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Acta Cryst. (1995). C**51**, 181–183

Lithium Berylloarsenate Hydrate, $LiBeAsO_4.H_2O$

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(*Received* 4 *August* 1994; *accepted* 1 *September* 1994)

Abstract

The full structure of lithium berylloarsenate hydrate, $LiBeAsO_4.H_2O$, as refined using X-ray powder data, is reported. This phase is briefly compared with other known Li–*A*-type materials.

Comment

Open-framework tetrahedrally connected berylloarsenates are part of the growing family of Group 2/12/15 (Be/Zn)(P/As) molecular sieves (Gier & Stucky, 1991; Harrison, Nenoff, Gier & Stucky, 1993). Berylloarsenate isostructures of zeolite rho (Parise *et al.*, 1992) and sodalite (Gier, Harrison & Stucky, 1991; Harrison, Gier & Stucky, 1994) have been described previously.

Lithium berylloarsenate hydrate is confirmed to be an aluminosilicate Li–*A*-type isostructure (Gier & Stucky, 1991). The Li–*A*-type framework topology has been described fully by Smith (1988) and consists of an open three-dimensional array built up from four, six and eight rings, enclosing one-dimensional channels, which propagate in the polar [001] direction. Like other known Li–*A*-type phases, $LiBeAsO_4.H_2O$ shows complete 1:1

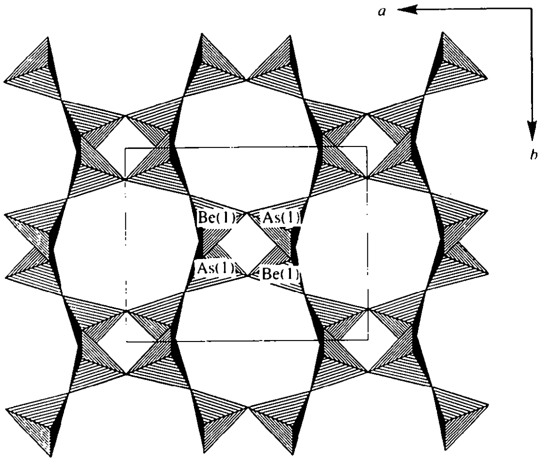

Fig. 1. Polyhedral view down [001] of the $LiBeAsO_4.H_2O$ framework structure, showing the ordered alternating BeO_4 and AsO_4 units.

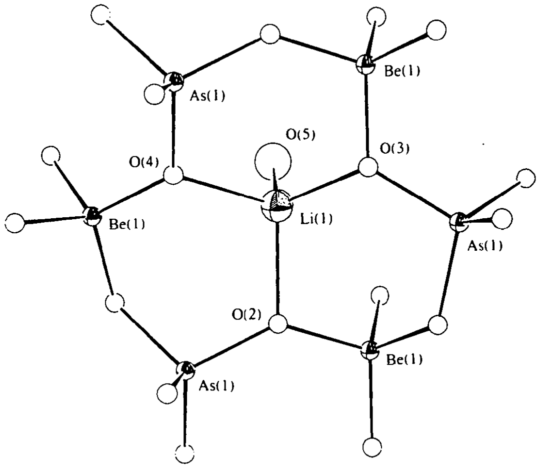

Fig. 2. View showing detail of the six-ring window environment in $LiBeAsO_4.H_2O$. The Li^+ cation makes three bonds to framework O atoms and a fourth tetrahedral vertex to the water molecule [atom O(5)], occupying the central region of the main [001] channel (arbitrary atomic radii).

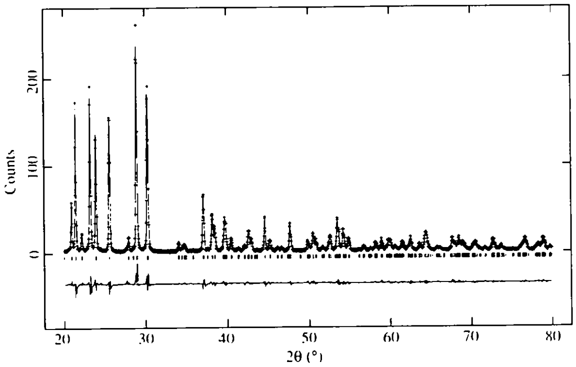

Fig. 3. Final observed (crosses), calculated (line) and difference profiles for the Rietveld refinement of the structure of $LiBeAsO_4.H_2O$. Allowed reflection positions are indicated by tick marks.

ordering of Be and As, and Be/As alternation over adjacent tetrahedral nodes, connected by Be—O—As bonds. Be—O and As—O bond lengths and angles (Table 2) are typical of the chemical species concerned [average Be—O = 1.618 (7), average As—O = 1.689 (6) Å] and compare well with those of other berylloarsenate phases (Harrison, Gier & Stucky, 1994). Brese–O'Keefe bond-valence sum (BVS) calculations (Brese & O'Keefe, 1991) give BVS(Be) = 2.11 (3) (expected 2.00) and BVS(As) = 4.94 (4) (expected 5.00). The BeO_4 tetrahedron [average O—Be—O = 109.4°, s.d. of individual angles about mean = 4.5°] is slightly more distorted than the AsO_4 moiety [average O—As—O = 109.5, s.d. = 2.3°]. For the framework O atoms, O(1) bridges As and Be atoms; O(2), O(3) and O(4) bond to As, Be and Li [average As—O—Be = 130.4, s.d. = 8.0°; average Li—O—Be = 110.6, s.d. = 4.4°; average As—O—Li = 117.7, s.d. = 2.1°].

Unlike $LiAlSiO_4.H_2O$ (Kerr, 1974) in which the Li^+ species occupies two disordered sites near the six-ring window, in $LiBeAsO_4.H_2O$ the Li^+ cation is ordered, as was also found for the lithium species in $LiZnPO_4.H_2O$ (Harrison, Gier, Nicol & Stucky, 1995). In $LiBeAsO_4.H_2O$, the Li^+ cation occupies a site near a framework six-ring and makes three Li—O bonds to framework O atoms and a fourth vertex to an extra-framework water molecule [O atom O(5)], completing a distorted tetrahedron [average Li—O = 1.95 (3) Å, average O—Li—O = 109.3, s.d. = 4.5°]. The water molecule occupies the central region of the main eight-ring channel. Although proton positions were not located in this X-ray study of $LiBeAsO_4.H_2O$, the water-molecule O atom [O(5)] occupies a similar site to the corresponding atom in $LiZnPO_4.H_2O$ (Harrison, Gier, Nicol & Stucky, 1995). In the study of $LiZnPO_4.H_2O$, the proton sites were located and refined using powder neutron diffraction data. This suggests that the hydrogen-bonding scheme, which links water molecules along the main eight-ring channel, is similar for the two phases. This structural study complements that of the gallosilicate Li–*A*-type phase $LiGaSiO_4.H_2O$ (Newsam, 1986), where an ordered Li^+ cation and in-channel hydrogen-bonding scheme were also observed.

The structure of $LiBeAsO_4.H_2O$ is illustrated in Figs. 1 and 2.

Experimental

The title compound was prepared by mild-condition hydrothermal reaction, as described previously (Gier & Stucky, 1991). A pure crystalline white powder was produced which was suitable for full structure determination by the Rietveld method (Rietveld, 1969).

Crystal data

$LiBeAsO_4.H_2O$	$Z = 4$
$M_r = 172.89$	$D_x = 2.934$ Mg m^{-3}
Orthorhombic	Cu $K\alpha$ radiation
$Pna2_1$	$\lambda = 1.54178$ Å
$a = 10.0416 (4)$ Å	$\mu = 11.14$ mm^{-1}
$b = 8.0285 (3)$ Å	$T = 298 (2)$ K
$c = 4.8553 (2)$ Å	White
$V = 391.43 (4)$ Å^3	

Data collection

Scintag PAD-X powder diffractometer	1499 data points in the processed diffractogram
θ/θ powder scans	$2\theta_{\min} = 20$, $2\theta_{\max} = 80°$
Absorption correction: none	Wavelength of incident radiation: 1.54178 Å

Refinement

Refinement on powder data points	$(\Delta/\sigma)_{\max} < 0.01$
$R_p = 0.073$	$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$R_{wp} = 0.098$	$\Delta\rho_{\min} = -0.29$ e Å^{-3}
$R_{\rm exp} = 0.041$	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)
294 reflections	
40 parameters	
$w = 1/\sigma^2(y)$	

Table 1. *Fractional atomic coordinates and isotropic displacement parameters* (Å^2)

	x	y	z	$U_{\rm iso}$
Be(1)	0.1518 (16)	0.102 (2)	0.333 (3)	0.0058 (9)
As(1)	0.34704 (18)	0.4026 (3)	0.331 (3)	0.0058 (9)
Li(1)	0.176 (3)	0.292 (4)	−0.155 (13)	0.01
O(1)	0.0013 (10)	0.1634 (13)	0.266 (3)	0.007 (3)
O(2)	0.2388 (11)	0.2578 (14)	0.210 (3)	0.007 (3)
O(3)	0.1838 (11)	0.0812 (17)	0.657 (2)	0.007 (3)
O(4)	0.1839 (11)	−0.0664 (14)	0.171 (2)	0.007 (3)
O(5)	0.5023 (8)	0.0904 (12)	0.827 (4)	0.015 (4)

Table 2. *Geometric parameters* (Å, °)

Be(1)—O(1)	1.623 (12)	As(1)—O(3$^{\rm ii}$)	1.694 (12)
Be(1)—O(2)	1.640 (12)	As(1)—O(4$^{\rm iii}$)	1.698 (10)
Be(1)—O(3)	1.613 (13)	Li(1)—O(2)	1.90 (7)
Be(1)—O(4)	1.594 (12)	Li(1)—O(3$^{\rm iv}$)	1.93 (4)
As(1)—O(1$^{\rm i}$)	1.667 (10)	Li(1)—O(4$^{\rm v}$)	2.00 (4)
As(1)—O(2)	1.698 (12)	Li(1)—O(5$^{\rm vi}$)	1.99 (3)
O(1)—Be(1)—O(2)	100.9 (10)	O(2)—Li(1)—O(5$^{\rm vi}$)	113.7 (31)
O(1)—Be(1)—O(3)	114.2 (11)	O(3$^{\rm iv}$)—Li(1)—O(4$^{\rm v}$)	105.7 (27)
O(1)—Be(1)—O(4)	110.4 (11)	O(3$^{\rm iv}$)—Li(1)—O(5$^{\rm vi}$)	115.5 (22)
O(2)—Be(1)—O(3)	109.1 (11)	O(4$^{\rm v}$)—Li(1)—O(5$^{\rm vi}$)	109.3 (19)
O(2)—Be(1)—O(4)	111.1 (11)	Be(1)—O(1)—As(1$^{\rm vii}$)	137.0 (9)
O(3)—Be(1)—O(4)	110.8 (10)	Be(1)—O(2)—As(1)	137.6 (9)
O(1$^{\rm i}$)—As(1)—O(2)	108.2 (5)	Be(1)—O(2)—Li(1)	105.9 (11)
O(1$^{\rm i}$)—As(1)—O(3$^{\rm v}$)	110.2 (5)	As(1)—O(2)—Li(1)	115.8 (11)
O(1$^{\rm i}$)—As(1)—O(4$^{\rm iii}$)	113.6 (6)	Be(1)—O(3)—As(1$^{\rm viii}$)	122.5 (9)
O(2)—As(1)—O(3$^{\rm v}$)	106.8 (5)	Be(1)—O(3)—Li(1$^{\rm ix}$)	111.5 (21)
O(2)—As(1)—O(4$^{\rm iii}$)	108.7 (6)	As(1$^{\rm viii}$)—O(3)—Li(1$^{\rm ix}$)	120.0 (19)
O(3$^{\rm v}$)—As(1)—O(4$^{\rm iii}$)	109.2 (5)	Be(1)—O(4)—As(1$^{\rm x}$)	124.5 (8)
O(2)—Li(1)—O(3$^{\rm iv}$)	107.5 (19)	Be(1)—O(4)—Li(1$^{\rm viii}$)	114.5 (18)
O(2)—Li(1)—O(4$^{\rm v}$)	104.2 (19)	As(1$^{\rm x}$)—O(4)—Li(1$^{\rm viii}$)	117.2 (19)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iv) $x, y, z-1$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (vi) $x-\frac{1}{2}, \frac{1}{2}-y, z-1$; (vii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (viii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (ix) $x, y, 1+z$; (x) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$.

The $LiBeAsO_4.H_2O$ crystal structure was optimized by X-ray Rietveld refinement (Rietveld, 1969) following a similar procedure to that described by Harrison, Gier & Stucky

(1994). A white powder sample of $LiBeAsO_4.H_2O$ was carefully packed into a 2 × 1 cm flat-plate sample holder and mounted horizontally in air. Unfiltered Cu $K\alpha$ radiation (λ = 1.54178 Å) was used to collect the step-scan diffraction data. No monochromation was used.

Starting unit-cell parameters were obtained by unit-cell powder refinements and starting atomic coordinates were obtained from the structure determination of $LiZnPO_4.H_2O$ (Harrison, Gier, Nicol & Stucky, 1995) with Be substituting for Zn and As replacing P. Proton positions were not included in the structural model, and Be—O bond-distance restraints [Be—O = 1.63 (2) Å] were used to stabilize the refinement. The relative weight of these extra observations was progressively reduced as the model converged. The Rietveld refinement progressed smoothly, with the usual profile parameters (scale factor, zero-point error, pseudo-Voigt peak-width variation parameters, six-term Fourier-cosine series background coefficients, unit-cell parameters) treated as least-squares variables in the usual fashion. Refined peak-shape descriptors of GU = 0, GV = 0, GW = 19.2 (7), LX = 2.0 (3) and LY = 16.4 (9) resulted. Refined background coefficients were 3.2 (5), 0.8 (5), −4 (2), 7 (3), −5 (2) and 2.1 (5). All atom positions and isotropic displacement factors [$U_{\rm iso}$(Li) fixed at 0.01 Å^2] were refined subject to the constraints $U_{\rm iso}$(Be) = $U_{\rm iso}$(As) and an atom-type $U_{\rm iso}$ for the framework O atoms. No corrections for preferred orientation, extinction or absorption were applied.

Program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976) and *STRUPLO* (Fischer, 1985).

We thank the National Science Foundation and Office of Naval Research for partial financial support.

Lists of raw power data and complete geometry have been deposited with the IUCr (Reference: BR1093). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 183–185

Strontium Dibromide Hexahydrate

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(*Received* 6 *July* 1994; *accepted* 19 *September* 1994)

Abstract

The structure of $SrBr_2.6H_2O$ has been solved by single-crystal X-ray analysis. Each Sr atom has tricapped trigonal prismatic coordination geometry involving six bridging and three terminal water molecules. The bridging arrangement results in a linear polymeric cation $[Sr(H_2O)_6]_n^{2n+}$ with charges balanced by Br^- ions in the lattice.

Comment

The title compound is readily crystallized from hot solutions of Sr^{2+} in HBr and is often formed as an impurity in the preparation of binary metal bromides. Several crystallographic studies of anhydrous (Sass, Brackett & Brackett, 1963; Smeggil & Eick, 1971) and monohydrated (Dyke & Sass, 1964; Engelen, Freiburg & Lutz, 1983; Lutz, Buchmeier & Engelen, 1987) strontium bromides have been carried out. Early studies (Herrmann, 1931; Jensen, 1940) showed that the title compound was likely to be isostructural with the analogous chloride. The present study, however, constitutes the first full determination of the structure of $SrBr_2.6H_2O$.

The title compound contains nine-coordinate Sr in tricapped trigonal prismatic coordination geometry (Fig. 1) involving six bridging and three terminal water molecules. The bridging water molecules at the apices of the trigonal prism link the Sr^{2+} ions at the centre of each prism, resulting in a linear cationic polymer, $[Sr(H_2O)_6]_n^{2n+}$, which is balanced in charge by Br^- ions in the lattice. The Br^- ions are hydrogen bonded to the water molecules.

$SrBr_2.6H_2O$ is isostructural with $CaBr_2.6H_2O$ (Leclaire & Borel, 1977). The strontium and calcium dichloride hexahydrates are also isostructural. The bridging and terminal contacts to water in these compounds are compared in Table 3.

It is clear that the interatomic distances observed in $SrBr_2.6H_2O$ compare well with those found in $SrCl_2.6H_2O$, particularly in the case of the bridging contacts. The structure of $MgBr_2.6H_2O$ (Andress & Gundermann, 1934) is also known, but contains isolated $[Mg(H_2O)_6]^{2+}$ ions with no bridging water molecules. The hydrogen-bonding contacts in the title compound lie in the range 3.35–3.37 Å, and are comparable to those observed in $HBr.3H_2O$ (Lundgren, 1970).

Acta Crystallographica Section C
ISSN 0108-2701 ©1995