

## THE PREPARATION AND TIN-119 MÖSSBAUER SPECTRA OF NEW ADDUCTS OF THE TYPE ORGANOTETRACHLOROSTANNATE(IV) BASE (1/1)

DESMOND CUNNINGHAM \*, MARK LITTLE and KEVIN McLOUGHLIN

*Department of Chemistry, University College, Galway (Ireland)*

(Received August 2nd, 1978)

### Summary

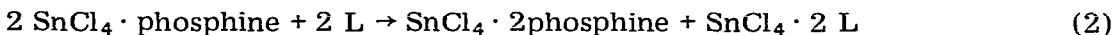
New adducts  $\text{Et}_4\text{N}(\text{R}\text{SnCl}_4 \cdot \text{L})$  (R butyl and phenyl; L pyridine, trimethylamine, tri-n-butylphosphine, triphenylphosphine oxide, triphenylarsine oxide, dimethylsulphoxide, dimethylformamide) have been isolated and their Mössbauer spectra studied. Definite structural assignments are made for the phosphine and phosphine oxide adducts from Mössbauer quadrupole splitting data. Comments are made on the choice of partial splitting values for phenyl and butyl groups.

### Introduction

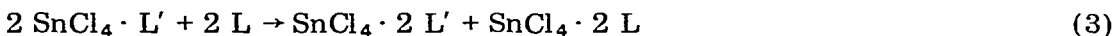
Recently we have examined the acceptor properties of the pentachlorostannate(IV) anion [1] and found that only in a few isolated cases was it possible to obtain the expected adducts  $\text{SnCl}_5 \cdot \text{L}^-$  (L neutral donor molecule). For a wide variety of donors a reaction occurred resulting in the formation of the stannic chloride 1/2 adduct and the hexachlorostannate(IV) anion (reaction 1).



Subsequently it was established [2] that 1/1 phosphine adducts,  $\text{SnCl}_4 \cdot \text{PPh}_3$  and  $\text{SnCl}_4 \cdot \text{PBu}_3$ , react with many donor molecules via reaction 2 rather than to yield mixed adducts  $\text{SnCl}_4 \cdot \text{phosphine} \cdot \text{L}$ .



Thus, it appears that reactions 1 and 2 are merely examples of a more general reaction 3 often favoured by tin (L and L' in reaction 3 represent different donor groups)

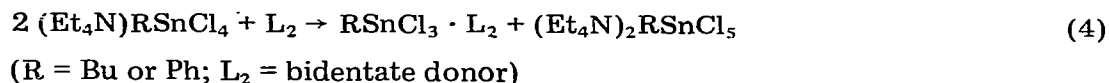


These observations prompted us to extend on our previous work to include a

study of the behaviour of anions  $\text{RnSnCl}_4^-$  (R organo group) towards Lewis bases. Adducts of the type  $\text{RnSnCl}_4 \cdot \text{L}^-$  have not previously been reported but the existence of  $\text{RnSnCl}_5^{2-}$  is in itself suggestive of the feasibility of forming such adducts, at least with strong donor groups.

## Results and discussion

Contrary to the behaviour of  $\text{SnCl}_5^-$  both  $\text{BuSnCl}_4^-$  and  $\text{PhSnCl}_4^-$  reacted straightforwardly with monodentate donor molecules to yield adducts  $\text{RnSnCl}_4 \cdot \text{L}^-$  (R butyl or phenyl) and in no case was a rearrangement reaction 3 observed. However, with the bidentate donors 2,2'-bipyridyl and *o*-phenanthroline, reaction 4 occurred.



The reactivity of the anionic species towards a range of donor molecules suggested that they are, as expected, weaker Lewis acids than  $\text{SnCl}_5^-$  and also weaker than alkyltin trihalides. For example, it was not possible to form adducts with acetonitrile, tetrahydrofuran, acetone and diethyl ether whereas  $\text{SnCl}_5^-$  forms adducts with acetonitrile and tetrahydrofuran [1] and  $\text{MeSnCl}_3$  appears to form complexes with the oxygen donors [3].  $\nu(\text{E}=\text{O})$  stretching frequency data in Table 1 are consistent with the formulation of adduct structures for the complexes and indicate that the donor-acceptor interactions are greater in the phenyl than in the butyl complexes.

A noteworthy feature of  $\text{PhSnCl}_4^-$  is its rearrangement reaction 5 to give  $\text{Ph}_2\text{SnCl}_2$  and  $\text{SnCl}_6^{2-}$  (see Experimental).



This reaction occurs fairly rapidly in dichloromethane but not at all in the donor solvents methanol, acetonitrile and acetone. In fact, previous molecular weight and conductivity measurements on  $(\text{Ph}_4\text{As})\text{PhSnCl}_4$  were made in the two latter solvents [4]. While attempts to isolate solid adducts with methanol, acetonitrile

TABLE 1  
 $\nu(\text{E}=\text{O})$  STRETCHING FREQUENCY DATA

Complex <sup>a</sup>	$\nu(\text{E}=\text{O})$ ( $\text{cm}^{-1}$ )	
	Free ligand	Complex
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{DMF}$	1684	1642
$(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{DMF}$		1630
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{Ph}_3\text{AsO}$	880	854
$(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{Ph}_3\text{AsO}$		850
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{Ph}_3\text{PO}$	1189	1148
$(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{Ph}_3\text{PO}$		1140
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{DMSO}$	1040	944

<sup>a</sup> DMF = dimethylformamide,  $\text{Ph}_3\text{AsO}$  = triphenylarsine oxide,  $\text{Ph}_3\text{PO}$  = triphenylphosphine oxide, DMSO = dimethylsulphoxide.

and acetone were unsuccessful it does seem likely that in solution these solvents coordinate weakly to  $\text{PhSnCl}_4^-$  and it may be this interaction which is responsible for the stability of the anion in the donor solvents.

Mössbauer data for the new complexes are in Table 2. The chemical shift data for the butyl complexes are of interest since they represent chemical shift values for a series of six coordinate tin complexes and for the parent acid  $\text{BuSnCl}_4^-$  which is known to contain five coordinate tin [4] and consequently the effect of increasing the coordination of tin on Mössbauer chemical shift data for an organotin(IV) series can be evaluated. This effect cannot be gauged from chemical shift data for adducts  $\text{R}_2\text{SnCl}_2 \cdot 2\text{L}$  and  $\text{RSnCl}_3 \cdot 2\text{L}$  since  $\text{R}_2\text{SnCl}_2$  species contain octahedral tin [5] and the coordination of tin in both  $\text{BuSnCl}_3$  and  $\text{PhSnCl}_3$  (in the frozen solids) remains in doubt. It is seen from the data in Table 2 that with the exception of  $\text{BuSnCl}_4 \cdot \text{PBU}_3^-$  other adducts  $\text{BuSnCl}_4 \cdot \text{L}^-$  have lower chemical shifts than the parent acid  $\text{BuSnCl}_4^-$ . This is the normal chemical shift trend associated with increasing coordination of tin and is attributed to the greater involvement of *d*-orbitals and increasing polarity of bonds as a result of the coordination increase [6]. However, the chemical shift of  $\text{BuSnCl}_4 \cdot \text{PBU}_3^-$  is an important exception to this trend since it is significantly greater than that of  $\text{BuSnCl}_4^-$ . The anomalous behaviour parallels that of the phosphine (and arsine) adducts of stannic chloride [7–9]. For the latter adducts there is

TABLE 2  
TIN-119 MÖSSBAUER PARAMETERS

Complex <sup>a</sup>	$\delta$ ( $\text{mm s}^{-1}$ ) ( $\pm 0.03$ )	$\Delta$ (obs) ( $\text{mm s}^{-1}$ ) ( $\pm 0.02$ )	$\Delta$ (calc.) ( $\text{mm s}^{-1}$ ) <sup>b</sup>	
			<i>cis</i>	<i>trans</i>
(Et <sub>4</sub> N)BuSnCl <sub>4</sub>	1.16	1.73		
(Et <sub>4</sub> N) <sub>2</sub> BuSnCl <sub>5</sub>	1.09	1.86		
(Ph <sub>4</sub> As) <sub>2</sub> BuSnCl <sub>5</sub>	1.09	1.88		
(Et <sub>4</sub> N) <sub>2</sub> BuSnCl <sub>3</sub> Br <sub>2</sub> <sup>e</sup>	1.20	1.85		
(Et <sub>4</sub> N)BuSnCl <sub>4</sub> · PBU <sub>3</sub>	1.27	2.42	1.66	2.39
(Et <sub>4</sub> N)BuSnCl <sub>4</sub> · Ph <sub>3</sub> PO	1.07	2.10	2.04 <sup>c</sup> (2.15) <sup>d</sup>	1.54 <sup>c</sup> (1.36) <sup>d</sup>
(Et <sub>4</sub> N)BuSnCl <sub>4</sub> · Ph <sub>3</sub> AsO	0.94	1.84	1.84	1.90
(Et <sub>4</sub> N)BuSnCl <sub>4</sub> · DMF	1.10	1.90	1.90	1.78
(Et <sub>4</sub> N)BuSnCl <sub>4</sub> · DMSO	0.98	1.88	1.87	1.84
(Et <sub>4</sub> N)BuSnCl <sub>4</sub> · Py	1.04	1.65	1.77	2.06
(Et <sub>4</sub> N)BuSnCl <sub>4</sub> · NMe <sub>3</sub>	0.98	1.91		
(Et <sub>4</sub> N) <sub>2</sub> PhSnCl <sub>5</sub>	0.90	1.65		
(Ph <sub>4</sub> As) <sub>2</sub> PhSnCl <sub>5</sub>	0.93	1.64		
(PyH) <sub>2</sub> PhSnCl <sub>5</sub>	1.01	1.72		
(Et <sub>4</sub> N)PhSnCl <sub>4</sub> · PBU <sub>3</sub>	0.96	2.10	1.47	2.18
(Et <sub>4</sub> N)PhSnCl <sub>4</sub> · Ph <sub>3</sub> PO	0.81	1.81	1.84 <sup>c</sup> (1.96) <sup>d</sup>	1.33 <sup>c</sup> (1.15) <sup>d</sup>
(Et <sub>4</sub> N)PhSnCl <sub>4</sub> · Ph <sub>3</sub> AsO	0.74	1.63	1.64	1.69
(Et <sub>4</sub> N)PhSnCl <sub>4</sub> · DMF	0.83	1.55	1.70	1.57
(Et <sub>4</sub> N)PhSnCl <sub>4</sub> · Py	0.89	1.57	1.57	1.85
(Et <sub>4</sub> N)PhSnCl <sub>4</sub> · NMe <sub>3</sub>	0.82	1.77		

<sup>a</sup> PBU<sub>3</sub> = tri-*n*-butylphosphine, Py = pyridine, NMe<sub>3</sub> = trimethylamine. Other symbols as in Table 1.

<sup>b</sup> Partial quadrupole splitting values ( $\text{mm s}^{-1}$ ) used for calculating the data in this table were: butyl  $-0.93$ ; phenyl  $-0.83$ ; PBU<sub>3</sub>  $-0.27$  (see text); Ph<sub>3</sub>AsO  $-0.02$  [14]; DMF  $+0.04$  [14]; DMSO  $+0.01$  [13]; Py  $-0.10$  [13]. <sup>c</sup> Calculated values using a partial quadrupole splitting ( $\text{mm s}^{-1}$ ) of  $+0.16$  [14] for Ph<sub>3</sub>PO. <sup>d</sup> Calculated using a partial quadrupole splitting ( $\text{mm s}^{-1}$ ), cf.  $0.25$  for Ph<sub>3</sub>PO (obtained from quadrupole splitting data for  $\text{SnCl}_4 \cdot 2\text{Ph}_3\text{PO}$  [20]). <sup>e</sup> Data from ref. 22.

now strong evidence in support of the contention that the Sn—P bonds contain enhanced *s*-character [7,10] and since the electronegativity of phosphorus is low this has the effect of maintaining *s*-electron density at the tin nucleus despite the other factors (already referred to) associated with increasing coordination which have the opposite effect. Thus, it may be assumed that the chemical shift of  $\text{BuSnCl}_4 \cdot \text{PBu}_3$  is a reflection of enhanced *s*-character in the Sn—P bond of this complex also. In contrast to  $\text{BuSnCl}_4 \cdot \text{PBu}_3^-$  the chemical shift of the phenyl analog would not appear to be anomalously high (e.g. the chemical shift of  $\text{BuSnCl}_4 \cdot \text{PBu}_3^-$  is  $0.18 \text{ mm s}^{-1}$  greater than that of  $\text{BuSnCl}_5^{2-}$  whereas the chemical shift of  $\text{PhSnCl}_4 \cdot \text{PBu}_3$  is comparable to that of  $\text{PhSnCl}_5^{2-}$ ) and this may be a reflection of the greater electronegativity of phenyl compared to butyl. In both phosphine adducts the phosphorus atom is *trans* to the organo group (see discussion on quadrupole splitting data) and is thus likely to involve the same *SP* hybrid orbital as carbon for bonding to tin [11]. Clearly, more electron density, in particular *s*-electron density, will be concentrated in the Sn—P bond when it is *trans* to a butyl group than when it is *trans* to the much more electron withdrawing phenyl group.

Quadrupole splitting parameters (see Table 2) are typical of those found for octahedral tin complexes in which there is one tin—carbon bond and are mostly very similar to those for  $\text{RSnCl}_5^{2-}$  species. This latter observation is consistent with the small quadrupole splittings associated with most of the 1/2 stannic halide adducts containing the donors in Table 2 [12].

Quadrupole splitting parameters which have been calculated on the basis of the point charge model are also included in Table 2. Figure 1 shows the two possible structures for the adducts along with the directions of the principal components of the electric field gradient. In the case of the *trans* structure there is no ambiguity as to the choice of the  $V_{zz}$  axis. However, in the case of the *cis* structure the point charge expressions for the electric field gradient components are

$$V_{11} = \{2[\text{R}] - [\text{Cl}] - [\text{L}]\}e$$

$$V_{22} = \{2[\text{Cl}] - [\text{R}] - [\text{L}]\}e$$

$$V_{33} = \{2[\text{L}] - [\text{R}] - [\text{Cl}]\}e$$

([R], [Cl] and [L] represent point charge contributions of organo group, chloride and donor respectively) and the choice of  $V_{zz}$  will therefore be dictated by

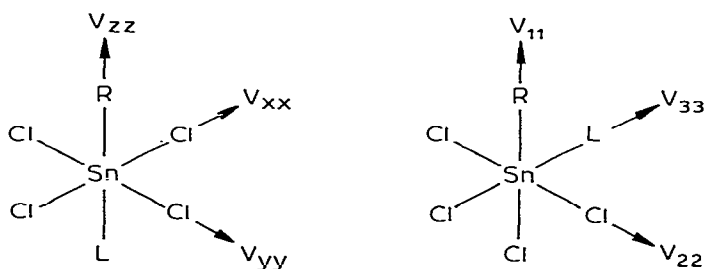


Fig. 1. Possible structures for the adducts and directions of the principal components of the electric field gradient. R = butyl or phenyl, L = donor molecule.

the relative magnitudes of [L] and [R]. For the donor groups in Table 2 [L] is always less than 0.5 [R] and consequently  $V_{11}$  corresponds to  $V_{zz}$ .

Partial quadrupole splitting (PQS) values which have previously been employed [13,14] for donor molecules are also adopted for the present calculations and the value of  $-0.27 \text{ mm s}^{-1}$  for  $\text{PBu}_3$  is from Mössbauer data for  $\text{SnCl}_4 \cdot 2 \text{PBu}_3$ . Since the sign of the quadrupole splitting has been determined [15] for this adduct the sign of the PQS value for  $\text{PBu}_3$  is definitely established. PQS values for butyl and phenyl are average estimates from quadrupole splitting data for salts of  $\text{R}_2\text{SnCl}_4^{2-}$  (included in Table 2). Quadrupole splitting values for these salts are not significantly dependent on the nature of the counter ions and thus the average estimates of the PQS values so obtained can justifiably be considered as good working values for other monophenyl and monobutyl octahedral tin(IV) complexes.

Only in the case of the phosphine and phosphine oxide adducts is it possible to make confident structural assignments from calculated data. In other instances differences between data calculated for *cis* and *trans* structures are too small (as a result of the small PQS values of the neutral donor groups). In the case of the phosphine adducts, the calculated *cis* and *trans* quadrupole splittings values differ by more than  $0.7 \text{ mm s}^{-1}$  and the values for the *trans* structures are in remarkably good agreement with the experimental values. Calculated data based on *cis* and *trans* structures for the phosphine oxide adducts differ by more than  $0.5 \text{ mm s}^{-1}$  but in those instances it is the *cis* values which show good agreement with the experimental data. Steric considerations certainly favour the *trans* structure for the phosphine adducts. On the other hand they cannot rule out the possibility of a *cis* structure for the phosphine oxide adducts since spectroscopic data suggest a *cis* structure for  $\text{SnCl}_4 \cdot 2 \text{Ph}_3\text{PO}$  [9] and X-ray crystallographic data have established the *cis* structure for  $\text{SnCl}_4 \cdot 2 \text{Cl}_3\text{PO}$  [16].

The PQS values for butyl and phenyl groups which have been used in the present calculations (estimated from quadrupole splitting data for monoorganotin(IV) complexes) are of the order of  $0.1 \text{ mm s}^{-1}$  lower than values previously employed for these groups (estimated from quadrupole splitting data for diorganotin(IV) complexes mostly) [13]. In other words, quadrupole splitting values for the octahedral anions  $\text{R}_2\text{SnCl}_4^{2-}$  [13] are on average greater than what would be predicted on the basis of the data for the anions  $\text{R}_2\text{SnCl}_5^{2-}$  in

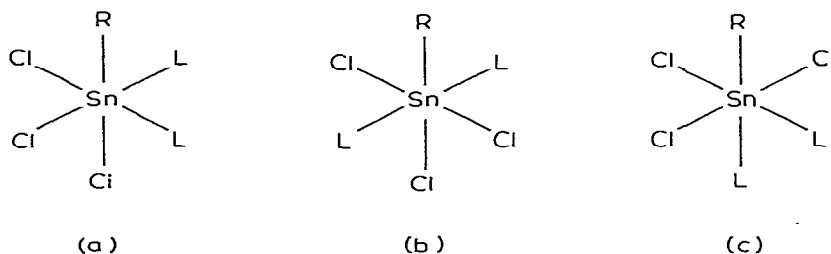


Fig. 2. Three possible isomers for the adducts. R = alkyl or phenyl, L =  $\text{Ph}_3\text{PO}$ .

TABLE 3

OBSERVED AND CALCULATED QUADRUPOLE SPLITTING DATA FOR  $\text{BuSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$  AND  $\text{PhSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$ 

	$\Delta$ (exp.) ( $\text{mm s}^{-1}$ ) <sup>a</sup>		$\Delta$ (calc.) ( $\text{mm s}^{-1}$ ) <sup>b</sup>	
$\text{BuSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$	2.34	Structure 2a	2.38 <sup>c</sup>	2.26 <sup>d</sup>
		Structure 2b	2.36	2.18
		Structure 2c	1.67	1.72
$\text{PhSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$	2.01	Structure 2a	2.17	1.98
		Structure 2b	2.15	1.97
		Structure 2c	1.46	1.51

<sup>a</sup> Data from ref. 21. <sup>b</sup> Calculated data are for structures in Fig. 2. <sup>c</sup> Data in this column were obtained using a partial quadrupole splitting of  $+0.25 \text{ mm s}^{-1}$  for triphenylphosphine oxide. <sup>d</sup> Data in this column were obtained using a partial quadrupole splitting of  $+0.16 \text{ mm s}^{-1}$  for triphenylphosphine oxide. See text and Table 2 for the origins of both partial quadrupole splitting values.

Table 2 and assuming the point charge model relationship

$$\Delta(\text{trans-R}_2\text{SnCl}_4^{2-}) = 2\Delta(\text{RSnCl}_5^{2-})$$

Similar type deviations from point charge model predictions have been encountered and discussed for tetrahedral molecules [17] though in these latter instances deviations are much more pronounced. Clearly, in view of their origin, the lower PQS values for butyl and phenyl would be expected to be the more suitable ones for all monobutyl and monophenyl octahedral tin(IV) complexes and this is generally fairly well reflected. For example, all calculated data in Table 2 would increase by approximately  $0.2 \text{ mm s}^{-1}$  by using the higher PQS values and thus the agreement between experimental and calculated data would always be less than that already achieved, and the lower values also generally give better results for adducts  $\text{RSnCl}_3 \cdot 2 \text{L}^*$ . However, calculated data for the latter adducts using the smaller PQS values for butyl and phenyl are generally no more helpful than previously calculated data from the point of view of making structural assignments (since PQS values of the donor molecules involved are generally very small). In this latter respect the situation for adducts  $\text{RSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$  (R butyl or phenyl) is possibly different and worth considering.

Three isomers are possible for these adducts (Fig. 2). In view of the approximate nature of the point charge model calculated data cannot distinguish between isomers (a) and (b) since their quadrupole splitting values differ only as a result of a non-zero asymmetry parameter in (b). However, the quadrupole splitting for isomer (c) will differ from those of the other two isomers by approximately  $3[\text{L}]$ . The data in Table 3 have been calculated using two different PQS values for triphenylphosphine oxide, one obtained from quadrupole splitting data for a compound containing no tin-carbon bonds ( $\text{SnCl}_4 \cdot 2 \text{Ph}_3\text{PO}$  [20]) and the other from data for a complex containing two tin-carbon bonds ( $(\text{Me}_2\text{Sn}(\text{Ph}_3\text{PO})_4)^{2-}$  [14]), and this reduces bias resulting from the choice of PQS value for  $\text{Ph}_3\text{PO}$ . It is seen from the data in Table 3 that irrespective of the choice of PQS value for triphenylphosphine oxide isomer (c) can be fairly

\* For example, all calculated data for butyl and phenyl complexes in Table 3 of ref. 18 would be lowered by approximately  $0.2 \text{ mm s}^{-1}$ . Data in ref. 19 were calculated using the lower values.

reliably ruled out for both  $\text{BuSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$  and  $\text{PhSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$  and this is consistent with a dipole moment measurement which suggests structure (a) for  $\text{BuSnCl}_3 \cdot 2 \text{Ph}_3\text{PO}$  [21].

## Experimental

### *Tetraethylammonium monobutyltetrachlorostannate and tetraethylammonium monophenyltetrachlorostannate*

The butyl complex was prepared by the slow addition of a dichloromethane solution of tetraethylammonium chloride (1 mol) to a dichloromethane solution of  $\text{BuSnCl}_3$  (1 mol).  $(\text{Et}_4\text{N})\text{BuSnCl}_4$  was precipitated on addition of petroleum spirit. A similar procedure using  $\text{PhSnCl}_3$  led to the precipitation of a white solid which was shown by an X-ray powder diffractogram to be a mixture of  $\text{Ph}_2\text{SnCl}_2$  and  $(\text{Et}_4\text{N})_2\text{SnCl}_6$ .

### *Adducts $(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{L}$ and $(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{L}$*

Adducts  $(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{L}$  (L pyridine, dimethylsulphoxide, dimethylformamide and tri-n-butylphosphine) were prepared by adding dichloromethane solutions of base (1 mol) to dichloromethane solutions of acid (1 mol) and precipitating the adducts with petroleum spirit. The trimethylamine adduct was prepared by bubbling gaseous trimethylamine through a dichloromethane solution of the acid and precipitating the product with petroleum spirit. When triphenylarsine oxide and triphenylphosphine oxide were used as base the addition of petroleum spirit resulted merely in the precipitation of unreacted base.

TABLE 4  
ANALYTICAL DATA FOR THE DONOR—ACCEPTOR COMPLEXES

Complex	Found (calcd.) (%)			
	C	H	Cl	N
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{PBu}_3$	44.52 (44.29)	8.23 (8.61)	22.12 (21.81)	2.10 (2.15)
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{Py}$	38.62 (38.71)	6.36 (6.45)	26.53 (26.91)	5.28 (5.31)
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{NMe}_3$	35.83 (35.51)	7.61 (7.50)	28.45 (27.98)	5.49 (5.52)
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{DMSO}$	31.99 (31.94)	6.82 (6.65)	26.74 (26.96)	2.56 (2.66)
$(\text{Et}_4\text{N})\text{BuSnCl}_4 \cdot \text{DMF}$	34.82 (34.55)	6.83 (6.91)	26.88 (27.22)	5.31 (5.37)
$(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{PBu}_3$	46.48 (46.55)	7.71 (7.76)	21.42 (21.16)	1.87 (2.09)
$(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{Py}$	41.31 (41.68)	5.56 (5.48)	25.56 (25.92)	5.23 (5.12)
$(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{NMe}_3$	38.90 (38.72)	6.59 (6.45)	27.05 (26.92)	5.48 (5.31)
$(\text{Et}_4\text{N})\text{PhSnCl}_4 \cdot \text{DMF}$	37.39 (37.71)	6.02 (5.91)	25.91 (26.21)	5.29 (5.18)

In these instances the adducts were obtained by adding acid and base in a 1/1 molar ratio to dichloromethane and removing solvent under reduced pressure. Evidence for adduct formation is obtained from shifts in As=O and P=O stretching frequency data (see Table 1) and from the fact that the solid products do not contain reactants (as indicated by X-ray diffractograms).

Adducts  $(Et_4N)PhSnCl_4 \cdot L$  were prepared by adding dichloromethane solutions of tetraethylammonium chloride (1 mol) to dichloromethane solutions of  $PhSnCl_3$  (1 mol) followed immediately by addition of base (1 mol). Procedures beyond this were as described for the butyl complexes. A dimethylsulphoxide adduct giving satisfactory elemental analyses could not be isolated in this case. Elemental analyses are in Table 4.

Acetonitrile, diethyl ether, acetone, methanol and tetrahydrofuran did not give adducts with  $(Et_4N)PhSnCl_4$  and  $(Et_4N)BuSnCl_4$  using the procedures described.

Addition of 2,2'-bipyridyl and *o*-phenanthroline (1 mol) to dichloromethane solutions of  $(Et_4N)PhSnCl_4$  and  $(Et_4N)BuSnCl_4$  (1 mol) followed by precipitation with petroleum spirit gave mixtures of organotin trihalide 1/1 adducts and  $(Et_4N)_2R_2SnCl_5$  (see reaction 4). Similar products were obtained when solutions were evaporated to dryness.

### Acknowledgement

We thank the Department of Education for financial support for M.L. and K. McL.

### References

- 1 D. Cunningham, J. Finnegan, J.D. Donaldson and M.J. Frazer, *J. Chem. Soc. Dalton*, (1977) 162.
- 2 K. McLaughlin, M.Sc. Thesis, National University of Ireland, 1977.
- 3 V.S. Petrosyan, N.S. Yashina, S.G. Sacharov, O.A. Reutov, V. Ya Rochev and V.I. Goldanskii, *J. Organometal. Chem.*, 52 (1973) 333.
- 4 P. Zanella and G. Tagliavini, *J. Organometal. Chem.*, 12 (1968) 355.
- 5 A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, *J. Chem. Soc. A*, (1970) 2862.
- 6 See for example N.N. Greenwood and T.C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971.
- 7 A.J. Carty, T. Hinsperger, L. Mihichuk and H.D. Sharma, *Inorg. Chem.*, 9 (1970) 2573.
- 8 D. Cunningham, M.J. Frazer and J.D. Donaldson, *J. Chem. Soc. A*, (1971) 2049.
- 9 P.G. Harrison, B.C. Lane and J.J. Zuckerman, *Inorg. Chem.*, 11 (1972) 1537.
- 10 G.G. Mather, G. McLaughlin and A. Pidcock, *J. Chem. Soc. Dalton*, (1973) 1823.
- 11 R.S. Tobias, *Inorg. Chem.*, 9 (1970) 1296.
- 12 G.M. Bancroft and R.H. Platt, *Adv. Inorg. Radiochem.*, 15 (1972) 59 and references therein.
- 13 M.G. Clark, A.G. Maddock and R.H. Platt, *J. Chem. Soc. Dalton*, (1972) 281.
- 14 G.M. Bancroft, V.G. Kumar Das and K.D. Butler, *J. Chem. Soc. Dalton*, (1974) 2355.
- 15 D. Cunningham, M.J. Frazer and J.D. Donaldson, *J. Chem. Soc. (A)*, (1971) 2049.
- 16 C.I. Branden, *Acta Chem. Scand.*, 17 (1963) 759.
- 17 A.P. Marks, R.S. Drago, R.H. Herber and M.J. Potasek, *Inorg. Chem.*, 15 (1976) 259.
- 18 R. Barbieri, L. Pellerito, N. Bertazzi and G.C. Stocco, *Inorg. Chim. Acta*, 11 (1974) 173.
- 19 D. Cunningham and M. Little, *J. Organometal. Chem.*, 142 (1977) C58.
- 20 P.A. Yeats, J.R. Sams and F. Aubke, *Inorg. Chem.*, 9 (1970) 740.
- 21 F.P. Mullins, *Can. J. Chem.*, 49 (1971) 2719.
- 22 A.G. Davies, L. Smith and P.J. Smith, *J. Organometal. Chem.*, 23 (1970) 135.