enables us to classify these solvating solvents in a spectro-chemical sequence $Dq(Me_2SO) < Dq(PC)$. This sequence has also been observed for ocahedral Ni(II) and Cr(III).[23]

The anions are less solvated, and this property is reflected in the very small absorption maxima differences. But the bathochromic shift of about 200 nm is good evidence for a structural change from square-planar to D_{2d} symmetry, even for the trichlorocuprate. The characteristics of the unsolvated $CuCl_4{}^{2-}$ are identical regardless of the solvents and for this complex the D_{2d} structure is well established. As opposed to aqueous solution, the absorption maxima for the highest complexes are located under 1000 nm, indicating clearly nonconfigurational changes from the square-planar structure.[19]

Summary

The spectrophotometric analysis of the copper(II) chloride solutions in two different solvents, Me₂SO and PC, shows contributions of the solvents and the solvation to the stability, the electronic spectra, and the structure of the copper(II) chloro complexes. In Me₂SO, the system can be characterized by three species. The absence of the dichloro complex is due to similar donor numbers of the solvent and the ligand.

As in the DMF solutions,[1] the overall stability constants are much higher in both solvents than in water and a drastic increase of the β_j's is found in the propylene carbonate medium. The complexes formed and their stability constants are very similar in DMF and Me₂SO, which are solvents of analogous properties.

The charge-transfer bands of the individual calculated spectra show maxima at 294 and 274 nm for $CuCl^+$, for $CuCl_3{}^-$ at 298 and 440 nm, and at 252, 312, and 470 nm for Me₂SO and for PC, respectively; for the unsolvated $CuCl_4{}^{2-}$, the maxima are identical and located at 295 and 410 nm. Their d–d transition bands are located at 908 and 840 nm for $CuCl^+$, at 1050 and 1080 nm for $CuCl_3{}^-$, and at 1200 nm for $CuCl_4{}^{2-}$, in both solvents. These quantitative IR results are given for the first time in these solvents and enable some structural conclusions: $CuCl^+$ is the square-planar CuCl-$(Me_2SO)_3{}^+$ ion in Me₂SO and $CuCl_3{}^-$ and $CuCl_4{}^{2-}$ are flattened tetrahydra with one molecule of Me₂SO coordinated to copper in $CuCl_3(Me_2SO)^-$ of D_{2d} symmetry.

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Use of Ligand Probes in Light Scattering. 3. Preresonance-Enhanced Depolarized Rayleigh Scattering of Dibenzoylmethane and Selected Diorganotin(IV) Complexes

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The depolarized Rayleigh light scattering of cyclohexane solutions of 1,3-diphenyl-1,3-propanedione (dibenzoylmethane) and its neutral, six-coordinate dibutyltin(IV) and dicyclohexyltin(IV) complexes has been studied interferometrically at the wavelengths 514.5, 488.0, and 457.9 nm. The data clearly indicate that significant preresonance enhancement of the central Rayleigh line occurs for the solutions studied. Rayleigh intensities and line shapes for the ligand and complexes support the conclusion that the complexes are monomeric and predominantly of "trans" or distorted "trans" structure. The complexes cannot be "cis".

Introduction

In principle, depolarized Rayleigh scattering can be used to determine the structure of molecules in solution. If a vertically polarized incident light beam is incident on a solution containing molecules with molecular optical anisotropy, γ, the depolarized scattered-light intensity I_{VH} is given by[1]

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

where G_n is a geometric factor, L_n a local field correction, ρ the number density of scattering molecules, g_2 is a static orientation correlation parameter, and n is the refractive index of the solution. Estimates of L_n and g_2 may present problems,[2–4] but if these quantities can be calculated or estimated, the relation between the measurable I_{VH} and the structurally sensitive, calculable γ^2 is direct for many relatively simple molecules.

Potentially one should be able to calculate molecular optical anisotropies from bond polarizabilities,[5] and to identify a solute molecule's structure by comparing[6] measured and calculated depolarized scattered-light intensities. In practice there are severe problems with such an approach even if the local field corrections and static orientation correlation parameters are reliably known. One of the most severe problems concerns the difficulty in calculating reliable bond polarizability components and then combining these to provide reasonable molecular optical anisotropies for candidate structures. Values of the molecular optical anisotropy calculated from bond polarizability components have been shown to be uncertain by 1 order of magnitude or more.[7]

More recently, we have noted the possibility of using ligands as optical probes[8] in complexes. If a ligand is highly anisotropic and polarizable, nearly all of the depolarized scattering of an associated complex will be due to the ligands alone. Furthermore, the depolarized scattering will be very sensitive to the relative positions of the ligands if two or more ligands

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Table I. Variation of $I_{VH(solute)}/I_{VH(benzene)}$ with Incident-Beam Wavelength and Related Data

solute	concn range, M	$I/I_{benzene}$ (514.4 nm) (19 436 cm^{-1})	$I/I_{benzene}$ (488 nm) (20 492 cm^{-1})	$I/I_{benzene}$ (457.9 nm) (21 839 cm^{-1})	f_n	$\bar{\nu}_n$, cm^{-1}
dibenzoylmethane	0.016–0.088	10.1	11.4	14.4	0.004	29 500
$(C_4H_9)_2Sn(DBZM)_2$	0.010–0.013	28.4	30.9	39.4	0.008	29 718
$(C_6H_{11})_2Sn(DBZM)_2$	0.009–0.010	29.9	31.1	36.6	0.008	29 028
Ph(C≡C)$_2$Ph	0.135	119	138	173	0.77	28 410
Ph(C≡C)$_5$Ph	0.0001	1490	2400	4000		23 590

are present. For a six-coordinate, regular-octahedral complex of the type R_2MCh_2, where R is a monodentate substituent of low optical anisotropy and Ch$^-$ is a bidentate, planar, highly anisotropic ligand, it is easily shown[8] that γ^2 for the cis (C_2) complex equals γ^2 for the free ligand. On the other hand if the complex is trans (D_{2h}), γ^2 will be 4 times as great and the depolarized scattered-light intensities will be very large and characteristically different for such complexes with magnitudes depending upon the nature of the ligands. Structures can be assigned with relative ease with that technique, but the relatively high concentrations of complex required, 0.01–1.0 M, is a serious limitation.

One possible way to improve the usefulness of this method would be sensitivity enhancement. Strong resonance enhancement of the depolarized scattering may provide one means of significantly increasing the sensitivity of the depolarized Rayleigh scattering method of determining molecular structure. Several years ago, it was noted that Rayleigh scattering from diphenylpolyenes[9] is very strongly resonance enhanced. It is apparent that carotenoids behave in similar fashion.[10] If ligands can be identified that are subject to strong resonance or preresonance scattering enhancement to the same degree as diphenylpolyenes or carotenoids, it is likely that their complexes can be studied by light scattering at very low concentrations and their molecular structures determined. Specifically, if the scattering from a ligand is as strongly resonance enhanced as that from polyenes, concentrations of ligands or complexes as low as 10^{-5} M could be studied with ease. Furthermore, potentially the studies could be made in the presence of higher concentrations of other non-resonance-enhanced species.

In this paper we report the depolarized scattered-light intensities of cyclohexane solutions of dibenzoylmethane and its six-coordinate dibutyl- and dicyclohexyltin(IV) complexes at 514.5, 488.0, and 457.9 nm. Observation of the Rayleigh line widths for the complexes allows for supporting estimates of molecular size and shape to be made as well. Since the ligand and complexes have relatively strong absorptions near 350 nm, but are only slightly yellow in color, it was anticipated that they should be good candidates for an initial study of preresonance enhancement of depolarized Rayleigh scattering.

Experimental Section

Light-Scattering Apparatus. All spectra were obtained with an apparatus described previously.[11] The light source was a stabilized Spectra-Physics Model 165 argon ion laser equipped with an intracavity etalon that allowed the isolation of a single longitudinal mode. Experiments were run at laser powers which varied from 10 to 600 mW (single line). Lower power at 457.9-nm wavelength, especially, was required to prevent the samples from heating. Each solution was observed with several different laser powers to assess the extent of sample heating. Heating could be detected very easily as a time-dependent change in the effective laser beam diameter in the sample cell.

The incident vertically polarized laser beam was focused by a lens into the center of a standard 1-cm sealed glass cuvette. The depolarized

scattered beam was observed at 90° to the incident laser beam after passing through a Glan-Thompson prism with an extinction ratio of 5×10^{-6}. The spectral analysis of the columnated scattered light was accomplished by means of a Fabry-Perot interferometer manufactured by Grandt Associates of Oakland, CA. The interferometer was equipped with mirrors coated for maximum reflectance at 488 nm. Finesse varied approximately from 40 to 80. The free spectral range was checked with the observed Brillouin doublet of liquid toluene at 20 °C.

The photomultiplier was an ITT FW 130 cooled to −20 °C to give low noise and dark current. The signal was amplified by an SSR Model 1105 photon-counter system, and the data were recorded digitally on a magnetic disk. Data were processed by the program MODELAIDE[12] to give the best fit of the central peak to a single Lorentzian. Hard copy was obtained by line printer through the program NEWDRAW.[12] Data averaging though occasionally used for dilute solutions was not required because of the sensitivity of the apparatus. Typical scan times were 2 min.

Solution Clarification. Dust was removed from solutions by a single filtration through 0.1 μm Millipore filters into clean cells. Absence of dust was confirmed by careful microscopic examination of the laser beam passing through each solution in its stoppered sealed cell. Solutions in which dust was observed were discarded. Filter mounts were judged clean when cyclohexane passing through them did not show evidence of dust. Cells were cleaned by immersion for 24 h in chromic acid followed by thorough rinsing with distilled water and hot distilled ethanol.

Materials and Reagents. Cyclohexane, toluene, and benzene were reagent grade. Dibenzoylmethane was obtained from Aldrich and recrystallized from ethanol. Complexes were prepared and purified as described earlier.[13]

Intensity Calculations. Depolarized scattered-light intensities of complexes were compared to the depolarized Rayleigh intensity of dibenzoylmethane because of the similarity in line widths of the species. Dibenzoylmethane depolarized central-line intensities were compared directly to those of benzene at 20 °C. The solute depolarized Rayleigh scattered light is composed of both a central relatively narrow component, the intensity of which is proportional to the square of the molecular optical anisotropy, and a much broader component due to collisional scattering. At the free spectral ranges used (50–100 GHz) the collisional depolarized scattering appeared as an increment to the base line. Only the central component contributed to the Lorentzian portion of the spectrum.

It is estimated that intensities were reproducible to ±10% for any given experiment. Since intensities due to complexes were calibrated against dibenzoylmethane solutions, the ratios of the intensities of the complexes to dibenzoylmethane should be most reliably known. Larger systematic errors may be present in the intensity ratios expressed in comparison with benzene since benzene is a much weaker scatterer and has a much broader central line that is more difficult to separate from the cyclohexane solvent contribution. Fortunately, it is the intensity ratio of the ligand to the complexes that is most important in determining the molecular structure of the complexes in solution. Solvent scattering like collisional scattering was much broader than the solute scattering of either ligand or complexes and contributed only to the flat base line of the spectrum. Figure 1 shows overlaid spectra of a strongly scattering polystyrene solution and that of bis(1,3-diphenyl-1,3-propanedionato)dibutyltin(IV), $(C_4H_9)_2Sn(DBZM)_2$, in cyclohexane. There is virtually no increase above 0 in

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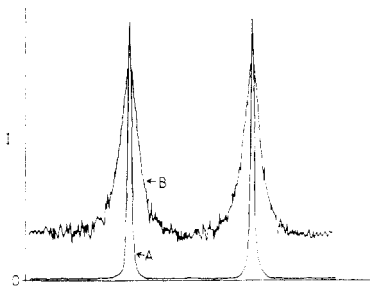(13) C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, **8**, 138 (1969).

Figure 1. Overlaid spectra of polystyrene (A) and complex (B) solutions.

Table II. Depolarized Rayleigh Line Half-Widths at Half-Height (WHH) and Corresponding Reorientation Times, τ, of Solutes in Cyclohexane and CCl_4

solute	10^{-9} WHH, Hz	solvent	$\tau,^a$ ps
dibenzoylmethane	7.58	C_6H_{12}	21
$(C_6H_{11})Sn(DBZM)_2$	1.98	C_6H_{12}	80
$(C_4H_9)_2Sn(DBZM)_2$	2.00	C_6H_{12}	80
$Ph(C=C)_2Ph$		CCl_4	80_v

^{a} $2\pi\tau = 1/(\text{half-width})$.

the base line of the polymer solution, and the line width is the instrumental line width. The solution of the complex in cyclohexane, however, shows a substantially raised base line due to collisional and solvent contributions as well as the characteristic central line.

The intensity of depolarized scattering of dibenzoylmethane and the complexes in solution is shown relative to that of benzene at 514.5, 488.0, and 457.9 nm in Table I. Table II shows corresponding line widths and calculated reorientation times.

Discussion

Resonance Enhancement of Scattering. The data of Table I show quite clearly that the Rayleigh scattering from dibenzoylmethane and its two complexes is resonance enhanced. The intensity of depolarized Rayleigh scattering increases for all solutions nearly 50% as the wavelength of incident light decreases from 514.5 to 457.9 nm. The normal dispersion in polarizability anisotropies has been studied recently and has been shown[14] to be small. Moreover, Table I shows that the change in depolarized scattering with wavelength for the solutions in question is very close to that of 1,4-diphenyl-1,3-butadiene which has been shown[9] to be preresonance enhanced. It is notable that the latter molecule's absorption maximum is very close to the maximum of the ligand and the complexes. All scattering intensities fit rather closely to the equation for resonance-enhanced scattering.

$$I/I_{\text{benzene}} = K[f_n/(\nu_n^2 - \nu^2) + b_n]^2$$

K is constant, f_n is the oscillator strength, ν_n is the first absorption maximum of the solute, and ν is the energy of the laser line in cm^{-1}. The constant b_n includes contributions to the polarizability anisotropy due to higher energy transitions. The oscillator strength has been estimated from optical spectra according to the method of Bayliss.[15]

The lower scattered-light intensities of dibenzoylmethane and the complexes as opposed to the diphenylpolyenes undoubtedly can be attributed in part to the substantially lower oscillator strength. The term $(\nu_n^2 - \nu^2)$ also is larger for the complexes and the ligand because of their lowest energy transitions being somewhat displaced into the UV. It seems likely that stronger resonance enhancement of Rayleigh scattering will come only through use of ligands which have
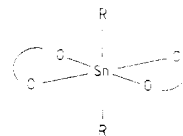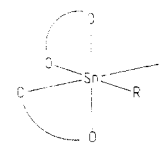

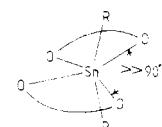**Figure 2.** Trans structure.

Figure 3. Cis structure.

Figure 4. Skew trapezoidal bipyramidal structure.

oscillator strengths similar in magnitude to those of the diphenylpolyenes. In short, "dye-type" chelates that are highly anisotropic may be even better candidates for use as ligand probes in structural studies.

Rayleigh Line Widths. Examination of Table II shows that the line widths for orientational scattering, and the corresponding orientation times, are within a reasonable range if we assume weak solute–solvent interactions. That reorientation times are substantially more rapid for dibenzoylmethane than for 1,4-diphenyl-1,3-butadiene as determined previously in CCl_4 may be attributed to the more "spherical" shape of dibenzoylmethane. That reorientation times of the complexes are substantially slower than that of dibenzoylmethane in cyclohexane is expected on the basis of calculated larger effective volumes of the complexes. In fact, if differences in shape are discounted, the relaxation times indicate a 4/1 complex/ligand molecular volume ratio. It is reasonable to suggest that the complex which is composed of two ligands and two alkyl groups slightly smaller than the ligand should occupy a volume about 4 times that of a single ligand. Because the complexes have a larger effective volume than 1,4-diphenyl-1,3-butadiene but the same relaxation time, it seems reasonable to suggest that the complex interacts very weakly indeed with the solvent. Part of the reason for the rapid relaxation time of the complexes may be the much more "spherical" shape, however. Nonetheless, since the relaxation time for the polyene is only slightly longer than that predicted by a "slip model";[11,16] any strong solute–solute or solute–solvent interaction appears unlikely.

Structure of the Complexes. The 3/1 complex/ligand depolarized scattering intensity ratio observed at 514.5, 488.0, and 457.9 nm not only shows that the resonance enhancement of the ligand and complexes is large but also indicates that both complexes must be 100% trans (Figure 2), only slightly distorted from the trans geometry, or a cis–trans mixture with the trans isomer predominating. If the ligands are symmetrical rotors, one predicts the complex/ligand depolarized scattered-light intensity ratio to be 4/1 for trans while the ratio must be 1/1 for a regular cis-type complex (Figure 3).

That the line shape of the scattering from dibenzoylmethane fits a single Lorentzian is consistent with the suggestion that the symmetric rotor approximation for that ligand is reasonably good.[11] It is likely that the complexes both are distorted from the regular, octahedral-trans geometry. A most likely possibility is that of a skew trapezoidal bipyramid which has

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been noted for related systems previously by Keppert[17] (Figure 4). NMR spectra[13] have shown no evidence for an equilibrium mixture. The "skew-trapezoidal" geometry should be characterized by an intensity ratio only slightly lower than 4/1. The actual value will depend upon the angle between the ligands. An earlier calculation[8] indicates that a 3/1 ratio corresponds to a 160° angle between the ligands; i.e., the ligand should be 20° out of plane.

In summary, this study definitely shows that dibenzoylmethane is characterized by resonance-enhanced Rayleigh depolarized scattering which increases modestly as scattered-light wavelengths decrease from 514.5 to 457.9 nm. The complexes also show similar amounts of resonance-enhanced scattering and the constancy of the $I_{complex}/I_{ligand}$ ratio shows that the dibenzoylmethane is relatively unaffected in its optical

properties by complexation. The 3/1 $I_{complex}/I_{ligand}$ ratio strongly suggests that the complex is approximately "trans" in geometry with only moderate distortion from ligand–ligand coplanarity observed. The relaxation times calculated from the half-widths at half-height of the central Rayleigh peaks show that the ligand and complexes are not strongly associated with the solvent or each other. This latter condition is necessary for the simple relation of the light-scattering intensities to molecular optical anisotropies.

Registry No. DBZM, 120-46-7; (C$_4$H$_9$)$_2$Sn(DBZM)$_2$, 22673-17-2; (C$_6$H$_{11}$)$_2$Sn(DBZM)$_2$, 80327-43-1.

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Absorption and Circular Dichroism Studies of Rhodium(I) Complexes Containing Chiral Isocyanides[1]

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Absorption and CD spectra of mono- and dinuclear Rh(I) complexes containing chiral isocyanide ligands such as (1*R*,2*R*)- or (1*S*,2*S*)-diisocyanocyclohexane (ICH) and (*R*)- or (*S*)-phenylethyl isocyanide (PEI) were examined. The ICH complexes showed an intermolecular metal–metal interaction in the solid state but not in solution. A metal–metal interaction in the PEI complexes was observed in the solid state and in a mixture of CH$_3$CN and H$_2$O. The CD spectra of ICH and PEI complexes showed a characteristic band at 310 nm, in which the CD band with plus sign was assigned to *S* configuration and that with minus sign to *R* configuration.

Square-planar d^8 rhodium complexes of isocyanide, Rh-(RNC)$_4^+$, have been found to show oligomerization in solution and redox chemistry.[2] There has been considerable interest in the electronic properties of their compounds. Many studies on their electronic spectra are known,[2] but there are few electronic and circular dichroism studies on the complexes containing chiral isocyanides. This paper reports the synthesis of some rhodium(I) complexes coordinated by chiral isocyanides such as (*R*)- and (*S*)-phenylethyl isocyanide (PEI) and (1*R*,2*R*)- and (1*S*,2*S*)-diisocyanocyclohexane (ICH), and their spectroscopic studies.

Results and Discussion

Preparation. Mono- and dinuclear Rh(I) complexes containing chiral isocyanides, Rh(PEI)$_4$Cl and [Rh$_2$(ICH)$_4$]X$_2$,

were prepared by the reaction of [Rh(COD)Cl]$_2$ with the corresponding isocyanide. They are reddish violet or yellow crystalline solids. The reddish violet color was reminescent of a metal–metal interaction.

Electronic Spectra. Absorption spectral data of Rh(PEI)$_4$Cl and [Rh$_2$(ICH)$_4$]X$_2$ in solution and in the solid state are given in Table I together with those of related complexes. Figures 1 and 2 show absorption spectra of some Rh(I) complexes.

Absorption spectra of all dinuclear complexes in solution show the transition at ca. 400 nm, which is identified as d$_{z^2}$–π^* metal to ligand charge-transfer absorption. The positions of these transitions are independent of solvents and concentrations in the range from 1.3×10^{-5} to 6.2×10^{-2} M. Furthermore, the spectra are closely similar to those of mononuclear complexes at concentration. These observations suggest that dinuclear Rh(I) complexes do not exhibit intra- and intermolecular metal–metal interaction in solution. However, dinuclear complexes of 1,3-diisocyanopropane derivatives[3] and 1,3-*cis*-diisocyanocyclohexane[2j,4] exhibit the presence of intra- and intermolecular metal–metal interaction in solution. This difference is unexpected on the basis of the molecular models (vide infra).

In the electronic spectrum of reddish violet solid, [Rh$_2$-(1*S*,2*S*-ICH)$_4$](PF$_6$)$_2$, in a pressed KBr pellet, there exists a

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