

[Tris(2-aminoethyl)amine]manganese(II) heptasulfidotetraantimony(III) hemihydrate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

H-atom completeness 97%

Disorder in solvent or counterion

R factor = 0.028

wR factor = 0.083

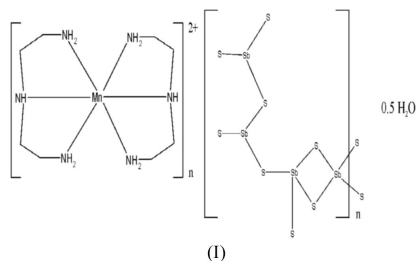
Data-to-parameter ratio = 26.6

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

Yellow crystals of the title compound, $[\text{Mn}(\text{dien})_2][\text{Sb}_4\text{S}_7] \cdot 0.5\text{H}_2\text{O}$ (dien = diethylenetriamine = $\text{C}_4\text{H}_{13}\text{N}_3$) were synthesized under solvothermal conditions by reacting MnSb_2S_4 with pure dien. The Mn^{2+} ion is in an octahedral environment of six N atoms of the tridentate dien molecules. The $[\text{Sb}_4\text{S}_7]^{2-}$ units, and anions are joined together to form two-dimensional layers. In the layered anion, Sb_2S_2 , Sb_4S_4 and Sb_8S_8 heterorings are found.

Comment

Until now, more than a dozen thioantimonates(III) with the $[\text{Sb}_4\text{S}_7]^{2-}$ anion with different dimensionalities have been reported (Sheldrick & Häusler, 1988; Dittmar & Schäfer, 1978*a,b*; Cordier *et al.*, 1984; Dittmar & Schäfer, 1977; Bensch & Schur, 1997; Stephan & Kanatzidis, 1997). For example, in $\text{K}_2\text{Sb}_4\text{S}_7$ (Graf & Schäfer, 1972), a three-dimensional network is observed. Incorporation of water yields a layered $[\text{Sb}_4\text{S}_7]^{2-}$ anion (Eisenmann & Schäfer, 1979). To the best of our knowledge, most of the $[\text{Sb}_4\text{S}_7]^{2-}$ compounds were prepared by reacting elements under solvothermal conditions or in a reactive flux. During our systematic search for new materials which are suitable as educts for solvothermal reactions, we synthesized the layered compound $[\text{Mn}(\text{dien})_2] \cdot \text{Sb}_4\text{S}_7 \cdot 0.5\text{H}_2\text{O}$, (I), applying the ternary compound MnSb_2S_4 and dien as the solvent.



The structure of (I) is composed of isolated $[\text{Mn}(\text{dien})_2]^{2+}$ cations and layered $[\text{Sb}_4\text{S}_7]^{2-}$ anions (Fig. 1). The Mn^{2+} ion is surrounded by six N atoms of two dien ligands forming a distorted octahedron (MnN_6), which adopts the *mer* configuration. The $\text{Mn}-\text{N}$ distances range from 2.241 (4) to 2.326 (4) Å, with $\text{N}-\text{Mn}-\text{N}$ angles between 75.2 (1) and 176.2 (1)°. All values are in the normal ranges for MnN_6 octahedra (von Zelewsky, 1996; Ellermeier & Bensch, 2002; Schaefer *et al.*, 2003). In the anionic part of the structure, two SbS_3 trigonal pyramids and two SbS_4 units are the primary building units. Both SbS_3 moieties share a common corner, forming an Sb_2S_5 unit. The $\text{Sb}-\text{S}$ bond lengths vary between 2.388 (1) and 2.479 (1) Å, with $\text{S}-\text{Sb}-\text{S}$ angles between 90.01 (3) and 104.79 (4)°. The two SbS_4 units share a common

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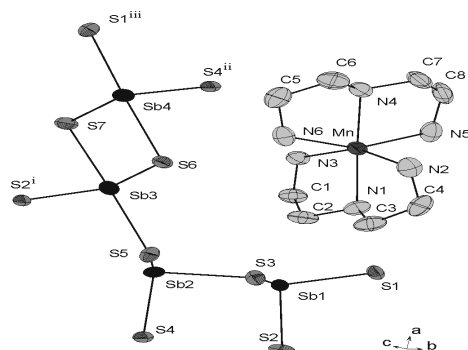


Figure 1
The asymmetric unit of $[\text{Mn}(\text{dien})_2]\text{Sb}_4\text{S}_7 \cdot 0.5\text{H}_2\text{O}$, together with some symmetry-equivalent S atoms to complete the coordination of Sb. Displacement ellipsoids are drawn at the 50% probability level. The symmetry codes are given in Table 1. H atoms have been omitted.

edge, forming an Sb_2S_2 hetero-ring within a Sb_2S_6 unit. In both SbS_4 units, two longer distances are found [2.692 (1) and 2.832 (1) Å for Sb3, and 2.728 (1) and 2.746 (1) Å for Sb4]. The longer separations are in *trans*-position to each other, with angles of 171.92 (3)° for S5–Sb3–S7 and 174.53 (3)° for S6–Sb4–S1ⁱⁱⁱ (see Table 1). Angles and distances are comparable with those reported in the literature (Sheldrick & Häusler, 1988; Dittmar & Schäfer, 1978*a,b*; Cordier *et al.*, 1984; Schur & Bensch, 1997). The secondary building blocks Sb_2S_5 and Sb_2S_6 share a common corner (S5) and further condensation leads to Sb_4S_4 and Sb_8S_8 rings. The eight-membered rings are fused to each other parallel to the *a* and *b* axis (Fig. 2). The *mer*- $[\text{Mn}(\text{dien})_2]^{2+}$ cations and the water molecules are found above and below the Sb_8S_8 hetero-rings. The coordination numbers of the Sb1 and Sb2 atoms are enhanced from three to four by S atoms at longer distances of 3.118 (1) and 3.264 (1) Å, respectively. We note that (I) is isostructural with $[\text{Ni}(\text{dien})_2]\text{Sb}_4\text{S}_7 \cdot \text{H}_2\text{O}$ (Stähler *et al.*, 2003). The unit-cell volume of the latter compound is 40 Å³ smaller than that of the title compound.

Experimental

$[\text{Mn}(\text{dien})_2]\text{Sb}_4\text{S}_7 \cdot 0.5\text{H}_2\text{O}$ was obtained in nearly 30% yield by the reaction of MnSb_2S_4 (Pfitzner & Kurowski, 2000) (0.100 g, 0.234 mmol) in a pure solution of 3 ml dien (99%) (Merck). The mixture was heated in Teflon-lined steel autoclaves with an inner volume of 30 ml for 14 d at 403 K and then cooled to room temperature within 3 h. After washing with water, dried under vacuum, yellow crystals of $[\text{Mn}(\text{dien})_2]\text{Sb}_4\text{S}_7 \cdot 0.5\text{H}_2\text{O}$ were obtained. The compound is stable in air and water. Analysis calculated for $[\text{Mn}(\text{dien})_2]\text{Sb}_4\text{S}_7 \cdot 0.5\text{H}_2\text{O}$: C 9.78, H 2.87, N 8.55, S 22.84%; found: C 9.59, H 2.61, N 8.75, S 22.15%.

Crystal data

$[\text{Mn}(\text{C}_6\text{H}_{13}\text{N}_3)_2][\text{Sb}_4\text{S}_7] \cdot 0.5\text{H}_2\text{O}$
 $M_r = 980.71$
 Monoclinic, $P2_1/c$
 $a = 9.7216$ (19) Å
 $b = 16.113$ (3) Å
 $c = 17.339$ (4) Å
 $\beta = 91.88$ (3)°
 $V = 2714.6$ (9) Å³
 $Z = 4$

$D_x = 2.400$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8000 reflections
 $\theta = 2.5$ – 28°
 $\mu = 4.93$ mm⁻¹
 $T = 293$ (2) K
 Polyhedron, yellow
 $0.2 \times 0.2 \times 0.1$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: numerical
 [*X-SHAPE* (Stoe & Cie, 1998)
 and *X-RED* (Stoe & Cie, 1998)]
 $T_{\min} = 0.390$, $T_{\max} = 0.609$
 31130 measured reflections

6508 independent reflections
 5824 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\max} = 28.0^\circ$
 $h = -12 \rightarrow 12$
 $k = -21 \rightarrow 21$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.083$
 $S = 1.05$
 6508 reflections
 245 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 3.6221P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.25$ e Å⁻³
 $\Delta\rho_{\min} = -1.12$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00169 (13)

Table 1

Selected geometric parameters (Å, °).

Mn–N4	2.241 (4)	Sb3–S6	2.3893 (12)
Mn–N2	2.256 (4)	Sb3–S2 ⁱ	2.4451 (11)
Mn–N5	2.259 (4)	Sb3–S7	2.6917 (13)
Mn–N1	2.270 (4)	Sb3–S5	2.8322 (13)
Mn–N3	2.320 (4)	Sb4–S7	2.3907 (13)
Mn–N6	2.326 (4)	Sb4–S4 ⁱⁱ	2.4495 (11)
Sb1–S1	2.4076 (10)	Sb4–S1 ⁱⁱⁱ	2.7279 (13)
Sb1–S2	2.4539 (11)	Sb4–S6	2.7459 (13)
Sb1–S3	2.4790 (10)	S1–Sb4 ^{iv}	2.7279 (13)
Sb2–S5	2.3883 (10)	S2–Sb3 ^v	2.4451 (11)
Sb2–S4	2.4682 (11)	S4–Sb4 ^{vi}	2.4495 (11)
Sb2–S3	2.4701 (10)		
N4–Mn–N2	107.09 (13)	S1–Sb1–S2	99.30 (4)
N4–Mn–N5	77.15 (16)	S1–Sb1–S3	92.19 (4)
N2–Mn–N5	98.22 (16)	S2–Sb1–S3	92.35 (4)
N4–Mn–N1	176.26 (13)	S5–Sb2–S4	104.82 (4)
N2–Mn–N1	76.64 (13)	S5–Sb2–S3	92.03 (4)
N5–Mn–N1	102.89 (16)	S4–Sb2–S3	91.09 (4)
N4–Mn–N3	100.00 (15)	S6–Sb3–S7	87.18 (4)
N2–Mn–N3	152.13 (15)	S6–Sb3–S5	87.83 (4)
N5–Mn–N3	93.99 (16)	S7–Sb3–S5	171.94 (3)
N1–Mn–N3	76.26 (15)	S7–Sb4–S6	85.92 (4)
N4–Mn–N6	75.19 (15)	Sb2–S3–Sb1	102.56 (4)
N2–Mn–N6	90.53 (14)	Sb2–S5–Sb3	88.68 (3)
N5–Mn–N6	152.33 (17)	Sb3–S6–Sb4	92.68 (4)
N1–Mn–N6	104.66 (15)	Sb4–S7–Sb3	94.02 (4)
N3–Mn–N6	90.12 (15)		

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

The H atoms were positioned with idealized geometry [C–H(methylene) = 0.97 Å and N–H(amine) = 0.90 Å] and refined with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}\text{C}_{\text{methylene}}$ and $C(\text{amine}) = 1.2U_{\text{eq}}\text{N}(\text{amine})$] using a riding model.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

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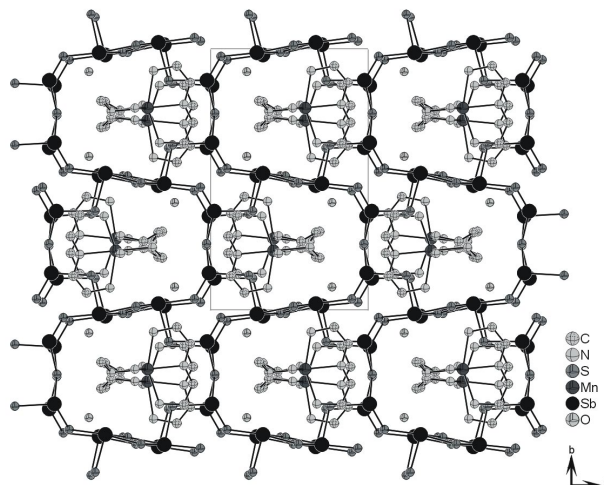


Figure 2

Arrangement of the cations and anions in $[\text{Mn}(\text{dien})_2]\text{Sb}_4\text{S}_7 \cdot 0.5\text{H}_2\text{O}$, viewed along $[001]$. The cations are located above and below the Sb_4S_8 rings. The H atoms of the dien ligands have been omitted for clarity.