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

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.008 Å
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.

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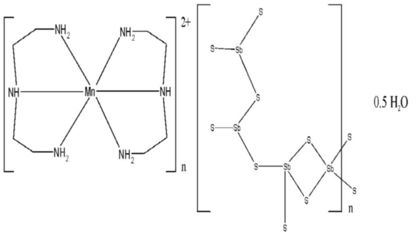
Yellow crystals of the title compound, $[Mn(dien)_2][Sb_4S_7]\cdot 0.5H_2O$ (dien = diethylenetriamine = $C_4H_{13}N_3$) were synthesized under solvothermal conditions by reacting $MnSb_2S_4$ with pure dien. The $Mn^{2+}$ ion is in an octahedral environment of six N atoms of the tridentate dien molecules. The $[Sb_4S_7]^{2-}$ 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 $[Sb_4S_7]^{2-}$ 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 $K_2Sb_4S_7$ (Graf & Schäfer, 1972), a three-dimensional network is observed. Incorporation of water yields a layered $[Sb_4S_7]^{2-}$ anion (Eisenmann & Schäfer, 1979). To the best of our knowledge, most of the $[Sb_4S_7]^{2-}$ 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 $[Mn(dien)_2]Sb_4S_7\cdot 0.5H_2O$, (I), applying the ternary compound $MnSb_2S_4$ and dien as the solvent.



(I)

The structure of (I) is composed of isolated $[Mn(dien)_2]^{2+}$ cations and layered $[Sb_4S_7]^{2-}$ 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 Mn—N distances range from 2.241 (4) to 2.326 (4) Å, with N—Mn—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 Sb—S bond lengths vary between 2.388 (1) and 2.479 (1) Å, with S—Sb—S angles between 90.01 (3) and 104.79 (4)°. The two $SbS_4$ units share a common

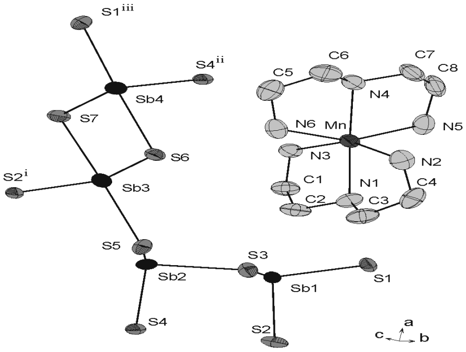


**Figure 1**
The asymmetric unit of $[Mn(dien)_2]Sb_4S_7\cdot 0.5H_2O$, together with some symmetry-equivalent S atoms to complete the coordination of Sb. Displacement ellipsoids are drawn at the 50% probability level. The symmetry codes are given in Table 1. H atoms have been omitted.

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—S1$^{iii}$ (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*-$[Mn(dien)_2]^{2+}$ 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 $[Ni(dien)_2]Sb_4S_7\cdot H_2O$ (Stähler *et al.*, 2003). The unit-cell volume of the latter compound is 40 Å$^3$ smaller than that of the title compound.

## Experimental

$[Mn(dien)_2]Sb_4S_7\cdot 0.5H_2O$ 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 $[Mn(dien)_2]Sb_4S_7\cdot 0.5H_20$ were obtained. The compound is stable in air and water. Analysis calculated for $[Mn(dien)_2]Sb_4S_7.0.5H_20$: 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*

$[Mn(C_4H_{13}N_3)_2][Sb_4S_7]\cdot 0.5H_2$
$M_r = 980.71$
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) Å$^3$
$Z = 4$

$D_x = 2.400$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 8000 reflections
$\theta = 2.5$–28°
$\mu = 4.93$ mm$^{-1}$
$T = 293$ (2) K
Polyhedron, yellow
0.2 × 0.2 × 0.1 mm

*Data collection*

Stoe IPDS diffractometer
$\varphi$ 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 $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 28.0°$
$h = -12 \rightarrow 12$
$k = -21 \rightarrow 21$
$l = -22 \rightarrow 22$

*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: *SHELXL*97
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 [$U_{iso}(H) = 1.2U_{eq}C_{methylene}$ and C(amine) = $1.2U_{eq}N$(amine)] using a riding model.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

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**m184** Michael Schaefer *et al.* • $[Mn(C_4H_{13}N_3)_2][Sb_4S_7]\cdot 0.5H_20$ *Acta Cryst.* (2004). E**60**, m183–m185

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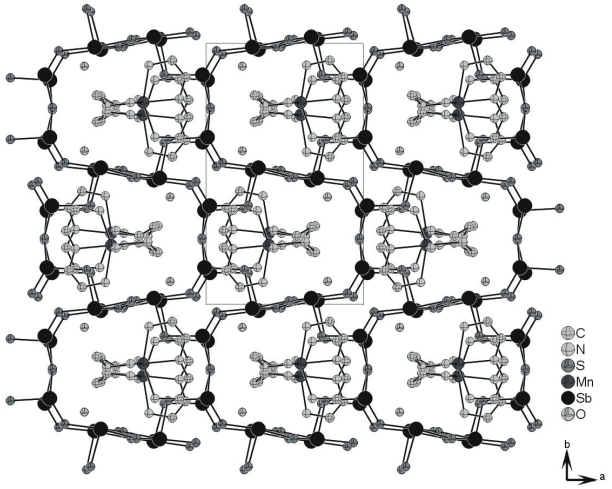

**Figure 2**

Arrangement of the cations and anions in [Mn(dien)$_2$]Sb$_4$S$_7$·0.5H$_2$O, viewed along [001]. The cations are located above and below the Sb$_8$S$_8$ rings. The H atoms of the dien ligands have been omitted for clarity.

*Acta Cryst.* (2004). E**60**, m183–m185 Michael Schaefer *et al.* • [Mn(C$_4$H$_{13}$N$_3$)$_2$][Sb$_4$S$_7$]·0.5H$_2$0 **m185**

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

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In the paper by Schaefer, Kurowski, Pfitzer, Näther & Bensch [*Acta Cryst.* (2004), E**60**, m183–m185], the chemical name in the title is incorrect. The title should be '(Diethylenetriamine)manganese(II) heptasulfidotetraantimony(III) hemihydrate'.

**e12** Michael Schaefer *et al.* • $[Mn(C_4H_{13}N_3)_2][Sb_4S_7]\cdot0.5H_20$

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