systems in detail. Possibility (a) represents the α-hydroxycarboxyl mode of attachment associated with LAC, HIC, ARG, MAN, and PLA ligands. Comparison of Figures 2–5 and 6–9 shows that the band shapes are very similar, with the ICT spectra being the mirror image of the illustrated MAN spectra. However, the absolute configuration of the MAN ligand is *S* and the analogous carbon in the ICT ligand is *R*, so this difference would be expected if the mode of bonding were the same. In addition, if one compares the dissymmetry factors of the Tables, one finds that the degree of optical activity is roughly equivalent. Possibilities b and c represent a similar bonding mode as already shown for the aspartic acid complexes, and an examination of our published spectra and g_{lum} values for the 4–5 emission band[11] (and unpublished data for the 4–6, 4–4, and 4–3 bands) shows that no similarities exist. Possibility d reflects the bonding situation presented by MAL at high pH, and a simple examination of Figures 6–9 demonstrates a clear difference. We can discount possibility e since this would require the existence of two seven-membered rings, and we have already shown that these are unstable.[11] We therefore believe that the ICT ligand binds predominately in a bidentate manner through the α-hydroxycarboxyl functionality and that any CPL line shapes that do exist must be a reflection of a small amount of terdentate bonding through participation of the carboxyl group at carbon 4.

The formation constants of Table IV represent trends that one would predict from simple arguments. We have already mentioned that the K_1 constants of Tb^{3+}/α-hydroxycarboxylic acid complexes range from 300 to 800.[17] The binding of one DPA ligand by Tb(III) reduces the overall positive charge of the complex as $Tb(DPA)^+$ is formed, and we now find that the K_1 constants range from 110 to 255. The effect on K_2 is even more pronounced; while for Tb^{3+}, K_2 is usually almost equal to K_1, for $Tb(DPA)^+$ we find that K_2 (if a second ligand is bound at all!) is only one-tenth that of K_1. Finally, a further decrease in positive charge must occur with formation of the $Tb(DPA)_2^-$ species, and now one finds that the association constants range from 30 to 90.

The data we have presented in the present study permit a critical evaluation of the selection rules for lanthanide optical activity recently proposed by Richardson.[20] In this work, Richardson developed predictions for the electric dipole strengths, rotatory strengths, and dissymmetry factor magnitudes solely on the basis of the *S*, *L*, and *J* quantum numbers of the states involved in the transitions. Details of the lanthanide crystal field were omitted in this treatment, but the conclusions should be good estimates of the relative magnitudes of the various properties. Richardson predicts that the 4–5, 4–4, and 4–3 transitions should all have approximately equal degrees of optical activity and the dissymmetry factors associated with the 4–6 transition ought to be much smaller. In fact, we find that while the 4–5 and 4–3 transitions do have approximately the same degree of CPL, the 4–4 transition actually has the same order of magnitude as the 4–6. Our observations simply point out the necessity for including the crystal field in the optical activity calculations, which shows that crystal field effects in lanthanide complexes are perhaps more significant than is generally thought.

The results presented in our present work demonstrate the usefulness of CPL spectroscopy as a probe of lanthanide ion stereochemistry. Given the current state of existing CPL theory as applied as lanthanide ions, our discussions have remained qualitative in nature. Nevertheless, by a systematic variation of functionality on the chiral ligands, one can deduce a fair amount of stereochemical information from a study of the CPL spectra of a chiral lanthanide complex.

Acknowledgment. This work was supported by Research Corp. through Grant No. 8926 of the Cottrell Research Program and by the Camille and Henry Dreyfus Foundation through a Teacher-Scholar grant to H.G.B.

Registry No. Tb, 7440-27-9; DPA, 499-83-2; LAC, 79-33-4; HIC, 13748-90-8; ARG, 157-07-3; MAN, 17199-29-0; PLA, 20312-36-1; MAL, 97-67-6; HGT, 41014-93-1; ICT, 20591-42-8.

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Optical Activity Induced in the Europium(III) Complexes of β-Diketones through Association with Phenylalkylamines and Phenylalkylamino Alcohols

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The optical activity induced in the Eu(III) chelates of two fluorinated β-diketones upon complexation with two chiral phenylalkylamines and six phenylalkylamino alcohols was studied by means of circularly polarized luminescence (CPL) spectroscopy. In addition, association constants for the adducts were computed from emission titrations of the chelates with substrates. These results were used to deduce the manner in which the substrate bound to the chelate, and arguments are presented regarding the major type of chirality experienced by the Eu(III) ion. Depending on the nature of the substrate, the chiral ligands could function as mono-, bi-, or terdentate chelators. The optical activity was found to arise solely from vicinal or vicinal/conformational effects, with no evidence being obtained to indicate the presence of configurational optical activity.

Introduction

The use of paramagnetic lanthanide complexes of β-diketones as shift reagents in NMR spectroscopy is a well-known phenomenon, with literally hundreds of articles having been published regarding applications of these materials. In general, most of the interest has been focused on questions of spectral resolution and simplification or of structure elucidation.[2-4] Structural aspects of the shift reagent adducts have been probed by means of X-ray crystallography, and it has been

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generally recognized that details obtained from the solid-state structure analysis may have no correspondence to features present in fluid solution. One has generally been forced to assume the presence of axial symmetry in the adduct complexes in order to carry out any sort of theoretical analysis of NMR shift data, in spite of crystal structures to the contrary. The labile nature of the chelates coupled with fast observed rates of β-diketone and substrate exchange have permitted wholesale discarding of the possibility that the adduct complexes might not be axially symmetric in solution.

Chiroptical methods of spectroscopy are most useful in providing details of solution structure, and a recent study of circularly polarized emission induced in achiral shift reagent adducts of dimethyl sulfoxide and dimethylformamide by magnetic fields clearly revealed the lack of axial symmetry in these complexes.[5] We have been carrying out systematic studies of the adduct formation that takes place when Eu(III) chelates of achiral β-diketones form complexes with chiral substrates and have used the circular polarization associated with the luminescence spectrum (CPL spectroscopy) as our probe of the solution-phase complexes. By examining the CPL resulting from the coordination of a monofunctional amine donor to a $Ln(DK)_3$ chelate (Ln = any lanthanide ion, and DK = any β-diketone ligand), we have been able to establish that the sign of the observed CPL can be correlated to the absolute configuration of the amine donor for both Tb(III)[6] and Eu(III)[7] complexes.

In studies of lanthanide-induced shifts in NMR spectra, most of the experimental work has concentrated on monofunctional substrates. It is well-known that adducts of $Ln(DK)_3$ can be formed with bidentate substrates such as 2,2′-bipyridyl or 1,10-phenanthroline.[8] It has been recognized that such a bifunctional substrate donor could act either as a bidentate ligand or as a monodentate ligand capable of exhibiting configurational isomerism.[9,10] Our first CPL study of optical activity induced in $Eu(DK)_3$ by a bidentate substrate concerned the complexes of $Eu(TTFA)_3$ (TTFA = theonyltrifluoroacetone) with chiral amino alcohols.[11] It proved difficult to compare the results of this study to the earlier work involving $Eu(TTFA)_3$ and the cinchona alkaloids[7] due to the difficulty of being absolutely sure that the alkaloids functioned only as monodentate donors, but it did appear that the interaction of the bifunctional amino alcohols with $Eu(TTFA)_3$ led to the observation of stronger optical activity than with the alkaloids.

Since it is established that when a chelate ring is formed that contains an asymmetric atom, this conformational effect usually leads to much greater degrees of optical activity than would be expected from a sole vicinal effect (chirality due to monodentate attachment of a chiral ligand to a metal ion).[12] By examining the CPL associated with $Eu(DK)_3$ adducts containing only monodentate chiral substrates and then examining the CPL of structurally related bi- and terdentate substrates, one ought to be able to evaluate the possible existence of multidentate bonding in shift reagent adducts.

These studies proved feasible since a wide variety of chiral amines and related chiral amino alcohols are available. In our present study, we report the optical activity induced in the Eu(III) chelates of TTFA and FOD (FOD = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione) with chiral amines and amino alcohols. In addition, formation constants for the 1:1 adducts were calculated for both $Eu(DK)_3$ chelates by means of luminescence titration techniques. In addition to the chiral substrates, data were obtained for two achiral parent monodentate amines as well. The structures of all substrates and a numbering system may be found in Figure 1. The systematic variation of substrate functional groups permits one to evaluate the relative contribution of vicinal and conformational effects and to determine the effect of the substrate bonding mode on the observed optical activity.

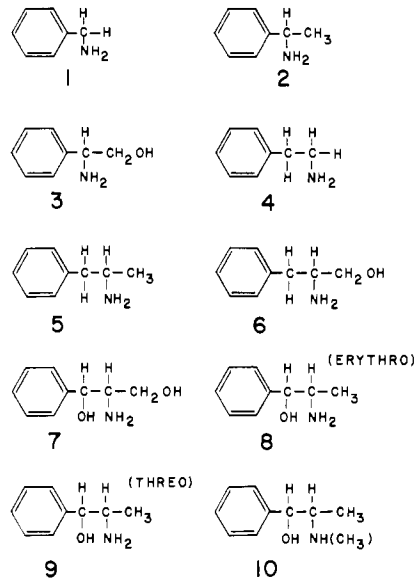

Figure 1. Structures of the chiral substrates used in this work.

Experimental Section

The $Eu(TTFA)_3$ chelate was prepared as the dihydrate according to the literature,[13] while $Eu(FOD)_3$ was obtained from Aldrich. Benzylamine (**1**), D-α-phenylglycinol (**3**), β-phenethylamine (**4**), L-phenylalaninol (**6**), (+)-2-amino-1-phenyl-1,3-propanediol (which we shall call APPD) (**7**), (+)-norephedrine (**8**), (−)-norpseudoephedrine (**9**), and D- or L-ephedrine (**10**) were all obtained from Aldrich. Compounds **8** and **9** were actually obtained as the hydrochloride salts and were converted to the free bases by neutralization with NaOH, extraction of the free amine into diethyl ether, and subsequent removal of the ether. (+)- or (−)-α-phenethylamine (**2**) was obtained from Norse laboratories, while D-amphetamine sulfate (**5**, or D-α-methylphenethylamine sulfate) was obtained from Sigma. Compound **5** was converted to the free base by a procedure similar to that described for the **8** and **9** hydrochlorides. The absolute configuration of each asymmetric atom in the substrates can be obtained from the literature.[14]

Stock solutions of the $Eu(DK)_3$ chelates were made up in dried $CHCl_3$, with the initial $Eu(TTFA)_3$ concentration being 3.75×10^{-4} M and the initial $Eu(FOD)_3$ concentration being 1.03×10^{-3} M. Stock solutions of each substrate were made up in the concentration range of 0.1–0.15 M, and these were added in microliter quantities to 3.0 mL of the $Eu(DK)_3$ solution already in a fluorescence cuvette. By adding relatively small amounts of substrate per addition, one could follow both the total luminescence (TL) and circularly polarized luminescence (CPL) as a function of the number of equivalents of substrate added and therefore obtain TL and CPL titrations. At the end of each titration, an excess amount of neat substrate was added to the cuvette to ensure complete formation of the $Eu(DK)_3$ adduct.

All luminescence and CPL spectra were obtained on an instrument constructed in this laboratory, which has recently been described in detail.[15] An excitation wavelength of 365 nm was used for all studies

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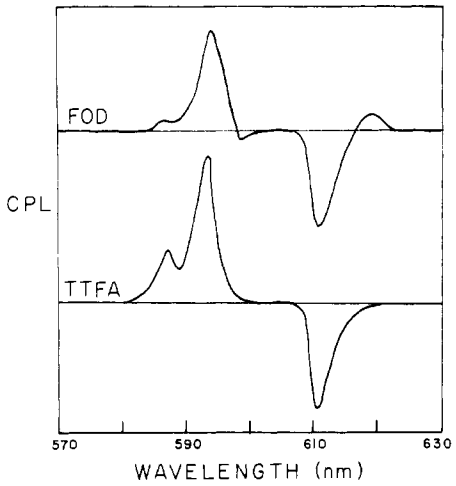

Figure 2. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*S*)-α-phenethylamine within the 0–1 and 0–2 emission bands. The spectra are reported in arbitrary units, and all quantitative features should be obtained from Tables II and III.

(obtained by passing the output of a 200-W Hg–Xe arc lamp through a 0.1-m grating monochromator), and a 20-nm bandpass was employed. The emission was collected at 180° to the exciting light in order to eliminate any possible linear polarizations in the emission, and therefore the light emitted by the $Eu(DK)_3$ samples was passed through a concentrated solution of $NaNO_2$ to filter out the unabsorbed exciting light. The emission was analyzed by a 0.5-m grating monochromator (using a 1-nm bandpass) and detected by an EMI 9798B photomultiplier tube (S-20 response). No attempt was made to correct the emission spectra for system response since the wavelength regions scanned were exceedingly narrow and any correction would be minor at most.

Results

Irradiation of $Eu(DK)_3$ complexes in the near-UV region of the spectrum results in efficient absorption of the excitation energy and frequently in fairly intense emission in red spectral regions. In fluid solution at room temperature, luminescence orginates from the $^5D_0$ Eu(III) level and terminates in the $^7F_0$ (580 nm), $^7F_1$ (595 nm), and $^7F_2$ (615 nm) levels. In usual situations, the 0–0 and 0–1 transitions (we shall label the transitions by their *J* quantum numbers) exhibit TL intensities of roughly the same magnitude, and the TL of the 0–2 transition is generally an order of magnitude more intense. No CPL is ever observed within the 0–0 transition, and the CPL of the 0–1 and 0–2 transitions is approximately equal in magnitude. Much weaker luminescence bands can be found at still lower energy (corresponding to the 0–3 and 0–4 transitions), but the low intensity of these precluded CPL measurements for all but the most chiral Eu(III) adducts.

As in the case of most luminescence measurements, the TL and CPL observables are recorded in arbitrary units. If we define

$$I = I_L + I_R \quad (1)$$

as the TL intensity and

$$\Delta I = I_L - I_R \quad (2)$$

as the CPL intensity, then the luminescence dissymmetry factor has been defined as[16]

$$g_{lum} = \Delta I/(\tfrac{1}{2}I) \quad (3)$$

One may immediately see that the unit dependence of the observables has been eliminated by taking the ratio of the TL and CPL. In our work, the value of the dissymmetry factor

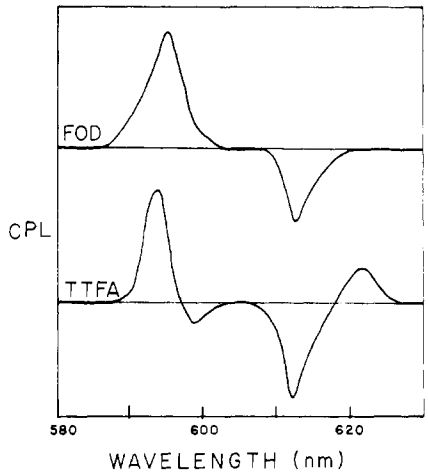

Figure 3. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*S*)-α-methylphenethylamine (**5**).

Table I. Association Constants[a] for the 1:1 $Eu(DK)_3$/Substrate Adducts

substrate	log *K* DK = TTFA	log *K* DK = FOD
1, benzylamine	3.08	2.14
2, α-phenethylamine	3.02	1.93
3, α-phenylglycinol	4.38	3.21
4, β-phenethylamine	3.38	2.04
5, α-methylphenethylamine	3.28	2.26
6, phenylalaninol	4.41	3.34
7, APPD	4.87	3.58
8, norephedrine	4.29	3.21
9, norpseudoephedrine	4.12	2.59
10, ephedrine	4.22	3.15

[a] All constants are accurate to approximately 5%.

depends on the degree of complexation existing between the chelate and the substrate.

In a previous study,[17] we reported the CPL spectrum of the adduct formed between $Eu(FOD)_3$ and α-phenethylamine. We have reported this experimentation in our present study and have obtained essentially the same spectral features. In addition to the FOD system, we have also examined the $Eu(TTFA)_3$ adduct with compound **2**; the CPL of the 0–1 and 0–2 transitions is found in Figure 2. The CPL spectra obtained when the same two $Eu(DK)_3$ chelates were complexed to **5** is shown in Figure 3, and one may immediately note a similarity among the four line shapes. All spectra were recorded by using substrates of the *S* configuration, and one may easily see that while small differences exist in the line shapes, the major CPL peak of each transition is of the same sign. In accord with our earlier work,[6] the sign of the CPL obtained for monodentate substrates correlates exactly with the absolute configuration of the substrate. This relation appears to hold for all Eu(III) emission bands.

Luminescence titrations could be carried out for both $Eu(DK)_3$ systems by monitoring the intensity of Eu(III) luminescence as a function of the quantity of substrate added, and we have previously described methods by which one can obtain the association constant for the chelate/substrate adduct.[18] Titrations for substrates **1**, **2**, **4**, and **5** form a series of monodentate amines, and in general the titration curves for a particular metal chelate were almost identical. We calculated the association constants for the adducts, and these may be found in Table I. From the values we have obtained, we

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Table II. Dissymmetry Factors for the $Eu(DK)_3$ Adducts within the $^5D_0 \rightarrow {}^7F_1$ Luminescence Band

substrate	$10^2 g_{lum}$ DK = TTFA	DK = FOD
2, (−)-phenethylamine	+2.20	+4.60
5, *d*-α-methylphenethylamine	+2.50	+3.30
3, α-phenylglycinol	−5.80	−10.40
6, phenylalaninol	+4.20	+9.40
7, APPD	−28.02	−58.00
10, *d*-ephedrine	+8.22	+7.00/+14.00
8, norephedrine	+7.60/−7.42	+9.20/−9.62
9, norpseudoephedrine	+7.50	−5.22

Table III. Dissymmetry Factors for the $Eu(DK)_3$ Adducts within the $^5D_0 \rightarrow {}^7F_2$ Luminescence Band

substrate	$10^3 g_{lum}$ DK = TTFA	DK = FOD
2, (−)-α-phenethylamine	−2.20	−5.00
5, *d*-α-methylphenethylamine	−2.46	−3.60
3, α-phenylglycinol	+6.22	+10.60
6, phenylalaninol	−4.76	−8.86
7, APPD	+20.02	+50.06
10, *d*-ephedrine	−7.16	−12.22
8, norephedrine	−7.42	−9.06
9, norpseudoephedrine	−6.60	+5.80

conclude that little steric effects arise as a result of replacement of a H atom by a CH_3 group in the **1**,**2** and **4**,**5** pairs. The titration curves were essentially complete with the formation of the 1:1 adduct, and if the 1:2 adduct does form, we believe that its formation constant must be at least 2 orders of magnitude smaller than that for the 1:1 adduct.

However, since the TL and CPL of each compound are obtained simultaneously, we have computed values for the dissymmetry factors. The 0–1 constants are located in Table II, while the 0–2 constants may be found in Table III. We observe that the optical activity of the 0–2 transition is generally an order of magnitude smaller than that of the 0–1 emission band. Since the **2** and **5** substrates must function only as monodentate ligands, two possibilities for the origin of the chirality immediately suggest themselves: the optical activity is either due to (a) an induction of chirality at the Eu(III) ion by virtue of monodentate attachment of the amine substrate (vicinal effect) or (b) a stereoselective rearrangement of the chelate rings caused by the binding of the chiral amine. The latter effect would recognize that the original $Eu(DK)_3$ tris chelate is used as a racemic mixture of rapidly interconverting isomers, and somehow the enantiomer conversion would be perturbed as a result of the adduct formation. This effect would be analogous to the Pfeiffer effect[19] and would represent configurational optical activity.

It is our belief that the first explanation given above is the correct one, and the chirality resulting from adduct formation with monodentate amines is due solely to vicinal effects. Our evidence is based on CPL data from two other sources; one involving a pure vicinal effect, and the other detailing pure configurational effects. We have recently synthesized and characterized a series of Eu(III) chelates having the general formula $Eu(DK)_2(CDK)$, where CDK represents an inherently chiral β-diketone ligand (such as trifluoroacetyl-*d*-camphor).[20] In these complexes, only vicinal effects can contribute to the overall optical activity, and we find that the dissymmetry factors are of the same order of magnitude as those reported in our present work when monodentate amines were used to induce the CPL. The second evidence comes from a study of

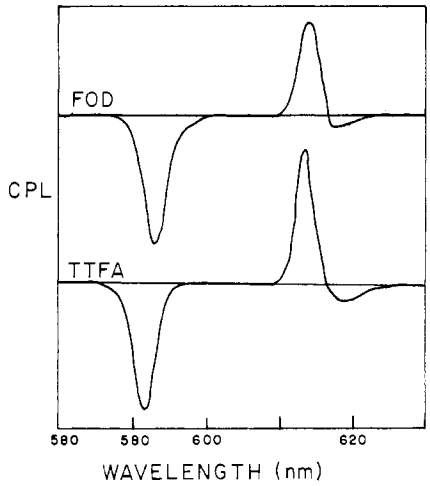

Figure 4. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*R*)-α-phenylglycinol (**3**).

$Eu(CDK)_3$/dimethyl sulfoxide adducts, where exceedingly strong CPL was observed (even though none was seen in the uncomplexed chelate) and the added substrate was achiral.[2] Here, the dissymmetry factors were almost an order of magnitude greater than any seen in the present work. Since the $Eu(CDK)_3/Me_2SO$ adduct certainly is an example of pure configurational optical activity, we again conclude that the monodentate amines lead only to vicinal effects.

Replacement of a terminal hydrogen atom on the **2** and **4** monodentate amines by a hydroxyl group results in the potentially bidentate amino alcohol substrates, **3** and **6**, respectively. Another set of amino alcohols are obtained by replacing a different hydrogen on substrate **5** by a hydroxyl group, and depending on the stereochemistry at this β-carbon one can obtain either an erythro (**8**) or a threo (**9**) isomer. Performance of the luminescence titrations for both $Eu(DK)_3$ chelates with **3**, **6**, **8**, and **9** again yields curves that resemble each other quite strongly, and one subsequently finds that the association constants (see Table I) are all essentially the same. A small steric effect associated with the phenyl ring may be noted in that the adducts formed between the $Eu(DK)_3$ and substrates **8** and **9** (which have the phenyl ring one position from the hydroxyl group) are somewhat weaker than the adducts containing substrates **3** and **6** (which have the phenyl ring three positions from the hydroxyl group).

However, the most striking feature of the association constants is the large difference in magnitude noted for the values obtained for monodentate amines when compared to those for the potentially bidentate amino alcohols. With the amino alcohols, the adducts are more stable by over an order of magnitude. One must ascribe this extra stability to the formation of a chelate ring where bidentate attachment of the substrate is through the amine group and through the unionized hydroxyl group. Presumably, the usual chelate effect accounts for the extra stability. One notable exception to this trend was found for the $Eu(FOD)_3$/norpseudoephedrine adduct. Here, the association constant was found to be significantly lower than any of the other amino alcohols and is actually of a magnitude that would indicate monodentate binding to the Eu(III) chelate.

Further proof that amino alcohols usually bind to the Eu(III) chelates in a bidentate fashion can be obtained from the CPL spectra. The 0–1 and 0–2 CPL spectra obtained for the $Eu(TTFA)_3$ and the $Eu(FOD)_3$ adducts with **3**, **6**, **8**, and **9** are found in Figures 4–7. If one calculates the dissymmetry factors for each band, one obtains the values shown in Table II for the 0–1 bands and in Table III for the 0–2 bands. It is quite clear that the optical activity obtained for the amino

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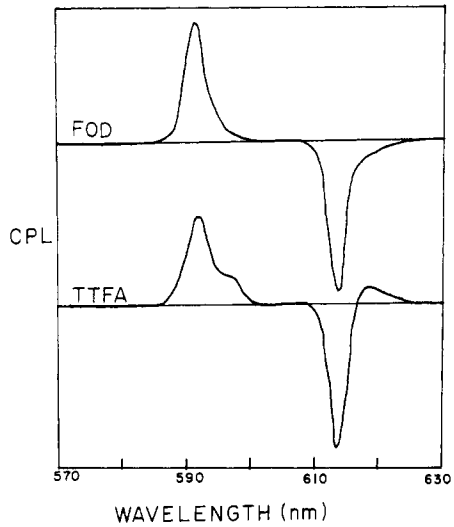

Figure 5. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*S*)-phenylalaninol (**6**).

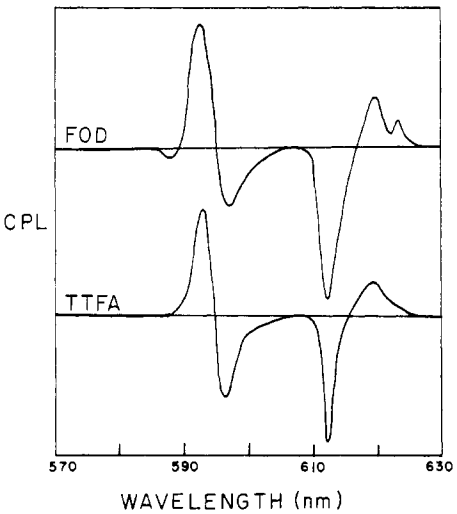

Figure 6. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*R,S*)-norephedrine (**8**).

alcohol adducts is measurably stronger than that obtained for the monodentate amines. Formation of a chelate ring containing an asymmetric atom would lead to the existence of a conformational contribution of the overall chirality (in addition to the vicinal effect), and in general the conformational effect is larger in magnitude than is the vicinal effect.[12] Comparison of these dissymmetry factors to those found when a configurational effect was operative[20] reveals that the CPL obtained on the amino alcohol adducts must be a sum of the vicinal and conformational effects only.

For the simple amino alcohols containing only one asymmetric atom, the sign of the CPL in the 0–1 and 0–2 bands correlates with the absolute configuration of that atom. Substrate **3** is of the *R* configuration, and substrate **6** is of the *S* configuration; one notes immediately that the sign of the observed CPL in corresponding bands is opposite. In addition, the CPL sign matches the pattern found for the monodentate amines, and we therefore conclude that as long as only one asymmetric atom is present on the chiral substrate, the Eu(III) atom will exhibit the sense of the chirality of that substrate regardless of the coordination mode. This rule will be helpful in evaluating the coordination modes of the other two amino alcohols.

Substrates **8** and **9** represent erythro and threo isomers of the same compound, α-(1-aminoethyl)benzyl alcohol. It is

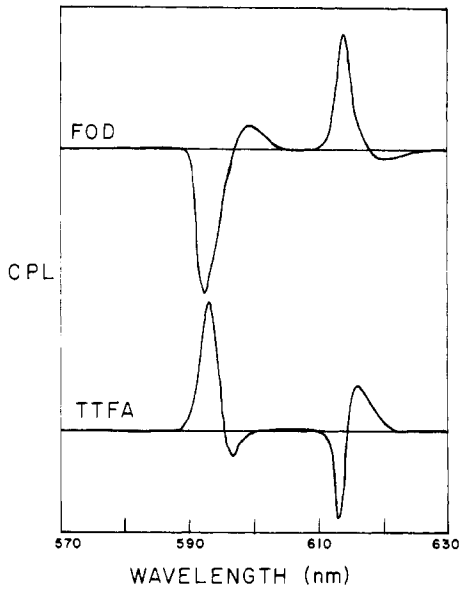

Figure 7. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*R,R*)-norpseudoephedrine (**9**).

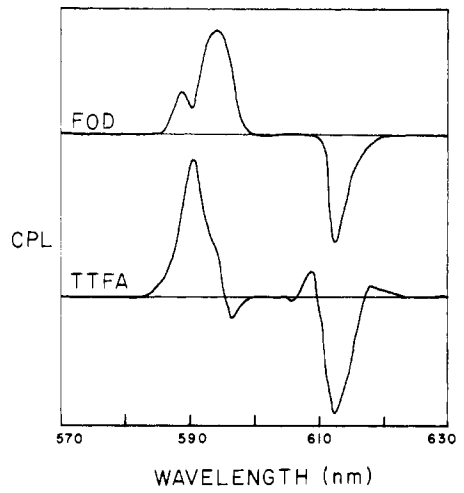

Figure 8. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*R,S*)-*d*-ephedrine (**10**).

interesting to note that the CPL of $Eu(TTFA)_3$/(**8** or **9**) is the same as that of $Eu(FOD)_3$/**8**, and also opposite in sign to that of $Eu(FOD)_3$/**9**. However, we have established through the association constants that $Eu(FOD)_3$ binds **9** in a monodentate fashion, while the other three adducts bind in a bidentate manner. Examination of the magnitudes of the dissymmetry factors for the four adducts confirms this bonding prediction. The rule regarding the sign of the CPL induced by a monodentate substrate is upheld for the $Eu(FOD)_3$/**9** adduct, since we worked with *R,R*-**9**. It is equally clear that when the substrate contains two asymmetric atoms in the chelate ring, the chirality experienced by the Eu(III) ion may *not* be easily related to the absolute configurations present on the substrate. In fact, we obtained essentially identical CPL for the $Eu(FOD)_3$/*R,R*-**9**, $Eu(TTFA)_3$/*R,S*-**8**, and $Eu(FOD)_3$/*R,S*-**8**.

Substrate **10** is our only example of a substituted amine group in the amino alcohol sequence. The formation constant of this ligand with the $Eu(DK)_3$ chelates is essentially the same as seen for substrates **8** and **9** (when these functioned in the bidentate model), and we conclude that ephedrine binds to both chelates as a bidentate ligand. The CPL spectra are shown in Figure 8, and the dissymmetry factors are in Tables II and III; these results also confirm the prediction of a bidentate

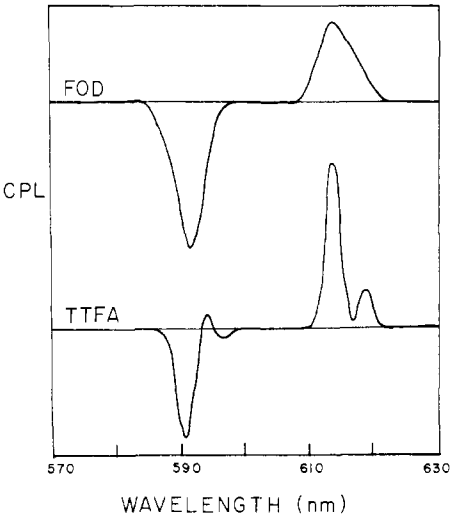

Figure 9. CPL spectra obtained for the $Eu(FOD)_3$ and $Eu(TTFA)_3$ adducts of (*S*,*S*)-2-amino-1-phenyl-1,3-propanediol (**7**).

mode of attachment for the **10** substrate. This substrate also contains two asymmetric atoms (and is of the erythro configuration), and we note that the sign of the observed CPL is more complicated than would be predicted if there were only one asymmetric atom in the ligand. It would appear that the presence of a methyl group on the **10** amine group does not interfere in any way with the adduct formation.

Finally, we have one substrate that contains two asymmetric atoms in a threo configuration and is potentially terdentate. Substrate **7**, 2-amino-1-phenyl-1,3-propanediol (APPD), contains three functional groups capable of bonding to a Eu(III) chelate, and it was of interest to determine whether such bonding could exist. Examination of the association constants in Table I reveals that this ligand binds to the chelates with the greatest degree of efficiency of any substrate studied. The CPL spectra are shown in Figure 9, and if one examines the dissymmetry factors of Tables II and III, one can immediately see that the degree of chirality is vastly greater than any of the bidentate amino alcohols or monodentate amines. The chirality if almost half that seen when configurational effects led to the observed CPL,[20] and one cannot rule out a possible contribution from configurational effects adding to the certain vicinal and conformational effects. Regardless, the evidence is quite clear that the APPD substrate binds in a radically different fashion when compared to all other substrates, and we take these observations to imply the presence of terdentate bonding existing in the $Eu(DK)_3$/**7** adducts.

Conclusions

From the results presented in this paper, it is abundantly clear that Eu(III) complexes of β-diketones are capable of forming adducts in which substrates exhibit mono-, bi-, and terdentate modes of coordination. Such conclusions are not highly surprising, since bidentate attachment of substrates has been demonstrated.[8,22] Our work has shown that terdentate attachment of substrate is also possible, and to our knowledge this has not hitherto been shown. CPL spectroscopy is a most powerful method to probe substrate attachment to Eu(III) chelates. The formation of such adducts suggests that unless exchange of these substrates is fast on the NMR time scale, the assumption of axial symmetry is polyfunctional substrates may be unwarranted.

We have shown that a rule exists which enables the prediction of the absolute configuration of an unknown material that has only one asymmetric atom. If the sign of the 0–1 CPL is positive, then the asymmetric atom must be of the *S* configuration, and this rule appears to hold whether the substrate is mono- or bidentate. However, when two asymmetric atoms are present, we cannot yet predict the sign of the CPL, and further work is called for. Such a method is of great use in synthesis. Since the strongest adducts are formed with amine and alcohol substrates,[3] the correlation of absolute configurations will be most useful for materials containing these functional groups.

A final note concerns the adducts formed with β-diketones that bind less well with the Eu(III) ion (such as dibenzoylmethane, dipivaloymethane, or benzoylacetone). We have found that the CPL spectra of these adducts differ considerably at low and high substrate concentrations and have identified the source of these changes as being due to Schiff base formation.[23] The strongly binding β-diketone ligands (such as TTFA or FOD) show no sign of this Schiff base formation. We have independently prepared several of the Eu(III) Schiff bases already and have found that a Schiff base can be prepared with almost any β-diketone ligand we choose. Another factor which contributes to the lack of Schiff base formation with the TTFA or FOD ligands is the well-known behavior of hydrolysis associated with fluorinated Schiff base ligand complexes.[24] These observations suggest caution in use of nonfluorinated Eu(III) β-diketone complexes as NMR shift reagents during investigation of polyfunctional substrates which contain one or more amine groups.

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Registry No. **1**, 100-46-9; **2**, 2627-86-3; **3**, 56613-80-0; **4**, 64-04-0; **5**, 51-64-9; **6**, 3182-95-4; **7**, 28143-91-1; **8**, 492-41-1; **9**, 37577-07-4; **10**, 299-42-3; $Eu(TTFA)_3$, 14054-87-6; $Eu(FOD)_3$, 17631-68-4.

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