

## Potassium sodium tin selenide, $K_3NaSn_3Se_8$

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The title compound, tripotassium sodium tritin octaselenide,  $K_3NaSn_3Se_8$ , has a molecular (zero-dimensional) structure containing trimeric  $[Sn_3Se_8]^{4-}$  units which consist of three edge-sharing  $SnSe_4$  tetrahedra. The  $[Sn_3Se_8]^{4-}$  anions and the tetrahedrally coordinated  $Na^+$  cations are arranged in an alternating fashion along the  $c$  axis to form  $SiS_2$ -like chains, which are then separated by eight-coordinate  $K^+$  cations. The Sn—Se bond distances are normal, being in the range 2.477 (1)–2.612 (1) Å.

### Comment

In recent years, a number of intermetallic compounds in the  $A$ –Sn–Se system have been detected and structurally characterized. These include  $A_4SnSe_4$  ( $A$  is Na or K; Klepp, 1992*a*) with isolated  $SnSe_4$  tetrahedra,  $K_4Sn_2Se_6$  (Eisenmann & Hansa, 1993*a*) and  $K_4Sn_3Se_8$  (Sheldrick, 1988) with dimers and trimers of edge-sharing tetrahedra,  $Na_2SnSe_3$  (Klepp, 1995) with one-dimensional chains of corner-sharing  $SnSe_4$  tetrahedra,  $K_2Sn_2Se_5$  (Klepp, 1992*b*) with chains of edge-sharing  $SnSe_5$  bipyramids which are connected *via* apical Se atoms to form an infinite anionic framework, and  $K_2Sn_4Se_8$  (Klepp & Fabian, 1992) containing layers of corner-sharing  $Sn^{IV}Se_4$  tetrahedra which are connected by  $Sn^{II}$  atoms to form an open three-dimensional network. During our investigation of the quaternary K–Ni–Sn–Se system using the molten alkali-metal polychalcogenide flux method, we unexpectedly obtained single crystals of the novel title trimeric compound,  $K_3NaSn_3Se_8$ . In this paper, we report its crystal structure determination.

The crystal structure of  $K_3NaSn_3Se_8$  projected approximately on the  $ab$  plane is shown in Fig. 1. Interestingly,  $Na^+$  cations and  $[Sn_3Se_8]^{4-}$  anions are aligned in an alternating fashion along the  $[001]$  direction to form a chain-like structure. These chains are then separated by  $K^+$  cations. The  $[NaSn_3Se_8]^{3-}$  chain (Fig. 2), which looks very similar to those observed in  $KFeS_2$  (Boon & MacGillavry, 1942) and  $K_2MnSn_2Se_6$  (Chen *et al.*, 2000), may be described as a substitutional variant of the  $SiS_2$ -type (Peters & Krebs, 1982). However, because Na–Se interactions are ionic in character,

it is more appropriate to describe the title compound as having a molecular (zero-dimensional) structure containing highly charged trimeric  $[Sn_3Se_8]^{4-}$  units which consist of three edge-sharing  $SnSe_4$  tetrahedra. In the  $[Sn_3Se_8]^{4-}$  unit, the central atom Sn1 has a site symmetry of  $\bar{4}2m$ , giving a single Sn–Se bond distance [ $4 \times 2.517$  (1) Å], while the external Sn2 atom lies on a twofold axis, resulting in two sets of bond lengths [Sn2–Se1 ( $\times 2$ ) 2.612 (1) and Sn2–Se2 ( $\times 2$ ) 2.477 (1) Å]. The terminal Sn2–Se2 bonds are markedly shorter than the bridging Sn–Se1 bonds, as expected, and both are close to those observed in the discrete di- and tritetrahedral species  $K_4Sn_2Se_6$  (Eisenmann & Hansa, 1993*a*) and  $K_4Sn_3Se_8$  (Sheldrick, 1988). The Se–Sn–Se angles range from 97.01 (5) to 116.04 (3)° for Sn1 and from 92.42 (6) to 114.16 (7)° for Sn2, with their respective smallest angles being associated with the constrained  $Sn_2Se_2$  four-membered rings.

There are two crystallographically independent  $K^+$  ions and one unique  $Na^+$  ion surrounding the  $[Sn_3Se_8]^{4-}$  anions. Each  $K^+$  is coordinated by eight Se atoms in a square antiprismatic arrangement, with K–Se distances in the range 3.333 (2)–3.5955 (8) Å, which are comparable with those observed in  $K_2MnSn_2Se_6$  [3.352 (2)–3.642 (3) Å; Chen *et al.*, 2000]. In contrast, each  $Na^+$  cation is four-coordinate to Se atoms, with shorter Na–Se distances of 2.895 (1) Å ( $\times 4$ ). Tetrahedrally coordinated  $Na^+$  is rare. Several limited examples include  $Na_2Se$  (Na–Se 2.948 Å; Zintl *et al.*, 1934) and  $Na_6Sn_2Se_7$  [Na–Se 2.880 (6)–2.926 (7) Å; Eisenmann & Hansa, 1993*b*].

It is noted that  $K_4Sn_3Se_8$  is related to the title compound in its stoichiometry but differs in its structure. This compound crystallizes in the orthorhombic space group  $Ccca$ . The adjacent  $[Sn_3Se_8]^{4-}$  groups are not arranged into linear arrays as in  $K_3NaSn_3Se_8$ , but are shifted with respect to each other by  $(a+b)/2$ . As a result, no tetrahedral voids are formed and the trimers are separated by six- and eight-coordinate  $K^+$  cations.

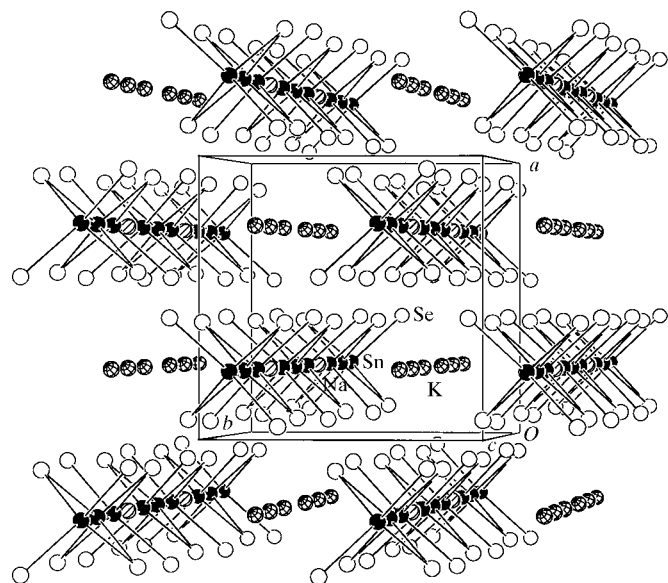
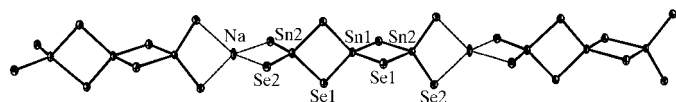


Figure 1  
The unit cell of  $K_3NaSn_3Se_8$  projected approximately along the  $c$  axis.

To the best of our knowledge,  $K_3NaSn_3Se_8$  represents a new structure type and it is also the first structurally characterized  $A-Sn-Q$  ternary chalcogenide ( $A$  is an alkali metal and  $Q$  is  $S$ ,  $Se$  or  $Te$ ) containing mixed alkali metal cations.



**Figure 2**

A fragment of the  $[NaSn_3Se_8]^{3-}$  chain, with Na–Se interactions indicated by dashed lines. Displacement ellipsoids are drawn at the 50% probability level.

Thermal analysis *via* differential scanning calorimetry shows that  $K_3NaSn_3Se_8$  melts congruently at about 741 K. The optical diffuse reflectance spectrum of  $K_3NaSn_3Se_8$  displays a steep absorption edge with an estimated band gap of about 2.2 eV, confirming its expected semiconducting nature.

## Experimental

Single crystals of the title compound were extracted from an experiment attempting to prepare K–Ni–Sn–Se quaternary chalcogenides.  $K_2Se$  (0.080 g, 0.5 mmol), Ni (0.015 g, 0.25 mmol), Sn (0.060 g, 0.5 mmol) and Se (0.158 g, 2 mmol) were weighed in a glove box under an atmosphere of argon. The mixture was introduced into a thin-walled Pyrex tube and sealed under vacuum (about  $10^{-3}$  Torr; 1 Torr = 133.322 Pa). The tube was gradually heated to 773 K, where it was kept for 6 d, then cooled at a rate of  $4\text{ K h}^{-1}$  to 423 K. Several orange block-like crystals were observed after washing the reaction product with dimethylformamide and anhydrous ethanol and drying with anhydrous diethyl ether. Structural refinements indicated the composition of these crystals to be  $K_3NaSn_3Se_8$ . The sodium constituent may come from the impure potassium source. Subsequently, direct reaction of a stoichiometric mixture of  $K_2Se$ ,  $Na_2Se$ , Sn and Se at 723 K for one week yielded an almost single-phase polycrystalline sample with small amounts of Se and  $SnSe_2$  impurities which were confirmed by powder X-ray analysis.

### Crystal data

$K_3NaSn_3Se_8$   
 $M_r = 1128.04$   
 Tetragonal,  $P4/nbm$   
 $a = 8.121(1)\text{ \AA}$   
 $c = 13.672(3)\text{ \AA}$   
 $V = 901.7(3)\text{ \AA}^3$   
 $Z = 2$   
 $D_x = 4.155\text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 7.17\text{--}13.93^\circ$   
 $\mu = 20.956\text{ mm}^{-1}$   
 $T = 293(2)\text{ K}$   
 Block, orange  
 $0.10 \times 0.08 \times 0.05\text{ mm}$

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (Kopfmann & Huber, 1968)  
 $T_{\min} = 0.121$ ,  $T_{\max} = 0.348$   
 879 measured reflections  
 491 independent reflections  
 387 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$   
 $\theta_{\text{max}} = 25.95^\circ$   
 $h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 10$   
 $l = 0 \rightarrow 16$   
 3 standard reflections every 150 reflections  
 intensity variation:  $\pm 1.5\%$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.071$   
 $S = 1.228$   
 491 reflections  
 27 parameters  
 $w = 1/[\sigma^2(F_o^2) + 12P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.83\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.75\text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient: 0.0026 (2)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Sn1–Se1 ( $\times 4$ )	2.517 (1)	K2–Se1 ( $\times 4$ )	3.333 (2)
Sn2–Se2 ( $\times 2$ )	2.477 (1)	K2–Se2 ( $\times 4$ )	3.468 (2)
Sn2–Se1 ( $\times 2$ )	2.612 (1)	Na–Se2 ( $\times 4$ )	2.895 (1)
K1–Se2 ( $\times 8$ )	3.5955 (8)		
Se1–Sn1–Se1 ( $\times 4$ )	116.04 (3)	Se2–Sn2–Se1 ( $\times 4$ )	112.09 (2)
Se1–Sn1–Se1 ( $\times 2$ )	97.01 (5)	Se1–Sn2–Se1	92.42 (6)
Se2–Sn2–Se2	114.16 (7)		

Direct phase determination yielded the positions of the Sn and Se atoms. The K and Na atoms were located from the subsequent difference Fourier synthesis. All atoms were refined anisotropically. The highest residual electronic density peaks were located  $0.74\text{ \AA}$  from the Sn2 atoms.

Data collection: *CAD-4/PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD-4/PC Software*; data reduction: *XCAD4/PC* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SCHAKAL97* (Keller, 1992); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1296). Services for accessing these data are described at the back of the journal.

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