

1,4,8,11-Tetraazacyclotetradecane antimony(III) sulfide

Rachel J. E. Lees,^a Anthony V. Powell,^{a*} David J. Watkin^b
and Ann M. Chippindale^c

^aDepartment of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland,

^bChemical Crystallography Laboratory, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, England, and ^cSchool of Chemistry, The University of Reading, Whiteknights, Reading RG6 6AD, England

Correspondence e-mail: a.v.powell@hw.ac.uk

Received 24 October 2006

Accepted 22 November 2006

Online 23 December 2006

Poly[1,4,8,11-tetraazacyclotetradecane(2+) [hepta- μ -sulfido-trisulfidohexaantimony(III)]], $\{(C_{10}H_{26}N_4)[Sb_6S_{10}]_n\}$, consists of novel $[Sb_6S_{10}]^{2-}$ layers containing Sb_2S_2 , Sb_4S_4 and Sb_7S_7 hetero-rings, which are separated by macrocyclic amine molecules. The macrocyclic amine molecules are disordered over two crystallographically distinct positions and are diprotonated in order to balance the charge of the anionic layers.

Comment

Template-directed synthesis of antimony(III) sulfides under solvothermal conditions has produced a wide variety of novel structures. The structural diversity arises from the stereochemical effect of the lone pair of electrons associated with Sb^{III} , together with the potential for antimony to exhibit coordination numbers that range from 3 to 6. The primary building units in solvothermally synthesized antimony sulfides are $[SbS_3]^{3-}$ trigonal pyramids. These may be connected through corner- or edge-sharing to create larger secondary building units, including a variety of Sb_xS_x hetero-rings and $[Sb_3S_6]^{3-}$ semicubes. Condensation of these building units can form chain, layered and three-dimensional antimony-sulfide structures, such as $[Fe(C_2H_8N_2)_3]_2[Sb_4S_8]$ (Lees *et al.*, 2005), $[Fe(C_4H_{13}N_3)_2][Sb_6S_{10}] \cdot 0.5H_2O$ (Stahler *et al.*, 2001) and $[Co(C_2H_8N_2)_3]_2[Sb_{12}S_{19}]$ (Vaqueiro, Chippindale *et al.*, 2004), respectively. The synthesis of these materials is generally performed using organic amines as structure-directing agents. The amines used to date have been principally linear and branched long-chain aliphatic amines and polyamines and alicyclic amines, such as ethylenediamine (Tan *et al.*, 1994), tris(2-aminoethyl)amine (Vaqueiro, Darlow *et al.*, 2004) and piperazine (Parise & Ko, 1992). The organic species is generally protonated in order to balance the negative charge of the anionic antimony-sulfide framework. Recently, we demonstrated that the macrocyclic amine cyclam can act as a structure-directing agent for solvothermally synthesized antimony

sulfides (Powell *et al.*, 2006). We prepared $(C_{10}H_{26}N_4)[Sb_4S_7]$, which represents a rare example of a truly three-dimensional antimony-sulfide framework and contains diprotonated cyclam molecules in the framework pores. We report here the structure of $(C_{10}H_{26}N_4)[Sb_6S_{10}]$, a layered antimony sulfide containing diprotonated cyclam, which was obtained as a minor product during the synthesis of $(C_{10}H_{26}N_4)[Sb_4S_7]$.

The asymmetric unit of the title compound contains three Sb and five S atoms, all of which occupy general positions. Atoms Sb1 and Sb3 show trigonal-pyramidal coordination, with Sb–S bond distances ranging from 2.4072 (16) to 2.4855 (15) Å and S–Sb–S angles ranging from 84.00 (5) to 100.8 (2)° (Table 1). Atom Sb2 is coordinated by four S atoms, with two shorter bonds and two longer bonds. The distances range from 2.4059 (15) to 2.8920 (15) Å, which is less than the sum of the van der Waals radii of antimony and sulfur (3.8 Å; Bondi, 1964), and the S–Sb–S angles lie in the range 87.44 (5)–96.27 (5)°. The bond lengths and angles are consistent with those found in other solvothermally synthesized antimony-sulfide materials containing $[SbS_3]^{3-}$ and $[SbS_4]^{5-}$ units (Stahler *et al.*, 2001; Spetzler *et al.*, 2004). The bond-valence sums (Brese & O’Keeffe, 1991) for atoms Sb1, Sb2 and Sb3 are 2.83, 2.98 and 2.98, respectively. These values are consistent with the presence of Sb^{III} in the framework. Vertex-linking of four $[SbS_3]^{3-}$ trigonal-pyramidal units generates an Sb_4S_4 hetero-ring, in which atoms Sb1 and Sb3 alternate around the ring. Each of the four terminal S atoms of the Sb_4S_4 hetero-ring is shared with an $[SbS_4]^{5-}$ unit (Fig. 1). These

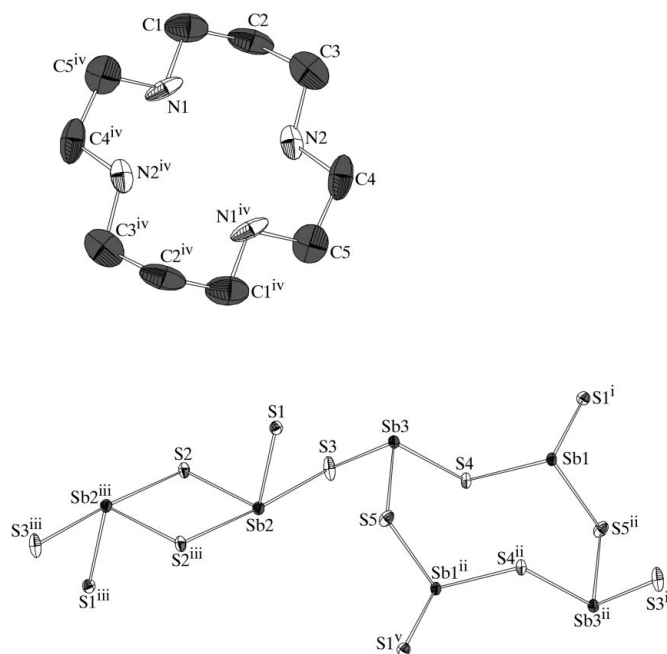


Figure 1

Local coordination of Sb and S atoms showing the Sb_4S_4 hetero-ring and an $[SbS_4]^{5-}$ unit connected through a shared S3 atom (bottom), and one of the two disordered and diprotonated cyclam molecules (top), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y + 2, -z + 1$; (iii) $-x + 2, -y + 1, -z + 1$; (iv) $-x + 1, -y + 2, -z$; (v) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.]

serve to link the rings into $[\text{Sb}_6\text{S}_{10}]^{2-}$ layers. Edge-sharing of two adjacent $[\text{Sb}_4\text{S}_4]^{5-}$ units generates Sb_2S_2 hetero-rings within the layers (Fig. 2). The anionic antimony–sulfide layers lie parallel to the *bc* crystallographic plane and are stacked directly above one another along $[100]$, separated by charge-balancing diprotonated macrocyclic cations (Fig. 3). Diprotonated cyclam molecules have been observed previously, examples being $(\text{C}_{10}\text{H}_{26}\text{N}_4)[\text{Sb}_4\text{S}_7]$ (Powell *et al.*, 2006) and $(\text{C}_{10}\text{H}_{26}\text{N}_4)[\text{ClO}_4]_2$ (Nave & Truter, 1974). The distance across the cyclam ring is 3.785 (6) Å for $\text{N1}\cdots\text{N1}^{\text{iv}}$ and 4.161 (6) Å for $\text{N2}\cdots\text{N2}^{\text{iv}}$ (Fig. 1). The shortest distance between the macrocyclic cation and the antimony–sulfide framework is 3.351 (4) Å ($\text{N2}^{\text{i}}\cdots\text{S2}$), which is short enough to allow hydrogen bonding between the macrocycle and the antimony–sulfide framework.

The structure of the $[\text{Sb}_6\text{S}_{10}]^{2-}$ layers of the title compound represents a new antimony–sulfide structural motif in which Sb_2S_2 , Sb_4S_4 and Sb_7S_7 hetero-rings form the anionic layers. The structure of the layers is significantly different from those of previously reported examples of antimony–sulfide layers with the same antimony–sulfur ratio. For example, the layers within $[\text{Fe}(\text{C}_4\text{H}_{13}\text{N}_3)_2][\text{Sb}_6\text{S}_{10}] \cdot 0.5\text{H}_2\text{O}$ (Stahler *et al.*, 2001) are composed of Sb_2S_2 , Sb_4S_4 and Sb_5S_5 hetero-rings which surround $\text{Sb}_{16}\text{S}_{16}$ rings, whilst in (*trans*-1,4- $\text{C}_6\text{H}_{15}\text{N}_2$) $[\text{Sb}_3\text{S}_5]$ and (*trans*-1,2- $\text{C}_6\text{H}_{15}\text{N}_2$) $[\text{Sb}_3\text{S}_5]$ (Engelke *et al.*, 2002), Sb_2S_2 ,

Sb_4S_4 and $\text{Sb}_{10}\text{S}_{10}$ hetero-rings are arranged to form the anionic layers.

Experimental

$(\text{C}_{10}\text{H}_{26}\text{N}_4)[\text{Sb}_6\text{S}_{10}]$ was synthesized by the reaction of cyclam (1.5 mmol), Sb_2S_3 (2 mmol) and sulfur (5 mmol) in deionized water (3 ml). The mixture was heated in a 23 ml Teflon-lined stainless steel autoclave at 438 K for 4 d before cooling to room temperature at a rate of 20 K h^{-1} . The solid product was filtered off, washed with deionized water and acetone, and dried at room temperature. The product consisted of orange blocks of the title compound as a minor phase, as well as a larger proportion of yellow blocks of $(\text{C}_{10}\text{H}_{26}\text{N}_4)[\text{Sb}_4\text{S}_7]$ (Powell *et al.*, 2006) and red blocks of $(\text{C}_2\text{H}_8\text{N}_2)[\text{Sb}_8\text{S}_{13}]$ (Tan *et al.*, 1994), identified by single-crystal X-ray diffraction and present in approximately equal amounts, together with a small amount of unreacted Sb_2S_3 , as identified by powder X-ray diffraction.

Crystal data

$(\text{C}_{10}\text{H}_{26}\text{N}_4)[\text{Sb}_6\text{S}_{10}]$	$Z = 2$
$M_r = 1253.46$	$D_x = 2.732 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.4872$ (9) Å	$\mu = 5.97 \text{ mm}^{-1}$
$b = 15.4477$ (14) Å	$T = 100 \text{ K}$
$c = 10.7567$ (9) Å	Block, orange
$\beta = 105.878$ (4)°	$0.16 \times 0.12 \times 0.06 \text{ mm}$
$V = 1516.3$ (2) Å ³	

Data collection

Bruker–Nonius APEX-2 CCD area-detector diffractometer	49836 measured reflections
$\omega/2\theta$ scans	4612 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4008 reflections with $I > 3.0\sigma(I)$
$T_{\text{min}} = 0.44$, $T_{\text{max}} = 0.70$	$R_{\text{int}} = 0.083$
	$\theta_{\text{max}} = 30.6^\circ$

Refinement

Refinement on F	Modified Chebyshev polynomial (Watkin, 1994) with coefficients 1.00, -1.11 , 0.479 and -0.402
$R[F^2 > 2\sigma(F^2)] = 0.049$	$(\Delta/\sigma)_{\text{max}} = 0.007$
$wR(F^2) = 0.038$	$\Delta\rho_{\text{max}} = 3.16 \text{ e \AA}^{-3}$
$S = 1.08$	$\Delta\rho_{\text{min}} = -2.81 \text{ e \AA}^{-3}$
4008 reflections	
150 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Sb1–S1 ⁱ	2.4855 (15)	Sb2–S2	2.4059 (15)
Sb1–S5 ⁱⁱ	2.469 (9)	Sb2–S3	2.6319 (16)
Sb1–S4	2.4621 (14)	Sb3–S3	2.4072 (16)
Sb2–S2 ⁱⁱⁱ	2.8920 (15)	Sb3–S4	2.4826 (15)
Sb2–S1	2.4723 (15)	Sb3–S5	2.4730 (15)
S1 ⁱ –Sb1–S5 ⁱⁱ	84.00 (5)	S1–Sb2–S3	87.09 (5)
S1 ⁱ –Sb1–S4	93.80 (5)	S2–Sb2–S3	91.97 (5)
S5 ⁱⁱ –Sb1–S4	92.05 (5)	S3–Sb3–S4	88.13 (5)
S2 ⁱⁱⁱ –Sb2–S1	88.66 (5)	S3–Sb3–S5	100.8 (2)
S2 ⁱⁱⁱ –Sb2–S2	87.44 (5)	S4–Sb3–S5	97.4 (3)
S1–Sb2–S2	96.27 (5)		

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

During refinement, inspection of the anisotropic displacement parameters indicated that the macrocyclic ring atoms were disordered. The C atoms were modelled as split over two positions, with both site occupancies fixed at 0.5. One set of U_{ij} values was refined for each pair of related C atoms. Bond length and angle similarity

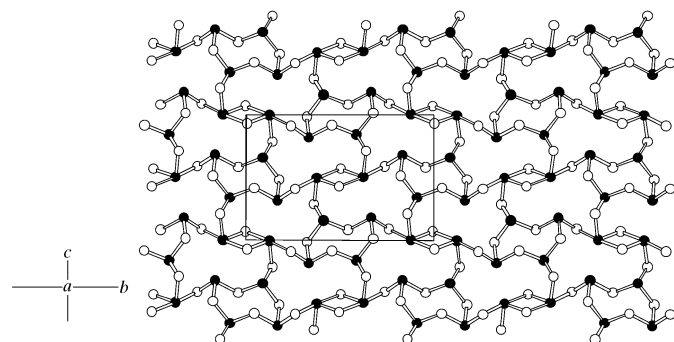


Figure 2
The $[\text{Sb}_6\text{S}_{10}]^{2-}$ layers viewed along $[100]$, with the unit cell outlined. Key: Sb atoms are large solid circles and S atoms are large open circles.

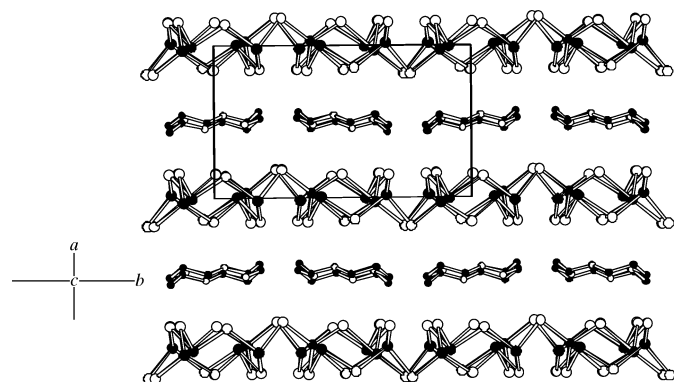


Figure 3
The $[\text{Sb}_6\text{S}_{10}]^{2-}$ layers separated by diprotonated cyclam molecules, with the unit cell outlined. H atoms have been omitted. Key: Sb atoms are large solid circles, S atoms are large open circles, C atoms are small solid circles and N atoms are small open circles.

restraints were applied between the two disordered threads and Hirshfield restraints applied to the U_{ij} values along the bonds. C-bound H atoms were positioned geometrically [$C-H = 0.97(1) \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$] and allowed to ride on the carrier atoms. The three H atoms attached to N1 and N2, which are required for charge balancing the antimony–sulfide framework, were not included in the refinement. The largest residual peak in the final Fourier map was located 0.506 \AA from C31 and the largest electron density trough was located 0.883 \AA from Sb2. The position of the beam stop precluded proper measurement of the omitted reflections.

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* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS*.

We thank the UK EPSRC for grants in support of a single-crystal CCD diffractometer and a studentship for RJEL. AMC thanks The Leverhulme Trust for a Research Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3032). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Bruker (2005). *APEX2*. Version 1.27. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dowty, E. (2000). *ATOMS*. Version 6.1. Shape Software, Hidden Valley Road, Kingsport, Tennessee, USA.
- Engelke, L., Näther, C. & Bensch, W. (2002). *Eur. J. Inorg. Chem.* **11**, 2936–2941.
- Lees, R. J. E., Powell, A. V. & Chippindale, A. M. (2005). *Polyhedron*, **24**, 1941–1948.
- Nave, C. & Truter, M. R. (1974). *J. Chem. Soc. Dalton Trans.* **21**, 2351–2354.
- Parise, J. B. & Ko, Y. (1992). *Chem. Mater.* **4**, 1446–1450.
- Powell, A. V., Lees, R. J. E. & Chippindale, A. M. (2006). *Inorg. Chem.* **45**, 4261–4267.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Spetzler, V., Kiebach, R., Näther, C. & Bensch, W. (2004). *Z. Anorg. Allg. Chem.* **630**, 2398–2404.
- Stahler, R., Nather, C. & Bensch, W. (2001). *Eur. J. Inorg. Chem.* **7**, 1835–1840.
- Tan, K., Ko, Y. & Parise, J. B. (1994). *Acta Cryst.* **C50**, 1439–1442.
- Vaqueiro, P., Chippindale, A. M. & Powell, A. V. (2004). *Inorg. Chem.* **43**, 7963–7965.
- Vaqueiro, P., Darlow, D. P., Powell, A. V. & Chippindale, A. M. (2004). *Solid State Ionics*, **172**, 601–605.
- Watkin, D. (1994). *Acta Cryst.* **A50**, 411–437.