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(3,4)-Connected Zincophosphites as Structural Analogues of Zinc Hydrogen Phosphate

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The synthesis and crystal structures of three new open-framework zincophosphites with helical channels are reported here in the context of the synthetic design of an open architecture from three- and four-connected polyhedral centers. These zincophosphites were prepared under hydrothermal conditions from HF-containing media in mixed water–ethylene glycol solvents. Their three-dimensional frameworks consist of alternating ZnO_4^{6-} tetrahedra and HPO_3^{2-} trigonal pyramids with an overall framework composition of $[Zn_3(HPO_3)_4]^{2-}$. The topology was analyzed by converting these zincophosphites from their (3,4)-connected network into a four-connected framework. The symmetry and charge density of three different structure-directing agents dictate the symmetry and framework density of resulting inorganic frameworks. These zincophosphites are structural analogues of a known hydrogen phosphate, suggesting that the bonding difference between –P–H and –P–OH plays an insignificant role in the formation of phosphite and hydrogen phosphate open frameworks.

Introduction

Crystalline microporous materials have found widespread applications as catalysts, adsorbents, ion-exchangers, and so forth.[1] Among the most important microporous materials are aluminosilicate zeolites.[2] In the past several decades, efforts to create new microporous materials have resulted in the synthesis of many different types of open-framework or miroporous materials such as metal phosphates and germanates,[3−6] metal chalcogenides (mostly sulfides),[7,8] and metal-organic framework materials.[9] These new materials further broaden potential applications of microporous solids to areas such as photocatalysis, solid electrolytes, enantioselective catalysis, and gas storage (e.g., H_2) and separation.

In the synthetic design of new open-framework materials, one of most important considerations is the coordination chemistry of cationic species used for the construction of the framework. The local geometric feature surrounding individual cationic (polyhedral) centers also plays a vital role in the overall topological features of the resulting open-framework architecture. In general, a low coordination number (<6) with more directional covalent bonds is desirable for creating an open architecture. For example, in known microporous oxides such as zeolites, one key structural feature is the tetrahedral coordination of its constituent Al^{3+} and Si^{4+} cations. Compared to octahedral units, tetrahedral blocks are far more likely to lead to open architectures.

It is, therefore, not surprising that there has been increasing interest in the use of three-connected centers as basic structural units for the construction of open-framework materials.[10] Three-connected centers, when used alone, tend to form low-dimensional structures. However, when used in combination with four-connected centers, a variety of three-dimensional open-framework architectures are possible.[11]

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There exist a number of different three-connected building blocks, both organic and inorganic. Among inorganic units, oxoanions are most common. Such oxoanions include planar BO_3^{3-} and CO_3^{2-} and pyramidal SnO_3,$^{4-}$ SO_3^{2-}, SeO_3^{2-}, and HPO_3^{2-}. In addition to these inherently three-connected centers, some four-connected centers can serve as three-connected centers when one of the four corners is terminated with a dangling group. The most common examples in this category are $HO-PO_3^{2-}$ and $R-PO_3^{2-}$ where R is an alkyl group. Several well-known zeolite-type structures (e.g, −CLO, JDF-20) contain $HO-PO_3^{2-}$.[12−14]

The presence of three-connected centers has been recognized to lead to large pore sizes and a low framework density (e.g, −CLO, JDF-20), both of which are desirable for applications. However, compared to four-connected framework topologies that have been extensively studied and tabulated,[12] (3,4)-connected framework topologies have received much less attention. Recently, metal phosphites have attracted some attention, in part because of their relationship to microporous phosphates that have already been shown to display a variety of compositional and topological features.[15−19]

We report here the synthesis and structure of three new zinc phosphites (denoted $ZnPO_3$-1, $ZnPO_3$-2, and $ZnPO_3$-3) that possess three-dimensional open frameworks with alternating three-connected HPO_3^{2-} and four-connected Zn^{2+} centers. The work is a part of our research program aimed at the systematic study of (3,4)-connected open-framework architectures.[20]

Experimental Section

Synthesis. A. $[N(CH_3)_4]_2Zn_3(HPO_3)_4$. A total of 0.3759 g of zinc carbonate, 2.1342 g of water, 2.0302 g of ethylene glycol, 0.7546 g of phosphorous acid, 0.0414 g of hydrogen fluoride−pyridine, and 4.0617 g of tetramethylammonium hydroxide (25 wt % in water) were mixed in a 23 mL Teflon-lined stainless steel autoclave and stirred for 45 min. The pH of the resulting mixture was 8.10. The vessel then was sealed and heated at 180 °C for 6 days. After cooling to room temperature, clear bipyramid-shaped crystals (0.5304 g), most of which were microcrystalline, were obtained with a 79.9% yield. Results of the elemental analysis (in wt %) are 14.25 (calcd 14.46) for C, 3.85 (calcd 4.25) for H, and 4.04 (calcd 4.22) for N. The X-ray powder diffraction pattern was consistent with that calculated from single-crystal data, showing no impurity peaks. Microscopic examination using a Nikon SMZ-1500 stereomicroscope showed no amorphous phase.

B. $[HN(CH_3)_3]_2Zn_3(HPO_3)_4$. A total of 0.3750 g of zinc carbonate, 1.9388 g of water, 1.5198 g of ethylene glycol, 0.7569 g of phosphorous acid, 0.0611 g of hydrogen fluoride−pyridine, and 3.737 g of trimethylamine (25∼27 wt % in water) were mixed together and stirred for 45 min in a 23 mL Teflon-lined stainless steel autoclave to reach a pH of 9.38. The vessel then was sealed and heated at 120 °C for 5 days. After cooling to room temperature, plate-shaped clear crystals were found mixed with an unidentified polycrystalline powder. The X-ray powder diffraction pattern showed the presence of an unidentified crystalline phase that occurred as a minor phase on the basis of diffraction intensity.

C. $[H_2N(CH_3)_2]_2Zn_3(HPO_3)_4$. A total of 0.3748 g of zinc carbonate, 1.9383 g of water, 1.5193 g of ethylene glycol, 1.0351 g of phosphorous acid, 0.0610 g of hydrogen fluoride−pyridine, and 2.425 g of dimethylamine (40 wt % in water) were mixed and stirred for 45 min in a 23 mL Teflon-lined stainless steel autoclave to reach a pH of 8.97. The vessel then was sealed and heated at 120 °C for 5 days. After cooling to room temperature, irregular-shaped clear crystals were obtained as a minor phase. The X-ray powder diffraction pattern showed a predominantly unidentified crystalline phase. Microscopic examination showed the crystals of the major phase to be fibrous and too small for single-crystal analysis.

X-ray Powder Diffraction. X-ray powder diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA (Cu Kα radiation, $\lambda = 1.5418$ Å). The data collection was carried out with a step size of 0.03° and a counting time of 1 s per step. The 2θ angular range is from 3 to 60°.

Single-Crystal Structure Analysis. Each crystal was glued to a thin glass fiber with epoxy resin and mounted on a Bruker APEX II diffractometer equipped with a fine focus, 2.0 kW sealed-tube X-ray source (Mo Kα radiation, $\lambda = 0.710\,73$ Å) operating at 50 kV and 30 mA. The empirical absorption correction was based on equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. Each structure was solved by direct methods followed by successive difference Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SHELXTL, and final full-matrix refinements were against F^2. The crystallographic results are summarized in Table 1. ORTEP diagrams for all three structures are shown in Figure 1.

Thermal Analysis. The simultaneous differential scanning calorimetry−thermogravimetric analysis (DSC-TGA) was performed on TA Instruments SDT Q600 under a flowing nitrogen atmosphere. The flow rate of the nitrogen gas was controlled at about 100 L/min. A total of 11.201 mg was heated between room temperature and 1000 °C at a heating rate of 5°/min.

Results and Discussion

Compositional Analysis. In (3,4)-connected nets with alternating four-connected vertexes (denoted A) and three-connected vertexes (denoted B), the stoichiometry is always A_3B_4, because the composition (the A/B ratio) is inversely proportional to the ratio between the coordination numbers of A and B (4/3). For three zincophosphites reported here, tetrahedral Zn^{2+} sites alternate with trigonal pyramidal HPO_3^{2-} sites (not considering terminating P−H) to form a

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Table 1. Summary of Crystal Data and Refinement Results

name	$ZnPO_3$-1	$ZnPO_3$-2	$ZnPO_3$-3
formula	$[(CH_3)_4N]_2Zn_3(HPO_3)_4$	$[(CH_3)_3NH]_2Zn_3(HPO_3)_4$	$[(CH_3)_2NH_2]_2Zn_3(HPO_3)_4$
size (mm)	$0.26 \times 0.10 \times 0.10$	$0.12 \times 0.10 \times 0.10$	$0.080 \times 0.080 \times 0.080$
temp (K)	293	293	293
a (Å)	9.0606(6)	16.1749(16)	15.7891(3)
b (Å)	15.7587(8)	8.3247(9)	8.4306(2)
c (Å)	32.0453(16)	17.0673(17)	16.1358(5)
β (deg)	90	114.781(2)	112.357(1)
V (Å^3)	4575.5(4)	2086.5(4)	1986.41(9)
Z	8	4	4
space group	$Fddd$	$C2/c$	$C2/c$
$2\theta_{max}$ (deg)	50	63	55
total data	8339	12982	10821
unique data	1014	3536	2318
data, $I > 2\sigma(I)$	750	2484	1485
parameters	72	135	109
$R(F)$ (%)	3.59	5.03	3.90
$R_w(F^2)$ (%)	10.5	12.9	8.63
GOF	1.07	1.05	1.03

three-dimensional framework with a framework composition of $[Zn_3(HPO_3)_4]^{2-}$.

The negative framework charge is balanced by extra-framework $(CH_3)_4N^+$, $(CH_3)_3NH^+$, and $(CH_3)_2NH_2^+$. These organic cations also play a space-filling role and serve to stabilize the inorganic framework by occupying extraframework spaces that represent 49.4%, 44.2%, and 41.5% of the crystal volumes respectively for $ZnPO_3$-1, $ZnPO_3$-2, and $ZnPO_3$-3 as calculated by the program PLATON.[21] The decreasing extraframework volume going from $ZnPO_3$-1 to $ZnPO_3$-2 to $ZnPO_3$-3 is consistent with the decreasing size of the corresponding structure-directing agent [i.e., $(CH_3)_4N^+$, $(CH_3)_3NH^+$, and $(CH_3)_2NH_2^+$].

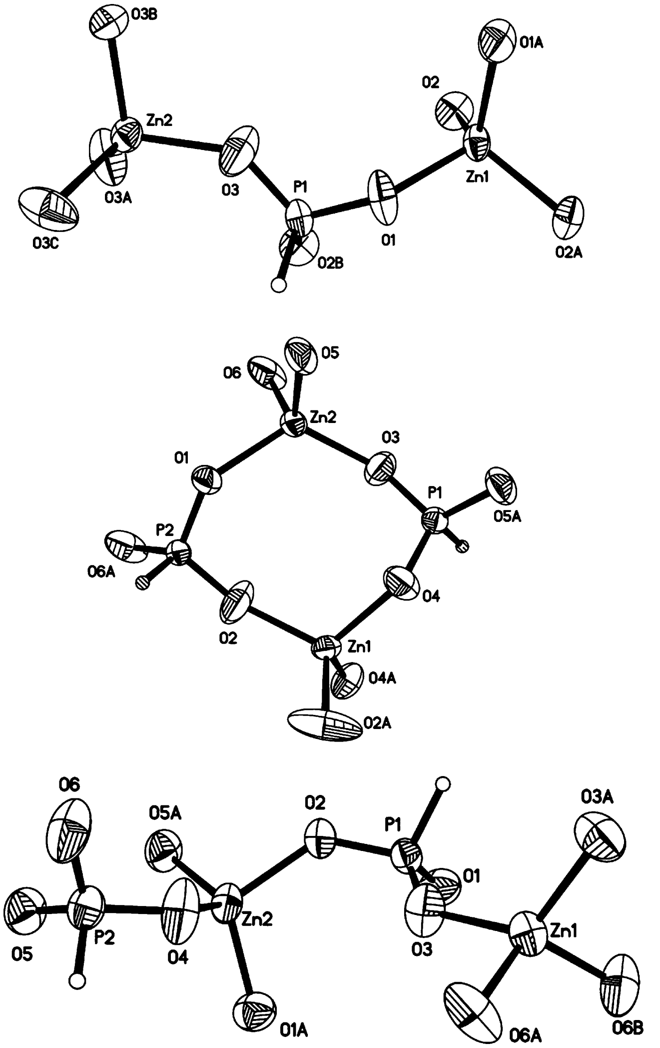

Figure 1. ORTEP diagrams of $ZnPO_3$-1 (top), $ZnPO_3$-2 (middle), and $ZnPO_3$-3 (bottom) showing the local coordination environment and connectivity for atoms in the asymmetric unit. Atom labels containing "A" and "B" indicate symmetry-generated sites.

In the synthetic design of the (3,4)-connected framework, the charge of three-connected and four-connected centers is an important consideration. There are two opposite situations depending on the sign of the charge on three- and four-connected centers. For zincophosphites, four-connected centers (Zn^{2+}) are positive and three-connected centers (HPO_3^{2-}) are negative (the $3^-/4^+$ case). The second situation opposite to zincophosphites involves positive three-connected centers and negative four-connected centers (the $3^+/4^-$ case). Open-framework tin phosphates represent one such example with the general framework composition of $Sn_4(PO_4)_3^-$.[22] Some other possibilities (both real and hypothetical) are listed in Table 2. Open-framework materials crystallized under hydrothermal conditions generally form a negative framework. The selection of three- and four-connected chemical units requires a different strategy for two different situations. For example, in the $3^-/4^+$ case, it is a good practice to have the same charge (but the opposite sign) for both three-connected and four-connected units as in zincophosphites. However, for the $3^+/4^-$ combination, the same charge is not preferred because it would necessarily lead to a positive framework that may be quite difficult to synthesize.

Topological Analysis. The framework density defined as the number of polyhedral centers (Zn and P in this case) in 1000 Å^3 is 12.2, 13.4, and 14.1, respectively for $ZnPO_3$-1, $ZnPO_3$-2, and $ZnPO_3$-3. Such framework density values are comparable to those lowest values for zeolite-type topologies (e.g., 12.1 for UCSB-10GaZn and tschortnerite, the lowest observed values for fully cross-linked four-connected frame-

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Table 2. Compositional Possibilities for (3,4)-Connected Open-Framework Structures[a]

three- and four-connected centers	framework compositions	charge per polyhedral center
M^{+} and NO_3^{-}	$[Li_3(NO_3)_4]^{-}$ (hypothetical)	−0.14
M^{2+} and CO_3^{2-} (or SO_3^{2-}, SeO_3^{2-}, etc.)	$[Zn_3(CO_3)_4]^{2-}$ (ref 10)	−0.29
M^{2+} and HPO_4^{2-}	$[Zn_3(HPO_4)_4]^{2-}$ (ref 23)	−0.29
M^{2+} and HPO_3^{2-}	$[Zn_3(HPO_3)_4]^{2-}$ (this work and refs 11−15)	−0.29
M^{3+} and BO_3^{3-}	$[Al_3(BO_3)_4]^{3-}$ (hypothetical)	−0.42
M^{2+} and PO_4^{3-}	$[Sn_4(PO_4)_3]^{-}$ (ref 22)	−0.14
M^{2+} and GeO_4^{4-}	$[Sn_4(GeO_4)_3]^{4-}$ (hypothetical)	−0.57

[a] Different three- and four-connected centers are selected so that the resulting framework carries a negative charge. Possible positive frameworks are not considered here.

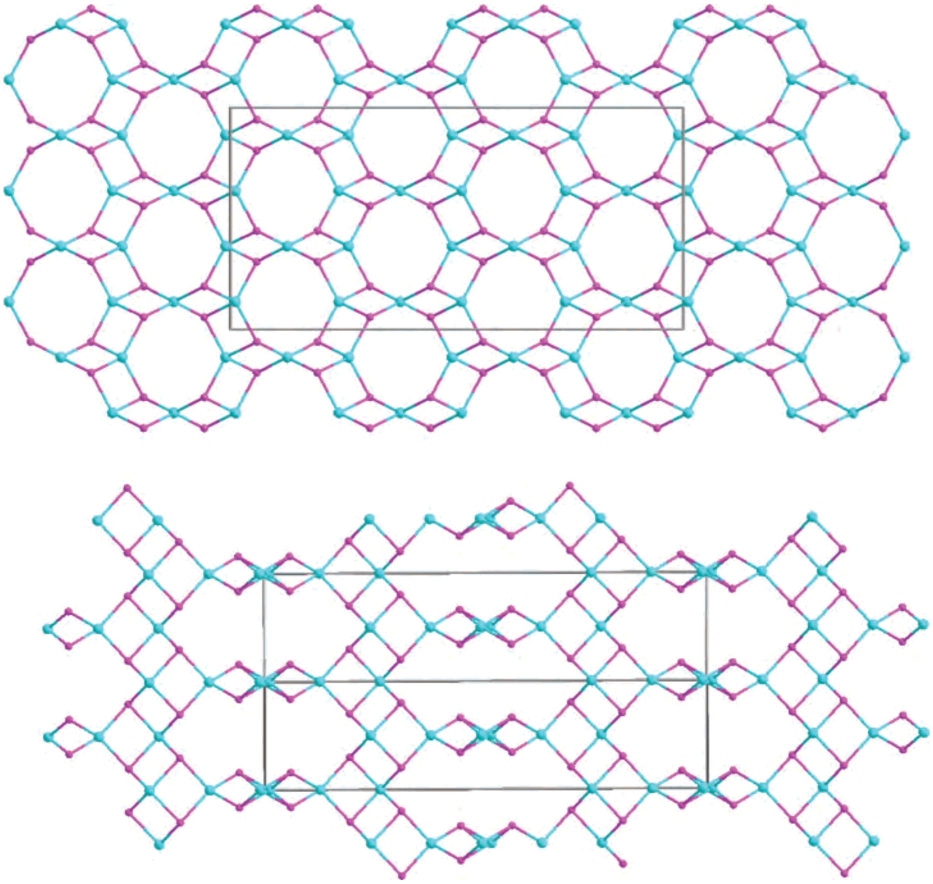

Figure 2. (3,4)-Connected framework in the orthorhombic $ZnPO_3$-1 showing the three-dimensional structure (a) viewed down the crystallographic *a* axis and (b) viewed down the crystallographic (110) axis. Framework oxygen and hydrogen atoms and extraframework species are omitted for clarity.

works),[12] further demonstrating that the use of three-connected centers represents a feasible approach toward the design of highly open framework topologies.

The three-dimensional framework of $ZnPO_3$-1 is shown in Figure 2. When projected down the *a* axis, it appears that there are eight-ring channels along the *a* axis (Figure 2a). However, $ZnPO_3$-1 does not have any eight-ring windows, and it only has 4- and 16-ring windows (Figure 2b). The actual channels along the *a* axis are helical, as shown in Figure 3.

In the synthetic design of the (3,4)-connected framework, one important factor to consider is the topological possibilities between three- and four-connected centers. While mathematical possibilities are numerous, the number of topologies that can be realized in a chemical system is limited because of the restriction by the availability of basic chemical building units and their bonding requirements.

On the basis of topological patterns, (3,4)-connected frameworks with alternating three- and four-connected centers can be divided into two types. The first type can be called an interrupted four-connected framework, which means that these (3,4)-connected frameworks can be derived from a four-connected framework by selectively removing *one-eighth* of all of the tetrahedral nodes. For example, $Na_2Zn_3(CO_3)_4(H_2O)_3$ can be considered as the diamond-type framework with one-eighth of the tetrahedral sites removed.[10] The second type of (3,4)-connected framework is inherently (3,4)-connected and cannot be reasonably converted into a four-connected framework through the insertion of additional tetrahedral nodes.

One practical method to determine the type of (3,4)-connected framework is to calculate the centroid position of four adjacent three-connected sites. If it is a type I framework, the addition of a tetrahedral node at the centroid

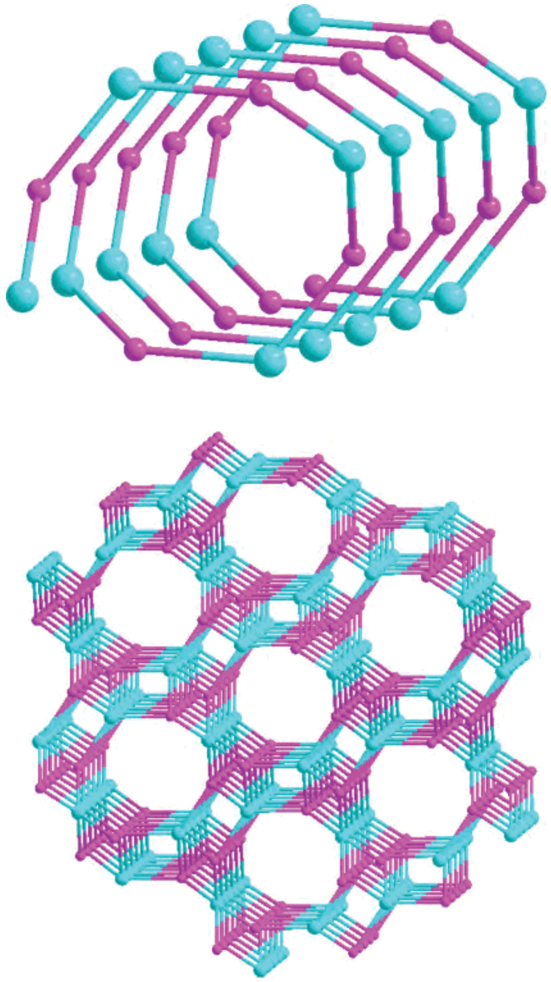

Figure 3. Helical channel along the crystallographic *a* axis. (a) One single channel; (b) hexagonal arrangement of helical channels.

position (or a position near it) would generally convert the (3,4)-connected network into the four-connected network.

One benefit of converting a (3,4)-connected framework into four-connected frameworks is that we can take advantage of the well-established methodology employed for the study and classification of four-connected nets (e.g., zeolites). The topological types of four-connected nets that have been realized in a chemical system have been tabulated.[12]

Three new structures reported here belong to the interrupted type, and it is possible to convert them from a (3,4)-connected topology into a four-connected topology by adding tetrahedral nodes. In these structures, the distribution of four P−H groups adopts the tetrahedral pattern surrounding a vacant tetrahedral node. The centroid of these four phosphorus positions would correspond to the position of missing tetrahedral nodes.

For ZnPO$_3$-1 with the *Fddd* symmetry, the crystallographic site position for the unoccupied tetrahedral node is (1/8, 5/8, 1/8) located at the crystallographic special position (222). This site is 3.431 Å away from its four neighboring phosphoruses. Such a distance between tetrahedral centers is typical in four-connected chemical structures. For ZnPO$_3$-2, the crystallographic site position for the unoccupied tetrahedral node is (1/2, 0.6455, 1/4) located at the crystallographic special position (2-fold axis). This site is 3.042 Å away from its two neighboring phosphorus sites and 3.339 Å away from two other neighboring phosphorus sites. For ZnPO$_3$-3, the crystallographic site position for the unoccupied tetrahedral node is (1, 0.6176, 1/4) also located at the crystallographic special position (2-fold axis). This site is 3.166 Å away from its two neighboring phosphorus sites and 3.235 Å away from two other neighboring phosphorus sites.

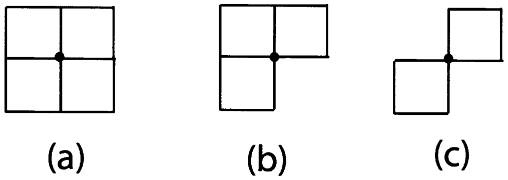

Figure 4. Three types of T-atom loop configurations observed in the hypothetical topological type ZPO, obtained by converting (3,4)-connected ZnPO$_3$-1, ZnPO$_3$-2, and ZnPO$_3$-3 frameworks into a four-connected zeolite-type framework. The loop configuration of a tetrahedral site is a graph showing how many three- and four-rings of which this particular site is a part.[12] In ZnPO-1 with two unique Zn sites and one P site, two Zn sites adopt *a* and *b* configurations shown here and the P site adopts the *b* type. The *c* type is for the vacant tetrahedral site.

Once these crystallographic positions for unoccupied tetrahedral nodes are determined, these (3,4)-connected nets can be converted into four-connected nets and can be characterized and compared using concepts such as coordination sequences, vertex symbols, secondary building units, loop configuration of tetrahedral atoms, channel structures (ring size, channel dimension, etc.), and framework density. All of these concepts have been well-established for four-connected networks.[12]

Three compounds reported here (ZnPO$_3$-1, ZnPO$_3$-2, and ZnPO$_3$-3) are found to have the same topological type, even though they have different framework symmetries resulting from different structure-directing agents. The four-connected topology that they correspond to (denoted as the ZPO type here) has not so far been found in known tetrahedral framework materials. This can be confirmed by examining the loop configurations of tetrahedral atoms in the compounds reported here. The loop configuration of a tetrahedral site is a graph showing how many three- and four-rings of which this particular site is a part.[12] The three different loop configurations found in the ZPO type (for four different tetrahedral sites in ZnPO$_3$-1) are the same as those in the chiral zeolite structural type CZP that occurs in NaZnPO$_4$·H$_2$O.[12] No other four-connected frameworks contain all three of these types of loop configurations (Figure 4). This is because one loop configuration (Figure 4a) is extremely rare in four-connected structures and only occurs in one known type (i.e., CZP). A major difference between CZP and ZPO types is that the largest ring size in CZP is 12 whereas the ZPO type consists of only 4- and 16-rings.

Thus, it is clear that three different structure-directing agents employed in this work led to only one topological type, possibly because of their similar size and charge. On the other hand, the subtle difference in the size and symmetry of these structure-directing agents is reflected in the structures of the resulting inorganic framework. Because of the smaller size and lower symmetry of $HN(CH_3)_3^+$ and $H_2N(CH_3)_2^+$ as compared to $N(CH_3)_4^+$, inorganic frameworks directed by $HN(CH_3)_3^+$ or $H_2N(CH_3)_2^+$ have a higher distortion and a lower symmetry (*C*2/*c*) than that directed by $N(CH_3)_4^+$ (*Fddd*). In addition, the framework density is increasingly lower when structure-directing agents become larger because of additional methyl groups.

Synthetically, possibly because of the proper geometrical fit of $(CH_3)_4N^+$ within the cavity of ZnPO-1, the crystallization of ZnPO-1 is strongly favorable under the hydrothermal conditions employed here. No other crystalline phase is found to cocrystallize with ZnPO-1. However, for ZnPO-2 with the smaller $N(CH_3)_3H^+$, other competing crystallization processes become significant. The fit becomes even worse for $N(CH_3)_2H_2^+$ in ZnPO-3. As a result, ZnPO-3 only occurs as a minor phase. Attempts with methylamine as the structure-directing agent have failed to obtain similar 3D zincophosphites.

Comparison with Open-Framework Hydrogen Phosphates ($H-PO_3^{2-}$ vs $HO-P-O_3^{2-}$). Zincophosphites share some similarities with zinc hydrogen phosphates. Both have one terminated corner, and very importantly, both have the same charge (−2) and geometry (trigonal pyramidal for $H-PO_3^{2-}$ vs $HO-P-O_3^{2-}$). However, from the chemical perspective, zincophosphite and zincophosphate systems are quite different. One difference is that phosphites are redox-active whereas phosphates have negligible redox activity. In the synthesis of zincophosphites, it is not uncommon to observe the formation of phosphates from phosphites. Furthermore, the P−H bond is expected to be highly covalent because of the same electronegativity (2.1) for P and H, whereas the O−H bond within the P−OH group is highly polar and can lead to hydrogen bonds or electrostatic interaction.

It is therefore quite surprising to find that phosphites can form structural analogues of phosphates in open-framework structures where the only difference is the replacement of P−OH by P−H. $[(CH_3)_4N]_2Zn_3(HPO_3)_4$ reported here is isostructural to $[(CH_3)_4N]_2Zn_3(HOPO_3)_4$ reported earlier.[23] In such a case, the replacement of −P−OH by −P−H only leads to a slight decrease in the unit-cell volume by 10.5 Å^3, which is only 0.2% of the total volume. The formation of nearly identical structures despite the large difference in the chemical properties of P−OH and P−H suggests that P−OH or P−H plays an insignificant role in the condensation of phosphate (or phosphite) precursors into extended solids. In addition, it appears that hydrogen bonding involving the terminating P−OH bond is either nonexistent or insignificant compared to other forces that exist during the crystal formation process.

Because a large number of open-framework materials with HPO_4^{2-} are known, the synthesis of the phosphite analogue of the zincophosphate $[(CH_3)_4N]_2Zn_3(HOPO_3)_4$ demonstrated here raises a general question about whether other phosphite analogues of metal hydrogen phosphates may be accessible under similar synthetic conditions.

Table 3. Comparison of the Framework Charge Density for Different Compositional Domains[a]

examples	charge/polyhedral atom
$ZnPO_4^-$ or $AlSiO_4^-$	−0.5
$ZnAlP_2O_4^-$ or $AlSi_3O_8^-$	−0.25
$AlPO_4$	0
$[Zn_3(HPO_3)_4]^{2-}$	−0.29
$[Sn_4(PO_4)_3]^-$	−0.14

[a] Here, the charge density is estimated in terms of charge per polyhedral site.

The combined DSC-TGA experiment on ZnPO-1 shows that there is no thermal event or weight change until 400 °C, suggesting a relatively high thermal stability of ZnPO-1. A sharp weight loss of 17.3% occurs between 400 and 450 °C, followed by a gradual weight loss of 5.6% between 450 and 650 °C. The total weight loss of 22.8% between 400 and 650 °C is close to the calculated percentage of the organic component (22.0%) in ZnPO-1. In comparison, the corresponding hydrogen phosphate begins the weight loss at 425 °C with a total weight loss of 24.0% (calcd 27.5%) up to 837 °C.[23]

Host−Guest Charge-Density Matching and Strategy for Structure Direction. Compared to four-connected frameworks, (3,4)-connected frameworks have been much less studied. How to develop a strategy for structure direction is key to continued successes for the creation of new (3,4)-connected frameworks. Because the strategies for structure directing in aluminosilicates, aluminophosphates, and metal-substituted aluminophosphates have been well-studied, it is worthwhile to compare zincophosphites reported here to those known silicates and phosphates.

One key to the development of novel open-framework materials is the proper host−guest charge-density matching.[5] Many chemical systems are capable of fine-tuning the host charge density (even for a fixed topology) through modifying chemical compositions (e.g., changing the Si/Al ratio in aluminosilicates or changing the Zn/Al ratio in zinc-substituted aluminophosphates). Compared to these four-connected frameworks, the binary (3,4)-connected systems described here, however, are quite inflexible in adjusting the host charge density because of the fixed ratio between three-connected and four-connected centers [e.g., $Zn_3(HPO_3)_4^{2-}$]. Thus, the creation of novel (3,4)-connected frameworks can only be achieved with a much smaller group of structure-directing agents.

Aluminosilicates can be divided into low-charged silicates (Si/Al ≥ 3) and high-charged silicates (Si/Al < 3). In terms of framework charge density, high-charged silicates correspond to zinc-substituted aluminophosphates with Zn/Al ≥ 1 and low-charged silicates correspond to zinc-substituted aluminophosphates with Zn/Al < 1. Table 3 shows a comparison in the framework charge density in terms of charge per tetrahedral atom for different compositional domains. On the basis of this comparison, it appears that zincophosphites are more similar to highly charged aluminophosphates, that is, those metal-substituted aluminophosphates in which over 50% of the Al^{3+} sites are replaced by divalent metal cations such as Zn^{2+}. On the other

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(23) Wiebcke, M. *J. Mater. Chem.* **2002**, *12*, 421−425.

hand, tin phosphates are more similar to low-charged aluminophosphates. Therefore, a structure-directing strategy for high- and low-charged silicate (or phosphate) systems may be applicable respective to the corresponding (3,4)-connected systems such as zincophosphites and tin phosphates.

In conclusion, three open-framework zincophosphites with helical channels have been synthesized and structurally characterized. The structure-directing effect by organic cations on the symmetry and framework density of the resulting inorganic framework has been identified. The compositional and topological features of these new crystals are discussed in terms of the general synthetic design of open-framework architectures from three- and four-connected polyhedral chemical units.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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