The Mössbauer Effect in Tin(II) Compounds. Part XII.[1] The Spectra of the Chloro- and Bromo-stannates(II)

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The ^{119}Sn Mössbauer parameters for the solid phases isolated from the aqueous and molten MX–SnX_2 systems are reported (M = Na, K, Rb, Cs, NH_4; X = Cl, Br). Data for complexes of types $MSnX_3$, MX,$MSnX_3$, and MSn_2X_5 are discussed in terms of the likely environments for tin(II) and of the use of tin bonding orbitals in complex formation.

THE ^{119}Sn Mössbauer parameters for the Et_4N^+, $Bu^n{}_4N^+$, and Ph_4As^+ derivatives of the trihalogenostannate(II) ions SnX_3^-, SnX_2Y^-, and $SnXYZ^-$ (X, Y, Z = Cl, Br, or I) have been reported.[2,3] The data for a number of trifluoro- and pentafluorodi-stannates(II) have also been described[4-6] but there has been no systematic study of the alkali-metal and ammonium derivatives of the complex tin(II) chloride and bromide species.

Studies[7-10] on tin(II) halide solutions have shown that the stable and predominant species present is the trihalogenostannate(II) ion, SnX_3^-. In concentrated solutions of tin(II) fluoride with insufficient fluoride to complex all of the tin as SnF_3^-, the polynuclear ion $Sn_2F_5^-$ is formed.[10] No evidence has been found for the presence of polynuclear anions in solutions of tin(II) chloride or bromide but this may be because all reported studies on these systems have been on dilute solutions. Earlier reports[9] of the existence of the tetrahalogenostannate(II) ion, SnX_4^{2-}, appear to be erroneous. Detailed studies on the derivatives of the tin(II) fluoride species have been reported[4-6,11] and some alkali-metal and ammonium trichloro-[11] and tribromo-stannates(II)[12,13] have been described. We have described[1] the preparation and properties of a series of caesium tin(II) trihalide compounds which have cubic unit cells and we now report a Mössbauer study of the other phases isolated from aqueous MX–SnX_2 systems (M = Na, K, Rb, Cs, NH_4; X = Cl, Br) and the molten MBr–$SnBr_2$ systems (M = Na, K, Rb, NH_4).

TABLE 1

Analyses of trihalogenostannates(II)

Compound	Found (%) Sn	Found (%) M(NH_4)	Found (%) X	Found (%) H_2O	Required (%) Sn	Required (%) M(NH_4)	Required (%) X	Required (%) H_2O
$KnSnCl_3,H_2O$	42·7		37·6	5·9	42·1		37·7	6·4
KSn_2Cl_5,H_2O	49·4		37·1	3·7	49·6		37·3	3·8
$KCl,KSnCl_3,H_2O$	33·3		39·1	5·4	33·3		39·7	5·1
$RbSnCl_3H_2O$	36·6		32·6	5·3	36·1		32·4	5·5
$RbSn_2Cl_5,H_2O$	46·5		34·3	3·1	45·8		34·2	3·5
$CsSnCl_3,H_2O$	32·0		28·5	4·7	31·6		28·4	4·8
$CsCl_2CsSnCl_3$	24·6				22·6			
NH_4SnCl_3,H_2O	46·0		40·6	6·7	45·5		40·7	6·9
$NH_4Sn_2Cl_5$	54·7	4·3	40·4		54·9	4·2	41·0	
NH_4Cl,NH_4SnCl_3,H_2O	37·7	11·7	45·0	5·4	37·7	11·5	45·1	5·7
$CsSn_2Cl_5$	44·1		33·6		43·4		34·2	
$KSnBr_3,2H_2O$	27·3		61·5	6·1	27·3		59·1	9·2
$KBr,KSnBr_3,2H_2O$	20·4		56·6	5·3	21·5		58·0	6·5
$RbSnBr_3$	27·2		55·3		26·8		54·1	
$RbBr,RbSnBr_3$	21·3		53·0		19·5		52·5	
$CsSn_2Br_5$	24·5		48·9		24·2		48·8	
$CsSn_2Br_5$	31·1		51·2		30·8		51·9	
NH_4SnBr_3	33·2		63·3		31·4		63·8	
NH_4Br,NH_4SnBr_3	25·0		66·2		26·5		67·5	

SnX_2–MX–H_2O *Systems*.—The phases isolated from solutions containing various mole ratios SnX_2 : MX from 1 : 6 to 6 : 1 were identified by chemical analysis and by their *X*-ray diffraction powder data. Three distinct complex phases were identified, $MSnX_3$ (M = K, Rb, Cs, NH_4; X = Cl, Br), MSn_2X_5 (M = K, Rb, Cs, NH_4; X = Cl; M = Cs, X = Br), and MX,$MSnX_3$ (M = K, NH_4, Cs; X = Cl; M = K, Rb, NH_4; X =

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Br). Some of the complexes also contained lattice water. No complex phase was isolated from the Li and Na systems presumably because these ions are too small to form a stable lattice from solution with the complex tin(II) halide species. Pure samples of the distinct phases were prepared from aqueous solutions containing the appropriate molar proportions of MX and SnX_2. Analyses for typical complexes are in Table 1.

The Molten $SnBr_2$–MBr *Systems*.—The products obtained from molten 1 : 1 and 1 : 2 MBr : $SnBr_2$ systems were identified by their *X*-ray diffraction powder data. Distinct complex phases of composition $MSnBr_3$ (M = Na, K, Rb, Cs, NH_4) and MSn_2Br_5 (M = K, Rb, Cs, NH_4) were identified.

Mössbauer Data.—The ^{119}Sn Mössbauer parameters for the complex tin(II) chlorides and bromides are in Table 2.

TABLE 2

Mössbauer parameters for halogenostannates(II)

Compound	δ/mm s⁻¹ rel. α Sn ±0·03	Δ/mm s⁻¹ ±0·03	Γ/mm s⁻¹ ±0·10
1. $SnCl_2$	2·07	*ca.* 0	
2. $KSnCl_3,H_2O$	1·44	1·10	2·10
3. $KSnCl_3$	1·71	0·77	1·97
4. $RbSnCl_3,H_2O$	1·57	1·14	2·40
5. $RbSnCl_3$	1·51	0·89	2·30
6. $CsSnCl_3,H_2O$	1·58	0·99	2·10
7. $CsSnCl_3$	1·59	0·90	1·80
8. NH_4SnCl_3,H_2O	1·62	1·18	2·35
9. NH_4SnCl_3	1·51	0·91	2·44
10. KSn_2Cl_5,H_2O	1·73	0·88	2·30
11. $RbSn_2Cl_5,H_2O$	1·75	0·98	2·38
12. $NH_4Sn_2Cl_5$	1·77	1·00	2·40
13. $CsSn_2Cl_5$	1·72	1·00	1·60
14. $KCl,KSnCl_3,H_2O$	1·65	0·70	2·10
15. NH_4Cl,NH_4SnCl_3,H_2O	1·59	0·95	2·30
16. $CsCl,CsSnCl_3$	1·54	0·75	2·15
17. $SnBr_2$	1·93	*ca.* 0	
18. $NaSnBr_3$ *	1·74	*ca.* 0	1·09
19. $KSnBr_3,2H_2O$	1·61	0·69	
20. $KSnBr_3$	1·72	*ca.* 0	1·96
21. $KSnBr_3$ *	1·76	*ca.* 0	1·33
22. $RbSnBr_3$	1·78	*ca.* 0	1·90
23. $RbSnBr_3$ *	1·72	0·76	1·77
24. $CsSnBr_3$ *	1·93	*ca.* 0	0·84
25. NH_4SnBr_3	1·69	0·68	
26. NH_4SnBr_3 *	1·77	0·77	1·55
27. KSn_2Br_5 *	1·77	1·01	1·69
28. $NH_4Sn_2Br_5$ *	1·75	0·91	1·63
29. $RbSn_2Br_5$ *	1·75	0·86	1·55
30. $CsSn_2Br_5$ *	1·77	0·81	1·63
31. $KBr,KSnBr_3,2H_2O$	1·58	0·76	
32. $RbBr,RbSnBr_3$	1·74	*ca.* 0	1·90
33. NH_4Br,NH_4SnBr_3	1·54	0·67	

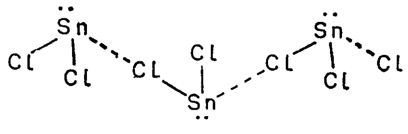
* From molten systems.

The chemical shifts (δ) of the trichlorostannates(II) (compounds 1—9) are all lower than that of $SnCl_2$. This is consistent with the replacement of a bridging Cl atom in the known environment[9] of Sn in tin(II) chloride with an additional chloride ion to form $SnCl_3^-$. The data for the trifluorostannates(II) have been interpreted in a similar manner.[4-6] Compounds 14—16 which are of the type $MCl,MSnCl_3,H_2O$ also contain discrete $SnCl_3^-$ ions and their Mössbauer parameters are similar to those of the trichlorostannates(II). The known crystal structure[14] for this type of complex is for a hydrated material in which the water is associated with the cation. The Mössbauer data for the anhydrous $CsCl,CsSnCl_3$ show that the Sn in this material has a similar environment to that in the hydrates and confirm that the water molecules are not bonded to the tin.

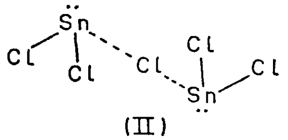
Many of the trisubstituted stannates(II) are hydrated when first precipitated. The water is easily removed and must be associated with the alkali metal rather than the tin environment. This is confirmed by the data for $KSnCl_3$ and $KSnCl_3,H_2O$ in that the hydrated material has a lower chemical shift as would be expected[6] if the polarising power of the K^+ ion was reduced by a sheath of H_2O.

The *X*-ray data for compounds 5, 7, and 9 show that they form an isostructural series and their Mössbauer parameters are similar. The structure of $CsSnCl_3$ is known[15] to contain discrete pyramidal $SnCl_3^-$ ions with Sn–Cl bond distances of 2·55, 2·52, and 2·50 Å and Cl–Sn–Cl bond angles of 92·3, 90·2, and 86·9°. $KSnCl_3$ is found to be isostructural with $KSnBr_3$ but not with $CsSnCl_3$.

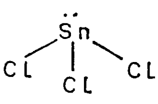
The compounds MSn_2Cl_5 (10—13) form an isostructural group and their *X*-ray data confirm that any water present in them when first precipitated must simply occupy spaces in the lattices; *e.g.*, the *X*-ray data for KSn_2Cl_5,H_2O are identical with those for the anhydrous material obtained from a melt. The bromide complexes MSn_2Br_5 (27—50) are isostructural with the corresponding chlorides. The chemical shifts for the MSn_2Cl_5 compounds are intermediate between that for $SnCl_2$ and the corresponding trichlorostannate(II). This is consistent with the existence of a polynuclear pentachlorodistannate(II) ion in these materials. Such an ion would maintain the stable pyramidal three-co-ordination of tin(II) by means of a bridging chloride. The Sn environment in $Sn_2Cl_5^-$ (II) would then be intermediate between that of $SnCl_2$ (I) and $SnCl_3^-$ (III).



(I)



(II)



(III)

The quadrupole splittings (Δ) for all of the chloride complexes in Table 2 are small. It has been suggested[16, 17] that the *p*-electron density in the non-bonding lone-pair

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[17] J. D. Donaldson, E. J. Filmore and M. J. Tricker, *J. Chem. Soc. (A)*, 1971, 1109.

tin orbital provides the major contribution to the field gradient in tin(II) materials. The relatively high chemical shifts for the chloride complexes should mean that there is a relatively low *p*-electron density in the lone-pair orbital. It is therefore probable that the *p*-electron density the lone-pair orbital of a chloride complex is much more similar to that in the bonding orbitals involving tin than is the case for the tin(II) fluorides.[4-6] The quadrupole splittings for the bromide complexes are generally lower than those of the chlorides as might be expected from their higher chemical shifts.

The Mössbauer parameters of the tin(II) bromide complexes, except for the Cs derivatives, show similar trends to those of the chlorides. We have shown [1] that $CsSnBr_3$ (compound 24) has a perovskite lattice and that it does not contain discrete complex tin(II)–bromide species. The shifts for the other tribromostannates(II) (compounds 18—23, 25, and 26) are all lower than that for $SnBr_2$ and the compounds of the type $MBr,MSnBr_3$ (31—33) generally have similar parameters to the tribromostannates(II). The compounds $MSnBr_3$ ($M = K$, Rb, and NH_4) obtained from molten systems are isostructural and have similar Mössbauer data. The slightly higher chemical shifts and quadrupole splittings for the isostructural tetragonal MSn_2Br_5 derivatives (27—30) are consistent with the formation of a polynuclear $Sn_2Br_5^-$ ion similar to that suggested for $Sn_2Cl_5^-$ (II). The chemical shifts for the bromide complexes are higher than those of the corresponding chloride derivatives and the increase in shift in the order $SnF_3^- < SnCl_3^- < SnBr_3^- < SnI_3^-$ follows the decrease in the stability constants of the trihalogenostannate(II) ions from fluoride to iodide.[9]

In view of the anomalous shift data for $KSnCl_3$ (compound 3) and the fact that perovskite-type halides containing tin(II) can be prepared, it is worth considering the effects of the packing of the ions present in some of the tin(II) halide materials. Although the stable and predominant species in tin(II) halide solutions is the trihalogenostannate(II) ion, it is clear from the formation of the cubic caesium tin trihalides [1] that lattice forces can have a major effect on the final structure of the solid materials obtained. In the formation of the perovskite $CsSnBr_3$ the stability of the cubic lattice must be high enough to cause the breakdown of the discrete $SnBr_3^-$ species. Anomalous Mössbauer parameters may therefore be expected for any tin(II) material in which packing to give a very stable lattice is possible. We suggest that the tin(II) in materials such as $KSnCl_3$, which have anomalously high chemical shifts, has an environment closer to the regular octahedral co-ordination of $CsSnBr_3$ than to the pyramidal species found in $CsSnCl_3$.

EXPERIMENTAL

All compounds obtained from aqueous systems except those discussed below were prepared from solutions containing the molar proportions of the pure Sn^{II} and M^{I} halides required for the desired product. The solutions were made up with the minimum of water and in an atmosphere of oxygen-free nitrogen. Molar ratios of 1·5 : 1 of $NH_4Cl : SnCl_2$ are, however, required for the formation of NH_4SnCl_3 because of the relatively low solubility of the alternative product NH_4Cl,NH_4SnCl_3,H_2O. An excess of SnX_2 is required for the formation of MSn_2X_5 and $MX : SnX_2$ ratios of 1 : 2·5 were found to be the most satisfactory. All the products were washed with the minimum of cold water and dried *in vacuo* over P_2O_5 to give the anhydrous materials.

The products from the molten systems were obtained by use of the correct molar proportions of MX and SnX_2 for the desired product.

All products were identified by their chemical analyses and *X*-ray diffraction powder data. Tin analyses were carried out by Donaldson and Moser's method,[18] Cl and Br were determined potentiometrically by titration with silver nitrate solution, and water was determined by loss of weight (collection in a weighed anhydrone absorption tube).

X-Ray diffraction powder data were obtained with Cu-K_α radiation and with Phillips 11·64 cm cameras.

X-*Ray Diffraction Powder Data for the Halogenostannates*-(II).—The data are reported with *d*-spacings to 2·0 Å and relative intensities.

$NH_4SnCl_3(H_2O)$. 8·96ms, 7·20s, 5·97ms, 4·66m, 4·50m, 4·07m, 3·93vw, 3·84s, 3·69w, 3·60w, 3·55w, 3·16w, 3·11mw, 2·87m, 2·75m, 2·67m, 2·62w, 2·48w, 2·44mw, 2·31w, 2·28w, 2·24w, 2·18w, 2·09vw, 2·03vw.

$RbSnCl_3(H_2O)$. 7·18m, 5·95vw, 4·52w, 4·18ms, 3·99mw, 3·87ms, 3·77ms, 3·60mw, 3·54mw, 3·08m, 3·02vw, 2·94m, 2·89m, 2·77m, 2·70m, 2·66m, 2·34w, 2·27w, 2·22w, 2·19w, 2·12w, 2·07w.

$KSnCl_3(H_2O)$ *and* $MSnBr_2$ ($M = K$, Rb, NH_4). These form an isostructural series.

$KSnCl_3(H_2O)$. 9·21vvw, 7·90vs, 7·76vs, 6·42w, 6·28w, 4·67w, 4·62vw, 4·37vw, 4·31vw, 4·29vw, 4·21vw, 4·13vw, 4·06vw, 3·59s, 3·40s, 3·30vvw, 3·07s, 2·92m, 2·90m, 2·82w, 2·76s, 2·62w, 2·38m, 2·18m, 2·04w.

$KSnBr_3$. 9·12w, 8·29s, 7·14m, 6·61m, 4·81vw, 4·27w, 4·63vw, 4·00w, 3·67s, 3·55s, 3·39vw, 3·31w, 3·16vs, 3·11w, 3·03s, 2·84vs, 2·68w, 2·64m, 2·55vs, 2·45w, 2·38w, 2·14s, 3·09s, 2·06s.

NH_4SnBr_3. 9·31w, 7·37vs, 6·46m, 6·07w, 5·08ms, 4·63w, 4·44w, 4·02m, 3·92w, 3·59s, 3·21vs, 3·05w, 2·98vvs, 2·86w, 2·77w, 2·70w, 2·67m, 2·59w, 2·56m, 2·50m, 2·44w, 2·38, 2·31mw, 2·18w, 2·08w, 2·04w, 2·03w.

$RbSnBr_3$. 8·15vw, 7·36m, 6·46w, 6·15vw, 5·21w, 4·65vvw, 4·04w, 3·87w, 3·65m, 3·45w, 3·31ms, 3·21w, 3·14m, 3·09m, 3·04ms, 2·99s, 2·95vw, 2·91vvw, 2·85vvw, 2·77mw, 2·73m, 2·67s, 2·58m, 2·53m, 2·50w, 2·47m, 2·33s, 2·23m, 2·19w.

$KSnBr_3,2H_2O$. 8·19s, 6·61m, 6·11vw, 5·31vw, 4·79vw, 4·25vw, 4·15w, 3·68m, 3·55m, 3·38s, 3·31w, 3·16s, 3·01s, 2·93vw, 2·83s, 2·74m, 2·63w, 2·49s, 2·33w, 2·25vw, 2·21m, 2·15m, 2·10w, 2·06w.

The structure of $KSnCl_3,KCl,H_2O$ is known,[14] and NH_4SnCl_3,NH_4Cl,H_2O is isomorphous with it. The powder data for the latter are: 6·98vs, 6·20ms, 4·67m, 4·20w, 3·88ms, 3·71ms, 3·48w, 3·41vvw, 3·12s, 3·10vvw, 3·03ms, 2·94m, 2·90m, 2·78ms, 2·73vvw, 2·69vvw, 2·63vvw, 2·57w, 2·48w, 2·46vw, 2·40vvw, 2·35m, 2·32mw, 2·29w, 2·21ms, 2·20ms, 2·10m, 2·07m, 2·04w.

$RbBr,RbSnBr_3$. 9·71w, 7·31w, 6·51w, 6·15w, 5·01w, 4·65vw, 4·43vw, 4·15m, 3·99w, 3·86w, 3·62vw, 3·55m,

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[18] J. D. Donaldson and W. Moser, *Analyst*, 1959, **84**, 10.

TABLE 3

$NH_4Sn_2Br_5$ $a = b = 11{\cdot}912$ $c = 14{\cdot}628$

$h = k$

I	*d*(obs)	*d*(calc)	(*hkl*)	*I*	*d*(obs)	*d*(calc)	(*hkl*)
s	7·314	7·314	002	s	1·674	1·674	624
m	4·206	4·211	202	vw	1·560	1·558	408
w	3·648	3·648	222	vw	1·538	1·539	606
mw	3·121	3·118	206	s	1·508	1·506	644
vvs	2·978	2·978	400	s	1·490	1·489	800
m	2·760	2·760	402	w	1·445	1·444	820
s	2·663	2·664	420	w	1·421	1·421	2010
m	2·501	2·502	422	w	1·406	1·404	660
m	2·437	2·440	006	m	1·382	1·382	2210
s	2·316	2·316	406	m	1·345	1·344	826
w	2·108	2·111	226	w	1·308	1·309	664
m	1·986	1·986	600	m	1·269	1·270	806
s	1·884	1·883	610	m	1·253	1·251	844
m	1·824	1·824	444	m	1·242	1·242	826
m	1·797	1·797	246	w	1·213	1·215	666
vw	1·743	1·745	604				

	a = *b*	*c*		*a* = *b*	*c*
$NH_4Sn_2Cl_5$	11·39	14·10	$RbSn_2Br_5$	11·94	14·51
$RbSn_2Cl_5$	11·66	14·25	$CsSn_2Cl_5$	11·57	14·57
KSn_2Cl_5	11·33	13·94	$CsSn_2Br_5$	12·09	15·52
KSn_2Br_5	11·84	14·46			

3·23s, 3·09s, 3·06s, 2·97s, 2·86m, 2·70w, 2·64w, 2·58vw, 2·44m, 2·37vw, 2·32vw, 2·281vw, 2·24m, 2·19vw, 2·09w, 2·01vw.

$KBr,KSnBr_3,2H_2O$. 8·12s, 7·20m, 6·66w, 4·74vw, 3·95w, 3·79w, 3·68w, 3·55w, 3·38m, 3·30w, 3·18s, 3·09m, 3·02s, 2·98vw, 2·85s, 2·74m, 2·63m, 2·56vw, 2·49m, 2·36vw, 2·34vw, 2·25w, 2·21w.

NH_4Br,NH_4SnBr_3. 7·20s, 6·46m, 5·15vw, 4·82w, 4·58vw, 4·13w, 4·00w, 3·82w, 3·59m, 3·23s, 3·143s, 3·05s, 2·73vw, 2·66w, 2·57w, 2·45m, 2·41m, 2·28m, 2·20w, 2·16m, 2·12vw.

$CsCl,CsSnCl_3$. 6·02vvw, 4·26ms, 3·78vs, 3·66vw, 3·56vs, 3·25w, 3·20vw, 3·00vs, 2·93s, 2·81vs, 2·59vw, 2·55vw, 2·25vw, 2·20m, 2·11w, 2·09m, 2·00m, 1·89vw, 1·84vw, 1·83vw, 1·76m.

Pentahalogenostannates(II). The MSn_2X_5 (M = K, Rb, NH_4, and Cs, X = Cl, Br) series are all tetragonal. Indexed data are given for $NH_4Sn_2Br_5$ in Table 3. The powder data for the other complex are similar but based on the cells listed.

The Mössbauer spectra were obtained with the absorber and a $BaSnO_3$ source at 80 K. The chemical shift for the reference material (α-Sn) from the source was 2·10 mm s^{-1} at 80 K. The Mössbauer apparatus has been described.[19]

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[19] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 1311.