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NEW SULFOXIDE AND AMIDE COMPLEXES OF METHYLTIN CATIONS

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INTRODUCTION

The coordination chemistry of organometallic cations is a subject of much current interest, and a number of recent reports have described complexes of the di- and trimethyltin cations (for leading papers in the area see ref. 1). Dissolution of tetrahedral $(CH_3)_2SnX_2$ and $(CH_3)_3SnX$ ($X = Cl$, Br) in oxygen donor solvents such as water[1a], sulfoxides[2] and amides[1c] is generally agreed to cause profound changes in the carbon–tin skeletal geometries, such that the $(CH_3)_2Sn(IV)$ moiety is essentially linear, while the $(CH_3)_3Sn(IV)$ species becomes planar. In view of the propensity of $(CH_3)_2Sn(IV)$ and $(CH_3)_3Sn(IV)$ to form six- and five-coordinate complexes, respectively[1], the feeling seemed to be that the former housed four ligands[3], and the latter two[1c], in their primary coordination spheres. The questions naturally arise whether such complexes [$(CH_3)_3SnL_2^+$ and $(CH_3)_2SnL_4^{2+}$, L = neutral oxygen donor] are isolable, and how do their chemistries differ from those of the species present in the bulk media. A very brief report[4] has discussed the di-aquo complex, $[(CH_3)_3Sn(H_2O)_2]^+ \cdot Ph_4B^-$, but no description of the $(CH_3)_2SnL_4^{2+}$ type has appeared. It seemed of considerable importance to survey this area more generally, and we presently report on the isolation and spectra of complexes of the types $[(CH_3)_2SnL_4]^{2+} \cdot 2\,Ph_4B^-$ where L = DMSO, DMF, DMA, and $[(CH_3)_3SnL_2]^+ \cdot Ph_4B^-$ where $L = H_2O$, DMSO, DMF, DMA, and speculate on their structures.

EXPERIMENTAL

Dimethyltin dichloride was purchased from Alfa Inorganics, and trimethyltin bromide was prepared by redistribution of tetramethyltin with stannic bromide[5]. Dimethyl sulfoxide (DMSO) and the amides (DMA, DMF) were the purest available commercial products. Reactions and manipulations were performed with minimum exposure times and the complexes were maintained under vacuum in the dark.

Preparation of complexes $[(CH_3)_2SnL_4]^{2+} \cdot 2\,Ph_4B^-$

Since the synthetic modus operandi was essentially the same for all complexes, the procedure is described for the DMSO complex only.

Tetrakis(dimethylsulfoxide)dimethyltin(IV) bis(tetraphenylborate). To a warm solution of 0.96 g (0.004 mole) of dimethyltin dichloride and 3.0 g (0.008 mole) of

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sodium tetraphenylborate in DMSO was added with stirring an excess of water. A white crystalline material was precipitated which was filtered and washed repeatedly with warm water and finally dried. The yield (4.8 g) was quantitative, m.p. 92–93°. The compound has no serious survival problem and may be kept for considerable periods under vacuum. (Found: C, 63.39; H, 6.44; Cl, <0.2; S, 11.73. $C_{58}H_{70}B_2O_4S_4Sn$ calcd.: C, 63.38; H, 6.37; Cl, 0.00; S, 11.65%.)

Tetrakis(dimethylformamide)dimethyltin(IV) bis(tetraphenylborate). The procedure was similar to that described for the DMSO complex. A white micro-crystalline product, m.p. 116–118° was obtained. (Found: C, 68.54; H, 7.06; N, 4.95. $C_{62}H_{74}B_2N_4O_4Sn$ calcd.: C, 69.00; H, 6.86; N, 5.15%.)

Tetrakis(dimethylacetamide)dimethyltin(IV) bis(tetraphenylborate). This white complex, m.p. 80–85°, is appreciably hygroscopic and an entirely satisfactory analysis could not be obtained. However, rapid manipulation under a dry atmosphere permitted the recording of IR and NMR spectra, on which the formulation is based.

Attempted preparation of tetraaquodimethyltin(IV) bis(tetraphenylborate). Employment of the general route did not afford any characterisable complex, although on occasions there were indications of a low melting crystalline complex, that has so far defied adequate characterisation.

The $(CH_3)_2Sn(IV)$ complexes are insoluble in alcohol, ether, chloroform, benzene and dioxane but dissolve in acetone, dichloromethane, DMF, DMA, DMSO and sulfolane.

Preparation of complexes $[(CH_3)_3SnL_2]^+ \cdot Ph_4B^-$

The general procedure is described only for the DMA complex. The $(CH_3)_3Sn(IV)$ complexes are hygroscopic to varying degrees, with the DMSO complex most stable.

Bis(dimethylacetamide)trimethyltin(IV) tetraphenylborate. 2 g of sodium tetraphenylborate (0.005 mole) and 1.22 g of trimethyltin bromide (0.005 mole) were dissolved in a slight excess of warm ($\not> 60°$) DMA. Ice was added and the mixture was refrigerated. White needles of the complex appeared which were filtered, dried and stored under vacuum in the dark, m.p. 80°. (Found: C, 64.48; H, 7.94; N, 4.02. $C_{35}H_{47}BN_2O_2Sn$ calcd.: C, 64.01; H, 7.10; N, 4.26%.)

Bis(dimethylsulfoxide)trimethyltin(IV) tetraphenylborate. White crystals, m.p. 107°, of this fairly stable complex (usual precautions) were obtained by the general synthetic procedure. (Found: C, 58.3; H, 6.43; Br, 0.0; S, 10.03. $C_{31}H_{41}BO_2S_2Sn$ calcd.: C, 58.4; H, 6.61; Br, 0.0; S, 10.00%.)

Bis(dimethylformamide)trimethyltin(IV) tetraphenylborate. No entirely satisfactory analysis was obtained for this complex, due to its hygroscopic nature, but rapid manipulation allowed IR and NMR spectra to be obtained, m.p. 144–145°.

Diaquotrimethyltin(IV) tetraphenylborate. This white complex, m.p. 82°, was prepared in the manner described by Wada and Okawara[4], and had an IR spectrum essentially identical with that reported. The NMR spectrum is discussed in the text.

The $(CH_3)_3Sn(IV)$ complexes are more soluble than their $(CH_3)_2Sn(IV)$ relatives, and chloroform, benzene, alcohol and acetone were suitable solvents.

Spectra

The proton NMR spectra were recorded with a Varian A-60 instrument and

NMR solvents (reagent grade and distilled before use) were examined at high amplification to ensure the absence of spurious peaks. Spectra were obtained largely on CH_2Cl_2 solutions but occasionally dioxane and acetone were employed. IR spectra were recorded either as Nujol mulls or sometimes on CH_2Cl_2 solutions. It was established that IR spectra of samples recovered after the recording of NMR spectra was essentially unchanged.

RESULTS AND DISCUSSION

Since the parent cations, $(CH_3)_3Sn(IV)$ and $(CH_3)_2Sn(IV)$ exhibit different coordination behaviour[1], it seems better to discuss the two series of complexes separately.

$(CH_3)_2Sn(IV)$ complexes

The analytical figures leave little doubt that the complexes are of the type $[(CH_3)_2SnL_4]^{2+} \cdot 2\,Ph_4B^-$, and the integrated proton resonance spectra confirm this. The proton resonance data is assembled in Table 1, and the Sn-CH_3 region of the DMSO complex is illustrated in Fig. 1(a).

TABLE 1

PROTON NMR DATA[a] OF $[(CH_3)_2SnL_4]^{2+} \cdot 2Ph_4B^-$

L	*τ(Ph)*	*τ(L-CH₃)*	*τ(Sn-CH₃)*	*J(¹¹⁹Sn–CH₃) (cps)*
DMSO	*ca.* 2.58 (40)	7.57 (24)	9.25; 9.55 (6)[b]	65; 57
DMF[c]	*ca.* 2.58 (44)	7.08 (24)	9.55 (6)	56
DMA[d]	*ca.* 2.58 (40)	7.03 (24); 8.25 (12)	9.14; 9.48 (6)	57

[a] CH_2Cl_2 medium. τ values are based on CH_2Cl_2 as secondary internal standard (τ 4.68). Relative intensities are located in brackets following the τ values. Where necessary, corrections have been applied for the isotopic composition of tin. [b] The relative intensities of these signals are *ca.* 2:3. [c] The aldehydic proton signal, which arises at 2.0 τ in free DMF is presumably smothered in the 40 aromatic multiplet of tetraphenyl borate. The N-$(CH_3)_2$ "doublet" separation was *ca.* 2–6 cps (*cf.* 6–8 cps in free DMF). [d] The N-$(CH_3)_2$ protons appeared as a single line. The intensity ratio of the Sn-CH_3 signals was *ca.* 1:4 and the tin satellites about the less intense τ 9.14 resonance were not observable.

That these complexes represent new examples of hexa-coordinate tin seems clear, and a description in terms of an octahedral ligand array is probably appropriate. For an undistorted octahedral arrangement, the isomers with *trans*- or *cis*-methyl groups would lead to single Sn-CH_3 resonance. The observation of two Sn-CH_3 resonances in the spectra of the DMSO and DMA complexes raises several interesting questions. Since the intensities of the Sn-CH_3 resonances are not equal, more than one $(CH_3)_2Sn(IV)$ species must be present in solution. In other words, distortion of the octahedron, leading to environmentally distinct methyl groups within the one complex, cannot be the complete explanation.

The following points require evaluation as possible explanations of the Sn-CH_3 resonance duality.

(1). Dissociation in the sense, $(CH_3)_2SnL_4^{2+} \rightleftharpoons (CH_3)_2SnL_3^{2+} + L$ would demand the existence of two distinct DMSO signals, since the presence of two Sn-CH_3

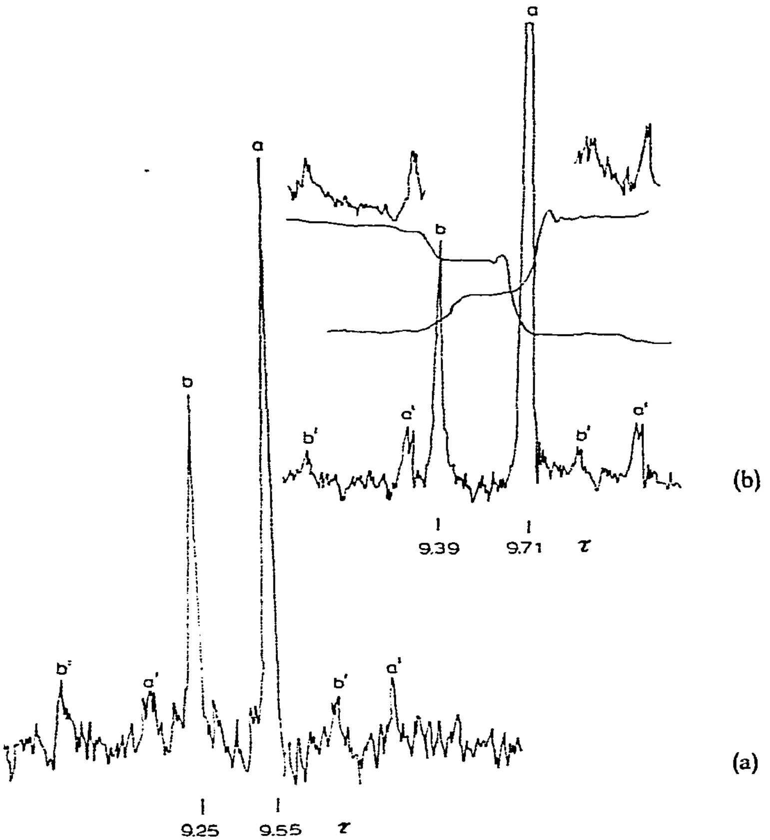


Fig. 1. (a) Sn-CH$_3$ region of proton spectrum of $[(CH_3)_2Sn(DMSO)_4]^{2+} \cdot 2\,Ph_4B^-$; (b) Sn-CH$_3$ region of $[(CH_3)_3Sn(DMA)_2]^+ \cdot Ph_4B^-$.

signals with their satellites (in DMSO case) implies appreciable NMR exchange times. Since comparison spectra indicate a difference of 4–6 cps between the resonance positions of free and complexed DMSO, the sharpness of the DMSO resonance suggests dissociation as an unlikely explanation.

Certainly dissociation cannot be the explanation in the DMA case, since the N-$(CH_3)_2$ protons appeared as a single line, whereas free DMA exhibits signals for the non-equivalent N-CH$_3$ groups under the same conditions[5]. The same type of argument may be successfully applied to the DMF case, since the N-$(CH_3)_2$ "doublet" separation of *ca.* 2–6 cps is appreciably less than in free DMF (*ca.* 6–8 cps)[6].

(2). The co-existence of *cis* and *trans* isomers is another possible explanation, but we have no real evidence on this matter. Infrared examination in the C–Sn stretching region, in principle can answer this question, since a *cis* arrangement should lead to two and a *trans* arrangement to one C–Sn stretching vibration. However, our attempts in this direction have been hampered by solubility problems and complicating ligand absorptions. The facts that the relative intensities of the Sn-CH$_3$ resonances fluctuate and that the addition of benzene simplified the region to one signal ($J(^{119}Sn\text{–}CH_3) = 56$ cps) are of course, not inconsistent with geometrical isomerism. However, what seems to be a mechanistic problem, immediately arises. Dissolution of $(CH_3)_2SnCl_2$ in DMSO produces a $(CH_3)_2Sn(IV)$ species with a $J(^{119}Sn-CH_3)$ of 113 cps[2] essentially the same as that observed when $(CH_3)_2SnCl_2$ is dissolved in water[7,3]. In the latter case, the geometry of the $(CH_3)_2Sn(IV)$ species has been established as linear by Raman spectra[8], and there seems no good reason to doubt that the $(CH_3)_2Sn$ moiety is linear in DMSO also. How the addition of water to precipitate the complex (see *Experimental*) could modify this to a *cis* geometry is not presently clear. The available evidence strongly indicates that complexes of the type $SnX_2(acac)_2$ (X = halogen, acac = acetylacetone) have a preferred *cis* configuration in solution[9], but just as certainly $(CH_3)_2Sn(acac)_2$ adopts the *trans*[10]. The present complexes, not incorporating the constraining features of the chelating ligands, may represent a blend of the characteristics responsible for predominantly *cis* or *trans* configuration. *Cis-trans* isomerism does seem to constitute one cogent explanation of the proton spectrum.

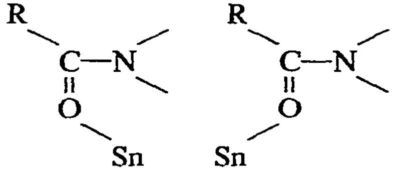
(3). So far, the role of the counter ions (Ph_4B^-) has been neglected, but it appears that the philosophies on organic ion-pairs may well be applicable to the present cases. Dichloromethane is a poor ion-solvator, and consequently a considerable energy barrier would exist to ionisation in such a medium. In other words, ion-pairing (or higher aggregation) between the complexed dipositive cation and the counter ions (Ph_4B^-) is expected to be extensive and probably complete under such conditions. It seems to us unreasonable to suppose that the cation and anion lead independent existences in CH_2Cl_2. It is not clear how rapidly such ion-aggregates may dissociate and re-associate, but we would anticipate it to be slow on an NMR time scale. The preferred geometries of the ion-pairs become of importance. Considering the anion, which may be approximated as spheroidal for the purposes of the following discussion, and a formal octahedral geometry for the cation, we can conceive of a number of situations in which two contiguous or non-contiguous faces of the octahedron are engaged, resulting in dissimilar ion-pairs. If each of the two signals in the NMR spectrum corresponds to a unique ion-pair, then certain restrictions must be placed on allowed geometries. Any ion-pair arrangement, leading to distinct $Sn\text{-}CH_3$ groups within that arrangement, seems to be ruled out, since a total of at least three signals would be expected. [The necessity for the presence of more than one $(CH_3)_2Sn(IV)$ species has already been explained]. Thus, it appears, that ion pairs, within which the $Sn\text{-}CH_3$ groups are equivalent, are consistent with the spectrum. Intuitively, we feel that the ion-pair, in which faces related by reflection through the center of symmetry are engaged would be energetically most favourable. The spectral simplification as a result of benzene addition seems consistent with some sort of π-electron interaction with the counter-ions. (For a description of what may be a related effect see ref. 11.) The fact that the surviving signal has $J(^{119}Sn-CH_3) = 56$ cps indicates only a shift in the equilibrium, since a weighted J value (*ca.* 60–61 cps as calculated from the equilibrium intensities of the $Sn\text{-}CH_3$ signals) somewhere between 56 cps and 65 cps would be expected for completely mobile counter ions.

It is possible to calculate the magnitude of the free energy change necessary to account for the spectral changes. For an ion-pair equilibrium of the type

$$A^{2+}2B^- \rightleftharpoons A^{2+}2B'^- \qquad \Delta\Delta F = 2.303\,RT\log(K/K')$$

Since only one $Sn\text{-}CH_3$ peak is observable after the benzene addition, then the equilibrium constant cannot be less than nine. Thus $K = 9$ and $K' = 1.5$, (*i.e.* 60 : 40 intensity ratio), leading to $\Delta\Delta F \sim 1$ Kcal/mol. This type of change seems consistent with the kinds of interactions that may develop between the counter-ions and benzene*.

Similar arguments may apply to the DMA complex but here an added complication must be recognised. As postulated for ester and ketone complexes[14], it may be that the hybridisation of the oxygen atom of the carbonyl group approaches sp^2 and this permits alternative formulations for the complexes as shown. However, we have no evidence on this problem. Similar considerations apply to the DMF complex,



but the fact that only one Sn-CH_3 resonance is observable may indicate that isomerism of the above type is not an important consideration for the amide complexes.

Shier and Drago[15] have recently described the complex, $[(CH_3)_2Pb(DMSO)_4](ClO_4)_2$, but unfortunately NMR data for the complex in non-coordinating media was unavailable.

The proton spectra of the complexes $[(CH_3)_2SnL_4]^{2+} \cdot 2\ Ph_4B^-$ in solutions of their respective ligands exhibited one Sn-CH_3 resonance with $J(^{119}Sn\text{-}CH_3) =$ 110–113 cps essentially the same as that observed for $(CH_3)_2SnCl_2$ in DMSO[2]. The J values found for the present complexes appear to be the lowest reported for $(CH_3)_2$-Sn(IV) species. If one accepts the usual rationale[7], that the J values are some function of *s*-electron density at tin (Fermi contact) then certainly the tin–carbon bonds in these complexes are different from those present in the bulk media. Although these new complexes seem to demonstrate that the $(CH_3)_2Sn$(IV) cation can accommodate four neutral oxygen donors in the primary coordination sphere in the solid and in non-coordinating media, extrapolation of this finding to donor solutions may not be straightforward. A larger number of ligands may be held by relatively weak polar bonds in solution, while in the solid (and in non-coordinating media) the Sn–O bonds are more covalent. Thus, one would not expect to see a Sn–O stretching vibration in the Raman spectra of these complexes in solutions of their ligands. This

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* From the NMR spectrum of $(CH_3)_2Sn(DMSO)_4^{2+} \cdot 2\ BF_4^-$, in which there is an 18 cps difference between the resonance positions of the Sn-CH_3 signals, it is possible to calculate some rough thermodynamic quantities of activation for ion-pair interconversion (for the mathematical techniques see ref. 12). These calculations lead to a value of $\Delta F^* = \Delta H^* - T\Delta S^* > 16.5$ Kcal/mole, for conversion of the least to the more stable ion-pair geometry. (ΔS^* is probably largely composed of statistical factors). Since ion-pair interconversion at least involves the migration of one BF_4^- species to an adjoining face, *i.e.* the negotiation of an edge of the octahedron, it is possible to make calculations on a simple electrostatic model with distances estimated from known crystallographic data (see *e.g.* ref. 13). Thus treating the cation as a dipositive point charge and the counter-ion as a point negative charge, an electrostatic barrier to interconversion of at least 30 Kcal/mole exists, if the negative charge, originally *ca.* 3 Å from the positive point, was required to move *ca.* 0.5 Å further away from the positive point to negotiate the edge of the octahedron. These admittedly crude calculations suggest that the NMR data and an electrostatic ion-pair model are at least compatible.

change from more covalent Sn–O bonds in the solid to far weaker polar Sn–O bonds in donor solution, must certainly involve appreciable hybridisation changes, with consequent *s*-electron redistribution. Not understood, however, is the possible effect of cation-anion pairing in CH_2Cl_2 on the coupling constants.

Taking a value of 1053 cm^{-1} for ν(S–O) in free DMSO, complexation lowers this value by 120 cm^{-1} for $[(CH_3)_2Sn(DMSO)_4]^{2+}$. There seems little doubt, then, that oxygen is the donor atom[16]. In the case of the amides, for which ν(C=O) = 1673 cm^{-1} (DMF) and ν(C=O) = 1649 cm^{-1} (DMA), low frequency movements of 23 cm^{-1} for the DMF complex, and 47 cm^{-1} for the DMA complex were observed, indicating oxygen donation[17,18]. Oxygen coordination should have the effect of increasing ν(C–N)[17,18], and we have made observations on bands, thought to be ν(C–N). However, no completely satisfactory assignments of the spectra of the free amides seem available and in view of the very recent evidence[18] for coupling of ν(C–N) and ν(C=O), we feel discussion of our data would serve no useful purpose at this time.

$(CH_3)_3Sn(IV)$ complexes

A brief report discussed the preparation of diaquotrimethyltin(IV) tetraphenylborate, and the presence of only one band (562 cm^{-1} asymmetric Sn–C stretch) in the 500–580 cm^{-1} region was interpreted to mean a planar $(CH_3)_3Sn$ arrangement[4]. Since subtle structural differences may escape detection by the IR technique, we undertook an NMR study of this compound, together with the new complexes $[(CH_3)_3SnL_2]^+ \cdot Ph_4B^-$ (L = DMSO, DMA, DMF) to furnish additional structural information. To be sure, reconciliation of IR spectra (Nujol mulls) and solution NMR spectra may not be a simple task. The NMR data is collected in Table 2 and the $Sn\text{-}CH_3$ region of the DMA complex is illustrated in Fig. 1(b).

TABLE 2

PROTON NMR DATA[a] OF $[(CH_3)_3SnL_2]^+ \cdot Ph_4B^-$

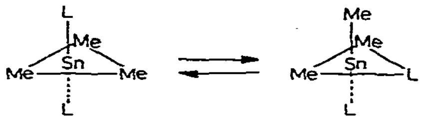
L	*τ(Ph)*	*τ(L-CH₃)*	*τ(Sn-CH₃)*	*J(¹¹⁹Sn–CH₃) (cps)*
H_2O[b]			9.71; 9.74 (9)	62, 56
DMSO	*ca.* 2.58 (20)	7.62 (12)	9.50; 9.71 (9)	66, 56
DMF[c]	*ca.* 2.58 (22)	7.01 (12)	9.35; 9.70 (9)	62, 56
DMA[d]	*ca.* 2.60 (20)	7.05 (12); 8.03 (6)	9.39; 9.71 (9)	64, 56

[a] Data is for CH_2Cl_2 (τ 4.68) solutions except where indicated. Intensities are located in brackets after τ values. [b] For dioxane (τ 6.38) solution. H_2O peak (broad) at τ 6 in acetone solution. [c] The N-$(Me_2)_2$ "doublet" separation was in the range 10–15 cps. [d] The N-Me_2 protons appeared as a single line.

In the aquo, DMA and DMF complexes, the higher field $Sn\text{-}CH_3$ resonance was essentially twice as intense as the lower field $Sn\text{-}CH_3$ resonance. This seems a serious question of Okawara's suggestion of a planar $(CH_3)_3Sn$ group, with the two water ligands occupying apical sites, and this cannot be the complete description of the structure in dioxane, if we ignore possible counter ion effects. The type of argument advanced against complex dissociation in the $(CH_3)_2Sn(IV)$ series has equal merit in the present cases. Thus, since the N-$(CH_3)_2$ protons in the DMA complex appear as a single line, and the N-$(CH_3)_2$ protons in the DMF have a doublet separation of *ca.* 10–15 cps (*cf.* 6–8 cps in free DMF) dissociation is certainly ruled out. The single DMSO resonance, and its sharpness and comparative spectra of free and complexed DMSO, argue against dissociation in this case also. We have no direct evidence in the aquo case, but the facts that the ^{119}Sn–CH_3 coupling constants are essentially the same for all four complexes, and that the Sn-CH_3 signal intensities are 1:2 for the complexes seem too much for coincidence, and we assume that the cause of the Sn-CH_3 resonance duality has a common origin.

There appear to be two possible explanations of the NMR data. The first, which we favour least, is that the structure may be trigonal bipyramidal with one axial and two equatorial methyl groups. There seeems to be no reasonable precedent for this proposal[1] and it certainly is contrary to the IR data for the aquo complex[4], if one assumes no profound reorganisation on transference from solid to dioxane solution. On the other hand, if we assume that the arrangement is trigonal bipyramidal, with a planar $(CH_3)_3$Sn group it is apparent that there is only one possible ion-pair geometry, if only faces are engaged. Further, such a geometry, environmentally distinguishes between the three Sn-CH_3 groups, such that two are identical and clearly different from the third. What may be relevant is that the doubly intense signal is at higher field (*ca.* 0.2–0.3 ppm) and may be associated with the proximity of the counter-ion*.

What appears slightly troublesome to this interpretation is that in the case of $[(CH_3)_3Sn(DMSO)_2]^+ \cdot Ph_4B^-$, the Sn-$CH_3$ signals were not initially in the ratio of 1:2, but fairly quickly approached this value on standing. This approach was hastened by addition of benzene. If ion association is an acceptable explanation of the data, the behaviour of the DMSO complex may reflect breakdown of, or a rearrangement among higher ionic aggregates than pairs. Further work will be required to clarify this point. An interconversion of the type below seems inconsistent with the presence of only two peaks, barring accidental resonance coincidence.



Dissolution of the DMSO and DMA $(CH_3)_3$Sn(IV) complexes in solutions of their respective ligands led to one Sn-CH_3 resonance (*ca.* 9.30 τ) with $J(^{119}\text{Sn–CH}_3) = 70$ cps[1c]. The diaquo complex dissolved in DMSO and one Sn-CH_3 resonance (τ 9.36) with $J = 70$ cps was observed. These values are very similar to those observed for $(CH_3)_3$SnBr in DMSO *i.e.* one signal at τ 9.28 with $J(^{119}\text{Sn–CH}_3) =$

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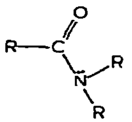
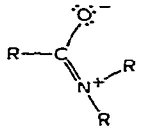
* In both series of complexes, we have observed that the phenyl region (Ph_4B^-) of the proton spectrum is prone to variation. Although we have not seriously attempted to understand this completely, it certainly seems to indicate environmental changes for the counter ions. For CH_2Cl_2 solutions, such changes most reasonably have their origin in cation–anion interactions. It appears that ion-pair phenomena of the type described here may be of importance in strictly inorganic complexes, but the absence of a suitable spectral probe (*e.g.* the Sn-CH_3 behaviour in the present complexes) to monitor such interactions has probably made their detection difficult. Spectroscopic methods, in general, cannot efficiently distinguish between ion-pairs and dissociated ions.

70 cps. Presumably the same species, the solvated planar trimethyltin cation is under observation. The reasons for the changes in coupling constants on going from $[(CH_3)_3SnL_2]^+ \cdot Ph_4B^-$ to the bulk donor media are probably essentially the same as those advanced in the $(CH_3)_2Sn(IV)$ cases.

Utilising values for ν(S–O) (DMSO), ν(C=O) (DMA) and ν(C=O) (DMF) already listed, a $\Delta\nu$(S–O) of 103 cm^{-1} to lower frequencies strongly indicates oxygen donation. $\Delta\nu$(C=O) (DMA) of -54 cm^{-1} and $\Delta\nu$(C=O) (DMF) of -28 cm^{-1} are similarly interpreted. The diaquo complex exhibited IR bands at 3450 cm^{-1} (OH stretch), 1591 cm^{-1} (H_2O deformation) and 790 cm^{-1} (CH_3-rock).

Although in principle, amides are bifunctional donors, there appears to be no authenticated example of coordination via nitrogen[18]. However, a consequence of this mode of binding would be a reduction in the C–N rotational barrier since the resonance form (I) would now be a more important contributor. Conversely, oxygen donation should increase the importance of (II), implying an increase in the C–N rotational barrier.


(I)


(II)

During our proton NMR studies of these methyltin complexes, we have made some observations on the NMR behaviour of N-$(CH_3)_2$ protons in complexed amides. The first point is that such protons appear as single, sharp lines in $[(CH_3)_2Sn(DMA)_4]^{2+}$ and $[(CH_3)_3Sn(DMA)_2]^+$. There appear to be two explanations of this. Firstly, because of the structural complexity of these compounds, neighbour anisotropy effects may be important, and tend to remove the chemical shift difference that exists for free DMA. The other rationale is that the C–N rotational barrier has been reduced, but this does not seem consistent with oxygen coordination. However, in spectra of cooled solutions of the DMA complexes (*ca.* $-20°$) the N-$(CH_3)_2$ "doublet" emerged, and collapsed to a singlet on gradual warming. The Sn-CH_3 region of the spectrum was insensitive to these operations. This seems to us best explicable in terms of a C–N rotational phenomenon. To investigate this area further, we prepared the structurally simpler bis-DMA adduct of stannic chloride, $SnCl_4 \cdot 2$ DMA[19] and examined its proton spectrum. Again, the N-$(CH_3)_2$ protons gave rise to a single line at ambient temperatures but at *ca.* $-30°$, the N-$(CH_3)_2$ "doublet" definitely appeared. Thus the argument that peculiar anisotropic effects are operative in the organotin–DMA complexes seems to be invalidated. Another example concerns the $BCl_3 \cdot$DMA complex described by Gerrard and Lappert[17] who, because of a serious oversight, mis-interpreted their own data. The crux of their error lies in the assumption that "the free amide (*i.e.* DMA) shows a single line for the methyl protons of the NMe_2 group". This is incorrect, and published spectra[6] showing the N-Me_2 "doublet" were available prior to the paper by Gerrard and Lappert. However, these authors found that the N-Me_2 group in $BCl_3 \cdot$DMA shows "some sign of a chemical shift" but the separation was slight and unsymmetrical. Thus, it is apparent that $[(CH_3)_2Sn(DMA)_4]^{2+}$, $[(CH_3)_3Sn(DMA)_2]^+$, $SnCl_4 \cdot 2$ DMA and $BCl_3 \cdot$DMA are similar in that the N-Me_2 protons appear essentially as a single line in contrast to free DMA. We are currently exploring the generality and significance of this phenomenon.

However, the DMF complexes behave in a fairly straightforward manner, except that the N-Me_2 "doublet" separations vary appreciably from that in free DMF (*ca.* 6–8 cps). Thus, the separations are *ca.* 10–15 cps in the $(CH_3)_3Sn(IV)$ complex but only 2–6 cps in the $(CH_3)_2Sn(IV)$ complex. The separation is *ca.* 7–8 cps in $SnCl_4 \cdot 2$ DMF. The causes of these fluctuations are not clear, but differential shielding, depending on structural details not presently clear, may be responsible. There appears to be no significant temperature effect on the magnitude of the N-Me_2 "doublet" separation. We could observe no spin coupling between the N-$(CH_3)_2$ group and the aldehydic proton, in the organotin complexes, as was observed in $BCl_3 \cdot$DMF. However, there are clear signs of a small coupling (< 1 cps) in $SnCl_4 \cdot 2$ DMF.

It is clear that the different NMR behaviour of complexed DMA and DMF (both almost certainly via oxygen) must be due to the C-CH_3 group in DMA. Further, its effect must be largely steric in origin and some of this effect must reduce effective conjugation between nitrogen and the carbonyl group. It is probably significant that the magnitude of $\Delta\nu(C{=}O)$ is much greater for the DMA complexes (*cf. ca.* 50 cm^{-1} for DMA and *ca.* 25 cm^{-1} for DMF).

Further work on the isolation and study of new complexes of methyl tin cations is currently under way, and we will report on amine and phosphine oxide complexes in the near future.

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SUMMARY

Complexes of the types $[(CH_3)_3SnL_2]^+ \cdot Ph_4B^-$ (where L = DMSO, DMF, DMA, H_2O) and $[(CH_3)_2SnL_4]^{2+} \cdot 2\ Ph_4B^-$. (L = DMSO, DMF, DMA) have been prepared and characterised, and their structures investigated by infrared and nuclear magnetic resonance spectroscopy.

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