Journal of Organometallic Chemistry, 273 (1984) 47–59
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SYNTHESIS AND STRUCTURAL STUDY OF FIVE-COORDINATE TRIORGANOTIN(IV) TROPOLONATES AND DIBENZOYLMETHANATES

S.K. BRAHMA *, W.H. NELSON **
Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881 (U.S.A.)

and W.F. HOWARD, JR.
Department of Chemical Engineering, University of Delaware, Newark, Delaware 19711 (U.S.A.)

(Received January 26th, 1984)

Summary

The complexes [1,3-diphenyl-1,3-propanedionato]tricyclohexyltin(IV), (tropolonato)triphenyltin(IV), and (tropolonato)tricyclohexyltin(IV) have been prepared for the first time and have been found to be five-coordinate in the solid state. These and related five-coordinate complexes prepared previously have been studied by a variety of physical methods; ^{13}C NMR, UV, IR, Raman, dipole moments and the Kerr effect. While all structures are demonstrably five-coordinate, and all chelates bidentate in the solid state, the geometries of two of the complexes in solution appear to vary somewhat from the expected *fac* or *mer*. There is evidence from the solution Kerr effect and ^{13}C NMR that cyclohexyl derivatives may disproportionate.

Introduction

Neutral, penta-coordinate tin complexes are relatively rare, probably due to a pronounced tendency to "disproportionate" to form compounds of coordination number four and six in solution. For example, it has been noted [1] that:

$$2(CH_3)_3Sn(bzac) \rightarrow (CH_3)_4Sn + (CH_3)_2Sn(bzac)_2 \qquad (1)$$

(bzac = benzoylacetonate)

Like other coordinatively unsaturated structures five-coordinate tin complexes can form polymers in the solid state. In solution, however, all of these species have been observed to be monomers. Simple monomers of the type R_3SnCh (Ch^- = a bidentate chelate) can adopt two distinctly different structures based on the trigonal bipyramid, the *fac* and the *mer* (Fig. 1).

---

[*] On leave from the Chemistry Department, Asutosh College, Calcutta (India).

[**] To whom correspondence should be addressed.

0022-328X/84/$03.00

The first known penta-coordinate tin complex was prepared by Roncucci et al. [2,3]. The compound, $(C_6H_5)_3Sn(ox)$, ($ox^- =$ 8-quinolinolate) was reported to be four-coordinate with the oxinate nitrogen not bonded to tin. However, Okawara [4] later demonstrated that this molecule is five-coordinate and that the structure must be essentially trigonal bipyramidal. Martin [5] and co-workers prepared a series of compounds of the type $R_2Sn(ox)X$ where $R = CH_3$, C_2H_5 and C_6H_5 and $X^- = Cl^-$ or I^- Trigonal bipyramidal geometries were assigned primarily on the basis of infrared and proton magnetic resonance data. Tin–carbon bonds were shown to occupy axial positions in these species. More recently, Harrison et al. [6,7] carried out synthesis and X-ray analyses of crystalline, monomeric triphenyltin-*N*-phenyl, *N*-benzoylhydroxylamine derivatives. All of these have been shown to be very nearly *fac*. Later, Bancroft et al. [8] synthesized and structurally studied trimethyl- and triphenyl-tin complexes with single acetylacetonate ($acac^-$), benzoylacetonate ($bzac^-$), and dibenzoylmethanate ($dbzm^-$) rings. His X-ray studies showed $(C_6H_5)_3Sn(dbzm)$ to be *fac*. Accompanying Mössbauer quadrupole splitting pointed toward all triphenyl analogs being *fac* as well, while trimethyl derivatives appeared to be *mer*.

Because compounds containing a single chelate ring are rare, and because they are valuable as model compounds in the study of chelation behavior, we have attempted to synthesize additional derivatives and to compare those with previously prepared molecules. To more unambiguously determine solution structures, measurements of molecular Kerr constants and dipole moments have been made, and visible and infrared absorption spectra carefully measured and interpreted. Raman spectral data have been obtained as well, along with ^{13}C NMR chemical shift data.

Experimental

Materials and synthesis. Chlorotrimethyltin(IV), bromotris(cyclohexyl)tin(IV) and chlorotriphenyltin(IV) were purchased from Alpha and were used as received. Tropolone and dibenzoylmethane obtained from Aldrich or Eastman did not have to be purified prior to use in synthesis. The compounds studied were prepared by mixing the thallous salt of the ligand with the triorganotin halide in a fashion previously outlined [8–10]. The thallous salts were prepared by mixing thallous ethoxide with pure ligands in appropriate solvents as reported earlier [9,10]. Purities of thallous salts used as intermediates were checked by chemical analysis and by observing other known physical properties [9,10] including melting points. The trimethyltin dibenzoylmethanate and triphenyltin dibenzoylmethanate were prepared by the method of Bancroft [8] and checked by chemical analysis and melting

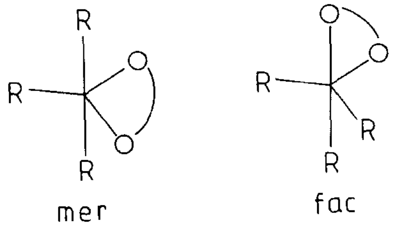

Fig. 1. *Mer*- and *fac*-isomers.

point. Elemental analyses were performed by Micro-Analysis, Inc. (Wilmington, DE). The following compounds have been synthesized for the first time.

[1,3-Diphenyl-1,3-propanedionato]tricyclohexyltin(IV), $(C_6H_{11})_3Sn(dbzm)$

Tricyclohexyltin bromide (1.12 g, 0.00250 mol) was added to thallous dibenzoylmethanate (1.073 g, 0.00250 mol) dissolved in 5 ml of dry benzene. The mixture was thoroughly stirred, and TlBr was removed by filtration. The solvent was removed on a rotary evaporator. After addition of a few drops of petroleum ether to facilitate precipitation, the liquid was cooled to −20 °C overnight. The pale yellow precipitate was filtered, washed with petroleum ether, and dried. Results: m.p. 135–137 °C. Analysis: Found: C, 68.37; H, 7.39. $C_{33}H_{44}O_2Sn$ calcd.: C, 67.02; H, 7.50%.

(Tropolonato)triphenyltin(IV), $(C_6H_5)_3Sn(trop)$

Triphenyltin chloride (1.926 g, 0.0050 mol) was added to thallous tropolonate (1.637 g, 0.0050 mol) in 50 ml of dry benzene and thoroughly stirred. TlCl was removed by filtration through paper, and the solvent removed under reduced pressure without warming. The faintly yellow product was recrystallized from benzene with a few drops of petroleum ether. The solution stood at 0 °C for several days before crystals formed. Results: m.p. 125–127 °C. Anal. Found; C, 62.74; H, 4.11. $C_{25}H_{20}O_2Sn$ calcd.: C, 63.74; H, 4.28%.

(Tropolonato)tricyclohexyltin(IV), $(C_6H_{11})_3Sn(trop)$

Thallous tropolonate (0.8190 g, 0.0025 mol) in 50 ml dry benzene was mixed with tricyclohexyltin bromide (1.1205 g, 0.0025 mol) and the mixture was thoroughly stirred. TlBr was removed by filtration through paper, and the solvent was removed under reduced pressure. The resulting product was stored at −20 °C after addition of a few drops of pentane to facilitate precipitation. The yellow product was filtered, washed with petroleum ether, and dried overnight. Results: m.p. 120–122 °C. Anal. Found: C, 60.70; H, 7.07. $C_{25}H_{38}O_2Sn$ calcd.: C, 61.37; H, 7.83%.

UV-VIS spectra

Spectra were obtained with a Cary Model 15 Spectrometer. Standard 10 mm quartz cells were used throughout. Experimental error in readings was ±2 nm. Data appear in Table 1.

Raman spectra

All Raman spectra were obtained with a Spex Model 1401 spectrometer. A 2 W argon ion laser was used as source providing lines at 488 and 514.5 nm. Samples were mounted in capillary tubes and viewed at 90 ° to the incident beam. Calibration by sulfate internal standard yielded accuracies of ± 2 cm^{-1}. Power levels were reduced until no sample heating effects were observed. Data are summarized in Tables 2 and 3.

IR spectra

Infrared absorption spectra were obtained with a Beckman Model·IR 4260 spectrometer. All samples were mounted as pressed KBr discs. Experimental error was ± 2 cm^{-1}. These data can be observed in Table 4.

Dipole moments

All measurements of the dielectric constants were by means of a WTW Model DM01 dipolemeter. Calculations were made using a method outlined by Guggenheim [11] and Smith [12].

The measurements of the dielectric constant increments appearing in Table 5 should be reliable to ±1%, even though very dilute solutions were used. Atomic polarizations have been neglected.

Refractive indices

Refractive index increments were determined at the Hg(435.8 nm) line to a precision of ±5% using a Phoenix BP-2000V differential refractometer. Solution densities exceeded solvent densities by less than 0.1% and were set equal to solvent densities in all calculations. These data also appear in Table 5.

A set of dipole moments measured for these complexes in solution, as well as values calculated for *fac*- and *mer*-isomers appear in Table 6.

Kerr effect data

Techniques for the measurement of the Kerr effect in non-conducting liquids have been described in detail [13,14]. Aroney has reviewed [15] progress in the application of the technique. Our apparatus used for measuring the Kerr effect is a modifiation of the one used by the Sydney group [10,13]. A 2 mW HeNe laser was used as a light source, and the intensity minima were measured with the aid of a photomultiplier.

Incremental changes in the dielectric constants, densities, refractive indices, and Kerr constants ($\Delta\varepsilon$, Δd, Δn and ΔB, respectively) were measured for solutions having solute weight fractions, w_2. The coefficients $\alpha\varepsilon_1$, β, γ and δ were derived by using the relationships

$$\begin{aligned} &\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/w_2 \\ &B = \Sigma\Delta d/(d_1\Sigma w_2) \\ &\gamma = \Sigma\Delta n/(n_2\Sigma w_2) \\ &\delta = \Sigma\Delta B/(B_2\Sigma w_2) \end{aligned}$$

The subscripts 1 and 2 refer to solvent and solute components, respectively. From these data tabulated in Table 7 can be calculated the solute dipole moments [16], and molar Kerr constants [13] shown in that table. Table 8 compares the experimentally determined Kerr constants with those calculated assuming a *fac*- or *mer*-structure. The term $_{\infty}(_{\mathrm{m}}K_2)$, which refers to the solute molar Kerr constant at infinite dilution, is obtained as

$$_{\infty}(_{\mathrm{m}}K_2) = {_{\mathrm{s}}K_1}(1 - \beta + \alpha + \delta - H\gamma - J\alpha\varepsilon)M_2$$

where $_{\mathrm{s}}K_1$ (the specific Kerr constant of the solvent), H, and J are solvent constants [17] and M_2 is the solute molecular weight.

^{13}C NMR

These were obtained in $CDCl_3$ at 20 °C using a Varian CFT 20 or a Bruker WM-250. The average acquisition time was 17 min for the five-coordinate complexes. Data are presented in Table 9.

Discussion

UV spectra

The spectra of Table 1 which show large extinction coefficients are consistent with the expected absorptions of ($\pi \rightarrow \pi^*$) ligand transitions. A comparison of absorption maxima in cyclohexane and benzene, respectively, shows the expected "red shift" for dibenzoylmethanates as the dielectric constant of the solvent increases. Tropolonates, on the other hand, show a "blue shift" even though extinction coefficients are high. It is possible that the "blue shift" is due to weak solvent adduct formation although there is no confirming spectral evidence.

Vibrational spectra

Infrared and Raman spectra and assignments are listed in Tables 2, 3, and 4. Assignments are tentative only since they are made on the basis of comparisons with assigned spectra of related compounds. In molecules of this size, it is not simple to make totally unambiguous assignments for a variety of experimental and theoretical reasons. A number of assignments are relatively certain, however. Most of these are associated with the ligand vibrations between 650 and 1600 cm^{-1}. The vibrations below 600 cm^{-1} associated with Sn–C and Sn–O modes are most useful in assessing the structures of the complexes (Table 3).

The vibrations associated with the phenyl groups [17–19] themselved are remarkably similar from compound to compound and provide the main source of features above 900 cm^{-1}. Nakamoto et al. [20], have studied Cu^{II} and Ni^{II} dibenzoylmethanates. Tin tropolonate infrared spectra have been studied by Okawara et al. [21]. Our assignments depend heavily upon the assumptions made in the early papers.

Infrared and Raman spectra very strongly indicate that both the dibenzoylmethanato and the tropolonato ligands are bidentate. Both ligands show marked and predicted decreases in the asymmetric C=O stretch. For tropolonates, infrared spectra are very similar to those of Rein and Herber [22] observed for similar six-coordinate tin complexes. For example, in $(C_6H_5)_3$Sn(trop) the C=O asymmetric

TABLE 1

ULTRAVIOLET ABSORPTION MAXIMA (nm) WITH CORRESPONDING EXTINCTION COEFFICIENTS, ε, ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}) IN FOUR SOLVENTS

Complexes	Ethanol	Chloroform	Cyclohexane	Benzene
$(C_6H_5)_3$Sn(dbzm)	343 (2.62)	341 (2.22)	337 (2.177)	346 (1.959)
$(CH_3)_3$Sn(dbzm)	342 (2.587)	342 (3.522)	337 (3.235)	345 (2.879)
$(C_6H_{11})_3$Sn(dbzm)	348 (3.19)	342 (4.192)	338 (2.84)	343 (2.939)
$(C_6H_5)_3$Sn(trop)	392 (0.314)	388 (0.813)	396 (0.644)	394 (0.604)
	370 (0.322)	370 (1.001)	386 (0.431)	382 (0.447)
	327 (0.604)	354 (1.177)	375 (0.329)	372 (0.377)
		326 (2.132)	365 (0.180)	326 (0.942)
			327 (0.879)	
$(C_6H_{11})_3$Sn(trop)	380 (1.075)	380 (1.059)	400 (1.103)	385 (0.549)
	325 (2.248)	329 (2.199)	390 (1.187)	332 (1.039)
			380 (1.117)	
			332 (2.42)	

TABLE 2

RAMAN DATA (cm^{-1}) FOR CRYSTALS (Relative intensities of peaks listed in brackets)

$(C_6H_5)_3$Sn(dbzm)	$(CH_3)_3$Sn(dbzm)	$(C_6H_{11})_3$Sn(dbzm)	$(C_6H_5)_3$Sn(trop)	$(C_6H_{11})_3$Sn(trop)	Assignment
1598 (89)	1598 (50)	1597 (86)	1594 (100)	1614 (82)	C=C stretch (A_1)
	1546 (4)				
1518 (13)	1518 (3)	1522 (5)	1522 (8)	1522 (9)	C=O stretch
1492 (32)	1490 (28)	1488 (27)	1472 (69)	1474 (44)	C=C stretch (A_1)
1444 (4)					
1441 (9)	1441 (10)	1440 (9)	1439 (85)	1430 (31)	C=C stretch (B_1)
1365 (84)	1360 (6)	1370 (5)		1372 (13)	
1312 (65)	1316 (50)	1314 (63)	1338 (20)		C=C stretch (B_1)
	1309 (43)				
1280 (100)	1289 (100)	1282 (100)	1256 (18)	1251 (10)	CH in plane bend (B_1)
1234 (5)	1230 (5)	1227 (3)		1222 (25)	
1182 (20)	1180 (10)	1183 (14)	1192 (23)	1177 (13)	CH in plane bend (A_1)
1159 (3)	1159 (3)	1159 (2)			CH in plane bend (B_1)
1126 (4)	1130 (3)	1133 (5)			
1065 (31)	1054 (43)	1055 (32)	1065 (16)	1078 (13)	CH in plane bend (B_1)
1023 (5)	1019 (8)	1021 (9)		1078 (13)	CH in plane bend (A_1) + ring vibr. (A_1)
999 (35)	1000 (15)	998 (36)	999 (92)		sym. ring vibr. (A_1)
941 (7)	932 (11)	938 (9)	969 (31)	972 (44)	CH-out of plane bend (B_2)
	852 (4)				
	810 (4)				
790 (5)	789 (6)				CH out of plane (B_2)
689 (5)	684 (4)	684 (5)			
666 (3)	670 (10)	658 (5)			

stretch drops from 1543 to 1510 cm^{-1}. The corresponding six-coordinate complexes showed the vibration between 1504 and 1509 cm^{-1}. The $(C_6H_{11})_3Sn(trop)$ complex absorbs at 1495 cm^{-1}. The reduction in the energy of the C=O stretching mode presumably is due to the reduction in the C=O bond order associated with coordination to tin. The 1510 cm^{-1} vibration of the triphenyl derivative is identical to the

TABLE 3

LOW ENERGY INFRARED[a] AND RAMAN DATA[b]

	$(C_6H_5)_3$-Sn(dbzm)	$(CH_3)_3$-Sn(dbzm)	$(C_6H_{11})_3$-Sn(dbzm)	$(C_6H_5)_3$-Sn(trop)	$(C_6H_{11})_3$-Sn(trop)	Assignment
IR	215w	500w	6600w	238vw	650w	Sn–R (ν_s)
R	220 (4)	498 (4)	–	221 (8)	659 (13)	Stretch
IR	257m	530w	615w	260w	695m	Sn–R (ν_{as})
R	260 (7)	538 (2)	616 (5)	267 (8)	–	Stretch
IR	365w	415w	410w	530w	520w	Sn–O
R	385 (4)	405 (8)	402 (5)	538 (16)	543 (19)	

[a] KBr disc. [b] Strength of peak in brackets (max = 100).

TABLE 4

INFRARED DATA (cm^{-1}) (KBr disc)[a]

$Ph_3Sn(dbzm)$	$Me_3Sn(dbzm)$	$Cyh_3Sn(dbzm)$	Ph_3SnT	Cyh_3SnT	Assignment
1594s	1588s	1595s	1594s	1590s	C=C stretch (A_1)
1550m	1550m	1550m			
1510m	1500m	1510m	1510s	1495m	C=O stretch
1475m	1480m	1466m	1478m		C=C stretch (A_1)
1450w	1450m	1448m			C=C stretch (B_1)
1427m					
1360s	1355s	1380s		1400s	
1310s	1300s	1305s		1320s	C=C stretch (B_1)
1285s	1285s	1285s	1260s	1250m	CH in plane bend (B_1)
1180m	1180m	1170s	1188m	1165s	CH in plane bend (A_1)
1157w	1160w	1150m	1158m		CH in plane bend (B_1)
1116m	1130m	1129m			
1090w	1090w	1090w			
1060s	1065w	1068w	1070s	1070s	CH in plane bend (B_1)
	1050s	1055s		1040w	
1020s	1015s	1022s	1025s	1020w	CH in plane bend (A_1) ring vibr. (A_1)
994m	995m	990s	1000s	985s	Sym. ring vibr. (A_1)
				970s	
938s	930s	932s	930s	910s	CH out of plane bend (B_2)
855w	–	875m	875vs	872s	CH bend (A_2)
–	–	835w		838s	
807vw	–	805vw			
780m	–				CH out of plane bend (B_2)
748m	760s	750s	765vs		
725s	715s	714s	720m		
692s	–	680s	690m		
674m	675s	668sh	–		

[a] Cyh = (C_6H_{11}); T = Tropolonate.

value shown by Cu(trop)$_2$ which has been shown by X-ray analysis [23] to possess two bidentate tropolonate groups. Raman spectra in these regions verify the infrared results.

Vibrational spectra for the penta-coordinate tin-dibenzoylmethanate complexes show that the dibenzoylmethanato ligand behaves as expected for a bidentate ligand. The C=O stretching vibration in Cu^{II} dibenzoylmethanate drops from above 1600 to 1544 cm^{-1}. The corresponding infrared vibrations in $(C_6H_5)_3$Sn(dbzm), $(CH_3)_3$Sn(dbzm), and $(C_6H_{11})_3$Sn(dbzm) lie between 1500 and 1550 cm^{-1}. Interestingly enough, the infrared spectra [9] of Sn(dbzm)$_2$Cl$_2$ reported earlier show C=C and C=O energies nearly identical to those of $(C_6H_5)_3$Sn(dbzm) and $(C_6H_{11})_3$Sn(dbzm). Once again, Raman spectra are consistent with the observation of a C=C stretching mode near 1595 cm^{-1}, but the C=O mode is nearer 1520 cm^{-1}. All data point to the presence of a bidentate dibenzoylmethanate ligand with C=O bonds of reduced order. In fact, the similarity of the infrared spectra of the dibenzoylmethanate ligand bound in vastly different environments suggests that the ligand retains its basic structural identity throughout.

The presence of Sn–R symmetric and antisymmetric vibrations active both in the infrared and Raman (Table 3) suggests that the *fac*-configuration predominates throughout the five-coordinate complexes. However, it could be consistent with the *mer*, or especially a structure intermediate between *fac* and *mer* as well. It is noticed also that the Sn–O stretching vibrations of the tropolonates are at substantially higher energy than those of corresponding dibenzoylmethanates. This suggests that the degree of covalent character in the Sn–O bonds of tropolonates may be higher than that of corresponding dibenzoylmethanates. Greater Raman intensities for tropolonate Sn–O vibrations also support this suggestion. The energies of the Sn–CH$_3$ vibrations are a little lower than those expected on the basis of earlier studies [24]. Sn–C modes associated with phenyl and cyclohexyl substituted tin complexes are also of lower energy than observed for analogous picolonates and oxides [25].

Dipole moments

Complexes of the sort studied here can exhibit large amounts of atom polarization which must be subtracted from the total polarization before dipole moments can be calculated with accuracy. The temperature dependence of $\Delta\varepsilon/w_2$ (Table 5) indicates that atom polarization is relatively small and can be ignored in this study. Actually, a comparison of calculated values of the orientation moments for *fac*- and *mer*-structures (Table 6) shows that there is little difference between the predicted moments for these candidate structures, and, as a consequence, the measured value of the dipole moment is of little use in distinguishing between the two. However, it is of definite interest to note that the experimental moments are near the calculated moments. This is additional evidence for the chelates being bidentate. It strongly suggests as well that the chelate ring moments must be very similar to the values measured [26] earlier for similar organometallic complexes.

The Kerr effect

Because the direction of the dipole moments with respect to the principal axis is the same for *fac*- and *mer*-isomers, it is not surprising that Kerr constants are positive and of similar magnitude for both isomer types. Data are probably consistent with the assignment of either a *fac*- or *mer*-geometry, although they do slightly favor the *fac*. The unusually large Kerr constants associated with the cyclohexyl derivatives suggest disproportionation in solution to tetracyclohexyl tin and the six-coordinate $(C_6H_{11})_2Sn(dbzm)_2$, since a distorted *trans* structure will

TABLE 5

DIELECTRIC CONSTANT AND REFRACTIVE INDEX DATA FOR CYCLOHEXANE SOLUTIONS AT DIFFERENT TEMPERATURES

Compound	T (°C)	$n_2^2 - n_1^2/w_2$	$\Delta\varepsilon/w_2$	μ(D)
$(C_6H_5)_3Sn(dbzm)$	25	0.328	2.07	4.21
	40	0.223	1.8	4.10
	60	0.20	1.75	4.19
$(C_6H_{11})_3Sn(dbzm)$	25	0.373	2.0	4.12
	40	0.30	1.75	3.99
	60	0.166	1.67	4.19
$(C_6H_5)_3Sn(trop)$	25	0.263	2.26	4.08
	40	0.167	2.095	4.10
	60	0.163	1.91	4.03
$(C_6H_{11})_3Sn(trop)$	25	0.208	2.02	3.96
	40	0.18	2.00	4.06
	60	0.166	1.7	3.85
$(CH_3)_3Sn(dbzm)$	25	0.205	4.167	5.21
	40	0.224	3.64	4.96
	60	0.183	3.33	4.91

TABLE 6

A COMPARISON OF OBSERVED MOLECULAR MOMENTS WITH MOMENTS CALCULATED FOR REGULAR *fac*- AND *mer*-TRIGONAL BIPYRAMIDAL STRUCTURES (D)

Compound	Sn–R Moment (calcd.)	Sn–Ring Moment (calcd.)	Mol. Moment (obsd.)	Calcd. molecular moments	
				fac	*mer*
$(C_6H_5)_3Sn(dbzm)$	1.1	2.0	4.21	3.56	3.1
$(C_6H_{11})_3Sn(dbzm)$	1.0	2.0	4.12	3.414	3.0
$(C_6H_5)_3Sn(trop)$	1.0	2.9	4.08	4.46	4.0
$(C_6H_{11})_3Sn(trop)$	1.0	2.9	3.96	4.31	3.9
$(CH_3)_3Sn(dbzm)$	0.6	2.0	5.21	2.85	2.6

TABLE 7

KERR EFFECT DATA AT 25 °C (Solvent cyclohexane)

Complex	$J\alpha\varepsilon_1$	β	γ	δ	$10^{12}\,({}_mK_2)$[a,b]
$(C_6H_5)_3Sn(dbzm)$	1.03	1.44	0.328	212	1601
$(CH_3)_3Sn(dbzm)$	2.073	3.928	0.175	825	4355
$(C_6H_{11})_3Sn(dbzm)$	0.995	3.17	0.277	1880	14747
$(C_6H_5)_3Sn(trop)$	1.124	1.65	0.263	530	3306
$(C_6H_{11})_3Sn(trop)$	1.005	1.92	0.208	1466	9477

[a] Kerr constant are expressed in e.s.u. mol^{-1}. $1m^5\ V^{-2}\ mol^{-1} = 0.8988 \times 10^{15}$ e.s.u. mol^{-1}. [b] Experimental error ~ ±10%.

have a large positive Kerr constant [27]. Light scattering studies not yet complete also show evidence for formation of the six-coordinate complex in solution.

Molecular optical anisotropies, $\gamma = b_2 - b_1$, (b_2, b_1 are principal molecular polarizability components) were calculated using previously determined anisotropy values of ligands [10,27,28] and other groups [15] and bonds. Simple group polarizability component additivity was assumed.

^{13}C NMR data

In order to determine the sensitivity of the ^{13}C chemical shift in organotin complexes as a probe of structural change, a number of four- and six-coordinate organotin compounds of known geometry have been studied along with penta-coordinate complexes (Table 9). With the aid of spin decoupling, the assignments become quit simple, especially since other substituted β-diketonate complexes have been studied previously [29].

Structure-related changes in the ^{13}C chemical shift are noted for the CH_2–Sn group comparing $(CH_3)_2SnCl_2$, octahedral *cis*-$(CH_3)_2Sn(ox)_2$, octahedral *trans*-$(CH_3)_2Sn(dbzm)_2$ and penta-coordinate $(CH_3)_3Sn(dbzm)$. Although the Sn–CH_3 methyl chemical shift is not very sensitive to the nature of the bonding at adjacent sites or even coordination number, the value of the shift in the penta-coordinate complex is closest to that of the "*trans*" structure, suggesting the presence of methyl groups in axial positions. However, a *mer*-isomer should have non-equivalent methyl groups, and only one peak is noted.

Related butyl derivatives which should be related closely to cyclohexyl derivatives also show small chemical shifts of α, β, γ and δ carbons as bond angle and coordination number change. It is obvious, however, that the carbon of the butyl group associated with the 1,10-phenanthroline and 2,2′-bipyridine adducts of dibutyltin dichloride are characterized by a very large down-field shift; i.e., from 27 to 42 ppm vs. TMS. This shift may be due either to steric crowding or the greater polarity of the bonding in the adducts.

An equally promising region is associated with the carbonyl carbons. Substantial differences appear in tropolonate, dibenzoylmethanate and benzoylacetylacetonate complex "carbonyl group" chemical shift values. The C=O chemical shift data, in

TABLE 8

A COMPARISON OF CALCULATED AND MEASURED KERR CONSTANTS

Complex	Structure	$10^{12}({}_{\mathrm{m}}K)$ (calcd.)	$10^{12}({}_{\mathrm{m}}K)$[a] (obsd.)
$(C_6H_5)_3Sn(dbzm)$	*fac*	2935	
$(C_6H_5)_3Sn(dbzm)$	*mer*	1463	1603
$(CH_3)_3Sn(dbzm)$	*fac*	4388	4355
$(CH_3)_3Sn(dbzm)$	*mer*	2211	
$(C_6H_{11})_3Sn(dbzm)$	*fac*	2819	14747
$(C_6H_{11})_3Sn(dbzm)$	*mer*	1404	
$(C_6H_5)_3Sn(trop)$	*fac*	3156	3306
$(C_6H_5)_3Sn(trop)$	*mer*	1729	
$(C_6H_{11})_3Sn(trop)$	*fac*	3293	9477
$(C_6H_{11})_3Sn(trop)$	*mer*	1635	

[a] See Table 7.

fact, should best discriminate between the *fac*- and *mer*-isomers. Clearly, for dibenzoylmethanates or tropolonates, both carbonyl carbons are equivalent for the *mer*-structures and should give rise to a single chemical shift value, while in the *fac*-structure the carbonyl oxygens occupy non-equivalent axial and equitorial sites and may be distinguishable. Unhappily, a *fac*-structure and a *mer*-structure will not be distinguishable if the differences between the axial and equitorial-bound carbonyl chemical shifts are small, or if ligand exchange is rapid.

The chemical shift data of $(CH_3)_3Sn(dbzm)$ are supportive of a *mer*-structure since there is only one observed C=O resonance. Unhappily, there is only one $Sn-CH_3$ peak also. This is consistent with neither the *fac*- nor *mer*-structures unless shifts of non-equivalent methyl groups bound to tin are unresolved. This is likely in light of the spectra of the complexes of known structure. The single C=O resonance makes a four-coordinate system very unlikely, of course, and is in agreement with conclusions of infrared data. Because Mössbauer and vibrational spectral data [8] also support the *mer*-structure, that structure is favored.

Somewhat surprisingly, the C=O shift data of the triphenyl and tricyclohexyltin dibenzoylmethanates also seem to support a *mer*-structure. Structure in the four major phenyl and cyclohexyl peaks is supportive of either *fac*- or *mer*-structures, but the sharp single C=O peak observed is more supportive of the *mer*. Of course, it is

TABLE 9

CHEMICAL SHIFTS (ppm) vs. TMS IN $CDCl_3$

Compound	Alkyl or phenyl	Ligand
$(CH_3)_2SnCl_2$	6.8	
$(C_4H_9)_2SnCl_2$	26.8(α), 26.7(β), 26.0(γ), 13.3(δ)	
$(CH_3)_2Sn(ox)_2$	7.0	112.9, 113.5, 121.2, 129.8, 130.2, 136.2, 138.4, 142.2, 157.5 (rings)
$(CH_3)_2Sn(dbzm)_2$	7.7	94.1(CH); [127.5, 128.3, 131.6, 139.5-rings]; 184.9 (C=O)
$(CH_3)_2Sn(bzac)_2$	7.6	97.0(CH); 28.7(CH-C) [127.3, 128.2, 131.2, 138.9-ring] [182.7, 192.9 (C=O)]
$(C_4H_9)_2SnCl_2\cdot$ophen	42.3(α); 27.7(β); 25.3(γ); 13.0(δ)	[124.9, 127.6, 129.7, 139.7, 140.0, 148.3] (rings)
$(C_4H_9)_2SnCl_2\cdot$bipy	41.6(α); 28.1(β), 25.8(γ); 13.4(δ)	[122.9, 126.4, 140.9, 148.5, 149.4] (rings)
$(CH_3)_3Sn(dbzm)$	7.5	93.7(CH); [127.3, 128.4, 131.8] (rings); 185.1 (C=O)
$(C_6H_{11})_3Sn(dbzm)$	45.8(α); 29.7(β); 28.8(γ); 26.8(δ)	93.8(CH) [127.3; 128.3, 131.3] (rings); 184.8 (C=O)
$(C_6H_5)_3Sn(dbzm)$	127.5, 128.1, 128.9, 136.9	94.9(CH); [127.4, 128.4, 131.7] (rings); 186.8 (C=O)
$(C_6H_{11})_3Sn(trop)$	43.5(α); 30.3(β); 28.8(γ); 26.8(δ)	[125.7, 126.2, 138.4, 138.7] (ring); [174.5, 177.0] (C=O)
$(C_6H_5)_3Sn(trop)$	127.6, 128.1, 128.8, 136.8	[129.9, 126.5, 137.9, 139.1] (ring)

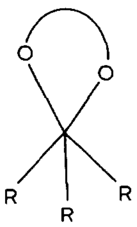

Fig. 2. A symmetrical tripod.

possible that the molecules are *fac* and the expected splitting has not been resolved. Such a possibility cannot be ignored, especially for $(C_6H_5)_3$Sn(dbzm) which has been shown to be *fac* [8] in the solid state. However, in that somewhat distorted crystal structure the phenyl groups occupy what appear to be nearly equivalent positions (Fig. 2). This alone could cause the lack of splitting of the C=O peaks.

In analogy with butyl derivatives, it is assumed that chemical shifts of the carbons of the cyclohexyl groups are in the order of $\alpha > \beta > \gamma > \delta$. What is very surprising is the large down-field shift of the carbon resonance. This may be due to strain associated with the bulk of the cyclohexyl groups, or to electronic effects. It is possible that the strained Sn–C bond may be the cause of the unexpectedly large Kerr constants shown by these derivatives if the strain has resulted in a Sn–C bond of unusually large polarizability anisotropy. Such a correlation is not unexpected, but has not been noted previously.

Tropolonate derivatives show cyclohexyl and phenyl chemical shifts which are very similar to those of the corresponding dibenzoylmethanates. This fact in itself is not very helpful in structural assignment. That the tricyclohexyl derivative shows a splitting of the C=O carbon peak is strongly supportive of the regular *fac*-structure for that molecule. It is unlikely that the splitting is due to the chelate binding at only one site, since the infrared and Raman spectra show a pronounced "red shift" associated with this bidentate tropolonate. While a single C=O peak for the triphenyl derivative might support a *mer*-structure, it is likely that the structure is analogous to the dibenzoylmethanate and has a structure closer to the *fac*-geometry with all these phenyl groups nearly equivalent in position showing a "tripod-like" arrangement (Fig. 2). Such a symmetrical tripod-type geometry would result in equivalent phenyl groups, as well as carbonyl carbon atoms. It should be noted that all structures except $(C_6H_{11})_3$Sn(trop) appear to behave in this general fashion with apparently equivalent monodentate organic groups and equivalent carbonyl carbon atoms.

Conclusions

Infrared and Raman spectra have demonstrated conclusively that the complexes studied are five-coordinate with the ligands bound through both oxygen atoms. ^{13}C NMR data support this finding. The vibrational spectra also support the assertion that the three carbon atoms attached to tin do not lie in the same plane. Dipole moments and Kerr constants in solution produce results best explained by a more symmetrical "tripod-like" structure which is very close to the trigonal bipyramidal *fac*-isomeric form, but which has three equivalent Sn–C bonds. It is noted that all the data is consistent with the assignment of a "symmetrical tripod" structure in solution.

Acknowledgement

Equipment used in this study was provided by grants from the National Science Foundation and Research Corporation. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. Thanks are due to the Department of Medicinal Chemistry for use of the Varian CFT 20 spectrometer.

References

1 R.C. Poller, Chemistry of Organotin Compounds, Academic Press, New York, 1970.
2 R. Barbieri, C. Faraglia, M. Guistiani, and L. Roncucci, J. Inorg. Nucl. Chem., 26 (1964) 203.
3 L. Roncucci, G. Faraglia, and R. Barbieri, J. Organomet. Chem., 1 (1964) 427.
4 K. Kawakami and R. Okawara, J. Organomet. Chem., 6 (1966) 249.
5 A.H. Westlake and D.F. Martin, J. Inorg. Nucl. Chem., 27 (1965) 1579.
6 P.G. Harrison, J. Organomet. Chem., 38 (1972) C5.
7 T.J. King and P.G. Harrison, J. Chem. Soc., Chem. Commun., (1972) 815.
8 G.M. Bancroft, B.W. Davies, N.C. Pyne, and T.K. Sham, J. Chem. Soc., Dalton Trans., (1975) 973.
9 W.H. Nelson and D.F. Martin, J. Inorg. Nucl. Chem., 27 (1965) 89.
10 W.H. Nelson and M.J. Aroney, Inorg. Chem., 12 (1973) 132.
11 E.A. Guggenheim, Trans. Faraday Soc., 45 (1949) 714.
12 J.W. Smith, Trans. Faraday Soc., 46 (1950) 394.
13 C.G. LeFevre and R.J.W. LeFevre in A. Weissberger (Ed.), Physical Methods of Organic Chemistry, Vol. 1, 3rd Ed., Interscience, N.Y., 1960, Ch. XXXVI.
14 C.G. LeFevre and R.J.W. LeFevre in C.A. Weissberger (Ed.), Techniques in Chemistry, Vol. I/III Wiley, N.Y., 1972, p. 399.
15 M.J. Aroney, Angew. Chem. Int. Ed. Engl., 16 (1977) 663.
16 R.J.W. LeFevre, Dipole Moments, Metheun, London, 1953.
17 R.J.W. LeFevre and R.K. Pierens, Aust. J. Chem., 25 (1972) 413.
18 R.R. Randle and D.H. Whiffen, Molecular Spectroscopy, Report on the Conference held in London in October, 1954, by the Institute of Petroleum, pp. 111–128, Institute of Petroleum, London, 1955.
19 D.H. Wiffen, Phil. Trans. Roy. Soc., A248 (1955) 131.
20 K. Nakamoto, Y. Morimoto, and A.E. Martell, J. Phys. Chem., 66 (1962) 346.
21 M. Komula, T. Tanaka, and R. Okawara, Inorg. Chim. Acta, 22 (1966) 1571.
22 A.J. Rein and R.H. Herber, J. Chem. Phys., 63 (1975) 1021.
23 J.M. Robertson, J. Chem. Soc., (1951) 1222.
24 M.M. McGrady and R.S. Tobias, J. Am. Chem. Soc., 87 (1965) 1909.
25 W.F. Howard, Jr. and W.H. Nelson, J. Mol. Struct., 53 (1979) 165.
26 C.Z. Moore and W.H. Nelson, Inorg. Chem., 8 (1969) 143.
27 S.K. Brahma and W.H. Nelson, Inorg. Chem., 21 (1982) 4076.
28 W.H. Nelson, W.F. Howard, Jr., and R. Pecora, Inorg. Chem., 21 (1982) 1483.
29 J.C. Hammel and J.A.S. Smith, J. Chem. Soc. A, (1970) 1855.