

Molecular building blocks for solid-state chalcogenides: solvothermal synthesis of $[\text{Mn}(\text{en})_3]\text{Te}_4$ and $[\text{Fe}(\text{en})_3]_2(\text{Sb}_2\text{Se}_5)$

Zhen Chen,^a Ru-Ji Wang,^{b*} Xiao-Ying Huang^a and Jing Li^a

^aDepartment of Chemistry, Rutgers University, Camden, NJ 08102, USA, and

^bDepartment of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Correspondence e-mail: wangrj@sam.chem.tsinghua.edu.cn

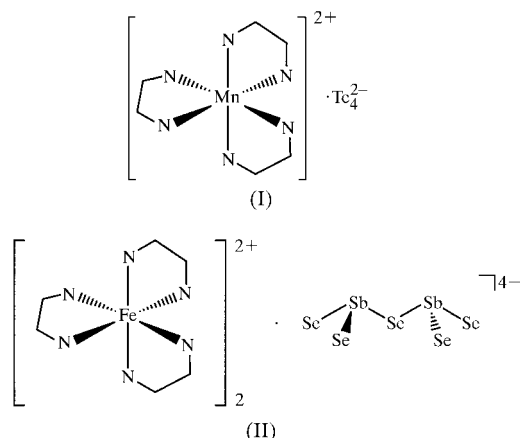
Received 18 October 1999

Accepted 8 May 2000

Two new molecular metal chalcogenides, tris(ethylenediamine-*N,N'*)manganese(II) tetratelluride, $[\text{Mn}(\text{C}_2\text{H}_8\text{N}_2)_3]\text{Te}_4$, (I), and bis[tris(ethylenediamine-*N,N'*)iron(II)] pentaselenodiantimonate(III), $[\text{Fe}(\text{C}_2\text{H}_8\text{N}_2)_3]_2(\text{Sb}_2\text{Se}_5)$, (II), containing the isolated molecular building blocks Te_4^{2-} and $\text{Sb}_2\text{Se}_5^{4-}$, have been synthesized by solvothermal reactions in an ethylenediamine solution at 433 K. The anion Te_4^{2-} in (I) is a zigzag oligometric chain with Te–Te bond lengths in the range 2.709–2.751 Å. There is a very short contact [3.329 (1) Å] between a pair of neighboring Te_4^{2-} anions. In (II), each Sb atom is surrounded by three Se atoms to give a tripodal coordination. One of the three independent Se atoms is a μ_2 -bridging ligand between two Sb atoms; the other two are terminal.

Comment

Polychalcogenide compounds with open frameworks are potentially useful materials for phase separation, ion



exchange, catalytic and optical applications. Several important open-framework chalcogenides have been reported (Li, Laine

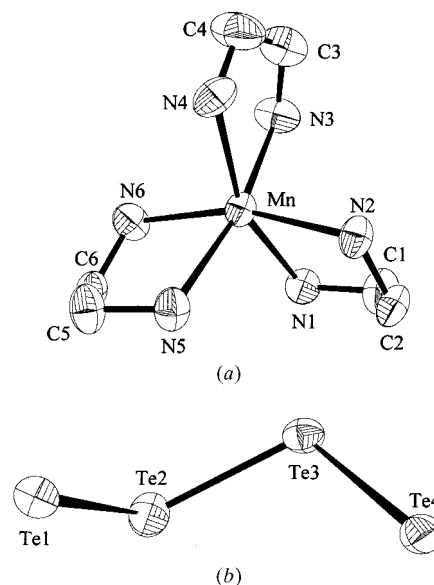


Figure 1

Views of (a) the cation and (b) the anion of (I), drawn with 50% probability ellipsoids. H atoms have been omitted for clarity.

et al., 1999; Hanko & Kanatzidis, 1998; McCarthy *et al.*, 1995). Using different structure-directing agents, such as the organic cations NR_4^+ , PR_4^+ ($R = \text{CH}_3$, CH_2CH_3 , Ph *etc.*) and metal complex cations $[\text{M}(\text{en})_3]^{m+}$ (where M^{m+} is a transition metal ion and en is ethylenediamine), numerous microporous and some mesoporous polychalcogenides have been prepared by soft synthetic methods. These chalcogenides exhibit a diverse and rich structural chemistry. Some examples include $(\text{Ph}_4\text{P})[\text{M}(\text{Se}_6)_2]$ ($M = \text{Ga}$, In , Tl ; Dhingra & Kanatzidis, 1992), $[(\text{CH}_3)_4\text{N}][\text{Sb}_3\text{S}_5]$ (Parise, 1991), $[(\text{C}_2\text{H}_5)_4\text{N}][\text{CuGe}_2\text{S}_5]$ (Tan *et al.*, 1995), $[(\text{C}_3\text{H}_7)_4\text{N}][\text{Sb}_3\text{S}_5]$ (Parise & Ko, 1992), and $[\text{Co}(\text{en})_3][\text{CoSb}_4\text{S}_8]$ (Stephan & Kanatzidis, 1996). Recently, we have focused on solvothermal reactions in neat ethylenediamine at temperatures generally below 453 K to

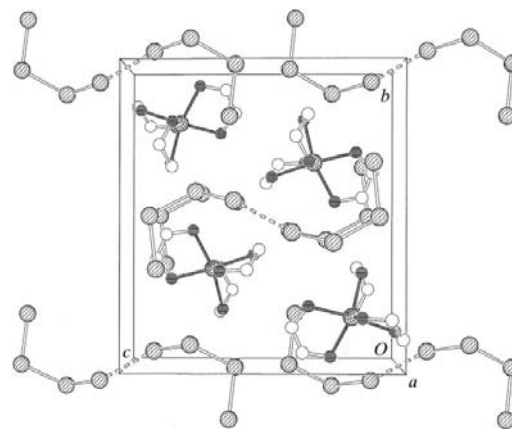


Figure 2

A packing view of (I) along the *a* direction with broken lines for non-covalent $\text{Te}\cdots\text{Te}$ interactions, double-shaded circles for Mn, single-shaded circles for Te, solid circles for N and open circles for C atoms.

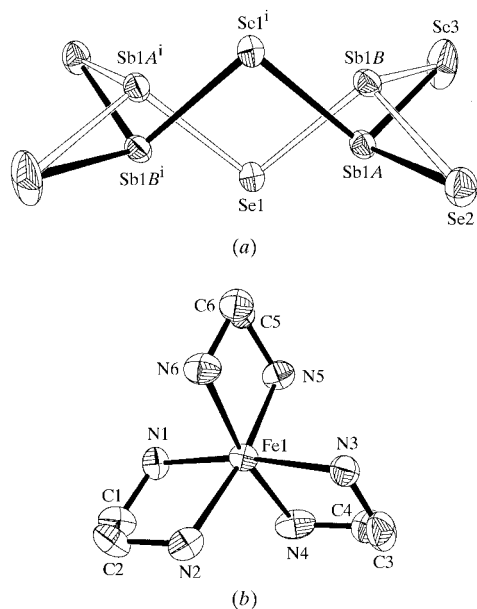


Figure 3
Views of (a) the disordered anion and (b) the cation of (II), drawn with 50% probability ellipsoids. H atoms have been omitted for clarity. See Table 3 for symmetry code.

synthesize porous metal polychalcogenides by the molecular building-block approach. The retention of molecular building blocks (such as polychalcogenide oligomers and molecular chalcogenido-metalates) during the reaction provides an effective means to obtain open-framework structures. The mild conditions often make it possible to leave the molecular building blocks intact during the reorganization and reformation of the crystal structure and we have succeeded in obtaining a number of new compounds in this category,

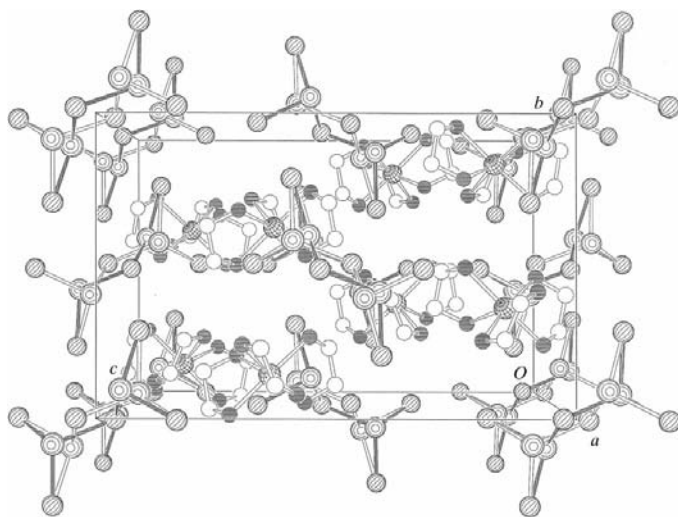


Figure 4
A packing view of (II) along the *a* direction. The two orientations of the anion are distinguished by black and open bonds. Double-shaded circles are shown for Fe, multi circles for Sb, single-shaded circles for Se, solid circles for N and open circles for C atoms.

including Cs_2PdSe_8 (Li, Chen, Wang & Lu, 1998) and $\text{Cs}_2\text{PdSe}_{16}$ (Li, Chen & Wang, 1999). We show here that two molecular building blocks, namely Te_4^{2-} and $\text{Sb}_2\text{Se}_5^{4-}$, may be isolated and stabilized in neat ethylenediamine.

Tris(ethylenediamine-*N,N'*)manganese(II) tetratelluride, $[\text{Mn}(\text{en})_3]\text{Te}_4$, (I), and bis[tris(ethylenediamine-*N,N'*)iron(II)] pentaselenodiantimonate, $[\text{Fe}(\text{en})_3]_2(\text{Sb}_2\text{Se}_5)$, (II), have been synthesized solvothermally in ethylenediamine solutions. Compound (I) consists of discrete complex cations, $[\text{Mn}(\text{en})_3]^{2+}$, and molecular anions, Te_4^{2-} , in a 1:1 ratio. As shown in Fig. 1(a), the Mn atom is surrounded by six N atoms to give a distorted octahedral environment. Ethylenediamine (en) functions as a bidentate ligand and forms a five-membered chelate ring with the Mn atom. The Mn–N bond lengths are in a narrow range [2.264 (7)–2.290 (7) Å] and are comparable with those found in analogous compounds (Li, Chen, Emge *et al.*, 1998). The conformation of $[\text{Mn}(\text{en})_3]^{2+}$ is le_2ob according to Saito's description (Saito, 1992). Its configuration should be $\Delta(\lambda\lambda\delta)$ or $\Lambda(\delta\delta\lambda)$, as (I) is meso-meric. The oligomer Te_4^{2-} is shown in Fig. 1(b). It is a zigzag chain with Te–Te bond distances in the range 2.709 (1)–2.751 (1) Å. There is a very short contact between a pair of neighboring Te_4^{2-} anions [$\text{Te}_4 \cdots \text{Te}_4$ 3.329 (1) Å], shown as broken lines in Fig. 2.

Compound (II) consists of discrete $[\text{Fe}(\text{en})_3]^{2+}$ complex cations and $\text{Sb}_2\text{Se}_5^{4-}$ anions in a 2:1 ratio. Each Sb atom is surrounded by three Se atoms to give a tripodal geometry (Fig. 3a). Atom Se1 bridges two Sb atoms as a μ_2 ligand, while the other two Se atoms are terminal ligands. In the $[\text{Fe}(\text{en})_3]^{2+}$ groups, each ethylenediamine functions as a bidentate ligand coordinating to iron to give rise to a five-membered chelate ring. The Fe atom has a distorted octahedral environment with an average Fe–N bond length of 2.192 (12) Å. The conformation of $[\text{Fe}(\text{en})_3]^{2+}$ is le_1e_3 , while its configuration is $\Delta(\lambda\lambda\lambda)$ (Fig. 3b) or $\Lambda(\delta\delta\delta)$. Fig. 4 is a packing view of (II) along the *a* direction.

Both (I) and (II) exhibit significant hydrogen bonding. The N–H to Te (or Se) distances shorter than 3 Å and the N–H \cdots Te (or Se) angles are listed in Tables 2 and 4.

Experimental

Rb_2Q ($Q = \text{Se}, \text{Te}$) was prepared in liquid ammonia by stoichiometric reactions of rubidium metal (Rb, 99.5%, Aldrich Chemical Company) and elemental tellurium (99.8%, Strem Chemicals Inc.) or selenium. Single crystals of $[\text{Mn}(\text{en})_3]\text{Te}_4$, (I), were grown from solvothermal reactions containing Rb_2Te (0.075 g, 0.25 mmol), MnCl_2 (0.032 g, 0.25 mmol; 97%, Strem Chemicals Inc.) and Te (0.096 g, 0.75 mmol). The reactants were weighed and mixed in a glove-box under an argon atmosphere. The sample was then transferred to a 9 mm OD thick-wall Pyrex tube and approximately 0.37 ml of en solvent (99%, anhydrous, Fisher Scientific) was added. After the liquid had been condensed by liquid nitrogen, the tube was sealed under vacuum ($\sim 10^{-3}$ Torr; 1 Torr \approx 133.322 Pa). The reaction took place at 433 K for 6 d. After the reaction was complete, the sample was washed with 30% and 95% ethanol followed by drying with

Table 1

Selected geometric parameters (Å, °) for (I).

Te1—Te2	2.7091 (12)	Mn1—N3	2.271 (8)
Te2—Te3	2.7500 (12)	Mn1—N1	2.287 (7)
Te3—Te4	2.7509 (12)	Mn1—N5	2.289 (7)
Mn1—N6	2.264 (7)	Mn1—N4	2.290 (7)
Mn1—N2	2.267 (7)		
Te1—Te2—Te3	109.17 (3)	Te2—Te3—Te4	107.39 (3)

anhydrous diethyl ether. [Fe(en)₃]₂(Sb₂Se₅), (II), was also synthesized in solvothermal reactions using ethylenediamine as a solvent. A mixture of Rb₂Se (0.06 g, 0.25 mmol), FeCl₂ (0.032 g, 0.25 mmol; 98%, Alfa-Aesar Chemical Company), SbCl₃ (0.057 g, 0.25 mmol; 99%, Aldrich Chemical Company) and Se (0.04 g, 0.5 mmol) was weighed in a glove-box and en (~0.4 ml) was added. The solvent was condensed and the tube was sealed under vacuum. The sample was heated at 433 K for 7 d. The same wash procedure as for (I) was applied to isolate the final product.

Compound (I)

Crystal data

[Mn(C ₂ H ₈ N ₂) ₃] ₂ Te ₄	$D_x = 2.622 \text{ Mg m}^{-3}$
$M_r = 745.65$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 8.461 (2) \text{ \AA}$	$\theta = 8.0\text{--}13.8^\circ$
$b = 15.653 (3) \text{ \AA}$	$\mu = 6.746 \text{ mm}^{-1}$
$c = 14.269 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.37 (3)^\circ$	Block, black
$V = 1889.2 (7) \text{ \AA}^3$	$0.33 \times 0.30 \times 0.30 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.042$
ω scans	$\theta_{\text{max}} = 24.97^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.120$, $T_{\text{max}} = 0.132$	$k = 0 \rightarrow 18$
3444 measured reflections	$l = 0 \rightarrow 16$
3306 independent reflections	3 standard reflections
2382 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 5.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0010P)^2 + 5.00P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.343$	$\Delta\rho_{\text{max}} = 1.37 \text{ e \AA}^{-3}$
3306 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
155 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.00129 (4)

Table 2

Intermolecular geometry (Å, °) for (I).

$D\text{--}H\cdots A$	$H\cdots A$	$D\text{--}H\cdots A$
N2—H2A···Te4 ⁱ	2.994	152
N2—H2B···Te1 ⁱ	2.887	170
N5—H5B···Te1 ⁱⁱ	2.987	158

 Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $x, y - 1, z$.

Table 3

Selected geometric parameters (Å, °) for (II).

Sb1A—Se3	2.438 (2)	Fe1—N4	2.161 (12)
Sb1A—Se2	2.481 (2)	Fe1—N2	2.185 (13)
Sb1A—Se1 ⁱ	2.590 (3)	Fe1—N6	2.192 (11)
Sb1B—Se3	2.383 (2)	Fe1—N5	2.198 (11)
Sb1B—Se2	2.537 (2)	Fe1—N1	2.206 (11)
Sb1B—Se1	2.609 (3)	Fe1—N3	2.211 (11)
Se3—Sb1A—Se2	103.72 (8)	Se3—Sb1B—Se1	107.37 (11)
Se3—Sb1A—Se1 ⁱ	108.24 (10)	Se2—Sb1B—Se1	100.20 (9)
Se2—Sb1A—Se1 ⁱ	102.03 (9)	Sb1A ⁱ —Se1—Sb1B	92.51 (10)
Se3—Sb1B—Se2	103.66 (9)		

 Symmetry code: (i) $-x, 1 - y, 1 - z$.

Table 4

Intermolecular geometry (Å, °) for (II).

$D\text{--}H\cdots A$	$H\cdots A$	$D\text{--}H\cdots A$
N1—H1A···Se2 ⁱ	2.81	159
N2—H2A···Se3 ⁱⁱ	2.67	158
N2—H2B···Se3	2.68	175
N3—H3A···Se3 ⁱⁱⁱ	2.91	151
N3—H3B···Se2 ⁱⁱⁱ	2.78	173
N4—H4A···Se2 ⁱ	2.77	158
N5—H5B···Se2 ⁱⁱⁱ	2.90	150
N6—H6A···Se3 ⁱⁱ	2.76	150
N6—H6B···Se2 ^{iv}	2.86	172

 Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $-x, 2 - y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (iv) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

[Fe(C ₂ H ₈ N ₂) ₃] ₂ (Sb ₂ Se ₅)	Mo $K\alpha$ radiation
$M_r = 1110.62$	Cell parameters from 25 reflections
Orthorhombic, Pbc	$\theta = 7.5\text{--}12.0^\circ$
$a = 15.774 (3) \text{ \AA}$	$\mu = 7.837 \text{ mm}^{-1}$
$b = 11.739 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 18.239 (4) \text{ \AA}$	Block, brown
$V = 3377.3 (11) \text{ \AA}^3$	$0.5 \times 0.3 \times 0.2 \text{ mm}$
$Z = 4$	
$D_x = 2.184 \text{ Mg m}^{-3}$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.115$
ω scans	$\theta_{\text{max}} = 26.02^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -18 \rightarrow 19$
$T_{\text{min}} = 0.018$, $T_{\text{max}} = 0.211$	$k = -13 \rightarrow 14$
6283 measured reflections	$l = -22 \rightarrow 21$
3321 independent reflections	3 standard reflections
1719 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 5.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 2.0077P]$
$R[F^2 > 2\sigma(F^2)] = 0.082$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.171$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.067$	$\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$
3321 reflections	$\Delta\rho_{\text{min}} = -0.95 \text{ e \AA}^{-3}$
163 parameters	
H-atom parameters constrained	

Although the anion, Sb₂Se₅⁴⁻, is not centrosymmetric, its disordered orientations in different cells give statistical centrosymmetry

with overlap of Se2 and Se3. Therefore, the occupancies of Sb1A, Sb1B and Se1 are 0.5 in the refinement.

For both compounds, data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4/PC* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SCHAKAL92* (Keller, 1992) and *ORTEX* (McArdle, 1993); software used to prepare material for publication: *SHELXL97*.

We are grateful to the National Science Foundation for financial support through grant DMR-9553066 and supplement.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1117). Services for accessing these data are described at the back of the journal.

References

Dhingra, S. & Kanatzidis, M. G. (1992). *Science*, **258**, 1769–1772.

- Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
- Hanko, J. A. & Kanatzidis, M. G. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 342–344.
- Harms, K. (1997). *XCAD-4*. University of Marburg, Germany.
- Keller, E. (1992). *SCHAKAL92*. University of Freiburg, Germany.
- Li, J., Chen, Z., Emge, T. J., Yuen, T. & Proserpio, D. M. (1998). *Inorg. Chim. Acta*, **273**, 310–315.
- Li, J., Chen, Z. & Wang, R.-J. (1999). *Coord. Chem. Rev.* **190–192**, 707–735.
- Li, J., Chen, Z., Wang, R.-J. & Lu, J. Y. (1998). *J. Solid State Chem.* **140**, 149–153.
- Li, H., Laine, A., O’Keeffe, M. & Yaghi, O. M. (1999). *Science*, **283**, 1145–1147.
- McArdle, P. (1993). *J. Appl. Cryst.* **26**, 752.
- McCarthy, T. J., Tanzer, T. A. & Kanatzidis, M. G. (1995). *J. Am. Chem. Soc.* **117**, 1294–1301.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Parise, J. B. (1991). *Science*, **251**, 293–294.
- Parise, J. B. & Ko, Y. (1992). *Chem. Mater.* **4**, 1446–1450.
- Saito, Y. (1992). *Inorganic Molecular Dissymmetry*, pp. 56–59. Berlin: Springer-Verlag.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stephan, H.-O. & Kanatzidis, M. G. (1996). *J. Am. Chem. Soc.* **118**, 12226–12227.
- Tan, K., Darovsky, A. & Parise, J. B. (1995). *J. Am. Chem. Soc.* **117**, 7039–7040.