Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

$K_2ScSn(AsO_4)_3$: an arsenate-containing langbeinite

William T. A. Harrison

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

Received 15 April 2010
Accepted 7 June 2010
Online 17 June 2010

The title compound, dipotassium tri-μ-arsenato-scandium(III)-tin(IV), is the first arsenate-containing langbeinite to be characterized by single-crystal methods and crystallizes in the aristotype $P2_13$ cubic symmetry for this structure type in which the K^+ ions and the octahedral scandium and tin cations lie on crystallographic threefold axes. The Sc^{III} and Sn^{IV} ions show a slight segregation over the two octahedral sites, with Sc/Sn populations of 0.582 (5):0.418 (5) on one site and 0.418 (5):0.582 (5) on the other. Bond-valence-sum calculations indicate that the K^+ ions are significantly underbonded in this structure and the O atoms show large anisotropic displacement parameters, as also seen in other langbeinites. The crystal studied was found to be a merohedral twin with a 0.690 (16):0.310 (16) domain ratio.

Comment

Langbeinites of the simplest generic formula $A_2B_2(XO_4)_3$ are an important and well studied family of inorganic solids with respect to minerals (Zemann & Zemann, 1957), phase transitions (Nalini & Guru Row, 2002) and magnetic behaviour (Battle *et al.*, 1986). In the langbeinite crystal structure, the two A cations occupy nominal nine-coordinate sites, the two B cations occupy octahedral sites and the tetrahedral XO_4 oxoanion completes the structure. The relationship of the langbeinite structure to the garnet and NASICON [sodium (Na) super-ionic conductor] structure types in terms of the connectivity of the BO_6 and XO_4 polyhedra has been discussed (Pet'kov *et al.*, 1999; Norberg, 2002). However, unlike NASICONs, langbeinities show poor ionic conductivity (Isasi & Daidouh, 2000), due to the small windows connecting the extra-framework cages where the univalent ions are located.

In terms of the identity of the oxoanion, sulfate and phosphate dominate the list of known langbeinites and many such langbeinites have been studied by single-crystal methods (Ogorodnyk *et al.*, 2007). Other $(XO_4)^{2-}$ ions are possible, including selenate, chromate, molybdate and manganate (Norberg, 2002), but surprisingly it seems that no $(XO_4)^{3-}$-containing analogues of phosphate langbeinites, such as arsenate or vanadate, have yet been reported. It should also be noted that no fewer than 40 fluoroberyllate $(BeF_4)^{2-}$ langbeinites were reported many years ago (Le Fur & Aleónard, 1969).

In terms of the A and B cations, the only plausible charge-balancing scheme for sulfate and other $(XO_4)^{2-}$ langbeinites is for the A cations to be univalent and the B cations to be divalent, as, for example, in $K_2Mg_2(SO_4)_3$ (Mereiter, 1977) or $Tl_2Cd_2(SO_4)_3$ (Guelylah *et al.*, 1996). The situation is more complex for phosphate langbeinites: to achieve a total cation charge of +9, one univalent and one divalent cation may be assigned to the A sites, along with two trivalent cations on the B sites, as in $KBaCr_2(PO_4)_3$ (Battle *et al.*, 1988). Alternately, two univalent cations on the A sites may accompany a trivalent and tetravalent pairing on the B sites, as in $K_2YbTi(PO_4)_3$ (Norberg, 2002). Yet another way to attain charge balance is a 'defect' langbeinite, such as $Ba_{1.5}V_2(PO_4)_3$ (Dross & Glaum, 2004), in which the A sites are 75% occupied by divalent cations and the B sites are fully occupied by trivalent cations.

In this paper, we describe the title arsenate langbeinite, (I), which contains a univalent (A) plus trivalent/tetravalent (B) combination of cations. Compound (I) crystallizes in the aristotype (Megaw, 1973) cubic (space group $P2_13$) langbeinite structure (Figs. 1 and 2). Both K1 and K2 have crystallographic site symmetry 3 and are nine-coordinated by O atoms (Table 1). The mean K$\cdots$O separations and their estimated errors (Taylor & Kennard, 1983) for K1 and K2 are 3.03 (4) Å and 3.16 (15) Å, respectively. Their bond valence sums (BVSs), calculated by the Brown & Altermatt (1985) formalism, are 0.79 and 0.62, respectively (expected 1.00); thus, they are both significantly 'underbonded' (Kahlenberg, 2001) (a 'back calculation' starting from a BVS of 1.00 yields a

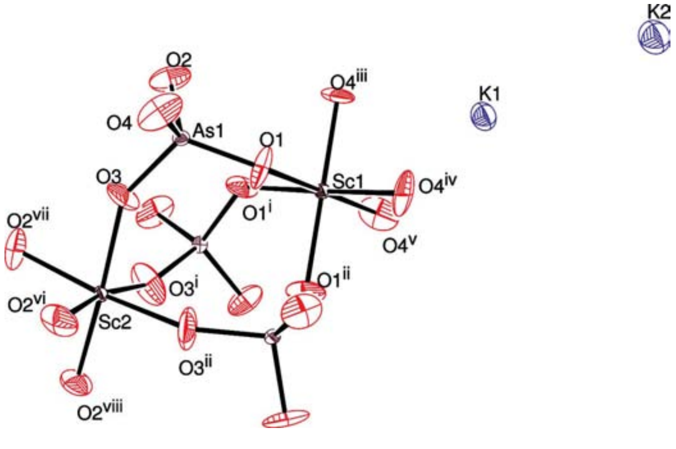

Figure 1
A fragment of (I), showing the characteristic 'lantern'-shaped motif (Norberg, 2002) of two octahedra linked by three tetrahedra (50% displacement ellipsoids). [Symmetry codes: (i) y, z, x; (ii) z, x, y; (iii) $1 - y, \frac{1}{2} + z, \frac{1}{2} - x$; (iv) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (v) $\frac{1}{2} + z, \frac{1}{2} - x, 1 - y$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (vii) $\frac{1}{2} - y, -z, x - \frac{1}{2}$; (viii) $-z, x - \frac{1}{2}, \frac{1}{2} - y$.]

doi:10.1107/S0108270110021670

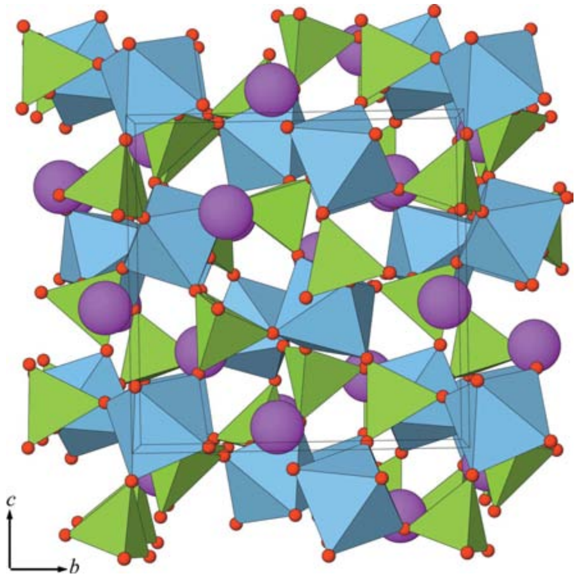

Figure 2
The unit-cell packing in (I), viewed down [100], showing the Sc/SnO$_6$ + AsO$_4$ network as polyhedra (blue and green, respectively, in the electronic version of the paper) and the K$^+$ ions as spheres (purple) of arbitrary radius.

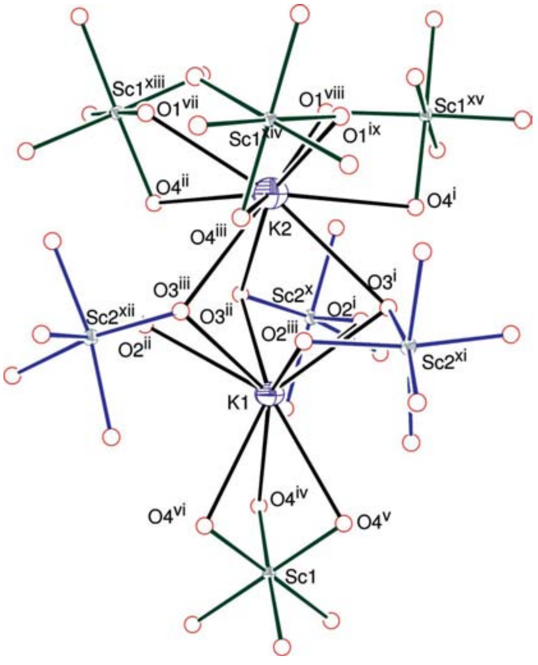

Figure 3
Fragment of (I), showing the coordination environments of K1 and K2 and the adjacent Sc/Sn octahedra (O atoms shown as arbitrary spheres). In the electronic version of the paper, the K—O bonds are black, the Sc1/Sn1—O bonds are green and the Sc2/Sn2—O bonds are blue. [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - z, 1 - x, \frac{1}{2} + y$; (iii) $\frac{1}{2} + y, \frac{1}{2} - z, 1 - x$; (iv) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (v) $1 - y, \frac{1}{2} + z, \frac{1}{2} - x$; (vi) $\frac{1}{2} + z, \frac{1}{2} - x, 1 - y$; (vii) $1 - z, \frac{1}{2} + x, \frac{3}{2} - y$; (viii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (ix) $\frac{3}{2} - y, 1 - z, \frac{1}{2} + x$; (x) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (xi) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (xii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (xiii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (xiv) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$; (xv) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.]

predicted K···O separation of about 2.95 Å for nine-coordination). We note that the $U_{\rm eq}$ value for K2 [0.0496 (7) Å^2] is significantly larger than that for K1 [0.0332 (5) Å^2], which may correlate with the longer mean K2···O distance. The next-nearest O atoms to K1 and K2 are 3.523 (5) and 3.701 (5) Å distant, respectively, and can hardly be considered to be significant bonding interactions (their individual bond valences are 0.02 and 0.01, respectively). Underbonding or 'loose bonding' of the *A* cations is a known feature of langbeinites [for example, in $Tl_2Cd_2(SO_4)_3$ (Guelylah *et al.* 1996) the thallium-ion BVSs of 0.83 and 0.61 compared to an expected value of 1.00 are very similar to those for the K$^+$ ions in (I)] and may be connected with their phase-transition behaviour. It is however notable that a different situation occurs in phosphate langbeinites containing large *A* cations such as Cs$^+$ (Ogorodnyk *et al.*, 2007), in which a BVS analysis indicates 'overbonding' of the metal ions.

As well as being underbonded, the K1 coordination sphere is highly asymmetrical with respect to the [111] body diagonal axis of the unit cell. This can be understood in terms of the polyhedra that its coordinated O atoms are also part of: three O4 atoms form a common face with the Sc1/Sn1 octahedron, whereas the triplet of (O2 + O3) displaced in the opposite sense form an octahedral edge of an Sc2/Sn2O$_6$ unit. For K2, the coordination geometry is significantly different and more regular; it shares corners with a triplet of Sc2/Sn2O$_6$ octahedra and edges with three Sc1/Sn1O$_6$ groups (Fig. 3).

The Sc^{3+} and Sn^{4+} ions show a slight segregation over the two octahedral sites in (I). For the Sc1/Sn1 site, the populations are 0.582 (5) and 0.418 (5) for Sc and Sn, respectively, and the reverse situation applies to the Sc2/Sn2 site. The mean bond lengths for the two sites are 2.05 (4) and 2.036 (6) Å for Sc1/Sn1 and Sc2/Sn2, respectively. The expected separations using Shannon (1976) ionic radii for octahedral Sc^{3+}—O and Sn^{4+}—O are 2.09 and 2.04 Å, respectively; thus the observed mean separations are closer to those for tin rather than for scandium. This feature of the larger cation being 'squeezed' onto a shared octahedral site in a langbeinite has also been seen in the series $K_2LnTi(PO_4)_3$ (Ln = Er^{3+}, Yb^{3+}, Y^{3+}; Norberg, 2002), in which the observed mean separation of (Ti + Ln) and O coincides closely with that expected for the tetravalent Ti^{4+} ion.

The mean As—O separation of 1.663 (8) Å in (I) is typical (Lin *et al.*, 1995) and the O—As—O angles lie between 103.4 (3) and 113.7 (3)°, representing an essentially regular [AsO$_4$] tetrahedron. It is notable that the displacement parameters of the As and O atoms are somewhat large. This appears to be a common feature of mixed-metal phosphate langbeinites: for example, $Rb_2YbTi(PO_4)_3$ (Gustafsson *et al.*, 2005) and $K_2YTi(PO_4)_3$ (Norberg, 2002) display the same feature. This is explainable in terms of static disorder of the O and As atoms in terms of their slightly different locations with respect to randomly distributed adjacent cations [Sc^{3+} or Sn^{4+} in (I)]. An alternative explanation applied to sulfate langbeinites is an incipient phase transition involving a concerted reorientation of the XO$_4$ tetrahedra (Abrahams *et al.*, 1978; Guelylah *et al.*, 1996).

Experimental

In an exploratory attempt to prepare new scandium-doped analogues of $KSnOAsO_4$ (Lin *et al.*, 1995), a mixture of K_2CO_3, NH_4AsO_4, Sc_2O_3 and SnO_2 (molar ratio = 1:3:1:1) was heated in a fused silica crucible to 1173 K and then cooled slowly ($10\ K\ h^{-1}$) to 773 K and finally cooled overnight to room temperature. A few small cubes of (I) were recovered from the crucible, accompanied by unreacted Sc_2O_3 and SnO_2. Semiquantitative (standardless) EDAX (energy dispersive X-ray spectroscopy) (Yamane & DiSalvo, 1996) indicated an Sc:Sn ratio of close to unity.

Crystal data

$K_2ScSn(AsO_4)_3$
$M_r = 658.62$
Cubic, $P2_13$
$a = 10.3927\ (4)$ Å
$V = 1122.50\ (7)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 12.41\ mm^{-1}$
$T = 298$ K
0.10 × 0.10 × 0.10 mm

Data collection

Bruker SMART1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.370$, $T_{max} = 0.370$
12634 measured reflections
1522 independent reflections
1423 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.063$
$S = 0.97$
1522 reflections
60 parameters
$\Delta\rho_{max} = 1.43$ e Å^{-3}
$\Delta\rho_{min} = -1.40$ e Å^{-3}
Absolute structure: Flack (1983), 638 Friedel pairs
Flack parameter: 0.310 (16)

Table 1
Selected bond lengths (Å).

K1—O2^{i}	2.980 (6)	Sc1—O1	2.086 (4)
K1—O4^{ii}	3.046 (6)	Sc2—O3	2.032 (5)
K1—O3^{i}	3.068 (7)	Sc2—O2^{iv}	2.040 (4)
K2—O1^{iii}	2.956 (5)	As1—O2	1.651 (4)
K2—O4^{i}	3.185 (6)	As1—O3	1.674 (5)
K2—O3^{i}	3.322 (6)	As1—O4	1.659 (4)
Sc1—O4^{ii}	2.008 (4)	As1—O1	1.669 (4)

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$.

The site occupancies of the K^+ ions were refined, but they did not vary significantly from being fully occupied and were fixed at 1.00. The (Sc1 + Sn1) and (Sc2 + Sn2) positional and anisotropic displacement parameters were constrained to be equal. The (Sc1 + Sn1) and (Sc2 + Sn2) site occupancies were refined with a constraint to maintain full occupations for both sites and an overall 1:1 Sc:Sn ratio. The degree of merohedral twinning was determined by refinement with the *SHELXL* TWIN/BASF instruction (Sheldrick, 2008), which is equivalent (Müller *et al.*, 2006) to determining the Flack (1983) absolute structure parameter. The highest difference peak is 0.82 Å from O3 and the deepest difference hole is 0.32 Å from Sc2/Sn2.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3025). Services for accessing these data are described at the back of the journal.

References

Abrahams, S. C., Lissalde, F. & Bernstein, J. L. (1978). *J. Chem. Phys.* **68**, 1926–1935.
Battle, P. D., Cheetham, A. K., Harrison, W. T. A. & Long, G. J. (1986). *J. Solid State Chem.* **62**, 16–25.
Battle, P. D., Gibb, T. C., Nixon, S. & Harrison, W. T. A. (1988). *J. Solid State Chem.* **75**, 21–29.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Bruker (1999). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dross, T. & Glaum, R. (2004). *Acta Cryst.* E**60**, i58–i60.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Guelylah, A., Madariaga, G. & Breczewski, T. (1996). *Acta Cryst.* C**52**, 2954–2956.
Gustafsson, J. C. M., Norberg, S. T., Svensson, G. & Albertsson, J. (2005). *Acta Cryst.* C**61**, i9–i13.
Isasi, J. & Daidouh, A. (2000). *Solid State Ionics*, **133**, 303–313.
Kahlenberg, V. (2001). *Mineral. Mag.* **65**, 533–541.
Le Fur, Y. & Aleónard, S. (1969). *Mater. Res. Bull.* **4**, 601–616.
Lin, K.-J., Lin, H.-C. & Lii, K.-H. (1995). *J. Chin. Chem. Soc.* **42**, 913–918.
Megaw, H. D. (1973). *Crystal Structures: a Working Approach*, p. 216. Philadelphia: WB Saunders.
Mereiter, K. (1977). *J. Chem. Phys.* **67**, 2146–2150.
Müller, P., Herbst-Irmer, R., Spek, A. L., Schneider, T. R. & Sawaya, M. R. (2006). *Crystal Structure Refinement: a Crystallographer's Guide to SHELXL* (IUCr Texts on Crystallography 8), p. 121. Oxford: IUCr/OUP.
Nalini, G. & Guru Row, T. N. (2002). *Chem. Mater.* **14**, 4729–4735.
Norberg, S. T. (2002). *Acta Cryst.* B**58**, 743–749.
Ogorodnyk, I. V., Baumer, V. N., Zatovsky, I. V., Slobodyanik, N. S., Shishkin, O. V. & Domasevitch, K. V. (2007). *Acta Cryst.* B**63**, 819–827.
Pet'kov, V. I., Dorokhova, G. I. & Orlova, A. I. (1999). *Crystallogr. Rep.* **46**, 69–74.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Taylor, R. & Kennard, O. (1983). *Acta Cryst.* B**39**, 517–525.
Yamane, H. & DiSalvo, F. J. (1996). *J. Alloys Compd*, **240**, 33–36.
Zemann, A. & Zemann, J. (1957). *Acta Cryst.* **10**, 409–413.