Two novel selenidostannates from mixed structure-directing systems: The
large ten-membered ring of \([\text{Sn}_3\text{Se}_4]\) semicubes and the 3D \([\text{Sn}_4\text{Se}_9]^{2n_-}\)
with multi-channels

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1. More Structural details

Figure S1. (a) Perspective views along the \(b\)-axis of the packing diagram of 1 showing the intensive hydrogen bonds among cations and anionic \([\text{Sn}_3\text{Se}_7]^{2-}\) layers. (b) Intensive hydrogen bonds for the cations between two adjacent anionic \([\text{Sn}_3\text{Se}_7]^{2-}\) layers of 1. Some of the hydrogen atoms on MACs and \([\text{Bmmim}]^+\) cations are omitted for clarity. (c) Stacking of \([\text{Sn}_3\text{Se}_7]^{2-}\) layers and the two different channels viewed along the \(c\)-axis (windows of the two kinds of channels are shaped in green and purple, respectively).
Figure S2. (a) The window of the large rectangular channel is defined by the interlinkages of \([\text{Sn}_6\text{Se}_{18}]\) and \([\text{SnSe}_4]\) units. (b) A perspective view along the $b$-axis of the packing diagram of $2$ showing the intensive hydrogen bonds among cations and anionic \([\text{Sn}_2\text{Se}_9]^{2-}\) framework of $2$. Some of the hydrogen atoms on MACs and \([\text{Bmmim}]^+\) cations are omitted for clarity.
Figure S3. (a) Linkages of [Sn$_3$Se$_{10}$] and [SnSe$_5$] in 3D-[Fe(bipy)$_3$]Sn$_4$Se$_9$·2H$_2$O. [SnSe$_5$] units were drawn in polyhedra. (b) Linkages of dimeric [Sn$_6$Se$_{18}$] and [Sn$_2$Se$_8$] in 3D-(Bmmim)$_2$[Ni(1,2-pda)$_3$][Sn$_4$Se$_9$]$_2$. [Sn$_2$Se$_8$] units were drawn in polyhedra. (c) Linkages of dimeric [Sn$_6$S$_{18}$] SBUs and [SnS$_4$] tetrahedra in 2D-[Sn$_4$S$_9$]$_n^2$· [SnS$_4$] units were drawn in polyhedra.

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<th>d(D⋯A) (Å)</th>
<th>∠(D–H⋯A) (°)</th>
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Table S2. Hydrogen bonds [Å and \(^\circ\)] for 2.

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<th>d(D···A)</th>
<th>(\angle(D-H···A))</th>
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<td>3.630(9)</td>
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<td>N(5)-H(5C)...Se(9)#3</td>
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<td>C(3)-H(3A)...Se(17)#1</td>
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<td>3.983(10)</td>
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Symmetry codes: #1 x,y+1,z; #2 x,y+1/2,z+1/2; #3 x,y+3/2,z+1/2; #4 -x,-y+1/2,-z+1/2; #5 -x+1,y+1,z+1; #6 -x+1,y+1/2,z+1/2; #7 x,y+1,z; #8 -x+1,-y+1,z+1

Symmetry codes: #1 x,y+1,z; #2 x,y+1/2,z+1/2; #3 x,y+3/2,z+1/2; #4 -x,-y+1/2,-z+1/2; #5 -x+1,y+1,z+1; #6 -x+1,y+1/2,z+1/2; #7 x,y+1,z; #8 -x+1,-y+1,z+1
2. Physical measurements

2a) PXRD

All the crystalline samples were manually selected and used for PXRD characterizations. The PXRD patterns of compounds 1 and 2 match well with those simulated from single-crystal X-ray data, indicating the phase purity of the two compounds.

![Figure S4. PXRD pattern of compound 1 and the simulated one from single-crystal X-ray structure.](image)

![Figure S5. PXRD pattern of compound 2 and the simulated one from single-crystal X-ray structure.](image)

The post-TGA residues for the two compounds were characterized by PXRD. The residues are a mixture of SnSe$_2$ (PDF NO. 89-3197, red lines), SnSe (PDF NO. 48-1224, pink lines) and Ni$_3$Se$_4$ (PDF NO. 89-7162, blue lines) for 1 and a mixture of SnSe$_2$ (PDF NO. 89-3197, red lines), SnSe (PDF NO. 48-1224, pink lines) and NiSe$_2$ (PDF NO. 88-1711, green lines) for 2, respectively.

![Figure S6. PXRD pattern of the post-TGA residue of compound 1 compared to that of the binaries.](image)
Figure S7. PXRD pattern of the post-TGA residue of compound 2 compared to that of the binaries.

2b) EDX spectra

Figure S8. EDX spectrum of compound 1.

Table S3. Atomic percentages from EDX analyses for compound 1.

<table>
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<tr>
<th>Elements</th>
<th>Atomic percentages from EDX analysis</th>
<th>Theoretical molar ratio of elements (Ni: Sn: Se)</th>
<th>Experimental molar ratio of elements (Ni: Sn: Se)</th>
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<td>Ni K</td>
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<td>1: 6.28: 16.13</td>
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<tr>
<td>Sn L</td>
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<tr>
<td>Se L</td>
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Figure S9. EDX spectrum of compound 2.

Table S4. Atomic percentages from EDX analyses for compound 2.

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<th>Theoretical molar ratio of elements (Ni: Sn: Se)</th>
<th>Experimental molar ratio of elements (Ni: Sn: Se)</th>
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