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Use of Ligand Probes in Light Scattering. 2. Structure of Labile, Six-Coordinate Organotin(IV) Complexes Having Octyl and Cyclohexyl Groups

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The molecular optical anisotropy has been determined for the ligands 1,3-diphenylpropane-1,3-dione (dibenzoylmethane) and tropolone in cyclohexane at 20 °C, by means of a depolarized Rayleigh light-scattering method. Illumination at 632.8 nm was used. Complexes of the type R_2SnCh_2 have been synthesized ($R = C_8H_{17}$, C_6H_{11} ; $Ch^- =$ dibenzoylmethanate). Two narrow-band-pass filters of differing breadth, 19 and 45 cm^{-1} , respectively, were employed to allow separation of the broad, transient, collision-induced contributions from that of the intrinsic molecular scattering, which is observed as the much narrower reorientational Rayleigh component of the solutions. The depolarized scattering data show conclusively that the complexes possess a "trans" structure with coplanar dibenzoylmethanate rings.

Introduction

Many neutral, six-coordinate, monomeric compounds of the type R_2SnCh_2 have been prepared.¹⁻⁶ The unidentate substituent, R , can be one of a variety of alkyl, aromatic, or halo groups, and the bidentate chelate, Ch^- , can possess various combinations of nitrogen-, oxygen-, and sulfur-donor sites. If the ligand Ch^- has C_{2v} symmetry, only two simple, regular, octahedral isomers are possible, a cis and a trans, although complexes having chelates of small normalized bite have been observed to exhibit a skew-trapezoidal structure. Crystal studies⁸⁻¹⁰ quite clearly show that chelates of large bite such as diketonates favor a trans structure⁸ while chelates of smaller bite such as tropolonates and 8-quinolinolates generally favor a cis configuration.⁹

Results of solution studies have not been easily interpreted. For example, there is good evidence for cis structures being stable for a number of β -keto-enolates such as $Cl_2Sn(acac)_2$ ¹¹ and $(C_6H_5)_2Sn(acac)_2$ ¹² in benzene and even $(CH_3)_2Sn(acac)_2$ and $(CH_3)_2Sn(dbzm)_2$ ($dbzm =$ dibenzoylmethanate) in carbon disulfide.¹³ Most complexes of this type are highly labile^{3,15} and do not lend themselves easily to NMR studies even at low temperatures. Dipole moments³ and vibrational spectra¹³ suggest that both isomers coexist in solution in a number of instances.

Because of the difficulty in determining the solution structures of complexes of the type R_2SnCh_2 by conventional techniques, we have attempted to study several complexes of interest by means of depolarized Rayleigh light scattering.⁴ This is attractive because cis and trans isomers are predicted to have large and substantially different optical anisotropies, which should give rise to very different, depolarized, Rayleigh scattered-light intensities.¹⁵

Since very little has been done to characterize the structures of complexes of this sort having bulky alkyl groups, complexes of the type R_2SnCh_2 have been prepared ($R = C_8H_{17}$, C_6H_{11} and $Ch^- = dbzm^-$), and they have been studied with use of the depolarized Rayleigh scattering technique. Special care

has been taken to remove collisional contributions to the depolarized scattered-light intensities.

Experimental Section

Light-Scattering Photometer. Intensities of horizontally polarized Rayleigh scattered light were measured with a specially constructed photometer¹⁶ described elsewhere. The light source was a 15-mW Spectra-Physics Model 120 CW He-Ne laser, which provided a vertically polarized light beam of wavelength 632.8 nm. Interference filters used were of 19 ± 1 and 45 ± 1 cm^{-1} breadth, respectively, and were purchased from Baird Atomic and Perkin-Elmer Corp., respectively. The cell compartment was maintained at 20 °C. Photometer calibration was by means of a previously reported method.¹⁵ Solutions were clarified by membrane filtration.¹⁶

Solution Densities, Refractive Indices, and Absorption Spectra. Specific gravities were measured at 20 °C with a Westphal-type balance. The refractive indices were measured at 20 °C as well with a Brice-Phoenix Model BA-2000V differential refractometer. Absorption spectra were determined between 250 and 700 nm with a Cary 15 spectrometer.

Reagents and Syntheses. Solvents were obtained from Mallinckrodt. Cyclohexane was distilled from CaH_2 . Dibenzoylmethane was obtained from Aldrich, Inc. Oxides and complexes were prepared with use of a modification of the method of McGrady and Tobias.¹

Bis(1,3-diphenyl-1,3-propanedionato)dicyclohexyltin(IV). Dibenzoylmethane (4.4948 g, 20.04 mmol) and dicyclohexyltin oxide (3.0171 g, 10.02 mmol) were added to 150 mL of cyclohexane and refluxed for 3.5 h. After vacuum elimination of the solvent, the yellow residue was recrystallized from pentane-benzene (5:1), mp 164.5-166 °C. Anal. Calcd for $C_{42}H_{44}O_4Sn$, $(chx)_2Sn(dbzm)_2$: C, 68.96; H, 6.06. Found: C, 69.23; H, 6.08.

Bis(1,3-diphenyl-1,3-propanedionato)di-*n*-octyltin(IV). Dibenzoylmethane (5.0032 g, 22.31 mmol) and di-*n*-octyltin oxide (4.1039 g, 11.36 mmol) were reacted overnight in 180 mL of petroleum ether-benzene (5:1) at reflux. After the solution was filtered through Celite and sintered glass, the solvent was flash evaporated, and the orange product, an oil, was stored at -20 °C without further purification. Anal. Calcd for $C_{46}H_{56}O_4Sn$, $(n-oct)_2Sn(dbzm)_2$: C, 69.79; H, 7.13. Found: C, 70.00; H, 7.16.

Measurement of the Molecular Polarizability Anisotropy. Depolarized Rayleigh scattered-light intensities are proportional to the square of the polarizability anisotropy, γ^2 :

$$\gamma^2 = \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]$$

α_{xx} , α_{yy} , and α_{zz} are the diagonal elements of a diagonalized molecular polarizability tensor. For a symmetric rotor $\gamma = \alpha_{||} - \alpha_{\perp}$ if $\alpha_{||}$ and $\alpha_{\perp}$ are respectively the diagonal elements of differing value. The depolarized scattered-light intensity, I_{VH} , due to a vertically polarized incident beam can be related to the anisotropy as described by Burnham, et al:¹⁷

$$I_{VH} = G_n L_n \gamma^2 P g_2$$

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Table I. Light-Scattering Data (Cyclohexane Solutions)

concn, M	n	c°/d°	10 ⁶ R _{VH}			10 ⁴⁸ γ ² , cm ⁶
			no filter	σ = 45 cm ⁻²	σ = 19 cm ⁻¹	
Dibenzoylmethane						
0.0248	1.4277	0.9954	0.191		0.051	119.6
0.0313	1.4281	0.9942			0.056	
0.0458	1.4288	0.9915		0.114	0.075	
0.0672	1.4298	0.9871	0.326	0.139	0.098	
0.0850	1.4306	0.9832	0.391	0.166	0.115	
0.0920	1.4309	0.9821	0.404	0.194		
Tropolone						
0.0415	1.4274	0.9961	0.127	0.040	0.026	15.4
0.0573	1.4277	0.9936	0.139	0.043	0.029	
0.0738	1.4281	0.9923		0.049	0.036	
0.1082	1.4288	0.9871	0.169	0.061	0.040	
0.1245	1.4292	0.9856	0.189	0.064	0.044	
(n-oct) ₂ Sn(dbzm) ₂						
0.00590	1.4273	0.9952	0.316	0.140	0.106	407
0.00878	1.4277	0.9938	0.372	0.168	0.119	
0.01245			0.441	0.209	0.146	
0.01512	1.4286	0.9902	0.481	0.226	0.161	
0.01796	1.4289	0.9885	0.536	0.255	0.182	
0.02435	1.4297	0.9846	0.670	0.326	0.232	
(chx) ₂ Sn(dbzm) ₂						
0.00482	1.4276	0.9961	0.295	0.144	0.102	489
0.00716	1.4279	0.9957	0.344	0.165	0.127	
0.00966	1.4280	0.9932	0.393	0.188	0.147	
0.01219	1.4287	0.9928	0.434	0.210	0.161	
0.01544			0.499	0.242	0.191	

G_n is a geometric correction, L_n is the local field correction, P is the solute number density, n is the refractive index, and g_2 is the static orientation correlation parameter. Experimentally, I_{VH} , the contribution for the solute, is proportional to the area of a sharp central peak, which can be easily separated in most instances from much broader contributions due to solvent and collisional scattering.

Calculations of I_{VH} and the associated Rayleigh constant, R_{VH} , for both solution and solvent were made with a method similar to that of Carlson and Flory.¹⁸ Simply, two different interference filters centered at 632.8 nm but having different band breadths for transmittance were used to selectively remove, in turn, portions of the broad part of the Rayleigh line. The filters were chosen with band breadths that do not significantly attenuate the solute peak due to orientational scattering but substantially and to differing predictable extents attenuate the broad collisional portions of the peak.

If σ is the Gaussian constant for the filter, b is the bandwidth for solute orientational scattering, and w_0 is the band width for collisional scattering, $R_{VH}(\sigma)$ is the apparent Rayleigh constant associated with solute scattering with a particular filter in place:

$$R_{VH}(\sigma) = [x(\sigma, b)]R_{VH}(\text{orientation}) + [y(\sigma, w_0)]R_{VH}(\text{collision})$$

Filter transmittance $T_w = T_0 \exp(-w^2/\sigma^2)$. For both filters $x = 1$ because of the narrowness of the peak due to orientational scattering. The transmission coefficient for collisional scattering, y , however, is not equal to 1.0 and differs markedly for the two filters used. Values of $R_{VH}(\text{orientation})$ calculated by means of the equation below are expressed in terms of $R_{VH}(\sigma_1)$ and $R_{VH}(\sigma_2)$ measured for each solution and the ratio y_1/y_2 , which is not a strong function of w_0 . For example, Carlson and Flory showed that $y_1/y_2 = 0.438$ for filters of $\sigma = 18$ and 48 cm^{-1} , respectively, for w_0 between 12 and 18 cm^{-1} . Since our filters were of slightly different bandwidth, we calculated our y_1/y_2 value independently. For our system $y_1/y_2 = 0.446$ with $w_0 = 20 \text{ cm}^{-1}$. Then R_{VH} becomes

$$R_{VH}(\text{orientation}) = \frac{R_{VH}(\sigma_1) - 0.446[R_{VH}(\sigma_2)]}{1 - 0.446}$$

The depolarized scattering has been measured with no filter in place, with the 19-cm^{-1} filter, and with the 45-cm^{-1} filter. R_{VH} measured for no filter in place is of no direct use in calculations but serves as

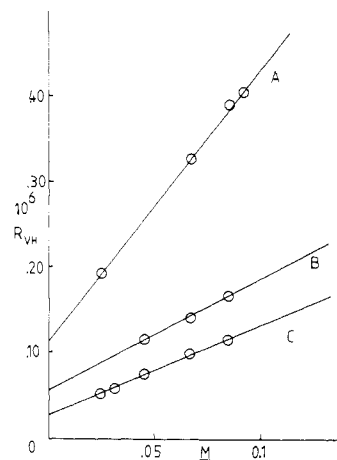


Figure 1. Plots of R_{VH} vs. [dibenzoylmethane] (M) in cyclohexane for (A) no filter, (B) $\sigma = 45 \text{ cm}^{-1}$, and (C) $\sigma = 19 \text{ cm}^{-1}$.

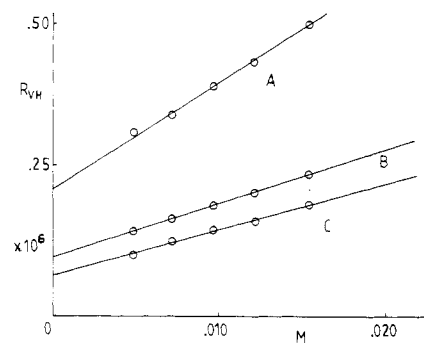


Figure 2. Plots of R_{VH} vs. [(chx)₂Sn(dbzm)₂] (M) in cyclohexane for (A) no filter, (B) $\sigma = 45 \text{ cm}^{-1}$, and (C) $\sigma = 19 \text{ cm}^{-1}$.

Table II. Optical Spectra

compd	solvent	abs max, nm (log ε)
(n-oct) ₂ Sn(dbzm) ₂ ^a	C ₆ H ₁₂	336 (4.60), 251.5 (4.35)
	CHCl ₃	341 (4.36), 254 (4.00)
(chx) ₂ Sn(dbzm) ₂	C ₆ H ₁₂	346.5 (4.57), 251 (4.42)
	CHCl ₃	341.5 (4.62), 255 (4.30)
n-Bu ₂ Sn(dbzm) ₂	C ₆ H ₁₂	337 (4.49), 252 (4.31)
	CHCl ₃	341.5 (4.65), 252 (4.39)

^a dbzm ≡ dibenzoylmethanate.

a means of assessing the total magnitude of all extra contributions besides collisional and orientational scattering. To obtain the R_{VH} for the pure solvent, one need only measure the scattering from the pure solvent. In practice it was useful to measure $R_{VH}(\text{soln})$ and to extrapolate it to infinite dilution. This value obtained with a filter in place is subtracted from the solution scattering to yield the contribution due to the solute, $R_{VH}(\sigma)$. All $R_{VH}(\sigma)$ values are obtained by multiplying R_{VH} for a standard Lucite block by $I_{VH}(\text{soln})/I_{VH}(\text{std})$. $R_{VH}(\text{std})$ was determined to be 1.438×10^{-4} , and usually a 20× neutral filter was placed in the scattered standard beam to reduce the scattered-light intensity values for the standard to values very near those of the solutions.

Typical plots of $R_{VH}(\text{soln})$ vs. solute concentration are shown in Figures 1 and 2. L_n was taken as $(n^2 + 2)/3$.⁴ Table I presents the results of the complete scattering data. Table II reports absorption spectra. Figure 3 shows a typical plot of refractive index vs. solute molarity.

Results and Discussion

As noted in Table I, the scattering from tropolone is much less intense than that from dibenzoylmethane. The value of γ^2 for tropolone is slightly larger than that of benzene itself, 15.4×10^{-48} vs. $13.0 \times 10^{-48} \text{ cm}^6$, which is doubtlessly reflective of their very similar structures. On the other hand, dibenzoylmethane is expected to be a much stronger scatterer than tropolone since it can be considered as roughly equivalent

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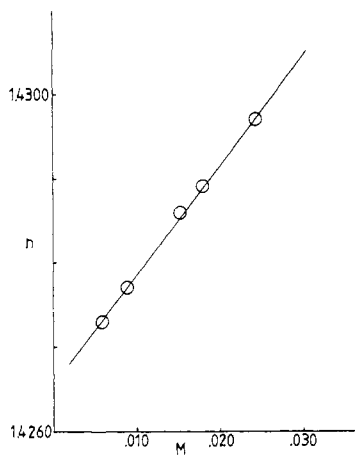


Figure 3. Refractive index vs. $[(n\text{-oct})_2\text{Sn}(\text{dbzm})_2]$ (M) in cyclohexane.

to three coplanar benzene rings, which should give rise collectively to a much larger optical anisotropy. Assuming that molecular polarizability anisotropies can be calculated as the sum of the three separate benzene-ring-like polarizability components, one predicts γ^2 to be $117 \times 10^{-48} \text{ cm}^6$. The observed value of $119.6 \times 10^{-48} \text{ cm}^6$ is remarkably close to the predicted one. Considering that the dibenzoylmethane molecule is a conjugated system, it is surprising that observed and predicted values fall this closely together. However, at the very least, it appears that the reported γ^2 value for dibenzoylmethane falls within a reasonable range unlike previously reported values,⁴ which were too large because of inclusion of collisional scattering.

The linearity of the $R_{\text{VH}}(\text{soln})$ vs. solute concentration plots for ligands and complexes strongly indicates that static correlations between solute molecules can be neglected in anisotropy calculations. That is, if $g_2 \neq 1$, plots of R_{VH} vs. solute molarity would be markedly curved. Thus, in all calculations " g_2 " has been set equal to 1.0.

Because for dibenzoylmethane γ^2 is large, $120 \times 10^{-48} \text{ cm}^6$, it follows that the intensity of depolarized scattering from solutions of dibenzoylmethanate complexes will be relatively great. Previously published calculations⁴ for six-coordinate octahedral complexes containing two planar bidentate and two monodentate ligands show that the octahedral cis geometry requires that γ^2 for the ligand equal γ^2 for the complex. In contrast, the octahedral trans geometry is shown to have a

value of γ^2 that is 4 times that of the single ligand or of the cis complex. Thus, one expects $\gamma^2 = 120 \times 10^{-48} \text{ cm}^6$ for a cis-type complex and $\gamma^2 = 480 \times 10^{-48} \text{ cm}^6$ for the trans. The observed values of 489×10^{-48} and $407 \times 10^{-48} \text{ cm}^6$ for the cyclohexyl and *n*-octyl derivatives, respectively, strongly indicate that little, and probably no, cis isomer is present.

Figures 1 and 2 show that Rayleigh wing scattering (collisional scattering) is very large for both the ligands and the complexes. It follows that in studies of this type care must be taken to measure intensities associated with the central Lorentzian lines, which are characterized by half-widths that are in the order of GHz as opposed to those of the wing scattering, which may extend for many wavenumbers above and below the central peak.

The difference in anisotropies of the two tin complexes is marginally significant, considering the experimental error associated with the use of filters and assumed collisional scattering line shapes. Future work in this laboratory will be done with an interferometer, which should allow a more accurate quantitative comparison of central-peak relative intensities.

It is noted from Table II that the octyl derivative, which has the lower γ^2 value, has its intense ligand-absorption band in the ultraviolet "blue shifted" as opposed to that of the cyclohexyl derivative. If preresonance enhancement of γ^2 is important, it is likely that the cyclohexyl derivative would show the greater enhancement. Nonetheless since neither of these complexes shows any measurable absorption below about 500 nm, it is unlikely that the scattering of either complex is significantly preresonance enhanced. Because the contributions of the cyclohexyl and *n*-octyl groups to the overall molecular anisotropy have been neglected, it may be that the reduced value of γ^2 for the octyl derivative is, in part, due to the contribution of the octyl group. The contribution of the cyclohexyl group to γ^2 must be negligibly small.

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Registry No. $(\text{chx})_2\text{Sn}(\text{dbzm})_2$, 80327-43-1; $n\text{-Bu}_2\text{Sn}(\text{dbzm})_2$, 81130-68-9; $(n\text{-Bu})_2\text{Sn}(\text{dbzm})_2$, 22673-17-2; dibenzoylmethane, 120-46-7; tropolone, 533-75-5; dicyclohexyltin oxide, 22771-17-1; di-*n*-octyltin oxide, 870-08-6.