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Key indicators

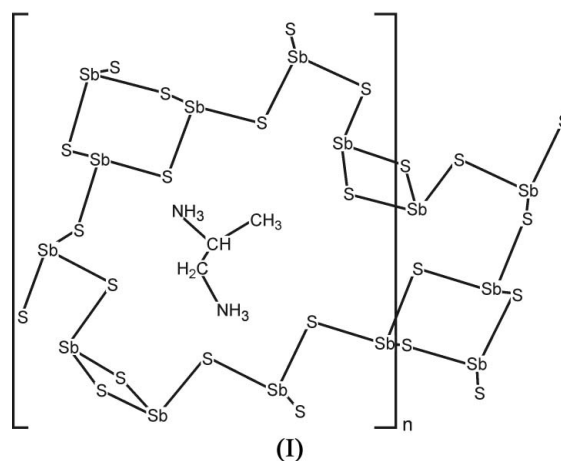
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$
 R factor = 0.024
 wR factor = 0.056
Data-to-parameter ratio = 25.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2-Ammoniopropylammonium dodeca- μ -sulfido-
tetrasulfidodecaantimony

In the structure of the title compound, $(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Sb}_{10}\text{S}_{16}]$, the SbS_3 pyramids are interconnected to form a one-dimensional $[\text{Sb}_6\text{S}_{10}]^{2-}$ chain anion which contains 24-membered $\text{Sb}_{12}\text{S}_{12}$ rings that are interconnected. The structure-directing cations are located above and below this ring. Accepting $\text{Sb}-\text{S}$ distances up to 3.2 \AA , a three-dimensional thioantimonate(III) network results.

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Comment

The number of known thioantimonates(III) with organic cations acting as structure directors has significantly increased during the past few years. One interesting aspect of thioantimonate(III) structures is the fact that for a given $\text{Sb}:\text{S}$ ratio different structures with differing dimensionality are observed. One example is the $\text{Sb}:\text{S}$ ratio of 1:1.667 for which $[\text{Sb}_3\text{S}_5]^-$ (Parise, 1991; Volk & Schäfer, 1979; Parise & Ko, 1992; Gostojic *et al.*, 1982; Engelke *et al.*, 2002), $[\text{Sb}_6\text{S}_{10}]^{2-}$ (Rijnberk *et al.*, 2000; Stähler *et al.*, 2001; Spetzler *et al.*, 2004), $[\text{Sb}_9\text{S}_{15}]^{3-}$ (Spetzler *et al.*, 2004) and $[\text{Sb}_{12}\text{S}_{20}]^{4-}$ (Wang *et al.*, 1998) anions have been reported. The dimensionality of thioantimonates(III) with organic structure directors ranges from one-dimensional chains to three-dimensional networks. The trend shows that the dimensionality decreases with the size of the organic molecules but a strict relationship cannot be deduced. In our ongoing work in the field of solvothermal syntheses of thioantimonate(III) network compounds we prepared another member of the series of compounds with an $\text{Sb}:\text{S}$ ratio of 1:1.667 applying 1,2-diaminopropane as structure director.



The structure of the title compound, (I), is constructed by interconnection of ten unique SbS_3 trigonal pyramids. $\text{Sb1}-\text{Sb3S3}$ and $\text{Sb8}-\text{Sb10S3}$ are joined to form the well known

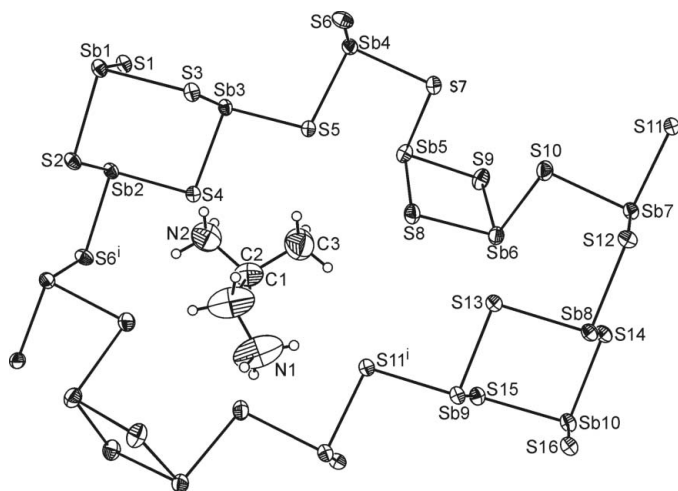


Figure 1

The structure of the title compound, with atom labeling and with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.]

Sb_3S_4 semicube. Sb_5S_3 and Sb_6S_3 share a common edge yielding an Sb_2S_4 group. The semicubes and the Sb_2S_4 group are interconnected by Sb_4S_3 and Sb_7S_3 pyramids to form an $\text{Sb}_{10}\text{S}_{16}$ unit (Fig. 1). These large units are condensed into a chain anion which is directed along [101]. A remarkable feature of the anion is a 24-membered $\text{Sb}_{12}\text{S}_{12}$ ring (Figs. 1 and 2). The Sb—S bonds are in the range observed for other thioantimonates(III). The charge-compensating organic structure directors are located above and below the large rings (Figs. 2 and 3). Relatively short $\text{N} \cdots \text{S}$ separations indicate weak hydrogen-bonding interactions. The shortest interchain $\text{Sb} \cdots \text{S}$ distance is below 3 Å and, treating such $\text{Sb} \cdots \text{S}$ contacts as secondary bonds, a layered anion is formed. Three-dimensional interconnection is achieved by expanding bonding $\text{Sb} \cdots \text{S}$ separations to about 3.2 Å, a distance which is markedly shorter than the sum of the van der Waals radii (3.8 Å). We note that the thioantimonate(III) network topology is closely related to that of $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3][\text{Sb}_{10}\text{S}_{16}]$ (Wang *et al.*, 1998).

Experimental

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Sb}_{10}\text{S}_{16}]$ was synthesized under solvothermal conditions from a mixture of elemental antimony (1 mmol), sulfur (3 mmol) and 10% aqueous 1,2-diaminopropane solution in a Teflon-lined steel autoclave. The mixture was heated for 6 d at 433 K. The title compound crystallized as dark-red crystals in 40% yield based on antimony. The product was washed with water and ethanol.

Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Sb}_{10}\text{S}_{16}]$
 $M_r = 1806.61$
 Monoclinic, $P2_1/n$
 $a = 17.480$ (3) Å
 $b = 10.922$ (2) Å
 $c = 18.030$ (3) Å
 $\beta = 111.415$ (10)°
 $V = 3204.5$ (10) Å³
 $Z = 4$

$D_x = 3.745$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 92 reflections
 $\theta = 11$ –20°
 $\mu = 9.34$ mm⁻¹
 $T = 293$ (2) K
 Block, red
 0.2 × 0.1 × 0.1 mm

Data collection

Stoe AED-II four-circle diffractometer
 ω - θ scans
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
 $T_{\min} = 0.345, T_{\max} = 0.401$
 11455 measured reflections
 6992 independent reflections
 5739 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 27.0^\circ$
 $h = 0 \rightarrow 22$
 $k = -13 \rightarrow 6$
 $l = -23 \rightarrow 21$
 4 standard reflections every 120 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.056$
 $S = 1.03$
 6992 reflections
 280 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 5.0622P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.92 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.80 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Sb1—S1	2.4099 (12)	Sb6—S10	2.4753 (13)
Sb1—S3	2.5604 (12)	Sb6—S8	2.5113 (13)
Sb1—S2	2.5777 (12)	Sb7—S12	2.4392 (13)
Sb2—S2	2.4477 (12)	Sb7—S11	2.4727 (12)
Sb2—S4	2.5408 (12)	Sb7—S10	2.4983 (13)
Sb2—S6 ⁱ	2.5475 (12)	Sb8—S14	2.4368 (12)
Sb3—S3	2.4551 (12)	Sb8—S13	2.5353 (12)
Sb3—S5	2.5082 (12)	Sb8—S12	2.5397 (12)
Sb3—S4	2.5490 (12)	Sb9—S15	2.4669 (13)
Sb4—S6	2.4451 (13)	Sb9—S11 ⁱ	2.5288 (12)
Sb4—S7	2.5055 (13)	Sb9—S13	2.5472 (12)
Sb4—S5	2.5115 (12)	Sb10—S16	2.4070 (13)
Sb5—S8	2.4561 (13)	Sb10—S15	2.5317 (12)
Sb5—S9	2.4583 (13)	Sb10—S14	2.6014 (12)
Sb5—S7	2.5340 (13)	S6—Sb2 ⁱⁱ	2.5475 (12)
Sb6—S9	2.4747 (14)	S11—Sb9 ⁱⁱ	2.5288 (12)
S1—Sb1—S3	92.29 (4)	S9—Sb6—S10	89.95 (5)
S1—Sb1—S2	90.73 (4)	S9—Sb6—S8	87.72 (4)
S3—Sb1—S2	94.07 (4)	S10—Sb6—S8	97.01 (4)
S2—Sb2—S4	91.28 (4)	S12—Sb7—S11	94.18 (4)
S2—Sb2—S6 ⁱ	92.40 (4)	S12—Sb7—S10	94.30 (4)
S4—Sb2—S6 ⁱ	93.04 (4)	S11—Sb7—S10	89.48 (4)
S3—Sb3—S5	89.41 (4)	S14—Sb8—S13	93.03 (4)
S3—Sb3—S4	91.37 (4)	S14—Sb8—S12	95.60 (4)
S5—Sb3—S4	95.80 (4)	S13—Sb8—S12	95.68 (4)
S6—Sb4—S7	95.06 (4)	S15—Sb9—S11 ⁱ	89.67 (4)
S6—Sb4—S5	91.59 (4)	S15—Sb9—S13	90.36 (4)
S7—Sb4—S5	91.11 (4)	S11 ⁱ —Sb9—S13	95.83 (4)
S8—Sb5—S9	89.34 (4)	S16—Sb10—S15	92.12 (4)
S8—Sb5—S7	89.91 (5)	S16—Sb10—S14	90.89 (4)
S9—Sb5—S7	99.13 (4)	S15—Sb10—S14	95.24 (4)

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

Table 2

Hydrogen-bond geometry (Å, °).

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
N1—H1C \cdots S7 ⁱⁱⁱ	0.89	2.53	3.341 (7)	151
N1—H1C \cdots S10 ⁱⁱⁱ	0.89	3.37	3.905 (8)	121
N2—H2A \cdots S7 ⁱ	0.89	2.53	3.309 (5)	147
N2—H2B \cdots S4	0.89	2.52	3.340 (6)	153
N2—H2C \cdots S13 ⁱⁱⁱ	0.89	2.48	3.343 (6)	163

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

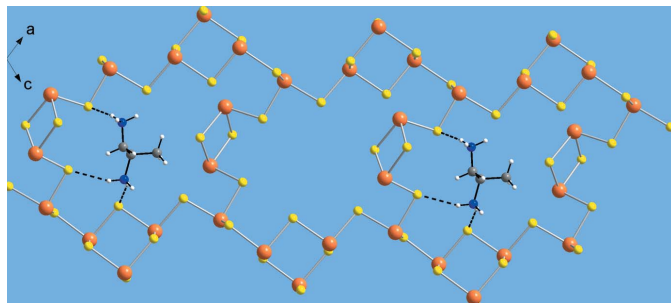


Figure 2
Part of the crystal structure of the title compound, showing the connection of the SbS rings (hydrogen bonding is shown as dashed lines).

All H atoms were positioned with idealized geometry and were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C},\text{N})$ for methyl and ammonium H atoms and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine and methylene H atoms using a riding model, with $\text{C},\text{N}-\text{H} = 0.96 \text{ \AA}$ for methyl, 0.89 \AA for ammonium, 0.98 \AA for methine and 0.97 \AA for methylene H atoms.

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: *SHELXTL* (Bruker, 1998) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: CIFTAB in *SHELXL97*.

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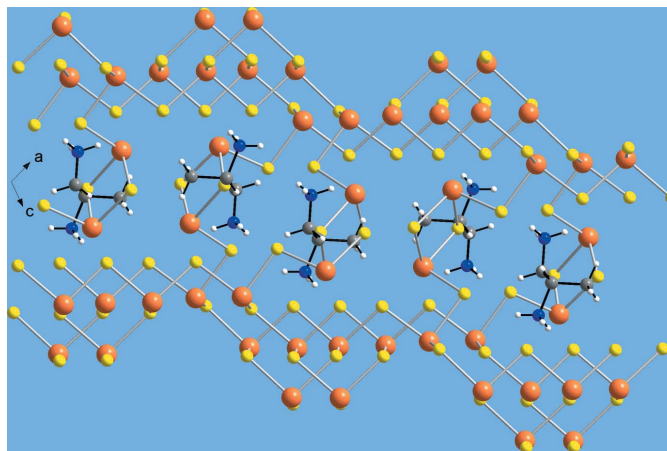


Figure 3
The crystal structure of the title compound, viewed along the *b* axis.

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