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The Crystal Structure of the Ternary Tin(II) Chalcogenide Halide $Sn_7Br_{10}S_2$

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The X-ray crystal structure of $Sn_7Br_{10}S_2$ is reported. $Sn_7Br_{10}S_2$ is hexagonal with $a = b = 12.185$, $c = 4.418$ Å, $Z = 1$. *Space group* $P6_3$. *There are three distinct tin sites and each tin atom lies in a partially occupied sixfold general site of the hexagonal lattice. Two of the sites have tin environments that are typical of tin(II) materials but the third site is unusual. The arrangement of tin atoms in the cell requires the operation of co-operative disorder in the lattice. The anions occupy two sets of general positions in the cell with one set consisting only of Br atoms and the other having randomly distributed Br and S atoms.*

Introduction

Tin in most tin(II) compounds is in a distorted environment because of the presence of a stereochemically active lone-pair of non-bonding electrons. The most common type of distorted environment found [1] has a trigonal pyramidal distribution of three nearest-neighbour tin–ligand bonds. Three longer non-bonding tin–ligand contacts completing the distorted octahedral environment, arise because close approach of ligands to the tin is prevented by lone-pair orbitals. The main structural feature found in the less common distorted four pyramidal environment is the existence of two short bonds and of two bonds of considerably greater length than those normally found in tin(II) compounds, as nearest-neighbour contacts. In addition to the low symmetry tin(II) compounds that have one of these two types of site, a small number of compounds with tin in environments of intermediate type are known. Although most tin(II) compounds have low symmetry lattices, a few structures have tin in high symmetry regular octahedral sites. Such environments for tin(II) are generally found in the heavier halide and chalcogenide derivatives, in lattices where these anions are in close contact and in which unusual optical and electrical properties are to be found.

Very few detailed crystal structure determinations have been carried out on tin(II) sulphides and tin(II) bromides. The tin(II) environments in SnS [2], Sn_2S_3 [3], $SnGeS_2$, $BaSnS_2$ [5] and $Sn[S_2P(OC_6H_5)_2]_2$ [6] have the common distorted trigonal pyramidal sites, whilst in bis(N,N-diethyldithiocarbamato)tin(II) [7] and bis-O-methyl-dithiocarbonatetin(II) [8], tin is in a square pyramidal environment. These are the only tin(II) compounds in which the details of the tin–sulphur environments are known. Partial crystal structures of a number of hydrated tin(II) bromide phases have been reported [9] but no real details of the tin–bromide environ-

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ments were given. Caesium tin tribromide, $CsSnBr_3$ [10], has the perovskite structure and is an example of a tin(II) compound with a high symmetry octahedral tin environment. The high symmetry structure arises because the distorting effects of the non-bonding electron pair on the tin are removed by direct population of solid-state bands arising from overlap of empty bromide orbitals.

We now report the structure of a mixed halide chalcogenide derivative of tin(II) in order to establish whether the tin(II) environments are of high symmetry, like $CsSnBr_3$ or low symmetry, like SnS. Previously reported data [11] suggested that $Sn_7Br_{10}S_2$ was isostructural with $Pb_7Br_{10}S_2$, which structure, although not fully determined was said [12] to be similar to that of Th_7S_{12} [13].

Experimental

$Sn_7Br_{10}S_2$ was prepared as the product from a cooled melt of $5SnBr_2$:2SnS under an atmosphere of oxygen-free nitrogen. A yellow hexagonal prismatic needle was taken from the bulk material and was used to obtain the cell data.

Crystal Data

$Sn_7Br_{10}S_2$, M = 1693.99, hexagonal: $a = b$ = 12.185(5), c = 4.418(4) Å, U = 568.08 Å^3, Z = 1, Dc = 4.95 g cm^{-3}, $F(000)$ = 732. Space group $P6_3$-(C_6 No. 173) or its centrosymmetric alternative $P6_{3/m}$(C_{6h} No. 176). Least squares refinement showed convergence towards the lower symmetry space group positions ($P6_3$) which were used in the complete refinement. Mo-K_α radiation (λ = 0.7107 Å, μ = 244.7 cm^{-1} was used).

Structure Determination

Intensity data collected with a Philips PW1100 four-circle diffractometer by use of monochromatized Mo-K_α radiation. 1176 intensities were recorded and 325 independent hexagonal reflections having $I \geqslant 3\sigma(I)$ were obtained and considered observed. Data were corrected for Lorentz and polarization factors but not for absorption.

Attempts to fit the data to the Th_7S_{12} atomic structure parameters failed, the high residual obtained from even the best fit to the data cast doubt on the validity of the assumption that $Sn_7Br_{10}S_2$ had a structure closely related to Th_7S_{12}. The structure was therefore solved using the non-centrosymmetric space group, with the usual heavy atom Patterson and Fourier methods being applied.

Initial refinement by full-matrix least-squares methods was performed with all atoms vibrating isotropically. Refinement was continued with the introduction of anisotropic thermal parameters for all atoms.

The calculations were carried out using SHELX-76 [14] and BONDLA from 'X-RAY 72' [15]. Stereographic projections of the unit cell were obtained using CELLPLOT [16].

The atomic positions were located as a result of a heavy atom Patterson synthesis. From the Patterson vector density map none of the top ten peaks could be uniquely assigned to Sn–Sn vectors, but instead could be accounted for by placing two heavy atoms in the two sets of sixfold positions (x_1 = 0.6200, y_1 = 0.1400, z_1 = 0.2500, x_2 = 0.9800, y_2 = 0.2200, z_2 = 0.2500). These positions were not considered close enough in the lattice to represent one tin and one anion (Br or S) atom site so in the initial stage they were assumed to be two sets of anion (Br) positions. These positions were refined using full matrix least squares to a residual of 0.409. A three dimensional difference Fourier map with phasing based on the refined anion (Br) positions gave a large peak with coordinates at x = 0.1128, y = 0.6871, z = 0.2375. This peak was assigned to a tin atom which had bond distances of the order of 2.85 Å to the two atoms now confirmed to be anions. The residual fell on refinement to 0.259. At this stage eighteen of the nineteen atoms in $Sn_7Br_{10}S_2$ had apparently been located, so a further Fourier synthesis was expected to reveal the position of the remaining tin atom. In fact one of the highest peaks in the Fourier map was at a position with coordinates close to 0, 0, ¼. Refinement of this seventh tin atom position, at 0, 0, ¼ with half occupancy of the twofold site, resulted in a residual of 0.1705. This unexpectedly high R value was explained by the appearance of a Fourier difference synthesis map peak corresponding to about eleven electrons. This peak with coordinates at x = 0.5948, y = 0.8328, z = 0.2936, lay at a distance of 0.82 Å from Sn(1). It was therefore necessary to consider the possibility that the Sn(1) atoms were not distributed over one sixfold site, but were instead distributed over two sixfold general positions (Sn(1) and Sn(2)). The relative site electron densities were calculated on the basis of possible site occupancies neglecting any structural requirements. The relative site densities reported in Table I are for the only two calculated site occupancies that are consistent with the experimental site electron densities. The first calculated set is for four Sn atoms distributed in site Sn(1), two Sn atoms distributed in site Sn(2), six Br atoms in site Br(1), four bromine and two sulphur atoms in site Br(2) and one Sn atom distributed in site Sn(3). The second calculated set has Sn and anions distributed on sites Sn(1), Br(1), and Br(2) but not only is this second set improbable in chemical terms it also leads to a much higher final residual. Refinement of the structure was then continued on the basis of the site occupancies suggested by the first calculated set with four Sn atoms distributed in the Sn(1) site

TABLE I. Electron Numbers (EN) found and calculated for the Various Site Occupancies considered.

Site	EN Found	EN 1st hypothesis	EN 2nd hypothesis
Br(2)	38	35.0(6Br)	37.5(5Br + 1Sn)
Br(1)	30	27.7(4Br + 2S)	28.7(4Br + 2S)
Sn(1)	31	33.3(4Sn)	30.8(3Sn + 1Br)
Sn(2)	18	16.7(2Sn)	16.7(2Sn)
Sn(3)	5	8.3(1Sn)	8.3(1Sn)

TABLE II. Final Atomic Parameters for $Sn_7Br_{10}S_2$.

	X	Y	Z	Site Occupation Factor
Sn(1)	0.5761	0.8845	0.2392	0.6667
Sn(2)	0.5939	0.8327	0.2916	0.3333
Sn(3)	0.9757	0.0370	0.2251	0.1667
Br(1)	0.6200	0.1352	0.2664	1.0000
Br(2)	0.7777	0.7618	0.2664	0.6667
S(2)	0.7777	0.7618	0.2664	0.3333

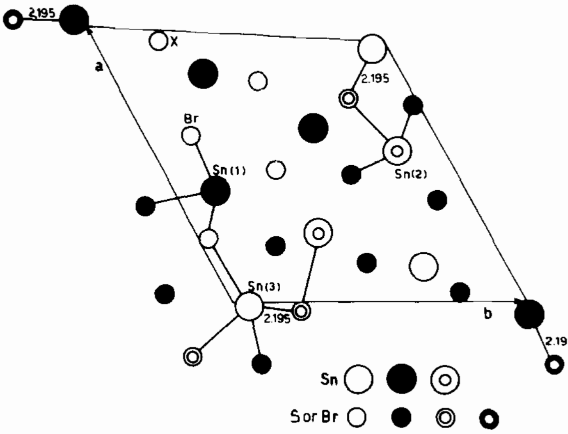

Fig. 1. Projection of the unit cell.

at x = 0.4241, y = 0.1158, z = 0.7500, and the remaining two tin atoms were distributed in the Sn(2) site at x = 0.5948, y = 0.8328, z = 0.2936. This distribution of tin atoms in two rather than one six-fold general position explains why the Sn–Sn vectors appear so low in the Patterson map.

After location and refinement of all atoms, refinements made with anisotropic temperature factors on all atoms gave a residual with $R = 0.061$. All three possible arrangements of sulphur atom positions in the structure arising either from location of the two sulphur atoms at the Br(1) or the Br(2) site or from an even distribution of the two sulphur atoms over the two bromide sites were considered. However, the lowest residual was achieved for a distribution of the two sulphur atoms on the Br(2) site only, as suggested by the calculated site occupancy numbers in Table I.

A total of twenty-nine reflections were then removed for which $|F_o| \geqslant 2|F_c|$ or $|F_c| \geqslant 2|F_o|$ and a final refinement was made with anisotropic temperature factors on all atoms to give a final residual of 0.0591. The final atomic parameters are given in Table II.

Discussion

The crystal structure determination of $Sn_7Br_{10}S_2$ shows that it is not similar to Th_7S_{12} but instead consists of an unusual set of disordered atomic positions. It is not surprising that the presence of a total of twelve anions in a hexagonal cell results in the occupation of two complete sets of six-fold positions. The data however, are not consistent with completely random distribution of bromide and sulphide ions within the structure but only with random distribution of these ions on one of the two sets of six-fold positions. The second set of six positions is occupied only by bromide ions.

The distribution of tin atoms within the cell is very unusual. With a total of seven tin atoms in the hexagonal cell, the expected distribution of cations based on a Th_7S_{12} structure would have been six in a general six-fold site and one randomly distributed on a twofold special position. The situation is, however, much more complicated than this. Attempts to fit the data to a set of six tin atoms in a general site failed and so it was necessary to redistribute the atoms as a set of four distributed in a general six-fold position based on a final tin atom position for Sn(1) at 0.576, 0.884, 0.239 and a set of two distributed in a general sixfold position based on a final tin atom position for Sn(2) at 0.594, 0.833, 0.292. These two sets of positions in which the tin atoms are distributed are only 0.814 Å apart. This means that the distribution of tin atoms and vacancies within the two sites cannot be a simple random distribution. There must be some type of cooperative disorder that avoids the positioning of tin atoms in the two sites 0.814 Å apart, but instead ensures that the positions associated with these short distances are always tin-vacancy distances. Figure 1 shows the projection of the unit cell of $Sn_7Br_{10}S_2$.

The environments of the tin atoms Sn(1) and Sn(2) differ, but are typical of environments found in many tin(II) compounds. Table III contains details

TABLE III. Bond Lengths and Bond Angles for $Sn_7Br_{10}S_2$.

(a) *Tin Coordination Sn(1)*

Bond Distances	(Å)	Bond Angles	(°)
Sn(1)–Br	2.831	Br–Sn(1)–Br	85.9
Sn(1)–Br	2.907	Br–Sn(1)–Br	96.8
Sn(1)–Br	3.002	Br–Sn(1)–Br	83.0
Sn(1)–Br	3.133	Br–Sn(1)–Br	83.3
Sn(1)–Br	3.209	Br–Sn(1)–Br	79.8
Sn(1)–Br	3.461	Br–Sn(1)–Br	82.9
		Br–Sn(1)–Br	81.5
		Br–Sn(1)–Br	78.5

(b) *Tin Coordination Sn(2)*

Bond Distances	(Å)	Bond Angles	(°)
Sn(2)–Br/S	2.764	Br–Sn(2)–Br/S	85.6
Sn(2)–Br/S	2.850	Br–Sn(2)–Br/S	97.1
Sn(2)–Br/S	3.044	Br–Sn(2)–Br/S	79.2
Sn(2)–Br	3.050	Br–Sn(2)–Br/S	81.4
Sn(2)–Br	3.244	Br–Sn(2)–Br/S	79.1
Sn(2)–Br	3.576	Br–Sn(2)–Br/S	75.9
		Br–Sn(2)–Br/S	78.2
		Br–Sn(2)–Br	89.1

(c) *Tin Coordination Sn(3)*

Bond Distances	(Å)	Bond Angles	(°)
Sn(3)–Br/S	2.195	Br/S–Sn(3)–Br/S	85.5
Sn(3)–Br/S	3.037	Br/S–Sn(3)–Br/S	133.4
Sn(3)–Br/S	3.239	Br/S–Sn(3)–Br/S	100.2
Sn(3)–Br/S	3.271	Br/S–Sn(3)–Br/S	69.4
Sn(3)–Br/S	3.307	Br/S–Sn(3)–Br/S	79.8
Sn(3)–Br/S	3.493	Br/S–Sn(3)–Br/S	123.3
Sn(3)–Br/S	3.523	Br/S–Sn(3)–Br/S	136.5
		Br/S–Sn(3)–Br/S	79.0

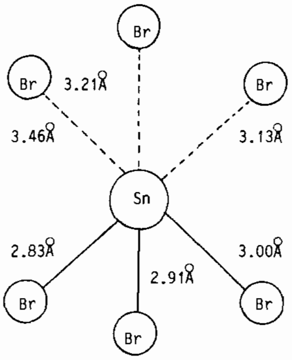

Fig. 2. The environment of Sn(1): Trigonal pyramidal.

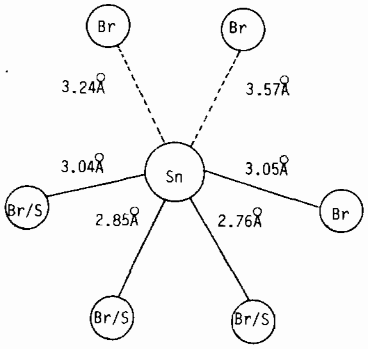

Fig. 3. The environment of Sn(2): Square pyramidal.

of bond lengths and angles associated with the Sn(1) and Sn(2) and Sn(3) sites. Sn(1) has a pyramidal environment of three short bonds to bromine atoms at distances of 2.83, 2.91 and 3.00 Å and Br–Sn–Br angles of 82.89, 81.48 and 96.74°. Three longer Sn–Br contacts of 3.13, 3.21 and 3.46 Å complete the distorted octahedral coordination about Sn(1) (Fig. 2). The atom Sn(2) on the other hand, lies in the less common four-coordinate environment, which consists of two short bonds and two longer Sn-anion distances. The short bonds to sulphur or bromine atoms are 2.76 and 2.85 Å, which are typical of Sn–S and Sn–Br bond lengths respectively. Two longer Sn–Br/S distances of 3.04 and 3.05 Å complete the square pyramidal coordination and even longer contacts (greater than 3.24 Å) complete a distorted octahedral environment about Sn(2) (Fig. 3). The environment of the third tin atom is most unusual, with an extremely short Sn–L bond of 2.19 Å which is most likely to be a Sn–S rather than Sn–Br bond. This distance together with six tin–ligand distances (in the range 3.04–3.52 Å) give an irregular coordination about the tin atom, Sn(3). Most of these Sn–L contact distances (3.24–3.25 Å) are longer than the sum of the Sn–S and Sn–Br ionic radii and must be considered as weak interactions rather than Sn–L bonds.

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