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Studies on Phases from the M:Sn(II):I:F Systems (M = Na, K, Rb, and NH_4)

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The products obtained from molten and aqueous SnF_2:MI systems (M = Na, K, Rb, and NH_4) have been studied. The Mössbauer data for phases with 1:1, 2:1, and 3:1 SnF_2:MI molar ratios are reported. The MSnIF_2 phases show evidence of two tin sites, one of which has Mössbauer parameters attributable to an octahedral tin(II) environment. The materials obtained are all colored and the reasons for these colors are discussed.

Introduction

Although a number of tin(II)-mixed halide systems have been studied (*1–5*) there are very few reports on phases obtainable from systems containing tin(II) and both fluoride and iodide ions. The ternary iodide fluorides SnIF and Sn_2IF_3 have been reported (*1*) and their Mössbauer data have the relatively low chemical isomer shifts and large quadrupole splittings associated with Sn–F bonds.

The compounds Sn_2F_3Cl (*6*), Sn_2BrF_5 (*7*), Sn_3F_8 (*8*), $NaSn_2F_5$ (*9*), $2KSnF_3 \cdot H_2O$ (*10*), contain distorted tin(II) fluoride environments with which their Mössbauer parameters are consistent. The products obtained on cooling the molten system $CsSnF_3$–$CsSnX_3$ (X = Br, I) depend upon the halide concentrations (*5*). The distinct phases $CsSnF_2X$ (X = Br, I) can be obtained from mixtures containing an excess of fluoride and the Mössbauer data on these materials suggest the presence of distorted tin(II) halide environments found in compounds containing the trihalogenstannate(II) ions in their structures. The products from mixtures containing greater than 1:1 mole ratios of X^- to F^-, however, form a continuous range of colored solid solutions $CsSnF_{3-n}X_n$ ($n > 1.5$) with cubic (X = Br) and orthorhombic (X = I) unit cells (*5*). The Mössbauer parameters for these solid solutions are similar to those found for the high symmetry phases in the $CsSnBr_3$–$CsSnCl_3$ system (*4*). The data for the chloride–bromide system have been interpreted in terms of random replacement of Br^- ions in the cubic perovskite $CsSnBr_3$ lattice by Cl^- ions. The retention of the narrow Mössbauer resonance lines for these products must mean that the electronic environment of the tin is not affected by the replacement of Br^- by Cl^-. Similar effects must occur in the $CsSnF_3$–$CsSnX_3$ (X = Br, I) systems, and therefore we consider that the F^- ions are on Br^- and I^- sites in these compounds and that the fluoride ions are not approaching close enough to the tin atoms to disturb their electronic environments. The X-ray diffraction powder data for these systems are consistent with such an interpretation. We now describe the phases obtained from the aqueous and molten systems SnF_2–MI (M = Na, K, Rb, and NH_4) and discuss their Mössbauer data and optical properties.

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Experimental and Results

The first precipitate from the aqueous MI–SnF_2 system depends upon which component is in excess. The products obtained from the Na, K, and NH_4 systems with SnF_2 in excess are MSn_3IF_6 phases. The ammonium phase is very unstable but has X-ray data similar to these of the sodium material. No reproducible product was obtained from the rubidium system. A second phase, $NaSn_2IF_4$ was obtained from the sodium system. The products obtained from the Na and K systems with MI in excess are $MSnIF_2$ phases. No reproducible products could be obtained from the ammonium and rubidium systems. Analytical data for typical products are given in Table I. These data are reproducible for a

TABLE I

ANALYSES OF COMPOUNDS OBTAINED FROM SOLUTION[a]

Compounds	I (%)	F (%)	Sn (%)
$NaSnIF_2$	37.4	14.2	37.5
	(41.5)	(12.4)	(38.7)
$NaSn_2IF_4$	29.6	17.9	49.0
	(29.6)	(16.4)	(51.2)
$KSnIF_2$	43.6	9.5	36.1
	(39.0)	(11.8)	(36.8)
KSn_3IF_6	20.2	17.8	54.5
	(20.0)	(17.9)	(56.0)
$NaSn_3IF_6$	18.5	16.5	55.2
	(20.5)	(18.4)	(57.4)

[a] Calculated values for the formulas given in parentheses.

TABLE II

MÖSSBAUER DATA FOR THE M–Sn–F–I SYSTEMS AT 80°K[a]

Compound	δ^* (± 0.03 mm sec^{-1})	Δ (± 0.03 mm sec^{-1})	Γ (± 0.05 mm sec^{-1})	Color at room temperature
1. $NaSnIF_2$	3.23	1.71	1.26	Yellow
2. $KSnIF_2$	*a* 3.37	1.75	1.32	Orange
	b 3.82	0	0.94	
3. $RbSnIF_2$	*a* 3.31	1.79	0.90	Orange
	b 3.93	0	1.27	
4. NH_4SnIF_2	*a* 3.45	1.68	0.83	Orange
	b 3.92	0	1.03	
5. NH_4SnIF_2[c]	*a* 3.41	1.55	0.81	
	b 2.92	0	1.03	
6. NH_4SnIF_2[d]	*a* 3.46	1.47	0.63	
	b 3.92	0	1.03	
7. $NaSn_2IF_4$	3.46	1.63	1.35	Yellow
8. KSn_2IF_4	3.33	1.84	1.41	Yellow
9. $RbSn_2IF_4$	3.35	1.86	1.38	Yellow
10. $NH_4Sn_2IF_4$	3.48	1.48	1.34	Yellow
11. $NaSn_3IF_6$[e]	3.52	0	3.80	Yellow
12. KSn_3IF_6[e]	3.66	0	3.04	Yellow
13. $NaSn_3IF_6$	3.56	1.51	0.76	White
14. KSn_3IF_6	3.39	1.60	0.82	Yellow
15. $RbSn_3IF_6$	3.37	1.60	0.81	Yellow
16. $NH_4Sn_3IF_6$	3.39	1.58	0.81	Yellow

[a] * = relative to $BaSnO_3$; a = low symmetry site; b = high symmetry site; c = room temperature; d = room temperature after heating; e = from solution.

given sample but the phases are difficult to obtain pure because they are precipitated as gelatinous masses which absorb much of their mother liquors. In addition to the analytical difficulties associated with absorption of mother liquors, these results also may be influenced by the possibility of some hydrolysis and/or oxidation.

The products from cooled melts containing SnF_2 and MI (M = Na, K, Rb, and NH_4) in the molar ratios 3:1, 2:1, and 1:1 were prepared in a nitrogen atmosphere.

The ^{119}Sn Mössbauer data (Table II) of the products were recorded with the sample and source at 80°K. Barium stannate was used as the source and the spectra were calibrated with a cobalt–stainless steel source and iron absorber at room temperature. The percentage resonance dips were 5–15% for compounds 1 and 3–6, and 20–25% for compounds 2 and 7–16 when approximately 65,000 counts had been accumulated in 256 channels. The data for all compounds except Nos. 11 and 12 were curve-fitted using a standard least-squares Mössbauer curve-fitting program. Room-temperature Mössbauer data were only collected for compounds whose resonance lines were very asymmetric at 80°K. The spectra for compounds 11 and 12 were complex and could have been fitted in various ways. The Mössbauer equipment has been described previously (*11*).

The X-ray diffraction powder data (not given) for the products were obtained with filtered CuKα radiation using Philips 11.64 cm cameras. The compounds MSnIF_2 (M = K, Rb, NH_4) from the melt form an isostructural series. The K and Rb phases $M$$Sn_2IF_4$ are isostructural but the Na and NH_4 species do not belong to the same series, nor are they isostructural with each other. The K, Rb, and NH_4 $M$$Sn_3IF_6$ phases from molten systems are isostructural.

The $KSnIF_2$ and $NaSn_2IF_4$ phases from the aqueous systems yield the same X-ray data as the corresponding phases from the melts. $NaSnIF_2$ is very hygroscopic. The $M$$Sn_3IF_6$ (M = Na or NH_4) compounds from aqueous solutions are isostructural but the K material has a different powder pattern. All of the $M$$Sn_3IF_6$ compounds from solution have different X-ray data from the corresponding molten system products.

Discussion

The Mössbauer data for the $M$$SnIF_2$ phases (M = Na, K, Rb, and NH_4) are given in Table II. The spectrum of $NaSnIF_2$ is a fairly symmetrical doublet, but at 80°K the spectra of the other compounds (M = K, Rb, NH_4) are very asymmetric, low energy:high energy peak heights ratio for Rb and NH_4 compounds being 2:3. The spectrum of NH_4SnIF_2 at room temperature is even less symmetrical, and heating the sample before the spectrum is taken increases the asymmetry of the doublet to 2:5. The Mössbauer data therefore suggest the presence of more than one tin site. Since the molten $RbSnIF_2$ and NH_4SnIF_2 systems give a small quantity of another crystalline phase in addition to the bulk material, the two sites could arise from the existence of two modifications of these compounds. The minor crystalline phases are orthorhombic with cell dimensions a = 19.97 Å, b = 6.23 Å, c = 6.08Å for the Rb system, and a = 20.07 Å, b = 6.18 Å, c = 6.01 Å for the NH_4 system.

Fitting the Mössbauer data to two sites proved to be much better than any fit to one site. The normalized squares errors were reduced by >10% for the two-site fit compared with the one-site fit and gave statistically significant agreement. All of the fitted spectra indicate the presence of one site similar to that in $NaSnIF_2$ and a second site that has a relatively high chemical shift and narrow line width. The quadrupole splittings of the sites with lower chemical isomer shifts are consistent with the presence of Sn(II) as a trihalostannate(II) species, with shifts lower than that of monoclinic SnF_2 (*12*), as expected (*5*). The chemical isomer shifts are all greater and the quadrupole splittings lower than in the corresponding fluorides, $M$$SnF_3$. This would be in keeping with the presence of SnF_2I^- ions with two Sn–F bonds similar to those in the SnF_3^- ion and one longer Sn–I bond. The spectra for the second sites are similar to those obtained from the CsSnX_3 system (*5*) in the orthorhombic tetragonal or cubic structures (*4*, *5*). The relatively high chemical shifts

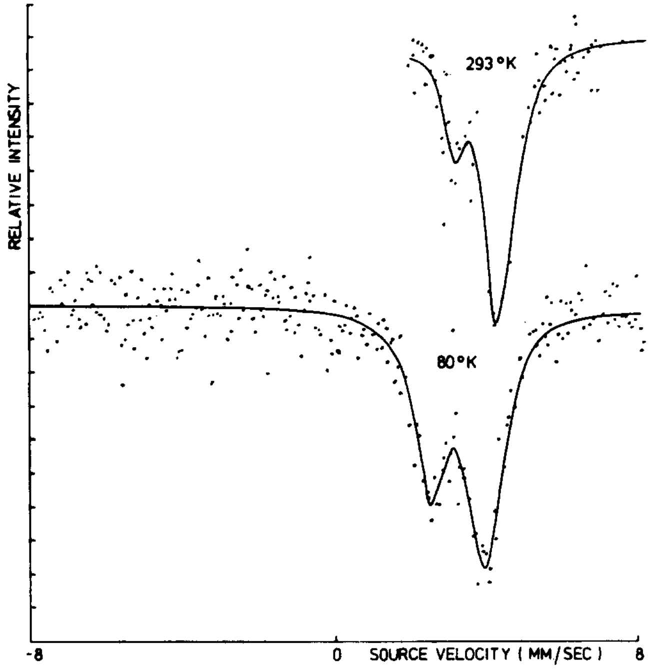

FIG. 1. Mössbauer spectra for NH_4SnF_2I at 80 and 293°K.

and narrow line widths indicate the presence of Sn(II) in an octahedral environment. Figure 1 shows the differences between the spectra for NH_4SnF_2I at 80 and 293°K. The observed variation in the intensities of the spectra for the two types of site with temperature are consistent with a temperature-dependent reversible solid-state equilibrium between two tin sites.

The Mössbauer spectra for the MSn_2IF_4 show the presence of only one site. These compounds have higher chemical isomer shifts and smaller quadrupole splittings than the pentafluorodistannates(II) (*13*). $NaSn_2F_5$ is known to contain discrete $Sn_2F_5^-$ ions and, if the compounds of the series MSn_2IF_4 contain $Sn_2IF_4^-$ ions, it seems likely that the I must be bridging as only one Sn(II) site is seen in the Mössbauer spectra. The spectra of the isomorphous KSn_2IF_4 and $RbSn_2IF_4$ are very similar. The chemical isomer shifts and quadrupole splittings for the MSn_2IF_4 compounds are closer to monoclinic SnF_2 (*12*) than those of the corresponding MSn_2F_5. This means that there must be more *s*-electron density at the Sn nucleus in the fluoride iodides and that the Sn(II) electronic environments are less distorted than in the $Sn_2F_5^-$ ion. Presumably these observations result from the fact that the I^- does not polarize the Sn(II) electrons to the same extent as F^-.

Figure 2 shows where the Mössbauer data for the MSn_2IF_4 compounds fit with the data for the other complex tin(II) fluoride species.

The two products $NaSn_3IF_6$ and KSn_3IF_6 obtained from solution have spectra which are asymmetric and seem to contain more than one tin(II) site. It has not been possible to fit the data to any definite parameters because of the number of different ways in which the spectra

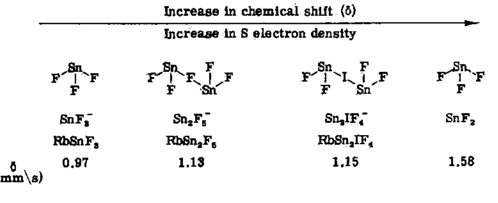

FIG. 2. Mössbauer data for complex tin(II) fluoride species.

can be fitted. Their approximate chemical isomer shifts are, however, close to that of SnF_2, as would be expected if the Sn atoms are bonded to fluorine rather than iodine.

The data for the melts MSn_3F_6I ($M = K$, NH_4, and Rb) show much lower chemical shifts and resolvable quadrupole splittings than the KSn_3F_6I phases from aqueous solution. The Mössbauer data for these three melts are identical within experimental error in agreement with the X-ray results which show them to be isomorphous. The $NaSn_3IF_6$ phases from molten and aqueous system have different Mössbauer data, neither of which are similar to the data of the other MSn_3IF_6 melts ($M = K$, NH_4, and Rb). The chemical isomer shift of the phase from the molten system $NaSn_3IF_6$ is closer to SnF_2 but its quadrupole splitting is of the same order as the other MSn_3IF_6 cooled melt products.

Color in the Fluoride–Iodide Systems

Many of the products are highly colored. The colors are given in Table II. The most strongly colored are those with the highest proportion of iodine (i.e., the $MSnIF_2$ phases). The room-temperature colors of the K, Rb, and NH_4 phases are similar to the orange of SnI_2 while the Na derivative is yellow, like the ternary halides $SnIX$ ($X = F$, Cl). The colors of the $MSnIF_2$ compounds deepen with increasing temperature; above 200°C the Na compound is orange and the others are red. The MSn_2IF_4 phases are all yellow at room temperature and orange at higher temperatures. The MSn_3IF_6 phases are white (Na) and yellow (K, Rb, and NH_4) at room temperature and yellow and orange, respectively, at higher temperatures. All color changes are reversible.

Intense colors in compounds containing tin(II) are usually found only when the tin(II) is present in highly symmetrical, often octahedral, environments (*14*). We have suggested (*4*, *14*, *15*) that these colors and associated electrical properties are due to the population by the tin(II) nonbonding electrons of low-lying nonvalence shell bands formed by the overlap of empty *d*-orbitals either on ligands (e.g., Br in $CsSnBr_3$) or on the Sn(II) itself if the Sn–Sn distance is short enough (e.g., in SnO). If there are no low lying empty *d*-orbitals on the ligands and no Sn–Sn distances less than 4.2 Å, the compounds are usually white (e.g., Sn(II) fluorides (*13*)) and the Sn(II) nonbonding lone-pair distorts its environment.

The Sn(II) iodides and their complexes are intensely colored. The direct population of nonvalence shell bands (formed from the mutual overlap of orbitals on iodine atoms in close contact) by the ns^2 nonbonding electrons is a possible mechanism for the development of these colors. The fact that many iodides not containing electron donors, such as Sn(II), are colored suggests, however, that the iodine atoms themselves can also act as donors in population of solid-state bands. This view would be consistent with the color and electrical properties of solid iodine itself (*16*).

Three possible mechanisms for the production and population of bands in the solids can be considered: (1) that the bands are formed by overlap of empty *d*-orbitals of the iodides and are self-populated by the iodide electrons; (2) that the bands are formed by overlap of empty *d*-orbitals of both the iodide and tin ions and that these are populated only by iodide electrons; and (3) that there is direct population of the band formed by overlapping empty *d*-orbitals on the iodide or iodide and tin by the Sn(II) nonbonding electron pair.

Direct population of nonvalence shell bands in solids containing ions with ns^2 outer electronic configurations seems to be associated with high-symmetry environments for these ions. There is no evidence from the Mössbauer data of the MSn_2IF_4 or MSn_3IF_6 phases for the presence of high-symmetry Sn(II) sites; their data are in fact typical of distorted Sn–F environments. It therefore seems likely that the colors in these phases result from electronic transitions involving only the iodide electrons. The compounds in the series $MSnIF_2$, however, show two distinct tin(II) sites, one of which has the relatively high chemical shift and narrow line width associated with Sn(II) in an octahedral environment. Direct population of nonvalence shell bands by the Sn(II) nonbonding electrons therefore seems likely to be a major contributory mechanism to the solid-state properties of these materials.

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References

1. J. D. Donaldson and B. J. Senior, *J. Chem. Soc.* (*A*) 2358 (1969).
2. M. Goldstein and G. C. Tok, *J. Chem. Soc* (*A*) 2303 (1971).
3. R. J. H. Clark, L. Maresca, and P. J. Smith, *J. Chem. Soc.* (*A*) 2687 (1970).
4. J. Barrett, S. R. A. Bird, J. D. Donaldson, and J. Silver, *J. Chem. Soc.* (*A*) 3105 (1971).
5. J. D. Donaldson and J. Silver, *J. Chem. Soc.* (*A*) 666 (1973).
6. D. R. Laughlin, Thesis, University of London (1974).
7. J. D. Donaldson and D. C. Puxley, *J. C. S. Chem. Comm.* 298 (1972).
8. M. F. A. Dove, R. King, and T. J. King, *J. C. S. Chem. Comm.* 944 (1973).
9. R. R. McDonald, A. C. Larsen, and D. T. Cromer, *Acta Crystallogr.* **17**, 1104 (1964).
10. G. Bergerhoff, L. Goost, and E. Schultz-Rhonhof, *Acta Crystallogr.* **B24**, 803 (1968).
11. S. R. A. Bird, J. D. Donaldson, S. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*) 1311 (1971).
12. J. D. Donaldson, R. Oteng, and B. J. Senior, *Chem. Comm.* 618 (1965).
13. J. D. Donaldson and B. J. Senior, *J. Chem. Soc.* (*A*) 1798 (1966).
14. J. D. Donaldson and J. Silver, *Inorg. Nucl. Chem. Letters* **10**, 537 (1974).
15. J. D. Donaldson, D. R. Laughlin, S. D. Ross, and J. Silver, *J. C. S. Dalton* 1985 (1973).
16. C. H. L. Goodman, private communication.