

44. Complex Tin(II) Fluorides.

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The solid phases obtained from the systems $\text{SnF}_2\text{-NaF-H}_2\text{O}$, $\text{SnF}_2\text{-KF-H}_2\text{O}$, and $\text{SnF}_2\text{-NH}_4\text{F-H}_2\text{O}$ have been studied. X-Ray diffraction data and complete analyses show that two distinct phases, MSnF_3 and MSn_2F_5 , exist ($\text{M} = \text{Na}^+$, K^+ , or NH_4^+). Preliminary evidence for the existence of the pentafluorodistannate(II) ion is discussed.

Of the reports of complex formation between bivalent tin and fluorine, the earliest is that of Wagner,¹ who described the preparation of compounds $2\text{NH}_4\text{F}\cdot\text{SnF}_2\cdot 2\text{H}_2\text{O}$; $2\text{KF}\cdot 3\text{SnF}_2\cdot 2\text{H}_2\text{O}$, and $2\text{NaF}\cdot 3\text{SnF}_2$. More recent studies^{2,3} concern the ions present in aqueous tin(II) fluoride solutions, but the solid derivatives of these ions have received little attention. The existence of the pyramidal trifluorostannate(II) ion, SnF_3^- , has been established by polarography,² infrared and Raman spectroscopy,⁴ and a study of some of its solid derivatives.⁵ Because of the evidence in favour of the pyramidal ion, reports^{3,6} of the existence of the tetrafluorostannate(II) ion, SnF_4^{2-} , appear to be erroneous. Other evidence, such as the fact that tin(II) fluoride is primarily a monofunctional acceptor and that other stannate(II) complexes, e.g., the trichloro- and tribromo-stannate(II) ions,^{7,8} and the dichloroaoquostannate(II) group,⁹ are known to be pyramidal, supports the existence of a trifluoro-complex. A polarographic study² of the ions present in aqueous tin(II) fluoride solutions indicated that the trifluorostannate(II) ion, with a dissociation constant of 1.2×10^{-10} at $\mu 0.8$ and 1.1×10^{-11} at $\mu 2.5$, was the stable and predominant species even at low fluoride concentrations. From this study there was no evidence for the existence of polymeric fluorostannate(II) ions in the system. Muettterties,⁵ in agreement with these results, reported that the only solid derivatives obtainable from aqueous tin(II) fluoride solutions had the composition MSnF_3 ($\text{M} = \text{NH}_4^+$, K^+ , or Cs^+). Aqueous solutions of these derivatives were found to deposit blue-black tin(II) oxide slowly, and to take up oxygen, presumably by complex formation with the oxygen molecule. The only other tin(II) fluoride ion for which there is any evidence is the ion SnF_4^{2-} .^{4,10}

The only recent work on the solid derivatives of the fluorostannate(II) ions, apart from that of Muettterties, is a report¹¹ of the preparation of a salt NH_4SnF_3 and a compound $\text{NaF}\cdot 2\text{SnF}_2$, which have been studied by infrared spectroscopy. Surprisingly, the preparation of sodium trifluorostannate(II) has not been reported. We have studied the systems $\text{SnF}_2\text{-NaF-H}_2\text{O}$, $\text{SnF}_2\text{-KF-H}_2\text{O}$, and $\text{SnF}_2\text{-NH}_4\text{F-H}_2\text{O}$ and have shown by

¹ Wagner, *Ber.*, 1886, **19**, 896.

² Schapp, Davis, and Nebergall, *J. Amer. Chem. Soc.*, 1954, **76**, 5226.

³ Davies, *Trans. Inst. Metal Finishing*, 1954, **31**, 401.

⁴ Kriegsmann and Kessler, *Z. anorg. Chem.*, 1962, **318**, 277.

⁵ Muettterties, *Inorg. Chem.*, 1962, **1**, 342.

⁶ Pugh, *J.*, 1953, 1934.

⁷ Woodward and Taylor, *J.*, 1962, 407.

⁸ Vanderzee and Rhodes, *J. Amer. Chem. Soc.*, 1952, **74**, 4806.

⁹ Grdenić and Kamenar, *J.*, 1961, 3954.

¹⁰ Connick and Poulson, *J. Phys. Chem.*, 1959, **63**, 568.

¹¹ Kriegsmann and Kessler, *Z. anorg. Chem.*, 1962, **318**, 266.

analysis and X-ray diffraction that two distinct phases, MSnF_3 and MSn_2F_5 , can be obtained from each system. We also report some comparative properties of the two types of fluorostannate(II) complex.

EXPERIMENTAL

Preparations and Analyses.—Addition of a solution of alkali-metal, or ammonium, fluoride to a solution of tin(II) fluoride produces a precipitate which is soluble in an excess of the alkali-metal or ammonium fluoride. Precipitation continues until the molar ratio of tin(II) fluoride to alkali-metal or ammonium fluoride is 2 : 1; thereafter, the precipitate redissolves on addition of an excess of fluoride solution, until at molar ratio 1 : 1 the precipitate is completely redissolved. This suggests that the initial precipitate should have the composition MF_2SnF_2 (MSn_2F_5), and dissolves with the formation of the trifluorostannate(II) ion as the fluoride concentration increases. Crystalline derivatives of the trifluorostannate(II) ion can be obtained by evaporation of solutions of tin(II) fluoride and an excess of alkali-metal, or ammonium, fluoride.

Compounds MSn_2F_5 ($\text{M} = \text{Na}^+, \text{K}^+, \text{or } \text{NH}_4^+$) were prepared by addition of alkali-metal or ammonium fluoride to a solution of tin(II) fluoride until the $\text{SnF}_2 : \text{MF}$ ratio was 2 : 1. The precipitates were filtered off, washed with a minimum of cold water, and dried *in vacuo* over potassium hydroxide.

The MSnF_3 complexes were prepared by dissolving tin(II) fluoride and a slight excess of alkali-metal or ammonium fluoride in a minimum of hot water, filtration from any insoluble material, and allowing the filtrate to cool. The crystalline products were filtered off, washed with a minimum of cold water, and dried *in vacuo* over potassium hydroxide. It has been reported⁵ that the trifluorostannates(II) can be recrystallised from water, but we have found that recrystallisation of the pure sodium and potassium derivatives in the absence of an excess of alkali fluoride gave the corresponding pentafluorodistannate(II). Ammonium trifluorostannate(II) can, however, be recrystallised from water.

We determined stannous and total tin by Donaldson and Moser's method.¹² It has been reported¹³ that the presence of fluoride ion interferes with the determination of stannous tin, but no evidence of this was found in the present work. We determined the alkali-metal content by flame photometry, and ammonia by boiling a weighed quantity of the complex in an excess of sodium hydroxide solution. The ammonia evolved was collected in an excess of standard acid, and determined by back-titration of the acid with standard alkali.

We determined fluoride by the following method. A weighed sample, containing about 0.05–0.10 g. of fluoride, was dissolved in water, and the fluoride precipitated as calcium fluoride by addition of an excess of standard calcium solution. The tin was then precipitated as hydrous oxide by addition of a dilute solution of ammonia, and the mixture filtered. Determination of the excess of calcium in the filtrate by titration against standard ethylenediaminetetra-acetic acid¹⁴ solution gave the fluoride content.

The average results of analyses on the six solid fluorostannates(II) are tabulated. These results are in agreement with the percentages calculated for the formulæ given.

Suggested compounds	NH_4SnF_3	$\text{NH}_4\text{Sn}_2\text{F}_5$	NaSnF_3	NaSn_2F_5	KSnF_3	KSn_2F_5
Sn(II) (%)	61.3	68.5	59.9	67.2	55.3	64.3
Total Sn (%)	60.5	68.7	59.2	66.8	54.5	64.3
Metal/ NH_3 (%)	9.3	5.1	11.4	6.1	17.6	10.2
F (%)	29.7	27.9	28.4	26.4	26.4	26.0

Solubility of the Complexes.—The solubilities of the complexes in water and 0.1N-hydrofluoric acid (see below) under a non-oxidising atmosphere at various temperatures were determined by titration¹² of the bivalent tin in the solution. Although the SnF_3^- ion can be extracted from aqueous solutions into ether,¹⁵ we found that none of the complexes was appreciably soluble in any common organic solvent.

Because of the high solubility of some of the complexes, the error in the determination is about 1%; results are therefore quoted only to one part in 100.

¹² Donaldson and Moser, *Analyst*, 1959, **84**, 10.

¹³ Collins and Nebergall, *Analyt. Chem.*, 1962, **34**, 1511.

¹⁴ Schwarzenbach, "Complexometric Titrations," transl., Irving, Methuen, 1957, p. 63.

¹⁵ Kitahara, *Report Sci. Res. Inst. (Japan)*, 1949, **25**, 165.

Solubility of fluorostannate(II) complexes (g. of complex per 100 ml. of solution).

Temp.	In H ₂ O			In 0.1N-HF		
	25°	40°	60°	25°	40°	60°
NH ₄ SnF ₃	59	74	78	59	65	79
NH ₄ Sn ₂ F ₅	4.4	6.4	10.6	8.6	9.3	10.5
NaSnF ₃	9.6	26.6	*	13.5	15.2	*
NaSn ₂ F ₅	5.6	8.4	11.7	6.0	8.1	10.4
KSnF ₃	9.1	13.7	*	11.4	12.8	*
KSn ₂ F ₅	2.50	6.8	12.3	5.1	6.9	9.9

* The pentafluorodistannates(II) recrystallised from these solutions at 60°.

Stability of the Complexes.—All the fluorostannates(II) are stable for several months in contact with dry air, there being no change in analytical composition. On exposure to a moist atmosphere for several days the complexes showed no significant increase in weight and are therefore not hygroscopic. The complexes are fairly resistant to hydrolysis, although a small quantity of material containing about 30% of stannous tin is produced on shaking a dilute (<0.01N) solution of any of the complexes for several hours at room temperature.

The fluorostannates(II) are also fairly resistant to atmospheric oxidation. When air was passed through solutions of the complexes at 25°, only about 2% of the stannous tin had been oxidised after 3 hr. Under the same conditions, most other tin(II) ions in solution would be oxidised appreciably. The thermal decomposition of each of the solid fluorostannates(II) was investigated by heating samples in sealed glass tubes in an oxygen-free atmosphere and identifying the products by X-ray diffraction powder photography.

The complexes decomposed over a range of temperatures; in each case the main products of the decomposition were the alkali-metal, or ammonium, fluoride and tin(II) fluoride. In the case of the ammonium complexes the dissociation products of ammonium fluoride were detected. The decomposition ranges of the complexes are: NH₄SnF₃, 165—210°; NH₄Sn₂F₅, 160—200°; NaSnF₃, 255—260°; NaSn₂F₅, 255—280°; KSnF₃, 260—290°; KSn₂F₅, 260—290°.

Potentiometric Studies of Tin(II) Fluoride Solutions.—Potentiometric measurements were made on the tin-tin(II) ion couple to determine which ions exist in tin(II) fluoride solutions. The cell used consisted of two half-cells Sn|SnClO₄.3M-HClO₄, containing equimolar quantities of tin(II) perchlorate,¹⁶ connected by means of a liquid bridge containing 3M-perchloric acid. To prevent oxidation of the bivalent tin the half-cells were kept in a non-oxidising atmosphere throughout these experiments. The changes in voltage of the cell on addition of solutions of alkali-metal fluoride to one half-cell, and of alkali-metal perchlorate to the other, were measured and plotted against the ratio of the concentrations of tin(II) and fluoride in the solutions. These measurements were carried out for cells containing initial concentrations of tin(II) perchlorate ranging from 0.14M to 1M. The graphs for the more dilute solutions showed only one significant inflection (at an Sn : F ratio of 1 : 3), but those for the more concentrated solutions (initial concentration of tin > 0.3M) also had a significant inflection at an Sn : F ratio of 2 : 5.

Crystallography.—(1) Ammonium trifluorostannate(II) consists of colourless elongated rectangular crystals with cleavage parallel to the elongation. The crystals show parallel extinction and have positive elongation; $n = 1.52$.

Crystal data: NH₄SnF₃, $M = 193.7$. Orthorhombic, $a = 9.43 \pm 0.02$, $b = 6.80 \pm 0.02$, $c = 6.62 \pm 0.02$ Å, $U = 422$ Å³, $D_m = 2.99$ g./c.c. (by displacement of organic solvents). $Z = 4$. $D_c = 3.04$ g./c.c. Filtered Cu- $K\alpha$ radiation; single-crystal rotation and Weissenberg photographs about a .

(2) Ammonium pentafluorodistannate(II) consists of six-sided colourless plates which are pseudohexagonal with $n = 1.51$.

Crystal data: NH₄Sn₂F₅, $M = 350.4$. Orthorhombic $a = 12.86 \pm 0.03$, $b = 10.05 \pm 0.02$, $c = 7.91 \pm 0.02$ Å, $U = 1022$ Å³, $D_m = 3.55$ g./c.c. (by displacement of organic solvents). $Z = 6$. $D_c = 3.42$ g./c.c. Filtered Cu- $K\alpha$ radiation by comparison with the isomorphous potassium pentafluorodistannate(II).

(3) Sodium trifluorostannate(II) consists of colourless elongated rhombohedral crystals with rhombohedral cleavage. The crystals have positive elongation, and are anisotropic with the extinction angle at 20° to the direction of elongation; $n = 1.50$.

Crystal data: NaSnF₃, $M = 198.7$. Monoclinic $a = 10.00 \pm 0.04$ Å, $b = 12.34 \pm 0.04$ Å,

¹⁶ Noyes and Toabe, *J. Amer. Chem. Soc.*, 1917, **39**, 1537.

X-Ray diffraction powder data for complex tin(II) fluorides.

(s, m, w, etc., denote relative intensities; dif. = diffuse.)

	Index of refln.	Calc. d spacings	d (Å)	d (Å)		Index of refln.	Calc. d spacings	d (Å)	d (Å)						
<i>Ammonium trifluorostannate(II).</i>															
5-54	ms	110	5-51	1-965	m	1-468	vvw	10-05	1-961	m	1-326	vw			
5-25	s	101	5-42	1-941	s	1-435	vww	5-04	020	5-03	1-873	m	1-284	vw	
4-72	m	{ 011	4-74	1-877	m	1-407	m	4-13	w	121	4-03	1-824	m	1-273	vw
3-41	vs	200	4-72	1-841	ms	1-387	w	3-58	vs	{ 221	3-54	1-794	ms	1-256	vw
3-28	s	002	3-31	1-797	m	1-332	w	3-36	s	{ 202	3-37	1-695	ms	1-232	vw
2-86	s	{ 310	2-85	1-722	m	1-296	m	3-29	s	{ 030	3-35	1-629	vw	1-212	vw
2-37	s	{ 301	2-84	1-645	mw	1-268	vww	3-19	ms	{ 320	3-26	1-532	vw	1-141	vw
2-20	m	{ 022	2-37	1-627	m	1-258	m	2-81	ms	{ 212	3-19	1-470	vw	1-132	vw
2-16	w	{ 003	2-21	1-590	ms	1-242	vww	2-54	m	{ 222	2-80	1-443	vw		
2-11	m	321	2-19	1-532	vw	1-215	w	2-81	ms	{ 312	2-79	1-407	w		
2-09	m	411	2-11	1-484	mw	1-167	w	2-54	m	{ 013	2-55	1-385	vw		
		113	2-09			1-141	vww	2-34	w	{ 141	2-35	1-369	vww		
								2-34	w	{ 240	2-34				
										{ 023					
								2-21	ms	521	2-20				
								2-12	s	{ 042	2-12				
										{ 512	2-11				
								2-08	m	{ 341, 142	2-09				
										{ 033, 601	2-07				
								2-04	m	{ 403	2-04				
										{ 530					
<i>Sodium trifluorostannate(II).</i>															
6-03	ms	020	6-17	2-99	s	1-764	w	4-53	vs	110	4-50	1-990	s	1-334	w
5-41	s	101	5-52	2-93	m	1-735	vww	3-47	vvs dif.	{ 004	3-43	1-888	m	1-317	w
4-98	ms	{ 201	4-98	2-86	m	1-713	m	3-43	ms	{ 004	3-43	1-806	s	1-296	w
		{ 102		2-70	s	1-664	m	3-20	ms	200	3-19	1-713	m	1-219	w
4-80	vs	{ 121	4-95	2-59	w	1-621	w	3-02	m	104	3-02	1-627	m	1-198	m
		{ 121		2-50	mw	1-598	m	2-85	ms	210	2-85	1-600	vww	1-161	vw
4-55	m	{ 002	4-60	2-42	ms	1-570	w	2-73	s	114	2-73	1-578	s	1-147	vw
		{ 200		2-29	w	1-500	w	2-27	m	220	2-25	1-550	m	1-129	w
4-13	mw	{ 211	4-13	2-25	m	1-461	vww	2-23	vww	221	2-23	1-506	m		
		{ 112		2-20	w	1-417	vww	2-19	m	214	2-19	1-466	m		
3-82	m	{ 022	3-78	2-13	m	1-384	vww	2-12	m	300	2-12	1-411	m		
		{ 220		2-08	m	1-354	w	2-09	vs	301	2-09	1-379	ms		
3-66	vs dif.	{ 131	3-69	2-03	w	1-336	w	2-01	m	310	2-01	1-351	w		
		{ 131		1-986	m	1-326	w								
3-48	s	{ 222	3-46	1-949	w	1-233	vw								
3-33	w	{ 131		1-917	mw	1-212	vw								
3-13	m	{ 221		3-29	1-899	mw	1-186	vw							
		{ 122		3-10	1-866	m	1-162	vw							
				1-848	m	1-131	vw	1-820	mw						
<i>Potassium trifluorostannate(II).</i>															
9-51	m	100	9-45	1-998	m			9-94	mw	010	9-80	1-961	m	1-317	vvw
7-20	m	101	7-17	1-941	w			4-91	m	020	4-90	1-929	m	1-322	vw
4-95	ms	002	4-88	1-892	w			4-13	w	021	4-14	1-791	m	1-310	w
4-48	ms	I02	4-53	1-873	m			3-63	mw	012	3-60	1-767	ms	1-292	m
4-13	ms	102	4-16	1-831	ms			3-41	vs	311	3-44	1-728	m	1-211	vw
3-97	ms	I12	3-96	1-797	m			3-30	m	202	3-31	1-701	m	1-200	w
3-87	vw	211	3-90	1-780	vww			3-27	s	030	3-27	1-634	m	1-164	w
3-49	m	121	3-53	1-747	w			2-94	s	321	2-94	1-593	vvw	1-141	vw
								2-44	w	{ 331	2-44	1-504	w	1-128	w
3-25	vvs	003	3-25	1-732	vww					{ 113		1-474	m		
3-18	s	300	3-15	1-713	vww			2-39	vw	203	2-38	1-437	w		
3-09	s	301	3-10	1-698	vw			2-10	s	502	2-10	1-361	m		
2-98	w	I13	2-96	1-661	vww			2-02	ms	{ 610					
2-87	m	221	2-88	1-629	m					{ 341	2-04				
2-80	w	113	2-80	1-593	w					{ 142					
2-62	m	210	2-61	1-553	w										
2-56	vvw	203	2-56	1-523	vw										
2-48	w	321	2-46	1-476	vww										
2-36	ms	401	2-35	1-433	w										
2-31	w	231	2-31	1-415	vw										
2-25	ms	231	2-26	1-395	w										
2-21	ms	402	2-20	1-365	vww										
2-16	w	223	2-16	1-312	vww										
2-07	w	330	2-05	1-214	vww										
2-09	w	240	2-09	1-200	vww										
<i>Potassium pentafluorodistannate(II).</i>															
9-94	mw		9-94	mw				9-94	mw	010	9-80	1-961	m	1-317	vvw
4-91	m		4-91	m				4-91	m	020	4-90	1-929	m	1-322	vw
4-13	w		4-13	w				4-13	w	021	4-14	1-791	m	1-310	w
3-63	mw		3-63	mw				3-63	mw	012	3-60	1-767	ms	1-292	m
3-41	vs		3-41	vs				3-41	vs	311	3-44	1-728	m	1-211	vw
3-30	m		3-30	m				3-30	m	202	3-31	1-701	m	1-200	w
3-27	s		3-27	s				3-27	s	030	3-27	1-634	m	1-164	w
2-94	s		2-94	s				2-94	s	321	2-94	1-593	vvw	1-141	vw
2-44	w		2-44	w				2-44	w	{ 331	2-44	1-504	w	1-128	w
										{ 113		1-474	m		
2-39	vw		2-39	vw				2-39	vw	203	2-38	1-437	w		
2-10	s		2-10	s				2-10	s	502	2-10	1-361	m		
2-02	ms		2-02	ms				2-02	ms	{ 610					
										{ 341	2-04				
										{ 142					

$c = 10.00 \pm 0.04$ Å, $\beta = 113^\circ$. $U = 1135$ Å³, $D_m = 3.52$ g./c.c. (by displacement of organic solvents). $Z = 12$. $D_c = 3.49$ g./c.c. Filtered Cu- $K\alpha$ radiation; single-crystal rotation and Weissenberg photographs about b .

(4) Sodium pentafluorodistannate(II) consists of colourless acicular crystals with straight extinction and positive elongation: $n = 1.55$.

Crystal data: NaSn_2F_5 , $M = 355.4$. Tetragonal $a = 6.37 \pm 0.02$ $c = 13.71 \pm 0.02$ Å, $U = 556$ Å³, $D_m = 4.29$ g./c.c. (by displacement of organic solvents). $Z = 4$. $D_c = 4.24$ g./c.c. Filtered Cu- $K\alpha$ radiation; single-crystal rotation and Weissenberg photographs about c .

(5) Potassium trifluorostannate(II) consists of colourless rectangular crystals with parallel cleavage, straight extinction and positive elongation: $n = 1.51$.

Crystal data: KSnF_3 , $M = 214.8$. Monoclinic $a = 9.51 \pm 0.02 \text{ \AA}$, $b = 8.12 \pm 0.02 \text{ \AA}$, $c = 9.81 \pm 0.02 \text{ \AA}$, $\beta = 96^\circ$, $U = 754 \text{ \AA}^3$, $D_m = 3.88 \text{ g./c.c.}$ (by displacement of organic solvents). $Z = 8$, $D_c = 3.79 \text{ g./c.c.}$ Filtered $\text{Cu}-K_\alpha$ radiation; single-crystal rotation and Weissenberg photographs about b .

(6) Potassium pentafluorodistannate(II) consists of colourless six-sided plates; $n = 1.54$.

Crystal data: KSn_2F_5 , $M = 371.5$. Orthorhombic $a = 12.54 \pm 0.03 \text{ \AA}$, $b = 9.80 \pm 0.02 \text{ \AA}$, $c = 7.71 \pm 0.02 \text{ \AA}$, $U = 948 \text{ \AA}^3$, $D_m = 4.07 \text{ g./c.c.}$ (by displacement of organic solvents). $Z = 6$, $D_c = 3.90 \text{ g./c.c.}$ Filtered $\text{Cu}-K_\alpha$ radiation; single-crystal rotation and Weissenberg photographs about c .

An annexed Table contains the X -ray diffraction powder data of all six complexes, obtained by using an 11.64-cm. camera with $\text{Cu}-K_\alpha$ radiation. The d spacings longer than 2.00 \AA [3.00 \AA in the case of sodium trifluorostannate(II)] have been indexed.

DISCUSSION

Two distinct solid phases can be obtained from the system $\text{MF}-\text{SnF}_2-\text{H}_2\text{O}$ ($\text{M} = \text{Na}^+$, K^+ , or NH_4^+), with compositions MSnF_3 and MSn_2F_5 , respectively, their existence being proved by complete analyses and by X -ray diffraction studies. The compounds MSnF_3 are derivatives of the stable and well-documented trifluorostannate(II) ion, but the series MSn_2F_5 is not obviously derived from any known ion. The fact that the MSn_2F_5 phases are immediately precipitated on addition of an alkali-metal or ammonium ion to an excess of tin(II) fluoride suggests the presence of an ion Sn_2F_5^- in solution. Moreover, we have shown that recrystallisation of pure sodium or potassium trifluorostannate(II) from hot water gives the corresponding pentafluorodistannate(II); this also suggests that the pentafluorodistannate(II) ion is present, in considerable concentration, in solutions with an insufficient excess of fluoride for conversion of all the tin into trifluorostannate(II). This argument can be strengthened by studies of a solution of tin(II) fluoride of concentration just sufficient to give a precipitate of the KSn_2F_5 phase on addition of a trace of potassium ion. For such a solution, it can be shown that the concentration of tin present as pentafluorodistannate(II) (estimated from the solubility of KSn_2F_5) is more than half the total tin present in anionic form (estimated by ion-exchange). The evidence of potentiometric titration is also consistent with the existence of a polynuclear Sn_2F_5^- ion. Additional physicochemical studies of the solid pentafluorodistannates(II) and their solutions are in progress in order further to characterise this ion. The existence of the polynuclear ion is easily explained on the basis of the outer electronic configuration of the tin(II) ion because, in view of the stability² of the pyramidal trifluorostannate(II) ion, in which hybridisation of the tin atom is sp^3 , it would be reasonable to suppose that tin would tend to adopt this configuration whenever possible.

The formation of the pentafluorodistannate(II) ion, containing a bridging fluorine atom, would thus occur in solutions containing insufficient fluoride to convert all the tin into trifluorostannate(II), in this way maintaining a pyramidal configuration of fluorine atoms about the tin atom. This is supported by the observation that precipitation of the MSn_2F_5 phases on addition of a solution of alkali-metal, or ammonium, fluoride to a solution of tin(II) fluoride is a maximum when the molar ratio of tin(II) fluoride to alkali fluoride is $2 : 1$, and that further addition of the alkali-metal, or ammonium, fluoride dissolves some of the precipitate. Dissolution is complete when the molar ratio is $1 : 1$. Although the existence of a polynuclear basic tin(II) ion $[\text{Sn}_3(\text{OH})_4]^{2+}$ containing bridging oxygen atoms¹⁷ is well established, this is the first report of the existence of a polynuclear fluorotin(II) ion containing a bridging fluorine atom.

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¹⁷ Tobias, *Acta Chem. Scand.*, 1958, **12**, 198; Donaldson and Moser, *J.*, 1961, 1996; Donaldson, Moser, and Simpson, *J.*, 1963, 1727.