100% larger. The buffer has at least two effects: (1) the acetate ion complexes Pb(II) reducing the effect of Pb(II) suppression and (2) the acetic acid acts as a general acid catalyst with $k_{\mathrm{HAc}}{}^{\mathrm{CdCy}} \simeq 5 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$. As shown in Table III the acetate reduction of the Pb(II) suppression is the larger effect as can be seen for the data at pH 5. The acetic acid acceleration is more important at pH 4 but is still a minor contribution to k_0. There may be additional effects but they were not sorted out.

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A Dipole Moment Study of Six-Coordinate Organotin Chelate Compounds

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Diphenyl-, dimethyl-, diethyl-, and dibutyltin acetylacetonates, dibenzoylmethanates, and hexafluoroacetylacetonates have been synthesized, and their structures have been studied in benzene and cyclohexane solutions. Polarization measurements obtained at several temperatures show that the complexes possess orientation dipole moments of 2.0–4.0 D. It appears likely that the molecules possess structures of the *cis*-octahedral type with most exhibiting some distortion from the regular geometry. The distortion appears to vary regularly with the electronegativities of the organic substituents. Supplementary infrared, ultraviolet, and nmr data, respectively, are consistent with the assumptions (1) that the complexes are six-coordinate, (2) that tin–oxygen bonds are of a simple polar type lacking $(p \rightarrow d)\pi$ character, and (3) that exchange is very rapid at room temperature for the β-ketoenolate groups.

Introduction

Several groups of workers[1-5] in the past few years have prepared neutral organotin complexes of the type R_2SnCh_2. The organic substituent, R, apparently can be either an alkyl or an aromatic group while the ligand, Ch^-, can be one of a variety of bidentate types possessing oxygen or nitrogen donor atoms. In prior work the complexes studied have been shown to be monomeric and six-coordinate.[1,2] An extensive structural study[1] of bis(2,4-pentanedionato)dimethyltin(IV) and several closely related compounds has indicated that only one of three possible isomers, the *trans* (D_{2h}), is stable in benzene and chloroform solutions. A very recent X-ray study[6] of bis(8-quinolinolato)dimethyltin(IV), on the other hand, points to the stability of a distorted *cis*-type structure for that molecule.

Most evidence accumulated[1,2] using physical techniques is consistent with the assignment of *trans* structures to phenyl and methyl derivatives, but the same evidence is not basically inconsistent with the assignment of structures of lower symmetry. For instance, the observation[2] that bis(2,4-pentanedionato)diphenyltin(IV) is not resolved upon passing in solution through a *d*-lactose column is consistent with the assignment of a *trans* structure. Yet a *cis*-type molecule would behave in similar fashion if rates of racemization were rapid enough to result in the loss of optical activity. The fact that chloroform solutions of bis(2,4-pentanedionato)dimethyltin(IV) exhibit only two methyl proton nmr peaks with areas under them showing a ratio of 2:1 can be explained in terms of a *cis* structure characterized by a rapid rate of ligand exchange as well as a *trans* structure. Infrared spectral data are hardly definitive since spectra of acetylacetonate complexes have been shown to be very similar regardless of structure. The Raman spectra[1] provide the most convincing argument in favor of the *trans* structure of bis(2,4-pentanedionato)dimethyltin(IV) since lines have been observed corresponding to both Sn–C and Sn–O symmetrical stretching vibrations. Yet, the totally symmetrical C–O vibration expected to be Raman active is missing in the above compound. Bis(2,4-pentanedionato)diphenyltin(IV) in solution has been shown[2] to exhibit large values of the polarization which could be due to an orientation dipole moment of 3.9 D or to a very large value of the atomic polarization.

The large polarization value is worth further investigation since dielectric constant measurements over a temperature range should clearly allow the distinction to be made between true orientation polarization and atomic polarization. A zero value of the dipole moment would be strong evidence for a *trans* (D_{2h}) structure. To determine the structures of molecules of the type R_2SnCh_2 a number of compounds have been synthesized and their electronic and total polarizations have been measured in solution.

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

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(3) R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.* (Amsterdam), **4**, 237 (1965).

(4) R. Barbieri, G. Faroglia, M. Gustiniani, and L. Roncucci, *J. Inorg. Nucl. Chem.*, **26**, 203 (1964).

(5) L. Roncucci, G. Faroglia, and R. Barbieri, *J. Organometal. Chem.* (Amsterdam), **1**, 427 (1964).

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Experimental Section

Reagents.—All solvents were of reagent grade and were used without further purification in synthetic work. Benzene and cyclohexane used in dipole moment measurements were distilled from a sodium–potassium amalgam and were used immediately. Dimethyltin dichloride and diethyltin dichloride obtained from City Chemical Corp. and dibutyltin dichloride donated by Carlisle Chemical Works were found to be pure and were used without further purification. Pure dibutyltin oxide and diethyltin oxide were obtained from M and T Corp. 1,3-Diphenylpropanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, and thallous formate purchased from Eastman Organic Chemicals, Inc., and 2,4-pentanedione obtained from Aldrich Chemical Corp. were pure enough to use without further treatment. 2,4-Pentanedionatothallium(I),[7] 1,3-diphenyl-1,3-propanedionatothallium(I), 1,1,1,-5,5,5-hexafluoro-2,4-pentanedionatothallium(I), and dimethyltin oxide were prepared using established techniques. The melting or boiling points of all reagents were checked against literature values and found to be in close agreement.

Analyses.—All analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

Molecular Weights.—Molecular weights were determined for most compounds using a Mechrolab Model 301A vapor pressure osmometer. Solutions were usually 0.1% solute by weight. All weights were determined cryoscopically in benzene. Actually the cryoscopic method was found to be by far the most satisfactory, especially for the acetylacetonates and hexafluoroacetylacetonates which react rapidly with moisture in the atmosphere.

Infrared Spectra.—The infrared spectra were obtained with either a Baird-Atomic or a Beckman IR-8 spectrometer.

Ultraviolet Spectra.—All spectra were obtained at 25° using a Beckman Model DK-2 or a Cary 15 recording spectrometer.

Dielectric Constants.—Values were measured using a WTW Model DM01 dipolemeter. The instrument was calibrated at several temperatures with dry reagent grade benzene and cyclohexane. Refractive indices (4358 Å) were obtained at 25° using a Phoenix Model BP-2000V differential refractometer.

Preparation of Complexes.—Although acetylacetone will react directly with tin oxides, it is impossible to prepare pure diethyltin and dibutyltin acetylacetonates by that route, because of the difficulty of separating acetylacetone remaining in excess from the products. The thallous salt synthesis described below appears at present to be the only satisfactory technique reported to date for ethyl or butyl derivatives. Techniques which require the distillation of the product are to be avoided since all derivatives appear to decompose upon melting to form oils from which extraction of the pure product is very difficult.

Bis(1,3-diphenyl-1,3-propanedionato)diphenyltin(IV), $(C_6H_5)_2$Sn(dbzm)$_2$.—Thallous dibenzoylmethane (9.95 g, 0.0233 mol) was added to diphenyltin dichloride (4.00 g, 0.01165 mol) in 30 ml of benzene. The mixture was warmed slightly and thoroughly stirred. TlCl was removed by filtering the warm solution through paper. Purification was accomplished by recrystallizaion from benzene. The yellow crystals precipitated only after several hours at 0°; mp 240–242°. *Anal.* Calcd for $C_{42}H_{32}O_4Sn$: C, 70.20; H, 4.46; mol wt, 719. Found: C, 70.06; H, 4.28; mol wt, 729 (in benzene).

Bis(1,3-diphenyl-1,3-propanedionato)dimethyltin(IV), $(CH_3)_2$Sn(dbzm)$_2$.—Dimethyltin oxide (1.00 g, 0.00607 mol) was added to dibenzoylmethane (2.75 g, 0.0122 mol) dissolved in 30 ml of dry benzene and refluxed for 15 hr. The clear solution was decanted and the solvent was removed on a rotary evaporator. The yellow product was purified by recrystallization from petroleum ether (bp 90–110°) with a few drops of benzene added at reflux to effect solution; mp 189–191°. *Anal.* Calcd for $C_{32}H_{28}O_4Sn$: C, 64.51; H, 4.71; mol wt, 595. Found: C, 64.64; H, 4.88; mol wt, 392 (in benzene).

Bis(1,3-diphenyl-1,3-propanedionato)diethyltin(IV), $(C_2H_5)_2$Sn(dbzm)$_2$.—Dibenzoylmethane (3.635 g, 0.0162 mol) was added to diethyltin oxide (1.560 g, 0.0081 mol) in 30 ml of benzene and refluxed for 5 hr. The clear solution was decanted and the solvent was removed on a rotary evaporator. The yellow product was purified by recrystallization from acetonitrile with a few drops of benzene added at reflux to complete solution; mp 146–148°. *Anal.* Calcd for $C_{34}H_{32}O_4Sn$: C, 65.47; H, 5.21; mol wt, 623. Found: C, 65.36; H, 5.08; mol wt, 585 (in benzene).

Bis(1,3-diphenyl-1,3-propanedionato)dibutyltin(IV), $(C_4H_9)_2$Sn(dbzm)$_2$.—Dibenzoylmethane (4.852 g, 0.02165 mol) was added to dibutyltin oxide (2.490 g, 0.010 mol) in 30 ml of benzene and refluxed for 2 hr. The clear solution was decanted and the benzene was removed on a rotary evaporator. The yellow product was crystallized from acetonitrile with a few drops of benzene added at reflux; mp 92–94°. *Anal.* Calcd for $C_{38}H_{40}O_4Sn$: C, 67.18; H, 5.95; mol wt, 679. Found: C, 66.17; H, 5.91; mol wt, 586 (in benzene).

Bis(2,4-pentanedionato)dimethyltin(IV), $(CH_3)_2$Sn(acac)$_2$.—Dimethyltin oxide (8.00 g, 0.05 mol) was added to 40 ml of acetylacetone and was refluxed for 5 hr. The clear solution was decanted and cooled overnight at 0°. The colorless product crystals were recrystallized twice from benzene; mp 177–179°. *Anal.* Calcd for $C_{12}H_{20}O_4Sn$: C, 41.49; H, 5.84; mol wt, 347. Found: C, 41.63; H, 5.74; mol wt, 362 (in benzene).

Bis(2,4-pentanedionato)diethyltin(IV), $(C_2H_5)_2$Sn(acac)$_2$.—Thallous acetylacetonate (4.5955 g, 0.0164 mol) was added quantitatively to diethyltin dichloride (1.8750 g, 0.0082 mol) in warm petroleum ether (bp 65–70°) with mixing. TlCl was removed by filtration through paper. The colorless product was recovered pure after removing solvent on a rotary evaporator and drying under vacuum for 12 hr; mp 87–89°. *Anal.* Calcd for $C_{14}H_{24}O_4Sn$: C, 44.80; H, 6.49; mol wt, 375. Found: C, 43.75; H, 6.19; mol wt, 387 (in benzene).

Bis(2,4-pentanedionato)dibutyltin(IV), $(C_4H_9)_2$Sn(acac)$_2$.—Thallous acetylacetonate (5.00 g, 0.0164 mol) was added slowly to dibutyltin dichloride (2.490 g, 0.0082 mol) in 25 ml of hot petroleum ether (bp 65–70°) and thoroughly stirred. TlCl was removed by filtering through paper and solvent was removed under reduced pressure without warming. The colorless product was recovered pure after placing under vacuum overnight; mp 31–33°. Decomposition to a yellow oil occurs upon melting. *Anal.* Calcd for $C_{18}H_{32}O_4Sn$: C, 50.11; H, 7.49; mol wt, 431. Found: C, 48.42; H, 7.33; mol wt, 426 (in benzene).

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)diphenyltin(IV), $(C_6H_5)_2$Sn(hfacac)$_2$.—Thallous hexafluoroacetylacetonate (3.00 g, 0.00704 mol) was added to diphenyltin dichloride (1.21 g, 0.0352 mol) in 25 ml of dry benzene with stirring. TlCl was removed by filtering through paper and solvent was removed on a rotary evaporator. The colorless product was recrystallized from petroleum ether (bp 90–110°) with a few drops of benzene added at reflux; mp 68–70°. *Anal.* Calcd for $C_{22}H_{12}O_4F_{12}Sn$: C, 38.42; H, 1.75; mol wt, 687. Found: C, 38.22; H, 1.77; mol wt, 679 (in benzene).

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)dimethyltin(IV), $(CH_3)_2$Sn(hfacac)$_2$.—Dimethyltin oxide (2.00 g, 0.01215 mol) was added to hexafluoroacetylacetone (4.97 g, 0.0243 mol) in 25 ml of petroleum ether (bp 65–70°) and warmed slightly until the reaction had gone to completion. The reaction was rapid and exothermic. The volume of the clear solution was reduced to 10 ml on an evaporator. Colorless crystals deposited upon cooling overnight at 0°; mp 57–59°. *Anal.* Calcd for $C_{12}H_8F_{12}O_4Sn$: C, 25.65; F, 40.50; mol wt, 563. Found: C, 25.92; F, 35.87; mol wt, 565 (benzene).

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)dibutyltin(IV), $(C_4H_9)_2$Sn(hfacac)$_2$.—Hexafluoroacetylacetone (3.50 g, 0.0168 mol) was added to dibutyltin oxide (2.00 g, 0.00805 mol) in 25 ml of petroleum ether (bp 65–70°). The reaction was rapid. The colorless product was recovered pure by evaporating off all solvent; mp −2°. *Anal.* Calcd for $C_{18}H_{20}F_{12}O_4Sn$: C, 33.40; H, 3.09; mol wt, 647. Found: C, 33.69; H, 3.19; mol wt, 654 (in benzene).

Bis(3-bromo-2,4-pentanedionato)dimethyltin(IV), $(CH_3)_2$Sn-

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[7] W. H. Nelson, W. J. Randall, and D. F. Martin, *Inorg. Syn.*, **9**, 52 (1967).

((Br)acac)$_2$.—To an excess of freshly prepared 3-bromo-2,4-pentanedione in 30 ml of dry benzene was added dimethyltin oxide. The mixture was refluxed for 2 hr. The clear solution was decanted and the benzene was removed on a rotary evaporator. Recrystallization was from petroleum ether (bp 90–110°) with a few drops of benzene added at reflux. The product was tan and remarkably air and water sensitive; mp 230–232° dec. *Anal.* Calcd for $C_{12}H_{18}O_4Br_2Sn$: C, 28.52; H, 3.56. Found: C, 23.43; H, 4.03.

Bis(1,3-diphenylpropanedionato)diphenyltin(IV), $(C_6H_5)_2$Sn-(dbzm)$_2$.—The method of synthesis was reported earlier.[2] *Anal.* Calcd for $C_{42}H_{34}O_4Sn$: C, 70.10; H, 4.49. Found: C, 70.06; H, 4.28; mp 240–242°.

Dipole Moments.—Calculations were made using a variation of the "refractivity method" outlined by Guggenheim[8] and Smith.[9] The measurements of the dielectric constant increments, $\Delta\epsilon$, should be reliable to ±1% even though very dilute solutions were used. Dipole moments tabulated in Table I have been calculated assuming that atomic polarization can be neglected. Refractive index increments (4358 Å) were determined to a precision of ±5% with a Phoenix BP-2000V differential refractometer. Solution densities exceeded solvent densities by less than 0.1% and were set equal to solvent densities in the calculations. Uncertainties in dipole moments measured did not exceed 0.1 D. In Table I, w_2 is the weight fraction of the solute, ϵ is the dielectric constant of the solution, n_1 is the refractive index of the solvent, and n_{12} is the refractive index of the solution. Note that the orientation polarization is proportional to $(\Delta\epsilon/w_2) - [(n_{12}^2 - n_1^2)/w_2]$ and should vary as $1/T$. It can be seen that the polarization is strongly a function of temperature for compounds listed in Table II.

TABLE I

DIELECTRIC CONSTANT AND REFRACTIVE INDEX DATA FOR SOLUTIONS AT 25°

Compound	Concn, 10^3w_2	$(n_{12}^2 - n_1^2)/w_2$	$\Delta\epsilon/\Delta w_2$	Dipole moment, D	Solvent
$(C_6H_5)_2Sn(acac)_2$	3.52–17.3	0.075	3.55	3.78	C_6H_6
$(C_6H_5)_2Sn(acac)_2$	2.36–11.7	0.093	3.18	4.02	C_6H_{12}
$(CH_3)_2Sn(acac)_2$	1.389–6.47	0.050	2.70	2.95	C_6H_6
$(CH_3)_2Sn(acac)_2$	1.67–8.03	0.077	2.75	3.19	C_6H_{12}
$(C_2H_5)_2Sn(acac)_2$	1.80–9.70	0.060	2.11	2.56	C_6H_6
$(C_2H_5)_2Sn(acac)_2$	1.80–9.70	0.066	2.05	2.66	C_6H_{12}
$(C_4H_9)_2Sn(acac)_2$	3.26–20.6	0.050	1.72	2.58	C_6H_6
$(C_4H_9)_2Sn(acac)_2$	3.26–11.1	0.065	1.54	2.73	C_6H_{12}
$(C_6H_5)_2Sn(dbzm)_2$	1.03–11.4	0.63	2.88	3.86	C_6H_6
$(CH_3)_2Sn(dbzm)_2$	0.626–8.17	0.63	2.30	3.02	C_6H_6
$(CH_3)_2Sn(dbzm)_2$	0.59–4.9	0.593	2.23	3.18	C_6H_{12}
$(C_2H_5)_2Sn(dbzm)_2$	3.95–15.0	0.65	1.41	2.09	C_6H_6
$(C_2H_5)_2Sn(dbzm)_2$	2.02–16.2	0.682	1.14	1.84	C_6H_{12}
$(C_4H_9)_2Sn(dbzm)_2$	1.48–19.7	0.58	1.32	2.15	C_6H_6
$(C_4H_9)_2Sn(dbzm)_2$	2.24–16.9	0.615	1.16	2.07	C_6H_{12}
$(C_6H_5)_2Sn(hfacac)_2$	1.083–9.46	−0.0175	0.883	2.38	C_6H_6
$(CH_3)_2Sn(hfacac)_2$	2.245–15.53	−0.19	0.630	2.05	C_6H_6
$(C_4H_9)_2Sn(hfacac)_2$	3.185–13.50	−0.030	0.618	1.96	C_6H_6

TABLE II

DIELECTRIC CONSTANT AND REFRACTIVE INDEX DATA FOR BENZENE SOLUTIONS AT SEVERAL TEMPERATURES

Compound	Concn, 10^3w_2	$(n_{12}^2 - n_1^2)/w_2$	$\Delta\epsilon/\Delta w_2$	Dipole moment, D	Temp, °C
$(CH_3)_2Sn(acac)_2$	1.095–6.80	0.050	2.97	2.99	16
$(CH_3)_2Sn(acac)_2$	1.389–6.47	0.056	2.70	2.95	25
$(CH_3)_2Sn(acac)_2$	0.91–9.80	0.055	1.82	2.64	60
$(C_6H_5)_2Sn(dbzm)_2$	1.03–11.40	0.63	2.88	3.86	25
$(C_6H_5)_2Sn(dbzm)_2$	0.617–5.07	0.60	2.71	3.87	40
$(C_6H_5)_2Sn(dbzm)_2$	0.83–10.7	0.62	2.45	3.81	60
$(C_4H_9)_2Sn(dbzm)_2$	1.46–10.79	0.58	1.41	2.22	16
$(C_4H_9)_2Sn(dbzm)_2$	1.48–19.79	0.60	1.32	2.15	25
$(C_4H_9)_2Sn(dbzm)_2$	2.05–13.60	0.60	1.26	2.15	40
$(C_4H_9)_2Sn(dbzm)_2$	1.46–11.2	0.60	1.22	2.18	60

TABLE III

ULTRAVIOLET SPECTRAL DATA

Compound	Solvent	mμ	$10^{4}\epsilon$, M^{-1} cm^{-1}
$(CH_3)_2Sn(acac)_2$	Ethanol	273	1.68
$(CH_3)_2Sn(acac)_2$	Chloroform	273	1.575
$(CH_3)_2Sn(acac)_2$	Cyclohexane	270	1.64
$(CH_3)_2Sn(acac)_2$	Carbon tetrachloride	272	1.18
$(C_2H_5)_2Sn(acac)_2$	Ethanol	273	1.55
$(C_2H_5)_2Sn(acac)_2$	Chloroform	282	0.785
$(C_2H_5)_2Sn(acac)_2$	Cyclohexane	273	1.38
$(C_4H_9)_2Sn(acac)_2$	Ethanol	273	0.264
$(CH_3)_2Sn(dbzm)_2$	Ethanol	343	4.60
$(C_2H_5)_2Sn(dbzm)_2$	Ethanol	343	0.177
$(C_4H_9)_2Sn(dbzm)_2$	Ethanol	343	0.264

TABLE IV

NMR CHEMICAL SHIFT DATA

Compound	Sn–CH$_3$	C–CH$_3$	C–H	Solvent
$(CH_3)_2Sn(acac)_2$	9.72	8.88	5.48, 4.7, 4.16	Benzene
$(CH_3)_2Sn(acac)_2$	9.50	8.08	4.71	Chloroform
$(CH_3)_2Sn(acac)_2$	9.60	8.07	4.72	Carbon tetrachloride
$(C_6H_5)_2Sn(acac)_2$		8.10	4.76	Chloroform
$(C_2H_5)_2Sn(acac)_2$		8.05	4.73	Chloroform
$(C_4H_9)_2Sn(acac)_2$		8.03	4.70	Chloroform
$(C_6H_5)_2Sn(dbzm)_2$			3.18	Chloroform
$(CH_3)_2Sn(dbzm)_2$	9.07		3.30	Chloroform
$(C_2H_5)_2Sn(dbzm)_2$			3.17	Chloroform
$(C_4H_9)_2Sn(dbzm)_2$			3.30	Chloroform
$(C_6H_5)_2Sn(hfacac)_2$			3.98	Chloroform
$(CH_3)_2Sn(hfacac)_2$	8.91		3.81	Chloroform
$(C_4H_9)_2Sn(hfacac)_2$			3.98	Chloroform
Mixtures				
$(CH_3)_2Sn(acac)_2$ $(C_4H_9)Sn(acac)_2$	9.51	8.07	4.70	Chloroform
$(CH_3)_2Sn(acac)_2$ $(CH_3)_2Sn(hfacac)_2$	9.13	8.00	4.57, 3.98	Chloroform

Infrared Spectra.—Between 4000 and 700 cm^{-1} the spectra closely resemble those reported earlier[1] for the methyl derivatives for which assignments have been made. In no case does a carbonyl band appear above 1600 cm^{-1}.

Ultraviolet Spectra.—The data listed in Table III suggest that there may be rather strong solvent effects. Extinction coefficients vary strongly from solvent to solvent.

Nmr Chemical Shift Data.—All data reported in Table IV were obtained at 25° using a Varian Model A-60 spectrometer. Data are reported in ppm with tetramethylsilane (τ = 10.0) used as an internal standard.

Discussion

Dipole Moments.—Polarization measurements obtained at several temperatures in cyclohexane and benzene solutions have shown that the complexes studied possess orientation dipole moments of 2.0–4.0 D. The presence of such moments definitely rules out the nonpolar, regular, *trans*-octahedral structure (D_{2h}) as the one belonging to the predominant species in solution. Rather, it appears likely that the molecules in solution possess structures of the *cis*-octahedral type with most of them exhibiting some degree of distortion from the regular geometry shown in Figure 1.

In an attempt to estimate the extent of the distortion, metal–chelate "ring moments" calculated from known molecular moments of compounds have been used. Unfortunately, because of uncertainties in the values of the Sn–Cl bond moments, the metal–chelate "ring moments" can be calculated with a reliability not better than ±0.5 D. Specifically, depending upon which value between 3.0 and 3.5 is used for the Sn–Cl bond moment, values between 1.7

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(8) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

(9) J. W. Smith, *ibid.*, **46**, 394 (1950).

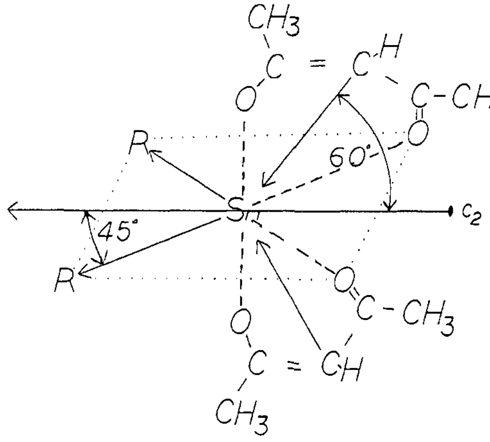

Figure 1.—The regular *cis*-octahedral structure.

TABLE V

A COMPARISON OF OBSERVED MOLECULAR MOMENTS WITH MOMENTS CALCULATED FOR A REGULAR *cis*-OCTAHEDRAL MODEL STRUCTURE (DEBYES)

Compound	Estd Sn–R group moment × 1.41	Calcd ring moment resultant	Calcd mol moment	Obsd mol moment	Calcd Sn–R group moment
$(C_6H_5)_2Sn(acac)_2$	0.71	2.0	2.71	3.78	1.26
$(CH_3)_2Sn(acac)_2$	0.71	2.0	2.71	2.95	0.67
$(C_2H_5)_2Sn(acac)_2$	0.71	2.0	2.71	2.56	0.40
$(C_4H_9)_2Sn(acac)_2$	0.71	2.0	2.71	2.58	0.41
$(C_6H_5)_2Sn(dbzm)_2$	0.71	2.0	2.71	3.86	1.32
$(CH_3)_2Sn(dbzm)_2$	0.71	2.0	2.71	3.02	0.72
$(C_2H_5)_2Sn(dbzm)_2$	0.71	2.0	2.71	2.09	0.08
$(C_4H_9)_2Sn(dbzm)_2$	0.71	2.0	2.71	2.15	0.11
$(C_6H_5)_2Sn(hfacac)_2$	0.71	1.7	0.99	2.38	−0.48
$(CH_3)_2Sn(hfacac)_2$	0.71	1.7	0.99	2.05	−0.35

and 2.7 D are obtained for the tin–acetylacetonate and tin–dibenzoylmethanate "ring moments." A likely value is 2.0 D. Likewise a value of 1.7 D pointing in the opposite direction has been used as the calculated "ring moment" for the tin–hexafluoroacetylacetonate rings. Sn–R bond moments have been estimated on the basis of earlier work[10] to be in the vicinity of 0.5 D.

The tin–acetylacetonate ring moment has been calculated as follows. The molecular moment of *cis*-$Sn(acac)_2Cl_2$ has been determined[11,12] at several temperatures in at least two different laboratories to be 6.7 D. Estimating that the Sn–Cl bonds[13] contribute 3.3 D each, the two bonds will produce a resultant of about 4.7 D along the molecular C_2 axis. Subtracting 4.7 from 6.7 D gives the Sn–acac moment of 2.0 D since the C_2 axis of each ligand, along which each "ring moment" lies, forms an angle of 60° with the molecular C_2 axis. Similarly, given a value of 2.97 D for the *cis*-$Sn(hfacac)_2Cl_2$ molecular moment, the Sn–hfacac "ring moment" will be 1.7 D. On the basis of group moment values[14,15] it is expected that Sn–acac and Sn–dbzm "ring moments" should differ by no more than 0.1–0.2 D.

Two model structures are proposed as worthy of consideration as representative of the systems studied. The regular *cis*-octahedral configuration is one of these. That model requires a C–Sn–C bond angle of 90° and "ring moments" oriented at an angle of 60° to the molecular C_2 axis (Figure 1). Estimated Sn–R group moments are combined with "ring moments" to give calculated molecular moments (Table V) which can be compared with the actual values of the molecular moments. Then, in the last column of Table V are listed calculated values of the Sn–R bond moments needed to give the observed molecular moments. Because the substantial differences from derivative to derivative between such Sn–R bond moments could reflect "R group" electronegativity differences, differences between such moments are expecially significant.

Although agreement between calculated and experimental values of the molecular dipole moments appears to be less than excellent, still, if possible variations of polarity in the Sn–C bond moments are considered, the calculated molecular moments are not inconsistent with those calculated for a *cis* structure. Group moments, Sn–R, calculated assuming constant values for ring moments are all within a reasonable range. The tin–phenyl moment is larger than might be expected on the basis of molecular moments[13] of organotin halides but is not unreasonable considering the much greater ease with which the phenyl group is cleaved from tin by electrophilic reagents.[16] The values of the Sn–R group moments belonging to hexafluoroacetylacetonates may reflect uncertainties in the choice of the tin–hexafluoroacetylacetonate ring moment. Reasonable values of the Sn–R group moment are obtained for those complexes if the ring moment value is assumed to be about 2.5 D. In short, the data can be fitted to the above model without serious difficulty if it is considered that the uncertainities in the values of the group moments very likely are in the vicinity of 0.5 D.

Because recent X-ray work[6] has shown the C–Sn–C bond angle to be 110° in bis(8-quinolinolato)-dimethyltin(IV) it is worthwhile calculating molecular moments based on a model structure with C–Sn–C bonds at an angle of 109° 28′ and with ring moments also in a tetrahedral arrangement. In fact, because d orbitals are of very high energy on tin atoms unless halogens are attached, it appears quite likely that the orbitals used by tin are basically of the sp^3-hybrid type. It is reasonable to speculate that the oxygens of the β-ketoenolate groups may be bonded *via* a three-center molecular orbital such as that recently proposed by Okawara[17] for a five-coordinate tin oxinate complex. In Table VI molecular moments are calculated assuming that group moments point toward the apex of a tetrahedron, that is, at 54° 44′ from the molecular C_2 axis (Figure 2).

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TABLE VI

MOMENTS CALCULATED USING BOND ANGLES OF 109° 28′ COMPARED WITH OBSERVED MOMENTS

Compound	Estd Sn–R group moment × 1.16	Calcd ring moment resultant along C_2 axis	Calcd mol moment	Obsd mol moment	Calcd Sn–R group moment
$(C_6H_5)_2Sn(acac)_2$	0.58	2.3	2.88	3.78	1.28
$(CH_3)_2Sn(acac)_2$	0.58	2.3	2.88	2.95	0.56
$(C_2H_5)_2Sn(acac)_2$	0.58	2.3	2.88	2.56	0.23
$(C_4H_9)_2Sn(acac)_2$	0.58	2.3	2.88	2.58	0.24
$(C_6H_5)_2Sn(dbzm)_2$	0.58	2.3	2.88	3.86	1.34
$(CH_3)_2Sn(dbzm)_2$	0.58	2.3	2.88	3.02	0.62
$(C_2H_5)_2Sn(dbzm)_2$	0.58	2.3	2.88	2.09	−0.18
$(C_4H_9)_2Sn(dbzm)_2$	0.58	2.3	2.88	2.15	−0.04
$(C_6H_5)_2Sn(hfacac)_2$	0.58	2.0	1.42	2.38	−0.33
$(CH_3)_2Sn(hfacac)_2$	0.58	2.0	1.42	2.05	−0.04

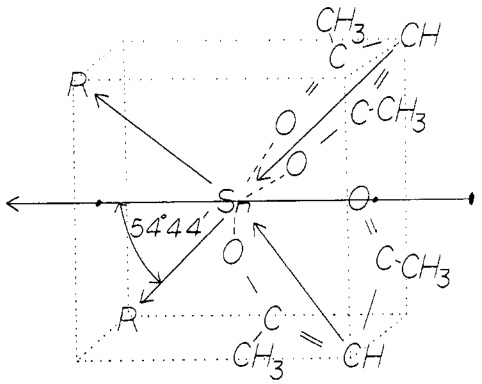

Figure 2.—The tetrahedral structure.

Using the second model, values of the molecular moment are not far from the observed ones. Yet, for the ethyl and the butyl derivatives the calculated values are a little large. It is suspected that although the C–Sn–C bond angles may approach or even exceed 109°, the ring moments very likely are separated by an angle of approximately 120°. Also, the decrease in molecular moments in the series phenyl > methyl > ethyl ~ butyl for the various β-ketoenolate derivatives may in a large part be due to an increase in the s character of the tin orbitals interacting with carbon.

According to Bent,[18] an atom concentrates s character in bonds to less electronegative substituents. In that fashion it is entirely possible that the C–Sn–C bond angles increase from perhaps 90° for the chloro and phenyl derivatives to 110° or more for the ethyl and butyl derivatives. Thus, the very substantial drop in molecular moments in a series of compounds such as the acetylacetonates may be due to both a decrease in Sn–C bond polarity and an increase in the C–Sn–C bond angle. There is no evidence for a *cis–trans* equilibrium. It appears that the molecules are best described by a structure which is basically of the *cis* type.

Infrared and Ultraviolet Spectra.—Infrared spectra show that there are no uncoordinated carbonyl groups belonging to any of the complexes studied. No definite conclusions can be made relative to *cis–trans* isomerism on the basis of these spectra. Ultraviolet spectra show $n \rightarrow \pi^*$ transitions which are characteristic of acetylacetonates not involved in π bonding through oxygen. No π bonding is expected between tin and oxygen in the compounds studied.

Nuclear Magnetic Resonance Spectra.—The nmr spectra of phenyl and methyl $R_2Sn(acac)_2$ complexes in chloroform solution are identical with those reported earlier.[1] Spectra of ethyl and butyl derivatives reported for the first time also exhibit only one resonance associated with acetylacetonate methyl protons, as predicted for a *trans* complex. A F^{19} spectrum of $(CH_3)_2Sn(hfacac)_2$ also shows only one peak belonging to the four CF_3 groups.

Since the presence of large dipole moments definitely rules out the possibility of *trans*-type structures, it seems reasonable to suppose that the splitting of the acetylacetonate methyl group resonance observed earlier for *cis*-$Sn(acac)_2Cl_2$ is not observed for the above derivatives because of rapid exchange or because of nonrigidity of the β-ketoenolate groups.

Chemical shift data of the $(CH_3)_2Sn(acac)_2$–$(CH_3)_2Sn(hfacac)_2$ mixture in chloroform at 25° demonstrate unambiguously that the simplicity of the $C–CH_3$ spectra is due to rapid ligand exchange. For the mixture only one $Sn–CH_3$ peak was observed at τ 9.13 approximately midway between $Sn–CH_3$ peaks for $(CH_3)Sn(acac)_2$ (τ 9.50) and for $(CH_3)Sn(hfacac)_2$ (τ 8.91). Since methyl groups bound to tin do not exchange rapidly at 25°, the observation of an average value of the methyl resonance must result from the rapid exchange of β-ketoenolate groups. As expected, all complexes of the type R_2SnCh_2 tend to be labile. They react with 8-quinolinol, for example, causing the displacement of the β-ketoenolate groups upon mixing.

Summary

Large values of the molecular dipole moment can be explained only in terms of the predominance of *cis*-type (C_2) structures for molecules of the type R_2SnCh_2. It is expected that because of the very different nature of the interaction in tin–carbon bonds as opposed to tin–oxygen bonds, such structures may be distorted substantially from the regular *cis*-octahedral geometry. Although the calculations do not allow a choice to be made between the two structural models proposed (Figures 1 and 2), the *trans* structure assigned on the basis of earlier work must be ruled out. Also, it is very likely that the R–Sn–R bond angles have values between 90 and 110° since structures with R–Sn–R angles much larger than 110° must show very much smaller dipole moments than those measured. Angles much less than 90° are unlikely because of crowding.

Proton nmr spectra show that β-ketoenolate ligand exchange is rapid. Such findings are consistent with the finding that tin–carbon bonds are much less polar than tin–oxygen bonds.

In spite of the rapid rate of ligand exchange, no appreciable fraction of the ligands is unbound. For

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instance, molecular weight measurements demonstrate conclusively that all complexes are monomeric, and infrared spectra[1] show no evidence of free ligands. The fact that solution dielectric constants and refractive index increments are precisely linear functions of the weight fraction of the solute also supports the claim that dissociation did not occur over the concentration range studied.

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Group Dipole Moments of Metal-β-Ketoenolate Rings in Thallium, Indium, and Tin Complexes

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Dipole moments of selected thallium, indium, and tin acetylacetonates, dibenzoylmethanates, and hexafluoroacetylacetonates have been measured in benzene solution at 25° using a refractivity method. The metal-acetylacetonate and metal-dibenzoylmethanate group moments have been found to be less than 2 D. Metal-hexafluoroacetylacetonate group moments have been observed to differ from acetylacetonate moments by about 3 D, as expected. All group moment values obtained are much smaller than those predicted in the literature.

Introduction

In spite of a lack of supporting experimental data, the opinion appears widespread[1-3] that metal-acetylacetonate group moments should vary between 6 and 9 D, presumably with the vector pointing away from the metal ion toward the ligand along the ligand C_2 axis. Such estimates should be viewed with suspicion since they are based on the use of metal-oxygen bond moments belonging to ether adducts[4,5] of beryllium, boron, and aluminum halides.

Directly related to the assignment of large ring moments to metal acetylacetonates has been the questionable practice of attributing the unusually large values of the polarization exhibited by supposedly highly symmetrical acetylacetonates to atomic polarization. Atomic polarization, the calculated difference between the total polarization of a molecule and the sum of its orientation and electronic polarizations, results from the movement of atomic nuclei in response to an electric field of moderately low frequency. The largest values of the atomic polarization are associated with molecules possessing highly polar groups characterized by relatively low frequency bending processes. Assuming that bending results in changes in the angle between two dipole moments and that the moments are both of magnitude u, Coop and Sutton[2] calculated for the atomic polarization $P_a = 4\pi N u^2/9V_i$, where N is Avogadro's number and V_i is the bending force constant. Thus, knowledge of the atomic polarization should allow calculation of the force constant of bending, V_i, for a chelate ring if permanent group moments, u, of the rings are known.

To investigate the potential usefulness of the atomic polarization as a probe of molecular electronic structure, the authors, in a related study, carried out an extensive dipole moment study of six-coordinate organotin chelate compounds. On the basis of earlier studies[6-8] these compounds had been assigned a *trans* (D_{2h}) geometry, and hence it was thought they should have orientation polarization values of zero. Unexpectedly, temperature-dependent polarization studies[9] showed that the complexes possessed very large permanent dipole moments. This study represents an attempt to investigate and explain the unexpectedly low values of the atomic polarization belonging to β-ketoenolate complexes of tin. It is believed that this work is the first attempt to measure the group moments of metal-β-ketoneolate rings directly.

Experimental Section

Reagents.—Commercially available materials were used without further purification in all syntheses. Reagent grade benzene and cyclohexane were distilled from a sodium-potassium mixture and used immediately to prepare solutions used for all dielectric constant measurements.

Preparation of Complexes. 2,4-Pentanedionatothallium(I), Tl(acac).—A previously described method[10] of synthesis was used. The molecular weight of this compound was calculated to be 303.5 while that found in benzene by cryoscopy was 418; mp 152–154°. Difficulty was encountered in measuring the molecular weight precisely because of the low solubility of this complex in benzene.

1,3-Diphenylpropanedionatothallium(I), Tl(dbzm).—A previously described method[10] of synthesis was used. The molecular weight was calculated to be 428 while that found by osmometry was 440; mp 158–160°.

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