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Key indicators

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(C-C)$  = 0.014 Å  
 R factor = 0.036  
 wR factor = 0.106  
 Data-to-parameter ratio = 23.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

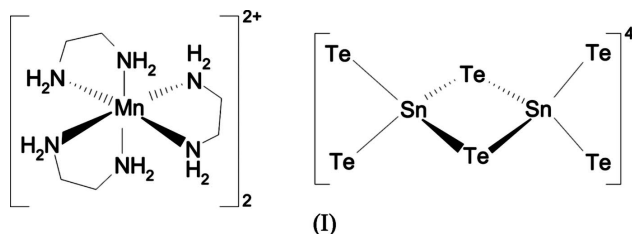
Bis[tris(ethylenediamine)manganese(II)] di- $\mu$ -tellurido-bis[ditelluridostannate(IV)] (monoclinic modification)

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The title compound,  $[Mn(C_2H_8N_2)_3]_2[Sn_2Te_6]$ , contains  $[Mn(en)_3]^{2+}$  (en is ethylenediamine) complex cations and crystallographically centrosymmetric  $[Sn_2Te_6]^{4-}$  anions in its monoclinic crystal structure. The five-membered chelate rings of symmetry-related cations exhibit either  $\lambda\lambda\lambda$  or  $\delta\delta\delta$  conformations. Two  $SnTe_4$  tetrahedra edge-share to afford the hexatelluridodistannate(IV) anions, whose terminal Sn—Te bonds are significantly shorter than the bridging Sn—Te bonds.

Comment

Tetrahedral  $[SnE_4]^{4-}$  ( $E = S, Se, Te$ ) anions exhibit a characteristic tendency to condense in polar solvents to generate corner- or edge-bridged oligomeric or polymeric chalcogenidostannates(IV) (Sheldrick & Wachhold, 1997, 1998; Sheldrick, 2000). Ditetrahedral anions  $[Sn_2E_6]^{4-}$  composed of two edge-sharing tetrahedra are particularly common and have been structurally characterized for  $E = Te$  in the salts  $Li_4[Sn_2Te_6] \cdot 8en$  (Dehnen *et al.*, 2002),  $K_4[Sn_2Te_6]$  (Evenson & Dorhout, 2000),  $K_2[K(2,2,2-crypt)]_2[Sn_2Te_6]$  (Campbell *et al.*, 1996),  $K_2[K(2,2,2-crypt)]_2[Sn_2Te_6] \cdot en$  (Fässler & Schütz, 1997),  $(Me_4N)_2[Sn_2Te_6]$  (Huffman *et al.*, 1984),  $(Et_4N)_2[Sn_2Te_6]$  (Ansari *et al.*, 1993),  $[M(en)_3]_2[Sn_2Te_6]$  ( $M = Mn, Zn$ ) (Li *et al.*, 1998),  $[Zn(en)_3]_2[Sn_2Te_6] \cdot en$  (Shreeve-Keyer *et al.*, 1997) and  $(enH)_4Sn_2Te_6 \cdot en$  (Dehnen & Zimmermann, 2002), where 2,2,2-crypt is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane and en is ethylenediamine. Interestingly, the telluridostannates(IV)  $[M(en)_3]_2Sn_2Te_6$  are not isostructural, but crystallize in the space groups  $Pbca$  ( $M = Mn$ ) and  $P2_1/n$  ( $M = Zn$ ). It was argued by the authors (Li *et al.*, 1998) that the packing differences are due to the different cation conformations, with  $\delta\delta\delta/\lambda\lambda\lambda$  being observed for  $M = Mn$  and  $\delta\delta\lambda/\lambda\lambda\delta$  for  $M = Zn$ .



We recently prepared  $[Mn(en)_3]_2[Sn_2Te_6]$ , (I), as a precursor for the construction of quaternary chalcogenidometalates and discovered that the compound crystallizes in a new modification (monoclinic,  $P2_1/n$ ) in the presence of  $Cs_2CO_3$  as a mineralizer. Somewhat surprisingly, this modification is not isostructural with the analogous zinc compound  $[Zn(en)_3]_2[Sn_2Te_6]$ , although both adopt the same monoclinic space group. The cell constants are  $a = 9.048(2)$  Å,  $b =$

22.300 (6) Å,  $c = 9.360$  (3) Å,  $\beta = 103.19$  (2)° and  $V = 1838.7$  (9) Å<sup>3</sup> for the latter telluridostannate(IV). It was, therefore, of interest to determine whether the cation conformation is the same in the Mn compound. The monoclinic modification of (I) contains crystallographically centrosymmetric [Sn<sub>2</sub>Te<sub>6</sub>]<sup>4-</sup> anions, whose more polar terminal Sn—Te distances of 2.6965 (8) and 2.7018 (8) Å are significantly shorter than the bridging Sn—Te distances of 2.8022 (8) and 2.8102 (9) Å. Although slightly longer than the analogous distances in the orthorhombic modification of [Mn(en)<sub>3</sub>]<sub>2</sub>[Sn<sub>2</sub>Te<sub>6</sub>] [terminal (*t*) 2.684 (1) and 2.681 (1) Å; bridging (*b*) 2.782 (1) and 2.780 (1) Å], these values do lie well within the typical ranges previously observed for other [Sn<sub>2</sub>Te<sub>6</sub>]<sup>4-</sup> anions with either alkylammonium or encapsulated alkali metal cations [Sn—Te<sub>t</sub> = 2.664–2.704 Å and Sn—Te<sub>b</sub> = 2.780–2.834 Å]. The Sn—E bond distances in anions [Sn<sub>2</sub>E<sub>6</sub>]<sup>4-</sup> are influenced by either the strength of E··H—N hydrogen bonding to organic counter-cations (Dehnen & Zimmermann, 2002) or the degree of covalency in the E··A interactions to alkali metal counter-cations (Sheldrick & Braunbeck, 1993). In the monoclinic modification of [Mn(en)<sub>3</sub>]<sub>2</sub>[Sn<sub>2</sub>Te<sub>6</sub>], the terminal Te1 and Te3 atoms both participate in six weak Te··H—N hydrogen bridges, each in the distance and angle ranges 3.764 (7)–4.115 (8) Å (Te··N) and 137–173° (Te··H—N). By contrast, the bridging atom Te2 exhibits only two Te··H—N contacts to an en ligand in the above distance range [Te2··N9 = 3.959 (7) Å], whose small angles of only 107° for both H9A and H9B rule out significant hydrogen bonding.

As depicted in Fig. 1, the [Mn(en)<sub>3</sub>]<sup>2+</sup> cation once again exhibits the λλλ/δδδ conformation of the orthorhombic modification. The number, strength and relative orientation of the Te··H—N contacts between the anions and cations must, therefore, be responsible for the adoption of a particular crystal system and not, as suggested by Li *et al.* (1998), the conformation of the complex cation *per se*. A total of ten rather than 12 weak Te··H—N hydrogen bridges in the somewhat wider range 3.688–4.102 Å are observed for the terminal Te atoms in the orthorhombic modification.

## Experimental

Sn (127.0 mg, 1.07 mmol), Te (325.4 mg, 2.55 mmol) and Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (253.6 mg, 1.04 mmol) were heated to 463 K in a 1:1 mixture (1 ml) of CH<sub>3</sub>OH and ethylenediamine in the presence of Cs<sub>2</sub>CO<sub>3</sub> (391.0 mg, 1.2 mmol). After 30 h, the solution was cooled to 293 K at a rate of 2 K h<sup>-1</sup> to afford deep-red crystals of [Mn(en)<sub>3</sub>]<sub>2</sub>[Sn<sub>2</sub>Te<sub>6</sub>], (I) (monoclinic modification) in 75% yield.

### Crystal data

[Mn(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]<sub>2</sub>[Sn<sub>2</sub>Te<sub>6</sub>]  
 $M_r = 1473.44$   
 Monoclinic,  $P2_1/n$   
 $a = 9.1006$  (18) Å  
 $b = 18.019$  (4) Å  
 $c = 12.701$  (3) Å  
 $\beta = 95.23$  (3)°  
 $V = 2074.1$  (7) Å<sup>3</sup>  
 $Z = 2$

$D_x = 2.359$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 20 reflections  
 $\theta = 12.4$ – $32.1$ °  
 $\mu = 5.94$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, dark-red  
 $0.5 \times 0.4 \times 0.3$  mm

### Data collection

Siemens P4 four-circle diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (XPREP in SHELXTL; Sheldrick, 1995)  
 $T_{\min} = 0.067$ ,  $T_{\max} = 0.169$   
 3807 measured reflections  
 3639 independent reflections

3055 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -10 \rightarrow 10$   
 $k = 0 \rightarrow 21$   
 $l = 0 \rightarrow 15$   
 3 standard reflections every 100 reflections  
 intensity decay: 1%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.106$   
 $S = 1.38$   
 3639 reflections  
 154 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.95$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.03$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|                            |             |                                          |           |
|----------------------------|-------------|------------------------------------------|-----------|
| Sn—Te1                     | 2.6965 (8)  | Mn—N8                                    | 2.270 (7) |
| Sn—Te3                     | 2.7018 (8)  | Mn—N1                                    | 2.283 (8) |
| Sn—Te2 <sup>1</sup>        | 2.8022 (8)  | Mn—N5                                    | 2.287 (7) |
| Sn—Te2                     | 2.8102 (9)  | Mn—N4                                    | 2.291 (7) |
| Te2—Sn <sup>1</sup>        | 2.8022 (8)  | Mn—N12                                   | 2.301 (7) |
| Mn—N9                      | 2.266 (7)   |                                          |           |
| Te1—Sn—Te3                 | 111.17 (2)  | N8—Mn—N5                                 | 77.3 (3)  |
| Te1—Sn—Te2 <sup>1</sup>    | 114.38 (3)  | N1—Mn—N5                                 | 168.5 (3) |
| Te3—Sn—Te2 <sup>1</sup>    | 111.04 (3)  | N9—Mn—N4                                 | 164.1 (3) |
| Te1—Sn—Te2                 | 111.36 (3)  | N8—Mn—N4                                 | 96.0 (3)  |
| Te3—Sn—Te2                 | 113.23 (3)  | N1—Mn—N4                                 | 77.1 (3)  |
| Te2 <sup>1</sup> —Sn—Te2   | 94.78 (2)   | N5—Mn—N4                                 | 98.3 (3)  |
| Sn <sup>1</sup> —Te2—Sn    | 85.22 (2)   | N9—Mn—N12                                | 77.0 (2)  |
| N9—Mn—N8                   | 97.5 (3)    | N8—Mn—N12                                | 167.3 (3) |
| N9—Mn—N1                   | 93.7 (3)    | N1—Mn—N12                                | 99.2 (3)  |
| N8—Mn—N1                   | 92.5 (3)    | N5—Mn—N12                                | 91.4 (3)  |
| N9—Mn—N5                   | 93.0 (3)    | N4—Mn—N12                                | 91.5 (3)  |
| Te1—Sn—Te2—Sn <sup>1</sup> | -118.52 (3) | Te2 <sup>1</sup> —Sn—Te2—Sn <sup>1</sup> | 0.0       |
| Te3—Sn—Te2—Sn <sup>1</sup> | 115.34 (3)  |                                          |           |

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

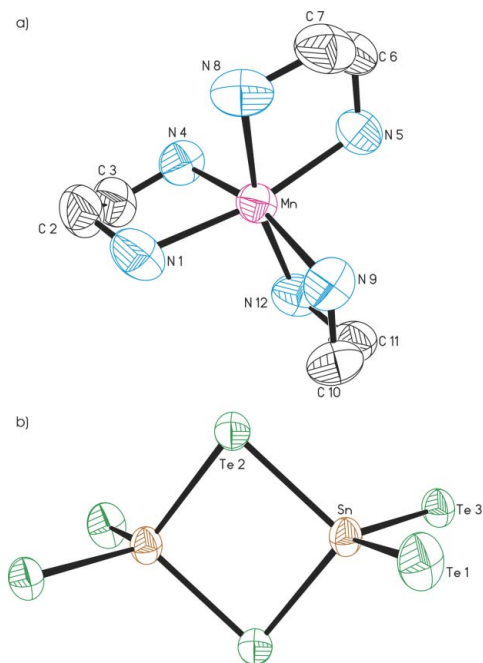
**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------|-------|-------------|-------------|---------------|
| N1—H1A···Te1 <sup>ii</sup>   | 0.90  | 3.34        | 4.039 (8)   | 137           |
| N1—H1B···Te3 <sup>iii</sup>  | 0.90  | 3.31        | 4.115 (8)   | 151           |
| N4—H4A···Te3                 | 0.90  | 3.04        | 3.931 (7)   | 173           |
| N4—H4B···Te1 <sup>iv</sup>   | 0.90  | 3.05        | 3.851 (8)   | 149           |
| N5—H5A···Te1 <sup>v</sup>    | 0.90  | 2.99        | 3.880 (7)   | 173           |
| N5—H5B···Te1 <sup>iv</sup>   | 0.90  | 2.95        | 3.798 (7)   | 157           |
| N8—H8A···Te3                 | 0.90  | 3.19        | 3.994 (8)   | 150           |
| N8—H8B···Te3 <sup>iii</sup>  | 0.90  | 3.05        | 3.895 (7)   | 158           |
| N9—H9A···Te1 <sup>v</sup>    | 0.90  | 3.19        | 4.052 (8)   | 161           |
| N9—H9B···Te3 <sup>iii</sup>  | 0.90  | 3.01        | 3.849 (7)   | 157           |
| N12—H12A···Te3 <sup>ii</sup> | 0.90  | 2.88        | 3.764 (7)   | 166           |
| N12—H12B···Te1 <sup>iv</sup> | 0.90  | 2.99        | 3.816 (7)   | 154           |
| N9—H9A···Te2 <sup>v</sup>    | 0.90  | 3.60        | 3.959 (7)   | 107           |
| N9—H9B···Te2 <sup>v</sup>    | 0.90  | 3.61        | 3.959 (7)   | 107           |

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

All H atoms were refined using a riding model, with C—H = 0.97 Å and N—H = 0.90 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{C})$ . The highest peak in the final difference synthesis is located 1.09 Å from Te3 and the deepest hole 0.91 Å from Te3.

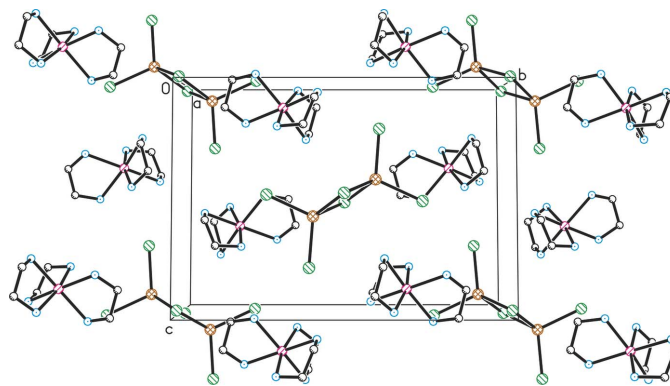


**Figure 1**  
The tris(ethylenediamine)manganese(II) cation and centrosymmetric hexatelluridostannate(IV) anion of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. The symmetry code for the unlabelled atoms is  $(1 - x, -y, -z)$ .

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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**Figure 2**  
The packing of the cations and anions of (I), shown in projection perpendicular to the *bc* plane with the following colouring scheme: Sn orange (cross-hatched), Mn pink (hatched circle), Te green (hatched circle), N blue (dotted circle) and C white (semi-hatched circle). H atoms have been omitted.

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