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$Be_3(AsO_4)_2 \cdot 2H_2O$, a New Berylloarsenate Phase Containing "Bridged" Tetrahedral 3-Rings

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The high-temperature/high-pressure hydrothermal synthesis and X-ray single crystal structure of $Be_3(AsO_4)_2 \cdot 2H_2O$ are described. The title compound contains a three-dimensional network of BeO_4 and AsO_4 tetrahedra, whose structural motif includes infinite layers of "bridged" tetrahedral 3- and 4-rings. ^9Be MAS NMR data are consistent with the Be-atom environments in the crystal structure. Crystal data for $Be_3(AsO_4)_2 \cdot 2H_2O$: M_r = 340.91, monoclinic, space group $C2/c$ (No. 15), a = 16.318(2) Å, b = 4.6664(3) Å, c = 9.8755(7) Å, β = 93.777(3)°, V = 750.37 Å^3, Z = 4. Final disagreement values of R = 3.59% and R_w = 3.79% were obtained for 1289 observed reflections with $I > 3\sigma(I)$.

INTRODUCTION

Molecular sieves containing tetrahedral 3-rings as part of their structures are currently of interest (1), and it has been suggested (2) that phases containing 3-rings as part of their three-dimensional structure may have a particularly low tetrahedral-framework atom density. The new aluminosilicate phase ZSM-18 (3) contains 3-rings of T atoms (T = Si, Al) and is notable as a large-pore material containing one-dimensional channels, which may have technologically valuable properties. The novel microporous beryllosilicate phase lovdarite (4) also contains 3-rings, as does a zincosilicate phase (5), which contains a framework subunit built up from three TO_4 units. Many possible topologies of 3-ring-containing structures have been recently elucidated (6).

We have previously described several materials containing various types of tetrahedral 3-rings in the (beryllo/zinco)(phosphate/arsenate) (Be/Zn)(P/As)O phase space (7), which are conveniently categorized according to their framework dimensionality. The *one-dimensional* chainions found in $Na_2ZnPO_4OH \cdot 7H_2O$ and synthetic berylloarsenate bearsite, $Be_2AsO_4OH \cdot 4H_2O$, contain tetrahedral 3-rings as part of their chain structures (8). The *two-dimensional* structures of the (nonisostructural) $CsH(ZnPO_4)_2$ and $NaH(ZnPO_4)_2$ contain "bridged" 3-rings as part of anionic Zn/P/O/H layers sandwiching cesium and sodium cations (9). Finally, the novel *three-dimensional* structure of $Zn_3(PO_4)(HPO_4)_2 \cdot HN_2C_6H_{12}$ contains similar "bridged" 3-rings, as part of its open, 8-ring channel-containing framework (10). Here, the term "bridged" 3-ring refers to the fact that one of the oxygen-atom T–O–T' bridges in the tetrahedral 3-ring is bonded to three neighboring tetrahedral atoms, compared to the usual two T-atom neighbors for other T–O–T' bridges (Fig. 1).

In this paper we describe the synthesis, characterization, and ^9Be MAS NMR spectrum of $Be_3(AsO_4)_2 \cdot 2H_2O$, a new beryllium arsenate hydrate phase, which also contains "bridged" 3-rings of BeO_4 and AsO_4 groups as part of its three-dimensional structure.

SYNTHESIS AND STRUCTURAL CHARACTERIZATION

The title compound was prepared by a high-temperature/high-pressure hydrothermal reaction: 0.087 g of $Be(OH)_2$, 0.3 ml of H_2O, and 0.644 g of 4M H_3AsO_4 solution were sealed in a gold tube and heated to 550°C for 135 hr in a Leco TemPres bomb. Upon cooling, numerous needle- and shard-like crystals were recovered from the mother liquor (pH = 2) by vacuum filtration. *Warning:* Beryllium and arsenic compounds are extremely toxic. Take all normal safety precautions in handling these materials, especially with respect to dust contamination.

The structure of $Be_3(AsO_4)_2 \cdot 2H_2O$ was determined by standard single-crystal X-ray methods (11). As-synthesized transparent $Be_3(AsO_4)_2 \cdot 2H_2O$ crystals are shard- or needle-like and have a maximum linear dimension of ~0.5 mm, and are indefinitely stable in air.

A suitable shard of $Be_3(AsO_4)_2 \cdot 2H_2O$ was selected and mounted on a thin glass fiber with cyanoacrylate adhesive, and room-temperature [25 (2)°C] intensity data were collected on a Huber automated 4-circle diffractometer (graphite-monochromated Mo$K\alpha$ radiation, λ = 0.71073

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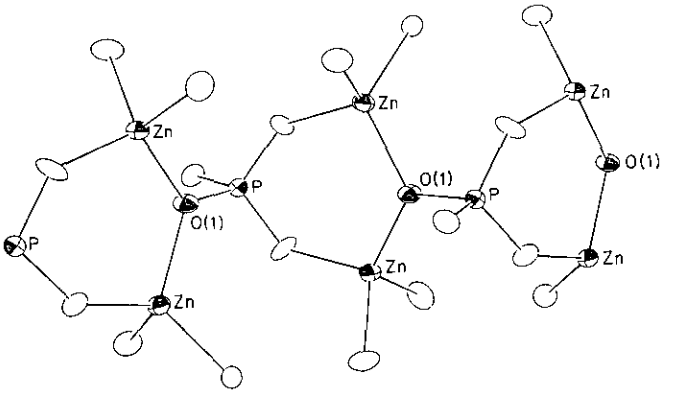

FIG. 1. Partial view of tetrahedral-Zn/P 3-rings linked via a "bridgehead" oxygen atom, O(1) in the three-dimensional phase $Zn_3(PO_4)(HPO_4)_2 \cdot HN_2C_6H_{12}$ (see text and Ref. (10)).

TABLE 1
Crystallographic Parameters for $Be_3(AsO_4)_2 \cdot 2H_2O$

Empirical formula	$As_2O_{10}Be_3H_4$
Formula wt.	340.91
Habit	Colorless shard
Crystal system	Monoclinic
a (Å)	16.318(2)
b (Å)	4.6664(3)
c (Å)	9.8755(7)
β(°)	93.777(3)
V (Å^3)	750.37
Z	4
Space group	$C2/c$ (No. 15)
T(°C)	25(1)
λ(Mo$K\alpha$) (Å)	0.71073
ρ_{calc} (g/cm^3)	3.02
μ(Mo$K\alpha$) (cm^{-1})	89.2
Absorption correction	DIFABS
hkl limits	±24, +7, +14
Total data	1609
Observed data[a]	1289
$R(F)$[b] (%)	3.59
$R_w(F)$[c] (%)	3.79

[a] $I > 3\sigma(I)$ after merging.
[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, with w_i as described in the text.

Å). After the locating and centering of 25 reflections, unit cell constants were optimized by least-squares refinement, resulting in monoclinic lattice parameters of a = 16.318(2) Å, b = 4.6664(3) Å, c = 9.8755(7) Å, β = 93.777(3)° (esd's in parentheses). Intensity data were collected in the θ-2θ scanning mode with standard reflections monitored for intensity variation throughout the course of the 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. The raw data were reduced using a Lehmann–Larsen profile-fitting routine (12) and the normal corrections for Lorentz and polarization effects were made. The systematic absences in the merged (R_{Int} = 5.1%), reduced data (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) indicated space groups Cc (No. 9) or $C2/c$ (No. 15).

The crystal structure of $Be_3(AsO_4)_2 \cdot 2H_2O$ was partially solved in space group $C2/c$ using the direct-methods program SHELXS-86 (13), and the centrosymmetric space group was assumed for the remainder of the crystallographic analysis. Other atom positions, including proton sites, were located from Fourier difference maps during the refinement procedure; after isotropic refinement, an empirical absorption correction (DIFABS) (14) was applied (minimum correction = 0.9, max. = 1.6). The final cycles of full-matrix least-squares refinement were against F and included anisotropic thermal factors (atom-type isotropic thermal factors for the protons) and a secondary extinction correction (15). Complex, neutral-atom scattering factors were obtained from the "International Tables" (16), and a 2-term Tukey–Prince weighting scheme (17) with Chebychev coefficients of 7.3(2) and 5.4(8) was applied to the data. Final residuals of R = 3.59% and R_w = 3.79% were obtained for the observed [$I > 3\sigma(I)$] data; for all data (1300 reflections), values of R = 3.62% and R_w = 3.79% resulted.

Hydrogen-atom positions were refined with bond distance [d(O–H) = 0.95(1) Å] and bond angle [θ(H–O–H) = 109(1)°] restraints. At the end of the refinement, analysis of the various trends in F_0 versus F_c revealed no unusual effects. The least-squares, Fourier, and subsidiary calculations were performed using the Oxford CRYSTALS system (18), running on a DEC Micro VAX 3100 computer. Supplementary tables of observed and calculated structure factors are available from the authors. Crystallographic data are summarized in Table 1.

^{9}Be MAS NMR data for the Be/As/O sample were collected on a Brücker/Nicolet NT-200 hybrid spectrometer system, at 28.12 MHz (field strength 4.0 T) with 785 acquisitions, using a 7 mm broadband MAS NMR probe from Doty Scientific, spinning at a speed of approximately 5 KHz. Data were collected in a single-pulse mode, with a 45° pulse length of 3 μsec and a recycle delay time of 60 sec. A broad singlet at −1.38 ppm is evident, as referenced to $2M$ $Be(NO_3)_2$ solution (downfield shifts defined as positive).

RESULTS

Final atomic positional and equivalent isotropic and anisotropic thermal parameters for $Be_3(AsO_4)_2 \cdot 2H_2O$ are listed in Table 2, with selected bond distance/angle data given in Table 3. The asymmetric unit and atom-labeling scheme of $Be_3(AsO_4)_2 \cdot 2H_2O$ are illustrated in Fig. 2. $Be_3(AsO_4)_2 \cdot 2H_2O$ is built up from BeO_4 and AsO_4 sub-

TABLE 2

Atomic Positional/Thermal Parameters for $Be_3(AsO_4)_2 \cdot 2H_2O$

Atom	x	y	z	U_{eq}[b]
Be(1)[a]	1/2	0.195(2)	1/4	0.0098
Be(2)	0.2528(3)	−0.056(1)	−0.1606(5)	0.0048
As(1)	0.34532(2)	0.05276(8)	0.09835(4)	0.0034
O(1)	0.4526(2)	0.4238(8)	0.3494(4)	0.0151
O(2)	0.3350(2)	−0.0772(7)	−0.0597(3)	0.0057
O(3)	0.4399(2)	−0.0159(8)	0.1646(4)	0.0103
O(4)	0.2764(2)	−0.1100(7)	0.1984(3)	0.0046
O(5)	0.3237(2)	0.4018(7)	0.0993(3)	0.0060
H(1)	0.474(8)	0.58(3)	0.40(1)	0.05(2)[c]
H(2)	0.419(7)	0.33(3)	0.41(1)	0.05(2)[c]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Be(1)	0.008(3)	0.013(3)	0.011(3)	0	0.003(2)	0
Be(2)	0.006(2)	0.003(2)	0.007(2)	−0.000(1)	0.001(2)	0.000(1)
As(1)	0.0032(2)	0.0035(2)	0.0036(2)	0.0004(1)	0.0000(1)	−0.0006(1)
O(1)	0.017(2)	0.017(2)	0.019(2)	−0.003(1)	0.009(1)	−0.006(1)
O(2)	0.007(1)	0.011(1)	0.003(1)	0.001(1)	0.0013(9)	−0.0017(9)
O(3)	0.008(1)	0.013(1)	0.021(2)	0.002(1)	−0.007(1)	−0.008(1)
O(4)	0.009(1)	0.006(1)	0.003(1)	−0.0014(9)	0.0037(9)	−0.0008(9)
O(5)	0.006(1)	0.006(1)	0.014(1)	0.0006(9)	0.007(1)	−0.000(1)

[a] Wyckoff site 4*e* (symmetry 2).
[b] $U_{eq}(Å^2) = (U_1U_2U_3)^{\frac{1}{3}}$.
[c] Atom-type U_{iso}.

units, as illustrated in Fig. 3 in polyhedral representation (19).

TABLE 3

Bond Distances (Å)/Angles (°) for $Be_3(AsO_4)_2 \cdot 2H_2O$

Be(1)–O(1)	1.674(7)	Be(1)–O(1)′	1.674(7)
Be(1)–O(3)	1.591(6)	Be(1)–O(3)′	1.591(6)
Be(2)–O(2)	1.621(6)	Be(2)–O(4)	1.667(6)
Be(2)–O(4)	1.660(6)	Be(2)–O(5)	1.593(6)
As(1)–O(2)	1.673(3)	As(1)–O(3)	1.668(3)
As(1)–O(4)	1.722(3)	As(1)–O(5)	1.667(3)
O(1)–H(1)	0.9(1)	O(1)–H(2)	0.9(1)
O(2) ··· H(2)[a]	1.8(1)		
O(1)–Be(1)–O(1)′	100.7(5)	O(3)–Be(1)–O(1)	114.4(2)
O(3)–Be(1)–O(1)′	112.1(2)	O(3)′–Be(1)–O(1)	112.1(2)
O(3)′–Be(1)–O(1)′	114.4(2)	O(3)–Be(1)–O(3)′	103.6(5)
O–Be(1)–O	109.6[5.9][b]		
O(4)–Be(2)–O(2)	107.0(3)	O(4)–Be(2)–O(2)	108.5(3)
O(4)–Be(2)–O(4)	109.0(3)	O(5)–Be(2)–O(2)	115.6(3)
O(5)–Be(2)–O(4)	106.7(3)·	O(5)–Be(2)–O(4)	109.8(3)
O–Be(2)–O	109.4[3.2][b]		
O(3)–As(1)–O(2)	109.3(2)	O(4)–As(1)–O(2)	110.3(1)
O(4)–As(1)–O(3)	108.2(2)	O(5)–As(1)–O(2)	110.6(2)
O(5)–As(1)–O(3)	112.1(2)	O(5)–As(1)–O(4)	106.3(1)
O–As(1)–O	109.5[2.0][b]		
As(1)–O(2)–Be(2)	125.4(3)	As(1)–O(3)–Be(1)	127.7(3)
Be(2)–O(4)–Be(2)′	123.1(2)	As(1)–O(4)–Be(2)	118.2(2)
As(1)–O(4)–Be(2)′	118.2(2)	As(1)–O(5)–Be(2)	127.9(3)

[a] H-bond contact.
[b] Average bond angle, with standard deviation in [ ], about central atom.

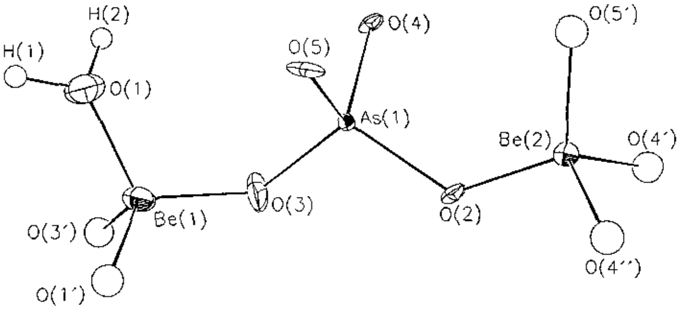

FIG. 2. Asymmetric unit of $Be_3(AsO_4)_2 \cdot 2H_2O$, showing the atom-labeling scheme: 50% thermal ellipsoids, arbitrary radii for H atoms.

This connectivity of tetrahedral nodes in $Be_3(AsO_4)_2 \cdot 2H_2O$ leads to a three-dimensional network, built up from infinite *bc*-plane layers of As(1) and Be(2) tetrahedral groups, which are linked together by the $Be(1)O_4$ groups. The As(1)/Be(2) layers (Fig. 4) are built up from infinite tetrahedral "bridged" 3- and 4-rings. The "backbone" of the layer is an edge-sharing chain of 4-rings, each of configuration –Be(2)–As(1)–Be(2)–As(1)–, which propagates in the **b**-direction. Adjacent 4-ring chains are fused together by 3-rings (configuration –Be(2)–As(1)–Be(2)–), which are fused edge-to-edge themselves, resulting in an infinite sheet structure. A notable feature of this connectivity is the fact that each Be(2) atom makes contact with *six* nearest-neighbor tetrahedral atoms [four distinct As(1)s and two distinct Be(2)s], and each As(1) atom bonds to *six* different Be(2) atoms, rather than the usual four nearest-neighbor *T* atoms, as found in zeolite molecular sieves.

Be(1) has two water-molecule oxygen atoms [atom O(1)] in its coordination sphere, and also makes two bonds to two different As atoms via O(3), with d_{av}(Be–O) = 1.633(4) Å. Be(2) makes four distinct bonds to As via O(2), O(4), O(4)′, and O(5) [d_{av}(Be–O) = 1.635(3) Å]. The tetrahedrally coordinated As(1) atom [d_{av}(As–O) = 1.683(2) Å] makes four As–O–Be bonds; an As(1)–O(3)–Be(1) bond and links to Be(2) via O(2), O(4), and O(5). The bridging oxygen atoms fall into two groups; O(2), O(3), and O(5) link adjacent Be and As species, as noted above, with θ_{av}(Be–O–As) = 127(1)°. O(4) bonds to three nearest-neighbor tetrahedral species; 2 × Be(2) and As(1), with the geometrical parameters listed in Table 3. Of the two protons attached to O(1), H(2) is involved in an H-bonding contact to O(2) [d(O ··· H) = 1.80(1) Å], while H(1) has no near neighbors.

Brown/Wu bond valence sum (BVS) values (20) accord with these bonding geometries; Be(1) has a BVS of 2.02, Be(2) is 2.00, and As(1) is 5.02 (expected values for Be and As = 2.00 and 5.00, respectively). The values for the O-atom species are O(1), neglecting protons 0.45; O(2), 1.81; O(3), 1.88; O(4), 2.02; and O(5), 1.88 (expected values 2.00). In this phase, it therefore appears that the 3-coordinated oxygen atom has a "typical" BVS value,

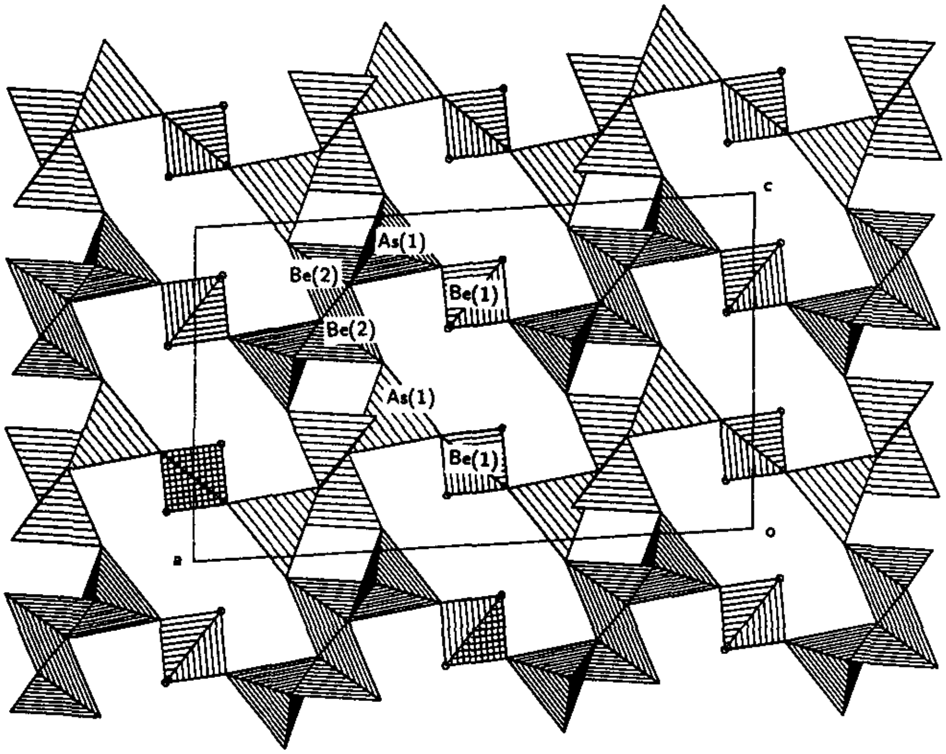

FIG. 3. Polyhedral plot of the crystal structure of $Be_3(AsO_4)_2 \cdot 2H_2O$, viewed down the **b**-direction, with some tetrahedra labeled. The "hanging" tetrahedral vertices of the interlayer $Be(1)O_4$ groups are occupied by water molecules (see text).

while the oxygen atoms which bridge two tetrahedral neighbors are slightly "underbonded." This situation is reversed in the layered phases $MH(ZnPO_4)_2$ (M = Cs, Na) (9), where the bridgehead (3-coordinate) oxygen atom appears to be somewhat "overbonded," with a BVS of ~2.2, compared to the typical value of ~2 for the other O atoms.

The ^9Be MAS NMR spectrum of $Be_3(AsO_4)_2 \cdot 2H_2O$ (Fig. 5) indicates that only one magnetically distinct Be atom site is observable at this resolution, even though there are two crystallographically distinct Be-atom sites in the structure. The chemical shift observed is in agreement with previous studies (21, 22). The observation of a single resonance may be rationalized by considering the consistent singular local environment (orthoberyllate group, BeO_4) of the Be atoms throughout the crystal, regardless of the fact that the next-nearest-neighbors are not equivalent. Similar instances have been documented in one-, two-, and three-dimensional systems containing BeO_4

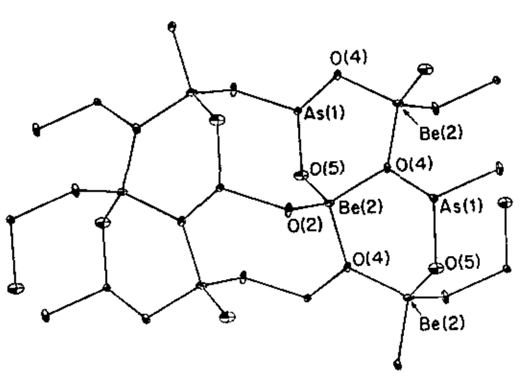

FIG. 4. ORTEP view of the Be(2)/As(1)-centered tetrahedral layers in the *bc*-plane of $Be_3(AsO_4)_2 \cdot 2H_2O$, showing the interlinked 3- and 4-rings of tetrahedra.

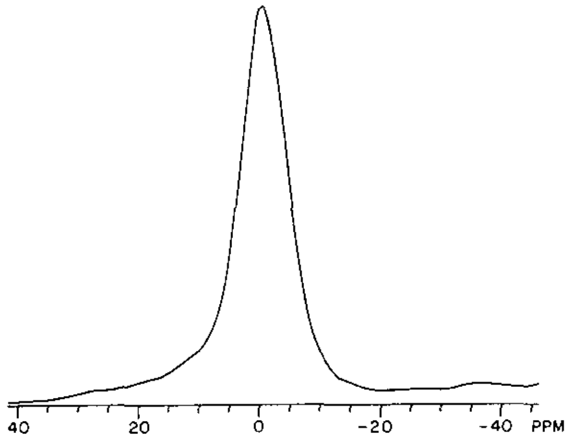

FIG. 5. ^9Be MAS NMR spectrum of $Be_3(AsO_4)_2 \cdot 2H_2O$, referenced to 2 M $Be(NO_3)_2$.

units (8, 21) and also by $^{31}P/^{9}Be$ MAS NMR studies of other beryllophosphate phases (22).

DISCUSSION

Rather similar sheet configurations to the three- and four-ring layers found in $Be_3(AsO_4)_2 \cdot 2H_2O$ have been found in the layered, anionic zincophosphate phases $CsH(ZnPO_4)_2$ and $NaH(ZnPO_4)_2$ (9). However, the precise nature of the tetrahedral-atom connectivity is different in each case; in $Be_3(AsO_4)_2 \cdot 2H_2O$, the 3-rings are fused with each other as described above. In $CsH(ZnPO_4)_2$, the tetrahedral 3-rings are joined "head to tail" and no two 3-rings share a common oxygen atom, while in $NaH(ZnPO_4)_2$, the 3-rings are isolated (from each other) and interlinked by tetrahedral 4-rings. Conversely, the one-dimensional phases $Na_2ZnPO_4OH \cdot 7H_2O$ and $Be_2AsO_4OH \cdot 4H_2O$ contain "true" (unbridged) tetrahedral 3-rings as part of their chain structures (8), although in these phases, hydroxide-ion bridges (i.e., Zn–(OH)–Zn and Be–(OH)–Be in $Na_2ZnPO_4OH \cdot 7H_2O$ and $Be_2AsO_4OH \cdot 4H_2O$, respectively) bonds replace the bridgehead 3-coordinate O atom found in $Be_3(AsO_4)_2 \cdot 2H_2O$.

In conclusion, the synthesis and structure of $Be_3(AsO_4)_2 \cdot 2H_2O$, a new beryllium arsenate hydrate phase, have been described. Like several other phases in the (Be/Zn)(P/As)O-structure field, this material contains tetrahedral 3-rings, although they are bridged or "fused," by way of a 3-coordinate oxygen atom which links the 3-ring group with another tetrahedral-atom center. By way of contrast, such tri-bridging oxygen atoms appear to be unknown in tetrahedral aluminosilicate structures. The non-1 : 1 Be : As ratio in $Be_3(AsO_4)_2 \cdot 2H_2O$ leads to a neutral "framework," as opposed to the typical anionic framework found in other BeAsO sieves (7), which suggests the possibility of synthesizing other three-dimensional, neutral BeAsO materials containing 3-rings. Efforts are now being made to that effect.

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