581. *Tin*(IV) *Fluoride Complexes and Their Infrared Spectra*

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The tin(IV) fluoride complexes with pyridine, 2,2′-bipyridyl, *NNN′N′*-tetramethylethylenediamine, tetrahydrofuran, 1,2-dimethoxyethane, pyridine *N*-oxide, and triphenylphosphine oxide have been prepared. Compositions correspond to six-co-ordination around tin. Evidence on the configurations is discussed. Infrared spectra of the pyridine *N*-oxide and triphenylphosphine oxide derivatives indicate that the ligand–tin bonds are stronger in the fluoride than in the chloride complexes. Dimethyltin fluoride forms a fluoride complex but does not co-ordinate with the foregoing ligands.

WHILE recent studies[1,2] have shown that tin(IV) fluoride co-ordinates with a variety of ligands, information on its behaviour towards simple donor molecules is less extensive than for the remaining tin(IV) halides. We have examined products from its reactions with several nitrogen and oxygen bases whose co-ordination was unlikely to be complicated by secondary processes, and whose behaviour towards the other tin(IV) halides had for the most part been determined. Pyridine, pyridine *N*-oxide, triphenylphosphine oxide, and tetrahydrofuran all yield complexes of the type SnF_4,L_2. The tin content of the tetrahydrofuran complex was somewhat high, but no evidence was found for a 1 : 1 complex previously reported.[1] The bidentate ligands 2,2′-bipyridyl, *NNN′N′*-tetramethylethylenediamine (tmen), and 1,2-dimethoxyethane (dme) give equimolar adducts. Such compositions afford evidence of six-co-ordination, uniformly with the majority of the adducts from the other tin(IV) halides.

Of the classes of ligand here examined ethers have the lowest capacity for co-ordination with tin(IV) fluoride. The fluoride (in contrast to the chloride) forms no complex with diethyl ether at ordinary temperatures.[1] Its complexes with tetrahydrofuran and dimethoxyethane, though suffering no loss in weight under a high vacuum, are very sensitive to atmospheric moisture. With this lower stability of the etherates can be linked the higher infrared absorption frequencies which they show in the Sn–F stretching region (Table 1) as compared with the remaining complexes. The stability of a co-ordinate link to a "*p*-block" element in a particular environment is determined largely by the electron availability from the ligand[3] (provided that this molecule is not sterically hindered). It can therefore be assumed that the relatively small charge-transfer from an ether does not weaken the tin–fluorine bond through reduction in the π-component as much as does the larger charge-transfer from the more strongly electron donating ligands.

[1] A. A. Woolf, *J. Inorg. Nuclear Chem.*, 1956, **3**, 285.

[2] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.

[3] I. Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, New York, 1963, pp. 86—114.

Dimethyltin difluoride co-ordinates with none of the foregoing ligands, so that the presence of the organic substituents leads to the usual reduction in electron-acceptor properties of the tin.[4] The high melting point, low volatility, and low solubility of dimethyltin difluoride,[5] as compared with dimethyltin dichloride, are indicative of a polymeric structure, presumably through halogen bridging, as found in tin(IV) fluoride.[6] Significantly, the difluoride does co-ordinate with fluoride ion. It dissolves more readily in fluoride solutions than in water and yielded the crystalline salts $(NH_4)_2Me_2SnF_4$, $NH_4Me_2SnF_3$, $K_2Me_2SnF_4,2H_2O$, and $K_2Me_2SnF_4$.

The spectra (Table 1) of most of the complexes in the Sn–F stretching region (620—540 cm.$^{-1}$) fall clearly into two classes characteristic of *cis*- and *trans*-configurations.[7] The single sharp absorption shown by the pyridine and tetrahydrofuran adducts and by the dimethylfluorostannates are grounds for assuming a *trans*-octahedral configuration,* or for ammonium dimethyltrifluorostannate a *trans*-trigonal bipyramidal arrangement with the fluorines in equivalent equatorial positions. A band characteristic of dimethyl- and trimethyl-tin compounds,[4,8] and assigned to Sn–Me asymmetric stretching, is shown at 553 cm.$^{-1}$ by the dimethylfluorostannates, but they do not give the corresponding symmetric vibration which should arise from a *cis*-configuration.

Co-ordination of the bidentate ligands and of triphenylphosphine oxide and pyridine *N*-oxide produces a multiple Sn–F absorption, to be associated with a *cis*-configuration.[7,9] The spectrum of the phosphine oxide complex in the P–O stretching region confirms this structure. This absorption (1202 cm.$^{-1}$ in the free ligand[10]) is now represented by at least two bands (1137 and 1082 cm.$^{-1}$; Table 2). The pyridine *N*-oxide complex gives a broad band in the Sn–F stretching region with four barely resolved components. While a ligand absorption shown by the remaining $SnX_4,2C_5H_5NO$ complexes within this range (Table 1) must contribute to the complexity of the band, there seems no reason to doubt

TABLE 1

Infrared spectra[a] in the low-frequency region

Compound	Bands (cm.$^{-1}$)	Compound	Bands (cm.$^{-1}$)
SnF_4[b]	720m, 550s	$SnF_4,2C_5H_5N$[d]	568s, 245s
Cs_2SnF_6	570sh, 555s,[e] 260—200vbr	$SnF_4,2[CH_2]_4O$[b,d]	600s
SnF_4,bipy[b,c]	592m, 578s, 567s	$K_2Me_2SnF_4$[b,d]	580s, 553w
SnF_4,tmen[b,c]	593m, 570s, 549s, 523w	$K_2Me_2SnF_4,2H_2O$[b,d]	576s, 553w[f]
SnF_4,dme[b,c]	620m, 600s, 585m	$(NH_4)_2Me_2SnF_4$[b,d]	582s, 553w[f]
$SnF_4,2Ph_3PO$[c]	581s, 555m, 548m, 535s[g]	$NH_4Me_2SnF_3$[b,d]	592s, 553w[f]
$SnF_4,2C_5H_5NO$[c]	572s, 560s, 548sh, 538sh, 447m,[g] 398m,[h] 351w,[g] 255s, 248m, 230s		
$SnCl_4,2C_5H_5NO$[c]	567m,[g] 444m,[g] 382s,[h] 351w,[g] 325msh, 316s, 303s		
$SnBr_4,2C_5H_5NO$[c]	565m,[g] 444m,[g] 372s, 350sh.[g] 238s[i]		
$SnI_4,2C_5H_5NO$	563m,[g] 442m,[g] 355s		

[a] Ligand bands without particular significance are omitted. [b] Spectrum not recorded below 400 cm.$^{-1}$. [c] Assigned *cis* configuration. [d] Assigned *trans* configuration. [e] Assymetric and symmetric stretching frequencies (see H. Kriegsmann and G. Kessler, *Naturwiss.*, 1960, **47**, 393). [f] Sn–Me asymmetric stretching. [g] Ligand frequency. [h] Band broadened by shoulders. [i] Sn–Br stretching frequency. It is possible that others occur below 220 cm.$^{-1}$. *X*-Ray powder photographs show that $SnCl_4,2C_5H_5NO$ and $SnBr_4,2C_5H_5NO$ are isomorphous.

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* Dr. E. L. Muetterties has informed the authors that the n.m.r. evidence for *cis*-configurations of a number of tin(IV) fluoride complexes (ref. 2) does not extend to the pyridine compound, whose low solubility prevented measurement.

[4] I. R. Beattie and G. P. McQuillan, *J.*, 1963, 1519.

[5] E. Krause, *Ber.*, 1918, **51**, 1447.

[6] R. Hoppe and W. Dähne, *Naturwiss.*, 1960, **47**, 254.

[7] References quoted by K. Nakamoto, " Infra-red Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 154.

[8] E. R. Lippincott, P. Mercier, and M. C. Tobin, *J. Phys. Chem.*, 1953, **57**, 939.

[9] I. R. Beattie, T. Gilson, M. Webster, and G. P. McQuillan, *J.*, 1964, 238.

[10] M. Halmann and S. Pinchas, *J.*, 1958, 3264.

the *cis*-assignment. The fluoride complex gives three distinct bands, at 255, 248, and 230 cm.$^{-1}$, whereas the *trans*-pyridine compound shows but one in this range. The pyridine *N*-oxide adduct from tin(IV) chloride, with three bands (325, 316, and 303 cm.$^{-1}$) in the Sn–Cl stretching region, also appears to be the *cis*-isomer.

Comparison of the available stereochemical evidence on SnX_4L_2 complexes [11,12] indicates that the structures are determined primarily by the ligand rather than by the halogen. The evidence can be systematised if it be assumed that those ligands having a polarisable π-bond linkage behind the spearhead atom (*e.g.*, acetonitrile, acetone, phosphoryl trichloride, and triphenylphosphine oxide) give *cis*-complexes with tin halides, but that otherwise a *trans*-complex develops (as with tetrahydrofuran and trimethylamine). This generalisation implies that overlap of the π-bonding charge cloud of the ligand with an empty *d*-orbital of the central atom plays a significant part in the linkage, and that stronger bonding of the ligands develops through the use of the two different *d* orbitals required for the *cis*-complex. The behaviour of pyridine may be marginal because there is evidence that it can produce either *cis*- or *trans*-isomers with different Group IV elements.[11] It must be remembered, however, that in critical cases where significant relative concentrations of the two isomers exist in solution, solubility relationships could determine which isomer crystallises.

In the low-frequency region the simplicity of the spectra of the tin(IV) halide complexes with pyridine *N*-oxide (in contrast to triphenylphosphine oxide) enables the strong band which moves from 398 cm.$^{-1}$ for the fluoride to 355 cm.$^{-1}$ for the iodide to be assigned as an Sn–O stretching vibation. The displacement of the band to higher frequency with increasing electronegativity of the halogen is of interest as indicating a progressive increase in the Sn–O bond strength. In comparison, shifts in ligand (N–O or P–O) stretching frequencies will not necessarily reflect so directly variations in the Sn–O bond strength, particularly since the effects produced by charge withdrawal and by kinematic coupling of the ligand and Sn–O vibrations can act in opposition.[13] In the triphenylphosphine oxide complexes the two closely related P–O stretching bands, 2 and 4, in Table 2 show lower frequencies for the fluoride than the chloride, despite a reversed trend from chloride to iodide. The lower fluoride frequency is explicable if weakening of P–O π-bonding through charge withdrawal from oxygen outweighs the effect of kinematic coupling which raises the frequency. It can be argued that ligand–tin bonding is here again stronger in the fluoride than in the chloride complex.

On this evidence from tin(IV) fluoride complexes the reluctance of dimethyltin difluoride to form crystalline complexes when dimethyltin dichloride does so,[4] cannot be attributed to weakness of the ligand–tin bond. Lattice energy effects and low solubility of difluoride are more likely to be important.

TABLE 2

Infrared bands (cm.$^{-1}$) of $SnX_4,2Ph_3PO$ complexes in the range 1175—1050 cm.$^{-1}$

X	1	2	3	4	5	6
F	—	1137s	1124s	1082s	1074w	
Cl	1162w	1143s	1124s	1089s	—	1071w
Br	1160w	1139s	1124s	1086s	1076vw [a]	1069m
I	1162w	1138s	1124s	1084m	1072w, sh [a]	1063s

[a] Approximate values only.

Detail of the high-resolution spectra of the triphenylphosphine oxide and the pyridine *N*-oxide complexes in the P–O and N–O stretching regions is given in Tables 2 and 3. Bands 2 and 4 of the phosphine oxide spectra have been discussed. Band 6 is very weak at the top of the series and indistinguishable from 5 in the fluoride. Its movement to

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[11] I. R. Beattie, *Quart. Rev.*, 1963, **17**, 382.

[12] I. R. Beattie and L. Rule, *J.*, 1964, 3267.

[13] F. A. Cotton, R. D. Barnes, and E. Bannister, *J.*, 1960, 2199.

TABLE 3

Infrared bands (cm.$^{-1}$) of $SnX_4,2C_5H_5NO$ complexes in the ranges 1275—1165 and 870—820 cm.$^{-1}$

X	1	2	3	4	5	6	7
F	[a]	1238s	—	1203s	1180m	—	835s
Cl	1257m	—	1211w, sh	1201s	1177m	840w	833s
Br	1257m	—	1210m	1197s	1177m	838m	831s
I	1253m	—	1202s	1190s	1171s	834s	825s

[a] This band probably contributes to a broadening of band 2.

lower frequency down the series suggests that it may be a further component of the P–O stretching mode to be expected from a *cis*-complex.[9] The positions of the weak unassigned band 1, and of band 3, due to a C–H in-plane bending vibration [10] remain unchanged.

In the spectra of the pyridine *N*-oxide complexes, bands 4 (N–O stretching) and 7 (N–O bending) move to lower frequencies from the fluoride to the iodide. So does band 5, assigned as a C–H in-plane deformation.[14] " Splitting " of bands 4 and 7 develops down the series. The strong band shown by the fluoride complex at 1238 cm.$^{-1}$ is distinctive, but other evidence makes it unlikely that the fluoride and chloride complexes are different isomerically.

The general picture given by the high-resolution spectra of the present complexes emphasises the need for caution in drawing conclusions from an individual spectrum. Splitting of bands may vary progressively in a series of complexes having the same configuration. The relative positions of corresponding ligand bands in the present compounds are for the most part determined by kinematic effects. Decreased coupling as the frequency of the oscillator falls apparently offsets this factor. Steric interference would produce the same trend, but examination of molecular models with an oxygen valence angle of about 150°, as in *cis*-$SnCl_4,2POCl_3$,[15] shows this not to be important. Moreover, the ligand frequency shifts shown through the pyridine *N*-oxide and triphenylphosphine oxide series are similar despite the very different space requirements of the two molecules.

EXPERIMENTAL

Tin(IV) *Fluoride and its Complexes.*—Tin(IV) fluoride was prepared by direct fluorination of tin(II) oxide [16] in a nickel boat. Reaction began at 200°. Passage of fluorine was continued for 5 hr. while the temperature was slowly raised to 500°. The fluoride was removed *via* a transfer sleeve into a dry-box (conditioned with phosphorus pentoxide, and flushed with dry nitrogen) in which all manipulations were made (Found: Sn, 60·6; F, 38·3. Calc. for SnF_4: Sn, 61·0; F, 39·0%).

Tin(IV) fluoride has a higher solubility in boiling tetrahydrofuran (about 1 g./100 ml.) than in other common solvents not causing solvolysis. The crystalline tetrahydrofuran complex is itself obtained by cooling this clear solution. Other complexes were precipitated under rigorously anhydrous conditions by running a hot solution of the fluoride into a slight excess of the ligand, also dissolved in tetrahydrofuran. Products were collected on a sintered glass filter, washed in turn with tetrahydrofuran and light petroleum (b. p. 30—60°), and dried on the filter under a stream of nitrogen. The low solubilities of the complexes often enabled preliminary information on composition to be obtained by direct weighing of the product. The dimethoxyethane complex was obtained by allowing the finely powdered tetrafluoride to remain under the liquid for 2 weeks, with occasional grinding. Surprisingly, the complex from this bidentate ligand is readily converted into the tetrahydrofuran derivative by treatment with the mono-ether.

The triphenylphosphine oxide complex was highly retentive of adsorbed light petroleum. This was removed by pumping to constant weight under a high vacuum. Complexes containing

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[14] S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, 1963, **19**, 189.

[15] C. I. Branden, *Acta Chem. Scand.*, 1963, **17**, 759.

[16] H. M. Haendler, S. F. Bartram, W. J. Bernard, and D. Kippax, *J. Amer. Chem. Soc.*, 1954, **76**, 2179.

volitale ligands suffered no loss in weight under a high vacuum. The pyridine and tetramethylethylenediamine complexes are slowly decomposed by atmospheric moisture.

The following analyses were obtained. Pyridine complex[1] (Found: Sn, 34·6; F. 21·0. Calc. for $C_{10}H_{10}F_4N_2Sn$: Sn, 33·7; F, 21·8%). *Bipyridyl complex* (Found: Sn, 33·2; C, 33·3; H, 2·8; N, 8·0. $C_{10}H_8F_4N_2Sn$ requires Sn, 33·8; C, 34·2; H, 2·3; N, 8·0%). NNN′N′-*Tetramethylethylenediamine complex* (Found: Sn, 38·7; F, 24·0. $C_6H_{16}F_4N_2Sn$ requires Sn, 38·2; F, 24·6%). *Pyridine* N-*oxide complex* (Found: Sn, 31·4; N, 7·3. $C_{10}H_{10}F_4N_2O_2Sn$ requires Sn, 30·9; N, 7·3%). *Triphenylphosphine oxide complex* (Found: C, 57·3; H, 4·05. $C_{36}H_{30}F_4O_2P_2Sn$ requires C, 57·5; H, 4·0%). *Tetrahydrofuran complex* (Found: Sn, 36·2; 36·0, on two different preparations. $C_8H_{16}F_4O_2Sn$ requires Sn, 35·1%). 1,2-*Dimethoxyethane complex* (Found: Sn, 41·4. $C_4H_{10}F_4O_2Sn$ requires Sn, 41·7%).

Tetrahydrofuran and 1,2-dimethoxyethane were distilled fractionally (range <0·2°) and dried over sodium. Pyridine and tetramethylethylenediamine were dehydrated over barium oxide and distilled from calcium hydride before storage over Linde 4A molecular sieve pellets. Pyridine *N*-oxide was purified by distillation under low pressure.

Pyridine N-*Oxide Complexes*.—These were precipitated from absolute ethanol (in which they are but slightly soluble) using excess ligand, and washed with light petroleum (b. p. 30—60°). The *chloride* and bromide[17] complexes are white crystalline solids, and the *iodide* is orange-red. $SnCl_4,2PyO$ (Found: Sn, 26·8; Cl, 31·1; N, 6·1. $C_{10}H_{10}Cl_4N_2O_2Sn$ requires Sn, 26·35; Cl, 31·5; N, 6·2%). $SnBr_4,2PyO$ (Found: Sn, 19·0; Br, 50·6; N, 4·6. Calc. for $C_{10}H_{10}Br_4N_2O_2Sn$: Sn, 18·9; Br, 50·9; N, 4·45%). $SnI_4,2PyO$ (Found: Sn, 14·7; I, 61·3; N, 3·6. $C_{10}H_{10}I_4N_2O_2Sn$ requires Sn, 14·5; I, 62·1; N, 3·6%).

Triphenylphosphine Oxide Complexes.—The triphenylphosphine oxide complexes of the remaining halides crystallised upon mixing benzene solutions of ligand and halide in 2 : 1 molar proportions. The chloride and bromide[18] are white, and the *iodide* red-brown (Found: Cl, 17·5; Br, 32·2; I, 42·6. Calc. for $C_{36}H_{30}Cl_4O_2P_2Sn$: Cl, 17·4%. Calc. for $C_{36}H_{30}Br_4O_2P_2Sn$: Br, 32·3%. $C_{36}H_{30}I_4O_2P_2Sn$ requires I, 42·9%.

Dimethyltin Difluoride and Dimethylfluorostannate.—Dimethyltin difluoride was prepared according to Krause,[5] but recrystallised from dilute hydrofluoric acid to eliminate basic impurity (Found: C, 12·8; H, 3·1; F, 20·05. Calc. for $C_2H_6F_2Sn$: C, 12·85; H, 3·2; F, 20·35%). The compound neither dissolves appreciably in, nor reacts with, acetonitrile, dimethylformamide, *NNN′N′*-tetramethylethylenediamine, pyridine, tetrahydrofuran, or molten bipyridyl.

Potassium dimethyltetrafluorostannate dihydrate crystallises upon evaporation of an aqueous solution containing dimethyltin difluoride (0·5 mole) and potassium fluoride (1·0 mole) (Found: C, 7·4; H, 2·9; H_2O, 10·0. $C_2H_{10}F_4K_2OSn$ requires C, 7·1; H, 2·95; H_2O, 9·8%). The water was determined as weight loss upon complete dehydration (as confirmed by the infrared spectrum) under a high vacuum.

Crystallisation of an aqueous solution containing dimethyltin difluoride (0·5 mole) and ammonium fluoride (1·0 mole) gave *ammonium dimethyltrifluorostannate* (I) in the first fraction and *diammonium dimethyltetrafluorostannate* (II) in the later fractions. Progress of the separation was followed by *X*-ray powder photography. (I) gives *d* values 6·17s, 5·45s, 4·04s, 3·72m, 3·57m, 3·26w, 3·19w, 2·72w, 2·41m. (II) gives 5·76s, 5·28m, 4·87s, 3·74m, 3·65w, 3·42w, 3·35m, 2·46w, 2·22m [Found: (I), C, 10·9; H, 4·8; N, 6·1. $C_2H_{10}F_3NSn$ requires C, 10·7; H, 4·5; N, 6·3%. Found: (II) C, 9·5; H, 5·5; N, 11·0. $C_2H_{14}F_4N_2Sn$ requires C, 9·2; H, 5·4; N, 10·7%].

Infrared Spectra.—These were run as mulls, and in a few cases, *e.g.*, Cs_2SnF_6, as KBr discs, to 400 cm.$^{-1}$ on a Perkin-Elmer 337 spectrophotometer. Spectra to 200 cm.$^{-1}$ were kindly recorded by Dr. D. W. A. Sharp of Glasgow. The high-resolution spectra of triphenylphosphine oxide and pyridine *N*-oxide complexes were determined on a Beckman IR-9 spectrophotometer (with 4 × scale expansion) through the courtesy of Dr. D. W. Meek of The Ohio State University. The error in these frequencies is believed to be less than 1 cm.$^{-1}$.

Analyses.—Tin was determined gravimetrically as the dioxide, and fluorine as calcium fluoride. A Coleman Analyzer was used for nitrogen. Other halogens were determined as the silver salts.

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[17] J. C. Sheldon and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.

[18] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 3770.

The research was supported in part by the U.S. Atomic Energy Commission. One of the authors (C. J. W.) participated during study leave from the University of Canterbury, New Zealand. Funds for the acquisition of the 337 spectrophotometer were made available by the National Science Foundation.

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[*Received, October 26th,* 1964.]