

Synthesis of a Selenidostannate(IV), $[\text{Mn}(\text{tepa})\cdot\text{Sn}_3\text{Se}_7]_n$, Demonstrating the Transformation from Achiral to Chiral and Dimeric to Polymeric Structure

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Although a number of chalcogenostannates have been obtained by using $[\text{M}(\text{amine})_m]^{n+}$ as the structure director, these materials with chiral metal complex ions are usually achiral because they are a racemic mix of chiral complex cations. A chiral selenidostannate, $[\text{Mn}(\text{tepa})\cdot\text{Sn}_3\text{Se}_7]_n$ (**1**; tepa = tetraethylenepentamine), containing incorporated $[\text{Mn}(\text{tepa})]^{2+}$ units, is reported herein. The unique structure is just like a grapevine appended with chiral grapes. In the same reaction, a centrosymmetric compound, $[\text{Mn}(\text{tepa})]_2(\mu_2\text{-Sn}_2\text{Se}_6)$ (**2**), in which the $\text{Sn}_2\text{Se}_6^{4-}$ anion acts as a bridge coordinating to $[\text{Mn}(\text{tepa})]^{2+}$ cations, has also been obtained. This is a reaction-time-related process in which compound **2** transformed gradually to **1** after prolonging the reaction time. This phenomenon demonstrates a transformation from achiral to chiral and dimeric to polymeric selenidostannate.

The synthesis of an inorganic–organic hybrid chiral framework is of great interest not only for the diversity of their structural chemistry but also for many potential applications.¹ Typically, these solids are obtainable through two methods. One of the synthetic approaches is that a self-assembled chiral framework is constructed by suitable achiral bridging ligands and metal centers.² The other effective strategy is to use the available chiral ligands or chiral

fragments as synthons to impart their chirality into the frameworks.³ Recently, chiral $[\text{M}(\text{amine})_m]^{n+}$ complexes as structure directors have been used in the synthesis of these chiral materials, and a number of the chiral metal phosphates have been prepared.⁴ However, although numerous chalcogenostannates have been synthesized using $[\text{M}(\text{amine})_m]^{n+}$ complexes as structure directors under hydro/solvothermal conditions, surprisingly, chiral compounds with metal complex ions as structure directors have not been obtained until now to the best of our knowledge. These materials with chiral metal complex ions have been all achiral⁵ because they are a racemic mix of chiral metal complex cations. In this Communication, we report a first 1-D chiral selenidostannate(IV) polymer $[\text{Mn}(\text{tepa})\cdot\text{Sn}_3\text{Se}_7]_n$ (**1**; tepa = tetraethylenepentamine), in which the flexible achiral amine ligand coordinates to the Mn^{2+} ion, forming a chiral center without the enantiomorph. The directional bonding of a complex cation with a selenidostannate anion and the noncentrosymmetric packing prevent the formation of a racemic structure. In addition, two achiral chalcogenostannates(IV), $[\text{Mn}(\text{tepa})]_2(\mu_2\text{-Sn}_2\text{Se}_6)$ (**2**) and $[\text{Mn}(\text{tepa})]_2(\mu_2\text{-Sn}_2\text{S}_6)$ (**3**), are also reported. The crystal conversion from achiral to chiral selenidostannates has been observed.

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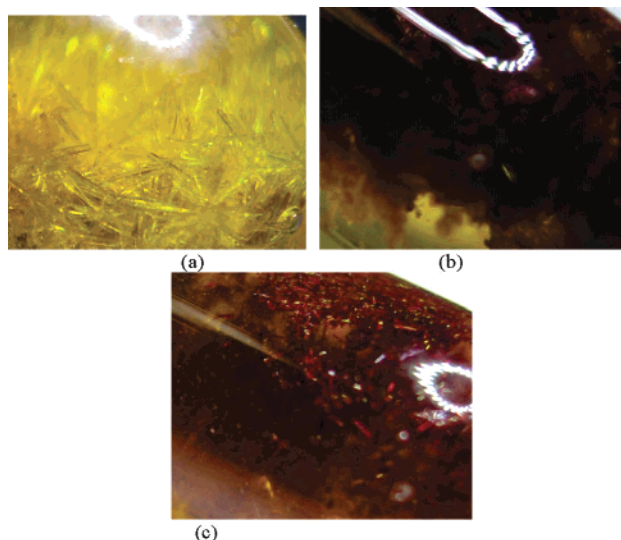


Figure 1. Photos of the transformation from **2** to the more stable **1** under solvothermal conditions: (a) 1 day; (b) 4 days; (c) 10 days.

Single crystals of **1** and **2** were prepared under solvothermal conditions from $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, and Se at the same molar ratio of $\text{Mn}/\text{Sn}/\text{Se} = 1:1:2$ in a mixed solvent of $\text{tepa}/\text{H}_2\text{O}$ at 157°C for several days (see the Supporting Information). Yellow clavate crystals **2** and red block-shaped crystals **1** were obtained in a thick Pyrex tube (yield 65% and 53%, respectively, based on Mn). Because the two new compounds were obtained under identical synthetic conditions and starting materials, their relationship aroused our curiosity. Then we found that it is a reaction-time-related process, in which compound **2** is transformed gradually to **1** after prolonging the reaction time. At first, nearly pure crystals of **2** were formed for about 1 day, and then they turned slowly to a brown milky state. At the same time, crystals of **1** formed gradually, and finally nearly pure compound **1** was obtained after about 10 days (Figure 1). This observation demonstrates that the phase of **1** is more stable than the phase of **2** under solvothermal conditions. It also demonstrates a transformation from achiral to chiral selenidostannates and dimeric to polymeric selenidostannates (see the discussion of the structure). The colorless block crystals of **3** were prepared by a similar method used in the synthesis of the crystals of **1** and **2**, except that the Se powder was replaced by a S powder (see the Supporting Information). With the aim of preparation of the analogue of **1**, the reaction time had been extended beyond 10 days. However, the attempts failed, and compound **3** was the only product in the same reaction conditions. This phenomenon reflects that the tendency of selenide to polymeric structure is stronger than that of sulfide, which might result from the extended atomic orbitals of the Se atom and the p-d orbitals coparticipating in the Se bridge bond.

Compounds **2** and **3** crystallize in the tetragonal centrosymmetric geometry with space group $I4_1/a$ and are isostructural (Figure 2a). The $[\text{Sn}_2\text{Se}_6]^{4-}$ anion in **2**, located at a center of inversion, connects two $[\text{Mn}(\text{tepa})]^{2+}$ units by the trans terminal Se atoms to form neutral $[\text{Mn}(\text{tepa})]_2-$

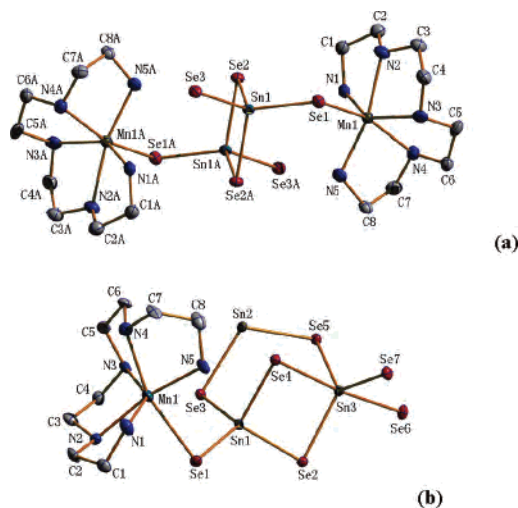


Figure 2. Crystal structures of **2** (a) [symmetry code A: $1 - x, 1 - y, 1 - z$] and **1** (b) with labeling schemes. The probability ellipsoids are drawn at the 50% level. H atoms are omitted for clarity.

$(\mu_2\text{-Sn}_2\text{Se}_6)$. Each Mn^{2+} ion in the $[\text{Mn}(\text{tepa})]^{2+}$ units is in a 6-fold coordination of five N atoms of one teпа ligand and one Se atom of the $[\text{Sn}_2\text{Se}_6]^{4-}$ anion, and the coordination polyhedron may be viewed as a heavily distorted octahedral geometry. Usually, the $\text{Sn}_x\text{Q}_y^{z-}$ anions are discrete from the metal-amine coordination cations in crystals. There are few reports of the incorporation of $[\text{M}(\text{amine})_m]^{n+}$ complex cations into the anionic $\text{Sn}_x\text{Q}_y^{z-}$ ($\text{Q} = \text{S}$ and Se) framework through $\text{M}-\text{Q}$ bonds, for example, $[\{\text{Co}(\text{tren})\}_2(\mu\text{-Sn}_2\text{S}_6)]$,^{5a} $[\{\text{Mn}(\text{tren})\}_2(\mu\text{-Sn}_2\text{Se}_6)]$,^{5c} and $[\{\text{Mn}(\text{en})_2\}_2(\mu\text{-en})(\mu\text{-Sn}_2\text{S}_6)]_n$.⁶ In order to prevent the formation of discrete anions and cations, we chose a pentadentate amine teпа as the ligand, which leaves one coordination site at the Mn^{n+} center, enabling bond formation to the S/Se atoms of the $\text{Sn}_x\text{Q}_y^{n-}$ anion. The terminal Se atoms of $\text{Sn}_2\text{Se}_6^{4-}$ in **2** are involved in intermolecular $\text{N}-\text{H}\cdots\text{Se}$ hydrogen bonding with adjacent molecules, resulting in a 3-D hydrogen-bond network structure (see the Supporting Information). A similar structure and molecular packing are found in **3**. Though the metal complex cations in **2** and **3** are chiral, the neutral $[\text{Mn}(\text{tepa})]_2-(\mu_2\text{-Sn}_2\text{Q}_6)$ molecule possesses a symmetrical center, leading to an achiral configuration.

Compound **1** crystallizes in chiral space group $P2_12_12_1$, and the fundamental structure is given in Figure 2b. It is notable that the flexible achiral teпа coordinates to Mn^{2+} ions, leading to a chiral center. The $[\text{Sn}_3\text{Se}_7]^{2-}$ structure contains a pseudo-semicube cluster unit (Sn_3Se_4). Semicube clusters are commonly seen in other reported $\text{R}_2\text{Sn}_3\text{Q}_7$ ($\text{Q} = \text{S}, \text{Se}$)^{7,8} structures. The so-called pseudo-semicube cluster

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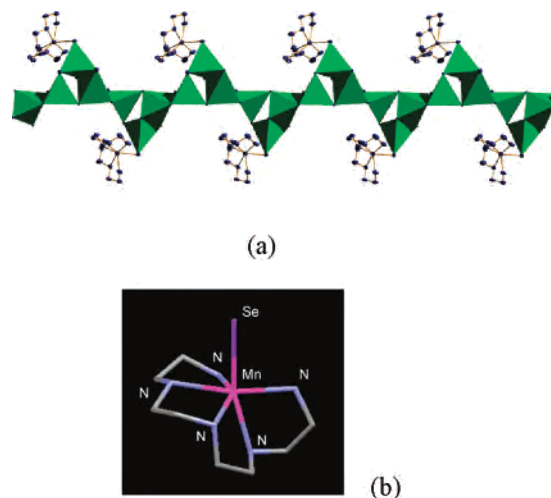


Figure 3. (a) Polyhedral connection of the polymeric anion $\{[\text{Sn}_3\text{Se}_7]^{2-}\}_n$ and (b) the only conformation of the $[\text{Mn}(\text{tepa})]^{2+}$ units in compound **1**.

of **1** is somewhat different from the semicube cluster because Sn2 and Se4 are separated with a long distance of 3.142 Å, which shows nonbonding or very weak bonding in the semicube Sn_3Se_4 structure.

The polymeric anion $\{[\text{Sn}_3\text{Se}_7]^{2-}\}_n$ is a 1-D chain that propagates in the [001] direction (Figure 3a). Some $\{[\text{Sn}_3\text{Q}_7]^{2-}\}_n$ chains similar to **1** have been reported.⁸ However, in this case, the chiral metal complex cations, just like grapes, are regularly appended to both sides of the chain (grapevine), connected by the terminal Se atoms of the anion. The chiral $[\text{M}(\text{amine})_m]^{n+}$ cations directly bonded into polymeric frameworks here appear to be unique because the reported examples only were concerned with the dimeric chalcogenometalate.^{5,6} The topology of this framework has not been previously observed in either chalcogenometalate chains or networks. A combination of N–H⋯Se and C–H⋯Se hydrogen bonds further links all chains into a 2-D layer structure parallel to the (100) plane (see the Supporting Information).

There are several unique characteristics of **1** that prevent the chiral complex cations from a racemic mix (Figure 3). The first is that the chiral complex cations are regularly fixed to both sides of the chain around a 2_1 helical axis. The second is the infinite chains are arranged in a parallel manner with the same orientation, while, in general, they are easily aligned in an antiparallel fashion.⁹ The unique structure of **1** results in a first chiral selenidostannate material.

Optical diffuse-reflection spectra were measured at room temperature. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function.¹⁰ The optical band gaps (E_{onset}) obtained by extrapolation of the

linear portion of the absorption edges are estimated as 2.20 eV for **1**, 2.61 eV for **2**, and 3.2 eV for **3** (see the Supporting Information). The band gap E_{onset} of **1** is close to values of $\text{K}_2\text{MnSn}_2\text{Se}_6$ (2.00 eV)¹¹ and $[\text{K}_{10}(\text{H}_2\text{O})_{16}(\text{MeOH})_{0.5}][\text{Mn}_4(\mu_4\text{-Se})(\text{SnSe}_4)_4]$ (2.27 eV),¹² which exhibits properties of the semiconductor. The larger band gaps of **2** and **3** might be the result of their nonpolymeric structures. The crystals of **1** are stable up to 228 °C. Above this temperature, the tepla ligand decomposes slowly, and at a temperature of about 380 °C, the decomposition gives a distinct step. The decomposition of tepla in compounds **2** and **3** is similar to that of **1**, and the volcanic decomposition is around 350 and 340 °C, respectively.

In summary, although a number of chalcogenostannates have been obtained by using $[\text{M}(\text{amine})_m]^{n+}$ as the structure director, these materials with chiral metal complex ions are all achiral because they are a racemic mix of chiral complex cations. We have presented the first chiral selenidostannate, **1**, containing an incorporated $[\text{Mn}(\text{tepa})]^{2+}$ unit and a unique structure just like a grapevine appended with chiral grapes. In the same reaction, a centrosymmetric compound, **2**, in which the $\text{Sn}_2\text{Se}_6^{4-}$ anion acts as a bridge coordinating to $[\text{Mn}(\text{tepa})]^{2+}$ cations, has also been obtained. It is a reaction-time-related process in which compound **2** transformed gradually to **1** after prolonging the reaction time. Though the reactions are complex, Loose and Sheldrick have proposed a self-assembling mechanism.^{8c} The phenomenon of transformation from dimeric to polymeric selenidostannate found in this work further demonstrates this mechanism. Furthermore, a transformation from achiral to chiral selenidostannate was revealed. Therefore, this work makes progress in the solvothermal synthesis of chiral chalcogenostannate by using chiral metal complexes as templates.

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Supporting Information Available: Experimental preparation, CIF tables, molecular packings, and spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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