$Q = (\Sigma D_i^2/21)^{1/2}$ and the variance in an observation of unit weight as

$$\sigma^2 = {}^1/_{21}\sum D_i^2/\sigma^2(X_i)$$

The quantity σ^2 may be tested as $(\chi^2/21)$ with 21 degrees of freedom (24 observations, three variables—the rotation angles). The values of $(\chi^2/21)$ with probability P of being exceeded in a random sampling for 21 degrees of freedom are 10%, 1.41; 5%, 1.56; and 1%, 1.84. On this basis we may assess whether D_{2d} symmetry holds for this orientation of the M_4Y_4 core. The process is repeated for the other two possible orientations of the principal axis with respect to the M–M vectors. If D_{2d} symmetry holds for all three orientations, then the molecular symmetry is T_d.

Inspection of Table IX leads to the conclusion that for the majority of the entries the values of σ^2 are too large to enable one to assign symmetry by the above criterion. Thus either the hypothesis of D_{2d} or T_d symmetry is not true, or the standard deviations associated with the atomic parameters are too small. (Because the information is lost in publication, the effects of correlation between atomic parameters were not included in this analysis, and only a diagonal weight matrix was employed. This could have some effect on the values of σ^2.) On the basis of evidence accumulated over the years[62] on careful X-ray structure determinations, in particular from comparative studies of the same structure carried out in different laboratories, it is reasonable to assume that the σ's reported in crystal structure investigations should be increased by a factor of 3 or 4 before chemical information is derived from the structure. It is on this basis that the probable symmetry assignments are made in Table IX. It is clear that the definite assignment of symmetry to molecules in a crystal structure is very difficult, unless such symmetry is required by crystallographic constraints. Thus the assessment of minor apparent variations in symmetry between related molecules in different crystal structures is risky at best and cannot be used objectively to support theoretical calculations.

[62] See, for example, S. C. Abrahams, *Acta Crystallogr., Sect. B*, **28**, 2886 (1972).

Complex Formation between Eu(fod)$_3$, a Lanthanide Shift Reagent, and Organic Molecules

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Abstract: The complex formation between Eu(fod)$_3$, a lanthanide shift reagent, and acetone, dimethyl sulfoxide (DMSO), 2-propanol, and β-picoline dissolved in carbon tetrachloride was studied as a function of the reagent-to-substrate ratio, ρ, using the chemical shifts induced in the methyl proton resonances as an indicator. Detailed data analysis shows that the total stoichiometry of the reagent–substrate adduct is 1:2, with complexes of the type RS and RS$_2$ present in equilibrium. The dissociation constants of the two complexes differ greatly in magnitude: $K_2 > 4K_1$ for acetone and DMSO; $K_2 < 4K_1$ for 2-propanol and β-picoline. A substrate-induced ligand rearrangement around the central lanthanide ion is suggested to account for these observations. The calculated relative contributions of the two complexes to the observed shifts vary with ρ and with the substrate. The approach to the data analysis is presented in detail.

Following the original communication of Hinckley[1] in 1969 and as a result of the methodological investigations subsequently conducted by him and his coworkers, by Williams and coworkers,[2] as well as by others,[3] some paramagnetic lanthanide β-diketonates that are soluble in organic solvents and are able to expand their coordination sphere and form adducts with organic molecules are now routinely used as chemical shift inducing agents in organic nmr spectroscopy. The proper interpretation of chemical shifts induced by lanthanide shift reagents in the spectra of substrate molecules requires some knowledge regarding the nature of the complex species present in solution, *viz.*, their stoichiometry, structure, and dissociation constants. In most of the published work 1:1 stoichiometry is implied. However, the existence in the solid state of reagent–substrate adducts of 1:2 stoichiometry has been demonstrated with Eu(dpm)$_3$ both chemically[1] and crystallographically.[4–6] Recently Evans and Wyatt showed that a 1:2 adduct is formed at low temperatures (−80°) between the deuterated analog of Eu(fod)$_3$ and DMSO in CD$_2$Cl$_2$ solution.[7] It is possible that an equilibrium between 1:1 and 1:2 adduct is present in solution at room temperature. Such an equilibrium may have unexpected effects on the chemical shifts induced on nuclei at different parts of the organic molecule thereby com-

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

[2] J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *ibid.*, **94**, 5325 (1972), and references cited therein.

[3] For a recent review, see J. Reuben, *Progr. Nucl. Magn. Resonance Spectrosc.*, **9**, Part 1 (1973).

[4] W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

[5] R. E. Cramer and K. Seff, *J. Chem. Soc., Chem. Commun.*, 400 (1972).

[6] Abbreviations used: dpm, dipivaloylmethanate; fod, 1,1,1,-2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate; pta, pivaloyltrifluoroacetonate; DMSO, dimethyl sulfoxide; TMS, tetramethylsilane.

[7] D. F. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972).

plicating the interpretation of the relative shift magnitudes in terms of molecular geometry. The kind of complication that may be encountered has been clearly depicted by Sanders, Hanson, and Williams with the shifts of the quinoline protons induced by Eu(pta)$_3$ as a function of the reagent-to-substrate ratio.[2] For some of the protons the shift increases monotonically toward a limiting value whereas other show a maximum. Similar behavior can be seen in the results for quinoline and Eu(fod)$_3$ reported by Roth, Grosse, and Rewicki.[8]

As a part of a general investigation of the lanthanides as probes for molecular structure elucidation, the effects of Eu(fod)$_3$ on the chemical shifts of a series of representative organic substrates were studied in order to gain a better insight into the problems of complex formation of this important shift reagent. Reported here are the results obtained for the methyl protons of acetone, DMSO, 2-propanol, and β-picoline in carbon tetrachloride solutions. The induced shifts were measured as a function of the reagent-to-substrate molar ratio, and the approach to the analysis of data of this type is outlined in detail.

Experimental Section

Nmr spectra were recorded on the Varian A-60 spectrometer at ambient probe temperature (*ca.* 30°) using TMS as an internal standard for chemical shift referencing. Chemical shifts are reported as the incremental shift, Δ, induced by the shift reagent relative to a similar solution but in the absence of reagent. In all the cases investigated Eu(fod)$_3$ induced downfield shifts which for convenience are reported as positive. The accuracy of the measured shifts is believed to be ±0.3 Hz.

The solvent and solutes were analytical grade reagents from freshly open containers and were used without further treatment, except for DMSO which was stored over molecular sieves. The shift reagent Eu(fod)$_3$ was supplied by Norell & Co., Landing, N. J. Freshly made solutions were used for each run. They were prepared in the following manner. A stock solution of the substrate in CCl$_4$ (containing *ca.* 0.2% v/v TMS) was made up volumetrically in a volumetric flask. The molar concentration of the solute was calculated from the known density and molecular weight of the substance. Part of the stock solution was then used to dissolve a sample of Eu(fod)$_3$ weighed in a volumetric flask. In this way both solutions are of the same concentrations in substrate. The nmr spectrum of an 0.4-ml sample of the stock solution was recorded first, and its chemical shift is referred to as $\Delta = 0$. Small aliquots (10–100 μl each) of the reagent containing solution were then successively introduced using Hamilton syringes. The nmr spectrum was recorded after each addition. Thus each run consists of 16–17 points of progressively increasing reagent–substrate molar ratio (hereafter referred to as ρ) at constant substrate concentration.

Computations were carried out at the Weizmann Institute Computer Center on the IBM 370/165 computer equipped with a CalComp plotter. The latter was used to plot the experimental points as well as the calculated curves.

Approach to Data Analysis

Bearing in mind the findings of Evans and Wyatt[7,9] and anticipating the results of the present study, we consider the system of the coupled complex formation equilibria between the reagent, R, and the substrate, S

$$\mathrm{R} + \mathrm{S} \rightleftarrows \mathrm{RS} \qquad K_1 = [\mathrm{R}][\mathrm{S}]/[\mathrm{RS}] \quad (1)$$

$$\mathrm{RS} + \mathrm{S} \rightleftarrows \mathrm{RS_2} \qquad K_2 = [\mathrm{RS}][\mathrm{S}]/[\mathrm{RS_2}] \quad (2)$$

where K_1 and K_2 are dissociation constants. Solving for [S] one obtains

$$[\mathrm{S}]^3 + (2R_t - S_t + K_2)[\mathrm{S}]^2 + K_2(R_t - S_t + K_1)[\mathrm{S}] - K_1K_2S_t = 0 \quad (3)$$

where $R_t = [\mathrm{R}] + [\mathrm{RS}] + [\mathrm{RS_2}]$ is the toal reagent concentration and $S_t = [\mathrm{S}] + [\mathrm{RS}] + 2[\mathrm{RS_2}]$ is the total substrate concentration. Thus, from eq 3 and knowing the dissociation constants, [S] can be calculated for any given solution composition.[10] With [S], the equilibrium concentrations of the other components of the system are then easily obtained, *e.g.*

$$[\mathrm{R}] = R_t/(1 + [\mathrm{S}]/K_1 + [\mathrm{S}]^2/K_1K_2)$$

There are two important questions to be asked. What is the relation between K_1 and K_2? If, *e.g.*, $K_2 = 4K_1$, then the reagent has two equivalent and independent coordinating positions for the substrate.[11] In this case we can describe the two steps with the single dissociation constant $K_D = 2K_1 = K_2/2$. If $K_2 > 4K_1$, the affinity for the second substrate is lower than that for the first, an often encountered case with small molecules and ions in solution. If, however, $K_2 < 4K_1$, then the affinity for the second substrate molecule is higher than that for the first implying a cooperative process. The case of complex formation equilibria involving n equivalent and independent coordination sites is best described[11] by the Scatchard equation of the form

$$\bar{\nu}/S_f = n/K_D - \bar{\nu}/K_D \quad (4)$$

where $S_f = [\mathrm{S}]$, $\bar{\nu} = S_b/R_t$, and $S_b = [\mathrm{RS}] + 2[\mathrm{RS_2}]$. This is a useful representation since a plot of $\bar{\nu}/S_f$ *vs.* $\bar{\nu}$ is a straight line, the intercept of which on the abscissa is n and that on the ordinate n/K_D. Negative ($K_2 > 4K_1$) or positive ($K_2 < 4K_1$) cooperativity will cause a curvature in the line making it concave or convex, respectively.

The second question is related to the magnetic equivalence of the substrates in the two complexes. Is the induced shift of a given proton in RS the same as that in RS$_2$? The related question regarding the magnetic equivalence between the two molecules in RS$_2$ is irrelevant in the present context, since the two substrate molecules by virtue of the rapid chemical exchange are, at least apparently, equivalent. The chemical shift observed under conditions of fast exchange is given by

$$\Delta = [\mathrm{RS}]\Delta_1/S_t + 2[\mathrm{RS_2}]\Delta_2/S_t \quad (5)$$

where Δ_1 and Δ_2 are the limiting shifts for the RS and RS$_2$ species, respectively. For the case of chemical ($K_2 = 4K_1$) and magnetic ($\Delta_1 = \Delta_2 \equiv \Delta_M$) equivalence

$$\Delta = S_b\Delta_M/S_t \quad (6)$$

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(8) K. Roth, M. Grosse, and D. Rewicki, *Tetrahedron Lett.*, 435 (1972).

(9) Evans and Wyatt[7] found that the DMSO line of a CD$_2$Cl$_2$ solution containing the deuterated analog of Eu(fod)$_3$ at $\rho = 0.336$ separated at −80° into two components corresponding to coordinated and free DMSO molecules. Integration of the peaks led to the conclusion that 2.0 ± 0.2 mol of DMSO are bound per mole of reagent. We reached a similar conclusion by repeating the experiment with normal Eu(fod)$_3$ and comparing the integrals of the complexed DMSO and the *tert*-butyl groups of the reagent.

(10) Newton's method of tangents was used to solve the cubic eq 3 by successive approximations. First the point of the lowest ρ was treated using S_t as initial approximation. For the next point [S] of the previous one was used as initial approximation. In this way convergence is obtained very rapidly, usually within less than ten steps. Also this procedure makes sure that a root of proper physical meaning is obtained.

(11) For an illuminating discussion of the theory of measurement of weak molecular complexes, *cf.* D. A. Deranleau, *J. Amer. Chem. Soc.*, **91**, 4044, 4050 (1969).

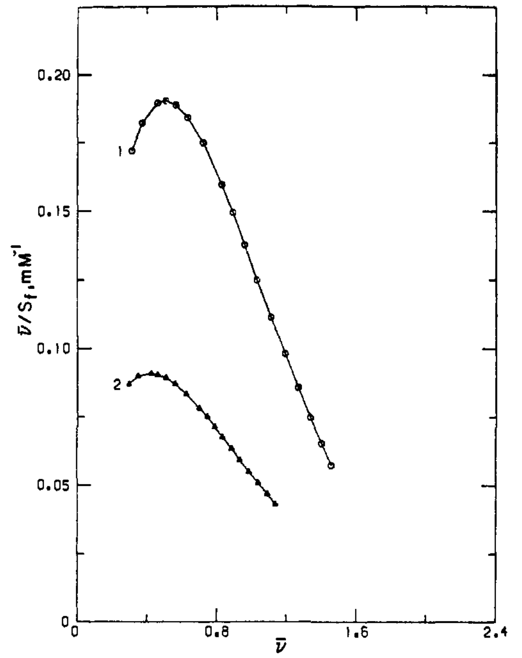

Figure 1. Scatchard plots of computer generated data with four parameters ($\Delta_1 = \Delta_2$) and then fitted with two parameters. Constants are given in Table I.

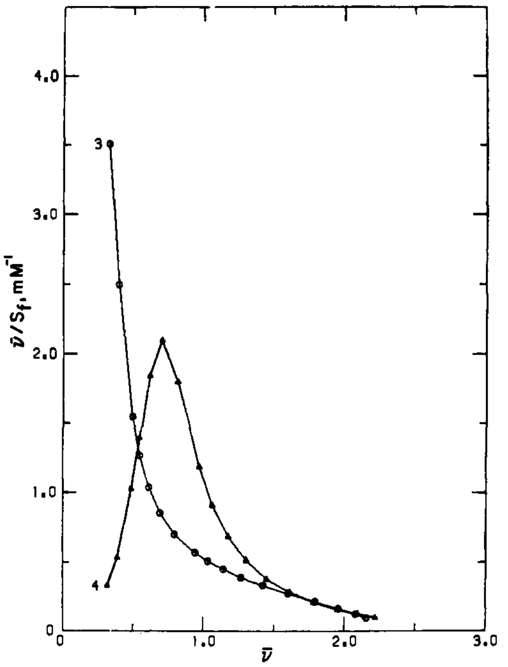

Figure 2. Scatchard plots of computer generated data with four parameters ($\Delta_1 < \Delta_2$) and then fitted with two parameters. Constants are given in Table I.

It has become customary in the art to plot shifts against ρ ($=R_t/S_t$). Denoting S_b/S_t by σ, eq 4 can be rearranged in the form

$$\sigma = \frac{n\rho}{1 + K_D/(S_t - S_b)} \tag{7}$$

and eq 6 becomes

$$\Delta = \frac{n\rho\Delta_M}{1 + K_D/(S_t - S_b)} \tag{8}$$

Thus, a plot of Δ *vs.* ρ at constant S_t consists of an (*almost*) linear portion at vey low ρ ($S_t \gg S_b$) of slope $n\Delta_M/(1 + K_D/S_t)$, followed by curvature and asymptotic approach to Δ_M. If a series of experiments is carried to sufficiently high values of ρ then the limiting shift and the initial slope can be used to estimate n, provided that $K_D/S_t \ll 1$. However, since usually K_D is unknown *a priori*, only values of $n > 1$ should be taken as a definitive indication (of higher than 1:1 stoichiometry), whereas if $n < 1$ only a computational analysis can give an answer. If only the linear portion of the Δ *vs.* ρ curve has been covered experimentally, then (*vide infra*) the problem (at least for 1:2 stoichiometry) is insufficiently determined and no conclusions can be drawn. As will become clear from the results of this study, this statement applies also to molecular structure determination from the intramolecular relative shifts based on the pseudocontact shift relationship.

The complexity of the problem is by now conspicuous. There are four parameters determining the shape of the Δ *vs.* ρ curve: K_1, K_2, Δ_1, and Δ_2. The simplest case, that of $K_2 = 4K_1$ and $\Delta_1 = \Delta_2$, can be managed relatively easily by first obtaining K_D and Δ_M which fit the data best. Then using Δ_M and the experimental shifts, a Scatchard plot can be constructed in which now $\bar{\nu} = \Delta/\rho\Delta_M$ and $\bar{\nu}/S_f = \Delta/(\Delta_M - \Delta)R_t$. This approach can also be used for a general case. An attempt can be made to fit the data with a single K_D and a single Δ_F and to construct a Scatchard plot using this Δ_F and the experimental shifts. The shape of the Scatchard plot will be quite characteristic and will show the approximate relation between the actual parameters which will best fit the data. To verify and illustrate this point a series of Δ *vs.* ρ curves were generated (on the computer) for given values of K_1, K_2, Δ_1, and Δ_2. A "best fit" was then obtained with a single K_D and Δ_F.[12] Some of the constructed Scatchard plots are shown in Figures 1 and 2. The constants used for the data generation and the "best fit" are summarized in Table I. While the values of the standard deviation of the "best fit" could be considered satisfactory, the constants of this fit are not even close to the actual values used to generate the data points. Moreover, it is seen that the shape of the curves (anything but a straight line) as well as their extent along the axes is quite characteristic. Such curves were used as a guide in the analysis of the experimental data obtained in this work.

Table I. Constants Used to Generate the Points and Curves of Figures 1 and 2. S_t = 30 m*M*

	1	2	3	4
K_1, m*M*	2.0	5.0	30.0	5.0
K_2, m*M*	20.0	50.0	1.0	10.0
Δ_1, Hz	1000	1000	600	600
Δ_2, Hz	1000	1000	1000	1000
K_D, m*M*	7.9	17.4	1.44	1.15
Δ_F, Hz	1034	1051	861	683
Std, Hz	8.2	7.6	17.9	12.9

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(12) The closeness of the fit is judged by the magnitude of the standard deviation (std) defined by $[\Sigma_N(\Delta_{\mathrm{obsd}} + \Delta_{\mathrm{calcd}})^2/(N - 1)]^{1/2}$, where N is the number of points.

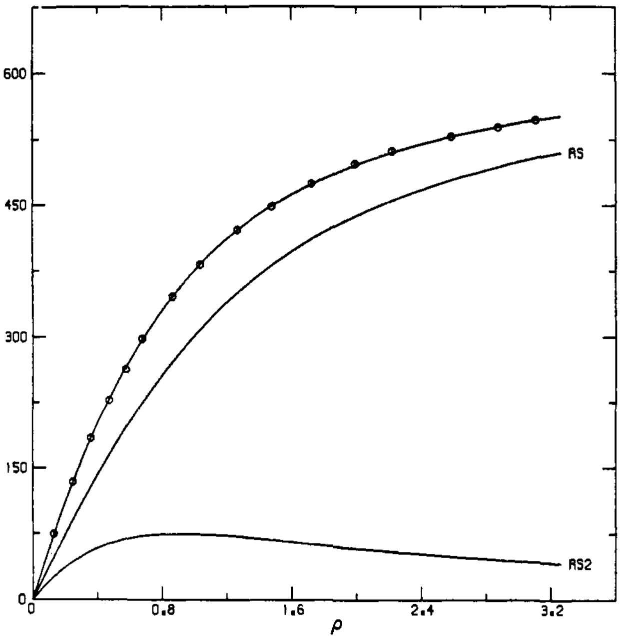

Figure 3. Experimental induced shifts of acetone plotted *vs.* the reagent-to-substrate ratio, ρ. Curves are calculated with four parameters (*cf.* Table II).

Results

Acetone. The results obtained with acetone as the substrate are graphically presented in Figure 3. The "initial slope" given in Table II (fourth entry) is the slope of the straight line drawn through the first two experimental points and the origin of the Δ *vs.* ρ plot. Its comparison to the shift observed at the highest ρ, Δ at ρ_{max}, would suggest $n \approx 1$. We note, however, that the curvature of the plot extends over a wide range of ρ indicating that the dissociation constant is of magnitude comparable to S_t. A two-parameter fit (K_D and Δ_F) gives a standard deviation of 2.7 Hz. Using Δ_F with the experimental data the Scatchard plot shown in Figure 4 is obtained. Its shape and magnitude along the axes is similar to that of curve 2 in Figure 1. It can thus be anticipated that a better fit should be obtained with $K_2 > 4K_1$ and $\Delta_1 \approx \Delta_2$. Indeed the standard deviation becomes 1.2 Hz with K_1 = 8.2 mM, K_2 = 67.4 mM, and $\Delta_1 = \Delta_2$ = 636 Hz. The individual contributions due to the RS and RS_2 species were calculated separately and are shown appropriately labeled in Figure 3. Their sum is the solid line through the points. It is seen that the RS complex makes the dominant contribution. Some observed quantities as well as the constants obtained in the fitting procedures are summarized for easy reference and comparison in Table II.

Table II. Experimental Data and Results of Fitting Procedures

	Acetone	DMSO	2-Propanol	β-Picoline
S_t, mM	20.3	21.2	26.0	31.1
ρ_{max}	3.107	2.386	2.518	2.915
Δ at ρ_{max}, Hz	546.5	376.0	500.0	190.5
Initial slope, Hz	560	548	824	407
	Two-Parameter Fit			
K_D, mM	22.77	6.37	7.48	1.76
Δ_F, Hz	665.0	412.0	536.5	191.5
Std, Hz	2.7	3.8	3.7	4.7
	Four-Parameter Fit			
K_1, mM	8.2	1.6	11.9	39.5
K_2, mM	67.4	15.7	26.1	1.2
Δ_1, Hz	636.0	395.0	502.0	115.0
Δ_2, Hz	636.0	395.0	897.0	229.0
Std, Hz	1.2	2.2	0.7	1.0

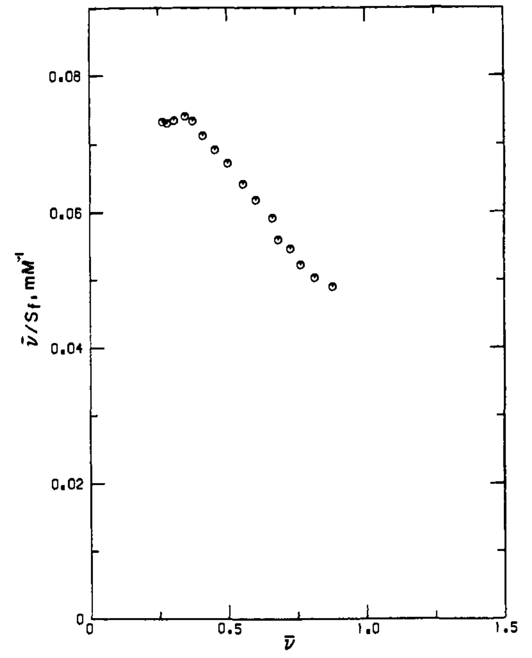

Figure 4. Scatchard plot for acetone and $Eu(fod)_3$ obtained from the experimental shifts and using the results of a two-parameter fit (*cf.* Table II).

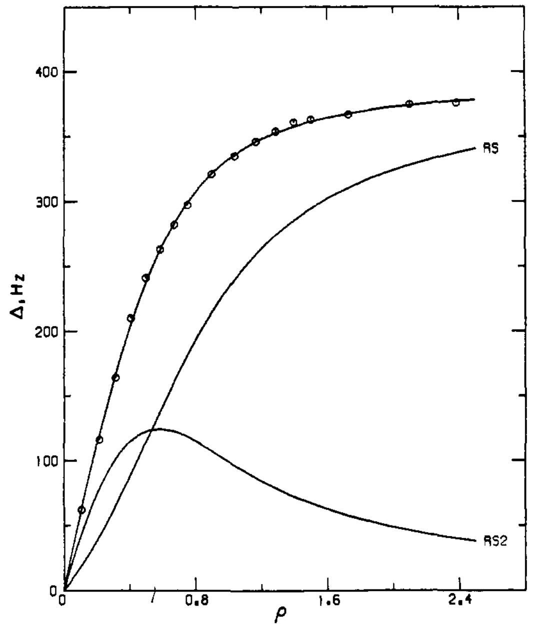

Figure 5. The experimental shifts of DMSO plotted *vs.* ρ. Curves are calculated with four parameters (*cf.* Table II).

DMSO. The results for DMSO are shown in Figure 5. Here the comparison of the initial slope to the Δ at ρ_{max} already suggests that $n > 1$. The Scatchard plot obtained using the experimental shifts and

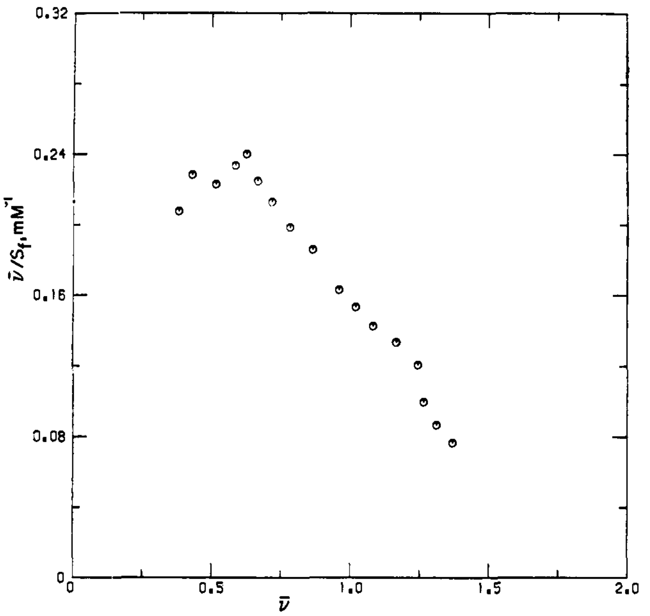

Figure 6. Scatchard plot for DMSO and Eu(fod)$_3$ obtained using the results of a two-parameter fit (*cf.* Table II).

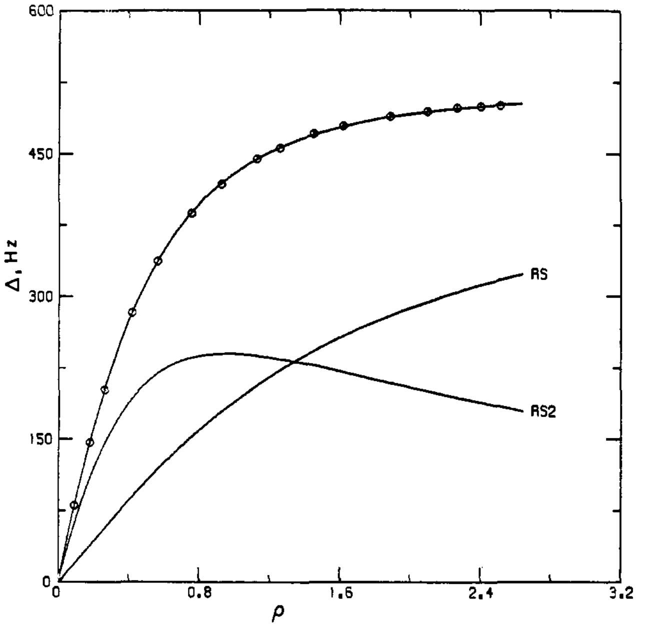

Figure 7. The experimental shifts of 2-propanol plotted *vs.* ρ. Curves are calculated with four parameters (*cf.* Table II).

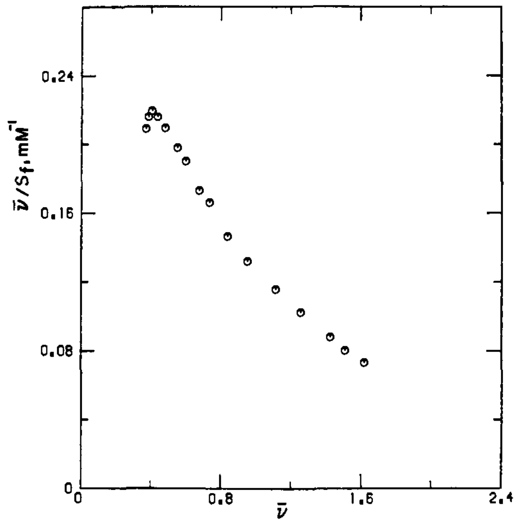

Figure 8. Scatchard plot for 2-propanol and Eu(fod)$_3$ obtained using the results of a two-parameter fit (*cf.* Table II).

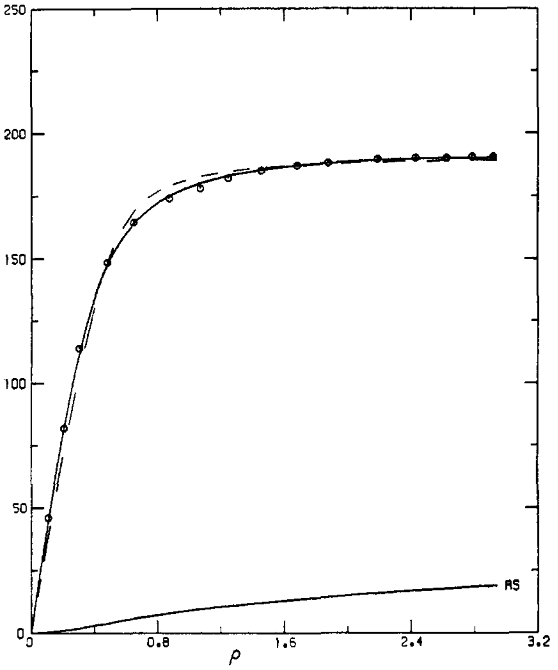

Figure 9. The experimental shifts of β-picoline plotted *vs.* ρ. The solid line was calculated with four parameters and the broken line with two parameters (*cf.* Table II).

the Δ_F fitting best the data with K_D is shown in Figure 6. Its shape resembles that of curve 1 in Figure 1, suggesting that the actual situation is one with $K_2 > 4K_1$ and $\Delta_1 \approx \Delta_2$. This is confirmed by the improvement in the standard deviation under such conditions (*cf.* Table II). For DMSO the RS$_2$ species make a larger contribution to the observed shifts up to $\rho \approx 0.5$, but becomes smaller at higher values of ρ.

2-Propanol. For 2-propanol the induced shifts in the resonance of the methyl doublet only were measured. The results are plotted *vs.* ρ in Figure 7. The methine septet is of much lower intensity and at the low substrate concentration used could be observed with difficulty and only at the lowest values of ρ. The initial slope compared to Δ at $\rho_{\max}$ shows that $n > 1$. While the two-parameter fit might be considered satisfactory, the Scatchard plot presented in Figure 8 shows characteristic irregularities similar to those seen in curve 4 of Figure 2. The latter was generated with $K_2 < 4K_1$ and $\Delta_2 > \Delta_1$. Indeed a much better fit is obtained with constants obeying these inequalities. The larger contribution of the RS$_2$ species extends for 2-propanol over a wider range of ρ, up to $\rho \approx 1.3$.

β-Picoline. The methyl protons of β-picoline, which were the only ones measured, showed the smallest induced shifts observed in this study. This was intuitively expected on the basis of the pseudo-contact shift model since here the methyl group is one bond further from the atom at which coordination occurs. The results are depicted in Figure 9. The Δ *vs.* ρ curve shows the steepest initial slope the magnitude of which already indicates that $n \approx 2$. The two-parameter fit is the poorest among the substrates investigated. It is shown by the broken line in Figure 9. The Scatchard plot on Figure 10 shows a prominent deviation from linearity with a characteristic break very similar to that of curve 3 in Figure 2. Thus, it was anticipated that $K_2 \ll 4K_1$ and $\Delta_2 \approx 2\Delta_1$, which was indeed substantiated by the calculation; the closeness of the fit as measured by the standard deviation improved significantly using constants obeying these relations. The contribution of the RS_2 species is dominant over the whole experimental range of ρ (for clarity the curve for RS_2 is omitted from Figure 9).

Discussion

The results of this study clearly demonstrate that the adducts formed in solution between Eu(fod)$_3$ and organic substrate molecules have a total 1:2 stoichiometry. Complex formation takes place in two steps characterized by different dissociation constants, and adducts of the type RS and RS_2 are present in equilibrium. The important outcome of the analysis of the experimental data is that the lanthanide induced shifts in the protons of the substrate molecule may be different for the RS and RS_2 species and that the relative contributions of these species to the total observed effect depends on the relations between the dissociation constants and between the limiting shifts. It thus appears that no general predictions can be made and for each case a complete analysis should be carried out. The implication of this conclusion is that the intuitive geometrical interpretation often given to the relative shifts induced in different parts of the same molecule may be in error unless the same (or approximately the same) relation between Δ_1 and Δ_2 holds for each proton. The data of Shapiro and Johnston show that for Eu(fod)$_3$ and 3-(*p*-chlorophenyl)-3,5,5-trimethylcyclohexanone, Δ_1/Δ_2 for ten of the protons spans the narrow range of 2.24–2.50.[13] On the other hand, the data for quinoline[8] suggest that the divergence there is greater. Clearly more examples and careful study are needed before making any generalizations.

The relations between the dissociation constants of the two types of adducts are $K_2 > 4K_1$ for acetone and DMSO and $K_2 < 4K_1$ for 2-propanol and β-picoline. This finding can be interpreted in terms of a substrate induced ligand rearrangement around the central lanthanide ion of the complex. Such rearrangements are well known for β-diketonate complexes of high coordination number.[14,15] The ligand rearrangement is probably induced by the formation of the RS complex. The binding of the second substrate molecule is either inhibited, as found with acetone and DMSO, or facilitated, as observed with 2-propanol and β-picoline, depending upon the nature of the new ligand arrangement around the central ion. It might be expected that such processes would show in the chemical shifts of the β-diketonate protons themselves. Preliminary observations support this expectation. The *tert*-butyl resonance of Eu(fod)$_3$ in CCl_4 solution appears at δ = 106 Hz. With the addition of substrate it moves usually upfield. By far the largest shift is observed with β-picoline where the upfield displacement (at saturation) amounts to 147 Hz.[16] It is with β-picoline that the study of the substrate resonance showed the strongest cooperative effect suggesting that the ligand rearrangement there is the most prominent.

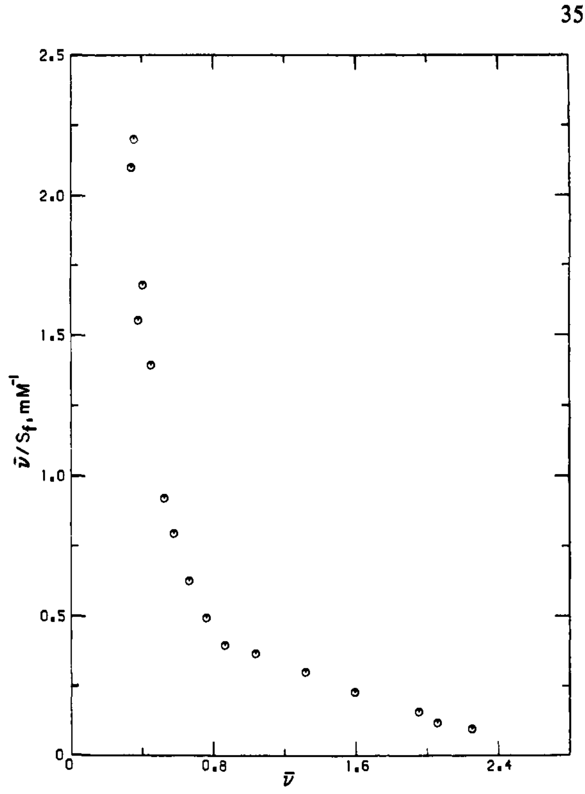

Figure 10. Scatchard plot for β-picoline and Eu(fod)$_3$ obtained using the results of a two-parameter fit (*cf.* Table II).

Effects of Reagent Dimerization. Evidence is accumulating in the literature suggesting that lanthanide shift reagents form dimers in solution.[2,15,17] Recently Desreux, Fox, and Reilly conducted a vapor-phase osmometric study of the phenomenon.[18] They found that Ln(dpm)$_3$ compounds were essentially monomeric in solution, whereas for Ln(fod)$_3$ the dimerization is substantial. The dissociation constant for Eu(fod)$_3$ dimers in carbon tetrachloride at 37° is reported to be 10 m*M*.[18] Thus the equilibrium has to

$$2R \rightleftharpoons R_2 \qquad K_d = [R]^2/[R_2] \quad (9)$$

be taken into consideration in discussing shift reagent data. With it the equation for free substrate becomes

$$[S]^5 + (3K_2/2 + 2R_t - S_t)[S]^4 + K_2(K_1 + K_2/2 + 2R_t - 3S_t/2)[S]^3 + K_2^2(K_1/2 + R_t/2 - K_1^2/K_d - K_1S_t/K_2 - S_t/2)[S]^2 + K_1K_2^2S_t(2K_1/K_d - {}^1/_2)[S] - K_1^2K_2^2S_t^2/K_d = 0 \quad (10)$$

The effect of reagent dimerization will be to shift the Δ *vs.* ρ curve to the right with a concomitant broadening of its curvature, thus leading to an apparently weaker binding of the substrate. Using eq 10 (with K_d = 10 m*M*) instead of eq 3 in the fitting procedure

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Table III. Results of Data Fitting with Reagent Dimerization Taken into Account (K_d = 10 mM)

	Acetone	DMSO	2-Propanol	β-Picoline
K_1, mM	4.64	1.39	4.1	7.01
K_2, mM	>120	21.86	40.0	5.75
Δ_1, Hz	784.0	424.0	590.0	178.0
Δ_2, Hz	0	406.0	788.0	252.0
Std, Hz	3.0	2.4	2.4	0.7

and assuming that the dimers do not react with substrate, a new set of adduct dissociation constants and limiting shifts was obtained. The results are summarized in Table III.

It is seen that as far as general trends are concerned the results are only slightly altered compared to those in Table II; for β-picoline still $K_2 < 4K_1$ and $\Delta_1 < \Delta_2$ and for DMSO $\Delta_1 \approx \Delta_2$. The only dramatic change is that acetone appears to be forming practically only 1:1 adducts. This lends further support to our tentative interpretation (*vide supra*) that substrate binding induces a ligand rearrangement around the central ion of the shift reagent molecule and that the new arrangement determines the affinity of the 1:1 adduct toward a second substrate molecule.

Acknowledgment. The assistance of Leonard Feigenbaum, a summer research student, in the early stages of this work, is gratefully acknowledged.

Nickel(II) and Palladium(II) Complexes with Polyfluoroaryl Polydentate Phosphorus–Sulfur Ligands[1-3]

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Abstract: Several different types of nickel(II) and palladium(II) complexes of the polyfluoroaryl ligands 2-methylthio-3,4,5,6-tetrafluorophenyldiphenylphosphine (fsp) and bis(2-methylthio-3,4,5,6-tetrafluorophenyl)phenylphosphine (fdsp) have been prepared and characterized. Conductance, magnetic, nmr, and electronic spectral data indicate that all the palladium complexes, except Pd(fdsp)I_2, possess planar geometries, whereas the nickel complexes have planar, tetrahedral, and octahedral structures. The potentially tridentate ligand fdsp functions as a bidentate ligand in the palladium complexes with only one of the two sulfur atoms coordinated. Several mercaptide complexes have also been prepared by demethylation of the corresponding fsp and fdsp complexes. Complexes of analogous fluorinated and unfluorinated ligands are compared, and the effect of fluorination on the σ- and π-bonding properties of the ligands is discussed.

Unusual coordination numbers and different geometries are often observed when the steric or electronic properties of the polydentate phosphine, arsine, thioether, and selenoether ligands are changed only slightly.[5-8] Unfortunately, both steric and electronic parameters are generally changed simultaneously when one of the substituents on a tertiary phosphine or arsine is varied. In order to separate these two parameters we have chosen sets of ligands whose donor groups and structural features are comparable, but whose coordination properties can be influenced by changing the electronic properties of the molecule. Thus we have been investigating the effect of substituting a fluoroaryl group for an aryl group in aryl and *o*-phenylene polydentate ligands. Since the van der Waals radii of hydrogen and fluorine are very similar (1.2 and 1.35 Å, respectively),[9] steric considerations should be minimal in comparisons of the donor properties of ligands containing comparable aryl and fluoroaryl substituents.

The electronegativity of the fluoroaryl group is higher than that of an aryl group.[10,11] A variety of

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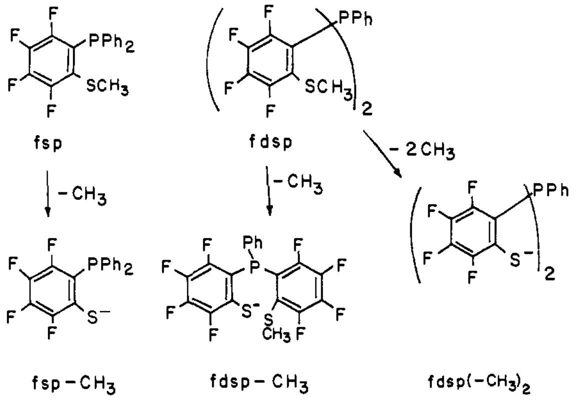
(1) The term "fluoro ligand" will be used to refer to a ligand in which some of the hydrogen atoms have been replaced by fluorine, *e.g.*, fsp or fdsp; the term "perfluoro ligand" will be reserved for those cases where *all* hydrogen atoms are replaced by fluorine, *e.g.*, PF_3, $P(CF_3)_3$, etc. Because the thioethers fsp and fdsp lose one (or two) methyl groups in certain reactions to form complexes nominally of anionic mercaptide ligands, establishing a brief but descriptive acronym for the different forms of the ligands is necessarily somewhat complex. We believe the following nomenclature scheme presents a minimum of confusion and a maximum of brevity.



(2) Presented in part at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 1970.

(3) Abstracted from the M.S. thesis of J. R., Aug 1970, and from the Ph.D. dissertation of P. G. E., The Ohio State University, Dec 1971.

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