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Circularly Polarized Emission Studies on the Chiral Nuclear Magnetic Resonance Lanthanide Shift Reagent Tris(3-trifluoroacetyl-*d*-camphorato)europium(III)

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Abstract: Total emission (TE) and circularly polarized emission (CPE) spectra are reported for the optically active rare earth chelate system, tris(3-trifluoroacetyl-*d*-camphorato)europium(III) or Eu(facam)$_3$, in powder form at liquid nitrogen temperature and in a variety of pure solvent and mixed solvent systems at room temperature. The detailed features of the TE and CPE spectra are related to structural characteristics of the chelate system and to the nature of chelate:solvent interactions. The emission anisotropy factor, g_{em}, is found to be an especially sensitive probe for studying chelate:solvent adduct formation and for deducing information about the relative coordinative strengths of various solvent molecules which possess nucleophilic donor moieties.

I. Introduction

The spectroscopic and structural properties of lanthanide β-diketonate complexes have been studied extensively over the past 15 years. Many of the earlier spectroscopic studies were stimulated by the potential of these systems as possible lasing materials in solution media. Weissman[1] first reported that certain rare earth chelates, when irradiated by ultraviolet radiation, emit visible light characteristic of the metal ion. The first systematic studies and interpretation of the mechanism of this process were provided by Crosby and co-workers.[2,3] Since these early investigations, a great many additional studies have been reported on the luminescence properties of rare earth chelates both in solution media and in the solid state.[4]

Hinckley[5] first demonstrated (in 1969) the potential application of paramagnetic tris(β-diketonato)lanthanide(III) complexes for inducing shifts in NMR spectra and, since that time, research activity in this area has grown prodigeously.[6] Lanthanide induced shift reagents, or lanthanide shift reagents (LSR), are now used routinely to enhance spectral resolution and clarification of the NMR spectra obtained for functional organic substrate molecules. Additionally, some success has been achieved in using observed lanthanide induced shifts (LIS) to deduce quantitative or semiquantitative structural information about substrate molecules in solution. Crucial to the eventual widespread acceptance and utility of this latter application of LSRs is an understanding or knowledge of: (1) LSR structure in solution in a variety of solvent systems (neat *and* mixed); (2) the stoichiometric and stereochemical characteristics of LSR:substrate binding as a function of various solution conditions (such as solvent, concentration ratios, temperature, etc.); and (3) the detailed nature of the magnetic interactions between the paramagnetic LSR and diamagnetic substrate molecules.

Little is known about the detailed structural characteristics of LSR complexes in solution. In the solid state these complexes are known to form dimers or oligomers, and it is quite possible that in solution at the concentrations normally used in NMR experiments (on the order of 0.5 M), these dimeric or oligomeric species also predominate or exist in significant amounts. The stoichiometries of various LSR:substrate systems under various conditions are, perhaps, better characterized and understood, but the symmetries and coordination geometries of these complexes in solution have not been well characterized. In using LIS data to deduce structural information, it is usually assumed that the LSR:substrate complexes possess axial symmetry (about an axis which includes the lanthanide metal ion and the donor atom(s) of the substrate molecules(s)). This assumption of axial symmetry simplifies enormously the quantitative treatment of the LIS data and its use in making spectra–structure correlations; however, a static axis of symmetry would in most cases not be expected from what structural information does exist on adducts of lanthanide tris(β-diketonate) compounds.[7-9]

In the present study we examine the total emission (TE) and circularly polarized emission (CPE) spectra of the optically active rare earth chelate system, tris(3-trifluoroacetyl-*d*-camphorato)europium(III), in a variety of solvents. Earlier studies in our laboratory have shown CPE (and TE) to be an extremely sensitive technique for probing the structure and structural changes of chiral lanthanide ion complexes in solution.[10-13] This technique combines the structural and stereochemical sensitivity of chiroptical spectroscopy with the instrumental sensitivity of emission spectroscopy.

Tris(3-trifluoroacetyl-*d*-camphorato)europium(III), or Eu(facam)$_3$, is just one member of a series of chiral lanthanide shift reagents which have been used for direct determination of enantiomeric composition and purity by NMR.[14] In the presence of these optically active chelates, enantiomers (that respond to LSRs) generally have nonequivalent NMR spectra. The crystal structure of the dimethylformamide (DMF) adduct of Pr(facam)$_3$ has just recently been reported.[9] In crystalline form this complex was found to exist as a dimer, (facam)$_3$Pr(DMF)$_3$Pr(facam)$_3$, with the DMF oxygen atoms forming bridges between the two Pr(facam)$_3$ moieties. Each Pr atom is nine-coordinate with the oxygen donor atoms occupying the vertices of a distorted monocapped square anti-

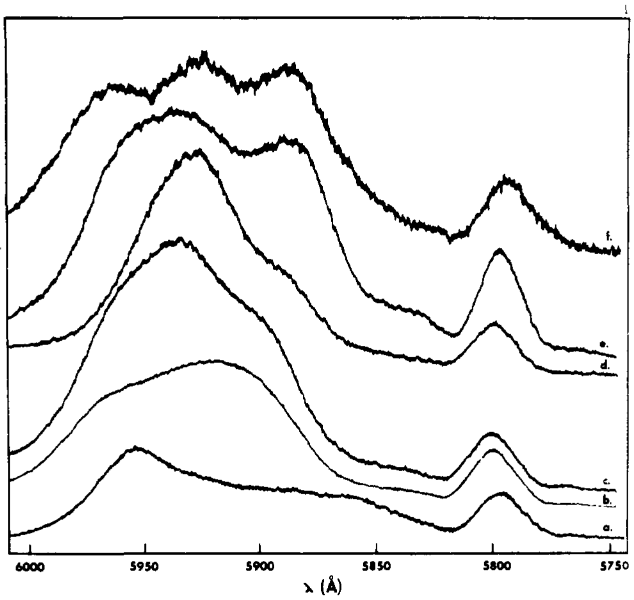


Figure 1. Total emission spectra in the 575-600-nm region for Eu(facam)$_3$ in solvents with nitrogen donor atoms: (a) triethylamine, (b) *n*-propylamine, (c) *n*-butylamine, (d) *tert*-butylamine, (e) piperidine, (f) pyridine. All lines represent exact tracings of recorded spectra.

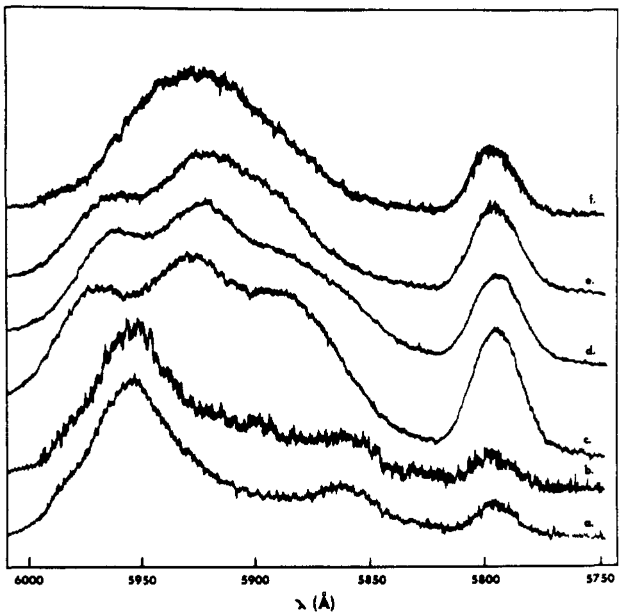
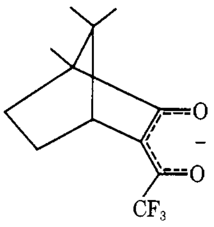


Figure 2. Total emission spectra in the 575-600-nm region for Eu(facam)$_3$ in solvents with oxygen donor atoms: (a) dimethyl ketone (acetone), (b) methyl ethyl ketone, (c) methanol, (d) ethanol, (e) *n*-butyl alcohol, (f) isopropyl alcohol. All lines represent exact tracings of recorded spectra.

prism. This nine-coordination and the accomodation of three DMF molecules into the inner coordination sphere is somewhat surprising in view of the considerable bulk of the facam ligands.



facam

For highly luminescent ions such as Eu^{3+} and Tb^{3+} only small concentrations of chelate are required to produce a measurable spectrum change revealing small structural changes in the chelate system. Recently the total emission spectra of the nonchiral NMR shift reagent tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III) and some of its adducts were reported and deductions were made regarding equilibria and conformations in solution.[15] Furthermore, a number of previous emission studies on europium β-diketonate complexes in solution revealed that total emission intensities and emission band shapes were altered upon formation of adducts with Lewis bases.[16-18] While the intensities, band positions, and band shapes and splittings in total emission spectra are useful in unraveling the structural features of these complex systems, CPE is expected to provide a somewhat more sensitive structure probe.

II. Experimental Section

A. Chelates and Solvents. Tris(3-trfluoroacetyl-*d*-camphorato)europium(III), Eu(facam)$_3$, was purchased from Aldrich and was used without further purification. The emission spectra of Eu(facam)$_3$ in 28 different *neat* solvents were examined in this study. These solvents were: *n*-propylamine, isopropylamine, *n*-butylamine, *sec*-butylamine, *tert*-butylamine, diethylamine, triethylamine, pyridine, piperidine, methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol, *n*-pentyl alcohol, dimethyl ketone (acetone), methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, cyclohexanone, carbon tetrachloride, chloroform, carbon disulfide, dimethyl sulfoxide, and dimethylformamide. Additionally, the emission spectra of Eu(facam)$_3$ were measured in a number of *mixed* solvent systems. Spectroquality grade solvents were used throughout.

Solutions were prepared by dissolving a weighed amount of chelate in ~2.0 ml of solvent directly in the fluorescence cuvette. For all the solution spectra reported in this paper chelate concentrations were in the range 0.005-0.008 M.

B. Emission Measurements. All total emission (TE) and circularly polarized emission (CPE) spectra were measured at 180° ("head-on") using instrumentation constructed in this laboratory.[11,19] TE and CPE were measured at room temperature, with a spectral band-pass of 2 nm (higher resolution spectra were recorded in some instances but these failed to reveal any new features). The excitation source was the 367-nm output of a 1000-W mercury-xeon arc lamp selected by a Spex "minimate" monochromator and appropriate filters. The spectral bandwidth of the exciting light was ~10 nm.

Both TE and CPE are reported in arbitrary units. We denote TE intensity by $I = I_L + I_R$ and CPE intensity by $\Delta I = I_L - I_R$ (where I_L and I_R are respectively the observed intensities of left and right circularly polarized emission). Although I and ΔI were measured in relative intensity units, absolute values of the ratio $\Delta I/(I/2)$ (= g_{em} or emission anisotropy factor)[11] were measured. In the present study it is g_{em} which is, perhaps, the most sensitive diagnostic probe of structural changes within the Eu(facam)$_3$ complex, of solvent perturbations on the Eu^{3+} ion, and of Eu(facam)$_3$:substrate formation.

III. Results

Representative TE spectra in the 575-600-nm region are displayed in Figures 1 and 2 for Eu(facam)$_3$ dissolved in a number of pure solvents. The spectral region 575-600 nm spans the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ transitions of Eu^{3+} in Eu(facam)$_3$. The band structure appearing around 580 nm is assigned to $^5D_0 \rightarrow {}^7F_0$ Eu^{3+} emission, and the emission appearing in the 585-600-nm region is assigned to components of the $^5D_0 \rightarrow {}^7F_1$ Eu^{3+} transition.

CPE from Eu(facam)$_3$ was observed for only 8 of the 28 pure solvents examined in this study. CPE was *never* observed in the region of $^5D_0 \rightarrow {}^7F_0$ Eu^{3+} emission and was observed in the regions of $^5D_0 \rightarrow {}^7F_J$ Eu^{3+} emission (where $J > 2$) only for dimethyl sulfoxide solvent. The strongest TE and CPE intensities were always observed in the $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transition. The emission anisotropy factors, $g_{em} = 2\Delta I/I$, were found to be largest, however, within the $^5D_0 \rightarrow {}^7F_1$ transition. Representative emission anisotropy factors are listed in Table

Table I. Representative Emission Anisotropy Factors Measured for Eu(facam)$_3$/Pure Solvent Systems

Solvent	$^5D_0 \rightarrow {}^7F_1{}^a$	$^5D_0 \rightarrow {}^7F_1{}^b$	$^5D_0 \rightarrow {}^7F_2{}^c$
Me$_2$SO^d	−0.84	−1.98	0.38
DMF^e	−0.58	−1.40	0.11
Triethylamine	−0.26	−0.98	0.11
Piperidine	−0.062	−0.12	0.014
Isopropylamine	--	−0.10	0.022
Dimethyl ketone	−0.54	−1.16	0.090
Methyl ethyl ketone	−0.58	−1.34	0.094
Cyclohexanone	−0.58	−1.64	0.20

[a,b] The CPE spectra in the $^5D_0 \rightarrow {}^7F_1$ region each show two separate bands. The two g_{em} ($^5D_0 \rightarrow {}^7F_1$) values reported here were measured at the λ_{max} of these two bands. [c] The g_{em} ($^5D_0 \rightarrow {}^7F_2$) values reported here were measured at the λ_{max} of the single CPE band appearing in the $^5D_0 \rightarrow {}^7F_2$ region. [d] Me$_2$SO = dimethyl sulfoxide. [e] DMF = dimethylformamide.

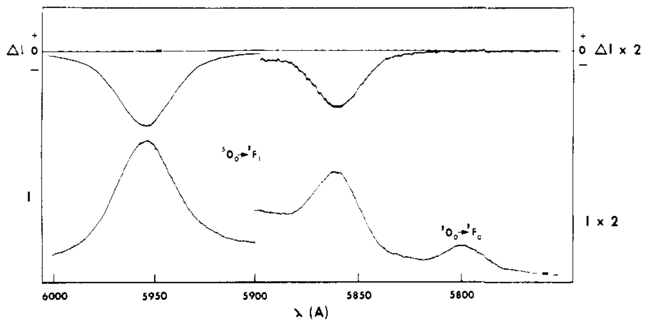


Figure 3. Circularly polarized emission (ΔI) and total emission (I) in the 575-600-nm region for Eu(facam)$_3$/Me$_2$SO. The two bands at ~5955 Å and ~5860 Å are assigned to components of the $^5D_0 \rightarrow {}^7F_1$ transition.

I for measurements made on Eu(facam)$_3$/pure solvent systems. g_{em} is, of course, a function of wavelength and the values reported in Table I were measured at specific wavelengths. For each of the cases represented in Table I, two separate CPE maxima (bands) were observed in the region of $^5D_0 \rightarrow {}^7F_1$ Eu^{3+} emission. The two g_{em} ($^5D_0 \rightarrow {}^7F_1$) values listed for each Eu(facam)$_3$/pure solvent system were measured at the λ_{max} of each of these two bands. Only one well-defined CPE band was observed in the region of $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} emission for each Eu(facam)$_3$/pure solvent system, and the reported g_{em}($^5D_0 \rightarrow {}^7F_2$) values were measured at the λ_{max} of this band. The CPE band shapes and splitting patterns were found to be identical for all the Eu(facam)$_3$/pure solvent systems in which CPE was observed.

Of all the solvents studied, dimethyl sulfoxide (Me$_2$SO) yielded the strongest TE and CPE spectra for Eu(facam)$_3$. CPE and TE spectra for Eu(facam)$_3$/Me$_2$SO are shown in Figures 3-6. In Me$_2$SO, $^5D_0 \rightarrow {}^7F_2$ emission is about two orders of magnitude more intense than any of the other Eu^{3+} transitions. The emission from one component of the $^5D_0 \rightarrow {}^7F_1$ transition (λ_{max} ~5955 Å) is almost completely circularly polarized in Me$_2$SO ($|g_{em}| = 2$ for complete circular polarization).

In order to assess the ability of Me$_2$SO to compete as a ligand with other solvent molecules around Eu(facam)$_3$, increments of Me$_2$SO were added to solutions of the complex in other solvents. The CPE and TE of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transitions were monitored. Data are shown in Table II and in Figure 7. It is seen that g_{em} for one component (λ ~5955 Å) of the $^5D_0 \rightarrow {}^7F_1$ emission increases rapidly then reaches a limiting value (Figure 7). Structural changes in solvated Eu(facam)$_3$ complexes appear to be induced by Me$_2$SO. The fact that different limiting g_{em} values were reached for different solvents (Table II) indicates that the interaction is with solvated complexes.

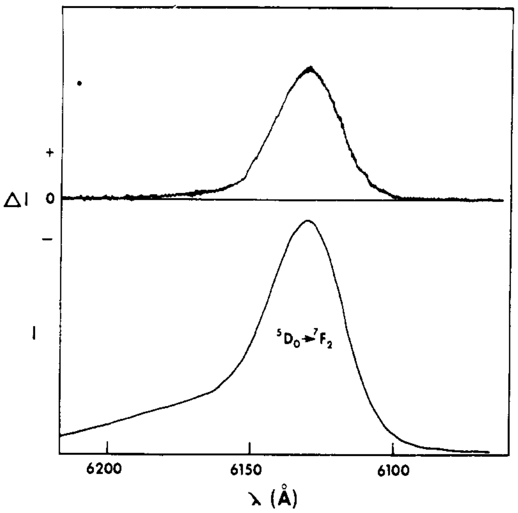


Figure 4. Circularly polarized emission (ΔI) and total emission (I) in the 610-620-nm region for Eu(facam)$_3$/Me$_2$SO.

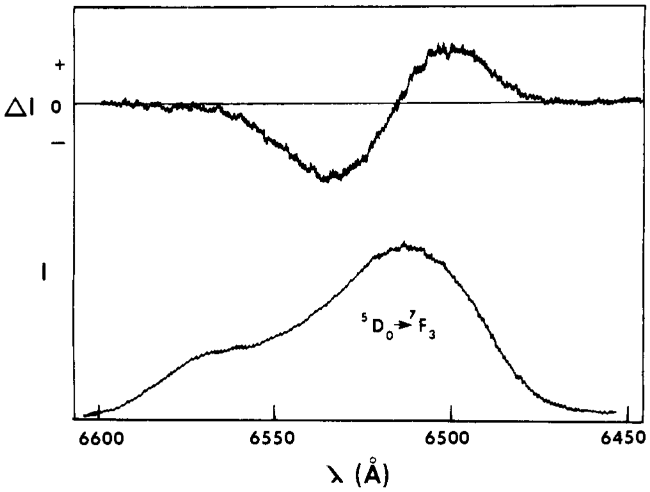


Figure 5. Circularly polarized emission (ΔI) and total emission (I) in the 645-660-nm region for Eu(facam)$_3$/Me$_2$SO.

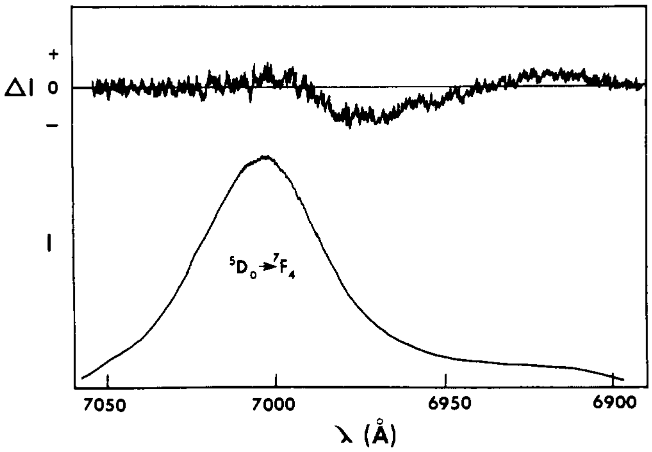


Figure 6. Circularly polarized emission (ΔI) and total emission (I) in the 690-705-nm region for Eu(facam)$_3$/Me$_2$SO.

Finally, the high-resolution emission spectrum ($\Delta\lambda_{em}$ ~ 2 Å) of Eu(facam)$_3$ powder was measured at room temperature

Table II. Emission Anisotropy Factors Measured for Eu(facam)$_3$/Solvent Systems with Me$_2$SO Added

Solvent	$^5D_0 \rightarrow {}^7F_1$ [a]	$^5D_0 \rightarrow {}^7F_1$ [b]	$^5D_0 \rightarrow {}^7F_2$ [c]
n-Propylamine	−0.12	−0.34	0.038
Isopropylamine	−0.38	−1.78	0.17
n-Butylamine	−0.30	−0.50	0.088
sec-Butylamine	−0.76	−1.78	0.16
tert-Butylamine	−0.76	−1.98	0.14
Diethylamine	−0.68	−1.70	0.13
Pyridine	−0.56	−0.70	0.11
Piperidine	−0.60	−1.56	0.072
Methanol	−0.38	−1.04	0.074
Ethanol	−0.54	−1.42	0.068
n-Propyl alcohol	−0.62	−1.56	0.082
isoPropyl alcohol	−0.64	−1.68	0.082
n-Butyl alcohol	−0.78	−1.90	0.20
sec-butyl alcohol	−0.80	−1.98	0.20
tert-Butyl alcohol	−0.84	−1.98	0.22
n-Pentyl alcohol	−0.76	−1.92	0.20
Dimethyl ketone	−0.66	−1.54	0.15
Methyl ethyl ketone	−0.72	−1.74	0.15
Methyl isopropyl ketone	−0.72	−1.78	0.17
Methyl isobutyl ketone	−0.66	−1.64	0.15
Cyclohexanone	−0.72	−1.88	0.20
Carbon tetrachloride	−0.82	−1.98	0.22
Chloroform	−0.80	−1.88	0.19
DMF	−0.64	−1.56	0.14

[a,b,c] See footnotes *a*, *b*, and *c* of Table I.

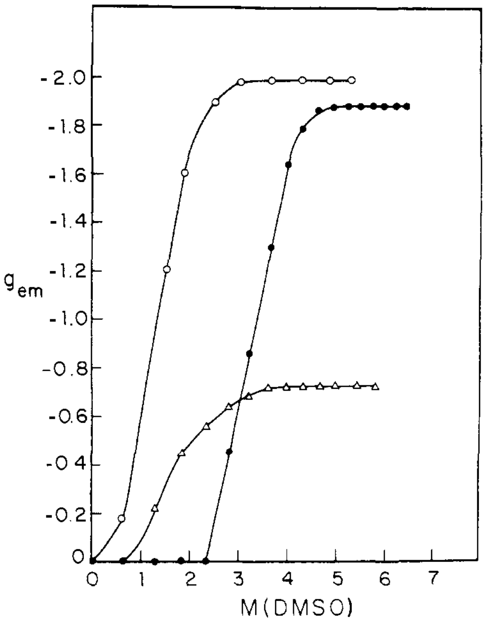


Figure 7. Emission anisotropy factors measured for variable amounts of Me$_2$SO added to three different Eu(facam)$_3$/solvent systems. g_{em} was measured for the $^5D_0 \rightarrow {}^7F_1$ CPE component appearing at ~5955 Å. The solvents are: △ = pyridine; ○ - *tert*-butylamine; ● = chloroform. M = molarity of added Me$_2$SO.

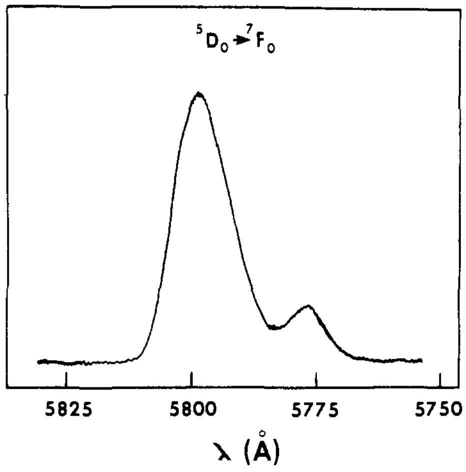


Figure 8. Total emission spectrum of Eu(facam)$_3$ powder in the 575-582-nm region. Spectral band-pass for emission ~2 Å. T = 77 K.

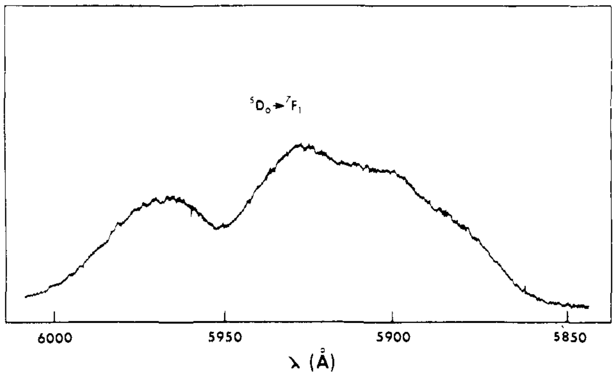


Figure 9. Total emission spectrum of Eu(facam)$_3$ powder in the 585-600-nm region. $\Delta\lambda_{em} \sim 2$ Å, T = 77 K.

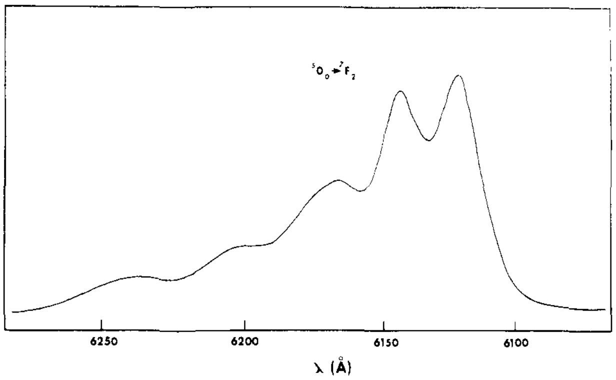


Figure 10. Total emission spectrum of Eu(facam)$_3$ powder in the 610-625-nm region. $\Delta\lambda_{em} \sim 2$ Å, T = 77 K.

and at liquid nitrogen temperature. Considerably more detail in the TE was found in the powder spectra vs. the solution spectra, but no CPE was observed. The TE spectra of the powder obtained at 77 K are shown in Figures 8-10. One feature of the powder spectrum not seen in any of the solution spectra is the apparent splitting of the $^5D_0 \rightarrow {}^7F_0$ band *or* the presence of two bands in the $^5D_0 \rightarrow {}^7F_0$ transition region (see Figure 8).

IV. Discussion

The TE spectra of Figures 1 and 2 and the g_{em} values listed in Table I suggest substantial solvent-induced perturbations on the stereochemical and/or electronic structural features of the Eu(facam)$_3$ system. These perturbations most likely involve direct chelate:solvent interactions resulting in formation of chelate:substrate (solvent molecules) complexes *and* alterations in the stereochemical and configurational dispositions of the facam ligands about the Eu^{3+} ion. The spectral perturbations appear to be much too large to be accounted for in terms of nonspecific or noncoordinative chelate:solvent interactions. The appearance of two and, in some cases, three components in the $^5D_0 \rightarrow {}^7F_1$ emission suggests a low-symmetry crystal-field environment about the Eu^{3+} ions, and the observed variations in the apparent splittings between these components in different solvents suggests that Eu^{3+}-solvent interactions are a major determinant of the effective crystal-field potential acting on the Eu^{3+} chromophore.

The intensity of Eu^{3+} emission is roughly proportional to the coordinative strength of the solvent. Weakly coordinating solvents (such as CCl_4, CS_2, and *tert*-butyl alcohol) give emission spectra which are much weaker than that observed in strongly coordinating solvents (such as Me_2SO and DMF). CPE is extraordinarily sensitive to solvent type and is found to be strong only in a few pure solvents (each of which involves a carbonyl or sulfoxide donor group *except* for triethylamine).

The TE of $Eu(facam)_3$ is most intense in Me_2SO (indicative of strong chelate–solvent interaction), and the largest g_{em} values were observed using this solvent. In most of the neat solvents examined in this study, $Eu(facam)_3$ does not exhibit CPE; however, CPE always appears when Me_2SO is added to $Eu(facam)_3$/other-solvent solutions. This latter observation most likely can be attributed to displacement of solvent molecules from the inner solvation sheath of $Eu(facam)_3$ or from chelate:solvent complexes by Me_2SO molecules. That is, Me_2SO is expected to form stronger adducts with the chelate system than do other solvent molecules and (or) to solvate more strongly. The displacement of other solvent molecules by Me_2SO will then produce a complex species more closely similar to that found in $Eu(facam)_3$/pure Me_2SO solutions and, consequently, will lead to an enhanced CPE. Assuming that displacement of other solvent molecules by Me_2SO is related to the relative chelate:solvent coordinative strengths, the degree of CPE intensity enhancement (or the increase in g_{em} values) upon addition of Me_2SO can be used to qualitatively or semiquantitatively probe the relative coordinative strengths of the various solvents considered in this study. That is, the degree of CPE enhancement upon addition of Me_2SO can be related (inversely) to the coordinative strength of the displaced solvent. This correlation must be considered somewhat crude, of course, since factors other than relative coordinative strength may enter into the competition between Me_2SO and other solvents for binding to the chelate, and the mechanism responsible for CPE in "mixed" solvent systems may be entirely different from that in pure solvents. However, it is unlikely that these other factors will dominate (if indeed they are important at all), and the proposed correlations would appear to have considerable validity. The data shown in Table II may be used to make these correlations.

The g_{em} values associated with the second component of the $^5D_0 \rightarrow {}^7F_1$ emission (~5995 Å) clearly illustrate the competition between Me_2SO and various other solvents for coordinating with, or preferentially solvating, the $Eu(facam)_3$ chelate in "mixed" Me_2SO–"other" solvent systems (see the data of Table II). In pure Me_2SO, the $g_{em}(^5D_0 \rightarrow {}^7F_1)$ value is -1.98 at ~5995 Å. In a 2:1 mixture of *n*-propylamine:Me_2SO, the g_{em} value of this band drops to -0.34. In a 2:1 mixture of isopropylamine:Me_2SO, however, the g_{em} value of this band was found to be -1.78. These observations suggest that whereas isopropylamine is readily displaced by Me_2SO, the *n*-propylamine molecules are less readily displaced. The *n*-propylamine molecules apparently interact more strongly with the chelate than do the isopropylamine molecules and are more difficult to displace. For 2:1 mixtures of *n*-butylamine:Me_sSO, *sec*-butylamine:Me_2SO, and *tert*-butylamine:Me_2SO, the observed g_{em} values for the 5995 Å $^5D_0 \rightarrow {}^7F_1$ component were determined to be -0.50, -1.78, and -1.98, respectively. Again it would appear that whereas the bulkiest of the solvent molecules, *tert*-butylamine, is quite readily displaced by Me_2SO, the least bulky, straight-chain solvent molecule, *n*-butylamine, is somewhat less readily displaced.

Throughout the data shown in Table II there exists a strong and persistent correlation between g_{em} values and the bulkiness or steric characteristics of the hydrocarbon framework attached to solvent molecules with a given type of donor moiety. For solvent molecules of a particular donor atom class, those with the bulkiest groups attached close to the donor moiety yield the largest g_{em} values (that is, g_{em} values close to those observed in pure $Eu(facam)_3/Me_2SO$). This suggests that chelate:solvent coordinative propensity is related to the shape and overall steric nature of the solvent molecules, and that bulky groups near the donor site of these solvent molecules tend to inhibit strong chelate:solvent interactions. Less bulky solvent molecules with less sterically crowded donor moieties appear to be less easily displaced by Me_2SO and, presumably, can coordinate more strongly to the chelate system.

Correlation between solvent molecule bulkiness and chelate:solvent coordinative strength (for solvents of a given donor type) would appear to be quite compatible with the traditional views of how chelate:solvent adducts are formed and what their structural features are. In chelate:substrate formation the nucleophilic strength of the substrate ligand as well as intramolecular steric factors are expected to be of paramount importance in determining chelate:substrate stability and structure. For substrate molecules of like donor moieties, steric factors should provide the differentiating influence—although the nucleophilicity of a given donor moiety may be somewhat dependent upon the nature of substituent groups attached at other sites in the substrate molecule. The chelate system itself in $Eu(facam)_3$ is somewhat bulky due to the rather large camphorato ligands, and this suggests that spatial access to the Eu^{3+} ion in $Eu(facam)_3$ will be somewhat restricted. The crystal structure study[9] on the DMF adduct of $Pr(facam)_3$ clearly showed that the space about the chelate system available for substrate attachment is considerably larger than had been previously assumed.[20] However, DMF is a relatively small ligand. For many of the solvent molecules (potential substrate ligands) examined in the present study, intramolecular steric factors would be expected to make chelate:substrate formation exceedingly difficult and the resulting adducts would be relatively unstable—especially in the presence of an excellent competing substrate ligand like Me_2SO. Given the bulk of the $Eu(facam)_3$ chelate, solvent molecules such as *tert*-butylamine, diethylamine, *sec*-butyl alcohol, *tert*-butyl alcohol, and methyl isopropyl ketone would not be able to gain easy or close access to the Eu^{3+} ion. They would not fit easily into the available "pockets" in the coordination sphere of the chelate.

There is some danger in carrying the correlation of relative g_{em} values, chelate:solvent coordinative strengths, and solvent molecule bulkiness too far; however, certain rather subtle features appear in the data which merit comment. For example, we note that the g_{em} value for the 5995 Å component of the $^5D_0 \rightarrow {}^7F_1$ emission is -1.78 in methyl isopropyl ketone, but is only -1.64 in methyl isobutyl ketone. Both of these solvent molecules contain a $-CH(CH_3)_2$ group; however, the $-CH(CH_3)_2$ group in methyl isopropyl ketone is adjacent to the carbonyl donor moiety whereas in methyl isobutyl ketone this group is removed from the carbonyl donor moiety by a $-CH_2-$ linkage. Although methyl isobutyl ketone is the larger of the two molecules, its bulky group does not sterically crowd the carbonyl moiety and, consequently, it can fit more easily into available "pockets" of the chelate's coordination sphere.

The g_{em} values also permit one to distinguish between solvents whose binding characteristics might not otherwise be expected to vary. *n*-Propylamine ($g_{em} = -0.34$) is shown to bind "tighter" to the $Eu(facam)_3$ than *n*-butylamine ($g_{em} = -0.50$). The series of methanol (-1.04), ethanol (-1.42), *n*-propyl alcohol (-1.56), *n*-butyl alcohol (-1.90), and *n*-pentyl alcohol (-1.92) clearly illustrates that even for nonbranched alkyl groups interaction with the lanthanide chelate is still sterically controlled. It seems clear that the wide range in NMR chemical shifts observed with lanthanide shift reagents is a reflection of (a) how well the substrate is able to interact with the shift chelate, and (b) how well the substrate is able to displace solvent molecules from the coordination sphere of lanthanide shift reagent.

In CCl_4 and $CHCl_3$, TE from Eu(facam)$_3$ was found to be extremely weak and CPE was nonobservable. In 2:1 CCl_4:Me_2SO and $CHCl_3$:ME_2SO mixtures, both the TE and CPE were essentially the same as that observed in pure Me_2SO solvent. These data indicate very weak interactions between the chelate and CCl_4 and $CHCl_3$, which is to be expected given the very weak nucleophilicity of these solvent molecules.

Previous work on NMR shift reagents has been concerned with the possibility of chelate dimers existing in solution. The powder spectrum of Eu(facam)$_3$ in Figure 8 shows the presence of more than one peak in the $^5D_0 \rightarrow {}^7F_0$ emission. Since this band cannot be split by *any* crystal field, it follows that there must be more than one kind of europium ion giving rise to the emission. The more intense of the two peaks occurs at the same wavelength as was found in the solution spectra and is assigned to a monomer species, since no chelate dimers are expected in 10^{-3} M solution samples. The other, blue-shifted peak is assigned to a Eu(facam)$_3$ dimer. The rest of the powder spectra shown in Figures 9 and 10 show several more bands than do the corresponding solution spectra which supports the conclusion that dimeric forms exist in the solid state.

Previous work[14] on Eu^{3+}/L-malic acid complexes in H_2O and D_2O showed that all Eu^{3+} emission features could be explained on the basis of Eu^{3+} free ion $^5D_0 \rightarrow {}^7F_J$ transitions split by low symmetry crystal-field interactions. It seems equally likely that all the features in the solution spectra of Eu(facam)$_3$ presented in this report can be attributed to crystal-field split components of $^5D_0 \rightarrow {}^7F_J$ Eu^{3+} free ion transitions. There was no splitting observed in the $^5D_0 \rightarrow {}^7F_0$ band in any of the solution spectra, even at the highest resolution possible with our instrument. The solvents in which no CPE was observed all showed three peaks in the $^5D_0 \rightarrow {}^7F_1$ region, while only two peaks were seen in the same region in solvents where CPE was observed. This suggests that the symmetries of the chelate: solvent adducts differ in CPE-inducing solvents vs. solvents in which CPE is not observed. This point remains entirely speculative, however, since almost nothing is known about the mechanisms whereby lanthanide f-f transitions acquire optical activity in a chiral ligand environment nor about the influence of specific chelate:solvent interactions on optical activity in metal complexes in general.

The complexity of the systems studied and the lack of well-developed or reliable theoretical models for the spectroscopic properties reported (especially CPE) preclude our offering more than qualitative conclusions regarding the data obtained. While it seems clear that circularly polarized emission and total emission spectra provide very useful probes for examining the structural characteristics of lanthanide shift reagents in solution media, it is also quite apparent that a great deal of additional experimental and theoretical work is required before *quantitative* structural information can be acquired. We are extending our emission studies on lanthanide shift reagents to optically inactive chelate systems dissolved in optically active solvents to probe further the nature of chelate: solvent interactions.

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