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Review

STABILITY OF ORGANO-MERCURY, -THALLIUM, -TIN AND -LEAD COMPLEXES WITH ANIONIC AND NEUTRAL LIGANDS

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ABBREVIATIONS

acac	acetylacetone	hfacac	hexafluoroacetylacetone
bipy	2,2-bipyridyl	HMTAP	hexamethyltriamidophosphate
bzac	benzoylacetone	HMTATP	hexamethyltriamidothiophosphate
dbzm	dibenzoylmethane	oxin	8-oxyquinoline
DEE	1,2-diethoxyethane	phen	1,10-phenanthroline
DEF	diethylformamide	phos	1,2-bis(diphenylphosphino)ethane
DMA	dimethylacetamide	Py	pyridine
DME	1,2-dimethoxyethane	TBF	tributylphosphate
DMF	dimethylformamide	tet	2,4,7,9-tetramethyl-1,10-phenanthroline
dmp	2,9-dimethyl-1,10-phenanthroline	THF	tetrahydrofuran
DMSO	dimethylsulphoxide	TMF	trimethylphosphate
DMTA	dimethylthioacetamide	tmp	3,4,7,8-tetramethyl-1,10-phenanthroline
DTDS	dithiane disulphoxide	TMSO	tetramethylene sulphoxide
DTM	dithiane monosulphoxide		

1. INTRODUCTION

This paper deals with the quantitative evaluation of the stability of complexes of σ-bonded organometallic compounds with anionic and neutral ligands.

A great number of organometallic reactions are carried out in complex-forming solvents and, furthermore, the rates of these reactions are often increased on addition of other substances to the reaction mixture, this being attributed to the facilitation of C—metal bond heterolysis or electron displacement along the C—metal bond in the most favourable direction for reaction[1]. Substances capable of such behaviour are usually anions having a noticeable affinity for the metal atom of the organometallic compound (*e.g.* Cl^-, Br^- and I^- for mercury, OH^- for tin etc.).

Solvent molecules may also exert a catalytic influence when they are able to specifically solvate a given metal atom when one or several molecules of the solvent are particularly strongly bound to the metal (solvent complex). Dipolar aprotic solvents (DMF, DMSO, etc.) generally form such complexes with metals. Obviously, the subsequent reaction rates depend on the concentration and on the stability of the complexes formed in solution.

In view of this, quantitative evaluation of the stability of organometallic complexes is of great interest in kinetic and mechanistic studies of these compounds in solution. The influence of coordination on reactivity has been discussed in a series of reviews[2–8], but very little attention has been devoted to quantitative results and to a comparison of the characteristic complexing ability as a function of the metal and organic groups in the organometallic compound and of the properties of the ligand.

In inorganic chemistry, the stability of metal ion complexes has been studied extensively as is reflected by the considerable volume of quantitative data on this subject, *e.g.* stability constants as measured by a variety of techniques. The situation in organometallic chemistry is quite different. The data at present available in the literature are mainly concerned with the stability constants of complexes of organometallic cations of the type $R_nM^{(m-n)+}$ (where m = valence of the metal) with neutral or charged ligands X, studied for the most part in aqueous media.

However, hydrolatically stable organometallic cations derived from non-transition metal compounds are not particularly numerous (being confined to those of mercury, thallium, thin and lead), and for this reason this review will be concerned with these particular cations. Other organometallic cation complexes, *i.e.*, transition metal complexes, have been reviewed by Tobias[9].

In addition to complex formation associated with organometallic cations of the metals mentioned above, it seems important to discuss complex formation associated with other organic derivatives of these metals, in particular organometallic compounds of the type R_mM. This problem is in fact most pertinent to mercury and tin compounds since these have been most commonly employed in mechanistic studies involving organometallics (*e.g.*, studies of electrophilic substitution mechanisms).

II. THE INFLUENCE OF THE NATURE OF THE METAL OR LIGAND UPON THE RELATIVE STABILITY OF COMPLEXES

An organometallic compound may be considered to function as a Lewis acid during complex formation where the corresponding equilibrium may be depicted in a similar manner to an acid–base equilibrium as

$$A + :B \rightleftharpoons A:B \qquad (1)$$

where A is the Lewis acid (electron acceptor) and :B the Lewis base (electron donor).

Since solvent molecules which often solvate organometallic compounds may also be regarded as ligands, complex formation in solution may be depicted by the competing equilibrium

$$A\,(\mathrm{solv}) + :B \rightleftharpoons A:B + \mathrm{solv} \qquad (2)$$

The position of equilibrium depends both on the nature of the metal atom and of the organic group bonded to it, as well as on the nature of the solvent and of the competing donor ligand.

Chatt, Ahrland and Davies[10] have suggested that all metals may be subdivided into two groups, A and B, depending on the stability of the complexes they form with various ligands.

The A-group metal ions form the most stable complexes with ligands whose coordinating atoms occur early in a particular group of the Periodic Table. The more electronegative the coordinating metal atom and the higher the positive charge possessed by the metal ion, the more stable are the complexes formed, *i.e.* $F > O > N > Cl > Br > I > S$ and $Al^{3+} > Mg^{2+} > Na^{+}$.

The most stable complexes of B-group metal ions are those formed with the heavier metal atoms. As a rule, these complexes are more stable the more polarizable the ligand and the lower the positive charge on the metal ion, *i.e.* $S > I > Br > Cl > N > O > F$ and $Ag^{+} > Cd^{2+} > Au^{3+} > Sn^{+}$

These metal ions also form adducts with olefins or aromatic hydrocarbons.

According to Chatt, the difference in properties between the A- and B-group metal ions is due to the difference in the structures of their electronic shells. Usually, A-group metals (unlike typical B metals) have no high *d*-electron levels, so no dative d_π–d_π interaction may occur which could additionally stabilise bonds involving ligands with lower energy vacant *d*-orbitals (*e.g.* S, P, I, etc.). In contrast, the extraordinary stability of B-metal complexes containing such elements as S, P, I, etc. may be directly attributed to such interaction. Dative displacement plays an insignificant part, if at all, in strengthening the metal–ligand bond of an A-type metal complex. In this case, the stability of the compound formed is merely a function of the difference between the electronegativities of the metal and the ligand; thus, the most stable compounds formed by the A metals are those containing elements which occur early in Groups of the Periodic Table (O, N, etc.).

In 1963, Pearson[13] introduced another notation for acid–base equilibria of type (1), and formulated the "hard–hard" and "soft–soft" interaction rule. Pearson hard bases are those in which the atom carrying an integral or partial negative charge has a low polarizability, is strongly electronegative, does not undergo mild oxydation and forms hydrogen bonds readily.

In soft bases, the atom carrying the negative charge is easily polarizable, less electronegative and readily oxidizable; in other words, its external occupied orbitals are at a higher energy level.

In a similar fashion, Lewis acids may be subdivided into hard and soft varieties. The A-metal cations may thus be placed in the hard acid group while the B-metal species belong to the soft acid group which also embraces organic cations and some organic molecules.

Hard acids prefer to interact with hard bases and soft acids with soft bases. Complexes of these two types are more stable than those formed from partners belonging to different groups.

Klopman[14] has applied perturbation theory in an attempt to rationalize this behaviour. Thus the donor–acceptor interaction mode depends on the difference between the energies of the interacting orbitals, *i.e.* on the difference between the highest occupied orbital energy of the donor (E_m) and the lowest vacant orbital energy of the acceptor (E_n). If the difference $E_m - E_n$ is high, then the energy gained from donor–acceptor interaction will be a function of only the Coulomb energy term, in other words, electrostatic interaction will prevail. If, however, the difference is small, *i.e.* if the energies of the interacting orbitals are close, then the interaction will be a function of the orbital overlap, that is, it will be a soft–soft interaction.

The Pearson rule represents an empirical approach which is often invalidated by the fact that there is no clear boundary between the two different types of acid and base. In addition, solvation effects or other factors may interfere. However, the approach discussed above is used quite commonly to explain both complex formation and reactivity in general[15].

A large number of nucleophiles have been treated with a selected substrate in order to obtain the relative reactivity series, *i.e.* the relative softness or hardness of bases. A number of empirical equations which inter-relate the reactivity and the properties of the substrate and the reagent have been proposed[16–19]. Various parameters contained in these equations have often been used as a quantitative measure of the relative softness of nucleophiles. These equations have been discussed in detail elsewhere[20].

The extent of a given coordination equilibrium in solution is also strongly affected by the solvent which cannot be considered as an inert medium and often acts as a ligand competing with the nucleophile. For this reason, the classification of donor properties of solvents with respect to a given acceptor poses a challenging problem. Generally, the standard acceptor is a proton or a compound capable of forming hydrogen bonds, for example, phenylacetylene[22].

Gutmann and his co-workers[23] have characterised the donor properties of a great number of solvents in a quantitative manner. They have suggested that the enthalpy of complex formation between a ligand and antimony pentachloride should be a measure of the ligand donor strength, *i.e.*

$$DN \text{ (donor number)} = -\Delta H\,(\mathrm{D\cdot SbCl_5})$$

The donor numbers listed in Table 1 were measured calorimetrically in dichloroethane.

This type of donor number scale is rather useful since it permits preliminary conclusions to be made regarding the stability of a given complex in a given medium. However, such a scale cannot be used generally, since donor numbers are usually specific to one definite acceptor. Hence, in going from one acceptor to another, specific donor/acceptor interactions are variable and this often leads to noticeable changes in a given stability series. In addition, donor numbers are also sensitive to spatial factors, for example, to large variations in acceptor size.

An attempt which has been made to correlate donor properties of anionic ligands with those of solvent molecules is quite interesting. Thus, using $VO(acac)_2$ as a standard acceptor instead of $SbCl_5$, thus preventing halide exchange, and taking into account the fact that the donor properties were almost unaffected by this replacement, the authors[24] have obtained the following ligand–donor property series which also includes data for

TABLE 1

DONOR NUMBERS (*DN*) FOR NEUTRAL MOLECULES (after Gutmann)

Donor	*DN*	ϵ	*Donor*	*DN*	ϵ
1,2-Dichloroethane	0	10.1	Ethylene carbonate	16.4	89.1
Sulphuryl chloride	0.1	10.0	Methyl acetate	16.5	6.7
Thionyl chloride	0.4	9.2	n-Butyronitrilie	16.6	20.3
Acetyl chloride	0.7	15.8	Acetone	17.0	20.7
Benzoyl chloride	2.3	23.0	Ethyl acetate	17.1	6.0
Nitromethane	2.7	35.9	Water	18.0	81.0
Nitrobenzene	4.4	34.8	Diethyl ether	19.2	4.3
Acetic anhydride	10.5	20.7	Tetrahydrofuran (THF)	20.0	7.6
Benzonitrile	11.9	25.2	Trimethylphosphate (TMP)	23.0	20.6
Acetonitrile	14.1	38.0	Tributylphosphate (TBP)	23.7	6.8
Sulpholan	14.8	42.0	Dimethylformamide	26.6	36.1
Propane-1,2-dicarbonate	15.1	69.0	Dimethylacetamide (DMA)	27.8	38.9
Benzyl cyanide	15.1	18.4	Tetramethylurea (TMU)	29.64[a]	
Ethylene sulphite	15.3	42.0	Dimethylsulphoxide (DMSO)	29.8	45.0
Isobutyronitrile	15.4	20.4	Diethylformamide (DEF)	30.9	-
Propionitrile	16.1	27.7	Diethylacetamide	32.2	-
			Pyridine (Py)	33.1	12.3
			Hexamethyltriamidophosphate	38.8	30.0

[a] G. Olofsson, *Acta Chem. Scand.*, 18 (1964) 1022.

halide and pseudo-halide ligand ions: $N_3^- > NCS^- > Py \geqslant HMTAP > Ph_3PO > DMSO > Cl^- \sim DMF > TMF > Br^- > I^-$.

The results help to explain the stability of anionic complexes in aprotic solvents. It was found[25] that not only is solvent-ligand competition important, but ligand solvation must also be taken into account, the latter effect being strongly dependent on the nature of the solvent. Dipolar aprotic solvents are known to predominantly solvate cationic centres (basic solvents). Protic solvents, on the other hand, solvate mainly anionic centres since these are capable of hydrogen bond formation[26]. The total solvation effect must include interaction of the solvent with all the species shown in eqn. (2). On solvating an anionic centre, a protic solvent diminishes the donor properties of the centre. Such solvation would be more important for hard anions in comparison to soft anions; for this reason the solvent will either level the effects or differentiate them, depending of the nature of the acceptor. The formation constant for the complex is a characteristic of the system as a whole; since numerous factors affect this constant, it cannot be used to relate any general characteristics associated solely with donor–acceptor interaction. However, donor numbers can be used for predicting the behaviour of a donor–acceptor pair in a system where the solvation effects are similar providing there is no specific interaction with the solvent or steric hindrance. With anionic complexes, the dielectric properties of the medium become increasingly important while for polydentate ligands the chelate effect noticeably increases the stability of the complex.

In summary, however useful the donor properties series may be, the best method of analysis remains experimental investigation of the particular case in question. In this article examples of typical experimental data are discussed and analysed.

III. ORGANOMERCURY COMPOUNDS

The reactivity of organomercury compounds is strongly dependent on specific solvation by solvent molecules and on coordination with anions and neutral molecules present in the solution[1]. However, quantitative data relating to the stability of organomercurial complexes were obtained only recently and are not numerous. The most stable complexes are those formed by RHg^+ cations, the order of stability decreasing for complexes with organomercury halides, while complexes with R_2Hg are so unstable that quantitative data for them have only been obtained in special cases, *e.g.* when R is a polyfluorinated group.

1. Organomercury cations

Organomercurial compounds of the type RHgX may be considered as complexes of the organomercury cation RHg^+. In order to form the cation in solution it is necessary that the Hg–X bond in the organomercury halide is polar while the solvent should be strongly ionizing. For these reasons, organomercury cations should be expected to form complexes in solution when X is ClO_4, NO_3, BF_4 or SO_4.

Goggin and Woodward[27], who studied the Raman spectra of solutions of CH_3HgClO_4 and CH_3HgNO_3 in water, have concluded that these salts are completely ionized in this solvent to give hydrated $CH_3HgOH_2^+$ and ClO_4^- and NO_3^- ions respectively, the donor–acceptor bond involving the oxygen of the hydrated cation being covalent. Spectroscopic studies showed that in non-ionizing solvents such as benzene only undissociated molecules of the type CH_3HgNO_3 exist. Addition of dimethylsulphide affects the spectra of both aqueous and benzene solutions of CH_3HgNO_3, presumably through formations of complexes of the type $[CH_3HgS(CH_3)_2]NO_3$ [27].

Of all the organomercurial cations, the methylmercury cation has been most extensively studied, and was proposed as a model for a soft Lewis acid by Schwarzenbach. Stoichiometrically the cation CH_3Hg^+ resembles the proton in complex formation[11]. When coordinated to a water molecule, the cation forms $CH_3HgOH_2^+$, which is analogous to the hydroxonium ion, H_3O^+. The methylmercury cation is also very capable of forming polynuclear complexes in those cases when the ligand remains sufficiently basic after addition of the first cation. $L^{n-} \rightarrow CH_3HgL^{1-n} \rightarrow (CH_3Hg)_2L^{2-n} \rightarrow (CH_3Hg)_3L^{3-n}$. This is similar to the series $OH^- \rightarrow OH_2 \rightarrow OH_3^+$.

Raman spectroscopy data obtained for solutions of CH_3HgL (where $L = CH_3SO_3^-$, NO_3^- or SO_4^{2-}) predict that the dissociation constant for CH_3HgL should be approximately equal in magnitude to the dissociation constant for HL when the *O*-donor ligand is a weak base ($-2 < \log K_{HL} < +2$).

Like the proton, the methylmercury cation most frequently adds just one ligand. However, since the maximum coordination number for the mercury cation is four, the possibility that a further two ligands may be complexed also exists. The complexes $CH_3HgL_2^{1-2n}$ and $CH_3HgL_3^{1-3n}$, which are similar to those containing a hydrogen bridge (*e.g.*, HF_2^-), are formed at higher concentrations of the ligand but have lower stability constants.

Despite the similarities in the stoichiometries of their complex formation, the methylmercury cation differs considerably from the proton in the stability of the complexes which it forms with different ligands. This is not surprising, for the proton is a hard Lewis acid while the methylmercury cation must be classified as soft. The proton gives more stable complexes with O and N donors while the methylmercury cation gives stable complexes with S and P donors. Thus, two stoichiometrically similar equilibria may be presented.

$$H^+ + CH_3HgOH \overset{K_1}{\rightleftharpoons} H_2O + CH_3Hg^+; \quad \log K_1 = 6.3;$$

$$H^+ + CH_3HgS^- \overset{K'_1}{\rightleftharpoons} HS^- + CH_3Hg^+; \quad \log K'_1 = -8.4;$$

The first quantitative data on the stability of complexes of methyl-, ethyl- and phenylmercury cations with anions such as OH^-, Cl^-, Br^- and I^- were obtained potentiometrically[25], while stability constants for the methylmercury cation have been obtained polarographically by Simpson[30].

Schwarzenbach[11] and his co-workers have made an extensive study of the coordination equilibrium between the methylmercury cation and a number of anionic ligands in water. The results obtained by various authors for stable methylmercury cation complexes with organic or inorganic ligands are listed in Tables 2 and 3.

These data demonstrate once more that the proton is a very different Lewis acid from the methylmercury cation. Comparison of the logarithms of the stability constants for the formation of complexes with the species CH_3HgL and HL (Fig. 1a) shows that a linear relationship may be obtained for each series of ligands where the coordinating atom is the same. If however the stability constants for the formation of complexes with the species CH_3HgL and AgL are compared (Fig. 1b), a slight linear relationship is obtained since both acids (CH_3Hg^+ and Ag^+) are soft. Thus, sharp differences in the properties of the cations lead to the stability constants of the complexes following a series of linear relationships. If, however, the nature of the base varies smoothly (*e.g.* during the addition of ligands with the same donor atom), the similarity in Lewis acid properties is apparently retained

TABLE 2

LOGARITHMIC STABILITY CONSTANTS FOR COMPLEXES OF THE METHYLMERCURY CATION CONTAINING INORGANIC LIGANDS

Ligand	T(°C)	*logK₁*	*pKa*	*Ref.*
OH^-	25	10.41	-	31
OH^-	25	9.5	14	30
OH^-	25	9.51	-	29a
OH^-	20	9.37	15.7	11
CN^-	20	14.1	9.14	11
CN^-	25	14.2	9.3	20
SCN^-	20	6.05	negative	11
SCN^-	25	6.1	< 1	20
NH_3	20	7.6	9.42	11
NH_3	25	8.4	9.3	30
$Co(CN)_6{}^{3-}$	20	4.15	negative	11
$HPO_4{}^{2-}$	20	5.03	6.79	11
$HPO_3{}^{2-}$	20	4.67	6.3	11
S^{2-}	20	21.2	14.2	11
$S_2O_3{}^{2-}$	20	10.90	negative	11
$SO_3{}^{2-}$	20	8.11	6.79	11
$[Co(SCN)(NH_3)_5]^{2+}$	20	3.20	-	11
F^-	20	1.50	2.85	11
Cl^-	20	5.25	–7	11
Cl^-	25	5.46	-	29a
Cl^-	25	5.45	< 1	30
Br^-	20	6.62	–9	11
Br^-	25	6.7	-	29a
Br^-	25	6.7	< 1	30
I^-	20	8.60	–9.5	11
I^-	25	8.7	-	29a
I^-	25	8.7	< 1	30

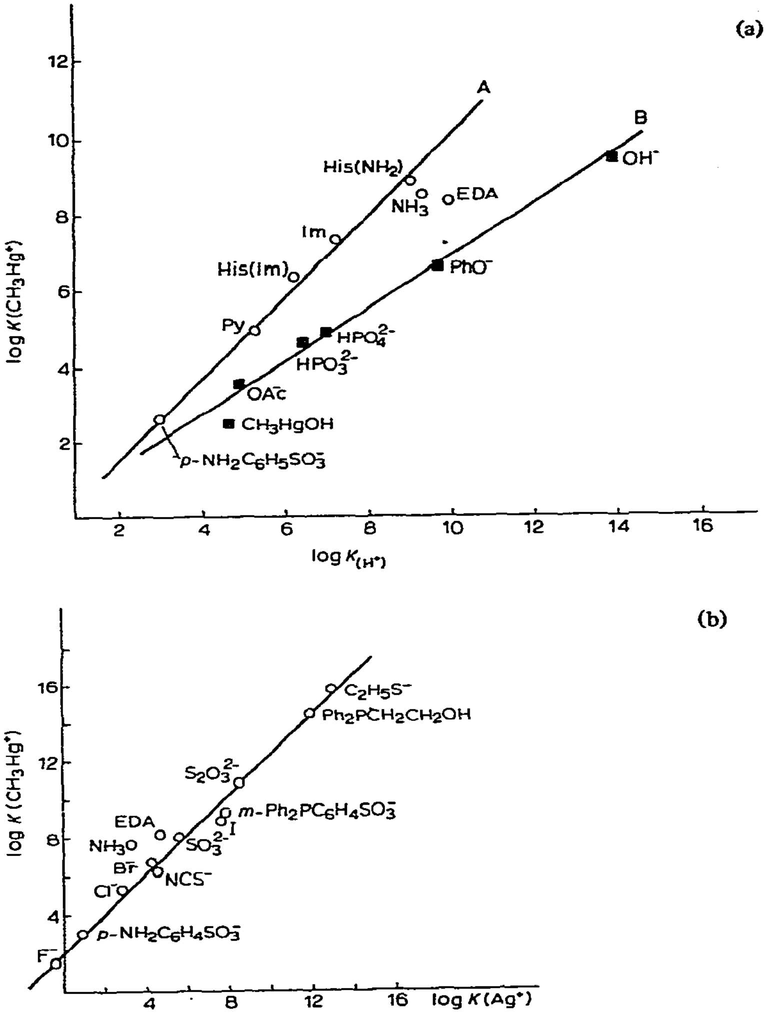

Fig. 1. Plots of the logarithms of the formation constants for the complex CH_3HgL *versus* those for (a) the acid HL and (b) the salt AgL.

over a wider range.

The NMR data obtained for complexes containing the methylmercury cation are interesting[36]. The $J(^{199}Hg-^{1}H)$ spin–spin coupling constants obtained for CH_3HgL apparently vary in a linear fashion in relation to the logarithm of the stability constants as measured by Schwarzenbach[11] (Fig. 2). This suggests therefore that NMR spectra should be capable of supplying useful information regarding cation–ligand bond stability.

This suggestion is supported by the fact (recently reported by the same authors[37])

TABLE 3

LOGARITHMIC STABILITY CONSTANTS FOR COMPLEXES OF THE METHYLMERCURY CATION CONTAINING ORGANIC LIGANDS

Ligand	*T(°C)*	*pK_a*	*$\log K_1$*	*Ref.*
CH_3HgOH	20	4.59	2.37	11
CH_3COO^-	25	4.8	3.6	30
$C_6H_5O^-$	25	9.8	6.5	30
p-$NH_2C_6H_4SO_3^-$	20	3.06	2.60	11
C_5H_5N	25	5.3	4.8	30
Imidazole	25	7.1	7.3	30
$H_2NCH_2CH_2NH_2$	20	10.05	8.25	11
Histidine (amine nitrogen complexed)	25	9.1	8.8	30
Histidine (imidazole nitrogen complexed)	25	6.1	6.4	30
$EDTA^{3-}$	25	6.2	6.2	30
$(C_6H_5)_2PC_6H_4SO_3^-$	20	0	9.15	11
$(C_2H_5)_2PCH_2CH_2OH$	20	8.12	14.6	11
$(C_2H_5)_3P$	20	8.8	15	11
CH_3HgS^-	20		16.3	11
CH_3HgSCN	20	negative	1.65	11
$(CH_3Hg)_2S$	20	negative	ca. 7	11
$HOCH_2CH_2S^-$	20	9.52	16.12	11
$HOCH_2CH_2SHgCH_3$	20	negative	6.27	11
Cysteine (RS^-)	25	8.6	15.7	30
Glutathione (RS^-)	25	9.0	15.9	30

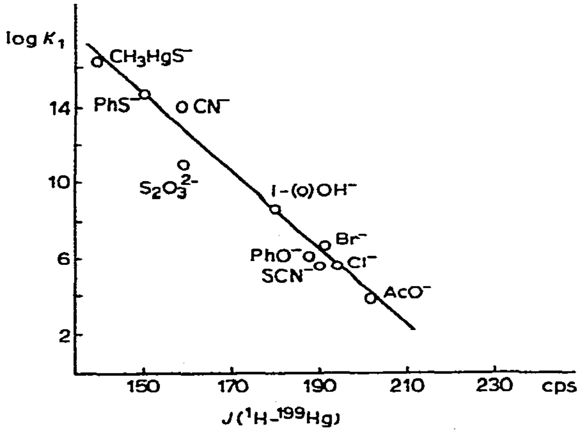

Fig. 2. Plot of the stability constants for the complex CH_3HgL *versus* the corresponding values of $J(^1H$—$^{199}Hg)$.

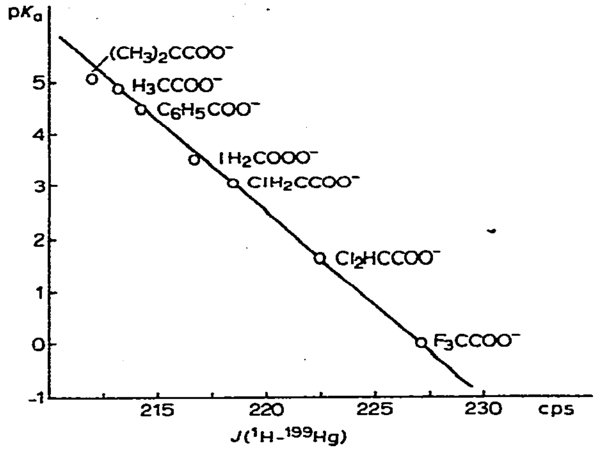

Fig. 3. Plot of the pK_a values for various carboxylic acids *versus* $J(^1H-^{199}Hg)$ for their respective complexes with methylmercury.

that the $J(CH_3-^{199}Hg)$ spin–spin coupling constants for methylmercury complexes of the type CH_3HgL vary both with the oxidative dimerization potentials (E) of the ligands L,

$$2L^- \overset{E}{\rightleftharpoons} L_2 + 2\bar{e}$$
$$(L = Cl^-, Br^-, OH^-, SCN^-, I^-, S_2O_3^{2-}, CN^-)$$

and with the relative S_N2 reactivity parameters which feature in the Swain–Scott equation.

Since ligands having the same donor atom and a similar structure exhibit an affinity for methylmercury similar to that for the proton, a linear relationship between the pK_a values for the parent ligands and the $J(CH_3-^{199}Hg)$ spin–spin coupling constants for the corresponding methylmercury complexes may be expected to exist. An NMR study of mercury carboxylates[37] has provided support for this suggestion (Fig. 3) *. The influence of the organic group bound to the mercury atom in the organomercury cation on the coordination properties of the latter has, however, received only limited study. It might be expected that the stability of such complexes would increase with the polarity of the carbon—metal bond, i.e. with the effective positive charge on the mercury. However, this may be a somewhat oversimplified picture since rather contradictory results have often been reported. Thus, for the OH^- complexes[29a] the increasing stability series $C_2H_5Hg^+ < CH_3Hg^+ < C_6H_5Hg^+$ has been found, while for the corresponding SCN^- [39] complexes a different series is found: $CH_3Hg^+ < C_6H_5Hg^+ < n\text{-}C_3H_7Hg^+ < i\text{-}C_3H_7Hg^+ < n\text{-}C_4H_9Hg^+ < i\text{-}C_4H_9Hg^+$. In this instance it is difficult to decide whether a difference in the nature of

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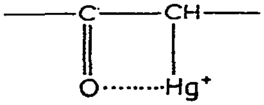
* A linear relationship between $J(^1H-^{199}Hg)$ for the complexes $(R_1R_2CH)_2Hg$ and the pK_a values for $R_1R_2CH_2$ has also been demonstrated[38].

the ligand (OH^- being a hard base while SCN^- is soft) or experimental errors are responsible for this discrepancy.

Table 4 summarizes the effect of the organic group R on the coordination properties of RHg^+. It should be noted that the introduction of fluorine into the group R markedly increases the stability of the resulting complexes. Furthermore, the stability order in a series of complexes of the type R_FHg^+ depends on the nature of the ligand (*cf.* I^- and OH^-).

The varying properties of anions as ligands may be responsible for the substantial alterations in the stability of a series of organomercury complexes containing different R groups[40], *e.g.* when $L = Cl^-, Br^-, OH^-$ the following stability series is obtained, $BuHg^+ < PrHg^+ < EtHg^+ < MeHg^+$ but when $L = I^-$, the order is inverted: $MeHg^+ < EtHg^+ < PrHg^+$. This behaviour may be explained on the basis of the "soft–soft, hard–hard" principle.

Stability constants have been measured polarographically for a number of bromide/organomercury cation complexes in 60% aqueous DMF[23]. In this case the following order was observed: $C_6H_5Hg^+ < C_6H_5CH_2Hg^+ < C_6H_5CH_2CH_2Hg^+$. Such an order agrees with the electronic effect of the organic group bound to the mercury atom. The observed values are, however, rather low for α-oxoorganomercury cations. This may be explained by assuming the existence of intramolecular coordination of the type:



which would tend to diminish the affinity of the cation for the bromide anion. Some support for this assumption is provided by the fact that the stability constants for the addition of a second ligand have "normal" values, since the cationic centre in the complex $RCOCH_2HgBr$ has already been eliminated by the addition of the first ligand (Br^-) so that no internal coordination may be expected to occur.

Although normally only one unidentate ligand may be readily added to an organomercury cation, the addition of a second and third ligand has also been observed. Barbieri and co-workers[41–43] applied paper electrophoresis and ion-exchange techniques to establish the existence of $RHgL_n^{1-n}$ ($L = SCN^-$) species in aqueous solution. Later, an attempt was made by Barbieri and Bjerrum[32] to clarify the effect of the organic group and the ligand anion on the ability of organomercury cations to add second and third ligands. The stability constants of some organomercury (halide or pseudo-halide) complexes were measured using the solubility method in 1 *M* ($NaClO_4 + NaX$) aqueous or 50% methanol solutions. No substantial anionic complex formation was detected when $X = Cl^-$ or Br^- and when $X = I^-$ or SCN^- the measured values of K_2 and K_3 were found to be close to those reported earlier[43].

Polarographic studies in 60% aqueous dimethylformamide[33] have been used to estimate

TABLE 4

STABILITY CONSTANTS FOR COMPLEXES OF ORGANOMERCURY CATIONS WITH INORGANIC ANIONS (25°)

Cation	*Ligand*	*Solvent*	*logK_1*	*K_2*	*K_3*	*Ref.*
$C_2H_5Hg^+$	OH^-	H_2O	9 to 10	-	-	29a
	Br^-	H_2O	-	0.3	1.1	29b
	SCN^-	H_2O; $\mu = 1$	-	0.80	1.59	32
	SCN^-	50% MeOH $\mu = 1$	-	1.73	0.56	32
	I^-	H_2O, $\mu = 1$	-	0.215	5.63	32
$C_4H_9Hg^+$	SCN^-	50%, MeOH, $\mu = 1$	-	2.30	0.565	32
$C_6H_5Hg^+$	OH^-	H_2O	10.00	-	-	29a
	Br^-	60%, DMF–H_2O	5.3	5.5	-	33
$C_6H_5CH_2Hg^+$	Br^-	60% DMF–H_2O	5.4	12.5	-	33
$C_6H_5CH_2CH_2Hg^+$	Br^-	60% DMF–H_2O	8.3	17.0	-	33
$C_6H_5CH(COOEt)Hg^+$	Br^-	60% DMF–H_2O	4.4	850	-	33
t-$BuCOCH_2Hg^+$	Br^-	60% DMF–H_2O	5.2	560	-	33
CF_3Hg^+	OH^-	H_2O	10.76	-	-	34
	Cl^-	H_2O	5.78	-	-	34
	Br^-	H_2O	7.24	-	-	34
		H_2O	9.63	-	-	34
$C_2F_5Hg^+$	OH^-	H_2O	10.58	-	-	34
	Cl^-	H_2O	5.64	-	-	34
	Br^-	H_2O	7.16	-	-	34
	I^-	H_2O	9.66	-	-	34
n-$C_3F_7Hg^+$	OH^-	H_2O	10.50	-	-	34
	Cl^-	H_2O	5.56	-	-	34
	Br^-	H_2O	7.16	-	-	34
	I^-	H_2O	9.96	-	-	34
$(NO_2)_3CHg^+$	OH^-	H_2O	11.26	-	-	35b
$(CF_3)_2CFHg^+$	OH^-	H_2O	10.64	-	-	35a
	Cl^-	H_2O	5.84	-	-	35a
	Br^-	H_2O	7.62	-	-	35a
	I^-	H_2O	9.88	-	-	35a
CF_3CHFHg^+	OH^-	H_2O	10.28	-	-	35a
	Cl^-	H_2O	5.55	-	-	35a
	Br^-	H_2O	7.22	-	-	35a
	I^-	H_2O	9.06	-	-	35a
$CF_3CH_2Hg^+$	OH^-	H_2O	10.20	-	-	35a
	Cl^-	H_2O	5.58	-	-	35a
	Br^-	H_2O	7.18	-	-	35a
	I^-	H_2O	8.98	-	-	35a

the stability constants for anionic complexes of the type $RHgBr_2^-$ (where R = phenyl, benzyl, β-phenylethyl, α-carboethoxybenzyl or pivaloylmethyl). The results given in Table 4 indicate that the formation constants for the complexes $RHgL_2^-$ and $RHgL_3^{2-}$ are much lower than those for RHgL. However, in general, the effect of the organic group R upon the stabilities of the complexes RHgL and $RHgL_2^-$ appears to follow the same trend, except for those compounds in which internal coordination may interfere.

Since the stability of charged anionic complexes is rather low, quantitative studies of equilibria involving such complexes are difficult. On the other hand, these complexes play an important part in organometallic reactions altering the rate, and sometimes the mechanism, quite significantly[44]. The effect of anions as catalysts (referred to as anion catalysis[45]) is a particular case of nucleophilic catalysis (also including specific solvation by the solvent), and is a very common phenomenon in organometallic chemistry.

A recent paper[95] dealing with organomercury chloride complexes in an aprotic solvent (acetonitrile), with triphenylchloromethane as the chloride source, has reported abnormally large values for the stability constants of methyl- and ethyl-mercury chloride anionic complexes $RHgCl_2^-$ (1×10^3 and 1.63×10^3, respectively). This striking difference is most probably attributable to the effect of exchanging a protic for an aprotic solvent. Most surprisingly, however, anionic complex formation was absent in the case of propyl- and phenyl-mercury chlorides.

Such a significant difference in the behaviour of the organic group can hardly be explained by spatial or electronic factors. Complexes of the type $RHgX_3^{2-}$ were not reported in this study.

2. *Complexes containing neutral ligands*

Generally, adducts of organomercury salts with neutral ligands may be isolated when the neutral molecule is coordinated more strongly to the mercury atom than the counter-ion. Under these circumstances, the ligand replaces the anion which is forced out into the outer sphere of the complex.

During the course of their studies on symmetrization reactions of organomercury salts of the type RHgX (where R = Me, Ph, Bu; X = Cl, Br, ClO_4, BF_4) by phosphines and arsines, Coates and his co-workers[46] noted that in some cases crystalline adducts were formed which slowly transformed to give the final products.

$$2RHgX + 2Et_3P \rightarrow (\text{complex}) \rightarrow R_2Hg + (Et_3P)_2HgX_2$$

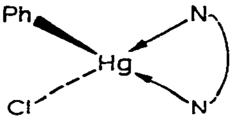
No crystalline adduct was isolated for phenylmercury chloride. It was found[47], however, that when triphenylphosphine was added to a dilute aqueous solution of PhHgCl in dioxane, the conductivity of the solution gradually increased until the reactant ratio attained a value of 1/1.

Coates and his co-workers[46,48] have isolated and identified a great number of complexes of the type [RHgL]X, where R may be Me, Et, Pr or Bu; X = Cl, Br, I, ClO_4 or BF_4; L = Me_3P, Et_3P, Me_2PhP, Et_3As or Ph_3As.

The dismutation rate of complexes of the type $[RHg \cdot PR_3]X$ increased both with the affinity of the halide ion for the alkylmercury cation[11] ($X = Cl < Br < I$) and also with the polarity of the solvent (benzene < THF < acetone < MeOH). No complexes were isolated with the triphenylphosphine ligand when X was a halogen, since under the circumstances the symmetrization rate was too great. When $X = ClO_4$, the complexes did not undergo immediate dismutation. Thus, methylmercury perchlorate gave isolable complexes not only with phosphines, but also with triethyl- and triphenyl-arsine and with pyridine. With aromatic organomercury derivatives, only the phenylmercury nitrate/triphenylphosphine complex was isolated; this complex eliminated diphenylmercury in the presence of NaBr or NaI.

In contrast to the lack of success in isolating an adduct of phenylmercury chloride with triphenylphosphine, bidentate ligands such as 1,10-phenanthroline (phen) or 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp) readily added a phenylmercury chloride molecule to give crystalline complexes[49,50].

On the basis of IR data obtained for these complexes, the authors[49,50] have suggested the following structure:



An attempt to obtain a similar complex with 2,2′-bipyridyl, *i.e.* PhHgCl • bipy, was unsuccessful. The attempted isolation of complexes of the type PhHgBr • tmp and PhHgBr • phen led only to symmetrization products.

Conductivity and molecular weight measurements in acetone solutions of the complex PhHgCl • phen indicate that in this solvent the complex is completely dissociated. In boiling benzene, however, dissociation occurs:

$$2PhHgCl\cdot phen \rightarrow phen\cdot HgCl_2 + Ph_2Hg + phen \text{ (Ref. 45)}$$

However no dissociation occurs for PhHgCl • tmp even after boiling for 8 h in benzene.

Chelate complexes of RHg^+ cations (R = Me, Ph)[57] with 8-hydroxyquinoline have also been isolated and characterized.

It must be pointed out, however, that in spite of many common features (*e.g.* facile dissociation), RHgL ($L = R_3P$, R_3As) (I) and $PhHgL_2$ (L_2 = phen, tmp) (II) adducts apparently possess different structures. For species (I), a structure of the type $[RHgL]^+X^-$ is most probable in view of the observed increase in conductivity on addition of R_3P to aqueous dioxane solutions of RHgX[47]. This agrees with the apparent dependence of the rate of dissociation on the nature of the anion X^-. The structure of complexes containing bidentate ligands is not as yet clear. In contrast to (I), these complexes are apparently non-ionic. Some evidence in favour of this suggestion is provided by the fact that acetone solu-

TABLE 5

LOGARITHMIC STABILITY CONSTANTS FOR SOLVATE COMPLEXES INVOLVING THE PHENYLMERCURY CATION (IN CH_2Cl_2 AT 25°) [52]

Ligand	$\log K_1$
Tetrahydrothiophene	10.0
Pyridine	8.1
Hexamethyltriamidophosphate	6.2
Tetramethylurea	3.8
Dimethylsulphoxide	3.3
Dimethylformamide	2.8
Methanol	1.4
Acetonitrile	1.1
Tetrahydrofuran	0.6

tions of (II) are non-conducting, the Hg—Cl bond remaining intact (IR data).

Complex formation involving neutral ligands has been extensively studied by polarographic methods for phenylmercury cations in methylene chloride[52]. The logarithms of the observed stability constants calculated according to the De Ford—Hume method are listed in Table 5.

The effect of ligand concentrations on the half-wave potentials of $PhHgClO_4$ solutions have also been studied from which it has been deduced that 1/1 complexes were present *.

Stable solvent complexes (with thiophane, pyridine etc.) have been isolated in the crystalline state and their 1/1 composition verified by chemical analysis.

The data listed in Table 5 embrace a series of solvents widely employed in organic chemistry. They enable an estimation of the respective nucleophilicity of solvents towards the phenylmercury cation, one of the softest Lewis acids. The data indicate that the affinity of solvents for the phenylmercury cation in general parallels the "donor numbers" of Gutmann[23].

The logarithms of the stability constants obtained for the phenylmercury cation (Table 5) correlate fairly well with the *ortho*-proton — ^{199}Hg spin—spin coupling constants $J(^1H-^{199}Hg)$ [52] (Fig. 4). A similar correlation has been obtained by Scheffold[37] for methylmercury complexes with anions, as has been discussed above.

3. *Organomercury compounds of the type R_2Hg*

Introduction of a second organic group into an organomercury compound generally decreases its coordination ability. The mercury—ligand interaction becomes so weak that in most cases it is hardly measurable quantitatively. This is the reason why data on the

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* For DMF and DMSO, the $E_{1/2}$ *vs.* log L plots exhibit inflections probably associated with the formation of 1/2 complexes at higher ligand concentrations.

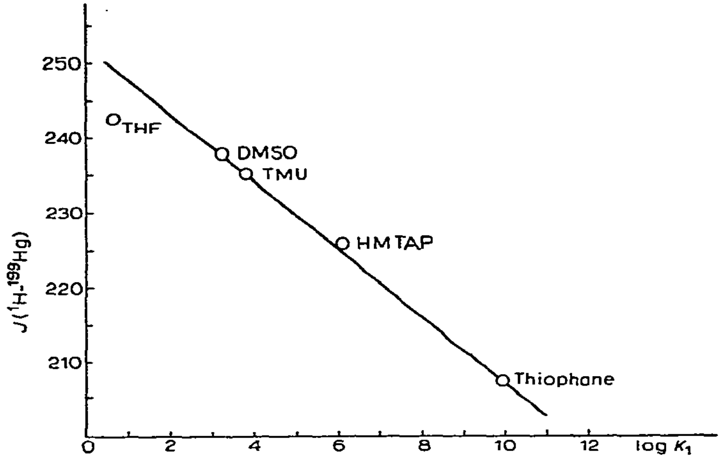


Fig. 4. Plot of the formation constants for the complexes PhHgL *versus* $J(^1H-^{199}Hg)$ for phenylmercury perchlorate dissolved in L.

coordination properties of symmetrical organomercurials is, to date, somewhat scarce.

Attempts to isolate dialkylmercury adducts with hexamethyltriamidophosphate (HMTAP), diazabicyclooctane and 2,2′-bipyridyl[53] have been unsuccessful. Some indications have been obtained, however, regarding the extent of mercury–ligand interaction in compounds of the type R_2Hg.

Lagowski and co-workers[54], using oscillometric titration techniques, have found that diphenylmercury forms very weak 1/1 and 1/2 adducts with neutral donors such as pyridine, triphenylphosphine, dimethylsulphoxide etc. However, diphenylmercury has been reported[50] as forming no complex with triphenylphosphine.

NMR spectra of diphenyl-[55], dimethyl-[56,57], bis(trifluoromethyl)-[59], di-t-amyl-[60] and dibenzyl-mercury[61] have demonstrated that the chemical shifts of protons in organic groups, as well as the spin–spin coupling constants $J(^1H-^{199}Hg)$ are largely solvent-dependent. This may be attributed to specific solvation of the mercury atom in these compounds.

According to ^{19}F NMR data obtained for bis(*p*-fluorophenyl)mercury[62], the solvation of the mercury atom in various solvents increases according to the following sequence: $CH_3Cl < CH_3NO_2 < C_6H_6 < CH_3CN <$ dioxane $<$ acetone $<$ ethyl acetate $<$ THF $<$ DME $<$ pyridine $<$ thiophane $<$ DMSO $<$ HMTAP.

Assuming that the Fermi contact mechanism is predominant in spin–spin coupling, the authors[58] have attributed the increase of $J(^1H-^{199}Hg)$ in relation to the solvating ability of the solvent to an increase in the *s* character of the sp^n hybride orbitals of the mercury atom, due to the greater displacement of the *p*-electrons towards the carbon atom on coordination.

It should be pointed out, however, that NMR data alone are not sufficient to provide complete information on the composition and structure of complexes, so conclusions regarding relative stabilities based on such data are not necessarily correct. In addition, it is necessary to take into account the variation of the dielectric constant in going from one solvent to another. Such differences may explain the observed discrepancies in the series of solvation abilities obtained for different R_2Hg-type organomercurial compounds[56,57,62].

Recently[63], the isolation of crystalline adducts of diphenylmercury with bidentate ligands such as 2,9-dimethyl-1,10-phenanthroline (dmp), 1,10-phenanthroline (phen) or 2,4,7,9-tetramethyl-1,10-phenanthroline (tet) has been reported. The adducts obtained, $Ph_2Hg\cdot(phen)_2$, m.p. 121°, $Ph_2Hg\cdot(dmp)_2$, m.p. 102° and $Ph_2Hg\cdot(tet)_2$, m.p. 230–233°, differ from the 1/1 complexes obtained with bis(perfluorophenyl)mercury and bidentate ligands, *i.e.* R_2HgL_2 (L_2 = phen, dmp, etc.).

Molecular weight measurements in benzene and chloroform have shown that these complexes are completely dissociated in such solvents:

$$Ph_2Hg\cdot(phen)_2 \rightleftharpoons Ph_2Hg + 2phen$$

Although spectroscopic data have provided some evidence for coordination in these species, a clathrate structure cannot be completely ruled out, especially when the unusual composition of these complexes is taken into account.

When the R groups in R_2Hg-type compounds are more electronegative, complex formation becomes much more favourable. For example, the bis(phenylethynyl)mercury complex with 1,10-phenanthroline may be isolated[66] while stable 1/1 phenanthroline complexes are also formed with carborane mercury derivatives[67].

A number of complexes containing neutral ligands have been synthesized for bis(trinitromethyl)mercury, *i.e.* $[(NO_2)_3C]_2Hg\cdot L$, where L is THF, dioxane, thiophane, DMSO, DMF, dimethylsulphone, 3-picoline-*N*-oxide, acetoxime, etc.[68].

The complexes of perfluorinated organomercurials have been studied most extensively. It has been found that fluorinated organomercurials differ markedly from their hydrocarbon analogues in their coordination properties. Table 4 demonstrates that the association constants found for fluorinated alkylmercury cations with OH^-, Cl^-, Br^- and I^- anions are in all cases greater than those for the respective alkylmercury cations[34]. Because of the high electronegativity of fluorinated organic groups, $(R_F)_2Hg$ compounds are markedly different from the analogous R_2Hg compounds both in their physical and chemical properties.

In contrast to $(CH_3)_2Hg$, which is a liquid and insoluble in water, crystalline $(CF_3)_2Hg$ is water-soluble and its aqueous solutions have a small but appreciable conductivity[69]. This may be explained by assuming that the following equilibria exist in solution

$$(CF_3)_2Hg + H_2O \rightleftharpoons (CF_3)_2HgOH_2 \rightleftharpoons (CF_3)_2HgOH^- + H^+$$

In contrast to R_2Hg, $(R_F)_2Hg$ compounds are capable of forming complexes with a variety of ligands.

Conductometric titration data[70] obtained for $(CF_3)_2Hg$–KX (X = Cl, Br, I) and CF_3HgX–KX (X = Br, I) systems have shown that 1/1 and 1/2 complexes may be formed in aqueous solution depending on the nature of X. For example, CF_3HgBr gave a 1/1 complex with KBr, whereas no complex formation was observed with KCl. When treated with zinc(II), copper(II) or nickel(II) ethylenediamine complexes, solutions containing $(CF_3)_2Hg$, CF_3HgI, C_3F_7HgI and KI gave coloured precipitates which were claimed[70] to contain $[Hg(CF_3)_2I_2]^{2-}$, $[Hg(CF_3)I_3]^{2-}$ and $[Hg(C_3F_7)I_3]^{2-}$ anions.

The analysis of IR and Raman spectral data[76] failed to provide support for complex formation in solutions containing $(CF_3)_2Hg$ and KI. Apparently, if any interaction between $(CF_3)_2Hg$ and I^- exists, it will be rather weak. Indeed, the organomercurial compound may be extracted unchanged by ether extraction from aqueous solutions containing KI, while $(CF_3)_2Hg$ has only a slight effect on the solubilities of alkali metal halides or pseudo halides[72]. Cryoscopic measurement have shown[72] that the stability of bis(trifluoromethyl)mercury anionic complexes is quite low.

	$[(CF_3)_2HgCl]^-$	$[(CF_3)_2HgBr]^-$	$[(CF_3)_2HgI]^-$
log*K*	−0.52	0.20	0.98

Both R_FHgX and $(R_F)_2Hg$ form complexes with neutral ligands. Stepwise complex formation of the type:

$$(R_F)_2Hg + L \rightleftharpoons (R_F)_2HgL \text{ and } (R_F)_2HgL + L \rightleftharpoons (R_F)_2HgL_2$$

where R = CF_3, C_2F_5, $(CF_3)_2CF$, CF_3CFH, CF_3CH_2 and L = $C_5H_{11}N$, C_5H_5N, C_5H_5NO, $(C_6H_5)_3P$, $(CH_3)_2CO$, $(CH_3)_2SO$, C_2H_5OH, $(CH_3)_2S$ occurs in benzene as demonstrated by oscillometric titration studies[54].

IR data have led to the conclusion[73] that $(R_F)_2Hg$ compounds [where R_F = CF_3, $(CF_3)_2CF$, C_2F_5, CF_3CHF, CF_3CH_2] form complexes with pyridine *N*-oxide, tetramethylene sulphoxide, piperidine and ethylene diamine in CCl_4. The shifts in the N→O and S→O stretching frequencies have been studied in an attempt to obtain the relative stability series which was found to agree with the corresponding electronegativity series for R_F groups attached to the mercury atom (Table 6): $[(CF_3)_2CF]_2Hg > (CF_3)_2Hg > (C_2F_5)_2Hg > (CF_3CFH)_2Hg > (CF_3CH_2)_2Hg$. Some of the $(R_F)_2HgL$ and R_FHgL_2 complexes have been isolated and identified.

Bis(pentafluorophenyl)mercury forms stable complexes with 2,2′-bipyridyl(bipy) and 1,2-bis(diphenylphosphinoethane)[64]. In addition, complexes of bis(tetrafluoro-4-pyridyl)- and bis(tetrafluoro-2-pyridyl)mercury with 2,2′-bipyridyl have also been isolated and identified.

Fluorinated organomercury complexes $(R_F)_2Hg \cdot L_2$ also result from the decarboxylation

TABLE 6

PAULING ELECTRONEGATIVITIES FOR SOME PERFLUOROALKYL COMPOUNDS [a]

	CF_3	CF_3CF_2	$(CF_3)_2CF$	$(CF_3)_2CHF$	CF_3CH_2
Electronegativity	3.3	3.2	3.4	2.8	2.7

[a] x_F 4.0, x_{Cl} 3.0.

of mercuric salts of the respective carboxylic acids $(R_FCO_2)_2HgL_2$ [67,65].

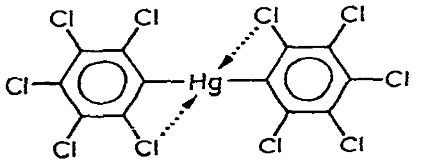
$$(R_FCO_2)_2HgL_2 \xrightarrow[\text{Py}]{t^\circ} (R_F)_2HgL_2$$

$R_F = CF_3, C_2F_5, C_3F_7; L_2 =$ bipy, phen

$R_F = C_6F_5; L_2 =$ bipy, phen, phos

Complexes of unsymmetrical fluorinated organomercurials, $R_FHgX \cdot L_2$ (where L_2 is a neutral bidentate ligand) are difficult to study since they are apt to readily disproportionate. Canty and Deacon[49,76], however, have succeeded in isolating a number of complexes of the type $C_6F_5HgX \cdot L_2$ (where X is Cl, Br; L_2 is 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline). IR data suggest that these complexes are four-coordinate and tetrahedral. Nevertheless, conductivity and molecular weight measurements have shown that even the most stable of these complexes is dissociated in acetone solution.

Bis(pentachlorophenyl)mercury, in contrast to its fluorinated analogue, gives no complexes with 2,2′-bipyridyl and 1,10-phenanthroline. Only a very unstable complex with 3,4,7,8-tetramethyl-1,10-phenanthroline could be isolated[77]. This may be related not only to the lower electronegativity of the pentachlorophenyl group compared to that of the pentafluorophenyl group but also to the possibility of intramolecular coordination which would completely satisfy the coordination sites on the mercury atom[78].



For the unsymmetrical compound C_6Cl_5HgCl, complexes with 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 2,4,7,9-tetramethyl-1,10-phenanthroline have been isolated[49]. The $C_6Cl_5HgX \cdot L_2$ complexes obtained, unlike the analogous $C_6F_5HgX \cdot L_2$ complexes, disproportionate much less readily. The authors[49] have suggested that the ease of disproportionation decreases with an increase in the difference between the electronegativities of the organic group R and the halogen X.

IV. ORGANOTHALLIUM COMPOUNDS

Of the organic derivatives of thallium, only compounds of the type R_2TlX are of relevant interest. Other organic derivatives, such as R_3Tl and $RTlX_2$, are much less stable and their coordination chemistry has been studied much less extensively[79].

Dialkyl- and diaryl-thallium(III) derivatives are isoelectronic with the corresponding organomercury compounds and usually resemble these as far as chemical reactivity or stability of their complexes are concerned[79, 80]; they are quite stable towards water or oxygen.

A very characteristic feature of R_2TlX-type compounds (where X is a halide) is their ability to form ionic crystals. Neither organotin nor organolead compounds are ionic in the crystalline state, the respective organometallic cations being formed only in highly ionizing solvents. Solid organomercury halides are well established as being covalent.

Structural investigations[81] of solid $(CH_3)_2TlI$ have demonstrated that the crystal lattice is essentially ionic, each linear $CH_3{-}Tl{-}CH_3$ unit being surrounded by four iodide ions and each iodide ion having four $CH_3{-}Tl{-}CH_3$ units near it.

The existence of organothallium cations in solution has been demonstrated by conductivity measurements of aqueous solutions of $(CH_3)_2TlOH$ [82], as well as by Raman spectral data[83] obtained for solutions of $(CH_3)_2TlNO_3$ and $(CH_3)_2TlClO_4$. The compounds $(CH_3)_2TlCN$ [84] and $(CH_3)_2TlCNO$ [85] have also been shown to be ionized in solution.

Dimethylthallium dissolved in water is a very weak acid. This suggests that the water molecules in the first coordination sphere are only weakly coordinated to thallium. This fact, as well as the high degree of dissociation found for a number of R_2TlX organothallium salts in solution, suggests that organothallium cations have only a weak acceptor ability.

The anionic complexes $[R_2TlX_2]^-$ and $[R_2TlX_3]^{2-}$ (R = Me, Ph; X = Cl, Br, I, SCN) have been obtained as the salts of tetraphenylarsonium and tetrabutylammonium cations[86]. The singly charged complex anions have a coordination number of four and are apparently tetrahedral. The authors[86] have suggested that the complex anions of the type $[R_2TlX_3]^{2-}$ have a coordination number of five, which is rather unusual for thallium.

Huber and Ernst[87] have isolated a number of complexes of general formulae $(C_6H_5)_2TlX \cdot 2L$, where X = Cl, Br; L = Py, DMSO, DMF and $(C_6H_5)_2TlX \cdot L$, where L = DMF (X = I), phen (X = Cl, Br, I). These complexes were very labile and dissociated in solution. Attempts to isolate $(C_6H_5)_2TlX$ (X = Hal) complexes with 2,9′-bipyridyl,

Ph_3PO and Ph_3AsO were unsuccessful. However, $(CH_3)_2TlClO_4$ complexes with pyridine and 1,10-phenanthroline have been shown to be stable[88] and in addition bis(β-chlorovinyl)thallium chloride complexes with pyridine and piperidine have been isolated[94].

Shier and Drago[89] studied the effect of solvent on dimethyl- and diethyl-thallium perchlorates in a wide variety of solvents using IR and PMR spectroscopy. It was found that the organothallium moiety retains its linear configuration in all solvents studied with the exception of pyridine. The IR spectrum of the $(CH_3)Tl^+$ cation observed in pyridine was strikingly different from that in other solvents[88]. The authors[88, 89] have suggested that this is due to the formation of a distorted T-shape complex cation $[(CH_3)_2Tl \cdot Py]^+$ with a non-linear $(CH_3)_2Tl^+$ unit in pyridine.

The spin–spin coupling constants $J(Tl{-}CH_3)$ measured for dimethylthallium perchlorate in various solvents increase in the following sequence: $(CH_2)_4SO_2 \sim CH_3CN \sim H_2O \sim CH_3OH \sim (CH_3)_2CO \leqslant HCON(CH_3)_2 \sim (CH_3)_2SO \sim CH_3CON(CH_3)_2 \sim (CH_2)_4SO < [(CH_3)_2N]_3PO$. The series essentially resembles those for donor strength[28] and solvation ability towards the phenylmercury cation[52].

Although the number of organothallium complexes isolated with various ligands is quite large, the only quantitative data at present available for these complexes are those for organothallium chelates containing β-diketones or β, δ-triketones[90] (see Table 7).

The logarithms of the stability constants measured for organothallium β-diketone enolates correlate quite well with the pK_a values for these complexes.

The stability of the complexes is also affected by the nature of the organic group attached to the thallium atom, the stability increasing as follows: $(CH_3)_2Tl^+ < (C_2H_5)_2Tl^+ < (n\text{-}C_3H_7)_2Tl^+ < p\text{-}CH_3C_6H_4(C_6H_5)Tl^+ < (C_6H_5)_2Tl^+$. The resulting stability series cannot be explained on the basis of the electronic effects arising from the groups attached to the thallium atom. The authors[90] suggest that as the size of the organic group increases the hydrophobic nature of the organothallium cation increases and chelation becomes more favourable.

As with organomercurial compounds, perfluorinated organothallium compounds form complexes more readily than their hydrocarbon analogues. Thus, for $(C_6F_5)_2TlX$ (where

TABLE 7

LOGARITHMIC STABILITY CONSTANTS FOR THALLIUM CHELATES OF β-DIKETONES IN 75% DIOXANE SOLUTION AT 30°

$[\beta\text{-}R_1COCHCOR_2]^-$ R_1	R_2	Me_2Tl^+ ClO_4^-	Et_2Tl^+ ClO_4^-	Et_2Tl^+ NO_3^-	Pr_2Tl^+ NO_3^-	Ph_2Tl^+ ClO_4^-	$Ph(p\text{-}Tol)Tl^+$ ClO_4^-
CH_3	CH_3	5.56	5.60	5.67	5.92	6.89	6.69
C_6H_5	CH_3	5.79	6.04	6.12	6.34	7.36	7.13
C_6H_5	C_6H_5	6.90	7.07	6.96	7.51	8.43	8.29
CH_3	$CH_2COC_6H_5$	5.25	5.46	5.49	5.83	6.88	6.64
C_6H_5	$CH_2COC_6H_5$	5.69	5.94	5.96	6.34	7.33	7.07

$X = Cl, Br$) four-coordinate anionic bromide and chloride complexes were isolated as their tetraethylammonium and tetraphenylphosphonium salts[91]. In contrast to $(C_6H_5)_2TlX$, complexes with 2,2′-bipyridyl, triphenylphosphine oxide ans triphenylarsine oxide of general formulae $(C_6F_5)_2TlX\cdot L$ ($X = CO_2CF_3$; $L = Ph_3PO, Ph_3AsO$) and $(C_6F_5)_2TlX\cdot 2L$ ($2L$ = bipy; $L = Ph_3PO, Ph_3AsO$) have been synthesized in addition to complexes with 1,10-phenanthroline, triphenylphosphine and triphenylarsine[91,92].

Again in contrast to R_2TlX compounds which are known to be monomeric and possess linear R–Tl–R units, compounds of the type $(C_6F_5)_2TlX$ are believed to be dimeric with a non-linear arrangement of the organic groups[91].

Dimethylthallium sulphate, $[(CH_3)_2Tl]_2SO_4$, is thought to be ionic. However, in $[(C_6F_5)_2Tl]_2SO_4$, covalent Tl–O bonds are present, as has been demonstrated by IR spectroscopy[93]. This latter fact may also provide evidence in favour of the stronger acceptor ability of fluorinated organothallium compounds in comparison to their hydrocarbon analogues.

A comparison of the coordination properties of alkylmercury and dialkylthallium compounds leads to conclusion that the organomercury complexes are more stable. This behaviour cannot be due to the difference between electronegativities of the elements (2.00 for mercury, 2.04 for thallium, Pauling scale) since this is rather small. More probably, the destabilizing effect of the second organic group attached to the metal atom (*cf.* RHg^+ and R_2Tl^+) and the high stability of the linear R–Tl–R structure, which would have to be distorted upon complex formation, are more important. Furthermore, changes in the nature of the metal (softness) may also be significant.

V. ORGANO-TIN AND -LEAD COMPOUNDS

It is well known that tin and lead tetrahalides are capable of adding two further ligands to form six-coordinate complexes, and for this reason organometallic derivatives may be expected to behave in a similar fashion. The presence of an organic group in a molecule usually diminishes its tendency to form complexes, and hence the observed stability of the complexes should decrease as follows: $MX_4 > RMX_3 > R_2MX_2 > R_3MX > R_4M$.

The configuration of the complexes readily follows from the type of metal hybridization involved. In R_4M complexes sp^3-hybrid orbital exist and tetrahedral configurations are attained. In MX_6^{2-}, the other limiting case, the six sp^3d^2-hybrid orbitals of the metal are directed towards the ligands so that the resulting complex will be octahedral. When only one ligand adds to an organometallic molecule, a trigonal-bipyramidal complex (coordination number five) should be formed through the participation of the sp^3d-hybrid orbitals of the metal. In the following discussion, a number of experiments will be described which show agreement with these simple rules, although in many cases the structures mentioned are often distorted, due to the different nature of the ligands in an organometallic complex.

Unlike organothallium compounds, organo-tin or -lead compounds do not form ionic crystals. Thus, trimethyltin fluoride is a bridged polymer containing a penta-coordinated tin atom[99]. Even R_3SnX compounds ($X = ClO_4$ [96], NO_3 [96], BF_4 [97], AsF_6 [98]) which may be thought as being ionic in the solid state are bridged polymers according to IR data. A planar arrangement has been suggested for the organic group. although the results obtained for Me_3SnNO_3 were not unambiguous (*cf.* refs. 96 and 108).

Organotin compounds R_3SnX and R_2SnX_2 (X = Cl, Br, I) are monomeric whereas their organolead analogues are bridged polymers[100]. This suggests that organolead compounds are possibly more efficient at complex formation than the similarly structured organotin compounds.

Crystalline organotin compounds are usually monomeric when the group X is a chelating ligand, *e.g.*, a carboxylate of the $R_2Sn(OOCR)_2$ type[101,102], or when the organic group is so bulky that it does not allow the R_3Sn group to become planar and to lead to bridged coordination. Thus, Me_3SnOAc forms a penta-coordinated, bridged polymer in the solid state while i-Pr_3SnOAc is a tetra-coordinated monomer[103].

Addition of a solvent usually destroys these polymeric structures and produces solvated organometallic monomers, and in some cases the M—X bond dissociates to give organometallic cations.

Organotin compounds of the type R_3SnX were shown some time ago to be strong conductors of electricity in polar solvents. This was explained by assuming that solvated organotin cations and anions X^- were present in the solution[104].

$$R_3SnX + \text{solv.} \rightarrow [R_3Sn \cdot \text{solv.}]^+ + X^-$$

Spectroscopic studies[105,106] revealed that in solution the R_2Sn^{2+} ions possess a linear structure while the R_3Sn^+ ions are planar. Similar results were obtained for solutions of Me_2Pb^{2+} in water[107].

IR spectroscopic data obtained for the solid aquo complex of formula (Me_3SnOH_2)-NO_3 [108] indicated that the bridged structure of anhydrous Me_3SnNO_3 was retained in this compound. The water molecule was apparently arranged in the Me_3Sn plane and weakly coordinated to the tin atom. It should be pointed out that structural data obtained for solid organotin compounds, when based solely on IR spectra, are often controversial and should be checked by other methods.

1. Anionic complexes

Tin or lead tetrahalides have long been known to form anionic complexes.

$$MX_4 + 2X^- \text{——} MX_6^{2-} \quad (X - Hal)$$

Organo-tin or -lead halides may be expected to behave similarly, although somewhat less actively since covalent bonding exists between the organic group and the metal atom in tin compounds. Such anionic complex formation has indeed been verified via Ramann spectra[109], potentiometric titrations[110] and ion-exchange chromatography[111]. Various salt-like compounds involving organo-tin or -lead complexes as the anions have also been isolated (Table 8).

The results presented in Table 8 demonstrate that the structures of the complex anions generally correspond to those assumed on the basis of hybridization involving *d*-orbitals. However, some controversy regarding this point exists in the literature (see *e.g.* refs. 115, 118 and 120). The spatial arrangement of the ligands (whether they are *cis* or *trans*) remains an unresolved problem in some complexes.

Quantitative data regarding the stability of organotin complexes containing halide ligands have been reported[110, 111, 122–129].

In Table 9 the stability constants for anionic complexes of organotin cations, measured by different methods in water, are summarized.

As seen from Table 9, the ability to form complexes decreases as the number of organic groups attached to the metal atom in the organometallic cation increases. The complex formed between $MeSn^{3+}$ and fluoride is quite stable ($K_5 = 1.7 \times 10^2$), whereas the

TABLE 8

SOLID ANIONIC COMPLEXES OF ORGANO-TIN OR -LEAD COMPOUNDS

Composition	*Structure assumed*	*Technique*	*Ref.*
$[Et_4N]_2^+ [BuSnCl_5]^{2-}$	Distorted octahedron	Mössbauer	112
$[Et_4N]_2^+ [BuSnCl_3Br_2]^{2-}$			
$\left.\begin{matrix}Cs^+\\ Me_4N^+\\ Et_4N^+\end{matrix}\right\}\begin{matrix}Me_2SnX_4^{2-}\\ Me_2SnX_3^-\end{matrix}$	Distorted octahedron *trans*-Me Distorted trigonal bipyramid	IR	113
$[Me_2SnCl \cdot tpy]^+ [Me_2SnCl_3]^-$	Distorted octahedral cation, trigonal bipyramidal anion	X-ray	114
$[Me_4N]_2^+ [Me_2Sn(NCS)_4]^{2-}$	Octahedron, *trans*-Me	IR	115
$[Me_4N]^+ [Me_3Sn(NCS)_2]^-$	Trigonal bipyramid, planar Me's		
$[Me_2SnCl \cdot tpy]^+[Me_2SnCl_3]^-$			
$[Et_4N^+][Me_3SnCl_2]^-$	Trigonal bipyramidal anion	Mössbauer	116
$[Et_4N]^+[Me_2SnCl_3]^-$			
$[ArN_2]_2^+[MeSnCl_5]^{2-}$			117
$[Me_4N]^+[PhSnCl_4]^-$	Trigonal bipyramid	IR	118
$[Ph_4As]^+[RSnCl_4]^-$			119
$[Ph_4As]^+[R_2SnCl_3]^-$			
$[Et_4N]^+[Me_3SnBr_2]^-$	Anion, bridged dimer (?)		120
$[Me_4N]^+[Ph_3PbX_2]^-$			
$[Me_4N]^+[Me_3PbCl_2]^-$			121
$[Me_4N]^+[Ph_2PbCl_3]^-$			
$[Me_4N]_2^+[Ph_2PbI_4]^{2-}$			
$Cs^+[Ph_2Pb(OAc)_3]^-$			
$Cs^+[Ph_2PbBr_3]^-$			

TABLE 9

STABILITY CONSTANTS FOR SOME ANIONIC ORGANOTIN COMPLEXES, AS MEASURED AT 25° IN WATER

Ligand	*Method*	K_1	K_2	K_3	K_4	K_5	*Ref.*
	$MeSn^{3+}$						
F^-	potentiometry ion exchange	1.26×10^5	5.7×10^4	1.25×10^4	1.2×10^4	1.7×10^2	123
Cl^-	ion exchange	–	2.24	0.56	1.6×10^{-2}	–	111
Cl^-	potentiometry	49	6.8	–	–	–	129
SCN^-	ferri	30	5.3	12.5	–	–	136
Br^-	potentiometry	4	–	–	–	–	129
	Me_2Sn^{2+}						
F^-	potentiometry ion exchange	5×10^3	7.5×10^2	29	1.2	–	124
Cl^-	ion exchange	2.35	0.59	3.5×10^{-2}	–	–	111
SCN^-	ferri	2.7	3.7	–	–	–	126
	Me_3Sn^+						
F^-	potentiometry	1.85×10^2	4	–	–	–	125
F^-	solubility	1.93×10^2	4	–	–	–	125
F^-	ion exchange	2.2×10^2	6.8	–	–	–	122
Cl^-	ion exchange	0.68	2.7×10^{-2}	–	–	–	111

similar hexa-coordinated complex of Me_2Sn^{2+} is very labile (K_4 = ca. 1.2) and no complexes of any description are found for chloride or bromide ions. The maximum coordination number is five for R_3Sn^+ indicating that the cation can add only two further anions.

Fluoride complexes are found to be more stable than chloride complexes in all cases. This is a characteristic of all A-class cations (hard Lewis acids).

The system ($R_{4-n}SnCl_n + R_4NCl$) (R = Ph, Bu; n = 2, 3; R = Me, Et) has been studied both potentiometrically and conductometrically in acetonitrile indicating that the ability to form complexes decreases in the following sequence for penta-coordinated anionic complexes: $PhSnCl_3 > BuSnCl_3 > Ph_2SnCl_2 > Ph_3SnCl > Bu_3SnCl$. This agrees with the series found by Kocheshkov and co-workers earlier[130]. Phenyltin derivatives form more stable complexes than the analogous butyl species, in agreement with the presumed greater electronegativity of the phenyl group. The stability constants of organotin complexes with chloride anions supplied by triphenylchloromethane have been measured spectrophotometrically in acetonitrile[127] (Table 10).

The series of stability constants obtained is similar to that obtained for the same complexes in water; in other words, the constants decrease as the number of organic groups attached to the metal atom increases or as the electronegativities decrease (Fig. 5).

The observed increase in the stability of chloride complexes in going from an aqueous

TABLE 10

STABILITY OF ANIONIC ORGANOTIN COMPLEXES CONTAINING THE CHLORIDE ANION AS MEASURED IN CH_3CN AT 35°

	$PhSnCl_4^-$	$EtSnCl_4^-$	$BuSnCl_4^-$	$Ph_2SnCl_3^-$	$Me_2SnCl_3^-$	$Et_2SnCl_3^-$	$Pr_2SnCl_3^-$
Relative stability	5400	246	140	68	3.3	1.2	1

to an acetonitrile medium is very significant. In water, it was found possible to obtain quantitative data of sufficient accuracy only for the fluoride anion complexes whereas in acetonitrile even the influence of structure on the stability could be studied for the chloride complexes $R_{4-n}SnCl_{n+1}^-$. This difference in stability may be attributed both to variations in the solvation ability of the medium and to the reactivity of the anion ligand. Water is a stronger solvating solvent, and is therefore more efficient at competing with anions than is the weakly solvating acetonitrile. As a result, the stability constants of the anionic complexes $R_{4-n}SnCl_{n+1}^-$ in acetonitrile increase. Complex formation with organotin compounds in water is possible only for such hard bases as the fluoride anion (Table 9).

In acetone, even stability constants for R_3SnBr/I^- complex formation could be measured[131] (Table 11).

It should be noted that the formation of anionic complexes plays a very important part in many electrophilic substitution reactions involving organotin compounds

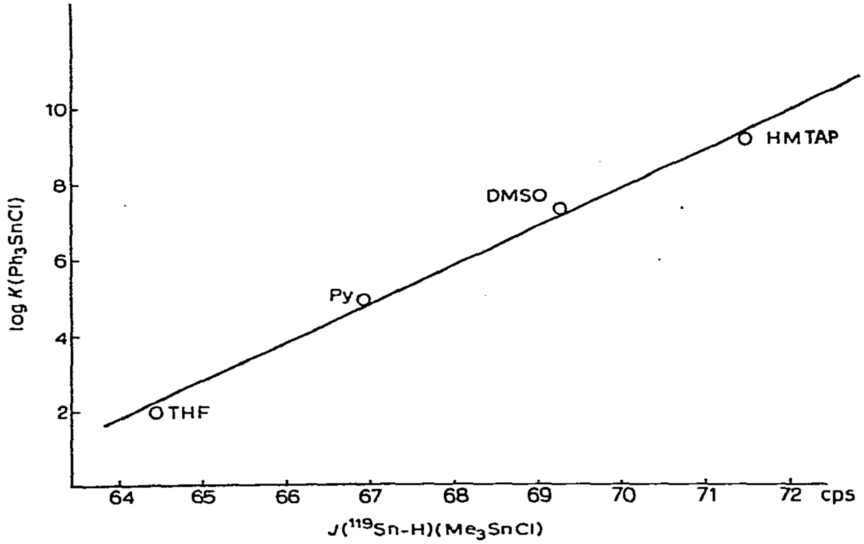


Fig. 5. Plot of the logarithms of the stability constants for the complex Ph_3SnCl (as obtained by polarography in CH_2Cl_2) *versus* $J(^1H-^{119}Sn)$ for $(CH_3)_3SnCl$ in the same solvents.

TABLE 11

STABILITY CONSTANTS FOR $[R_3SnBrI]^-$ IN ACETONE AT 20°

	CH_3	C_2H_5	i-C_3H_7	n-C_4H_9
K (l mol^{-1})	91 ± 6	168 ± 1	71 ± 8	123 ± 16

(nucleophilic catalysis)^3. Thus, iododemetallation of R_4Sn and R_4Pb compounds is enhanced only by iodide addition to those solvents which NMR techniques revealed complex formation between the organometallic compound and the I^- ion[132].

2. *Complexes containing neutral ligands*

(a) Solvation. The ability of various solvents to solvate organotin compounds has been studied by PMR spectroscopy.

On the basis of the spin–spin coupling constants $J(^{119}Sn{-}H)$ and $J(^{117}Sn{-}H)$ for Me_3SnBr, the following sequence of solvating ability was obtained[133]: DMSO ~ DMF > HOH > Py > MeOH > MeCOMe ~ MeCOOMe > dioxane > MeCN ~ MeCOOH > $MeNO_2$ > PhCl ~ CCl_4.

Stability constants for a series of triphenyltin chloride solvent complexes in methylene dichloride have been obtained polarographically (Table 12).

The structural similarity between R_3SnCl compounds allows the collation of data obtained for Ph_3SnCl and Me_3SnCl. In this way the spin–spin coupling constants associated with Me_3SnCl, $J(^{119}Sn{-}H)$, have been related linearly with the logarithms of the stability constants obtained for the corresponding Ph_3SnCl complexes (Fig. 5).

Again it should be noted that the ability of a solvent to solvate Ph_3SnCl follows a somewhat different sequence from that used to describe the ability to solvate $SbCl_5$ (donor numbers (DN)). In this case the quantities DN($SbCl_5$) and log K do not correlate which is not surprising when the difference between the acceptors is taken into account.

For the same reason there are similar inconsistencies between the stability series for organotin and organomercury compounds.

Gol'danskii and co-workers[135] studied Bu_2SnCl_2 by Mössbauer techniques and observed

TABLE 12

LOGARITHMIC STABILITY CONSTANTS FOR Ph_3SnCl SOLVENT COMPLEXES MEASURED POLAROGRAPHICALLY[134] AND VIA SPIN–SPIN COUPLING CONSTANTS $J(^{119}Sn{-}H)$ FOR Me_3SnCl IN THE RESPECTIVE SOLVENT (Drago)

	HMTAP	*DMSO*	*DMF*	*TMU*	*Py*	*MeOH*	*THF*
log K	9.2	7.3	7.3	6.2	5.1	2.7	1.3
$J(^{119}Sn{-}H)$	71.6	69.2	–	–	67.0	–	64.5

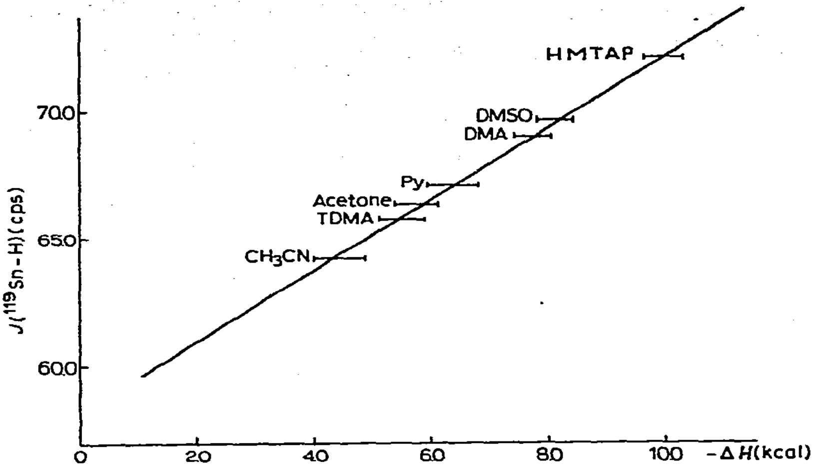


Fig. 6. Plot of $J(^1H-^{119}Sn)$ *versus* the enthalpies of formation for solvate complexes of $(CH_3)_3SnCl$.

a considerable increase in quadrupole splitting when coordinating solvents were added. The following series relating to increasing solvation was thus obtained: DMSO > DMF > HMTAP > DME > THF > DEE > Et_2O.

Bolles and Drago[136] have found a linear correlation between the $J(^{119}Sn-H)$ spin–spin coupling constants and the enthalpies of formation ($-\Delta H$) of Me_3SnCl complexes with various solvents (see Fig. 6).

The spin–spin coupling constants $J(^{119}Sn-H)$ increase as the solvating ability of the medium increases which is somewhat hard to explain merely in terms of the variation in effective positive charge ($\delta+$) on the tin atom. Based on the earlier assumption[137] that $J(^{119}Sn-H)$ may be used a measure of the *s*-character of the carbon–tin bond, the authors[136] have explained the solvent-induced variation in the spin–spin coupling constants by assuming that the hybridization on the tin atom is affected by complex formation with the solvent. The stronger the coordination of the solvent molecule to the tin atom, the closer the configuration of the complex approaches trigonal bipyramid. The arrangement of the three methyl groups attached to the tin atom becomes more and more planar and hence the hybridization of the Me–Sn bond becomes more and more sp^2 in character; hence the *s*-orbital contribution increases. The d_{z^2} and p_z orbitals are mainly used for ligand binding.

The donor strength of the solvents studied[136] decreased as follows: HMTAP > DMSO > DMA > Py > Me_2CO > THF > MeCN > Et_2O > Et_2S. Similar series for the solvation of organotin compounds have been reported by other authors[134,135,136]. It should be noted that O- or N-donor solvents solvate organotin compounds more efficiently than S and P donors, *e.g.*, $Et_2S < Et_2O$, DMTA < DMA, HMTAPT < HMTAP, Bu_3P < Py. This behaviour is typical for hard Lewis acids. Complexes of $Bu_2Sn(NCS)_2$

and $(C_8H_{17})_2Sn(NCS)_2$ with 2,2′-bipyridyl in benzene are more stable than the corresponding complex of $(C_8H_{17})_2SnCl_2$ by a factor of ca. 500 (ref. 187).

(b) Crystalline complexes. A very large number of crystalline complexes of the general formula $R_{4-n}MX_n \cdot L$ (where L is a neutral ligand) have been described. The main types are listed in Table 13.

Tables 13 and 14 summarize the most important types of individual complexes of organo-tin or -lead compounds with neutral donor ligands. The techniques used for studying these complexes as well as their presumed configuration are also listed in these Tables. As demonstrated by the data, no significant deviations from the structures assumed occur; on the other hand, each of the complexes exhibits its own peculiarities depending on the ligands and on the nature and number of organic groups bonded to the metal. It is not possible in a review such as this to try to embrace the whole of the information available and for this reason only general trends will be discussed.

Three main methods of studying the structures of organotin complexes are worthy of mention: (i) estimation of the coordination number and configuration of the complexes, (ii) of the spatial arrangement of the organic groups and ligands around the metal atom and (iii) of the nature of the metal—ligand bond and of the changes in the character of the metal—carbon bond upon coordination. The techniques applied have been mainly X-ray, IR, Raman, NMR and Mössbauer spectroscopy.

Data relating to the coordination number and configuration are, in the main, quite self-consistent. The results obtained may be concisely summarized as follows. Most RMX_3 compounds form six-coordinate octahedral complexes whereas R_2MX_2 complexes are sometimes octahedral and sometimes trigonal-bipyramidal. R_3MX compounds form only trigonal-bipyramidal complexes while R_4M form no complexes whatsoever and always exist in a tetrahedral configuration.

The spatial arrangement of the ligands has, as yet, defied resolution in terms of a unit concept. Linearity of R_2M and planarity of R_3M are more often encountered than non-planar arrangements for these groups. However, strong complexes always occur in planar or linear configurations whereas with weak complexes the C—M bond angles only deviate slightly from a tetrahedral configuration. The arrangement of the ligands in the complexes (as either *cis* or *trans*) does not unfortunately fall into any regular pattern, at least on the basis of the results obtained to date.

Even less is known regarding the nature of the metal—ligand bonding in these complexes, *i.e.* whether $p_\pi - d_\pi$ bonding plays an important part in the behaviour of Pb—L and Sn—L bonds.

As listed in Table 14, a considerable number of organo-tin and -lead complexes containing bidentate ligands, *e.g.*, 1,10-phenanthroline or 2,2′-bipyridyl or chelate-forming anions such as 8-oxyquinolinate or acetylacetonate and related compounds, have been studied.

This Table also shows that the structural regularities found for other organo-tin and -lead complexes are also generally present in complexes containing bidentate ligands.

(continued on p. 35)

TABLE 13

COMPLEXES WITH NEUTRAL MONODENTATE LIGANDS, AS ISOLATED IN THE SOLID STATE

Composition	*Structure*	*Method*	*Ref.*
$Me_2SnCl_2 \cdot 2DMSO$	octahedral, *cis*-Me, *cis*-DMSO, *cis*-Cl	X-ray	138
$Me_2SnCl_2 \cdot 2PyO$	octahedral, *trans*-Me, *trans*-PyO *trans*-Cl	X-ray	139
$Me_3SnCl \cdot Py$	trigonal bipyramid, *trans*-Py–Cl	X-ray	140
$Me_3SnCl \cdot NH_3$	trigonal bipyramid;		
$Me_3SnBr \cdot NH_3$	1/1 adducts are covalent,		
$Me_3SnCl \cdot Py$	1/2 adducts ionic	IR	141
$Me_3SnBr \cdot Py$			
$Me_3SnCl \cdot 2NH_3$			
$Me_3SnBr \cdot 2NH_3$			
$Me_3SnClO_4 \cdot 2Py$			
$Me_3Sn^+ \cdot 2NH_3$	trigonal bipyramid	IR	142
$Me_2SnCl_2 \cdot 2Py$	octahedral	IR	143
$Me_2SnCl_2 \cdot 2PyHCl$			
$MeSnCl_3 \cdot 2Py$			
$Me_3SnCl \cdot Py$	trigonal bipyramid		
$Me_2SnSO_4 \cdot Py$	trigonal bipyramid		
$Me_2SnSO_4 \cdot DMSO$		IR	144
$Me_2SnCl_2 \cdot 2DMSO$	octahedral, *trans*-Me		
$Me_2SnCl_2 \cdot 2Py$			
$Me_3SnCl \cdot NH_3$			
$Me_3SnCl \cdot PhNH_2$			
$Me_3SnI \cdot NH_3$			145
$Me_3SnI \cdot 2NH_3$	unstable		
$Me_3SnCl \cdot Py$			
$n\text{-}BuSnCl_3 \cdot 2Ph_3PO$			
$n\text{-}BuSnCl_3 \cdot 2DMA$			
$n\text{-}BuSnCl_3 \cdot 2Py$	octahedral	Mössbauer	112
$n\text{-}BuSnCl_3 \cdot 2DMSO$			
$n\text{-}BuSnCl_3 \cdot 2PyO$			
$Me_2SnCl_2 \cdot 2PyO$			
$Me_2SnCl_2 \cdot 2DMSO$			
$Me_2SnCl_2 \cdot 2Py$			
$Et_2SnCl_2 \cdot 2Py$			146
$n\text{-}Pr_2SnCl_2 \cdot 2Py$			

(to be continued)

TABLE 13 (continued)

Composition	*Structure*	*Method*	*Ref.*
$[Me_2Sn(DMSO)_4]^{2+} \cdot 2Ph_4B^-$			
$[Me_2Sn(DMF)_4]^{2+} \cdot 2Ph_4B^-$	octahedral		
$[Me_2Sn(DMA)_4]^{2+} \cdot 2Ph_4B^-$		PMR	147
$[Me_3Sn(H_2O)_2]^+Ph_4B^-$			
$[Me_3Sn(DMF)_2]^+ Ph_4B^-$	trigonal bipyramid		
$[Me_3Sn(DMA)_2]^+ Ph_4B^-$			
$[Me_3Sn(DMSO)_2]^+ Ph_4B^-$			
$PhSnCl_3 \cdot$ *cis*-DTDS			
$PhSnCl_3 \cdot$ *trans*-DTDS	*cis*-DTDS monodentate		
$Ph_2SnCl_2 \cdot$ *cis*-DTDS	*trans*-DTDS bidentate	IR	148
$Ph_2SnCl_2 \cdot$ *trans*-DTDS			
$Ph_2SnCl_2 \cdot 2DTM$			
$Ph_3SnCl \cdot DTM$			
$n\text{-}Bu_2SnCl_2 \cdot 2(4\text{-}PhPy)$		IR	149
$Ph_3SnCl \cdot (4\text{-}PhPy)$			
$Bz_2SnCl_2 \cdot 2DMSO$		NMR	150
$Me_2SnCl_2 \cdot 2DMSO$			
$Ph_2Sn(NCS)_2 \cdot 2DMSO$	*cis*-NCS	IR	151
$(o\text{-}CH_3C_6H_4)_2Sn(NCS)_2 \cdot 2DMSO$			
$PhSnCl_3 \cdot 2DMSO$			
$Ph_2SnCl_2 \cdot 2DMSO$			
$Ph_2SnCl_2 \cdot 2TMSO$	coordination number 6		
$MeSnCl_3 \cdot 2DMSO$	octahedral	IR	152
$Me_2SnCl_2 \cdot 2DMSO$			
$Me_3SnCl \cdot DMSO$	coordination number 5		
$Ph_3SnCl \cdot DMSO$	trigonal bipyramid		
$Me_3SnCl \cdot TMSO$			
$Et_3SnCl \cdot TMSO$	coordination number 5	IR	
$Me_3SnCl \cdot DMA$	trigonal bipyramid	PMR	113
$Et_3SnCl \cdot DMA$			
$Me_3SnCl \cdot DMF$			
$Et_3SnCl \cdot DMF$			
$[Me_3SnL_2]BPh_4$			
$(L = Ph_3PO, Ph_3AsO, p\text{-}Tol_3AsO)$	distorted trigonal		
	bipyramid, planar Me_3Sn	PMR	153
$[Me_3SnL_4][BPh_4]_2$	distorted octahedron		
$R_3SnX \cdot L$; $R = Me, Ph$;	trigonal bipyramid	IR	
$(X = Cl, Br; L = Ph_3PO, Ph_3AsO, PyO$		PMR	154
$R_2SnCl_2 \cdot 2L$	octahedral,		
$(R = Me, Ph, PhCH_2)$	organic group is *trans*		

(to be continued)

TABLE 13 (continued)

Composition	*Structure*	*Method*	*Ref.*
$Me_2SnCl_2 \cdot 2Et_2SO$ $Me_2SnCl_2 \cdot 2Me(PhCH_2)SO$ $Ph_2SnCl_2 \cdot 2Bz_2SO$ $Ph_2SnCl_2 \cdot 2(i\text{-}Pr_2MeSO)$	octahedral, ligands are *cis*	IR PMR	155
$Me_2SnCl_2 \cdot Bz_2SO$ $Me_2SnCl_2 \cdot MeBzSO$ $Me_3SnBr \cdot Bz_2SO$	trigonal bipyramid		
$MeSnBr_3 \cdot 2Py$ $PhSnCl_3 \cdot 2Py$ *p*-Tol$SnCl_3 \cdot 2Py$ *o*-Tol$SnCl_3 \cdot 2Py$; $Me_2SnCl_2 \cdot 2Py$ $Me_2SnBr_2 \cdot 2Py$ $Et_2SnBr_2 \cdot 2Py$ $Pr_2SnBr_2 \cdot 2Py$ $Me_3SnCl \cdot 2Py$			156
$R_2SnX_2 \cdot 2DMF$ (R = Ph, *o*-Tol, n-Tol, Br; X = Cl, Br, I)	octahedral, *cis*-Ph, *trans*-Cl	IR	186
$Me_3SnCl \cdot L'$(L = *p*-MePyO, Ph_3PO, DMSO, DMA, HMTAP, Py)	distorted trigonal bipyramid	Mössbauer	157
$R_2SnCl_2 \cdot 2(n\text{-}MePy)$ (R = Me, Et, Pr, Bu)	*trans*-alkyl *cis* ligand	PMR	158
$Me_2SnX_2 \cdot DMF$	trigonal bipyramid Me non-linear	IR	159
$Me_2SnX_2 \cdot 2DMF$ (X = Cl, Br)	distorted octahedron, Me non-linear.		
$Ph_2PbX_2 \cdot 4Py$	stable		
$Ph_2PbX_2 \cdot 2Py$ (X = Cl, Br, NO_3)	unstable		160
$Ph_2PbCl_2 \cdot 2Py$ $Ph_2PbCl_2 \cdot 2DMSO$ $Ph_2PbCl_2 \cdot 2DMF$ $Ph_2PbBr_2 \cdot 2DMSO$			161
$Ph_2PbCl_2 \cdot 2DMSO$			152
$R_3PbCl \cdot L$ (R = Me, Et; L = DMSO, DMF, DMA)			106
$R_3PbX \cdot L'$(R = Me, Et; X = Cl, Br; L = Ph_3PO, Ph_3AsO, PyO) $R_2PbCl_2 \cdot 2L$ (R = Me, Ph, Bz)			154
$Me_2Pb(ClO_4)_2 \cdot 4DMSO$	Me_2Sn almost linear	IR	162
$Me_2Pb(ClO_4)_2 \cdot 2Py$			
$Me_3PbClO_4 \cdot 2HMTAP$	Me_3Sn almost planar	PMR	
$Me_3PbClO_4 \cdot HMTAP$			
$Me_3PbClO_4 \cdot Py$			

TABLE 14

ORGANO-TIN AND -LEAD COMPLEXES WITH NEUTRAL BIDENTATE LIGANDS ISOLATED AS CRYSTALLINE COMPOUNDS

Composition	*Structure*	*Method*	*Ref.*
$\text{n-BuSnCl}_3\cdot\text{L}_2$ (L_2 = bipy, phen)	coordination number 6		
$\text{n-Oct}_2\text{SnCl}_2\text{L}_2$ (L_2 = bipy, phen)	distorted octahedron	Mössbauer	112
$\text{MeSnCl}_3\cdot\text{L}_2$ $\text{Me}_2\text{SnCl}_2\cdot\text{L}_2$ (L_2 = bipy, phen)	distorted octahedron	IR	143
$\text{n-Bu}_2\text{SnCl}_2\cdot\text{L}_2$ $\text{Ph}_2\text{SnCl}_2\cdot\text{L}_2$ $\text{n-Oct}_2\text{SnCl}_2\cdot\text{L}_2$ (L_2 = 4,4'-bipy) $\text{n-Bu}_2\text{SnBr}_2\cdot\text{L}_2$ $\text{PhSnCl}_3\cdot\text{L}_2$ $\text{Ph}_3\text{SnCl}\cdot\text{L}_2$	coordination number 6 polymer coordination number 5	IR	149
$\text{Et}_2\text{SnCl}_2\cdot\text{L}_2$ $\text{n-Bu}_2\text{SnCl}_2\cdot\text{L}_2$ $\text{n-Bu}_2\text{SnBr}_2\cdot\text{L}_2$ (L_2 = bipy, phen) $\text{n-Bu}_2\text{SnI}_2\cdot$ bipy $\text{Ph}_2\text{SnCl}_2\cdot\text{L}_2$			163
$\text{n-Pr}_2\text{Sn(NO}_3)_2\cdot$ 2phen $\text{n-Bu}_2\text{Sn(NO}_3)_2\cdot$ 2phen			164
$\text{Ph}_2\text{SnCl}_2\cdot\text{L}_2$ (L_2 = bipy, phen)	*trans*-Ph	Mössbauer	165
$\text{n-Bu}_2\text{SnX}_2\cdot\text{L}_2$(X = Cl, Br; L_2 = bipy, phen) $\text{n-Bu}_2\text{SnI}_2\cdot$ phen	*trans*-alkyl	electric moment	166
$\text{Et}_2\text{SnCl}_2\cdot\text{L}_2$ $\text{n-Bu}_2\text{SnX}_2\cdot\text{L}_2$ (X = Cl, Br, I, CNS) $\text{n-Oct}_2\text{SnCl}_2\cdot\text{L}_2$ (L_2 = bipy, phen) $\text{Ph}_2\text{SnCl}_2\cdot\text{L}_2$			163
$\text{R}_2\text{Sn(NCS)}_2\cdot\text{L}_2$ (L_2 = bipy, phen; R = Ph, $o\text{-CH}_3\text{C}_6\text{H}_4$	*cis*-NCS	IR	151
$\text{Ph}_2\text{Sn(NCO)}_2\cdot$ bipy	coordination number 5 bridged	IR	167
$\text{R}_2\text{Sn(NCS)}_2\cdot$ bipy (R = Me, Et, Pr, Bu)			168
$\text{Ph}_2\text{PbCl}_2\cdot$ bipy $\text{Ph}_2\text{PbCl}_2\cdot$ phen			161
$\text{R}_2\text{PbX}_2\cdot\text{L}_2$ (L = bipy, phen; X = Cl, Br; R = Et, Bu) $\text{Ph}_2\text{PbCl}_2\cdot$ phen $\text{Bu}_2\text{SnCl}_2\cdot$ phen $\text{R}_2\text{SnX}_2\cdot\text{L}_2$ (R = Me, Bu; X = Cl, OAc; L_2 = bipy, phen)			169

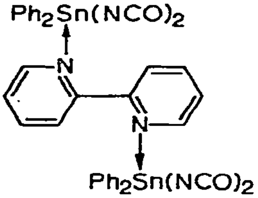
(*to be continued*)

TABLE 14 (continued)

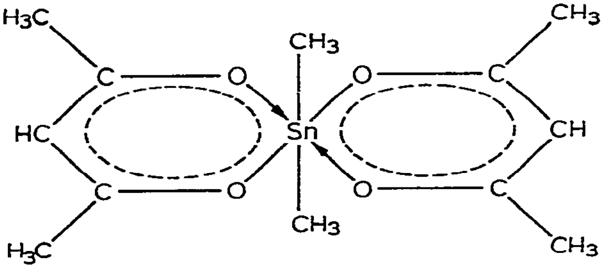
Composition	*Structure*	*Method*	*Ref.*
$\mathrm{Me_2Sn(oxin)_2}$	strongly distorted octahedron; C–Sn–C angle is close to tetrahedral		170
$\mathrm{R_2Sn(oxin)_2}$ (R = Me, Et, Pr, Bu, Oct, Ph) $\mathrm{R_2SnX(oxin)}$ (R = Me, Et, Pr; X = Cl, Br, I, NCS) $\mathrm{BuSn(oxin)_3}$	Presumably covalent coordination number 7	Mössbauer	171
$\mathrm{Ph_3Sn(oxin)}$ $\mathrm{Ph_3Pb(oxin)}$	chelates in $\mathrm{C_6H_6}$ no chelates in MeOH	UV	172
$\mathrm{R_2Sn(oxin)}$ (R = Me, Et, Pr, Bu, Ph) $\mathrm{R_2SnX(oxin)}$ (X = Cl, NCS) $\mathrm{RSnCl(oxin)_2}$	chelates monomers	UV	173
$\mathrm{Me_2Sn(acac)_2}$ $\mathrm{Me_2Pb(acac)_2}$	octahedron, *trans*-Me, M–O bonds equivalent	IR Raman	174
$\mathrm{Ph_2SnCh_2}$ (Ch = acac, bzac, dbzm, oxin)	coordination number 6 monomers *trans*	IR	175
$\mathrm{R_2SnCh_2}$ (R = Me, Et, Bu, Ph; Ch = acac, dbzm, hfacac)	coordination number 6 octahedral organic groups are *cis*	dipole moments PMR IR	176
$\mathrm{R_2Sn(acac)_2}$ $\mathrm{R_2Pb(acac)_2}$ (R = Me, Et, $\mathrm{CH_2 = CH}$, Ph) $\mathrm{RSnX(acac)_2}$ (R = Me, Et, Ph; X = Cl, Br, I)			177
$\mathrm{R_2XnL_2}$ (R = Me, Ph) $\mathrm{L_2}$ = 2,4-pentanedione, 1-phenyl-1,3-butanedione, picolinic acid, *o*-hydroxyquinoline	organic groups are *trans*	IR PMR	178

$\mathrm{R_3SnX}$ compounds which have only one coordination site form no complexes with bidentate ligands. Thus, $\mathrm{Ph_3SnCl}$ forms a (bridged) complex with 4,4′-bipyridyl[149], but no complex with 2,2′-bipyridyl[143]. The compounds $\mathrm{R_2SnX_2}$ and $\mathrm{RSnX_3}$ where X is Hal or OAc give 1/1 octahedral complexes, the organic groups in the resulting complex $\mathrm{R_2SnX_2\ L_2}$ (where $\mathrm{L_2}$ is a bidentate ligand) forming, as a rule, a linear C—M—C. skeleton. When the anion X is only weakly bonded to the tin atom (*e.g.*, when X = $\mathrm{NO_3}$, ref. 164), the anions may be forced out into the outer sphere.

An interesting complex of diphenyltin diisocyanate with 2,2′-bipyridyl has been reported[167]. Unlike the analogous $\mathrm{R_2SnX_2 \cdot bipy}$ complex this compound exists as a bridged penta-coordinated species (according to IR data).



For a long time controversy existed regarding the spatial arrangement of the methyl groups in dimethyltin oxyquinolinate, $Me_2Sn(oxin)_2$. X-ray studies have now shown that the C—Sn—C angle is close to the tetrahedral value in this compound[170]. However, the data obtained for dimethyltin and dimethyllead acetylacetonates[174] agree with the assumption that the C—M—C group is linear with the four coordinated oxygen atoms completely equivalent.



The Mössbauer quadrupole splittings measured for the $[Me_2SnCl\cdot tpy]^+[Me_2SnCl_3]^-$ (where tpy is 2,2′, 2′-tripyridyl) cation and anion were equal and so a linear R—Sn—R group was assumed[116] to be present in both cases.

X-Ray data have shown[114] that the cation is a distorted octahedron with the methyl groups in a *trans* orientation whereas the anion is a trigonal bipyramid with the methyl groups arranged equatorially, the C—M—C angle being 140°. These data show that structural data obtained for complexes containing mono- or bi-dentate ligands often need further study.

In general, the geometry may be predicted on the basis of a simple model but, unfortunately, in many complexes the structure and the arrangement of the ligands around the metal atom need further clarification.

(c) Stability of complexes. Despite the number of complexes isolated, in general their stability has been estimated purely on a qualitative basis. In most cases quantitative data are quite scarce.

Wardell[179] has measured the formation constants for complexes between tin compounds of the type $RSnCl_3$ (Me, Bu, Ph) and substituted anilines spectrophotometrically (see Table 15).

TABLE 15

STABILITY CONSTANT VALUES (pK) FOR $RSnCl_3$ COMPLEXES WITH SUBSTITUTED ANILINES, IN ETHER AT 25°

$K = \frac{[B \cdot RSnCl_3]}{[B] \cdot [RSnCl_3]}$ AND pK RELATES TO THE DISSOCIATION CONSTANT OF BH^+ IN WATER AT 25°

No.	*Aniline B*	*pK_a BH^+*	*pK*		
			$MeSnCl_3$	*$BuSnCl_3$*	*$PhSnCl_3$*
1	2-amino-4-nitro	2.70	−1.95	−1.66	−2.70
2	3-amino-4-nitro	1.01	−0.75	−0.66	−0.66
3	4-amino-3-nitro	–	−1.90	−1.62	−2.30
4	4-methyl-3-nitro	2.90	−0.35	+0.10	−0.93
5	3-nitro	2.50	−0.03	+0.47	−0.62
6	2-methyl-5-nitro	2.32	+0.40	–	−0.21
7	4-chloro-3-nitro	1.86	–	–	−0.05
8	3-methyl-4-nitro	2.32	–	–	+0.22
9	4-nitro	0.99	–	–	+0.44
10	2,5-dimethyl-4-nitro	1.52	–	–	+0.33
11	2-methyl-4-nitro	0.94	–	–	+0.62

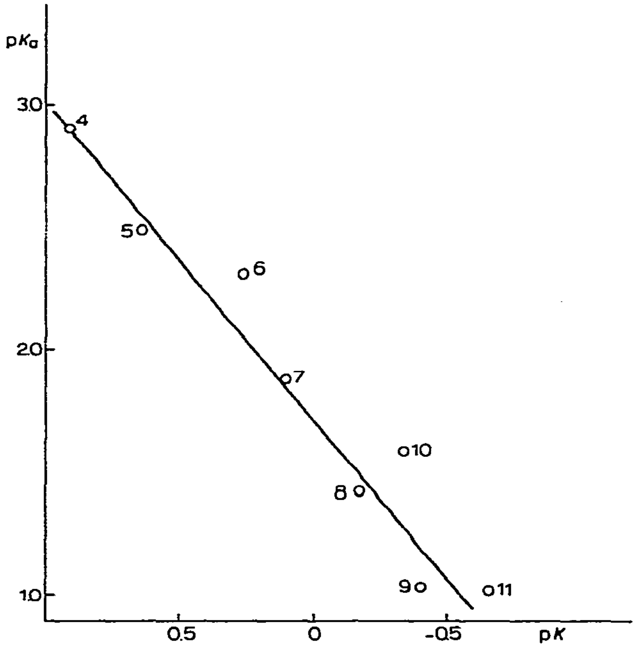


Fig. 7. A plot of pK_a for BH^+ *versus* pK for $PhSnCl_3 \cdot B$. (The numbers on the points correspond to those listed for the compounds in Table 15.)

Plots of the pK_a values for various aromatic monoamines may be correlated with the negative logarithms of the stability constants for the respective complexes (Fig. 7).

The effect of a substituent in the aromatic ring of $RC_6H_4SnCl_3$ on the stability of complexes formed with substituted anilines has also been studied[180] (Table 16).

The stability series obtained for complexes of $RC_6H_4SnCl_3$ with monoamines as a function of R was found to be Me > H > Cl > Ph. With diamines, however, a different sequence of stability relationships was observed: Cl > H > Me > Ph. This result was assumed[180] to be related to the competing effect of the solvent. The stability constants for complexes of Me_3SnCl or Me_2SnCl_2 with substituted pyridine *N*-oxides in acetonitrile have been measured spectrophotometrically[181] (Table 17).

As expected, the stability of the complexes increases with the electron donor properties of the substituents in the pyridine ring. The logarithms of the stability constants correlate with the Hammett σ-parameters for the substituents in the ring. The greater the pK_a value of a particular ligand, the more stable the complexes formed with the organotin compound studied.

TABLE 16

EFFECT OF THE SUBSTITUENT R ON THE p*K* VALUES OF $RC_6H_4SnCl_3$ COMPLEXES WITH SUBSTITUTED ANILINES AS MEASURED BY SPECTROPHOTOMETRY IN ETHER AT 25°

No.	*Aniline substituent*	pK_a	*pK*			
			R in $RC_6H_4SnCl_3$			
			p-Cl	*H*	*p-Me*	*p-Ph*
1	4-methyl-3-nitro	2.90	−0.70	−0.93	−1.10	+0.06
2	3-nitro	2.50	−0.39	−0.62	−0.78	–
3	6-methyl-3-nitro	2.32	−0.01	−0.21	−0.36	–
4	3-amino-4-nitro	1.01	−1.36	−0.06	−0.21	–
5	4-amino-3-nitro	4	−2.71	−2.30	−1.98	−1.80
6	2-amino-4-nitro	2.70	−3.30	−2.68	–	–

TABLE 17

STABILITY CONSTANTS FOR COMPLEXES OF THE TYPE Me_3SnCl/RC_5H_4NO

R in RC_5H_4NO	*T(°C)*	*logK*	$pK_a(RC_5H_4NOH)^+$
$C_6H_5CH_2O$	15	2.57	2.05
C_2H_5	16	2.42	–
CH_3	17	2.40	1.29
H	17	1.53	0.79
Cl	17	1.08	0.36
C_2H_5OCO	16	0.46	−0.41
NO_2	17	−0.19	−1.7

The stability of complexes of R_2Sn^{2+} with substituted 1,10-phenanthrolines has been correlated with the basicity of the ligand[182]. The linear plots obtained for different aliphatic groups ($ClCH_2$ and C_2H_5 in Fig. 8) have the same slope, whereas the slope for $(CH_2{=}CH)Sn^{2+}$ is much greater. This reflects the greater sensitivity of the latter organotin cation to the donor properties of the ligands.

Complexes of Bu_2SnCl_2 and Me_2SnCl_2 with another bidentate ligand (2,2′-bipyridyl) in acetonitrile turned out to possess an almost identical stability (log K being equal to 3.19 and 3.36, respectively)[183]. As a function of the solvent, the stability constant varies linearly with the dielectric constant, the following sequence being obtained: MeOH > EtOH > PrOH > BuOH; diethyl malonate > MeOAc > BuOAc.

Okawara and co-workers[159] have measured the respective stability constants for complexes of Me_2SnCl_2 with carbonyl donors in dichloroethane (see Table 18). The values of these constants increase as the electron-donor properties of the substituents attached to

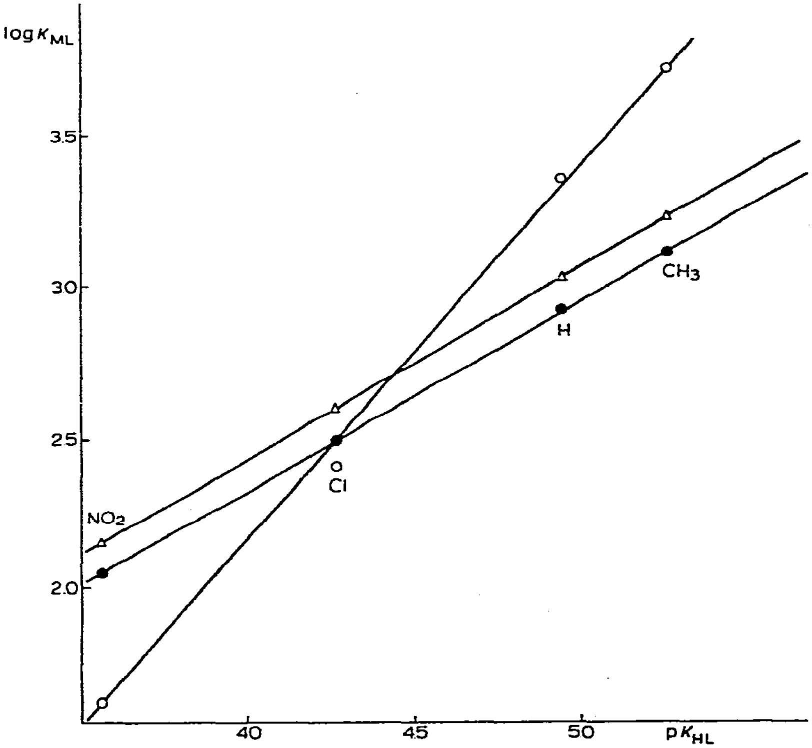


Fig. 8. Plot of the logarithms of the stability constants *versus* the basicity of the ligand for various complexes. Δ, $(ClCH_2)_2Sn^{2+}$; •, $(C_2H_5)_2Sn^{2+}$; o, $(CH_2{=}CH)_2Sn^{2+}$.

TABLE 18

STABILITY CONSTANTS FOR Me_2SnCl_2 COMPLEXES WITH CARBONYL-CONTAINING COMPOUNDS (in dichloroethane)

Donor	$CH_3OC_6H_4COCH_3$	$(CH_3)_2NC_6H_4COCH_3$	$(CH_3)_2NC_6H_4CHO$	$[(CH_3)_2NC_6H_4]_2CO$
K ($l\ mol^{-1}$)	1.06	3.17	7.78	8.90

the carbonyl group increase despite the fact that their magnitudes demonstrate that in each individual case the donor—acceptor interaction is very weak.

VI. CONCLUSIONS

The "softness" of organometallic cations decreases over the series Hg, Tl, Pb, Sn if these cations are regarded as typical Lewis acids. Because of this, the ability of these cations to form complexes with various ligands varies. In all cases, the ability to form complexes decreases as the number of alkyl groups attached to the metal atom increases. Complexes with the organometallic compounds R_4Sn or R_4Pb have not been isolated in any case. Unstable adducts with triethylamine or ether have been found in the case of R_3Tl, (refs. 184, 185). No data exist for complexes of the symmetrical organomercurial compounds R_2Hg (where R is an alkyl or an aryl group), although some indirect evidence for such interactions have been reported. The stability of complexes of these organometallic materials may be estimated qualitatively on the basis of Gutman donor numbers or the Pearson hard-soft concept. These two approaches, however, permit only preliminary estimates to be made of such stabilities, and to obtain a quantitative estimate, a particular complex should be examined experimentally in an appropriate medium.

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