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CONCERNING DIMETHYL SULFOXIDE COMPLEXES OF SOME ORGANOTIN HALIDES

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The recent report of Langer and Blut[1], which focussed on preparative and infra-red spectral studies of some sulfoxide complexes of Group IV derived organometallic halides, prompts a report from this laboratory describing nuclear magnetic resonance (proton) spectroscopic studies of several such complexes[2]. The nature of these complexes suggested n.m.r. spectroscopy as the tool of choice for probing solution phenomena[3].

The proton spectrum of a chloroform solution of dimethyl tin dichloride consists of a sharp methyl resonance at 8.92τ for methyl groups bound to magnetically inactive tin, and two sets of symmetrically disposed "satellite" resonances for methyl groups bound to magnetically active ($I = \frac{1}{2}$) tin. (Sn^{117} and Sn^{119})[4]. The observed magnitudes[5] of these proton-tin spin interactions are $J_{Sn^{119}-CH_3} = 70$ c.p.s. and $J_{Sn^{117}-CH_3} = 67$ c.p.s., values in excellent agreement with those previously reported[6]. The n.m.r. spectrum of the bis-DMSO complex of $(CH_3)_2SnCl_2$ exhibits major resonances (intensity ratio 2:1) at 7.47τ and 9.01τ, assignable only to the DMSO and $\underline{CH_3}$-Sn functions. Of interest and considerable importance is the observation that J_{Sn-CH_3} have now substantially increased, the values being

$$J_{Sn^{119}-CH_3} = 86 \text{ c.p.s.} \quad \text{and} \quad J_{Sn^{117}-CH_3} = 82.5 \text{ c.p.s.}$$

The proton spectrum of a DMSO solution of $(CH_3)_2SnCl_2$ yields values of

$$J_{Sn^{119}-CH_3} = 113 \text{ c.p.s.} \quad \text{and} \quad J_{Sn^{117}-CH_3} = 107 \text{ c.p.s.}$$

These findings at first suggested that complex dissociation

$$\begin{array}{ccl} (CH_3)_2SnCl_2.2DMSO & \rightleftarrows & (CH_3)_2SnCl_2.DMSO + DMSO \\ & & \quad\quad \uparrow\downarrow \\ & & (CH_3)_2SnCl_2 + DMSO \end{array}$$

in $CHCl_3$ may have been important[7], since the observed Sn-CH_3 coupling constants would then be dependent on the equilibrium constants for the above processes, provided ligand exchange was sufficiently rapid. However, no variation in the magnitudes of the Sn-CH_3 coupling constants were observed over the temperature range 35°C-70°C and our present, but necessarily tentative, rationale[8] is that the ligand disposition about tin in $(CH_3)_2SnCl_2.2DMSO$ is different from that when $(CH_3)_2SnCl_2$ is dissolved in DMSO[9]. The J values of 113 c.p.s. and 107 c.p.s. are the highest observed for the $(CH_3)_2Sn(IV)$ system[9], and appear to demand substantial rehybridisation of the bonding orbitals about tin[10]. Interpolation from the function[6] relating $J_{Sn^{119}-CH_3}$ to the apparent S-character of the tin atomic orbital in the Sn-C bond indicates greater than 50% S-character, suggesting a linear geometry for the $(CH_3)_2Sn$ moiety[9]. Actual displacement of chloride from tin by DMSO molecules may be involved in the dissolution process[11].

$$(CH_3)_2SnCl_2. + x\ DMSO \rightarrow (CH_3)_2Sn^{++}(DMSO)_x + 2Cl^{\ominus}$$

A $J_{Sn^{119}-CH_3} = 86$ c.p.s. corresponds to ca. 40% S-character in the Sn atomic orbital in the Sn-C bond in $(CH_3)_2SnCl_2.2DMSO$.

Rapid intermolecular DMSO exchange appears to be an explanation for the spectra of equimolar mixtures of $(CH_3)_2SnCl_2.2DMSO$ and $(CH_3)_2SnCl_2$. One sharp DMSO resonance, one sharp $\underline{CH_3}$-Sn resonance and only two sets of $\underline{CH_3}$-Sn satellites indicate that all methyl groups are equivalent n.m.r.

wise, and rapid ligand re-organisation about tin, necessitating DMSO exchange, seems demanded. Since the gross composition of such a system is $(CH_3)_2SnCl_2$.DMSO, a reduction in the Sn-CH_3 coupling constant would be anticipated[7], and a slight, but probably real, variation is observed. The addition of further quantities of $(CH_3)_2SnCl_2$ to the system results in corresponding small reductions in the coupling constants.

The n.m.r. spectrum of the bis-DMSO complex of bibenzyl tin dichloride exhibits resonance at 3.0τ, 6.92τ and 7.64τ, corresponding to the aromatic, benzylic and DMSO protons. The Sn^{119} and Sn^{117} spin couplings with the benzylic protons yield values of $J_{Sn^{119}-\underline{CH_2}} = 101$ c.p.s. and $J_{Sn^{117}-\underline{CH_2}} = 96$ c.p.s., significantly greater than those (*ca.* 79 c.p.s. and 76 c.p.s.) observed for uncomplexed $(C_6H_5CH_2)_2SnCl_2$. Essentially no variation in the J values for the bis-DMSO complex were observed over the temperature range 30-70°C.

That ligand "scrambling" on tin is important follows from observations of changes in the proton-tin coupling constants when species R_2SnCl_2.2DMSO and $R_2'SnCl_2$ are mixed in chloroform. Thus admixture of $(C_6H_5CH_2)_2SnCl_2$.2DMSO and $(CH_3)_2SnCl_2$ apparently results in very efficient capture of the DMSO ligands by the $(CH_3)_2SnCl_2$, since the benzylic proton-tin spin coupling constants decrease markedly, while the CH_3-Sn coupling constants enjoy a corresponding increase. $J_{Sn^{119}-\underline{CH_2}}$ falls from 101 c.p.s. to 90 c.p.s. and $J_{Sn^{117}-\underline{CH_2}}$ falls from 96 c.p.s. to 86 c.p.s. $J_{Sn^{119}-CH_3}$ and $J_{Sn^{117}-CH_3}$ increase from 70 c.p.s. and 67 c.p.s. to 80.5 c.p.s. and 77 c.p.s. respectively. In a similar way $(C_6H_5)_2SnCl_2$ captures DMSO initially bound to $(C_6H_5CH_2)_2SnCl_2$, since $J_{Sn^{119}-\underline{CH_2}}$ falls from *ca.* 101 c.p.s. to *ca.* 91 c.p.s. Completion of the experimental triad *viz.* $(C_6H_5)_2SnCl_2$.2DMSO + $(CH_3)_2SnCl_2$ indicates the $(CH_3)_2Sn$ function to largely gain control of the available DMSO.

$(CH_3)_2SnCl_2$.2DMSO is water soluble and such dissolution is accompanied by a rather large increase in J_{Sn-CH_3}, the values observed being $J_{Sn^{119}-CH_3}$ = 107 c.p.s. and $J_{Sn^{117}-CH_3}$ = 103 c.p.s. These values are essentially the same as those observed for $(CH_3)_2SnCl_2$ in aqueous media, where the aquated $(CH_3)_2Sn^{++}$ ion is apparently under scrutiny. Hence complete displacement of DMSO by H_2O seems indicated, and is consistent with the known affinity of the $(CH_3)_2$Sn(IV) ion for water molecules[9].

Langer and Blut[1] have asserted that their solution spectral studies of a variety of complexes in DMSO and chloroform indicated complete dissociation into DMSO and the organometallic compound. If the magnitude of the proton-tin coupling constant is an acceptable criterion for probing rehybridisation and coordination phenomena on tin[6], then the above conclusion seems to require some modification in view of the herein reported results.

Although the present work yields no information on the identity of the donor atom in the sulfoxide molecule (oxygen and sulfur both possess unshared electron pairs), a considerable reduction in the S-O stretching frequency on complexation has been observed and interpreted[1 12] to indicate donor action by oxygen. This would decrease pπ→dπ bonding and consequently the S-O bond order and stretching frequency. It is of interest that sulfur apparently is the donor atom toward palladium[12] in $PdCl_2$.2DMSO, and this is consistent with the known importance of dπ-dπ back bonding in palladium chemistry[13].

The chemistry of this area is being actively explored and further results on the lead and tin systems will be reported at a later date.

References

1. H.G. Langer and A.H. Blut, J. Organometal. Chem. 5, 288 (1966).
2. Leading references to and a brief history of the area are contained in Ref. 1.
3. Langer and Blut (Ref. 1) concluded from a variety of studies that complicated systems existed in solution.

4. The natural abundances of Sn^{119} and Sn^{117} are 8.68% and 7.67% respectively.

5. The magnitudes of the CH_3-Sn coupling constants depend not only on electronic effects, but on the magnetogyric ratios of the tin nuclei.

6. J.R. Holmes and H.D. Kaesz, J. Am. Chem. Soc. 83, 3903 (1961).

7. Certain assumptions are implicit here, and relate to the dependence of the proton-tin coupling constants on the geometry of the ligands about the tin atom. Organotin compounds appear to be fairly versatile in their coordination behaviour (see, for example, R.C. Poller, J. Organometal. Chem. 3, 321 (1965) and references therein) and how the coupling constants would alter with geometry is not fully understood.

8. The temperature range studied may have been insufficient to produce a measurable effect. More complete studies are currently underway.

9. For a lucid account of important aspects of the chemistry of the $(CH_3)_2Sn(IV)$ system see H.N. Farrer, M.M. McGrady and R.S. Tobias, J. Am. Chem. Soc. 87, 5019 (1965).

10. The Fermi contact term, which is non-zero for S-atomic states, appears to dominate the coupling (see H. Dreeskamp, Z. Naturforsch 19a, 139 (1964)) and a large increase in J implies an increase in S-character.

11. Aquation of methyltin halides occurs rapidly and a synchronous displacement at tin has been suggested. (See R.H. Prince, J. Chem. Soc. 1783 (1959)).

12. F.A. Cotton and R. Francis, J. Am. Chem. Soc. 82, 2986 (1960).

13. See, for example, G.F. Coates, "Organo-metallic Compounds", p. 318. Methuen & Co., New York (1956).