

# Dimensional Reduction of a Selenido Stannate Salt in Ionic Liquids to form 2D-K<sub>2</sub>Sn<sub>2</sub>Se<sub>5</sub>, a Direct Heavy Analogue of an Oxo Silicate

Bertram Peters,<sup>[a]</sup> Silke Santner,<sup>[a]</sup> and Stefanie Dehnen\*<sup>[a]</sup>

*Dedicated to Professor Bernd Harbrecht on the Occasion of his 70th Birthday*

**Abstract.** The structural motifs of SiO<sub>2</sub> or silicates, on one hand, and their heavier homologues of group 14 (T) and group 16 (E) elements, on the other hand, commonly differ, as the strict adherence to corner-sharing is not necessary in the latter owing to larger interatomic distances. On the contrary: larger coordination numbers as well as edge-sharing of the coordination polyhedra are preferred in [T<sub>x</sub>E<sub>y</sub>] subunits with T = Si, Ge, Sn and E = S, Se, Te. Hence, we were surprised to find a new modification of the selenido stannate K<sub>2</sub>Sn<sub>2</sub>Se<sub>5</sub>, which is comprised of exclusively corner-sharing [SnSe<sub>4</sub>] tetrahedra in a layer-

type anionic substructure 2D-{{[Sn<sub>2</sub>Se<sub>5</sub>]}<sup>2-</sup>. While the structure of the title compound 2D-K<sub>2</sub>Sn<sub>2</sub>Se<sub>5</sub> (**1**) differs significantly from the known parent compound, 3D-K<sub>2</sub>Se<sub>2</sub>Se<sub>5</sub>, it shows similarities with layered silicates of the apophyllite family. To the best of our knowledge, **1** represents the first known selenido stannate with an oxo silicate-like 2D structure. It formed besides known selenido stannates upon heating 3D-K<sub>2</sub>Sn<sub>2</sub>Se<sub>5</sub> in imidazolium-based ionic liquids (C<sub>2</sub>C<sub>2</sub>Im)[BF<sub>4</sub>] or (C<sub>2</sub>C<sub>2</sub>Im)[BF<sub>4</sub>] in the presence of DMMP and Cd<sup>2+</sup> or Zn<sup>2+</sup>.

## Introduction

SiO<sub>2</sub> and oxo silicates formed under ambient pressure strictly follow the construction principle of corner sharing [SiO<sub>4</sub>] units in their structures, owing to the electrostatic repulsion of two tetravalent Si atoms if being in closer contact than via one Si–O–Si bridge. However, this is not the case for heavier homologues owing to much larger interatomic distances. SiS<sub>2</sub> and the dichalcogenides of the heavier group 14 elements commonly feature edge-sharing of [TE<sub>4</sub>] units (T = group 14 atom, E = group 16 atom),<sup>[1–3]</sup> corresponding chalcogenido tetrelates comprise also [TE<sub>5</sub>] units upon increase of the central atom's coordination number.<sup>[4–6]</sup> In these cases, a higher density or more bonds per group 14 atom overcompensate the repulsive interaction. The latter is much lower here anyway, owing to the larger T–E bond lengths and the lower partial charge of the group 14 atoms. This holds especially for chalcogenides with much smaller differences in the electronegativity of T and E. For these compounds, corner-sharing [TE<sub>4</sub>] units are rare: they are known from one-dimensional strands 1D-{{[TE<sub>3</sub>]}<sup>2-</sup> in salts of the *meta*-metalates such as ((CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>)(NH<sub>4</sub>)SnS<sub>3</sub>,<sup>[7]</sup> yet 2D-layered structures that re-

semble the subunits of oxo silicates have not been known, to the best of our knowledge.

A very prominent structural motif of tin chalcogenides, for instance, is a trigonal bipyramidal coordination of tin atoms that assemble in defect-heterocubane-type [Sn<sub>3</sub>E<sub>4</sub>] moieties (d-HC) as a secondary building unit. These are further assembled into different tertiary structures, or further combined with other structural motifs, such as [SnE<sub>4</sub>] tetrahedra (TD) or [Sn<sub>2</sub>E<sub>6</sub>] double-tetrahedra (DT), into extended 1D, 2D, or 3D extended structures or clusters.<sup>[4–6,8]</sup> Many sulfido and selenido stannates have been reported to possess a 2D inorganic framework based on the [Sn<sub>3</sub>E<sub>4</sub>] d-HC unit,<sup>[4–6,9–11]</sup> some of which were obtained by ionothermal syntheses, for instance, 2D-[BMMIm]<sub>16</sub>[Sn<sub>24</sub>Se<sub>56</sub>].<sup>[12]</sup> Edge-sharing of such d-HC units with [SnSe<sub>4</sub>] TD units was found in 2D-[BMMIm]<sub>2</sub>[Ge<sub>0.83</sub>Sn<sub>3.17</sub>Se<sub>9.06</sub>], for example.<sup>[13]</sup>

Herein, we report a compound that does not follow any of these patterns, but rather behaves like an oxo silicate in spite of the presence of heavy congeners Sn and Se. The compound was accessed by ionothermal reactions of 3D-K<sub>2</sub>Sn<sub>2</sub>Se<sub>5</sub> (**A**)<sup>[14]</sup> in the presence of Lewis-acidic metal cations.

## Results and Discussion

While the reaction of 60 mg 3D-K<sub>2</sub>Sn<sub>2</sub>Se<sub>5</sub> (0.08 mmol, 1 equiv.) with 20 mg of MnCl<sub>2</sub> (0.16 mmol, 2 equiv.) in 0.5 mL of the imidazolium-based ionic liquid (C<sub>4</sub>C<sub>1</sub>Im)[BF<sub>4</sub>] in the presence of 50 mL of DMMP at 120 °C for 4 days affords single-crystals of (DMMPH)<sub>6</sub>[Mn<sub>4</sub>Sn<sub>4</sub>Se<sub>13</sub>(Se–Me)<sub>4</sub>] (**B**),<sup>[15]</sup> a different observation is made upon employing the transition metal salts ZnCl<sub>2</sub> or CdCl<sub>2</sub>, or upon using the ionic liquid (C<sub>2</sub>C<sub>2</sub>Im)[BF<sub>4</sub>]: The treatment of 60 mg of 3D-

\* Prof. Dr. S. Dehnen

E-Mail: dehnen@chemie.uni-marburg.de

[a] Fachbereich Chemie und Wissenschaftliches Zentrum für Materialwissenschaften

Philipps-Universität Marburg

Hans-Meerwein-Straße 4

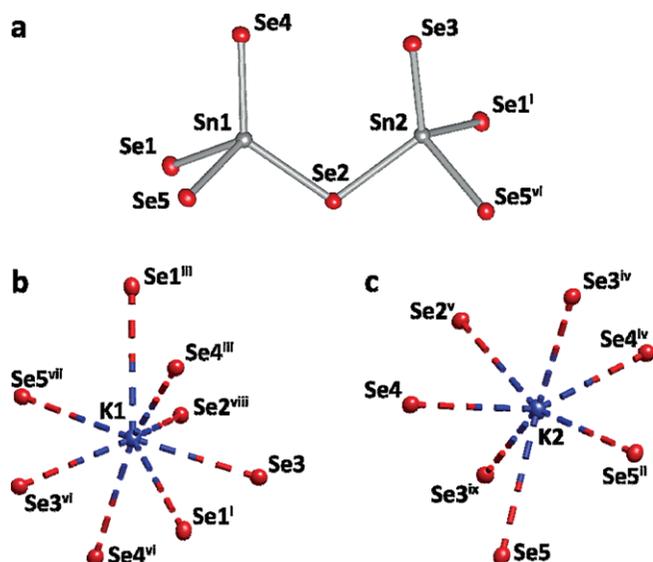
35043 Marburg, Germany

© 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



with the same orientation take turns in each eight-membered ring. As a consequence of the respective connection of the subunits, the  $\text{Sn}_2\text{Se}_5$  layers are shifted against each other in **1**, thus covering the voids of every second layer (Figure 1c and d), while in the apophyllites, they are congruent (Figure 1h), with the tetrahedra alternating in their orientation along  $c$  (Figure 1g).

The potassium cations in **1** are located between the selenido stannate layers and separate them from each other by filling the corresponding voids (see Figure 1c). In the (extended) asymmetric  $\text{Sn}_2\text{Se}_7$  subunit of **1** (Figure 2a), Sn–Se bond length ranging from 2.4268(6) Å (Sn2–Se3) to 2.5809(6) Å (Sn1–Se4). By interactions with Se atoms of the selenido stannate network, the two crystallographically independent cations in **1** are hexacoordinate ( $\text{K1}\cdots\text{Se}$  3.237–3.443 Å; two further neighbors at slightly longer distances:  $\text{K1}\cdots\text{Se1}^{\text{iii}}$  3.740 Å and  $\text{K1}\cdots\text{Se1}^{\text{i}}$  3.906 Å) or pentacoordinate ( $\text{K2}\cdots\text{Se}$  3.197–3.382 Å; two further neighbor at slightly longer distances:  $\text{K1}\cdots\text{Se2}^{\text{v}}$  3.702 Å and  $\text{K1}\cdots\text{Se5}$  3.705 Å) (see Figure 2b).



**Figure 2.** (a) Asymmetric unit of **1** without  $\text{K}^+$  cations. (b) Coordination environment of the  $\text{K}^+$  cations. Symmetry codes: <sup>i</sup> 2– $x$ , 1– $y$ , 1– $z$ ; <sup>ii</sup> 2– $x$ , 2– $y$ , 1– $z$ ; <sup>iii</sup> 2– $x$ , –1/2 +  $y$ , 1/2– $z$ ; <sup>iv</sup> 2– $x$ , 1/2 +  $y$ , 1/2– $z$ ; <sup>v</sup>  $x$ , 3/2– $y$ , –1/2 +  $z$ ; <sup>vi</sup> 5/2– $x$ , –1/2 +  $y$ ,  $z$ ; <sup>vii</sup> 5/2– $x$ , 1– $y$ , –1/2 +  $z$ ; <sup>viii</sup> 5/2– $x$ , 1– $y$ , –1/2 +  $z$ ; <sup>ix</sup> 5/2– $x$ , 1/2 +  $y$ ,  $z$ .

Notably, the composition of the starting material,  $3\text{D-K}_2\text{Sn}_2\text{Se}_5$  was not changed by this reaction, which therefore represents a mere dimensional reduction of the anionic framework from a three-dimensional to a two-dimensional substructure. A similar observation was made previously with the two-dimensional vs. one-dimensional substructures of the related selenido stannates  $2\text{D}-(\text{C}_4\text{C}_1\text{C}_1\text{Im})_4[\text{Sn}_6\text{Se}_{14}]$  and  $1\text{D}-(\text{C}_4\text{C}_1\text{C}_1\text{Im})_4[\text{Sn}_6\text{Se}_{14}]$ .<sup>[12]</sup> In these compounds, a two-dimensional honeycomb structure was cut into one-dimensional double-strands, thereby reducing the coordination number of the involved third of the Sn atoms from 5 to 4. In **1**, the change is more dramatic: (a) all Sn atoms turn from penta-coordination to tetra-coordination, and (b) all coordination polyhedra

move from edge-sharing to corner-sharing, which has been unprecedented in layered selenido stannate structures to date.

## Conclusions

The first selenido stannate salt with a layered anionic substructure comprising exclusively corner-sharing  $[\text{SnSe}_4]$  units,  $2\text{D-K}_2\text{Sn}_2\text{Se}_5$  (or  $\beta\text{-K}_2\text{Sn}_2\text{Se}_5$ ; **1**), was obtained upon ionothermal treatment of  $3\text{D-K}_2\text{Sn}_2\text{Se}_5$  (or  $\alpha\text{-K}_2\text{Sn}_2\text{Se}_5$ ) with a three-dimensional anionic network structure, in  $(\text{C}_4\text{C}_1\text{Im})[\text{BF}_4]$  or  $(\text{C}_2\text{C}_2\text{Im})[\text{BF}_4]$  at 120 °C for 4 days. This is another example for dimensional reduction of a solid state compound by application of ionic liquids, as “solid state methods near room temperature”.

## Experimental Section

**General:** All reactions and measurements were carried out under dry Ar atmosphere using Schlenk technique or a glovebox (type Unilab plus; MBraun). Elements were used as received: K lumps (Acros Organics, 98%), Sn powder (Sigma–Aldrich, 99%), and Se powder (Alpha Aesar, 99,999%). 2,6-Dimethylmorpholine (DMMP; 97%; Acros Organics) was distilled from  $\text{CaH}_2$  and stored over molecular sieves (3 Å). 1-Butyl-2,3-dimethylimidazolium chloride,  $(\text{C}_4\text{C}_1\text{Im})[\text{BF}_4]$  (Sigma–Aldrich, 98%) and  $(\text{C}_2\text{C}_2\text{Im})[\text{BF}_4]$  (abcr, 98%) were vacuum-dried for several days. The starting material  $\text{K}_2[\text{Sn}_2\text{Se}_5]$  (**A**) was prepared by solid state reaction of  $\text{K}_2\text{S}$ , Sn and Se according to the literature.<sup>[14]</sup>

**Synthesis of  $2\text{D-K}_2[\text{Sn}_2\text{Se}_5]$  (**1**):** 60 mg of  $\text{K}_2[\text{Sn}_2\text{Se}_5]$  (**A**, 0.08 mmol, 1.0 equiv.),  $\text{MCl}_2$  (0.16 mmol, 2.0 eq,  $M = \text{Zn}$ : 23 mg,  $M = \text{Cd}$ : 31 mg), 500 mg of  $(\text{C}_2\text{C}_2\text{Im})[\text{BF}_4]$ , and 50  $\mu\text{L}$  of DMMP were sealed in a Duran glass ampoule, heated to 120 °C for 4 d. After the heating was terminated, the ampoule was stored for 12 h for the purpose of cooling-down. Red crystals of **1** were obtained as rods in approximately 15% yield. The compound is highly air sensitive and must be handled under inert conditions. It can be handled under highly viscous oil (e.g., perfluoropolyether oil Fomblin® YR-1800), yet after several minutes, decomposition is visible from a color change to dark reddish-black.

**X-ray Diffraction:** X-ray data were collected with a Stoe StadiVari diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54186$  Å;  $T = 100$  K) equipped with an Oxford Cryosystems module. Structure solution by dual space methods and full-matrix least-squares refinement against  $F^2$  were carried out using using SHELXT15, SHELXL15, and OLEX2 software.<sup>[19]</sup> The non-hydrogen atoms were refined using anisotropic displacement parameters.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1996048 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

## Acknowledgements

This work was supported by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) within the framework of SPP 1708. Open access funding enabled and organized by Projekt DEAL.

**Keywords:** Ionic liquids; Selenido stannates; Layered structures; Dimensional reduction; X-ray diffraction

## References

- [1] C. T. Prewitt, H. S. Young, *Science* **1965**, *149*, 535–537.
- [2] J. Peters, B. Krebs, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *38*, 1270–1272.
- [3] H. P. Nayek, Z. Lin, S. Dehnen, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1737–1740.
- [4] B. Seidlhofer, N. Pienack, W. Bensch, *Z. Naturforsch. B* **2010**, *65*, 937–975.
- [5] W. S. Sheldrick, M. Wachhold, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 206–224.
- [6] S. Santner, J. Heine, S. Dehnen, *Angew. Chem. Int. Ed.* **2016**, *55*, 876–893.
- [7] P. Nørby, E. Eikeland, J. Overgaard, S. Johnsen, B. B. Iversen, *CrystEngComm* **2015**, *17*, 2413.
- [8] B. Peters, N. Lichtenberger, E. Dornsiepen, S. Dehnen, *Chem. Sci.* **2020**, *11*, 16–26.
- [9] a) J. B. Parise, Y. Ko, J. Rijssenbeck, D. M. Nellis, K. Tan, S. Koch, *J. Chem. Soc., Chem. Commun.* **1994**, 527–527; b) T. Jiang, A. Lough, G. A. Ozin, *Adv. Mater.* **1998**, *10*, 42–46; c) N. Pienack, D. Schinkel, A. Puls, M.-E. Ordolff, H. Lühmann, C. Näther, W. Bensch, *Z. Naturforsch. B* **2012**, *67*, 1098–1106; d) X.-H. Qi, K.-Z. Du, M.-L. Feng, Y.-J. Gao, X.-Y. Huang, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2017**, *139*, 4314–4317; e) M. Hvid, P. Lamagni, N. Lock, *Sci. Rep.* **2017**, *54*, 45822.
- [10] a) W. S. Sheldrick, B. Schaaf, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1041–1045; b) H. Ahari, C. L. Bowes, T. Jiang, A. Lough, G. A. Ozin, R. L. Bedard, S. Petrov, D. Young, *Adv. Mater.* **1995**, *7*, 375–378.
- [11] a) W. S. Sheldrick, H. G. Braunbeck, *Z. Naturforsch. B* **1990**, *45*, 1643–1646; b) W. S. Sheldrick, H. G. Braunbeck, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1300–1306; c) J. Zhou, G. Bian, Y. Zhang, A. Tang, Q. Zu, *Inorg. Chem.* **2007**, *46*, 1541–1543; d) G. Xu, C. Wang, P. Guo, *Acta Crystallogr., Sect. C* **2009**, *65*, m171–m173; e) J.-R. Li, W.-W. Xiong, Z.-L. Xie, C.-F. Du, G.-D. Zou, X.-Y. Huang, *Chem. Commun.* **2013**, *49*, 181–183; f) C.-F. Du, J.-R. Li, M.-L. Feng, G.-D. Zou, N.-N. Shen, X.-Y. Huang, *Dalton Trans.* **2015**, *44*, 7364–7372; g) Z. Wang, C.-F. Du, C.-C. Cheng, N.-N. Shen, J.-R. Li, X.-Y. Huang, *Inorg. Chem. Commun.* **2016**, *74*, 58–61; h) K.-W. Kim, M.-Y. Heo, *Z. Kristallogr. NCS* **2018**, *233*, 255–257; i) S. Li, Z. Wei, N. Chen, Y. Gao, D. Jia, *J. Coord. Chem.* **2020**, *73*, 3562–3574.
- [12] Y. Lin, D. Xie, W. Massa, L. Mayrhofer, S. Lippert, B. Ewers, A. Chernikov, M. Koch, S. Dehnen, *Chem. Eur. J.* **2013**, *19*, 8806–8813.
- [13] Y. Lin, W. Massa, S. Dehnen, *Chem. Eur. J.* **2012**, *18*, 13427–13434.
- [14] K. O. Klepp, *Z. Naturforsch. B* **1992**, *47*, 197–200.
- [15] B. Peters, S. Santner, C. Donsbach, P. Vöpel, B. Smarsly, S. Dehnen, *Chem. Sci.* **2019**, *10*, 5211–5217.
- [16] W. S. Sheldrick, *Z. Naturforsch. B* **1988**, *43*, 249–252.
- [17] A. A. Colville, C. P. Anderson, P. M. Black, *Am. Mineral.* **1971**, *56*, 1222–1233.
- [18] For the definition of the net structure, see <http://rcsr.anu.edu.au/layers/fes>.
- [19] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8; b) G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8; c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

Received: April 10, 2020

Published Online: June 18, 2020