

## 단 신

### [dabcoH]<sub>2</sub>[(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Sn<sub>2</sub>Se<sub>6</sub>]의 DMF 용매열 합성과 구조 분석

김 강 우\*

인천대학교 자연과학대학 화학과  
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### DMF Solvothermal Synthesis and Structural Characterization of [dabcoH]<sub>2</sub>[(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Sn<sub>2</sub>Se<sub>6</sub>]

Kang-Woo Kim\*

Department of Chemistry, University of Incheon, Incheon 402-749, Korea  
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#### INTRODUCTION

For the last two or three decades, a solvothermal synthetic method has proven to be effective and versatile for the exploration of new metal chalcogenides.<sup>1</sup> Although several solvents such as water, methanol, ethylenediamine(en), and ethyleneglycol have been extensively employed for the solvothermal synthesis of metal chalcogenides, DMF has been rarely used. Here we report the solvothermal synthesis of [dabcoH]<sub>2</sub>[(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Sn<sub>2</sub>Se<sub>6</sub>] (I) with *N,N*-dimethylformamide (DMF) as a solvent and its structural characterization by a single-crystal X-ray diffraction study.

Tin (poly)chalcogenides have been of special interest as some of these possess open framework structures.<sup>2</sup> It may lead to the new or at least advanced applications if we can combine the microporosity of metal chalcogenides and their characteristics such as catalytic activity, semiconductivity, and optoelectronic properties. A variety of organic cations have been incorporated as the counter cations into the salts of anionic chalcometallates, because of the belief that the templating capability of large organic cations is mainly responsible for directing the open

framework structures. As one of the unique organic cations with a certain value of the charge/size ratio, dabcoH<sup>+</sup> (=N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup>) was adopted for the stabilization of (dabcoH)<sub>2</sub>Sn<sub>3</sub>S<sub>7</sub><sup>2(b)</sup> but never appeared in the selenostannates. We attempted to stabilize new selenostannates with open framework structures by using dabcoH<sup>+</sup> as counter cations, but only found the [Sn<sub>2</sub>Se<sub>6</sub>]<sup>4-</sup> molecular anion to be yielded, instead.

#### EXPERIMENTAL SECTION

All experiments and manipulations were performed under an atmosphere of dry argon or nitrogen using either a Vacuum Atmosphere Dri-Lab glove box or Schlenk line.

Potassium diselenide, K<sub>2</sub>Se<sub>2</sub>, was prepared by dissolving the stoichiometric amount of potassium metal and elemental selenium in liquid ammonia. Tin(IV) bis(acetylacetonate) dichloride (98%) and 1,4-diazabicyclo[2.2.2]octane (dabco) (98%) were purchased from Aldrich and used without further purification. Dimethylformamide (DMF) (A.C.S. reagent) was purchased from J. T. Baker and distilled under reduced pressure after being stored over KOH for

more than a week and over Linde 4A molecular sieves for several days. Diethyl ether (Anhydrous, A.C.S. reagent) was also purchased from J. T. Baker and distilled after refluxing over potassium metal in the presence of benzophenone and triethylene-glycol-dimethyl ether for several hours.

Tin(IV) bis(acetylacetonate) dichloride (0.020 g, 0.052 mmol),  $K_2Se_2$  (0.025 g, 0.11 mmol), and dabco (0.012 g, 0.11 mmol) were charged into a 9 mm  $\phi$  pyrex tube under an inert argon atmosphere and about 0.5 mL DMF was added as a solvent. While the solvent was being frozen, the pyrex tube was evacuated up to about  $2.0 \times 10^{-3}$  torr and sealed with the use of a flame. The sealed tube was placed in a furnace and heated at 170 °C for 24 hours, then cooled to room temperature. Yellow needle crystals were isolated from the tube and washed with diethyl ether several times. Crystals of (I) were obtained in 42% yield, based on Sn(IV) metal ion content used. EPMA analysis on these crystals showed the Sn/Se ratio as 1 : 2.8.

A single crystal of (I) with dimensions 0.48  $\times$  0.08  $\times$  0.04 mm was selected for the study of structural determination. The single crystal was mounted on the tip of a glass fiber with epoxy adhesive. Crystallographic data for (I) was collected on a MXC3 four-circle single crystal automated diffractometer with  $\omega/2\theta$  scan mode. The intensities of two standard reflections were checked every 100 reflections to monitor crystal and instrument stability. No serious decay was observed during the data collection period. Final data set contained 1831 total reflections, of which 1689 reflections are unique. Accurate unit cell parameters were determined from 27 centered reflections in the range of  $20^\circ \leq 2\theta \leq 28^\circ$ .

After the structure was solved using a direct method with SHELXS-86, positional parameters and anisotropic displacement parameters were refined using full-matrix least squares techniques on  $F_o^2$  with SHELXL-97.<sup>3</sup> The final  $R$ -factors for all data were as follows:  $R_1=0.0514$ ,  $wR_2=0.0877$ . All non-hydrogen atoms were refined anisotropically. The hydrogen positions were calculated but not refined. The crystallographic data and details for the structural analysis of (I) are summarized in Table 1.

Table 1. Summary of crystallographic data and structural analysis for (I)

formula	$[N(CH_2CH_2)_3NH_2]_2[(CH_3)_2NH_2]_2[Sn_2Se_6]$
formula weight	1029.70
crystal habit	yellow needle
crystal size (mm <sup>3</sup> )	0.48 $\times$ 0.08 $\times$ 0.04
space group	$C2/m$ (No. 12)
$a$ (Å)	20.172(6)
$b$ (Å)	11.674(4)
$c$ (Å)	6.476(2)
$\beta$ (deg)	103.15(3)
$F$ (Å <sup>3</sup> ), $Z$	1485.0(8), 2
$D_{calc}$ (g/cm <sup>3</sup> )	2.303
temperature (K)	190
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71070
$\mu$ (mm <sup>-1</sup> )	9.051
$F(000)$	968
$\theta_{min}$ - $\theta_{max}$ (deg)	2.03 - 27.48
index ranges	$-26 \leq h \leq 25$ , $0 \leq k \leq 15$ , $0 \leq l \leq 8$
no. of reflections collected	1831
no. of independent reflections	1689
parameters/restraints	78/0
$R$ indices for all data	$R_1=0.0514$ , $wR_2=0.0877$
$R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.0396$ , $wR_2=0.0831$
GOF on $F^2$	0.993

## RESULTS AND DISCUSSION

Compound (I) consists of discrete molecular  $[Sn_2Se_6]^{4-}$  anions and charge-balancing organic cations, dabcoH<sup>+</sup> and  $[(CH_3)_2NH_2]^+$ . The geometry of the  $[Sn_2Se_6]^{4-}$  anion (see Fig. 1), which has a crystallographically imposed center of symmetry on the center of its  $Sn_2Se_2$  rhombus, is based on two edge-sharing  $SnSe_4$  tetrahedra and isostructural to the other dibor-

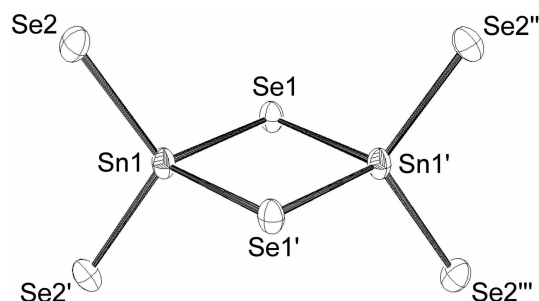


Fig. 1. ORTEP<sup>4</sup> representation of the  $[Sn_2Se_6]^{4-}$  anion in (I) with labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters(Å<sup>2</sup>) for (I)

atom	x	y	z	U <sub>eq</sub> (Å <sup>2</sup> ) <sup>a</sup>
Sn(1)	0.0783(1)	0	0.1842(1)	0.021(1)
Se(1)	0.0461(1)	0	-0.2262(1)	0.023(1)
Se(2)	0.1386(1)	0.1772(1)	0.3240(1)	0.029(1)
N(1)	0.3350(4)	0	1.0548(11)	0.026(2)
N(2)	0.2384(4)	0	0.7264(12)	0.029(2)
N(3)	0	0.2584(6)	0.5000	0.031(2)
C(1)	0.3621(4)	0	0.8607(14)	0.035(2)
C(2)	0.3049(4)	0	0.6569(14)	0.035(2)
C(3)	0.2923(3)	0.1023(6)	1.0495(10)	0.034(2)
C(4)	0.2335(3)	0.1050(6)	0.8501(10)	0.036(2)
C(5)	0.0326(4)	0.3269(7)	0.6890(12)	0.049(2)

<sup>a</sup> Equivalent isotropic U<sub>eq</sub> is defined as one-third of the trace of the orthogonalized U<sub>i</sub> tensor.

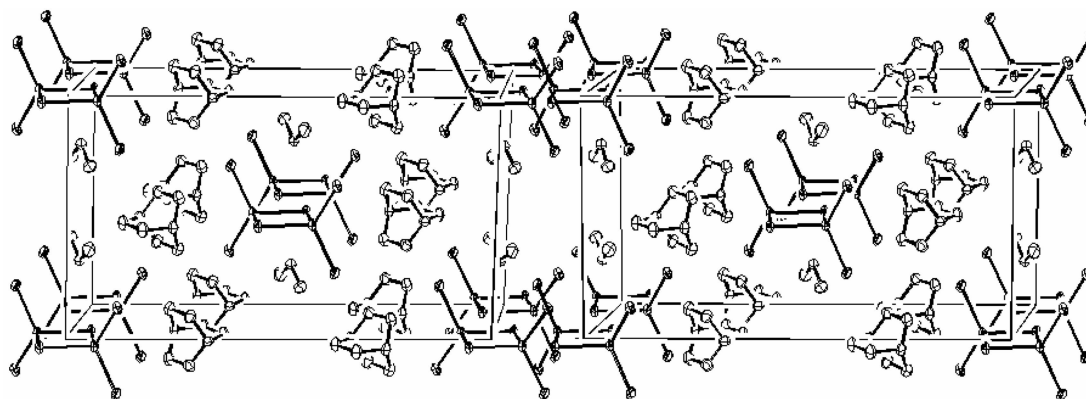


Fig. 2. Unit cell packing diagram (stereo-view) of (I). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

rane-type [M<sub>2</sub>Q<sub>6</sub>]<sup>4-</sup> (M=Metal; Q=S, Se, Te) anions, such as [W<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup>,<sup>5</sup> and [Ge<sub>2</sub>Se<sub>6</sub>]<sup>4-</sup>.<sup>6</sup> In the Sn<sub>2</sub>Se<sub>6</sub> rhombus, both tin and bridging selenium atoms are sitting on the special positions of (x, 0, z) with a site symmetry of mirror plane, as found in Table 2. Thus, the Sn<sub>2</sub>Se<sub>6</sub> rhombus plane itself is the mirror plane and the axis, normal to the Sn<sub>2</sub>Se<sub>6</sub> plane and passing through its center, is 2-fold rotation axis.

Fig. 2 shows the packing diagram of the [Sn<sub>2</sub>Se<sub>6</sub>]<sup>4-</sup> anions and the organic cations, dabcoH<sup>+</sup> (= [N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]<sup>+</sup>) and [(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> in the unit cell of (I). For the [N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]<sup>+</sup> cation, both nitrogen atoms, N(1) and N(2) are sitting on the aforementioned special positions of (x, 0, z) and one ethylene ring backbone is also in the mirror plane, as C(1) and C(2) are on the same special positions.

The other two ethylene ring backbones containing C(3) and C(4) atoms are related each other as the mirror images. In the case of another cation, [(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>, the only nitrogen atom, N(5) is placed on the special position of (0, y, 1/2) with a site symmetry of 2-fold axis. Further information about the fractional atomic coordinates of all non-hydrogen atoms of (I) can be found in Table 2.

The organic cations, [N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]<sup>+</sup> and [(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> in (I), are supposed to be originated from the protonation of dabco (1,4-diazabicyclo [2.2.2]octane) and the breakdown of the solvent DMF, respectively. In the [N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]<sup>+</sup> cation, the one nitrogen atom, N(1) has the average N-C bond distance of 1.47Å and the average C-N-C bond angle of 108.3°, whereas the other nitrogen

Table 3. Selected Bond Distances(Å) and Angles(°) for (I)

Sn(1)-Se(1)	2.5888(14)	Sn(1)-Se(1) <sup>ii</sup>	2.5847(12)
Sn(1)-Se(2)	2.4649(9)	Sn(1)-Se(2) <sup>i</sup>	2.4648(9)
N(1)-C(1)	1.480(11)	N(1)-C(3)	1.468(7)
N(1)-C(3) <sup>i</sup>	1.468(7)	N(2)-C(2)	1.508(11)
N(2)-C(4)	1.480(8)	N(2)-C(4) <sup>i</sup>	1.480(8)
N(3)-C(5)	1.485(8)	N(3)-C(5) <sup>iii</sup>	1.485(7)
C(1)-C(2)	1.543(12)	C(3)-C(4)	1.542(8)
Se(1)-Sn(1)-Se(1) <sup>ii</sup>	94.85(4)	Se(1)-Sn(1)-Se(2)	111.41(3)
Se(1)-Sn(1)-Se(2) <sup>i</sup>	111.41(3)	Se(1) <sup>ii</sup> -Sn(1)-Se(2)	111.76(2)
Se(1) <sup>ii</sup> -Sn(1)-Se(2) <sup>i</sup>	111.76(2)	Se(2)-Sn(1)-Se(2) <sup>i</sup>	114.13(4)
Sn(1)-Se(1)-Sn(1) <sup>ii</sup>	85.15(4)	C(1)-N(1)-C(3)	108.0(5)
C(1)-N(1)-C(3) <sup>i</sup>	108.0(5)	C(3)-N(1)-C(3) <sup>i</sup>	108.9(7)
C(2)-N(2)-C(4)	109.6(4)	C(2)-N(2)-C(4) <sup>i</sup>	109.6(4)
C(4)-N(2)-C(4) <sup>i</sup>	111.8(7)	C(5)-N(3)-C(5) <sup>iii</sup>	114.7(8)
N(1)-C(1)-C(2)	112.2(7)	N(2)-C(2)-C(1)	106.7(7)
N(1)-C(3)-C(4)	111.8(6)	N(2)-C(4)-C(3)	107.6(6)

Symmetry codes: (i) x, -y, z; (ii) -x, -y, -z; (iii) -x, y, -z-1.

atom, N(2) has 1.49Å and 110.3°. Detailed values of selected bond distances and angles for (I) can be found in Table 3. The protonation of dabco is believed to occur on N(2) atom, which has longer N-C bond distances and larger C-N-C bond angles. In the process of structural analysis, one hydrogen atom was included as attached to the N(2) atom and its position was calculated. Apparent difference in geometry around the above two nitrogen atoms exclude the possibility for divalent  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}]^{2-}$  cations to be incorporated in (I).

The reduction of  $\text{Se}_2^{2-}$  to  $2\text{Se}^{2-}$  must have taken

place during the synthetic reaction for compound (I), as we used  $\text{K}_2\text{Se}_2$  as the starting reagent for the source of selenides. This kind of reduction of polychalcogenides have been encountered in numerous examples.<sup>1</sup> When we used  $\text{K}_2\text{Se}$  instead of  $\text{K}_2\text{Se}_2$ , we were not able to isolate the crystalline products of (I).

Several compounds containing  $[\text{Sn}_2\text{Se}_6]^{4-}$  anions have been characterized previously by X-ray crystallographic studies. These include  $\text{Tl}_2\text{Sn}_2\text{Se}_6$ ,<sup>7</sup>  $\text{Na}_4\text{Sn}_2\text{Se}_6 \cdot 13\text{H}_2\text{O}$ ,<sup>8</sup>  $\text{K}_4\text{Sn}_2\text{Se}_6$ ,<sup>9</sup>  $\text{Rb}_4\text{Sn}_2\text{Se}_6$ ,<sup>10</sup>  $\text{Cs}_4\text{Sn}_2\text{Se}_6$ ,<sup>11</sup>  $\text{K}_2(18\text{-crown-6-K})_2[\text{Sn}_2\text{Se}_6]$ ,<sup>12</sup>  $\text{K}(\text{NMe}_4)_3[\text{Sn}_2\text{Se}_6]$ ,<sup>13</sup>  $(\text{enH})_2(2,2,2\text{-crypt-K})_2[\text{Sn}_2\text{Se}_6]$ ,<sup>13</sup>  $(\text{enH})_2\text{Sn}_2\text{Se}_6$ ,<sup>14</sup>  $(\text{enH})_4\text{Sn}_2\text{Se}_6$ ,<sup>15</sup>

Table 4.  $\text{S}_p \cdots \text{S}_q$  Distances(Å) and Sn-Se<sub>p</sub>-Sn, Se<sub>p</sub>-Sn-Se<sub>q</sub>, and Se<sub>p</sub>-Sn-Se<sub>q</sub> Bond Angles(°) Observed in the  $[\text{Sn}_2\text{Se}_6]^{4-}$  Salts

counter-cation	$\text{S}_p \cdots \text{S}_q$	Sn-Se <sub>p</sub> -Sn	Se <sub>p</sub> -Sn-Se <sub>q</sub>	Se <sub>p</sub> -Sn-Se <sub>q</sub>	ref.
$\text{TT}^-$	3.577	87.1	92.9	110.5	7
$\text{Na}^+$	3.529(2)	86.07(5)	93.94(5)	117.68(6)	8
$\text{K}^+$	3.514	85.5	94.5	121.2	9
$\text{Rb}^+$	3.518	85.4(1)	94.6(1)	120.1(1)	10
$\text{Cs}^+$	3.504(1)	85.26(5)	94.74(5)	118.91(6)	11
$(\text{K}^+)_2(18\text{-crown-6-K}^+)_2$	3.4930(9)	84.823(12)	95.176(12)	117.748(12)	12
$\text{K}^+(\text{NMe}_4)_3$	3.578(4)	87.06(7)	92.94(7)	119.12(3)	13
$(\text{enH})_2(2,2,2\text{-crypt-K}^+)_2$	3.557(1)	87.05(2)	92.95(2)	111.95(6)	13
$(\text{enH}_2^{2+})_2$	3.480(1)	84.91(1)	95.1(1)	115.1(1)	14
$\text{enH}^+$	3.522(2)	85.77(4), 85.99(4)	93.69(4), 94.51(3)	112.17(3), 115.70(4)	15
$(n\text{-Bu})_2\text{NH}_2^+$	3.498	85.6	94.4	117.3	16
$(\text{dabcoH}^+)_2(\text{Me}_2\text{NH}_2^+)_2$	3.5002(16)	85.15(4)	94.85(4)	114.13(4)	this work

and [(*n*-Bu)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Sn<sub>2</sub>Se<sub>6</sub>].<sup>16</sup> As given in *Table 3*, the Sn-Se<sub>6</sub> bond distances are 2.589(1) and 2.585(1) Å, while the Sn-Se<sub>7</sub> bond distance is 2.465(1) Å (*b* is bridging and *t* terminal) for compound (**I**). Average bridging (2.587 Å) and terminal (2.465 Å) bond distances in (**I**) are similar to those found in the previously reported [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> structures. The Sn-Se<sub>6</sub> distances are much shorter than the Sn-Se<sub>7</sub> distances in all [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> structures, as expected due to the higher bond orders of the Sn-Se<sub>6</sub> bonds. This trend has been frequently observed in most of chalcometalates including [Sn<sub>2</sub>S<sub>6</sub>]<sup>2-</sup>,<sup>17</sup> and [Sn<sub>2</sub>Te<sub>6</sub>]<sup>2-</sup>.<sup>12,18</sup>

S<sub>n</sub>⋯S<sub>n</sub> distances and Sn-Se<sub>6</sub>-Sn, Se<sub>6</sub>-Sn-Se<sub>6</sub>, Se<sub>7</sub>-Sn-Se<sub>6</sub> bond angles in (**I**) and other previously characterized [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> anions are summarized in *Table 4*. The S<sub>n</sub>⋯S<sub>n</sub> distance in (**I**), 3.500(2) Å is close to those in Cs<sub>2</sub>Sn<sub>2</sub>Se<sub>6</sub>, K<sub>2</sub>(18-crown-6-K)<sub>2</sub>[Sn<sub>2</sub>Se<sub>6</sub>], and [(*n*-Bu)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Sn<sub>2</sub>Se<sub>6</sub>]. S<sub>n</sub>⋯S<sub>n</sub> distances in all the known [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> anions range between 3.480 and 3.578 Å. It is noteworthy that the divalent enH<sub>2</sub><sup>2+</sup> salt has the shortest S<sub>n</sub>⋯S<sub>n</sub> distance, 3.480 Å. The Sn-Se<sub>6</sub>-Sn, Se<sub>6</sub>-Sn-Se<sub>6</sub>, and Se<sub>7</sub>-Sn-Se<sub>6</sub> bond angles in (**I**) are similar to those observed in the other [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> anions.

## CONCLUSIONS

A new metal chalcogenide compound, [dabcoH]<sup>+</sup>[(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> (**I**) was prepared by adopting a DMF solvothermal synthetic approach. (**I**) is the rare example showing that DMF can be employed as a solvent for the solvothermal synthesis of metal chalcogenides. However, the usability of the DMF solvothermal technique should be limited, because DMF solvent can decompose under the solvothermal conditions and (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup> cation, resulting from the above decomposition, can integrate into the product as a counter-cation. As the first selenotannate stabilized with dabcoH<sup>+</sup> organic cations, (**I**) contains the well known molecular [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> anion. Geometric parameters for the [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> anion in (**I**) are found to be close to those in the other [Sn<sub>2</sub>Se<sub>6</sub>]<sup>2-</sup> salts previously known.

**Supporting Information Available.** Crystallographic data for (**I**) have been deposited at the

Cambridge Crystallographic Data Centre with the deposition number of CCDC-284697. Data can be obtained free of charge via the Internet at <http://www.ccdc.cam.ac.uk>.

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