

Potassium silver tin selenide,
 $K_2Ag_2Sn_2Se_6$ Hongyou Guo,^{a*} Zenghe Li,^a Lin Yang,^a Ping Wang,^a
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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 $[Ag_2Sn_2Se_6]^{2-}$ anions. The chain is constructed by edge-sharing bitetrahedral $[Sn_2Se_6]$ 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 $K_4Ti_3S_{14}$ 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, $KGaSn_4$ (Wu *et al.*, 1992), $A_2Hg_3Sn_2S_8$ ($A = Rb$ and Cs ; Marking *et al.*, 1998), and $K_2MnSn_2Se_6$, $K_2MnSnSe_4$ and $K_2Ag_2SnSe_4$ (Chen *et al.*, 2000). For the $A_2M_2Sn_2Q_6$ family ($A =$ alkali metal; $M = Cu, Ag$ or Au ; $Q = S$ or Se), the members with $M = Cu$ and Au , including $A_2Cu_2Sn_2S_6$ ($A = Na, K, Rb$ and Cs), $A_2Cu_2Sn_2Se_6$ ($A = K$ and Rb), $K_2Au_2Sn_2S_6$ and $K_2Au_2Sn_2Se_6$, have been investigated (Liao & Kanatzidis, 1993). We report here a new member to the family, namely $K_2Ag_2Sn_2Se_6$.

$K_2Ag_2Sn_2Se_6$ has a one-dimensional structure containing a chain of $[Ag_2Sn_2Se_6]^{2-}$ anions separated by K^+ ions. The packing, viewed along the c axis, is shown in Fig. 1(a). The $[Ag_2Sn_2Se_6]^{2-}$ chain is constructed by edge-sharing bitetrahedral Sn_2Se_6 units and Ag^+ ions in a 1:2 ratio (see Fig. 1b). In the Sn_2Se_6 dimer, the bridging Se1 atoms form Sn—Se1 bonds of 2.5839 (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 $SnSe_1_2Sn$ four-membered ring. There are two nearly linear Se—Ag—Se bridging bonds between adjacent Sn_2Se_6 units, forming eight-membered $Sn(SeAg_2Se)_2Sn$ rings. The Se—Ag—Se fragments of the ring are not

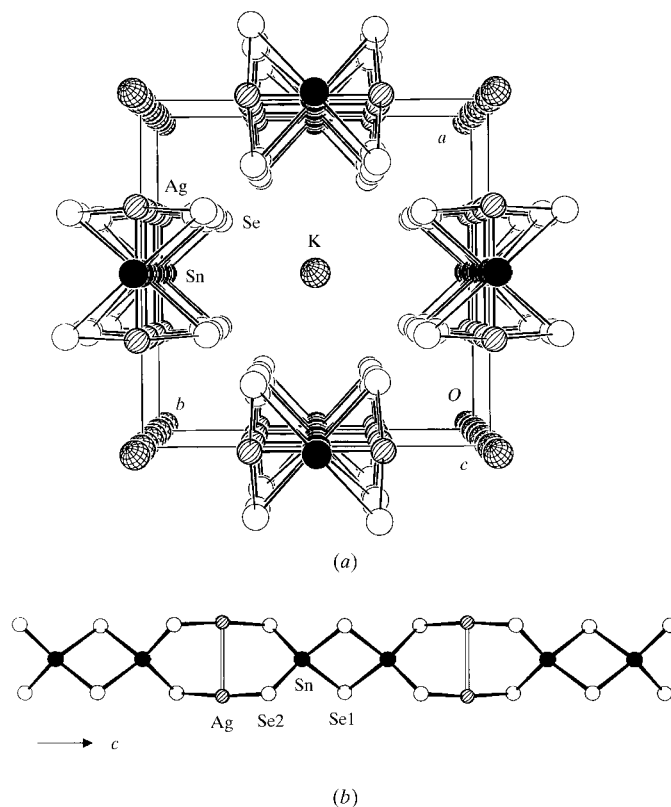


Figure 1

(a) View of $K_2Ag_2Sn_2Se_6$ along the c axis, with double-shaded circles for K , solid circles for Sn , single-shaded circles for Ag and open circles for Se atoms. The unit cell is outlined. (b) An illustration of the $[Ag_2Sn_2Se_6]^{2-}$ chain extending along the c axis, showing 70% probability displacement ellipsoids.

parallel to each other, while an $Ag—Ag$ bond occurs inside the ring, with a distance of 3.0717 (19) Å. The $[Ag_2Sn_2Se_6]^{2-}$ 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 3.3244 (13) to 3.550 (3) Å. $K3$ is statistically distributed among the available sites, with a 50% probability.

The title compound, $K_2Ag_2Sn_2Se_6$, is isostructural with $K_2Au_2Sn_2S_6$ and $K_2Au_2Sn_2Se_6$, but has a different structure type from $A_2Cu_2Sn_2Q_6$ ($A = Na, K, Rb$ or Cs ; $Q = S$ or Se ; Liao & Kanatzidis, 1993). Cu^+ prefers tetrahedral coordination in $A_2Cu_2Sn_2Q_6$, while Ag^+ and Au^+ tend to adopt a linear coordination, as in $K_2Ag_2Sn_2Se_6$, $K_2Au_2Sn_2S_6$ and $K_2Au_2Sn_2Se_6$.

Experimental

A mixture of K_2Se (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-810Q) using energy dispersive spectroscopy (EDS), indicated the composition to be $\text{KAgSnSe}_{2.5}$. A single crystal was selected for X-ray crystal structure determination.

Crystal data

| | |
|---|-------------------------------------|
| $\text{K}_2\text{Ag}_2\text{Sn}_2\text{Se}_6$ | Mo $K\alpha$ radiation |
| $M_r = 1005.08$ | Cell parameters from 25 reflections |
| Tetragonal, $P4/mcc$ | $\theta = 5.9\text{--}11.7^\circ$ |
| $a = 8.1730$ (10) Å | $\mu = 23.18$ mm $^{-1}$ |
| $c = 20.278$ (4) Å | $T = 293$ (2) K |
| $V = 1354.5$ (4) Å 3 | Block, orange-red |
| $Z = 4$ | $0.08 \times 0.05 \times 0.05$ mm |
| $D_x = 4.929$ Mg m $^{-3}$ | |

Data collection

| | |
|--|--|
| Enraf-Nonius CAD-4 diffractometer | $R_{\text{int}} = 0.036$ |
| ω scans | $\theta_{\text{max}} = 30.0^\circ$ |
| Absorption correction: ψ scan (Kopfmán & Huber, 1968) | $h = 0 \rightarrow 11$ |
| $T_{\text{min}} = 0.208$, $T_{\text{max}} = 0.314$ | $k = 0 \rightarrow 11$ |
| 1946 measured reflections | $l = 0 \rightarrow 28$ |
| 1029 independent reflections | 3 standard reflections every 300 reflections |
| 546 reflections with $I > 2\sigma(I)$ | intensity decay: $\pm 1.6\%$ |

Refinement

| | |
|---------------------------------|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2)]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $wR(F^2) = 0.048$ | $\Delta\rho_{\text{max}} = 1.68$ e Å $^{-3}$ |
| $S = 0.99$ | $\Delta\rho_{\text{min}} = -1.61$ e Å $^{-3}$ |
| 546 reflections | Extinction correction: <i>SHELXL97</i> |
| 35 parameters | Extinction coefficient: 0.00190 (4) |

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, °).

| | | | |
|---------------------------|------------|---|-------------|
| Sn1—Se2 | 2.5075 (7) | Ag1—Se2 ⁱⁱⁱ | 2.4935 (7) |
| Sn1—Se2 ⁱ | 2.5075 (7) | Ag1—Se2 | 2.4935 (7) |
| Sn1—Se1 | 2.5839 (8) | Ag1—Ag1 ⁱ | 3.0717 (19) |
| Sn1—Se1 ⁱⁱ | 2.5839 (8) | | |
| Se2—Sn1—Se2 ⁱ | 114.74 (3) | Se2 ⁱ —Sn1—Se1 ⁱⁱ | 111.76 (3) |
| Se2—Sn1—Se1 | 111.76 (3) | Se1—Sn1—Se1 ⁱⁱ | 93.08 (3) |
| Se2 ⁱ —Sn1—Se1 | 111.78 (3) | Se2 ⁱⁱⁱ —Ag1—Se2 | 174.72 (5) |
| Se2—Sn1—Se1 ⁱⁱ | 111.78 (3) | | |

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

(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).

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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.

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