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Circularly Polarized Luminescence Studies of the Adducts Formed Between Tris(6,6,7,7,8,8,8-Heptafluoro-2,2-Dimethyl-3,5-Octanedionato)Europium(III) and Chiral Amino Alcohols

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The adduct formation between the title compound and five chiral amino alcohols was studied using circularly polarized luminescence (CPL) spectroscopy. In addition, association constants for the 1:1 adducts were calculated from emission titrations. The adducts were all found to contain the amino alcohol bound to the metal ion in a bidentate manner, resulting in eight-fold coordination of the Eu(III) ion. The signs of the CPL in the various emission bands could be correlated with the absolute configuration of the chiral substrate, and the CPL is postulated to arise from a combination of chiral vicinal and conformational effects. The CPL spectra contained evidence indicating that effective axial symmetry is not present in the adducts.

Introduction

While a great deal is known about the usefulness of lanthanide chelates as shifting reagents in nmr spectroscopy [1], much less information is available regarding the stoichiometries and stereochemistries of the adducts formed when a chelate combines with a substrate. Since quantitative analysis of LIS (lanthanide induced shift) data clearly requires the existence of this information, several groups have attempted to study the equilibria and stereochemistries associated with the adducts. Most of these efforts have involved an examination of the shift data itself [2, 3], but others have employed absorption spectra [4]. Other progress has been made by crystallizing the adducts and attempting to extrapolate the solid-state features determined from X-ray diffraction studies to the solution-phase chemistry [5, 6].

In our laboratory, we have investigated this problem by studying the changes in luminescence spectra as a function of adduct formation in Eu(III) complexes. We have developed methods whereby one can compute association constants for the chelate/substrate adducts [7–9] by carrying out an emission titration, and have studied the stereochemistries of the adducts by means of circularly polarized luminescence (CPL) spectroscopy [10–13]. These studies have proved quite fruitful in the characterization of these chelate adducts.

Recently, we examined the adduct formation of $Eu(TTFA)_3$ (TTFA = theonyltrifluoroacetone) and $Eu(FOD)_3$ (FOD = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) with a variety of chiral phenylalkylamines and phenylalkylamino alcohols with CPL spectroscopy, and were able to characterize for the first time a series of experimental observables which could be used to predict the mode of bonding between the chelate and the substrate [14]. In this latter study, evidence was presented which clearly indicates that a polyfunctional substrate can bind in a bidentate or in a terdentate manner to the $Eu(DK)_3$ chelate (DK = any achiral β-diketone ligand). In our current study, we wish to present investigations of the adduct formation between $Eu(FOD)_3$ and a series of potentially bidentate amino alcohols. We have already reported a preliminary investigation involving the $Eu(TTFA)_3$ adducts of the same amino alcohol substrates [13], but with the advances made recently [14] we are able to obtain further conclusions regarding this series of adducts. The amino alcohols we will discuss form a series in which steric effects vary in a systematic way and, therefore, enable an evaluation of the role which these effects play in the adduct formation. Structures of the amino alcohols used in this study are found in Fig. 1.

Experimental

The $Eu(FOD)_3$ chelate was purchased from Aldrich, as were all of the chiral amino alcohols. Each

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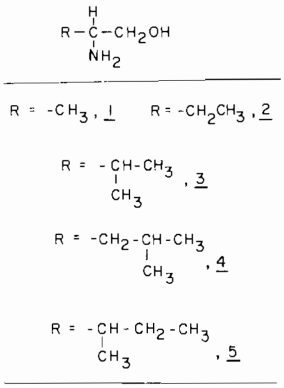

Fig. 1. Structures of the amino alcohols used in the present study.

material was used as received. The absolute configurations of (S)-2-amino-1-propanol (*1*, or alaninol), (R)-2-amino-1-butanol (*2*), (S)-2-amino-3-methyl-1-butanol (*3*, valinol), (S)-2-amino-4-methyl-1-pentanol (*4*, leucinol), and (S)-2-amino-3-methyl-1-pentanol (*5*, isoleucinol) were all obtained from the literature [15]. Stock solutions of Eu(FOD)$_3$ were made up in dried CHCl$_3$, using an initial concentration of 1.03 m*M*. Slow decomposition of the chelate was evident in old solutions by the formation of insoluble material, and as a result only fresh solutions were used. A stock solution (approximately 25 m*M*) of each amino alcohol was made up in CHCl$_3$, and this solution was added in microliter quantities to 3.0 ml of the Eu(FOD)$_3$ solution already in the fluorescence cuvette. The total luminescence (TL) and CPL spectrum was taken after the addition of each increment, and therefore TL and CPL titrations could be acquired. At the end of each titration, excess solid substrate was added to the cuvette to insure that complete formation of the adduct was achieved.

All CPL and luminescence spectra were obtained on an instrument constructed in this laboratory, and which has recently been described [16]. An excitation wavelength of 290 nm was used for all studies, and this excitation was selected by passing the output of a 200 watt Hg-Xe arc lamp through a 0.1 meter grating monochromator (model H-10-UV-V, Instruments SA). The emission was collected at 180° to the exciting light to eliminate the possible presence of any linear polarization in the emission; this beam was passed through a long-pass filter (consisting of a concentrated solution of NaNO$_2$) to remove any exciting light not absorbed by the sample. The emission was analyzed by a 0.5 meter grating monochromator (model 1870, Spex Industries) whose resolution was equal to a 10 A bandpass. Further increase in resolving power did not reveal any new spectral features. The emission was detected by an EMI 9798B photomultiplier tube (S-20 response), whose output was converted to a voltage and split. One signal was fed directly to one channel of a dual-channel recorder, and the other underwent phase-sensitive detection to obtain the CPL component (which was then displayed on the second recorder channel).

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 leads to fairly intense emission in red spectral regions. In fluid solution at room temperature, luminescence 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 most cases, 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 observed with the 0–0 transition, and the CPL intensities of the 0–1 and 0–2 transitions are 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 the Eu(III) adducts examined in the present work.

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

$$I = I_L + I_R \tag{1}$$

as the TL intensity, and

$$\Delta I = I_L - I_R \tag{2}$$

as the CPL intensity, then the luminescence dissymmetry factor can be defined as [17]:

$$g_{lum} = 2\Delta I/I \tag{3}$$

Note that the latter quantity is independent of intensity units.

The association between chelate and substrate is governed by equilibrium considerations, for if the equation for formation of the 1:1 chelate: substrate adduct is:

$$\mathrm{Eu(DK)_3} + \mathrm{S} \rightleftharpoons \mathrm{Eu(DK)_3S} \tag{4}$$

then the equilibrium constant is defined as:

$$K = \frac{[\mathrm{Eu(DK)_3S}]}{[\mathrm{Eu(DK)_3}[\mathrm{S}]]} \tag{5}$$

TABLE I. Total Luminescence Properties of the Eu(FOD)$_3$ Complexes.

(a) Limiting TL values (arbitrary units)

Substrate	0–0	0–1	0–2
None	23	17.5	345
1	32	50	690
2	36	52.5	660
3	47	67	712
4	43	58	780
5	32	46	491

(b) Band Intensity Ratios

Substrate	Ratio (0–1/0–0)	Ratio (0–2/0–0)	Ratio (0–2/0–1)
None	0.76	15.07	19.71
1	1.56	21.56	13.80
2	1.49	18.12	12.51
3	1.41	15.00	10.65
4	1.34	18.12	13.49
5	1.44	15.44	10.70

Using the luminescence titration method [7–9] one can determine the value of K. Since the absolute value of g_{lum} is proportional to the concentration of Eu(DK)$_3$S so long as the adduct is not fully formed, we have chosen to define a new parameter, the molar dissymmetry factor:

$$G_{lum} = \frac{2\Delta I/I}{[Eu(DK)_3S]} \tag{6}$$

The use of the molar dissymmetry factor permits one to evaluate the equilibrium constants *via* the CPL/TL data, and also permits the comparison of optical activities associated with other Eu(DK)$_3$ systems. While g_{lum} has no units and may range from 0 to 2, C_{lum} has the units of mol^{-1} and may range from 0 to infinity.

Addition of any of the amino alcohols to a solution of Eu(FOD)$_3$ resulted in an approximate doubling of the TL intensity. Titration curves resemble those we have presented in earlier works for other substrates [9, 13] in that one typically observed a rapid initial increase in TL intensity as substrate is first added, and a subsequent leveling-off of the TL to some constant value at high substrate concentrations. However, on closer examination one finds that the different bands increase by different amounts, and that the ratio of the 0–0, 0–1, and 0–2 band intensities for a given adduct can be very different. The limiting TL intensities and band ratios are summarized in Table I.

Examination of Table I reveals that the 0–1 band exhibits the greatest degree of emission enhancement, with enhancements ranging from 2.5 to 3.9 being found. Enhancements associated with the 0–0 and 0–2 bands were somewhat less, and ranged from 1.5 to 2.3. In the absence of any substrate (and with the assumption that CHCl$_3$ is a noncoordinating solvent), the highest possible symmetry of the Eu(FOD)$_3$ chelate is C_{3v}. Consideration of the selection rules associated with the Eu(III) transitions reveals that for C_{3v} symmetry, the 0–0 band consists of 1 electric dipole allowed transition, the 0–1 contains 1 magnetic dipole allowed and 1 electric/magnetic dipole allowed set of transitions, and the 0–2 band contains 2 electric/magnetic dipole allowed and 1 electric dipole allowed set of transtions [18]. It is important to note that the rotational strength of any of these transitions will be zero unless the particular transition is both electric and magnetic dipole allowed [17]. Further lowering of the symmetry of the chelate adduct results in a relaxation of the above selection rules and, in general, an increase in TL intensity.

TABLE II. Association Constants for the 1:1 Eu(FOD)$_3$/Substrate Adducts.

Substrate	K	log K
2-amino-1-propanol, *1*	2890	3.46
2-amino-1-butanol, *2*	2595	3.41
2-amino-3-methyl-1-butanol, *3*	2465	3.39
2-amino-3-methyl-1-pentanol, *4*	2025	3.31

Examination of the titration curves using the methods we have outlined [7–9] leads to the association constants collected in Table II. There is not a great deal of difference between the constants, but a trend does exist whereby the most sterically hindered substrates have the smallest association constants. The constants are essentially of the same magnitude as those found for the bidentate phenylalkylamino alcohols of our earlier study [14] (log K = 3.21 for α-phenylglycinol and 3.34 for phenylalaninol), which implies that all of the substrates bind to the Eu(FOD)$_3$ chelate in a bidentate manner.

While no CPL was observed for Eu(FOD)$_3$/CHCl$_3$, addition of any one of the amino alcohol substrates led to the immediate observation of strong optical activity in the luminescence bands. The lineshapes of all CPL were essentially the same, and the sign of the most intense CPL band could be directly related to the absolute configuration of the chiral substrate. Representative examples of the 0–1 CPL are shown in Fig. 2, while analogous spectra within the 0–2 emission bands may be found in Fig. 3. The general rule that we have developed in our earlier works [13, 14] continues to hold: *when a chiral substrate binds*

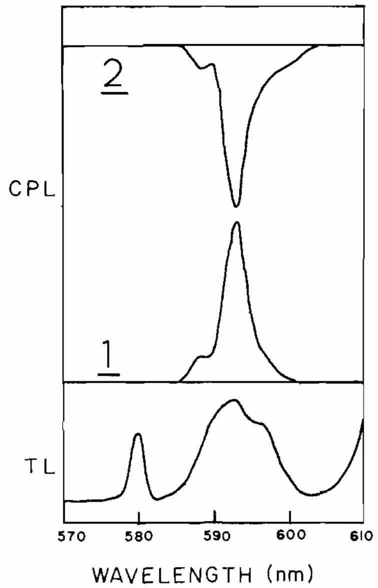

Fig. 2. TL and CPL spectra of Eu(FOD)$_3$/(S)-2-amino-1-propanol (middle) and Eu(FOD)$_3$/(R)-2-amino-1-butanol (upper), within the $^5D_0 \rightarrow {}^7F_1$ Eu(III) transition. The intensity scales are in arbitrary units.

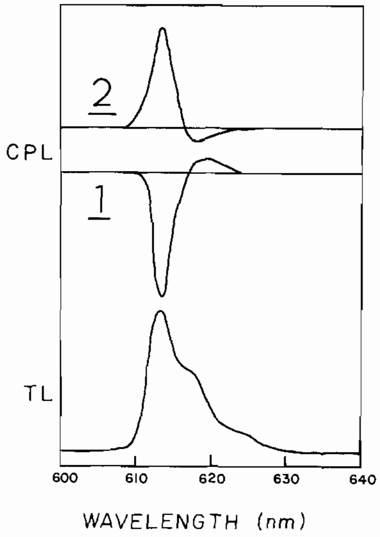

Fig. 3. TL and CPL spectra of the $^5D_0 \rightarrow {}^7F_2$ Eu(III) emission band system for Eu(FOD)$_3$/(S)-2-amino-1-propanol (middle) and Eu(FOD)$_3$/(R)-2-amino-1-butanol (upper).

to a Eu(DK)$_3$ complex in either a mono- or a bidentate fashion, the sign of the CPL in the 0–1 band will be positive if the substrate is of the (S)-configuration. For the same substrate, the sign of the dominant 0–2 CPL band will be negative. We have verified this rule extensively when DK = FOD or TTFA, but have trouble extending it to other β-diketone chelates due to their tendency to form Schiff bases as well as adducts. The only consideration that needs to be remembered is that the presence of more than one asymmetric atom invalidates the rule.

TABLE III. Luminescence Dissymmetry Factors for the major CPL bands of the Eu(FOD)$_3$/Substrate Adducts.

Substrate	0–1 Band		0–2 Band	
	$g_{lum} \times 10^2$	G_{lum}	$g_{lum} \times 10^3$	G_{lum}
1	+5.1	+49.6	−5.5	−5.34
2	−3.5	−34.0	+4.2	+4.08
3	+4.3	+41.8	−6.4	−6.22
4	+4.1	+39.8	−4.1	−3.98
5	+3.9	+37.9	−6.1	−5.93

The degree of optical activity (as reflected by the dissymmetry factors) varies somewhat with the different substrates used, but in general all g_{lum} and G_{lum} values are within the range [14] which certifies the presence of bidentate binding between the chelate and the substrate. Results for both the 0–1 and 0–2 emission bands have been collected in Table III. As in the case of the emission intensity enhancements, little pattern appears to exist among the dissymmetry factors. We cannot yet develop more quantitative discussions of the data, for while the theory associated with the CPL effect exists in an abstract form [17], its application to lanthanide complexes is still forthcoming [19]. One must remember that each $^5D_0 \rightarrow {}^7F_J$ ($J \neq 0$) band contains a number of crystal field components which overlap in fluid solution at room temperature (and whose resolution is not instrument-limited), and which most likely have different signs. Slight differences in overlap will have a profound effect on the magnitude of the observed CPL.

The CPL of the 0–1 band (which contains the fewest number of crystal field components and is by far the easiest band to interpret) clearly contains at least two components, and is often suggestive of a third. Attempted matching of some of these transitions with known energy levels of Eu(III) in crystals [20] (and making use of the observation that the energy levels of lanthanide ions in general are relatively insensitive to the environment) revealed that none of the CPL bands could be ascribed to emission from the $^5D_1$ excited state and, therefore, all emission results could be interpreted within the 0–1 selection rules. As noted earlier, as long as an axis of symmetry exists, the 0–1 emission band will consist of two electric/magnetic dipole allowed components. The observation of three components within this band is a clear indication that nonaxial symmetry exists [14]. It is our contention, therefore, that the adducts formed between Eu(FOD)$_3$ and bidentate amino alcohols are *not* axially symmetric.

A final note concerns the type of chirality experienced by the Eu(III) ion which leads to the observed CPL. In general, a metal complex can contain three distinctive contributions to the overall optical activity: (a) a vicinal effect (due to asymmetric centers in the ligand environment), (b) a conformational effect (due to the formation of a chelate ring containing an asymmetric atom, and this ring having dissymmetric conformations), and (c) a configurational effect (due to a dissymmetric distribution of ligands about the metal). We have observed vicinal and conformation effects in our earlier work [14] and have contrasted these with the CPL of Eu(III) complexes where only pure configurational effects are found [20]. The g_{lum} values associated with the pure configurational effects are much larger than those observed in the present work, and the dissymmetry factors associated with a vicinal/conformational mechanism are consistent with those we have in the present work. Similar values were obtained in the $Eu(TTFA)_3$/amino alcohol study [13] which identifies the same mechanism as operating for that chelate as well.

The results of the present study demonstrate that CPL spectroscopy is a useful method for the study of chelate stereochemistry. The lack of configurational optical activity implies that no diastereomer preferences exist for the Eu(III) chelates. We conclude that in these very labile chelates, ligand exchange takes place at such a rate that a time-averaged adduct is observed over the approximately 500 μsec lifetime of the excited state. Many workers have argued that this fast exchange leads to the existence of an 'effective' axial symmetry [1–3], but the emission results show that this may not be the case. We are confident in applying our excited-state results to ground-state properties, since the 4-f electrons are quite nonbonding in nature and one would not expect geometrical changes to take place upon excitation. The existence of a predominant species in solution (as evidenced by the consistency in optical activity parameters) permits detailed study of the adduct complexes *via* CPL spectroscopy, and therefore points the way for future research.

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