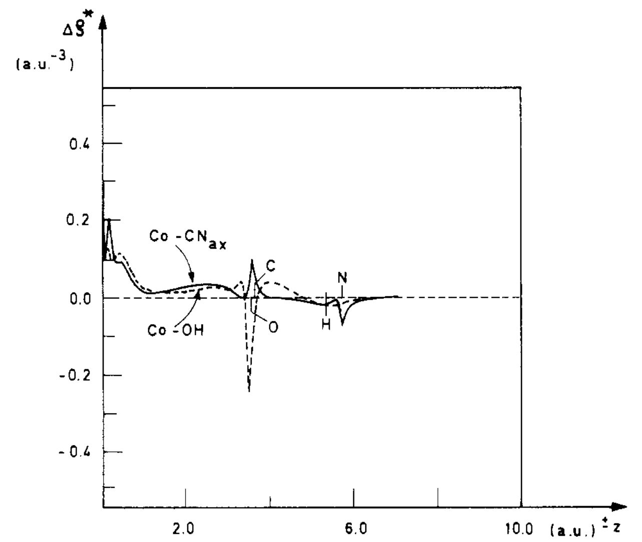

Figure 11. Total density difference plot $\Delta\rho^* = \rho(\text{complex}) - \rho(\text{metal-ligand system})$ for the photoactive ^3E_a state of $Co(CN)_5(OH)^{3-}$ along the $\pm z$ axis. In this case the separated metal–ligand system is considered to be made up of $Co^{3+}[(xy)^2(z^2)^1(xz,yz)^3;{}^3E]$ plus five CN^- ($^1\Sigma^+$) and one OH^- ($^1\Sigma^+$) ligand. The figure describes the electronic shift upon bond formation in the excited state. The full line describes the density shift along the axial Co–CN bond; the dashed line describes the corresponding shift along the Co–OH bond.

evidenced by the positive density contours on the ligands, especially on the carbon atoms: obviously the chemical bond is weaker in the excited state.

Similar plots can be obtained for the photoactive ^3E_a state of the substituted complex, as shown in Figures 9 and 10. Since the excitation in this case corresponds to $xz,yz \rightarrow z^2$, ligand field theory predicts only a small labilizing effect on the equatorial bonds.[11] Figure 9 shows the difference density plot in the xy plane: apart from the population increase on the central metal ion (due to z^2 occupation) no drastic changes can be detected in the metal–ligand interaction zones. Quite to the contrary, the axial bonds (Figure 10) are modified significantly: the decrease of the σ bonding and of the π back-bonding are even more pronounced than in the octahedral case. Obviously, the SCF calculations basically confirm the LF rationalization of the selective (axial) labilization of the metal–ligand bonds.

This conclusion is reinforced by calculating the corresponding density difference plots for the next excited state $^3A_2$. Since the latter corresponds to an $xy \rightarrow x^2 - y^2$ excitation, LF theory predicts only an equatorial labilization from this state. The SCF density plots are in complete agreement with this conclusion: the total density difference $\rho(^3A_2) - \rho(^1A_1)$ in the xy plane is quite similar to Figure 8; in contrast, along the z axis no significant density shifts are taking place.

As for the axial labilization from the photoactive ^3E_a state, a more difficult question remains: which one of the two axial ligands, OH^- or $(CN^-)_{ax}$, is expelled by excitation. Figure 11 shows the density difference upon bond formation in the excited state, for the two bonds Co–OH and Co–$(CN)_{ax}$. In comparison with Figure 6, where the corresponding plots were given for the ground state, one sees that both the σ donation toward the metal and the height of the covalent plateau have decreased in the excited state. This again indicates that both axial bonds are weakened, but from the ab initio point of view, there is no obvious reason why CN^- release should be the dominant photoreaction mode.

V. Conclusion

1. The effect of ligand substitution on the LF spectrum is reasonably well predicted by SCF calculations. The sign of certain energy splittings is sometimes at variance with classical ligand field theory, but the general features of the metal–ligand interactions are found to be as expected from semiempirical considerations: the CN^- ligand behaves as a strong σ donor and a weak π acceptor and the OH^- ligand as a weaker σ donor and as a π donor. This conclusion follows both from the analysis of the SCF excited energies and from the analysis of the density shifts; it does not follow from the relative order of the orbital energies in the ground state.

2. The AOM postulate of ligand additivity is to some extent substantiated by the ab initio calculations. This conclusion follows both from energy and from electron density calculations.

3. In our Hartree–Fock treatment, the bond labilization induced by photoexcitation can be rationalized essentially in the same way as in simple ligand field theory: ^3E_a is characterized by axial labilization, whereas $^3A_2$ is characterized by equatorial labilization.

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Contribution from the National Bureau of Standards,
Gaithersburg, Maryland 20899

Structure Determination by NMR Spectroscopy. Correlation of $|^2J(^{119}Sn,^1H)|$ and the Me-Sn-Me Angle in Methyltin(IV) Compounds

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New and published tin–carbon ($|^1J(^{119}Sn,^{13}C)|$, $|^1J|$) and tin–hydrogen ($|^2J(^{119}Sn,^1H)|$, $|^2J|$) J coupling data for 25 methyltin(IV) compounds (several in a variety of solvents) have been collected. From a relationship between $|^1J|$ and the Me–Sn–Me angle, θ, described previously, $|^2J|,\theta$ data pairs have been derived. A plot of these data reveals that θ and $|^2J|$ are related by a smooth curve described by $\theta\ (\text{deg}) = 0.0161|^2J|^2 - 1.32|^2J| + 133.4$; data for most methyltin(IV) compounds lie within 4° of this empirical line. Data for dimethyltin dichloride and dibromide in solvents of varying coordinating ability are described by a somewhat different relationship: $\theta\ (\text{deg}) = 0.0105|^2J|^2 - 0.799|^2J| + 122.4$. Several applications of the former equation for determining the structures of methyltin(IV) compounds in solution are briefly described, including its use in the assignment of tin coordination number.

NMR spectroscopy is an important tool for investigating molecular structure in solution. The interpretation of chemical shifts and coupling constants, however, is generally based on crystal structure data (X-ray) and is consequently subject to uncertainties

Table I. $|^1J(^{119}\text{Sn},^{13}\text{C})|$, $|^2J(^{119}\text{Sn},^1\text{H})|$, and Estimated Me–Sn–Me Angles of Methyltin(IV) Compounds in Solution

no.	compd[a]	solvent[b]	ref[b]	$\lvert^1J(^{119}\text{Sn},^{13}\text{C})\rvert$, Hz	$\lvert^2J(^{119}\text{Sn},^1\text{H})\rvert$, Hz	estd Me–Sn–Me angle, deg[c]
1	Me_4Sn	*d*	17	336.3	54.7	109.5
2	$(Me_3Sn)_2Se$	CH_2Cl_2	*e*	340	56.1	106.6
3	$(Me_3Sn)_2S$	CH_2Cl_2	*e*	356	57.1	108.0
4	Me_3SnOAc	$CDCl_3$	*f, g*	401	58.5	111.9
5	Me_3SnCl	CCl_4	17	379.7	58.1	110.1
6	Me_3SnCl	acetone-d_6	17	433.4	64.4	114.8
7	Me_3SnCl	pyridine	*h, i*	472	67.0	118.2
8	Me_3SnCl	DMF-d_7	17	513.4	70.0	121.8
9	Me_3SnBr	CCl_4	17	368.9	57.8	109.1
10	Me_3SnBr	DMF-d_7	17	490.8	69.8	119.3
11	$Me_3Sn(o\text{-}OC_6H_4NMe_2)$	nr	*j*	422	56.6	113.8
12	Me_3Sn(oxinate)	CD_2Cl_2, $CDCl_3$	*k, l*	427	57.0	114.2
13	$Me_2SnBr(O_2CC_6H_5)$	$CDCl_3$	*m*	500	70.5	120.6
14	$Me_2SnCl(O_2CC_6H_5)$	$CDCl_3$	*m*	568	76.1	126.6
15	Me_2SnCl(pen)	D_2O	*n*	614.4	79.1	130.6
16	$Me_2Sn(\text{oxinate})_2$	$CDCl_3$	27	632	71.2	132.2
17	$Me_2Sn(\text{trop})_2$	$CDCl_3$	27	643	72.2	133.2
18	$Me_2Sn(S_2PMe_2)_2$	$CDCl_3$	*f*	553	78.8	125.3
19	$Me_2Sn[S_2CN(CH_2)_4]_2$	$CDCl_3$	*f*	655	85.9	134.2
20	$Me_2Sn(O_2CC_6H_5)_2$	$CDCl_3$	27	660	84.0	134.6
21	$Me_2Sn(S_2CNMe_2)_2$	$CDCl_3$	27	664	84.0	135.0
22	$Me_2Sn(S_2CNEt_2)_2$	$CDCl_3$	27	664	84.0	135.0
23	$Me_2Sn(OAc)_2$	C_6D_6, CCl_4	*f*, 8	665	82.5	135.1
24	$Me_2Sn(\text{koj})_2$	Me_2SO	27	748	83.3	142.4
25	$Me_2Sn(\text{dbm})_2$	$CDCl_3$	27	913	97.0	156.8
26	$Me_2Sn(\text{bac})_2$	$CDCl_3$	27	931	98.4	158.4
27	$Me_2Sn(\text{acac})_2$	$CDCl_3$	27	977	99.3	162.5
28	Me_2SnCl_2	C_6H_6	17	469.4	69.0	117.9
29	Me_2SnCl_2	CD_3CN	17	584.9	81.2	128.1
30	Me_2SnCl_2	acetone-d_6	17	601.8	85.0	129.5
31	Me_2SnCl_2	DMF-d_7	17	886.9	104.5	154.6
32	Me_2SnCl_2	Me_2SO	*f, o*	1009	113	165.3
33	Me_2SnBr_2	C_6H_6	17	442.6	67.0	115.6
34	Me_2SnBr_2	CD_3CN	17	523.9	77.3	122.7
35	Me_2SnBr_2	acetone-d_6	17	533.4	79.1	123.5
36	Me_2SnBr_2	DMF-d_7	17	820.8	101.5	148.8

[a] Abbreviations: OAc = acetate; oxinate = anion of 8-hydroxyquinoline; DMF = *N*,*N*-dimethylformamide; Me_2SO = dimethyl sulfoxide; acac = acetylacetonate; pen = penicillaminate; trop = tropolonate; dbm = dibenzoylmethanate; bac = benzoylacetonate; koj = kojate. [b] When two solents or references are listed, the first refers to $|^1J|$ and the second to $|^2J|$; nr = not reported. [c] Estimated from $|^1J|$ by using eq 1. [d] $|^1J|$ and $|^2J|$ are averages of values determined in nine solvents; tetrahedral geometry is assumed. [e] Kennedy, J. D.; McFarlane, W. *J. Organomet. Chem.* **1975**, *94*, 7. [f] This work. [g] Simons, P. B.; Graham, W. A. G. *J. Organomet. Chem.* **1967**, *10*, 47. [h] Mitchell, T. N. *J. Organomet. Chem.* **1973**, *59*, 189. [i] Bolles, T. F.; Drago, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 3921. [j] Tzschach, A.; Weichmann, H.; Jurkshat, K. *J. Organomet. Chem. Libr.* **1981**, *11*, 293. [k] Clark, H. C.; Jain, V. K.; McMahon, I. J.; Mehrotra, R. C. *J. Organomet. Chem.* **1983**, *243*, 299. [l] Kawakami, K.; Okawara, R. *J. Organomet. Chem.* **1966**, *6*, 249. [m] Honnick, W. D.; Zuckerman, J. J. *J. Organomet. Chem.* **1979**, *178*, 133. [n] Domazetis, G.; Magee, R. J.; James, B. D. *J. Organomet. Chem.* **1978**, *162*, 239. [o] Kennedy, J. D.; McFarlane, W. *J. Chem. Soc., Perkin Trans. 2* **1974**, 146.

arising from solvation and dynamic effects. Recently, we showed[2,3] that solid-state NMR measurements made on structurally characterized, crystalline samples can allow the relationship between NMR parameters and molecular structure to be probed in detail. Through such experiments with methyltin(IV) compounds we found[3] that the magnitude of tin–carbon J coupling, $|^1J(^{119}\text{Sn},^{13}\text{C})|$ ($|^1J|$), depends linearly on the Me–Sn–Me angle for tetramethyltin and a number of tetra-, penta-, and hexacoordinated di- and trimethyltin(IV) compounds (eq 1, where θ

$$|^1J| = 11.4\theta - 875 \qquad (1)$$

= the Me–Sn–Me angle (deg) and $|^1J|$ is measured in Hz). X-ray studies[4] have confirmed the accuracy of Me–Sn–Me angle estimates made for structurally uncharacterized methyltin(IV) compounds using eq 1. The J coupling parameter is easily measured in solution and thus provides, through application of eq 1, a method of reasonable accuracy for determining the structure of these compounds in solution.[3]

The availability[5] of tin–proton J coupling constants, $^2J(^{119}\text{Sn},^1\text{H})$ ($|^2J|$), measured over the past 25 years for an enormous number and variety of methyltin(IV) compounds, and the fact that ^{1}H remains the most commonly observed NMR nucleus encouraged a similar search for a ^{1}H NMR/structure correlation. Only in rare circumstances, however, can J coupling of any nucleus to ^{1}H be observed for solid samples,[6] so a *direct* $|^2J|$/angle study was not possible. The alternate, *indirect* approach we have followed is to measure both $|^2J|$ and $|^1J|$ by solution NMR spectroscopy for a series of methyltin(IV) compounds and then to estimate the solution Me–Sn–Me angle from $|^1J|$ by using eq 1. This approach yields a new, useful correlation between $|^2J|$ and the Me–Sn–Me angle.

Experimental Section

Me_3SnOAc,[7] $Me_2Sn(OAc)_2$,[8] $Me_2Sn(\text{oxinate})_2$,[9] and $Me_2Sn[S_2CN$-

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(2) Manders, W. F.; Lockhart, T. P. *J. Organomet. Chem.* **1985**, *297*, 143.

(3) Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 4546. Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J., manuscript in preparation.

(4) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O. *J. Am. Chem. Soc.* **1985**, *107*, 7451.

(5) For compilations see: Petrosyan, V. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 115. Poller, R. C. "Chemistry of Organotin Compounds"; Academic Press: New York, 1970; pp 235–237.

(6) Graham, J. D.; Darby, J. S. *J. Magn. Reson.* **1976**, *23*, 369. Terao, T.; Miura, H.; Saika, A. *J. Magn. Reson.* **1982**, *49*, 365. Zilm, K. W.; Grant, D. M. *J. Magn. Reson.* **1982**, *48*, 524. Rothwell, W. P.; Shen, W. X.; Lunsford, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 2452.

(7) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459.

(8) Maeda, Y.; Okawara, R. *J. Organomet. Chem.* **1967**, *10*, 247.

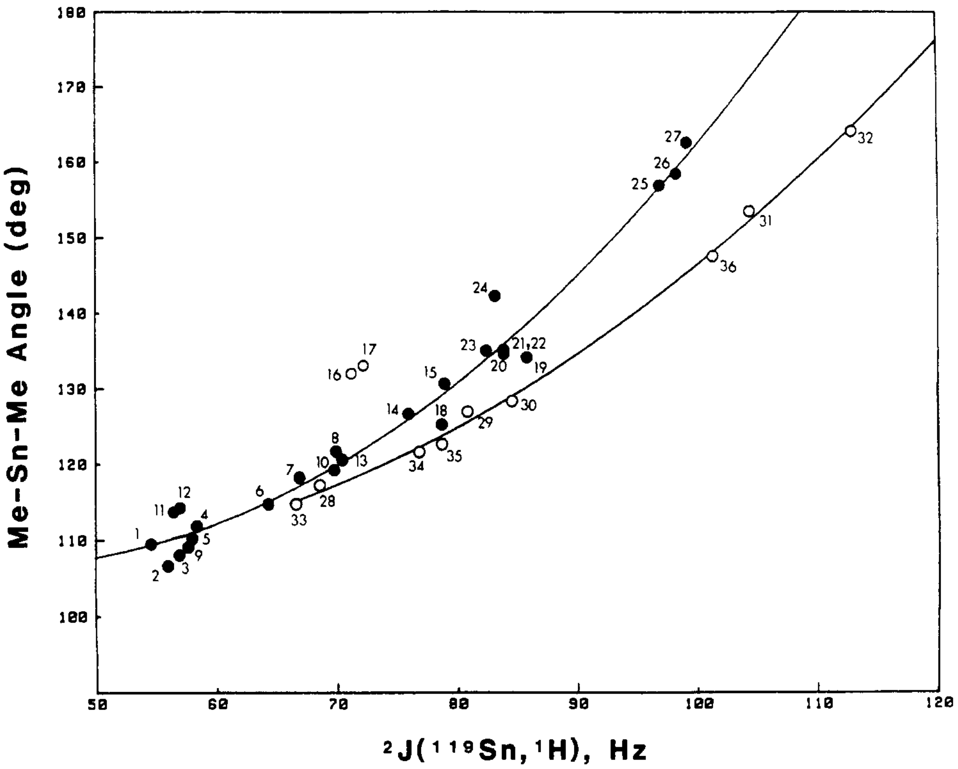

Figure 1. Plot of Me–Sn–Me angle vs. $|^2J|$ for methyltin(IV) compounds. Filled circles were used in the empirical calculations of the upper curve (eq 2); open circles (except points 16 and 17) were used in the calculation of the lower line (eq 3). The numbers are defined in Table I.

$(CH_2)_4]_2$[10] were prepared as described in the literature. A sample of $Me_2Sn(S_2PMe_2)_2$[11] was generously provided by Prof. F. P. Mullins (Mount St. Vincent University). Me_2SnCl_2 was obtained from a commercial source. Solution NMR spectra were recorded on a Bruker WM-400 spectrometer (400 MHz for ^1H, 100.6 MHz for ^{13}C). Solutions were <10% methyltin(IV) by weight; $CDCl_3$ was used as solvent except for the run with Me_2SnCl_2 in dry Me_2SO-d_6. ^{13}C line widths at half-height were <5 Hz except those for $Me_2Sn(S_2PMe_2)_2$, which were ca. 10 Hz. $|^1J(^{119}Sn,^{13}C)|$ values are reproducible to ±3 Hz. A least-squares method was used to compute polynomial expressions (eq 2 and 3) to fit the experimental data. Linear-regression ($r = 0.971$) and logarithmic methods gave less satisfactory fits of the 25 points used to obtain eq 2.

Results and Discussion

^1H and ^{13}C NMR data for solutions of 25 methyltin(IV) compounds (several studied in solvents of different coordinating abilities), taken largely from the literature, and Me–Sn–Me angles, θ, estimated from $|^1J|$ by using eq 1, are given in Table I. A plot of Me–Sn–Me angle vs. $|^2J|$ is shown in Figure 1.

The $|^2J|$/angle data divide into two main groups of points, both indicating a nonlinear relationship of $|^2J|$ to the Me–Sn–Me angle. First, all of the compounds (filled circles, Figure 1) but four follow a smooth curve described by the quadratic expression in eq 2.

$$\theta = 0.0161|^2J|^2 - 1.32|^2J| + 133.4 \qquad (2)$$

Curiously, the $|^2J|$/angle data for dimethyltin dibromide and dichloride in various solvents (open circles 28–36, Figure 1) describe a quadratic expression (eq 3) distinct from that of the other

$$\theta = 0.0105|^2J|^2 - 0.799|^2J| + 122.4 \qquad (3)$$

compounds, although in a noncoordinating solvent, benzene, the dimethyltin dihalides (points 28 and 33, Figure 1) fall close to the main curve. The data suggest that the deviation may be connected with the expansion of the tin coordination number from 4 in benzene to 6 in strongly coordinating solvents, although it is difficult to understand why this should influence the $|^1J|$ and $|^2J|$ coupling constants differently. Unlike the dimethyltin dihalides, trimethyltin chloride and bromide in a variety of solvents (points 5–10, Figure 1) closely follow the main curve.

Distinct from either of the above groups are data for $Me_2Sn(oxinate)_2$ (point 16) (oxinate = anion of 8-hydroxyquinoline) and $Me_2Sn(trop)_2$ (point 17) (trop = tropolonate). We have found[3] in solid-state ^{13}C NMR experiments that certain hexacoordinated *cis*-dimethyltin(IV) compounds [$Me_2Sn(oxinate)_2$ and bis(*N*-hydroxyacetamidato)dimethyltin(IV), θ = 110.7[12] and 109.1°,[13] respectively] deviate strongly from the $|^1J|/\theta$ plot, giving values of $|^1J|$ much higher (>200 Hz) than predicted from their Me–Sn–Me angles.[14] The similar $|^1J|$ and $|^2J|$ data for points 16 and 17 suggest that point 17 also has a small (cis) Me–Sn–Me angle. Interestingly, the solution $|^2J|$ data for point 16 indicate a smaller Me–Sn–Me angle than does $|^1J|$, suggesting that $|^2J|$ may track θ somewhat better for compounds of this type.

Several sources may introduce errors in the $|^2J|$/angle data. First, on the basis of the scatter of data in the original $|^1J|/\theta$ plot,[3] an accuracy of not better than about ±3° is expected for values of θ derived from eq 1. Further, $|^1J|$ and $|^2J|$ were not measured under identical conditions for all of the methyltin(IV) compounds, so there may have been slight differences between the molecular structures in the ^1H and ^{13}C NMR solutions. The complicated relationship between $|^1J|$ and $|^2J|$ values of methyltin(IV) com-

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(9) Tanaka, T.; Komura, M.; Kawasaki, Y.; Okawara, R. *J. Organomet. Chem.* **1964**, *1*, 484.

(10) Fitzsimmons, B. W.; Owusu, A. A.; Seeley, N. J.; Smith, A. W. *J. Chem. Soc. A* **1970**, 935.

(11) Mullins, F. P. *J. Inorg. Nucl. Chem.* **1979**, *41*, 633.

(12) Schlemper, E. O. *Inorg. Chem.* **1967**, *6*, 2012.

(13) Harrison, P. G.; King, T. J.; Phillips, R. C. *J. Chem. Soc., Dalton Trans* **1976**, 2317.

(14) This effect may have its source in the presence of four "hard"[15] basic ligands (O, N) in the Sn coordination sphere; in contrast, $|^1J|$ of $Me_2Sn(S_2PMe_2)_2$ (with four soft sulfur atoms in the tin coordination sphere, θ = 122.6°) measured in the solid state[3] lies on the $|^1J|/\theta$ line. Substituent effects may also account for the anomalously large $|^1J|$ and $|^2J|$ values of some pentacoordinated trimethyltin(IV) compounds. For example, $|^2J|$ values[16] of several compounds of the type $Me_3Sn(XP(Y)R_2)$ (X, Y = O, S) tend to be too high, indicating average Me–Sn–Me angles of up to 127° (the highest possible average angle is 120°). Our current efforts are directed toward identifying, and understanding, compound types that deviate from the simple $|^1J|$ and $|^2J|$ structure correlations.

(15) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(16) Molloy, K. C.; Nasser, F. A. K.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 1711. Nasser, F. A. K.; Zuckerman, J. J. *J. Organomet. Chem.* **1983**, *244*, 17.

pounds[17] may contribute further to scatter. In spite of these considerations, however, $|^2J|$ *values of only 2 of 25 measurements indicate Me–Sn–Me angles 4° or more from the empirical line* (eq 2). The relationship should provide estimates of Me–Sn–Me angles of comparable accuracy.[18]

Equation 2 can be used to obtain rapid insight into the molecular structure of methyltin(IV) compounds from ^{1}H NMR data. Given the similar shapes and gentle slopes of the two curves (eq 2 and 3), differences in $|^2J|$ for a group of closely related compounds, or one compound in different solvents, can be used with confidence to estimate changes in θ.

Tin coordination is of general interest in synthetic and structural organotin studies. On the basis of data in Table I and Figure 1, several general comments can be made concerning the range of $|^2J|$ values expected for di- and trimethyltin(IV) compounds of different coordination number. Tetracoordinated trimethyltin(IV) compounds have $|^2J|$ values <59 Hz. $|^2J|$ of tetracoordinated dimethyltin(IV) compounds can be much larger if the substituents are highly electronegative [cf. data for Me_2SnX_2 (X = Cl, Br) in Table I], reflecting changes in θ due to orbital rehybridization.[19] For pentacoordinated dimethyltin(IV) compounds, θ can vary between about 115 and 130°, corresponding to $|^2J|$ values of 64–79 Hz. Hexacoordinated dimethyltin(IV) compounds with Me–Sn–Me angles from 109.1 to 180° are known[20] from X-ray studies; for $\theta > 135°$ ($|^2J| > 83$ Hz) it appears that $|^2J|$ faithfully indicates the Me–Sn–Me angle. As noted above, θ of hexacoordinated *cis*-dimethyltin(IV) compounds can be much smaller than predicted from eq 2, so the equation should be employed cautiously if $|^2J|$ is less than about 80 Hz (or $|^1J|$ is less than about 650 Hz[3]) and the dimethyltin(IV) is likely to be hexacoordinated.

The utility of the new $|^2J|$/angle relationship for determining methyltin(IV) structures in solution can be demonstrated for $Me_2Sn(S_2COEt)_2$, whose X-ray and solution structures have recently been reported.[21] X-ray studies revealed that Sn is hexacoordinated and that the complex adopts a geometry similar to that of the well-characterized dimethyltin bis(dithiocarbamates)[22] with the exception that the Me–Sn–Me angle in $Me_2Sn(S_2COEt)_2$, 130.1°, is somewhat smaller. On the basis of the ^{119}Sn chemical shift of $Me_2Sn(S_2COEt)_2$ in CH_2Cl_2 solution, it was argued that Sn is only tetracoordinated in solution, the two *O*-ethyl xanthate ligands no longer being bidentate.[23] From the $|^2J|$ reported (79.1 Hz), however, a Me–Sn–Me angle in solution of about 130° is calculated by using eq 2, a result that rules out the proposed tetracoordinated Sn solution structure. Instead, it can be argued with confidence that the solution structure is essentially unchanged from that in the solid state.

To date, only a few hexacoordinated *cis*-dimethyltin(IV) compounds have been identified by X-ray crystallography.[20] Since they represent an unusual and, apparently, energetically unfavorable configuration, there is considerable interest in the steric and electronic factors that lead to such geometries.[25] With use of the new NMR/structure correlation (eq 2), published ^{1}H NMR data of various Me_2Sn(chelating ligand)$_2$ compounds can be reexamined to identify additional compounds likely to fall into the *cis*-dimethyltin(IV) group. Several such compounds include $Me_2Sn(S(O)CC_6H_5)_2$ ($|^2J| = 76.4$ Hz),[26] $Me_2Sn(trop)_2$ ($|^2J| = 72.2$ Hz),[27] and $Me_2Sn(pic)_2$ (pic = picolinate) ($|^2J| = 77.6$ Hz).[28]

Equilibration of different methyl sites in pentacoordinated trimethyltin(IV) compounds is expected to be fast on the NMR time scale,[29] and measured values of $|^1J|$ and $|^2J|$ should correspond to an average of the different Me–Sn–Me angles in the molecule. This is exemplified by data for trimethyltin chelates: the average θ values predicted from $|^1J|$ for points 11 and 12 are 113.8 and 114.2°, respectively, and those predicted for trimethyltin acetylacetonate, benzoylacetonate, and dibenzoylmethanate from $|^2J|$ values[30] lie in the range 111–113°. For comparison, X-ray analysis[31] of the two forms of pentacoordinated $Me_3Sn(S_2CNMe_2)$ indicated average values of $\theta = 113.7$ and 114.0°.

Other attempts[22a,b,27,32] have been made to investigate the relationship between $|^2J|$ and the Me–Sn–Me angle. The failure of those approaches can be attributed to the fact that solution geometries were of necessity assumed to be the same as in the crystalline state. Thus, Otera and co-workers[27] used $|^2J|$ values for dimethyltin dithiocarbamates (points 21 and 22) (for which the solution and X-ray structures are very similar), $Me_2Sn(acac)_2$, (which has $\theta = 180°$ in the solid, ca. 162.5° in solution), and $Me_2Sn(oxinate)_2$ [whose $|^2J|$ value does not accurately reflect its Me–Sn–Me angle (vide supra)]; the resulting (linear) plot[27] bears little resemblance to that reported here.

Conclusions

We have used a large number of $|^2J|,|^1J|$ data pairs obtained in solution NMR experiments and an equation relating $|^1J|$ to the Me–Sn–Me angle to construct a new plot of $|^2J|$ vs. Me–Sn–Me angle. Unlike the earlier,[3] linear $|^1J|$/angle plot, the $|^2J|$/angle data separate into two distinct curves, one for dimethyltin dihalides in coordinating solvents and another for the large number of remaining compounds. It is suggested that eq 2 should be applied to ^{1}H NMR data for methyltin(IV) compounds for the purpose of estimating methyltin(IV) molecular structures. The wide distribution and use of ^{1}H NMR spectrometers make eq 2 an important, new tool for structural organotin chemistry. It should be useful for obtaining rapid estimates of the molecular structures of new methyltin(IV) compounds and for comparing solution and solid-state structures (known from X-ray or solid-state ^{13}C NMR); we are aware of no other method that is both so widely available and simple in execution and that provides structural information of comparable detail for these compounds. Not least important, eq 2 provides a means of estimating the solution structures of the large number of structurally uncharacterized methyltin(IV) compounds for which ^{1}H NMR data ($|^2J|$) are available.[5]

Registry No. Me_3SnOAc, 1118-14-5; $Me_2Sn(S_2PMe_2)_2$, 85708-76-5; $Me_2Sn[S_2CN(CH_2)_4]_2$, 22484-02-2; $Me_2Sn(OAc)_2$, 13293-57-7; Me_2SnCl_2, 753-73-1.

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(17) Petrosyan, V. S.; Permin, A. B.; Reutov, O. A.; Roberts, J. D. *J. Magn. Reson.* **1980**, *40*, 511.

(18) The accuracy of eq 2 for classes of compounds outside those described here is uncertain. ^1J and ^2J have been shown to change sign for certain methyltin(IV) compounds (e.g., trimethylstannate anions, for which the magnitudes of ^1J and ^2J were small: Kennedy, J. D.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1974**, 983).

(19) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(20) A bibliography of organotin X-ray structural studies has been published: Smith, P. *J. Organomet. Chem. Libr.* **1981**, *11*, 97.

(21) Dakternieks, D.; Hoskins, B. F.; Tiekink, E. R. T.; Winter, G. *Inorg. Chim. Acta* **1984**, *85*, 215.

(22) (a) Kimura, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1649. (b) Morris, J. S.; Schlemper, E. O. *J. Cryst. Mol. Struct.* **1979**, *9*, 13. (c) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O.; Zuckerman, J. J. *J. Am. Chem. Soc.*, in press.

(23) In our opinion the arguments employed by Dakternieks et al.[21] do not justify this conclusion; the ^{119}Sn chemical shift of $Me_2Sn(S_2COEt)_2$, −267 ppm at −90 °C, falls within the range observed for other hexacoordinated dimethyltin(IV) compounds such as $Me_2Sn(acac)_2$, $Me_2Sn(S_2CNEt_2)_2$, and $Me_2Sn(oxinate)_2$ (−365, −333, and −237 ppm, respectively).[24] As these data indicate, the ^{119}Sn chemical shift varies widely with the bonding geometry of the hexacoordinate dimethyltin(IV) and it must be used cautiously for determining tin coordination number.

(24) Otera, J. *J. Organomet. Chem.* **1981**, *221*, 57.

(25) Tse, J. S.; Sham, T. K.; Bancroft, G. M. *Can. J. Chem.* **1979**, *57*, 2223. Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1; *J. Organomet. Chem.* **1976**, *107*, 49. Zahrobsky, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 3313.

(26) Coldea, V.; Coldea, M.; Haiduc, I. *Rev. Roum. Chim.* **1981**, *26*, 71.

(27) Otera, J.; Hinoishi, T.; Kawabe, Y.; Okawara, R. *Chem. Lett.* **1981**, 273.

(28) McGrady, M. M.; Tobias, R. S. *J. Am. Chem. Soc.* **1965**, *87*, 1909.

(29) See discussion in: Tzschach, A.; Jurkschat, K. *Comments Inorg. Chem.* **1983**, *3*, 42.

(30) Bancroft, G. M.; Davies, B. W.; Payne, N. C.; Sham, T. K. *J. Chem. Soc., Dalton Trans.* **1975**, 973.

(31) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1970**, 490. Sheldrick, G. M.; Sheldrick, W. S.; Dalton, R. F.; Jones, K. *Ibid.* **1970**, 493.

(32) Howard, W. F.; Crecely, R. W.; Nelson, W. H. *Inorg. Chem.* **1985**, *24*, 2204.