

## Poly[[pentaethylenhexamine)manganese(II)] [hepta- $\mu$ -selenido-tritin(IV)]: a tin–selenium net with remarkable flexibility

Guo-Hai Xu,<sup>a,b</sup> Cheng Wang<sup>a\*</sup> and Peng Guo<sup>a,b</sup>

<sup>a</sup>State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China, and <sup>b</sup>Graduate School of the Chinese Academy of Sciences, Changchun 130022, People's Republic of China  
Correspondence e-mail: cwang@ciac.jl.cn

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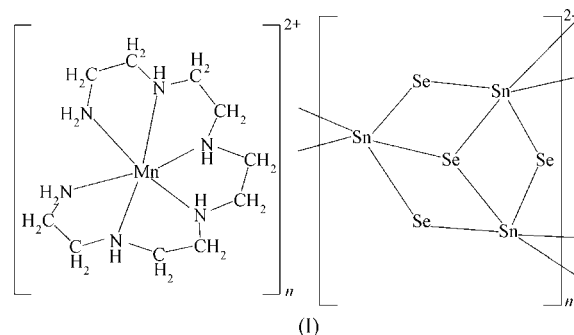
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The title compound,  $\{[\text{Mn}(\text{C}_{10}\text{H}_{28}\text{N}_6)][\text{Sn}_3\text{Se}_7]\}_n$ , consists of anionic  $\infty\{[\text{Sn}_3\text{Se}_7]^{2-}\}$  layers interspersed by  $[\text{Mn}(\text{peha})]^{2+}$  complex cations (peha is pentaethylenhexamine). Pseudocubic ( $\text{Sn}_3\text{Se}_4$ ) cluster units within each layer are held together to form a  $6^3$  net with a hole size of  $8.74 \times 13.87 \text{ \AA}$ . Weak  $\text{N}-\text{H} \cdots \text{Se}$  interactions between the host inorganic frameworks and metal complexes extend the components into a three-dimensional network. The incorporation of metal complexes into the flexible anion layer dictates the distortion of the holes.

### Comment

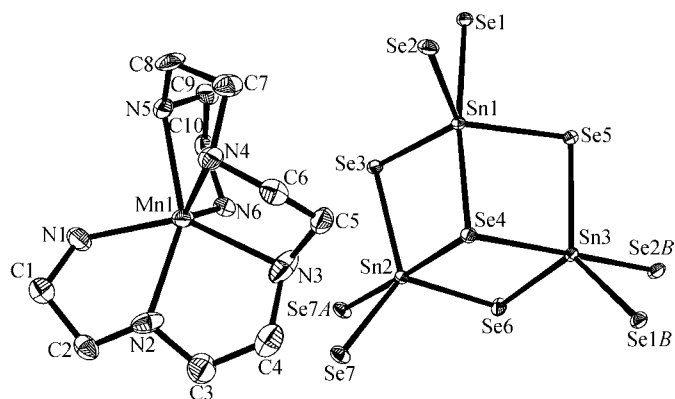
Since the extension of established synthetic methodologies for zeolites to metal sulfides (Bedard *et al.*, 1989), chalcogenido-metalates have been of considerable interest because of their combination of the microporous features of zeolites and their intrinsic semiconducting behaviour. Organic amines play an important role in the formation of these materials by acting as templates and charge-balancing counter-ions. Synthesis of organic–inorganic hybrid tin chalcogenides is generally performed in the presence of nonchelating organic amines, and a series of dimeric anions with general formula  $[\text{Sn}_2\text{Q}_6]^{4-}$  ( $\text{Q} = \text{S}, \text{Se}$  and  $\text{Te}$ ; Li *et al.*, 1999) has been prepared with *in-situ*-generated metal–amine complexes. However, little (Li *et al.*, 2000) is known about the incorporation of metal complexes into two- or three-dimensional networks of tin chalcogenides. It is known that the tendency of  $\text{Sn}^{\text{IV}}$  to extend its coordination number from 4 to 5 or 6 allows the formation of a variety of two- and three-dimensional anionic structures. The most important feature of metal complexes is the integration of their electronic, optical and magnetic properties with those of the host inorganic frameworks, which helps to provide complementary properties and synergistic effects. We

report here the crystal structure of such a compound, *viz.*  $\{[\text{Mn}(\text{peha})][\text{Sn}_3\text{Se}_7]\}_n$  (peha is pentaethylenhexamine), (I).



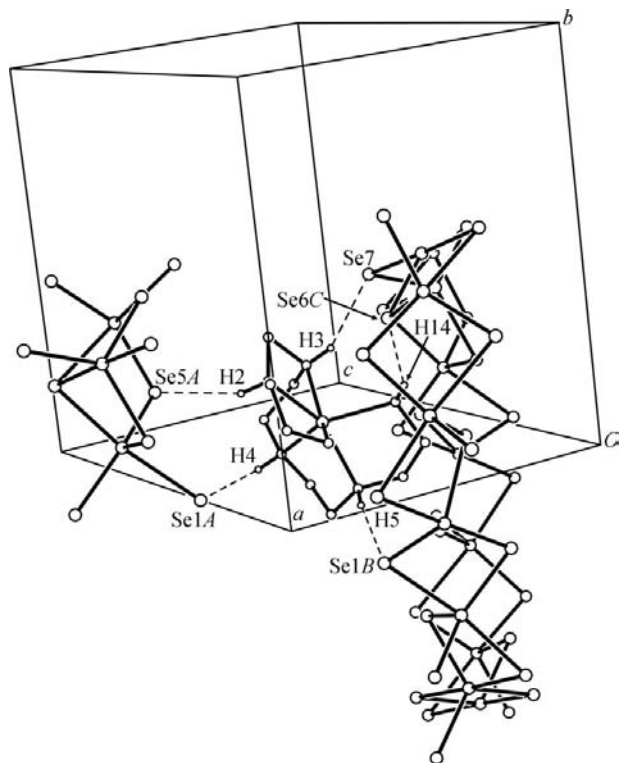
As shown in Figs. 1 and 2, compound (I) consists of anionic  $\infty\{[\text{Sn}_3\text{Se}_7]^{2-}\}$  layers interspersed by  $[\text{Mn}(\text{peha})]^{2+}$  complex cations. Within the  $\infty\{[\text{Sn}_3\text{Se}_7]^{2-}\}$  layer, pseudocubic ( $\text{Sn}_3\text{Se}_4$ ) cluster units are connected by edge sharing to form a  $6^3$  net with cavities surrounded by 12 Sn–Se polyhedra (Fig. 3). While all Sn atoms are coordinated in a trigonal bipyramidal fashion, the Se4 atom located centrally between three Sn atoms (Sn1, Sn2 and Sn3) is trigonally coordinated, and the remaining Se atoms are bicoordinated. In the  $[\text{Mn}(\text{peha})]^{2+}$  complex cation, the Mn centre is six-coordinated by N atoms from the peha molecule, displaying a distorted octahedral coordination geometry. Atoms N1, N2 and N3 are meridional, as are the other three N atoms (N4, N5 and N6). The peha molecules are generated from the decomposition and rearrangement of triethylenetetramine (teta).

Each Sn atom of (I) adopts a coordination environment with the  $\mu_3$ -Se atoms in axial (ax) positions [the opposite axial atoms are Se1 for Sn1, Se7<sup>ii</sup> for Sn2 and Se2<sup>iii</sup> for Sn3; symmetry codes: (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ]. The axial Se–Sn bond lengths are significantly longer than those for the equatorial sites (Table 1), which are similar to the distances found in the literature (Parise *et al.*, 1994). The deviations of the  $\text{Se}_{\text{ax}}-\text{Sn}-\text{Se}_{\text{ax}}$  angles from linearity (Table 1) indicate that the Sn atoms have slightly distorted trigonal bipyramidal coordination geometry.



**Figure 1**

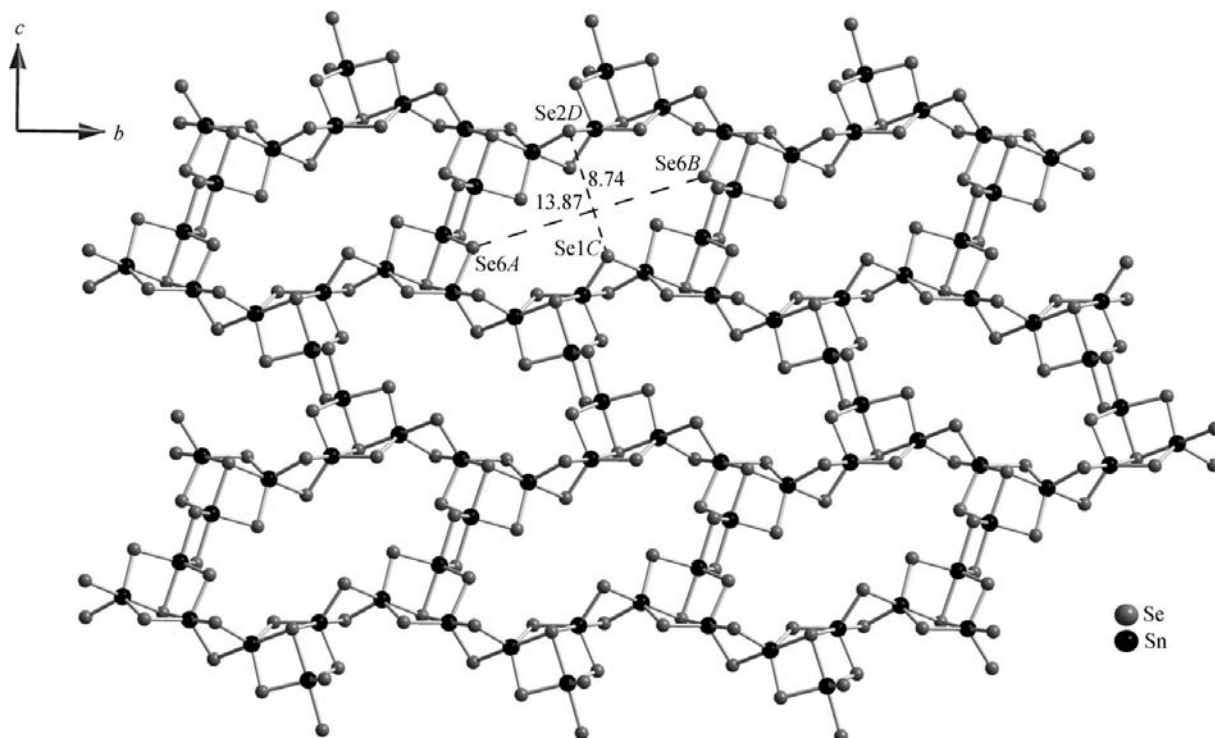
The structure of (I). Displacement ellipsoids are drawn at the 30% probability level and all H atoms have been omitted for clarity. Atoms labelled with the suffixes A and B are at the symmetry positions  $(-x + 1, -y + 1, -z)$  and  $(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$ , respectively.



**Figure 2**  
A packing diagram for (I), showing the three-dimensional network formed *via* weak N—H...Se interactions (dashed lines). Atoms labelled with the suffixes A, B and C are at the symmetry positions  $(x + 1, y, z)$ ,  $(-x + 1, -y, -z)$  and  $(-x + 1, -y + 1, -z)$ , respectively.

In the  $[\text{Mn}(\text{peha})]^{2+}$  complex cations, the Mn—N distances range from 2.254 (9) to 2.340 (9) Å and are in the normal range (Wendland *et al.*, 1998). The heavy distortion of the octahedral environment around the metal centre is manifested by the *trans* angles, which range from 128.9 (3) to 151.0 (3)°, and the *cis* angles, which lie in the range 73.2 (3)–129.1 (3)°.

As shown in Fig. 2 and Table 2, the title compound forms a three-dimensional network *via* weak N—H...Se interactions between N atoms of peha molecules and  $\mu_2$ -Se atoms from two adjacent polyanion layers. The layers are oriented parallel to the (101) plane. All Sn atoms within each layer are nearly coplanar (the mean deviation from the plane is 0.0597 Å). The average interlayer separation as measured between the tin planes is 9.23 Å. Both (I) and the previously reported compound TMA—SnSe (TMA is tetramethylammonium; Ahari, Ozin *et al.*, 1995; Ahari, Bowes *et al.*, 1995) contain anionic  $\infty\{[\text{Sn}_3\text{Se}_7]^{2-}\}$  layers, but the steric requirements of charge-balancing cations in the two structures are different. The flexibility of the  $\text{Sn}_3\text{Se}_7$  framework has been verified by varying the organic template or including molecular guests in the two structures. It is obvious that the distortion of the cavities in the title compound is a result of the bulk of the Mn complexes. On the basis of the Se...Se distances (Fig. 3), the holes have approximate dimensions of 8.74 13.87 Å and are significantly distorted from a regular hexagonal shape. Therefore, the incorporation of metal complexes into such structures not only explores their flexibility but may be able to introduce new properties into semiconductors.



**Figure 3**  
The  $\text{Sn}_3\text{Se}_7$  framework in the crystal structure of (I). Atoms labelled with the suffixes A, B, C and D are at the symmetry positions  $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ ,  $(x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$ ,  $(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$  and  $(x - \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2})$ , respectively.

Experimental

A mixture of Sn powder (0.0594 g, 0.5 mmol) and Se (0.0789 g, 1.0 mmol) with MnCl<sub>2</sub>·4H<sub>2</sub>O (0.1980 g, 1.0 mmol) in 3.0 ml of tetra/glycol (1:2 v/v) was stirred for 30 min in a 17.0 ml Teflon-lined stainless steel vessel. The vessel was sealed and heated at 463 K for one week. Orange block-shaped crystals were isolated by washing with ethanol and water.

Crystal data

[Mn(C<sub>10</sub>H<sub>28</sub>N<sub>6</sub>)] [Sn<sub>3</sub>Se<sub>7</sub>]  
*M<sub>r</sub>* = 1196.11  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 11.893 (5) Å  
*b* = 13.322 (5) Å  
*c* = 17.097 (5) Å  
 β = 96.659 (5)°  
*V* = 2690.5 (17) Å<sup>3</sup>  
*Z* = 4  
 Mo *K*α radiation  
 μ = 12.69 mm<sup>-1</sup>  
*T* = 207 K  
 0.12 × 0.12 × 0.08 mm

Data collection

Bruker SMART APEX CCD diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.230, *T*<sub>max</sub> = 0.308 (expected range = 0.271–0.362)  
 14868 measured reflections  
 5291 independent reflections  
 3945 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.055

Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.042  
*wR*(*F*<sup>2</sup>) = 0.079  
*S* = 0.99  
 5291 reflections  
 256 parameters  
 6 restraints  
 H atoms treated by a mixture of independent and constrained refinement  
 Δρ<sub>max</sub> = 1.20 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.88 e Å<sup>-3</sup>

All H atoms bound to C atoms were refined using a riding model, with C–H distances of 0.97 Å and *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub>(C). The imine H atoms were refined using a riding model, with N–H distances of 0.91 Å and *U*<sub>iso</sub>(H) values set at 1.2*U*<sub>eq</sub>(N). The amine H atoms were located in a difference Fourier map and their positions were refined under the application of an N–H bond-length restraint of 0.90 (2) Å, with *U*<sub>iso</sub>(H) values set at 1.5*U*<sub>eq</sub>(N).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3102). Services for accessing these data are described at the back of the journal.

Table 1

Selected geometric parameters (Å, °).

N1–Mn1	2.340 (9)	Se4–Sn1	2.6826 (12)
N2–Mn1	2.287 (8)	Se4–Sn2	2.7701 (12)
N3–Mn1	2.308 (8)	Se4–Sn3	2.8200 (13)
N4–Mn1	2.299 (8)	Se5–Sn3	2.5584 (13)
N5–Mn1	2.306 (7)	Se5–Sn1	2.5764 (12)
N6–Mn1	2.254 (9)	Se6–Sn2	2.5402 (12)
Se1–Sn3 <sup>i</sup>	2.5197 (12)	Se6–Sn3	2.5429 (12)
Se1–Sn1	2.8592 (13)	Se7–Sn2	2.5142 (14)
Se2–Sn1	2.5044 (12)	Se7–Sn2 <sup>ii</sup>	2.6703 (13)
Se2–Sn3 <sup>i</sup>	2.7211 (14)	Sn2–Se7 <sup>ii</sup>	2.6703 (13)
Se3–Sn1	2.5540 (12)	Sn3–Se1 <sup>iii</sup>	2.5197 (12)
Se3–Sn2	2.5776 (13)	Sn3–Se2 <sup>iii</sup>	2.7211 (14)
N6–Mn1–N2	122.1 (3)	N5–Mn1–N3	127.5 (3)
N6–Mn1–N4	128.9 (3)	N6–Mn1–N1	90.3 (3)
N2–Mn1–N4	101.9 (3)	N2–Mn1–N1	73.2 (3)
N6–Mn1–N5	77.5 (3)	N4–Mn1–N1	129.1 (3)
N2–Mn1–N5	151.0 (3)	N5–Mn1–N1	86.6 (3)
N4–Mn1–N5	74.6 (3)	N3–Mn1–N1	144.9 (3)
N6–Mn1–N3	89.9 (3)	Se4–Sn1–Se1	170.79 (3)
N2–Mn1–N3	77.1 (3)	Se7 <sup>ii</sup> –Sn2–Se4	178.20 (3)
N4–Mn1–N3	75.0 (3)	Se2 <sup>iii</sup> –Sn3–Se4	176.02 (4)

Symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2...Se5 <sup>iv</sup>	0.91	2.85	3.699 (8)	155
N3–H3...Se7	0.91	2.60	3.380 (9)	144
N4–H4...Se1 <sup>iv</sup>	0.91	2.76	3.607 (8)	156
N5–H5...Se1 <sup>v</sup>	0.91	2.65	3.542 (7)	168
N6–H14...Se6 <sup>ii</sup>	0.91 (2)	2.77 (4)	3.603 (8)	152 (7)

Symmetry codes: (ii)  $-x + 1, -y + 1, -z$ ; (iv)  $x + 1, y, z$ ; (v)  $-x + 1, -y, -z$ .

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