and $pK_1 + pK_2$ (or pK_1, pK_2) if it is assumed that the linear relation between pK_1 and pK_2 can be extended to 4-carboxy and 4-sulfonate substituents. The failure of previous workers[9] to observe this relation between $\log \beta_1$ and $pK_1 + pK_2$ is apparently due to erroneous experimental values of pK_2 for catechol and its 4-chloro and carboxy derivatives. The effect of ligand substituents on the stability of o-diphenol complexes with Ge(IV), Si(IV), and divalent metals appears therefore to be in line with the general relations between complex stability and ligand basicity.

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Polar Six-Coordinate Tin(IV) Complexes of Type SnX_2L_2: Synthesis, Structure, and Bonding

BY W. H. NELSON

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The structures of several six-coordinate tin complexes of the type SnX_2L_2 have been studied, where X is Cl, Br, or I, and L is acetylacetonate or dibenzoylmethanate. Dipole moment measurements in benzene solution at 25 and 60° as well as nmr chemical shift data indicate that the complexes are of the *cis* configuration. Infrared and ultraviolet spectra suggest, respectively, that tin–halogen bonds are stronger than those of simple six-coordinate adducts, and that tin–oxygen bonds are primarily ionic in character. An improved method of synthesis has been reported for bromo and iodo derivatives.

The ability of silicon, germanium, tin, and lead to increase their coordination numbers beyond four has been attributed to the availability of empty d orbitals.[1] However, such orbitals belonging to an isolated atom are too diffuse for effective overlap with ligand orbitals. In fact, calculations[2-4] have shown that the d orbitals in question contract enough to allow the formation of bonds only in the presence of highly electronegative ligands.

The majority of investigations to date have concerned bonding in silicon compounds. Calculations[5] have demonstrated that about silicon the order of effectiveness of ligands in contracting 3d orbitals is $F > Cl > C \gg H$. A large body of experimental evidence indicates that for silicon compounds[6] there is effective overlap between ligand p orbitals and metal d orbitals to form π bonds. Evidence for such $(p \rightarrow d)$ π bonding is based largely on the analysis of bond characteristics such as bond lengths, bond energies, infrared spectra, and electric dipole moments. It has been suggested[7,8] that trends in donor and acceptor strengths of compounds of silicon and its heavier cogeners are strongly influenced by such $(p \rightarrow d)$ π bonding effects, which decrease in magnitude as the central atom increases in size and as the d orbitals available for bonding become more diffuse. In particular, it is claimed that $(p \rightarrow d)$ π bonding is very important in most silicon–oxygen bonds, of lesser importance for germanium–oxygen bonds, and small or nonexistent for tin–oxygen bonds. That does not mean that the orbitals of tin cannot be used for π bonding with atoms other than oxygen. In fact, halogen atoms probably quite effectively contract the 5d orbitals of tin, since the acceptor properties of tin halides are well known.[1]

On the other hand, the nature of the bonding in true six-coordinate tin complexes has been investigated to only a very limited extent.[9] This is especially the case for compounds such as dichlorobis(2,4-pentanedionato)-tin(IV).

Beyond doubt, $SnCl_2(acac)_2$ has been demonstrated to be monomeric in boiling benzene,[10] and it has been shown that nitrobenzene solutions are very poor conductors[11] of electricity. The disclosure that the molecule exhibits a large (8.8 D.) dipole moment[12] in benzene solution suggests that a *cis*-type configuration is likely. Recently, nmr and infrared data have been reported which are consistent with the assignment of a *cis* configuration.[13,14] Similar nmr data have been interpreted in terms of an unlikely equilibrium be-

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tween localized double bonds in acetylacetonate groups.[15]

In this paper an attempt has been made to characterize beyond doubt structures of $SnCl_2(acac)_2$ and closely related compounds, and to explain in terms of proposed electronic structures the observed properties of these compounds.

Experimental Section

Reagents.—Reagent grade solvents were used without further purification in all synthetic work. Tetrabromotin(IV) and tetraiodotin(IV) obtained from Alpha Inorganics, Inc., were used without further purification as were the tetraphenyltin(IV) and acetylacetone obtained from Aldrich Chemicals, Inc. Reagent grade tetrachlorotin(IV) purchased from Fisher Scientific, Inc., was also used without further purification. Reagent grade benzene and cyclohexane used for dipole moment work were distilled from sodium–potassium amalgam and used immediately.

Analyses.—Samples were analyzed for carbon, hydrogen, and halogen by Micro-Analysis, Inc., Wilmington, Del.

Molecular Weights.—Molecular weights were determined using a Mechrolab Model 301A vapor phase osmometer with benzene and chloroform as solvents. Solutions were 0.1% by weight solute.

Infrared Spectra.—Spectra of samples in KBr disks were obtained with a Perkin-Elmer Model 521 grating spectrometer.

Nuclear Magnetic Resonance Spectra.—Proton spectra were determined at 25° in $CDCl_3$ with a Varian A-60 spectrometer operating at 60 Mc/sec. Tetramethylsilane was used as an internal standard.

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

Dipole Moments.—Dielectric constants were measured at 25 and 60° with a WTW Model DM01 dipolemeter. The instrument was calibrated with dry reagent grade benzene and cyclohexane as well as with dry air. Refractive indices (4358 A) were obtained at 25° with a Phoenix Model BP-2000V differential refractometer.

Preparation of Complexes.—Dichlorobis(2,4-pentanedionato)-tin(IV) was prepared according to the method of Morgan and Drew;[10] that is, by allowing acetylacetone and tetrachlorotin(IV) to react directly in benzene. Since the bromo and iodo derivatives could not be prepared by the above route, a phenyl–tin cleavage technique was used. This cleavage technique is recommended since yields are high and the starting materials are inexpensive and readily available. Crystals analyzed and used for measurements were recrystallized twice from benzene without special precautions being taken to maximize yields. Bromo and iodo derivatives were dried overnight in a vacuum oven at 80° to remove benzene.

Dichlorobis(2,4-pentanedionato)tin(IV).—Mp 203–204°. *Anal.* Calcd for $C_{10}H_{14}O_4Cl_2Sn$: C, 30.97; H, 3.64; Cl, 18.28; mol wt, 387.7. Found: C, 31.25; H, 3.61; Cl, 19.21; mol wt in benzene, 371.

Dibromobis(2,4-pentanedionato)tin(IV).—Tetraphenyltin-(IV) (4.27 g, 0.01 mole) and tetrabromotin(IV) (4.38 g, 0.01 mole) were heated together in a moisture-free atmosphere for 2.0 hr at 225°. To the mixture upon cooling was added 5.0 ml of acetylacetone. This mixture was refluxed for 2.0 hr and cooled. The product was separated as yellow crystals by adding 20 ml of petroleum ether (bp 90–110°); yield 7.6 g (80%); mp 183–184°. *Anal.* Calcd for $C_{10}H_{14}O_4Br_2Sn$: C, 25.20; H, 2.96; Br, 33.52; mol wt, 476.7. Found: C, 25.03; H, 3.01; Br, 33.71; mol wt in benzene, 485; in chloroform, 489.

Diiodobis(2,4-pentanedionato)tin(IV).—Tetraiodotin(IV) (5.08 g, 0.01 mole) and tetraphenyltin(IV) (4.27 g, 0.01 mole) were heated together for 2.0 hr at 225°. From that point the procedure followed was identical with that used to prepare the bromo derivative; yield 7.5 g (66%) after recrystallization; mp 178–179°. *Anal.* Calcd for $C_{10}H_{14}O_4I_2Sn$: C, 21.05; H, 2.47; I, 44.47; mol wt, 570.7. Found: C, 21.55; H, 2.52; I, 47.93; mol wt in benzene, 591; in chloroform, 549.

Dichloro(1,3-diphenylpropanedionato)tin(IV).—This compound was prepared by the method of Morgan and Drew,[10] mp 263–264°. *Anal.* Calcd for $C_{30}H_{22}O_4Cl_2Sn$: C, 56.65; H, 3.48; Cl, 11.14; mol wt, 636. Found: C, 56.40; H, 3.32; Cl, 11.72; mol wt in benzene, 594.

Dibromo(1,3-diphenylpropanedionato)tin(IV).—Dibromodiphenyltin(IV) (2.163 g, 0.005 mole) and 1,3-diphenylpropanedione (2.2426 g, 0.01 mole) were mixed directly and then heated in a moisture-free atmosphere at 200° until the evolution of benzene stopped. The light yellow product which was produced in nearly 100% yield was purified by recrystallization from pure benzene; mp 281–283°. *Anal.* Calcd for $C_{30}H_{22}O_4Br_2Sn$: C, 49.70; H, 3.06; Br, 22.04; mol wt, 725. Found: C, 49.95; H, 3.02; Br, 22.23; mol wt in benzene, 701.

Diiodo(1,3-diphenylpropanedionato)tin(IV).—In a moisture-free atmosphere a mixture of diiododiphenyltin(IV) (2.853 g, 0.005 mole) and 1,3-diphenylpropanedione (2.2426 g, 0.01 mole) was heated at 200° until the evolution of benzene stopped. The light yellow product produced in nearly 100% yield was purified by recrystallization from pure benzene; mp 282–283°. *Anal.* Calcd for $C_{30}H_{22}O_4I_2Sn$: C, 44.00; H, 2.71; I, 30.99; mol wt, 819. Found: C, 44.32; H, 2.99; I, 30.25; mol wt in benzene, 839.

Results

Nuclear Magnetic Resonance Data.—Nmr data are presented in Table I.

Table I

The Proton Chemical Shifts in Deuterated Chloroform

Compound	$\tau(CH_3)^a$		τ(CH)
$SnCl_2(C_5H_7O_2)_2$	7.80	7.89	4.31
$SnBr_2(C_5H_7O_2)_2$	7.81	7.90	4.28
$SnI_2(C_5H_7O_2)_2$	7.83	7.93	4.27

[a] Tetramethylsilane = 10.0.

Dipole Moments.—Calculations were made according to the methods of Guggenheim[16] and Smith,[17] but no corrections were made for atomic polarization. The measurements of the dielectric constant increments, $\Delta\epsilon$, should be reliable to ±1% even though very dilute solutions were used. Dipole moment data are given in Table II.

Ultraviolet and Visible Spectra.—All solutions of acetylacetonates exhibited a strong absorption (ϵ 1.7 $\times 10^4$ M^{-1} cm^{-1}) at 273 mμ. Those of the iodo derivative showed a strong peak (ϵ 2.0 $\times 10^4$ M^{-1} cm^{-1}) at 218 mμ and a relatively wak absorption at 357 mμ (ϵ 1.1 $\times 10^3$ M^{-1} cm^{-1}) as well. Identical spectra were observed using both chloroform and ethanol solutions.

Infrared Spectra.—Between 4000 and 400 cm^{-1} the spectra of $SnCl_2(acac)_2$, $SnBr_2(acac)_2$, and $SnI_2(acac)_2$ closely resembled one another and that of $Pd(acac)_2$, for which assignments had been made.[18] The similarities are to be expected since interactions between acetylacetonate groups are weak. In the $SnCl_2(acac)_2$ spectra an important characteristic absorption appeared at 332 cm^{-1} which had been assigned in an earlier

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Table II

Dipole Moment Data

Compound	Solvent	Concn range in w_2[a]	$\Delta\epsilon/\Delta w_2$[b]	$\Delta n/\Delta w_2$[c]	Dipole moment, D.	Temp, °C
$SnCl_2(C_5H_7O_2)_2$	C_6H_6	0.000626–0.00922	13.1	0.0692	6.77	25
$SnBr_2(C_5H_7O_2)_2$	C_6H_6	0.00273–0.01070	10.2	0.0749	6.61	25
$SnI_2(C_5H_7O_2)_2$	C_6H_6	0.00256–0.01980	7.5	0.0896	6.25	25
$SnCl_2(C_{15}H_{11}O_2)_2$	C_6H_6	0.001014–0.00504	9.9	0.21	7.3	25
$SnBr_2(C_{15}H_{11}O_2)_2$	C_6H_6	0.000805–0.00298	7.3	0.22	6.6	25
$SnI_2(C_{15}H_{11}O_2)_2$	C_6H_6	0.000425–0.00387	6.1	0.22	6.3	25
$SnCl_2(C_5H_7O_2)_2$	C_6H_6	0.000348–0.00478	10.5	0.06	6.6	60
$SnBr_2(C_5H_7O_2)_2$	C_6H_6	0.00320–0.0113	8.5	0.07	6.4	60
$SnI_2(C_5H_7O_2)_2$	C_6H_6	0.00129–0.00615	6.0	0.08	6.1	60

[a] w_2 = weight fraction solute. [b] n = refractive index. [c] ϵ = dielectric constant.

paper[19] to an Sn–Cl vibration. Sn–Br and Sn–I absorptions probably appear below 250 cm^{-1} since they were not observed. $SnCl_2(C_{15}H_{11}O_2)_2$ showed a characteristic absorption at 330 cm^{-1}.

Discussion

Nuclear Magnetic Resonance.—The splitting of the methyl resonances into two peaks of equal height separated by 5.5 cps at 60 Mc strongly suggests that the compounds studied are exclusively of the *cis* configuration. They cannot be *trans*. The observed splittings are slightly greater in magnitude than those noted by Piper, *et al.*,[20,21] as characteristic of other *cis*-type octahedral diketonate complexes.

Dipole Moments.—Although the value of 6.8 D. observed for $SnCl_2(acac)_2$ is substantially lower than the 8.8 D. reported earlier,[12] a perusal of the data used to calculate the larger value shows that the dielectric constant measurements were made imprecisely. As a result, a value of 6.8 D. is really not in conflict with the results of the earlier work. At any rate, all reported dipole moment data remain consistent with the assumption of a *cis*-type structure. The very similar values of the dipole moments exhibited by all complexes studied are not especially surprising since bond moments have been observed to drop rather slowly in the sequence Sn–Cl, Sn–Br, Sn–I;[22,23] presumably because of the effects of π bonding. Specifically, if it is assumed that equal or small values of the atomic polarization are assigned to each complex, the dipole moments can be explained in terms of decreasing effectiveness of (p→d) π overlap in tin–halogen bonds as one considers, respectively, the chloro, bromo, and iodo complexes. That is, the chloro group which should most effectively contract d orbitals on tin and form the strongest π bonds would have its electron density reduced through π bonding to a greater extent than would the bromo or iodo groups. Thus bond moments for Sn–Cl, Sn–Br, and Sn–I might be very much nearer the same value than otherwise would be anticipated from consideration of electronegativity differences.

The temperature independence of the dipole moments indicates that atomic polarization must be too small to measure conveniently for the acetylacetonates. Specifically, it must be less than 1% of the total polarization and can be safely ignored here. Certainly it is extremely doubtful that any important *cis–trans* equilibrium occurs. All evidence points toward a solution containing only *cis*-type isomers.

Ultraviolet and Visible Spectra.—These spectra indicate that the acetylacetonate groups are not strongly perturbed by the central tin atom. The charge-transfer band at 273 mμ characteristic of acetylacetone does not undergo an appreciable change either in energy or in intensity upon complex formation. The dibenzoylmethanate groups attached to tin are characterized by charge-transfer bands shifted only 4 to 26 mμ toward the red end of the spectrum.

Infrared Spectra.—Beattie and McQuillan[24] have noted that the Sn–Cl stretching modes found between 330 and 336 cm^{-1} for trimethyltin chloride and between 320 and 350 cm^{-1} for dimethyltin chloride are shifted below 250 cm^{-1} when pyridine or *o*-phenanthroline adducts are formed in benzene solution. This effect occurs largely because of bond lengthening due to increased ligand–ligand repulsion forces, decreased effectiveness of (p→d) π bonding, or both. Thus a Sn–Cl absorption at 332 cm^{-1} in a six-coordinate complex such as $Cl_2Sn(acac)_2$ suggests unusually great bond strength. Such an observation is consistent with the assumption that the Sn–Cl bond in the complex possesses a significant amount of double-bond character. The absence of any strong carbonyl absorption above 1600 cm^{-1} indicates that acetylacetonate groups are acting as bidentate[25] ligands.

In an octahedral complex (p→d) π bonding between tin and chlorine will be most easily accomplished if the two chloro groups are *cis* to one another. This will be true especially if there is little or no π bonding between tin and ligands bound *trans* to the chloro groups. Little if any π bonding between acetylacetonate groups and tin is expected.[7,8] π bonding should also effectively lower electron density on the adjacent halogen groups, thus lowering not only bond moments, but ligand–ligand repulsion forces as well which might other-

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wise destabilize the *cis* structures. π bonding also would decrease the positive charge on the central tin atom and make it less susceptible to nucleophilic attack. Such a suggestion explains the compounds' unusual reluctance to hydrolyze. Quite evidently, the suggestion that (p→d) π overlap is important between tin and halogen atoms is consistent with the observed stability of the *cis* isomers of type X_2SnL_2.

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Stereochemistry and Lability of Dihalobis(β-diketonato)titanium(IV) Complexes. I. Acetylacetonates[1]

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The preparation and characterization of dihalobis(acetylacetonato)titanium(IV) complexes, $Ti(acac)_2X_2$ (X = F, Cl, Br), is reported. X-Ray powder patterns suggest that the crystalline solids may be isomorphous. Molecular weight, conductivity, and proton nmr data demonstrate that the complexes are monomeric nonelectrolytes which exist in solution as *cis* geometrical isomers. Variable temperature nmr spectra show that the acetylacetonate rings undergo rapid configurational changes which exchange acetylacetonate methyl groups between the two nonequivalent sites of the *cis* isomer. First-order rate constants, extrapolated to 25°, for exchange of methyl groups, activation energies, and entropies of activation have been determined to be, respectively, 1.6×10^4 sec^{-1}, 11.6 ± 0.5 kcal/mole, and -2.4 ± 2.3 eu (X = F); 6.7×10^2 sec^{-1}, 11.2 ± 0.6 kcal/mole, and -10.0 ± 2.3 eu (X = Cl); 2.3×10^3 sec^{-1}, 11.6 ± 0.4 kcal/mole, and -6.3 ± 1.6 eu (X = Br). Possible mechanisms for the configurational changes are discussed briefly.

Introduction

The structure of the product obtained from the reaction of acetylacetone (Hacac) with titanium(IV) chloride has been of considerable interest. This reaction was first studied in ether solution by Rosenheim,[2] who formulated the product as the ether addition compound, $Ti(acac)Cl_3 \cdot (C_2H_5)_2O$. Dilthey[3] repeated Rosenheim's preparation, but Dilthey's analytical data indicated that the composition of the product was $Ti(acac)_2Cl_2$. The absence of ether was confirmed by the fact that the same product was obtained when the reaction was carried out in glacial acetic acid or in chloroform. Dilthey suggested the ionic structure, $[Ti(acac)_3]_2[TiCl_6]$, on the basis of similarities in the chemical behavior of the titanium compound and the analogous silicon compound, $[Si(acac)_3]Cl \cdot HCl$.[4] In particular, both compounds react with certain anhydrous metal chlorides, for example, iron(III) chloride and platinum(IV) chloride, yielding "double salts" of the type $[M(acac)_3][FeCl_4]$ and $[M(acac)_3]_2[PtCl_6]$.

Although the existence of the $[Ti(acac)_3]^+$ cation in double salts such as $[Ti(acac)_3][FeCl_4]$ is now well established,[5-8] the ionic formulation, $[Ti(acac)_3]_2[TiCl_6]$, for the original reaction product appears to be incorrect. Mehrotra and coworkers[9-11] have contended, on the basis of chemical, molecular weight, and conductivity evidence, that the product should be formulated as the monomeric nonelectrolyte, $[Ti(acac)_2Cl_2]$. Mehrotra's conclusion has been confirmed by Cox, Lewis, and Nyholm,[6] who have studied an entire series of dichlorobis(β-diketonato)metal complexes.[12] In view of the considerable evidence for the nonelectrolyte structure, it is unfortunate that the ionic formulation appears in the recent literature.[13]

We, also, have been investigating the constitution of $Ti(acac)_2Cl_2$. In this connection, we have prepared and characterized the difluoro and dibromo analogs. The present paper reports the results of molecular weight, conductance, X-ray powder diffraction, and nmr studies of the $Ti(acac)_2X_2$ complexes (X = F, Cl, Br). The nmr results are especially significant because they reveal the molecular stereochemistry and kinetic lability of the complexes.

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