Bis(methyl-L-cysteinato)zinc(II), $Zn(SCH_2CHNH_2-CO_2CH_3)_2$ (III). Methyl L-cysteinate hydrochloride (1.72 g., 0.01 mole) was dissolved in a solution of 0.8 g. of sodium hydroxide (0.02 mole) in 50 ml. of water at 0°; to it was added with vigorous stirring a cold aqueous solution of 0.68 g. of zinc chloride (0.005 mole). The white precipitate formed was quickly filtered, washed three times with cold water, and recrystallized from a small amount of hot water. The white fine crystals were dried in vacuo over $CaCl_2$. Anal. Calcd. for $C_8H_{16}N_2S_2O_4Zn$: C, 28.79; H, 4.83; N, 8.39. Found: C, 28.84; H, 4.81; N, 8.59.

Bis(S-methyl-L-cysteinato)zinc(II), $Zn(CH_3SCH_2-CHNH_2CO_2)_2$ (IV). S-Methyl-L-cysteine (1.35 g., 0.01 mole) was dissolved in a solution of 0.4 g. of sodium hydroxide (0.01 mole) in 50 ml. of water; to it was added with stirring an aqueous solution of 0.68 g. of zinc chloride (0.005 mole). A white precipitate began to form soon after the addition. After stirring for 2 hr., the precipitate was filtered, washed several times with water until the filtrate gave a negative chloride test, and dried in vacuo over $CaCl_2$. Anal. Calcd. for $C_6H_{16}N_2S_2O_4Zn$: C, 28.79; H, 4.83; N, 8.39. Found: C, 28.63; H, 5.09; N, 8.30.

Synthesis, Structure, and Bonding of Complexes of Dimethyl- and Diphenyltin Ions With Bidentate Ligands[1]

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A series of coordination compounds of the general type R_2SnL_2 (R = methyl or phenyl; HL = 2,4-pentanedione, 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, picolinic acid, and 8-hydroxyquinoline) has been synthesized. Data are also reported for solutions of the complex with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. Studies of the infrared and Raman crystal and solution spectra together with proton n.m.r. measurements indicate that the bis(2,4-pentanediono)dimethyltin complex has the trans configuration, and vibrational assignments are made for this complex. The same structure is indicated by the infrared and n.m.r. spectra for the other complexes with β-diketones. For these trans octahedral complexes, a direct correlation is observed between the tin-methyl proton coupling constants and tin-oxygen bond strength deduced from the spectral data. The vibrational spectra and proton chemical shifts of the chelated acetylacetonato ligands are very similar to those observed in other acetylacetonates. The structure and bonding in these complexes is compared with that for the trans-aquodimethyltin(IV) cation and the trans-tetrahydroxidodimethylstannate(IV) anion where the structures have been established. The picolinato and 8-hydroxyquinolinato ligands appear to be coordinated primarily through the oxygen atoms.

Introduction

Several years ago, it was noted that the dimethyltin cation $[(CH_3)_2Sn(aq)]^{+2}$ was rather stable and behaved in aqueous solution very much like the tin(II) ion.[3]

More recently, there has been some discussion in the literature concerning the existence of cations of the type R_2Sn^{+2} in various compounds. It was suggested that dimethyltin formate contained linear $CH_3-Sn-CH_3^{+2}$ ions, since but one infrared active vibration was observed in the tin-carbon stretching region.[4] It was also suggested that interactions between the dimethyltin cation and the formate anions were very weak, because there were only slight differences in the carbonyl stretching region between the infrared spectra of sodium formate and dimethyltin formate. It was pointed out by Beattie and Gilson that the effective symmetry of a free and of a bridging carboxylate ion is the same, and the bands in the carbonyl stretching region could be explained equally well with a model involving bridging carboxylate groups.[5]

The question of whether dialkyltin cations exist or not is essentially one of semantics. In solution $[(CH_3)_2Sn(aq)]^{+2}$ behaves much like other divalent cations. On the other hand, most multivalent ions in complexes containing nitrogen or oxygen donor atoms form bonds with sufficient covalent character to give metal–ligand vibrations detectable in the Raman and infrared spectra. Using this as a criterion for the nonexistence of free ions, one is hard pressed to find free cations in compounds with other than alkali or alkaline earth ions.

Recent Raman, infrared, and n.m.r. studies on aqueous solutions of dimethyltin compounds have shown that the linear $CH_3-Sn-CH_3^{+2}$ structure exists in these solutions.[6] It would be expected that four water oxygens would coordinate to the tin atom in a

(3) E. G. Rochow, D. Seyferth, and A. C. Smith, Jr., J. Am. Chem. Soc., 75, 3099 (1953).

(4) R. Okawara, D. E. Webster, and E. G. Rochow, ibid., 82, 3287 (1960).

(5) I. R. Beattie and T. Gilson, J. Chem. Soc., 2585 (1961).

(6) M. M. McGrady and R. S. Tobias, Inorg. Chem., 3, 1157 (1964).

plane giving essentially octahedral coordination about the tin. It is convenient to picture the dimethyltin species in solution as a simple aquated linear cation, since the tin–oxygen bonds are so polar that no Sn–O vibration is observed in the Raman spectrum of 1 M solutions. It was suggested by McGrady and Tobias[6] that diorganometallic ions would generally adopt such a linear configuration in aqueous solution. Studies on the hydrolysis of the dimethyltin cation indicated the existence of four stepwise proton transfer equilibria.[7–9] The tetrahydroxidodimethylstannate(IV) anion which is formed in strongly alkaline solutions was shown by Raman and proton n.m.r. spectra to have the *trans* configuration.[9] The hydroxo groups are considerably better donors than water, and a Raman line due to tin–oxygen bond stretching is observed for the anion.

From these observations, it can be concluded that the dimethyltin cation behaves in many ways like other divalent cations. From the stereochemical point of view, the methyl groups tend to adopt *trans* positions in the species that have been studied which have contained rather electronegative donor atoms. This leads to a coordination number of four for the dimethyltin cation and the square-planar configuration for these four ligands. This effect can be attributed, at least partially, to a tendency to maximize the s-character in the bonds to carbon.[6] This is in accord with Bent's generalization that the s-character tends to be a maximum in the bonds to the least electronegative elements.[10] An analogous effect has been noted in five-coordinate stereochemistry where maximization of the s-character in the bonds to carbon leads to the more electronegative groups adopting axial positions in R_3MX_2 compounds.[11]

On the basis of these considerations, the dialkyl- and diaryltin ions would be expected to form a new class of complexes with four donor atoms arranged in a square plane. The ligand stereochemistry should resemble that of Pd(II) where the d_{z^2} electron pair has the same stereochemical effect as the alkyl or aryl groups in R_2Sn^{+2}. Probably the first case in which this effect has been noted was in $[(CH_3)_2SnCl_4]^{-2}$, where the square-planar arrangement of the chlorides occurs.[12] A complex of the dimethyltin ion with acetylacetone was noted several years ago,[13] and we[6] as well as Kawasaki, *et al.*,[14] have noted that bis(2,4-pentanediono)dimethyltin appeared to have the same linear $CH_3–Sn–CH_3^{+2}$ skeleton as did the aquodimethyltin cation and hence should have coplanar chelate rings.

In this paper we describe the syntheses and structures of several complexes of the dimethyltin and diphenyltin ions with bidentate ligands which have nitrogen and oxygen donor atoms.

(7) R. S. Tobias, I. Ogrins, and B. A. Nevett, *Inorg. Chem.*, **1**, 638 (1962).
(8) R. S. Tobias and M. Yasuda, *Can. J. Chem.*, **42**, 781 (1964).
(9) R. S. Tobias and C. E. Freidline, *Inorg. Chem.*, **4**, 215 (1965).
(10) H. A. Bent, *J. Inorg. Nucl. Chem.*, **19**, 43 (1961).
(11) E. L. Muetterties, W. Mahler, K. J. Packer, and N. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).
(12) I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).
(13) R. F. Riley and W. Erby, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 1957, p. 11-N.
(14) Y. Kawasaki, T. Tanaka, and R. Okawara, *Bull. Chem. Soc. Japan*, **27**, 903 (1964).

Experimental

Reagents. Reagent grade benzene, chloroform, carbon tetrachloride, absolute ethanol, methanol, anhydrous ether, and practical petroleum ether were used without further purification.

Dimethyltin dichloride was obtained from M and T Chemicals, Inc., Rahway, N. J., and was purified by recrystallization from benzene and petroleum ether "C" (observed m.p. 108°; lit.[15] m.p. 107.5–108.5°).

Diphenyltin dichloride was also obtained from M and T Chemicals and was purified by recrystallization from benzene, observed m.p. 41–42°; lit.[15] m.p. 42–44°.

Dimethyltin oxide was precipitated from an aqueous solution of dimethyltin dichloride by the addition of aqueous ammonia. The precipitate was washed with water until it was free of chloride ion and dried overnight in a vacuum oven at 60°. *Anal.* Calcd. for $(CH_3)_2SnO$: Sn, 72.0. Found: Sn, 72.4.

Acetylacetone obtained from Matheson Coleman and Bell was purified by distillation from $CaCl_2$, b.p. 134–135°.

The ligands 1,3-diphenyl-1,3-propanedione, 1-phenyl-1,3-butanedione, and 8-hydroxyquinoline were used as obtained from Eastman Chemicals.

Eastman picolinic acid was recrystallized from benzene; 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was used as obtained from Columbia Organic Chemicals Co. *Anal.* Calcd. for $C_5H_2F_6O_2$: C, 28.86; H, 0.97; F, 54.79. Found: C, 29.99; H, 1.67; F, 53.25.

Analyses. Tin was determined gravimetrically as SnO_2 in Vycor test tubes according to the method of Luijten and van der Kerk.[16] In the compound with hexafluoroacetylacetone, tin was oxidized to SnO_2 in a platinum crucible as described by Okawara and Rochow.[17] Samples were analyzed for carbon, hydrogen, fluorine, and nitrogen by Clark Microanalytical Laboratories, Urbana, Ill.

Molecular Weights. These were determined cryoscopically using a Beckmann thermometer freezing point apparatus. Reagent grade benzene was used as a solvent without further purification. Bromoform was distilled from $CaCl_2$ at *ca.* 2.6 mm. pressure and stored in the dark.

Raman Spectra. The Raman spectra were recorded photoelectrically with a Cary Model 81 spectrophotometer using the general procedure described earlier.[6] The crystal spectra were obtained using both a conical cell patterned after that of Busey and Keller[18] and a straight cell with an internal diameter of 4 mm., both using the 7-mm. cell optics of the Cary 81 spectrophotometer. Although the conical cell is far more efficient than the straight cell, fairly good spectra could be obtained with the latter cell because of the high Raman intensities of these complexes. It was found possible to identify the strongly polarized lines even in the crystal spectra by using the cylindrical polarizers supplied with the instrument. Frequencies

(15) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).
(16) J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, Middlesex, England, 1955, p. 84.
(17) R. Okawara and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3285 (1960).
(18) R. H. Busey and O. L. Keller, Jr., *J. Chem. Phys.*, **41**, 215 (1964).

for sharp lines are believed to be accurate to ±2 cm.$^{-1}$.

Infrared Spectra. The infrared spectra were obtained with a Perkin-Elmer Model 521 grating spectrometer. Calibration of the instrument was effected with polystyrene film.

Nuclear Magnetic Resonance Spectra. Proton n.m.r. spectra were determined with either a Varian DP-60 spectrometer operating at 56.4 Mc./sec. and with a sample temperature of 28° or with a Varian A-60 spectrometer at 32°. Coupling constants and chemical shifts were determined by the side-band technique. The coupling constants are believed to be accurate to ±1 c.p.s. and the chemical shifts to ±0.02 p.p.m.

Preparation of Complexes. Most of the complexes were synthesized several times. The analyses and molecular weights reported are the mean of the results on the different preparations.

Bis(2,4-pentanediono)dimethyltin [(CH₃)₂Sn(acac)₂]. A suspension of 8.0 g. (0.05 mole) of dimethyltin oxide in 40 ml. of acetylacetone was refluxed for several hours. On cooling, colorless crystals of bis(2,4-pentanediono)-dimethyltin precipitated from the solution. The product was filtered and dried overnight in a vacuum oven at 60°. Recrystallization was from benzene in the presence of a small amount of free acetylacetone. The compound did not appear to melt or decompose below 300°. *Anal.* Calcd. for $C_{12}H_{20}O_4Sn$: C, 41.54; H, 5.81; Sn, 34.21; mol. wt., 347. Found: C, 41.25; H, 5.69; Sn, 34.2; mol. wt. (in benzene), 335.

Bis(2,4-pentanediono)diphenyltin [(C₆H₅)₂Sn(acac)₂]. A solution of 6.9 g. (0.02 mole) of diphenyltin dichloride in 100 ml. of absolute ethanol was added to a solution of 4.9 g. (0.04 mole) of sodium acetylacetonate in 100 ml. of absolute ethanol. The sodium acetylacetonate was prepared by adding thin strips of sodium metal to a solution of acetylacetone in anhydrous ether. The mixture containing the complex was cooled in an ice bath, and the sodium chloride produced was filtered off. The ethanol was removed on a rotary evaporator; the colorless product was recrystallized from benzene containing a small amount of free acetylacetone. The product was stored in a desiccator since it hydrolyzes readily. Decomposition begins at 125°. *Anal.* Calcd. for $C_{22}H_{26}O_4Sn$: C, 56.08; H, 5.14; Sn 25.20. Found: C, 55.31; H, 5.01; Sn, 26.0.

Bis(1-phenyl-1,3-butanediono)dimethyltin [(CH₃)₂Sn(bzac)₂]. A suspension of 1.6 g. (0.01 mole) of dimethyltin oxide in a solution containing 6.4 g. (0.04 mole) of 1-phenyl-1,3-butanedione in 50 ml. of benzene was refluxed for several hours. After the (CH₃)₂SnO had dissolved completely, the benzene was removed, and the colorless product was washed several times with small amounts of ethanol, m.p. 134–135°. *Anal.* Calcd. for $C_{22}H_{24}O_4Sn$: C, 56.08; H, 5.14; Sn, 25.20. Found: C, 56.16; H, 5.11; Sn, 25.0.

Bis(1,3-diphenyl-1,3-propanediono)dimethyltin [(CH₃)₂Sn(dbzm)]. A suspension of 2.2 g. (0.13 mole) of dimethyltin oxide in a solution containing 9.0 g. (0.04 mole) of 1,3-diphenyl-1,3-propanedione in 50 ml. of benzene was refluxed for several hours. After the oxide had dissolved completely, the benzene was removed, and the yellow product was washed several

times with small amounts of ethanol to remove the excess ligand, m.p. 189–191. *Anal.* Calcd. for $C_{32}H_{28}O_4Sn$: C, 64.57; H, 4.74; Sn, 19.94. Found: C, 64.32; H, 4.85; Sn, 19.9.

Bis(picolinato)dimethyltin [(CH₃)₂Sn(pic)₂]. A suspension of 3.3 g. (0.02 mole) of dimethyltin oxide and 4.9 g. (0.04 mole) of picolinic acid in a mixture of 150 ml. of benzene and 50 ml. of methanol was heated until all of the oxide had dissolved. The solvent was removed on a rotary evaporator, and the colorless complex was recrystallized from a benzene–methanol mixture, m.p. 267–268°. *Anal.* Calcd. for $C_{14}H_{14}N_2O_4Sn$: C, 42.80; H, 3.59; N, 7.13; Sn, 30.20: mol. wt., 393. Found: C, 42.54; H, 3.82; N, 7.03; Sn, 29.7; mol. wt. (in bromoform), 435.

Bis(8-hydroxyquinolinato)dimethyltin [(CH₃)₂Sn(oxinate)₂]. This compound, which together with the di-n-butyl analog[19] has been reported earlier,[20] was synthesized according to the procedure of Tanaka, et al.[20] *Anal.* Calcd. for $C_{22}H_{18}N_2O_2Sn$: C, 54.97; H, 4.11; N, 6.41. Found: C, 55.24; H, 3.94; N, 6.57.

Attempted Synthesis of Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanediono)dimethyltin [(CH₃)₂Sn(hfacac)₂]. Dimethyltin oxide reacts readily with hexafluoroacetylacetone at room temperature, indicating that a complex is formed easily. In the presence of any excess ligand, it is extremely difficult to isolate any solid from the mixture. The white solid which was isolated from solutions containing a 2:1 mole ratio mixture of hexafluoroacetylacetone and dimethyltin oxide in inert solvents varied over a rather wide range in composition from synthesis to synthesis. Attempts to purify the product by sublimation were also unsuccessful. *Anal.* Calcd. for $C_{12}H_8F_{12}O_4Sn$: C, 25.61; H, 1.43; F, 40.50; Sn, 21.1. Found for a typical sample: C, 22.41; H, 2.43; F, 27.25; Sn, 35.0. N.m.r. spectra were obtained in the presence of a slight excess of ligand.

Results

Raman and Infrared Spectra. The frequencies observed in the infrared spectrum of bis(2,4-pentanediono)dimethyltin and of bis(2,4-pentanediono)diphenyltin are tabulated in Table I. For comparison, the frequencies for the *trans*-tetraaquodimethyltin(IV) cation[6] are given as are the frequencies for bis(2,4-pentanediono)palladium(II).[21] In the case of the spectrum of the complex of diphenyltin(IV), the vibrations of the phenyl groups have been deleted. This can be done with some certainty, since these vibrations vary little from one phenyltin compound to another. The data of Griffith and Derwish for diphenyltin dichloride[22] and of Poller for diphenyltin dichloride and diphenyl tin oxide[23] were used for this purpose.

Figure 1 shows the infrared spectra of bis(2,4-pentanediono)dimethyltin, bis(2,4-pentanediono)di-

(19) G. E. Coates, "Organometallic Compounds," 2nd Ed., Methuen, London, 1960, p. 190.
(20) T. Tanaka, M. Komura, Y. Kawasaki, and R. Okawara, *J. Organometal. Chem.*, **1**, 484 (1964).
(21) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).
(22) V. S. Griffith and G. A. W. Derwish, *J. Mol. Spectry.*, **5**, 148 (1960).
(23) R. C. Poller, *J. Inorg. Nucl. Chem.*, **24**, 593 (1962).

Table I. Infrared Spectra of the Acetylacetonato Complexes

$\bar{\nu}$, cm.$^{-1}$ ^{a}				
$(CH_3)_2Sn(acac)_2$	$[(CH_3)_2Sn(OH_2)_4]^{+2}$ ^{b}	$(C_6H_5)_2Sn(acac)_2$	$Pd(acac)_2$ ^{c}	Assignment
3070 w, bd		d, e	d	$\nu(C_2-H)(acac)$
2995 w, bd	3020			$\nu_{as}(C-H)(Sn-CH_3)$
2970 m, shoulder				$\nu_{as}(C-H)(C-CH_3)$
2920 w, bd	2935			$\nu_s(C-H)$
1565 s, m sh		1582 m, sh	1570	$\nu(C\cdots C)(B_2)$
		1555 m, sh	1547	
				$\nu(C\cdots O)(A_1)$
1515 s, sh		1518 s, sh	1523	
1445 m, v bd		1420 vw, sh	1430	$\nu(C\cdots O) +$
				$(C-H) (B_2)$
				$\delta_s(CH_3)(acac)$
1370 s, v bd	1403	1365 s, m bd	1395	
				$\delta_{as}(CH_3)(Sn-CH_3)$
1253 s, bd		1262 s, sh	1273	$\nu(C\cdots C) +$
				$(C-CH_3)(A_1)$
1198 w, sh	1202	1190 vvw, sh	1199	$\delta(C-H)(B_2)$
1181 w, sh		1175 vvw, sh		$\delta_s(CH_3)(Sn-CH_3)$
1012 s, sh		1011 m, sh	1022	$\rho_r(CH_3)$
918 s, sh		920 s, sh	936	$\nu(C-CH_3) +$
				$(C\cdots O)(A_1, B_2)$
798 m, sh		794 w, sh		$\rho_r(CH_3)(Sn-CH_3)$
775 w, m sh		781 w, sh	781	$\pi(C-H)$
712 vvw, sh		723 m, sh		
655 m, sh		660 w, sh	697	νRing def. $+$
				$(M-O)(A_1)$
645 m, sh		649 w, sh	676	$\nu(C-CH_3) +$
				$(M-O)(B_2)$
570 m, sh	582			$\nu_{as}(Sn-C_2)$
550 m, sh		558 m, sh	659	$\pi(C-H)$
400 m, m bd		450 m, v sh	464	$\nu_{as}(M-O_4)$
		443 w, sh	442	
				$\pi(C-H)$
		402 w, sh		

^{a} v = very, w = weak, m = medium, s = strong, sh = sharp, bd = broad. ^{b} Data of McGrady and Tobias.[8] ^{c} Data of Nakamoto, *et al.*[21] ^{d} C–H stretching vibrations omitted. ^{e} Phenyl vibrations omitted.

Table II. Raman Spectra of Bis(acetylacetonato)dimethyltin(IV)

$\bar{\nu}$, cm.$^{-1}$			
Crystalline $(CH_3)_2Sn(acac)_2$	Solution^a $(CH_3)_2Sn(acac)_2$	Aqueous^b $[(CH_3)_2Sn(OH)_4^{-2}]$	Assignment
3090 m, sh			$\nu(C_2-H)(acac)$
3010 m, bd	3000	3000	$\nu_{as}(C-H)(Sn-CH_3)$
2980 m, bd			
			$\nu_{as}(C-H)(C-CH_3)$
2965 m, bd			
2920 s, sh, p	2920 w, sh	2924	$\nu_s(C-H)$
1590 vw, vv bd	1600 m, bd		$\nu(C\cdots C)(B_2)$
	1525 w, bd		$\nu(C\cdots O)(A_1)$
1368 s, sh, p	1365 m, sh		$\delta_s(CH_3)(acac)$
1311 w, sh, dp	1300 w, bd		
1262 vvs, sh, p	1262 ms, sh		$\nu(C\cdots C) +$
			$(C-CH_3)(A_1)$
1207 m, sh		1200	$\delta_s(CH_3)(Sn-CH_3)$
1198 m, sh	1195 w, sh		$\delta(C-H)(B_2)$
1033 w, bd, dp	1030 w, bd		$\rho_r(CH_3)$
928 ms, sh, dp	929 m, sh		$\nu(C-CH_3) +$
			$(C\cdots O)(A_1, B_2)$
668 ms, sh, p(?)	665 mw, m bd		Ring def. $+$
			$(Sn-O)(A_1)$
567 w, sh, dp	560 w, bd		$\pi(C-H)$
514 s, sh, p	518 s, sh	523	$\nu_s(Sn-C_2)$
414 s, sh, p	415 s, m sh	555	$\nu_s(Sn-O_4)$
220 m			

^{a} Average of values for benzene and carbon tetrachloride solutions. ^{b} Data from Tobias and Freidline.[9]

phenyltin, bis(1-phenyl-1,3-butanediono)dimethyltin, bis(1,3-diphenyl-1,3-propanediono)dimethyltin, bis(picolinato)dimethyltin(IV), and bis(hexafluoroacetylacetonato)dimethyltin in the region from 400 to 700 cm.$^{-1}$ where Sn–C$_2$ and Sn–O$_4$ skeletal stretching vibrations would be expected.

Table II gives the frequencies from the Raman crystal spectrum of bis(2,4-pentanediono)dimethyltin together with the solution frequencies. Benzene and carbon tetrachloride were used as solvents in order to cover the entire region from 400 to 3000 cm.$^{-1}$. For comparison, the Raman spectrum for the *trans*-tetra-hydroxidodimethylstannate(IV) anion in aqueous solution is included in the table.
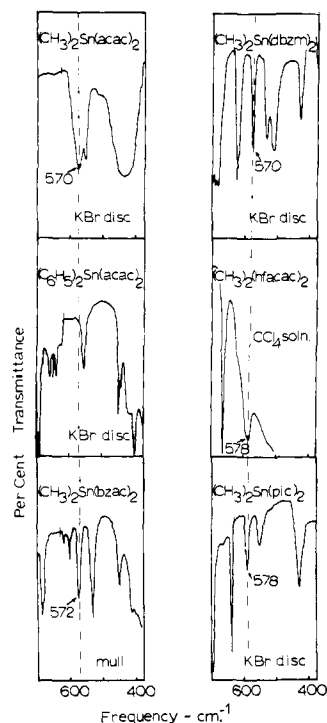
Figure 1. Infrared spectra of the β-diketo complexes in the Sn–C$_2$ stretching region.

Figure 2. Infrared spectrum of bis(2,4-pentanediono)dimethyltin in a KBr disk.

Figure 2 shows the infrared spectrum of bis(2,4-pentanediono)dimethyltin taken using a KBr disk, and Figure 3 gives the corresponding Raman crystal spectrum for comparison. Relatively few solid compounds have been studied by photoelectric Raman spectroscopy and to our knowledge this is the first such measurement on a coordination compound. In addition to the usual advantages which accrue from having both the Raman and infrared spectra, there are certain additional benefits. The Raman lines are much sharper than the infrared bands with the crystalline samples, and the low frequency region where metal ligand vibrations appear is especially easy to investigate. The spectrum illustrated is one of the poorest which we have obtained, for the compound showed a rather high background radiation, presumably because of fluorescence. This effect has been noted previously for pure liquid dimethyltin dichloride.[24] Surprisingly, it also has proved to be possible to identify the Raman lines arising from totally symmetrical vibrations when these give strongly polarized scattering in spite of the optical inhomogeneity of the sample, and this information is noted in Table II.

N.m.r. Spectra. Table III gives values for the ^{117}Sn–C–H and ^{119}Sn–C–H coupling constants for the dimethyltin chelates. Values are also given for the chemical shifts of the protons in methyl groups bound

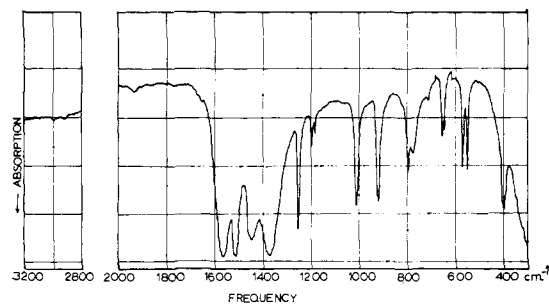(24) W. F. Edgell and C. H. Ward, *J. Mol. Spectry.*, **8**, 343 (1962).

to tin. In addition, values are tabulated for the chemical shifts of the single hydrogen attached to the central carbon in the β-diketo ligands.

Table III. Tin Proton Coupling Constants and Proton Chemical Shifts for Several Dimethyltin Chelates in Deuteriochloroform Solution

Compound	$J(^{117}SnCH)$, c.p.s.	$J(^{119}SnCH)$, c.p.s.	τ^a (SnCH$_3$), p.p.m.	τ^a (C$_2$H), p.p.m.
(CH$_3$)$_2$Sn(hfacac)$_2$	99.0	103.4	8.91	3.79
(CH$_3$)$_2$Sn(acac)$_2$	95.0	99.3	9.51	4.73
(CH$_3$)$_2$Sn(dbzm)$_2$	93.8	96.9	9.07	3.25
(CH$_3$)$_2$Sn(pic)$_2$	73.5	77.6	9.40	. . .
(CH$_3$)$_2$Sn(oxinate)$_2$	67.9	71.2	9.56	. . .

^{a} $\tau_{\text{tetramethylsilane}} = 10$.

The value for the chemical shift of the C$_2$–H proton in the acetylacetonato ring was found to be $\tau = 4.62$ p.p.m. for the bis(2,4-pentanediono)diphenyltin compared to 4.73 for bis(2,4-pentanediono)dimethyltin, both measured in CDCl$_3$ solution. In the n.m.r. spectrum, only a single, sharp resonance was observed under high resolution for the protons of the acetylacetonato methyl groups.
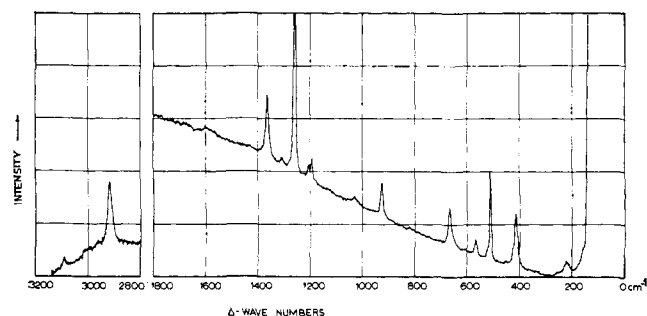
Figure 3. Raman crystal spectrum of bis(2,4-pentanediono)-dimethyltin.

Because of the relatively low solubility of the chelate compounds, it was not possible to obtain values for the ^{13}C–H coupling constants for the methyl groups bonded to tin. Studies on other compounds have indicated that these spin–spin coupling constants vary little even when the coordination number of tin increases from four to six. Values for some typical dimethyltin

Compound	Concn.	Solvent	$J(^{117}Sn-CH)$, c.p.s.	$J(^{119}Sn-CH)$, c.p.s.	$(J^{13}C-H)$, c.p.s.
(CH₃)₂SnCl₂	14.4%	CDCl₃	66.5	69.8	137.2
(CH₃)₂Sn(ClO₄)₂	2.0 M	H₂O	102.0	107.0	135.2
(CH₃)₂Sn(NO₃)₂	1.9 M	H₂O	104.3	108.7	135.4
K₂[(CH₃)₂Sn(OH)₄]	0.6 M	1 M KOH	78.4	82.7	. . .
(CH₃)₂Sn(OCH₃)²⁵	1.5 M	CCl₄	71.3	74.4	. . .

compounds are given in Table IV together with data for the tin–proton coupling constants.

Discussion

Structure of the Complexes. Studies on the hydrolysis of the dimethyltin(IV) ion in aqueous solution have indicated that dimethyltin oxide should be rather strongly basic.[7,8] This is borne out by the successful synthesis of the β-diketo and picolinato complexes by the direct reaction of dimethyltin oxide and the ligand conjugate acid.

With the symmetrical ligands, only two geometrical isomers are possible, and these are illustrated in Figure 4. The isomer with the *trans* R groups should have effective D₂ₕ symmetry assuming planar chelate rings and free rotation of the R groups. The effective symmetry of the complex with *cis* R groups would be C₂ with the same assumptions.
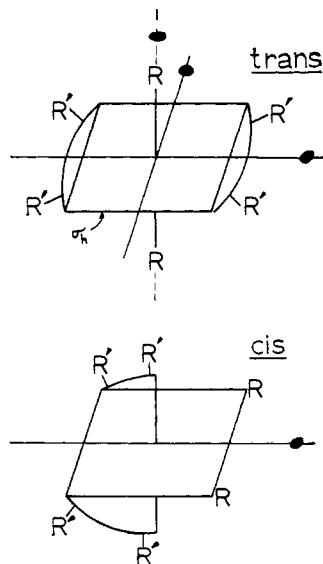

Figure 4. Possible geometrical isomers for a bis complex of a diorganotin cation with a symmetrical bidentate ligand.

Since the isomer with *trans* R groups possesses an effective center of symmetry, skeletal modes symmetrical with respect to inversion should be Raman active only and those antisymmetrical should be infrared active only. In the case of the *cis* complex, all skeletal modes should be both Raman and infrared active. The highest skeletal frequency would be expected to arise from tin–carbon bond stretching. In the case of the

linear aquo [(CH₃)₂Sn⁺²] cation with D₃d symmetry, which for skeletal vibrations can be treated in terms of point group D∞ₕ, the symmetrical tin–carbon stretching frequency is found at 529 ± 2 cm.⁻¹ in the Raman solution spectra and the antisymmetrical tin–carbon vibration at ca. 582 cm.⁻¹ in the infrared spectra of thin films of the solution.[6] For solutions of the *trans*-tetrahydroxidodimethylstannate(IV) anion, the tin–carbon symmetric stretch is observed at 523 ± 2 cm.⁻¹ in the Raman solution spectra.[9] For the aquo-monochloro complex of the dimethyltin(IV) cation which has effective C₂ᵥ symmetry, the symmetrical stretch is observed at 518 cm.⁻¹ and the antisymmetrical stretch at 577 cm.⁻¹ in the Raman solution spectra.[6]

Since (CH₃)₂Sn(acac)₂ is the simplest of all of the complexes structurally, its spectra given in Tables I and II will be considered in detail. In the Raman spectra, lines are observed at 567 cm.⁻¹ in the crystal spectrum and at 560 cm.⁻¹ in the solution spectra; but these lines are tentatively assigned to an out-of-plane vibration of the ligand. No lines attributable to the antisymmetric Sn–C₂ stretch were therefore observed. The symmetrical stretch is observed as a strong, polarized line at 514 cm.⁻¹ in the crystalline sample and at 518 cm.⁻¹ in solution. Examination of the infrared spectra illustrated in Figure 1 shows that all of the dimethyltin complexes have a band at 570 to 578 cm.⁻¹ which is absent in the diphenyltin chelate, and this is assigned to the antisymmetrical tin–carbon stretch. In addition the ligand out-of-plane vibration gives a band at ca. 550 to 560 cm.⁻¹ in the spectra of the acetylacetone complexes. There is no band which can be assigned logically to the symmetrical stretch. The Raman and infrared spectra then indicate that (CH₃)₂-Sn(acac)₂ has the *trans* arrangement of methyl groups; however, because of the complexity of the spectra these assignments are by no means certain.

By examination of Figure 4, it is seen that for symmetrical β-diketo ligands, all four ligand R' groups form a symmetrically equivalent set in the *trans* complex. Since there is only a twofold axis in the *cis* complex, the molecule has two sets of two symmetrically equivalent R' groups. Fay and Piper[26] have found splittings of 0.6–1 c.p.s. at 60 Mc./sec. for nonequivalent methyl protons in tris(1-phenyl-1,3-butanediono) complexes. In complexes such as *cis*-diamminebis-(ethylenediamine)cobalt(III) perchlorate, the splittings of nonequivalent protons bound to nitrogen in the ethylenediamine ligand are of the order of 10–20 c.p.s.[27] measured in aqueous solution. Since no splitting of the ring methyl proton signal could be observed in any of the spectra for (CH₃)₂Sn(acac)₂, this too indicates that the complex has the *trans* structure. It is also possible that the splittings were too small to be resolved by our spectrometer; however, this seems unlikely, for the line widths of sharp proton resonances run under comparable conditions are less than 0.3 c.p.s. In the case of (C₆H₅)₂Sn(acac)₂ also, only a single methyl signal was obtained, indicating that this complex too has the *trans* configuration and that the phenyl groups probably are rotating freely.

Finally, as a means of examining the structure of these complexes, the tin–proton spin–spin coupling constants

(25) W. Gerrard, J. B. Leane, E. F. Mooney, and R. G. Rees, *Spectrochim. Acta*, **19**, 1964 (1963).

(26) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).
(27) Private communication, Dr. S. T. Spees, Jr.

were measured. It has been noted that the coupling constants in dimethyltin compounds are very sensitive to the nature of the bonding in the compound.[28] It has also been suggested that a linear relation holds between the degree of s-character in the tin orbitals directed to·carbon and the coupling constants.[29,30] The approximate validity of this linear relation is supported by the fact that the coupling constants for the linear aquodimethyltin cation lead to a value of 49% for the s-character in the tin–carbon bonds relative to an assumed 25% s-character in tetrahedral $(CH_3)_4Sn$.[6] The hybridization in the C orbitals appear, to remain essentially constant, since the ^{13}C–H coupling constants are about the same from one dimethyltin compound to another as is shown by the data in Table IV. Recent measurements of the tin–proton coupling constants for the *trans*-tetrahydroxidodimethylstannate-(IV) anion,[8] however, gave considerably smaller values than observed for the aquo cation as is indicated by the data in Table IV. If the Fermi contact term is the only important one in determining the coupling constants, this would indicate that the distribution of s-character among the tin orbitals is influenced not only be changes in the C–Sn–C angle but also by variations of the donor strength of the ligands. Nevertheless, the fact that the coupling constants for bis(2,4-pentanediono)dimethyltin are intermediate between the values for the aquo and hydroxo complexes, both of which have the *trans* structure, gives strong support to the postulated *trans* structure for $(CH_3)_2Sn(acac)_2$. The similar values listed in Table III for the coupling constants in the complexes with the other β-diketo ligands indicates that these have the same *trans* arrangement of the methyl groups bound to tin.

Vibrational Assignments. The fundamentals of $(CH_3)_2Sn(acac)_2$ were assigned on the basis of the normal coordinate studies by Nakamoto and co-workers on metal acetylacetonates[21,31,32] and the measurements at low frequencies carried out by Dismukes, Jones, and Bailar[33] together with the assignments of McGrady and Tobias[6] for *trans*-$[(CH_3)_2Sn(aq)]^{+2}$ and of Tobias and Freidline[9] for *trans*-$[(CH_3)_2Sn(OH)_4]^{-2}$. These assignments are given in Tables I and II.

Since $(CH_3)_2Sn(acac)_2$ appears to have the *trans* configuration and studies on the *trans*-tetrahydroxidodimethylstannate(IV) ion have indicated that there is essentially no coupling between the tin–carbon and tin–oxygen vibrations, the assignments were made assuming local C_{2v} symmetry for the chelate ring and D_{3d} symmetry for the dimethyltin ion. Although there should be coupling between the tin–oxygen vibrations of the two chelate rings, this treatment of the ligand vibrations in terms of a 1:1 complex has proved fairly satisfactory.[31] Assignments were readily made for the dimethyltin group, and the ligand fundamentals other than those involving metal–oxygen bond stretching contributions are very similar in all acetylacetonate

complexes.[21,31,32,34] The corresponding ligand vibrations for $(C_6H_5)_2Sn(acac)_2$ are also listed in Table I.

The normal coordinate analysis of Nakamoto, *et al.*, considered only the in-plane vibrations of the acetylacetonato group which belong to symmetry species A_1 and B_2, and our Raman spectra are in reasonable agreement with their assignments. One curious feature of the Raman spectra is that the totally symmetrical C∸O vibration which would be expected above 1500 cm.$^{-1}$ is not observed in the Raman crystal spectrum and only weakly if at all in the solution spectrum. A similar effect occurs in the solution spectra of $Al(acac)_3$, $Ga(acac)_3$, and $In(acac)_3$.[35] The Raman spectrum of acetylacetone itself has a very strong line at 1596 cm.$^{-1}$[36] which has no counterpart in the complex spectrum.

The strong, polarized line in the Raman crystal spectrum at 414 cm.$^{-1}$ and in solution at 415 cm.$^{-1}$ can be assigned definitely to a totally symmetrical tin–oxygen stretching vibration. The band assigned to tin–oxygen stretching in the infrared is at 400 cm.$^{-1}$ indicating relatively weak coupling of the stretching vibrations involving the two rings. The low frequency line at 220 cm.$^{-1}$ is a ligand vibration, for a similar line is observed for pure acetylacetone[36]; and a ligand in-plane deformation is predicted at *ca.* 200 cm.$^{-1}$ by the normal coordinate calculations.[31]

Bonding. All of the complexes which have been discussed have two relatively nonpolar tin–carbon bonds and four highly polar tin–oxygen bonds. Because of the appreciable s–p separation in the post-transition elements, it would be expected that the tin 5s-orbital would be involved almost entirely in the two tin–carbon bonds. Taking the z axis along the C–Sn–C skeleton, both the tin $5p_z$ and the $5d_{z^2}$ as well as the 5s have the proper symmetry to be used in bonding the methyl carbons. Because of the high energy and diffuse character, little d-orbital mixing should occur, and the axial bonds would be expected to be primarily sp-hybrids.

The fact that the tin–proton coupling constants double in going from $(CH_3)_4Sn$ with essentially sp^3 hybridization to $[(CH_3)_2Sn(aq)]^{+2}$ where sp hybridization is expected tends to support the interpretation of these coupling constant changes in terms of the Fermi contact term.

For σ-bonding to the four oxygens in the equatorial plane, only the tin $5d_{z^2}$, $5d_{x^2-y^2}$, $5p_x$, and $5p_y$ have the proper symmetry, since the 5s is maximized in the axial bonds. Considering the highly ionic character of the tin–oxygen bonds, it is likely that the bonding orbitals are derived mainly from the tin $5p_x$ and $5p_y$ orbitals as suggested originally by Pimentel for ICl_4^{-} [37] and considered in the context of molecular orbitals by Rundle.[38]

As the bonds in the equatorial plane become more like the axial bonds, the tin 5s-character should become more uniformly distributed among all six bonds. If the Fermi contact term dominates in the spin–spin

(28) J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 326 (1961).

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

(30) G. P. van der Kelen, *Nature*, **193**, 1069 (1962).

(31) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(32) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

(33) J. P. Dismukes, L. H. Jones, and J. C. Bailar, *J. Phys. Chem.*, **65**, 792 (1961).

(34) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 217.

(35) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 513 (1964).

(36) K. W. F. Kohlrausch and A. Pongratz, *Ber.*, **B67**, 1465 (1934).

(37) G. Pimentel, *J. Chem. Phys.*, **19**, 447 (1951).

(38) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

coupling, the tin–methyl proton coupling constants would be expected to decrease as the equatorial bonds become more covalent. A regular decrease is noted in the data of Table III for the series of *trans* complexes: $[(CH_3)Sn(OH_2)_4]^{+2}$ $(CH_3)_2Sn(hfacac)_2$, $(CH_3)_2Sn(acac)_2$, $(CH_3)_2Sn(dbzm)_2$, and $[(CH_3)_2Sn(OH)_4]^{-2}$. This is also the order of the metal–oxygen bond strength. The bonds to water are very polar; Nakamoto, *et al.*,[39] have observed an increase in the metal–oxygen stretching force constants for complexes in the order hfacac < acac < dbzm; and from the Raman data for the hydroxo complex,[9] the tin–oxygen stretching force constant is of the order of 3.7 mdynes/Å. and larger than for acetylacetonato chelates.

The coupling constants for the complexes with picolinate and 8-hydroxyquinolinate are surprisingly small and comparable to the value for dimethoxy-dimethyltin. In solution, these ligands may be co-ordinated primarily through oxygen, although the visible spectra tend to indicate some interaction of the nitrogen.[20,40]

Much has been written in recent years concerning the question of p_π–d_π bonding in acetylacetonato complexes. The vibrational spectra of the chelate ring in these complexes are typical for acetylacetonates and the proton n.m.r. spectra are also similar to those for chelated acetylacetone. In deuteriochloroform, the signal for the hydrogen on the central carbon of the chelate ring appears at τ = 4.73 p.p.m. in $(CH_3)_2$-$Sn(acac)_2$ and at 4.62 p.p.m. in $(C_6H_5)_2Sn(acac)_2$. Smith and Thwaites found an average τ of 4.66 p.p.m. for acetylacetonato complexes in carbon tetrachloride.[41] In $[Si(acac)_3][HCl_2]$ where appreciable π-bonding would be expected, a τ of 3.74 p.p.m. was observed in chloroform solution.[42,43]

(39) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962).

(40) R. Roncucci, G. Faraglia, and R. Barbieri, *J. Organometal Chem.*, **1**, 427 (1964).

(41) J. A. S. Smith and J. D. Thwaites, *Discussions Faraday Soc.*, **34**, 143 (1962).

(42) R. E. Hester, *Chem. Ind.* (London), 1397 (1963).

(43) NOTE ADDED IN PROOF. Since the preparation of this paper, the syntheses of several β-diketo complexes of diphenyltin(IV) have been reported [W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 89 (1965)]. Attempts to resolve the complexes with D-lactose columns failed, and this is in accord with the *trans* structure assigned in this paper to $(C_6H_5)_2Sn(acac)_2$.