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PMR Studies of Trimethyltin Bromide, Dimethyltin Dibromide and Dimethyltin Diiodide [1]

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Introduction

During the past decade, there have been numerous studies on the alkyltin chlorides [2]. However, in this same period of time, there has been only a limited number of studies on the bromide and iodide analogs. Therefore, our laboratory has initiated a pmr study of trimethyltin bromide, dimethyltin dibromide and dimethyltin diiodide. Also, there has been much interest in the structural configuration of organotin complexes [2, 3]. Previous workers have been able to correlate the structural configuration as a function of the tin–methyl coupling constant [4–6].

The chemical shifts and the tin–methyl coupling constants for trimethyltin bromide, dimethyltin dibromide and dimethyltin diiodide have been measured in twenty-nine organic solvents using pmr spectroscopy.

Experimental

Trimethyltin bromide obtained from Alpha Inorganics was distilled, b.p. 165 °C/760 mm (lit. [7] b.p. 165 °C/760 mm).

TABLE 1. Chemical Shifts (δ, ppm) of the Methyl Protons and the Coupling Constants (J, cps) Between the Methyl Protons and the Tin Atom at Ambient Temperature Relative to TMS.

No.	Solvent	$(CH_3)_3SnBr$		$(CH_3)_2SnBr_2$		$(CH_3)_2SnI_2$	
		$\delta(Sn–CH_3)$	$J(^{119}Sn–CH_3)$	$\delta(Sn–CH_3)$	$J(^{119}Sn–CH_3)$	$\delta(Sn–CH_3)$	$J(^{119}Sn–CH_3)$
1	Dimethylsulfoxide	0.70	71.4	1.23	116.0	1.24	110.2
2	N,N-Dimethylformamide	0.73	70.5	1.37	106.0	1.67	102.0
3	Formamide	0.73	69.9	1.35	106.0	1.42	104.0
4	Pyridine	1.06	68.4	—[a]	—[a]	—[a]	—[a]
5	Methanol	0.71	68.2	1.31	93.3	1.63	74.9
6	Ethanol	0.74	68.0	1.17	86.0	1.66	75.0
7	2-Picoline	0.99	67.8	—[a]	—[a]	—[a]	—[a]
8	Acetone	0.76	65.4	1.39	83.6	1.77	74.8
9	Acetonitrile	0.73	65.0	1.39	80.6	1.70	73.0
10	Tetrahydrofuran	0.71	64.2	1.35	83.0	1.66	73.9
11	2,4,6,-Trimethyl-pyridine	0.79	63.6	—[a]	—[a]	—[a]	—[a]
12	1,4-Dioxane	0.72	62.3	1.33	76.0	1.67	70.2
13	*o*-Toluidine	0.53	62.0	—[a]	—[a]	—[a]	—[a]
14	Nitrobenzene	0.87	60.9	1.56	73.0	1.79	67.2
15	Diethyl ether	0.70	60.8	1.31	70.4	1.37	64.4
16	*p*-Bromoanisole	0.65	59.3	1.13	68.8	1.46	64.8
17	Methylene Chloride	0.76	59.2	1.37	69.0	1.66	64.5
18	1,2-Dichloroethane	0.73	59.2	1.36	69.4	1.67	65.0
19	*p*-Bromotoluene	0.61	59.1	1.03	68.0	1.37	63.4
20	Phenylisothiocyanate	0.70	59.0	1.23	69.0	1.39	63.5
21	Toluene	0.42	58.8	0.65	68.6	1.05	64.0
22	Bromobenzene	0.59	58.8	1.03	68.0	1.32	63.2
23	Anisole	0.53	58.8	0.93	69.4	1.22	64.0
24	*o*-Dichlorobenzene	0.66	58.8	1.17	67.2	1.48	64.4
25	Chloroform	0.83	58.8	1.36	68.0	1.65	63.5
26	Carbon Tetrachloride	0.75	58.6	1.33	67.4	1.65	63.5
27	Phenyl Ether	0.54	58.6	0.90	68.4	1.22	63.2
28	Chlorobenzene	0.56	58.2	1.00	68.0	1.31	64.0
29	Benzene	0.43	57.6	0.66	69.2	0.95	64.0

[a] Solution precipitated upon addition of the tin compound.

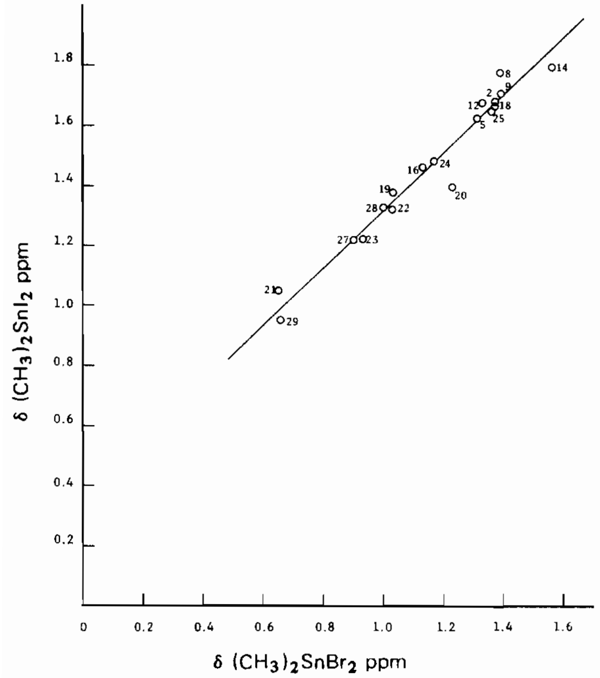

Figure 1. Effect of halogen on complex formation between dimethyltin diiodide and dimethyltin dibromide. The numbers in the figure refer to the solvents in Table 1.

Dimethyltin dibromide obtained from Alpha Inorganics was purified by recrystallization from benzene, m.p. 74 °C (lit. [8] m.p. 74 °C).

Dimethyltin diiodide obtained from Orgmet Inc. was purified by recrystallization from $CHCl_3$, m.p. 30 °C (lit. [9] m.p. 30 °C).

Solvents used in the pmr measurements were reagent or spectro grade and were used without purification. The solvents gave no detectable impurities in their pmr spectra.

The pmr spectra were recorded on a Varian T-60 spectrometer. The chemical shifts were measured relative to TMS. The chemical shifts are within ±0.05 ppm. Expanded spectra were used to measure the $J(^{119}Sn{-}CH_3)$ coupling constants and are within ±0.2 cps. The concentration of the samples were 3–5% and the pmr spectra were recorded at ambient temperatures.

Results and Discussion

The chemical shift of the methyl protons and the $J(^{119}Sn{-}CH_3)$ coupling constants for trimethyltin bromide, dimethyltin dibromide and dimethyltin diiodide measured in twenty-nine organic solvents are tabulated in Table I. Holmes and Kaesz have used the $J(^{119}Sn{-}CH_3)$ coupling constant to estimate the per cent s-character in the tin–methyl orbitals for a series of methyltin chlorides [10]. Also, a model for coordination of trimethyltin chloride with Lewis bases has been suggested based on the $J(^{119}Sn{-}CH_3)$ coupling constants [5]. Using this criterion, the twenty-nine solvents can be divided into three groups: 1) strong donating solvents such as DMSO $J(^{119}Sn{-}CH_3)$ coupling constant of 67.8 to 71.4 cps; 2) moderate donating solvents such as acetone

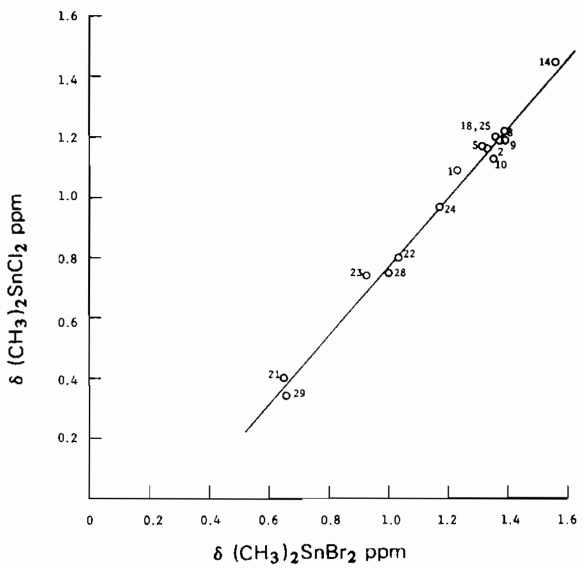

Figure 2. Effect of halogen on complex formation between dimethyltin dichloride and dimethyltin dibromide.

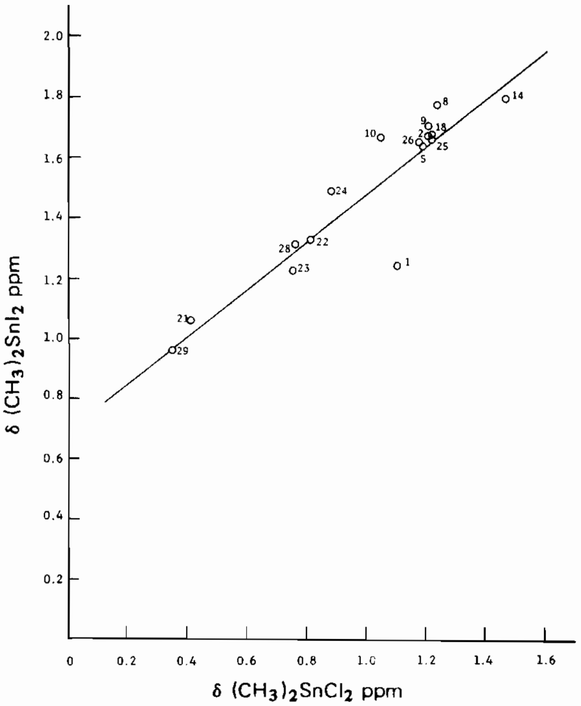

Figure 3. Effect of halogen on complex formation between dimethyltin diiodide and dimethyltin dichloride.

TABLE II. Comparison of the Chemical Shift (δ, ppm) of the Methyl Protons in $(CH_3)_3SnX$ and $(CH_3)_2SnX_2$ at Ambient Temperature Relative to TMS.

No.	Solvent	$(CH_3)_3SnX$		$(CH_3)_2SnX_2$		
		Br	Cl[b]	Br	Cl[b]	I
1	Dimethylsulfoxide	0.70	0.54	1.23	1.09	1.24
2	N,N-Dimethylformamide	0.73	0.63	1.37	1.19	1.67
4	Pyridine	1.06	0.94	–[a]	–[c]	–[a]
5	Methanol	0.71	0.61	1.31	1.17	1.63
7	2-Picoline	0.99	0.79	–[a]	1.53	–[a]
8	Acetone	0.73	0.64	1.39	1.22	1.77
9	Acetonitrile	0.73	0.60	1.39	1.19	1.70
10	Tetrahydrofuran	0.71	0.59	1.35	1.13	1.66
12	1,4-Dioxane	0.72	0.59	1.33	–[c]	1.67
14	Nitrobenzene	0.87	0.79	1.56	1.45	1.79
18	1,2-Dichlorobenzene	0.73	0.68	1.36	1.20	1.67
21	Toluene	0.42	0.27	0.65	0.40	1.05
22	Bromobenzene	0.59	0.46	1.03	0.80	1.32
23	Anisole	0.53	0.41	0.93	0.74	1.22
24	*o*-Dichlorobenzene	0.66	0.55	1.17	0.97	1.48
25	Chloroform	0.83	0.65	1.36	1.20	1.65
26	Carbon tetrachloride	0.77	0.66	1.33	1.16	1.65
28	Chlorobenzene	0.56	0.45	1.00	0.75	1.31
29	Benzene	0.43	0.22	0.66	0.34	0.95

[a] Solution precipitated upon addition of the tin compound. [b] G. Matsubayashi *et al.*, *Bull. Chem. Soc. (Japan)*, *40,* 1566 (1967). [c] No data reported.

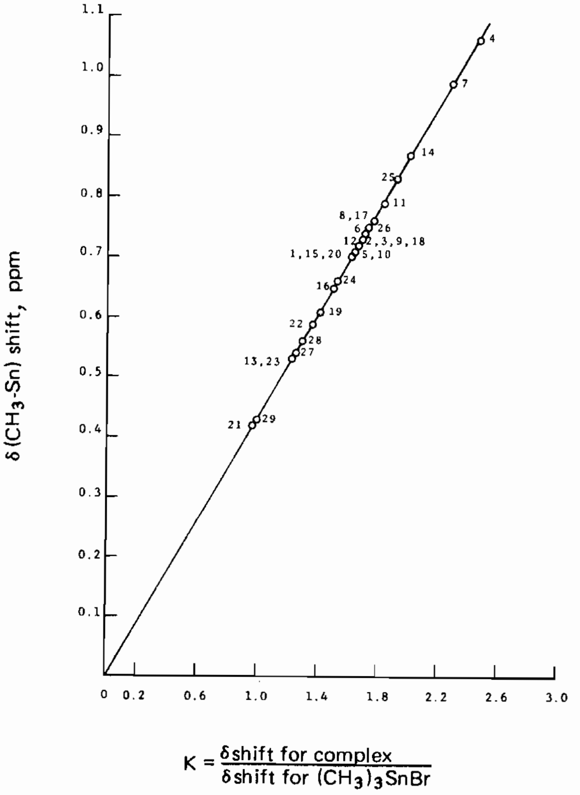

Figure 4. Effect of different ligands on the CH_3 shift values for trimethyltin bromide complexes.

$J(^{119}Sn{-}CH_3)$ coupling constant of 60.8 to 65.4 cps and 3) non-donating solvents such as CCl_4 $J(^{119}Sn{-}CH_3)$ coupling constants of 59.3 to 57.6 cps.

The relationship between the effect of the halogen on complex formation in dimethyltin dihalides is shown in Fig. 1–3. The presence of a straight line in these figures is interpreted as there being minimal or no effect of the halogen on complex formation. Thus, it appears that the Lewis base rather than the halogen is the predominant factor in complexation. This is confirmed by the values obtained from the slope of the lines. If the effect of the ligands is absent then the slope is expected to have a value of one. However, our calculated values in all cases were greater than one, indicating that the ligands do play a role. Similar results were obtained for the trimethyltin halides.

Tabulated in Table II is the comparison of the chemical shift in trimethyltin halides and dimethyltin dihalides. The data supports dπ–pπ bonding between the halogen atom and the tin atom since the shielding order is Cl > Br > I. This is not unexpected since the chloro group being the smallest will have the greatest per cent overlap with the tin atom. This back bonding argument has been forwarded to explain the dipole moment data for SnX_4 [1]].

Also confirmed in Table II is the relative order of acidity as a function of the halogen (I > Br > Cl) since the iodo group is the least able to donate its

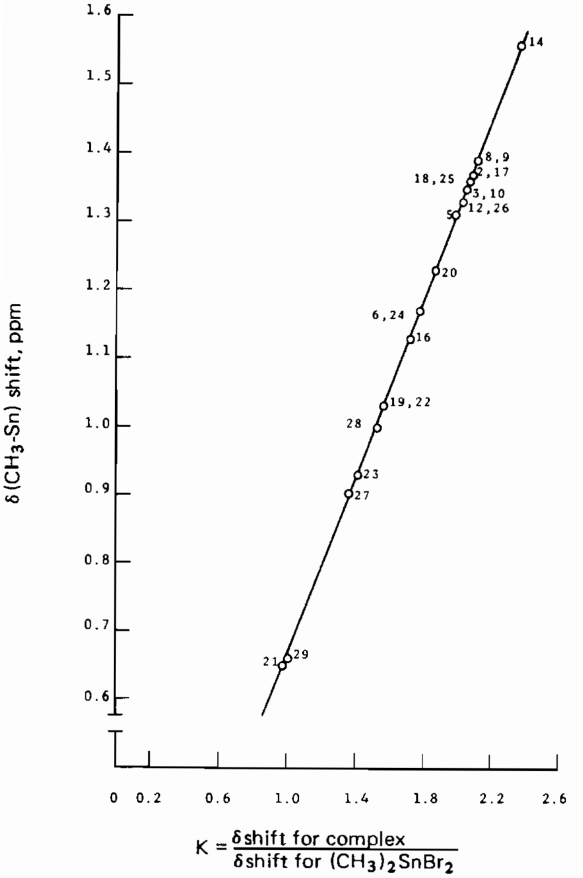

Figure 5. Effect of different ligands on the CH_3 shifts values for dimethyltin dibromide complexes.

p-electrons to the tin atom. The data are also in agreement with earlier studies that substitution of a methyl group by a halogen increases the acidity of the organotin halide [12].

The effect of different ligands on the CH_3 chemical shift values can be seen in Fig. 4 and 5. The appearance of a straight line indicates that the ligands do have an effect in an orderly manner. As seen in Fig. 4, pyridine and 2-picoline had the greatest effect on trimethyltin bromide. It is further assumed that these ligands have a strong effect on dimethyltin dibromide since precipitation occurred upon addition of the Lewis base to the dimethyltin dibromide. Similar results were obtained for dimethyltin diiodide.

The structural similarity between trimethyltin chloride and the bromo and iodo analogs would suggest that a similar mode of coordination can be expected for the trialkyltin complexes studied. In a similar manner, the dimethyltin diiodide complexes can be expected to have a similar structures to dimethyltin dichloride, namely formation of a hexacoordinated complex.

The relative coordinating ability of the twenty-nine solvents based on the $J(^{119}Sn{-}CH_3)$ coupling constant can be grouped into the following:

Strong donors: DMSO ~ DMF ~ Formamide > pyridine ~ EtOH ~ 2-picoline

Moderate donors: Acetone ~ acetonitrile > THF ~ 2,4,6-trimethylpyridine > 1,4 dioxane ~ *o*-toluidine > nitrobenzene ~ Et_2O.

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