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^{119}Sn NMR Spectra of Tin(II) Halides

HO-MEI MIMI YEH and R. A. GEANANGEL
Department of Chemistry, University of Houston Central Campus, Houston, Tex. 77004, U.S.A.

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The ^{119}Sn NMR spectra of tin(II) halides in solution in donor solvents consist of single resonances, the chemical shifts of which are markedly solvent, concentration and temperature dependent in most cases. The δ values increase in the order $SnF_2 < SnCl_2 < SnBr_2 < SnI_2$, the same order as seen earlier for heats of solution and adduct stabilities for the tin compounds. A rationale for the chemical shift dependence on solvent is proposed. Significant solution conductivity was found for SnI_2 in dimethylsulfoxide and hexamethylphosphoramide complicating analysis of δ values. An approximately linear relationship was found between infinite dilution shifts of a given SnX_2 compound and the dielectric constants of the solvents used.

Introduction

The potential of the magnetically active ^{119}Sn and ^{117}Sn nuclei for investigating divalent tin compounds has not been extensively developed, in part, as a result of the low solubilities of the such compounds and the NMR properties of the nuclei. The unusual electronic characteristics of tin(II) halides have led us to investigate their donor-acceptor behavior by thermodynamic measurements and through Mössbauer spectroscopy [1, 2]. We sought to extend the study of their solution interactions using ^{119}Sn NMR as a probe. Investigations such as that of Popov *et al.,* [3] where ^{133}Cs NMR parameters were used to determine stability constants of complexes in nonaqueous solvents suggested that ^{119}Sn NMR could also be used for such purposes.

The present investigation reports ^{119}Sn NMR shifts of the tin(II) halides in several donor solvents over a range of concentrations. The variation of the shifts as a function of halogen substituent, solvent properties and concentration is discussed.

Experimental

Instrumentation

^{119}Sn NMR spectra at 37.28 MHz were obtained on a Varian XL-100 instrument in the FT mode using a Nicholet 1080 data system and Nt-440 Mona multinuclear accessory. A YSI Model 31 conductivity bridge was employed for conductivity measurements.

Materials

All solvents were reagent grade, dried according to literature procedures and degassed. Solutions were

TABLE I. ^{119}Sn Chemical Shifts of SnF_2.

Solvent	M[a]	x_{SnF_2}	$-\delta$ (ppm)[c]	Regression Parameters[b]		
				−A	B	R^2
HMPA	1.58	0.2166	626.1	609.0	10.60	0.96
	1.26	0.1811	622.1			
	0.948	0.1423	618.9			
	0.632	0.0996	615.4			
	0.316	0.0524	612.7			
DMSO	0.462	0.0317	629.0	622.6	14.95	0.96
	0.277	0.0193	626.3			
	0.185	0.0129	626.3			
	0.0923	0.0065	624.3			

[a] Concentration (mol/liter). [b] $\delta = A + B\,M$, R is the correlation coefficient. [c] Positive δ signifies shift downfield from $Sn(CH_3)_4$.

TABLE II. ^{119}Sn Chemical Shifts of $SnCl_2$.

Solvent	M[a]	$\chi SnCl_2$	−δ (ppm)[c]	Regression Parameters[b]		
				−A	B	R^2
HMPA	1.70	0.2302	285.2	293.1	−4.75	0.92
	1.36	0.1927	286.3			
	1.02	0.1518	288.4			
	0.68	0.1066	289.9			
DMSO	1.09	0.0718	358.2	368.0	−9.76	0.60
	0.73	0.0490	357.9			
	0.674	0.0456	362.4			
	0.539	0.0368	364.4			
	0.404	0.0279	362.8			
	0.135	0.0095	363.4			
DMF	0.74	–	324.1	318.5	7.47	0.995
	0.38	–	321.2			
	0.21	–	320.2			
DME	2.6	0.2129	260.3	217.7	16.67	0.98
	1.3	0.1191	242.4			
	0.87	0.0827	229.9			

[a] See Table I for footnotes.

TABLE III. ^{119}Sn Chemical Shifts of $SnBr_2$.

Solvent	M[a]	$\chi SnBr_2$	−δ (ppm)[c]	Regression Parameters[b]		
				−A	B	R^2
DMSO	1.3	–	319.5	357	0.83	0.91
	0.98	–	322.2			
	0.87	–	319.9			
DMF	0.32	0.0242	202.1	171.9	94.9	0.999
	0.24	0.0183	194.9			
	0.19	0.0147	189.7			
DME	0.39	0.0390	72.3	38.34	85.9	0.997
	0.26	0.0263	59.9			
	0.20	0.0199	55.2			
	0.16	0.0171	52.9			

[a] See Table I for footnotes.

prepared in a nitrogen-filled glove box. Tin(II) oxide was prepared from metallic tin [4] and used to prepare SnF_2 [5]. Tin(II) chloride and bromide were prepared in a special apparatus described earlier [6]. Tin(II) iodide was prepared from tin metal as previously described [1]. The tin content of each of the halides was confirmed gravimetrically before use. Tetrabutylammonium bromide and iodide were commercial materials purified by recrystallization.

NMR Sample Preparation

First, the approximate solubility of each tin(II) halide was roughly determined. A nearly saturated solution of each halide in the desired solvents was then prepared accordingly. Known volumes of this stock solution were transferred to five 12 mm NMR tubes and four were diluted to progressively lower concentrations. A coaxial 5 mm tube filled with $(CD_3)_2SO$, the external lock, was then centered in each sample tube. The capped sample tubes were then removed from the glove box and spectra obtained without unnecessary delay.

NMR Spectra

Chemical shifts are reported (Tables I–IV) with respect to $(CH_3)_4Sn$ with positive δ values assigned to downfield shifts. No susceptibility corrections to the observed shifts were carried out. FT pulse times of 12 μsec and pulse delays of 1.2 sec were employed in the collection of the spectra. From 32

TABLE IV. ^{119}Sn Chemical Shifts of SnI_2.

Solvent	M[a]	χSnI_2	$-\delta$ (ppm)	Regression Parameters[b]		
				$-A$	B	R^2
HMPA	1.24	–	174.4	182.5	−9.40	0.57
	1.119	–	173.0			
	1.025	0.1521	171.6			
	0.820	0.1255	170.9			
	0.616	0.0973	173.6			
	0.410	0.0669	177.8			
	0.200	0.0348	184.7			
DMSO	1.29	–	586.0	702.2	−90.4	0.994
	1.03	–	608.6			
	0.903	–	617.9			
	0.774	0.0520	630.9			
	0.620	0.0421	643.1			
	0.496	0.0340	658.7			
	0.388	0.0267	669.9			
DMF	5.117	0.2857	152.6	89.9	11.8	0.96
	4.13	0.2422	138.9			
	3.10	0.1935	122.1			
	2.07	0.1381	117.5			

[a]See Table I for footnotes.

TABLE V. Molar Conductivities of Tin(II) Halides in DMSO and HMPA at 25 ± 0.001 °C.

Compound	DMSO		HMPA	
	Conc. ($\times 10^{-2}$ M)	Λ(cm^2 mol^{-1} Ω^{-1})	Conc. ($\times 10^{-2}$ M)	Λ(cm^2 mol^{-1} Ω^{-1})
SnF_2	2.80	1.78	1.59	4.63
$SnCl_2$	1.65	4.06	1.85	7.72
$SnBr_2$	2.17	13.78	1.60	8.65
SnI_2	2.38	30.20	1.83	14.83
TBABr[a]	2.27	22.66	2.15	10.48
TBAI[b]	1.78	25.78	1.97	13.51

[a]TBABr = Tetrabutylammonium bromide. [b]TBAI = Tetrabutylammonium iodide.

to 1200 acquisitions were required for acceptable signal to noise values depending on the sample and its concentration. Each sample was allowed to warm to probe temperature for 10–15 minutes then trial spectra were obtained. In most cases several spectra were necessary before consecutive observed shift values agreed within ±0.2δ because the chemical shifts of nearly all samples were temperature dependent.

Results and Discussion

In our initial application of ^{119}Sn NMR to study solution reactions of divalent tin compounds, unusual solvent and concentration dependence of chemical shifts were noted. Investigation of the shifts of all the tin(II) halides in several donor solvents (Table I–IV) confirmed the existence of such dependences and plots of δ *vs.* concentration (χ) (Table VI, Figs. 1–4) revealed both positive and negative slopes. The magnitude of the slopes vary widely with the halide and the solvent and the plots are reasonably linear (according to the correlation coefficients) for the lighter halides, but some curvature was evident (Fig. 4) in the SnI_2 plots.

The marginal solubilities of the tin(II) halides made it impractical for us to obtain a complete set of chemical shift-concentration data for the four

TABLE VI. Slopes and Intercepts of ^{119}Sn *vs.* Molar Concentration Plots.

Solvent Parameter	HMPA		DMSO		DMF		DME	
	Slope[a]	Intercept[a]	Slope	Intercept	Slope	Intercept	Slope	Intercept
SnF_2	10.60	−609.0	14.95	−622.6				
$SnCl_2$	−4.75	−293.1	−9.76	−368.0	7.47	−318.5	16.67	−217.7
$SnBr_2$			0.833	−357.0	94.9	−171.9	85.9	−38.34
SnI_2	−9.41	−182.5	−90.35	−702.2	11.84	−89.9		
ε[b]	30		46.68		36.71		7.20	
D.N.[c]	38.8		29.8		26.6		20.00	
Eb[d]	1.55		1.34		1.23		1.0–1.1	
Cb[d]	3.55		2.85		2.48		2.5–3.0	

[a] Slope (B) and intercept (A) as defined in footnote b, Table I. Positive intercept (δ_0) value signifies downfield from $Sn(CH_3)_4$. [b] Dielectric constant at 25 °C except HMPA at 30 °C. [c] Gutman's donor numbers from reference 18. [d] Drago's base parameters from references 19 and 20.

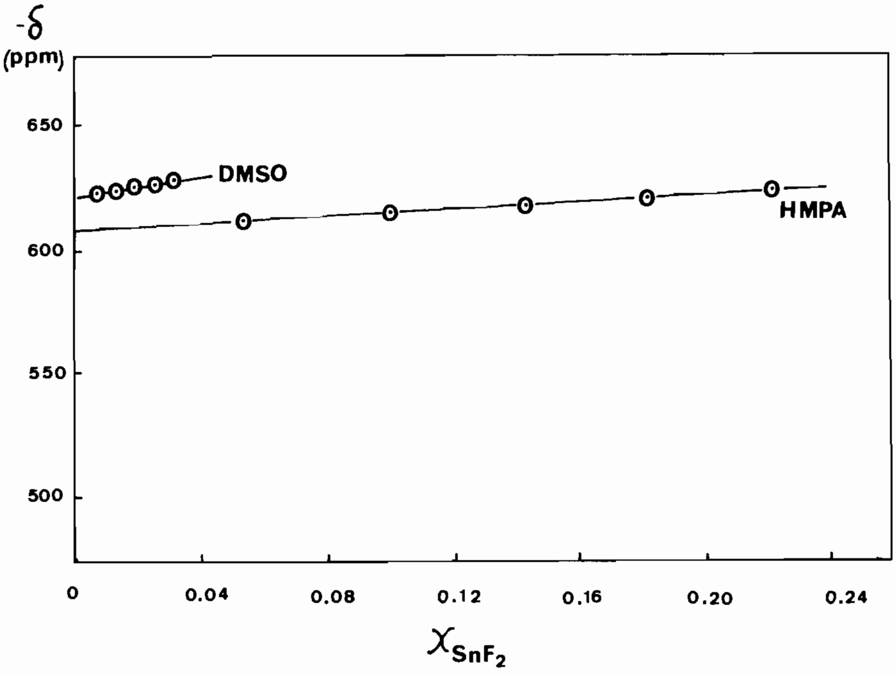

Fig. 1. ^{119}Sn Chemical Shifts of SnF_2 in DMSO and HMPA at Varying Concentrations.

solvents studied. This limits the scope of any correlations which may be detected with solvent parameters but we found it informative, nevertheless, to look for such relationships.

The molar conductivities of the tin(II) halides were measured in dilute HMPA and DMSO solutions (Table V). Conductivities of tetrabutylammonium bromide and iodide are included for comparison. Molar conductivities (Λ) in the range of 24–42 cm^2 mol^{-1} Ω^{-1} in DMSO solution are indicative [7, 8] of 1:1 electrolytes. It can be seen that the molar conductivity in both solvents increases in the order of solute molecular weight with SnI_2 acting as a uni-univalent electrolyte in both solvents at the concentrations used. This suggests that the dissociation shown in eqn. 1 plays a major role in the behavior of SnI_2 in DMSO and HMPA. Such ionization may be

$$SnI_2(solv.) \rightarrow SnI^+(solv.) + I^-(solv.) \quad (1)$$

responsible for the nonlinearity of δSnI_2 *vs.* concentration plots.

The lesser conductivities of the lighter halides indicate that molecular species, probably solvated

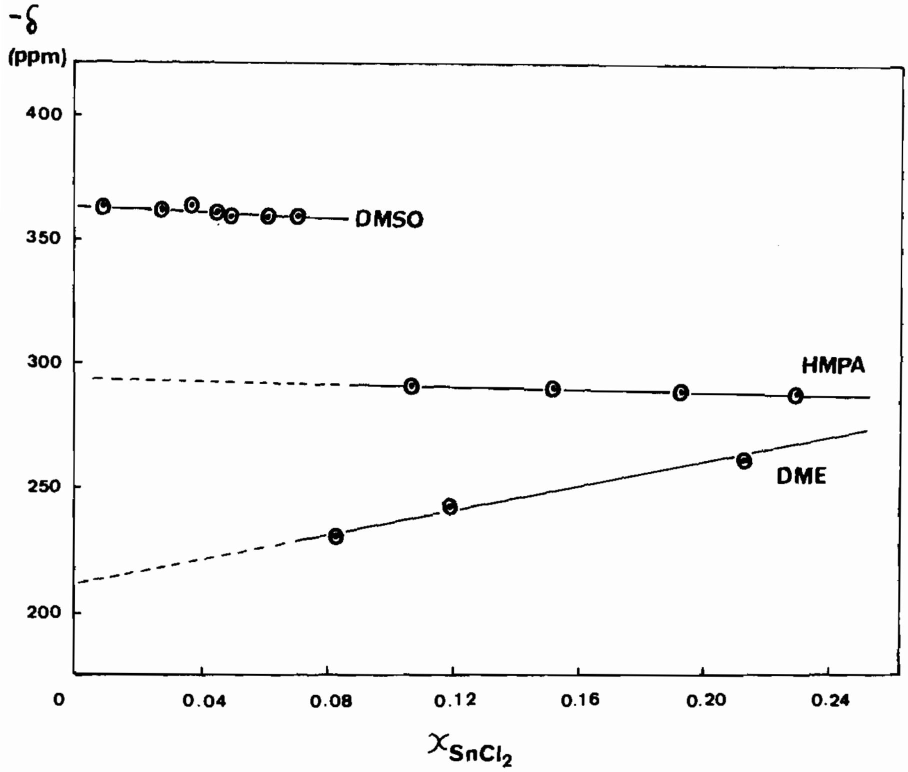

Fig. 2. ^{119}Sn Chemical Shifts of $SnCl_2$ in HMPA, DMSO and DME at Varying Concentrations.

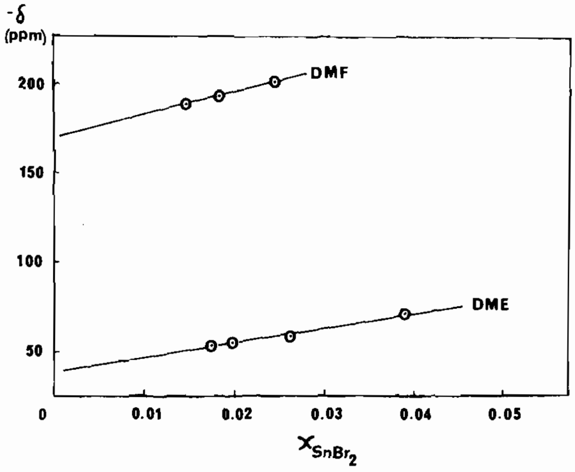

Fig. 3. ^{119}Sn Chemical Shifts of $SnBr_2$ in DMF and DME at Varying Concentrations.

adducts, are the principal forms in solution. Both 1:1 and 1:2 adducts of tin(II) halides with various sigma donors have been isolated [1, 9] and similar adducts with solvent molecules are likely to exist in these solutions, although we did not attempt to isolate them. In this respect the SnX_2 solutes are quite different from Tl(I), Na(I), *etc.*, solutes studied by others [3, 10–13] where the assumption is usually made that covalent interactions are negligible [10].

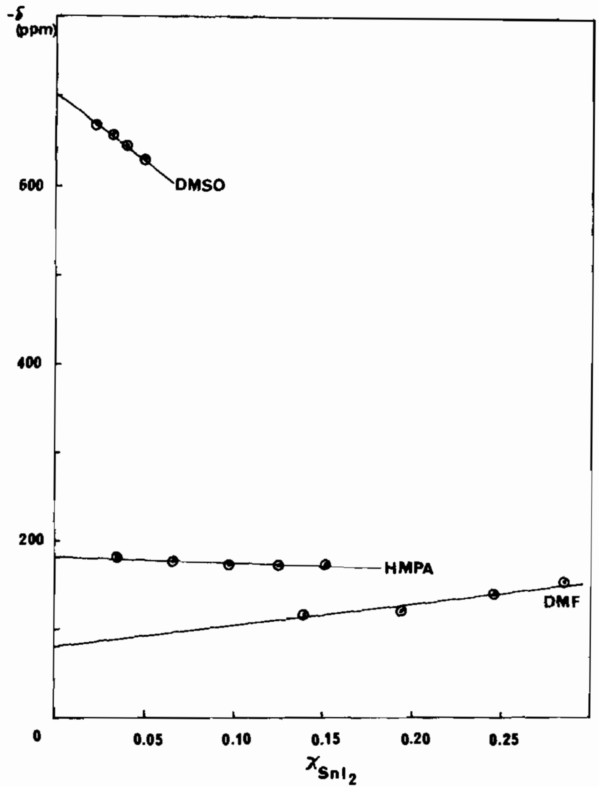

Fig. 4. ^{119}Sn Chemical Shifts of SnI_2 in HMPA, DMSO and DMF at Varying Concentrations.

Single NMR peaks were observed in all ^{119}Sn spectra suggesting that rapid exchange among tin species is operative. (In a few cases, expanded spectra showed asymmetry perhaps due to unresolved resonances). Thus, the observed shifts probably represent weighted averages of the species present and the large concentration dependence seen in some solute-solvent combinations could result from concentration related changes in the shift contributions of each species. Although there is little available information on ^{119}Sn chemical shifts of SnX_2 adducts [14], it is reasonable to expect large chemical shift differences among species of the type under consideration.

The factors usually considered in accounting for chemical shifts are contained in the Ramsey equation [15] as applied, for example, by Dechter and Zink [10] (eqn. 2).

$$\sigma = \sigma_d + \sigma_p + \sigma_o \qquad (2)$$

The total shielding is made up of σ_d, representing shielding by electrons in the ground state of the species, σ_p representing deshielding due to mixing of excited states with the ground state and σ_o representing all contribution from remote atoms. In considering shifts of heavy nuclei, σ_d and σ_o are usually regarded as negligible compared to σ_p [10]. The latter is a function of ΔE, the excitation energy, and of the symmetry of the charge cloud about the nucleus. Factors which cause asymmetry of p or d electron distribution produce downfield shifts.

In this context, we expect both the formation of SnX_2 adducts (eqn. 3) and ionization (eqn. 1) to effect large σ_p shifts because of the changes in hydridization and charge distribution involved as well

$$SnX_2(solv.) + S \rightarrow SnX_2 \cdot S(solv.) \qquad (3a)$$

$$SnX_2 \cdot S(solv.) + S \rightarrow SnX_2 \cdot 2S(solv.) \qquad (3b)$$

as the low symmetry in the coordination sphere of the tin. Therefore, it is reasonable that a marked concentration dependence of δ should exist in these systems, although the necessity for a linear relationship is not evident from these qualitative considerations.

The infinite dilution shift (δ_o) represent the solute in its most solvated state allowing comparison of solutes without concentration effects. In each of the solvents where data is available, δ_o values increase (shift to lower field) in the order $SnF_2 < SnCl_2 < SnBr_2$ (SnI_2 is omitted because of indicated ionization, *vide supra*). The same order has been found [2] for the heats of solution of the tin(II) halides in DMSO and DMF and for the stabilities of $SnX_2 \cdot nN(CH_3)_3$ adducts (X = F, Cl, Br, I: n = 1, 2) [1]. It seems possible that the binding of the donor to the tin creates deshielding *via* the σ_p term in proportion to the strength of the interaction.

The δ_o values of a given SnX_2 increase approximately linearly with dielectric constant of the solvent (Table VI). In view of the uncertainty of the extrapolation, a detailed analysis of the relationship is not warranted, but the dependence on the dielectric constant indicates that some dipolar interactions, possibly solute-solute, influence the chemical shift of the tin. Strong intermolecular interactions involving bridging halogens occur in solid tin(II) halides [16] but the degree to which they might persist in solution has not been established. Solvents with high dielectric constants should reduce the magnitude of such interactions and concurrently increase the solvation of the tin perhaps leading to the observed chemical shift relationship.

Although some workers [11, 17] have reported a linear correlation of chemical shifts of metal ions with Gutmann donor numbers for the solvents [18] we find no such relationship in the ^{119}Sn data nor is there any evident correlation with Drago's E_b and C_b parameters (Table VI) [19, 20].

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