Unfortunately, coupling constants for $(DMAC)_2BF_2^+$ and $(DMAC)(tmu)BF_2^+$ were not observed. Chemical shifts, however, are in the expected range. *Only* the coupling constant (37 Hz), and not the chemical shift, has been reported for $(Me_3N)_2BF_2^+$.[17] This value is in the expected range.

The insensitivity of the nmr parameters to the charge on the ion is notable in the series $(tmu)_2BF_2^+$, $tmu \cdot BF_3$, BF_4^-; $(DMAC)_2BF_2^+$, $DMAC \cdot BF_3$, BF_4^-. Much more sensitivity is shown to factors such as the nature of the donor, the number of heavier halogens, and whether boron is trigonal or tetrahedral.

Acknowledgments. We thank the National Research Council of Canada for financial support of this work and for the award of a scholarship (to G. J. S.). Thanks are also due to Dr. J. M. Miller for helpful discussions and to the Department of Chemistry, McMaster University, for making available to us their ^{19}F and ^{11}B nmr facilities.

Registry No. $tmu \cdot BF_3$, 23389-91-5; $(tmu)_2BF_2^+ \cdot BF_4^-$, 50600-95-8; $tmu \cdot BCl_3$, 50599-70-7; $tmu \cdot BF_2Cl$, 50599-71-8; $tmu \cdot BFCl_2$, 50599-72-9; $(tmu)_2BF_2^+$, 50600-94-7; BF_3Cl^-, 36503-32-9; $BF_2Cl_2^-$, 36503-34-1; $BFCl_3^-$, 36503-36-3; $(DMAC)(tmu)BF_2^+$, 50600-96-9; $(DMAC)_2BF_2^+$, 50600-97-0; $DMAC \cdot BF_3$, 15876-98-9; $DMAC \cdot BF_2Cl$, 50790-57-3; $DMAC \cdot BFCl_2$, 50790-58-4; tmu, 632-22-4; DMAC, 127-19-5; BF_3, 7637-07-2.

Contribution from the Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11790

Complexes of Nucleophiles with Rare Earth Chelates. II.[1] Self-Association and Adduct Formation of the Lanthanide Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) Chelates $Pr(fod)_3$ and $Eu(fod)_3$

ALAN H. BRUDER, STEPHEN R. TANNY, HARRY A. ROCKEFELLER, and CHARLES S. SPRINGER, Jr.*

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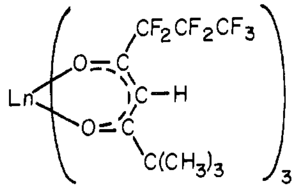
The self-association of the acidic chelates $Pr(fod)_3$ and $Eu(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) as well as the adduct formation of $Eu(fod)_3$ with methyl dimethylcarbamate (TMC) has been studied. All investigations were carried out in carbon tetrachloride solutions. The association quotients for the formation of dimers and trimers respectively are 140 ± 8 M^{-1} and 45 ± 5 M^{-1} for $Pr(fod)_3$ and 367 ± 22 M^{-1} and 12 ± 2 M^{-1} for $Eu(fod)_3$ at 37°. The association quotients for the formation of 1:1 and 1:2 adducts of $Eu(fod)_3$ with TMC are $(16 \pm 6) \times 10^2$ M^{-1} and 107 ± 10 M^{-1}, respectively, at 32°. The effects of water of hydration on the above interactions are also discussed.

Introduction

The paramagnetic tris lanthanide(III) chelates of the anion of Hfod, $Ln(fod)_3$ (I),[2] have been finding ever increasing usage as nmr shift reagents[3] since the first report of Rondeau and Sievers.[4] The chemical property which allows their use as nmr shift reagents is the Lewis acidity which they possess as a consequence of their coordinative unsaturation. Thus the neutral tris chelates dissolve in organic solvents and form labile adducts with a large variety of nucleophilic substrates.[1,3b] The paramagnetic lanthanide ions cause isotropic hyperfine shifts in the resonance frequencies of magnetic substrate nuclei.[3] The Lewis acidity of these chelates also causes two side interactions which can interfere with their usage as nmr shift reagents. These are the formation of hydrates[5-7] and the formation of self-associated oligomers.[1,8,9] We report here the results of our investigations on the effects of these interactions on shift reagent studies.



I

Results

Self-Association of $Pr(fod)_3$, $Eu(fod)_3$, and Their Hydrates. We have studied the self-association of $Pr(fod)_3 \cdot {\sim}^3/_2OH_2$, $Pr(fod)_3 \cdot {\sim}^1/_2OH_2$, $Pr(fod)_3$, $Eu(fod)_3 \cdot {\sim}^3/_2OH_2$, $Eu(fod)_3 \cdot {\sim}^1/_2OH_2$, and $Eu(fod)_3$ in carbon tetrachloride by vapor pressure osmometry.[7] The results of the experiments with the praseodymium complexes are shown in Figure 1. The

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[1] Part I: B. Feibush, M. F. Richardson, R. E. Sievers, and C. S. Springer, *J. Amer. Chem. Soc.*, 94, 6717 (1972).

[2] In this paper, Ln symbolizes all of the lanthanide elements from La to Lu and includes Y. The ligand abbreviations used in this paper are as follows: fod, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate; thd, 2,2,6,6-tetramethyl-3,5-heptanedionate, often referred to as dpm; dfhd, 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedionate; pta, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionate; hfhd, 1,1,1,2,2,3,3-heptafluoro-4,6-heptanedionate; tta, 1,1,1-trifluoro-4-thenoyl-2,4-butanedionate; hfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; acac, 2,4-pentanedionate.

[3] Reviews of lanthanide shift reagents: (a) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, 11, 675 (1972); (b) R. E. Sievers, M. F. Richardson, and C. S. Springer, to be submitted for publication.

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[5] (a) C. S. Springer, D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, 6, 1105 (1967); (b) C. S. Springer, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1967.

[6] R. E. Sievers, K. J. Eisentraut, C. S. Springer, and D. W. Meek, *Advan. Chem. Ser.*, No. 71, 141 (1968).

[7] For a discussion of the extent of hydration of $Ln(fod)_3$ chelates see C. S. Springer, A. H. Bruder, S. R. Tanny, M. Pickering and H. A. Rockefeller in "NMR Shift Reagents," R. E. Sievers, Ed., Academic Press, New York, N. Y., 1973, Chapter 14, p 283.

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[9] R. Porter, T. J. Marks, and D. F. Shriver, *J. Amer. Chem. Soc.*, 95, 3548 (1973).

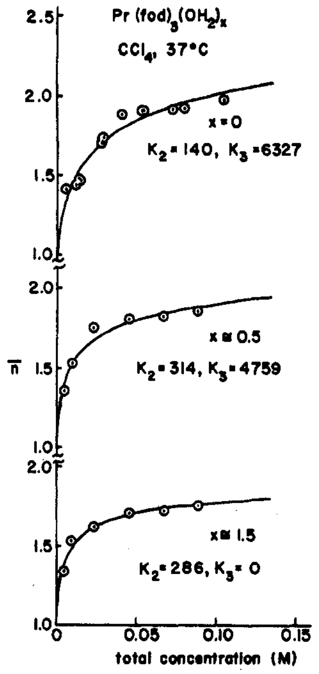

Figure 1. Self-association curves of $Pr(fod)_3$, $Pr(fod)_3 \cdot \sim ^1/_2OH_2$, and $Pr(fod)_3 \cdot \sim ^3/_2OH_2$ as a function of concentration in CCl_4 at 37°. $\bar{n}$ is the average number of monomers per solute molecule (determined from vapor pressure osmometry). The total concentration is calculated assuming that all solute molecules are monomers. The circles represent experimental data points. The lines are theoretical curves obtained with the values of the association quotients for dimerization and trimerization (K_2 and K_3) shown.

average number of monomeric units present in the solute molecules, $\bar{n}$, is plotted *vs.* the total concentration of monomeric units. It is obvious that the $Pr(fod)_3$ chelates are highly associated ($\bar{n} \geqslant 1.5$ at 0.01 M). It is also clear that decreasing the state of hydration increases the extent of self-association. At 0.1 M, $\bar{n} \simeq 2.0$ for $Pr(fod)_3$ while for $Pr(fod)_3 \cdot \sim ^3/_2OH_2$, $\bar{n}$ is only ~1.7. The curves shown in Figure 1 are the best least-squares fits to the data points found by a computer program which iterates the equilibrium quotients K_2 and K_3, defined by eq 1 and 2, respectively.

$$2Ln(fod)_3 \cdot xOH_2 \overset{K_2}{\rightleftarrows} (Ln(fod)_3 \cdot xOH_2)_2 \qquad (1)$$

$$3Ln(fod)_3 \cdot xOH_2 \overset{K_3}{\rightleftarrows} (Ln(fod)_3 \cdot xOH_2)_3 \qquad (2)$$

The program thus allows for competing dimerization and trimerization reactions. The values of K_2 and K_3 corresponding to the best theoretical curves are shown in the figure. Fits with $K_3 > 0$ for $Pr(fod)_3 \cdot \sim ^3/_2OH_2$ were definitely poorer than that shown, as were fits with $K_3 = 0$ for $Pr(fod)_3 \cdot \sim ^1/_2OH_2$ and $Pr(fod)_3$.

Similar results were obtained for the $Eu(fod)_3$ chelates and the best fit association quotients along with those of the $Pr(fod)_3$ complexes are set out in Table I. In the table, K_3 is replaced by K_3', defined by eq 3 and calculated from the

$$(Ln(fod)_3 \cdot xOH_2)_2 + Ln(fod)_3 \cdot xOH_2 \overset{K_3'}{\rightleftarrows} Ln(fod)_3 \cdot xOH_2)_3 \qquad (3)$$

relationship $K_3' = K_3/K_2$. The results obtained, in recent studies in several solvents, by other workers are also included in Table I. The state of hydration in most of these samples is uncertain because it is not clear *exactly* how the complexes were dried immediately prior to the vapor pressure osmometry studies. (This is an important consideration.[7]) Our results are in reasonably good agreement with the CCl_4 results of Reilley and coworkers considering the difficulty in attaining a specific state of hydration.[7] If the complexes studied by them were the sesquihydrates, the agreement would be excellent. For our $Eu(fod)_3 \cdot \sim ^1/_2OH_2$ data, we could get almost (but not quite) as good a fit with $K_2 = 109 \pm 6$ and $K_3 = 0$ (almost identical with their reported result). All of our other best fit results reported in Table I are much better than any alternatives studied by us.

Solution Adduct Formation of $Eu(fod)_3$ and Its Hemihydrate with Methyl Dimethylcarbamate. The formation of labile solution adducts with nucleophilic substrates by the acidic lanthanide tris(β-diketonate) chelates is readily studied by nmr spectroscopy.[3b] We have investigated the interaction of methyl dimethylcarbamate ($(H_3C)_2NC(O)OCH_3$, TMC) with $Eu(fod)_3 \cdot \sim ^1/_2OH_2$ and $Eu(fod)_3$ in carbon tetrachloride solution. The results of our experiments are shown in Figure 2. They are given in the form of plots of the isotropic hyperfine shifts, Δ, of the various substrate proton resonances as a function of the mole ratio, ρ, of the total concentration of monomeric units of the chelate to the total substrate concentration. (Thus, $\rho \equiv [Eu(fod)_3 \cdot xOH_2]_{total}/[TMC]_{total}$.) The total concentration of substrate, [TMC], remains constant at 0.23 ± 0.02 M for all points. The observed hyperfine shift of nucleus i in substrate D, Δ_{D_i}, is defined as the shift of that nucleus in a diamagnetic solution of the same concentration of D, $\delta^D{}_{D_i}$ (in ppm from TMS, negative if downfield), *i.e.*, in the absence of the paramagnetic shift reagent, minus the observed shift in the presence of the chelate, δ_{D_i}.[3b] (Thus, $\Delta_{D_i} \equiv \delta^D{}_{D_i} - \delta_{D_i}$.)

The hyperfine shifts of all resonances are to lower fields, as is usually true with europium(III)[3] and as has been previously reported for carbamates.[10,11] The cis and trans NCH_3 resonances are isochronous in the diamagnetic solution[12,13] and at very low values of ρ. At values of $\rho >$ ~0.04, however, these resonances become anisochronous and the variation in the exchange broadening of the peaks allows for a novel dynamic nmr method for studying the rate of rotation about the carbonyl carbon-nitrogen bond.[14] The lowest field peak in the diamagnetic solution has a relative area which is half that of the other peak. Thus, the downfield resonance is assigned to the OCH_3 group.[12,13] It undergoes the largest downfield shift in the presence of the paramagnetic Eu(III) complex. This is consistent with coordination through either the carbonyl or the ester oxygen atoms. Carbonyl groups usually show a greater interaction with Ln(β-diketonate)$_3$ chelates than do sterically crowded ethers.[3b] Coordination through the carbonyl oxygen is confirmed by the fact that, while TMC interacts with $Eu(thd)_3$,[2] methyl dimethylthiocarbamate ($(H_3C)_2NC(S)OCH_3$) does not.[10] The NCH_3 resonance shifted further downfield is assigned to the cis NCH_3 group because of its closer proximity to the site of complexation.[11]

The solid curves through the $Eu(fod)_3$ points (circles) are the best least-squares fits obtained by assuming the four competing equilibria shown in Figure 2 to be the important ones. The values of K_2 and K_3' for the dimerization and trimerization, respectively, of $Eu(fod)_3$ are those obtained

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Table I. Vapor Pressure Osmometry Studies

	Solvent							
	$CHCl_3$ (37°)		C_6H_6 (37°)	CCl_4 (37°)		n-C_6H_{14}		
Compd	K_2, M^{-1}	K_3', M^{-1}	K_2, M^{-1}	K_2, M^{-1}	K_3', M^{-1}	K_2, M^{-1}	K_3', M^{-1}	Ref
$Pr(fod)_3\cdot{\sim}{}^3/_2OH_2$				286 ± 20	0			This work
$Pr(fod)_3\cdot{\sim}{}^1/_2OH_2$				314 ± 20	15 ± 2			This work
$Pr(fod)_3$				140 ± 8	45 ± 5			This work
$Pr(fod)_3\cdot xOH_2$	1.6	0		339	0	5130	224	8
$Eu(fod)_3\cdot{\sim}{}^3/_2OH_2$				75 ± 5	0			This work
$Eu(fod)_3\cdot{\sim}{}^1/_2OH_2$				68 ± 5	6.9 ± 1			This work
$Eu(fod)_3$				367 ± 22	12 ± 2			This work
$Eu(fod)_3\cdot xOH_2$	1.6	0		100	0	5010	12	8
$Eu(fod)_3\cdot xOH_2$			60.9 ± 18					9
$Dy(fod)_3\cdot xOH_2$			13.8 ± 4.0					9
$Ho(fod)_3\cdot xOH_2$			11.6 ± 3.8					9
$Yb(fod)_3$			8.6 ± 3.6					9

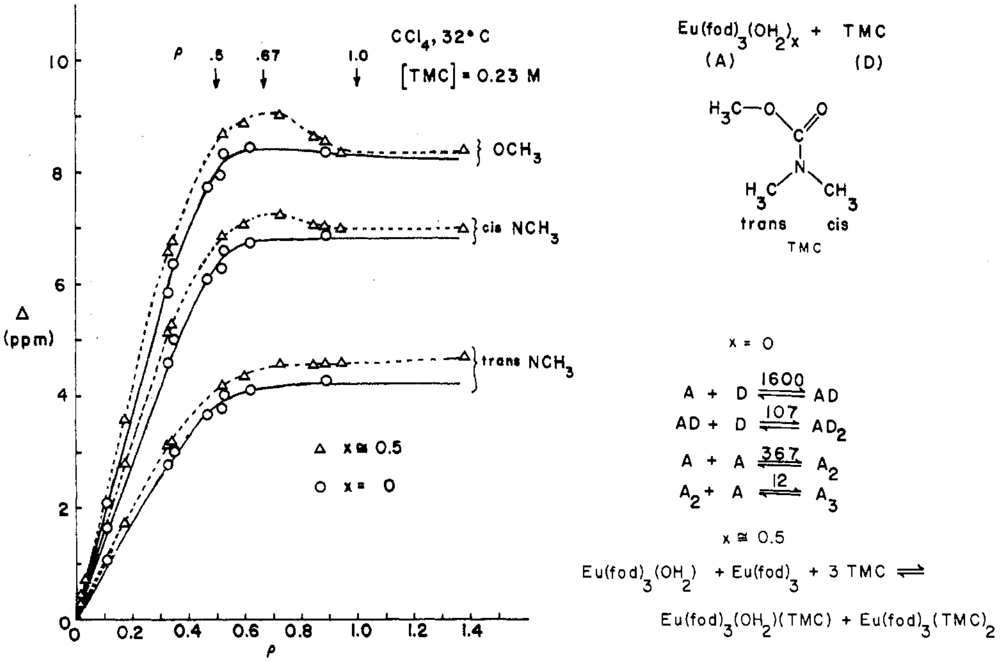

Figure 2. Mole ratio plots of the isotropic hyperfine shifts of the resonances of methyl dimethylcarbamate induced by $Eu(fod)_3$ and $Eu(fod)_3\cdot{\sim}{}^1/_2OH_2$ in CCl_4 at 32°. The circles and triangles represent experimental data points. The solid lines represent the theoretical curves obtained with the association quotients shown for the $Eu(fod)_3$ equilibria.

from the osmometry studies described above. These parameters are simply constants which regulate the amount of monomeric $Eu(fod)_3$ present. (Their values cannot be obtained from a fitting of the *substrate* resonance curves.)

Thus, the fitting problem reduces to one of four variable parameters, K^{AD}, K^{AD_2}, $\Delta_1°$, and $\Delta_2°$, which are defined in eq 4-7.[3b,15] The parameters $\Delta_1°$ and $\Delta_2°$ are the shifts of

$$A + D \overset{K^{AD}}{\rightleftharpoons} AD \tag{4}$$

$$AD + D \overset{K^{AD_2}}{\rightleftharpoons} AD_2 \tag{5}$$

$$\Delta_1° = \delta^{D}{}_{D_i} - \delta^{AD}{}_{D_i} \tag{6}$$

$$\Delta_2° = \delta^{D}{}_{D_i} - \delta^{AD_2}{}_{D_i} \tag{7}$$

the substrate resonances in the 1:1 and 1:2 complexes, respectively. A first fitting of each of the three curves (OCH_3, cis NCH_3, and trans NCH_3) was made in which all four parameters were allowed to vary. Then the three values each of K^{AD} and K^{AD_2} (which were similar) were weighted according to the goodness of their respective fits and averaged. Their averaged values are $K^{AD} = (16 \pm 6) \times 10^2$ (M^{-1}) and $K^{AD_2} = 107 \pm 10$ (M^{-1}) and are shown in Figure 2. (The error in the K^{AD_2} value is much smaller because most of the data points are in the low ρ (<0.5) region.) These values were then used as constants and the curves were refitted with only $\Delta_1°$ and $\Delta_2°$ as variables. The values which gave the fits shown in Figure 2 are given in Table II.

The dashed curves through the $Eu(fod)_3\cdot{\sim}{}^1/_2OH_2$ data (triangles) in Figure 2 are *not* computer fitted. They merely emphasize the effect of the water on the shift reagent plots in this case. It is clear that the presence of water causes a pronounced nonmonotonicity in the curves of the OCH_3 and cis NCH_3 resonances which go through maxima at $\rho \simeq 0.67$.

Discussion

Extensive investigations of transition metal β-diketonate

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(15) Other possible reactions $A_2 + D \rightleftarrows A_2D$ and $A_2D + D \rightleftarrows A_2D_2$ were ignored because they should be less important (especially at low values of ρ) and their inclusion would introduce two new parameters each. An eight-parameter fit to these data would not be of significance proportional to its difficulty. These reactions almost certainly become important at larger values of ρ (>1.5) and must be taken into account in that region.

Scheme I

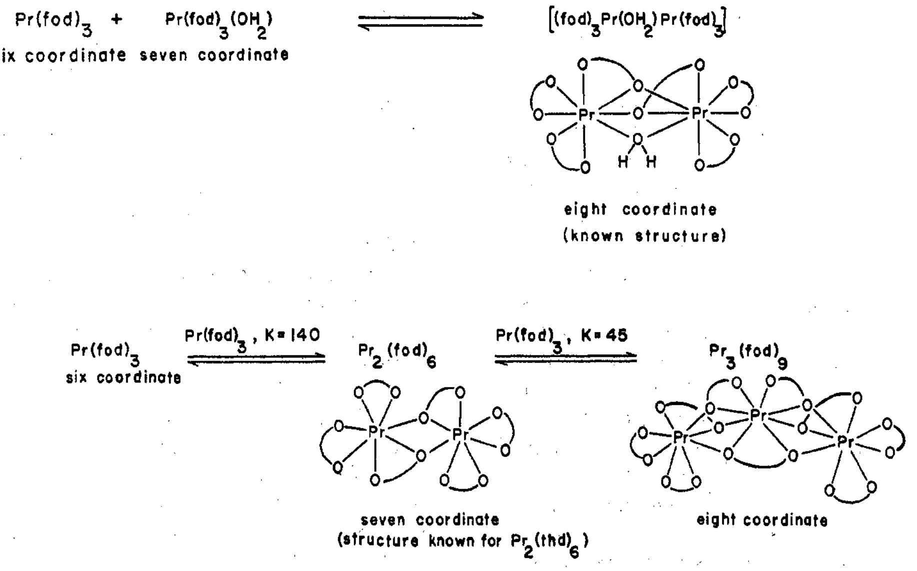

Table II. Nmr Shift Parameters for the Interaction of TMC with $Eu(fod)_3$

Resonance	$\Delta_1°$, ppm	$\Delta_2°$, ppm
OCH_3	6.94 ± 0.03	9.65 ± 0.01
Cis NCH_3	6.32 ± 0.02	7.49 ± 0.01
Trans NCH_3	4.14 ± 0.03	4.48 ± 0.01

complexes have shown that whenever the coordination number of the metal can exceed twice its ionic charge, the neutral (inner) β-diketonate chelate acts as a Lewis acid.[16,17] Since the ionic charge of the lanthanides in the present studies is 3+, a coordination number greater than 6 is requisite for Lewis acidity. There is much evidence that higher coordination numbers (*i.e.*, >6) are important for lanthanide β-diketonate complexes.[3b,18] Thus, much of the chemistry of the simple $(fod)_3$ complexes (I) can be understood in terms of their Lewis acidity, which for such coordinatively unsaturated compounds is manifest in two general ways: self-association and adduct formation with bases.

Self-Association. The self-association data for the $(fod)_3$ complexes of Pr(III) and Eu(III) given in Figure 1 and Table I can be interpreted in terms of a drive toward eight-coordination about these early lanthanide ions. Thus, for any state of hydration equal to or above that of the hemihydrate the extent of trimerization is small because the formation of a dimer with a bridging "water" molecule in which both metal ions become eight-coordinate (as in the known structure of a $Pr(fod)_3$ hydrate[7]) is possible. This is shown in Scheme I for $Pr(fod)_3 \cdot \sim {}^1/_2 OH_2$.

However, if the chelate is completely anhydrous, a simple topological analysis, according to Fackler,[19] indicates that the metal ions cannot both attain eight-coordination by simple dimerization.[20] The lowest oligomer in which all metal ions can become eight-coordinate is the trimer. There are two topologically allowed eight-coordinate trimers. One of these is cyclic and would presumably be quite crowded. A possible structure for the angular noncyclic trimer is shown in Scheme I. Also possible is one 8,8,7 trimer, one 8,7,7 trimer, and an 8,7 dimer. ($Zn(acac)_2$ has a 6,5,5 trimeric solid-state structure.[17])

Inspection of the data presented in Table I allows us to enumerate three factors which affect the extent of self-association of $Ln(\beta\text{-diketonate})_3$ chelates. One is the state of hydration as discussed above. Another is the polarity of the solvent. The data indicate that the extent of self-association has the following solvent dependence: $n\text{-}C_6H_{14} > CCl_4 > C_6H_6 > CHCl_3$. That is, *self-association is reduced in the more polar solvents.* The initial molecular weight studies of the $Ln(fod)_3$ chelates were made in $CHCl_3$[5] and indicated that the complexes were monomeric. The most popular solvents for shift reagent studies have been CCl_4 and $CHCl_3$, and it is clear that there can be significant differences in self-association in these media.

The third factor apparent from Table I is the effect of the size and/or acidity of the metal ion. *The chelates of the larger lanthanide ions are more highly associated than those of the smaller ions under the same conditions.* This is in agreement with the general trend across the entire lanthanide series as exemplified by the (+)-3-trifluoroacetylcamphorates[1] and the tropolonates.[21] Although the metal ions become more acidic as they get smaller[9] (and therefore more "highly" coordinatively unsaturated), the steric requirements for the hindered process of self-association become more detrimental and apparently override the increased acidity. The $Er(fod)_3$ complexes are even less associated than the Pr(III) and Eu(III) compounds.[1,22] For the later lanthanide β-diketonates, coordination numbers above 7 are rare.[3b]

A fourth factor is apparent upon consideration of recent self-association studies of the $Ln(thd)_3$ complexes, the other most popular class of shift reagents.[8,23-25] All of these studies indicate the monomeric nature of the chelates in all solvents and at all concentrations studied. These results are consistent with the observed monomeric molecular structures of the $(thd)_2$ complexes of the divalent first-row tran-

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(20) The only assumption involved in this analysis is the entirely reasonable one that, in any oligomer, the number of atoms shared between any two adjacent metal ions cannot exceed 3. A three-atom bridge is found in the known structure of a $Pr(fod)_3$ hydrate.[7]

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sition metal ions. (The Fe, Co, and Zn chelates are tetrahedral while the Ni and Cu analogs are square planar in the solid state.[17] The only instance of known self-association of a thd complex is the solid-state $Pr_2(thd)_6$ dimer (Scheme I).[26]) Graddon has pointed out that it is not clear whether the monomeric character of thd chelates is due to the bulky nature of the *t*-Bu substituents, as has often been supposed, or the great basicity of the thd anion[17] (the pK_a of H(thd) is 15.9). The latter factor would serve to lessen the acidic character of the metal ion and thus reduce its tendency toward coordinative expansion. This seems to be an important factor in nickel(II) β-diketonate chemistry[17] and most likely also for the Ln(III) complexes. The H(fod) ligand ($pK_a \simeq 8.7$) is, after all, not a great deal less sterically hindered than the H(thd) ligand. Proposals, based on "extra" nmr peaks, that the $Pr(thd)_3$ and $Eu(thd)_3$ complexes are dimerized in solution[27-29] are almost certainly incorrect. These "extra" peaks disappear upon rigorous predrying of the chelates.[8,25] Thus, the fourth factor affecting the self-association of Ln(β-diketonate)$_3$ complexes is the size and/or acidity of the chelate ligand. *The fod chelates are associated in nonpolar solvents; the thd chelates are not.*

Solution Adduct Formation. The importance of attaining eight-coordination about the metal ion in the *early* lanthanide β-diketonates is also manifest in the formation of 1:2 adducts (AD_2) with monodentate substrates in solution. Although much of the early shift reagent work with the $Ln(fod)_3$ chelates assumed the formation of only 1:1 adducts,[3] the appearance of the mole ratio plots for the interaction of the small nucleophilic substrate TMC with anhydrous $Eu(fod)_3$ (Figure 2) leaves no doubt as to the formation of 1:2 adducts. The curves begin to level off at values of $\rho \simeq 0.5$. This indicates significant amounts of 1:2 adduct formation at lower values of ρ.[3b] Thus the curves were fit for four competing equilibria: the formation of dimer (A_2), trimer (A_3), 1:1 adduct (AD), and 1:2 adduct (AD_2). The two self-association equilibria were known from the osmometry studies and therefore were not variables.

Recently published mole ratio plots also indicate the presence of solution 1:2 adducts of the $(fod)_3$ chelates of Pr,[9,30] Eu,[9,31] and Ho.[9] Although these curves do not begin to level off until $\rho \approx 1.0$, careful analysis reveals the presence of the 1:2 adducts. Shapiro and Johnston performed a total curve fitting of the mole ratio plot of the interaction of $Eu(fod)_3$ with a substituted cyclohexanone, taking into account the competetive formation of 1:1 and 1:2 adducts.[31] Significant amounts of the latter are formed but the plot does not level off until $\rho \approx 1.0$ because $\Delta_1°$ is greater than $\Delta_2°$.

For the carbamate results reported here, $\Delta_2°$ *is greater than* $\Delta_1°$ (Table II). In the mole ratio plots of systems containing 1:2 adducts, the initial slopes are equal to $2\Delta_2°$.[3b,28,31] That is, in the low ρ region where AD_2 adducts predominate, the observed shift is tending toward $\Delta_2°$ where it would level off at $\rho = 0.5$ if 1:2 complexes were exclusively formed.[3b] However as ρ increases, the AD species become more important and, when the $\Delta_1°$ values are smaller than the $\Delta_2°$ values, the curves begin to level off at values of Δ intermediate between $\Delta_2°$ and $\Delta_1°$ and therefore well below $\Delta_2°$. This is a significant observation because the values of $\Delta_1°$ have often been estimated from the initial slopes of mole ratio plots in shift reagent studies.[3b] Also, estimates of $\Delta_1°$ values have recently been made from the values of Δ on the level portion of the mole ratio plot.[30] The mole ratio plot is by far the most common type used in shift reagent studies.[3]

Figure 3 depicts the variation of the concentrations of the various species present in the $Eu(fod)_3$-TMC solution as ρ is changed. The concentrations were obtained using the association quotients given in Figure 2.

Further evidence for the formation of 1:2 adducts is found from linear Scott-type nmr plots[3b] of substrate binding to $Eu(fod)_3$,[32] the low-temperature nmr spectra of 1:2 adducts of $Ln(fod)_3$ complexes,[33,34] and a circular dichroism study of $Eu(fod)_3$ adducts in solution.[35] There is also evidence from mole ratio plots that Eu(III) chelates of other fluorinated β-diketonates; dfhd[2,36] and pta[2,28] form 1:2 adducts in solution. The latter curves begin to level off or go through maxima at $\rho \approx 0.5$, presumably for the same reason as those of the carbamate.

Although a number of crystal structures reveal eight-coordinate 1:2 adducts of $Ln(thd)_3$ chelates with monodentate substrates,[3b] no direct evidence has been noted of *solution* 1:2 adduct formation of these chelates. This would be expected to be less important if the high basicity of the thd anion is a dominant factor (as discussed above for self-association). Indeed, under the low-temperature conditions where Evans and Wyatt found direct evidence for 1:2 hexamethylphosphoramide adducts of fod, hfhd, tta, and hfa complexes, the nonfluorinated thd chelates form only 1:1 adducts.[34]

The importance of correcting for the competition of self-association is to be emphasized. Values of K^{AD} and K^{AD_2} of 375 M^{-1} and 99 M^{-1}, respectively, were obtained by fitting the cis NCH_3 curve of the interaction of anhydrous $Eu(fod)_3$ with TMC with the assumption that $K_2 = K_3 = 0$. The fit was just as good as that shown in Figure 2. Many of the literature values of association quotients for the interaction of early $Ln(fod)_3$ chelates with substrates in nonpolar solvents have not been corrected for self-association and this is an obvious source of error.[3b]

The effects of water, in the form of the hemihydrated $Eu(fod)_3$, are also evident in Figure 2. Nonmonotonicities in mole ratio plots which bear some resemblance to those observed in the $Eu(fod)_3 \cdot {\sim}{}^1/_2OH_2$ curves have been reported in the literature.[28,31,37] These are all for the interaction of substrates with chelates of fluorinated ligands. (The thd complexes do not show such a pronounced tendency to be hydrated.)

For the data presented here, the most likely source of the nonmonotonicities is the presence in solution of the adduct $Eu(fod)_3 \cdot OH_2 \cdot TMC$. When $Eu(fod)_3 \cdot {\sim}{}^1/_2OH_2$ is used as the

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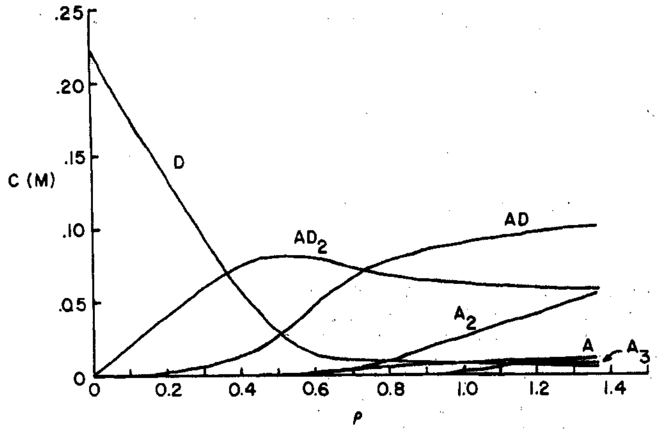

Figure 3. The dependence of the concentrations of the species present in the $Eu(fod)_3$-TMC solution on the mole ratio, ρ. The concentrations were calculated using the association quotients given in Figure 2.

acid, the values of Δ continue to rise past the point where they leveled off for the anhydrous chelate. They go through a maximum at $\rho \simeq 0.67$ before declining back toward the $\Delta_1°$ values. This would be consistent with a value of $\Delta°$ for the $Eu(fod)_3{\cdot}OH_2{\cdot}TMC$ complex larger than $\Delta_2°$. The fact that the curves go through maxima at $\rho \simeq 0.67$ may indicate the importance of the reaction given in eq 8 in

$$Eu(fod)_3 + Eu(fod)_3{\cdot}OH_2 + 3TMC \rightleftarrows Eu(fod)_3{\cdot}2TMC + Eu(fod)_3{\cdot}OH_2{\cdot}TMC \qquad (8)$$

which all europium ions become eight-coordinate. At values of ρ greater than 0.67, some seven-coordinate $Eu(fod)_3{\cdot}TMC$ must be formed.

Use of $Eu(fod)_3{\cdot}{>}{}^1/_2OH_2$ as a shift reagent results in mole ratio curves which are generally displaced to lower values of Δ, for a given ρ, than those shown in Figure 2.[38,39] This is presumably due to the more effective competition of the increased amount of water.

Experimental Section

Syntheses. The $Pr(fod)_3$ and $Eu(fod)_3$ chelates were prepared according to published procedures[5,6] from the metal oxides (Alpha, 99.9%) and H(fod) (Pierce) which were used as obtained. The purities of the isolated products were checked by comparison of the melting points and infrared spectra with the literature data.

Methyl dimethylcarbamate was prepared and purified by a method similar to that of Middaugh, Drago, and Niedzielski.[12] The nmr spectrum of the product so obtained is identical with the literature data (see Results) (bp 132.5°, atmospheric pressure).

Extent of Hydration of $Pr(fod)_3$ and $Eu(fod)_3$. Determination of the exact extent of hydration of $Ln(fod)_3$ complexes is extremely difficult.[7] In this work, the presence of an O–H stretching vibration at ~3300 cm^{-1} in the infrared spectrum was used as a convenient qualitative (and roughly quantitative) indication of the existence of hydration. The complexes could be rendered completely anhydrous (*i.e.*, no O–H stretching peak) *only* by vacuum pumping at elevated temperatures (~85°) for several days. Initially, the anhydrous complexes were removed from the drying chamber only in an inert-atmosphere box filled with dried N_2. The samples were prepared for ir analysis, by Nujol mulling, in the drybox. Later, it was determined that the anhydrous compounds could be handled (quickly) under a continuous stream of dried N_2 or argon with no apparent hydration. The approximate hemihydrates and sesquihydrates were prepared as described in ref 7.

Osmometry. The self-association studies were made with a Mechrolab Model 301 osmometer which was thermostated at 37°. The instrument was calibrated with carbon tetrachloride solutions of known concentrations of benzil. Spectrograde carbon tetrachloride (Fisher), used for the osmometer reference solvent and for the chelate solutions, was predried over molecular sieves. The solutions of the anhydrous $Ln(fod)_3$ complexes were prepared in the inert-atmosphere box. The experimental value of $\bar{n}$ for each solution was obtained by dividing the known total concentration of chelate in that solution (assuming only monomers present) by the observed concentration (obtained from the benzil calibration curve).

Nmr Spectroscopy. The methods of solution preparation and spectroscopic measurement have been described previously.[14] Sufficient precautions were taken to ensure the anhydrous nature of the glassware, solvents, and sample preparation.

Computer Programing. All programs for the self-association studies and the solution adduct formation studies were run on an IBM 1800 computer. For the self-association studies, a subroutine was written which calculates the equilibrium concentrations of monomer, dimer, and trimer present in a solution of any total concentration in which competing equilibria (eq 1 and 2) are present. The subroutine requires values of K_2 and K_3 and iterates the concentrations until self-consistency is obtained. The main program calculates the theoretical value of $\bar{n}$ according to eq 9.[40] The theoretical value of $\bar{n}$ is compared with the experimental value for each solution. The values of K_2 and K_3 are iterated until the best least-squares fit of the entire experimental curve is obtained. A grid least-squares search routine[41] is used.

$$\bar{n} = \frac{[\text{monomer}] + 2\,[\text{dimer}] + 3\,[\text{trimer}]}{[\text{monomer}] + [\text{dimer}] + [\text{trimer}]} \qquad (9)$$

A similar strategy was employed for the adduct formation computations. A subroutine calculates the equilibrium concentrations of A, A_2, A_3, AD, and AD_2 when the four equilibria shown in Figure 2 are in competition. The program requires values of K_2, K_3, K^{AD}, and K^{AD_2} (the latter two are defined in eq 4 and 5). The main program calculates the theoretical value of the isotropic hyperfine shift according to eq 10.[3b] For each resonance, the theoretical value of Δ is compared with the experimental value for each solution. The values of K^{AD}, K^{AD_2}, $\Delta_1°$, and $\Delta_2°$ are iterated until the best least-squares fit to the entire experimental curve is obtained.

$$\Delta = \frac{[AD]\Delta_1° + 2\,[AD_2]\Delta_2°}{[D] + [AD] + 2\,[AD_2]} \qquad (10)$$

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Registry No. $Pr(fod)_3{\cdot}xH_2O$, 49792-34-9; $Pr(fod)_3$, 17978-77-7; $Eu(fod)_3{\cdot}xH_2O$, 49792-35-0; $Eu(fod)_3$, 17631-68-4.

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