

Ionothermal syntheses and optical property of chromium selenidostannates containing linear polyamine ligand



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ABSTRACT

Ternary chromium selenidostannates $[\text{Cr}(\text{tepa})(\text{OH})_2\text{Sn}_2\text{Se}_6 \cdot \text{H}_2\text{O}]$ (tepa = tetraethylenepentamine) (**1**) and $[\text{Cr}(\text{peha})_2(\text{Sn}_2\text{Se}_6)\text{Cl}_2]$ (peha = pentaethylenhexamide) (**2**) were successfully synthesized by the reaction of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Sn, Se and tepa or peha in ionic liquid 1-ethyl-3-methylimidazolium chloride at 160 °C. In the ionic liquid, the Cr^{3+} ion forms $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ or $[\text{Cr}(\text{peha})]^{3+}$ chelating complex cations, which lead to the formation of chromium selenidostannates **1** and **2**. But the reactions in pure tepa or peha under solvothermal conditions produced amorphous powders. **1** and **2** are the first examples of TM-complex contained chalcogenidostannates synthesized by ionothermal technique. Both **1** and **2** form three-dimensional networks via intermolecular N–H···Se, O–H···Se and N–H···O or N–H···Cl interactions, respectively. **1** and **2** exhibit possible semiconducting properties with the band gaps at 2.08 and 2.19 eV, respectively.

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Ternary chalcogenidometallates based on metal chalcogenides of groups 14 and 15 have attracted increasing attention for their rich structural chemistry [1,2] and potential applications in different technological areas, such as thermoelectric, semiconductor, ion-exchange and optical materials [3–5]. Since the cobalt thioantimonate $[\text{Co}(\text{en})_3]\text{CoSb}_4\text{S}_8$ was prepared by the reaction of CoBr_2 and Na_3SbS_3 in ethylenediamine (en) solution under solvothermal conditions in 1996 [6], the solvothermal synthesis in ethylene polyamine has been developed to be a successful route for the preparation of ternary chalcogenidometallates combined with transition-metal (TM) complexes. In the case of tin chalcogenides, a number of ternary chalcogenidostannates had been prepared in the presence of TM^{n+} ion in a variety of ethylene polyamines using the solvothermal methods. The examples include $[\text{Ni}(\text{en})_3]_2\text{Sn}_2\text{S}_6$ [7], $[\text{TM}(\text{en})_3]_2\text{Sn}_2\text{Te}_6$ (TM = Mn, Zn) [8], $[\text{Zn}(\text{en})_3]_2\text{Sn}_2\text{Te}_6 \cdot \text{en}$ (en = ethylenediamine) [9], $[\{\text{TM}(\text{tren})\}_2(\mu\text{-Sn}_2\text{E}_6)]$ (E = S, TM = Co, Ni; E = Se, TM = Mn) (tren = tris(2-aminoethyl)amine) [7,10], $[\{\text{TM}(\text{tepa})\}_2(\mu\text{-Sn}_2\text{E}_6)]$ (E = S, Se, TM = Fe, Co; E = Te, TM = Zn) (tepa = tetraethylenepentamine) [11–13], and $[\text{Mn}(\text{peha})]\text{Sn}_3\text{Se}_7$ (peha = pentaethylenhexamide) [14]. In the solvothermal reactions, the ethylene polyamines act as not only the reaction solvents, but also the chelating ligands to bind the TM^{n+} ion to form complex cation $[\text{TM}(\text{polyamine})_m]^{n+}$ in situ, which acts as charge compensating ion and/or space filler in the final chalcogenidoantimonates. However, it is curious that the chromium chalcogenidostannate is not observed among above chalcogenidostannates across transition metal series. The only example of chromium chalcogenidostannate is $[\text{K}_6(\text{MeOH})_9][\text{Sn}_2\text{Se}_6]$

$[\text{Cr}(\text{en})_2(\text{SnSe}_4)]_2$, which was prepared by extraction method in MeOH/toluene solution using $\text{K}_4[\text{SnSe}_4]$ and $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ as precursors [15].

Ionic liquid (IL), which is usually constituted of large organic cations and weakly coordinating inorganic or organic anions, is a new type class of solvents with unique properties, such as high thermal stability, wide liquid range, and negligible vapor pressure. Ionic liquids have been widely employed as solvents in the preparation of metal-organic frameworks [16], and zeolites [17]. But the application of ionic liquid in the syntheses of crystalline metal chalcogenides is still less explored [5,18]. Recently, binary selenidostannates $[\text{Bmim}]_4\text{Sn}_9\text{Se}_{20}$ (Bmim = 1-butyl-3-methyl-imidazolium) [19], $[\text{P}_1\text{mmim}]_4\text{Sn}_9\text{Se}_{20}$, and $[\text{P}_1\text{mmim}]_2\text{Sn}_3\text{Se}_7$ (P_1mmim = 1-butyl-2,3-dimethyl-imidazolium) [20] were prepared using ionothermal methods. In the ionothermal syntheses, the ILs not only act as reaction solvent, but also provide counter cations for the selenidostannate anions. Here, we describe the ionothermal syntheses of TM-contained selenidostannates $[\text{Cr}(\text{tepa})(\text{OH})_2\text{Sn}_2\text{Se}_6 \cdot \text{H}_2\text{O}]$ (**1**), and $[\text{Cr}(\text{peha})_2(\text{Sn}_2\text{Se}_6)\text{Cl}_2]$ (**2**) in 1-ethyl-3-methylimidazolium chloride (EmimCl), which only serves as the reaction media. **1** and **2** are the first examples of TM complex-contained chalcogenidostannates synthesized by ionothermal technique, and also the first chalcogenidostannates combined with chromium complex of ethylene polyamine ligand.

Reaction of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Sn, Se, and tetraethylenepentamine (tepa) in 1-ethyl-3-methylimidazolium chloride at 160 °C for 6 days yielded selenidostannate $[\text{Cr}(\text{tepa})(\text{OH})_2\text{Sn}_2\text{Se}_6 \cdot \text{H}_2\text{O}]$ (**1**). Replacement of tepa with pentaethylenhexamide (peha) in the reaction afforded compound $[\text{Cr}(\text{peha})_2(\text{Sn}_2\text{Se}_6)\text{Cl}_2]$ (**2**). The reactions in tepa or peha under the same conditions produced black amorphous powders (for details, see ESI). Single-crystal X-ray diffraction study [21] reveals that **1** and **2** crystallize in the orthorhombic space group *Pbcn* and monoclinic

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space group $P2_1/n$, respectively. **1** consists of $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ and $[\text{Sn}_2\text{Se}_6]^{4-}$ ions, and a lattice water molecule (Fig. 1). The Sn atom binds with four Se atoms forming a SnSe_4 tetrahedron. Two SnSe_4 tetrahedra are joined via sharing a common edge, forming a bimeric $[\text{Sn}_2\text{Se}_6]^{4-}$ unit (Fig. 1). The $[\text{Sn}_2\text{Se}_6]^{4-}$ anion has two sets of Sn–Se bond lengths. The bridging Sn–Se_b bond [Sn–Se_b: 2.5802(9) Å] is longer than the terminal Sn–Se_t bond [Sn–Se_t: 2.4557(9) and 2.4704(11) Å] (Table S1). The Sn–Se_t and Sn–Se_b lengths are in the normal range of those observed in other compounds containing the $[\text{Sn}_2\text{Se}_6]^{4-}$ anions [10,12]. The Se–Sn–Se angles vary in 93.95(3)–115.04(3)°, indicating distortion of the tetrahedral SnSe_4 unit. The Cr^{3+} ion is coordinated to a pentadentate tepa ligand, and a OH^- group, forming an octahedral $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ complex cation. The Cr–N [2.037(5)–2.082(5) Å] and Cr–O [1.903(4) Å] (Table S1) bond lengths are in accordance with corresponding values observed in other Cr(III) complexes [15, 22], respectively. The solvothermal syntheses of TM/Sn/E system in tepa solvent have afforded a series of TM-chalcogenidostannates with general formula $[\{\text{TM}(\text{tepa})\}_2(\mu\text{-Sn}_2\text{E}_6)]$ (TM = Fe, Co, Zn; E = S, Se, Te) [11–13], in which the $[\text{Sn}_2\text{E}_6]^{4-}$ anion coordinates to the bivalent TM(II) centers. But the Cr^{3+} ion forms a $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ in tepa and leads to the formation of compound **1** containing a free $[\text{Sn}_2\text{Se}_6]^{4-}$ anion.

In **1**, a three-dimensional (3-D) network is caused by intermolecular H-bonding interactions. All Se atoms of the $[\text{Sn}_2\text{Se}_6]^{4-}$ unit are involved in the H-bonding interactions. Each $[\text{Sn}_2\text{Se}_6]^{4-}$ unit contacts four $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ neighbors via N–H⋯Se and O–H⋯Se interactions with N⋯Se separations of 3.263(5)–3.750(5) Å and O⋯Se separation of 3.372(4) Å (Table S3). In turn, each $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ unit interacts with two $[\text{Sn}_2\text{Se}_6]^{4-}$ neighbors (Fig. 2a). As a result, the $[\text{Sn}_2\text{Se}_6]^{4-}$ and $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ units are connected into a wavy layer $[\text{Sn}_2\text{Se}_6]^{4-}/[\text{Cr}(\text{tepa})(\text{OH})]^{2+}_2$ perpendicular to the *c* axis (Fig. 2a). The layers are further connected by the interlayered N–H⋯O hydrogen bond [N(1)⋯O(1)#2: 3.039(7) Å], forming a 3-D H-bonding network (Fig. 2b). The H_2O molecules are located between the layers.

2 consists of $[\text{Cr}(\text{peha})]^{3+}$, $[\text{Sn}_2\text{Se}_6]^{4-}$, and Cl^- ions (Fig. 3). The structure of $[\text{Sn}_2\text{Se}_6]^{4-}$ anion is similar to that of the $[\text{Sn}_2\text{Se}_6]^{4-}$ anion in **1** (Tables S1 and S2). The Cr^{3+} ion is coordinated to a hexadentate peha ligand, forming a $[\text{Cr}(\text{peha})]^{3+}$ complex cation, in which all the six N atoms of peha are involved in the coordination to the Cr^{3+} ion. So, the Cr^{3+} ion is in an octahedral coordination environment, with equatorial and axial N–Cr–N angles in the range of 80.7(2)–99.7(2) and 162.32(19)–179.2(2)° (Table S2), respectively. The Cr–N bond lengths [2.040(5)–2.090(5) Å] are in the range of those observed in **1**. The TM complexes of linear polyamino ligands of bidentate en, tridentate dien, tetradentate trien and pentadentate tepa are very common, and a variety of these TM complexes have been isolated and structurally characterized. However, the TM complexes with peha, a linear polyamino hexadentate ligand, are less explored. Compounds $[\text{Cd}(\text{peha})](\text{BPh}_4)_2$, $[\text{Cd}(\text{peha})](\text{BPh}_4)_2 \cdot 2\text{DMSO}$, $[\text{Cd}(\text{peha})](\text{BF}_4)_2$ [23] and $[\text{Mn}(\text{peha})]$

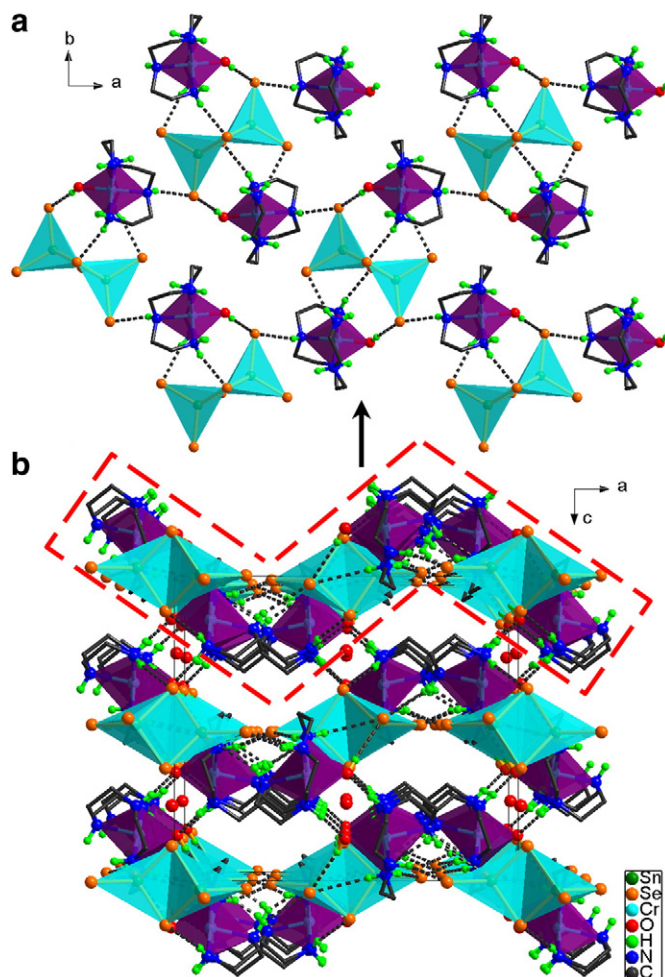


Fig. 2. (a) A view of the layer constructed by $[\text{Sn}_2\text{Se}_6]^{4-}$ and $[\text{Cr}(\text{tepa})(\text{OH})]^{2+}$ units via N–H⋯Se and O–H⋯Se hydrogen bonds (dashed lines) in **1**. (b) View of **1** along the *b* axis, showing the interlayered N–H⋯O hydrogen bonds (dashed lines). The hydrogen atoms of CH_2 are omitted for clarity. Cyan tetrahedra: SnSe_4 ; Purple octahedron: CrN_5O .

Sn_3Se_7 [14] are the fewer examples of the TM-peha complexes. Now the Cr(III)-peha complex of **2** was prepared with ionothermal method.

In **2**, the $[\text{Cr}(\text{peha})]^{3+}$, $[\text{Sn}_2\text{Se}_6]^{4-}$ and Cl^- ions form a 3-D network via intermolecular N–H⋯Se and N–H⋯Cl H-bonding interactions (Fig. 4a). Through the four terminal Se atoms, each $[\text{Sn}_2\text{Se}_6]^{4-}$ unit contacts four $[\text{Cr}(\text{peha})]^{3+}$ neighbors via N–H⋯Se hydrogen bonds

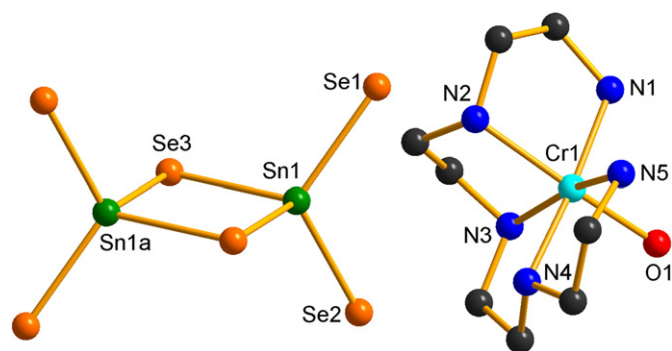


Fig. 1. Crystal structure of **1** with the labeling scheme. The H_2O molecule and hydrogen atoms of tepa are omitted for clarity.

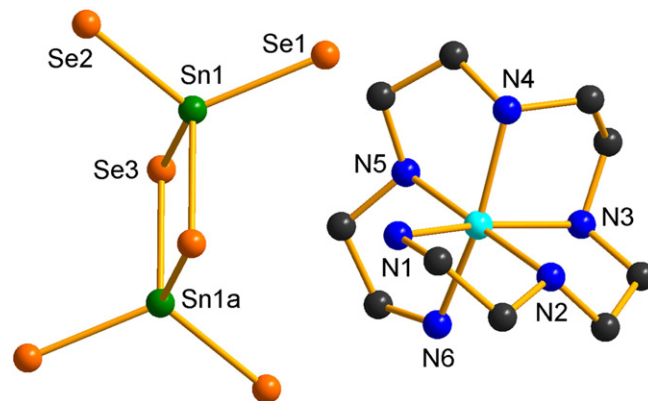


Fig. 3. Crystal structure of **2** with the labeling scheme. The Cl^- ions and hydrogen atoms of peha are omitted for clarity.

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