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REMARKABLE CONFIGURATIONAL CHANGES OF SOME DIMETHYLTIN COMPLEXES DERIVED FROM ONO TRIDENTATE SCHIFF BASES IN STRONG DONOR SOLVENTS

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SUMMARY

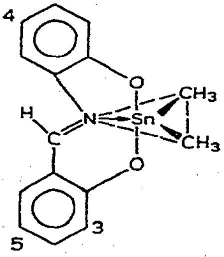
A series of coordinatively unsaturated pentacoordinated dimethyltin complexes have been prepared from dimethyltin dichloride and some ONO tridentate Schiff bases derived from substituted *o*-aminophenols and salicylaldehydes. Their proton magnetic resonance spectra indicate that an initially bent C–Sn–C moiety in these complexes in less donating solvents becomes nearly linear upon coordination with solvent molecules in strong donor solvents.

INTRODUCTION

Recently we have found that coordinatively unsaturated diorganotin halide oxinates disproportionate to give six-coordinate diorganotin dioxinates in donor solvents[1]. Some diorganotin complexes of ONO tridentate Schiff bases recently reported by Barbieri *et al.*[2,3] are also coordinatively unsaturated, although they have no chance to disproportionate owing to their tridentate chelated structure. It is anticipated that the central tin atom in these complexes may have some residual positive charge to interact with strong donor solvent molecules.

In this paper we report the synthesis of a series of dimethyltin complexes of ONO tridentate Schiff bases derived from substituted *o*-aminophenols and salicylaldehydes and discuss their remarkable changes in configuration and bonding in strong donor solvents such as dimethylsulphoxide (DMSO) and hexamethylphosphoramide (HMPA) by means of proton magnetic resonance spectroscopy.

Complexes are abbreviated as A-1, A-2, ..., and D-5. The abbreviations mean that the *o*-aminophenol part in the ligand carries substituent either methyl group (A),



none (B), chlorine (C), or nitro group (D) on the 4-position and the salicylaldehyde part has substituent either methoxy group (1) or nitro group (5) on the 3-position, or either none (2), chlorine (3), or nitro group (4) on the 5-position. Thus, a dimethyltin complex of [*N*-(5-nitrophenyl)formimidoyl]-4-nitrophenol, for example, is abbreviated as D-4 and so on.

EXPERIMENTAL

Materials

Dimethyltin dichloride was kindly donated by Prof. Matsuda, Department of Petroleum Chemistry of this University. Schiff bases were prepared by refluxing alchoholic solutions of substituted *o*-aminophenols and salicylaldehydes. 3- and 5-nitro-[4], and 5-chloro-[5] salicylaldehydes were prepared by literature methods. Solvents were all of reagent grade and were purified according to the standard method except deuterated solvents which were used as supplied.

TABLE 1

SOME DIMETHYLTIN COMPLEXES OF ONO TRIDENTATE SCHIFF BASES

Compound	*M.p.* (°C)	*Analysis found* (*calcd.*)(%)			*Mol.wt. found* (*calcd.*)	
		C	*H*	*N*	*In* $CHCl_3$	*In DMSO*
A-1	190.5–192.0	50.18	4.78	3.29	365	389
		(50.54)	(4.78)	(3.47)	(404)	(404)
A-2	172–176	51.97	4.69	3.30		391
		(51.38)	(4.58)	(3.75)		(374)
A-4	>260	44.82	4.02	7.08		
		(45.86)	(3.85)	(6.69)		
A-5	169–175(d)	45.46	3.92	6.56		
		(45.86)	(3.85)	(6.69)		
B-1	147–167(d)	48.03	4.74	3.55	368	373
		(49.28)	(4.39)	(3.59)	(390)	(390)
B-2	177–179	50.01	4.24	3.64	340	365
		(50.05)	(4.20)	(3.89)	(360)	(360)
B-3	158–159	45.03	3.70	3.57		
		(45.68)	(3.58)	(3.55)		
B-4	242–244	44.46	3.36	6.09	385	455
		(44.49)	(3.48)	(6.92)	(405)	(405)
B-5	258–261(d)	44.10	3.34	7.12	396	
		(44.49)	(3.48)	(6.92)	(405)	
C-2	186.5–187.5	45.38	3.55	3.70		
		(45.68)	(3.58)	(3.55)		
C-3	181–183	42.18	3.03	3.64		
		(42.02)	(3.05)	(3.27)		
D-1	222–223	43.67	3.75	6.34		
		(44.18)	(3.71)	(6.44)		
D-2	213–216	44.24	3.50	6.84		
		(44.49)	(3.48)	(6.92)		
D-4	>260	39.49	2.90	9.71		456
		(40.04)	(2.91)	(9.34)		(450)
D-5	>260	39.88	2.87	9.87		478
		(40.04)	(2.91)	(9.34)		(450)

Preparation of complexes

All complexes described here were prepared according to the following general procedure. Dimethyltin dichloride (0.44 g, 2 mmol) in anhydrous methanol (10 ml) was added dropwise under stirring to sodium methoxide prepared from sodium (0.10 g, 4.4 mmol) and methanol (4.4 ml). Then an appropriate Schiff base (2 mmol) in anhydrous methanol was added and the mixture was refluxed for 1 h. The solvent was removed under reduced pressure and the resulting product was recrystallized from methylene chloride/ligroin or *N,N*-dimethylformamide/ethanol depending on its solubility. Satisfactory melting point ranges and analytical data are obtained for 14 newly prepared complexes as shown in Table 1.

Molecular weights and conductivity measurements

Molecular weights were determined in chloroform at 25° and in DMSO at 65° by using a Mechrolab Vapor Pressure Osmometer for some representative complexes (Table 1). The electric conductivity was measured in DMSO solutions by using a Yokogawa F-255A Universal Bridge and a cell with the cell constant of $0.322\ cm^{-1}$. DMSO was distilled over calcium hydride twice to give $\kappa = 3.6 \times 10^{-7}\ \Omega^{-1} \cdot cm^{-1}$.

Proton magnetic resonance spectra

The PMR spectra were recorded on a Japan Electron Optics JNM-3H-60 Spectrometer or on a JNM-PS-100 Spectrometer operating at 60 and 100 MHz, respectively. Spectral data are summarized in Table 2 and 3. All these data were obtained in 5 wt. % or in saturated solutions with tetramethylsilane as internal standard at ambient temperature unless otherwise noted. Coupling constants were reproducible to ±0.6 Hz for three runs and chemical shifts to ±0.02 ppm for two runs.

TABLE 2

COUPLING CONSTANTS IN DEUTEROCHLOROFORM AND IN DIMETHYLSULPHOXIDE-d_6 (±0.6 Hz)

Compound	$J(^{119}Sn\text{–}CH_3)$		$J(Sn \leftarrow N{=}CH\text{–})$	
	$CDCl_3$	$DMSO\text{-}d_6$	$CDCl_3$	$DMSO\text{-}d_6$
A-1	79.0	86.3	48.9	47.9
A-2	78.5	83.7	50.0	46.6
A-4	78.5	92.9	46.7	32.9
A-5	80.8	96.0	47.3	32.9
B-1	77.8	87.6	49.3	45.2
B-2	78.1	85.2	49.0	44.7
B-3	79.2	87.2	49.8	43.4
B-4	79.2	93.1	45.9	31.9
B-5	80.3	94.8	46.0	30.5
C-2	79.2	86.6	48.1	43.9
C-3	79.1	88.6	47.7	40.1
D-1	80.1	92.7	46.2	33.0
D-2	78.9	89.8	46.8	36.0
D-4	78.8[a]	98.0	46.2[a]	24.0
D-5	79.9[a]	98.4	45.7[a]	24.2

[a] In $CHBr_3$ at 85°.

TABLE 3

SOLVENT EFFECTS ON PMR PARAMETERS[a]

Compound	*PMR parameters*	$CDCl_3$	*Nitromethane*	*Acetone*	*DMA*	*DMSO-d_6*	*HMPA*
A-1	$J(^{119}Sn-CH_3)$	79.0	82.7	83.8	86.2	86.3	95.9
	$J(Sn \leftarrow N=CH-)$	48.9	49.9	51.2	48.7	47.9	37.6
	$\tau(Sn-CH_3)$	9.19	9.25	9.33	9.33	9.43	9.44
	$\tau(Sn \leftarrow N=CH-)$	1.50	1.17	1.03	0.87	1.04	0.79
B-2	$J(^{119}Sn-CH_3)$	78.1	82.6	82.2	85.6	85.2	95.2
	$J(Sn \leftarrow N=CH-)$	49.0	51.1	51.0	49.3	44.7	38.5
	$\tau(Sn-CH_3)$	9.23	9.25	9.34	9.32	9.40	9.47
	$\tau(Sn \leftarrow N=CH-)$	1.38	1.19	0.99	0.83	0.97	0.66
B-4	$J(^{119}Sn-CH_3)$	79.2	85.7	85.2	93.0	93.1	105.0
	$J(Sn \leftarrow N=CH-)$	45.9	[c]	[c]	39.6	31.9	23.2
	$\tau(Sn-CH_3)$	9.16	9.15	9.20	9.22	9.33	9.37
	$\tau(Sn \leftarrow N=CH-)$	1.36	1.05	0.73	0.61	0.87	0.41
D-4	$J(^{119}Sn-CH_3)$	78.8[b]	83.3	86.6	96.4	98.0	109.8
	$J(Sn \leftarrow N=CH-)$	46.2[b]	[c]	[c]	30.7	24.0	16.6
	$\tau(Sn-CH_3)$	9.03[b]	9.09	9.10	9.16	9.28	9.40
	$\tau(Sn \leftarrow N=CH-)$	1.03[b]	0.88	0.43	0.44	0.63	0.15

[a] *J* values are ±0.6 Hz and τ values ±0.02 ppm. [b] In $CHBr_3$ at 85°. [c] Insufficiently soluble to measure.

RESULTS AND DISCUSSION

These complexes are yellow to red in color and quite stable in the solid state in air. However, solutions of those complexes having electron donating groups on the ligand became darkened on prolonged standing.

They are essentially monomeric in $CHCl_3$ and in DMSO (Table 1). The molar conductances of B-2, B-4, and D-4 in 1×10^{-2} and 10^{-3} *M* DMSO solutions are all found to be less than 1 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$. It can be said that these complexes do not show appreciable conductivity in DMSO. Moreover, distinct spin–spin couplings are observed between the tin nuclei and the azomethine proton through three bonds including a $N \rightarrow Sn$ coordination (see later). The complexes are, therefore, concluded not to dissociate even in a strong donor solvent.

Table 2 summarizes $J(^{119}Sn-CH_3)$ and $J(Sn \leftarrow N=CH-)$ values in $CDCl_3$ and in DMSO-d_6; the coupling constant between tin-119 nucleus and the methyl protons attached directly to the tin atom, and the average value for those between tin-117 and -119 nuclei and the azomethine proton, respectively. The concentration dependence of PMR parameters was checked by measuring 0.5, 1.0, and 2.0 wt. % solutions of B-4 in $CDCl_3$ and 0.5, 1.0, 2.0, 5.0, and 10.0 wt. % solutions of B-4 both in *N*,*N*-dimethylacetamide (DMA) and HMPA. The chemical shifts were constant to ±0.04 ppm and the coupling constants to ±1.0 Hz. The PMR parameters, therefore, are apparently only slightly dependent on concentrations both in non-coordinating and in coordinating solvents. In order to obtain values for $J(Sn \leftarrow N=CH-)$ as easily as possible, the data were obtained for 5 wt. % or saturated solutions throughout.

The configurational changes of the dimethyltin skeleton in these complexes are discussed mainly on the basis of $J(^{119}Sn-CH_3)$. It is generally assumed that the coupling mechanism for $J(^{119}Sn-CH_3)$ is governed by the Fermi contact term and that only rehybridization, and not the effective nuclear charge, need be considered[6]. The following discussions are based entirely on this assumption.

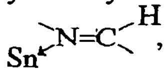
The $J(^{119}\mathrm{Sn{-}CH_3})$ value obtained here for the B-2 complex is in good agreement with that reported by Barbieri *et al.*[3]. In addition, we have obtained a value of about 50 Hz for $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$ in $CDCl_3$ or in $CHBr_3$ confirming unambiguously the existence of a strong N → Sn coordination bond. Ours appear to be the first values of this kind. These values are larger than the values of about 40 Hz for $J(\mathrm{Sn{-}N{-}CH_2{-}})$ in $R_2Sn[N(C_2H_5)_2]_2$ compounds ($R = C_2H_5$ and C_6H_5)[7] and larger than the value of 36 Hz for $J(\mathrm{Sn{\leftarrow}N{-}CH_2{-}})$ in bis(salicylaldehyde ethylenediiminato)dichlorotin-(IV)[8]. In the system of coupling nuclei, that is,  $\mathrm{Sn{\leftarrow}N{=}C{-}H}$, the tin nuclei and the azomethine proton must be situated *trans* to each other with respect to the C=N double bond according to a molecular model. It is well known that nuclei in this situation show larger coupling constant values than those between nuclei in *cis* positions[9]. Moreover, spin–spin couplings through σ and π electron systems as in our case are experimentally proved to be larger than those through only σ electron systems[9]. Thus, the larger value of 50 Hz for $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$ seems to indicate the N → Sn coordination in our system being, at least, comparable in strength with a N–Sn covalent bond. The hypothesis[3] is therefore quite reasonable that in $CDCl_3$ these complexes have trigonal bipyramidal configurations with two methyl groups and the nitrogen atom in the equatorial plane.

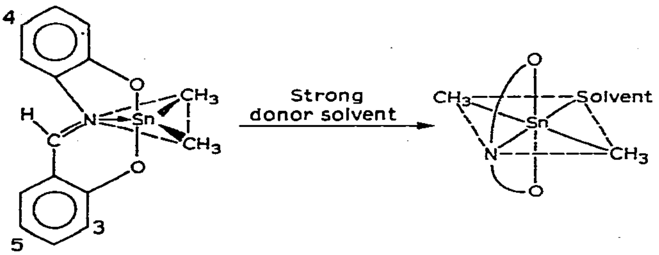
Table 2 also shows that both the $J(^{119}\mathrm{Sn{-}CH_3})$ and $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$ values for all complexes do not change much with change of substituents on the ligand in non-coordinating solvents such as $CDCl_3$ and $CHBr_3$. However in some cases, the former is significantly larger and the latter is much smaller in the strong donor solvent, DMSO-d_6. This is a general tendency observed for all substituents used in this investigation but when the complexes contain electron withdrawing groups *ortho* or *para* to hydroxylic oxygen atoms, the tendency is much intensified. Examples of such complexes include B-4, B-5, C-3, D-4, and D-5.

The trend mentioned above is further verified by inspection of Table 3, which gives the results of solvent effect studies on some representative complexes; A-1, B-2, B-4, and D-4. A-1 carries electron donating groups such as methyl and methoxy groups, B-2 none, B-4 one strongly electron withdrawing nitro group, and D-4 two nitro groups. The solvents chosen are $CDCl_3$, nitromethane, acetone, DMA, DMSO-d_6, and HMPA in order of coordinating ability.

For any complex in $MeNO_2$, the change in both coupling constants from those observed in $CDCl_3$, is much less than the corresponding changes obtained when DMA and HMPA were used as solvents. The solvents $MeNO_2$, DMA, and HMPA have comparable dielectric constant values (38.6, 37.8, and 34, respectively) indicating that they have comparable polarities. On the other hand, the greater the donor ability of the solvent, the larger is $J(^{119}\mathrm{Sn{-}CH_3})$, and the smaller is $J(\mathrm{Sn{\leftarrow}N{=}CH{-}})$. It is well known that dimethyltin compounds with a positive charge on the tin atom, such as halides, show a considerable increase in $J(^{119}\mathrm{Sn{-}CH_3})$ in donor solvents[10]. Hence, these results suggest that the solvent effect is not due to polarity but to the coordinating ability of the solvent molecules.

It is evident from Table 3, by comparing the data for A-1 with those for B-2, that electron donating groups on the ligand do not produce any significant effect on either coupling constant. On the other hand, comparison of the data for B-4 and D-4 with those for B-2 clearly indicates that electron withdrawing groups have profound influence on these coupling constants. Even the B-4 complex with one nitro group *para* to the hydroxylic oxygen atom leads to considerable change of the J values in the moderately strong donor solvent, DMA. A similar change is observed for B-2 only in the strongest donor solvent, HMPA. The change is more striking for D-4, which is thought to have the most residual positive charge on the tin atom due to the presence of two strongly electron withdrawing nitro groups. This complex shows 28% increase in $J(^{119}\text{Sn–CH}_3)$ and as high as 63% decrease in $J(\text{Sn}\leftarrow\text{N=CH–})$, when the solvent is changed from $CHBr_3$ to HMPA. According to the relationship postulated by Holmes and Kaesz[6], the value of 109.8 Hz for $J(^{119}\text{Sn–CH}_3)$ corresponds to about 51% *s* character in the hybrid orbital of the tin atom toward the methyl groups in the case of the D-4 complex in HMPA. This result strongly suggests the occurrence of an almost linear C–Sn–C skeleton in this case.

In accordance with the solvent effect on spin–spin coupling constants, $\tau(\text{Sn–CH}_3)$ values are generally larger in more donating solvents for all complexes. It seems that the methyl protons are more shielded because electron density on the tin atom is increased by donation from solvent molecules. The $\tau(\text{Sn}\leftarrow\text{N=CH–})$ values, on the other hand, decrease remarkably. Of several factors which may play relatively important roles, this effect is probably due to an increase in the electron current of the two phenyl rings in the ligand.



(I) (II)

Based on all these results, we suggest that in strong donor solvents, the dimethyltin moiety in these complexes undergoes remarkable configurational changes owing to coordination of solvent molecules with (I) giving (II). Strong donor solvent molecules are considered to attack the residual positive charge on the tin atom to form coordinatively saturated octahedral dimethyltin complexes with a nearly linear C–Sn–C skeleton. The *s* character of the hybrid orbital on the tin atom may be distributed predominantly around the C–Sn–C skeleton to account for the large increase in $J(^{119}\text{Sn–CH}_3)$ and the very large decrease in $J(\text{Sn}\leftarrow\text{N=CH–})$.

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