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Methylammonium antimony sulfide

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Bis(methylammonium) octaantimony(III) dodecasulfide persulfide, $(CH_3NH_3)_2[Sb_8S_{12}(S_2)]$, contains pairs of $[Sb_4S_7]^{2-}$ chains joined through an unusual persulfide bond to create infinite double $[Sb_8S_{14}]^{2-}$ chains. The double chains are interlocked by longer Sb···S interactions to form sheets approximately parallel to the (101) crystallographic plane. Methylammonium cations, formed by decomposition of 2-methylpropane-1,2-diamine during the synthesis, are located in large (Sb_8S_{10}) hetero-ring apertures created within the double chains.

Comment

Organic template-directed solvothermal synthesis of open-framework antimony(III) sulfides yields a wide variety of structural motifs. Hence, novel materials can be synthesized with potentially interesting electrical, optical and magnetic properties. The variety of structures is a result of the stereochemical effect of the lone pair of electrons on Sb^{III}, together with the possibility of Sb^{III} having coordination numbers ranging from 3 to 6. The primary building units are typically $[SbS_3]^{3-}$ trigonal pyramids, which are connected *via* corner- or edge-sharing to form isolated, chain, layered or three-dimensional structures (Sheldrick & Wachhold, 1998). The $[Sb_4S_7]^{2-}$ chain is a common structural motif and is frequently present as single isolated chains (Parise & Ko, 1992). In rare examples, the chains can be linked to form infinite double chains, such as in $[C_2N_2H_{10}]Sb_8S_{13}$ (Tan *et al.*, 1994) and $[C_3N_2H_{12}]Sb_{10}S_{16}$ (Wang, 1995). As part of our ongoing studies of antimony–sulfide materials, we report here the structure of the title compound, $[CH_3NH_3]_2Sb_8S_{12}(S_2)$, (I), synthesized under solvothermal conditions, using 2-methylpropane-1,2-diamine. During the reaction, the amine decomposes and the methylammonium fragment formed directs the crystallization of the antimony–sulfide structure. The structure contains the unusual feature of a persulfide linkage between antimony–sulfide chains, and represents, after $[(CH_3)_2NH_2]_2Sb_8S_{12}(S_2)$ (Tan *et al.*, 1996), only the second reported example of its occurrence.

In the asymmetric unit of (I), there are four Sb atoms and seven S atoms, all of which occupy general positions (Fig. 1). All of the Sb atoms show their expected pyramidal coordination (Table 1). The bond-valence sums (BVS) for atoms Sb1–Sb4, calculated using the procedure of Brese & O'Keeffe (1991), are 2.73, 2.92, 2.72 and 2.91, respectively. These are in satisfactory agreement with the expected value of 3.00 for Sb^{III}. Three $[SbS_3]^{3-}$ pyramidal units are corner-linked to form $[Sb_3S_6]^{3-}$ semi-cubes, which are linked by $[SbS_3]^{3-}$ trigonal pyramids to form infinite $[Sb_4S_7]^{2-}$ chains, in which semi-cubes and pyramids alternate (Fig. 2). Atoms S7 and S7($-x$, $1-y$,

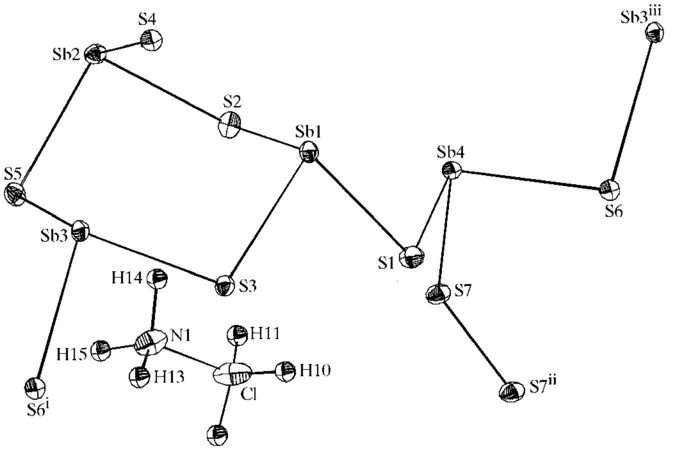

Figure 1
The $[Sb_4S_7]^{2-}$ repeating unit and one of the two positions of the disordered methylammonium cation in (I). Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are as given in Table 1.

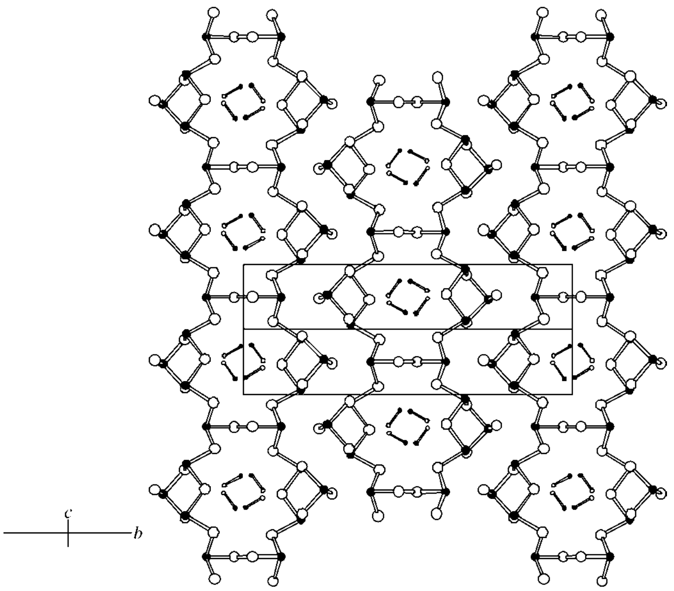

Figure 2
A view of (I) along the [$\bar{1}$01] direction (the *a* axis is eclipsed), showing the methylammonium cations within the (Sb_8S_{10}) hetero-rings. Both orientations of the disordered methylammonium cation are shown. Key: antimony, large solid circles; sulfur, large open circles; carbon, small solid circles; nitrogen, small open circles.

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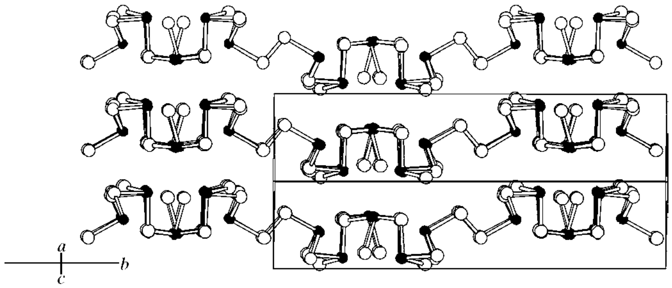

Figure 3
A view along the [101] direction, showing the undulating antimony sulfide layers. Methylammonium cations have been omitted for clarity. The key is as for Fig. 2.

$1 - z$) serve to link pairs of $[Sb_4S_7]^{2-}$ chains into double chains through a persulfide bond. The S—S bond length of 2.101 (2) Å is slightly longer than that of 2.085 (7) Å for the persulfide bond found in $(Me_2NH_2)_2Sb_8S_{14}$, the only other example of such a bond in these materials (Tan *et al.*, 1996).

18-membered (Sb_8S_{10}) hetero-rings are generated within the double chains, containing one methylamine molecule disordered over two crystallographically independent sites. The double negative charge of the antimony–sulfide framework requires the amine group to be monoprotonated. The shortest distance between the methylammonium ions and the surrounding framework atoms is the S5···N2 interatomic distance of 3.288 (7) Å, suggesting possible hydrogen bonding between the template and the antimony–sulfide framework. The $[Sb_8S_{12}(S_2)]^{2-}$ double chains are directed along [101]. Longer secondary Sb···S interactions in the range 3.22–3.37 Å serve to crosslink double chains in a zipper-like arrangement, forming layers approximately parallel to the (101) plane (Fig. 3) and linking individual layers into a three-dimensional structure.

The structure of (I) described in the space group $P2_1/n$ is closely related to that of $[(CH_3)_2NH_2]_2Sb_8S_{12}(S_2)$ reported by Tan *et al.* (1996), which crystallizes in the space group *Cmca*. However, there is a slight variation in the crystal packing, depending on the structure-directing amine used. In $[(CH_3)_2NH_2]_2Sb_8S_{12}(S_2)$, the antimony–sulfide layers are essentially planar, whereas in (I), the layers undulate along the [010] direction.

Experimental

Compound (I) was synthesized by the reaction of 2-methylpropane-1,2-diamine (2 mmol), Sb_2S_3 (2 mmol) and sulfur (5 mmol) in distilled water (3 ml). The mixture was heated in a Teflon-lined steel autoclave with an inner volume of 23 ml for 4 d at 438 K, and then cooled to room temperature over a period of 6 h. The product, consisting of red blocks of (I) and a small amount of unreacted Sb_2S_3, was filtered off, washed with water and acetone, and dried in air. CHN analysis of a handpicked sample of (I) found: C 1.64, H 0.60, N 1.79%; calculated: C 1.62, H 0.81, N 1.88%. Thermogravimetric analysis under flowing N_2 of handpicked ground crystals (7.29 mg) revealed a single weight loss of 8.20% over the range 541–559 K, which is consistent with the loss of the organic amine together with two moles of H_2S (8.61%). Powder X-ray diffraction of the decomposition product indicates that thermal decomposition produces poorly crystalline Sb_2S_3.

Crystal data

$(CH_6N)_2[Sb_8S_{12}(S_2)]$
$M_r = 743.60$
Monoclinic, $P2_1/n$
$a = 7.0984$ (9) Å
$b = 25.139$ (3) Å
$c = 7.937$ (1) Å
$\beta = 97.034$ (6)°
$V = 1405.6$ (3) Å^3
$Z = 4$
$D_x = 3.513$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4140 reflections
$\theta = 1.6$–30.1°
$\mu = 8.61$ mm^{-1}
$T = 100$ K
Plate, red
0.24 × 0.06 × 0.01 mm

Data collection

Bruker–Nonius APEX-2 CCD area-detector diffractometer
$\omega/2\theta$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.547$, $T_{max} = 0.918$
47592 measured reflections
4143 independent reflections
3187 reflections with $I > 3\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 30.2°$
$h = -10 \rightarrow 9$
$k = -35 \rightarrow 35$
$l = -11 \rightarrow 11$

Refinement

Refinement on F
$R[F > 2\sigma(F)] = 0.024$
$wR(F) = 0.027$
$S = 1.08$
3187 reflections
137 parameters
H-atom parameters constrained
Weighting scheme: Chebychev polynomial (Watkin, 1994), $w = 1/[0.562T_0(x) + 0.144T_1(x) + 0.274T_3(x)]$, where $x = F/F_{max}$; $W = w[1 - (\Delta F/6\sigma F)^2]^2$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.24$ e Å^{-3}
$\Delta\rho_{min} = -1.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sb1—S1	2.4983 (12)	Sb3—S6^{i}	2.5079 (12)
Sb1—S2	2.4731 (11)	Sb4—S1	2.4477 (11)
Sb1—S3	2.4819 (11)	Sb4—S6	2.4467 (12)
Sb2—S2	2.4944 (12)	Sb4—S7	2.4884 (11)
Sb2—S4	2.4074 (11)	S7—S7^{ii}	2.101 (2)
Sb2—S5	2.4833 (12)	N1—C1	1.464 (8)
Sb3—S3	2.4745 (11)	N2—C2	1.463 (8)
Sb3—S5	2.4771 (11)		
S1—Sb1—S2	91.41 (4)	S1—Sb4—S6	92.65 (4)
S1—Sb1—S3	85.14 (4)	S1—Sb4—S7	95.40 (4)
S2—Sb1—S3	96.37 (4)	S6—Sb4—S7	95.36 (4)
S2—Sb2—S4	96.17 (4)	Sb1—S1—Sb4	99.91 (4)
S2—Sb2—S5	95.24 (4)	Sb1—S2—Sb2	97.99 (4)
S4—Sb2—S5	95.83 (4)	Sb1—S3—Sb3	105.35 (4)
S3—Sb3—S5	98.44 (4)	Sb2—S5—Sb3	97.85 (4)
S3—Sb3—S6^{i}	83.26 (4)	Sb3^{iii}—S6—Sb4	99.69 (4)
S5—Sb3—S6^{i}	89.67 (4)	Sb4—S7—S7^{ii}	101.09 (7)

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

The methylammonium cations were modelled as disordered over two independent sites, each with an occupancy of 0.5. The C—N distances were restrained to be 1.45 (1) Å in each case. The six 0.5-occupancy H atoms of each 0.5-occupancy methylammonium cation were placed geometrically in a fully staggered orientation, as they could not be located from difference Fourier maps. H atoms were positioned geometrically and allowed to ride on their respective carrier atoms [C—H = N—H = 1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$]. Large residuals in the difference Fourier map revealed the presence of a minor twin component. The twin law was identified using the ROTAX procedure (Cooper *et al.*, 2002), implemented as a routine in *CRYSTALS* (Watkin *et al.*, 1996). The model was refined as a two-component twin, (100, 010, 001) and ($0.124\ 0\ \bar{0}.874$, $0\bar{1}0$, $\bar{1}.127\ 0\ \bar{0}.124$), with twin element scale factors 0.84 and 0.16.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure:

CRYSTALS (Watkin *et al*., 1996); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS* (Watkin *et al*., 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG1018). Services for accessing these data are described at the back of the journal.

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