Circularly Polarized Emission Studies on Chiral and Achiral Europium(III) β-Diketonate Complexes in an Optically Active Solvent

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Abstract: Circularly polarized emission (CPE) spectra of achiral europium(III) β-diketonate complexes dissolved in an optically active solvent are reported. The solvent-induced CPE intensities and the magnitudes of the observed emission anisotropy factors (g_{cm}) suggest strong chelate:solvent interactions which are highly specific and chiral. CPE spectra for optically active europium(III) β-diketonate complexes dissolved in pure DMSO solvent and in 2:1 α-phenylethylamine (optically active): DMSO solvent mixtures are also reported. The latter data suggest stereospecificity and chiral discrimination in the interactions between the chiral chelate systems and the optically active solvent molecules. This is the first reported study of solvent-induced CPE and the results demonstrate the sensitivity of the technique for monitoring solute-solvent interactions in solution media.

I. Introduction

It is well known that optical activity may be induced in achiral compounds or in racemic mixtures of chiral compounds by dissolution in an optically active solvent. In the former instance optical activity in the achiral solute molecules is generated by chiral perturbations upon the solute chromophoric group by the solvent molecules. The effects of these perturbations may be: (1) to chirally distort the nuclear configuration of the solute molecule making it inherently optically active; (2) to induce optical activity in chromophoric transitions of the solute molecule through direct (chiral) electrostatic interactions between the solute molecules and the electronic charge distributions on the inherently achiral chromophoric group of the solute molecule; or (3) a combination of the above. The induction of optical activity in achiral solute molecules by chiral solvent environments has been the subject of a number of recent experimental and theoretical studies.[1-9]

The optical activity observed for racemic mixtures of chiral solute molecules dissolved in an optically active solvent is presumed to arise from differential *d*(solute)–*d*(solvent) and *l*(solute)–*d*(solvent) interactions (in the case where a dextrorotatory solvent is used) which produce an equilibrium mixture of nonenantiomeric solute–solvent pairs. The net chirality generated in the formation of these nonenantiomeric solute-solvent pairs can lead to observable optical activity in transitions of the solute molecules.[10]

Induced optical activity arising from solute–solvent interactions in solution media is a potentially valuable source of information on the nature of solute–solvent interactions and on the structures of solute–solvent "complexes" formed under various physical and chemical conditions. Unlike solvent-induced frequency shifts and intensity changes in ordinary absorption spectra, induction of optical activity requires that a rather specific set of structural and interactive conditions be met by the solute–solvent pairs (or clusters).

The purpose of the present communication is to report the observation of circularly polarized emission (CPE) from *achiral* europium(III) β-diketonate complexes dissolved in an optically active solvent and the observation of changes in the CPE *chiral* europium(III) β-diketonate complexes dissolved in an optically active solvent. In the present study the optically active solvent was α-phenylethylamine. Lanthanide chelate systems are known to form specific adducts with solvent molecules which have nucleophilic functional moieties and it is presumed in the present case that the induced CPE arises from a specific and direct interaction between an optically active α-phenylethylamine molecule and the Eu^{3+} ion of the chelate.

Andersen and co-workers[11] have previously reported the observation of circular dichroism (CD) in the f–f transitions of tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato)europium(III), or $Eu(fod)_3$, codissolved in CCl_4 (or $CHCl_3$) with optically active compounds containing a nucleophilic functional group. In these cases the induced CD (ICD) is presumed to arise from the formation of chelate: substrate adducts involving the optically active compounds. Dillon and Nakanishi[12] have similarly observed induced CD in the transitions of tris(dipivalomethanato)praseodymium(III), or $Pr(dpm)_3$, when codissolved in achiral solvents with a series of chiral compounds known to form adducts with the chelate. In these studies the induced CD was used to probe the absolute configuration of the substrate molecules involved in adduct formation.

A wide variety of Eu^{3+} β-diketonate complexes are known to emit in solution when irradiated with near ultraviolet light.[13] The intensity of emission (and, to a lesser extent, the frequency maxima of the emission bands) depends quite sensitively on the solvent environment of the chelate systems and on the details of chelate:solvent coordination.[14] Recently, Cotton, Hart, and Moss[15] have reported an emission study of the lanthanide shift reagent, $Eu(dpm)_3$, and several of its adducts in solution at both room temperature and low temperatures. In this laboratory emission titration methods have been employed in studying the formation characteristics and structural features of various $Eu(fod)_3$:substrate adducts in CCl_4 solution.[16] Additionally, total (unpolarized) emission and circularly polarized emission spectra have been measured and reported[17] for the chiral lanthanide shift reagent, tris(3-trifluoroacetyl-*d*-camphorato)europium(III), or $Eu(facam)_3$, in a variety of neat and mixed solvent (achiral) systems. The latter study[17] demonstrated the extreme sensitivity of circularly polarized emission to the nature of chelate:solvent interactions and the structural details of chelate:solvent molecule adducts.

Solvent-induced CPE from achiral luminescent species has not heretofore been reported in the literature. However, owing to the known propensity of lanthanide β-diketonate chelates for interacting strongly with solvent molecules containing a nucleophilic functional group, the induction of CPE in achiral Eu^{3+} chelates by chiral α-phenylethylamine solvent molecules is not a surprising result. However, the magnitudes of the induced CPE effects reported in the present communication are quite remarkable and suggest that the chelate:solvent adducts

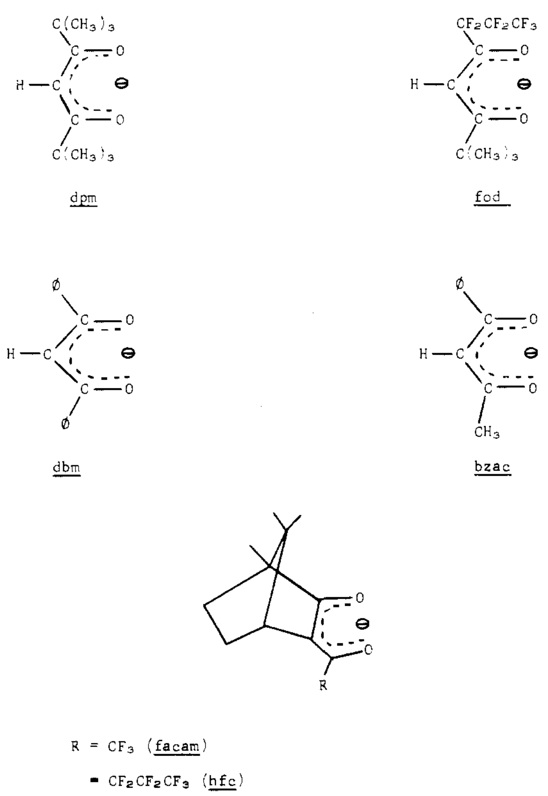

Figure 1. Structural formulas for β-diketonate ligands.

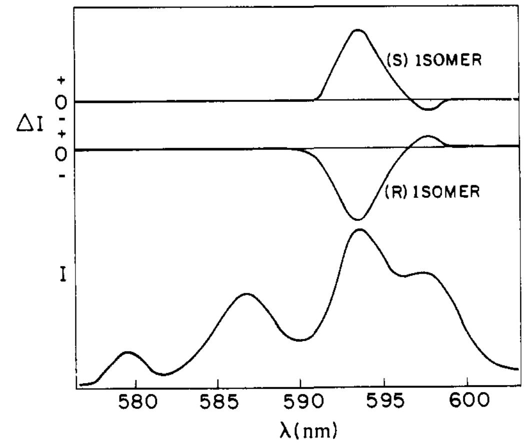

Figure 2. TE(I) and CPE(ΔI) for Eu(dpm)$_3$ in neat α-phenylethylamine solvent in the $^5D_0 \rightarrow {}^7F_0$ and $^7F_1$ regions.

that are formed are highly chiral and involve a very strong coordinative interaction between the achiral chelate system and the chiral molecule(s).

II. Experimental Section

(A) Chelates and Solvents. Tris(3-trifluoroacetyl-*d*-camphorato)europium(III), Eu(facam)$_3$, and tris(heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III), Eu(hfc)$_3$, were purchased from Aldrich and were used without further purification. Tris(dipivalomethanato)europium(III), Eu(dpm)$_3$, and tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro3,5-octanedionato)europium(III), Eu(fod)$_3$, were obtained from Willow Brook Laboratories and were also used without further purification. Tris(1-benzoylmethanato)europium(III), Eu(bzac)$_3$, and tris(dibenzoylmethanato)europium(III), Eu(dbm)$_3$, were prepared according to the method of Charles[18] and subsequently dehydrated by heating at 70 °C in a vacuum desiccator.

Structural formulas for the various ligands employed in this study are depicted in Figure 1.

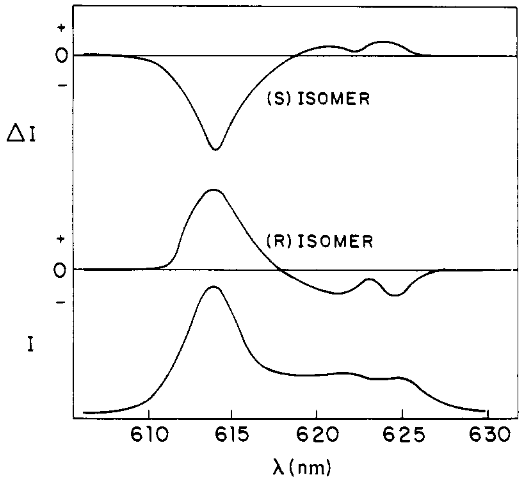

Figure 3. TE(I) and CPE(ΔI) for Eu(dpm)$_3$ in neat α-phenylethylamine solvent in the $^5D_0 \rightarrow {}^7F_2$ region.

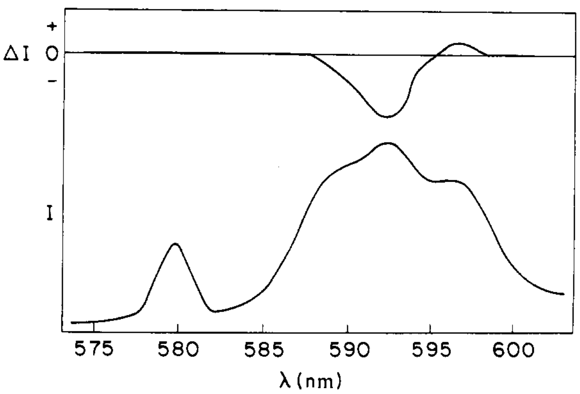

Figure 4. TE(I) and CPE(ΔI) for Eu(fod)$_3$ in neat (R)-α-phenylethylamine solvent in the $^5D_0 \rightarrow {}^7F_0$ and $^7F_1$ regions.

In all experiments involving the achiral chelates, Eu(dpm)$_3$, Eu(fod)$_3$, Eu(bzac)$_3$, and Eu(dbm)$_3$, α-phenylethylamine was employed as a *neat* solvent. Both the R and S isomers of α-phenylethylamine were obtained from Norse Laboratories. In the experiments involving the chiral chelates, Eu(facam)$_3$ and Eu(hfc)$_3$, a mixed solvent of 2:1 α-phenylethylamine:dimethyl sulfoxide (DMSO) composition was used as well as neat α-phenylethylamine. All solutions were prepared by dissolving a weighed amount of chelate in 2.0 ml of α-phenylethylamine directly in the fluorescence cuvette. For the two chiral chelates, 1.0 ml of DMSO was subsequently pipetted into the cell and the spectral measurements were rerun. Chelate concentrations were in the range of 0.007 to 0.009 M in all the experiments performed in this study.

(B) Emission Measurements. All total emission (TE) and circularly polarized emission (CPE) spectra were measured at 0° ("head-on") using instrumentation constructed in this laboratory.[19,20] TE and CPE were measured at room temperature, with a spectral bandpass of 2 nm. The excitation source was the 367-nm output of a 1000-W mercury-xenon 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)[21,22] were measured.

III. Results

All the Eu^{3+} chelates examined in this study showed strong red luminescence, extending from 580 to 730 nm. The emission centered near 580 nm is assigned to the $^5D_0 \rightarrow {}^7F_0$ Eu^{3+} transition, bands in the 585–600-nm region are assigned to

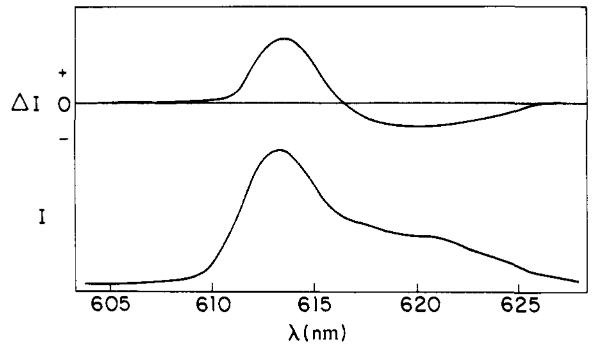

Figure 5. TE(I) and CPE(ΔI) for Eu(fod)$_3$ in neat (R)-α-phenylethylamine solvent in the $^5D_0 \rightarrow {}^7F_2$ region.

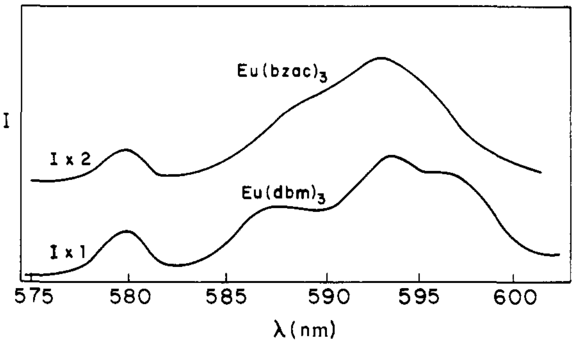

Figure 6. TE(I) for Eu(bzac)$_3$ and Eu(dbm)$_3$ in α-phenylethylamine solvent in the $^5D_0 \rightarrow {}^7F_0$ and $^7F_1$ regions.

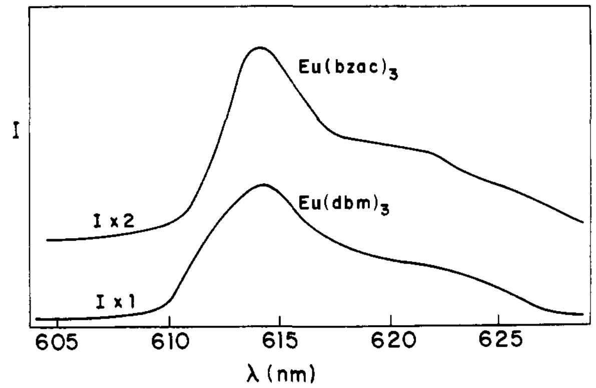

Figure 7. TE(I) for Eu(bzac)$_3$ and Eu(dbm)$_3$ in α-phenylethylamine solvent in the $^5D_0 \rightarrow {}^7F_2$ region.

Table I. Emission Anisotropy Factors for Achiral Chelates in (R)-α-Phenylethylamine

Chelate	Transition[a]	λ, nm	$g_{em} = \Delta I/(I/2)$
Eu(dpm)$_3$	0-1	587	
	0-1	594	−0.50
	0-1	597	0.14
	0-2	614	0.032
	0-2	622	−0.015
	0-2	624	−0.028
Eu(fod)$_3$	0-1	590	−0.032
	0-1	592	−0.086
	0-1	596	0.034
	0-2	602	
	0-2	613	0.0074
	0-2	620	−0.0048
Eu(dbm)$_3$	0-1	587	
	0-1	595	
	0-1	596	−0.024
	0-2	614	
	0-2	622	
Eu(bzac)$_3$	0-1	590	
	0-1	594	0.012
	0-2	613	
	0-2	620	

[a] 0-1 refers to a component of the $^5D_0 \rightarrow {}^7F_1$ Eu^{3+} transition. 0-2 refers to a component of the $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transition.

components of the $^5D_0 \rightarrow {}^7F_1$ Eu^{3+} transition, and emission in the 605–625-nm region is assigned to the $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transition. These assignments agree with those made previously[13,14] for a variety of Eu^{3+} β-diketonate complexes and appear to be secure. The splittings and multiple components observed in the regions of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emission arise from crystal-field induced splittings of the $^7F_1$ and $^7F_2$ free-ion states in the presence of the β-diketonate ligands. The detailed nature of these splittings depends upon the geometries (symmetries) of the tris-chelate species and upon the strength of the Eu^{3+}-ligand interactions. The geometries of Ln^{3+} β-diketonate complexes in solution have not been well-characterized and we do not attempt to deduce such information in the present paper. For this reason we shall avoid assigning specific emission features to transitions connecting specific crystal-field components of the emitting and final states. Instead, we shall label the various emission bands (and their components) according to their free-ion parentage with the tacit understanding that J becomes a "weak" quantum number in the presence of the low-symmetry crystal fields encountered in the chelate systems studied here.

We shall present results only for the emission spectra associated with the $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, and $^7F_2$ Eu^{3+} transitions. The additional emission observed at 645–660 nm ($^5D_0 \rightarrow {}^7F_3$) and at 690–725 nm ($^5D_0 \rightarrow {}^7F_4$) will not be discussed here due to the complex splitting patterns and very weak CPE intensities (low emission anisotropy values) exhibited by these bands.

The TE and induced CPE spectra measured for Eu(dpm)$_3$ in neat (R)- and (S)-α-phenylethylamine solvent are displayed in Figures 2 and 3. The TE and induced CPE spectra measured for Eu(fod)$_3$ in neat (R)-α-phenylethylamine are shown in Figures 4 and 5. The sign patterns of the induced CPE in Eu(dpm)$_3$ and Eu(fod)$_3$ are similar (for a given enantiomeric form of α-phenylethylamine) throughout the spectral region spanned by the Eu^{3+} $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, and no induced CPE is observed for the $^5D_0 \rightarrow {}^7F_0$ transition (~579 nm) in either Eu(dpm)$_3$ or Eu(fod)$_3$. The splitting of the $^5D_0 \rightarrow {}^7F_1$ transition (585–600 nm), as observed in the TE spectra, is somewhat different for these two chelates although the apparent *number* of components (3) is the same in each case.

TE spectra for Eu(dbm)$_3$ and Eu(bzac)$_3$ in neat α-phenylethylamine solvent are shown in Figures 6 and 7. The induced CPE for these systems is very weak and is observable in only one component of the $^5D_0 \rightarrow {}^7F_1$ transition. CPE spectra for these systems are not shown, but the emission anisotropy factors measured for the 594-nm component of the 0-1 transition are given in Table I. Emission anisotropy factors measured at emission extrema for Eu(dpm)$_3$ and Eu(fod)$_3$ are also presented in Table I.

Relative emission intensities (TE) associated with the $^5D_0 \rightarrow {}^7F_2$ transition (including all components) for all the chelates examined in this study are listed in Table II. These data are for measurements done in neat α-phenylethylamine solvent. The order of decreasing Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ emission intensity is seen to be I(fod) > I(dbm) > I(bzac) > I(dpm) among the achiral chelates.

Table II. Relative Intensities (TE) of the $^5D_0 \rightarrow {}^7F_2$ Transition for Chelates Dissolved in α-Phenylethylamine Solvent

Chelate	Relative intensity (TE)
$\mathrm{Eu(fod)_3}$	1.00
$\mathrm{Eu(dbm)_3}$	0.86
$\mathrm{Eu(bzac)_3}$	0.35
$\mathrm{Eu(dpm)_3}$	0.16
$\mathrm{Eu(facam)_3}$	0.022
$\mathrm{Eu(hfc)_3}$	0.020

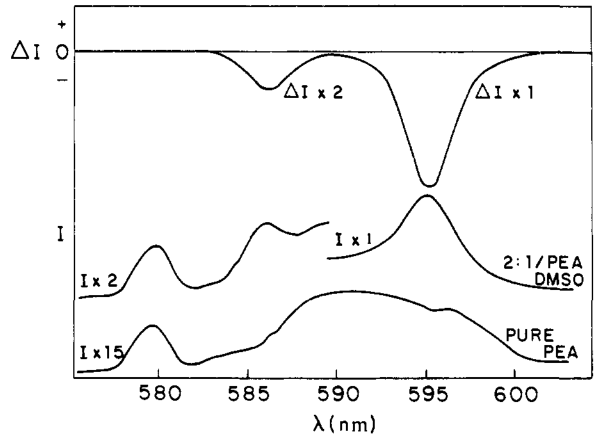

Figure 8. TE(I) and CPE(ΔI) for $\mathrm{Eu(facam)_3}$ in mixed 2:1 (R)-α-phenylethylamine/DMSO solvent in the $^5D_0 \rightarrow {}^7F_0$ and $^7F_1$ regions. TE(I) for $\mathrm{Eu(facam)_3}$ in pure α-phenylethylamine solvent. PEA = α-phenylethylamine.

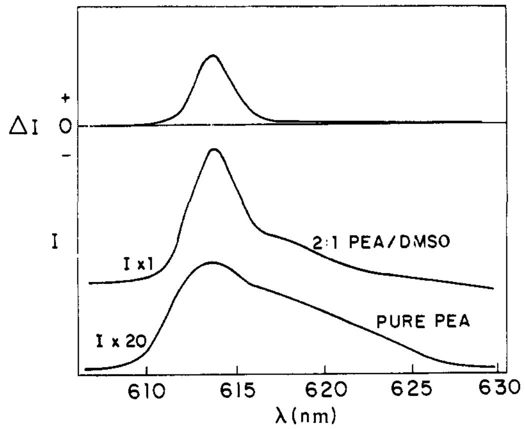

Figure 9. TE(I) and CPE(ΔI) for $\mathrm{Eu(facam)_3}$ in mixed 2:1 (R)-α-phenylethylamine/DMSO solvent in the $^5D_0 \rightarrow {}^7F_2$ region. TE(I) for $\mathrm{Eu(facam)_3}$ in pure α-phenylethylamine solvent. PEA = α-phenylethylamine.

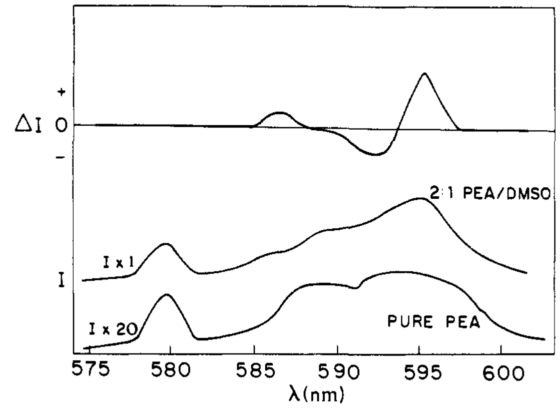

Figure 10. TE(I) and CPE(ΔI) for $\mathrm{Eu(hfc)_3}$ in mixed 2:1 (R)-α-phenylethylamine/DMSO solvent in the $^5D_0 \rightarrow {}^7F_0$ and $^7F_1$ regions. TE(I) for $\mathrm{Eu(hfc)_3}$ in pure α-phenylethylamine solvent. PEA = α-phenylethylamine.

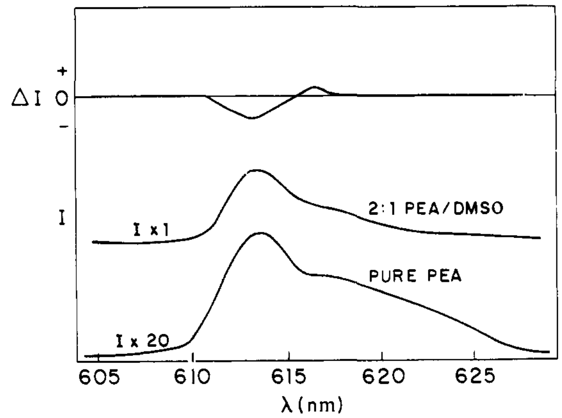

Figure 11. TE(I) and CPE(ΔI) for $\mathrm{Eu(hfc)_3}$ in mixed 2:1 (R)-α-phenylethylamine/DMSO solvent in the $^5D_0 \rightarrow {}^7F_2$ region. TE(I) for $\mathrm{Eu(hfc)_3}$ in pure α-phenylethylamine solvent. PEA = α-phenylethylamine.

No CPE was observed for either of the chiral chelates, $\mathrm{Eu(facam)_3}$ or $\mathrm{Eu(hfc)_3}$, dissolved in neat α-phenylethylamine (R or S). The data in Table II show that the total emission intensity of both $\mathrm{Eu(facam)_3}$ and $\mathrm{Eu(hfc)_3}$ in α-phenylethylamine is much less than that observed for the achiral chelate systems. Previous studies in this laboratory[17] showed that strong CPE could be observed for $\mathrm{Eu(facam)_3}$ if DMSO was added to the solution of chelate plus solvent and that the intensity of the CPE was directly related to the coordinative strength of the solvent relative to that of DMSO. A strongly coordinating solvent tended to quench CPE, whereas a weakly coordinating solvent (such as $\mathrm{CCl_4}$) tended to enhance CPE. TE and CPE spectra measured for $\mathrm{Eu(facam)_3}$ in 2:1 (R)-α-phenylethylamine/DMSO mixed solvent are shown in Figures 8 and 9, and analogous spectra for $\mathrm{Eu(hfc)_3}$ in mixed solvent are presented in Figures 10 and 11. TE spectra for $\mathrm{Eu(facam)_3}$ and $\mathrm{Eu(hfc)_3}$ in neat α-phenylethylamine are also given in Figures 8–11.

The TE and CPE spectra observed for $\mathrm{Eu(facam)_3}$ in the mixed 2:1 α-phenylethylamine/DMSO solvent are qualitatively the same as those reported previously[17] for $\mathrm{Eu(facam)_3}$ in pure DMSO. However, the TE and CPE spectra observed for $\mathrm{Eu(hfc)_3}$ in the mixed vs. pure DMSO solvent are both qualitatively and quantitatively different. The TE and CPE of $\mathrm{Eu(hfc)_3}$ in pure DMSO are shown in Figures 12 and 13. The g_{em} values measured at various emission extrema for $\mathrm{Eu(facam)_3}$ and $\mathrm{Eu(hfc)_3}$ in both pure DMSO and mixed 2:1 α-phenylethylamine/DMSO are listed in Table III. The data of Table III clearly demonstrate chiral discrimination between the two enantiomeric forms of α-phenylethylamine by the chiral chelates.

IV. Discussion

The TE and CPE data reported in this study suggest that these properties are sensitive probes of chelate–solvent interactions and of adduct formation involving tris(β-diketonate)-europium(II) complexes in solution. The magnitude of the induced CPE observed for the $\mathrm{Eu(dpm)_3}$ and $\mathrm{Eu(fod)_3}$ chelates in optically active α-phenylethylamine solvent suggest chelate–solvent interactions which are both strong and geometrically specific. The two most likely mechanisms for the induced CPE in these chelates are: (1) formation of stable chelate:solvent adducts in which the asymmetric center of the solvent molecule is held rigidly and close to the $\mathrm{Eu^{3+}}$ ion (i.e.,

Table III. Emission Anistropy Factors for Chiral Chelates in 2:1 α-Phenylethylamine/DMSO Mixed Solvent and in Pure DMSO

			g_{em}		
Chelate	Transition[a]	λ, nm	R^b isomer	S^c isomer	Pure DMSO
Eu(facam)	0-1	586	−0.60	−0.72	−0.84
	0-1	595	−1.7	−1.8	−1.98
	0-2	613	0.16	0.18	0.38
Eu(hfc)	0-1	586	0.094	0.13	0.32
	0-1	592	−0.078	−0.092	
	0-1	595	0.11	0.14	0.38
	0-2	613	−0.0064	−0.0058	−0.052

[a] 0-1 and 0-2 refer respectively to components of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transitions. [b] 2:1 (*R*)-α-phenylethylamine/DMSO. [c] 2:1 (*S*)-α-phenylethylamine/DMSO.

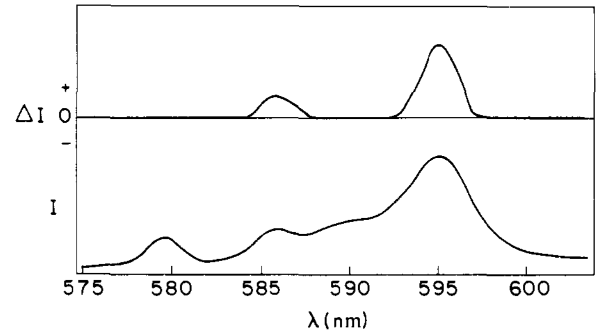

Figure 12. TE(*I*) and CPE(Δ*I*) for $Eu(hfc)_3$ in pure DMSO in the $^5D_0 \rightarrow {}^7F_0$ and $^7F_1$ regions.

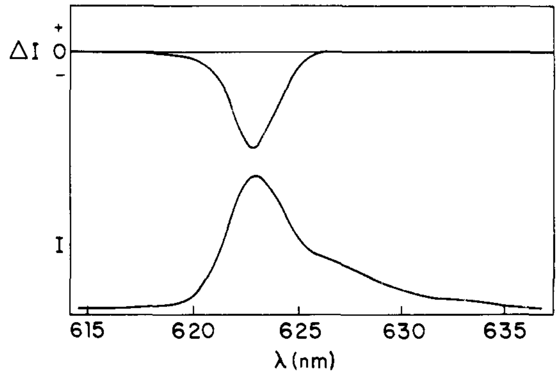

Figure 13. TE(*I*) and CPE(Δ*I*) for $Eu(hfc)_3$ in pure DMSO in the $^5D_0 \rightarrow {}^7F_2$ region.

inside the inner coordination sphere) and the chirality sensed by the chromophoric f electrons originates directly from the asymmetric center of the solvent molecule; (2) solvent-induced resolution of the chelate systems into a nonracemic mixture of enantiomeric configurational isomers. The latter mechanism generates an equilibrium mixture of inherently optically active chelate structures enriched in a specific enantiomeric form. In this case, the f–f transitions acquire optical activity due to the inherent chirality of the chelate structure and the solvent's role is indirect (it serves as a resolving agent). This mechanism is analogous to the Pfeiffer effect observed for racemic mixtures of (usually) labile transition metal coordination compounds.[10]

A third, but less likely, mechanism for the solvent induced CPE observed in $Eu(dpm)_3$ and $Eu(fod)_3$ involves chiral dispersive interactions between the achiral chelates and the optically active molecules in the bulk solvent. Given the magnitude of induced CPE and the known propensity of tris(β-diketonate)lanthanide(III) complexes for interacting strongly and specifically with solvent molecules having a nucleophilic functional group, it seems unlikely that a mechanism based on weak dispersive interactions is dominant.

The very weak induced CPE observed for $Eu(dbm)_3$ and $Eu(bzac)_3$ in optically active α-phenylethylamine suggest that these chelates interact weakly with the solvent molecules and that if significant adduct formation occurs the asymmetric center of the solvent molecule does not assume a rigid or close position with respect to the Eu^{3+} chromophoric site.

It is not clear why DMSO is required to generate an observable CPE in the inherently chiral chelates, $Eu(facam)_3$ and $Eu(hfc)_3$. In pure DMSO, the observed g_{em} (595 nm) value for $Eu(facam)_3$ approaches the limiting value of 2 (complete circular polarization). It is expected that DMSO will interact with (and solvate or bind to) the chelate more strongly than α-phenylethylamine, and in the mixed 2:1 α-phenylethylamine/DMSO solvent it is expected that DMSO will entirely occupy the available solvation sites within the inner coordination sphere of the chelate. However, the data of Table III demonstrate that the chirality of the α-phenylethylamine solvent molecules *does* influence the CPE of the Eu^{3+} f–f transitions and that there are apparent differences between chelate (*R*)-α-phenylethylamine and chelate (*S*)-α-phenylethylamine interactions. The mechanism most likely operative in this case involves a solvent-induced change in the equilibrium mixture of tris-chelate configurational (optical) isomers. The chirality due to the asymmetric sites on the facam and hfc ligands cannot be altered by the presence of an optically active solvent. However, chirality due to configurational (optical) isomerism within the labile tris-chelate system *can* be influenced by the chirality of the solvent.

We note that the signs of the respective CPE bands observed for $Eu(facam)_3$ and $Eu(hfc)_3$ in the $^5D_0 \rightarrow {}^7F_1$ and $^7F_2$ transitions are opposite (see Table III). Since the facam and hfc ligands each possess the same absolute configuration at the asymmetric carbon atom of the camphorato moiety, this result leads to the rather remarkable conclusion that the dominant configurational (optical) isomeric forms perferred by the two tris chelates are different. That is, the configurational dissymmetry generated by the relative dispositions of the three chelate rings about the metal ion is different in $Eu(facam)_3$ and $Eu(hfc)_3$. This observation also suggests that the optical activity of the f–f transitions in these chelate systems is determined primarily by configurational dissymmetry rather than by so-called vicinal interactions between asymmetric centers on the ligand and the chromophoric electrons of the metal ion.

The relatively low symmetries of the systems examined in this study lead to extensive "crystal-field" splittings of the $^5D_0 \rightarrow {}^7F_1$ and $^7F_2$ Eu^{3+} free-ion transitions. However, in no instance is the $^5D_0 \rightarrow {}^7F_1$ transition split into more than three components and in each case the $^5D_0 \rightarrow {}^7F_0$ transition yields a single, symmetrical emission band. These latter observations strongly suggest the absence of dimeric or oligomeric chelate species in solution at the low chelate concentrations used here (0.007 to 0.009 M).

A detailed analysis of the CPE results reported in this study must await further theoretical development of f-f optical activity in dissymmetric lanthanide complexes. Almost nothing is known about the mechanisms whereby lanthanide ion 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. It seems clear that both TE and CPE are very sensitive probes for investigating chelate-solvent interactions and that they can provide a great deal of qualitative (and, in some cases, semiquantitative) structural information not readily obtainable by other techniques. However, the development of detailed and specific spectra-structure relationships must await further experimental and theoretical study.

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Proton Magnetic Resonance Study of Divalent Metal Ions Binding to Adenosine 5′-Triphosphate

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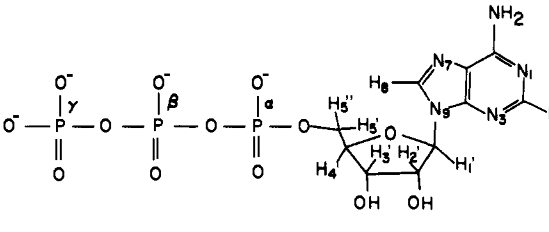
Abstract: The monometallic Co^{2+}, Ni^{2+}, Mg^{2+}, and Ca^{2+} complexes with adenosine 5′-triphosphate have been investigated by proton magnetic resonance. The experimental pD values were adjusted so as to have the adenine ring either protonated or unprotonated, and the phosphate chain triple or fully ionized. The effect of ring protonation or the secondary phosphate hydrogen ionization on the metal-ring and metal-chain interactions has been studied. The formation of a bis M^{2+}-ATP complex was established. The equilibria equations involving the formation of 1:1 and 1:2 metal-ligand complexes and the nucleotide molecules self-association are discussed, and a method for calculating the formation constants from the NMR shifts is presented. A model for the bis complex, compatible with the experimental results, is proposed.

Nuclear magnetic resonance has been extensively used in the study of adenine nucleotides and their metal complexes.[2] Concerning the complexes of adenosine 5′-triphosphate (1) and divalent metal ions, the main results may be summarized as follows. The paramagnetic ions (Mn^{2+}, Co^{2+}, Ni^{2+}) bind simultaneously to the three (α, β, γ) phosphates and to the adenine ring.[3-8] The binding to the ring is not direct but *via* a water molecule which is coordinated to the metal ion and hydrogen bonded to N_7 of the adenine ring.[9,10] In addition, the metal complex contains another two water molecules in the inner sphere of coordination.[9-11] A more recent ^{13}C NMR study of the Mn^{2+} complex of ATP indicated however a direct binding of the manganese ion to the N_7 ring nitrogen.[13] At high total ATP concentration it was found that 1:2 metal-ligand complexes are formed.[12,14] The diamagnetic ions (Mg^{2+}, Ca^{2+}) were found not to interact with the adenine ring[6,15] and their binding is to the β and γ phosphates[6] or to the β phosphate alone.[16]



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ATP has two major ionization sites: the phosphate moiety and the adenine ring. The three primary phosphate hydrogens were estimated to have $pK \lesssim 2$,[17] and the final hydrogen was found to have $pK \sim 7$.[18-23] Hence the major part of ATP will be fully ionized (ATP^{4-}) at $pH \gtrsim 8$. At a lower pH both ATP^{4-} and ATP^{3-} will be present, and at $pH \lesssim 5$ the major part will be ATP^{3-}. ^{31}P NMR studies[3,6,16] revealed almost no difference in the metal-phosphate interaction in the pH range 5.5-8.5. In the present work we show that the same is true also regarding the metal-ring interaction. This metal-ring interaction, however, may be expected to depend on the ionization