

Novel Sulphide Frameworks: Synthesis and X-Ray Structural Characterization of $\text{Cs}_6\text{Sb}_{10}\text{S}_{18}\cdot 1.2\text{H}_2\text{O}$

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New antimony sulphides have been synthesized and the crystal structure of one of these, $\text{Cs}_6\text{Sb}_{10}\text{S}_{18}\cdot 1.2\text{H}_2\text{O}$, has been determined to be two dimensional in nature, accommodating Cs^+ ions and the Sb^{3+} lone pairs in cavities within an open framework.

Recent advances in the synthesis of novel molecular sieves have included the replacement of both Al and Si in traditional aluminosilicates to produce new varieties of open zeotype framework structures. The line followed by this research was firstly to combine group III and V elements to produce compounds with open structures isoelectronic with SiO_2 , AlPO_4 and GaPO_4 for example.^{1,2} Subsequently, transition elements were employed to replace some of the tetrahedrally coordinated cations in these zeotypes³ and this has culminated in the discovery of a series of open molybdenum phosphates.⁴ The range of compositions to be accessed as the basis for new zeotypes has been further expanded by the replacement of the oxide anion in the traditional frameworks with sulphur.⁵

Reported in this communication is the crystal structure of a new framework produced from antimony sulphide. The technique used for the synthesis is similar to that described for other classes of open frameworks;¹⁻⁶ finely divided sulphides are treated hydrothermally in the presence of either alkali metals or tertiary amines, which occlude the channels formed about them and are thought to act as structure directing agents during crystallization.⁶ The syntheses performed for this study were effected by heating the slurries of antimony sulphide and alkali in thick-walled Pyrex tubes.

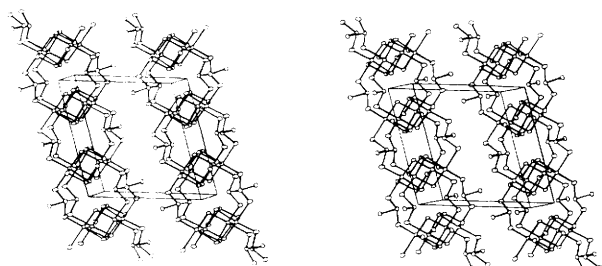


Fig. 1 Stereoscopic ORTEP drawing⁷ of the structure of $\text{Cs}_6\text{Sb}_{10}\text{S}_{18}\cdot 1.2\text{H}_2\text{O}$ close to down the a axial direction. The origin of the unit cell is in the back bottom left hand corner, with y to the right and z close to vertical. For the sake of clarity the Cs^+ ions, depicted in Fig. 3, and H_2O molecules are not shown.

A comparison of the X-ray powder diffraction patterns for the materials produced suggested they were unique. A chemical analysis was carried out on one of the materials, which crystallized as deep-red euhedral blocks up to 3 mm in size, using the electron micro-probe. The analysis was consistent with the empirical formula $\text{Cs}_3\text{Sb}_5\text{S}_9$.

The structure[†] (Fig. 1) consists of semi-cubes of antimony sulphide, shown in Fig. 2, which are stacked in columns along the a axis. These columns are linked by SbS_3 trigonal pyramids, an unusual coordination environment for Sb, to form ribbons along the c axial direction (Fig. 1). Four of the

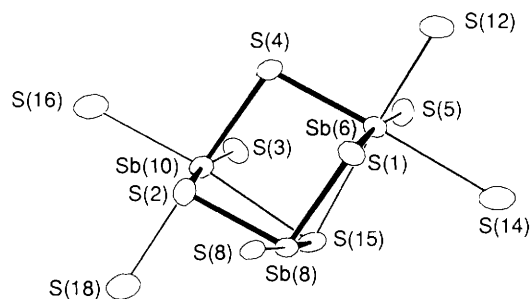


Fig. 2 The semi-cubes of antimony sulphide, which are linked along the a direction to form columns, and are cross-linked by SbS_3 -unit (Fig. 1). Short bonds (<2.7 Å) are shown as heavy lines.

[†] *Crystal data:* for $\text{Cs}_6\text{Sb}_{10}\text{S}_{18}\cdot 1.2\text{H}_2\text{O}$, triclinic, space group $P\bar{1}$, $a = 11.366(1)$, $b = 13.529(1)$, $c = 14.767(2)$ Å, $\alpha = 105.78(1)$, $\beta = 90.106(8)$, $\gamma = 102.104(7)^\circ$, $U = 2132.4$ Å³, $D_c = 4.06$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 121.5$ cm⁻¹, $Z = 2$, $\lambda = 0.7107$ Å, crystal arrow-head shape, dimensions 0.03 mm thick, 0.15 mm long and 0.10 mm at base, $R = 0.038$, $R_w = 0.035$, for 6643 reflections with $I > 3\sigma(I)$, collected at 24 °C on a CAD4-diffractometer ($R = 0.064$, $R = 0.050$ for $I > \sigma(I)$); solved and refined using a suite of programs written by J. C. Calabrese, E. I. Dupont de Nemours and Company. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300, Bonn.

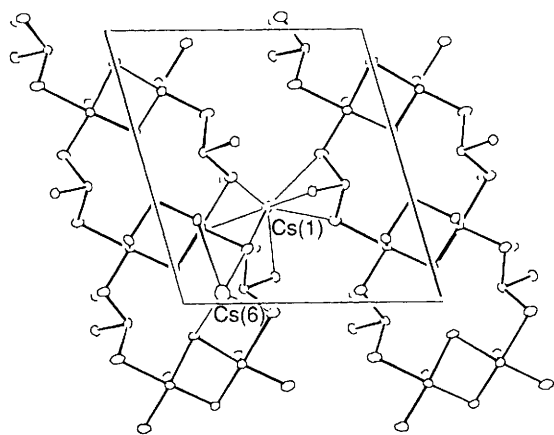


Fig. 3 ORTEP⁷ drawing of part of the structure of $\text{Cs}_6\text{Sb}_{10}\text{S}_{18} \cdot 1.2\text{H}_2\text{O}$ showing the two types of positions for the Cs^+ ions

Cs^+ -ions serve to link these ribbons in the b direction (Figs. 1 and 3) while the remaining two are positioned between the stacks of ribbons along the a direction. The structural elements shown in Fig. 2 are slightly disordered while the bridging SbS_3 pyramids are ordered. The disorder amounts to a partial occupancy (0.12) of sites, displaced from those shown in Fig. 2 by between 0.6 and 1.6 Å along the a direction. No such disorder is observed in either the SbS_3 polyhedra, which serve to connect the semi-cubes (Fig. 2), or in the Cs sites. Two partially occupied sites (0.6) in the channels were refined using the oxygen scattering factor and are the 1.2 molecules of water per formula unit included during crystallization.

The two dimensional nature of the structure (Figs. 1 and 3) is reminiscent of the clays rather than the molecular sieves. However, the motif of Sb-S connections should be more general and larger channel sizes may be realized using different templates. Indeed preliminary experiments, using the tetramethylammonium (TMA) ion as a template, have produced a unique material. It possesses a monoclinic cell, $P2_1/c$, and is light-orange in colour. Chemical analysis confirmed the crystals contain Sb, S and N in the ratio 3:5:1; this suggests that the TMA molecule is part of the crystal structure, as is to be expected if the new material is an open framework.

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