Varied forms of lamellar $[\text{Sn}_3\text{Se}_7]_{2n}^n$ anion: the competitive and synergistic structural directing effects of metal-amine complex and imidazolium cations

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Supporting Information.

1. Structure details

Figure S1. The four known lamellar $[\text{Sn}_3\text{Se}_7]_{2n}^n$ anions with six–membered rings (up) and two novel lamellar $[\text{Sn}_3\text{Se}_7]_{2n}^n$ anions with eight-membered heart-shaped rings (down) reported in this work.

When $[\text{Sn}_3\text{Se}_4]$ semi-cube was used as a node and $(\mu_2\text{Se})_2$ as a ligand, the lamellar $[\text{Sn}_3\text{Se}_7]_{2n}^n$ anions in compounds 1, 2, 3 and 4 can be simplified as those in Figs. S2-S4, that is, compounds 1 and 2 contains a simplified elliptic six-membered ring while a novel eight-membered heart shaped ring can be found in 3 and 4.
Figure S2. The simplified elliptic six-membered ring with $[\text{Sn}_3\text{Se}_4]$ semi-cube as a node and $(\mu_2-\text{Se})_2$ as a ligand in 1 and 2.

Figure S3. The simplified eight-membered heart shaped ring with $[\text{Sn}_3\text{Se}_4]$ semi-cube as a node and $(\mu_2-\text{Se})_2$ as a ligand in 3.

Figure S4. The simplified eight-membered heart shaped ring and six-membered ring with $[\text{Sn}_3\text{Se}_4]$ semi-cube as a node and $(\mu_2-\text{Se})_2$ as a ligand in 4.
Figure S5. (a) A view of the packing of [Sn₃Se₇]₂ⁿ⁻ layers in 3 along the b axis, (b) the connecting mode of eight-membered heart shaped ring chain in 3 and (c) the eight-membered heart shaped ring chain constructed from the [Sn₃Se₇]₂ⁿ⁻ single chain and [Sn₃Se₉] SBUs.

Figure S6. (a) A view of the packing of [Sn₃Se₇]₂ⁿ⁻ layers in 4 along the c axis and (b) the construction of eight-membered heart shaped ring chain in 4.
Figure S7. Perspective views of the mixed cations filling modes in compounds 3 (a) and 4 (b); the [Sn$_3$Se$_7$]$_{2n}$ layers are in a yellow ball-stick mode, and the [Bmmim]$^+$ cations in different positions are distinguished by different colors. (c) and (d) show the side views of the mixed cations located in the inter-lamellar space and voids; the green cylinders indicate the channels in 3 and 4.

2. Physical measurements

3a). PXRD

Figure S8. The PXRD pattern of the post-TGA residue of compound 1 along with the simulated ones of SnSe$_2$ and MnSe at bottom for comparison. The TGA residue of compound 1 is identified as a mixture of SnSe$_2$ and MnSe.
Figure S9. The PXRD pattern for the post-TGA residues of compound 2 along with the simulated ones of SnSe$_2$ and MnSe at bottom for comparison. The residue of compound 2 is identified as a mixture of SnSe$_2$ and MnSe.

Figure S10. The PXRD pattern for the post-TGA residue of compound 3 along with the simulated ones of SnSe and MnSe at bottom for comparison. The residue of compound 3 is identified as a mixture of SnSe and MnSe.

Figure S11. The PXRD pattern for the post-TGA residue of compound 4 along with the simulated ones of SnSe$_2$ and MnSe at bottom for comparison. The residue of compound 4 is identified as the mixture of SnSe$_2$ and MnSe.
3b). EDX spectra

**Figure S12.** EDX spectrum of compound 1.

**Figure S13.** EDX spectrum of compound 2.

**Figure S14.** EDX spectrum of compound 3.

**Figure S15.** EDX spectrum of compound 4.