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Dimensional Reduction of a Selenido Stannate Salt in Ionic Liquids to form 2D-K₂Sn₂Se₅, a Direct Heavy Analogue of an Oxo Silicate

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

Abstract. The structural motifs of SiO₂ 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 cornersharing 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 $[T_xE_y]$ subunits with T = Si, Ge, Sn and E = S, Se, Te. Hence, we were surprised to find a new modification of the selenido stannate K₂Sn₂Se₅, which is comprised of exclusively corner-sharing [SnSe₄] tetrahedra in a layer-

type anionic substructure 2D-{[Sn₂Se₅]²⁻}. While the structure of the title compound 2D-K₂Sn₂Se₅ (1) differs significantly from the known parent compound, 3D-K₂Se₂Se₅, 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 stannes upon heating 3D-K₂Sn₂Se₅ in in imidazolium-based ionic liquids (C₂C₂Im)[BF₄] or (C₂C₂Im)[BF₄] in the presence of DMMP and Cd²⁺ or Zn²⁺.

Introduction

SiO₂ and oxo silicates formed under ambient pressure strictly follow the construction principle of corner sharing [SiO₄] 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. SiS₂ and the dichalcogenides of the heavier group 14 elements commonly feature edge-sharing of $[TE_4]$ units (T = group 14 atom, E = group 16 atom, [1-3] corresponding chalcogenido tetrelates comprise also [TE₅] units upon increase of the central atom's coordination number.^[4–6] 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 [TE₄] units are rare: they are known from one-dimensional strands $1D-\{[TE_3]^{2-}\}$ in salts of the *meta*-metalates such as ((CH₃)₂NH₂)(NH₄)SnS₃,^[7] yet 2D-layered structures that resemble 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 $[Sn_3E_4]$ 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 $[SnE_4]$ tetrahedra (TD) or $[Sn_2E_6]$ double-tetrahedra (DT), into extended 1D, 2D, or 3D extended structures or clusters.^[4-6,8] Many sulfido and selenido stannates have been reported to possess a 2D inorganic framework based on the $[Sn_3E_4]$ d-HC unit, [4–6,9–11] some of which were obtained by ionothermal syntheses, for instance, 2D-[BMMIm]₁₆[Sn₂₄Se₅₆].^[12] Edge-sharing of such d-HC units TD units was with [SnSe₄] found in 2D-[BMMIm]₂[Ge_{0.83}Sn_{3.17}Se_{9.06}], for example.^[13]

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 $3D-K_2Sn_2Se_5$ (A)^[14] in the presence of Lewis-acidic metal cations.

Results and Discussion

While the reaction of 60 mg $3D-K_2Sn_2Se_5$ (0.08 mmol, 1 equiv.) with 20 mg of MnCl₂ (0.16 mmol, 2 equiv.) in 0.5 mL of the imidazolium-based ionic liquid (C₄C₁Im)[BF₄] in the presence of 50 mL of DMMP at 120 °C for 4 days affords single-crystals of (DMMPH)₆[Mn₄Sn₄Se₁₃(Se-Me)₄] (**B**),^[15] a different observation is made upon employing the transition metal salts ZnCl₂ or CdCl₂, or upon using the ionic liquid (C₂C₂Im)[BF₄]: The treatment of 60 mg of 3D-

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(DMMPH)₆[Mn₄Sn₄Se₁₃(Se-Me)₄] (B)

Scheme 1. Overview of the reaction conditions and products 1, B, C, and D upon ionothermal treatment of $3D-K_2Sn_2Se_5$ (A, reference^[14]) in the presence of MCl₂ (M = Mn, Zn, Cd) in the ionic liquids (IL) (C₄C₁Im)[BF₄] or (C₂C₂Im)[BF₄].

 $K_2Sn_2Se_5$ (0.08 mmol, 1 equiv.) with 2 equiv. of MCl₂ (0.16 mmol, M = Zn: 23 mg, M = Cd: 31 mg) in (C₂C₂Im)[BF₄] with 50 µL of DMMP at 120 °C for 4 days yields orange blocks of the known compound $K_4Sn_3Se_8$ (C),^[16] besides red rods of 2D-K₂Sn₂Se₅ (1, ca. 15%). The variations of reactions starting out from 3D-K₂Sn₂Se₅ are depicted in Scheme 1.

Compound 1 forms also (besides black rods of re-crystallized 3D-K₂Sn₂Se₅) when using ZnCl₂ in $(C_4C_1Im)[BF_4]$. Upon treatment of 3D-K₂Sn₂Se₅ with CdCl₂ in $(C_4C_1Im)[BF_4]$, the starting material re-crystallizes besides the simple complex compound CdCl₂•2DMMP (**D**). The reaction with MnCl₂ carried out in C₂C₂Im does not yield crystalline products besides simple binary salts.

In all cases, compound 1 (or β -K₂Sn₂Se₅) crystallizes in the orthorhombic space group *Pbca* with 8 formula units in the unit cell. To our surprise, the crystal structure analysis did not

reveal any variant of a [Sn₃Se₄]-based structure, nor the known 3D structure of this composition (A; α -K₂Sn₂Se₅).^[14] Instead, the atoms are arranged in a 2D-{[Sn₂Se₅]²⁻} inorganic framework consisting of exclusively [SnSe₄] TD building units which are all connected exclusively via corner-sharing. The structure of 1 exhibits a close relationship with silicates of the apophyllite family, $K_{0.84}Na_{0.16}Ca_4Si_8O_{20}(F,OH)\cdot 8H_2O$,^[17] still with some differences in structural details, which is highlighted in the comparison given in Figure 1. Both, 1 and the apophyllite silicates possess 2D inorganic frameworks build from corner-sharing $[ME_4]$ tetrahedra with layers parallel to (001). The tetrahedra are connected to two different types of rings, as shown in Figure 1 (a and e): (regular) four-membered rings on the one hand, and (distorted) eight-membered rings on the other hand. These are connected to form the well-known {4.8.8} net^[18] (Figure 1b and f). The Sn/Se and Si/O structures, respectively, differ in the orientation of the tetrahedra with regard to the M-layer. In 1, the triangular base areas of the tetrahedra are rotated out of the *ab* plane. Two directly linked tetrahedra in each four-membered ring possess the same orientation. This way, zigzag chains are formed that extend parallel to the b axis, as illustrated in Figure 1a (dark and light gray shading). Thus, each four-membered rings contain two tetrahedra of each orientation, and the eight-membered rings consist of two inversely oriented sets of four tetrahedra with the same orientation. In the apophyllite structure, in contrast, tetrahedra that belong to one four-membered ring possess the same orientation, and such rings are linked in the *ab* plane, with alternate orientation (Figure 1e). Thus, two tetrahedra



Figure 1. Fragments of the solid-state structure of compound 1 (a–d), and the related silicate structure of the hydroxylapophyllite $K_{0.84}Na_{0.16}Ca_4Si_8O_{20}(F,OH)\cdot8H_2O^{[17]}$ (e–h). The following atoms are shown as colored spheres: Na/K (indigo), Se/O (red), Sn/Si (grey), Ca (sky blue). F atoms are omitted for clarity. Grey and red tetrahedra represent [SnSe₄] and [SiO₄] units, respectively. For details, see the text.

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with the same orientation take turns in each eight-membered ring. As a consequence of the respective connection of the subunits, the Sn₂Se₅ 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).

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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 Sn₂Se₇ subunit of 1 (Figure 2a), Sn-Se bond length ranging from 2.4268(6) Å (Sn2–Se3) to 2.5809(6) (Sn1-Se4). By interactions with Se atoms of the selenido stannate network, the two crystallographically independent cations in 1 are hexacoordinate (K1···Se 3.237-3.443 Å; two further neighbors at slightly longer distances: K1...Se1ⁱⁱⁱ 3.740 Å and K1...Se1ⁱ 3.906 Å) or pentacoordinate (K2...Se 3.197-3.382 Å; two further neighbor at slightly longer distances: K1...Se2^v 3.702 Å and K1...Se5 3.705 Å) (see Figure 2b).



Figure 2. (a) Asymmetric unit of 1 without K⁺ cations. (b) Coordination environment of the K⁺ cations. Symmetry codes: ⁱ 2-x, 1-y, 1-z; ⁱⁱ 2-x, 2-y, 1-z; ⁱⁱⁱ 2-x, -1/2 + y, 1/2-z; ^{iv} 2-x, 1/2 + y, 1/2-z; ^v x, 3/22-y, -1/2 + z; vi 5/2-x, -1/2 + y, z; vii 5/2-x, 1-y, -1/2 + z; viii 5/2-x, -1/2 + z; viii 5/2-x; viii 51-y, -1/2 + z; ix 5/2-x, 1/2 + y, z.

Notably, the composition of the starting material, 3D-K₂Sn₂Se₅ 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 twodimensional vs. one-dimensional substructures of the related selenido stannates $2D-(C_4C_1C_1Im)_4[Sn_6Se_{14}]$ and 1D- $(C_4C_1C_1Im)_4[Sn_6Se_{14}]$.^[12] 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 [SnSe₄] units, $2D-K_2Sn_2Se_5$ (or $\beta-K_2Sn_2Se_5$; 1), was obtained upon ionothermal treatment of 3D-K₂Sn₂Se₅ (or α-K₂Sn₂Se₅) with a threedimensional anionic network structure, in (C₄C₁Im)[BF₄] or (C₂C₂Im)[BF₄] 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 gloveboxe (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 CaH₂ and stored over molecular sieves (3 Å). 1-Butyl-2,3-dimethylimidazolium chloride, $(C_4C_1Im)[BF_4]$ (Sigma-Aldrich, 98 %) and (C2C2Im)[BF4] (abcr, 98 %) were vacuumdried for several days. The starting material K2[Sn2Se5] (A) was prepared by solid state reaction of K2S, Sn and Se according to the literature.[14]

Synthesis of 2D-K₂[Sn₂Se₅] (1): 60 mg of K₂[Sn₂Se₅] (A, 0.08 mmol, 1.0 equiv.), MCl_2 (0.16 mmol, 2.0 eq, M = Zn: 23 mg, M = Cd: 31 mg), 500 mg of $(C_2C_2Im)[BF_4]$, and 50 µL 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 handeled under highly viscous oil (e.g., perfluoropolyether oil Fomblin® YR-1800), yet after several minutes, decomposition is visible from a color change to dark reddishblack.

X-ray Diffraction: X-ray data were collected with a Stoe StadiVari diffractometer using Cu- K_{α} 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.^[19] 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).

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