

INORGANIC COMPOUNDS

Acta Cryst. (1994). C50, 471–473

Two Lithium Chloroberyllo(Phosphate/Arsenate) Sodalites: $\text{Li}_4\text{Cl}(\text{BePO}_4)_3$ and $\text{Li}_4\text{Cl}(\text{BeAsO}_4)_3$

WILLIAM T. A. HARRISON

*Department of Chemistry, University of Houston,
Houston, TX 77204-5641, USA*

THURMAN E. GIER AND GALEN D. STUCKY

*Department of Chemistry, University of California,
Santa Barbara, CA 93106-9510, USA*

(Received 5 July 1993; accepted 20 September 1993)

Abstract

The full structures of lithium chloroberyllophosphate sodalite, $\text{Li}_4\text{Cl}(\text{BePO}_4)_3$ (I), and lithium chloroberylloarsenate sodalite, $\text{Li}_4\text{Cl}(\text{BeAsO}_4)_3$ (II), as refined using X-ray powder data, are reported. These phases are briefly compared with other known $M_4X(\text{ABO}_4)_3$ -type sodalites.

Comment

The sodalite framework, exemplified by $\text{Na}_4\text{Cl}(\text{AlSiO}_4)_3$, is built up from tetrahedral building blocks (*e.g.* SiO_4 and AlO_4), linked *via* Si—O—Al O-atom bridges. 24 of these units link together to form a truncated octahedral β -cage, containing eight six-ring openings and six four-ring openings (Pauling, 1930). In sodalite, the β -cages are built into a closely packed array and each sodalite cage is in contact with 14 neighbors: eight *via* six rings and six *via* four rings. The sodalite framework is particularly versatile with respect to accommodating a wide variety of framework tetrahedral species and various guest cations and anions (Stucky *et al.*, 1992). Typical zeolitic cation exchange (Stein, Ozin & Stucky, 1990) and dehydration/rehydration reactions (Felsche & Luger, 1987) have been demonstrated for various sodalites.

Two general types of sodalite structure may be distinguished, based on the extra-framework contents of each β -cage. Normal sodalites, of the formula $M_4X(\text{ABO}_4)_3$, contain four guest cations M and one anion X , which is located at the center of the β -cage. Empty-cage sodalites, *e.g.* $M_3(\text{H}_2\text{O})_{4-x}(\text{ABO}_4)_3$, contain three guest cations and (up to) four water molecules in a defective cubane arrangement in the β -cage. We have discovered varieties of both types of sodalite structure during our recent investigations of new group 2/12/15 molecular sieve structures: $\text{Na}_3(\text{H}_2\text{O})_4(\text{ZnPO}_4)_3$

and $\text{Na}_3(\text{H}_2\text{O})_4(\text{ZnAsO}_4)_3$, prepared using mild conditions [343 K, ambient pressure (Nenoff, Harrison, Gier & Stucky, 1991)], are empty-cage sodalites, while $\text{Li}_4\text{Br}(\text{BePO}_4)_3$, prepared at high temperatures and pressures [823 K, *ca.* 0.3447 GPa (Gier, Harrison & Stucky, 1991)], is a normal sodalite. In this paper we describe the structures of two further normal sodalites, $\text{Li}_4\text{Cl}(\text{BePO}_4)_3$ and $\text{Li}_4\text{Cl}(\text{BeAsO}_4)_3$, and briefly compare them with other $M_4X(\text{ABO}_4)_3$ materials.

Both $\text{Li}_4\text{Cl}(\text{BePO}_4)_3$ and $\text{Li}_4\text{Cl}(\text{BeAsO}_4)_3$ adopt the typical $P43n$ $M_4X(\text{ABO}_4)_3$ normal sodalite structure, which shows complete 1:1 tetrahedral ordering of the Be and P/As species. Bond lengths and angles are typical of the chemical species concerned. In particular, the Li—O and Li—Cl contacts in each structure are virtually identical. In both structures, the Li cation occupies a site near the inter- β -cage six-ring window (site symmetry $\bar{3}$.) and is three-coordinate with the framework O atoms. Its fourth tetrahedral vertex is to the Cl anion at the center of each β -cage. The Cl anion bonds to four Li cations in a regular tetrahedron (Cl[−] site symmetry: 23 .) The six-ring environment in $\text{Li}_4\text{Cl}(\text{BePO}_4)_3$ is illustrated in Fig. 1.

A key parameter in defining the geometry of the sodalite framework is the intertetrahedral atom angle $T\text{—O—}T'$ (Taylor & Henderson, 1978): $127.0(2)$ in $\text{Li}_4\text{Cl}(\text{BePO}_4)_3$ and $123.4(2)^\circ$ in $\text{Li}_4\text{Cl}(\text{BeAsO}_4)_3$, compared with $128.9(2)$ in $\text{Li}_4\text{Br}(\text{BePO}_4)_3$ (Gier, Harrison & Stucky, 1991) and $125.6(4)^\circ$ in $\text{Li}_4\text{Cl}(\text{AlSiO}_4)_3$ (Beagley, Henderson & Taylor, 1982). In normal alu-

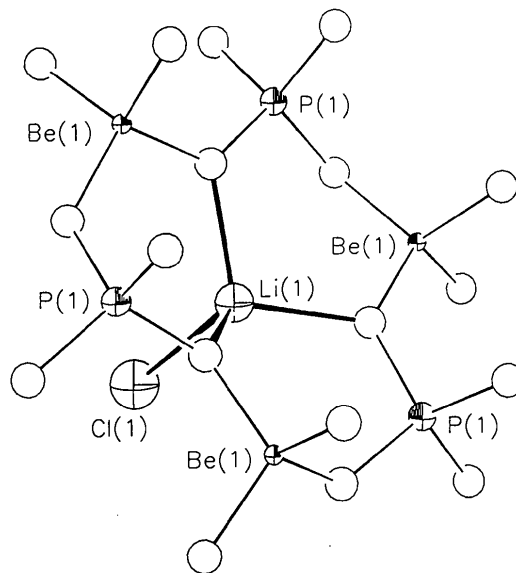


Fig. 1. View showing the six-ring window environment in $\text{Li}_4\text{Cl}(\text{BePO}_4)_3$. The Li^+ cation makes three bonds to the framework O atoms and a fourth tetrahedral vertex to the Cl^- species occupying the center of the β -cage. (Arbitrary atom radii; O atoms represented as unlabeled plain circles.)

minosilicate sodalites, correlations may be observed between the sizes (ionic radii) of the cage species and the intertetrahedral angle (Taylor & Henderson, 1978): here, there are insufficient data to offer any similar general predictions for the beryllio(phosphate/arsenate) sodalites, but we observe that the larger arsenate group in Li₄Cl(BeAsO₄)₃ leads to a smaller T—O—T' bond angle than observed in its phosphate-containing congener, Li₄Cl(BePO₄)₃. This suggests that correlations between the T—O—T' angle and unit-cell size (Taylor & Henderson, 1978) may not be so clearly apparent when sodalites of different framework compositions are compared.

A significant difference between Li₄Cl(AlSiO₄)₃ and Li₄Cl(BePO₄)₃ and Li₄Cl(BeAsO₄)₃ may be observed by comparing the Li—O bond lengths. In Li₄Cl(AlSiO₄)₃, Li—O = 2.09 (2) Å, while in Li₄Cl(BePO₄)₃ and Li₄Cl(BeAsO₄)₃ the comparable Li—O contacts are 1.928 (5) and 1.946 (6) Å, respectively. This may indicate that simple size-packing considerations are insufficient to explain the structural trends between sodalites with different framework compositions, and that other effects, such as electronegativities, may also be significant in determining crystal structure.

The Li cation/six-ring O-atom interaction may be quantified further (Stucky *et al.*, 1992) by defining a parameter $\delta(\text{Li})$ (Å), which denotes the displacement along the [111] direction, toward the center of the sodalite cage at (0,0,0), of the Li cation from the plane formed by its three near-neighbor O atoms in the sodalite six-ring; values of 0.69 for Li₄Cl(BePO₄)₃, 0.71 for Li₄Cl(BeAsO₄)₃, 0.89 for Li₄Cl(AlSiO₄)₃ and 0.60 Å for Li₄Br(BePO₄)₃ result. The δ parameter is useful for comparing structural trends between different extra-framework species in different zeolites; for example, typical δ values of 1.3 Å result for sodium aluminosilicate sodalites, while for the S_{II} site in hydrated sodium zeolite X, where a similar threefold sodium-framework O-atom coordination occurs, a δ value of 1.0 Å is found.

The sodalite T—O—T' angle is also significant in defining the area of the intercage six-ring window (Stucky *et al.*, 1992) and the cage-center-to-cage-center separation. The consequences for the resulting ion-exchange and spectroscopic behavior of these systems (Stucky *et al.*, 1992) are extremely important, offering the possibilities of microengineering the physical properties of these materials, such as blue shifting or red shifting a semiconductor band gap, based on the precise control of atomic separations of the guest species *via* controlled substitutions of the framework tetrahedral atoms (Moran *et al.*, 1994).

Experimental

Lithium chloroberyllophosphate sodalite, Li₄Cl(BePO₄)₃, and lithium chloroberylloarsenate sodalite, Li₄Cl(BeAsO₄)₃, were prepared by high-temperature/high-pressure methods, as described previously (Gier, Harrison & Stucky, 1991). In each

case, a highly crystalline white powder was produced, which was suitable for full structure determination by the Rietveld method (Rietveld, 1969).

Compound (I)

Crystal data

Li₄Cl(BePO₄)₃
M_r = 375.16
 Cubic
*P*4̄3*n*
a = 8.0269 (3) Å
V = 517.18 (4) Å³

Z = 2
D_x = 2.409 Mg m⁻³
 Cu Kα radiation
 μ = 8.484 mm⁻¹
T = 298 (2) K
 White

Data collection

Scintag PAD-X powder diffractometer
 θ/θ powder scans
 Absorption correction: none

1999 data points in the processed diffractogram
 $2\theta_{\min} = 20$, $2\theta_{\max} = 100^\circ$
 Wavelength of incident radiation: 1.54178 Å

Refinement

Refinement on powder data points
R_p = 0.103
R_{wp} = 0.131
 $\chi^2 = 4.85$
 130 reflections
 20 parameters
 $w = 1/\sigma^2(y)$

$(\Delta/\sigma)_{\max} < 0.01$
 $\Delta\rho_{\max} = 0.6 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.7 \text{ e } \text{Å}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and isotropic displacement parameters (Å²) for (I)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Be(1)	1/4	0	1/2	0.016 (4)
P(1)	1/4	1/2	0	0.0075 (7)
O(1)	0.14281 (28)	0.41448 (30)	0.13778 (27)	0.0020 (9)
Li(1)	0.1814 (10)	0.1814 (10)	0.1814 (10)	0.010
Cl(1)	0	0	0	0.013 (2)

Table 2. Selected geometric parameters (Å, °) for (I)

Be(1)—O(1 ⁱ)	1.6114 (21)	Li(1)—O(1)	1.928 (5)
P(1)—O(1)	1.5603 (22)	Li(1)—Cl(1)	2.523 (15)
O(1 ⁱ)—Be(1)—O(1 ⁱⁱ)	108.21 (8)	Be(1 ^{vi})—O(1)—Li(1)	115.22 (13)
O(1 ⁱ)—Be(1)—O(1 ⁱⁱⁱ)	112.03 (16)	P(1)—O(1)—Li(1)	117.84 (12)
O(1)—P(1)—O(1 ^{iv})	107.70 (8)	O(1)—Li(1)—O(1 ⁱ)	107.6 (4)
O(1)—P(1)—O(1 ^v)	113.07 (16)	O(1)—Li(1)—Cl(1)	111.2 (4)
Be(1 ^{vi})—O(1)—P(1)	126.95 (15)	Li(1)—Cl(1)—Li(1 ^{vii})	109.471

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

Compound (II)

Crystal data

Li₄Cl(BeAsO₄)₃
M_r = 507.01
 Cubic
*P*4̄3*n*
a = 8.23685 (8) Å
V = 558.83 (2) Å³

Z = 2
D_x = 3.013 Mg m⁻³
 Cu Kα radiation
 μ = 13.688 mm⁻¹
T = 298 (2) K
 White

Data collection

Scintag PAD-X powder diffractometer

2571 data points in the processed diffractogram

θ/θ powder scans
Absorption correction:
none

$2\theta_{\min} = 20$, $2\theta_{\max} = 120^\circ$
Wavelength of incident radiation:
1.54178 Å

Refinement

Refinement on powder data
points
 $R_p = 0.072$
 $R_{wp} = 0.101$
 $\chi^2 = 5.04$
200 reflections
24 parameters
 $w = 1/\sigma^2(y)$

$(\Delta/\sigma)_{\max} < 0.01$
 $\Delta\rho_{\max} = 0.9 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.5 \text{ e } \text{Å}^{-3}$
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography* (1974, Vol. IV, Table
2.2B)

Table 3. Fractional atomic coordinates and isotropic displacement parameters (Å^2) for (II)

	x	y	z	U_{iso}
Be(1)	1/4	0	1/2	0.005 (3)
As(1)	1/4	1/2	0	0.0046 (3)
O(1)	0.13390 (31)	0.4066 (4)	0.14093 (32)	0.009 (2)
Li(1)	0.1772 (11)	0.1772 (11)	0.1772 (11)	0.017 (5)
Cl(1)	0	0	0	0.018 (1)

Table 4. Selected geometric parameters (Å , $^\circ$) for (II)

Be(1)—O(1 ⁱ)	1.6174 (24)	Li(1)—O(1)	1.946 (6)
As(1)—O(1)	1.6895 (29)	Li(1)—Cl(1)	2.528 (16)
O(1 ⁱ)—Be(1)—O(1 ⁱⁱ)	107.97 (9)	Be(1 ^{vi})—O(1)—Li(1)	120.12 (17)
O(1 ⁱ)—Be(1)—O(1 ⁱⁱⁱ)	112.51 (19)	As(1)—O(1)—Li(1)	116.36 (13)
O(1)—As(1)—O(1 ^{iv})	108.69 (9)	O(1)—Li(1)—O(1 ⁱ)	107.4 (5)
O(1)—As(1)—O(1 ^v)	111.05 (18)	O(1)—Li(1)—Cl(1)	111.5 (5)
Be(1 ^{vi})—O(1)—As(1)	123.43 (19)	Li(1)—Cl(1)—Li(1 ^{vii})	109.471

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

Both crystal structures were optimized by X-ray Rietveld refinements (Rietveld, 1969), following a similar procedure to that described by Gier, Harrison & Stucky (1991). Starting unit-cell parameters were obtained by unit-cell powder refinements and starting atomic coordinates were obtained from the structure of $\text{Li}_4\text{Br}(\text{BePO}_4)_3$ (Gier, Harrison & Stucky, 1991), with Cl substituting Br and As replacing P in the $\text{Li}_4\text{Cl}(\text{BeAsO}_4)_3$ phase. The Rietveld refinements progressed smoothly in each case, with the usual profile parameters (scale factor, zero-point error, pseudo-Voigt peak-width variation parameters, six-term Fourier-cosine series background coefficients and unit-cell parameters) treated as least-squares variables in the usual fashion. All atom positions and isotropic displacement factors were refined. No corrections for preferred orientation, extinction or absorption were applied.

Program(s) used to refine structures: *GSAS* (Larson & Von Dreele, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976), with local modifications.

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

Lists of raw X-ray powder data and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71662 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1052]

References

- Beagley, B., Henderson, C. M. B. & Taylor, D. (1982). *Mineral. Mag.* **46**, 459–464.
Felsche, J. & Luger, S. (1987). *Thermochim. Acta*, **118**, 35–55.
Gier, T. E., Harrison, W. T. A. & Stucky, G. D. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 1169–1171.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Larson, A. C. & Von Dreele, R. B. (1990). *GSAS User's Guide*. Los Alamos National Laboratory, New Mexico, USA.
Moran, K. L., Gier, T. E., Harrison, W. T. A., Stucky, G. D., Eckert, H., Eichele, K. & Wasylishen, R. E. (1994). *J. Am. Chem. Soc.* In the press.
Nenoff, T. M., Harrison, W. T. A., Gier, T. E. & Stucky, G. D. (1991). *J. Am. Chem. Soc.* **113**, 378–379.
Pauling, L. (1930). *Z. Kristallogr.* **74**, 213–225.
Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
Stein, A., Ozin, G. & Stucky, G. D. (1990). *J. Am. Chem. Soc.* **112**, 904–905.
Stucky, G. D., Srdanov, V. I., Harrison, W. T. A., Gier, T. E., Keder, N. L., Moran, K. L., Haug, K. & Metiu, H. I. (1992). *Supramolecular Architecture*, *Am. Chem. Soc. Symp. Ser.* 499, edited by T. E. Bein, pp. 294–313. Washington: American Chemical Society.
Taylor, D. & Henderson, C. M. B. (1978). *Phys. Chem. Miner.* **2**, 325–336.

Acta Cryst. (1994). **C50**, 473–476

Synthesis and Structures of Two Isostructural Phosphites, $\text{Al}_2(\text{HPO}_3)_3$ and $\text{Ga}_2(\text{HPO}_3)_3$

RUSSELL E. MORRIS, MARTIN P. ATTFIELD
AND ANTHONY K. CHEETHAM

Materials Department, University of California,
Santa Barbara, CA 93106, USA

(Received 22 May 1992; accepted 31 August 1993)

Abstract

Aluminium hydrogen phosphite, $\text{Al}_2(\text{HPO}_3)_3$, and gallium hydrogen phosphite, $\text{Ga}_2(\text{HPO}_3)_3$, were prepared hydrothermally in Teflon-lined steel autoclaves at 473 K. The compounds are isostructural with $\text{Fe}_2(\text{HPO}_3)_3$. The structures consist of very distorted MO_6 octahedra which share faces to form a dimeric M_2O_9 unit. These dimers are interlinked by the phosphite groups, which link three different dimers into a three-dimensional arrangement having small proton-lined channels running parallel to the c axis.

Comment

Aluminium and gallium phosphates have received much attention in recent years because of their capacity to form framework structures with topologies similar to those of