Poly[propane-1,2-diammonium μ-disulfido-deca-μ-sulfido-disulfidooctaantimonate(III)]

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean σ(S–S) = 0.003 Å

Disorder in solvent or counterion

R factor = 0.033

wR factor = 0.094

Data-to-parameter ratio = 21.1

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

In the structure of the title compound, $\{(C_3H_{13}N_2)[Sb_8S_{14}]\}_n$, SbS_3 pyramids are joined to form an $[Sb_4S_7]$ chain. Two adjacent chains are joined *via* an S_2 bridge, yielding the final $[Sb_8S_{14}]^{2-}$ anion. The structure-directing organic cations are located in the plane of large rings composed of ten S and eight Sb atoms. If Sb—S bonds longer than 3.1 Å are considered, a three-dimensional network with two types of channels is observed.

Comment

In the overwhelming majority of thioantimonate(III) compounds, only Sb—S bonds occur, covering the large range from about 2.4 Å up to the sum of the van der Waals radii of S and Sb of 3.8 Å (Bondi, 1964), and S—S or Sb—Sb bonds are very rare. To date, there are only a few examples of thioantimonates with S—S bonds and these are $[P(C_6H_5)_4]_3[Sb_3S_{25}]$ (Schur & Bensch, 1998), $[P(C_6H_5)_4]_2[Sb_2S_{17}]$ (Bensch & Schur, 1997), $[Ph_4P]_2[Sb_2S_{15}]$ (Rijnberk *et al.*, 1998), $Rb_2[Sb_8S_{14}]\cdot 2H_2O$ (Berlepsch *et al.*, 2001), $[CH_3NH_3]_2[Sb_8S_{14}]$ (Powell *et al.*, 2005) and $[C_2H_8N][Sb_8S_{14}]$ (Tan *et al.*, 1996). To the best of our knowledge, only two thioantimonates(III) with Sb—Sb bonds have been reported to date containing the $[Sb_6S_6]^{2-}$ and $[Sb_4S_6]^{2-}$ anions (Martin *et al.*, 1995). The title compound, $[C_3H_{13}N_2][Sb_8S_{14}]$, (I), is another example of a thioantimonate(III) containing an S_2^{2-} anion.

(I)
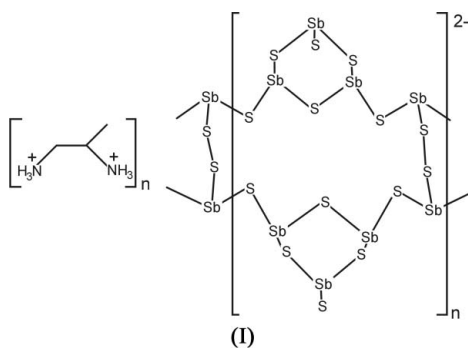
The four unique Sb atoms of (I) each have bonds to three S atoms to form the well known trigonal SbS_3 pyramids, with Sb—S bonds ranging from 2.399 (2) to 2.494 (2) Å. Three such pyramids are joined to form an Sb_3S_3 ring in a chair conformation by vertex sharing. These rings are connected by another SbS_3 pyramid, yielding an $[Sb_4S_7]^{2-}$ chain propagating along [101] (Fig. 1). Two adjacent chains are joined *via* the S_2 group into the final $[Sb_8S_{14}]^{2-}$ anion (Fig. 2). The S—S bond length of 2.089 (5) Å is typical for a single bond.
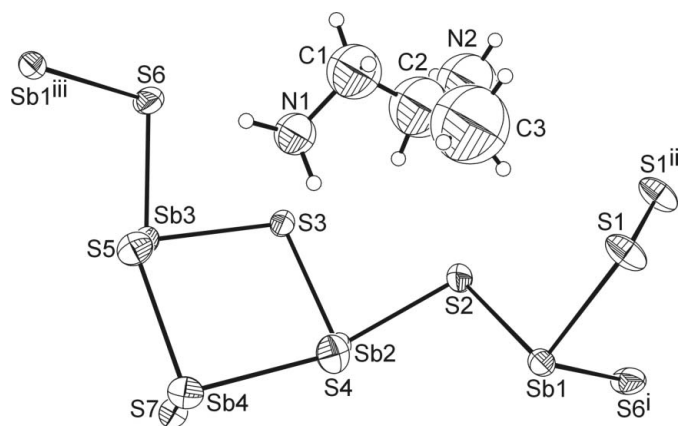
Figure 1
The structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x + 1$, y, $z + 1$; (ii) $-x + 2$, $-y + 1$, $-z + 3$; (iii) $x - 1$, y, $z - 1$.] Only one of the two disordered components of the cation is shown.
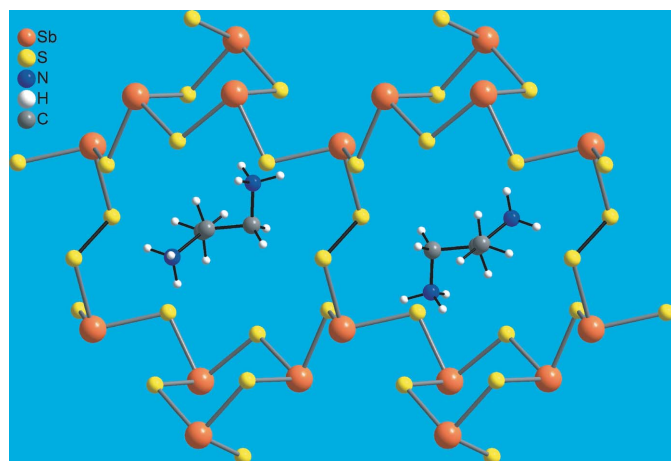
Figure 2
The crystal structure of (I), viewed along the a axis. Only one of the two disordered components of the cations is shown.

A central motif of the chain anion is a large ring composed of 18 atoms, *viz.* eight Sb and ten S atoms. The dimensions of the ring are about 7.8 × 10 Å. The $[(H_3N)(CH_3)-CH(CH_2)NH_3]^{2+}$ cations are located in the plane of the rings, demonstrating the structure-directing effect. The next-nearest S neighbours of the Sb atoms are at distances longer than 3.1 Å. Such long Sb—S distances are called secondary bonds and taking these bonds into account, atoms Sb1 and Sb4 are in a fourfold coordination environment, atom Sb2 in a fivefold coordination environment and atom Sb3 in a sixfold coordination environment. With these long bonds, a three-dimensional network is formed, with channels running along [001] which are occupied by the cations.

We note that the topology of the title compound is very similar to those of $[CH_3NH_3]_2[Sb_8S_{14}]$ (Powell *et al.*, 2005), $Rb_2[Sb_8S_{14}]\cdot 2H_2O$ (Berlepsch *et al.*, 2001) and $[C_2H_8N][Sb_8S_{14}]$ (Tan *et al.*, 1996).

Experimental

The title compound was synthesized under solvothermal conditions from a mixture of elemental antimony (1 mmol), sulfur (3 mmol) and 10% aqueous 1,2-diaminopropane solution (3 ml) in a Teflon-lined steel autoclave. The mixture was heated at 433 K for 6 d. The yield of the dark-red crystals of (I) was approximately 5 to 10% based on Sb. The main phase was $[C_3H_{13}N_2][Sb_{10}S_{16}]$. The product was washed with water and ethanol and dried under vacuum.

Crystal data

$(C_3H_{12}N_2)[Sb_8S_{14}]$	$Z = 2$
$M_r = 1498.99$	$D_x = 3.474$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.1404$ (13) Å	$\mu = 8.44$ mm^{-1}
$b = 25.522$ (4) Å	$T = 293$ (2) K
$c = 7.9316$ (9) Å	Block, red
$\beta = 97.558$ (11)°	$0.21 \times 0.1 \times 0.1$ mm
$V = 1432.9$ (4) Å^3	

Data collection

Stoe AED2 diffractometer	2160 reflections with $I > 2\sigma(I)$
ω/θ scans	$R_{int} = 0.037$
Absorption correction: numerical	$\theta_{max} = 25.0°$
(*X-SHAPE*; Stoe & Cie, 1998)	4 standard reflections
$T_{min} = 0.368$, $T_{max} = 0.450$	frequency: 120 min
4911 measured reflections	intensity decay: none
2537 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$+ 9.1338P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
2537 reflections	$\Delta\rho_{max} = 1.50$ e Å^{-3}
120 parameters	$\Delta\rho_{min} = -1.18$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Sb1—S6^i	2.430 (2)	Sb3—S3	2.481 (2)
Sb1—S2	2.439 (2)	Sb3—S6	2.489 (2)
Sb1—S1	2.494 (2)	Sb4—S7	2.399 (2)
Sb2—S4	2.466 (2)	Sb4—S4	2.479 (2)
Sb2—S3	2.468 (2)	Sb4—S5	2.487 (2)
Sb2—S2	2.495 (2)	S1—S1^{ii}	2.089 (5)
Sb3—S5	2.473 (2)	S6—Sb1^{iii}	2.430 (2)
S6^i—Sb1—S2	93.99 (9)	S7—Sb4—S4	96.43 (7)
S6^i—Sb1—S1	93.59 (9)	S7—Sb4—S5	95.33 (7)
S2—Sb1—S1	95.70 (8)	S4—Sb4—S5	95.20 (8)
S4—Sb2—S3	97.07 (8)	S1^{ii}—S1—Sb1	103.16 (14)
S4—Sb2—S2	90.73 (8)	Sb1—S2—Sb2	100.35 (8)
S3—Sb2—S2	85.28 (7)	Sb2—S3—Sb3	105.03 (8)
S5—Sb3—S3	99.69 (8)	Sb2—S4—Sb4	99.03 (7)
S5—Sb3—S6	90.93 (8)	Sb3—S5—Sb4	98.04 (8)
S3—Sb3—S6	82.26 (7)	Sb1^{iii}—S6—Sb3	101.50 (9)

Symmetry codes: (i) $x + 1$, y, $z + 1$; (ii) $-x + 2$, $-y + 1$, $-z + 3$; (iii) $x - 1$, y, $z - 1$.

The H atoms could not be located in a difference map and were positioned with idealized geometry, with C—H = 0.96 Å and N—H = 0.90 Å, and refined using a riding model, with U_{iso}(H) = $1.2U_{eq}$(parent), or $1.5U_{eq}$(parent) for methyl and N-bound H atoms. The 1,2-propanediammonium cation is disordered around a centre of inversion. Therefore, the site-occupancy factors must be 0.5.

According to the composition of the compound, both amino groups must be protonated. Because of the disorder, the C and N atoms were refined isotropically. The disorder remains identical in all space groups of lower symmetry and there are no hints of superstructure reflections. The largest peak is located 1.06 Å from Sb3 and the deepest hole 1.42 Å from Sb2.

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

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