Fluorostannates(II): The Non-transition-metal(II) Derivatives of the Complex Tin(II) Fluoride Ions

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The aqueous and molten SnF_2–MF_2 (M = Mg, Ca, Sr, Ba, and Pb) systems have been studied and the preparation of the crystalline trifluorostannates(II) $Sr(SnF_3)_2$, $Ba(SnF_3)_2$, $PbFSnF_3$, $Sr_2Sn_2NO_3F_7,2H_2O$, and $Pb_2SnNO_3F_5,2H_2O$ described. The infrared and ^{119}Sn Mössbauer spectra of these materials are consistent with the presence of the SnF_3^- ion in all of them. There is no evidence for tin–nitrate bonding in the nitrate-containing phases but there is an increase in the ionic character of the Sn–F bonds compared with the metal(II) trifluorostannates(II). No derivative of the $Sn_2F_5^-$ ion was isolated from aqueous solutions but features attributable to such compounds were found in the phase diagrams of the molten systems, and the solid complexes $Sr(Sn_2F_5)_2$ and $Ba(Sn_2F_5)_2$ were prepared.

THE existence of the trifluorostannate(II) and pentafluorodistannate(II) ions in aqueous solutions[1,2] of tin(II) fluoride and in metal fluoride–tin(II) fluoride melts[3] has already been confirmed. Well characterised alkali-metal derivatives of both complex ions have been prepared[2–5] from both aqueous and molten systems. The environment of the tin atom in these trifluoro- and pentafluorodi-stannate(II) derivatives is pyramidal[6,7] and can be explained on the basis of sp^3 hybridisation of the tin(II) orbitals. The Mössbauer spectra[8,9] of tin(II) fluorides do, however, suggest that electrostatic effects as well as sp^3 hybridisation may be important when describing the tin–fluorine bonds. The relative stability of the trico-ordination of tin in its 2+ compounds is a feature[10,11] of the chemistry of the element in this oxidation state. In the $Sn_2F_5^-$ ion, which forms in solutions containing insufficient fluoride to complex all of the tin as SnF_3^-, the pyramidal configuration of the tin atom is maintained in a polynuclear ion in preference to the formation of a species of lower co-ordination.

We now show that the addition of strontium(II), barium(II), or lead(II) ions to an aqueous solution of tin(II) fluoride results in the immediate precipitation of crystalline metal(II) trifluorostannate(II) phases and not of the insoluble metal(II) fluorides.

We also show that, although metal(II) derivatives of the pentafluorodistannate(II) ion could not be obtained from aqueous solution, some of them can be prepared from tin(II) fluoride–metal(II) fluoride melts.

In the study of the aqueous tin(II)–metal(II)–fluoride systems the metal(II) nitrates were used as the source of metal(II) ions, and it was found that the product obtained depended on which of the ions were present in excess at the onset of precipitation. The addition of solid metal(II) nitrate, or its saturated solution, to a solution of tin(II) fluoride resulted in the immediate precipitation of a metal(II) trifluorostannate(II). Pure crystalline Sr^{2+}, Ba^{2+}, and PbF^+ trifluorostannate(II) derivatives were prepared in this way, but no similar Mg^{2+} or Ca^{2+} material could be obtained. Presumably the magnesium and calcium ions are too small to form a stable crystalline arrangement with the trifluorostannate(II) ion. The addition of solid tin(II) fluoride, or its saturated solution, to a solution of some of the metal(II) nitrates, resulted in the precipitation not of the metal(II) trifluorostannate(II) but of tin(II) materials containing fluoride and nitrate.

Crystalline nitrate-containing phases were isolated from the strontium and lead but not from the barium systems. Again, no magnesium derivative could be isolated but the calcium system gave non-crystalline products, of variable tin(II) content, which decomposed on recrystallisation. The calcium derivatives had similar properties to the other nitrate-containing materials but could not be isolated as a pure distinct phase. The mean analytical data for two typical samples of each of the fluorostannates(II) and their suggested formulae are given in Table 1.

TABLE 1

Analyses of metal(II) fluorostannates(II)

Suggested compounds:	$Sr(SnF_3)_2$ 1	2	Reqd.	$Ba(SnF_3)_2$ 1	2	Reqd.	$PbF{\cdot}SnF_3$ 1	2	Reqd.
Sn^{II} (%) ...	54·3	54·3	54·1	48·1	48·4	48·6	29·6	29·3	29·5
Total Sn (%)	54·4	54·7	54·1	48·2	48·8	48·6	29·3	29·4	29·5
Metal(II) (%)	20·2	19·8	20·0	28·2	28·5	28·1	51·8	51·8	51·6
Fluoride (%)	26·0	26·2	26·0	23·3	23·3	23·3	18·7	18·8	18·9

Suggested compounds:	$Sr_2Sn_2NO_3F_7,2H_2O$ 1	2	Reqd.	$Pb_2SnNO_3F_5,2H_2O$ 1	2	Reqd.
Sn^{II} (%)	36·5	36·6	36·8	16·3	16·4	16·4
Total Sn (%) ...	36·6	36·5	36·8	16·4	16·6	16·4
Metal(II) (%) ...	27·0	27·1	27·2	57·1	57·2	57·1
Fluoride (%) ...	20·4	20·5	20·7	13·4	13·0	13·1
Nitrate (%) ...	9·4	9·7	9·6	9·9	9·6	8·5
Water (%)	5·9	5·5	5·6	4·7	4·8	5·0

Since the studies of aqueous solutions provided no

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[10] J. D. Donaldson, 'A Review of the Chemistry of Tin(II) Compounds,' Tin Research Institute Publication No. 348, 1964.

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evidence for the formation of metal(II) pentafluorodistannates(II), the possible existence of these materials was investigated by using transition-point data to plot the phase diagrams for the molten MF_2–SnF_2 systems (M = Ca, Sr, Ba, and Pb). The range of compositions studied by this technique was limited to samples containing more than 40 moles % of tin(II) fluoride because of the insolubility of an excess of the metal(II) fluorides in tin(II) fluoride. The phase diagrams (Figure 1) for the calcium, strontium, and barium systems display two features that can be attributed to congruently melting phases corresponding to trifluoro- and pentafluorodistannates(II), respectively. In the strontium and barium systems both the trifluoro- and pentafluorodi-stannates(II) were identified (*X*-ray powder data) in the products from the cooled melts and the trifluorostannate(II) phases were found to be identical with those prepared from aqueous solution. The stoicheiometry of the new pentafluorodistannate(II) phases, $M(Sn_2F_5)_2$ (M = Sr or Ba), was confirmed by chemical analysis. There was no evidence for the existence of calcium derivatives of the complex tin(II) fluoride ions in the cooled products and the *X*-ray powder patterns contained only lines attributable to calcium fluoride and tin(II) fluoride; their existence as high-temperature phases cannot, however, be ruled out. The phase diagram (Figure 2) for the PbF_2–SnF_2 system displays features attributable to three congruently melting phases corresponding to $Pb(Sn_2F_5)_2$, $Pb(SnF_3)_2$ or $PbFSn_2F_5$, and $PbFSnF_3$. Of these the only material, other than tin(II) fluoride or lead fluoride, which could be identified in the cooled melts was a $PbFSnF_3$ phase identical with that prepared from aqueous solution. Again the possibility of the existence of high-temperature phases corresponding to the other features on the phase diagram cannot be ruled out.

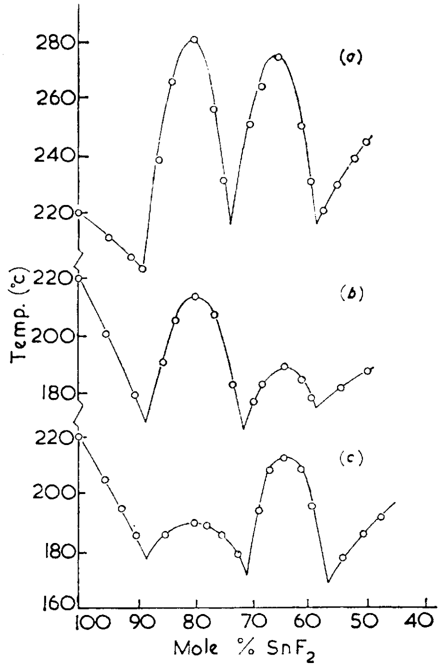

FIGURE 1 Phase diagrams for (*a*) SnF_2–CaF_2, (*b*) SnF_2–SrF_2, and (*c*) SnF_2–BaF_2

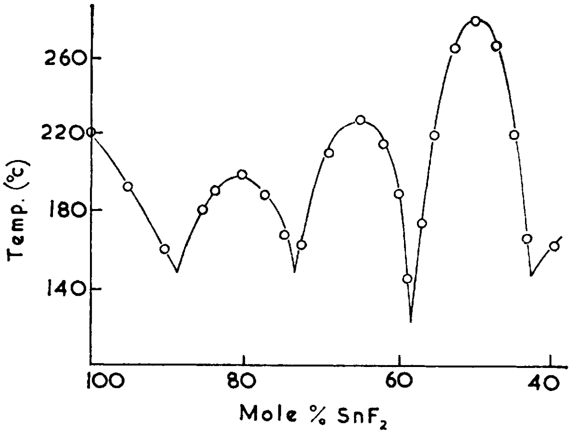

FIGURE 2 Phase diagram for the PbF_2–SnF_2 system

TABLE 2

Melting or decomposition temperatures of the trifluorostannates(II)

	$Sr(SnF_3)$	$Ba(SnF_3)_2$	$PbF{\cdot}SnF_3$
M. p.	630—625°	880—885°	494—497°
D. p.	—	—	—

	$Sr_2Sn_2NO_3F_7,2H_2O$	$Pb_2SnNO_3F_5,2H_2O$
M. p.	—	—
D. p.	220—222°	220—224°

The fluorostannates(II) described are stable when stored *in vacuo* over potassium hydroxide. After several months, no change was detectable in their analytical compositions, or in their *X*-ray diffraction powder patterns. On exposure to a moist atmosphere for several days the complexes showed no significant increase in weight and are therefore not hygroscopic. The thermal stability of the materials was studied by use of a vacuum grid and a melting point apparatus. The melting or decomposition temperatures are given in Table 2. The strontium, barium, and lead trifluorostannates(II) melted without decomposition, but the nitrate-containing phases decomposed explosively. The solid products resulting from decomposition *in vacuo* were tin(IV) oxide and metal(II) fluoride (*X*-ray diffraction powder data) and the main gaseous products were dinitrogen tetroxide, nitrogen dioxide, nitrous oxide, nitrosyl fluoride, nitryl fluoride, difluorodiazine, and water (infrared characterisation). The formation of tin(IV) oxide by an internal oxidation–reduction reaction [12] can be attributed to the presence of the oxidising nitrate group. The decomposition of the nitrate-containing phases, however, gives little indication of the environment of the tin atom in these materials because the thermal decomposition of a mixture of metal(II) trifluorostannate(II) and metal(II) nitrate gives the same solid products as the complexes. The solu-

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[12] J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 1961, 1966.

bilities of the complexes in water, 0·1N-hydrofluoric acid, and 0·1N-nitric acid are given in Table 3. None of the materials was appreciably soluble in organic solvents such as ethanol, dimethylformamide, or tetrahydrofuran.

TABLE 3

Solubility of the metal(II) fluorostannates(II) (g./100 ml. of solution)

Solvent	H_2O				0·1N-HF				0·1N-HNO_3			
Temp.	25°	40°	60°	80°	25°	40°	60°	80°	25°	40°	60°	80°
$Sr(SnF_3)_2$	0·313	0·423	0·663	0·755	0·396	0·514	0·761	1·09	1·06	1·48	1·79	2·32
$Ba(SnF_3)_2$	0·190	0·268	0·443	0·810	0·221	0·391	1·020	1·30	1·00	1·33	2·09	2·51
$PbF{\cdot}SnF_3$	0·159	0·196	0·369	0·473	0·209	0·297	0·576	1·33	1·09	1·90	2·15	2·42
$Sr_2Sn_2NO_3F_7,2H_2O$	0·145	0·159	0·241	0·344	0·153	0·228	0·678	1·03	0·820	1·33	2·44	3·04
$Pb_2SnNO_3F_5,2H_2O$	0·251	0·766	1·14	1·56	0·257	0·800	1·23	1·62	0·884	2·60	3·48	6·12

The Infrared Spectra of the Trifluorostannates(II).—An assignment of the vibrational spectra of the trifluorostannate(II) ion was included in a recent study [6] of the spectra of the triligandstannate(II) species. The infrared spectra of the trifluorostannates(II) prepared in this work are all consistent with the presence of the SnF_3^- ion in their structures (see Table 4). There is also some evidence, from the splitting of the ν_3 vibrations in the barium and lead derivatives, to suggest that the pyramidal co-ordination of the tin atom is not regular. The band at 562 cm.$^{-1}$ in the lead derivative is consistent with the presence of PbF^+ in this material. The spectra of the nitrate-containing phases also suggests the presence of the SnF_3^- group and the bands in these spectra in the region 550—590 cm.$^{-1}$ can be assigned to the librational modes of the water present in the lattice. The vibrational frequencies for the nitrate groups in the complex fluorides are very similar to those in the metal(II) nitrates (Table 5) and it seems likely that the nitrate is essentially ionic and that there is no tin–nitrate bonding.

TABLE 4

Infrared spectra of the metal(II) trifluorostannates(II) (cm.$^{-1}$)

Assignment	Librational modes of water	PbF	SnF_3^- $\nu_3+\nu_4$	ν_1	ν_3
$Sr(SnF_3)_2$			505	427	370
$Ba(SnF_3)_2$			495, 476	434	374, 362
$PbF{\cdot}SnF_3$		562	467	443	376, 350
$Sr_2Sn_2NO_3F_7,2H_2O$	588			417	
$Pb_2SnNO_3F_5,2H_2O$	560			400	375, 355

TABLE 5

Infrared spectra of strontium and lead nitrates and of the nitrate-containing phases (cm.$^{-1}$)

$Sr(NO_3)_2$	2450	2150	1790	1440	1360
$Pb(NO_3)_2$			1780	1390	1300
$Sr_2Sn_2NO_3F_7,2H_2O$		3440	1660	1380	
$Pb_2SnNO_3F_5,2H_2O$		3400	1660	1380	
$Sr(NO_3)_2$			850	815	740
$Pb(NO_3)_2$	1080	1020	830	808	726
$Sr_2Sn_2NO_3F_7,2H_2O$	1350	1050	820	710	
$Pb_2SnNO_3F_5,2H_2O$		1045	818	710	

The Mössbauer Spectra of the Nitrate-containing Fluorostannates(II).—The Mössbauer parameters of $Sr(SnF_3)_2$, $Ba(SnF_3)_2$, and $PbFSnF_3$, and of $Sr(Sn_2F_5)_2$ and $Ba(Sn_2F_5)_2$ have been described previously and were shown to be consistent with the presence of the SnF_3^- and $Sn_2F_5^-$ ions, respectively. The spectra of the nitrate-containing complex tin(II) fluorides are given in Table 6, together with those of the metal(II) trifluorostannates(II) for comparison. The similarity in the chemical shift (δ) and quadrupole splitting (Δ) results for $Sr_2Sn_2NO_3F_7,2H_2O$ and $Pb_2SnNO_3F_5,2H_2O$ suggests that the environment of the tin atoms in these materials is identical in spite of the difference in chemical composition. Since the disagreement over the sign of $\Delta R/R$ has now been resolved [13] in favour of a positive value, the chemical shifts for the complex fluorides can be discussed in terms of the tin–fluoride bond character. The increase in the positive chemical shift in going from a metal(II) trifluorostannate(II) to the corresponding nitrate-containing complex represents an increase in the 5*s*-electron density of the tin nucleus and therefore in the ionic character of the tin–fluorine bonds. This is consistent (Table 6) with the decrease in the ν_1 stretching frequency in the infrared spectra of these materials. Similar chemical shift and infrared correlations are to be found between $PbF{\cdot}SnF_3$ and $Sr(SnF_3)_2$ and between $Sr_2Sn_2{\cdot}NO_3F_7,2H_2O$ and $Pb_2SnNO_3F_5,2H_2O$. If a value of 5·6 mm./sec. relative to grey-tin is assumed [8] for the chemical shift of the $5s^2$ ion, the shifts of the materials described here correspond to 5*s*-electron densities at the tin nucleus that are 20—25% in excess of that for grey-tin. Comparison of the quadrupole splittings for the metal(II) trifluorostannates(II) with those of the corresponding nitrate-containing phases suggests that the overall asymmetry of the environment of the tin atom is greater in the latter materials.

TABLE 6

Mössbauer and infrared data for metal(II) fluorostannates(II)

	Mössbauer δ (mm./sec.) *	Δ (mm./sec.)	Infrared ν_1 (cm.$^{-1}$)
$Sr_2Sn_2NO_3F_7,2H_2O$	1·35	1·30	417
$Sr(SnF_3)_2$	1·19	1·75	427
$Pb_2SnNO_3F_5,2H_2O$	1·38	1·32	400
$PbF{\cdot}SnF_3$	1·22	1·66	443

* δ relative to α-Sn.

[13] J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and R. G. T. Emery, *Phys. Rev. Letters*, 1966, **17**, 809.

Crystallography.—$Sr(SnF_3)_2$ consists of colourless, elongated rectangular crystals, with cleavage parallel to the elongation. Crystal data: $n = 1{\cdot}74$, $M = 439{\cdot}0$, Orthorhombic, $a = 9{\cdot}83 \pm 0{\cdot}02$, $b = 8{\cdot}62 \pm 0{\cdot}02$, $c = 7{\cdot}17 \pm 0{\cdot}02$ Å, $U = 607{\cdot}7$ Å^3, $D_m = 4{\cdot}74$ g./c.c. (by displacement of organic solvents), $Z = 4$, $D_c = 4{\cdot}80$ g./c.c.

TABLE 7

X-Ray diffraction powder data for the metal(II) fluorostannates(II)

d (Å)	Index of reflection	Calc. *d* spacing (Å)	*d* (Å)	Index of reflection	Calc. *d* spacing (Å)
$Sr(SnF_3)_2$					
4·88mw	2 0 0	4·91	1·925mw	2 2 3	1·925
4·07mw	2 0 1	4·05	1·840m	0 3 3	1·837
3·67vvs	2 1 1	3·67	1·763mw	1 0 4	1·763
3·49w	1 2 1	3·46	1·735m	5 2 1	1·735
3·27vvs	3 0 0	3·28	1·702mw	1 5 0	1·698
3·16vs	1 1 2	3·14	1·691mw	5 1 2	1·690
2·99vs	3 0 1	2·98	1·635mw	1 2 4	1·632
2·57mw	1 3 1	2·57	1·607m	3 4 2	1·609
2·44mw	3 2 1	2·45	1·526vvw	3 5 0	1·526
2·30w	0 1 3	2·30	1·494w	5 1 3	1·495
2·13m	4 2 0	2·14	1·459w		
2·05m	4 2 1	2·05	1·424w		
1·969m	4 1 2	1·971	1·390vvw		
1·959m	5 0 0	1·965			
$Ba(SnF_3)_2$					
8·69w	0 1 0	9·30	2·14w	6 1 1	2·14
4·96w	3 0 0	5·06	2·10m	0 1 2	2·10
4·33vs	0 0 1	4·31	2·017m	2 1 2	2·02
3·99w	2 2 0	3·98	1·980m	2 4 1	1·978
3·84w	4 0 0	3·84	1·926vw	8 0 0	1·921
3·59vw	4 1 0	3·55	1·893vvw	2 2 2	1·895
3·47vs	2 1 1	3·48	1·826vw	3 2 2	1·827
3·29vs	3 0 1	3·30	1·799ms	7 2 1	1·803
3·20vs	0 2 1	3·16	1·765mw	5 0 2	1·764
3·10mw	1 2 1	3·10	1·720mw	6 4 0	1·722
2·92mw	5 1 0	2·92	1·648mw	6 0 2	1·649
2·48m	1 3 1	2·48	1·626vvw	6 1 2	1·623
2·39m	2 3 1	2·39	1·440vvw	0 0 3	1·436
2·25mv	6 2 0	2·24		4 6 0	1·438
PbF·SnF_3					
11·33s	0 0 1	11·35	2·06s	0 2 1	2·07
5·65vvw	0 0 2	5·68		2 0 1	
4·13vw	0 1 0	4·20	1·892vw	0 0 6	1·892
			1·787s	1 2 2	1·785
3·94vvw	0 1 1	3·94		2 1 2	
			1·729m	0 1 6	1·726
3·39vvs	1 0 3	3·38		1 0 6	
	0 1 2		1·692m	0 2 4	1·689
2·98s	1 1 0	2·97		2 0 4	
2·85s	0 0 4	2·84	1·518vvw	0 1 7	1·519
2·34vw	1 1 3	2·34	1·488vvw	2 2 0	1·486
2·27vw	0 0 5	2·27	1·421w		
2·11s	0 2 0	2·10	1·362mw		
			1·334w		
$Sr_2Sn_2NO_3F_7,2H_2O$					
12·11s	1 0 0	11·49	1·811w	3 1 2	1·810
6·01s	2 0 0	5·97	1·762w	0 4 1	1·763
3·96vvw	1 0 1	3·97	1·722ms	4 0 2	1·721
3·63w	1 1 1	3·65	1·682m	4 1 2	1·680
3·56s	3 1 0	3·54	1·619w	1 3 2	1·619
3·24s	2 2 0	3·26	1·584w	7 0 1	1·581
2·99s	4 0 0	2·99	1·497w	8 0 0	1·493
2·56w	2 2 1	2·56	1·446w	6 0 2	1·446
2·39w	5 0 0	2·39	1·415w	2 5 1	1·416
2·20w	0 3 1	2·21	1·349w		
2·10s	0 0 2	2·11	1·327w		
2·07vw	2 3 1	2·07	1·312w		
1·999w	6 0 0	1·990	1·294w		
1·981w	2 0 2	1·986	1·280w		
1·829mw	1 2 2	1·829			

TABLE 7 (*Continued*)

d (Å)	Index of reflection	Calc. *d* spacing (Å)	*d* (Å)	Index of reflection	Calc. *d* spacing (Å)
$Pb_2SnNO_3F_5,2H_2O$					
12·10m	2 0 0	12·09	2·97vs	6 0 1	2·93
6·07w	2 1 0	6·05	2·74vvw	8 1 0	2·77
4·16vvw	1 0 1	4·21	2·34w	0 3 0	2·33
4·01w	2 0 1	4·04	2·12w	9 2 0	2·13
3·65s	0 1 1	3·65	2·02vw	2 1 2	2·02
3·51s	2 1 1	3·50	1·886vw	5 1 2	1·885
3·34ms	3 1 1	3·33	1·858vw	8 3 0	1·844
3·15ms	4 1 1	3·13	1·762vw	7 1 2	1·761
3·03m	4 2 0	3·02	1·740vw	1 4 0	1·742
$Sr(Sn_2F_5)_2$					
5·66vw	2 0 0	5·80	2·08ms	3 2 0	2·09
4·08m	0 0 2	4·17	2·02m	4 0 3	2·01
3·76vvw	2 1 0	3·77	1·998w		
3·45m	2 1 1	3·44	1·960w		
3·23s	0 1 2	3·19	1·817vw		
2·89mw	4 0 0	2·90	1·781vw		
2·83m	3 0 2	2·84	1·763vvw		
2·49vvw	2 0 3	2·51			
	4 1 0				
$Ba(Sn_2F_5)_2$					
3·79w	0 2 0	3·78	2·68vvw	−1 1 3	2·66
3·64w	1 0 3	3·57		−3 1 1	
(diffuse)	3 0 1		2·61vvw	1 2 3	2·60
3·53w	−1 2 0	3·54		3 2 1	
	0 2 1		2·55vvw	2 2 3	2·54
3·45ms	−2 1 1	3·47		3 2 2	
	−1 1 2		2·43ms	1 3 1	2·43
3·31s	−3 0 0	3·31	2·15ms	2 0 5	2·15
	0 0 3			5 0 2	
3·20s	−1 2 1	3·20	2·10s	1 0 5	2·11
3·06ms	−3 1 0	3·04		5 0 1	
	0 1 3		2·04ms	2 3 3	2·04
	3 1 0			3 3 2	
2·83vvw	−3 0 1	2·84	2·00ms	−3 0 3	2·00
	−1 0 3		1·912s	−4 2 1	1·915
2·76vvw	3 1 3	2·76	1·819ms	−5 0 1	1·823
				−1 0 5	

$Ba(SnF_3)_2$ consists of colourless fibres. Crystal data: $n = 1{\cdot}68$, $M = 488{\cdot}8$, Orthorhombic, $a = 15{\cdot}38 \pm 0{\cdot}02$, $b = 9{\cdot}32 \pm 0{\cdot}02$, $c = 4{\cdot}31 \pm 0{\cdot}05$ Å, $U = 617{\cdot}8$ Å^3, $D_m = 4{\cdot}90$ g./c.c., $Z = 4$, $D_c = 5{\cdot}27$ g./c.c.

$PbFSnF_3$ consists of colourless elongated rectangular crystals with cleavage parallel to the elongation. Crystal data: $n = 1{\cdot}75$, $M = 401{\cdot}9$, Tetragonal, $a = 4{\cdot}20 \pm 0{\cdot}02$, $c = 11{\cdot}36 \pm 0{\cdot}03$ Å, $U = 200{\cdot}6$ Å^3, $D_m = 6{\cdot}60$ g./c.c., $Z = 2$, $D_c = 6{\cdot}65$ g./c.c.

$Sr(Sn_2F_5)_2$ consists of colourless elongated rectangular crystals. Crystal data: $n = 1{\cdot}69$, $M = 752{\cdot}4$, Orthorhombic, $a = 11{\cdot}62 \pm 0{\cdot}03$, $b = 4{\cdot}97 \pm 0{\cdot}02$, $c = 8{\cdot}33 \pm 0{\cdot}02$ Å, $U = 481{\cdot}1$ Å^3, $D_m = 4{\cdot}9$ g./c.c., $Z = 2$, $D_c = 5{\cdot}2$ g./c.c.

$Ba(Sn_2F_5)_2$ consists of colourless elongated rectangular crystals. Crystal data: $n = 1{\cdot}79$, $M = 802{\cdot}2$, Monoclinic, $a = 10{\cdot}73 \pm 0{\cdot}03$, $b = 7{\cdot}59 \pm 0{\cdot}02$, $c = 10{\cdot}73 \pm 0{\cdot}03$ Å, $\beta = 68°$, $U = 796{\cdot}0$ Å^3, $D_m = 6{\cdot}4$ g./c.c., $Z = 4$, $D_c = 6{\cdot}70$ g./c.c.

$Sr_2Sn_2NO_3F_7,2H_2O$ consists of colourless plates. Crystal data: $n = 1{\cdot}63$, $M = 643{\cdot}7$, Orthorhombic, $a = 23{\cdot}90 \pm 0{\cdot}04$, $b = 7{\cdot}77 \pm 0{\cdot}02$, $c = 4{\cdot}21 \pm 0{\cdot}02$ Å, $U = 781{\cdot}6$ Å^3, $D_m = 5{\cdot}00$ g./c.c., $Z = 4$, $D_c = 5{\cdot}47$ g./c.c.

$Pb_2SnNO_3F_5,2H_2O$ consists of colourless plates. Crystal data: $n = 1{\cdot}78$, $M = 726{\cdot}2$, Orthorhombic, $a = 24{\cdot}16 \pm 0{\cdot}04$, $b = 8{\cdot}80 \pm 0{\cdot}02$, $c = 4{\cdot}28 \pm 0{\cdot}02$ Å, $U = 910{\cdot}7$ Å^3, $D_m = 5{\cdot}10$ g./c.c., $Z = 4$, $D_c = 5{\cdot}27$ g./c.c.

The X-ray diffraction powder data for the materials are given in Table 7.

EXPERIMENTAL

Preparative.—The crystalline metal(II) trifluorostannate (II) materials, free from nitrate impurity, were prepared by the addition of hot saturated solution of metal(II) nitrate to an aqueous soution of tin(II) fluoride (30% w/v) at 90°, under oxygen-free nitrogen until the precipitate just formed. This precipitate was redissolved by the addition of a minimum of 1N-nitric acid and the resultant solution cooled. The product was filtered off, washed with a minimum of cold water, and recrystallised from 10% (w/v) aqueous solution of tin(II) fluoride. The *product* was again washed with a minimum of cold water and then dried *in vacuo* (KOH).

The nitrate-containing *phases* were prepared under the same experimental conditions except that hot tin(II) fluoride solution was added to the metal(II) nitrate solution, and the products were recrystallised from a solution of metal(II) nitrate (10% w/v in 1N-nitric acid).

Analysis.—Stannous and total tin were determined by Donaldson and Moser's method [14] and fluoride by Leonard's method [15] after distillation of the fluoride from the sample as hydrofluorosilicic acid. The metal(II) and nitrate contents were determined gravimetrically as metal(II) sulphate and nitron nitrate, respectively. Water was determined by decomposing the material in a stream of dry oxygen, and absorbing the water formed in 'anhydrone.'

Infrared Spectra.—The spectra in the region 500—200 cm.$^{-1}$ were recorded as Nujol mulls between Polythene plates on a Grubb–Parsons DM 4 spectrometer, and in the region 4000—500 cm.$^{-1}$ as Nujol mulls between potassium bromide plates on a GS2A spectrometer.

Mössbauer Spectra.—The experimental details have been described.[8]

X-*Ray Crystallography.*—Diffraction powder data were obtained using an 11·64 cm. camera and Cu-K_α radiation.

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

[15] M. A. Leonard, *Analyst*, 1963, **88**, 404.