

## METAL-ORGANIC COMPOUNDS

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**$(K^+)_2(18\text{-crown-6-K}^+)_2[Sn_2Se_6]^{4-} \cdot 4en$ : an  $[Sn_2Se_6]^{4-}$  Anion with a Short Sn...Sn Distance**

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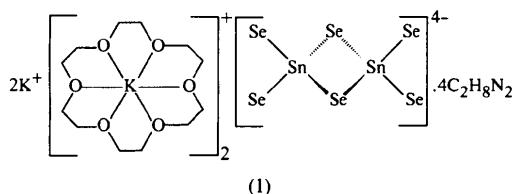
**Abstract**

The title compound, dipotassium(+) bis[(1,4,7,10,13,16-hexaoxacyclooctadecane)potassium(+)] hexaselenodistannate(4-) tetrakis(ethylenediamine) solvate,  $K_2[K(C_{12}H_{24}O_6)]_2[Sn_2Se_6] \cdot 4C_2H_8N_2$ , (1), has been prepared by the extraction of the alloy  $KSn_{0.67}Se_{1.93}$  in en (en is ethylenediamine) in the presence of 18-crown-6 followed by addition of tetrahydrofuran. The geometric parameters observed for the  $Sn_2Se_6^{4-}$  anion in (1) are significantly different from those previously reported in the  $(enH^+)_2(2,2,2\text{-crypt-K}^+)_2$  (2,2,2-crypt is 1,10-diazabicyclo-4,7,13,16,21,24-hexaoxa[8.8.8]hexacosane),  $K^+(NMe_3^+)_3$  and  $M^+$  ( $M = Na, K, Rb, Cs$ ) salts.

**Comment**

Compound (1) crystallizes in the space group  $P2_1/c$  and consists of a centrosymmetric  $Sn_2Se_6^{4-}$  anion (Fig. 1) bridging two symmetry-related unsequestered  $K^+$  cations, forming  $K^+ \cdots Sn_2Se_6^{4-} \cdots K^+$  layers. These layers are sandwiched between two symmetry-related 18-crown-6- $K^+$  cations and are bridged to these cations by ethylenediamine (en) solvent molecules. The unsequestered  $K^+$  ions are coordinated to an additional en solvent molecule (Fig. 2). The structure of the 18-crown-6- $K^+$  cation is similar to that determined previously in  $K^+(18\text{-crown-6-K}^+)_2GaTe_3^{2-}$  (Park, Salm & Ibers, 1995) and therefore will not be discussed. The geometry of the  $Sn_2Se_6^{4-}$  anion (approximate  $D_{2h}$  point symmetry) is based on two edge-sharing distorted  $SnSe_4$  tetrahedra and is isostructural with  $B_2H_6$  (Greenwood & Earnshaw, 1984),  $W_2Se_6^{2-}$  (Lu, Ansari & Ibers, 1989) and  $Ge_2Se_6^{4-}$  (Eisenmann & Hansa, 1993). Although the  $Sn_2Se_6^{4-}$  anion has been previously characterized by X-ray crystallography in  $(enH^+)_2(2,2,2\text{-crypt-K}^+)_2[Sn_2Se_6]^{4-}$  (Campbell, Devereux, Gerken, Mercier, Pirani & Schrobilgen, 1996),

$K^+(NMe_3^+)_3[Sn_2Se_6]^{4-}$  (Campbell, Devereux, Gerken, Mercier, Pirani & Schrobilgen, 1996),  $Na_4Sn_2Se_6 \cdot 13H_2O$  (Krebs & Uhlen, 1987),  $K_4Sn_2Se_6$  (Eisenmann & Hansa, 1993),  $Rb_4Sn_2Se_6$  (Sheldrick & Schaaf, 1994) and  $Cs_4Sn_2Se_6$  (Sheldrick & Braunbeck, 1989), the  $Sn_2Se_6^{4-}$  anion in (1) is compressed along the Sn...Sn vector, resulting in geometric parameters which vary significantly from those of the previously reported structures. The Sn...Sn distances and the Sn—Se<sub>b</sub>—Sn, Se<sub>b</sub>—Sn—Se<sub>b</sub> and Se<sub>t</sub>—Sn—Se<sub>t</sub> (*b* is bridging and *t* terminal) bond angles in (1) and in the previously characterized  $Sn_2Se_6^{4-}$  anions are summarized in Table 2. The Sn...Sn distance in (1), 3.4930(9) Å, is significantly shorter ( $> 3\sigma$ ) than those observed in the previously characterized anions, and the Sn—Se<sub>b</sub>—Sn and Se<sub>b</sub>—Sn—Se<sub>b</sub> bond angles are significantly smaller and larger, respectively, than in the previously reported structures. The Se<sub>t</sub>—Sn—Se<sub>t</sub> bond angle in (1) is similar only to that observed in  $Na_4Sn_2Se_6 \cdot 13H_2O$  but is significantly different from those observed in the other salts. The average terminal [2.464(2) Å] and bridging [2.590(4) Å] bond distances in (1) are similar to those established in the previously reported structures [average: terminal 2.460(8) and bridging 2.589(7) Å].



In all structures, the Sn—Se<sub>t</sub> distances are shorter than the Sn—Se<sub>b</sub> distances, which is consistent with the expected higher relative bond orders of the Sn—Se<sub>t</sub> bonds (Campbell *et al.*, 1996). A similar trend has also been observed in the related  $Sn_2Te_6^{4-}$  (Huffman, Haushalter, Umarji, Shenoy & Haushalter, 1984; Ansari, Bollinger & Ibers, 1993; Campbell *et al.*, 1996),  $Sn_2Te_7^{4-}$  (Brinkmann, Eisenmann & Schäfer, 1985)

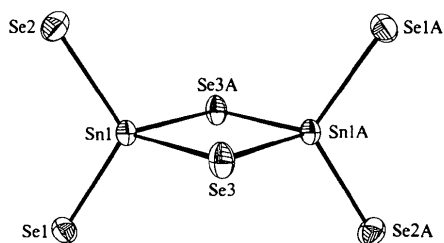


Fig. 1. View of the  $[Sn_2Se_6]^{4-}$  anion in (1) with displacement ellipsoids drawn at the 70% probability level.

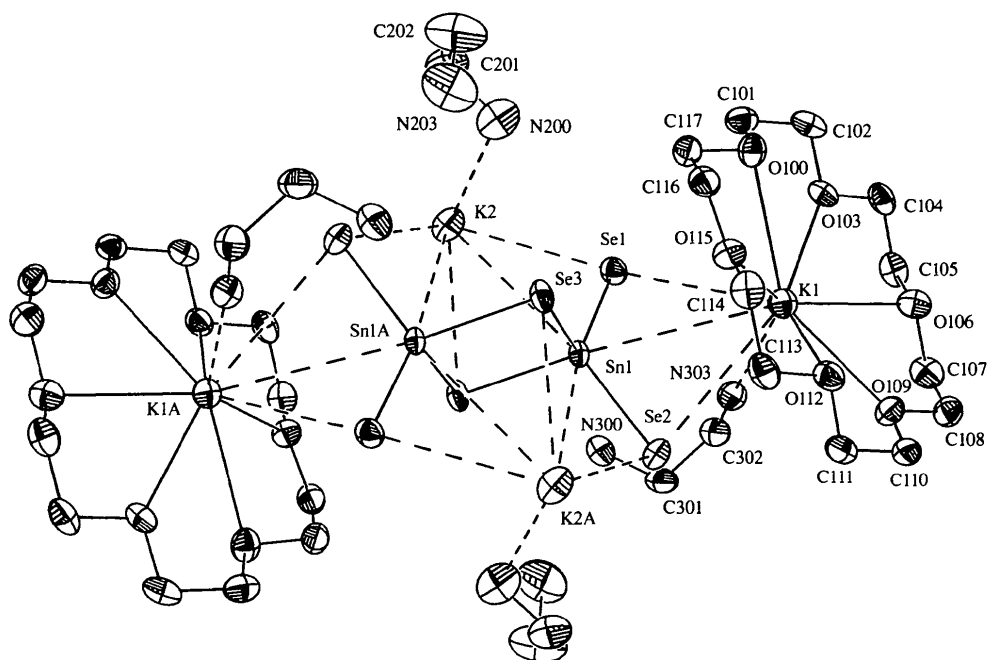


Fig. 2. View of the  $[18\text{-crown-6-K}^+]\cdot\text{en}\cdot\text{K}^+(\text{en})\cdot\text{Sn}_2\text{Se}_6^{4-}\cdot\text{K}^+(\text{en})\cdot\text{en}\cdot[18\text{-crown-6-K}^+]$  structural unit with displacement ellipsoids drawn at the 70% probability level. H atoms have been omitted for clarity.

and  $\text{Sn}_4\text{Se}_{10}^{4-}$  (Campbell, DiCiommo, Mercier, Pirani, Schrobilgen & Willuhn, 1995) anions.

It should be noted that the  $\text{Sn}_2\text{Se}_6^{4-}$  anion has also been structurally characterized by X-ray crystallography in  $(\text{enH}_2)_2\text{Sn}_2\text{Se}_6$  (Sheldrick & Braunbeck, 1993). Although the  $\text{Se}_b\text{—Sn—Se}_b$  bond angle  $[95.1(1)^\circ]$  in  $(\text{enH}_2)_2\text{Sn}_2\text{Se}_6$  is similar to that in (1), the  $\text{Sn—Se}_b\text{—Sn}$  bond angle  $[84.91(1)^\circ]$  is larger and the  $\text{Sn}\cdots\text{Sn}$  distance, which is anticipated to be slightly larger, is actually shorter  $[3.480(1)\text{ \AA}]$  than in the present and previously reported structures (Table 2). The  $\text{Sn—Se}_t$  and  $\text{Sn—Se}_b$  distances in  $(\text{enH}_2)_2\text{Sn}_2\text{Se}_6$  are  $2.460(1)$  and  $2.578(1)\text{ \AA}$ , respectively.

## Experimental

The extreme air and moisture sensitivity of the compounds used required all manipulations to be carried out under rigorously anhydrous and oxygen-free conditions in a nitrogen-atmosphere dry box (two-station Vacuum Atmospheres Model DLX, with moisture and oxygen levels  $< 0.1$  p.p.m.; for general solid and crystal handling), on a general-purpose grease-free glass vacuum line equipped with Pyrex/Teflon stopcocks (J. Young Scientific Glassware) and in a glove bag (for solution handling) which had been purged with dry nitrogen for at least 12 h prior to use. The ternary  $\text{KSnSe}_2$  alloy was prepared as previously described (Burns, Devereux, Granger & Schrobilgen, 1985) by fusion of the elements (K 0.9591 g, 24.53 mmol; Sn 2.7575 g, 23.23 mmol; Se 3.7318 g, 47.26 mmol) inside a thick-walled Pyrex glass tube. The resulting alloy was ground into a fine powder and

its composition was corrected for the recovered tin lump (0.8151 g, 6.87 mmol) to  $\text{KSn}_{0.67}\text{Se}_{1.93}$ . The  $\text{KSn}_{0.67}\text{Se}_{1.93}$  alloy (0.1040 g, 0.384 mmol) was transferred into one arm of a two-arm Pyrex vessel and extracted in en (5 ml) in the presence of 18-crown-6 (0.0930 g, 0.352 mmol) with an 18-crown-6: $\text{K}^+$  ratio of 1.00:0.92. After two weeks, the deep-yellow solution was carefully decanted off the alloy residue into the second arm of the reaction vessel. An excess of THF (1:2 v/v) was condensed under static vacuum at 273 K into the first arm of the reactor. Yellow platelets of (1) were obtained by the vapor-phase diffusion of the THF into the en solution under static vacuum.

## Crystal data

$\text{K}_2[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)]_2[\text{Sn}_2\text{Se}_6]\cdot 4\text{C}_2\text{H}_8\text{N}_2$   
 $M_r = 1636.58$   
 Monoclinic  
 $P2_1/c$   
 $a = 15.634(2)\text{ \AA}$   
 $b = 8.4790(10)\text{ \AA}$   
 $c = 23.404(3)\text{ \AA}$   
 $\beta = 108.600(10)^\circ$   
 $V = 2940.4(6)\text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.848\text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073\text{ \AA}$   
 Cell parameters from 1775 reflections  
 $\theta = 3\text{--}29^\circ$   
 $\mu = 4.900\text{ mm}^{-1}$   
 $T = 150(2)\text{ K}$   
 Platelet  
 $0.35 \times 0.32 \times 0.12\text{ mm}$   
 Yellow

## Data collection

Stoe Imaging Plate  
 Diffractometer System  
 (IPDS)

7794 independent reflections  
 $R_{\text{int}} = 0.070$   
 $\theta_{\text{max}} = 29^\circ$

Oscillation scans  $h = -22 \rightarrow 21$   
 Absorption correction:  $k = -11 \rightarrow 11$   
 redundant reflections  $l = -32 \rightarrow 33$   
 (Borrmann, 1997)  
 $T_{\min} = 0.433, T_{\max} = 0.646$   
 27 121 measured reflections

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.080$   
 $S = 1.033$   
 7733 reflections  
 449 parameters  
 All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.481P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 1.513 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.961 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

crystal oscillated through  $1^\circ$  in  $\varphi$ . The two data sets were merged and the final data set contained 92% of the calculated number of reflections.

All computations were carried out on a Silicon Graphics Inc. Model 4600 PC workstation. During refinement, 61 reflections with  $F^2 < -2\sigma(F^2)$  were suppressed. In the final difference map, the maximum electron density was located around the Sn<sub>2</sub>Se<sub>6</sub><sup>4-</sup> anion.

Data collection: *IPDS* (Stoe & Cie, 1995). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Table 1. Selected geometric parameters (Å, °)

Sn1—Sn1 <sup>i</sup>	3.4930 (9)	Se2—K2 <sup>i</sup>	3.5723 (8)
Sn1—Se1	2.4665 (4)	Se3—K2 <sup>i</sup>	3.6030 (8)
Sn1—Se2	2.4616 (4)	K1—O100	3.046 (2)
Sn1—Se3	2.5941 (4)	K1—O103	2.897 (2)
Sn1—Se3 <sup>ii</sup>	2.5852 (5)	K1—O106	3.052 (2)
Sn1—K1 <sup>iii</sup>	4.0218 (8)	K1—O109	2.879 (2)
Sn1—K2	4.0695 (8)	K1—O112	3.030 (2)
Sn1—K2 <sup>i</sup>	4.1397 (8)	K1—O115	2.843 (2)
Se1—K1 <sup>iii</sup>	3.6946 (7)	K1—N303 <sup>iv</sup>	3.330 (3)
Se1—K2	3.4534 (8)	K2—N200	2.890 (4)
Se1—K2 <sup>iii</sup>	3.5604 (8)	K2—N300 <sup>v</sup>	2.874 (3)
Se2—K1 <sup>iii</sup>	3.7952 (8)	K2—K2 <sup>iii</sup>	4.2403 (14)
Sn1 <sup>i</sup> —Se3—Sn1	84.823 (12)	Se2—Sn1—Se3	109.831 (13)
Se1—Sn1—Se3	113.149 (13)	Se2—Sn1—Se3 <sup>i</sup>	110.065 (14)
Se1—Sn1—Se3 <sup>i</sup>	108.506 (12)	Se3 <sup>i</sup> —Sn1—Se3	95.176 (12)
Se2—Sn1—Se1	117.748 (12)		

Symmetry codes: (i)  $1 - x, 1 - y, -z$ ; (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $1 - x, 2 - y, -z$ ; (iv)  $x, y, 1 + z$ ; (v)  $x, 1 + y, z$ .

Table 2. Sn···Sn distances (Å) and Sn—Se<sub>b</sub>—Sn, Se<sub>b</sub>—Sn—Se<sub>b</sub> and Se<sub>i</sub>—Sn—Se<sub>i</sub> bond angles (°) observed in known Sn<sub>2</sub>Se<sub>6</sub><sup>4-</sup> salts

Counter-cation	Sn···Sn	Sn—Se <sub>b</sub> —Sn	Se <sub>b</sub> —Sn—Se <sub>b</sub>	Se <sub>i</sub> —Sn—Se <sub>i</sub>
(K <sup>+</sup> ) <sub>2</sub> (18-crown-6-K <sup>+</sup> ) <sub>2</sub>	3.4930 (9)	84.823 (12)	95.176 (12)	117.748 (12)
(enH <sup>+</sup> ) <sub>2</sub> (2,2,2-crypt-K <sup>+</sup> ) <sub>2</sub>	3.557 (1)	87.05 (2)	92.95 (2)	111.95 (6)
K <sup>+</sup> (NMe <sub>3</sub> <sup>+</sup> ) <sub>3</sub>	3.578 (4)	87.06 (7)	92.94 (7)	119.12 (3)
Na <sup>+</sup>	3.529 (2)	86.07 (5)	93.94 (5)	117.68 (6)
K <sup>+</sup>	3.514	85.5	94.5	121.2
Rb <sup>+</sup>	3.518	85.4 (1)	94.6 (1)	120.1 (1)
Cs <sup>+</sup>	3.504 (1)	85.26 (5)	94.74 (5)	118.91 (6)
(enH <sub>2</sub> <sup>+</sup> ) <sub>2</sub>	3.480 (1)	84.91 (1)	95.1 (1)	115.1 (1)

Crystal data were collected on a single crystal which was sealed under dry nitrogen in a 0.5 mm Lindemann glass capillary. A Stoe Imaging Plate Diffractometer System equipped with a one-circle goniometer and a graphite monochromator was used for data collection. Data were collected in two stages: (a) 500 exposures (4 min per exposure) were obtained at 48 mm with  $0 < \varphi < 150^\circ$  and with the crystal oscillated through  $0.3^\circ$  in  $\varphi$ ; (b) 200 exposures (2 min per exposure) were obtained at 125 mm with  $0 < \varphi < 200^\circ$  and with the

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1163). Services for accessing these data are described at the back of the journal.

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