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Use of Ligand Probes in Light Scattering. 1. Structural Analysis of Some Organotin(IV) Complexes in Cyclohexane and Benzene Solutions

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Optical anisotropies have been determined for several complexes of the type R_2SnCh_2 (R = CH_3, C_2H_5; Ch^- = acetylacetonate, dibenzoylmethanate, or tropolonate) by measurement of depolarized Rayleigh-scattered light intensities at 632.8 nm. Results of studies in cyclohexane solutions confirm that several of these complexes exist as cis–trans mixtures. For example, solutions of bis(1,3-diphenyl-1,3-propanedionato)dimethyltin(IV) and bis(1,3-diphenyl-1,3-propanedionato)diethyltin(IV) have been characterized as being composed of approximately two-thirds trans and one-third cis isomers. Scattering from several benzene solutions also is consistent with the assumption of cis–trans mixtures, but in two instances involving bis(2,4-pentanedionato)dimethyltin(IV) and bis(tropolonato)diethyltin(IV) anisotropies are believed to have been enhanced measurably by solute–solvent interaction. Advantages and limitations in the use of the depolarized-light-scattering technique for the determination of isomer distributions have been discussed.

Introduction

Neutral, monomeric, six-coordinate organotin chelate compounds of the type R_2SnCh_2 are well-known.[1-8] The substituent, R, can be a halo, alkyl, or aromatic group and the bidentate ligand, Ch^-, can be one of a variety possessing nitrogen or oxygen donors. Complexes of β-keto enols, 8-quinolinol, and tropolone have been studied most extensively. If the ligand, Ch^-, has C_{2v} symmetry, only two isomeric forms of the complex are likely, a cis and a trans. Such systems, because of their simplicity, are of special interest. Unfortunately, no simple principle has been developed which allows the prediction of the most stable isomeric form for a particular derivative and both forms have been observed.

A number of physical methods have been applied. X-ray crystal studies have shown, for example, that bis(8-quinolinolato)dimethyltin(IV), $(CH_3)_2Sn(Ox)_2$, is cis while bis(2,4-pentanedionato)dimethyltin(IV),[9] $(CH_3)_2Sn(acac)_2$, is trans. Results of infrared, Raman, and Mössbauer studies are in substantial agreement with the findings of the x-ray work. Because of the lability of many of these complexes[10,11] in solution, NMR has been of limited use. Attempts[11] to assess the solution structure of $(CH_3)_2Sn(acac)_2$ by variable-temperature NMR, for example, have proved unsuccessful. On the other hand $Cl_2Sn(acac)_2$[12,13] and $(C_6H_5)_2Sn(acac)_2$[14] which are somewhat less labile have been shown to be 100% cis. Significantly, $CH_3ClSn(acac)_2$ is best characterized[15] in terms of a cis–trans equilibrium. Apparently conflicting data have been reported concerning $(CH_3)_2Sn(acac)_2$ in solution. Infrared[2] and Raman[2,16,17] studies have provided evidence for a predominant trans structure while dipole moment[10] and dielectric loss measurements[18] have indicated that the complex is cis or a mixture of cis and trans isomers.

Very recently, infrared spectra[19] of $(CH_3)_2Sn(acac)_2$, corresponding tropolonate and oxinate derivatives, $(CH_3)_2Sn(trop)_2$ and $(CH_3)_2Sn(Ox)_2$, and their deuteriomethyl analogues have been obtained in CS_2 solution. As expected for a cis structure[6,19] solutions of the oxinate possess two peaks at 517 and 529 cm^{-1}, assignable to the symmetrical and antisymmetrical $(CH_3)_2Sn$ skeletal stretching vibrations, which shift about 50 cm^{-1} to lower energies for the deuteriomethyl derivatives. Solutions of the corresponding tropolonates and acetylacetonates have been shown to possess corresponding peaks which shift in similar fashion. This indicates very strongly that a substantial amount of *cis*-$(CH_3)_2Sn(acac)_2$ is present in CS_2 solutions. However, the dimethyltin acetylacetonate spectra, in contrast with other spectra, include a third stronger peak at 578 cm^{-1} which also shifts 50 cm^{-1} upon deuteration. Since that peak is best assignable to the antisymmetrical stretching vibration of a linear $(CH_3)_2Sn$ moiety, it has been concluded that the dimethyltin acetylacetonate solutions are mixtures of cis and trans isomers. Dimethyltin oxinates and tropolonates[19,20] have been shown to be present exclusively as the cis isomers in solutions. Because it was not possible to determine quantitatively the relative amounts of cis and trans isomers present in equilibrium mixtures on the basis of the infrared solution study[19] and because the complexes are too labile to study effectively with NMR, it was decided to attempt another means of structural investigation capable of determining the amounts of cis and trans isomers.

A recent paper[21] reports the optical anisotropies of several ligands of C_{2v} symmetry. Because the ligands in question—acetylacetone, dibenzoylmethane, and tropolone—have very large optical anisotropies, simple complexes of the type $(CH_3)_2SnCh_2$ and $(C_2H_5)_2SnCh_2$ will have large optical anisotropies in solution. More importantly, these anisotropies will vary strongly as a function of structure. Since there is reasonable confidence[19] that the solutions are best described as possessing cis–trans equilibrium mixtures rather than single distorted intermediate type structures, apparent anisotropies, as measured in terms of the intensities of the depolarized Rayleigh scattered light, will allow calculation of the relative amounts of cis and trans isomers to be made.

This paper describes the first successful effort to determine the cis–trans isomer distributions for several highly labile complexes of type R_2SnCh_2.

Experimental Section

Light-Scattering Photometer. Intensities of Rayleigh-scattered light were measured by means of a specially constructed photometer described in detail elsewhere.[22] The instrument was equipped with a Spectra-Physics Model 122 He–Ne laser which provided vertically polarized light of wavelength 633 nm. Measurement of Rayleigh-scattered light intensities was made at 90° to the incident laser beam by means of a highly sensitive detection system capable of measuring either vertically or horizontally polarized scattered light. Solutions were contained in a 30 × 30 mm glass cell painted on the outside, except for the entrance and exit slits, with a flat black paint which minimized reflections. The photometer was calibrated using benzene–cyclohexane solutions as described previously.[21,23]

Solution Densities and Refractive Indexes. The refractive indexes were measured at 20.0 °C by means of a Bausch and Lomb Model 33-45-03 Series 021 precision refractometer, estimated to be precise to $n = \pm 0.00003$. Specific gravities were measured using a Westphal-type balance.

Solution Clarification. Dust-free solutions were obtained by using a Millipore stainless steel filter funnel Model 4004700 in conjunction with Millipore filters of Type VCWPO 4700 which have a uniform pore size of 100 nm. Solutions were forced through the filter under positive N_2 pressure of 1–2 psi adjusted to produce a flow rate of 1–2 ml/min. Solutions were judged to be dust free when scattered-light intensities converged to a reproducible value varying by only 1–2%. Generally, three filtrations were enough to produce "clean solutions", but as a general practice five or six filtrations were performed and intensities were measured after each filtration.

Synthesis. Oxides and complexes were prepared using a modification of the method of McGrady and Tobias.[2]

Dimethyl- and Diethyltin Oxides. These were prepared by placing the diorganotin dichloride in a convenient volume of 6 M aqueous ammonia. Precipitates were washed several times with water to remove chloride and then were washed with absolute alcohol to free the sample of starting material. The pure product was then dried in a vacuum oven at 60 °C.

Bis(2,4-pentanedionato)diethyltin(IV), $(C_2H_5)_2Sn(acac)_2$. Diethyltin oxide (2.71 g, 0.0141 mol) and acetylacetone (3.00 g, 0.0300 mol) were placed in a 500-ml round-bottom flask with 250 ml of dry pentane. The mixture was refluxed with stirring for 10 h while the water produced was removed azeotropically. The cooled solution was filtered through paper, and the solvent was removed on a rotary evaporator. The colorless product was recrystallized from dry pentane and dried overnight in a vacuum desiccator; mp 85–87 °C. Anal. Calcd for $C_{14}H_{24}O_4Sn$: C, 44.84; H, 6.45. Found: C, 45.24; H, 6.47.

Bis(1,3-diphenyl-1,3-propanedionato)diethyltin(IV), $(C_2H_5)_2Sn(dbzm)_2$. A slight excess of dibenzoylmethane (9.100 g, 0.0406 mol) was added to diethyltin oxide (3.910 g, 0.0203 mol) in 250 ml of dry cyclohexane. The mixture was refluxed with stirring for 4 h while water was removed azeotropically. After the oxide had reacted completely, the solution was filtered and the solvent evaporated. The pale yellow product was recrystallized from a dry cyclohexane–benzene mixture in which a few crystals of ligand had been added to suppress hydrolysis; mp 141–143 °C. Anal. Calcd for $C_{34}H_{32}O_4Sn$: C, 65.52; H, 5.17. Found: C, 65.50; H, 5.12.

Bis(tropolonato)diethyltin(IV), $(C_2H_5)_2Sn(trop)_2$. Tropolone (3.1979 g, 0.0262 mol) dissolved in 250 ml of dry cyclohexane was mixed with diethyltin oxide (2.5245 g, 0.0131 mol) and refluxed for 5 h. At the end of this period the warm solution was filtered through paper and the solvent removed by flash evaporation. The light tan product was recrystallized from a dry cyclohexane–benzene mixture and dried overnight in a vacuum desiccator; mp 175–177 °C. Anal. Calcd for $C_{18}H_{20}O_4Sn$: C, 51.59; H, 4.81. Found: C, 51.89; H, 4.61. Bis(2,4-pentanedionato)dimethyltin(IV), $(CH_3)_2Sn(acac)_2$, and bis(1,3-diphenyl-1,3-propanedionato)dimethyltin(IV), $(CH_3)_2Sn(dbzm)_2$, were prepared as reported earlier.[19]

Reagents. Reagent grade 2,4-pentanedione was purchased from Mallinckrodt Chemical Works and purified by fractional distillation. Reagent grade 1,3-diphenyl-1,3-propanedione was purchased from Eastman and recrystallized from 95% ethyl alcohol. Tropolone was obtained from the Aldrich Chemical Co. and recrystallized from cyclohexane. Diethyltin dichloride purchased from K & K Laboratories and dimethyltin dichloride obtained from City Chemical Co. were used without further purification.

Measurement of the Molecular Polarizability Anisotropy, γ^2

According to Bothorel,[24] γ^2, the molecular polarizability anisotropy (optical anisotropy) of a solute molecule can be determined by measurement of the intensity increments of depolarized Rayleigh-scattered light from solutions as in

$$\gamma^2 = \frac{135\lambda^4}{16\pi^4 p(n^2+2)^2}\left[R_i(\mathrm{soln}) - R_i(\mathrm{solv})\frac{c_0}{d_0}\left(\frac{n^2+2}{n_0+2}\right)^2\right]$$

If the molecular polarizability tensor is diagonalized

$$\gamma^2 = {}^1/_2\,[(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{xx}-\alpha_{zz})^2 + (\alpha_{yy}-\alpha_{zz})^2]$$

λ is the wavelength of incident radiation in centimeters, p is the number of solute molecules per milliliter, n is the refractive index of the solution, n_0 is the refractive index of the pure solvent, c_0 is the number of grams of solvent per milliliter of solution, and d_0 is the density of the pure solvent. R_i(soln) and R_i(solv) are respectively the Rayleigh constants of the solution and pure solvent which are proportional to corresponding depolarized scattered light intensities measured 90° to the incident polarized laser beam.

Calibration was done by measuring the depolarized scattering of four benzene solutions in cyclohexane. Concentrations of benzene ranged from 0.236 to 1.151 M. Turbidity increments due to the benzene were calculated by means of Bothorel's equation[24] assuming a γ^2 value of 28.0×10^{-48} cm^6 for benzene. Basically

$$R_i(\mathrm{soln}) = \frac{I_h(\mathrm{soln})}{I_h(\mathrm{std})}R_i(\mathrm{std})$$

I_h(soln) and I_h(std) are relative intensities of scattered light associated with the solution and a standard, respectively. Because

$$\frac{c_0}{d_0}\left(\frac{n^2+2}{n_0^2+2}\right)^2$$

was very nearly equal to 1.00, typically one could assume

$$\gamma^2 = \frac{135\lambda^4}{16\pi^2 p(n^2+2)^2}[R_i(\mathrm{soln}) - R_i(\mathrm{solv})]$$

It was assumed that both measured "R" values contained a small and equal contribution from parasitic light which canceled. Elimination of parasitic light was accomplished in standardization by taking advantage of that fact. That is, the increment in scattered light R_i(soln) − R_i(solv) of standard solution scattering was used to calibrate the instrument rather than the scattering from a pure liquid which it was feared would contain an unknown amount of parasitic light.

The quantity of greatest experimental interest R_i(soln) − R_i(solv) = R_i(solute) is proportional to the ratio I_h(solute)/I_h(std) assuming I_h(solute) = I_h(soln) − I_h(solv).

Cyclohexane was used as solvent when possible to minimize the magnitude of I_h(solv) as well as to minimize effects of solute–solvent interactions.

Table I summarizes the light-scattering data for the complexes studied. Table II allows a comparison to be made between the anisotropies of the free ligands and those of the complexes in solution.

Discussion

Light-Scattering Data. The data (Table I) indicate clearly that all of the complexes studied are highly optically anisotropic. That is expected[21] since anisotropies should range from single ligand values for cis (C_2) isomers (Figure 1) to 4 times that amount for trans (D_{2h}) isomers (Figure 2). Because dibenzoylmethane has a much larger free-ligand anisotropy,[21] its organotin derivatives also show much larger molecular anisotropies. In comparison with values associated with acetylacetonate and tropolonate complexes, which are also large by ordinary standards, the values of the dibenzoylmethanates are truly enormous.

Because depolarized Rayleigh scattering can be increased due to collisional complex formation[25,26] and solvent-dependent

Table I. Light-Scattering Data

Solute	[Solute], M	Solvent	n(6328 Å)	d^{20}	S^a	I_h(solute)/ I_h(std)	$10^{48}\gamma^2$, cm^6
$(C_2H_5)_2Sn(acac)_2$	0.039	C_6H_{12} + 0.1 M free acetylacetone	1.426 17	0.7920	0.9961	0.067	94
	0.078		1.427 05	0.7954	0.9830	0.138	97
	0.107		1.427 79	0.7981	0.9735	0.227	116
	0.160		1.429 29	0.8075	0.9621	0.342	117
$(C_2H_5)_2Sn(dbzm)_2$	0.017	C_6H_{12}	1.426 96	0.7851	0.9952	0.602	1934
	0.033		1.428 93	0.7902	0.9915	1.213	2003
	0.050		1.431 13	0.7955	0.9876	1.760	1912
	0.070		1.433 65	0.8008	0.9819	2.547	1969
$(C_2H_5)_2Sn(dbzm)_2$	0.050	C_6H_6	1.502 74	0.8926	0.9831	1.685	1654
$(CH_3)_2Sn(dbzm)_2$	0.008	C_6H_6 + 0.1 M free dibenzoylmethane	1.502 47	0.8893	0.9976	0.360	2081
	0.017		1.503 24	0.8913	0.9953	0.681	1964
	0.025		1.503 95	0.8933	0.9932	1.029	2018
	0.034		1.504 73	0.8953	0.9904	1.307	1882
$(CH_3)_2Sn(acac)_2$	0.089	C_6H_6 + 0.1 M acetylacetone	1.498 51	0.8957	0.9773	0.302	152
$(C_2H_5)_2Sn(trop)_2$	0.024	C_6H_6	1.499 56	0.8857	0.9950	0.224	459
	0.048		1.501 04	0.8903	0.9909	0.453	464
	0.072		1.502 56	0.8951	0.9871	0.651	444
	0.112		1.505 03	0.9030	0.9805	0.973	425

[a] $S = (c_0/d_0)[(n^2 + 2)/(n_0 + 2)]^2$; d_0 = solvent density; c_0 = g of solvent/p ml of solution; n_0 = refractive index of pure solvent.

Table II. Comparison of Ligand and Complex Anisotropies and Associated Calculated Isomer Distributions

Complex	Anisotropy, 10^{-48} cm^6			
	Ligand (L)	Complex (C)	C/L	% *trans*
$(C_2H_5)_2Sn(acac)_2$	40	106	2.65	55
$(C_2H_5)_2Sn(dbzm)_2$	677	1954	2.89	63
$(C_2H_5)_2Sn(trop)_2$	130	448	3.44	81
$(CH_3)_2Sn(dbzm)_2$	677	1986	2.93	65
$(CH_3)_2Sn(acac)_2$	40	152	3.80	93

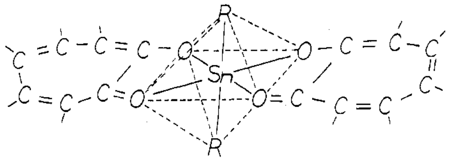

Figure 1. The trans structure.

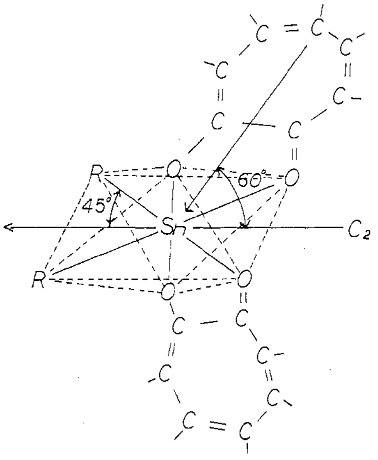

Figure 2. The cis structure.

electric field effects[27-30] proper choices of solvent are critical and determinations of anisotropies as a function of concentration are essential. Anisotropies listed in Table I show no evidence of significant concentration dependence. It is expected that use of solvents such as benzene and especially cyclohexane should minimize problems due to anisotropic electric fields. Cyclohexane should be nearly ideal as a solvent.

The interpretation of benzene solution data, unfortunately, must take into account the probability that benzene molecules may be interacting with the highly polar cis-type complexes to form transient collision complexes. Because dibenzoylmethanates have such large anisotropies, it is doubted that for them such an effect would be easily detectable. However, tropolonates and acetylacetonates may have apparent anisotropies which are significantly larger than expected due to such stereospecific associations of the benzene π system with electron-deficient sites.[31]

A comparison of anisotropies observed for complexes with those anisotropies known for the free ligands (Table II) strongly suggests the existence of a cis–trans equilibrium in solution. The calculation of the percent trans isomer population in a given solution can be determined easily from

$$\gamma^2(\text{complex}) = \frac{\%\ \text{cis}}{100}\gamma^2(\text{ligand}) + \frac{\%\ \text{trans}}{100}(4\gamma^2(\text{ligand}))$$

Since the first conclusive evidence for a cis–trans equilibrium involving the compounds studied was obtained spectroscopically,[19] it was expected that substantial amounts of both isomers would be present.

The similar isomer distributions for $(C_2H_5)_2Sn(acac)_2$, $(C_2H_5)_2Sn(dbzm)_2$, and $(CH_3)_2Sn(dbzm)_2$, ranging between 55 and 65% trans, are consistent with predictions of an earlier paper[18] in which it was noted that most dipole moment data can only be interpreted in terms of complexes in solution being predominantly cis or being in cis–trans equilibrium showing similar isomer distributions.

It is suspected that the anisotropies of $(CH_3)_2Sn(acac)_2$ and $(C_2H_5)_2Sn(trop)_2$, measured in benzene because of limited solubility in cyclohexane, have been significantly enhanced due to stereospecific interactions with benzene. Hence, the percentage trans isomer calculated and tabulated (Table II) may be relatively high for those two species. It is quite possible that in fact the isomer distributions of all of the compounds studied are quite similar.

Comparison with Results of Earlier Dipole Moment Studies

A direct comparison of optical anisotropies and previously determined dipole moment data[10] for the purpose of determining structure is not as simple as it might appear due to the presence of large values of the atom polarization which are difficult to measure. Extensive temperature-dependent dielectric constant measurements definitely have shown that complexes of the type R_2SnCh_2 possess very substantial orientation dipole moments and the magnitudes of several of such moments have been estimated by dielectric loss studies.[18] Dipole moment values determined previously appear along with

Table III. Dielectric Data Compared with Light-Scattering Data

Compd	Static dipole moment, D	Atomic polarizn, cm^3	μ_{loss}, D	% cis isomer[a]
$(C_6H_5)_2Sn(acac)_2$	3.78	160	2.55	100
$(CH_3)_2Sn(acac)_2$	2.95	115	1.76	07
$(C_2H_5)_2Sn(acac)_2$	2.56			45
$(C_6H_5)_2Sn(dbzm)_2$	3.86			
$(CH_3)_2Sn(dbzm)_2$	3.02			35
$(C_2H_5)_2Sn(dbzm)_2$	2.09			37
$(C_6H_5)_2Sn(trop)_2$	4.60	182	3.5	
$(CH_3)_2Sn(trop)_2$	3.65	83	3.0	100

[a] Experimentally determined.

experimentally determined amounts of the cis isomer in Table III.

Clearly the dipole moment data, even after correction for atom polarization, are not consistent with the assignment of 7% cis isomer to solutions of $(CH_3)_2Sn(acac)_2$. If one uses the components derived by Lorberth and Noth[32]

$$\mu(\mathrm{Sn}\rightarrow\mathrm{CH_3}) = 0.6\ \mathrm{D} \qquad \mu(\mathrm{Sn}\rightarrow\mathrm{C_6H_5}) = 1.1\ \mathrm{D}$$

dielectric-loss-derived dipole moments of $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(trop)_2$, based upon the assumption of a cis octahedral geometry, suggest a tin–acetylacetonate group dipole moment of 1.0 D and a tin–tropolonate group dipole moment of 2.15 D. Both values are about 1.0 D lower than predicted on the basis of previously reported static dipole moments.[10,20] A ring dipole moment of only 1.0 D is low enough to make the molecular dipole moment rather insensitive to changes in molecular structure or isomer distribution.

Original dipole moment data[10] were explained on the basis of complexes of the type R_2SnCh_2 being predominantly cis in solution. This conclusion was reached not only because of the substantial magnitudes of dipole moments measured in solution but also because of the differences between dipole moments of compounds in a homologous series, such as $(C_6H_5)_2Sn(acac)_2 > (CH_3)_2Sn(acac)_2 > (C_2H_5)_2Sn(acac)_2$, which were close to those predicted on the basis of group moments. There is no doubt concerning the correctness of the polarization data.

On the other hand, there is little doubt that very appreciable percentages of trans isomers are present in several of these solutions, and this fact must be reconciled with the polarization data. It has been noted previously[18] that atomic polarization values are larger for diphenyltin derivatives than for dimethyltin analogues. Possibly, diethyltin analogues have even lower atomic polarization values. If that is true, one would expect total polarization to vary, $(C_6H_5)_2SnCh_2 > (CH_3)_2SnCh_2 > (C_2H_5)_2SnCh_2$, even for solutions which are composed of 100% trans isomers. Furthermore, if differences in atom polarization equal about half the differences in orientation polarization expected for cis isomers in the above series and the isomer distribution is about 50% cis–50% trans, differences in total polarization should be very close to those predicted[10] for solutions composed of 100% cis isomers.

Spectral Studies

Raman and Infrared Spectra. Raman and infrared studies of both solid state[2] and solutions[16,17] have shown no trace of *cis*-$(CH_3)_2Sn(acac)_2$. Such work appeared to rule out the possibility that solutions were 100% cis as suggested earlier[10] and strongly indicated that the trans isomer predominated. A more recent solution infrared study[19] has shown conclusively that detectible amounts of the cis isomer are present. In fact infrared absorption intensities suggest that isomer distributions are very similar for $(CH_3)_2Sn(acac)_2$ and $(CH_3)_2Sn(dbzm)_2$. Certainly, such ratios are unlikely to differ by more than an order of magnitude. Since the light-scattering study has shown the dibenzoylmethanate to exist as 35% cis, it is suggested that the most likely range for the cis isomer distribution of the acetylacetonate is roughly 20–40%. A value in the lower end of that range would not be inconsistent with the spectroscopic findings of Ramos and Tobias.[16,17]

NMR Spectra. Results of light scattering are in substantial agreement with those of NMR studies. Unfortunately, frequently it is necessary to do NMR work at low temperatures[11] because of the rapid rates of exchange shown by these compounds. Consequently, the number of complexes of the type R_2SnCh_2 studied effectively by NMR has been limited.

Summary

The cis–trans isomer distribution of compounds of the type R_2SnCh_2 can be measured effectively by light scattering in solvents such as benzene or cyclohexane if compounds with highly anisotropic ligands such as dibenzoylmethane are used. Even compounds of much lower anisotropy such as $(C_2H_5)_2Sn(acac)_2$ can be studied in a relatively isotropic solvent such as cyclohexane. Molecules of low anisotropy are much more difficult to study effectively. This must be especially true of species which are not highly soluble in cyclohexane or CCl_4 and which must be dissolved in a polar or strongly interacting anisotropic solvent such as benzene. Benzene solutions very likely exhibit large increments to the anisotropy due to the formation of stereospecific complexes with the solvent. Anisotropies obtained from studies of such solutions should be treated as upper limits only.

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Registry No. *cis*-$(C_6H_5)_2Sn(acac)_2$, 20179-85-5; *cis*-$(CH_3)_2Sn(acac)_2$, 40866-48-6; *trans*-$(CH_3)_2Sn(acac)_2$, 60828-29-7; *cis*-$(C_2H_5)_2Sn(acac)_2$, 60873-34-9; *trans*-$(C_2H_5)_2Sn(acac)_2$, 16949-79-4; $(C_6H_5)_2Sn(dbzm)_2$, 22878-87-1; *cis*-$(CH_3)_2Sn(dbzm)_2$, 60828-30-0; *trans*-$(CH_3)_2Sn(dbzm)_2$, 53319-86-1; *cis*-$(C_2H_5)_2Sn(dbzm)_2$, 60828-31-1; *trans*-$(C_2H_5)_2Sn(dbzm)_2$, 60828-32-2; $(C_6H_5)_2Sn(trop)_2$, 21729-18-0; $(CH_3)_2Sn(trop)_2$, 21844-38-2; $(C_2H_5)_2Sn(trop)_2$, 21729-19-1; diethyltin oxide, 3682-12-0.

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Sandwich-Type Molecules of First-Row Atoms. Instability of Bis-(η^3-cyclopropenyl)beryllium

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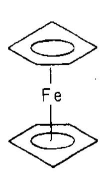
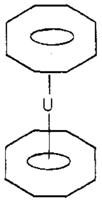
No symmetrical "sandwich" molecules involving only first short period elements and hydrogens are known. Beryllocene (IV) comes closest but possesses a fluctuating structure with nonequivalent cyclopentadienyl rings. Analysis of the more symmetrical (D_{5h} or D_{5d}) alternatives reveals that the HOMO's, degenerate pairs, possess two nodal planes passing through the central atom. Consequently, occupation of these orbitals does not contribute to binding between the rings and the central atom and less symmetrical structures are more stable. Only the lowest four valence molecular orbitals provide this bonding; therefore the optimum number of *interstitial* electrons is 8, provided that the ligand rings are large enough to accommodate six of these electrons in π orbitals which are bonding with respect to the rings themselves. Three- and four-membered ring sandwich complexes in the first short period should be possible only with *four* interstitial electrons. STO-3G ab initio calculations on partially optimized bis(η^3-cyclopropenyl)beryllium (IIIc) bears this out. The η^1,η^1 alternative is more stable. A first short period sandwhich complex was achieved computationally (if only marginally) with the four interstitial electron system VIIb. Other possible first-row sandwich complexes are suggested.

Introduction

Since E. O. Fischer and Wilkinson postulated the bonding scheme in ferrocene (I) (bis-(η^5-cyclopentadienyl)iron) nearly 25 years ago,[2] interest in such π-bonded sandwhich complexes has grown steadily.[3] It was proposed that metal orbitals of d symmetry were ideally disposed for interacting with π molecular orbitals of the two cyclopentadienyl rings, attaching the rings to the central metal in a highly symmetrical fashion.[2] R. D. Fischer[4a] and Streitwieser[4b] extended this idea to predict the stability of uranocene (II) (bis-(η^8-cyclooctatetraene)-uranium) in which orbitals of f symmetry are thought to help bind the ligands to the central atom.



I



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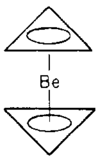
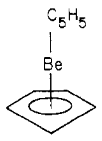


III



IV

We have investigated, by ab initio LCAO-MO-SCF calculations, the possibility of an extension of this idea in the opposite sense, namely, to symmetrical π complexes, such as III, comprised only of elements of the first short period in which the central atom is restricted to s and p orbitals.

Several half-sandwhich complexes of Be are known experimentally[5] as is "beryllocene" (bis(cyclopentadienyl)-beryllium) (IV).[6] However, IV has a dipole moment and the gas-phase structure confirms that the rings are not equivalent.[5b,7] In the gas the molecule possesses C_{5v} symmetry in which the Be atom oscillates in a double-well potential. In the solid a further distortion occurs to a structure described as having one π-bonded (η^5) and one σ-bonded (η^1) ligand.[8] A steric argument is generally offered[8] to account for this distortion. In the D_{5h} structures the rings are thought to approach too closely, thereby introducing strain which is relieved in the lower symmetry orientation.

Alternatively, it can be argued (vide infra), on the basis of orbital interaction diagrams (Figures 1 and 2), that D_{5h} or D_{5d} beryllocene has four too many electrons for the number of available ligand-metal bonding orbitals and relieves this surplus by a structural distortion.

Our search for symmetrical sandwich molecules utilized ligands designed to provide fewer electrons than cyclopentadienyl. The simpliest choice, and one that is both experimentally and computationally accessible, is cyclopropenyl (e.g., III). Several substituted cyclopropenyl complexes of transition metals have been reported and have been shown to possess local threefold axes.[9] In addition to cyclopropenyl we have studied the hypothetical ligands boracyclobutenyl, which has the same number of π electrons as cyclopropenyl, and diboracyclopropyl, which has two fewer π electrons.

Computational Method

All calculations were performed with the Gaussian 70[10] series of programs using the STO-3G basis set of Hehre et al.[11] in the restricted Hartree-Fock approximation (RHF/STO-3G).[12] Two levels of sophistication were employed in selecting the geometrical parameters of the molecules (Figure 3). In the first level a geometrical model was constructed from standard metal-carbon bond lengths[13] combined with calculated structures for the free ligands, where these are available, or standard geometries,[14] where they are not. For η^3-cyclopropenyl, the structure of $C_3H_3{}^+$ was employed;[15] for η^1-cyclopropenyl, the structure of cyclopropene itself[16] was used. In the second level the Be-ring distance was optimized since this parameter is subject to the greatest uncertainty, especially in the π complexes. In addition, some ligand parameters were optimized in the smaller complexes.[17] Total energies and optimized metal-ligand distances are given in Table I. Ligand geometries are found in Figure 3.

Results and Discussion

An analysis of the orbital interaction diagram in Figure 1 shows that first-row π complexes can accommodate no more than eight electrons in orbitals which bind ligands to a central