Stoe & Cie (1990*a*). *DIF4. Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1990*b*). *REDU4. Data Reduction Program*. Version 7.03. Stoe & Cie, Darmstadt, Germany.
Taffoli, P., Khodadad, P. & Rodier, N. (1981). *Bull. Soc. Chim. Fr.* pp. 429–432.
Wachhold, M. & Sheldrick, W. S. (1996). *Z. Naturforsch. Teil B*, **51**, 32–36.
Yun, R., Randall, C. R. & Ibers, J. A. (1988). *J. Solid State Chem.* **76**, 109–114.

Acta Cryst. (1999). C**55**, 1199–1200

Lithium barium arsenide, $Li_4Ba_3As_4$, containing isolated As^{3-} and As_2^{4-} anions

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(*Received 4 May 1999; accepted 18 May 1999*)

Abstract

$Li_4Ba_3As_4$ crystallizes in the orthorhombic space group *Immm* and is isostructural with $Li_4Sr_3Sb_4$ and $Li_4Ba_3Sb_4$ [Liebrich, Schäfer & Weiss (1970). *Z. Naturforsch. Teil B*, **25**, 650–651]. The structure contains two anionic moieties, namely As_2^{4-} dumbbells [As1—As1 2.487 (2) Å] and As^{3-}.

Comment

The structure of $Li_4Ba_3As_4$ has been determined in the centrosymmetric space group *Immm* (No. 71) and is isostructural with $Li_4Sr_3Sb_4$ and $Li_4Ba_3Sb_4$ (Liebrich *et al.*, 1970). The structure contains two anionic moieties, namely As_2^{4-} dumbbells [As1—As1 2.487 (2) Å] and isolated As^{3-} anions. This structure is best described by visualizing coordination polyhedra around the Ba atoms. Ba1 lies at the center of a pseudo-octahedron (symmetry *mmm*) formed by four As1 atoms at 3.320 (1) Å and two As2 atoms at 3.319 (1) Å. Ba2 is coordinated by six Li atoms [four at 3.28 (1) Å and two at 3.29 (2) Å] and six As atoms [four As1 and two As2 at 3.363 (1) and 3.392 (1) Å, respectively]. The large $BaAs_6$ octahedra are condensed along the [100] direction into a linear framework by edge sharing. These columns form a two-dimensional array through the As1—As1 dumbbell parallel to [010]. Interestingly, the planes of the octahedra are separated from each other by corrugated sheets of electropositive Li and Ba atoms. The As1 atoms that form the As_2^{4-} dumbbells are coordinated by six Li atoms [two at 2.75 (2) Å and four at 2.80 (1) Å]. The As1—As1 distance of 2.487 (2) Å is slightly longer than the single-bond length given by Pauling (2.42 Å; Pauling, 1947, 1949). This compound can be described using the Zintl formalism as the ionic compound: 4 Li^+, 3 Ba^{2+}, As_2^{4-}, 2 As^{3-}.

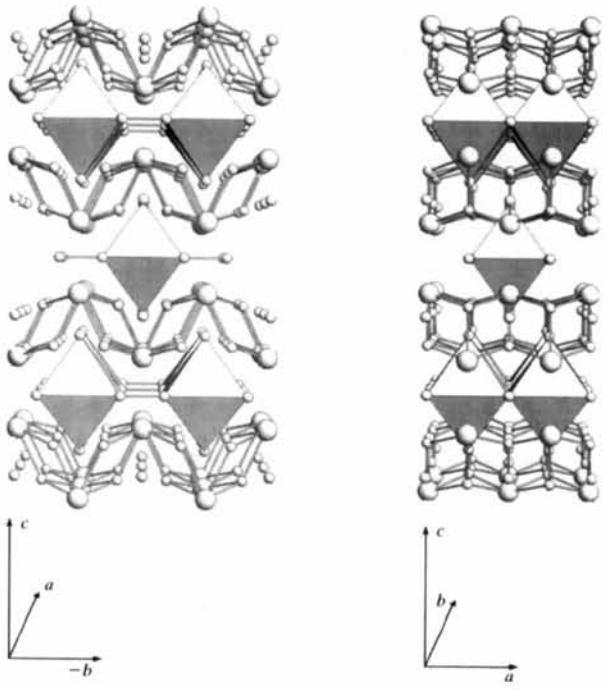

Fig. 1. Two views of the structural packing of $Li_4Ba_3As_4$. Ba1 lies at the center of the octahedron and the origin of the cell, Ba2 is represented by large circles, As1 is in the equatorial plane of the octahedron and forms dumbbells between adjoining octahedra, As2 is axial with respect to the octahedron and Li is represented by small circles between Ba2 atoms.

Experimental

With the aim of obtaining the quaternary phase $Li_3Ba_2VAs_4$, which is closely related to the recently discovered Li_7VAs_4 phase (Monconduit, 1999), Li_3As, As, Ba and V (ratio 1:3:2:1) were inserted into a niobium reactor weld-sealed under argon. The niobium reactor was protected in a quartz ampoule sealed under vacuum. Single crystals of $Li_4Ba_3As_4$ were obtained by heating to 1273 K for 10 h, heating for 8 d at 1123 K and then cooling the mixture at a rate of 150 K h^{-1}. The product contained a large amount of $Li_4Ba_3As_4$. Elemental analyses (SEM) of flat crystals confirmed the presence of barium and arsenic in a Ba/As ratio of 0.77, and the absence of vanadium. Atomic absorption analyses showed an Li/Ba ratio of 1.21.

Crystal data

$Li_4Ba_3As_4$
M_r = 739.46

Mo $K\alpha$ radiation
λ = 0.71069 Å

Orthorhombic
Immm
a = 4.7034 (10) Å
b = 7.1735 (13) Å
c = 15.643 (2) Å
V = 527.78 (16) Å^3
Z = 2
D_x = 4.654 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 10.48–21.33°
μ = 23.43 mm^{-1}
T = 293 (2) K
Wedge
0.08 × 0.07 × 0.05 mm
Silver/light grey

Data collection

Nonius CAD-4 diffractometer
ω–$\frac{1}{3}\theta$ scans
Absorption correction: numerical (Sheldrick, 1976)
T_{min} = 0.176, T_{max} = 0.332
463 measured reflections
463 independent reflections

430 reflections with $I > 3\sigma(I)$
θ_{max} = 29.89°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 21$
3 standard reflections
every 100 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.107
S = 1.217
463 reflections
23 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2 + 15.1135P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.031

$\Delta\rho_{max}$ = 2.651 e Å^{-3}
$\Delta\rho_{min}$ = −1.776 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0045 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Ba1	0	0	0	0.0081 (3)
Ba2	0	1/2	0.13150 (4)	0.0094 (3)
As1	1/2	−0.32666 (17)	0	0.0073 (3)
As2	0	0	0.21219 (7)	0.0082 (3)
Li	1/2	−0.199 (3)	−0.1789 (11)	0.019 (3)

Table 2. *Selected bond lengths (Å)*

Ba1—As2	3.3191 (13)	Ba2—As1^{ii}	3.3627 (7)
Ba1—As2^{i}	3.3191 (13)	Ba2—As2^{x}	3.3925 (10)
Ba1—As1^{ii}	3.3199 (10)	Ba2—As2^{xi}	3.3925 (10)
Ba1—As1^{iii}	3.3199 (10)	As1—As1^{xii}	2.487 (2)
Ba1—As1	3.3199 (10)	As1—Li^{xiii}	2.944 (19)
Ba1—As1^{i}	3.3199 (10)	As1—Li	2.944 (19)
Ba2—Li^{iv}	3.277 (15)	As2—Li^{vii}	2.751 (18)
Ba2—Li^{i}	3.277 (15)	As2—Li^{xiv}	2.751 (18)
Ba2—Li^{v}	3.277 (15)	As2—Li^{xv}	2.800 (12)
Ba2—Li^{ii}	3.277 (15)	As2—Li^{ii}	2.800 (12)
Ba2—Li^{vi}	3.292 (19)	As2—Li^{i}	2.800 (12)
Ba2—Li^{vii}	3.292 (19)	As2—Li^{xiii}	2.800 (12)
Ba2—As1^{i}	3.3627 (7)	Li—Ba2^{i}	3.277 (15)
Ba2—As1^{viii}	3.3627 (7)	Li—Ba2^{ii}	3.277 (15)
Ba2—As1^{ix}	3.3627 (7)	Li—Ba2^{xvi}	3.292 (19)

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

The parameters and crystallographic space group were initially determined by oscillation and Weissenberg techniques. The space group was found to be *Immm* (No. 71) and no violation of the I-centering conditions ($h + k + l = 2n$) was observed.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1246). Services for accessing these data are described at the back of the journal.

References

Dowty, E. (1993). *ATOMS. A Computer Program for Displaying Atomic Structures*. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Liebrich, O., Schäfer, H. & Weiss, A. (1970). *Z. Naturforsch. Teil B*, **25**, 650–651.

Monconduit, L. (1999). Unpublished results.

Pauling, L. (1947). *J. Am. Chem. Soc.* **69**, 542–543.

Pauling, L. (1949). *Proc. R. Soc. London Ser. A*, **196**, 343–354.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. University of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). C**55**, 1200–1203

Thallium titanium phosphate, $Tl_3Ti_3O(PO_4)_3(P_2O_7)$

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(*Received 17 September 1998; accepted 12 May 1999*)

Abstract

The title compound, trithallium trititanium oxide tris(phosphate) diphosphate, consists of a three-dimensional network of vertex-sharing TiO_6, PO_4 and P_2O_7 groups [d_{av}(Ti—O) = 1.940 (3) and d_{av}(P—O) = 1.536 (4) Å]. Extra-framework Tl^+ cations [d_{av}(Tl—O) = 3.090 (7) Å] complete the structure, which is isostructural with $M_3Ti_3O(PO_4)_3(P_2O_7)$ (M = K, Rb).

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