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–$\beta$-Ketoenolate Rings in Thallium, Indium, and Tin Complexes

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*Received June 12, 1968*

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 $P_a = 4\pi Nu^2/9V_i$, 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 $\beta$-ketoenolate complexes of tin. It is believed that this work is the first attempt to measure the group moments of metal–$\beta$-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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**1,1,1,5,5,5-Hexafluoro-2,4-pentanedionatothallium(I), Tl(hfacac).**—This compound was prepared by a method[10] of synthesis described earlier, except that recrystallization was from petroleum ether (bp 90–110°); mp 148–150°. *Anal.* Calcd for $C_5HO_2F_6Tl$: C, 14.60; F, 27.70; mol wt, 413. Found: C, 14.57; F, 26.35; Mol wt, 429 (in benzene by cryoscopy).

**2,4-Pentanedionatodimethylthallium(III), $(CH_3)_2Tl(acac)$.**—Dimethylthallium(III) iodide, 1.00 g, was mixed with 0.95 g of thallous acetylacetonate in 50 ml of benzene. The mixture was refluxed for 2 hr and filtered through paper while still warm to remove thallous iodide. Colorless crystals were obtained from the solution after cooling to 0° overnight; mp 215–217°. The compound[11] has been shown to be monomeric in benzene. *Anal.* Calcd for $C_7H_{13}O_2Tl$: C, 25.20; H, 3.90. Found: C, 26.36; H, 4.06.

**1,3-Diphenylpentanedionatodimethylthallium(III), $(CH_3)_2Tl(dbzm)$.**—Dimethylthallium(III) iodide, 2.60 g, and thallous dibenzoylmethanate, 2.97 g, were refluxed for 2 hr in 25 ml of absolute ethanol. The solution was filtered through paper while still warm to remove thallous iodide. Light yellow crystals were deposited after standing overnight at 0°; mp 176–178°. *Anal.* Calcd for $C_{17}H_{17}O_2Tl$: C, 44.65; H, 3.76. Found: C, 45.17; H, 3.89. The molecular weight in benzene[11] corresponds to that of a monomer.

**1,1,1,5,5,5-Hexafluoro-2,4-pentanedionatodimethylthallium(III), $(CH_3)_2Tl(hfacac)$.**—To 0.93 g of dimethylthallium(III) bromide was added 1.23 g of thallous hexafluoroacetylacetonate in 25 ml of absolute ethanol. The mixture was refluxed for 1 hr. The solution was filtered through paper at room temperature to remove thallous bromide. The crude product crystallized in good yield after the solution volume was reduced to below 5 ml and the temperature was reduced to 0°. Purification was accomplished by recrystallization from petroleum ether (bp 90–100°) with just enough ethanol added at the boiling point to bring the product into solution; mp 190–192°. *Anal.* Calcd for $C_7H_7O_2F_6Tl$: C, 19.04; H, 1.60; F, 25.82; mol wt, 441.5. Found: C, 19.13; H, 1.58; F, 22.78; mol wt, 485 (in benzene by osmometry).

**2,4-Pentanedionatodimethylindium(III).**—Preparation was according to a method described by Clark;[12] mp 170–172°.

**Dichlorobis(1,1,1,5,5,5-hexafluoropentanedionato)tin(IV).**—Hexafluoroacetylacetone, 5.00 g, was refluxed for 12 hr with 2.86 g of tin tetrachloride in 25 ml of benzene. Evaporation of the solvent at room temperature on a rotary evaporator left a light yellow liquid. *Anal.* Calcd for $C_{10}H_2O_4Cl_2F_6Sn$: C, 19.87; Cl, 11.75; mol wt, 603.7. Found: C, 20.76; Cl, 11.64; mol wt, 615 (in benzene by cryoscopy).

**Analyses.**—Samples were analyzed by Micro-Analysis, Inc., Wilmington, Del.

**Molecular Weights.**—Molecular weights were determined with a Mechrolab Model 301A vapor pressure osmometer with benzene as solvent or by means of standard freezing point lowering measurements in the same solvent. Solutions used were less than 1% solute by weight.

**Dipole Moments.**—Dielectric constants were measured at 25° with a WTW Model DM01 dipolemeter. The instrument was calibrated with dry reagent grade benzene and cyclohexane. Refractive indices (4358 Å) were determined at 25° with a Phoenix Model BP-2000V differential refractometer. Solution densities did not exceed those of the pure solvent by more than 0.1%.

## Results

**Dipole Moments.**—Calculations were made according to the methods of Guggenheim[13] and Smith[14] with no corrections shown in the tabulated data for atomic polarization. Reproductibility of the dielectric constant increments, $\Delta\epsilon$, was ±1% even though very dilute solutions were used. Uncertainties in dipole moments due to uncertainties in the refractive index were less than 1%. Reproducibility of the dipole moments was about ±0.1 D.

TABLE I

DIPOLE MOMENT DATA[a]

| Compound | Concn range, $10^3w_2$ | $\Delta\epsilon/w_2$ | $\Delta n^2/\Delta w_2$ | Mol dipole moment, D | Metal–$\beta$-ketoenolate group moment, D |
|---|---|---|---|---|---|
| Tl(acac) | 1.39–9.15 | 1.360 | 0.100 | 1.87 | 1.87 |
| Tl(dbzm) | 1.25–8.30 | 1.545 | 0.545 | 1.98 | 1.98 |
| Tl(hfacac) | 1.115–5.52 | 8.15 | −0.043 | 5.57 | 5.57 |
| $(CH_3)_2Tl(acac)$ | 0.553–4.14 | 1.045 | 0.100 | 1.70 | 1.9 |
| $(CH_3)_2Tl(dbzm)$ | 0.025–8.04 | 1.235 | 0.471 | 1.79 | 2.0 |
| $(CH_3)_2Tl(hfacac)$ | 1.197–3.76 | 4.64 | 0.01 | 4.55 | 4.7 |
| $(CH_3)_2In(acac)$ | 1.347–11.65 | 1.937 | 0.134 | 2.01 | 2.2 |
| $SnCl_2(hfacac)_2$ | 3.79–10.95 | 1.591 | −0.060 | 2.97 | 2.0 |

[a] $w_2$ = weight fraction solute; $\epsilon$ = dielectric constant (solution; $n$ = refracive index (solution).

## Discussion

**Thallium(I) $\beta$-Ketoenolates.**—The thallium(I) complexes studied possess molecular dipole moments consistent with the assumptions that the molecules studied are monomeric and that thallium–oxygen bonds are only moderately polar. The dipole moment of 1.87 D assigned to Tl(acac) in benzene certainly is much lower than the 6–9 D predicted[1–3] by some workers. The 5.57-D moment observed for Tl(hfacac) is 0.56 unit higher than expected assuming that Tl(acac) and Tl(hfacac) are monomeric and that they have similar planar carbon atom skeletons.

If it is assumed that the structures are like that determined by Roof[15] with C–$CH_3$ and C–$CF_3$ carbon–carbon bonds lying at angles of 57° 31′ to the molecular $C_2$ axis, the difference in moments between Tl(acac) and Tl(hfacac) should be $2(\cos 57° 31')(2.56 + 0.37) = 3.14$ D. Possible values of the Tl(hfacac) moment must be approximately $(1.87 - 3.14) = -1.24$ D or $1.87 + 3.14 = 5.01$ D. Since the moment of Tl(hfacac) is 5.57 D, it can be claimed safely that Tl(acac) and Tl(hfacac) moments both point along the $C_2$ axes toward the ligand away from the metal ions. Calculations have been made using group moment values of −0.37 and 2.56 D for the C–$CH_3$ and C–$CF_3$ groups, respectively. The positive direction is taken as that pointing away from the metal ion toward the ligand.

The arguments stated above rest on the assumptions that every complex studied is monomeric and that the carbon atom skeletons of the chelate rings are unchanged from compound to compound. It is recognized that there will be minor differences in bond angles for the different molecules, but it is felt that such changes will be relatively small. It must be admitted that the molecular weight of Tl(acac) is not known with precision due to the low solubility in benzene of that complex. Fortunately, it was possible to determine the molecular weights of Tl(hfacac) and Tl(dbzm) very precisely. Both unquestionably are monomers. It should be noted that the moment of Tl(dbzm) is

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slightly greater than that of Tl(acac) and much less than that of Tl(hfacac), just as should be predicted on the basis of group moments listed by Smith.[16]

**Thallium(III) Complexes.**—β-Ketoenolate group moments in the dimethylthallium(III) complexes studied are not substantially different from those belonging to corresponding thallium(I) complexes. For instance, the moment of $(CH_3)_2Tl(acac)$ is 1.70 D while that of Tl(acac) is 1.87 D. Assuming a reasonable value of the Tl–C bond moment[16] to be about 0.5 D pointing away from the metal toward carbon, the metal acetylacetonate group moment in $(CH_3)_2Tl(acac)$ is almost identical with that of Tl(acac). The other chelate rings have moments which roughly correspond to those predicted on the basis of group moments.

**2,4-Pentanedionatodimethylindium(III).**—This complex's moment of 2.01 D is close enough to that of $(CH_3)_2Tl(acac)$ to state that again the ring moment must be about 2 D with the vector pointing away from the metal ion toward the ring. It can be concluded that in all of the above complexes the metal–oxygen bonds are moderately polar. Specifically, metal–oxygen bond moments should be about 3.5 D if it is assumed that the acetylacetonate groups have a resultant moment[16,17] of about 3 D pointing toward the metal away from the ring after metal–oxygen bond moments have been subtracted.

**Dichlorobis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)tin(IV).**—The dipole moment of the corresponding acetylacetonate has been reported earlier[18] as 6.7 D at several temperatures in benzene. A *cis* ($C_2$) geometry has been assigned by several workers.[18-21] Dibenzoylmethanate derivatives[18] are also *cis* with no evidence for a *cis–trans* equilibrium. It seems likely that the hexafluoroacetylacetonate derivatives should also be *cis*. The moment of 2.97 D is consistent with the assignment of a *cis* structure only if it is assumed that Sn–O bonds in $SnCl_2(hfacac)_2$ are only slightly polar. The smaller value of the moment for the above complex implies that metal–β-ketoenolate group moments in the above complex and in $SnCl_2(acac)_2$-point toward the tin away from the chelate ring. The reasoning is as follows. Possible values of the $SnCl_2(hfacac)_2$ moment based on group moment additivity are $(6.77 + 3.14) = 9.91$ D or $(6.77 - 3.14) = 3.63$ D. The observed value of 2.97 D is reasonably close to the 3.63 D predicted for a *cis*-type structure with $C–CF_3$ group moments opposing the tin–acetylacetonate group moment. The nearly nonpolar character of the tin–oxygen bonds in $SnCl_2(acac)_2$ and $SnCl_2(hfacac)_2$ is interesting but not entirely surprising since it is widely held[22-24] that d orbitals of tin are lowered substantially in energy upon formation of tin–chlorine bonds. The reluctance of $SnCl_2(acac)_2$ to undergo displacement reactions may in part be due to the covalent character of the Sn–O bonds.

There is no way to calculate precisely the tin–β-ketoenolate group moments from the data, since the value of the Sn–Cl bond moment is not known for six-coordinate structures. However, it seems safe to assume that it will not be much greater than the 3–3.5 D found[16] for four-coordinate tin. If an Sn–Cl bond moment of 3.5 D is used, the resultant of two Sn–Cl moments will be about 5 D. It follows that the tin acetylacetonate group moment on $SnCl_2(acac)_2$ must be about 1.7 D pointing away from the ring toward the metal along the $C_2$ axis of each ring.

All of the complexes studied have surprisingly low group dipole moments. Use of the "rule of thumb" that acetylacetonate ring moments can be assigned values of 6–9 D has been shown to be unwarranted. No definite conclusion can be made regarding group moments of transition metal complexes such as $Hf(acac)_4$ and $Zr(acac)_4$ which have been assigned[1-3] large values of atomic polarization. Such moments indeed may be large, yet it must be emphasized that the assignment of atomic polarization values should be made only with the greatest caution. In complexes of $Tl^+$—$(CH_3)_2Tl^+$, $(CH_3)_2In^+$, and $SnCl^{2+}$—the low values of the group dipole moments suggest that atomic polarization will have a very small value indeed. Precise measurements of the atomic polarization which require a determination of the dielectric loss in the infrared and microwave regions have not been made.

**Acknowledgment.**—Thanks are due to Bristol-Myers Co., Hillside, N. J., for generous support of C. Z. M.

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