlP_2O_8{\cdot}C_2N_2H_9$ have been successfully built up through assembly of the corner-sharing 4-MR chains of AlPO-CSC via transition metal cations M^{2+} (M = Ni, Co, and Fe).[37,38] The interactions between M^{2+} species and the terminal P=O groups of the chains of AlPO-CSC lead to the formation of the 3-D open frameworks. It is believed that AlPO-CSC acts as a structural building unit for the construction of the 3-D open frameworks $MAlP_2O_8{\cdot}C_2N_2H_9$. Since AlPO-CSC and AlPO-ESC can transform to each other, we use AlPO-ESC as a structure building unit to assemble 3-D open frameworks through transition metal M^{2+} species. As in the assembly of AlPO-CSC to $NiAlP_2O_8{\cdot}C_2N_2H_9$, AlPO-ESC is first prepared and followed by the addition of Ni^{2+} cations. The appropriate molar ratio of $Ni(OAc)_2$:Al(*i*-PrO)$_3$ is 1.0−3.0. Interestingly, the 3D open-framework $NiAlP_2O_8{\cdot}C_2N_2H_9$ which is featured by the chains of AlPO-CSC is built up. The experimental powder XRD pattern is in good agreement with that simulated on the basis of the single-crystal structural

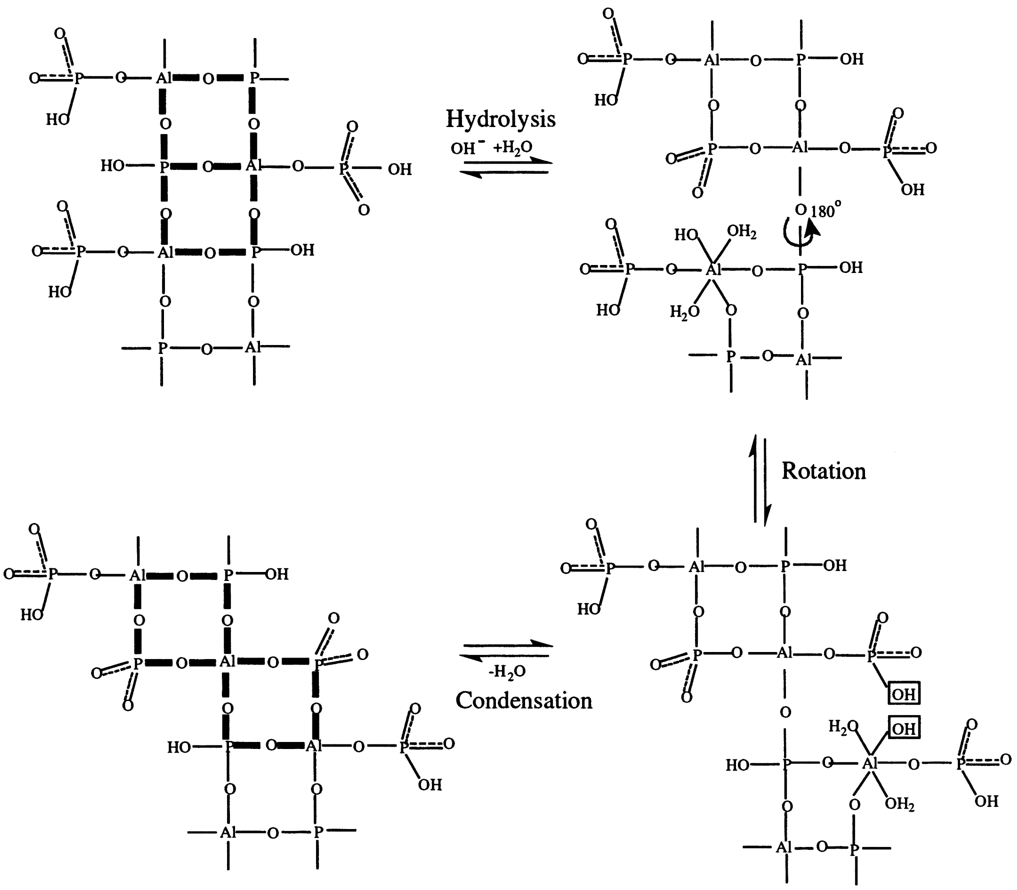

Figure 5. Possible structural transformation pathway from AlPO-ESC to AlPO-CSC.

analysis of $NiAlP_2O_8{\cdot}C_2N_2H_9$ (Figure 6).[37] It is believed that during this assembly process the edge-sharing 4-MR chains of AlPO-ESC might first transform to the corner-sharing 4-MR chains of AlPO-CSC and then assembly to 3-D open-framework $NiAlP_2O_8{\cdot}C_2N_2H_9$ through Ni^{2+} cations. This experimental result indicates that the chains of AlPO-ESC and AlPO-CSC built up by 4-MRs might be the parent chains for the crystallization of open-framework aluminophosphates.

Insight into the literature on the open-framework materials reveals that the 1-D chains constructed by corner-sharing or edge-sharing 4-MRs are ubiquitous. It has been shown recently by Rao et al that the edge-sharing 4-MR chains of $Zn(HPO_4)_2^{2-}$ are the building block in some layered and open-framework zinc phosphates.[41] Such 1-D 4-MR chains are also known in gallophosphates,[42−44] iron phosphates,[45] cobalt phosphates,[46,47] zirconium phosphates,[48] and chromium phosphite.[49] The transformation from 1-D chains to 3-D open frameworks provides an insight into the possible pathways involved in the built-up process of complex structures of metal phosphates. It is believed that using the low-dimensional metal phosphates as precursors, other multi-dimensional structures might be developed.

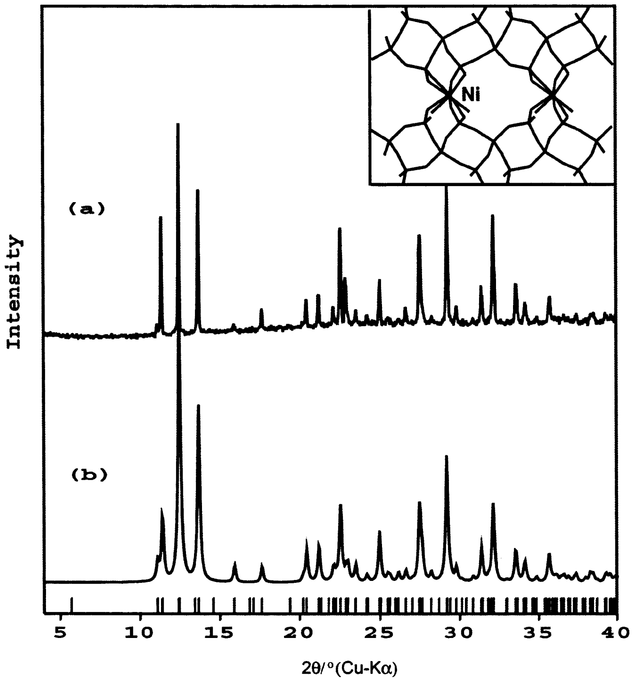

Figure 6. (a) Experimental XRD pattern of the product prepared by the assembly of AlPO-ESC via Ni^{2+} cations and (b) that simulated from single-crystal diffraction analysis of $NiAlP_2O_8{\cdot}C_2N_2H_9$ with the Cerius[2] software package.[40] The insert is a section of the structure of $NiAlP_2O_8{\cdot}C_2N_2H_9$ showing the connection between the chains of AlPO-CSC and Ni^{2+} cations.

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Conclusion

The synthesis conditions for two 1-D aluminophosphates with edge-sharing and corner-sharing 4-MR chains of AlPO-ESC and AlPO-CSC have been investigated. The alkalinity and acidity of the starting gel have an important influence on the final product. By addition of extra base or acid to the reactant mixture in which AlPO-ESC or AlPO-CSC is formed, the structures of these two types of chains can transform to each other. It is proposed that the transformation of these two aluminophosphate chains is achieved by the cleavages and reconstructions of some Al−O−P bonds. As with the 1-D chains of AlPO-CSC, AlPO-ESC can also be used to assembly to 3-D open-framework $NiAlP_2O_8 \cdot C_2N_2H_9$ through Ni^{2+} cations. The transformations provide an insight into the possible pathways involved in the built-up process of complex structures of metal phosphates.

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Note Added after ASAP: Due to a production error, this paper was posted ASAP on June 12, 2003, before all of its corrections had been made. The correct version was posted on June 26, 2003.

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