Potassium silver tin selenide, $\text{K}_2\text{Ag}_2\text{Sn}_2\text{Se}_6$

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Potassium silver tin selenide, 
K₂Ag₂Sn₂Se₆

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Received 1 August 2001
Accepted 30 August 2001

The title compound was synthesized by a reactive salt reaction at 773 K over a period of 5 d. It has a one-dimensional chain structure consisting of K⁺ cations and one-dimensional [Ag₂Sn₂Se₆]²⁻ anions. The chain is constructed by edge-sharing bitetrahedral [Sn₂Se₆] units connected in a 1:2 ratio via linear Ag⁺ ions.

Comment

Multi-component metal chalcogenides are of great interest due to their low-dimensional structures and unusual properties. Since Ibers and co-workers first synthesized K₄Ti₃S₁₄ crystals using a molten salt (alkali metal polysulfide flux) reaction at 648 K (Sunshine et al., 1987), great progress has been made in the flux growth of solid-state chalcogenides at intermediate temperatures. A number of Sn-containing quaternary systems have been reported so far, for example, KGaSnS₄ (Wu et al., 1992), A₂Hg₃Sn₂S₈ (A = Rb and Cs; Marking et al., 1998), and K₂MnSn₆Se₆, K₂MnSn₆S₆ and K₂Ag₂SnSe₄ (Chen et al., 2000). For the A₂M₂Sn₂Q₆ family (A = alkali metal; M = Cu, Ag or Au; Q = S or Se), the members with M = Cu and Au, including A₂Cu₂Sn₂S₆ (A = Na, K, Rb and Cs), A₂Cu₂Sn₂Se₆ (A = K and Rb), K₂Au₂Sn₆S₆ and K₂Au₂Sn₆Se₆, have been investigated (Liao & Kanatzidis, 1993). We report here a new member to the family, namely K₂Ag₂Sn₂Se₆.

K₂Ag₂Sn₂Se₆ has a one-dimensional structure containing a chain of [Ag₂Sn₂Se₆]²⁻ anions separated by K⁺ ions. The packing, viewed along the c axis, is shown in Fig. 1(a). The [Ag₂Sn₂Se₆]²⁻ chain is constructed by edge-sharing bitetrahedral Sn₆Se₆ units and Ag⁺ ions in a 1:2 ratio (see Fig. 1b). In the Sn₆Se₆ dimer, the bridging Se₁ atoms form Sn—Se bonds of 2.583 (8) Å, which are longer than the bonds formed between the terminal Se₂ and Sn atoms [2.5075 (7) Å]. This is due to the stress of the SnSe₁Sn four-membered ring. There are two nearly linear Se—Ag—Se bridging bonds between adjacent Sn₆Se₆ units, forming eight-membered Sn(SeAg-Se)₄Sn rings. The Se—Ag—Se fragments of the ring are not parallel to each other, while an Ag—Ag bond occurs inside the ring, with a distance of 3.0717 (19) Å. The [Ag₂Sn₂Se₆]²⁻ chains extend along the crystallographic c-axis direction and are separated by K⁺ ions. The shortest inter-chain Se—Se distance is 3.61 Å. There are three crystallographically distinct K⁺ ions. Each K⁺ ion is eight-coordinated by Se atoms in a square-antiprismatic arrangement, with K—Se distances ranging from 3.5244 (13) to 3.550 (3) Å. K₃ is statistically distributed among the available sites, with a 50% probability.

The title compound, K₂Ag₂Sn₂Se₆, is isostructural with K₂Au₂Sn₂S₆ and K₂Au₂Sn₂Se₆, but has a different structure type from A₂Cu₂Sn₂Q₆ (A = Na, K, Rb or Cs; Q = S or Se; Liao & Kanatzidis, 1993). Cu⁺ prefers tetrahedral coordination in A₂Cu₂Sn₂Q₆, while Ag⁺ and Au⁺ tend to adopt a linear coordination, as in K₂Ag₂Sn₂Se₆, K₂Au₂Sn₆S₆ and K₂Au₂Sn₆Se₆.

Experimental

A mixture of K₂Se (0.0640 g, 0.417 mmol), Ag (0.0450 g, 0.417 mmol), Sn (0.0459 g, 0.417 mmol) and Se (0.0998 g, 1.264 mmol) was loaded into a Pyrex tube in a glove-box under an argon atmosphere and then sealed under vacuum conditions (about 10⁻¹ Pa). The tube was gradually heated to 773 K and kept at that temperature for 5 d. It was then cooled at a rate of 4 K h⁻¹ to 473 K, followed by natural cooling.
to room temperature. Orange–red block-like crystals were isolated from the reaction product, washed with dimethylformamide and ethanol, and finally dried with anhydrous ether. Semi-quantitative elemental analysis for the crystal, performed on an electron probe micro-analyzer (Shimadzu EPM-8100Q) using energy dispersive spectroscopy (EDS), indicated the composition to be KAgSnSe$_{2.5}$. A single crystal was selected for X-ray crystal structure determination.

**Crystal data**

K$_2$Ag$_2$Sn$_2$Se$_6$

$M_r = 1005.08$

Tetragonal, $P4/mnc$

$a = 8.1730 (10)$ Å

$\mu = 23.18$ mm$^{-1}$

$V = 1354.5 (4)$ Å$^3$

$Z = 4$

$D_x = 4.929$ Mg m$^{-3}$

Mo $K\alpha$ radiation

Cell parameters from 25 reflections

$\theta = 5.9$–11.7$^\circ$

$T = 293$ (2) K

Block, orange–red

Intensity decay: 0.08 to 0.05 Å$^2$

**Data collection**

Enraf-Nonius CAD-4 diffractometer

$\omega$ scans

Absorption correction: $\psi$ scan

(Kopfman & Huber, 1968)

$T_{min} = 0.208, T_{max} = 0.314$

1946 measured reflections

1029 independent reflections

546 reflections with $I > 2\sigma(I)$

**Refinement**

Refinement on $F^2$

$R(F^2) = 0.031$

$wR(F^2) = 0.048$

$S = 0.99$

546 reflections

35 parameters

Direct phase determination yielded the positions of the Ag, Sn and Se atoms. The remaining K atoms were located from the subsequent difference Fourier synthesis. The highest residual electron-density peak was located 1.08 Å from K3.

Data collection: CAD-4-PC Software (Enraf–Nonius, 1992); cell refinement: CAD-4-PC Software; data reduction: XCAD4/PC

**Table 1**

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>Sn1–Se2</th>
<th>2.5075 (7)</th>
<th>Ag1–Se2$^{\text{iv}}$</th>
<th>2.4935 (7)</th>
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<tr>
<td>Sn1–Se2$^{\text{i}}$</td>
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<td>Ag1–Se2</td>
<td>2.4935 (7)</td>
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<tr>
<td>Sn1–Se1</td>
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<td>Ag1–Ag1$^{\text{i}}$</td>
<td>3.0717 (19)</td>
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<tr>
<td>Se2–Sn1–Se2$^{\text{ii}}$</td>
<td>114.74 (3)</td>
<td>Se2–Sn1–Se1$^{\text{ii}}$</td>
<td>111.76 (3)</td>
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<tr>
<td>Se2–Sn1–Se1</td>
<td>111.76 (3)</td>
<td>Se1–Sn1–Se1$^{\text{ii}}$</td>
<td>93.08 (3)</td>
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<tr>
<td>Se2$^{\text{iv}}$–Sn1–Se1$^{\text{iv}}$</td>
<td>111.78 (3)</td>
<td>Se2$^{\text{iv}}$–Ag1–Se2</td>
<td>174.72 (5)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry codes: (i) $-x, 1-y, z$; (ii) $-x, 1-y, -z$; (iii) $-x, y, 1/2-z$. (Harms, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SCHAKAL97 (Keller, 1997).

The authors wish to thank the National Science Foundation for its generous support through grant DMR-9553066.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1017). Services for accessing these data are described at the back of the journal.

**References**


