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Evidence for Schiff Base Formation in the Addition of Amino Alcohols to the Eu(III) Chelates of Benzoylacetone and Dibenzoylmethane

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The adduct formation between $Eu(DBM)_3$ (DBM = dibenzoylmethane) and $Eu(BZAC)_3$ (BZAC = benzoylacetone) has been studied by means of circularly polarized luminescence (CPL) spectroscopy. The Eu(III) chelates were titrated with small amounts of chiral substrates (phenylalkylamines and phenylalkylamino alcohols) and it was found that the spectra drastically changed both sign and magnitude during the course of the CPL titrations. The presence of Schiff base ligands resulting from condensation of the β-diketone ligands and the added amino alcohols was established from infrared spectra of the products. This Schiff base is capable of being formed even if the β-diketone is already coordinated to the Eu(III) ion.

Introduction

Since the first discovery by Hinckley [1] that lanthanide chelates of β-diketones are capable of functioning as paramagnetic shift reagents in NMR spectroscopy, an enormous amount of research has focused on the properties and applications of these compounds [2]. The field has been reviewed many times [3–5]. One of the features that is vital to the use of these reagents is their stability in the presence of chelating substrates, and any attempted conformational analysis must assume that formation of the chelate/substrate adduct does not perturb the configurational properties of the uncomplexed substrate.

We have carried out a number of studies in which the process of adduct formation involving Eu(III) β-diketonate complexes has been followed using techniques associated with luminescence spectroscopy. In a series of works primarily involving fluorinated β-diketone complexes, we have used luminescence intensity enhancements to evaluate association constants of the adduct complexes [6–9]. In addition, we have used circularly polarized luminescence (CPL) spectroscopy to study the stereochemistries and bonding modes in adducts containing chiral ligands [10–14]. One generally finds during the course of a CPL titration that a basic lineshape develops with the formation of small amounts of the adduct complex, and that this lineshape merely intensifies as the uncomplexed chelate is converted into the adduct. Once the chelate/substrate adduct is fully formed, no further change in CPL lineshape or intensity is observed.

However, while investigating the adduct formation associated with the addition of amino alcohol substrates to β-diketone complexes not containing fluorinated ligands it was observed that the CPL lineshape often underwent substantial modifications as substrate was added. In some cases, the spectra completely inverted, implying that the adduct had undergone a drastic change in stereochemistry as a result of interaction with the amino alcohol substrate. Such a change in CPL lineshape is unprecedented, and clearly must be due to a chemical reaction taking place between the Eu(III) chelate (or its coordinated ligands) and the substrate. It is well known that β-diketones and amines can undergo condensation to yield Schiff base ligands. The Schiff base derivatives containing fluorinated β-diketone functionalities are prone toward hydrolysis [15], which would explain the absence of such a condensation reaction in our earlier work [14]. In our present work, we present evidence to show that the Eu(III) chelates of 1-phenyl-1,3-butanedione (benzoylacetone, or BZAC) and 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, or DBM) are capable of forming Schiff base complexes with several chiral amino alcohols, *even if the β-diketone ligands are already coordinated to the Eu(III) ion.* Our primary evidence comes from detailed CPL titrations of the Eu(III) chelates with the substrates,

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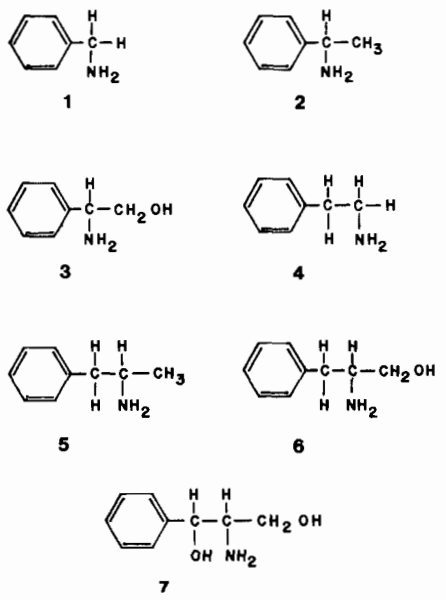


Fig. 1. Structures of the chiral substrates used in this study.

although other evidence is also available. Structures of the substrates used in the present study are shown in Fig. 1.

Experimental

$Eu(BZAC)_3$ was prepared and dehydrated according to the procedure of Charles [16], while a related procedure was employed for preparation of the $Eu(DBM)_3$ chelate [17]. For these syntheses, $EuCl_3 \cdot 6H_2O$ (99.9% pure, obtained from Alfa Inorganics) was used as the source of lanthanide ion, and the free DBM and BZAC ligands were used as received from Eastman. Benzylamine (*1*), D-α-phenylglycinol (*3*), β-phenethylamine (*4*), L-phenylalaninol (*6*), and (+)-2-amino-1-phenyl-1,3-propanediol (which shall be termed APPD) (*7*) were all obtained from Aldrich. (+)-α-phenethylamine (*2*) was obtained from Norse Laboratories, While D-α-methylphenethylamine sulfate (*5*) was purchased from Sigma. Substrate *5* was converted to the free base by neutralization with aqueous NaOH, extraction of the free amine into diethyl ether, and subsequent evaporation of the ether layer. The absolute configuration of each asymmetric atom in the chiral substrates is available in the literature [18].

Stock solutions of the Eu(III) chelates were made up in dried $CHCl_3$, with an initial $Eu(DBM)_3$ concentration of 1.1 m*M* and $Eu(BZAC)_3$ concentration of 1.4 m*M* being used. Stock solutions of each substrate were made up in the concentration range of 0.1 to 0.15 *M*, and these were added in microliter quantities to 3.0 ml of the $Eu(DK)_3$ solution already in 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 insure complete formation of the $Eu(DK)_3$ adduct.

All luminescence and CPL spectra were obtained on an instrument constructed in this laboratory, and which has recently been described in detail [19]. An excitation wavelength of 365 nm was used for all studies (obtained by passing the output of a 200 watt Hg-Xe arc lamp through a 0.1 meter grating monochromator), and a 16 nm bandpass was employed. The emission was collected at 180 °C 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 meter 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.

Further characterization of the chelate/substrate adduct complexes was obtained by measuring the low-temperature, high-resolution luminescence spectra of solid material obtained by evaporation of the $CHCl_3$ solvent after completion of a CPL titration. These spectra were obtained by exciting the Eu(III) sample with the 325 nm output of a He-Cd laser (Liconix model 4050), and analyzing the Eu(III) luminescence at right angles. The emission could be processed at 1 Å resolution through a 1-meter grating monochromator (Spex Industries model 1703), and was detected by an EMI 9558 B photomultiplier tube (S-20 response and cooled to −20 °C in an EMI Fact-50 thermoelectric cooler). The samples were routinely cooled to 15 K in a closed-cycle gaseous helium refrigerator system (Lake Shore Cryotronics model LTS-21-D80C).

Results and Discussion

Irradiation of $Eu(DK)_3$ complexes in the near-UV region of the spectrum results in efficient absorption of the excitation energy, and frequently to fairly intense emission in red spectral regions. In fluid solution at room temperature, luminescence

TABLE I. Association Constants for the 1:1 Adducts Formed Between Phenylalkylamines and $Eu(BZAC)_3$ and $Eu(DBM)_3$.[a]

Substrate	K_1 ($Eu(BZAC)_3$)	K_1 ($Eu(DBM)_3$)
1, Benzylamine	7.5	43.8
2, α-phenethylamine	5.8	35.0
4, β-phenethylamine	11.0	64.3
5, α-methylphenethylamine	8.5	51.4

[a]The formation constants associated with the $Eu(BZAC)_3$ adducts have approximately a 10% error associated with them, while only a 5% error is associated with results corresponding to the $Eu(DBM)_3$ adducts.

originates 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 one defines a new quantity, the luminescence dissymmetry factor, as:

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

While the TL and CPL are routinely obtained in arbitrary units, the luminescence dissymmetry is an absolute quantity having no unit dependence. In principle, the g_{lum} factor may be related to the rotational strength of the transition [20], although such calculations require more detailed knowledge regarding the spectral transitions than is currently available.

Addition of one of the simple phenalkylamines (substrates *1*, *2*, *4*, or *5*) to a $CHCl_3$ solution of either $Eu(BZAC)_3$ or $Eu(DBM)_3$ results in small increases in the TL intensity. No CPL appeared in the luminescence spectra, however, when the chiral *2* or *5* substrate adducts were formed. We had previously noted this behavior in a previous study of adducts formed between *2* and $Eu(BZAC)_3$ and $Eu(DBM)_3$ [21]. However, by using the computational methods described in our earlier works [6–9] one can use the luminescence intensity enhancements to obtain association constants for the 1:1 chelate substrate adducts.

The association constants thusly calculated have been collected in Table I, and the values are found to be one order of magnitude smaller than those found for the Eu(III) chelate of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione (FOD) and two orders of magnitude smaller than the Eu(III) chelate of theonyltrifluoroacetone (TTFA) [14]. This behavior is consistent with the lower Lewis acidity of the BZAC and DBM chelates compared to the TTFA and FOD chelates. It is general property of the Eu(III) chelates that Lewis acidity increases with increasing fluorine substitution on the β-diketone ligand [2]. The low values of the association constants are certainly a consequence of the requirement that the simple phenylakylamines can only bind the Eu(III) ion in a monodentate fashion.

The constants shown in Table I clearly demonstrate that the $Eu(DBM)_3$ chelate is a stronger Lewis acid toward monodentate phenylalkylamines compared to the less-substituted $Eu(BZAC)_3$. Both of these materials are much poorer Lewis acids than any chelate containing fluorinated groups [22], and a comparison of the present results with our previously communicated work involving fluorinated β-diketone complexes [14] is supportative of these general trends. The lack of discernable optical activity accompanying the adduct formation between $Eu(DBM)_3$ and $Eu(BZAC)_3$ and *2* or *5* argues that the weak adducts are characterized by rather non-specific binding.

A very different situation is observed when one adds either phenylglycinol or phenylalaninol to a $CHCl_3$ solution of either $Eu(BZAC)_3$ or $Eu(DBM)_3$. Here, the formation of the adduct complex is accompanied by the appearance of strong CPL and one can conclude immediately that the mode of substrate binding by the Eu(III) ion must be quite different in

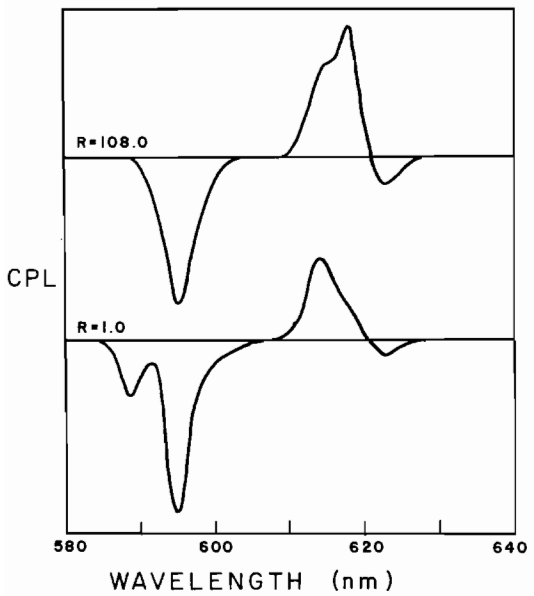


Fig. 2. CPL spectra obtained for $Eu(BZAC)_3$ during various stages of titration with L-phenylalaninol (substrate *6*). The spectra are shown in arbitrary units, and quantitative information should be obtained from Table II. Spectra corresponding to substrate/chelate ratios of 1.0 (lower) and 108.0 (upper) are shown.

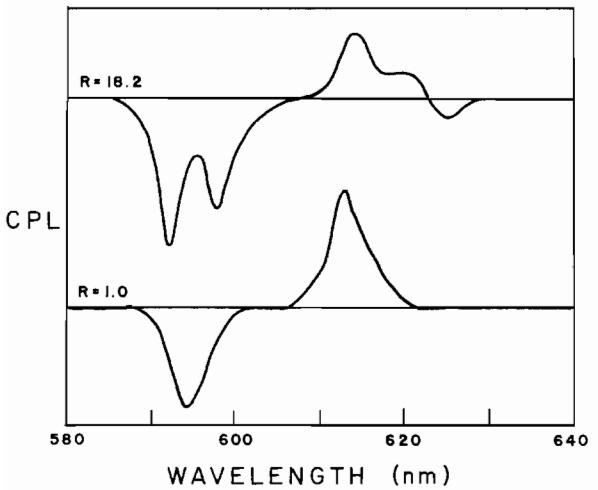


Fig. 3. CPL spectra obtained from $Eu(DBM)_3$ during titration with L-phenylalaninol (substrate *6*). Quantitative information is to be found in Table III, and spectra corresponding to substrate/chelate ratios of 1.0 (lower) and 18.2 (upper) are shown.

the case of the amino alcohols. A basic CPL lineshape develops almost immediately, but further addition of substrate results in drastic changes in the CPL spectra. The data shown in Figs. 2–5 clearly illustrate that complete sign inversions accompany the various stages of adduct formation. Our previous studies had shown that in all other cases, the basic

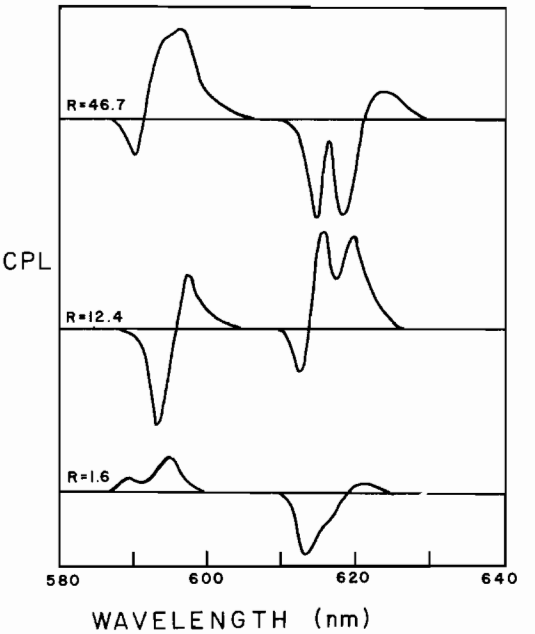


Fig. 4. CPL spectra obtained for $Eu(BZAC)_3$ during titration with D-phenylglycinol (substrate *3*). Spectra are shown for substrate/chelate ratios of 1.6 (lower), 12.4 (middle), and 46.7 (upper).

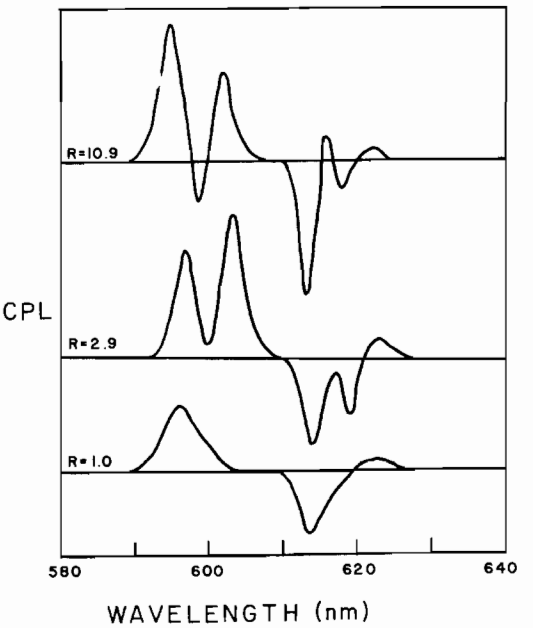


Fig. 5. CPL spectra obtained for $Eu(DBM)_3$ during titration with D-phenylglycinol (substrate *3*). Spectra are shown for substrate/chelate ratios of 1.0 (lower), 2.9 (middle), and 10.9 (upper).

CPL lineshape merely intensifies during the course of a CPL titration and this CPL eventually reached a limiting value as the adduct was fully formed.

TABLE II. Luminescence Dissymmetry Factors Associated with the Major CPL Peaks of the $Eu(BZAC)_3$ Complexes.

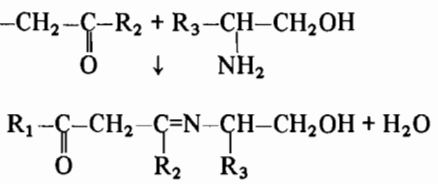
Ratio (substrate/chelate)	Wavelength (nm)	$g_{lum} \times 10^2$ (0–1)	Wavelength (nm)	$g_{lum} \times 10^3$ (0–2)
(*a*) Phenylglycinol (*3*) substrate				
1.6	589	+0.60	613	–1.6
	594	+1.1		
12.4	593	–1.6	612	–0.22
	597	+1.0	615	+0.60
			619	+0.93
46.7	590	–0.84	614	–2.8
	595	+2.2	617	–2.9
			623	+2.6
(*b*) Phenylalaninol (*6*) substrate				
1.0	588	–1.7	613	+4.2
	594	–4.0		
108.0	594	–2.1	617	+5.0
(*c*) APPD (*7*) substrate				
1.8	593	+16.0	612	–6.8
			617	–4.5
			620	–9.8
3.7	590	–7.5	613	+9.6
	596	–2.1	618	+5.1
			623	–15.0

TABLE III. Luminescence Dissymmetry factors Associated with the major CPL Peaks of the $Eu(DBM)_3$ Complexes.

Ratio (substrate/chelate)	Wavelength (nm)	$g_{lum} \times 10^2$ (0–1)	Wavelength (nm)	$g_{lum} \times 10^3$ (0–2)
(*a*) Phenylglycinol (*3*) substrate				
1.0	596	+1.7	613	–2.6
2.9	597	+2.0	614	–2.2
	604	+2.3	620	–2.4
			623	+2.5
10.9	595	+3.9	613	–2.9
	598	–1.8	615	+0.65
	601	+2.7	618	–1.1
			622	+1.6
(*b*) Phenylalaninol (*6*) substrate				
1.0	594	–1.8	612	+3.5
18.2	592	–1.3	613	+1.7
	598	–1.2	625	–2.0
(*c*) APPD (*7*) substrate				
0.25	594	+4.5	612	–4.8
			620	+5.3
3.1	590	–14.0	613	+9.3
	597	–5.6	618	+7.7
			622	–13.9

Eventually, the CPL associated with the $Eu(DBM)_3$ or $Eu(BZAC)_3$ chelate adducts did reach limiting values, but these limits were found to require the addition of large excesses of substrate relative to the amount of Eu(III) chelate that was present initially. It was noted that the BZAC adducts required 4–5 times as much substrate relative to the DBM complexes before the CPL reached its final lineshape and magnitude. The dissymmetry factors of the major CPL bands which correspond to the spectra of Figs. 2–5 are shown in Tables II and III.

It is quite clear that some sort of chemical reaction is taking place between the Eu(III) chelates and the amino alcohol substrates. It is well known that β-diketone ligands are capable of condensing with amino alcohols, forming Schiff base ligands in the process:



The Schiff base formed in this process is capable of binding the Eu(III) ion in a terdentate manner.

The formation of Schiff base ligands was proven by isolating the Eu(III) complex formed at the end of the CPL titrations, and obtaining the IR spectrum of the complex. In all cases, the new IR band appeared around 1630 cm^{-1}, which is exactly the spectral region in which a C=N band should appear [15, 24, 25]. The compound formed was shown to be pure by measuring the luminescence spectrum of the $^5D_0 \rightarrow {}^7F_0$ emission band at 77 K, since this particular band cannot be split by any crystal field and the presence of more than one line is proof of the existence of more than one emitting species. Under 1 Å resolution, only a single line was observed, which we take as confirmation that only one type of adduct complex is formed at the end of the titration.

With these observations in hand, it is possible to draw certain conclusions regarding the CPL spectra of Figs. 2–5. The first basic lineshape noted for each chelate cannot be due to simple adduct formation of the type:

$$Eu(DK)_3 + S \rightleftharpoons Eu(DK)_3(S) \quad (4)$$

(DK represents the DBM or BZAC β-diketone ligands and S represents the chiral amino alcohol substrate) since the sign of the CPL peaks of the $^5D_0 \rightarrow {}^7F_1$ (which shall be termed the 0–1 transition) and the $^5D_0 \rightarrow {}^7F_2$ transitions (the 0–2 transition) are found to be exactly opposite in sign to analogous complexes where simple adduct formation is known to take place [13, 14, 23]. In addition, the magnitude of the observed optical activity is significantly lower than found in the earlier work. It is presumed that the actual process which takes place can be described by:

$$Eu(DK)_3 + S \rightleftharpoons Eu(DK)_2(SDK) \quad (5)$$

where SDK represents the Schiff base formed by the condensation of the amino alcohol and the β-diketone.

We have verified that the absolute configuration of the asymmetric atom in the amino alcohol does not change on formation of the Schiff base (from measurements of optical rotation of the independently synthesized ligand), and therefore conclude that the opposite signs noted in the DMB and BZAC chelate products are indeed the result of a chemical reaction, and do not represent inversion of the asymmetric carbon. The sign of the CPL is still dictated by the chirality sense of the ligand, however, as the phenylalaninol complexes (S configuration) display opposite signs relative to the phenylglycinol complexes (R configuration).

With the absolute configuration of the ligand remaining unchanged, one must conclude that a simple vicinal effect (chirality resulting from the presence of an asymmetric atom in the bonded ligands) cannot account for the observed optical activity. Configurational effects (chirality resulting from an asymmetric placement of ligands about the Eu(III) ion) would not be anticipated since the remaining DK ligands are achiral. We conclude that in the early stages of the CPL titration, the observed optical activity is determined by conformational effects (chirality due to asymmetric chelate ring conformations). Simple adducts of amino alcohols are also characterized by conformational effects [14] and we propose here that a different conformation of the Schiff base ligand is responsible for the opposite sign found in the CPL spectra. The similarity of the two sets of DBM spectra (as well as similarities in the two sets of BZAC spectra) provide further support for a conclusion linking the observed optical activity to properties related solely to ligand conformations.

Continued addition of amino alcohol substrate to the $Eu(BZAC)_3$ or $Eu(DBM)_3$ solutions results in further changes in the CPL spectra. With phenylalaninol, the degree of optical activity remains approximately constant (with the TL intensity increasing drastically), and with only small changes taking place in the CPL spectra (see Figs. 2–5). However, with addition of phenylglycinol, much more dramatic changes are noted. The dissymmetry factors do not change a great deal, but new and unusual CPL lineshapes appear. These argue for the further formation of Schiff base products:

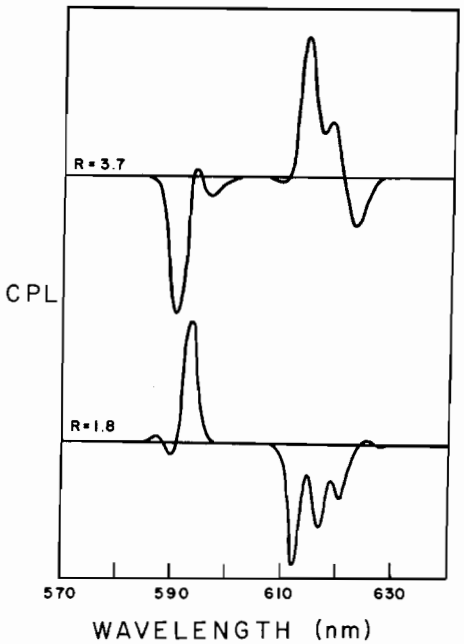


Fig. 6. CPL spectra obtained for $Eu(BZAC)_3$ during titration with (+)-2-amino-1-phenyl-1,3-propanediol (substrate *7*). Spectra are shown for substrate/chelate ratios of 1.8 (lower) and 3.7 (upper).

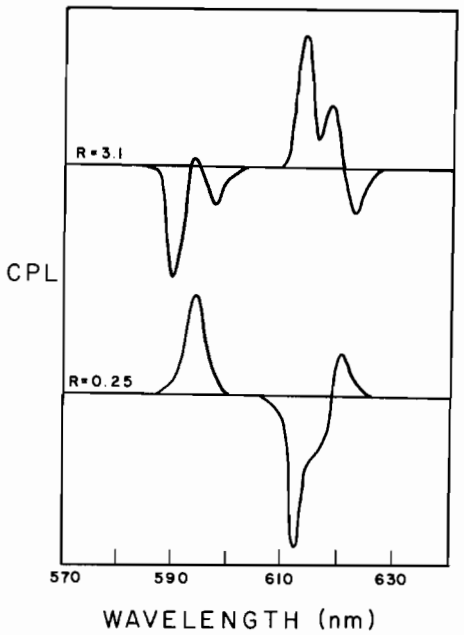


Fig. 7. CPL spectra obtained for $Eu(DBM)_3$ during titration with (+)-2-amino-1-phenyl-1,3-propanediol (substrate *7*). Spectra are shown for substrate/chelate ratios of 0.25 (lower) and 3.1 (upper).

$$Eu(DK)_2(SDK) + S \rightleftharpoons Eu(DK)(SDK)_2 \quad (6)$$

It is believed that the unreacted DK remains attached to the Eu(III) ion since independently synthesized $Eu(SDK)_2$ has completely different CPL spectra [26]. Coordinated DK is still visible in the IR spectrum of the isolated reaction product.

The Schiff base formation is much more efficient for the phenylglycinol complexes compared to the phenylalaninol complexes, and the DBM chelates form Schiff base complexes more readily than do the BZAC chelates (these conclusions are illustrated by the ratios of substrate/chelate required to achieve the spectra of Figs. 2–5). These trends are undoubtably a combination of steric and electronic effects and cannot be detailed properly at the present time. We have not been able to use our luminescence titration method to calculate association constants for the complexes as the presence of different ligands changes the inherent quantum yield of the Eu(III) ion in a way which may not be related to the degree of complexation.

With the APPD ligand (substrate *7*), the CPL spectra reveal that similar trends are followed. This ligand, however, contains two asymmetric atoms of the same (S,S) configuration, and each atom is capable of being placed in a chelate ring. We believe that all three atoms of the APPD ligand must be involved in the bonding, as the initial spectra shown in Figs. 6 and 7 are opposite in sign to those shown for S-phenylalaninol in Figs. 2 and 3. In addition, the degree of optical activity (as evidenced from the dissymmetry factors in Tables II and III) is significantly stronger for APPD relative to phenylalaninol. Formation of the Schiff base in the initial stages is indicated by the drastic differences in CPL spectra noted when one compares the results found for $Eu(DBM)_3$/APPD and $Eu(BZAC)_3$/APPD with corresponding spectra already obtained for the APPD adducts of $Eu(FOD)_3$ and $Eu(TTFA)_3$ [14]. The CPL spectra associated with the 0–1 emission bands are quite similar, but significant differences can be noted when one compares the 0–2 spectral results. In addition, comparison of the dissymmetry factors of Tables II and III reveals that the BZAC complex is much more chiral than the DBM complex. These observations suggest that while some degree of similarity in stereochemistry is present, each complex ultimately adopts a slightly different configuration. This feature is undoubtably a consequence of the extra steric bulk of the DBM ligand relative to the BZAC ligand.

Continued addition of APPD ligand to either $Eu(BZAC)_3$ or $Eu(DBM)_3$ results in a slight intensification of the TL spectrum, but also in a complete inversion of the CPL spectra. In the case of the DBM chelate, this inversion is quite dramatic and sudden, and occurs at fairly low concentrations of APPD

substrate (the entire inversion takes place when between 0.40 and 0.45 equivalents of APPD per mol of $Eu(DBM)_3$ are added). For the $Eu(BZAC)_3$ chelate, the change is not quite as sharp, and is complete by the time 2.6 equivalents of substrate are added. These ratios are considerably lower than those required for similar processes with the simple amino alcohols (substrates *3* and *6*), and indicate that the extra hydroxyl group of the APPD ligand must be involved in the complex bonding. The low ratios of substrate required to achieve further Schiff base formation argue that as the ligand is more able to fill coordinating positions on the Eu(III) ion, macrocyclic binding becomes more efficient. We are currently studying this problem in detail [26].

It is quite interesting to note that the CPL spectra reached after several equivalents of APPD are added are essentially the same for the DBM and BZAC complexes. In fact, the dissymmetry factors of the two sets of limiting CPL spectra are essentially the same. These results strongly suggest that the stereochemistry in the two products is essentially identical. Preliminary studies [26] on independently synthesized Schiff base complexes indicates that no uncomplexed β-diketone remains attached to the Eu(III) ion after formation of the second Schiff base ligand, which is not totally surprising when one considers that two APPD-Schiff base ligands would fill eight coordination positions on the metal.

We note finally, that in none of the Schiff base complexes were more than three bands observed in the 0–1 transition band, five in the 0–2 band, and one in the 0–0 band. These are the maximum number of allowed components possible for a single emitting Eu(III) species, and these results suggest that in each case, the spectra are characteristic of a single dominant Eu(III) complex.

Conclusions

In this work, we have demonstrated that the adduct formation which takes place when polyfunctional substrates are bound to lanthanide β-diketone complexes (and these are commonly used NMR shift reagents) can be accompanied by competing chemical reactions. Two important points must then be followed to minimize possible interferences in NMR work involving amines: (*a*) one should work *only* with fluorinated β-diketone ligands were Schiff base formation is unimportant, and (b) one should never work with large excesses of substrate relative to the amount of lanthanide chelate.

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