

Tetrahedral Networks Containing Beryllium: Syntheses and Structures of $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$

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Received February 24, 1999; in revised form April 21, 1999; accepted May 10, 1999

The hydrothermal syntheses and single crystal structures of $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ are described. These phases are built up from vertex-sharing tetrahedra, but their overall structures are quite different. In $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, BeO_4 , $\text{BeO}_2(\text{H}_2\text{O})_2$, and PO_4 groups build up a three-dimensional structure via Be–O–P and Be–O–Be bonds, resulting in tetrahedral 3- and 4-rings. $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ is layered and contains 6-rings of $\text{BeO}_3(\text{H}_2\text{O})$ and HAsO_4 building blocks fused via Be–O–As bonds. Similarities and differences to some other tetrahedral structures are discussed. Crystal data: $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $M_r = 253.01$, monoclinic, space group $C2/c$ (No. 15), $a = 15.9640(6) \text{ \AA}$, $b = 4.5842(2) \text{ \AA}$, $c = 9.5320(4) \text{ \AA}$, $\beta = 94.366(2)^\circ$, $V = 695.6(2) \text{ \AA}^3$, $Z = 4$, $R(F) = 3.79\%$, $R_w(F) = 4.44\%$ [812 reflections with $I > 2\sigma(I)$]. $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$, $M_r = 166.95$, orthorhombic, space group $Pca2_1$ (No. 29), $a = 9.7471(2) \text{ \AA}$, $b = 4.6794(1) \text{ \AA}$, $c = 8.5929(1) \text{ \AA}$, $V = 391.93(9) \text{ \AA}^3$, $Z = 4$, $R(F) = 3.93\%$, $R_w(F) = 4.32\%$ [795 reflections with $I > 2\sigma(I)$]. © 1999 Academic Press

INTRODUCTION

Nonaluminosilicate open framework phases are of significant current interest (1). Although beryllium has been recognised as being a suitable cation for tetrahedral framework structures (2, 3), its chemistry remains relatively unexplored, perhaps in part due to its high toxicity. Berylllophosphate (BePO) analogues of aluminosilicate zeolites include phases crystallising with the ABW (4), SOD (5), FAU (6), LOS (7), and RHO (2) topologies, where these three-letter codes are the International Zeolite Association official framework descriptors (8). As yet, the BPH (9) topology is only adopted by a BePO phase, with the sodium and potassium guest cations appearing to play a co-templating role. Beryllloarsenate (BeAsO) analogues of zeolites include the ABW (3), SOD (5), and RHO (3) frameworks. Two notable mineral berylllophosphates include the cancrinite-type tiptopite (10) and pahasapaite (11), a zeolite RHO type framework. As yet, only one organically templated berylllophosphate,

$(\text{N}_2\text{C}_6\text{H}_{13})_2 \cdot \text{Be}_4(\text{PO}_4)_2(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$, has been reported (12).

Here, we report the hydrothermal syntheses and single-crystal structures of $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$. These phases are built up from vertex-sharing tetrahedra, but their overall structures are quite different: the phosphate is three-dimensional and the arsenate is layered. These phases are briefly compared and contrasted to related compounds.

EXPERIMENTAL

Synthesis

$\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. A small gold tube (2 1/4" × 1/4") was loaded with 0.038 g BeO (1.5 mmol) and 0.60 g 4 M H_3PO_4 (2 mmol) and welded closed. The tube was heated in a Tempres apparatus to 600°C for 14 hours (estimated pressure 30,000 psi) and then cooled slowly to 300°C over a period of 40 hours. Recovery of the product (pH 1) yielded 0.053 g (42% based on Be) of small sparkling lath-tablets suitable for structure determination.

$\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$. The reactants, 6.98 g 2 M $\text{Be}(\text{NO}_3)_2$ (12 mmol), 4.74 g 4 M H_3AsO_4 (14 mmol), and 5.74 g 4 M NaOH (20 mmol) were sealed into a Teflon pouch and heated in a stainless steel autoclave (external support fluid = water) for three days at 195°C and autogenous pressure (about 200 psi). After cooling and recovery of the product, 1.437 g (72% yield, based on Be) of clear, small plates were obtained. *Warning!* Take all appropriate safety precautions when working with beryllium and arsenic containing materials, especially with respect to dust contamination.

Structure Determinations

A crystal of $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (dimensions 0.37 × 0.13 × 0.10 mm) was mounted on a thin glass fiber with cyanoacrylate adhesive, and room-temperature [$25 \pm 2^\circ\text{C}$] intensity measurements were made with a Siemens SMART CCD

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TABLE 1
Crystallographic Parameters

	Be ₃ (PO ₄) ₂ · 2H ₂ O	Be(HAsO ₄) · H ₂ O
Empirical formula	P ₂ O ₁₀ Be ₃ H ₄	AsO ₅ BeH ₃
Formula weight	253.01	166.95
Crystal system	Monoclinic	Orthorhombic
<i>a</i> (Å)	15.9640(6)	9.7471(2)
<i>b</i> (Å)	4.5842(2)	4.6794(1)
<i>c</i> (Å)	9.5320(4)	8.5929(1)
α (°)	90	90
β (°)	94.366(2)	90
γ (°)	90	90
<i>V</i> (Å ³)	695.5(2)	391.93(5)
<i>Z</i>	4	4
Space group	<i>C2/c</i> (No. 15)	<i>Pca2₁</i> (No. 29)
<i>T</i> (°C)	25 ± 2	25 ± 2
λ (MoK α) (Å)	0.71073	0.71073
ρ_{calc} (g/cm ³)	2.42	2.83
μ (cm ⁻¹)	6.49	85.38
Reflections measured	3853	3989
<i>R</i> _{int}	0.048	0.060
Significantly intense reflections ^a	812	795
Parameters	70	66
<i>R</i> (<i>F</i>) ^b	3.79	3.93
<i>R</i> _w (<i>F</i>) ^c	4.44	4.32

^a*I* > 2 σ (*I*) after the merging of systematically equivalent and multiply-measured reflections.

^b*R* = 100 × $\sum(|F_o| - |F_c|) / \sum|F_o|$

^c*R*_w = 100 × $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ with *w_i* as described in the text.

area-detector diffractometer as outlined in Table 1. The application of preliminary cell determination routines led to a *C*-centred monoclinic unit cell. Intensity data were collected in narrow-slice ω -scan mode (13), resulting in 3853 measured intensities for 4° ≤ 2 θ ≤ 55°. Data merging resulted in 842 unique reflections (*R*_{int} = 0.048) of which 812 were considered observed according to the criterion *I* > 2 σ (*I*). Absorption and incident beam decay corrections were applied on the basis of multiple and symmetry-equivalent reflections (14), with a resulting correction factor range of 0.67–1.00. The systematic absences indicated space groups *Cc* or *C2/c*.

A similar data collection protocol for Be(HAsO₄) · H₂O was carried out, as summarised in Table 1: rectangular plate 0.20 × 0.13 × 0.03 mm, primitive orthorhombic cell, ω -scan width = 0.3°, 3989 measured intensities (4° ≤ 2 θ ≤ 55°), 952 unique reflections (*R*_{int} = 0.060), 795 with *I* > 2 σ (*I*), empirical absorption correction factor range of 0.60–1.00. The systematic absences indicated space groups *Pca2₁* or *Pcam*.

Direct methods (15) established enough of each structure (P or As, and some O atoms) to enable the remaining nonhydrogen atoms to be located from difference maps without difficulty. For Be₃(PO₄)₂ · 2H₂O, a satisfactory solution was obtained in the centrosymmetric space group

C2/c (No. 15). For Be(HAsO₄) · H₂O, no model could be established in *Pcam*, and space group *Pca2₁* (No. 29) was assumed. For Be₃(PO₄)₂ · 2H₂O, the two distinct hydrogen atoms were located from difference maps and refined by riding on their O atom. These atoms were refined in their as-found locations, resulting in slightly different final O–H bond lengths. No H atoms could be located for Be(HAsO₄) · H₂O. The final cycles of full-matrix least-squares refinement (program CRYSTALS (16)), minimised the function $\sum w_i(F_o - F_c)^2$, with *w_i* described by a three-term Chebychev polynomial (17), and included anisotropic temperature factors for all the nonhydrogen atoms and a Larson-type secondary extinction correction (18). Refinement of the Flack absolute structure parameter (19) for Be(HAsO₄) · H₂O to 0.13 (3), where the number in parentheses represents the standard uncertainty derived from the least-squares process, suggested some degree of merohedral twinning. Anisotropic thermal factors will be deposited in an online database. Tables of observed and calculated structure factors are available from the authors.

RESULTS

Crystal Structure of Be₃(PO₄)₂ · 2H₂O

Final atomic positional and thermal parameters are listed in Table 2, with selected bond distance/angle data in Table 3. Be₃(PO₄)₂ · 2H₂O is a new beryllium phosphate hydrate based on a network of tetrahedral BeO₄ and PO₄ groups. The crystal structure of Be₃(PO₄)₂ · 2H₂O is shown in Fig. 1 with ORTEP-3 (20).

Be1 (site symmetry 2) makes two Be–O–P linkages to nearby phosphorus atoms and has two terminal Be–OH₂ links (*d*_{av}(Be1–O) = 1.633(2) Å). Be2 makes four bonds to P atoms with *d*_{av}(Be2–O) = 1.635(2) Å. P1 forms the centre of a phosphate group with *d*_{av}(P1–O) = 1.535(1) Å and

TABLE 2
Atomic Coordinates/Displacement Parameters for Be₃(PO₄)₂ · 2H₂O

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Be1	0	0.1924(7)	0.75	0.0118
Be2	0.25148(14)	0.5501(4)	0.8425(2)	0.0084
P1	0.15525(2)	0.04667(9)	0.89645(4)	0.0069
O1	0.06622(8)	−0.0139(3)	0.83553(14)	0.0151
O2	0.17532(8)	0.3698(3)	0.89376(13)	0.0111
O3	0.16755(8)	−0.0784(3)	1.04505(12)	0.0097
O4	0.21878(7)	−0.1110(3)	0.80262(11)	0.0092
O5	−0.04551(9)	0.4218(3)	0.85720(15)	0.0192
H1	−0.0853	0.3399	0.9039	0.02 ^b
H2	−0.0644	0.5824	0.8067	0.02 ^b

^a*U*_{eq} (Å²) = 1/3[*U*₁ + *U*₂ + *U*₃].

^b*U*_{iso} (Å²) not refined.

TABLE 3
Selected Bond Distances (Å) and Angles (°) for $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

Be1–O1 × 2	1.595(2)	Be1–O5 × 2	1.671(2)
Be2–O2	1.578(2)	Be2–O3	1.620(2)
Be2–O4	1.673(2)	Be2–O4	1.669(2)
P1–O1	1.519(2)	P1–O2	1.516(2)
P1–O3	1.527(2)	P1–O4	1.578(2)
O5–H1	0.89	O5–H2	0.92
H1–O3	1.87 ^a		
O1–Be1–O1	107.3(2)	O1–Be1–O5	111.27(7)
O1–Be1–O5	112.56(7)	O5–Be1–O5	102.0(2)
O2–Be2–O3	115.6(2)	O2–Be2–O4	108.8(2)
O3–Be2–O4	107.2(2)	O2–Be2–O4	107.4(2)
O3–Be2–O4	108.7(2)	O4–Be2–O4	109.0(2)
O1–P1–O2	111.40(8)	O1–P1–O3	109.67(7)
O2–P1–O3	111.72(7)	O1–P1–O4	108.82(7)
O2–P1–O4	106.99(7)	O3–P1–O4	108.13(7)
Be1–O1–P1	130.6(2)	Be2–O2–P1	133.3(2)
Be2–O3–P1	128.6(2)	Be2–O4–Be2	119.7(1)
Be2–O4–P1	120.0(1)	Be2–O4–P1	120.2(1)

^aHydrogen bond.

makes four P–O–Be bonds. The five distinct oxygen atoms divide into three Be–O–P bridges (O1 to O3 with $\theta_{\text{av}} = 130.8^\circ$), one trigonal O4 atom (to 2 Be + 1 P), and one terminal Be–O5H₂ vertex. O4 and its three neighbours are almost exactly planar, and rather long Be–O and P–O bonds result for this atom (Table 3). Bond valence sum (BVS) data for Be1 (2.04), Be2 (2.03), and P1 (5.00) are in

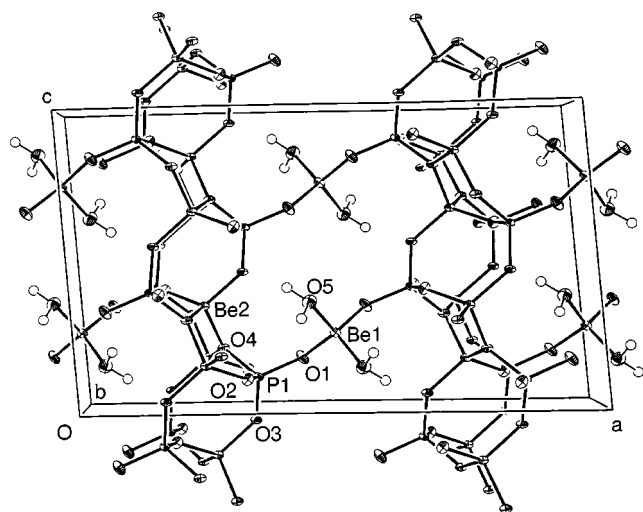


FIG. 1. View down [010] of the $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ crystal structure (50% thermal ellipsoids).

excellent agreement with the expected values of 2.00 for Be and 5.00 for P (21). The trigonally coordinated O4 also satisfies its valence (calculated 2.03, expected 2.00).

The polyhedral connectivity in $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ results in sheets of Be_2O_4 and PO_4 tetrahedra arrayed in the [011] plane. Because of the presence of 3-coordinated O4 atoms, the sheets (Fig. 2) contain “fused” tetrahedral 3-rings (nodes: 2 Be + 1 P) and 4-rings (2 Be + 2 P). Infinite, contorted–O–Be–O–Be–O– chains propagate in the [010] direction. The P–O1 vertex projects from the these sheets and bonds to Be1. Thus, the sheets are linked together along [100] into a three-dimensional framework by the $\text{Be}_1\text{O}_2(\text{H}_2\text{O})_2$ groups (Fig. 1). A hydrogen bonding link, as $\text{Be–O5–H1} \cdots \text{O3}$ ($d(\text{H} \cdots \text{O}) = 1.87 \text{ \AA}$, $d(\text{O} \cdots \text{O}) = 2.724(2) \text{ \AA}$) also stabilises the intersheet packing.

Crystal Structure of $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$

Final atomic positional and thermal parameters are listed in Table 4, with selected geometrical data in Table 5. $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ is a new beryllium hydrogen arsenate hydrate based on layers of tetrahedral BeO_4 and AsO_4 groups. The $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ structure is shown in Figures 3 and 4.

Be1 makes three Be–O–As linkages to nearby arsenic atoms and has one terminal Be–OH₂ bond ($d_{\text{av}}(\text{Be1–O}) = 1.625(8) \text{ \AA}$). As1 forms the centre of a hydrogen arsenate group with $d_{\text{av}}(\text{As1–O}) = 1.686(4) \text{ \AA}$ and makes three As–O–Be bonds. BVS data for Be1 (2.08) and As1 (4.99) are typical. The five distinct oxygen atoms thus divide into three Be–O–As bridges ($\theta_{\text{av}} = 126.2^\circ$), an As–O3H, and a Be–O1H₂ vertex.

The polyhedral connectivity in $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ results in a layered structure based on tetrahedral 6-rings

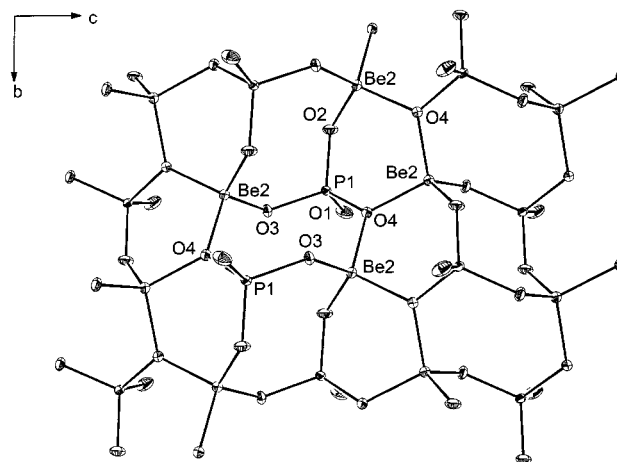


FIG. 2. View down [100] of a fragment of the $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ structure, showing the infinite network of “fused” tetrahedral 3- and 4-rings.

TABLE 4
Atomic Coordinates/Displacement Parameters for
 $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$

Atom	x	y	z	U_{eq}^a
Be1	0.9550(8)	0.3778(12)	0.275(1)	0.0099
As1	0.97643(4)	0.11406(7)	-0.03030(15)	0.0075
O1	0.8062(5)	0.5087(9)	0.2220(5)	0.0204
O2	0.9437(5)	0.3691(8)	-0.1618(5)	0.0147
O3	0.8238(5)	-0.0576(8)	0.0056(5)	0.0174
O4	1.0857(4)	-0.1376(7)	-0.0955(5)	0.0129
O5	1.0408(4)	0.2444(9)	0.1349(5)	0.0147

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

(Fig. 4), which stack along [100]. Strict alternation of Be- and As-centred tetrahedra occurs, and only Be–O–As bonds link the tetrahedral centres together. The Be–OH₂ and As–OH bonds project into the interlayer region. Hydrogen atoms were not located in the present experiment, but interlayer H bonds are probably present, based on several O1...O and O3...O contacts shorter than 3.0 Å.

DISCUSSION

Two new tetrahedral-network phases containing beryllium, $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$, have been prepared as single crystals and structurally characterised by X-ray methods. They consist of the typical polyhedral units of BeO_4 and XO_4 ($X = \text{P}, \text{As}$) tetrahedra, sharing vertices (1). Their structures differ significantly: $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is a three-dimensional phase containing both Be–O–Be and Be–O–P links, whereas $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ is layered and only contains Be–O–As bonds. The phosphate contains

TABLE 5
Selected Bond Distances (Å) and Angles (°) for $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$

Be1–O1	1.640(9)	Be1–O2	1.635(9)
Be1–O4	1.630(8)	Be1–O5	1.593(9)
As1–O2	1.674(4)	As1–O3	1.719(4)
As1–O4	1.684(4)	As1–O5	1.667(5)
O1–Be1–O2	110.9(4)	O1–Be1–O4	103.4(5)
O2–Be1–O4	114.9(6)	O1–Be1–O5	113.6(6)
O2–Be1–O5	102.6(5)	O4–Be1–O5	111.9(4)
O2–As1–O3	106.8(2)	O2–As1–O4	113.3(2)
O3–As1–O4	106.3(2)	O2–As1–O5	112.7(2)
O3–As1–O5	110.1(2)	O4–As1–O5	107.5(2)
Be1–O2–As1	128.7(4)	Be1–O4–As1	123.7(4)
Be1–O5–As1	126.1(4)		

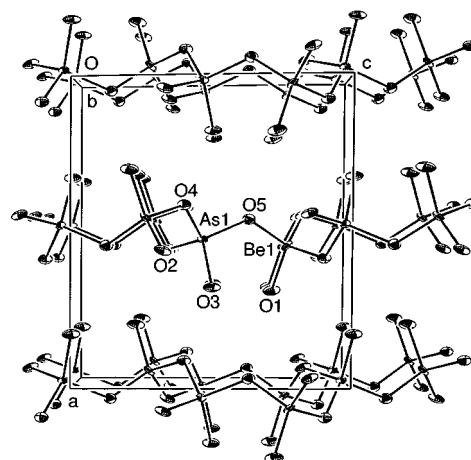


FIG. 3. View down [010] of the $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ crystal structure (50% thermal ellipsoids).

tetrahedral 3-rings and 4-rings, whereas the arsenate contains 6-rings. Both phases contain “dangling” terminal Be–OH₂ bonds.

$\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is isostructural with $\text{Be}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (22). Apart from the expected difference in P–O and As–O bond lengths, there is little structural disparity between these two phases. The average Be–O–As bond angle of 127.0° in $\text{Be}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ is some 3.8° less than the corresponding Be–O–P angle in $\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. $\text{Be}_2(\text{OH})\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (23) and $\text{Be}_2(\text{OH})\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (24) represent another isostructural pair of beryllium phosphates/arsenates. These materials contain interesting one-dimensional $[\text{Be}_2(\text{OH})\text{XO}_4]$ chains built up from tetrahedral 3- and 4-rings.

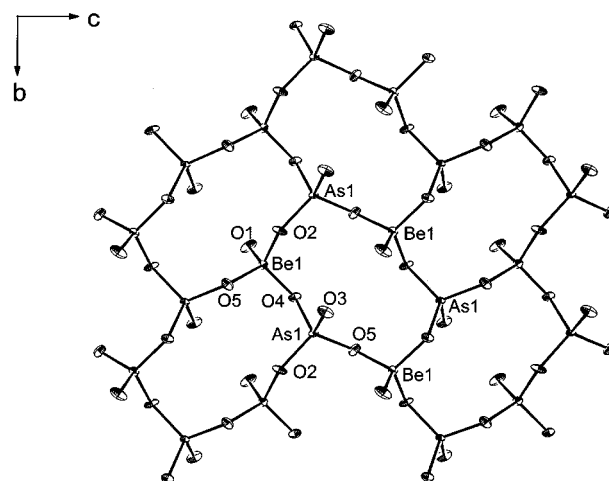


FIG. 4. View down [100] of a fragment of the $\text{Be}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$ crystal structure, showing the infinite network of 6-rings.

Be(HAsO₄)·H₂O adopts a new layered structure type. The connectivity of tetrahedra into 6-rings, with three in-layer linkages, and one terminal bond (either Be–OH₂ or As–OH) can be described topologically as a 6³ hexagonal net (25). In Be(HAsO₄)·H₂O, the fourth vertex of each tetrahedron may point either “up” or “down,” approximately along [100]. We assume that these out-of-plane links serve to fuse the sheets into a three-dimensional structure by way of intersheet O–H···O hydrogen bonds. There is one distinct 6-ring in Be(HAsO₄)·H₂O which may be classified following Smith (26) as type *SCCSCC* where *S* refers to a hexagonal node having its adjacent node pointing the same direction (both up or both down) and *C* refers to the adjacent nodes changing direction (one up, one down). When the intersheet links are through *T–O–T* bonds (*T* = tetrahedral atom), rather than via H bonds, the three-dimensional monoclinic Ca(SiAlO₄)₂ structure (27) results.

ACKNOWLEDGMENT

We thank the National Science Foundation (Grant DMR 95-20971) for partial funding.

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