

Hydrothermal Synthesis and Structural Characterization of Four Scandium Phosphate Frameworks

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The recent expansion of zeolitic synthesis toward mixed geometry frameworks reflects their potential applications in shape-selective catalysis and absorption. Four scandium phosphates with three-dimensional frameworks have been hydrothermally synthesized. All structures were solved from single-crystal X-ray diffraction and were supported by ³¹P MAS NMR and infrared spectroscopy. Structure **1** ((C₂N₂H₁₀)₈Sc₈(ScO₂)₄(PO₄)₄(HPO₄)₁₂·12H₂O) consists of a novel framework with 14-membered rings (MRs) and 10-MR channels along the *a* and *c* axes, respectively. Ethylenediamine and water reside in the resulting supercage. Structure **2** ((C₂N₂H₁₀)₂Sc₄(HPO₄)₈) consists of a framework built from the corner-sharing of ScO₆ octahedra with HPO₄ tetrahedra whose connection results in a 8-MR channel down the *a* axis, where hydrolyzed cyclam resides. This compound is isostructural to a number of existing synthetic materials including a scandium phosphate, an indium phosphate, and an iron phosphate. Structure **3** (Sc₄(HPO₄)₈·4(H₃O)) is a framework built in the same way as structure **2** but is described by a 12-MR channel down the *a* axis in which hydronium resides. This structure is isostructural to a ferric oxonium bis(hydrogenphosphate). Structure **4** (Sc₄(PO₄)₄·8H₂O) is a framework built by the corner-sharing of PO₄ tetrahedra with ScO₄·2H₂O octahedra to form 8-MR channels down the *a*-axis. This structure occurs in nature as sterrettite, a scandium-bearing phosphate mineral, and has an isostructural indium phosphate. Crystal data: structure **1**, *P*2₁/*n*, *a* = 8.603(2) Å, *b* = 15.476(3) Å, 16.504(4) Å, and β = 96.877(5)°, structure refinement converged at *R* = 0.0443; structure **2**, *P*2₁/*n*, *a* = 9.4111(15) Å, *b* = 9.1066(15) Å, *c* = 9.6950(15) Å, and β = 117.272(3)°, structure refinement converged at *R* = 0.032; structure **3**, *P*2₁/*n*, *a* = 5.3048(11) Å, *b* = 8.8230(18) Å, *c* = 14.779(3) Å, and β = 96.685(5)°, structure refinement converged at *R* = 0.0433; structure **4**, *P*2₁(1)/*n*, *a* = 5.4429(8) Å, *b* = 10.2513(15) Å, *c* = 8.9094(11) Å, and β = 90.253(7)°, structure refinement converged at *R* = 0.063.

Introduction

The classical definition of a zeolite is a crystalline, porous aluminosilicate with tetrahedral connectivity. However, this definition has been expanded by the possibility of producing a great variety of microporous materials with elements other than silicon and aluminum. Over the last 20 years we have seen the development of novel frameworks stem from the early aluminophosphates¹ to gallophosphates^{2–4} and many other

tetrahedrally coordinated metal phosphates we see today.^{5–7} The realization that most of the elements in the Periodic Table can be incorporated in solids of this type has stimulated the preparation of many new materials containing both tetrahedral and octahedral coordinated cations.^{8,9} A major goal of the study of these structurally and chemically diverse open frameworks is to arrive at novel topologies allowing for a greater variety of applications in areas such as shape-selective catalysis.

In the early 1990s Haushalter et al. reported the synthesis and structure of some molybdenum phos-

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phates with octahedral–tetrahedral microporous frameworks toward application in shape-selective catalysis.¹⁰ Around this time the first titanium silicate was disclosed in patent literature. Since then, other examples include a variety of titanium, yttrium, and rare earth silicates.^{11–15} These materials have found applications in areas such as catalysis and ion exchange.^{16,17} An example is the application of the ETS-10 titanosilicate in shape-selective photocatalytic degradation of large aromatic molecules.^{18,19} In addition to the silicates, a range of metal phosphates have been prepared in which the metals are octahedrally coordinated. Ferey et al. have synthesized a number of iron phosphates^{20–24} and oxyfluorinated iron phosphates.^{25–34} Several more iron phosphates have been produced.^{35–39} Other mixed geometry frameworks include indium,^{40–49} titanium,⁵⁰ and nickel phosphates,⁵¹ illustrating the potential for incor-

porating a range of metal cations into microporous frameworks through hydrothermal synthesis.

Recently, two groups reported the synthesis of scandium-containing open frameworks.^{52,53} Prior to this, no organically templated scandium-containing frameworks had been reported, probably due to scandium's high commercial cost. In this paper, we report the hydrothermal synthesis of four scandium phosphate frameworks using a variety of templates, solvents, and gel compositions. These phases are compared and contrasted to themselves and their isostructural phosphates where appropriate, focusing on structural aspects of the framework. By borrowing the concept of secondary building units (SBUs) from aluminosilicate zeolite chemistry we hope that we can elucidate some information toward understanding synthetic and structural influences on the formation of octahedral–tetrahedral frameworks. We also reveal the presence of the relatively rare 3-ring, which is the smallest SBU, and is said to be the key to unlocking the synthesis of even more open frameworks.

Experimental Section

Hydrothermal reactions were carried out in Parr acid digestion bombs with 23 mL of poly(tetrafluoroethylene) liners. All gels were prepared, mixed, and aged for 1 h in the Teflon liners, which were generally half-filled. All chemicals common to several reactions are from the same supplier. All reactions were quenched and the final products were filtered, washed with deionized water, and then dried in air. All products were fine crystalline white powders with the exception of structure 2, which was a coarse brown powder.

Synthesis of Compounds. Structure 1 ((C₂N₂H₁₀)₈Sc₈(ScO₂)₄(PO₄)₄(HPO₄)₁₂·12H₂O) was prepared from 0.487 g of Sc₂O₃ (99.9%, Aldrich), 1.467 g of H₃PO₄ (85 wt %, Aldrich), 5.99 g of H₂O, 0.425 g of ethylenediamine (98%, Aldrich), and 0.2886 g of hydrofluoric acid (49 wt % HF, Fisher) to give a gel composition of 1:1.8:100:2:2 Sc₂O₃:P₂O₅:H₂O:ethylenediamine:HF. The resulting solution had a pH of 2.2. The autoclave was heated at 190 °C for 72 h. Structure 2 ((C₂N₂H₁₀)₂·Sc₄(HPO₄)₈) was prepared from 0.378 g of ScCl₃·H₂O (99.99%, Aldrich), 0.845 g of H₃PO₄, 1.00 g of H₂O, 0.25 g of Cyclam (98%, Aldrich), and 0.05 g of HF to give a gel composition of 1:3:52:1:1 Sc₂O₃:P₂O₅:H₂O:cyclam:HF. The resulting solution had a pH of 2. The autoclave was heated at 220 °C for 72 h. Structure 3 (Sc₄(HPO₄)₈·4(H₂O)) was prepared from 0.5 g of ScCl₃·H₂O, 0.751 g of H₃PO₄, 6.0 g of H₂O, 0.124 g of 1,3-diaminopropane (99+%, Aldrich), and 0.051 g of HF to give

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Table 1. Data Collection and Refinement Parameters for Structures 1–4

| compound | structure 1 | structure 2 | structure 3 | structure 4 |
|------------------------------|--|--|---|--|
| chemical formula | (C ₂ N ₂ H ₁₀) ₈ Sc ₈ (ScO ₂) ₄ (PO ₄) ₄ (HPO ₄) ₁₂ ·12H ₂ O | (C ₂ N ₂ H ₁₀) ₂ Sc ₄ (HPO ₄) ₈ | Sc ₄ (HPO ₄) ₈ ·4(H ₂ O) | Sc ₄ (PO ₄) ₄ ·8H ₂ O |
| formula weight | 323.59 | 267.98 | 255.94 | 175.96 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ (1)/ <i>c</i> | <i>P</i> 2 ₁ (1)/ <i>n</i> |
| <i>Z</i> | 4 | 4 | 4 | 4 |
| <i>a</i> (Å) | 8.603(2) | 9.4111(15) | 5.3048(11) | 5.4429(8) |
| <i>b</i> (Å) | 15.476(3) | 9.1066(15) | 8.8230(18) | 10.2513(15) |
| <i>c</i> (Å) | 16.504(4) | 9.6950(15) | 14.779(3) | 8.9094(11) |
| β (deg) | 96.877(5) | 117.272(3) | 95.685(5) | 90.253(7) |
| <i>V</i> (Å ³) | 2181.5(8) | 738.5(2) | 688.3(2) | 497.11(12) |
| temperature | 293 | 173(2) | 173(2) | 293 |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.6845 |
| total no. of reflections | 4985 | 2161 | 2066 | 626 |
| no. of unique reflections | 4053 | 1902 | 1643 | 589 |
| R1 (<i>I</i> > 2 σ) | 0.0443 | 0.0320 | 0.0433 | 0.063 |
| R1 (all data) | 0.0548 | 0.0377 | 0.0584 | 0.0655 |

a gel composition of 1:2:210:1:1 Sc₂O₃:P₂O₅:H₂O:1,3-diaminopropane:HF. The resulting solution had a pH of 1. The autoclave was heated at 190 °C for 48 h. Structure 4 (Sc₄(PO₄)₄·(H₂O)₈) was prepared from 0.345 g of Sc₂O₃, 1.729 g of H₃PO₄, 3.164 g of pyridine (99.9+%, Aldrich), 0.72 g of H₂O, and 0.10 g of HF to give a gel composition of 1:3:8:8:8 Sc₂O₃:P₂O₅:pyridine:H₂O:HF. The resulting solution had a pH of approximately 6. The autoclave was heated at 180 °C for 72 h.

X-ray Crystallographic Studies. The experimental X-ray data for all structures are summarized in Table 1. All data were integrated using SAINT,⁵⁴ and empirical absorption corrections were performed in the program SADABS or TWIN-ABS.⁵⁵ Structures were solved in SHELXS using direct methods,⁵⁶ and successive refinements were performed in SHELXL-97 by difference Fourier synthesis.⁵⁷ All least-squares refinements were carried out against F^2 .

Structure 1. Data collection was carried out on a 4-circle Bruker 1K Smart-CCD diffractometer. X-rays were generated at 50 kV and 30 mA using a normal-focus X-ray tube with Mo as the target metal (Mo K α , λ = 0.71073 Å). Data were collected at room temperature with a φ and ω scans using 0.3° rotations/frame. A total of 1650 frames were collected for each crystal spanning one hemisphere of reciprocal space out to 0.75 Å.

Structures 2 and 3. Data collection and structure solution were conducted at the X-ray Crystallographic Laboratory, 160 Kolthoff Hall, Department of Chemistry, University of Minnesota. Suitable crystals of both structures were carefully collected and placed on the tip of a 0.1-mm-diameter glass capillary and mounted on a Bruker SMART system for data collection at 173(2) K. The data collections were carried out using Mo K α radiation. Many crystals of structure 3 were examined with a polarizing microscope, which suggested all to be twinned in some fashion. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames using GEMINI;⁵⁸ 82 reflections were used to index a two-component nonmerohedral twin. The twin law is by rows [1.0 0 0 / 0 -1 0 / -0.55495 0 -1], which corresponds to a 180° rotation about the (1 0 0) axis (in direct space). The intensity data were corrected for absorption and decay (TWIN-ABS).⁵⁵ Final cell constants were calculated from 2533 strong reflections from the actual data collection after integration (SAINT 6.35A, 2002).⁵⁴ The data were integrated as a two-component nonmerohedral twin.

Structure 4. Single-crystal X-ray diffraction was carried out at the CCLRC Synchrotron Radiation Source, Daresbury Laboratories, UK, using an X-ray diffractometer equipped with a Bruker Proteum 200 CCD detector. The metric symmetry of the crystal system appeared to be orthorhombic; however, no orthorhombic space group was found. Closer inspection showed the real symmetry to be monoclinic with a space group of *P*2₁(1)/*n*. The twin law was modeled by applying a 2-fold rotation about the *a*-axis in the monoclinic cell.

Solid-State NMR Spectroscopy. Room-temperature ³¹P MAS NMR experiments were performed with a double tuned Chemagnetics 5.0-mm probe on a Chemagnetics CMX-360 spectrometer in a magnetic field strength of 8.45 T at a Larmor frequency of 145.7 MHz. Powdered samples were packed inside zirconia MAS rotors and spun between 2.5 and 8 kHz. Continuous ¹H decoupling was applied during the acquisition of ³¹P MAS spectra. The Hartmann–Hahn condition for ¹H–³¹P CP/MAS NMR experiments was determined on a sample of (NH₄)₂HPO₄. Recycle delays and contact time in CP/MAS NMR were optimized experimentally. The reported chemical shifts were referenced to the external standard, 85% H₃PO₄ solution, which was set at 0 ppm. The ³¹P chemical shift anisotropy (CSA) simulation was done with the WSolid NMR simulation package developed by Dr. K. Eichele. The CSA convention used in this study was introduced by Haeblerlen.⁵⁹

Results and Discussion

Crystallography. *Crystal Structure of Structure 1.* Structure 1 presents a novel three-dimensional mixed framework (3Sc:4P) containing corner-sharing of ScO₆ octahedra to both HPO₄ tetrahedra and other ScO₆ octahedra. Each ScO₆ octahedra shares four coplanar corners with HPO₄ tetrahedral and two apical corners with another identical octahedra. There are also ScO₆ units which share four corners with three HPO₄ and one PO₄ tetrahedra, one corner with another ScO₆ octahedra and it is also bonded to water in the channel. The interatomic distances are very similar to those reported for similar scandium phosphate structures. The Sc–O distances involved in bonding between both tetrahedra and octahedra are in the range of 2.03–2.10 Å, whereas the Sc–H₂O bonds are considerably shorter (1.95–2.0 Å). Again, the P–O bond distances involved in framework bonding to octahedra are around 1.51–1.53 Å. However, three of the four crystallographically distinct P atoms have one longer distance in the range

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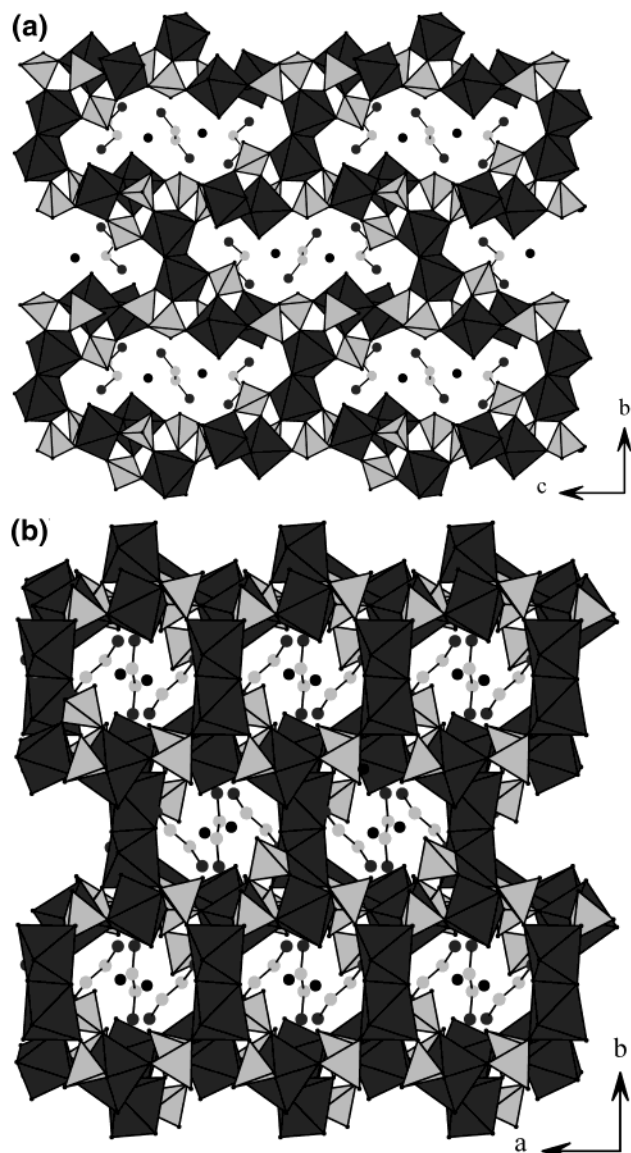


Figure 1. Framework of structure 1: scandium octahedra are dark gray; phosphorus tetrahedra are light gray; water, carbon, and nitrogen are represented by black, light gray, and dark gray circles, respectively. (a) Projection along [100] illustrating the 14-MR channels. (b) Projection along [001] illustrating the 10-MR channels.

of 1.56–1.58 Å, which is indicative of protonation of the dangling oxygen. The crystallography requires these three dangling oxygens to be protonated to give a unit cell composition of $(\text{C}_2\text{N}_2\text{H}_{10})_8\text{Sc}_{12}(\text{PO}_4)_4(\text{HPO}_4)_{12}\cdot 12\text{H}_2\text{O}$.

The framework can be thought of as being constructed of secondary building units, formula $\text{Sc}_3\text{P}_4\text{O}_{18}$, that can be described as an open $3^24^{35}1$ cage. These are connected nose to tail along the [001] direction to form chains. The corners of the 4-rings are connected via Sc–O–P bonds to four surrounding SBUs in parallel chains to form sheets of 6 rings. The Sc at the tail of the SBU then connects adjoining sheets along [010] with each neighboring SBU alternating between linking the layer above and below to form 14-MR channels down [100] as shown in Figure 1a. The connection of these SBUs also results in 10-MR channels down the [001] direction (see Figure 1b), which in turn produces a large cage which contains 2 water molecules and 8 diprotonated ethylenediamine molecules—3 in each 14-MR window and 1 in each 10-

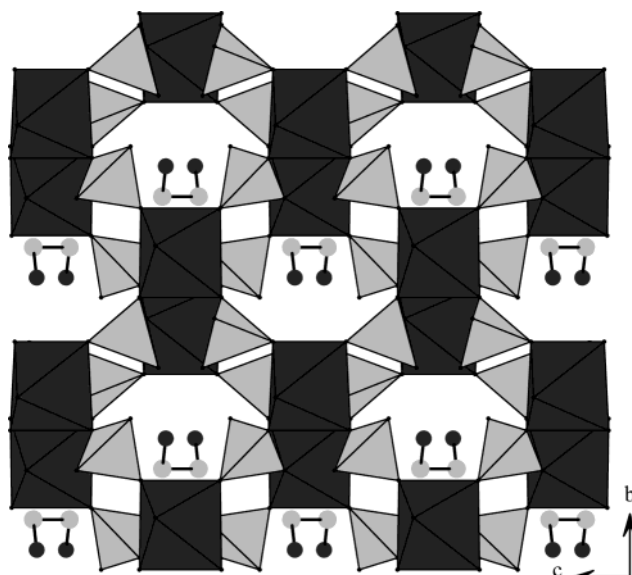


Figure 2. Projection along [100] illustrating the 10-MR channels containing hydrolyzed cyclam. Framework of structure 2: scandium octahedra are dark gray; phosphorus tetrahedra are light gray; water, carbon and nitrogen are represented by black, light gray, and dark gray circles, respectively.

MR window. The organic is strongly hydrogen-bonded to the framework.

Crystal Structure of Structure 2. The scandium-to-phosphorus ratio of this material is 1:2, with strict alternation between scandium octahedra and phosphorus tetrahedra similar to that seen in the aluminophosphates frameworks. Structure 2, $(\text{C}_2\text{N}_2\text{H}_{10})_2\text{Sc}_4(\text{HPO}_4)_8$, is isostructural to the scandium phosphate prepared by Riou et al.,⁵³ an indium phosphate⁴¹ and an iron phosphate material.³⁵ The interatomic distances of this structure agree with values previously seen in the Riou's scandium phosphate structure and are slightly shorter than that seen in the indium material (2.009–2.166 Å). Two crystallographically distinct scandiums are octahedrally coordinated to oxygen, exhibiting typical interatomic distances of 2.05–2.14 Å, whereas phosphorus is tetrahedrally coordinated to three framework oxygens (1.51–1.53 Å) and one dangling oxygen, which is protonated (longer distance of 1.57–1.59 Å). Each protonated phosphate group is involved in considerable hydrogen bonding with the other hydrogen phosphate oxygens.

Structure 2 is a one-dimensional framework with 8-MR channels down [100] as shown in Figure 2. The framework can be described by 4-ring helical chains, which propagate along [100] and join diagonally to neighboring chains to form intersecting diagonal rows. These 4-ring chains are formed by the head-to-tail connection of SBUs with formula $\text{Sc}_2(\text{HPO}_4)_4$. Four rows intersect to form the 8-MR channels. There is only a fragment of the expected cyclam molecule in the channel, probably due to its hydrolysis in the very acidic synthesis conditions. This hydrolysis results in an organic fragment analogous to the ethylenediamine template (bond distances and angles describing this organic fragment are very similar to those seen for the ethylenediamine) utilized by Riou et al., which explains its isostructural framework, but may highlight a lack

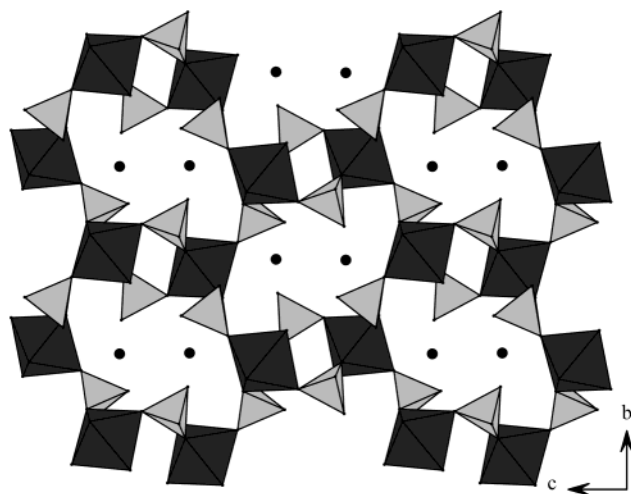


Figure 3. Projection along [100] illustrating the 12-MR channels containing water. Framework of structure 3: scandium octahedra are dark gray; phosphorus tetrahedra are light gray; water is represented by black circles.

of synthetic control allowed by the acidic conditions in this reaction.

Crystal Structure of Structure 3. Structure 3 presents a three-dimensional mixed framework (1Sc:2P) containing corner-sharing of ScO_6 octahedra to HPO_4 tetrahedra. Again, there is a strict alternation between the Sc and P polyhedra. The interatomic distances of this structure are very similar to those seen in structure 2. This structure has an isostructural iron phosphate framework.³⁹ Like iron, scandium is octahedrally coordinated to oxygen with typical interatomic distances of 2.04–2.13 Å. These distances are slightly longer than the distances seen in the iron material (1.990–2.073 Å). Again, phosphorus is tetrahedrally coordinated to three framework oxygens (1.49–1.53 Å) and one dangling oxygen, which is protonated (longer distance of 1.59–1.60 Å). As in the iron phosphate, this structure is charge-balanced by the presence of hydronium in the channels to give a unit cell composition of $\text{Sc}_4(\text{HPO}_4)_8 \cdot 4\text{H}_3\text{O}$. The presence of the hydronium cation is supported by the infrared spectrum, which exhibits a strong band at 3438 cm^{-1} .

Structure 3 is a three-dimensional framework with one-dimensional 12-MR channels down [100] as shown in Figure 3. The framework can be described as sheets of 4-MRs, which stack to form steps when viewed down [010]. Four of these sheets intersect to form four 4-MRs down [100], which are connected via Sc–P–Sc linkages to build the 12-MR channels. These sheets are formed by the side-to-side connection of SBUs with formula $\text{Sc}_2(\text{HPO}_4)_4$. Hydronium cations reside in the channel and are bonded to the framework via a hydrogen bond network with the dangling hydroxyl groups.

Crystal Structure of Structure 4. The scandium-to-phosphorus ratio in this material is 1:1, and there is a strict alternation between scandium octahedra and phosphorus tetrahedra in the framework. Structure 4 is isostructural with the scandium phosphate-bearing mineral, sterrettite,⁶⁰ and an indium phosphate prepared by Sugiyama et al.⁴⁹ Scandium is octahedrally

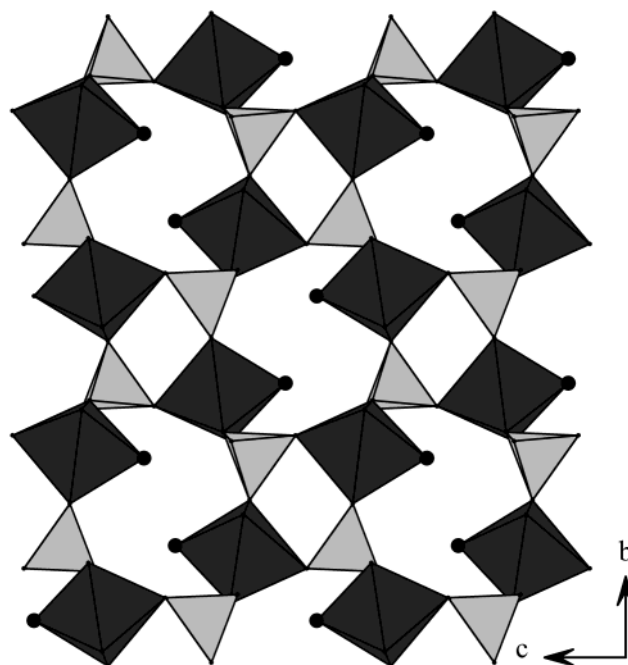


Figure 4. Projection along [100] illustrating the 8-MR channels containing water. Framework of structure 4: scandium octahedra are dark gray; phosphorus tetrahedra are light gray; water is represented by black circles.

coordinated to four framework oxygens with typical interatomic distances of 2.02–2.09 Å and two water molecules. As expected, the indium phosphate material contains slightly longer bond distances (2.097–2.17 Å). Both the indium and scandium materials have large thermal parameters associated with the water molecules, which may be indicative of disorder of the water within the channels. Phosphorus is tetrahedrally coordinated to framework oxygen (1.51–1.54 Å).

Structure 4 is a three-dimensional framework with 8-MR channels down [100] (see Figure 4) and 6-MR channels down both [010] and [001]. The framework can be described as diagonal rows of corner-sharing 4-MRs. These rows intercept parallel to the [100] direction to produce sheets with an 8-MR channel. These sheets form a three-dimensional framework through the bridging of the corners of 4-MRs by another polyhedra to form 6-rings in both the [010] and [001] directions. This results in a 4^26^4 cage and the structure can also be described by the stacking of this cage down [100].

Solid-State NMR Spectroscopy. *Structure 1.* The solid-state ^{31}P MAS NMR spectrum of structure 1 (Figure 5) shows four overlapping resonances at –6.7, –9.0, –12.8, and –16.4 ppm. ^{31}P chemical shielding anisotropies, CSAs (Table 2), were determined by simulation of the spectrum acquired at a spinning frequency of 2.5 kHz. The relative intensities of these four peaks are approximately 1:1:1:1. Because the CSA is much smaller for the PO_4^{3-} group than for the HPO_4^{2-} group [1], the resonance at –9.0 ppm can be assigned to PO_4^{3-} group (P(2) site) and the other three resonances to HPO_4^{2-} groups. The NMR line shapes of these two groups are consistent with the characteristic line shapes for HPO_4^{2-} and PO_4^{3-} reported in the literature.⁶¹ On

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(61) Rothwell, W. P.; Waugh, J. S.; Yesinowski, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2637–2643.

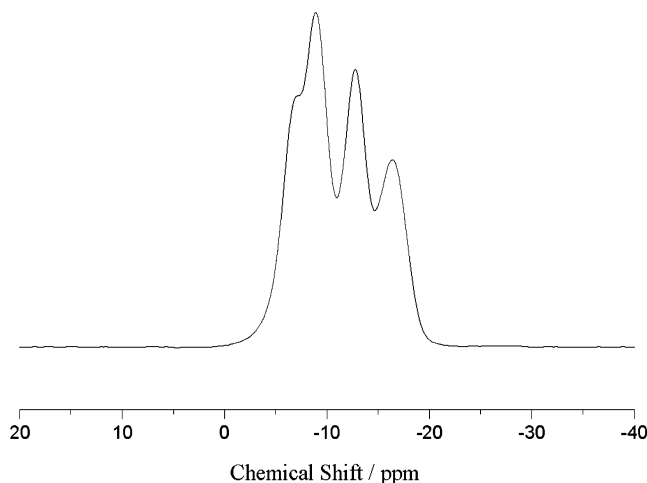


Figure 5. ^{31}P MAS NMR spectrum of structure **1** acquired at a spinning frequency of 8 kHz. Recycle delay: 15 s.

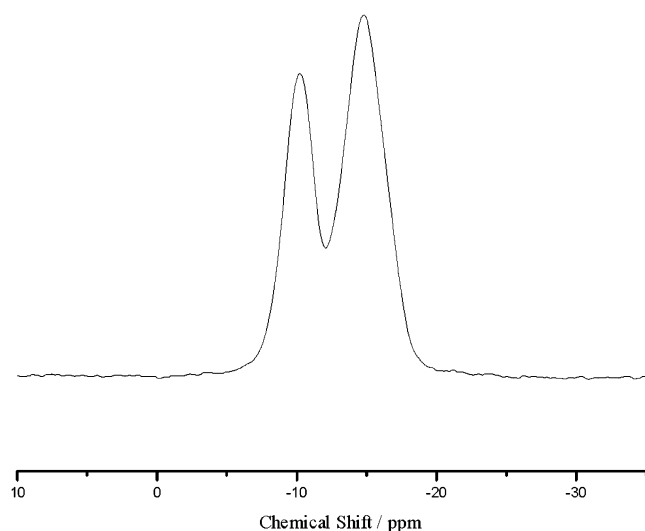


Figure 6. ^{31}P MAS NMR spectrum of structure **2** acquired at a spinning frequency of 8 kHz. Recycle delay: 2000 s.

Table 2. ^{31}P Chemical Shift Parameter of Structure **1**

| ^{31}P | δ_{iso} (ppm) | $\Delta\sigma$ (ppm) | η | ^{31}P | δ_{iso} (ppm) | $\Delta\sigma$ (ppm) | η |
|-----------------|-----------------------------|----------------------|--------|-----------------|-----------------------------|----------------------|--------|
| P(1) | -16.4 | 66 | 0.65 | P(3) | -12.8 | 71 | 0.50 |
| P(2) | -9.0 | 32 | 0.80 | P(4) | -6.7 | 68 | 0.55 |

the basis of the distribution of P–O bond distances, O–P–O bond angles determined by X-ray diffraction, and the CSA data, the resonances from HPO_4^{2-} at -6.7, -12.8, and -16.4 ppm can be tentatively assigned to P(4), P(3), and P(1) sites in structure **1**, respectively (see Supporting Information). The $\Delta\sigma$ values of these HPO_4^{2-} groups are larger than the values of a similar scandium phosphate compound reported recently⁵³ (41 and 51 ppm), but they are noticeably smaller than those of HPO_4^{2-} in the classic HPO_4 compound dicalcium phosphate dihydrate (103 ppm).⁶¹

Structure 2. ^{31}P MAS NMR (Figure 6) shows two resonances at -10.2 and -14.8 ppm. These two resonances arise from two different HPO_4^{2-} groups and agree with the values reported by Riou et al.⁵³ The relative intensities are close 1:1, which coincide with the ratio of the two types of HPO_4^{2-} groups determined by XRD. The resonance at -10.2 ppm is slightly lower in intensity than expected, which is ascribed to either the long relaxation time of this site or the presence of

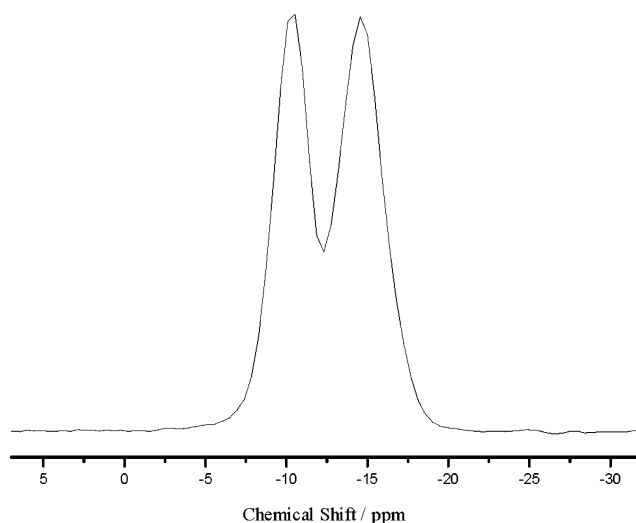


Figure 7. ^1H - ^{31}P CP/MAS NMR spectrum of structure **2** acquired at a spinning frequency of 8 kHz. Recycle delay: 8 s. Contact time: 0.1 ms.

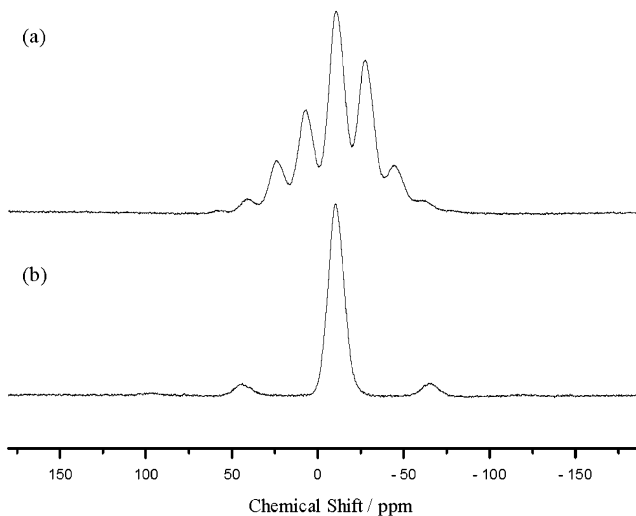


Figure 8. ^{31}P MAS NMR spectrum of structure **4** acquired at a spinning frequency of 2.5 kHz (a) and 8 kHz (b). Recycle delay: 60 s.

impurities associated with the resonances hidden underneath the -14.8 ppm resonance. The relative intensity of the resonance at -10.2 ppm increases in the ^1H - ^{31}P CP/MAS NMR spectrum (Figure 7), which indicates that the phosphorus atom at this site is more strongly coupled to the protons. See Supporting Information for the ^{31}P CSA analysis of this compound.

Structure 3. The ^{31}P spectrum contains a sharp resonance with shoulders on either side due to at least two broader resonances. Powder diffraction and SEM studies of this sample clearly illustrate a large concentration of amorphous impurities so no further analysis of this material was performed.

Structure 4. ^{31}P MAS NMR of structure **4** (Figure 8) shows only one broad resonance at -10.3 ppm, which corresponds to the only P site in structure **4**. The NMR line shape obtained at low spinning speed (2.5 kHz) resembles that seen for the other HPO_4^{2-} groups in this study, which is not consistent with the X-ray crystallography data. On the basis of the XRD, there is an indication that this material contains H_2O molecules coordinated to the scandium atoms, which may be

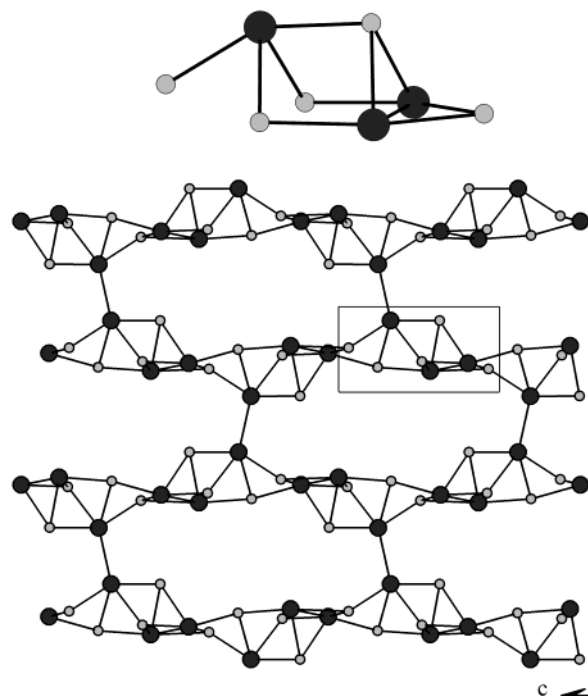


Figure 9. Repeat unit of structure **1** (top) illustrating the 3-ring formed as a consequence of direct Sc–O–Sc links. The repeat unit in the context of the complete framework is emphasized in the rectangle (bottom). In this representation oxygen atoms are omitted for clarity and are at the approximate midpoint of the straight line segments in both the illustration of the subunit and the complete structure. Scandium and phosphorus are represented by dark gray and light gray circles, respectively.

disordered within the channels. The ^{31}P NMR supports this and suggests that these H_2O molecules may be strongly hydrogen-bonded to the PO_4 groups. This may result in local distortions of the PO_4^{3-} groups, which may not be detected in the XRD structure, where the average PO_4 environments are determined. This distribution of local environments is consistent with the broad resonance seen for this material. More detailed experiments to examine the temperature dependence of the ^{31}P CSA and the $^1\text{H} \rightarrow ^{31}\text{P}$ CP dynamics are underway to explore this hypothesis in greater detail.

Discussion

Four scandium phosphates have been hydrothermally synthesized and structurally characterized. The single-crystal structures of these materials reveal characteristic building blocks. All of the structures contain octahedral scandium and tetrahedral phosphorus; however, only structure **1** contains direct bonding between scandium octahedra, while the remaining structures all have a strict alternation between Sc octahedra and P tetrahedra similar to that seen in the aluminophosphates. Reasons for direct bonding between scandium octahedra in structure **1** remain unclear. Initially, it seemed the direct bonding of scandium octahedra could be attributed to the higher scandium content in the framework (3:4 Sc:P). However, structure **4** has a higher scandium content (1:1 Sc:P) and no direct bonding of scandium octahedra. Instead, perhaps less obvious synthetic influences (e.g., pH, water content) may dictate the direct bonding between scandium octahedra.

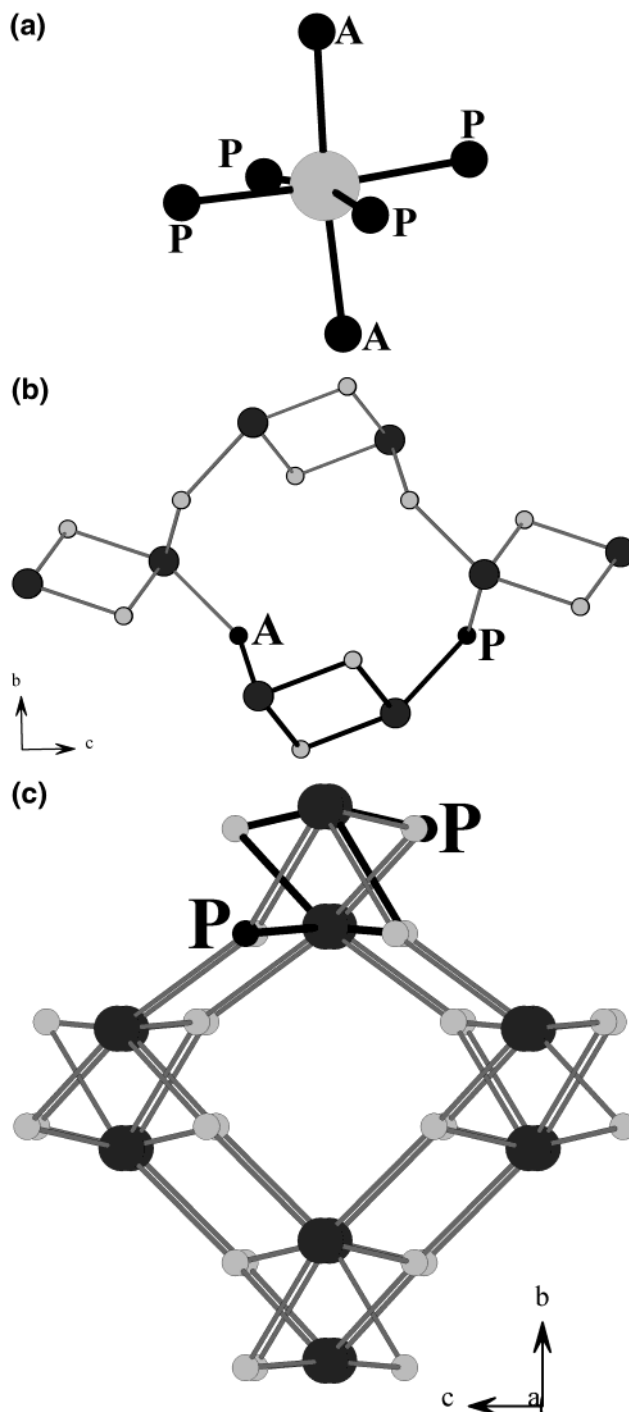


Figure 10. (a) Illustration of a scandium octahedrally coordinated by oxygen defining the planar oxygens (labeled P) and the trans apical oxygens (labeled A) SBUs of structures **2** (b) and **3** (c) are outlined with thick black lines. SBUs in structure **2** are linked parallel to [100] through phosphate groups which share planar oxygens (labeled P) with scandium octahedra to form an 8-MR, whereas in structure **3** the SBUs are linked down [100] through phosphate groups which share planar and apical oxygens of the scandium octahedra (labeled P and A, respectively) to produce a 12-MR. Within the highlighted SBU, the P-linking SBUs together are small black circles. Outside the highlighted SBU Sc and P are represented by dark grey and light grey circles, respectively. Oxygens are omitted for clarity.

All of the structures contain 4-MRs as part of their framework, suggesting these building units may have a large part to play in their synthesis and structures.

Only structure **1** contains a smaller building unit, the 3-ring unit that can be attributed to the direct corner-sharing of Sc octahedra (as illustrated in Figure 9). In addition, the presence of 6-MR and 5-MR units demonstrate a similarity to the building blocks of zeolitic structures in general.

The greatest similarity within the four frameworks is that structures **2** and **3** contain the structural building unit, $\text{Sc}_2(\text{HPO}_4)_4$, which can be linked in a variety of ways to form 8- or 12-MRs as shown in Figure 10. By borrowing Riou et al.'s description of the scandium octahedron in terms of 4 coplanar oxygens and 2 trans apical oxygens (see Figure 10a), one can obtain an understanding of building units. In structure **3**, the SBU is connected to another SBU (head to tail) via phosphate groups which share planar and apical oxygens of the scandium octahedra, whereas in structure **2** the SBUs are linked (head to head) via phosphate groups which share only planar oxygens of the scandium octahedra. The planar and apical links result in a chainlike structure which when linked into a three-dimensional framework produce a more open solid with 12-MRs as seen in structure **3**. In contrast, the planar links result in a fuller three-dimensional chain which when connected to form a three-dimensional framework result in a less open solid with the formation of an 8-MR.

Structure **2** (1:2 Sc:P) has a higher P content than structure **4** (1:1 Sc:P). However, in both structures we have an 8-MR. In structure **4** this is facilitated by a fully framework-connected phosphorus (i.e., it has no dangling bonds), allowing phosphorus to participate further in bridging, resulting in 6-MR units (see Figure 11). These 6MR units open up a larger degree of porosity than that expected for structure **4**'s smaller formula unit. In these two structures we see two ways of accomplishing a one-dimensional 8-MR structure.

This paper provides further evidence that scandium is a suitable element for the synthesis of open-framework phosphates. All the reactions to date have been carried out at an acid pH, resulting in incomplete frameworks perhaps due to the synthetic conditions favoring protonation of a framework oxygen as a means to charge balance rather than template incorporation, exclusively. The hydrolysis of the cyclic template, cyclam, during the synthesis of structure **2** highlights the lack of control associated with these acidic reactions. It is hoped that complete frameworks can be formed from

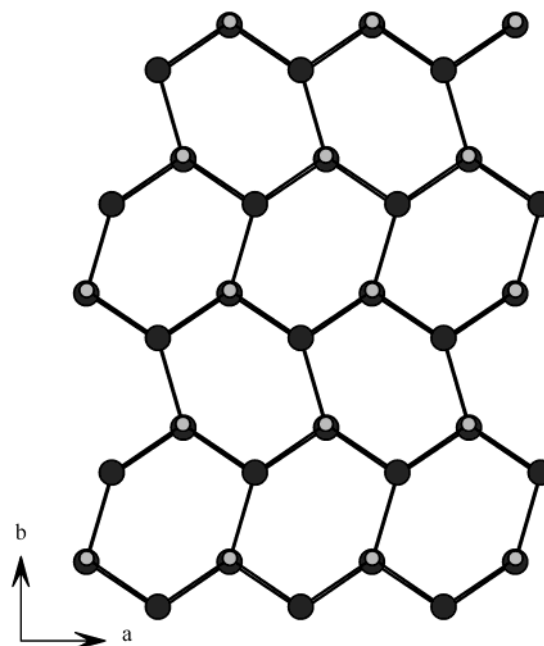


Figure 11. 6MRs formed as a consequence of a fully tetrahedrally framework-connected P, allowing the formation of an 8-MR in structure **4**, even though it has a lower P framework content than structure **2**. Scandium and phosphorus are represented by dark grey and light grey circles, respectively. Oxygen has been omitted for clarity.

this system via exploring synthesis at highly alkaline pH. These complete frameworks should allow applications in areas common for zeolitic materials.

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Supporting Information Available: IR spectroscopy and NMR details (PDF) and crystallographic information files (CIF) for all structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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