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^{119}Sn NMR IN COORDINATION CHEMISTRY

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CONTENTS

A. INTRODUCTION AND SCOPE

In this review we have two objectives. First, to describe the essential features of ^{119}Sn NMR as it is currently practiced. The level of the presentation was chosen to be informative to chemists who use the technique but who are not specialists in NMR. A number of other review articles concerning all aspects of ^{119}Sn NMR is available [1–6] to which the reader needing more detailed information is directed.

The second and primary objective of this review is to present the applications of ^{119}Sn NMR in all aspects of coordination chemistry. In this regard we have tried to present at least one example of each such application and have included illustrative data tabulations. The literature was surveyed through early 1981.

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B. NUCLEAR AND INSTRUMENTAL CONSIDERATIONS

Of the ten naturally-occurring tin nuclides, three, ^{115}Sn, ^{117}Sn, and ^{119}Sn, exhibit nonzero nuclear spin and have characteristics (Table I) suitable for NMR observation. The most favorable of these is ^{119}Sn and the majority of chemical NMR investigations have used this nuclide even though ^{117}Sn is nearly as favorable. ^{115}Sn has a much smaller abundance and has accordingly received less attention.

The first observations of ^{119}Sn resonance, reported in 1961 [7–10], were obtained in the continuous wave (CW) mode using rapid passage and high RF power to partially compensate for low isotopic abundance. The difficulties associated with CW ^{119}Sn stimulated the development of double resonance and INDOR techniques to improve sensitivity in the spectra of organotin compounds [11,12]. In these methods an easily obtained resonance such as ^{1}H or ^{19}F is observed in compounds where spin coupling occurs between ^{119}Sn and the resonant nucleus. (Twin satellites due to ^{117}Sn and ^{119}Sn are commonly observed in the ^{1}H spectra of organotin compounds.) The ^{119}Sn chemical shift is determined by sweeping the frequency of a second RF oscillator until the ^{119}Sn satellites collapse, establishing the ^{119}Sn frequency for the tin atoms in question at the magnetic field used in the experiment. Using the INDOR modification of the technique, a trace of the ^{119}Sn spectrum can be obtained [11]. The inherently greater sensitivity of the ^{1}H or ^{19}F resonance and modest equipment requirements of the method constitute advantages over direct observation ^{119}Sn NMR but there are also several drawbacks to the technique [5], not the least of which is that it can only be applied to systems where spin coupling involving ^{119}Sn is observable. Much of the ^{119}Sn chemical-shift data for organotin compounds in the literature was obtained by double resonance and INDOR methods.

TABLE I

NMR parameters of tin nuclides [a]

Nuclide	Abundance	Spin	Magnetogyric ratio [b]	Rel. sensitivity		NMR freq. [c] MHz
				Const. H	Const. ν	
^{115}Sn	0.35	1/2	−8.7475	0.0350	0.329	32.864
^{117}Sn	7.61	1/2	−9.5301	0.0452	0.356	35.626
^{119}Sn	8.58	1/2	−9.9707	0.0518	0.383	37.292

[a] Handbook of Chemistry and Physics, 51st edn., CRC, Cleveland, OH, 1970.
[b] Ref. 6. [c] At 23.487 kG.

The advent of the pulse Fourier Transform NMR technique and wide-band probes has made direct ^{119}Sn NMR much more accessible to chemists in general than previously [13,14]. Several commercial instruments are available, with which pulse FT ^{119}Sn NMR spectra can be obtained. The signal averaging capability of such instruments makes it possible to study even relatively dilute solutions of samples. In addition, the FT technique lends itself well to the determination of relaxation times [15,16]. Since the magnetogyric ratio of ^{119}Sn is negative (Table 1), the nuclear Overhauser effect (NOE) can be detrimental towards signal intensities [2] depending on the structure of the tin compound. Gated decoupling is commonly used to suppress this effect although longer spectral collection times are a consequence [5,6].

The generally-accepted chemical shift reference standard for ^{119}Sn is $(CH_3)_4Sn$(TMT). In this review, compounds which resonate at higher fields than TMT will be given negative δ values in accord with the IUPAC recommendation [17] that the signs of reported chemical shifts reflect the resonance frequency difference compared to the reference standard. Quoted literature data in this review have been modified where necessary to conform with the IUPAC convention.

C. NMR PARAMETERS

The three types of measurable quantities in NMR of primary interest to chemists are chemical shifts, coupling constants and relaxation times. Each of these parameters has been discussed in some detail for ^{119}Sn in earlier reviews and only the elements of those subjects pertinent to coordination chemistry will be presented here.

(i) Chemical shift

The relationship between ν_A, the Larmour frequency, B_0, the applied magnetic field, and σ_A, the magnetic shielding constant of nucleus A is given [6] by eqn. (1), where γ is the magnetogyric ratio (Table 1). Information about the electron

$$\nu_A = \frac{\gamma}{2\pi} B_0(1 - \sigma_A) \qquad (1)$$

cloud surrounding the nucleus is obtained from the measured chemical shift through consideration of the shielding indicated for the compound in question. The analysis is complicated by the fact that there are several factors which may contribute to the shielding of a nucleus in a molecular environment [2,5] (eqn. 2).

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

Here, σ_d and σ_p are the diamagnetic and paramagnetic contributions to the shielding respectively, arising from the local (Sn) electron cloud, and σ_n is comprised of all contributions from remote sources including other atoms in the molecule, solvent molecules, ring currents, etc. From Ramsey's treatment [18], equations exist with which σ_d and σ_p may be calculated for a given system but the theory has not yet been developed to the point where consistently accurate values can be calculated especially for atoms as heavy as tin [6]. The best results are usually obtained when calculating the differences in shielding among members of related series of compounds.

Most investigators interpret the large chemical shift range (> 2000 ppm) as indicating that σ_p is the controlling factor in ^{119}Sn chemical shifts. Even this simplifying assumption fails to clarify markedly the interpretation of the chemical shifts since σ_p is a function of at least three factors [19], the average excitation energy, ΔE, the p and d electron imbalance and the effective nuclear charge. These terms are usually interdependent to some extent and are not always readily determined. Thus, ^{119}Sn chemical shift interpretation is limited to an essentially qualitative level at present.

Additional factors which must be considered when ^{119}Sn chemical shifts are to be measured include solvent, concentration and temperature effects. Only in circumstances where solute–solvent interaction and self-association are minimal will solute chemical shifts be reasonably invariant with these factors.

^{119}Sn chemical shifts have been found to be influenced by the presence of electronegative substituents such as halogens, oxygen and sulphur on tin [2,11,20,21], $d\pi$–$p\pi$ bonding effects [11,21,22], bulky atom and dispersion effects [7,11,21–23], coordination number changes [11,21,23] and variation of bond angles at tin [2,6,24]. Some of these factors which relate to coordination chemistry are discussed further in Section D.

(ii) ^{119}Sn coupling constants

Most of the reported coupling constants between ^{119}Sn and ^{1}H, ^{13}C, ^{19}F and ^{31}P have been obtained from spectra of the latter nuclei. From data tabulated in ref. 6, the magnitudes of $^{1}J_{^{119}Sn-X}$ values (signs not considered) fall in the ranges 1740–2960 Hz (X = ^{1}H), 155–966 Hz(X = ^{13}C), 128–1956 Hz (X = ^{19}F) and 50–2383 Hz (X = ^{31}P). In compounds with Sn–Sn bonds $^{1}J_{^{119}Sn-^{119}Sn}$ values with magnitudes in excess of 4400 Hz have been reported [25,26]. Numerous two- and three-bond couplings have also been recorded between ^{119}Sn and the above nuclei.

Coupling constants involving ^{119}Sn appear to behave analogously to those of ^{13}C, at least insofar as ordinary Sn(IV) compounds are concerned. The magnitudes of the former are larger as a result of the greater Z_{eff} and different γ for Sn. While the $J_{^{119}Sn}$ values almost certainly vary with Sn hybridization, it is seldom possible to obtain reliable hybridization information from coupling constants alone.

D. APPLICATIONS IN COORDINATION CHEMISTRY

In the following sections, we interpret coordination chemistry as including all chemical interactions normally regarded as coordinate or donor–acceptor in nature.

(i) Solute–solvent interactions

The concentration dependence of ^{119}Sn chemical shifts has been used to gain insight into coordination of both Sn(IV) and Sn(II) compounds with donor solvents. Investigations of $(CH_3)_3SnX$ (X = Cl, Br) shifts in various donor solvents led to the determination of association constants between the tin compounds and the solvents [7,9,26,27]. The formation of a simple 1:1 solute–solvent adduct was assumed (eqn. 3)

$$R_3SnX + D \rightleftharpoons R_3SnX \cdot D \text{ (D = donor solvent)} \tag{3}$$

and the observed $\delta^{119}Sn$ was taken to be an averaged quantity (eqn. 4).

$$\delta_{obs} = (1-\alpha)\delta_0 + \alpha\delta_c \tag{4}$$

TABLE 2

Association constants for $(CH_3)_3SnX \cdot D$ complexes in donor solvents (D)

X	D	K (mole fraction)		K (mol^{-1})
		Ref. 7 [a]	Ref. 26	Ref. 27
Cl	Acetone	7.0	7.1 ± 2 (−34°C)	0.8 ± 0.1(−30°C)
Br	Acetone	3.0		0.6 ± 0.1(−30°C)
Cl	Acetonitrile	2.7	6.2 ± 2 (−20°C)	
Br	Acetonitrile	3.48		
Cl	Dioxane		2.1 ± 0.4 (20°C)	
Cl	Pyridine			36 ± 3 (−30°C)
Br	Pyridine			28 ± 3 (−30°C)
Cl	Dimethylformamide			3.0 ± 0.5(−30°C)
Br	Dimethylformamide			3.1 ± 0.3(−30°C)
Cl	Dimethylsulfoxide			2.3 ± 0.4(−10°C)
Br	Dimethylsulfoxide			3.1 ± 0.5(−10°C)
Cl	Hexamethylphosphoramide			231 ± 9 (−30°C)
Br	Hexamethylphosphoramide			232 ± 9 (−30°C)

[a] No temperature specified.

where $\delta_0 = {}^{119}Sn$ shift for uncomplexed R_3SnX, $\delta_c = {}^{119}Sn$ shift for pure $R_3SnX \cdot D$ complex, α = degree of complexation.

For an initial mole fraction, C, of R_3SnX, the equilibrium constant in mole fraction terms is given by eqn. (5), which was solved by a fitting procedure yielding the values in Table 2.

$$K = \delta_0(\delta_c - C\delta_0)/[\delta_0^2(1 - C) + C\delta_0^2 - \delta_0\delta_c] \quad (5)$$

The fact that temperatures were not specified in one report and differed in many cases limits the utility of the data. It is observed that the equilibrium constants for $(CH_3)_3SnCl$ and $(CH_3)_3SnBr$ with the same donor are usually indistinguishable given the error limits of the data. Also, the strong donors hexamethylphosphoramide and pyridine exhibit the largest K values as expected.

Another determination of the ^{119}Sn chemical shifts of $(CH_3)_3SnCl$ adducts with hexamethylphosphoramide, dimethylsulfoxide, N,N-dimethylacetamide, acetone, acetonitrile and pyridine revealed that the δ values varied linearly with the calorimetrically-measured enthalpies of adduct formation for all the oxygen donors [28]. The deviation of the values of the acetonitrile and pyridine adducts from linearity was explained in terms of paramagnetic shielding differences.

The special utility of ^{119}Sn NMR for such studies is demonstrated by the observation [7] that ^1H chemical shifts of the CH_3 protons in the above compounds were essentially unchanged by complex formation. It is true, however, that the ^{119}Sn–^1H coupling constants are sensitive to adduct formation and their variation with concentration has been analyzed to determine association constants in the same general manner as was described for δ values above [7,27].

The foregoing investigations also showed that ^{119}Sn shifts are nearly concentration independent when $(CH_3)_3SnX$ compounds are dissolved in non-coordinating solvents such as chloroform, carbon tetrachloride and benzene. Such invariance suggests that these compounds neither form chemical complexes with such solvents nor self-associate in their solutions.

The behavior of divalent tin halides in solution has been investigated by ^{119}Sn NMR [29]. Since such compounds do not dissolve to a significant extent in non-coordinating solvents, it was not possible to investigate self-association phenomena, but they do dissolve in donor solvents and their ^{119}Sn shifts exhibit marked solvent, concentration and temperature dependence in most cases. At normal probe temperature, 35°C, the variation of δ with concentration was very close to linearity (Figs. 1–4) with the exception of SnI_2 for which significant ionization was indicated by conductivity measurements in dimethylformamide and hexamethylphosphoramide solutions. The slopes of the plots vary widely in both positive and negative ranges.

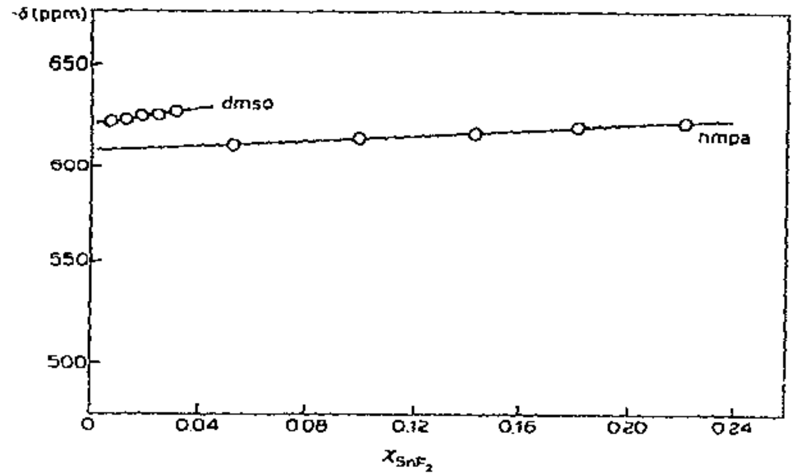


Fig. 1. Variation of $\delta^{119}Sn$ for SnF_2 in donor solvents [29].

Comparing infinite dilution shifts, the order of halogen dependence was generally: $\delta SnF_2 < \delta SnCl_2 < \delta SnBr_2 < \delta SnI_2$, with SnI_2 being uncertain because of the effect of ionization. An approximately linear relationship was found between the infinite dilution shifts for each SnX_2 compound and the dielectric constants of the solvents used but no correlation with other donor parameters was detected.

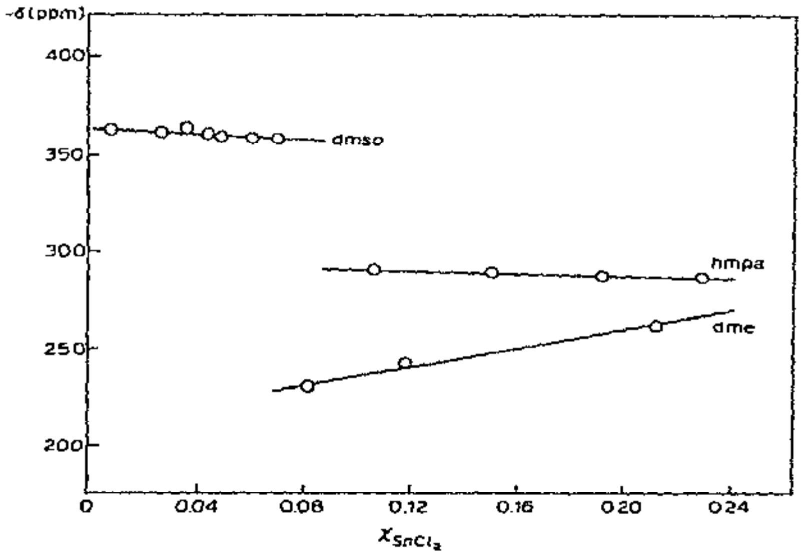


Fig. 2. Variation of $\delta^{119}Sn$ for $SnCl_2$ in donor solvents [29].

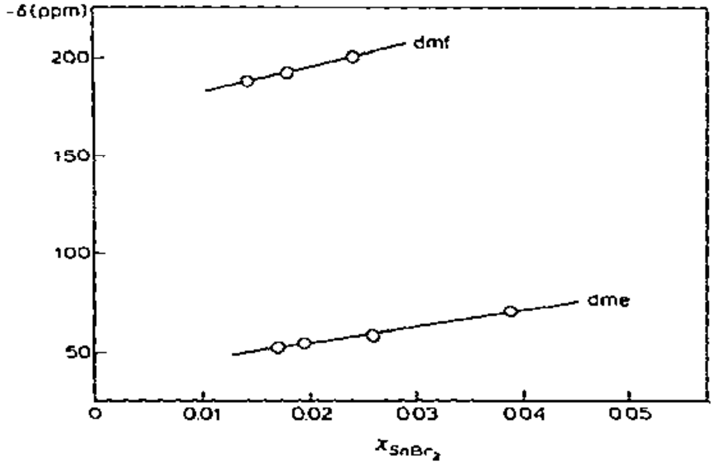


Fig. 3. Variation of $\delta^{119}Sn$ for $SnBr_2$ in donor solvents [29].

Attempts to calculate a consistent set of association constants for $SnX_2 \cdot D$ adducts by the methods described above were not fruitful, perhaps because of the formation of 1:2 adducts or solute self-association.

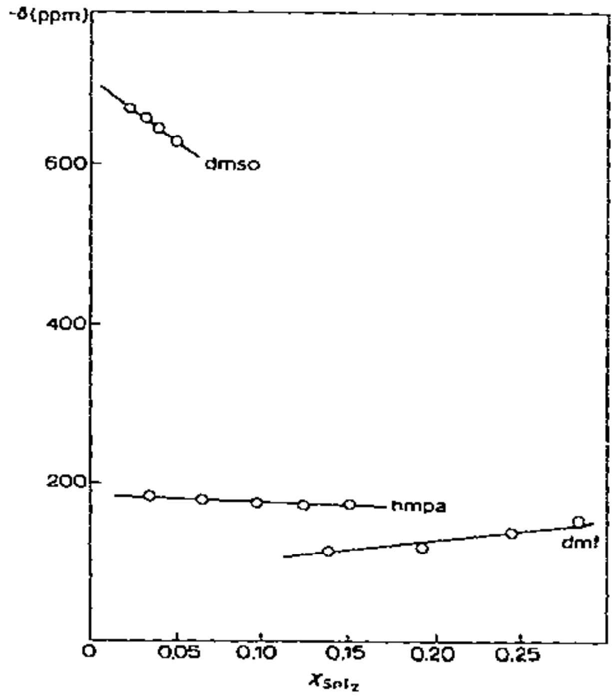
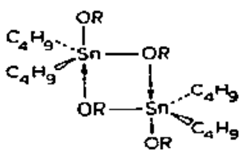


Fig. 4. Variation of $\delta^{119}Sn$ for SnI_2 in donor solvents [29].

(ii) Auto-association of tin compounds

Auto-association of tin compounds depends on both steric and electronic effects [30,31] and, as a result, tin NMR provides an effective means of studying such interactions. $\delta^{119}Sn$ is very sensitive to changes in the coordination number of tin which occur to varying degrees in auto-association depending on the number and type of substituents in the compounds. As mentioned previously, compounds such as $(CH_3)_3SnX$ (X = Cl, Br, I) exhibit essentially solvent and concentration independent $\delta^{119}Sn$ values in solvents of low polarity indicating that neither solvent coordination nor auto-association are occurring to a significant extent in these systems. Different behavior is seen for many tin–oxygen compounds. Alkyl tin(IV) alkoxides and phenoxides are among the more studied examples and serve to illustrate the application.

Molecular weight measurements and spectroscopic evidence showed that certain di-n-butyltindialkoxides, $(n\text{-}C_4H_9)_2Sn(OR)_2$ (R = CH_3, n-C_3H_7 and n-C_4H_9), are associated in the liquid state while the more sterically crowded $(n\text{-}C_4H_9)_2Sn(O\text{-}t\text{-}C_4H_9)_2$ is monomeric [30,31]. Table 3 shows the ^{119}Sn chemical shifts of the same series of compounds [32]. The associated compounds are believed to form dimers **I** increasing the coordination number of the tin to five with an accompanying low-frequency shift in δ of approximately 130 ppm.



(I)

TABLE 3

^{119}Sn chemical shifts (δ) of di-n-butyltin dialkoxides, $(n\text{-}C_4H_9)_2Sn(OR)_2$ [30]

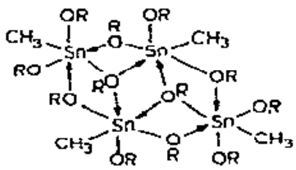
R	δ (ppm) [a,b]	State
CH_3	-165 ± 2	dimer
n-C_3H_7	-159 ± 5	dimer
n-C_4H_9	-161 ± 5	dimer
t-C_4H_9	-34 ± 5	monomer

[a] Negative δ values signify low frequency shifts from the reference $(CH_3)_4Sn$.

[b] Neat liquids.

Several other $R_2Sn(OR')_2$ (R and R' = alkyl) compounds exhibit chemical shifts suggesting auto-association in noncoordinating solvents and as neat liquids [33,34]. Making the assumption that the observed δ values of such species represent weighted averages of the limiting shifts of the monomer and dimer, the equilibrium constants for auto-association were calculated by a procedure similar to that described earlier for solute–solvent association. In addition, the variation of δ_{obs} with temperature was used to obtain estimates of the ΔH and ΔS values for the association process. Values of the former parameter ranged from -60 to -78 kJ mol^{-1} for the $R_2Sn(OR')_2$ compounds in the study and from -90 to -115 kJ mol^{-1} for the $RSn(OR')_3$ compounds.

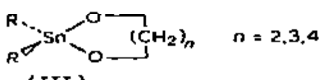
The ^{119}Sn δ values for two trialkoxy compounds, $CH_3Sn(OR)_3$ (R = C_2H_5, t-C_4H_9) were significantly low-frequency shifted, δ -434 and -452, respectively, compared to the compounds where dimers are formed (Table 3) and molecular weight measurements indicated that tetrameric species in a dynamic equilibrium with dimers and monomers were responsible. The structure suggested for the tetramer **II** involves six-coordinate tin accounting qualitatively for the difference in the ^{119}Sn shifts [33]. On the other hand, the ^{119}Sn shifts of the R_3SnOR' compounds studied suggest they have four-coordinate tin and are therefore monomeric in C_6H_6 solution.



(II)

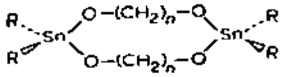
In using ^{119}Sn shifts to determine whether association is present, it should be recognized that it is only the large low-frequency shifts compared to the range of δ values for the monomer forms of the specific type of compound in question which indicate auto-association. Since δ values for monomeric $RSn(OR')_3$, $R_2Sn(OR')_2$, etc., vary considerably between formula types [33], comparisons should only be made with shifts of compounds of the same formula type [35,36].

Cyclic diorganotin(IV) alkoxides **III** are known to be associated in solvents

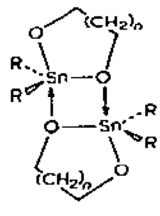


(III)

such as benzene at room temperature [31,37,38], but different structures have been suggested for the associated species **IV** and **V**. By comparison with values for analogous $R_2Sn(OR')_2$ compounds, structure **IV** would be ex-



(IV)



(V)

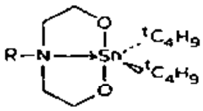
pected to exhibit δ near -30 ppm since only four-coordinate tin is involved whereas the expected shift for **V** with five-coordinate tin is near -160 ppm. The measured shifts [32] for several $R_2\overline{SnO(CH_2)_nO}$ ($R = n\text{-}C_4H_9$) compounds ($n = 2$, $\delta = -189 \pm 5$; $n = 3$, $\delta = -228 \pm 10$; $n = 4$, $\delta = -161$) confirm that **V** or some similar five-coordinate structure is present.

The observation [22] that the ^{119}Sn chemical shifts of $(CH_3)_nSn(SCH_3)_{4-n}$ ($n = 0$–4) are little affected by changes in the concentration of their solutions in noncoordinating solvents and the reports of similar behavior in other thioalkoxide compounds [32,39–41] indicate that the auto-association seen in some alkoxytin(IV) compounds is absent in their sulfur analogs. Factors contributing to the ^{119}Sn shielding in various Sn–S, Sn–Se, and Sn–Te compounds have been discussed [42,43].

Auto-association, as indicated by ^{119}Sn shifts, has also been detected in $(CH_3)_3SnOCHO$ [44], distannoxanes, $(XR_2Sn)_2O$ (X = F, Cl, Br; $R = C_4H_9$ [45,46]; X = NCS, $OCOCH_3$, $OSi(CH_3)_3$, $R = CH_3$, C_4H_9 [46,47]), $(C_4H_9)_3SnCN$ [11], tin carboxylates [44] and dithiocarbamates [11,48]. Evidence from ^{119}Sn coupling constants has been cited as supporting self-association of alkyl stannylamines through Sn–N–Sn bridges [49].

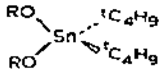
Direct complexation of $(CH_3)_3SnX$ (X = Cl, Br) acceptors with O, N and P donors has been investigated using ^{119}Sn NMR [9,21,39,50]. It has been pointed out [6] that ^{119}Sn NMR parameters of adducts such as $(CH_3)_3SnCl \cdot$ DMSO (DMSO = dimethylsulfoxide) can vary greatly owing to dissociation depending on the solvent used to dissolve the adduct.

The ^{119}Sn chemical shifts for certain stannatranes (*N*-alkyl-5,5-di-t-butyl-diptychoxazstannolidines) **VI** are nearly the same in CH_2Cl_2 as in $(CD_3)_2CO$ and they vary only slightly with temperature (-40 to $+32$°C) indicating that intermolecular association is minimal for these compounds [51]. Nevertheless, their δ values lie nearly 90 ppm towards lower frequency than those of analogous compounds [52] **VIII** differing primarily in the absence of the nitrogen donor functionality. This marked difference in shift demonstrates the presence of five-coordinate tin via an intramolecular N → Sn bond [51] characteristic of stannatranes [53,54]. Alkyl and phenyl stannatranes with the general structure **VIII** are reported to exist as surprisingly



R = H; δ-210
R = CH₃; δ-205

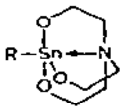
(VI)



R = CH₃; δ-115
R = ᵗC₄H₉; δ-123

(VII)

stable trimers associated through Sn-O → Sn links in $CHCl_3$ solution. At −40°C three separate ^{119}Sn resonances of equal intensity showing tin–tin



(VIII)

coupling are observed for the methylstannatrane suggesting a rather unsymmetrical trimeric structure [54].

Among the relatively few instances where tin is believed to exhibit seven-coordinate structures in solution are the compounds in Table 4 [55]. Although the observed shifts vary with the substituents on tin, there is a pronounced low-frequency shift between comparable six- and seven-coordinate compounds comparable to that seen between lower coordination numbers (see above). Thus, low-frequency shifts of δ appear to be a reasonably dependable criterion indicating increasing coordination number in organotin compounds. There are, however, occasional exceptions [21].

TABLE 4

^{119}Sn chemical shifts of selected six- and seven-coordinate tin compounds [55]

Compound	$\delta^{119}Sn$ [a]	CN	Conditions
$(CH_3)_2Sn(acac)_2$ [b]	−365	6	10% in $CHCl_3$
$(CH_3)_2Sn(pan)(acac)$ [c]	−463	7	30% in $CHCl_3$
$(CH_3)_2Sn(NCS)_2(DP)$ [d]	−363	6	20% in DMF
$(CH_3)_2Sn(NCS)_2(TP)$ [e]	−409	7	20% in DMF
$PhSn(dtc)_2Cl$ [f]	−361	6	5% in $CHCl_3$
$PhSn(dtc)_3$	−695	7	5% in $CHCl_3$

[a] Ref. $(CH_3)_4Sn$. [b] acac = acetylacetonate. [c] pan = 1-(2-pyridylazo)-2-naphtolate. [d] DP = 2,2′-dipyridyl. [e] TP = 2,2′,2″-terpyridyl. [f] dtc = *N,N′*-dimethyldithiocarbamate.

(iii) Tin–transition metal compounds

The rather complex bonding interactions between tin-based ligands and transition metals might be expected to produce unusual δ and J values in the ^{119}Sn resonance. For example, the trichlorostannate ion, $SnCl_3^-$, forms numerous complexes involving tin to transition metal bonds in which the ligand acts as a weak sigma donor but a strong pi acceptor [56]. Pi interactions may have very marked effects on the chemical shifts through the σ_p term insofar as they provide a low-energy electronic excited state and thereby reduce the magnitude of ΔE, the average excitation energy [57]. Unfortunately, the amount of ^{119}Sn data available is not sufficient at present to support a thorough analysis of the relationship between bonding parameters and NMR parameters.

In coordination compounds such as $(CH_3)_3SnC_6H_5 \cdot Cr(CO)_3$ which lack a direct tin–metal bond, complexation produces a change of ca. 30 ppm towards higher frequency in the ^{119}Sn shift of the organotin moiety [21]. The change is reduced to about +4 ppm when the tin is one carbon atom further removed, as in $(CH_3)_3SnCH_2C_6H_5 \cdot Cr(CO)_3$, but the shifts have not been rationalized.

The ^{119}Sn NMR spectra of a considerable number of complexes of the form $(CH_3)_3SnML_n$ have been obtained [9]. Examining the dependence of δ^{119}Sn on the electronegativity of X in $(CH_3)_3SnX$ compounds, it was determined that the δ value for $(CH_3)_3SnMn(CO)_5$ (i.e. X = $Mn(CO)_5$) departed substantially (toward positive δ) from the approximately linear relationship found between those variables in non-transition metal compounds [9,21], in which more positive δ values are associated with more electronegative substituents. On the other hand, the tin-methyl proton coupling constants, $^2J_{^{119}Sn-^1H}$, range from 24 to 53 Hz which is somewhat smaller than most ^2J values reported for other $(CH_3)_3SnR$ compounds [3]. A large value of $^2J_{^{119}Sn-^1H}$ in such compounds is usually associated with more electronegative X groups which, according to Bent [58], divert s character into the orbitals used by tin to bond to the methyl groups increasing $|\psi^2 s(O)|$. Thus, chemical shifts and coupling constants give opposing indications concerning the electronic character of ML_n suggesting that more than a simple inductive effect is operative, probably in the nature of a tin–transition metal d_π–d_π interaction [57].

Calculations of the σ_d chemical shift term for the Mn and Re compounds predicted a low-frequency shift of δ about 143 ppm between the compounds, in reasonable agreement with the difference in the observed values (Table 5). The same type of calculations for other complexes were in poor agreement, however, so the σ_d term alone apparently cannot account for such variations in the chemical shifts.

TABLE 5

^{119}Sn NMR chemical shifts and coupling constants for selected $(CH_3)_3SnML_n$ compounds [57]

Compound	$\delta^{119}Sn$ (ppm)	$^2J(^{119}Sn-^1H)$ (Hz)	Conditions
$(CH_3)_3SnMn(CO)_5$	$+63\pm1$	48.5	C_6H_6 soln.
$(CH_3)_3SnRe(CO)_5$	-89 ± 1	47.0	saturated C_6H_6 soln.
$[(CH_3)_3Sn)]_2Fe(CO)_4$	$+79\pm1$	49.5	C_6H_6 soln.
$(CH_3)_3SnCo(CO)_4$	$+151\pm0.2$	52.8	C_6H_6 soln.
$(CH_3)_3SnCr(CO)_3CP$ [a]	$+161\pm0.5$	48.1	C_6H_6 soln.
$(CH_3)_3SnMo(CO)_3CP$	$+121\pm0.5$	48.3	C_6H_6 soln.
$(CH_3)_3SnW(CO)_3CP$	$+42\pm0.5$	48.5	C_6H_6 soln.

[a] $CP=h^5$-C_5H_5.

The Cr, Mo and W complexes in Table 5 exhibit nearly identical $^2J_{^{119}Sn-^1H}$ values but the chemical shifts move considerably toward lower frequency with each step lower in the periodic table. The nearly constant coupling constants argue against significant changes in the electron density at tin in the series, so the shift variation is ascribed primarily to changes in the paramagnetic term [57].

A convincing analysis of the trends in NMR parameters of compounds with tin–transition metal bonds will probably not be forthcoming until more data are in hand. It will be particularly important to correlate ^{119}Sn NMR data (eventually of compounds in the solid state) with ^{119}Sn Mössbauer and NQR results in order to remove ambiguities as fully as possible.

Another type of complex with tin–transition metal bonds is those with stannylene (SnX_2 or SnR_2) ligands [59–61]. One report of ^{119}Sn NMR spectra of base-stabilized complexes has appeared [62] from which selected data are shown in Table 6. Complexes of the form $D \cdot SnX_2 \cdot ML_n$ (where D represents a donor molecule such as THF or R_3P and L is carbon monoxide) contain four-coordinate tin, as was the case with the R_3SnML_n complexes described earlier (Table 5). These exhibit high frequency δ values comparable to those in Table 5 when dissolved in noncoordinating solvents but when dissolved in the presence of THF they show a pronounced low-frequency shift ($>$ 140 ppm) in δ indicative of further THF coordination to Sn making it five-coordinate.

The coordination shifts, $\Delta\delta$ (the difference between δ complex and δ ligand), vary widely depending upon the nature of the donor, the halogen and particularly on the transition metal [62].

TABLE 6

^{119}Sn NMR chemical shifts of selected halogenostannylene complexes [62]

Complex	Solvent	$\delta^{119}Sn$ (ppm)	$\Delta\delta$ [a]
$SnCl_2 \cdot (THF)_x$	THF/C_6D_6	−238.0	
$SnBr_2 \cdot (THF)_x$	THF/C_6D_6	−70.7	
$(t\text{-}C_4H_9)_3PH^+ SnCl_3^-$	CH_2Cl_2/C_6D_6	−30.0	
$(t\text{-}C_4H_9)_3P \cdot SnCl_2$	$CH_3C_6H_5/C_6D_6$	21.0	
$THF \cdot SnCl_2 \cdot Cr(CO)_5$	C_6D_6	+193.0	
$(THF)_x \cdot SnCl_2 \cdot Cr(CO)_5$	THF/C_6D_6	+55.0	+293
$(C_6H_5)_3P \cdot SnCl_2 \cdot Cr(CO)_5$	C_6D_6	+238.0	
$THF \cdot SnCl_2 \cdot W(CO)_5$	C_6D_6	−54.6	
$(THF)_x \cdot SnCl_2 \cdot W(CO)_5$	THF/C_6D_6	−209.4	+19
$(C_6H_5)_3P \cdot SnCl_2 \cdot W(CO_5)$	C_6D_6	−15.1	
$THF \cdot SnBr_2 \cdot W(CO_5)$	C_6D_6	−2.6	
$(THF)_x \cdot SnBr_2 \cdot W(CO)_5$	THF/C_6D_6	−217.6	−147

[a] $\Delta\delta = \delta$ complex $- \delta$ ligand.

(iv) Tin cluster anions

Among the most innovative uses of ^{119}Sn is its application to the detection and structural elucidation of 'naked metal clusters' [63], such as Sn_9^{4-}, $(Sn_{9-x}Pb_x)^{4-}$, Sn_4^{2-}, $(Sn_{9-x}Ge_x)^{4-}$ ($x = 0$–9), and $TlSn_8^{5-}$ [64]. Such species are formed in solution from alloys between alkali metals and main-group metals or electrochemically [65]; in the former method agents such as ethylenediamine or a 2,2,2-cryptand coordinate with the alkali cation stabilizing the cluster in solution. Both the ^{119}Sn chemical shifts and coupling

TABLE 7

^{119}Sn NMR parameters [a] of selected 'naked metal cluster' polyanions [63–65]

Cluster anion	$\delta^{119}Sn$ (ppm)	$J^{119}Sn-^{117}Sn$
Sn_4^{2-}	−1895	1224
Sn_9^{4-}	−1230	254
$(SnGe_8)^{4-}$	−1227	
$(Sn_8Tl)^{5-}$	−1167	410 [b]
$(SnTe_4)^{4-}$	−1828	— [c]

[a] All spectra in ethylenediamine solution.
[b] $J(^{119}Sn-^{205,203}Tl) = 800$ Hz, solvent and temperature dependent.
[c] $J(^{119}Sn-^{125}Te) = 2804$ Hz.

TABLE 8

Multiplet patterns for $^{119}Sn-^{117}Sn$ coupling in $(Sn)_x^{4-}$ cluster anions [63]

X	Line [a]				
	1	2	3	4	5
8	0.034	0.276	1.000	0.276	0.034
9	0.044	0.311	1.000	0.311	0.044
10	0.056	0.345	1.000	0.345	0.056
Observed	0.046	0.312	1.000	0.312	0.046

[a] Relative intensities of five most intense lines in calculated multiplets assuming abundances of ^{117}Sn and ^{119}Sn are 7.61 and 8.58% respectively.

constants (Table 7) played important roles in the characterization of the solution species. In the homonuclear cluster Sn_9^{4-}, $^{119}Sn-^{117}Sn$ satellites were observed as quintets with intensities 0.046:0.312:1.000:0.312:0.046, and with a spacing between members of 127 Hz. The investigators calculated the intensities and multiplicities expected for clusters of various sizes asuming the natural abundances of the tin isotopes and the intensities of the five most intense lines are shown in Table 8. A match is seen for the Sn_9 cluster formulation suggesting that Sn_9^{4-}, the structure of which has been determined to be a capped C_{4v} antiprism in the solid state [66], is responsible for the resonance.

The observation of a single ^{119}Sn resonance for Sn_9^{4-} indicates that the solution structure of the cluster is neither the C_{4v} monocapped antiprism nor the D_{3h} tricapped trigonal prism thought to be close to it in energy [66], but rather a fluxional structure with averaged Sn environments. Fluxionality receives further support from the small magnitude of the $^{119}Sn-^{117}Sn$ coupling constants (believed to be weighted averages of one bond and two bond couplings [63]) compared with other one bond Sn–Sn couplings which usually exceed 1000 Hz [6] and compared with $^1J_{^{119}Sn-^{117}Sn}$ for Sn_4^{2-} (Table 7) which is probably not fluxional.

Finally, an approximate relationship between the average charge per tin atom and the ^{119}Sn chemical shift has been successfully used to estimate the formulas of $Na_xSn_y^{x-}$ and related clusters compounds for which spectra were observed [64]. The relationship was found not to apply to $Sn_{9-x}Ge_x^{n-}$ cluster anions, however.

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