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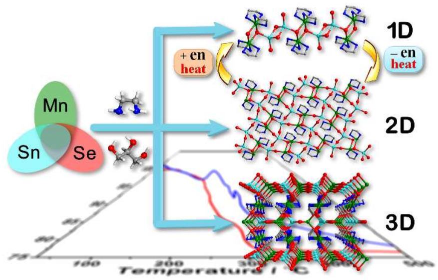
Assembly and structural transformation of organic–decorated manganese selenidostannates

Cheng–Feng Du,[a,b] Mei–Ling Feng,[a] Jian–Rong Li,[a] Guo–Dong Zou,[a,b] Ke–Zhao Du,[a] and Xiao–Ying Huang*[a]



Presented are the 1D, and the first 2D and 3D amine-decorated Mn-Sn-Se compounds, and structural transformation between the 1D and 2D ones.

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COMMUNICATION

Assembly and structural transformation of organic–decorated manganese selenidostannates

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Presented here are three organic-decorated manganese selenidostannates with various structural dimensionality (D), namely, 1D–$SnSe_3Mn(en)_2$ (en = ethylenediamine) (1), 2D–$SnSe_3Mn(en)$ (2) and 3D–$MnSnSe_4Mn(en)_2$ (3). 2 and 3 represent the first 2D and 3D organic-decorated Mn–Sn–Se compounds, respectively. A structural transformation was observed between 1 and 2.

Organic-decorated or inorganic-organic hybrid chalcogenidometalates are of great interest, because the incorporation of organics (typically amines) into the inorganic chalcogenido moieties can lead to large structural variation[1-8] and a change in the physical and chemical properties.[5, 9-16] It is well known that some transition-metal ions (especially Mn^{2+}) could easily form metal complexes in which the coordination sites of the cation are not fully occupied by the organic ligands and therefore, can bind to the chcalcogeno ions.[17-25] Previously much effort has been devoted to the incorporation of the $[Mn(amine)_m]^{n+}$ complex to the anionic $[Sn_xQ_y]^{z-}$ (Q = S and Se) moieties through Mn–Q bonds.[18, 20-22, 26-28] However, thus far only the 0D and 1D organic-decorated manganese selenidostannates structures have been obtained.

On the other hand, solid state crystal-to-crystal transformations triggered by external stimuli such as heat, light, exchange or loss of guest molecules are interesting phenomena that are often associated with property changes.[7, 15, 29-32] In the case of organic-decorated or hybrid chalcogenidometalates, however, such structural transformations are less reported.[7, 15, 25] Thus far there are only two examples concern the solid state transformations between amine-rich species and amine-poorer species, i.e. 0D–$[Mn(tren)]_2Sb_2S_5$ and 0D–$[Mn(tren)]_2Mn_2Sb_4S_{10}$,[25] and 1D–$(N_2H_4)_2ZnTe$ and 2D–$(N_2H_4)ZnTe$,[7].

In this paper, we report on the solvothermal syntheses, crystal structures and optical properties of three new organic-decorated manganese selenidostannates, namely, 1D–$SnSe_3Mn(en)_2$ (**1**), 2D–$SnSe_3Mn(en)$ (**2**) and 3D–$MnSnSe_4Mn(en)_2$ (**3**) (*en* = ethylenediamine). To our best knowledge, compounds **2** and **3** were the first 2D and 3D organic-decorated manganese selenidostannates, respectively. Interestingly, a reversible structural transformation was observed between **1** and **2**.

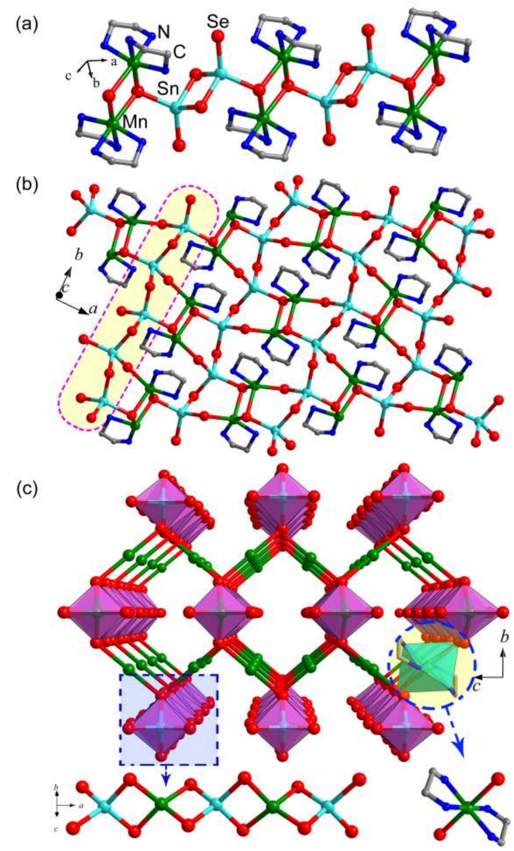

Fig. 1 (a) Chain-like structure of **1**; (b) layer of **2** with the $[SnSe_3]_n^{2-}$ chain highlighted; (c) prospective view of **3** along the *a*-axis with the $[MnSnSe_4]_n^{2-}$ chain and $[MnSe_2(en)_2]$ unit shown at the bottom. All the H atoms and most of the *en* molecules in **3** are omitted for clarity.

The title compounds were prepared by the solvothermal reactions of a mixture of $MnCl_2{\cdot}4H_2O$, $Na_2SnO_3{\cdot}3H_2O$, Se and en in glycerol (for details, see ESI†). The crystal structures were determined by single-crystal diffraction techniques‡.[33] Compound **1** features a neutral infinite chain-like structure of $[SnSe_3Mn(en)_2]_n$, Fig. 1a. In **1**, the Mn^{2+} ion is coordinated by two Se atoms and four N donors from two bidentate en molecules to conform to a $[MnN_4Se_2]$ octahedron. Two $[MnN_4Se_2]$ octahedra form a $[Mn_2(en)_4Se_2]$ dimer by sharing a Se–Se edge. The alternating arrangement of $[Mn_2(en)_4Se_2]$ dimers and

$[Sn_2Se_6]^{4-}$ units by sharing selenium corners results in an infinite chain extending along the *a*-axis in **1**. In comparison, the Mn^{2+} ion in **2** is coordinated by three Se atoms and two N donors from a chelating en molecule forming a $[MnN_2Se_3]$ square pyramid. Two $[MnN_2Se_3]$ units are fused into a $[Mn_2(en)_2Se_4]$ dimer by edge-sharing two Se^{2-} ions. While the $[SnSe_4]$ tetrahedra form the $[SnSe_3]_n^{2-}$ chains along the *b*-axis via corner-sharing. Then the $[Mn_2(en)_2Se_4]$ dimers inter-connect the $[SnSe_3]_n^{2-}$ chains through sharing Se atoms to generate a neutral 2D layer of $[SnSe_3Mn(en)]_n$ parallel to the *ab* plane in **2**, Fig. 1b. Whereas in **3** the $[SnSe_4]$ and $[Mn(1)Se_4]$ tetrahedra are alternatingly arranged to form a $[MnSnSe_4]_n^{2n-}$ chain by edge-sharing, and then the chains are further linked by the $[Mn(2)N_4Se_2]$ octahedra to give rise to a 3D network of $[MnSnSe_4Mn(en)_2]_n$, Fig. 1c. Note that the two Se atoms in the $[Mn(2)N_4Se_2]$ octahedron in **3** are in trans-configuration, in contrast to the cis-configuration of those in **1**. The overall structure of **3** is similar to that of a thiogallate compound $Mn(en)_2Ga_2S_4$.[34]

Although compounds **1** and **2** possess structures with different dimensionality, they possess the same inorganic formulae and their structures are closed related. In **2** there exist $[Sn_2Se_7Mn_2(en)_2]_n$ chains extending along the [110] direction; the chains are inter-connected by vertex-sharing the Se atoms of the $[Sn_2Se_7]$ units to result in a 2D sheet-like structure of **2** (Fig. 1b). Both the chains in **1** and **2** are constructed from the alternating connections of the $[Sn_2Se_x]$ units and $[Mn_2Se_2(en)_y]$ dimers. For the transformation from **1** to **2**, only one en molecule per Mn must be removed. Accompanying with the removal of one en per formula, one of the two bridging Se ions in the $[Sn_2Se_6]$ dimer becomes dangling, thus it could connect to the unsaturated four-coordinated Mn^{2+} ion in the same chain to fulfil a five-coordinated Mn^{2+}. Meanwhile the two dangling Se atoms in the $[Sn_2Se_6]$ unit could bond to one Sn^{4+} ion of the $[Sn_2Se_6]$ unit from an adjacent chain and one Mn^{2+} from another adjacent chain, respectively. Such structural relationship implies possible structural transformation between **1** and **2**. Indeed, we found that **1** could transform to **2** through thermal treatment in a thermogravimetric (TG) process under a N_2 atmosphere. Fig. 2 shows the PXRD patterns of structure transformation from **1** to **2** during the TG treatment. Such solid-state transformation is rarely observed for organic-inorganic metal chalcogenides.[7, 25] On the other hand, the crystals of **1** could be obtained through heating **2** at 160 ºC for 6 days with a moderate amount of the mixture of glycerol and en in a closed apparatus (for details, see ESI†). The structural transformation between compounds **1** and **2** demonstrated that by varying the amine content of $[Mn(amine)_m]^{n+}$ coordinated complex, the dimensionality of structure can be tuned.[5] In fact, since compound **1** is relatively easily synthesized in higher yield, compound **2** could be obtained more efficiently by the controlled TG decomposition of **1**, which provides us an alternative way to prepare new compounds.

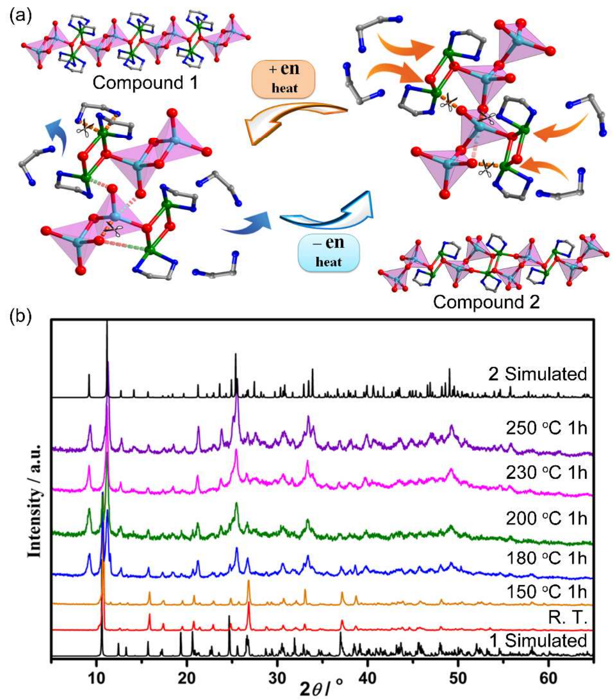

Fig. 2 (a) The schematic illustration of structural transition between **1** and **2**. (b) PXRD analysis of structure transformation from **1** to **2** during thermal treatment.

Fig. 3 shows the thermal decomposition and differential scanning calorimetry (DSC) profiles for **1**. As seen in the TG profile, the decomposition of **1** to $SnSe_2$ and MnSe occurred in approximately two steps. The overall observed weight loss (23.4% at 400 °C) was in good agreement with that expected for elimination of two *en* molecules per formula from **1**. The first thermal transition, beginning at 180 °C and yielding a weight loss of 13.4% at 260 °C, corresponded approximately to that expected for the loss of one *en* molecule per formula from 1D–$SnSe_3Mn(en)_2$ (11.3%), resulting in the formation of the 2D compound $SnSe_3Mn(en)$ (**2**).

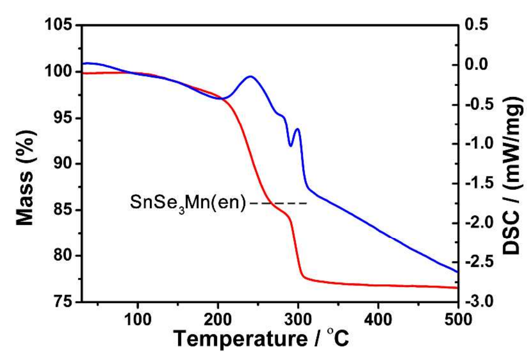

Fig. 3 TG and DSC curves of compound **1** at a heating rate of 5 °C/min in a N_2 atmosphere from 30 to 500 °C.

The optical diffuse reflectance spectra of compounds **1-3** investigated at room temperature are plotted in Fig. 4. The spectra indicate a sharp absorption edge at about 1.98 eV for **1**, 1.73 eV for **2** and 2.25 eV for **3**, respectively, consistent with their colours.

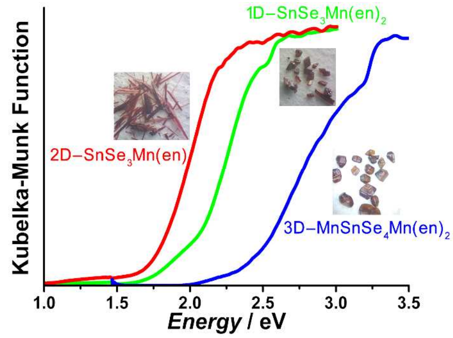

Fig. 4 Solid state optical absorption spectra of compounds **1**, **2** and **3**.

To gain further insight into the electronic structure of the title compounds, the band structures, density of states (DOS) and partial density of states (PDOS) of compounds **1**, **2** and **3** were calculated (for details, see ESI†). The variation tendency of the calculated band gaps of **1**, **2** and **3** was consistent with that of the experimental optical absorption edges. However, all the calculated values are smaller than their experimental optical band gaps, which may be related to the inaccurate description of eigenvalues of the electronic states by GGA.[35, 36] The components of each band of the compounds by DOS analyses are shown Fig. 5. It can be found that in all the compounds, the valence bands (VB) near the fermi level (E_F) mainly consist of Se-4p states with a small contribution from N-2p and Mn-3d states (Figs. S11, S12 and S13 in ESI†).

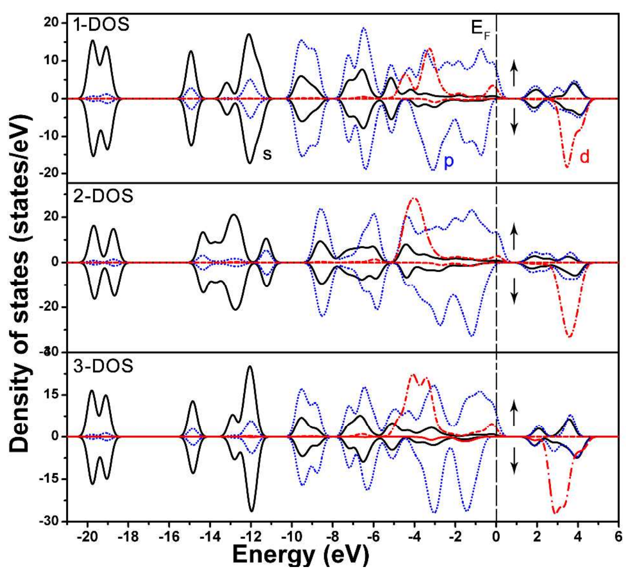

Fig. 5 The partial density of states calculation and density-of-states analyses for **1**, **2** and **3**.

In conclusion, by using glycerol as the solvent and *en* as the structural decorating ligand, a series of organic-decorated manganese selenidostannates with various structural dimensionality were prepared and structurally and optically characterized. It is worth mentioning that compounds **2** and **3** were the first 2D and 3D organic-decorated manganese selenidostannates, respectively. The successful preparation of these compounds not only enriches the field of hybrid heterometallic chalcogenides, but also provides us an alternative way to prepare new compounds in larger scale from relatively easily synthesized ones.

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Notes and references

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, People's Republic of China. Fax: +86 591 83793727; Tel: +86 591 83793727; E-mail: xyhuang@fjirsm.ac.cn*
[b] *University of Chinese Academy of Sciences, Beijing, 100049, People's Republic of China.*

† Electronic Supplementary Information (ESI) available: [Syntheses, more structural details, elemental analysis, TGA， PXRD and theoretical calculations. CCDC reference numbers 968733-968735]. See DOI: 10.1039/b000000x/

‡ Crystal and structure refinement details. For **1**: $C_4H_{16}MnN_4Se_3Sn$, λ = 0.71073 Å, M = 530.72, monoclinic, $P2_1/n$, a = 9.4565(4), b = 11.2896(4), c = 12.7937(5) Å, V = 1326.63(9) Å^3, Z = 4, T = 293(2) K, 5890 reflections measured, 2805 unique (R_{int} = 0.0274), 2266 observed [$I > 2\sigma(I)$], R_1 = 0.0291, wR_2 = 0.0555, GOF = 1.008, CCDC 968733; For **2**: $C_2H_8MnN_2Se_3Sn$, λ = 0.71073 Å, M = 470.61, orthorhombic, *Pbca*, a = 13.9290(5), b = 7.5261(2), c = 19.2572(9) Å, V = 2018.75(13) Å^3, Z = 8, T = 293(2) K, 5652 reflections measured, 2130 unique (R_{int} = 0.0329), 1709 observed [$I > 2\sigma(I)$], R_1 = 0.0478, wR_2 = 0.1338, GOF = 1.046, CCDC 968734; For **3**: $C_4H_{16}Mn_2N_4Se_4Sn$, λ = 0.71073 Å, M = 664.62, orthorhombic, *Pnma*, a = 13.1101(4), b = 14.8267(6), c = 7.9466(2) Å, V = 1544.66(9) Å^3, Z = 4, T = 293(2) K, 4008 reflections measured, 1641 unique (R_{int} = 0.0198), 1340 observed [$I > 2\sigma(I)$], R_1 = 0.0234, wR_2 = 0.0538, GOF = 1.041, CCDC 968735.

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