

Tetrahedral-Atom 3-Ring Groupings in 1-Dimensional Inorganic Chains: $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$

William T. A. Harrison,*† Tina M. Nenoff,‡ Thurman E. Gier,‡ and Galen D. Stucky*‡

Departments of Chemistry, University of California, Santa Barbara, California 93106-9510, and University of Houston, Houston, Texas 77204-5641

Received November 11, 1992

The hydrothermal syntheses and X-ray single-crystal structures of $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$, two phases which contain 3-ring groupings of tetrahedra as part of 1-dimensional chains of MXO_4 ($\text{M} = \text{Zn, Be; X} = \text{P, As}$) groups, are reported. MAS NMR and TGA data are reported for these phases, and the structures of these two materials are briefly compared with those of some other known extended tetrahedral species. Crystal data for $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ (BAO): $M_r = 246.01$; monoclinic, space group $P2_1/a$, with $a = 7.2349(8)$ Å, $b = 12.686(2)$ Å, $c = 8.6546(9)$ Å, and $\beta = 98.439(3)^\circ$; $Z = 4$. Final residuals of $R = 4.49\%$ and $R_w = 4.79\%$ were obtained for 2333 observed reflections [$I > 3\sigma(I)$]. BAO contains 1-dimensional stacks of interconnected BeO_4 and AsO_4 tetrahedra, including alternating 4-rings and 3-rings, the latter ring system containing $\text{Be}-(\text{OH})-\text{Be}$ bonds. The tetrahedral columns are held together by water molecules, via a network of H-bonds. Crystal data for $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ (NZPO): $M_r = 349.43$; monoclinic, space group $P2_1/a$, with $a = 6.4212(6)$ Å, $b = 21.612(2)$ Å, $c = 8.6813(6)$ Å, and $\beta = 109.899(3)^\circ$; $Z = 4$. $R = 5.85\%$ and $R_w = 5.61\%$ for 2654 observed reflections [$I > 3\sigma(I)$]. NZPO also contains 1-dimensional tetrahedral stacks (ZnO_4 and PO_4 moieties) made up only of 3-rings which include $\text{Zn}-(\text{OH})-\text{Zn}$ connections. Adjacent stacks are interconnected via a complex arrangement of sodium cations and water molecules.

Introduction

The "zeolitic" MXO_4 -based framework ($\text{M} = \text{Zn, Be; X} = \text{P, As}$) structure field has recently been shown to be a very extensive one by ourselves and others.¹⁻⁷ A seemingly general feature of these new zeolitic (Zn/Be,P/As,O)-framework phases is a preference for a 1:1 M to X ratio and strict alternation of MO_4 and XO_4 tetrahedra, akin to a "Lowenstein's rule":⁸ Al—O—Al avoidance and consequent Si/Al tetrahedral alternation for 1:1 Si:Al aluminosilicate phases. This feature would appear to militate against Zn/Be,P/As,O molecular sieves with odd- as opposed to even-membered ring systems and also against phases whose M:X ratio is non-unity.

Conversely, many aluminosilicate zeolites contain odd-membered ring systems, including the recently characterized ZSM-18⁹ [3-rings (3 T atoms and 3 oxygen atoms) and 7-rings], ferrierite¹⁰ and mordenite¹¹ (5-rings), and bikitaite¹² (5+1-rings), for example. The microporous beryllosilicate phase lovdatite also contains 3-rings.¹³ ZSM-18 is notable as a large-pore material containing 1-dimensional channels, which may have technologically-valuable properties. Odd-member ring zeolites are characterized by crystallographic disorder of the silicon/aluminum

atoms and usually contain a high silicon to aluminum (Si:Al $> 3 \rightarrow \infty$) atomic ratio. It has been proposed that 3-ring-containing systems may offer the lowest framework density possible, in terms of T atoms per unit volume, in microporous systems,^{14a} but further examples of such materials are required to test this theory.^{14b}

As part of our efforts to prepare new (Zn/Be,P/As,O) phases to mimic the behavior described in the above paragraph, we describe the preparations, structures, and properties of two new phases: a zincophosphate, $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ (NZPO), and a beryllarsenate, $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ (BAO), which are non-zeolitic but contain 1-dimensional chains, whose building blocks include tetrahedral 3-rings. These two phases complement the 3-ring zincophosphate *layered* materials described recently.¹⁵ As will be described below, $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ is a close analogue of the beryllphosphate phase moräsite, which was structurally characterized very recently.¹⁶

Experimental Section

Synthesis. *Warning!* Beryllium and arsenic compounds are highly toxic. Preparations must be carried out under appropriate safety conditions. $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ was prepared by the following hydrothermal method. A 0.437-g sample of beryllium hydroxide, $\text{Be}(\text{OH})_2$ (10 mmol), 3.707 g of 4 M arsenic acid (H_3AsO_4) solution (~ 11 mmol), and 10 cm^3 of water were sealed in a FEP fluorocarbon-film "pouch" and heated in an autoclave at 150 °C for 3 days. Water was used as the support fluid at autogenous pressure (70 psi). The product, which was filtered out, consisted of 0.71 g of transparent, rod-shaped crystals (maximum dimensions 1.0 \times 0.1 \times 0.1 mm), with some beryllium cations and other species remaining in solution (final pH = 1). All starting reagents were of analytical grade or better.

For $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$, a clear, basic solution containing Na^+ , phosphate, and zincate ions was prepared in a small Teflon bottle by adding 7.76 g of 2 M $\text{Zn}(\text{NO}_3)_2$ (12 mmol), 10.78 g of 4 M H_3PO_4 (36 mmol), and then 37.68 g of 4 M NaOH (132 mmol). The initial gel cleared rapidly to give complete solution. To this was added 2.39 g of 4 M H_3PO_4 (8 mmol), resulting in a gel-like suspension which transformed

* Authors for correspondence.

† University of Houston.

‡ University of California.

- (1) Peacor, D. R.; Rouse, R. C.; Ahn, J.-H. *Am. Mineral.* **1987**, *72*, 816.
- (2) Rouse, R. C.; Peacor, D. R.; Merlino, S. *Am. Mineral.* **1989**, *74*, 1195.
- (3) Harvey, G.; Meier, W. M. In *Zeolites: Facts, Figures, Future: Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1989; Vol. 49, p 411.
- (4) Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 378.
- (5) Gier, T. E.; Stucky, G. D. *Nature (London)* **1991**, *349*, 508.
- (6) Harrison, W. T. A.; Gier, T. E.; Moran, K. L.; Nicol, J. M.; Eckert, H.; Stucky, G. D. *Chem. Mater.* **1991**, *3*, 27.
- (7) Gier, T. E.; Harrison, W. T. A.; Stucky, G. D. *Angew. Chem.* **1991**, *103*, 1191.
- (8) Lowenstein, W. *Am. Mineral.* **1954**, *39*, 92.
- (9) Lawton, S. L.; Rohrbaugh, W. J. *Science (Washington, D.C.)* **1990**, *247*, 1319.
- (10) Vaughan, P. A. *Acta Crystallogr.* **1966**, *21*, 983.
- (11) Mortier, W. J. *J. Phys. Chem.* **1977**, *81*, 1334.
- (12) Kocman, V.; Gait, R. I.; Rucklidge, J. *Am. Mineral.* **1974**, *59*, 71.
- (13) Merlino, S. *Eur. J. Mineral.* **1990**, *2*, 809.

- (14) (a) Brunner, G. O.; Meier, W. M. *Nature (London)* **1989**, *337*, 146. (b) Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111.
- (15) Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Calabrese, J. C.; Stucky, G. D. *J. Solid State Chem.*, in press.
- (16) Merlino, S.; Pasero, M. *Z. Kristallogr.* **1992**, *201*, 253.

into a milky slurry upon shaking. After the mixture was allowed to stand at 70 °C for 40 h, many small needles ($\sim 0.2 \times 0.02 \times 0.02$ mm) were suspended in the supernatant liquid; these were recovered by filtration, washing, and drying. A nonsuspended mass of needles and a second sodium zinc phosphate phase was also present. These materials will be described later.

Powder Data. X-ray powder patterns were collected for these materials using techniques described previously.¹⁷ It became evident that $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ had a powder pattern similar to that of the beryllophosphate mineral bearsite,¹⁸ with the same reported formula as the material described here, and also that of the beryllophosphate mineral moräsite ($\text{Be}_2\text{PO}_4\text{OH}\cdot 4\text{H}_2\text{O}$).¹⁹ On the basis of X-ray photographs, the unit cells of these materials were reported to be C-centered monoclinic, with dimensions $\sim 8.6 \times 36.90 \times 7.15$ Å and $\beta \approx 98^\circ$, but no detailed structures were reported. Single-crystal measurements on synthetic $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$, described below, gave a unit cell with a unit-cell *b* periodicity $\approx 1/3$ of that quoted for the two mineral species (and transformed *a* and *c* axes), and the synthetic $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ was indexed on that basis. Conversely, some evidence for unit-cell *b* tripling was observed in the recent study of the structure of moräsite,¹⁶ which was attributed to a possible superstructure ordering of the H-bonds in the beryllophosphate material. It should be noted that the supercell reflections observed for $\text{Be}_2\text{PO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ were very weak and the presence of a supercell in $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ cannot be completely ruled out. However, our diffraction results indicate that the H atoms appear to be well-ordered in $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ (vide infra).

Thermogravimetric Analysis. TGA of the $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ rods showed the total weight loss equivalent to losing 4.5 H_2O by 825 °C (obs loss = 34%, calc loss = 33%). This occurred in two stages—a rapid loss of approximately 1.67 H_2O between 100 and 150 °C and subsequent loss of the rest of the water gradually to 800 °C. The anhydrous, crystalline product, whose X-ray powder pattern bore no resemblance to other beryllium/arsenic-containing phases might be formulated as $\text{Be}_4\text{As}_2\text{O}_9$, and further work is in progress to characterize this material.

TGA for $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ showed a smooth, rapid weight decrease, equivalent to the loss of 7 water molecules between 50 and 130 °C, with subsequent slow loss of another 0.5 weight-equivalent of a water molecule. When the sample was cooled from 700 °C, X-ray powder measurements indicated that the residue consisted of ZnO and an unidentified phase, perhaps a sodium pyrophosphate of stoichiometry $\text{Na}_4\text{P}_2\text{O}_7$. The X-ray data for this phase did not match those of any known Na/P/O or Na/As/O phases.

Structure Determination. Suitable single crystals for structure determination were selected for each phase and mounted on thin glass fibers with cyanoacrylate adhesive. Room-temperature [25(1) °C] intensity data were collected for each phase on a Huber automated four-circle diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å). For each phase, at least 20 reflections were located and centered by searching reciprocal space and indexed to obtain a unit cell and orientation matrix. Unit-cell constants were optimized by least-squares refinement, resulting in the lattice parameters shown in Table I. Intensity data were collected in the θ - 2θ scanning mode with standard reflections monitored for intensity variation throughout the course of each experiment. The scan speed was 6°/min with a scan range of 1.3° below $K\alpha_1$ to 1.6° above $K\alpha_2$. No significant variation in standards was observed, and crystal absorption was monitored for using ψ -scans through 360° for selected reflections with $\chi \approx 90^\circ$: Absorption was insignificant and no correction was applied. The raw data were reduced using a Lehmann-Larsen profile-fitting routine,²⁰ and the normal corrections for Lorentz and polarization effects were made. All the data collection and reduction routines were based on the UCLA crystallographic computing package.²¹ Systematic absences (*h*0*l*, *h*; 0*k*0, *k*) unambiguously established the space groups of both these phases as $P2_1/a$ (No. 14).

The structures were solved by a combination of direct methods and Fourier syntheses, assuming the space groups noted above. For BAO, the As and O positions were obtained from the direct-methods program

Table I. Crystallographic Parameters

	$\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$	$\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$
emp formula	$\text{AsO}_9\text{Be}_2\text{H}_9$	$\text{ZnPNa}_2\text{O}_{12}\text{H}_{15}$
mol wt	246.01	349.43
habit	colorless needle	colorless needle
crystal system	monoclinic	monoclinic
<i>a</i> (Å)	7.2349(8)	6.4212(6)
<i>b</i> (Å)	12.686(2)	21.612(2)
<i>c</i> (Å)	8.6548(9)	8.6813(6)
α (deg)	90	90
β (deg)	98.439(3)	109.899(3)
γ (deg)	90	90
<i>V</i> (Å ³)	785.8	1132.8
<i>Z</i>	4	4
space group	$P2_1/a$	$P2_1/a$
<i>T</i> (°C)	25(1)	25(1)
λ (Mo K α) (Å)	0.71073	0.71073
ρ_{calc} (g/cm ³)	2.08	2.04
μ (cm ⁻¹)	42.4	24.8
abs cor	none	none
<i>hkl</i> limits	$\pm 10, +19, +13$	$\pm 9, +32, +13$
no. of tot. data	3250	4516
no. of obs data ^a	2333	2654
no. of params	138	192
<i>R</i> (<i>F</i> _o) ^b (%)	4.49	5.85
<i>R</i> _w (<i>F</i> _o) ^c (%)	4.79	5.61

^a $I > 3\sigma(I)$. ^b $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

SHELXS-86,²² and the remaining atoms, including all the protons, were located from Fourier difference maps following anisotropic refinement of the known atoms positions. For NZPO, all the non-hydrogen atoms were located using SHELXS-86, all but one proton position was located from Fourier maps, and the remaining H atom was placed geometrically. For both materials, bond distance [$d(\text{O}-\text{H}) = 0.95(1)$ Å] and angle [$\theta(\text{H}-\text{O}-\text{H}) = 109(1)^\circ$] restraints were used during the refinement of the proton positions. The final full-matrix least-squares refinements were against *F* and included anisotropic temperature factors (atom type isotropic for hydrogens) and a secondary extinction correction.²³ Complex, neutral-atom scattering factors were obtained from ref 24. Final agreement factors, defined in Table I, of $R = 4.49\%$ and $R_w = 4.79\%$ ($w_i = 1$) were obtained for $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$; the corresponding values for $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ were $R = 5.85\%$ and $R_w = 5.61\%$ ($w_i = 1$). Final Fourier difference maps revealed no regions of electron density which could be assigned to atomic sites (for $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$, min = -0.2, max = 0.2 electron/Å³; for $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$, min = -1.3, max = 1.3 electron/Å³), and analysis of the various trends in *F*_o versus *F*_c revealed no unusual effects. The least-squares, Fourier, and subsidiary calculations were performed using the Oxford CRYSTALS system,²⁵ running on a DEC Micro VAX 3100 computer. Tables of observed and calculated structure factors are available as supplementary material directly from the authors.

Solid-State MAS NMR. ³¹P spectra were obtained on a General Electric GN-300 spectrometer at 121.65 MHz (field strength 7.05 T) with 20 acquisitions, using a multinuclear broad-band MAS NMR probe manufactured by Doty Scientific. Data were collected in a single-pulse mode, with a 45° pulse length of 3 μs and a recycle time of 300 s. A broad singlet at +8.4 ppm (downfield shift defined as positive) relative to 85% H_3PO_4 was observed. MAS NMR ⁹Be spectra were obtained on a GN-300 machine at 42.23 MHz (field strength 7.05 T) with 24 acquisitions, using a Doty Scientific multinuclear broad-band probe. Data were collected in a single-pulse mode with a 45° pulse length of 3 μs and a recycle delay time of 60 s. A sharp singlet at -0.767 ppm, relative to 2 M $\text{Be}(\text{NO}_3)_2$, was apparent.

Results

BAO. The crystal structure of $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ consists of a network of $(\text{Be,As})\text{O}_4$ tetrahedron-containing columns inter-

- (17) Gier, T. E.; Harrison, W. T. A.; Nenoff, T. M.; Stucky, G. D. In *Synthesis of Microporous Materials*; Ocelli, M. L., Robson, H. E., Eds.; Van Nostrand Reinhold: New York, 1992; Vol. 1, pp 407-426.
 (18) Kopchenova, E. V.; Sidorenko, G. A. *Am. Miner.* **1963**, *48*, 210.
 (19) Lindberg, M. L.; Pecora, W. T.; Barbosa, A. L. d. *Am. Miner.* **1953**, *38*, 1126.
 (20) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr.* **1974**, *A30*, 580.
 (21) The UCLA Crystallographic Computing Package, developed by C. E. Strouse, Department of Chemistry, University of California, Los Angeles, CA.

- (22) Sheldrick, G. M. *SHELXS-86* User Guide; Crystallography Department, University of Göttingen: Göttingen, Germany, 1986.
 (23) Larson, A. C. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 291.
 (24) Cromer, D. T. *International Tables for X-Ray Crystallography*; Kynoch Press; Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.
 (25) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory, Oxford University: Oxford, U.K., 1990.

Table II. Atomic Positional Parameters for $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$

atom	x	y	z	U_{eq}^a
Be(1)	0.6227(7)	0.1224(4)	0.3590(6)	0.0163
Be(2)	0.8508(7)	0.1265(4)	0.1107(6)	0.0170
As(1)	0.23796(5)	0.17406(3)	0.24214(4)	0.0121
O(1)	0.8251(4)	0.2545(2)	0.1070(3)	0.0172
O(2)	0.4017(4)	0.0923(2)	0.3342(4)	0.0159
O(3)	1.0697(4)	0.0928(2)	0.1546(4)	0.0157
O(4)	0.6568(4)	0.2488(2)	0.3741(3)	0.0174
O(5)	0.7200(4)	0.0733(2)	0.2216(5)	0.0234
O(6)	0.7096(5)	0.0778(3)	0.5335(5)	0.0265
O(7)	0.7905(5)	0.0883(3)	-0.0731(4)	0.0233
O(8)	0.4158(6)	0.1502(3)	0.8331(5)	0.0355
O(9)	0.0307(5)	0.1810(4)	0.6445(4)	0.0337

$$^a U_{eq} (\text{\AA}^2) = (U_1 U_2 U_3)^{1/3}.$$

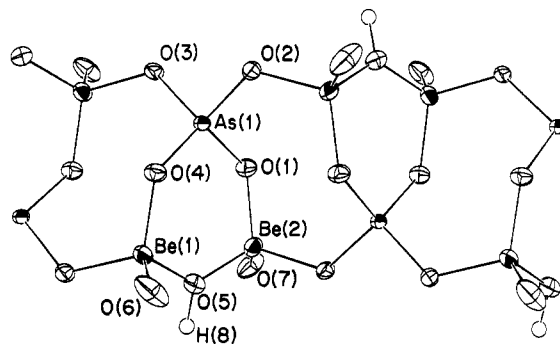
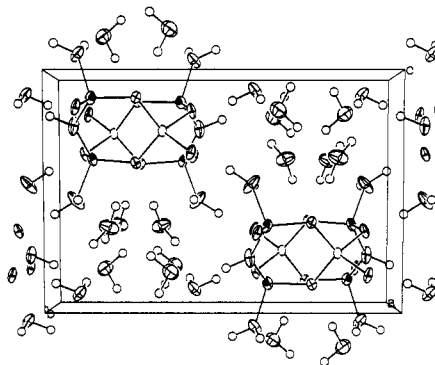
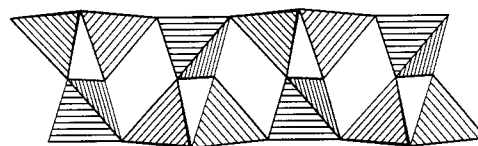
Table III. Selected Bond Distances (\AA) and Angles (deg) for $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$

Be(1)–O(2)	1.627(6)	Be(1)–O(4)	1.625(6)
Be(1)–O(5)	1.595(7)	Be(1)–O(6)	1.648(6)
Be(2)–O(1)	1.635(6)	Be(2)–O(3)	1.630(5)
Be(2)–O(5)	1.593(7)	Be(2)–O(7)	1.659(6)
As(1)–O(1)	1.674(3)	As(1)–O(2)	1.684(3)
As(1)–O(3)	1.688(3)	As(1)–O(4)	1.674(3)
O(4)–Be(1)–O(2)	112.1(3)	O(5)–Be(1)–O(2)	110.0(3)
O(5)–Be(1)–O(4)	111.5(3)	O(6)–Be(1)–O(2)	106.0(3)
O(6)–Be(1)–O(4)	103.4(3)	O(6)–Be(1)–O(5)	113.5(4)
O(3)–Be(2)–O(1)	111.7(3)	O(5)–Be(2)–O(1)	110.9(3)
O(5)–Be(2)–O(3)	113.0(4)	O(7)–Be(2)–O(1)	105.0(3)
O(7)–Be(2)–O(3)	104.8(3)	O(7)–Be(2)–O(5)	111.0(3)
O(2)–As(1)–O(1)	110.7(1)	O(3)–As(1)–O(1)	109.7(1)
O(3)–As(1)–O(2)	104.3(1)	O(4)–As(1)–O(1)	111.5(1)
O(4)–As(1)–O(2)	109.3(1)	O(4)–As(1)–O(3)	111.2(1)
As(1)–O(1)–Be(2)	125.2(3)	As(1)–O(2)–Be(1)	121.8(2)
As(1)–O(3)–Be(2)	123.8(2)	As(1)–O(4)–Be(1)	125.9(3)
Be(2)–O(5)–Be(1)	130.5(3)		

connected via a H-bonding network of hydroxide groups and water molecules. Final atomic positional and equivalent isotropic thermal parameters for $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ are listed in Table II, with selected bond distance/angle data in Table III. The atom-bonding scheme of BAO is illustrated in Figure 1 with ORTEP,²⁶ and the complete crystal structure is shown in Figure 2. BAO contains 2 Be, 1 As, 9 O, and 9 H atoms in the asymmetric unit. The beryllium and arsenic atoms are tetrahedrally coordinated to oxygen atoms, as expected. Four oxygen atoms [O(1) to O(4)] participate in Be–O–As links, one [O(5)] is part of a Be–(OH)–Be link, and there are 4 distinct water molecules [O(6) to O(9)].

The structure consists of two distinct parts: infinite, 1-dimensional, neutral chains of stoichiometry $\text{Be}_2\text{AsO}_4\text{OH}\cdot 2\text{H}_2\text{O}$, which propagate in the unit-cell *a* direction, and "channels", occupied by the two extra-chain water molecules, which link adjacent chains via a hydrogen-bond network (vide infra). Each crystallographically-distinct Be atom makes two bonds to arsenic via O [$d_{av}(\text{Be}–\text{O}) = 1.629(12) \text{\AA}$], one bond to a water molecule [$d_{av} = 1.655(9) \text{\AA}$], and one bond [$d = 1.594(9) \text{\AA}$, $\theta(\text{Be}–\text{O}–\text{Be}) = 130.5(4)^\circ$] to the other Be atom via a bridging hydroxide ion. The arsenic atom bonds to four different Be atoms via oxygen atom bridges [$\theta_{av} = 124.2(6)^\circ$], with a $d_{av}(\text{As}–\text{O})$ of 1.680(6) \AA . Bond valence sums (BVS)²⁷ for the tetrahedral species are as follows: $\text{BVS}[\text{Be}(1)] = 2.05$, $\text{BVS}[\text{Be}(2)] = 2.02$, $\text{BVS}[\text{As}(1)] = 5.05$. These are consistent with the expected values of 2.0 for tetrahedral Be and 5.0 for tetrahedral As.

This tetrahedral connectivity leads to two different types of ring linkages: first, a 3-ring consisting of Be(1)–Be(2)–As(1) (oxygen-atoms omitted), which lies approximately in the *bc* plane,

**Figure 1.** View of the 3-ring/4-ring chain in $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$, showing the atom-labeling scheme. Thermal ellipsoids are at the 50% level, and protons coordinated to O(6) and O(7) are omitted for clarity.**Figure 2.** View down *a* of the unit cell of $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$, showing the packing of tetrahedral chains and water molecules: Be atoms, shaded ellipsoids; As atoms, plain ellipsoids; O atoms, "open" ellipsoids; H atoms, plain circles.**Figure 3.** Polyhedral plot of the chain connectivity in $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$, showing the 4-/3-ring connectivity. The repeating unit of the chain is a T_3O_7 unit.

and, second, adjacent 3-rings in the 1-dimensional stacks that are connected via Be(1)–O(1)/O(2)–As(1) and Be(2)–O(3)/O(4)–As(1) links, thus forming 4-rings, of T atom configuration

Be(1)–As(1)–Be(2)–As(1). Thus, edge-sharing 3- and 4-rings alternate in the 1-dimensional chain, as illustrated in the polyhedral representation in Figure 3.

The H-bonding scheme, which involves both the Be-coordinated water molecules and the "free" water molecules, connects adjacent chains and includes 8 of the 9 distinct protons with $d(\text{H}\cdots\text{O}) < 2.1 \text{\AA}$. All four protons of the two water molecules directly attached to Be partake in H-bonds: two "direct" O–H \cdots O links to chain oxygen atoms [O(1) to O(4)] in adjacent chains ($d_{av} = 1.72(4) \text{\AA}$) and two slightly-longer links to extrachain water molecules ($d_{av} = 1.87(3) \text{\AA}$). In turn, three out of four of the free water molecule protons also make H-bonds: two of them to a Be–O–As tetrahedral bridge oxygen and one to the other water molecule oxygen atom. The remaining proton, H(7), is not involved in any H-bond links. Finally, the bridging hydroxy proton, Be–(OH)–Be, links via a weak H-bond to a water molecule oxygen atom [$d = 2.08(2) \text{\AA}$]. Thus, all the Be-/As-coordinated chain oxygen atoms, O_c [O(1) to O(4)], participate in H-bonds to water: two $O_c\cdots\text{H}–\text{O}–\text{Be}$ links and two $O_c\cdots\text{H}–\text{O}–\text{H}$ connections. The average O–H \cdots O angle of all the H-bonds in the structure is 169° .

The ^9Be MAS NMR spectrum of $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ shows one resolved resonance at -0.767 ppm , relative to aqueous 2 M

(26) Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN 37830, 1976; with local modifications.

(27) Brown, I. D.; Wu, K. K. *Acta Crystallogr.* 1975, B32, 1957.

Table IV. Atomic Positional Parameters for $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$

atom	x	y	z	U_{eq}^a
Na(1)	0.0339(4)	0.1927(1)	0.2686(3)	0.0324
Na(2)	0.0230(4)	0.0289(1)	0.1917(3)	0.0342
Zn(1)	0.49499(9)	0.74442(3)	0.36474(7)	0.0224
P(1)	0.6361(2)	0.85568(5)	0.1892(2)	0.0207
O(1)	0.3101(5)	0.7627(2)	0.4975(4)	0.0231
O(2)	0.4805(6)	0.8005(2)	0.1854(4)	0.0277
O(3)	0.3785(6)	0.6624(2)	0.2861(5)	0.0287
O(4)	0.5691(7)	0.9113(2)	0.2705(5)	0.0315
O(5)	0.6194(7)	0.8703(2)	0.0128(4)	0.0296
O(6)	0.2538(7)	0.2386(2)	0.1150(5)	0.0312
O(7)	0.9450(7)	0.1244(2)	0.0297(5)	0.0377
O(8)	0.6827(8)	0.1396(2)	0.2882(5)	0.0372
O(9)	0.7909(7)	0.0190(2)	0.3545(5)	0.0350
O(10)	0.2716(7)	0.0102(2)	0.0434(5)	0.0346
O(11)	0.2712(7)	0.1049(2)	0.3844(5)	0.0380
O(12)	0.8185(7)	0.0650(2)	0.6633(5)	0.0340

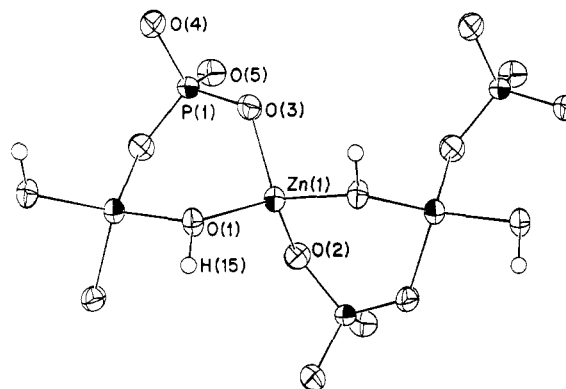
$$^a U_{\text{eq}} (\text{\AA}^2) = (U_1U_2U_3)^{1/3}.$$

$\text{Be}(\text{NO}_3)_2$. The crystal structure results (Table II) indicate that there are two crystallographically-distinct beryllium atoms with equal site occupancies in the structure of $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ —thus two, distinct, ^9Be NMR resonances of equal intensity might be expected a priori from this material. We attribute this single observed resonance to coincidental overlap of the signals from Be(1) and Be(2): both Be atom chemical environments are similar, involving two bonds to As via O, a bonded water molecule, and Be(1) and Be(2) share a common, bridging OH⁻ ion (see above). In particular, the 3-ring containing the Be(1) and Be(2) moieties (Figure 1) has pseudo-2-fold symmetry (about the O(5)—As(1) axis), again indicating that the two resonances are likely to have similar chemical shifts.

Little work has been carried out on MAS NMR of beryllium-containing molecular sieve materials. One example is provided by our structural study of the faujasite-type Na/BePO-X,⁶ where a single resonance at -1.7 ppm was observed. The smallest identifiable subunit in the BePO-X topology is a 4-ring. The Be atom environment in Na/BePO-X is more regular than that found in $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ —the single, crystallographically-distinct beryllium atom in Na/BePO-X makes four Be-O-P bonds to four different phosphorus atom neighbors, with a d_{av} (Be-O) of 1.61(5) Å. In MAS NMR studies of aluminosilicate and aluminophosphate molecular sieve systems, empirical correlations between isotropic MAS NMR shift (of ^{29}Si and ^{31}P) and Si/P atom chemical environments have been established.²⁸ However, any attempt to establish a correlation between ^9Be MAS NMR shift and ring size or Be-O-P bond angle is premature in the berylllophosphate phase space.

NZPO. In $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$, which contains $(\text{Zn},\text{P})\text{O}_4$ tetrahedral columns interconnected via a network of sodium ions and water molecules, there is just one type of tetrahedral ring

topology, namely, 3-rings of $\text{Zn}(1)-\text{P}(1)-\text{Zn}(1)$ (oxygen atoms omitted), essentially an infinite backbone of Zn-Zn T-links, each with a bridging P- group. Final atomic positional and equivalent isotropic thermal parameters for $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ are listed in Table IV, with selected bond distance/angle data in Table V. The atom-bonding scheme in NZPO is illustrated in Figure 4, with ORTEP, and the complete crystal structure is shown in Figure 5. $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ contains 2 Na atoms, 1 Zn atom, 1 P atom, 12 O atoms (5 oxide ions; 7 water molecules), and 15 protons in the asymmetric unit, all on general crystallographic positions. The zinc atom is tetrahedrally coordinated by 4 oxygen atoms [$d_{\text{av}} = 1.957(8)$ Å], three of which also bond to the phosphorus atom, the other forming the bridging hydroxide ion between adjacent zinc atoms, akin the hydroxy bridge in the beryllloarsenate described above. The phosphorus atom is also

**Figure 4.** View of the chain configuration in $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ showing the 3-ring tetrahedral chain linkage. Thermal ellipsoids are illustrated at the 50% level (arbitrary radius for the proton).**Table V.** Selected Bond Distances (Å) and Angles (deg) for $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$

Na(1)-O(1)	2.456(4)	Na(1)-O(6)	2.456(5)
Na(1)-O(6')	2.363(4)	Na(1)-O(7)	2.449(5)
Na(1)-O(8)	2.588(6)	Na(1)-O(11)	2.428(5)
Na(2)-O(7)	2.452(5)	Na(2)-O(9)	2.387(5)
Na(2)-O(10)	2.402(5)	Na(2)-O(10)	2.415(5)
Na(2)-O(11)	2.494(5)	Na(2)-O(12)	2.422(5)
Zn(1)-O(1)	1.964(3)	Zn(1)-O(1)'	1.956(3)
Zn(1)-O(2)	1.951(4)	Zn(1)-O(3)	1.955(4)
P(1)-O(2)	1.548(4)	P(1)-O(3)	1.547(4)
P(1)-O(4)	1.528(4)	P(1)-O(5)	1.531(4)
O(6)-Na(1)-O(1)	93.0(1)	O(6)-Na(1)-O(1)	95.6(1)
O(6)-Na(1)-O(6)'	84.7(1)	O(7)-Na(1)-O(1)	169.5(2)
O(7)-Na(1)-O(6)	78.2(1)	O(7)-Na(1)-O(6)	89.3(2)
O(8)-Na(1)-O(1)	109.8(1)	O(8)-Na(1)-O(6)	152.8(2)
O(8)-Na(1)-O(6)	78.6(2)	O(8)-Na(1)-O(7)	80.2(2)
O(11)-Na(1)-O(1)	96.8(1)	O(11)-Na(1)-O(6)	98.3(2)
O(11)-Na(1)-O(6)	167.1(2)	O(11)-Na(1)-O(7)	79.2(2)
O(11)-Na(1)-O(8)	93.7(2)		
O(9)-Na(2)-O(7)	111.6(2)	O(10)-Na(2)-O(7)	82.9(2)
O(10)-Na(2)-O(9)	164.9(2)	O(10)-Na(2)-O(7)	82.0(2)
O(10)-Na(2)-O(9)	90.1(2)	O(10)-Na(2)-O(10)	87.7(2)
O(11)-Na(2)-O(7)	77.8(2)	O(11)-Na(2)-O(9)	92.7(2)
O(11)-Na(2)-O(10)	94.6(2)	O(11)-Na(2)-O(10)	159.3(2)
O(12)-Na(2)-O(7)	166.2(2)	O(12)-Na(2)-O(9)	81.6(2)
O(12)-Na(2)-O(10)	84.2(2)	O(12)-Na(2)-O(10)	102.5(2)
O(12)-Na(2)-O(11)	98.3(2)		
O(1)-Zn(1)-O(1)'	112.4(2)	O(2)-Zn(1)-O(1)	118.1(2)
O(2)-Zn(1)-O(1)	106.1(1)	O(3)-Zn(1)-O(1)	98.8(2)
O(3)-Zn(1)-O(1)	109.2(1)	O(3)-Zn(1)-O(2)	112.1(2)
O(3)-P(1)-O(2)	109.9(2)	O(4)-P(1)-O(2)	109.5(2)
O(4)-P(1)-O(3)	109.7(2)	O(5)-P(1)-O(2)	108.2(2)
O(5)-P(1)-O(3)	108.1(2)	O(5)-P(1)-O(4)	111.4(2)
Zn(1)-O(1)-Zn(1)'	110.4(2)	P(1)-O(2)-Zn(1)	127.3(2)
P(1)-O(3)-Zn(1)	127.8(2)		

4-coordinate with oxygen atoms, two of which [O(2) and O(3)] bond to Zn [$d_{\text{av}} = 1.548(6)$ Å] and two of which [O(4) and O(5)] are uncoordinated by any other atoms, except by protons making H-bonds to those oxygen atoms [$d_{\text{av}}(\text{P}-\text{O}) = 1.530(6)$ Å]. These oxygen coordinations are supported by bond valence sums:²⁷ neglecting protons, values of 1.00, 1.73, 1.72, 1.29, and 1.28 result for O(1) through O(5), respectively. The average Zn-O-P angle is 127.6(4)°, and the Zn-(OH)-Zn angle is 110.4(2)°, substantially smaller than the Be-(OH)-Be bond angle noted above. The twisted, corner-sharing columns of 3-rings in NZPO propagate in the a direction, as indicated in Figure 6 (polyhedral representation).

The two crystallographically-distinct sodium atoms are both approximately octahedrally coordinated by oxygen atoms: Na(1) is surrounded by one oxygen atom from the Zn/P/O chain and five water molecules [$d_{\text{av}}(\text{Na}-\text{O}) = 2.457(12)$ Å], while Na-

(28) Cheetham, A. K.; Clayden, N. J.; Dobson, C. M.; Jakeman, R. J. B. *J. Chem. Soc., Chem. Commun.* 1986, 195.

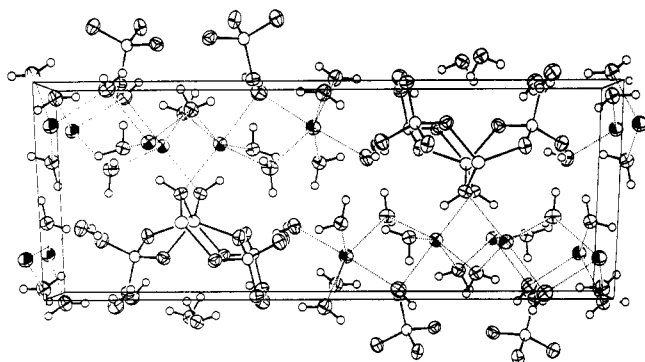


Figure 5. View down a of the unit cell of $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ showing the packing of chains: Zn and P atoms, plain ellipses; O atoms, "open" ellipses; sodium cations, shaded ellipses; hydrogen atoms, plain circles. Na-O bonds are indicated by dotted lines.

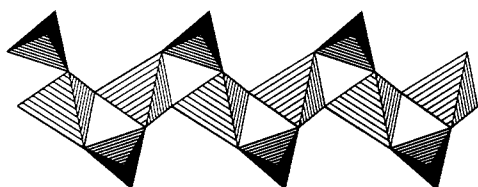


Figure 6. Polyhedral plot of the T_2O_5 chain in $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ ("backbone" of ZnO_4 groups, bridged by PO_4 units).

(2) coordinates to six water molecules as its neighbors [$d_{\text{av}} = 2.429(12)$ Å]. O-Na(1)-O cis bond angles vary from $78.2(1)$ to $109.8(1)^\circ$; for the Na(2) polyhedron these limits are $77.8(2)$ – $111.6(2)^\circ$. Neglecting protons, the NaO_6 octahedra form infinite, corrugated, layers which are aligned in the ac plane. The layers are composed of edge- and corner-sharing NaO_6 units; groups of 4 NaO_6 octahedra form isolated edge-sharing chains, aligned approximately in the unit-cell b direction, and these edge-sharing chain are corner-linked with their neighbors, to form the overall sheet configuration.

As in BaO , a network of H-bonds, also part of the sodium/water octahedral network, holds adjacent tetrahedral stacks together. All but two of the 14 water protons participate in H-bonds. Unlike the situation in BAO , the bridging hydroxide proton in the $\text{Zn}-(\text{OH})-\text{Zn}$ link sees no near neighbors. The two "free" phosphate oxygen atoms [O(4) and O(5)] each make 4 distinct H-bonds to water molecule protons [$d_{\text{av}} = 1.95(10)$ Å], to saturate their bond valences.²² These protons belong to all 7 water molecules in the structure: in particular, O(10) makes two O-H...O-P H-bonds, while O(7) and O(11) make their only H-bond to a phosphate oxygen, their other proton being uncoordinated. The two Zn-O-P bridging oxygens also make H-bonds to water protons as O(6)-H(2)...O(2) and O(12)-H(13)...O(3). Finally, two H-bonds are solely involved in the Na/water network: O(8)-H(6)...O(9) [$d = 1.83(3)$ Å] and O(9)-H(7)...O(12) [$d = 1.93(3)$ Å]. The average O-H...O H-bond angle is 167° .

In the ^{31}P MAS NMR spectrum of $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$, one signal is observed, corresponding to the sole crystallography-distinct phosphorus atom site in this material. The shift of +8.4 ppm is within the range quoted for a number of phosphorus-containing materials observed earlier.²⁸ Some compatible ^{31}P resonances in anionic, phosphorus-containing molecular sieve frameworks include values of -8.2 ppm in $\text{BePO}_4\text{-X}$ and +5.8 ppm in $\text{ZnPO}_4\text{-X}$, both of these materials crystallizing in the faujasite-type structure.⁶

Conclusions

The two three-dimensional phases described above are not zeolitic but do contain 3-membered rings ordered in 1-dimensional chains. The key bonding connections in $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ are

$\text{Be}-\text{O}-\text{As}$ and $\text{Be}-(\text{OH})-\text{Be}$ links; in $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$, $\text{Zn}-\text{O}-\text{P}$ and $\text{Zn}-(\text{OH})-\text{Zn}$ links build up the 3-rings. In the former case, $\text{As}-\text{O}-\text{As}$ and, in the latter case, $\text{P}-\text{O}-\text{P}$ bonds are excluded. This bridging hydroxide link between tetrahedra is not unprecedented and has a counterpart in 3-dimensional aluminosilicate zeolite phases, for example in the steam-treated H-zeolite ρ phase,²⁹ where $\text{Si}-(\text{OH})-\text{Si}/\text{Al}$ bonds are found, within a 4-/6-ring topology. However, there appear to be no other known extended 3-ring-containing structures containing such bridging hydroxide links.

It should be noted here that *isolated* T_3O_9 tetrahedral 3-rings are well-known for a number of tetrahedral species, for example, T = silicon (many phases, such as $\text{BaTiSi}_3\text{O}_9$ (benitoite)), T = germanium (e.g., $\text{BaTiGe}_3\text{O}_9$), and T = phosphorus (e.g., $\text{Na}_2\text{P}_3\text{O}_9\cdot \text{H}_2\text{O}$). In each case, the TO_4 tetrahedron makes two bonds to its neighbors via T-O-T links and two "unsaturated" T-O links. These and other tetrahedral ring systems are described elsewhere.^{30,31}

Some other recently-characterized phases in the $(\text{Be}/\text{Zn})(\text{P}/\text{As})\text{O}$ structure field also contain 3-ring tetrahedral groupings, albeit of a slightly-different type. The two layered zincophosphate materials $\text{CsH}(\text{ZnPO}_4)_2$ and $\text{NaH}(\text{ZnPO}_4)_2$ ¹⁵ both contain (different) 3-ring moieties consisting of $\text{Zn}-\text{O}-\text{P}$ and $\text{Zn}-\text{O}-\text{Zn}$ links (no $\text{P}-\text{O}-\text{P}$ bonds). In these systems, the proton of the bridging hydroxide link between the two divalent cations is replaced by a link to another phosphorus atom, resulting in chains of "bridging" 3-rings, via a 3-coordinated oxygen atom, cross-linked into 2-dimensional, anionic sheet structures, which sandwich the univalent cations. A 3-dimensional example of a zincophosphate material containing a 3-ring is provided by $\text{Zn}_3(\text{PO}_4)(\text{HPO}_4)_2\cdot \text{HN}_2\text{C}_6\text{H}_{12}$,³² which has a ring topology similar to that of the phases described here ($\text{Zn}-\text{O}-\text{Zn}$, $\text{Zn}-\text{O}-\text{P}$ links, no $\text{P}-\text{O}-\text{P}$ bonds). As with the layered $\text{MH}(\text{ZnPO}_4)_2$ materials, in $\text{Zn}_3(\text{PO}_4)(\text{HPO}_4)_2\cdot \text{HN}_2\text{C}_6\text{H}_{12}$ the 3-rings are bridged together via the $\text{Zn}-\text{O}-\text{Zn}$ link where the central O atom also bonds to an adjacent P atom.

The 1-dimensional structures of $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ indicate that it may be possible to synthesize 3-dimensional structures containing these small, odd-membered rings in the $(\text{Be}/\text{Zn})(\text{P}/\text{As})\text{O}$ phase space, to complement the "bridged" 3-ring phases noted above: Such efforts are now being made. Finally, it is notable that the overall charge of the chain in $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$, including protons, is neutral, while that in $\text{Na}_2\text{ZnPO}_4\text{OH}\cdot 7\text{H}_2\text{O}$ is more typically anionic. Thus, it may even be possible to prepare neutral, 3-dimensional, microporous frameworks in the $(\text{Be},\text{Zn})/(\text{P},\text{As})/\text{H}/\text{O}$ system: for instance, a hypothetical "condensation" reaction of $\text{Be}_2\text{AsO}_4\text{OH}\cdot 4\text{H}_2\text{O}$, where the water molecule bound to Be is replaced by a link to another tetrahedral center.

Acknowledgment. This work was partially funded by the National Science Foundation (Division of Materials Research; Grant DMR-9208511) and the Office of Naval Research.

Supplementary Material Available: Tables of anisotropic thermal factors and H atom positions (2 pages). Ordering information is given on any current masthead page.

(29) Fischer, R. X.; Baur, W. H.; Shannon, R. D.; Staley, R. H. *J. Phys. Chem.* **1987**, *91*, 2227.

(30) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: New York, 1986; see also references therein.

(31) Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: New York, 1985; see also references therein.

(32) Harrison, W. T. A.; Nenoff, T. M.; Eddy, M. M.; Martin, T. E.; Stucky, G. D. *J. Mater. Chem.* **1992**, *2*, 1127.