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Preliminary communication

Mössbauer and infrared spectra of some 1/1 and 1/2 sulphoxide complexes of diphenyltin dichloride

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Many addition compounds of organotin(IV) halides with Lewis bases are known. Almost all such complexes of the diorganotin dihalides with monodentate bases isolated thus far have 1/2 stoichiometry, *i.e.*, $R_2SnX_2 \cdot 2L$, with hexacoordination about the tin atom[1]. The only 1/1 adducts which seem to have been reported are those of Me_2SnCl_2 and Me_2SnBr_2 with *N,N*-dimethylformamide (DMF) and a few *p*-substituted aromatic carbonyl donors[2]. Tanaka and Kamitani[3] have reported a *mixture* of 1/1 and 1/2 complexes of Me_2SnCl_2 with dimethylselenoxide (DMSeO), but the former was not isolated in pure form.

We have obtained 1/1 adducts of Ph_2SnCl_2 with some sulphoxide donors when a stoichiometric quantity of base is added to a chloroform solution of the tin compound, and the solvent removed under reduced pressure. When 100% or greater excess of base is employed, 1/2 compounds are obtained. Microanalytical data and melting points are given in Table 1. That the 1/1 complexes are true addition compounds and not equimolar mixtures of Ph_2SnCl_2 and the corresponding 1/2 adduct is unequivocal in view of the melting points (Table 1), ^{119}Sn Mössbauer parameters (Table 2) and infrared spectra (Table 3).

TABLE 1

ANALYTICAL DATA AND MELTING POINTS

Compound	Found (%)		Calcd. (%)		M.p. (°C)
	C	H	C	H	
$Ph_2SnCl_2 \cdot Me_2SO$	39.89	3.79	39.83	3.82	80–82
$Ph_2SnCl_2 \cdot Pr_2SO$	45.01	5.08	45.20	5.06	75–77
$Ph_2SnCl_2 \cdot Bu_2SO$	47.45	5.44	47.44	5.58	100–102
$Ph_2SnCl_2 \cdot (CH_2)_4SO$	42.65	4.16	42.88	4.05	106–108
$Ph_2SnCl_2 \cdot 2Me_2SO$	38.04	4.34	38.41	4.44	132–135
$Ph_2SnCl_2 \cdot 2Pr_2SO$	47.22	6.12	47.06	6.26	105–108
$Ph_2SnCl_2 \cdot 2Bu_2SO$	49.74	6.61	50.29	6.94	109–111
$Ph_2SnCl_2 \cdot 2(CH_2)_4SO$	43.27	4.96	43.48	4.75	131–134

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TABLE 2

MÖSSBAUER DATA FOR Ph_2SnCl_2 ADDUCTS AT 80°K

Compound	IS[a,b]	QS[a]	Γ_1[a]	Γ_2[a]
Ph_2SnCl_2	1.37	2.83	0.78	0.79
$Ph_2SnCl_2 \cdot Me_2SO$	1.21	3.06	0.90	0.91
$Ph_2SnCl_2 \cdot (CH_2)_4SO$	1.23	2.91	0.87	0.83
$Ph_2SnCl_2 \cdot Pr_2SO$	1.27	3.01	0.83	0.86
$Ph_2SnCl_2 \cdot Bu_2SO$	1.25	3.20	0.96	0.98
$Ph_2SnCl_2 \cdot 2Me_2SO$	1.30	3.86	0.75	0.82
$Ph_2SnCl_2 \cdot 2(CH_2)_4SO$	1.24	3.76	0.76	0.67
$Ph_2SnCl_2 \cdot 2Pr_2SO$	1.24	3.86	0.88	0.82
$Ph_2SnCl_2 \cdot 2Bu_2SO$	1.20	3.65	0.87	0.84

[a] In mm/s, ±0.05 mm/s. [b] Relative to SnO_2 at 80°K; a $Ba^{119}SnO_3$ source at room temperature was employed.

TABLE 3

RELEVENT INFRARED ABSORPTIONS IN THE 1200–250 cm^{-1} REGION[a]

Compound	ν(S–O)	$\Delta\nu$(S–O)[b]	ν(Sn–O)	ν(Sn–Cl)
Ph_2SnCl_2	–	–	–	356s, 350s
$Ph_2SnCl_2 \cdot Me_2SO$	951 vs	96	421(sh), 417s, 414(sh)	328s, 322(sh)
$Ph_2SnCl_2 \cdot (CH_2)_4SO$	940 vs	80	380m, 376m, 372m	336s, 331(sh), 324m
$Ph_2SnCl_2 \cdot Pr_2SO$	938 vs	80	443s, 439(sh), 432m	328s, 321s, 317(sh)
$Ph_2SnCl_2 \cdot Bu_2SO$	931 vs	97	419s, 416s, 407(sh)	329(sh), 322s, 319s
$Ph_2SnCl_2 \cdot 2Me_2SO$	946 vs	101	418s, 408(sh)	–
$Ph_2SnCl_2 \cdot 2(CH_2)_4SO$	952 vs	68	378(sh), 374s, 367m	–
$Ph_2SnCl_2 \cdot 2Pr_2SO$	938 vs	80	416s, 413s	–
$Ph_2SnCl_2 \cdot 2Bu_2SO$	935 vs	93	419(sh), 415s, 410m	–

[a] Samples run as nujol mulls between CsI plates. All values in cm^{-1}. [b] $\Delta\nu$(S–O) is ν(S–O) for the neat free ligand minus ν(S–O) for the complex.

The 1/1 derivatives show quadrupole splitting values lying between those for Ph_2SnCl_2 and the 1/2 adducts, with no significant line broadening. Because of the large difference in splitting observed for Ph_2SnCl_2 and for the 1/2 complexes, mixture of the two would show either a four-line Mössbauer spectrum or an extremely broad apparent doublet. In all cases the isomer shift decreases on complexation, indicating a lower *s*-electron density at the tin nucleus than in the neat Ph_2SnCl_2. The lower isomer shift in the complexes could be due to an increase in *s*-electron withdrawal from tin, an increase in *p*- and/or *d*-electron donation to tin (which would enhance shielding of the *s* electrons), or both. The 1/1 adducts show essentially the same isomer shift as that reported[4] for $Ph_2SnCl_3^-$ (1.25 mm/s However, the shifts for the 1/2 derivatives are significantly lower than for $Ph_2SnCl_4^{2-}$ (1.44 mm/s)[5].

The IR spectra (Table 3) show substantial lowering of the S–O stretching frequencies on complexation. If the shift in ν(S–O) is taken as a measure of the donor–acceptor interaction strength[3,6], then such interaction appears about equally strong for corresponding 1/1 and 1/2 adducts. On the other hand, the bands assignable to ν(Sn–O) show considerable variation. For both complexes of $(CH_2)_4SO$, the Sn–O vibration is some 40 cm^{-1} lower than for the Me_2SO and Bu_2SO adducts. The Pr_2SO complexes are the only ones showing a significant change in ν(Sn–O) between 1/1 and 1/2 derivatives. The reason for this shift is not clear at present.

All the 1/1 adducts, which presumably have trigonal bipyramidal structures, show strong, complex bands at about 330 cm^{-1} which we assign to Sn–Cl vibrations. $Me_2SnCl_2 \cdot DMF$[2] shows two Sn–Cl bands at 309 and 258 cm^{-1}, but only ν_{as}(Sn–Cl) is found for $Me_2SnCl_2 \cdot DMSeO$[3]. This had led Tanaka[2,3] to assume the donor molecule occupies an apical position in the former and an equatorial position in the latter. The complexity of the Sn–Cl bands observed here, together with the fact that a band at $\sim$ 260 cm^{-1} could well be obscured by the strong ν_{as}(Sn–C) absorption, precludes any such structural assignments in these cases. It seems likely that the phenyl groups occupy equatorial positions, as the methyl groups do in the $Me_2SnCl_3^-$ ion[7], but spectra in the region below 250 cm^{-1} (not presently accessible to us) will be needed to clarify this point.

For the 1/2 complexes, the Mössbauer quadrupole splittings lead us to assign an octahedral structure with *trans*-phenyl groups, as a *cis*-Ph_2 arrangement should give a splitting $\lesssim$ 2 mm/s. In the context of Mössbauer spectroscopy, *cis* and *trans* arrangements of the more electronegative ligands are essentially degenerate, and either will give approximately the same splitting. The IR spectra are not helpful, since none of the present 1/2 complexes shows a band attributable to ν(Sn–Cl) above 250 cm^{-1}. However, on the basis of detailed far-infrared data, Tanaka[8] has postulated a *cis*-chlorine, *cis*-oxygen configuration for $Ph_2SnCl_2 \cdot 2Me_2SO$. This is consistent with the recently determined X-ray structure of $Me_2SnCl_2 \cdot 2Me_2SO$[9], and unlike that of $Me_2SnCl_2 \cdot 2C_5H_5NO$ in which all like groups are mutually *trans*[10].

Further studies on these and related complexes are in progress.

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