

A Mössbauer Study of the Adducts of Trimethyltin Chloride with Lewis Bases

James C. Hill,^{1a,b} Russell S. Drago,^{1b} and Rolfe H. Herber^{1c}

Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801, and R. G. Wright Laboratory, Rutgers University, New Brunswick, New Jersey 08903. Received June 19, 1968

Abstract: Mössbauer parameters for trimethyltin chloride and its 1 : 1 adducts with Lewis bases have been obtained. The isomer shifts for four of the six compounds studied are essentially constant (~ 1.44 mm/sec). This indicates similarity of the effective nuclear charge on the tin nucleus in the adducts studied even though $J_{\text{Sn}^{119}\text{-C-H}}$ changes significantly. The isomer shifts are inconsistent with the application of the model of Grant and Litchman to explain these coupling constant changes on the basis of changes in the tin effective nuclear charge. An increase in the quadrupole splittings occurs when trimethyltin chloride is complexed. The values for the adducts studied are essentially the same though the enthalpies of adduct formation vary from -6.5 to -10.1 kcal mole⁻¹. An alternative model to that previously offered involving π bonding is proposed to explain the quadrupole splitting in these tin compounds. The new model is consistent with the description of the bonding previously offered to explain changes in $J_{\text{Sn}^{119}\text{-C-H}}$ and with the results from other studies indicating the unimportance of π bonding in these systems.

There has been considerable interest in the chemical and physical properties of trimethyltin chloride and the 1 : 1 adducts it forms with Lewis bases. Trimethyltin chloride has a C_{3v} (local symmetry) structure in the gas phase² with nearly tetrahedral angles. The 1 : 1 adducts appear to have approximately a trigonal-bipyramidal structure both in solution^{3,4} and also on the basis of X-ray data for the pyridine adduct⁵ in the solid state. The base and chlorine are *trans* to each other along the axial bond, and the methyl groups are in a trigonal array.^{3,4} Bolles and Drago⁶ and Matsubayashi, *et al.*,⁴ have proposed that the fraction of "s" character that tin employs in bonding to the methyl groups is a function of the base strength. For strong donors approximately sp^2 hybrids are employed and the C-Sn-Cl angle is close to 90° , while for weak bases the hybridization is closer to sp^3 and the angle close to 109° . Matwiyoff and Drago³ proposed that in the adducts of strong donors the tin uses p_z or ($d_{z^2} + p_z$) orbitals in the axial bonds to the base and chlorine.

A linear relationship between the enthalpy of adduct formation and the $\text{Sn}^{119}\text{-C-H}$ coupling constant, $J_{\text{Sn}^{119}\text{-C-H}}$, for a series of adducts of trimethyltin chloride has been found.⁶ When the line was extrapolated to zero enthalpy, the $J_{\text{Sn}^{119}\text{-CH}}$ coupling constant for free trimethyltin chloride was obtained. This relationship was explained by the following model. It has been proposed that $J_{\text{Sn}^{119}\text{-C-H}}$ is related to the fraction of "s" character in the tin-carbon bond.^{6,7} This assumes the Fermi term makes the dominant contribution to $J_{\text{Sn}^{119}\text{-C-H}}$ and that

the amount of tin "s" orbital used in the bonding in the adducts and trimethyltin chloride is constant. The extrapolated value at zero enthalpy supports these assumptions. The extent of rehybridization and distortion of the methyl groups toward planarity is related to the magnitude of the interaction with the donor as manifested by the enthalpy of adduct formation, *i.e.*, rehybridization manifested by $J_{\text{Sn}^{119}\text{-C-H}}$ changes in a linear fashion with donor strength manifested by $-\Delta H^\circ$.

Grant and Litchman have proposed⁸ a model for $J_{\text{C}^{13}\text{-H}}$ based on changes in the effective nuclear charge of carbon as opposed to changes in "s" character. Although they have not suggested application of this model to our system involving $J_{\text{Sn}^{119}\text{-C-H}}$, we must consider such a contingency, for if there are changes in the effective nuclear charge of the tin atom, our explanation of $J_{\text{Sn}^{119}\text{-C-H}}$ would be incorrect. The model of Grant and Litchman would predict an increase in $J_{\text{Sn}^{119}\text{-C-H}}$ with an increase in effective nuclear charge on the tin atom toward the 5s electrons. This is contradicted by the fact that with increasing donor strength, which intuitively should lead to a smaller formal charge on the tin atom, the coupling constant increases. However, there could be changes in the Sn-CH₃ and Sn-Cl bond that effectively increase the charge on the tin atom when complexed.⁶

In order to observe changes in the effective nuclear charge on the tin atom as reflected in changes in the s electron density at the tin nucleus, we decided to obtain the Sn^{119} Mössbauer spectra for trimethyltin chloride and its adducts. The isomer shift obtained from the Mössbauer spectra can be related to the changes in s electron density at the tin nucleus.⁹ We also obtained the quadrupole splitting for the compounds studied. This parameter is of interest because it is a measure of the deviation from cubic symmetry of the p and d electron distribution in the bonds to the tin atom.⁹ In this article

(1) (a) Abstracted in part from the Ph.D. Thesis of J. C. Hill, University of Illinois, Urbana, Ill., 1968; National Aeronautic and Space Administration Traineeship in Chemistry, 1965-1968; (b) University of Illinois; (c) Rutgers University.

(2) H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

(3) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964). For other examples, see R. C. Poller, *J. Organometal. Chem.*, **3**, 321 (1965), and references therein.

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(6) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 5730 (1966).

(7) J. R. Holmes and H. D. Kaesz, *ibid.*, **83**, 3903 (1961).

(8) D. M. Grant and W. M. Litchman, *ibid.*, **87**, 3994 (1965).

(9) For a detailed discussion of this point, see V. I. Gol'danskii, *et al.*, "Chemical Applications of Mossbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapters 1 and 6, and references therein.

Table I. Mössbauer Parameters, $J_{\text{Sn}^{119}-\text{CH}}$, and Enthalpy of Adduct Formation

Absorber	Isomer shift, mm sec ⁻¹	Quadrupole splitting, mm sec ⁻¹	$J_{\text{Sn}^{119}-\text{CH}}$, cps	$-\Delta H^\circ$, kcal/mole
(CH ₃) ₃ SnCl	1.43 ± 0.03	3.32 ± 0.03		
(CH ₃) ₃ SnCl ^a	1.42 ± 0.03	3.36 ± 0.03	58.1	
(CH ₃) ₃ SnCl · HMPA	1.44 ± 0.03	3.52 ± 0.03	72.0	10.1 ^b
(CH ₃) ₃ SnCl · DMA	1.50 ± 0.04	3.69 ± 0.04	69.2	7.9 ^b
(CH ₃) ₃ SnCl · PMPO	1.44 ± 0.03	3.45 ± 0.03	68.9	7.8
(CH ₃) ₃ SnCl · TPPO	1.45 ± 0.03	3.49 ± 0.03	68.1	7.2
(CH ₃) ₃ SnCl · pyridine	1.53 ± 0.05	3.52 ± 0.05	67.4 ^c	6.5 ^b

^a 0.8 M benzene solution. ^b T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3921 (1966). ^c Reference 6.

we propose an alternative interpretation of the quadrupole splitting for tin compounds which is in contrast with one previously offered¹⁰⁻¹³ but which is consistent with our models for the bonding in these compounds.

Experimental Section

A. Purification of Chemicals. Mallinckrodt Analytical reagent carbon tetrachloride and Baker and Adams dichloromethane were dried over Linde 4A molecular sieves and used without further purification. Eastman White Label N,N-dimethylacetamide (DMA), Fischer Certified reagent dimethyl sulfoxide (DMSO), benzene, and hexamethylphosphoramide (HMPA), and Baker Analyzed pyridine (py) were stored over fresh barium oxide for 2 days, refluxed at reduced pressure over barium oxide for 4 hr, and fractionally distilled under reduced pressure through a 30-in. Vigreux column. The middle fractions were collected.

Metal and Thermit Chemicals trimethyltin chloride was sublimed under vacuum three times. Aldrich Chemicals triphenylphosphine oxide (TPPO) was washed with water and cold ether and recrystallized from carbon tetrachloride. Reilly Tar and Chemical *p*-methylpyridine N-oxide (PMPO) was recrystallized from absolute ethanol and sublimed, under vacuum, three times.

B. Preparation of Compounds. The DMA, HMPA, and pyridine complexes were prepared by the addition of excess base to trimethyltin chloride, slowly cooled in an ice-water bath, and allowed to stand until crystals formed. The crystals were transferred to a filter and washed five times with 10-ml portions of dry cyclohexane which had been cooled in an ice-water bath. The crystals were dried under vacuum at room temperature. The TPPO and PMPO complexes were prepared by adding excess trimethyltin chloride to the base in methylene chloride and removing the solvent and excess trimethyltin chloride under vacuum. *Anal.* Calcd for C₉H₂₇N₃-POSnCl: C, 28.56; H, 7.19; N, 11.10. Found: C, 28.20; H, 7.34; N, 10.99. Calcd for C₈H₄NSnCl: C, 34.52; H, 5.06; N, 5.04. Found: C, 34.72; H, 4.98; N, 4.87. Calcd for C₇H₁₈-ONSnCl: C, 29.35; H, 6.33; N, 4.89. Found: C, 29.51; H, 6.19; N, 4.68. Calcd for C₂₁H₂₄OPSnCl: C, 52.82; H, 5.06. Found: C, 52.90; H, 5.23. Calcd for C₈H₁₄NOSnCl: C, 32.65; H, 4.79; N, 4.76. Found: C, 32.85; H, 5.01; N, 4.74.

C. Mössbauer Measurements. The samples were sealed under nitrogen in glass tubes prior to shipment for the subsequent Mössbauer measurements. All samples were mounted in a drybox and immediately immersed in liquid nitrogen. All measurements were carried out with the absorber at a temperature of 80-100°K.

D. Nuclear Magnetic Resonance Measurements. The $J_{\text{Sn}^{119}-\text{C}-\text{H}}$ coupling constants were determined from proton spectra obtained on the Jeolco C-60H spectrometer equipped with Jeolco low-temperature apparatus. All runs were carried out in the one sample nmr control, fixed-field/frequency sweep mode, locking on the methylene proton resonance of CH₂Cl₂. Temperatures in the probe were measured to ±0.5°, with a YSI Model 42SL Tele-Thermometer.

The spectra were found to be reproducible to better than ±0.2 cps. The $J_{\text{Sn}^{119}-\text{C}-\text{H}}$ coupling constant was found by measuring

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(12) N. N. Greenwood and J. N. Ruddick, *ibid.*, 1679 (1967).

(13) N. N. Greenwood, P. G. Perkins, and D. H. Wall, *Discussions Faraday Soc.*, **1**, 90 (1968).

Table II. $J_{\text{Sn}^{119}-\text{CH}}$ Coupling Constants

Compound	Solvent	$J_{\text{Sn}^{119}-\text{CH}}$, cps	Temp, °C
(CH ₃) ₃ SnCl · PMPO	CH ₂ Cl ₂	68.9	-53
(CH ₃) ₃ SnCl · TPPO	CH ₂ Cl ₂	68.1	-60
(CH ₃) ₃ SnCl · DMSO	CH ₂ Cl ₂	69.6	-75
(CH ₃) ₃ SnCl · DMSO	DMSO	69.6 (69.2) ^a	27
(CH ₃) ₃ SnCl · DMA	CH ₂ Cl ₂	69.1	-72
(CH ₃) ₃ SnCl · DMA	DMA	69.2 (68.8) ^a	27
(CH ₃) ₃ SnCl · HMPA	CH ₂ Cl ₂	72.1	-73
(CH ₃) ₃ SnCl · HMPA	HMPA	72.0 (71.6) ^a	27
(CH ₃) ₃ SnCl	CH ₂ Cl ₂	59.1	27
(CH ₃) ₃ SnCl	CCl ₄	58.1 (57.6) ^a	27

^a Value in parentheses is $J_{\text{Sn}^{119}-\text{CH}}$ reported by Bolles and Drago.⁶

the difference in cycles per second of the Sn¹¹⁹-C-H split peaks with a frequency counter.

E. Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer 521 spectrometer. Solution spectra were obtained with matched 0.1-mm CsBr cells and the mull spectrum with CsBr plates.

F. Preparation of Solution and Complexes. All solutions and complexes were prepared in a nitrogen-filled glove bag or in a dry-box. Solutions were prepared using standardized volumetric flasks dried at 120° for several hours and flushed with dry nitrogen before use.

Results

The isomer shift, quadrupole splitting, enthalpy of adduct formation, and $J_{\text{Sn}^{119}-\text{C}-\text{H}}$ coupling constant for trimethyltin chloride and its adducts are summarized in Table I. The isomer shifts are reported relative to SnO₂. In order to check the effect a solvent would have upon the Mössbauer parameters, a frozen solution of trimethyltin chloride in benzene was prepared and the result is included in Table I. The error limits for the isomer shift and quadrupole splitting are also reported. The larger error associated with the DMA and pyridine adducts is partly due to the smaller signal-to-noise (nonresonant background) ratio for these samples. Line positions were calculated using the method-of-chords analysis previously reported.¹⁴

The $J_{\text{Sn}^{119}-\text{C}-\text{H}}$ values for the TPPO and PMPO adducts were obtained by lowering the temperature of a series of solutions of trimethyltin chloride with 5-10 M excess base in CH₂Cl₂ until a constant and identical $J_{\text{Sn}^{119}-\text{C}-\text{H}}$ was obtained at two different temperatures which were at least 10° apart. The final $J_{\text{Sn}^{119}-\text{C}-\text{H}}$ coupling constants measured for these adducts are reported in Table II with the lowest temperature observed.

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Table III. The Sn-C Asymmetric and Symmetric Stretching Frequencies and Their Relative Absorbances for Trimethyltin Chloride and the Pyridine Adduct

Compound	ν_{sym} , cm ⁻¹	ν_{asym} , cm ⁻¹	$A_{\text{sym}}/A_{\text{asym}}$
(CH ₃) ₃ SnCl (Nujol)	517	545	0.24
(CH ₃) ₃ SnCl (CCl ₄ soln)	517	545	0.23
(CH ₃) ₃ SnCl (C ₆ H ₆ soln)	518	546	0.22
(CH ₃) ₃ SnCl · pyridine (Nujol)	512	544	0.07

The $J_{\text{Sn}^{119}\text{-C-H}}$ values used in obtaining the linear plot⁶ of $-\Delta H^\circ$ vs. $J_{\text{Sn}^{119}\text{-C-H}}$ were obtained with trimethyltin chloride in neat base using a Varian A-60 while those reported here were measured in CH₂Cl₂ as solvent.⁶ As can be seen in Table II, the adduct values are insensitive to the solvent employed, but CH₂Cl₂ apparently interacts with trimethyltin chloride.

The $J_{\text{Sn}^{119}\text{-C-H}}$ values for free trimethyltin chloride in CCl₄ and adducts in neat base were found to be about 0.4 cps higher than those previously reported from this laboratory.⁶ The higher values are in agreement with the results of Matsubayashi, *et al.*⁴ A constant error was evidently present in the earlier work and +0.4 cps should be added to the $J_{\text{Sn}^{119}\text{-C-H}}$ values used to construct⁶ the $-\Delta H^\circ$ vs. $J_{\text{Sn}^{119}\text{-C-H}}$ plot. The ΔH° values for the TPPO and PMPO adducts were obtained from the corrected plot. The $J_{\text{Sn}^{119}\text{-C-H}}$ coupling constants for the DMSO, HMPA, and DMA adducts in CH₂Cl₂ were obtained in the same manner as for the TPPO and PMPO adducts and are included in Table II. A constant $J_{\text{Sn}^{119}\text{-C-H}}$ was not obtained for the pyridine adduct.

In Table III the Sn-C asymmetric and symmetric stretching frequencies with their relative absorbance values at maximum intensity are reported for the Nujol mull spectra of trimethyltin chloride and its pyridine adduct, and for the CCl₄ and C₆H₆ solution of trimethyltin chloride.

Discussion

Isomer Shift. Our first concern is with ascertaining the importance of formal charge on the metal atom. The Mössbauer Sn¹¹⁹ isomer shift is proportional to $(\Delta R/R)(|\Psi(0)|_A^2 - |\Psi(0)|_S^2)$, where $|\Psi(0)|_A^2$ is the electron density at the absorbing Mössbauer nucleus and $|\Psi(0)|_S^2$ the electron density at the source nucleus, and ΔR is the difference in the nuclear radii of the Sn¹¹⁹ nucleus in the excited state (R_{ex}) and the ground state (R_{gd}), $R_{\text{ex}} - R_{\text{gd}}$. Considerable disagreement has existed concerning the sign of ΔR . Earlier workers concluded ΔR to be positive on the basis of changes in electronegativity and hybridization with isomer shift.⁹ Goldanskii and Makarov^{15,16} concluded on the basis of calculations on SnX₄ (X = Cl, Br, I) that ΔR was negative. A pressure study by Panyushkin and Voronov¹⁷ on β -tin was interpreted on the basis that the isomer shift decreased with increas-

ing pressure in agreement with $\Delta R > 0$. From detailed self-consistent field calculation, Lees and Flinn¹⁸ have concluded that $\Delta R > 0$. Finally Bocquet, *et al.*,¹⁹ studied the internal electron conversion in SnO₂ and white tin and concluded $\Delta R > 0$, and this experiment is presently considered to be definitive with respect to the sign of this parameter. The sign of ΔR is essential to some of our arguments but not to the evaluation of the factors contributing to $J_{\text{Sn}^{119}\text{-CH}_3}$.

In considering the isomer shift data relative to the model for coupling constants proposed by Grant and Litchman,⁸ it is necessary to establish relationships between the effective nuclear charge on the tin nucleus, the Mössbauer isomer shifts, and $J_{\text{Sn}^{119}\text{-CH}_3}$ coupling constants. Their model yields the equation⁸

$$J(k) = \frac{\Delta_{\text{ref}}}{\Delta_k} \left(\frac{N_k}{N_{\text{ref}}} \right)^2 \left(\frac{\alpha_k}{\alpha_{\text{ref}}} \right)^2 \left(\frac{Z_k}{Z_{\text{ref}}} \right)^3 J(\text{ref}) \quad (1)$$

where $J(k)$ is the Sn¹¹⁹-CH₃ coupling constant in the k th Sn-C-H bond, $J(\text{ref})$ is the Sn¹¹⁹-CH₃ coupling constant of a reference compound, Δ is the average excitation energy, N is the bond normalization constant defined in another paper by Karplus and Grant,²⁰ α^2 is directly proportional to the fractional "s" character, and Z represents the effective nuclear charge appearing in the tin 5s orbital of the form $(Z_k/a_0)^{3/2}(A + BZr + CZ^2r^2 + DZ^3r^3 + EZ^4r^4)e^{-Zr/5}$. The ratios $\Delta_{\text{ref}}/\Delta_k$ and $(\alpha_k/\alpha_{\text{ref}})^2$ were assumed to be unity in their calculations.⁸ From eq 1, as the effective nuclear charge on the tin nucleus toward the 5s electrons increases, the Sn¹¹⁹-CH₃ coupling constant will increase. An increase in the effective nuclear charge will result in a radial contraction of the 5s orbital and a corresponding increase in $|\Psi(0)|^2$.

As both Z^3 and the isomer shift are proportional to $|\Psi(0)|^2$, we can substitute the isomer shift, IS, for Z^3 into eq 1 and obtain

$$J(k) = \frac{\Delta_{\text{ref}}}{\Delta_k} \left(\frac{N_k}{N_{\text{ref}}} \right)^2 \left(\frac{\alpha_k}{\alpha_{\text{ref}}} \right)^2 \left(\frac{\text{IS}_k}{\text{IS}_{\text{ref}}} \right) J(\text{ref}) \quad (2)$$

$J_{\text{Sn}^{119}\text{-C-H}}$ for tetramethyltin is 54.0 cps⁵ and its isomer shift is 1.22 mm/sec¹⁰ and $J_{\text{Sn}^{119}\text{-C-H}}$ for trimethyltin chloride is 58.2 cps and its isomer shift is 1.43 mm/sec. This requires $\Delta R > 0$, if the above assumptions are correct.

The values of the isomer shifts for the adducts and trimethyltin chloride (Table I) are essentially the same. The slightly larger isomer shifts values for the pyridine and DMA adducts are believed due to experimental uncertainties rather than changes in $|\Psi(0)|^2$. If the increases in the isomer shifts for the pyridine and DMA adducts are real, then the effective nuclear charges on the tin nucleus for the DMA and pyridine adducts must be greater than on the tin nucleus of trimethyltin chloride and its HMPA, TPPO, and PMPO adducts. On this basis of nuclear charge as manifested by the isomer shift, the predicted order of $J_{\text{Sn}^{119}\text{-CH}_3}$ for the adduct is py > DMA > HMPA ~

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(15) V. I. Gol'danskii and E. F. Makarov, *Zh. Eksperim. i Teor. Fiz.*, **2**, 48 (1965).

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(17) V. N. Panyushkin and F. F. Voronov, *J. Exptl. Theoret. Phys. Letters, Acad. Sci. USSR*, **2**, 153 (1965); see R. H. Herber, *Ann. Rev. Phys. Chem.*, **17**, 261 (1966).

PMPO ~ TPPO. This is inconsistent with the experimentally observed trend in Table I. Obviously if the isomer shifts in these compounds are the same, the model for $J_{\text{Sn}^{119}\text{-C-H}}$ based on changes in Z is also incorrect. Consequently, these studies support the interpretation of changes in $J_{\text{Sn}^{119}\text{-C-H}}$ in terms of a model based on changes in "s" character in the orbitals employed by tin to bond the CH_3 groups with any changes in Z being of insignificant consequence in affecting $J_{\text{Sn}^{119}\text{-C-H}}$.

Quadrupole Splitting. The Sn^{119} quadrupole splitting (ΔE_Q) is given by the equation

$$\Delta E_Q = \frac{e^2 q Q}{2} \left(1 + \frac{\eta^2}{3} \right)^{1/2} \quad (3)$$

where q is the negative of the electrostatic field gradient at the nucleus, η is the asymmetry parameter, and Q is the Sn^{119} nuclear quadrupole moment. The compounds studied have a local C_3 symmetry axis and η becomes zero. Since eQ is a constant, the magnitude of the quadrupole splitting is proportional to q .

Studies of the quadrupole splittings in four- and six-coordinate organotin(IV) compounds by Gibb and Greenwood¹¹ and Greenwood and Ruddick¹² were interpreted to indicate that electronic field gradients as evidenced by the quadrupole splitting will only be observed when there exists an imbalance in the presence of π interactions due to the presence of nonbonded electron pairs on the ligand which can form a π bond with the empty tin 5d or 6p orbitals. If all the ligands form π bonds with the tin atom, then no quadrupole splitting is observed. Ligands which are all σ donors, even though they differ in electronegativity, are reported not to give rise to an asymmetric electric field gradient. The absence of quadrupole splitting in compounds of type $\text{R}_n\text{SnH}_{4-n}$ was used to support this model.¹⁰

It is clearly established that π bonding involving oxygen and tin is not extensive in $(\text{alkyl})_3\text{SnOC}_6\text{H}_5$.²¹ Similar conclusions indicating the absence of p-d π bonding are drawn from a nuclear magnetic resonance and infrared study of N^{15} -substituted anilines and trimethylstannylaniline.²² Consequently the proposals of Gibb and Greenwood¹¹ and Greenwood, *et al.*,^{12,13} which are largely based upon π -bonding interactions involving systems with oxygen and nitrogen donors are inconsistent with the above results. Instead the following model is proposed to account for the quadrupole splitting in both the compounds reported¹⁰⁻¹² and the adducts reported here.

First consider why $(\text{CH}_3)_{4-n}\text{SnH}_n$ compounds show no quadrupole splitting but $(\text{CH}_3)_3\text{SnCl}$ does. In the tetrahedral compounds the donor strengths of hydride or methide or alternatively the bond strengths of tin with groups such as butyl, methyl, and H are very similar. For example, in the series $(\text{CH}_3)_{4-n}\text{SnH}_n$ the isomer shift is essentially constant.¹⁰ In this near-tetrahedral geometry the p_x , p_y , and p_z orbitals are distributed almost equally in all four bonds, the electron population charge densities in these three p orbitals is similar, and ΔE_Q is too small to be detected. In $(\text{CH}_3)_3\text{SnCl}$ (defining the Sn-Cl bond as the Z axis), the isovalent hybridization concept²³ predicts

increased p character in the bond toward the electronegative chlorine. This is borne out by the change in $J_{\text{Sn}^{119}\text{-CH}}$.³ Since p_z character toward the electron-withdrawing chlorine group increases, the differences in charge densities in p_z , on the one hand, and p_x and p_y , on the other hand, are increased and ΔE_Q is now large enough to be resolved. This is to be contrasted with the conclusion of Greenwood, *et al.*, that the distortion of the tetrahedrally symmetric charge distribution about $(\text{CH}_3)_3\text{-SnCl}$ would arise from chlorine donating electron density to the empty 5p or 5d orbitals of tin.

In this context it should be noted that, at least for ligands such as the heavy halogens, electronegativity differences or similarities alone do not account for the magnitude of the isomer shift and quadrupole splitting parameters observed in the Mössbauer spectra. However, even in CH_3X compounds, the electronegativity of the halogens does not correlate with $J_{\text{C}^{13}\text{-H}}$,²⁴ indicating the absence of a relationship between electronegativity of the halides and the populations of the orbitals.

Consider the results in the six-coordinate tin compounds reported by Greenwood, *et al.*¹¹⁻¹³ When the six groups around the tin are comparable in donor strength, the adducts SnX_4L_2 or SnL_4X_2 are often found to be *cis*.²⁵ The three p orbitals will be nearly equally distributed over all six ligands approaching the six equivalent sp^3d^2 hybrids of the valence-bond description for a purely octahedral complex. Equivalence also results for the multicentered bond description invoking not as much "d" orbital contribution as in sp^3d^2 . At any rate, near equal charge densities result in the p_x , p_y , and p_z orbitals, and small or unresolvable splittings result. When two of the groups are very strong donors or not very electronegative, as the methyls in $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ ²¹ and $[(\text{CH}_3)_2\text{Sn}(\text{SCN})_2]_n$,²⁶ the *trans* isomer is expected. Now the s and p_z orbitals (C-Sn-C bond axis is defined as the z axis) become extensively involved in bonding to the methyls with the p_x and p_y becoming more extensively involved in bonding the oxygens. The differences in charge densities in p_z , on the one hand, and p_x and p_y , on the other, increases and a quadrupole splitting results. For those cases which are in between these two extremes, a knowledge of whether the isomer is *cis* or *trans* is essential to an understanding of the magnitude of ΔE_Q . These arguments account for the major differences in the values of ΔE_Q for the tin compounds reported in the literature and is also consistent with the results of point-charge calculations²⁷ which predicts that $\Delta E_Q(\text{trans})$ is approximately twice $\Delta E_Q(\text{cis})$.

In conclusion these arguments can be employed to rationalize all of the results on the compounds reported by Greenwood, *et al.*, without recourse to π bonding. It should be pointed out that in compounds where tin has a very high formal charge the empty "d" orbital energy could be lowered and π bonding could be important. At present there is no information bearing on this problem and our model should be used with caution on systems of this type should they be encountered.

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There are two observable trends in the quadrupole splittings for the compounds reported in this study: an increase when trimethyltin chloride is complexed, and essentially the same quadrupole splitting for the adducts. In interpreting the splitting in $(\text{CH}_3)_3\text{SnCl}$, the possibility of the formation of a five-coordinate species due to molecular association must be considered. Trimethyltin chloride is reported to be associated *via* chlorine bridges in the solid state, on the basis of ir evidence,²⁸ and reported to be monomeric in carbon tetrachloride.³ The relative absorbances of the Sn–C asymmetric and symmetric stretching modes (Table III) indicate that the strength of the interaction in the solid must be weak. Since local C_{3v} symmetry is present for both the nonassociated tetrahedral species and for the five-coordinate associated species, the asymmetric and symmetric stretching modes are allowed. However, if the strength of the Sn–Cl bridge bond were large, the C–Sn–Cl bond angle should approach 90° , the dipole moment associated with the symmetric stretching modes would become small, and a low intensity should result. The similar absorbance ratios for the Sn–C asymmetric and symmetric stretching modes for solid trimethyltin chloride and trimethyltin chloride in C_6H_6 and CCl_4 , when compared to the low absorbance ratio for the pyridine adduct, indicates a very

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weak, if any, Sn–Cl bridge bond in the solid state.

The presence of Sn–Cl π -bond character has been proposed to exist in SnCl_4 , $(\text{C}_6\text{H}_5)\text{SnCl}_3$, and $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ from nuclear quadrupole resonances,^{29,30} but the possibility of intermolecular association in the solid causing an asymmetry in the field gradient has not been ruled out in these cases.

The increase in the quadrupole splitting when trimethyltin chloride is complexed can be explained in terms of the previously reported description of the bonding in these adducts.^{3,6} The p_z orbital is mainly involved in the three center bonds to the chlorine and the base while p_x and p_y are increasingly involved in bonding to the methyls compared to $(\text{CH}_3)_3\text{SnCl}$. Consequently, increased imbalance in the charge densities in these two sets of orbitals results in E_Q increases over that of $(\text{CH}_3)_3\text{SnCl}$.

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