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## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
 $R$  factor = 0.032  
 $wR$  factor = 0.092  
Data-to-parameter ratio = 30.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis[tris(1,3-diaminopropane)manganese(II)]  
octasulfidotetraantimonate(III) dihydrate

Yellow crystals of  $[\text{Mn}(\text{pn})_3]_2[\text{Sb}_4\text{S}_8] \cdot 2\text{H}_2\text{O}$  (pn = 1,2-diaminopropane) were synthesized under solvothermal conditions by reacting elemental Mn, Sb and S in an aqueous solution of 1,2-diaminopropane. The structure is composed of cyclic  $[\text{Sb}_4\text{S}_8]^{4-}$  anions and octahedral  $[\text{Mn}(\text{pn})_3]^{2+}$  cations, both stacked in a rod-like manner along the  $a$  axis. The anion sits on a centre of symmetry. Between the anions and the cations there is an extended hydrogen-bonding network.

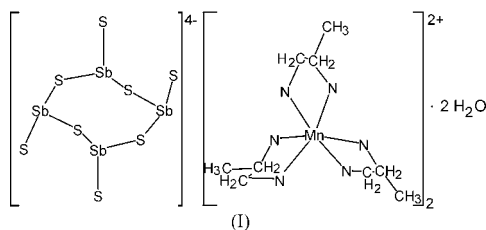
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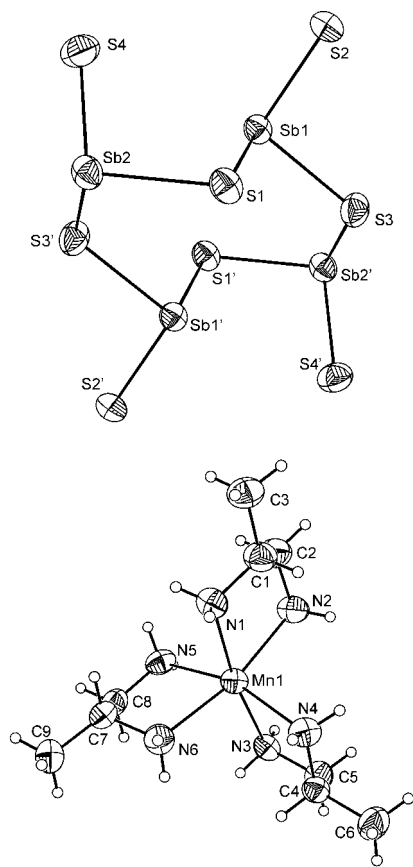
Online 31 May 2003

## Comment

During the last few years, a large number of thioantimonates(III) have been reported demonstrating the rich structural diversity of this class of compounds. In these structures, the primary  $\text{SbS}_3$  trigonal pyramids are often connected, forming so-called secondary building units (SBU), such as  $\text{Sb}_2\text{S}_2$ ,  $\text{Sb}_3\text{S}_3$ ,  $\text{Sb}_4\text{S}_4$  hetero-rings or the  $\text{Sb}_3\text{S}_4$  semicube. Until now only a few thioantimonates(III) have been reported containing isolated  $\text{SbS}$  anions. The isolated  $[\text{SbS}_3]^{3-}$  anion is found in  $M_3\text{SbS}_3$  ( $M = \text{Ag}, \text{Cu}, \text{Tl}$ ; Wattenberg & Hellner, 1966; Pfitzner, 1994; Rey *et al.*, 1984). Using a cut-off for the  $\text{Sb}-\text{S}$  distance of 3 Å, isolated  $\text{SbS}_3$  and  $\text{Sb}_2\text{S}_4$  units co-exist in  $\text{Ca}_2\text{Sb}_2\text{S}_5$  (Cordier & Schäfer, 1981). In  $\text{Ba}_8\text{Sb}_6\text{S}_{17}$  and in  $\text{BaSb}_2\text{S}_4$ , chain-like  $\text{Sb}_3\text{S}_8$  anions and isolated  $\text{SbS}_3$  pyramids were observed (Dörrscheidt & Schäfer, 1981; Cordier *et al.*, 1984). The isolated  $\text{Sb}_2\text{S}_5^{4-}$  anion is found in  $\text{Sr}_2\text{Sb}_2\text{S}_5 \cdot 15\text{H}_2\text{O}$  (Cordier *et al.*, 1985). It should be noted that, besides these isolated anions, only one compound with an isolated ring anion has been reported so far (Bensch *et al.*, 2001).

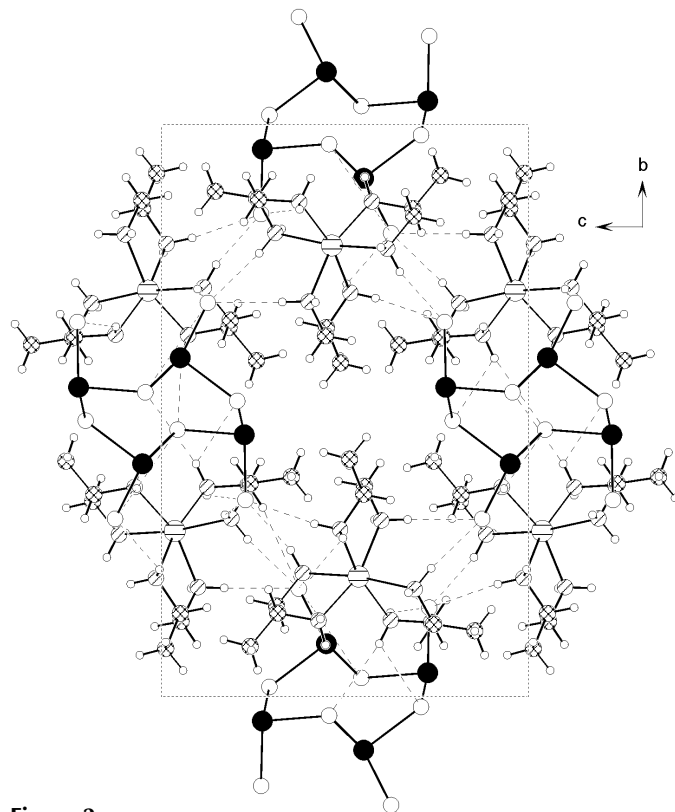


In the anion of the title compound, (I), four pyramidal  $\text{SbS}_3$  units, sharing corners, form an  $\text{Sb}_4\text{S}_4$  hetero-ring that adopts a chair conformation. The anion sits on a centre of symmetry. Each Sb atom has a terminal S atom to form the  $[\text{Sb}_4\text{S}_8]^{4-}$  ring anion (Fig. 1). The bridging  $\text{Sb}-\text{S}$  distances are between 2.4598 (10) and 2.4919 (10) Å (Table 1). As expected, the terminal  $\text{Sb}-\text{S}$  bonds ( $\text{Sb1}-\text{S2}$  and  $\text{Sb2}-\text{S4}$ ) are significantly shorter, with values of 2.3322 (11) and 2.3442 (10) Å. The  $\text{S}-\text{Sb}-\text{S}$  angles vary between 92.33 (4) and 104.37 (3)°. The terminal  $\text{Sb}-\text{S}$  distances in the recently reported compound  $[\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2]_2\text{Sb}_4\text{S}_8$  (Bensch *et al.*, 2001) are between 2.315 (3) and 2.337 (2) Å, and the bond lengths within the

**Figure 1**

The cation (top) and the anion (bottom) in the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (')  $1 - x, -y, 1 - z$ .]

$\text{Sb}_4\text{S}_4$  ring range from 2.426 (2) to 2.497 (2) Å. The S—Sb—S angles cover a larger range than in the title compound [87.92 (7)–107.53 (8)°]. The differences in the geometrical parameters in the two compounds demonstrate the considerable flexibility of the Sb—S bonds and S—Sb—S angles to accommodate an optimal arrangement of cations and anions in the structure. The  $\text{Mn}^{2+}$  cation is in an octahedral environment of six N atoms of three bidentate amine ligands (Fig. 1). The Mn—N distances are between 2.258 (3) and 2.322 (3) Å (Table 1) and are in accordance with literature data (Laskowski & Hendrickson, 1978; Wendland *et al.*, 2000). The *cis*-N—Mn—N angles vary from 76.37 (11) to 99.05 (12)° and the *trans* angles from 161.64 (12) to 171.97 (12)°, indicative of a relatively strongly distorted octahedral environment. The three-dimensional interconnection of anions and cations is achieved by ten N—H...S interactions. Only three of the four unique S atoms are involved, and the N—H...S distances range between 2.62 and 3.03 Å, with corresponding angles ranging from 136 to 172° (Table 2). We note that in  $[\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2]_2[\text{Sb}_4\text{S}_8]$  the H...S contacts are significantly shorter (2.513–2.837 Å), which may have an influence on the geometrical parameters of the anions, as mentioned above. The water molecule acts as a hydrogen-bond donor and acceptor. Two short contacts are observed to S2 and S4 and one from N5 (Table 2). Cations and anions form separate

**Figure 2**

The crystal structure of the title compound, viewed along the crystallographic *a* axis. O atoms have been omitted and hydrogen bonding is shown as dashed lines.

stacks parallel to the *a* and *c* axes. A view of the arrangement of the cations and anions, viewed along [100], is displayed in Fig. 2. The water molecule is situated between the cations.

## Experimental

The title compound was prepared by solvothermal synthesis from elemental Mn (54.94 mg, 1 mmol), Sb (121.75 mg, 1 mmol) and S (80.15 mg, 2.5 mmol) in a 70% aqueous solution of 1,2-diaminopropane (5 ml). The mixture was heated for 7 d in a Teflon-lined steel autoclave at 383 K. The yield was about 60% based on Mn, after washing with water and acetone.

### Crystal data

$[\text{Mn}(\text{C}_3\text{H}_{10}\text{N}_2)_3]_2[\text{Sb}_4\text{S}_8] \cdot 2\text{H}_2\text{O}$   
 $M_r = 1334.17$   
 Monoclinic,  $P2_1/n$   
 $a = 9.4773$  (19) Å  
 $b = 19.579$  (4) Å  
 $c = 12.592$  (3) Å  
 $\beta = 91.56$  (3)°  
 $V = 2335.6$  (8) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.897$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 126 reflections  
 $\theta = 12$ –19°  
 $\mu = 3.20$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Polyhedron, yellow  
 0.22 × 0.19 × 0.16 mm

### Data collection

Philips PW1100 diffractometer  
 $\omega$  scans  
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)  
 $T_{\min} = 0.495$ ,  $T_{\max} = 0.641$   
 7248 measured reflections  
 6515 independent reflections  
 5895 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = 0 \rightarrow 12$   
 $k = -27 \rightarrow 1$   
 $l = -17 \rightarrow 17$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.092$   
 $S = 1.18$   
 6518 reflections  
 214 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 2.9874P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 1.69 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.06 \text{ e } \text{\AA}^{-3}$

**Table 1**  
 Selected geometric parameters (Å).

Sb1—S2	2.3442 (10)	Mn1—N2	2.258 (3)
Sb1—S3	2.4598 (10)	Mn1—N4	2.262 (3)
Sb1—S1	2.4919 (10)	Mn1—N6	2.279 (3)
Sb2—S4	2.3322 (11)	Mn1—N5	2.279 (3)
Sb2—S3 <sup>i</sup>	2.4593 (10)	Mn1—N3	2.312 (3)
Sb2—S1	2.4602 (11)	Mn1—N1	2.322 (3)
S3—Sb2 <sup>i</sup>	2.4593 (10)		

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

**Table 2**  
 Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2B··S4	0.90	2.70	3.487 (4)	147
N1—H1A··S2 <sup>ii</sup>	0.90	2.88	3.692 (4)	150
N1—H1B··S4 <sup>iii</sup>	0.90	3.03	3.853 (4)	153
N2—H2A··S1 <sup>i</sup>	0.90	3.02	3.906 (4)	168
N3—H3A··S4 <sup>iv</sup>	0.90	2.62	3.464 (3)	157
N4—H4B··S2 <sup>iii</sup>	0.90	2.67	3.484 (4)	152
N4—H4B··S1 <sup>iii</sup>	0.90	2.90	3.454 (3)	121
N5—H5A··S2 <sup>ii</sup>	0.90	2.61	3.506 (3)	172
N5—H5B··O1	0.90	2.33	3.188 (8)	160
N6—H6A··S4 <sup>iv</sup>	0.90	2.81	3.662 (4)	159
N6—H6B··S2 <sup>iii</sup>	0.90	2.97	3.674 (4)	136
O1—H1O··S2	0.848 (10)	2.43 (5)	3.211 (5)	154 (9)
O1—H2O··S4	0.849 (10)	2.48 (7)	3.199 (5)	143 (10)

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

The positions of the H atoms were located in difference maps. H atoms bound to C atoms were positioned with idealized geometry and

refined with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ], using a riding model with C—H(tertiary) = 0.98 Å, C—H(secondary) = 0.97 Å and C—H(primary) = 0.96 Å. The positions of the H atoms of the NH<sub>2</sub> groups were idealized, with N—H distances of 0.90 Å, then refined as rigid groups allowed to rotate but not tip. These H atoms were refined using fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ ]. The H atoms of H<sub>2</sub>O were refined with restraints, setting the distances for O—H to 0.84 (1) Å and for H··H to 1.40 (1) Å. The isotropic displacement parameters were fixed [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ ].

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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