esters,[45] are found to be higher for the thio compounds. This suggests an increased contribution from resonance form III when X = S. Further support comes from a comparison of bond lengths in the tris(hydroximato) and -(thiohydroximato) complexes of chromium(III), where the C–N bond distance in the thio compound is somewhat shorter than found for the O compound.[46,47]

It is interesting to note that the rate constants for the dissociation of the last hydroxamate group of the siderophore ferrioxamine B from iron(III) by acid-dependent and acid-independent paths also follow the correlation shown in Figure 6 but are larger than the values found for $Fe(H_2O)_4(CH_3OC_6H_4C(S)N(O)H)^{2+}$.[48,49] The kinetic and thermodynamic stability of the thiohydroxamic acid ligand studied here suggests that the thiohydroxamates may also serve a biological function as an iron(III) chelator and that future research may establish the existence of a thiohydroxamate-based siderophore.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank C. P. Brink for a sample of the hydroxamic acid and for helpful discussions and A. B. Griffis for preliminary synthetic work with thiohydroxamic acids.

**Registry No.** I (X = O), 94944-52-2; I (X = S), 94944-53-3; $Fe(H_2O)_6^{3+}$, 15377-81-8; $Fe(H_2O)_5OH^{2+}$, 15696-19-2; $4\text{-}CH_3OC_6H_4C(O)N(OH)H$, 10507-69-4; $4\text{-}CH_3OC_6H_4C(S)N(OH)H$, 17650-20-3.

**Supplementary Material Available:** Rate constant data (Table II) (4 pages). Ordering information is given on any current masthead page.

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# Octahedral Dialkyltin Complexes: A Multinuclear NMR Spectral Solution Structural Study

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*Received February 3, 1984*

Octahedral dialkyltin complexes of type $R_2SnCh_2$ (R = alkyl, Ch = bidentate ligand) yield NMR tin–carbon $|^1J(^{119}Sn-^{13}C)|$ and tin–hydrogen, $|^2J(^{119}Sn-C-^1H)|$ coupling constants that allow the estimation of C–Sn–C bond angles. Complexes with β-keto enolate ligands show trans alkyl structure with calculated ∠C–Sn–C between 174 and 180°. Very nearly cis arrangements with ∠C–Sn–C between 109 and 126° characterize the 8-hydroxyquinolinolates. The sterically crowded 2-methyl-8-hydroxyquinolinolate family shows intermediate skew-cis structures. Skew (i.e., trapezoidal bipyramidal) frameworks were found for tropolonates and 1-picolinates. Finally, $^{119}Sn$ NMR spectra have been analyzed to yield $|^3J(^{119}Sn-C-C-^1H)|$ values for the first time in octahedral species. Syntheses of eight new benzoylacetonate, 2-methyl-8-hydroxyquinolinolate, and tropolonate derivatives are reported.

## Introduction

Even though it might appear that the structures of six-coordinate $R_2SnCh_2$ species should be simple octahedra, 20 years of structural investigations have shown a substantially different picture. Most early studies interpreted results on the basis of simple trans or cis structures,[1–7] and, indeed, there is little doubt that some structures are trans in solution[8,9] and the solid state.[10] Others certainly are cis.[11,12] More recently, Kepert[13] noted that many octahedral organometallic complexes, including several tin complexes, are of neither regular cis nor regular trans geometry, but that an intermediate geometry, skew or trapezoidal bipyramidal, is more stable (see Figure 1; skew structures have C–Sn–C angles of 135–155°). We have shown[14] by means of the Kerr effect that a number of structures previously believed to be trans are better described as skew in solution. Extensive studies involving dipole moments,[15] IR spectroscopy,[16] and depolarized light scattering[17–19] are better interpreted in terms of distorted structures rather than cis–trans mixtures.

Early proton NMR studies[15,20–22] showed little evidence for cis–trans equilibria. Although information concerning the mechanism of ligand exchange has been obtained, such studies have shown primarily that ligand exchange is very rapid. More recent $^{119}Sn$ and $^{13}C$ NMR experiments by Otera[23,24] indicate that NMR may provide a more useful means of probing the configurations of $R_2SnCh_2$-type complexes.

Much interesting Mössbauer data are available. Quadrupole splittings from $^{119}Sn$ Mössbauer spectra are related to molecular geometry in octahedral complexes and have been used to calculate

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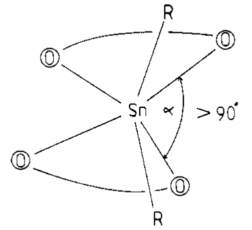

**Figure 1.** Skew, or irregular trapezoidal-bipyramidal, configuration found to be the in-solution structure of several $R_2SnCH_2$ complexes. The O–Sn–O angle, α, is greater than 90°.

**Table I.** Physical and Analytical Data for Previously Synthesized Octahedral Bischelated Dialkyltin Complexes[a]

| complex | % anal. hydrogen | % anal. carbon | mp, °C | ref |
|---|---|---|---|---|
| | dibenzoylmethanoates | | | |
| $(CH_3)_2Sn(dbzm)_2$ | 64.42 | 4.91 | 189–190 | 2 |
| | (64.57) | (4.74) | (189–191) | |
| $(C_2H_5)_2Sn(dbzm)_2$ | 65.50 | 5.12 | 141–143 | 17 |
| | (65.52) | (5.17) | (141–143) | |
| $(n\text{-}C_4H_9)_2Sn(dbzm)_2$ | 67.08 | (6.04) | 90–91.5 | 15 |
| | (67.18) | (5.93) | (92–94) | |
| | 1-Picolinates | | | |
| $(n\text{-}C_4H_9)_2Sn(pic)_2$ | 50.53 | 5.61 | 198.5–200 | 36 |
| | (50.35) | (5.49) | (198–200) | |
| $(n\text{-}C_8H_{17})_2Sn(pic)_2$ | 57.21 | 7.01 | 148–150 | 37 |
| | (57.07) | (7.18) | | |
| | 8-Hydroxyquinolinolates | | | |
| $(CH_3)_2Sn(ox)_2$ | 55.20 | 3.80 | 231–233 | 6 |
| | (54.97) | (4.11) | (231–233) | |
| $(C_2H_5)_2Sn(ox)_2$ | 56.83 | 4.66 | 172.5–174 | 38 |
| | (56.81) | (4.77) | (175–176) | |
| $(n\text{-}C_4H_9)_2Sn(ox)_2$ | 59.94 | 5.85 | 152–153.5 | 6 |
| | (59.91) | (5.80) | (150–152) | |
| $(n\text{-}C_8H_{17})_2Sn(ox)_2$ | 64.90 | 7.30 | 77.5–79.5 | 39 |
| | (64.47) | (7.32) | (78) | |
| | 2,2′-Bipyridine | | | |
| $(C_4H_9)_2SnCl_2\cdot bpy$ | 46.97 | 5.82 | 178–179 | 6 |
| | (47.00) | (5.70) | (177–179) | |
| $(C_8H_{17})_2SnCl_2\cdot bpy$ | 54.51 | 7.61 | 130–131 | |
| | (54.57) | (7.40) | (133–133.5) | 40 |
| | 1,10-Phenanthroline | | | |
| $(C_4H_9)_2SnCl_2\cdot phen$ | 49.78 | 5.48 | 198–199 | 40 |
| | (49.63) | (5.41) | (200) | |
| $(C_8H_{17})_2SnCl_2\cdot phen$ | 56.15 | 7.37 | 101.5–103 | 40 |
| | (56.40) | (7.10) | (101) | |

[a] Previously listed abbreviations are employed above, and both calculated elemental analyses and literature melting points are in parentheses.

solid-state C–Sn–C angles in $(CH_3)_2SnCh_2$ species.[25] Frozen-solution spectra have been used[26] to estimate solute structures, but the usefulness of Mössbauer relates primarily to the solid state.

Tin-119 NMR spectra exhibit a large chemical shift (δ) range. The $^{119}Sn$ chemical shift data are of little use in structural studies, though, since minor molecular structural and electronic changes are magnified into unpredictable δ changes of tens of ppm. Tin–carbon and tin–hydrogen coupling constants, however, show promise[23,24] as structural probes, and this study reports an effort to determine the structure of complexes of type $R_2SnCh_2$ using coupling constants. Results are compared with those obtained by means of several other physical methods including the Kerr effect and depolarized light scattering.

## Experimental Section

**Preparation.** Many of the complexes synthesized have been prepared previously[27] (see Table I). Syntheses of new species are described below. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE (see Table II).

**Table II.** Physical and Analytical Data for New $R_2SnCh_2$ Complexes[a]

| complex | color | mp, °C | % anal. carbon | % anal. hydrogen |
|---|---|---|---|---|
| | Benzoylacetonates | | | |
| $(CH_3)_2Sn(bzac)_2$ | pale yellow | 128.5–130.0 | 56.22 | 4.99 |
| | | | (56.09) | (5.13) |
| $(C_2H_5)_2Sn(bzac)_2$ | yellow | 88.0–89.5 | 58.04 | 5.65 |
| | | | (57.75) | (5.65) |
| $(n\text{-}C_4H_9)_2Sn(bzac)_2$ | yellow orange | 47.5–49.5 | 60.68 | 6.54 |
| | | | (60.57) | (6.53) |
| | 2-Methyl-8-hydroxyquinolinolates | | | |
| $(CH_3)_2Sn(Meox)_2$ | ivory | 310 dec | 57.32 | 4.88 |
| | | | (56.81) | (4.77) |
| $(C_2H_5)_2Sn(Meox)_2$ | ivory | 288.0–291.0 | 59.43 | 5.28 |
| | | | (58.45) | (5.31) |
| $(n\text{-}C_4H_9)_2Sn(Meox)_2$ | ivory | 231.0–233.0 | 61.39 | 6.20 |
| | | | (61.23) | (6.24) |
| $(n\text{-}C_8H_{17})_2Sn(Meox)_2$ | ivory | 74.0–75.0 | 65.27 | 7.55 |
| | | | (65.37) | (7.62) |
| | Tropolonate | | | |
| $(n\text{-}C_8H_{17})_2Sn(trop)_2$ | tan | 44.0–45.5 | 61.08 | 7.47 |
| | | | (61.35) | (7.55) |

[a] Eight tin complexes prepared for this study are reported for the first time. Previously listed abbreviations are used above, and calculated elemental compositions are in parentheses.

Benzoylacetone (Mallinckrodt, reagent), 2-methyl-8-hydroxyquinoline, and dialkyltin oxides (Pfaltz and Bauer) were used without further purification. Bischelated dialkyltin species were synthesized by suspending the dialkyltin oxide (0.01–0.02 mol) in cyclohexane or benzene, adding a stoichiometric amount of ligand (0.02–0.04 mol), and refluxing for 2–12 h.[17] The solvent was removed on a rotary evaporator, and the crude products were recrystallized from pentane or pentane/benzene as required.

Dialkyltin dichloride adducts were prepared by first dissolving equimolar amounts (generally 0.01–0.02 mol) of the starting materials separately in 25 mL of ethanol and then mixing the two solutions. The white products precipitated immediately and were washed 3–5 times with ethanol, filtered, and dried at 100 °C overnight. All the hexacoordinated tin complexes were produced quantitatively (>90% yields after recrystallization).

The following ligand abbreviations are used: acetylacetonate, acac; benzoylacetonate, bzac; dibenzoylmethanate, dbzm; tropolonate, trop; 8-hydroxyquinolinolate or oxinate, ox; 2-methyl-8-hydroxyquinolinate or 2-methyloxinate, Meox; 2-picolinate, pic; 2,2′-bipyridine, bpy; 1,10-phenanthroline, phen; *N*-acetal-*N*-methylhydroxylamine, amha; *N,N′*-dimethyldithiocarbamate, Medtc; *N,N′*-diethyldithiocarbamate, Etdtc.

**Instrumentation.** A Bruker WM250 was employed in the $^{119}Sn$ and $^{13}C$ NMR studies, operating at frequencies of 93.2 and 62.9 MHz, respectively. Negative chemical shift values are upfield from $(CH_3)_4Si$ for $^{13}C$ and $^{119}Sn$ measurements, respectively, and $(CH_3)_4Sn$ [=0.0 ppm] accuracies are estimated as ±0.2 ppm. Except where noted, all NMR samples were studied in $CDCl_3$ solution. Sample concentrations were 0.5g/mL (1–2 M) for *n*-butyl and *n*-octyl $SnCh_2$ species, and tetraalkyltin compounds were neat. All other complexes were studied in saturated solutions.

## Results and Discussion

**Nuclear Magnetic Resonance. (1) $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ Couplings.** Otera et al.[23] observed a linear relationship between Sn–C–H coupling constants (in solution) and the C–Sn–C angles (from X-ray crystal analyses) of dimethyltin complexes with bidentate ligands. Expanding Otera's graph with data from other octahedral organotin species yields a seven-point plot, depicted as Figure 2, with supporting information in Tables III and IV. Subjecting the data to linear regression analysis yields the equation

$$\angle C\text{–}Sn\text{–}C = 2.28|^2J(^{119}Sn\text{–}C\text{–}^1H)| - 46.4 \qquad (1)$$

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**Table III.** Chemical Shifts and Sn-H and Sn-C Coupling Constants of Selected Organotin Compounds

| ligands and alkyl groups | $\delta(^{119}Sn)$ vs. TMT | $\lvert ^1J(^{119}Sn-^{13}C)\rvert$, Hz | $\lvert ^2J(Sn-C-^{13}C)\rvert$,[a] Hz | $\lvert ^3J(Sn-C-C-^{13}C)\rvert$,[a] Hz | $\lvert ^2J(^{119}Sn-C-^1H)\rvert$, Hz |
|---|---|---|---|---|---|
| | | Benzoylacetonates | | | |
| Me | −353.5 | 933 | | | 98.4 |
| Et | −392.8 | 943 | 49.2 | | 97.8 |
| *n*-Bu | −390.4 | 902 | 41.2 | 129.9 | 96.9 |
| | | Dibenzoylmethanoates | | | |
| Me | −348.0 | 914 | | | 97.0 |
| Et | −386.9 | 919 | 49.2 | | 98.1 |
| *n*-Bu | −385.1 | 880 | 41.3 | 126.0 | 98.1 |
| | | Tropolonates | | | |
| Me[c] | −197.0 | 643 | | | 72.2 |
| *n*-Oct | −230.7 | 616 | 44.7 | 103.2 | 83.0 |
| | | 1-Picolinates | | | |
| Me[b] | NL[f] | NL | | | 77.6 |
| *n*-Bu | −312 ± 2 | 711 | 33.5 | 122.1 | 74 ± 2 |
| *n*-Oct | −337 ± 5 | 766 | 35.4 | 126.0 | NR[g] |
| | | 8-Hydroxyquinolinolates | | | |
| Me | −235.1 | 630 | | | 68.7 |
| *n*-Bu | −259.2 | 634 | 31.5 | | 68.1 |
| *n*-Bu | −260.7 | 612 | 23.6 | 102.4 | 72.6 |
| *n*-Oct | −260.3 | 608 | 35.0 | 96.5 | 72.7 |
| | | 2-Methyl-8-hydroxyquinolinolates | | | |
| Me | −227.3 | 862 | | | 90.0 |
| Et | −245.6 | 827 | 40.0 | | 74.7 |
| *n*-Bu | −248.7 | 805 | 45.3 | 122.1 | 72.6 |
| *n*-Oct | −248.7 | 803 | 43.3 | 114.2 | 75.4 |
| | | 2,2′-Bipyridine | | | |
| *n*-Bu, Cl | −238.5 ± 1 | 980 | 47.3 | 179.2 | NR |
| *n*-Oct, Cl | −248.5 ± 1 | 988 | 47.3 | 159.5 | NR |
| | | 1,10-Phenanthroline | | | |
| *n*-Bu, Cl | −262.5 ± 1 | 1016 | 47.3 | 185.1 | NR |
| *n*-Oct Cl | −262.5 ± 1 | 1015 | 46.6 | 163.5 | NR |
| | | Miscellaneous Compounds | | | |
| $(CH_3)_4Sn$ | 0.0 | 337 | | | 54.1 |
| $(n-C_4H_9)_4Sn$ | −11.5 | 307 | 25.0 | 51.2 | 48.3 |
| $(CH_3)_2SnCl_2$ | 140.7 | 476 | | | 68.0[e] |
| $(n-C_4H_9)_2SnCl_2$ | 125.7 | 421 | 33.0 | 83.8 | 53.4 |
| $(n-C_8H_{17})_2SnCl_2$ | 125.4 | 430 | 32.1 | 79.0 | 54.2 |
| $(CH_3)_2Sn(acac)_2$[b] | −365 | 977 | | | 99.3 |
| $(n-C_4H_9)_2Sn(acac)_2$[d] | NL | 914 | 41 | 130 | NL |

[a] $^{117,119}Sn$ isotopic splitting not resolved. [b] Reference 2. [c] Reference 23. [d] Reference 41. [e] δ 85.1 in acetone-$d_6$. [f] NL = not listed. [g] NR = not resolved.

**Table IV.** Crystallographic Data and Coupling Constants for Octahedral Tin Complexes Utilized in Figures 2 and 3

| | complex | ∠C-Sn-C, deg | $^1J(^{119}Sn-^{13}C)$, Hz | $^2J(^{119}Sn-C-^1H)$, Hz | ref[a] |
|---|---|---|---|---|---|
| 1 | $(CH_3)_2Sn(acac)_2$ | 180 | 977 | 99.3 | 10, 2 |
| 2 | $(CH_3)_2Sn(ox)_2$ | 110.7 | 630 | 68.7 | 42, *b* |
| 3 | $(CH_3)_2Sn(Medtc)_2$ | 142.3 | 664 | 84.0 | 42, 23 |
| 4 | $(CH_3)_2Sn(Etdtc)_2$ | 136 | 664 | 84.0 | 43, 23 |
| 5 | $(CH_3)_2Sn(NO_2)_2$ | 144 | 81.6 | 28, 28 | |
| 6 | $(CH_3)_2Sn(amha)_2$ | 145.8 | 81.5 | 29, 29 | |
| 7 | $(n-C_4H_9)_2Sn(dbzm)_2$ | 180 | 880 | 98.1 | 32, *b* |

[a] First reference for X-ray data, second for NMR values. [b] This work.

with a standard error of estimate of 5.6° and a correlation coefficient equal to 0.978. Note that the coupling constants were calculated from frequency-locked $^{119}Sn$ NMR spectra, and therefore there is no interference from $^{117}Sn$ isotopic partners. Values of $\lvert ^2J(^{119}Sn-C-^1H)\rvert$ from Table II were inserted into eq 1, and several structural predictions and observations follow.

As a rule,[13] $R_2SnCh_2$ complexes prefer a trans arrangement when the ligand bite (distance between the two coordinating atoms) is large and tend to cis when the bite is small. For example, acetylacetonate-type ligands form a six-membered chelate-metal ring, and trans configurations are expected. On the basis of eq 1, the calculated C-Sn-C angles are 175-178° for the benzoylacetonates and dibenzoylmethanates tested. That is, trans structures are predicted within experimental error. This is in accord with light-scattering and Kerr effect measurements on $R_2Sn(dbzm)_2$ complexes.[14,18,19]

Both picolinates and tropolonates have smaller bites than the acac family ligands, and the skew (trapezoidal bipyramid, as in Figure 1) structural assignment was previously made for $R_2Sn(trop)_2$.[28] Our structural estimates for these two groups (119-143° for ∠C-Sn-C) indicate skew or cis-skew configurations. In the quinolinolate groups of complexes, the oxinates, with less steric crowding about the central atom, are nearly cis (109-120°),

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(28) Sham, T. K.; Tse, J. S.; Wellington, V.; Bancroft, G. M. *Can. J. Chem.* **1971**, *55*, 3487.

**Table V.** Structural Predictions of Six-Coordinated Dialkyltin Complexes in Solution

| | C–Sn–C angle (deg) structure indicator | | | | |
|---|---|---|---|---|---|
| ligand family | $^2J(^{119}\mathrm{Sn}–\mathrm{C}–^1\mathrm{H})$[b] | $^1J(^{119}\mathrm{Sn}–^{13}\mathrm{C})$[c] | light scattering[d] | Kerr effect[e] | Mössbauer[f] |
| acetylacetonate[a] | 180 | 177–180 | trans | | trans |
| benzoylacetonate | 175–178 | 175–180 | | | |
| dibenzoylmethanoate | 175–178 | 171–178 | >165 | trans–skew | |
| tropolonate | 119–143 | 124–129 | >skew | cis–skew | 136–146 |
| 1-picolinate | 123–131 | 141–151 | | | trans |
| 8-hydroxyquinolinolates | 109–120 | 123–127 | | cis | cis |
| 2-methyl-8-hydroxyquinolinolates | 119–126, 159 | 157–162, 168 | | | |
| 2,2′-bipyridine | | trans | | | trans |
| 1,10-phenanthroline | | trans | | | trans |

[a] NMR data from ref 2 and 10. [b] Range predicted from eq 1. [c] Range predicted from eq 2. [d] Reference 18. [e] Reference 14. [f] Reference 26.

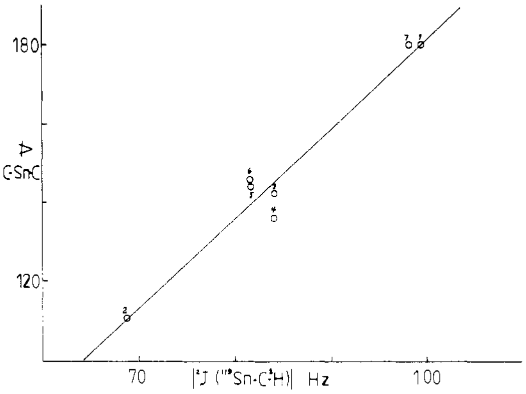

**Figure 2.** Plot of ∠C–Sn–C from crystallographic studies vs. $|^2J(^{119}\mathrm{Sn}–\mathrm{C}–^1\mathrm{H})|$ from octahedral tin complexes. Points referenced in Table IV.

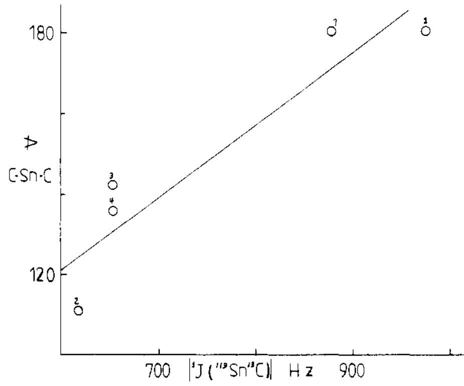

**Figure 3.** Plot of ∠C–Sn–C from crystallographic studies vs. $|^1J(^{119}\mathrm{Sn}–^{13}\mathrm{C})|$ from octahedral tin complexes. Points referenced in Table IV.

as reported earlier in a Kerr effect study.[14] The bulkier 2-methyloxinates force $R_2Sn(Meox)_2$ complexes into slightly larger C–Sn–C angles (119–126°). $(CH_3)_2Sn(Meox)_2$ (159°) is an extreme example of this effect, overriding the effects expected from the ligand bite size. These calculations are summarized in Table V.

Harrison and Richards[29] suggested that $|^2J(^{119}\mathrm{Sn}–\mathrm{C}–^1\mathrm{H})|$ values for $(CH_3)_2SnCh_2$ were consistent with structural retention in solution, but we note that complexes with highly unsymmetrical bidentate ligands appear to distort in solution from cis to skew. Our data indicate a similar, but weaker, effect on going from $-CH_3$ to $-n-C_8H_{17}$ within a $R_2Sn$ chelate family (such as tropolonates and oxinates). This is attributed to the larger alkyls repelling one another more strongly than do the methyl groups.

The presence of quadrupolar nuclei in the tin complexes broadens the signal and limits the resolution of fine structure in the $^{119}$Sn NMR spectra. This is especially true with the $R_2SnCl_2$ adducts, and to a lesser extent with $R_2Sn$ picolinates. Also, coordinating solvents lead to larger Sn–H coupling constants in $R_2SnCl_2$ species attributable to increased (4–6) Sn coordination number and forced trans structures as the solvent/chelate becomes more tightly bound to the tin. This effect was observed in the series with $(CH_3)_2SnCl_2$ in $CDCl_3$ ($|^2J|$ = 68.0 Hz), acetone-$d_6$ (85.1 Hz), and $Me_2SO$-$d_6$ (115 Hz)[30] but is not quantitatively related to the $R_2SnCh_2$ data herein.

**(2) $|^1J(^{119}\mathrm{Sn}–^{13}\mathrm{C})|$ Coupling.** The linear relationship noted in the previous section also exists for the C–Sn–C angle and the one-bond tin–carbon coupling constants, although the fit is not as good and there are only five points (see Figure 3). Therefore, the structural predictions are not as precise. A linear regression analysis of the data yields the equation

$$\angle \mathrm{C–Sn–C} = 0.178|^1J(^{119}\mathrm{Sn}–^{13}\mathrm{C})| + 14.74 \qquad (2)$$

Angles calculated from this relationship have a standard error calculated as ±12.1°, and the correlation coefficient for eq 2 equals 0.94.

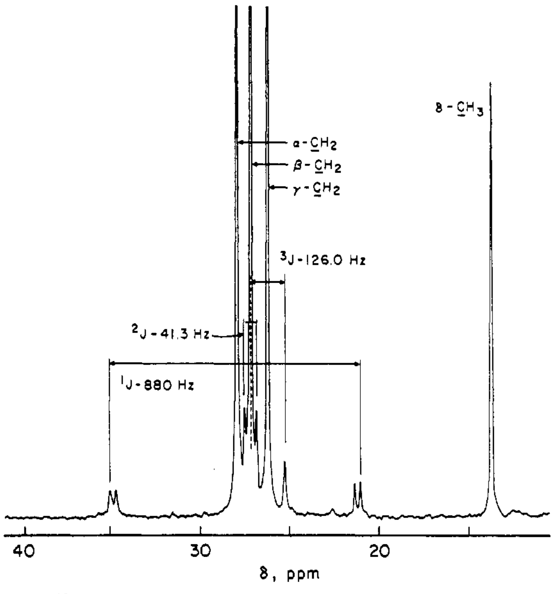

**Figure 4.** $^{13}$C NMR spectrum of $(n-C_4H_9)_2Sn(dbzm)_2$ relative to $Me_4Si$ (0.0 ppm).

Structural predictions are similar to those derived from $^2J(^{119}\mathrm{Sn}–\mathrm{C}–^1\mathrm{H})$ values (see Table V). acac-type ligands lead to trans organotin complexes; tropolonates and oxinates are associated with cis–skew structures; $R_2Sn$ picolinates have skew geometries; and complexes with 2-methyloxinate are trans–skew. The presence of covalently bound N and Cl in the phenanthroline and bipyrdine adducts, however, increases the Sn–C coupling constant, as reflected in the much-too-large "calculated" effective C–Sn–C angle of ~200°. This effect is noticeably weaker with the N-containing picolinates, oxinates, and 2-methyloxinates, which have only two N's and no Cl's bonded to the central atom.

**(3) Other $^{119}$Sn NMR Features. (a) $\delta(^{119}\mathrm{Sn})$.** The $^{119}$Sn NMR chemical shifts of related organotin complexes move upfield as the coordination number increases from 4 to 7 through a range of 600 ppm.[31] In this study, 22 six-coordinate tin complexes were

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(29) Harrison, P. G.; Richards, J. A. *J. Organomet. Chem.* **1980**, *185*, 9.
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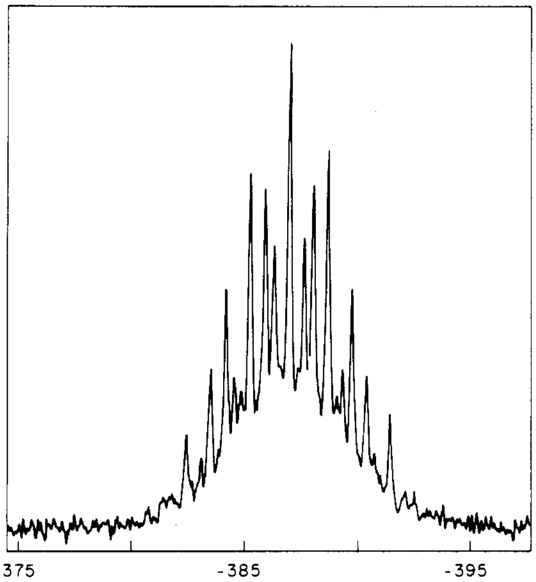

**Figure 5.** Proton-coupled $^{119}$Sn NMR spectrum of $(C_2H_5)_2$Sn(dbzm)$_2$ in $CDCl_3$. $|^2J(^{119}Sn–C–^1H) = 98.1$ Hz, $|^3J(^{119}Sn–C–C–^1H)| = 159.5$ Hz, and $\delta$ is relative to $(CH_3)_4$Sn.

examined, with $\delta(^{119}Sn)$ found to vary from −197 to −393 ppm (see Table II), and a trend to upfield shifts is noted with increasing ligand bite. The $\beta$-diketonates have large O,O bites. These ligands are labile, and the trans structure has a lower potential energy than the cis geometry. The time-averaged coordination number remains at or close to 6. The other ligands, having smaller N,O or O,O bites, attach within a distorted octahedral framework about Sn. The ($^{119}$Sn) values noted in this study are consistent with the earlier observation[31] of upfield shifts with increasing Sn coordination number.

**(b) $|^2J(^{119}Sn–C–^{13}C)|$ and $|^3J(^{119}Sn–C–C–^{13}C)|$.** As expected, $|^3J|$ exceeds $|^2J|$ (cf. Table II), but little structural information is available from these data. Both sets of coupling constants change by ligand family, similar to $|^1J(^{119}Sn–^{13}C|$ and $|^2J(^{119}Sn–C–^1H)|$, but as only one complex without a $(CH_3)_2$Sn skeleton[32] has been examined crystallographically, structural assignments from two- and three-bond Sn–C coupling constants are of questionable value.

**(c) $|^3J(^{119}Sn–C–C–^1H)|$.** Pereyre[33] noted that this coupling is not observed with complex R groups, even though $|^3J|$ should be greater than 100 Hz. This was true with all the $(n\text{-}C_4H_9)_2$Sn and $(n\text{-}C_8H_{17})_2$Sn complexes in this study, although each $^{119}$Sn NMR signal showed seven peaks instead of the expected five from ($-CH_2$–Sn–$CH_2-$). The two outermost peaks were weak and broad, and our conclusion is that $|^3J(^{119}Sn–C–C–^1H)| = 2|^2J(^{119}Sn–C–^1H)|$, within 1 Hz, for the *n*-butyl- and *n*-octyltin species. There is no suggested reason why this should be so, but the relation is consistent with the NMR spectra.

The $|^2J(^{119}Sn–C–^1H)|$ coupling constant from terminal $CH_3$ evolves from an electronic environment different from that of $\beta$-$CH_2$ and should differ in magnitude. This is attributable to the neighbor anisotropy effect, which is felt more strongly by $-CH_2-$ than $-CH_3$.[34] The complex $^{119}$Sn NMR spectrum of $(C_2H_5)_2$Sn(dbzm)$_2$, reproduced in Figure 5, has over 20 signals: this symmetric pattern was reduced to yield $|^3J(^{119}Sn–C–C–^1H)| = 159.5$ Hz. Similar spectra, although not as well resolved, were obtained from $(C_2H_5)_2$Sn(bzac)$_2$ [$|^3J| = 156.8$ Hz], $(C_2H_5)_2$Sn(ox)$_2$ [128.8 Hz], and $(C_2H_5)_2$Sn(Meox)$_2$ [141.1 Hz]. These coupling constants are slightly less than twice the corresponding $|^2J(^{119}Sn–C–^1H)|$ values listed in Table II. As with $|^1J$(Sn–C)$|$ and $|^2J$(Sn–C–C)$|$ values, $|^3J$(Sn–C–C–H)$|$ roughly parallels $|^2J$(Sn–C–H)$|$, but no structural characterization can be established due to the scarcity of data.

**(d) $|^1J(^{119}Sn–^{13}C)|$ vs. $|^2J(^{119}Sn–C–^1H)|$.** The two-bond Sn–C–H coupling constant was thought to measure the hybridization at the metal atom through the Fermi contact term, which is a primary contributor.[35] This approach is workable for tetraalkyl tin compounds, but electronegative atoms bonded to the tin alter the metal hybridization without concomitant changes in $|^2J(^{119}Sn–C–^1H)|$. The supposition of proportionality between $^2J$ and s-electron density on Sn is valid if a plot of $|^1J(^{119}Sn–^{13}C)|$ vs. $|^2J(^{119}Sn–C–^1H)|$ is linear and passes through the origin; otherwise, at least one of the coupling constants has appreciable contributions from other than the Fermi contact term. A plot of the appropriate *J* values from Table II is linear (correlation coefficient 0.987, standard error of estimate 1.5 Hz), but the *y* intercept is at 16.5 Hz. This further points out that there is no simple Fermi relationship between percent s character around the central Sn atom and the two-bond Sn–C–H coupling constants. Tin complexes are stabilized by donor–acceptor interactions between p–d orbitals, and much of the $|^2J(^{119}Sn–C–^1H)|$ variation is due to electron density changes on the H atom.

## Conclusions

Two-atom proton–tin NMR coupling constants have been shown to be a valuable structural aid for in-solution assignments of labile six-coordinated dialkyltin complexes. Because the $\alpha$-carbon protons are not in the tin coordination sphere, $|^2J(^{119}Sn–C–^1H)|$ is less affected by ligand-bonding variations than $|^1J(^{119}Sn–^{13}C)|$ and the Sn–H coupling constants yield a more consistent picture of molecular geometry. Backed by corroborating evidence from light-scattering[18] and Kerr effect[14] studies, dialkyltin species chelated to tropolonates, 2-methyloxinates, and picolinates are assigned trapezoidal-bipyramidal structures in solution. Similarly, the more common ligands ($\beta$-keto enolates and oxinates) have trans and cis geometries, respectively. Other NMR spectral parameters are dependent on the ligand bite size: namely, $\delta(^{119}Sn)$, tin electron density variations [as in plots of $|^1J(^{119}Sn–^{13}C)|$ vs. $|^2J(^{119}Sn–C–^1H)|$, and Sn–C dipole–dipole interactions [from $|^1J(^{119}Sn–^{13}C)|$]. $|^3J(^{119}Sn–C–C–^1H)|$ values from octahedral $(C_2H_5)$Sn complexes are reported for the first time.

Specifically, this study shows that multinuclear NMR can provide definitive structural information through metal–proton and metal–carbon coupling constants.

**Acknowledgment.** Many thanks to Dr. S. K. Brahma for supplying us with some of the required complexes and to Dr. Cecil Dybowski for several helpful discussions.

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