Stereoselectivity observed Upon Adduct Formation of Tris(3-trifluoroacetyl-D-camphorato)- and Tris-(3-heptafluorobutyryl-D-camphorato)-europium(III) * with Formamide and Acetamide Derivatives

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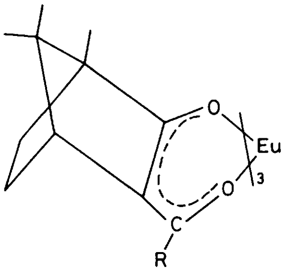
The adduct formation which takes place when the title compounds bind *N*-alkyl and *NN*-dialkyl derivatives of formamide and acetamide has been studied by means of circularly polarized luminescence (c.p.l.) spectroscopy. It was determined from examinations of emission enhancements that at least two molecules of substrate are bound by the chelates, but the luminescence titrations were too indeterminate to permit a calculation of association constants. No optical activity is observed within the emission of the free chelates, but strong c.p.l. could be detected if the 1 : 2 chelate : substrate adduct could be fully formed. This chirality was found to be most developed in neat substrate solvent, and takes place even though the substrates are not inherently chiral. It is concluded that the formation of the adduct complexes is accompanied by a stereoselective rearrangement of the camphorato-ligands, thus yielding a partial resolution of the labile Eu^{III} complexes.

The existence of stereoselectivity in the transition metal complexes of chiral β-diketone ligands has become well established, and studies of these effects can provide important information about the nature of interligand interactions in metal chelate systems. Most of these works have involved complexes in which the β-diketone ligand contains the camphorato-group (see below).



The most commonly studied systems are those of (+)-(3-hydroxymethylene)camphorate (where R = H, and abbreviated as hmc) and (+)-3-acetylcamphorate (R = CH_3, and abbreviated as atc). A racemic mixture of tris octahedral complex would contain four possible diastereomers: Δ-*cis* and Λ-*cis* (the *fac* isomers), as well as Δ-*trans* and Λ-*trans* (the *mer* isomers). The determination of the relative abundances of these isomers has proven to be a fertile ground for research.

Early work established that if the kinetically inert complexes of Co^{III} were prepared using either (+)-(*R*,*R*)-hmc or (+)-(*R*,*R*)-atc as starting materials, then the resulting product mixture contained the Λ-*trans* isomer in the greatest excess.[1,2] It was subsequently shown through *X*-ray diffraction studies that the absolute configuration of [Cr{(+)atc}$_3$] was indeed Λ-*trans*.[3] Later studies determined the relative abundances of the four diastereomers in the racemic preparations of [Co{(+)atc}$_3$],[4,5] [Cr{(+)atc}$_3$],[4] and [Ru{(+)atc}$_3$],[6] and found that while the Λ-isomer was present in the largest excess, considerable amounts of the Δ-isomer were also produced. One general conclusion associated with all the studies was that the existence of the two *trans* isomers was greatly favoured over the two *cis* isomers.

In our laboratory, we have been investigating the stereoselectivity associated with the lanthanide complexes of chiral β-diketones. Recently, it was demonstrated that the optical activity of labile [Tb{(+)atc}$_3$] was profoundly affected by the solvent the material was dissolved in.[7] The lanthanide chelates differ from the transition metal analogues somewhat in that the lanthanide complexes can expand their co-ordination number through adduct formation, and it was found that the steric nature of the substrate in the [Tb{(+)atc}$_3$] adduct determined the particular diastereoisomer which dominated *even though the substrates were not themselves chiral.*[7] This behaviour is quite analogous to work carried out on labile [V{(+)atc}$_3$] complexes in which the Δ-*trans* : Λ-*trans* ratio (as determined by n.m.r. methods) could be varied from 0.31 to 0.97 depending on the nature of the solvent used.[8]

Europium(III) chelates of fluorinated camphorato β-diketones have been used in the n.m.r. determination of enantiomeric purity,[9,10] but no attention has been paid to the effects which stereoselectivity might have on such measurements. Such effects have been shown to exist: [Eu(tfac)$_3$] [tfac = (+)-3-trifluoroacetylcamphorate, R = CF_3] shows no optical activity in non-co-ordinating solvents, but shows extremely intense optical activity when dissolved in dimethyl sulphoxide solvent.[11] Similar results were reported for [Eu(hfbc)$_3$] in dimethyl sulphoxide [hfbc = (+)-3-heptafluorobutyrylcamphorate, R = C_3F_7], but the sign of the optical activity was found to be opposite to that of [Eu(tfac)$_3$] even though the absolute configuration of both ligands was identical.[12] The synthesis of a series of mixed-ligand Eu^{III} chelates containing both chiral and achiral β-diketone ligands subsequently showed that this stereoselectivity is a consequence of adduct formation with the substrate molecules.[13]

In this paper, we detail the stereoselective effects which accompany the binding of a series of formamide and acetamide derivatives by [Eu(tfac)$_3$] and [Eu(hfbc)$_3$]. In many cases, adduct formation with these substrates leads to strong optical activity, with this chirality clearly being a stereoselective effect. The optical activity was measured *via* circularly polarized luminescence (c.p.l.) spectroscopy rather than the more conventional method of circular dichroism (c.d.), since the *f*–*f* absorptions of the lanthanide complexes are too weak to permit c.d. work except at high concentrations. Recent correlations relating the absolute configuration of tri-

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* The ligands are derivatives of bornan-2-one, *not* of camphoric acid.

gonal Eu^{III} complexes with the signs of c.d. and c.p.l. peaks permitted the prediction of which particular isomer predominated in the [Eu(tfac)$_3$] and [Eu(hfbc)$_3$] adduct systems.

Experimental

The compounds [Eu(tfac)$_3$] and [Eu(hfbc)$_3$] were purchased from Aldrich, and were dried for prolonged periods of time in a vacuum desiccator. Spectroquality $CHCl_3$ (dried over molecular sieves) was used as the solvent in most studies, except in the instances where the neat substrate itself was used as the solvent. Formamide, *N*-methylformamide (mf), *NN*-dimethylformamide (dmf), *NN*-diethylformamide (def), *NN*-dibutylformamide (dbf), acetamide, *N*-methylacetamide (ma), *NN*-dimethylacetamide (dma), and *N*-diethylacetamide (dea) were all obtained from Aldrich and were used as received. Each substrate was dried before use, as excessive water content in the solutions led to somewhat irreproducible results.

Luminescence titrations were carried out for each of the Eu^{III} chelates with each of the substrates. Stock solutions of [Eu(tfac)$_3$] and [Eu(hfbc)$_3$] were prepared to be 5 mmol dm^{-3}, and titrated with microlitre amounts of substrate solutions (whose concentrations ranged from 0.1 to 0.5 mol dm^{-3}, depending on the desired ratio of substrate : chelate) which were added to 3 cm^3 of the Eu^{III} solution in the fluorescence cuvette. The total luminiscence (t.l.) and c.p.l. spectra of the $^5D_0 \rightarrow {}^7F_0$ (580), $^5D_0 \rightarrow {}^7F_1$ (595), and $^5D_0 \rightarrow {}^7F_2$ (615 nm) was followed after each addition. Reproducibility in the Eu^{III} t.l. intensities was monitored by periodically recording the emission intensity of a piece of uranium glass.

All luminescence measurements were obtained on a medium-resolution c.p.l. spectrometer constructed in our laboratory, and whose basic operation has been described.[14] An excitation wavelength of 365 nm was used to excite the compounds (obtained by passing the output of a 200 W mercury-xenon arc lamp through a 0.1 m grating monochromator and suitable glass filters), with a width of 16 nm being used. As before, the emission was collected at 180° to the exciting light (to eliminate any possible linear polarization effects) and passed through a concentrated solution of $NaNO_2$ to remove any unabsorbed exciting light. The emission was analyzed by a 0.5 m grating monochromator at 1 nm bandpass, and detected by an EMI 9798B photomultiplier tube (S-20 response). No attempt was made to correct the spectra for system response since the wavelength regions scanned were quite narrow and any correction would be minor at best. The t.l. and c.p.l. signals were recorded simultaneously to ensure that the ratio of these quantities would account for any instrumental fluctuations.

Results and Discussion

Much work has centred on the u.v.-excited photoluminescence of Eu^{III} β-diketone complexes, and these numerous studies have been primarily aimed at understanding the photophysics of the emission process. It is known that the sharp-line emission observed in the luminescence spectra of the Eu^{III} chelates is dependent on the geometry of the complex [15] and on the presence of additional substrates bound in the complex inner-sphere.[16-18] In fluid solution at room temperature, all emission originates solely from the $^5D_0$ excited state. Transitions to the spin-orbit split components of the ^7F_J ground state occur at energy values close to those predicted for the free ion [19] due to the low covalency of the lanthanide–oxygen bonds in the complexes. The total luminescence (t.l.) intensity of the $^5D_0 \rightarrow {}^7F_0$ transition at 580 nm is approximately half the intensity of the $^5D_0 \rightarrow {}^7F_1$ band at 590 nm, while the t.l. intensity of the $^5D_0 \rightarrow {}^7F_2$ band at 615 nm is typically an order of magnitude more intense than the $^5D_0 \rightarrow {}^7F_1$ band. The bands corresponding to the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions are found at 645 and 690 nm respectively, but the intensities of these are extremely weak (usually an order of magnitude smaller than the $^5D_0 \rightarrow {}^7F_1$ band system).

The binding of a substrate by a Eu^{III} β-diketone chelate usually results in an enhancement of the t.l. intensities of all bands. Such increases have been attributed to protection of the metal ion from solvent quenching (energy is lost to high vibrational levels of the solvent) *via* formation of an insulating sheath,[18] and is a feature characteristic of adduct formation.[20-23] In general, the t.l. intensity increases from an extremely low value associated with free [Eu(tfac)$_3$] or [Eu(hfbc)$_3$] complexes to some limiting value, which is taken to be the emission intensity of the fully formed adduct. Since the intermediate points represent situations where both chelate and chelate–substrate adduct co-exist, then it is clear that the intensity values obtained between the extremes may be related to the association constant of the adduct complex.

Addition of either formamide or acetamide to a $CHCl_3$ solution of either [Eu(tfac)$_3$] or [Eu(hfbc)$_3$] resulted in absolutely no enhancement of the Eu^{III} t.l. intensity, and it was also found that neither chelate would even dissolve in neat formamide solvent. We conclude from these observations that no adduct formation takes place between these substrates and the two chelates of the present study. The chelates were found to be very slightly soluble in *N*-methylformamide, and it was found that the t.l. intensity (usually measured within the $^5D_0 \rightarrow {}^7F_2$ band) increased by approximately a factor of two upon dissolution in the neat solvent. Addition of *N*-methylacetamide to a $CHCl_3$ solution of [Eu(tfac)$_3$] also resulted in a modest enhancement, while no enhancement at all could be observed with [Eu(hfbc)$_3$]. In both cases, quite large amounts of solid substrate were added to the chelate solution in the cuvette, and these observations indicate that adduct formation with the *N*-methyl substrates is still not a very favourable process.

Quite different behaviour was noted when the *NN*-dialkyl substrates were added to the chelate solutions. Here, luminescence enhancements up to an order of magnitude were noted, although the actual amount of enhancement was found to depend critically on the nature of the solvent. It is possible to carry out a luminescence titration by adding microlitre amounts of substrate to a $CHCl_3$ solution of the chelate in the fluorescence cuvette, and it was found that the shapes of these titration curves were approximately the same for the formamide and acetamide substrates used in the current work. In Figure 1, the t.l. titration of [Eu(tfac)$_3$] with dimethyl-, diethyl-, and dibutyl-formamide substrates is shown, and it may be seen that the curves appear to contain a rapid initial rise which is followed by a gradual rise in the t.l. intensity with added substrate.

It did not prove possible to use the t.l. titrations of the present work to calculate the formation constant associated with the adduct-forming processes, as the titrations were never observed to level off in the normal manner. The t.l. intensity continued to rise and did not level off even at 30% dialkylformamide (or acetamide) solvent, and the maximum t.l. values were obtained in the neat solvents themselves. While the titration curves do indicate that addition of the first molecule of substrate, S [equation (1); L = achiral β-diketone], is fairly efficient, addition of the second (or more) substrate molecule [equation (2)] is a much more difficult process.

$$[\mathrm{Eu(L)_3}] + \mathrm{S} \rightleftharpoons [\mathrm{Eu(L)_3}]\cdot\mathrm{S} \qquad (1)$$

$$[\mathrm{Eu(L)_3}]\cdot\mathrm{S} + \mathrm{S} \rightleftharpoons [\mathrm{Eu(L)_3}]\cdot 2\mathrm{S} \qquad (2)$$

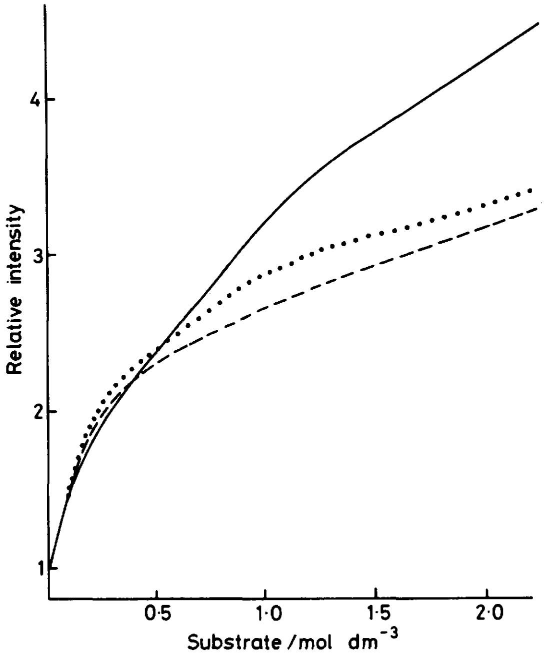

Figure 1. Luminescence titrations of [Eu(tfac)$_3$] with dmf (——), def (· · · ·), and dbf (– – – –). The intensity scale has been normalized by dividing all measured t.l. intensities by the t.l. intensities of uncomplexed chelate. The [Eu(tfac)$_3$] concentration used in these titrations was 5.8 mmol dm^{-3}

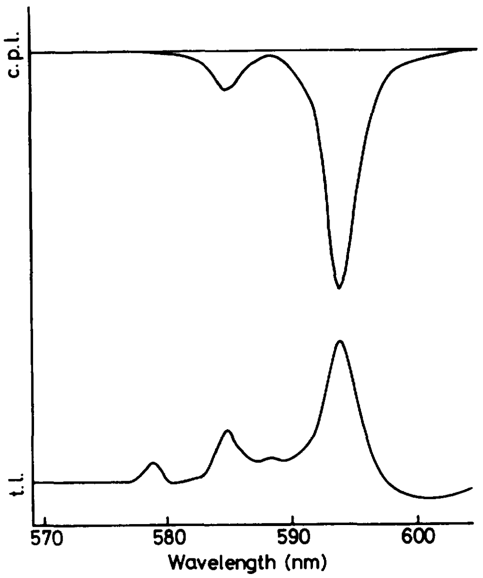

Figure 2. C.p.l. (upper) and t.l. (lower) spectra obtained within the $^5D_0\rightarrow{}^7F_0,{}^7F_1$ band systems of [Eu(tfac)$_3$]–def. The spectra were obtained at a concentration of 7.3 mmol dm^{-3} in neat def solvent, and are shown in arbitrary units

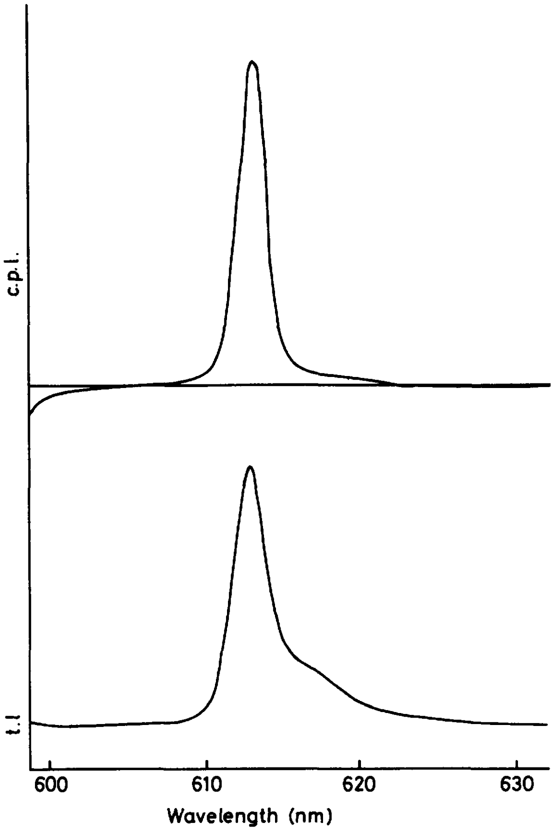

Figure 3. C.p.l. (upper) and t.l. (lower) spectra obtained within the $^5D_0\rightarrow{}^7F_2$ transition of [Eu(tfac)$_3$]–def

Dissolution of either [Eu(tfac)$_3$] or [Eu(hfbc)$_3$] into the neat dialkyl-formamide or -acetamide solvents invariably resulted in the observation of strong optical activity in the Eu^{III} emission bands. The lineshapes of the c.p.l. were essentially identical in all cases, and greatly resembled those reported earlier for [Eu(tfac)$_3$] dissolved in neat dimethyl sulphoxide.[11] In addition, the signs and lineshapes were also the same for the [Eu(hfbc)$_3$] chelate, and this behaviour may be contrasted to the sign inversion found when [Eu(hfbc)$_3$] was dissolved in dimethyl sulphoxide.[12] The t.l. and c.p.l. spectra were found to be more intense for [Eu(tfac)$_3$]–def, and representative spectra for the $^5D_0\rightarrow{}^7F_J$ ($J = 0$—4) are found in Figures 2—5. The lineshapes obtained with the [Eu(hfbc)$_3$] chelates are not identical to those of Figures 2—5, but are very closely related.

In pure CHCl$_3$ solvent, no c.p.l. is observed for either [Eu(tfac)$_3$] or [Eu(hfbc)$_3$]. This result is not surprising when one considers that in a racemic mixture of a highly labile chelate, all four diastereomers would be present and the c.p.l. of these would approximately cancel. This has been shown for the analogous transition metal complexes, where the c.d. of the two *cis* isomers is essentially equal in magnitude but opposite in sign to that of the two *trans* isomers.[4] While for the transition metal complexes, one finds an excess of the Λ-isomers [when starting with (+)-tfac or (+)-hfbc] in the free chelates,[4–6] the larger ionic radius of the lanthanide ions apparently allows the three β-diketone ligands to co-exist without significant interaction.

During the course of the luminescence titrations c.p.l. appears after the addition of a large excess of substrate, and none is observed in the initial portion of the titration where the sharpest rise in t.l. intensity is noted. These observations suggest that formation of the 1 : 2 chelate : substrate adduct is required for the observation of c.p.l., and the existence of such stoicheiometry for Eu^{III} β-diketonate complexes of dmf has been shown.[24] It is quite possible that expansion of the Eu^{III} co-ordination sphere causes crowding of the bulky camphorato ligands, resulting in the stabilization of the isomer which minimizes the interligand repulsion. Since the ligands are inherently chiral, this perturbation will yield a partial

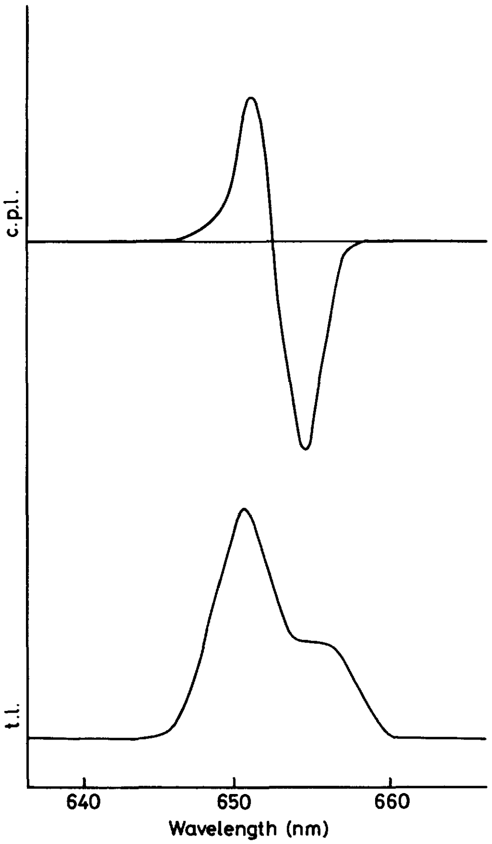

Figure 4. C.p.l. (upper) and t.l. (lower) spectra obtained within the ${}^5D_0\rightarrow{}^7F_3$ transition of [Eu(tfac)$_3$]–def

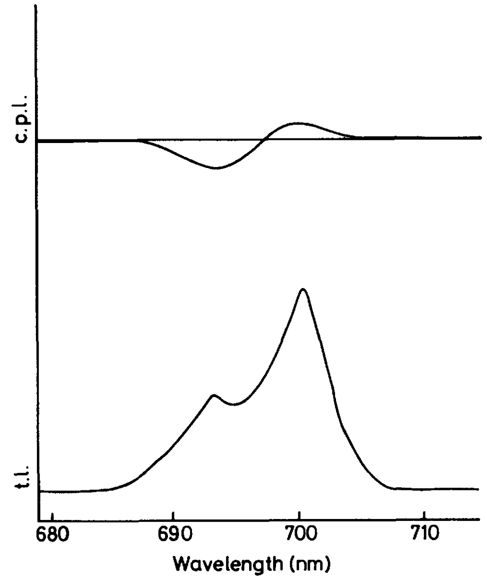

Figure 5. C.p.l. (upper) and t.l. (lower) spectra obtained within the ${}^5D_0\rightarrow{}^7F_4$ transition of [Eu(tfac)$_3$]–def

Table 1. Luminescence dissymmetry factors observed upon dissolution of [Eu(tfac)$_3$] in neat formamide and acetamide solvents

	${}^5D_0\rightarrow{}^7F_1$		
Solvent	Band A [a]	Band B [b]	${}^5D_0\rightarrow{}^7F_2$
Formamide	*c*	*c*	*c*
mf	−0.413	−1.023	+0.0804
dmf	−0.510	−1.175	+0.0950
def	−0.741	−1.697	+0.041
dbf	−0.459	−1.082	+0.0680
Acetamide [d]	*c*	*c*	*c*
ma [d]	−0.404	−0.938	+0.0452
dma	−0.588	−1.360	+0.115
dea	−0.662	−1.511	+0.119

[a] Band A is located at 587 nm. [b] Band B is located at 596 nm. [c] C.p.l. was not observed for this substrate. [d] These dissymmetry factors are those obtained by addition of large excesses of solid substrate to a CHCl$_3$ solution of the chelate, and are limiting values.

Table 2. Luminescence dissymmetry factors observed upon dissolution of [Eu(hfbc)$_3$] in neat formamide and acetamide solvents

	${}^5D_0\rightarrow{}^7F_1$		
Solvent	Band A [a]	Band B [b]	${}^5D_0\rightarrow{}^7F_2$
Formamide	*c*	*c*	*c*
mf	−0.102	−0.111	+0.006 75
dmf	−0.123	−0.135	+0.007 33
def	−0.148	−0.161	+0.008 72
dbf	−0.0529	−0.0601	+0.003 38
Acetamide [d]	*c*	*c*	*c*
ma [d]	*c*	*c*	*c*
dma	−0.0995	−0.108	+0.007 99
dea	−0.0850	−0.0921	+0.007 72

For definition of footnotes see Table 1.

resolution of the complex and result in the observation of optical activity.

As in the case of most luminescence measurements, the t.l. and c.p.l. observables are recorded in arbitrary units. If we define I [equation (3)] as the t.l. intensity, and ΔI [equation (4)]

$$I = \tfrac{1}{2}(I_{\mathrm{L}} + I_{\mathrm{R}}) \tag{3}$$

$$\Delta I = I_{\mathrm{L}} - I_{\mathrm{R}} \tag{4}$$

as the c.p.l. intensity, then the luminescence dissymmetry factor, g_{lum}, can be defined by equation (5).[25] One may immediately see that the unit dependence within the t.l. and c.p.l.

$$g_{\mathrm{lum}} = \Delta I/I \tag{5}$$

observables has been eliminated by taking their ratio. The luminescence dissymmetry factor may be related to the rotational strength of the transition.[25]

Values for the dissymmetry factors have been calculated for each of the c.p.l. bands observed within the ${}^5D_0\rightarrow{}^7F_1$ and ${}^5D_0\rightarrow{}^7F_2$ transitions as a function of solvent, and these are found in Tables 1 {[Eu(tfac)$_3$] compounds} and 2 {[Eu(hfbc)$_3$] adducts}. The very low t.l. intensity of the ${}^5D_0\rightarrow{}^7F_3$ and ${}^5D_0\rightarrow{}^7F_4$ emission bands does not make these systems well suited for the study of molecular chirality, and these were not examined in detail. These observations are in accord with the theoretical predictions of Richardson.[26]

Examination of the values in Tables 1 and 2 reveals several interesting features regarding the process of adduct formation, as long as one remembers that the values depend both on the steric nature of the substrate and on the formation constant of the adduct. We believe that no adduct formation takes place with the parent acetamide and formamide substrates, and find that no c.p.l. is observed with these systems. Increasing the steric size of the substrate generally results in greater optical activity, until the ligand becomes too bulky to bind effectively at the metal site and then presumably the degree of interaction becomes less. These observations support the notion that it is steric crowding of the chelate rings which leads to the observed optical activity.

It is quite interesting to note that the degree of optical activity associated with the [Eu(hfbc)$_3$] adducts is significantly smaller than for the [Eu(tfac)$_3$] adducts. One would normally expect that the extra fluorination of the hfbc ligands would produce a Eu^{III} chelate which would be a stronger Lewis acid, and thus interact more strongly with the substrate molecules. Since we observe the opposite trend, one may conclude that the extra length of the fluorocarbon side chain must provide less of a ' pocket ' on the co-ordination sphere of the Eu^{III} ion for the substrate to fit into.

It can be shown that a definite compound is being formed over the entire series of solvents. Within the $^5D_0 \rightarrow {}^7F_1$ transition, there can exist a maximum of three crystal field components if axial symmetry is not present. Close examination of the t.l. spectrum of Figure 2 shows that three t.l. peaks can be found (thus proving that axial symmetry is not present), while only two c.p.l. peaks are noted. If one takes the ratio of the dissymmetry factors for the 596 and 587 nm c.p.l. peaks, then a remarkable consistency is found. For the [Eu(tfac)$_3$] chelate a ratio of 2.35 ± 0.07 is found, while for the [Eu(hfbc)$_3$] series a ratio of 1.10 ± 0.02 was obtained. The constancy of this ratio is strongly suggestive of the existence of a single type of compound, although it is equally clear that the exact stereochemical nature must be somewhat different in the two chelate systems (given the differing t.l. patterns).

The observation that addition of an achiral substrate to a solution of either [Eu(tfac)$_3$] or [Eu(hfbc)$_3$] often leads to the observation of optical activity indicates that the aforementioned ligand arrangement can be accompanied by stereoselectivity. It is equally clear that the signs of the optical activities within the c.p.l. bands contain information regarding the absolute configuration of the Eu^{III} ion, but the source of the chirality experienced by the metal must first be established. It is well established that a metal ion interacts with a dissymmetric environment through three major mechanisms, (*a*) the vicinal effect (chirality induced at the metal by the simple presence of an asymmetric atom on the ligand), (*b*) the conformational effect (additional chirality arising when the asymmetric atom is part of a chelate ring), and (*c*) the configurational effect (chirality due to an asymmetric disposition of chelate rings about the metal).[27]

For the Eu^{III} β-diketone complexes studied here, only the vicinal and configurational effects can contribute to the Eu^{III} ion chirality, as the chelate ring is quite planar and does not contain an asymmetric atom. We have examined the nature of the vicinal effect in detail for Eu^{III} complexes containing camphorato ligands by synthesizing and studying chelates whose general formulae are Eu(L)$_2$(L′) and Eu(L′)$_2$(L) (where L = any achiral β-diketone and L′ = chiral β-diketone derived from D-camphor).[13] In this earlier work, it was shown that the optical activity arising from the vicinal effect was at least two orders of magnitude smaller than the effects found in the present work with formamide and acetamide substrates. It therefore appears quite safe to conclude that the chirality experienced by the Eu^{III} ion (and manifested through the c.p.l. spectra) in the adduct complexes is configurational in nature. We believe that the adduct formation causes crowding of the bulky camphorato-ligands and these adopt the configuration which minimizes these interactions. Since the ligands are themselves chiral, the isomer which forms in largest excess must be chiral and thus the adduct formation is accompanied by a spontaneous resolution of the very labile chelate.

The mirror images of dissymmetric six-co-ordinate trigonal metal complexes are denoted Λ and Δ.[27] This nomenclature is not really applicable to the Eu^{III} chelate adducts as these certainly are not trigonal, and do not even possess axial symmetry. Nevertheless, it is possible to speak of the free Eu^{III} β-diketone complexes as being six-co-ordinate and trigonal, and we suggest that the Λ and Δ labels might be used to identify an approximate stereochemistry for the adduct complexes.

Complicating the picture is the fact that no correlation has yet been made between the absolute configuration of a chiral Eu^{III} β-diketone complex and its chiroptical spectra. However, such a correlation has been made for [Eu{O(CH$_2$CO$_2$)$_2$}$_3$] (which happens to crystallize in an optically active space group), and it has been determined that the c.d. associated with the $^7F_0 \rightarrow {}^5D_1$ Eu^{III} absorption [28,29] and the c.p.l. of the $^5D_0 \rightarrow {}^7F_1$ Eu^{III} emission [30] is negative in sign if the absolute configuration of the Eu^{III} ion is Δ. We have used this information to correlate observed chirality with the Eu^{III} and Tb^{III} absolute configurations in a variety of solution-phase studies where the optical activity was induced in a trigonal complex through outer-sphere association (Pfeiffer effects).[31–33]

That the optical activity associated with the Eu^{III} β-diketone chelate adducts of the present study may be approximately described by the Λ and Δ nomenclature comes from examination of the c.p.l. spectra. The c.p.l. spectra of partially resolved [Eu(pyda)$_3$]$^{3-}$ (pyda = pyridine-2,6-dicarboxylate) are very distinctive and different from the c.p.l. spectra taken in a variety of studies we have made where conformational effects dominate. Since with [Eu(pyda)$_3$]$^{3-}$ we have shown that inner-sphere complexation is negligible,[32] we believe that the c.p.l. spectra shown in the Figures are indicative of trigonal, configurational optical activity (the magnitudes of the dissymmetry factors further support this assignment). Since the c.p.l. spectra of the Eu^{III} chelate adducts are absolutely identical in lineshape and of approximately the same order of magnitude as the earlier work, we conclude that the presence of negative c.p.l. in the $^5D_0 \rightarrow {}^7F_1$ luminescence band indicates that the diastereomer present in largest excess is that of the Δ configuration.

For transition metal complexes of camphorato β-diketones, it has been generally found that if one begins with (*R*,*R*)-ligand then the Λ isomer of the metal complex is formed to the greatest extent. The degree of stereoselectivity is solvent dependent for labile complexes; the Λ/Δ ratio runs from 3.2 to 1.03 for [V{(+)atc}$_3$].[8] In most of the Eu^{III} camphorato complexes studied to date, the opposite situation is found to hold: if the chelates are prepared from (+)-(*R*,*R*)-tfac or (+)-(*R*,*R*)-hfbc then the Δ-isomer is present in the largest amount. One of the few exceptions which has been noted is that of [Eu(hfbc)$_3$]–dimethyl sulphoxide, in which the Λ-isomer is found to predominate.[12]

It has been noted that plots of induced differential shifts (ΔΔδ), obtained during the course of n.m.r. experiments, ought to increase to a maximum as one titrates a substrate with a Eu^{III} shift reagent, but that frequently this is not the case.[10] It has been suggested that different magnetic environments [34] or varying stoicheiometries [10] account for these effects. The present study indicates that the both effects can contribute, as changing the stereochemistry of the Eu^{III} complex would certainly provide different magnetic effects and we have already shown how stoicheiometry can vary. It has proven very difficult to obtain absolute configurations of unknown materials by the action of chiral shift reagents, and these difficulties might be related to stereoselective effects provided by differing magnetic environments. Further studies are underway to clarify these processes.

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