Analogous V(II) complexes are formed from 2,4-, 2,5-, and 2,6-pyridinedicarboxylic acids.[17] Since, however, kinetic experiments involving the Co(III) derivatives of these acids were carried out in much more dilute solutions, formation of these complexes did not interfere with our measurements.

Acknowledgment. The authors are grateful to the National Science Foundation for sponsorship of this work.

(17) Visible absorption maxima are at 610 nm (ϵ = 600) for the 2,4 isomer, 572 nm (ϵ = 88) for the 2,5 complex, and 600 nm (ϵ = 95) for the 2,6 complex.

Registry No. 1-H-4-$COOCo(NH_3)_5$-$C_5H_4N^{3+}$, 42532-70-7; 1-CH_3-4-$COOCo(NH_3)_5$-$C_5H_4N^{3+}$, 74911-56-1; 2-$COOCo(NH_3)_5$-4-$CONH_2$-$C_5H_3N^{2+}$, 67598-21-4; 1-$CH_2COOCo(NH_3)_5$-4-$CONH_2$-$C_5H_4N^{3+}$, 69421-18-7; 1-$CH(CH_3)COOCo(NH_3)_5$-4-$CONH_2$-$C_5H_4N^{3+}$, 69421-20-1; 1-H-4-(4-CH=CH-C_5H_4N)$Co(NH_3)_5$-$C_5H_4N^{4+}$, 74911-57-2; 2-$COOCo(NH_3)_5$-4-COOH-$C_5H_3N^{2+}$, 67662-33-3; 2-$COOCo(NH_3)_5$-3-COOH-$C_5H_3N^{2+}$, 67598-28-1; 2-$COOCo(NH_3)_5$-3-$CONH_2$-$C_5H_3N^{2+}$, 67598-20-3; 2-$COOCo(NH_3)_5$-5-COOH-$C_5H_3N^{2+}$, 67598-29-2; 2-$COOCo(NH_3)_5$-5-$CONH_2$-$C_5H_3N^{2+}$, 67598-23-6; 2-$COOCo(NH_3)_5$-6-COOH-$C_5H_3N^{2+}$, 67662-34-4; 2-$COOCo(NH_3)_5$-6-$CONH_2$-$C_5H_3N^{2+}$, 67632-51-3; 2-$COOCo(NH_3)_5$-6-$COOCH_3$-$C_5H_3N^{2+}$, 67598-24-7; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3.

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Optical Activity Induced in Tris(4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione)europium(III) by Association with Chiral Amino Alcohols

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The optical activity induced in the title compound by complex formation with seven chiral amino alcohols was studied by means of circularly polarized luminescence (CPL) spectroscopy. The signs of the CPL peaks associated with the Eu(III) emission bands could be correlated with the absolute configuration of the added amino alcohol, and the magnitude of the CPL appeared to be dictated by steric considerations. It proved possible to calculate association constants for the chelate/substrate adducts from the enhancement of luminescence intensities that resulted from the formation of adduct species. For all substrates, the presence of 1:1 and 1:2 chelate/substrate adducts was noted, but the 1:2 adduct only formed at high concentrations of substrate. It was found that all log K_1 values were approximately 4.5, while the log K_2 values ranged from 1.1 to 1.8. The magnitude of the formation constants and of the induced optical activity appears to be a complicated function of steric and electronic effects.

Introduction

Complexes of lanthanide ions are finding increasing degrees of application in a wide variety of areas, and the solution-phase coordination chemistry of these ions is receiving a great deal of attention. While solutions of aquated metal ions have been investigated via diffraction techniques,[1] these methods cannot easily be applied to lanthanide complexes containing more complex ligands. Unlike transition metals, lanthanide ions can exhibit a wide range of coordination numbers,[2] and this situation greatly extends the range of available chemistry. Nevertheless, quantitative aspects of lanthanide chemistry require detailed knowledge of solution stereochemistries, and without this information the application of lanthanide ions as NMR shift reagents[3] or as probes of calcium-binding proteins[4] cannot hope to become more than qualitative.

A wide variety of physical methods have been brought to bear on solutions of lanthanide complexes in order to obtain the necessary stereochemical information. The most useful of these are chiroptical techniques, and circular dichroism studies have been used to probe solution stereochemistries.[5,6] Unfortunately, the intensity of lanthanide f-f absorptions are extremely weak and CD spectra are only obtained at relatively high concentrations of complex. Many of these complexes have been shown to associate into polynuclear species under these conditions, and this association is most extensive at alkaline pH where the CD signals are the strongest.[6,7]

A more recently developed technique that is better suited for the study of lanthanide complexes is that of circularly polarized luminescence (CPL) spectroscopy.[8] With this method, the differential emission of left and right circularly polarized light by a chiral luminescent molecule is detected, and this method has been shown to be extremely sensitive toward slight stereochemical changes. Lanthanide ions are best studied by emission methods such as CPL since the luminescence spectra are well characterized and the bands arising from various states are well separated. In addition, the f-f transitions are highly nonbonding in character, and one is then able to assume that any measurement of excited-state chirality must have its origin in the ground-state stereochemical effects.

The study of lanthanide complexes of β-diketones is very important due to the use of these chelates as NMR shift reagents.[3] These complexes are easily studied by CPL spectroscopy since the solution geometries can be reasonably well-defined, the Tb(III) and Eu(III) derivatives are often highly emissive, and most complexes are mononuclear. These features make this particular class of compounds especially useful in the development of spectra-structure correlations, and these in turn can be applied to new systems of unknown stereochemistry. When one prepares a lanthanide tris(β-diketone) complex, the compound that is produced is actually a racemic mixture of highly labile enantiomers. The observation of CPL therefore requires a stereoselective enrichment

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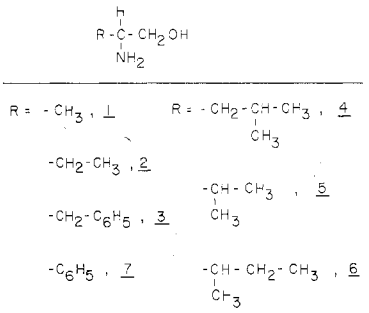

Figure 1. Structures and numbering system for the amino alcohols used in this work.

of one particular enantiomer or diastereomer, and consequently CPL studies are extraordinarily sensitive to subtle changes in stereochemical features.[8]

In the present work, optical activity induced in tris(4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione)europium(III) (Eu(ttfa)$_3$) by association with seven chiral amino alcohols is reported. The structures of and numbering system associated with the various amino alcohols is shown in Figure 1. The ttfa ligand itself is inherently achiral, and the tris Eu(III) complexes show no CPL in achiral solvents. Formation of an adduct with chiral amino alcohols results in the presence of reasonably strong CPL, and this chirality is a very sensitive probe of the association process.

Experimental Section

The Eu(ttfa)$_3$ chelate was prepared and purified according to the literature.[9] Optically active amino alcohols were obtained from Aldrich and were used as received. The amino alcohol substrates used during the course of this work were: (*S*)-2-amino-1-propanol (L-alaninol, **1**), (*R*)-2-amino-1-butanol (**2**), (*S*)-2-amino-3-phenyl-1-propanol (L-phenylalaninol, **3**), (*S*)-2-amino-4-methyl-1-pentanol (L-leucinol, **4**), (*S*)-2-amino-3-methyl-1-butanol (L-valinol, **5**), (*S*)-2-amino-3-methyl-1-pentanol (L-isoleucinol, **6**), and (*R*)-2-amino-2-phenylethanol (D-α-phenylglycinol, **7**). The absolute configuration of each amino alcohol was available from various sources.[10] Stock solutions of Eu(ttfa)$_3$ were made up in dried $CHCl_3$, with the initial concentration being 3.35×10^{-4} M. A 0.10 M stock solution of each amino alcohol was made up in $CHCl_3$, and these solutions were added in microliter quantities to 3.0 mL of the Eu(ttfa)$_3$ solution already in a fluorescence cuvette. In this fashion, the change in Eu(III) emission intensity could be followed as a function of the concentration of added substrate. In no case did the final volume increase by more than 5% relative to the initial volume. After approximately 10 equiv of substrate/mol of Eu(ttfa)$_3$ had been added, excess amino alcohol (in the form of neat material) was added to the cuvette to obtain a final data point.

All luminescence and CPL spectra were obtained on an instrument constructed in this laboratory, which has recently been described in detail.[11] An excitation wavelength of 365 nm was used for all studies (obtained by passing the output of a 200-W Hg–Xe arc lamp through a 0.1-m grating monochromator), and a 20-nm band-pass 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(ttfa)$_3$ 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 (with use of a 1-nm band-pass) 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 and Discussion

The irradiation of Eu(β-diketonate)$_3$ complexes by near-UV light results in the observation of fairly intense emission in the red region of the spectrum. This emission consists of transitions from the excited $^5D_0$ Eu(III) level to the $^7F_0$ ($\sim$580 nm), $^7F_1$ ($\sim$595 nm), and $^7F_2$ ($\sim$615 nm) ground-state levels. In most of these β-diketone complexes, the 0–0 and 0–1 transitions are of approximately equal intensity, and the 0–2 transition is typically 1 order of magnitude more intense (we shall label the emissions according to their J quantum numbers). In all chiral Eu(III) β-diketonate complexes whose CPL has been reported so far,[12] no CPL has ever been found in the 0–0 transition. The CPL of the 0–1 and 0–2 transitions has roughly the same intensity.

The CPL measurement actually results in the detection of two quantities. One is the total luminescence (TL) intensity, usually given by eq 1, and the other is the circularly polarized

$$I = \tfrac{1}{2}(I_L + I_R) \quad (1)$$

luminescence (CPL) intensity (eq 2). In eq 1 and 2, I_L and

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

I_R represent the emitted intensities of left and right circularly polarized light, respectively. Since I and ΔI are measured in arbitrary quantal units, it is common practice to calculate the luminescence dissymmetry factor, g_{lum}, by taking the ratio of these quantities (eq 3), and thus eliminating any unit dependence.[8] The g_{lum} has theoretical as well as experimental significance, as it may be related to the rotational strength of the transition[8] (eq 4), where R_{ab} is the rotatory strength (eq 5)

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

$$g_{lum} = 4R_{ab}/D_{ab} \quad (4)$$

$$R_{ab} = \mathrm{Im}\langle \Psi_a|\hat{\mu}|\Psi_b\rangle\langle \Psi_b|\hat{m}|\Psi_a\rangle \quad (5)$$

and D_{ab} is the dipole strength (eq 6). Equations 4–6 are valid

$$D_{ab} = \langle \Psi_a|\hat{\mu}|\Psi_b\rangle^2 \quad (6)$$

for randomly oriented emitting systems in which the luminescent excited state is thermally equilibrated prior to emission. It should be noted that, while the value of g_{lum} has little theoretical significance without a detailed analysis of the CPL line shape, values of g_{lum} may be compared to each other to evaluate trends in the data that may be correlated with changes in complex structure.[8]

When Eu(ttfa)$_3$ was allowed to complex with the amino alcohols in $CHCl_3$ solution, it was found that the TL intensity increased more than threefold relative to the TL of uncomplexed chelate. As may be seen in Figure 2, the TL typically increases very rapidly and finally reaches an apparently constant value after the addition of 4 equiv of amino alcohol/mol of Eu(ttfa)$_3$. Calculation of association constants from these intensity enhancements is quite easy in this low concentration region where only 1:1 complexes form, and we have previously outlined a method whereby this may be done.[13] An application of Job's method of continuous variations verified that only 1:1 chelate/substrate adducts formed when the substrate concentration was less than 2.1 mM. The formation constants have been collected in Table I.

In an earlier study, it was found that Eu(ttfa)$_3$ would form strong adducts with amine substrates but that apparently this chelate did not bind alcohol substrates.[14] It was found that log K_1 for primary amines was about 4.1 and log K_1 for sec-

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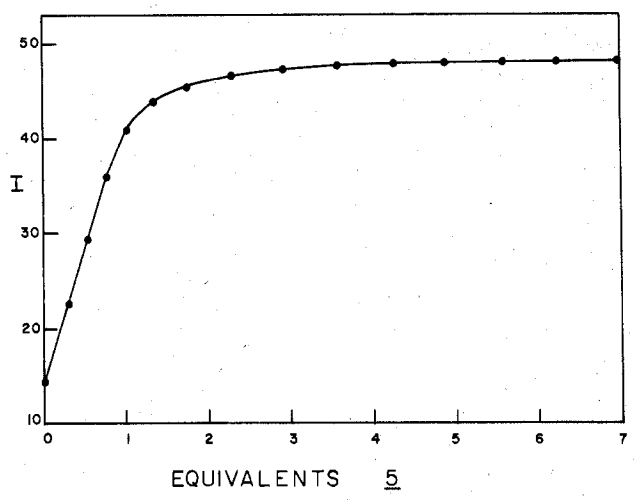

Figure 2. Luminescence titration of Eu(ttfa)$_3$ with (*S*)-2-amino-3-methyl-1-butanol (**5**). The intensity units are arbitrary.

Table I. Formation Constants of the Eu(ttfa)$_3$/Amino Alcohol Adducts

amino alcohol	log K_1 [a]	log K_2 [b]	log K_{12}
(*S*)-2-amino-3-phenyl-1-propanol (**3**)	4.39	1.18	5.57
(*S*)-2-amino-1-propanol (**1**)	4.40	1.84	6.24
(*R*)-2-amino-2-phenylethanol (**7**)	4.40	1.61	6.01
(*R*)-2-amino-1-butanol (**2**)	4.43	1.69	6.12
(*S*)-2-amino-4-methyl-1-pentanol (**4**)	4.49	1.08	5.57
(*S*)-2-amino-3-methyl-1-pentanol (**6**)	4.54	1.46	6.00
(*S*)-2-amino-3-methyl-1-butanol (**5**)	4.54	1.47	6.01

[a] Values are calculated from intensity data alone, and the associated error is estimated to be ±0.04 log units. [b] Values are calculated from both intensity and CPL data, and the error associated with these values is estimated to be ±0.07 log units.

ondary and tertiary amines was in the 4.35–4.40 range. These more hindered amine substrates bear a strong structural resemblance to compounds **1**–**3** and **7** of the present work, and indeed the formation constants fall within the same range. Compounds **4**–**6** clearly possess a better stereochemistry for binding to Eu(ttfa)$_3$. Since these compounds represent the most sterically hindered of all the substrates, it may be concluded that the "pocket" available on the inner coordination sphere of Eu(ttfa)$_3$ for substrate binding is fairly large and that most efficient binding of the substrate is possible if the substrate is capable of completely filling the available area.

Addition of large quantities of all amino alcohols resulted in an additional 10% increase in emission intensity after the apparent leveling off previously noted. This subsequent increase must be due to the formation of a 1:2 chelate/substrate adduct, and it proved possible to calculate formation constants for reaction 7. In eq 7, EuS stands for the Eu(ttfa)$_3$ chelate.

$$\mathrm{EuS} + \mathrm{S} \rightleftharpoons \mathrm{EuS_2} \qquad (7)$$

While the error associated with the calculation of log K_2 from the intensity data was somewhat larger than the error associated with the log K_1 values, it still proved possible to calculate values of reasonable accuracy. The set of log K_2 association constants are also found in Table I, and these results were actually confirmed from CPL data, as will be shown shortly.

It may be seen that Eu(ttfa)$_3$ only adds the second substrate molecule with difficulty, with the log K_2 values averaging nearly 3 orders of magnitude smaller than the log K_1 values. Considerable variation could be observed in association constants, and in general the less sterically hindered was the amino group, the greater the formation constant. This trend provides more information regarding the nature of the "pocket" available for adduct formation: after the first molecule of substrate is bound (and the largest substrates bind most efficiently), a second molecule experiences considerable difficulty in binding to this chelate and the steric nature of the substrate plays a vital role in determining the extent of this additional binding. The combination of these effects leads to an interesting set of overall association constants, calculated from eq 8. Because of the opposing trends in K_1 and K_2 values, Eu-

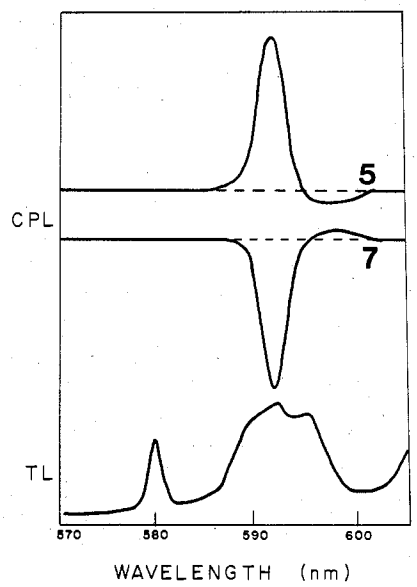

Figure 3. Total luminescence (bottom) of and circularly polarized luminescence associated with the $^5D_0 \rightarrow {}^7F_1$ transition of Eu(ttfa)$_3$ adducts. Spectra obtained for (*S*)-2-amino-3-methyl-1-butanol (**5**) and (*R*)-2-amino-2-phenylethanol (**7**) are shown; all intensity units are arbitrary.

$$\mathrm{Eu} + 2\mathrm{S} \rightleftharpoons \mathrm{EuS_2} \qquad (8)$$

(ttfa)$_3$ adducts with compounds **1**, **2**, and **5**–**7** have essentially identical values for log K_{12}, while the totally unrelated compounds **3** and **4** have considerably smaller and yet identical association constants, as may be seen in Table I.

When the 1:1 Eu(ttfa)$_3$/amino alcohol adducts are formed, a reasonably strong CPL appears in the 0–1 and 0–2 emission bands. The CPL associated with all adducts appeared qualitatively alike and only differed in the sign of the CPL. Representative examples of 0–1 TL and CPL are shown in Figure 3, and 0–2 spectra may be found in Figure 4. The CPL associated with each band system consisted of one major and one minor peak, and the sign of the CPL associated with the major CPL peak could be exactly correlated with the absolute configuration of the chiral amino alcohol. The general rule is that, when the chiral substrate has the *R* configuration, the CPL associated with the 0–1 peak will be predominantly negative and the CPL of the 0–2 band will be of positive sign. This observation agrees with earlier work[12] where a similar CPL was induced in a variety of Eu(III) β-diketone complexes by (*R*)-α-phenethylamine.

Two mechanisms may be proposed to account for the optical activity induced by the chiral substrates: (1) the chiral substrate might perturb the disastereomer interconversion of the labile tris chelates and generate one specific enantiomer, or (2) the formation of a stable adduct would bring the asymmetric center of the substrate into close contact with the Eu(III) ion and thus induce chirality in the f–f transitions by means of a vicinal effect. Since in the previous sections, it has been demonstrated that Eu(ttfa)$_3$ forms strong adducts with

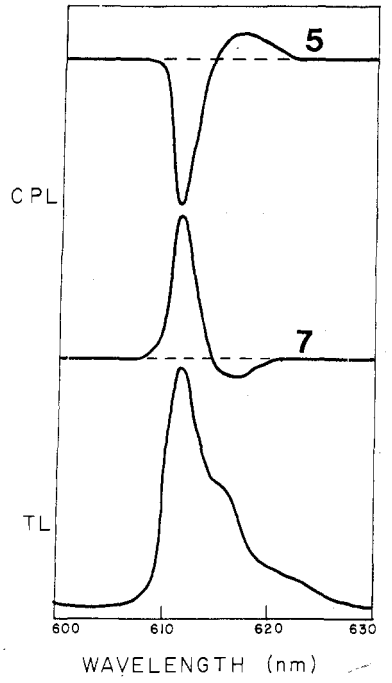

Figure 4. Total luminescence (bottom) and circularly polarized luminescence associated with the $^5D_0 \rightarrow {}^7F_2$ transition of $Eu(ttfa)_3$ adducts. Spectra obtained for (*S*)-2-amino-3-methyl-1-butanol (**5**) and (*R*)-2-amino-2-phenylethanol (**7**) are shown.

the substrates used in this work, the latter explanation is to be strongly favored.

Values for the luminescence dissymmetry factor were computed at each of the major CPL extrema according to eq 3, and the results obtained for the 0–1 and 0–2 transitions are shown in Table II. A general trend is immediately apparent, in that strongest CPL (as evidenced by the largest g_{lum} values) is associated with substrates that contain the greatest degree of steric crowding α to the coordinating amino group (**5**–**7**). When the alkyl side chain is moved β to the amino group (**3**, **4**), the degree of CPL decreases further, and when it is removed entirely (**1**, **2**), the observed CPL is found to be the weakest. This trend does not follow that found for the log K_1 constants and therefore suggests that electronic effects play a very important role in the inducement of optical activity. No correlation could be obtained in an attempted linear free-energy relationship involving g_{lum} values and steric constants.[15] It is significant to note that the strongest CPL intensities were obtained when an aromatic ring was attached α to the amino group but that the CPL intensity dropped drastically when this group was moved one carbon further away.

Addition of excess substrate to a solution containing 1:1 chelate/substrate adduct led to a modest increase in emission intensity but usually a large increase in CPL intensity. By examining the change in CPL intensity relative to the plateau values obtained after formation of the 1:1 adducts, it was possible to calculate reliable values for log K_2 according to eq 8. These values agreed excellently with the data presented in Table I. One is therefore able to conclude that the changes in CPL intensity that occur upon addition of excess substrate arise from further perturbation of the chelate stereochemistry. In most cases, the 1:2 adduct shows a greater degree of chirality, but for the substrate **7**, the addition of the second molecule of substrate clearly induces a stereochemistry whose CPL opposes that of the 1:1 adduct. This reinforcement or destruction of vicinal effects would properly be termed a configurational effect.

(15) E_s constants were obtained from: Fujita, T.; Takayama, C.; Nakajima, M. *J. Org. Chem.* **1973**, *38*, 1623. Mac Phee, J.-A.; Panaye, A.; DuBois, J.-E. *Ibid.* **1980**, *45*, 1164.

Table II. Luminescence Dissymmetry Factors Obtained for the $Eu(ttfa)_3$/Amino Alcohol Adducts

amino alcohol	$10^2 g_{lum}$ ($^5D_0 \rightarrow {}^5F_1$)		$10^3 g_{lum}$ ($^5D_0 \rightarrow {}^7F_2$)	
	a	*b*	*a*	*b*
(*S*)-2-amino-1-propanol (**1**)	+2.34	+5.20	−2.88	−4.28
(*R*)-2-amino-1-butanol (**2**)	−2.56	−4.50	+3.08	+4.56
(*S*)-2-amino-3-phenyl-1-propanol (**3**)	+3.50	+4.34	−3.24	−3.64
(*S*)-2-amino-4-methyl-1-pentanol (**4**)	+5.38	+6.20	−4.74	−5.32
(*S*)-2-amino-3-methyl-1-pentanol (**6**)	+5.62	+6.56	−5.68	−5.90
(*S*)-2-amino-3-methyl-1-butanol (**5**)	+5.84	+8.40	−6.12	−8.60
(*R*)-2-amino-2-phenylethanol (**7**)	−6.24	−2.84	+6.86	+5.00

[a] Results calculated at approximately 1:6 $Eu(ttfa)_3$:amino alcohol ratios. [b] Results calculated after addition of neat amino alcohol to $Eu(ttfa)_3$ solution in the fluorescence cuvette.

Taken together, the data enable one to draw certain conclusions regarding the process of adduct formation in $Eu(ttfa)_3$ chelates. Addition of one molecule of substrate is very favorable, and the better a substrate is able to fit into the coordination site available for bonding, the more robust the adduct will be. An interesting sidelight is that, were it not for the low solubility of the $Eu(ttfa)_3$ chelate in most common solvents, its large formation constants with amino substrates would make this compound a preferred NMR shift reagent.[14] The binding of a second molecule of substrate is much more difficult, and a certain degree of selectivity is found. When a bulky alkyl group is located two positions from the coordinating amino group (**3**, **4**), the weakest overall coordination is found. This observation strongly suggests that the steric interference with the alkyl groups of the β-diketone rings becomes quite important for long-chain substrates and is relatively unimportant for short-chain substrates.

In the TL spectra, three components are clearly visible within the 0–1 emission band. This transition only contains three possible crystal field transitions, and the observation of all three implies that axial symmetry is not present in the $Eu(ttfa)_3$ adducts (even in the 1:1 adducts). This last point is of considerable importance, since most quantitative calculations involving lanthanide shift reagents assume an axial symmetry.[3]

Finally, the g_{lum} values recorded during the course of the present work are 1 order of magnitude smaller than the values found for Eu(III) β-diketonate complexes exhibiting configurational optical activity.[12] One is then able to conclude that we have indeed observed vicinal effects in our present study of induced optical activity. CPL spectroscopy is therefore an excellent probe of lanthanide optical activity and has been shown to yield new information regarding the adduct formation process. Further studies are clearly called for and are presently under way in our laboratory.

Acknowledgment. This work was supported by the Research Corp., through Grant 8926 of the Cottrell Research Program.

Registry No. $Eu(ttfa)_3$·**1**, 74808-35-8; $Eu(ttfa)_3$·**21**, 74808-36-9; $Eu(ttfa)_3$·**2**, 74808-37-0; $Eu(ttfa)_3$·**22**, 74808-38-1; $Eu(ttfa)_3$·**3**, 74808-39-2; $Eu(ttfa)_3$·**23**, 74808-40-5; $Eu(ttfa)_3$·**4**, 74808-41-6; $Eu(ttfa)_3$·**24**, 74808-42-7; $Eu(ttfa)_3$·**5**, 74808-43-8; $Eu(ttfa)_3$·**25**, 74808-44-9; $Eu(ttfa)_3$·**6**, 74808-45-0; $Eu(ttfa)_3$·**26**, 74808-46-1; $Eu(ttfa)_3$·**7**, 74808-47-2; $Eu(ttfa)_3$·**27**, 74808-48-3; $Eu(ttfa)_3$, 14054-87-6.