The Mössbauer Effect in Tin(II) Compounds. Part 14.[1] Data for some Chalcogenide Halides

By **John D. Donaldson,*** **David R. Laughlin,** and **Jack Silver,** Department of Chemistry, Chelsea College, University of London, Manresa Road, London SW3 6LX

The ^{119}Sn Mössbauer data for $Sn_7Br_{10}S_2$, Sn_4Br_6Se, and $Sn_4Br_{10}Te$ and for compositions from the $SnCl_2$–SnS system are compared with those of the parent halides and chalcogenides. The data for $Sn_7Br_{10}S_2$ show the presence of two tin(II) sites but these are not associated with distinct Sn–Br and Sn–S environments. The data for all the phases studied are consistent with random distribution of halide and chalcogenide anions. The variation in Mössbauer parameters of $Sn_7Br_{10}S_2$ with temperature and the development of colour in the chalcogenide halides is discussed in terms of direct population of solid-state bands by non-bonding electron pairs.

ALTHOUGH a number of lead(II) chalcogenide halides have been described as a result of phase-diagram studies,[2,3] very little is known of the corresponding tin(II) compounds. The lead(II) chalcogenide halides Pb_4Br_6Se, Pb_4Cl_6S, $Pb_7Br_{10}S_2$, and $Pb_5I_6S_2$ are well documented and the likely existence of some other phases has been discussed. All of the known lead(II) chalcogenide halides are coloured. The Pb_4Br_6Se and Pb_4Cl_6S phases are isostructural and are said [4,5] to have a structure similar to that of $PbCl_2$ but with random distribution of halide and chalcogenide ions. The compound $Pb_5I_6S_2$ has a structure [5] containing three different distorted lead(II) sites, two of which are associated with S atoms. The structure of $Pb_7Br_{10}S_2$ has not been fully determined but it has been suggested [6] that it is similar to that of Th_7S_{12}. Less information is available on the corresponding tin(II) phases, and although much of it is contradictory [7,8] there is agreement that these materials are coloured. In view of our previous work [9,10] on the development of colour in tin(II) halide-containing compounds, we have carried out a detailed study of the products obtained from cooled melts of all the systems SnX_2–SnZ (X = Cl or Br; Z = S, Se, or Te). The ^{119}Sn Mössbauer data for the chalcogenide halides obtained are compared with those of their parent halides and chalcogenides and discussed in terms of possible band population by the tin non-bonding electrons.

RESULTS AND DISCUSSION

No new phases were found in the $SnCl_2$–SnZ systems (Z = Se or Te). *X*-Ray diffraction data for the cooled melts from these systems showed that they were mixtures of tin(II) chloride and the tin(II) chalcogenide and some separation of these compounds was, in fact, observed as the melts cooled. There were no new distinct phases in the products from the cooled melts of the $SnCl_2$–SnS system but their *X*-ray diffraction and Mössbauer data suggest that solid solution over a wide range of compositions is possible. The distinct new phases $Sn_7Br_{10}S_2$, Sn_4Br_6Se, and Sn_4Br_6Te were, however, identified as the only new phases from the $SnBr_2$–SnZ system (Z = S, Se, or Te respectively).

X-*Ray Data for the Tin*(II) *Bromide Chalcogenides*.—*X*-Ray powder-diffraction data for the compounds

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$Sn_7Br_{10}S_2$, Sn_4Br_6Se, and Sn_4Br_6Te obtained from cooled melts are in Table 1. Single crystals of all the three phases were obtained by annealing melts of the appropriate composition under a nitrogen atmosphere. The compounds Sn_4Br_6Se and Sn_4Br_6Te have similar orthorhombic cells with a 8.74, b 4.15, and c 10.50 Å and a 8.95, b 4.22, and c 10.65 Å respectively. These crystals showed the following systematic absences: $0kl$ for $k + l = 2n + 1$, $hk0$ for $h = 2n + 1$; they therefore must have the space group $Pnma$ or $Pn2_1a$. Density measurements gave D_m 4.45 g cm^{-3} and D_c 4.51 g cm^{-3} for the selenide and D_m 4.70 g cm^{-3} and D_c 4.75 g cm^{-3} for the telluride in unit cells with $Z = 1$. The compound $Sn_7Br_{10}S_2$ has a hexagonal unit cell with a 11.35 and c 4.40 Å and space group $P6_{3/m}$ or $P6_3$ from the systematic absence of $00l$ for $l = 2n + 1$. These data suggest that $Sn_7Br_{10}S_2$ is isostructural with $Pb_7Br_{10}S_2$ which is said to have the Th_7S_{12} type structure.[11] This would mean that two types of tin environment would be present in $Sn_7Br_{10}S_2$: *viz.* a set of 6 Sn on one crystallographic site (site 1) and the seventh on a different special position (site 2).

TABLE 1

X-Ray powder-diffraction data ($d > 2.0$ Å) for Sn_4Br_6Se, Sn_4Br_6Te, and $Sn_7Br_{10}S_2$

Sn_4Br_6Se d/Å			Sn_4Br_6Te d/Å	
obs.	calc.	Index	obs.	calc.
6.55	6.65	101	6.73	6.84
5.26	5.25	002	5.40	5.33
4.45	4.52	102	4.55	4.51
3.89	3.86	011	3.99	3.95
3.28	3.32	202	3.42	3.42
3.07	3.04	210	3.14	3.10
2.86	2.90	211	2.93	2.95
2.70	2.67	113	2.77	2.75
2.59	2.61	004	2.65	2.66
2.57	2.55	302	2.63	2.61
2.51	2.52	104	2.57	2.56
2.19	2.18	400	2.24	2.23
2.16	2.14	401	2.21	2.19

$Sn_7Br_{10}S_2$		
d/Å		
obs.	calc.	Index
5.90	5.75	110
3.84	3.90	011
3.41	3.42	111
3.24	3.22	021
2.82	2.81	121
2.39	2.38	221
2.35	2.36	131
2.23	2.24	230
2.16	2.15	140
2.11	2.13	041
2.02	2.02	231

^{119}Sn *Mössbauer Data for Tin*(II) *Chalcogenide Phases.*—The Mössbauer parameters obtained at 78 K, for the distinct tin(II) bromide chalcogenide compounds and for compositions from the $SnCl_2$–SnS system, are compared in Table 2 with the data for the parent halides and chalcogenides. Room-temperature data for the tin(II) chalcogenides are also reported.

The chemical-isomer shifts (δ) for the pure tin(II) chalcogenides increase in the order SnTe > SnSe > SnS reflecting the increasing electrostatic character of the longer tin–chalcogenide bonds. The high symmetry of the tin environment in the sodium chloride structure of tin(II) telluride is shown by the narrow single resonance line compared with the quadrupole-split spectra for tin(II) sulphide and selenide which have distorted tin(II) environments.[12] The constant values for the chemical shifts for the chalcogenides at 78 and 298 K could result from two opposing effects: *viz.* (*a*) the longer tin–chalcogenide bonds at high temperatures which should give higher shift values; and (*b*) any donation of the tin(II) non-bonding electrons into the band structure should increase with temperature and give lower shift values at higher temperatures.

The narrow linewidth of the SnTe spectrum at 298 K shows that the electronic environment of the tin is more symmetrical than at 78 K. Line-broadening effects in tin(II) compounds studied by ^{119}Sn enriching are found to be small. The narrowing of the resonance line must therefore reflect the increased population, at room temperature, of solid-state bands by the non-bonding tin(II) electrons which would decrease their distortive effects as lone pairs.

TABLE 2

Mössbauer data for tin(II) chalcogenide halides

	δ* ±0.03 mm s^{-1}	Δ ±0.03 mm s^{-1}	Γ ±0.05 mm s^{-1}	T/K
SnTe	1.40	0.00	1.32	78
SnTe	1.37	0.00	0.93	298
SnSe	1.29	0.83	1.38	78
SnSe	1.27	0.73	1.35	298
SnS	1.24	0.93	1.73	78
SnS	1.21	0.86	1.68	298
$SnCl_2$·SnS	1.26	0.82	1.50	78
$3SnCl_2$·2SnS	1.57	1.02	1.65	78
$3SnCl_2$·SnS	1.90	1.31	2.10	78
Sn_4Br_6Se	1.88	0.59	1.53	78
Sn_4Br_6Te	1.80	0.36	1.27	78
$Sn_7Br_{10}S_2$ Site 1	1.71	0.00		78
Site 2	1.36	0.00		
$Sn_7Br_{10}S_2$ Site 1	1.50	0.00		298
Site 2	1.15	0.00		
$Sn_6PbBr_{10}S_2$	1.71	0.00		78
$SnBr_2$	1.93	0.00		78
$SnCl_2$	2.07	0.00		78

* Relative to α-Sn.

The 1 : 1, 3 : 2, and 3 : 1 phase compositions from the cooled $SnCl_2$–SnS system all have the tin(II) sulphide *X*-ray powder-diffraction pattern and there is no evidence for the presence of tin(II) chloride. This suggests that the compounds can form solid solutions based on the SnS structure. The Mössbauer data for these phases are consistent with this suggestion in that they show no definite evidence for the presence of both Sn–S and Sn–Cl sites. The Mössbauer parameters for the 1 : 1 composition are very similar to those for SnS, but the shift and splitting increase with increasing

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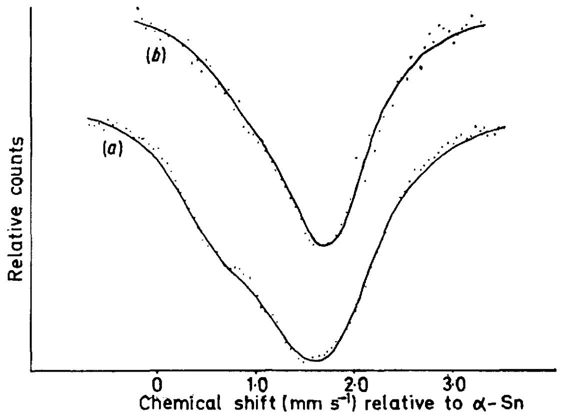
chloride content. The value of the shift for the 3 : 1 composition is closer to that of $SnCl_2$ but it has a much larger splitting indicating a lowering of the symmetry of the electronic environment of the tin.

The spectra of Sn_4Br_6Se and Sn_4Br_6Te consisted of asymmetric and symmetric quadrupole-split resonance lines, respectively. The spectrum of the bromide selenide can be fitted to a single tin(II) Mössbauer site. The *asymmetry* of the Sn_4Br_6Se spectrum might suggest the presence of more than one tin site, but since the observed asymmetry is less than that observed for SnSe itself, at 78 K, a single electronic environment is more likely. These results suggest that both structures are likely to contain randomly mixed chalcogenide and halide anions, with values of the chemical shifts between those of the corresponding parent compounds.

The Mössbauer spectra for $Sn_7Br_{10}S_2$ at 298 and 78 K (Figure) consisted of broad resonance lines with shoulders at lower chemical-shift values and these spectra cannot be fitted to single electronic sites. From the *X*-ray data and the suggested crystal structure for $Sn_7Br_{10}S_2$, it is reasonable to assume that six of the Sn atoms in the formula unit are on one crystallographic site and that the seventh has a different site. In order to test the effect of this on the Mössbauer data, a phase of composition $Sn_6PbBr_{10}S_2$ was prepared from a melt of the corresponding composition. The *X*-ray powder data for the product was that of a single phase, indistinguishable from $Sn_7Br_{10}S_2$. The new phase gave a single narrow Mössbauer peak (Figure) which was fitted to a single site. The data for this material were assumed to correspond to those for site 1 in $Sn_7Br_{10}S_2$. All the parameters for the second site were then calculated by fitting to the spectrum of $Sn_7Br_{10}S_2$, assuming them to be the difference between the data for $Sn_7Br_{10}S_2$ and $Sn_6PbBr_{10}S_2$ and that the single Pb atom in $Sn_6PbBr_{10}S_2$ preferentially occupies the high-symmetry site 2.



Tin-119 Mössbauer spectra of (*a*) $Sn_7Br_{10}S_2$ and (*b*) $Sn_6PbBr_{10}S_2$ at 78 K

The marked decrease in the Mössbauer chemical shift at 298 K compared with the shift at 78 K shows a decrease in *s*-electron density at the tin nucleus at higher temperatures. This trend is the opposite to that expected from an increase in the electrostatic nature of the tin–anion bond, at elevated temperatures. This observation is, however, readily explained by an increase in donation of the tin(II) *s*-electron lone pair into a solid-state band, as the temperature increases. Alternatively, a phase change may occur at lower temperatures, causing a change in the electronic environment of the tin atoms. The similar shape of the Mössbauer resonance line at all the three temperatures, however, suggests that this is not the case.

Colour of Tin(II) *Chalcogenide Halides*.—The Mössbauer data for $Sn_7Br_{10}S_2$ show the presence of two tin(II) sites. These sites are, however, not associated with distinct Sn–Br and Sn–S environments and must mean that the bromide and sulphide ions are randomly distributed in the structure. Such a random distribution of ions in $Sn_7Br_{10}S_2$ is similar to that found in the $CsSnBr_3$–$CsSnX_3$ (X = F, Cl, or I) system[1] in which a random distribution of halide ions is found in the high-temperature cubic phases. The development of colour and electrical conduction in the caesium tin(II) trihalides has been interpreted[9] in terms of direct population of solid-state bands by the non-bonding electron pairs on Sn^{II}. These bands could be formed in the chalcogenide halide phases by mutual overlap of bromide and chalcogen *d* orbitals. The colours of the tin(II) chalcogenide halides could then arise because of direct population of these bands by the tin(II) non-bonding electrons. It seems significant that the chemical shifts for both sites in $Sn_7Br_{10}S_2$ are lower at 298 than at 78 K. This decrease in *s*-electron density at the tin nucleus with temperature is contrary to the expected trend and is best explained in terms of more effective population of the *d* bands at the higher temperature giving rise to increased loss of tin *s*-electron density. Similar effects have been observed for $CsSnBr_3$.[13] The Mössbauer data for Sn_4Br_6Se and Sn_4Br_6Te are best interpreted in terms of single tin(II) sites and are therefore consistent with random distribution of the bromide and chalcogenide ions. The phases Sn_4Br_6Se and Sn_4Br_6Te are isostructural and their possible space groups (*Pnma* and *Pn*2_1*a*) suggest that, in addition to random distribution of chalcogenides replacing two Br^- ions, there must also be random distribution of anion vacancies.

In general, colours corresponding to lower energy transitions are found for the heavier chalcogenides and halides. For example, the perovskite phases of $CsSnCl_3$ and $CsSnBr_3$ are yellow and black respectively[14] and the isostructural compounds Pb_4Cl_6S and Pb_4Br_6Se are yellow and red respectively.[4] This suggests that band formation is more effective with the heavier anions and that they should be associated with higher-symmetry structures[9] and with more efficient band population by non-bonding electrons. In the present work the com-

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[14] J. Barrett, S. R. A. Bird, J. D. Donaldson, and J. Silver, *J. Chem. Soc.* (*A*), 1971, 3105.

pounds Sn_4Br_6Se and Sn_4Br_6Te are both black, but the greater effectiveness of the Te in forming bands is seen in the lower Mössbauer chemical shift of the telluride phase.

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