

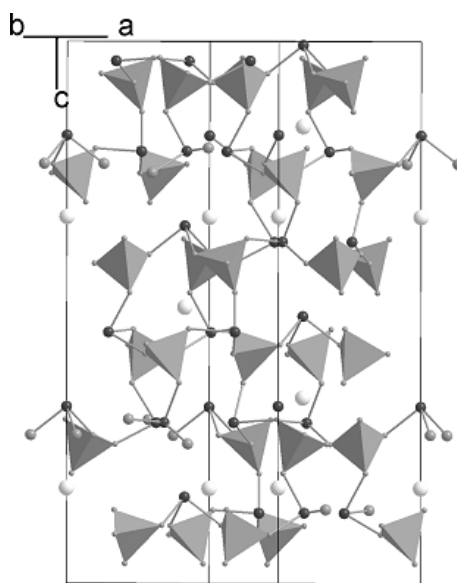
KSn₄(PO₄)₃Jin-Feng Deng,^a You-Jun Kang,^a
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symao@jingxian.xmu.edu.cn**Key indicators**Single-crystal X-ray study
T = 293 K
Mean σ (P–O) = 0.004 Å
R factor = 0.017
wR factor = 0.041
Data-to-parameter ratio = 15.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of potassium tetratin(II) tris(orthophosphate), KSn₄(PO₄)₃, obtained by hydrothermal synthesis, has been determined from single-crystal X-ray diffraction data. The structure consists of [Sn₄(PO₄)₃] units sharing common corners, which leads to a three-dimensional network structure and generates cages along the *c* direction. The cages are occupied by K atoms on threefold axes.

Comment

Compounds with open framework structures, including phosphates, have attracted great interest due to their potential applications (Cheetham *et al.*, 1999). While the Sn^{IV} compound KSnOPO₄, which is isotypic with KTiOPO₄, has been extensively studied for its non-linear optical properties (Thomas *et al.*, 1990; Phillips *et al.*, 1990), Sn^{II} phosphates have been less well investigated. To our knowledge, besides some organically templated compounds and recently reported ammonium and sodium tin(II) phosphate compounds (Ayyappan *et al.*, 2000; Mao *et al.*, 2004), no other phases with inorganic cations have been published. Here, we report the synthesis and characterization of the Sn^{II} title compound, (I), in the potassium phosphate system.

In the KSn₄(PO₄)₃ structure there are eight crystallographically independent atomic sites, *viz.* one K, two Sn, one P and four O atoms. The tetrahedron around the P atom is quite regular, with an average P–O distance of 1.531 (4) Å

Received 26 July 2004
Accepted 9 August 2004
Online 21 August 2004**Figure 1**

The crystal structure of KSn₄(PO₄)₃. K atoms are represented by white shaded spheres, Sn atoms by black spheres and O atoms by grey spheres. The PO₄ tetrahedra are shown in a polyhedral representation.

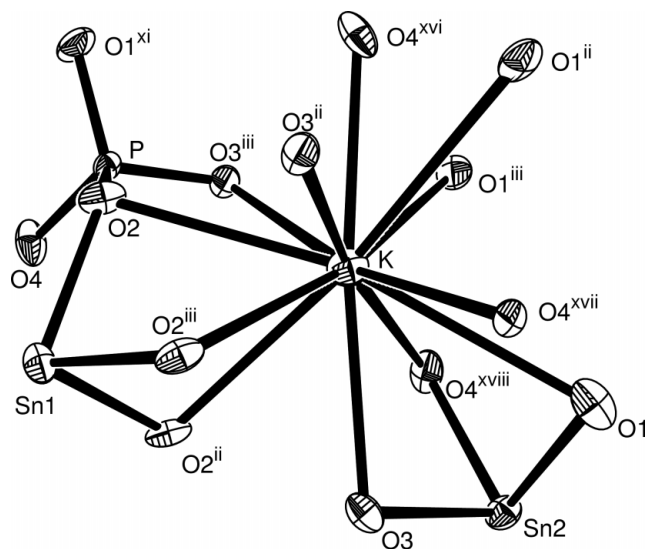


Figure 2

The coordination environment of the metal atoms in $\text{KSn}_4(\text{PO}_4)_3$, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (ii) $-x, x - y, z$; (iii) $-x + y, -x, z$; (xi) $\frac{1}{3} + x, \frac{2}{3} + x - y, \frac{1}{6} + z$; (xvi) $\frac{2}{3} - y, \frac{1}{3} - x, \frac{5}{6} + z$; (xvii) $\frac{2}{3} + x, \frac{1}{3} + x - y, \frac{5}{6} + z$; (xviii) $\frac{2}{3} - x + y, \frac{1}{3} + y, \frac{5}{6} + z$.]

and an average bond angle of $109.5(2)^\circ$ [ranging from $107.3(2)$ to $112.0(2)^\circ$]. These values are consistent with those typically observed in other orthophosphates.

In general, valences for Sn can be 4 or 2, with frequent coordination numbers of 6 and 3, respectively, as observed in KSnOPO_4 and $\text{Sn}_3(\text{PO}_4)_2$ (Thomas *et al.*, 1990; Mathew *et al.*, 1977). In (I), the coordination number of Sn is 3. The average Sn—O distances are 2.110 and 2.101 Å for Sn1 and Sn2, respectively. On the basis of bond-valence calculations (Brese & O'Keeffe, 1991), the bond-valence sums for P and Sn are calculated to be 4.87, 2.13 and 2.18, respectively, which confirms the formal assignment of the valences.

The structure of (I) can be described as constructed by linkages of $[\text{Sn}_4(\text{PO}_4)_3]$ units sharing common corners with Sn—O—P links. This construction leads to a three-dimensional network structure and cages are generated along the *c* direction. The cages are occupied by K atoms with 12 coordinations of O atoms.

Experimental

The title compound was obtained by a mild hydrothermal method. Starting materials were of analytical grade and used without further purification. A mixture of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.226 g), H_3BO_3 (0.432 g) and KH_2PO_4 (1.087 g) was prepared and dissolved in distilled water (10 ml) in a molar ratio of 1:7:8. The pH of the solution was about 1.5. The mixture was sealed in a glass tube about 20 cm in length, filled to about 30% of the tube volume. The glass tube was then placed in an oven and the temperature was increased slowly to about 413 K and maintained for two weeks before cooling to room temperature. The reaction proceeded under autogenous pressure. Colourless crystals of (I) with a trigonal prismatic shape were grown from this solution. X-ray powder diffraction showed that $\text{KSn}_4(\text{PO}_4)_3$ is the only crystalline phase obtained during these experiments.

Crystal data

$\text{KSn}_4(\text{PO}_4)_3$
 $M_r = 798.77$
 Trigonal, $R3c$
 $a = 9.7342(5)$ Å
 $c = 24.4754(14)$ Å
 $V = 2008.4(3)$ Å³
 $Z = 6$
 $D_x = 3.962$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 4440 reflections
 $\theta = 2.9\text{--}28.2^\circ$
 $\mu = 8.10$ mm⁻¹
 $T = 293(2)$ K
 Trigonal prism, colourless
 $0.16 \times 0.13 \times 0.13$ mm

Data collection

Bruker SMART Apex 2000 diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.290, T_{\max} = 0.349$
 4440 measured reflections

936 independent reflections
 927 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 28.2^\circ$
 $h = -12 \rightarrow 12$
 $k = -11 \rightarrow 12$
 $l = -32 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.041$
 $S = 1.25$
 936 reflections
 62 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0167P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.94$ e Å⁻³
 $\Delta\rho_{\min} = -0.69$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00092(5)
 Absolute structure: Flack (1983), with 446 Friedel pairs
 Flack parameter = 0.03(3)

Table 1

Selected geometric parameters (Å, °).

Sn1—O2	2.110 (3)	P—O4	1.523 (4)
Sn2—O4 ⁱ	2.095 (4)	P—O1 ⁱⁱ	1.524 (4)
Sn2—O1	2.101 (3)	P—O2	1.538 (3)
Sn2—O3	2.108 (4)	P—O3 ⁱⁱⁱ	1.541 (3)
O2—Sn1—O2 ^{iv}	86.44 (13)	O4 ⁱ —Sn2—O3	84.92 (14)
O4 ⁱ —Sn2—O1	88.16 (15)	O1—Sn2—O3	86.39 (14)
Symmetry codes: (i) $\frac{5}{3} - y, \frac{4}{3} - x, z - \frac{1}{6}$; (ii) $x - \frac{2}{3}, \frac{2}{3} + x - y, z + \frac{7}{6} - 1$; (iii) $1 - x + y, 2 - x, z$; (iv) $2 - y, 1 + x - y, z$.			

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 1996–2001); software used to prepare material for publication: SHELXL97.

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