286. *Addition Compounds of Organotin Halides with Lewis Bases.*

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Dimethyltin dichloride and methyltin trichloride form 1 : 1 addition compounds with 1,10-phenanthroline and 2,2′-bipyridyl, but give 1 : 2 addition compounds with pyridine and pyridinium chloride. Trimethyltin chloride under comparable conditions, gives Me_3SnCl,py as the only adduct. The absence of a symmetric Sn–C stretching vibration in the infrared spectrum of solid Me_3SnCl,py leads to the suggestion of a co-ordination number of five for the tin atom in this compound. The Sn–Cl stretching vibrations of Me_3SnCl and Me_2SnCl_2 are shifted to below 250 cm.$^{-1}$ on co-ordination. There appears to be a relation between the intensity of the Sn–C symmetric stretching vibration and the position of the Sn–Cl stretching vibration for trimethyltin chloride in certain solvents. Reasons for this behaviour are discussed and it is suggested that adducts of Me_2SnCl_2 and $MeSnCl_3$ are six co-ordinate (with *trans*-methyl groups in the case of co-ordinated Me_2SnCl_2).

ORGANOTIN HALIDES, like the tetrahalides of tin, react with certain electron-pair donors to form addition compounds. From a recent review of organotin compounds[1] it is clear that the majority of adducts are of the type R_xSnX_{4-x},2L (where R = organic radical, X = halogen, and L = an electron-pair donor). The range and stability of the addition compounds formed appears to decrease as the number of organic groups increases and for the tetraorganotins there is little evidence of Lewis acid behaviour. Very little is known of the stereochemistry of the adducts, even though in several cases the combining ratios are not those to be expected on the basis of (mononuclear) six-co-ordinate tin (for example, Me_3SnCl,py and $MeSnI_3$,4py,* where py = pyridine). Early work on the conductivity of trimethyltin chloride in nitrobenzene[2] suggested the absence of ionization unless a Lewis base was also present in the solution. Similarly, Prince[3] represented the ionization of triorganotin chlorides in ionizing solvents in the presence of an electron-pair donor by equilibria of the type:

$$L\colon + R_3SnCl \rightleftharpoons L\colon SnR_3^+ + Cl^-.$$

Further, the compound Me_2SnCl_2,2py is apparently a weak electrolyte in acetonitrile.[4] In aqueous solutions triethyltin bromide behaves as a typical uni-univalent electrolyte[5] with a Λ_0 value of about 112 ohm^{-1} cm.^{2}, while in the case of dimethyltin dichloride Rochow and Seyferth[6] write equilibria of the type:

$$Me_2SnCl_2 + nH_2O \rightleftharpoons Me_2Sn(H_2O)_n^{2+} + 2Cl^-$$
$$Me_2Sn(H_2O)_n^{2+} + H_2O \rightleftharpoons Me_2Sn(H_2O)_{n-1}(OH)^+ + H_3O^+$$

Earlier workers[7] favoured an ionic formulation for compounds such as Me_3SnCl,py, which were represented as based on quaternised nitrogen $[Me_3Sn\,py]^+Cl^-$. However, by

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* The addition of pyridine to a solution of methyltin tri-iodide in carbon tetrachloride gave a yellow precipitate (Found: I, 57·1. $C_{11}H_{13}I_3N_2Sn$ requires I, 56·5%); Sn–C stretching vibration at 495 cm.$^{-1}$. No evidence was found for a 1 : 4 adduct with pyridine. With methyltin tri-iodide 1,10-phenanthroline gave a 1 : 1 adduct.

[1] Ingham, Rosenberg, and Gilman, *Chem. Rev.*, 1960, **60**, 459.
[2] Kraus and Greer, *J. Amer. Chem. Soc.*, 1923, **45**, 2946.
[3] Prince, *J.*, 1959, 1783.
[4] Thomas and Rochow, *J. Inorg. Nuclear Chem.*, 1957, **4**, 205.
[5] Dennison, quoted in Ref. 3.
[6] Rochow and Seyferth, *J. Amer. Chem. Soc.*, 1953, **75**, 2877.
[7] See, *e.g.*, Kocheshkov, *Chem. Abs.*, 1936, **30**, 8184.

analogy with iodine, a co-ordination number of five has been suggested for tin in trimethyltin acetate.[8] More recently[9] the existence of five-co-ordinate tin has been proposed in compounds of the type R_3SnR', where R′ is an unsaturated organic radical containing two nitrogen atoms in the 1,3-position (*e.g.*, imidazolyl). A co-ordination number of six for tin in the related compounds $R_2SnX_2,2L$ and $RSnX_3,2L$ is indicated and it has been envisaged[10] (by dimerisation) in the anion of the compound $[Ph_3P{\cdot}CH_2{\cdot}SnMe_3][Me_3SnBr_2]$.

In agreement with the related work of Alleston and Davies,[11] we find that dimethyltin dichloride readily forms 1 : 1 addition compounds with chelate ligands such as 1,10-phenanthroline and 2,2′-bipyridyl. With pyridine or its hydrochloride, 1 : 2 addition compounds are formed. Similar reactions occur with methyltin trichloride and tin tetrachloride. In contrast, trimethyltin chloride yields a 1 : 1 adduct with pyridine, while with 1,10-phenanthroline or 2,2′-bipyridyl under similar conditions no compound formation is observed.

In Table 1 we record the infrared spectra of the addition compounds formed between pyridine and methyltin chlorides or tin tetrachloride in the range 14—30 μ. Previous assignments of Sn–C skeletal stretching vibrations for certain methyltin compounds are summarised in Table 2. By comparison of the spectra of the organotin adducts with the spectra[12] of $GeCl_4,2py$ and $SnCl_4,2py$, it is seen that the bands around 690, 630, and 430 cm.$^{-1}$ may be assigned to a ligand pyridine. The bands at 546 cm.$^{-1}$ for Me_3SnCl,py and at 560 cm.$^{-1}$ for $Me_2SnCl_2,2py$ are assigned to an antisymmetric Sn–C stretching mode, while that at 515 cm.$^{-1}$ for $MeSnCl_3,py$ is assigned to the Sn–C stretch. The small variations of the Sn–C stretching vibrations shown in Table 2 suggest that there will be only weak coupling with the Sn–Cl vibrations. Although assignment for the pyridine adducts is fairly straightforward, the assignment of the Sn–C vibrations for the 1,10-phenanthroline and 2,2′-bipyridyl adducts is more difficult in view of the complexity of these spectra even in the 15—30 μ region. Our assignments for the stretching vibrations of the addition compounds are given in Table 3. Under the heading Sn–Cl vibrations we list all bands

TABLE 1.

The infrared spectra of pyridine addition compounds of methyltin chlorides and tin tetrachloride in the range 14—30 μ (Nujol mulls).

Compound	Frequency (cm.$^{-1}$)			
Me_3SnCl,py	698s	617s	546s (510) *	417m
$Me_2SnCl_2,2py$	696s, 686s	625vs	560m	422m
$MeSnCl_3,2py$	688s	633s	515s	428s
$SnCl_4,2py$ †	681vs	638m	—	431m

* Extremely weak if present. † Ref. 12.

TABLE 2.

Some previous assignments of infrared active Sn–C stretching skeletal vibrations in methyltin compounds (cm.$^{-1}$).

Compound			Ref.	Compound			Ref.
Me_2SnI_2	513 (a_1)	544 (b_1)	A	Me_3SnCl	514 (a_1)	545 (e)	C
Me_3SnI	511 (a_1)	538 (e)	A	Me_2SnCl_2	524 (a_1)	563 (b_2)	C
Me_4Sn	[507 (a_1) Raman]	528 (f_2)	B	$MeSnCl_3$	548 (a_1)		C

References: (A) Lippincott, Mercier, and Tobin, *J. Phys. Chem.*, 1953, **57**, 939. (B) Lippincott and Tobin, *J. Amer. Chem. Soc.*, 1953, **75**, 4144. (C) Edgell and Ward, *J. Mol. Spectroscopy*, 1962, **8**, 343.

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[8] Beattie and Gilson, *J.*, 1961, 2585.
[9] van der Kerk, Luijten, and Janssen, *Chimia*, 1962, **16**, 10.
[10] Seyferth and Grim, *J. Amer. Chem. Soc.*, 1961, **83**, 1610.
[11] Alleston and Davies, *J.*, 1962, 2050.
[12] Beattie, McQuillan, Rule, and Webster, preceding paper.

observed in the range 25—40 μ with the exception of (*a*) weak broad bands at 388 and 395 cm.$^{-1}$ for $MeSnCl_3$,2pyHCl and Me_2SnCl_2,2pyHCl, respectively, assigned to pyridinium vibrations (by analogy with $SbCl_5$,pyHCl and $SnCl_4$,2pyHCl with bands at 383 and 391 cm.$^{-1}$ respectively), and (*b*) one band at 347 cm.$^{-1}$ for Me_2SnCl_2,bipy which we were unable to assign. 2,2′-Bipyridyl and $SiCl_4$,bipy show no bands below 400 cm.$^{-1}$, so that this band is unlikely to be a ligand vibration. It is equally unlikely to be associated with Sn–C or Sn–Cl vibrations. The most striking aspect of these spectra shown in Table 3 is the absence of vibrations associated with tin–chlorine stretching modes for addition compounds of trimethyltin chloride and dimethyltin dichloride.

If the addition compound Me_3SnCl,py is based on 5-co-ordinate tin, the most probable stereochemical distribution is that of a trigonal bipyramid with the chlorine and the pyridine axial and methyls equatorial. This would result in a very low intensity for the symmetric Sn–C stretching vibrations. As Table 3 shows, we have not been able to observe the symmetric Sn–C stretching vibration in the spectrum of Me_3SnCl,py in solution in pyridine, and in the solid state this band is extremely weak if present. Further, the Sn–Cl stretching vibration (which must be infrared-active) is not observed in solution in pyridine to the limit of our instrument (40 μ). Although an ionic formulation could be correlated with the absence of an Sn–Cl stretching vibration, it would not agree with the extremely low intensity of the symmetric Sn–C stretching vibration. Further, in pyridine the absence of a symmetric Sn–C vibration suggests the presence of an approximately planar Me_3Sn grouping which could be found either in the adduct Me_3SnCl,py or in the complex ion $[Me_3Sn,py_2]^+$. High solubility of an ionic compound in pyridine is unlikely. As Thomas and Rochow[4] find that trimethyltin chloride does not conduct appreciably in pyridine, it is probable that the observed spectrum is due to the molecular species Me_3SnCl,py. To account for our non-observance of the Sn–Cl stretching vibration in the compound Me_3SnCl,py we must assume that the force constant is approximately halved, or even further reduced. This at first appears to be a rather large change unless halogen bridging is involved. However, there are considerable analogies between the addition

TABLE 3.

Tentative assignments of Sn–C and Sn–Cl stretching vibrations in addition compounds of methyltin chlorides and tin tetrachloride (cm.$^{-1}$).

Compound *	State	Sn–C antisym.	Sn–C sym.	Sn–Cl
Me_3SnCl †	CCl_4 soln.	543s	513w	336vs
	C_6H_6 soln.	542s	513w	331vs
	Et_2O soln.	542s	512w ‡	335vs
	MeCN soln.	542s	510vw	~300s.br
	py soln.	544s	—	—
Me_3SnCl,py §	Mull	546s	510vvw	—
Me_2SnCl_2	Mull	566s	515s	~320vs.br. complex
	C_6H_6 soln.	559s	521s	350vs
Me_2SnCl_2,2py	Mull	560m	—	—
Me_2SnCl_2,2pyHCl	Mull	564s	—	—
Me_2SnCl_2,phen	Mull	576s	(553?)	—
Me_2SnCl_2,bipy	Mull	571s	—	—
$MeSnCl_3$	Mull	—	546s	~360vvs.br
	C_6H_6 soln.	—	547m	374vvs
$MeSnCl_3$,2py	Mull	—	515s	~306vs.br, ~285vs.vbr
$MeSnCl_3$,2pyHCl	Mull	—	523s	~305s.br, ~267vs.vbr
$MeSnCl_3$,phen	Mull	—	525s	~308s, 296s, ~284s, ~275s
$MeSnCl_3$,bipy	Mull	—	529s	~291vs.br, ~266m.br
$SnCl_4$	C_6H_6 soln.	—	—	403(f_2) [366 (a_1) ††]
$SnCl_4$,2py ¶	Mull **	—	—	~324vvs.br

* Phen = 1,10-Phenanthroline; bipy = 2,2′-bipyridyl. † No mull for Me_3SnCl owing to solubility in mulling agents. ‡ Close to peak in Et_2O. § Me_3SnCl,py is largely dissociated in solution in benzene. ¶ Regular octahedral $SnCl_6^{2-}$ has one band at 310 cm.$^{-1}$ (f_{1u}). ** Ref. 12. †† Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, 1945.

compounds Me$_3$SnCl,py and ICl,py; and iodine monochloride in solution in the mixed solvent pyridine–carbon tetrachloride shows an I–Cl stretching frequency at about 270 cm.$^{-1}$ compared with the value of 375 cm.$^{-1}$ found for carbon tetrachloride solutions, indicating a very considerable change in the force constant.[13] Similarly the adduct ICl,py was for many years thought to be ionic in the solid state until *X*-ray determination showed the presence of a linear N–I–Cl group,[14] while *X*-ray examination of Me$_3$SnCl,py [15] has fully confirmed the predictions made from the infrared work. Again, the slight ionization of ICl,py in solvents such as acetonitrile resembles the behaviour of Me$_3$SnCl,py.[16] The possibility of studying the intensity of the Sn–C symmetric stretching vibration as a function of the position of the Sn–X stretching frequency for compounds of the type Me$_3$SnX in a variety of solvents opens up an interesting field for comparison with the work already carried out on related iodine compounds.

It is probable [17] that *d*-orbitals do not have major participation in the bonding of ions such as ICl$_2^-$, and that the low force constant found from the I–Cl stretching frequencies in this ion may be interpreted in terms of "half-bonds," or three-centre molecular orbitals based on $p\sigma$-atomic orbitals.[18] It is reasonable to assume that the *d*-orbitals will be rather diffuse in compounds such as Me$_3$SnCl,py, where there are not a number of highly electronegative substituents around the tin. If we consider pyridine as a simple electron-pair donor, the chlorine atom is the most likely recipient of any attempt at charge adjustment by the tin in an attempt to maintain an overall charge close to zero. Thus we might expect larger changes in the Sn–Cl interaction for Me$_3$SnCl,py relative to Me$_3$SnCl than for SnCl$_4$,2py relative to SnCl$_4$. (It may be argued that in Me$_3$SnCl,py one observes the simple Sn–Cl stretch, whereas in SnCl$_4$,2py, if the compound is *trans*, the symmetric stretching vibration would be inactive. This is not a serious objection as the symmetric and the antisymmetric Sn–Cl vibrations would occur in similar regions of the spectrum.) The I–Cl distance in iodine monochloride is [19] about 2·31 Å, whereas that in the ICl$_2^-$ ion is [19] about 2·36 Å. In the case of trimethyltin chloride the Sn–Cl distance [19] is 2·37 Å and in Me$_3$SnCl,py this is increased [15] to about 2·42 Å. Although the increase in the Sn–Cl distance is smaller than might have been expected from the marked change in force constant, it is comparable with that for the iodine compounds. Further, it is possible that this large change in force constant, coupled with a small change in the interatomic distance, is due to different σ- and π-contributions to the Sn–Cl bond in the two compounds.[20]

On the assumption that the addition compounds of dimethyltin dichloride are examples of tin with a co-ordination number of six, the lack of symmetric Sn–C stretching vibrations may be accounted for in terms of a *trans*-alignment of the methyl groups. As the number of chlorine atoms about the central tin atom increases for related compounds, so the Sn–Cl stretching vibrations become more accessible. In the case of addition compounds of methyltin trichloride they occur around 300 and 270 cm.$^{-1}$, while for adducts of tin tetrachloride they occur around 320 and 280 cm.$^{-1}$. Our results show that in the addition compounds the co-ordination number around the central tin atom has increased, probably to six. In the symmetrical SnCl$_6^{2-}$ ion (found in the ammonium salt, for example) the antisymmetric Sn–Cl stretching vibration (f_{1u}) occurs at 310 cm.$^{-1}$.

The compound Me$_2$SnCl$_2$,2pyHCl (having four chlorine atoms about the proposed six-co-ordinate tin) might initially be expected to resemble adducts of tin tetrachloride. It is

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[13] Person, Humphrey, Deskin, and Popov, *J. Amer. Chem. Soc.*, 19 8, **80**, 2049.

[14] Hassel and Rømming, *Acta Chem. Scand.*, 1956, **10**, 696.

[15] Hulme, following paper; see also Beattie, McQuillan, and Hulme, *Chem. and Ind.*, 1962, 1429.

[16] Popov and Pflaum, *J. Amer. Chem. Soc.*, 1957, **79**, 570.

[17] See, *e.g.*, Person, Anderson, Fordemwalt, Stammreich, and Forneris, *J. Chem. Phys.*, 1961, **35**, 908 and reference therein.

[18] Pimentel, *J. Chem. Phys.*, 1951, **19**, 446; see also Wiebenga, Havinga, and Bowijk, "Advances in Inorganic and Radiochemistry," Academic Press, New York, 1961, Vol. III, p. 133.

[19] Sutton *et al.*, "Interatomic Distances," *Chem. Soc. Special Publ.* No. 11, London, 1958.

[20] For related discussions see Woodward, *Trans. Faraday Soc.*, 1958, **54**, 1271; Cruickshank, *J.*, 1961, 5486.

reasonable to compare $SnCl_4$,2py with the addition compound formed by adding two methide anions to tin tetrachloride. However, there is a possibility of charge delocalisation back to the ring in the case of $SnCl_4$,2py, whereas donation from $H_3C\colon^-$ must be regarded as the provision of a lone pair of electrons by a very powerful Lewis base with no possibility of additional interaction. The effect on the Sn–Cl stretching vibrations might reasonably be assumed to be much greater in the latter case. There is a close similarity between *trans*-$Me_2SnCl_4^{2-}$ and ICl_4^-, and for the latter ion the force constant for the I–Cl bond stretch is anomalously low.[17]

EXPERIMENTAL

Preparation of Reagents and Adducts.—Methyltin trichloride was prepared from methyltriphenyltin.[21] The addition compounds were prepared as precipitates by mixing solutions of the Lewis base and the acceptor compound in a suitable solvent. Solvents employed were benzene (for Me_2SnCl_2,2py; Me_2SnCl_2,bipy; Me_2SnCl_2, phen), light petroleum (b. p. 40—60°) (for Me_3SnCl,py), carbon disulphide (for $MeSnCl_3$,phen), carbon tetrachloride (for $MeSnCl_3$,2py and $MeSnCl_3$,bipy), and chloroform (for Me_2SnCl_2,2pyHCl and $MeSnCl_3$,2pyHCl. The excess of acceptor or base was removed by washing and the products were dried *in vacuo*. The methyltin trichloride compounds were prepared in a dry-box from rigorously dried solvents and donors: derivatives of dimethyltin dichloride and trimethyltin chloride were prepared in the open.

Analysis.—Chloride was determined by titration with silver nitrate, a glass electrode, silver electrode, and pH meter being used. For methyltin trichloride adducts it was necessary to heat the mixture under reflux to ensure complete hydrolysis in acid solution.

Results.—The following were obtained. (*a*) Me_3SnCl, m. p. 38° (Found: Cl, 17·9. Calc. for C_3H_9ClSn: Cl, 17·8%); Me_3SnCl,py, m. p. 40—41° (Found: Cl, 12·8. Calc. for $C_8H_{14}ClNSn$: Cl, 12·8%). (*b*) Me_2SnCl_2, m. p. 109° (Found: Cl, 32·2. Calc. for $C_2H_6Cl_2Sn$: Cl, 32·3%); Me_2SnCl_2,2py, m. p. 161° (sealed tube), sublimes at 145° (open tube) (Found: Cl, 18·7. Calc. for $C_{12}H_{16}Cl_2N_2Sn$: Cl, 18·8%); *2,2′-bipyridyl adduct* m. p. 240° (Found: Cl, 18·8. $C_{12}H_{14}Cl_2N_2Sn$ requires Cl, 18·9%); 1,10-*phenanthroline adduct*, m. p. 284° (Found: Cl, 17·7. $C_{14}H_{14}Cl_2N_2Sn$ requires Cl, 17·8%); Me_2SnCl_2,2pyHCl, m. p. 151° (Found: Cl, 31·5. Calc. for $C_{12}H_{18}Cl_4N_2Sn$: Cl, 31·5%); (*c*) $MeSnCl_3$, m. p. 42—44° (Found: Cl, 43·8. Calc. for CH_3Cl_3Sn: Cl, 44·2%); $MeSnCl_3$,2py (Found: Cl, 26·6. Calc. for $C_{11}H_{13}Cl_3N_2Sn$: Cl, 26·7%); *2,2′-bipyridyl adduct* (Found: Cl, 26·8. $C_{11}H_{11}Cl_3N_2Sn$ requires Cl, 26·9%); 1,10-*phenanthroline adduct* (Found: Cl, 25·3. $C_{13}H_{11}Cl_3N_2Sn$ requires Cl, 25·4%); $MeSnCl_3$,2pyHCl (Found: Cl, 37·4. Calc. for $C_{11}H_{15}Cl_5N_2Sn$: Cl, 37·6%).

Infrared Spectra.—These were determined on a Perkin-Elmer 221 infrared spectrometer equipped with cæsium bromide optics: mulls in Nujol and cæsium bromide windows were used for all spectra except those of the acetonitrile solution of trimethyltin chloride, for which Polythene windows were used.

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[21] Pavlovskaya and Kocheshkov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **49**, 263, *Chem. Abs.*, 1946, **40**, 5697.