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Circularly Polarized Luminescence Studies of the Adducts Formed with Eu(III) β-Diketone Complexes and (−)-Sparteine

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The optical activity resulting from the complexation of (−)-sparteine by a series of Eu(III) β-diketone compounds has been studied by means of circularly polarized luminescence spectroscopy. It was found that the presence of at least one perfluoro group was necessary for the formation of an adduct complex. With Eu(III) complexes containing achiral β-diketone ligands, it was found that the observed chirality could be considered to result from a combination of vicinal and conformational effects. With Eu(III) complexes containing chiral β-diketone ligands, the optical activity was found to be dominated by configurational effects.

Introduction

It is well established that lanthanide β-diketone complexes function as excellent nmr shift reagents, and that one may deduce conformational information from such work [1]. Studies of the adducts formed between the β-diketone complexes and substrates are essential to any theoretical interpretation of the induced paramagnetic shifts. It is common practice to treat LIS data by assuming the existence of axial symmetry in the adduct complexes [2], in spite of the fact that such symmetry might not exist [3].

Chiroptical techniques are ideally suited for studies of the stereochemistry of the adduct complexes, with circularly polarized luminescence (CPL) spectroscopic studies of Eu(III) derivatives being the most useful [4]. Of particular significance have been the works in which optical activity has been induced in achiral Eu(III) compounds through complexation with chiral substrates. In these studies, systematic variation of the substrate functionalities have permitted deductions to be made regarding the mode of substrate interaction [5–7].

The studies have largely been carried out employing chiral amines and amino alcohols as substrates. With certain β-diketone ligands, it has been noted that these substrates were capable of forming Schiff bases with the coordinated ligands [8]. In such a situation, no structure–spectra correlations were possible. It is therefore important to study the adducts formed between Eu(III) β-diketone and chiral amines incapable of forming Schiff bases. Such a substrate is the alkaloid, (−)-sparteine, which is able to function as a bidentate ligand in its all-chair conformation [9–11] (Fig. 1):

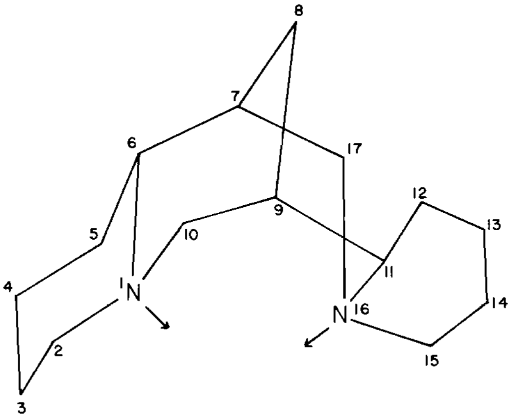

Fig. 1. Structure and numbering system for (−)-sparteine in the all-chair conformation.

In the present work, the results of these investigations will be detailed.

Experimental

Eu(FOD)$_3$ [FOD = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione], Eu(DPM)$_3$ [DPM = 2,2,6,6-tetramethylheptane-3,5 dione], Eu(DFHD)$_3$ [DFHD = 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione], Eu(TFAC)$_3$ [TFAC = trifluoroacetyl-d-camphor], and Eu(HFBC)$_3$ [HFBC = heptafluorobutryl-d-camphor] were all purchased from Aldrich and used as received. Eu(TTFA)$_3$ [TTFA = 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionate] was prepared in the manner described by Melby *et al.* [12], Eu(BZ-

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AC)$_3$ (BZAC = benzoylacetone] was prepared according to the method of Charles [13], and Eu(DBM)$_3$ [DBM = dibenzoylmethane] was prepared by a similar route [14]. After their synthesis, all compounds were dried over P_2O_5. Spectrograde $CHCl_3$ was used as the solvent. (–)-sparteine was used as received from Sigma.

Stock solutions of the metal complexes and sparteine substrate were made up in $CHCl_3$, and normally a 3 ml aliquot of the Eu(III) compounds was titrated with microliter amounts of the sparteine stock solution. After the addition of 3–5 equivalents of substrate, several additions of pure substrate were performed to insure that the titration endpoint had been reached. These titration procedures have been adequately summarized in our earlier work [5–8]. All measurements were thus performed in $CHCl_3$ solution at room temperature.

All CPL and TL (total luminescence) measurements were obtained on apparatus constructed in our laboratory. In all cases, the 365 nm output of a 200 W Hg–Xe arc lamp was used to excite the complexes. This wavelength was selected by a combination of a 0.1 meter grating monochromator and UV-transmitting filters. Measurements of the TL and CPL spectra were carried out simultaneously within the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2) band systems associated with the Eu(III) ion. The emission was analyzed by a 0.5 m grating monochromator at 5 Å resolution, and it was determined that further increases in resolving power did not yield any significant improvement in the spectral features. The emission was detected by a photomultiplier tube (S-20 response), which was cooled to –25 °C in an effort to reduce noise and dark currents.

The chiroptical measurements produce two quantities normally measured in arbitrary units. One of these is the total luminescence (TL) intensity, defined by:

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

and the other is the circularly polarized luminescence intensity, defined by:

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

In eqns. (1) and (2), I_L and I_R represent the emitted intensities of left- and right-circularly polarized light, respectively. One may remove the unit dependence associated with I and ΔI by taking the ratio of these, and this quantity is termed the luminescence dissymmetry factor [15]:

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

The g_{lum} factor has theoretical as well as experimental significance in that it may be related to the rotational strength of the transition [15].

Results and Discussion

Eu(III) Complexes Containing Achiral β-Diketone Ligands

The β-diketone ligands denoted by DK = FOD, TTFA, DFHD, DPM, BZAC, or DBM are all inherently achiral, as is clearly evident from the flat planar structures illustrated in Fig. 2. Thus, no Eu(III) chirality may arise from intrinsic ligand chirality, and the lability of the compounds insures that the Eu(DK)$_3$ complexes will always exist as racemic mixtures. In non-coordinating solvents, one may speak of an Eu(DK)$_3$ compound, but in coordinating solvents one deals with adduct complexes. Upon interaction with a substrate, S, the formation of 1:1 adducts:

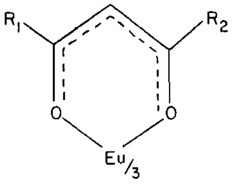
$$\mathrm{Eu(DK)_3 + S \rightleftharpoons Eu(DK)_3(S)} \tag{4}$$

and 1:2 adducts:

$$\mathrm{Eu(DK)_3 + 2S \rightleftharpoons Eu(DK)_3(S)_2} \tag{5}$$

may be observed. Given the steric bulk of sparteine, it is likely that only the 1:1 adduct complex described in eqn. (4) would be formed. When the substrate is optically active, then chirality may be observed in the f–f emission bands of the Eu(III) ion [4].

This optical activity may be considered to arise from two effects. The first of these is a vicinal contribution, where the Eu(III) ion becomes dissymmetric by the simple presence of an asymmetric carbon atom on one of the ligands. The other contribution would come from the conformational effect, which represents additional chirality resulting when the asymmetric carbon is bound as part of a chelate ring In that situation the entire ring must be considered dissymmetric (its mirror images are non-superimposable), and the Eu(III) ion experiences this additional dissymmetry. Of the two effects, the conformational



$R_1 = C_3F_7$	$R_2 = C(CH_3)_3$	FOD
$R_1 = C_3F_7$	$R_2 = CF_3$	DFHD
$R_1 = CF_3$	$R_2 = C_4H_3S$	TTFA
$R_1 = R_2$	$= C(CH_3)_3$	DPM
$R_1 = R_2$	$= C_6H_5$	DBM
$R_1 = CH_3$	$R_2 = C_6H_5$	BZAC

Fig. 2. Structures of the achiral β-diketone ligands used in the present work.

effect is anticipated to be the dominant mechanism. With (–)-sparteine acting as a bidentate ligand in the all-chair form, one would predict that both effects would contribute to the observed optical activity.

The rather low absorptivities of the Eu(III) *f–f* transitions make the measurement of circular dichroism difficult, but fortunately one may also study *f–f* optical activity by means of CPL spectroscopy. Excitation of Eu(III) β-diketone complexes by near-UV radiation can result in the observation of strong luminescence in the red region of the spectrum. This emission consists of a series of well-resolved transitions from the excited $^5D_0$ level to the ^7F_J levels of the ground state. We shall henceforth label the spectroscopic transitions by their defining J quantum numbers, and have observed the 0–0 (580 nm), 0–1 (595 nm), and 0–2 (615 nm) bands during the course of our work. The formation of adduct complexes is normally accompanied by strong intensification of the 0–1 and 0–2 bands, and the lack of such intensity enhancements may be taken to imply that adduct formation has not taken place. When the substrates are inherently chiral, the adduct formation process is also signified by the presence of measurable optical activity within the Eu(III) emission bands. CPL within the 0–0 transition is not permitted [15], but strong CPL was normally observed within the 0–1 and 0–2 transitions.

The interaction of (–)-sparteine with the Eu(DK)$_3$ complexes was found to depend critically on whether the β-diketone ligand contained perfluoro groups. With Eu(DPM)$_3$, Eu(BZAC)$_3$, or Eu(DBM)$_3$, no evidence for adduct formation was noted. Little (if any) intensification of the TL intensities was observed, and no CPL was observable in any of the emission bands. Even the addition of relatively large excesses of neat sparteine did not yield measurable differences in the spectra. These observations imply that the sparteine is too bulky to bind at the inner coordination sphere of the Eu(III) ion, and that the acidity of the complexes is too low to promote such interactions.

With fluorinated ligands, however, the acidity of the Eu(III) is greatly increased through the inductive effects of the fluorines. With Eu(FOD)$_3$, Eu(DFHD)$_3$, or Eu(TTFA)$_3$, sizeable TL enhancements were observed upon addition of sparteine and quite strong CPL was also evident. The CPL lineshapes observed within the 0–1 and 0–2 emission bands were found to be independent of the identity of the DK ligand. These may be found in Fig. 3. The CPL intensities (as measured by the luminescence dissymmetry factors) were found to increase smoothly with the concentration of added sparteine. Eventually a limiting value was reached, which clearly represents the dissymmetry factor associated with the fully formed Eu(DK)$_3$(sparteine) complexes.

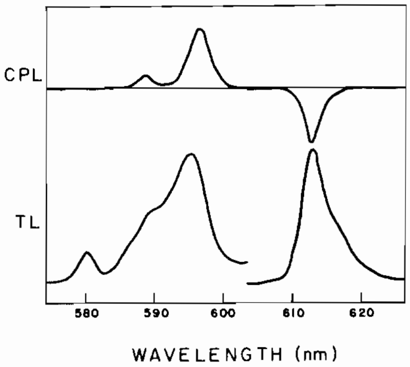


Fig. 3. Total luminescence (lower trace) and circularly polarized luminescence (upper trace) spectra obtained for the Eu(FOD)$_3$(sparteine) adduct complex. The intensity of the 0–2 TL spectrum has been reduced by a factor of 10; no such reduction has been applied to the CPL spectrum.

The limiting dissymmetry factors observed with the chelates where DK = FOD, DFHD, or TTFA have been collected in Table I. It is very significant to note that the limiting dissymmetry factors are almost equal in magnitude, since this result would imply that the observed chirality is independent of the nature of the DK substituents. This would in turn imply that these factors represent the chirality associated with the chelate ring formed by Eu(III) and sparteine in the all-chair form.

The CPL lineshapes reported here for the sparteine adduct complexes are essentially identical to those reported earlier when working with amino alcohol

TABLE I. Wavelengths, Assignments, and Dissymmetry Factors Observed for the (–)-Sparteine Adduct Complexes with Eu(III) β-Diketonates.

β-diketone ligand	Wavelength (nm)	Band origin	g_{lum}
FOD	589	0–1 (a)	0.0154
	596	0–1 (b)	0.0291
	613	0–2	–0.0026
DFHD	589	0–1 (a)	0.0120
	596	0–1 (b)	0.0282
	613	0–2	–0.0028
TTFA	589	0–1 (a)	0.0126
	596	0–1 (b)	0.0294
	613	0–2	–0.0022
TFAC	586	0–1 (a)	–0.74
	596	0–1 (b)	–2.00
	614	0–2	0.28
HFBC	586	0–1 (a)	0.80
	596	0–1 (b)	1.94
	614	0–2	–0.19

substrates [5–7]. In addition, the luminescence dissimmetry factors of the sparteine adducts are approximately equal to those measured for the amino alcohol adducts. These observations provide support that the data reported in these earlier works [5–7] do not contain a contribution from Schiff base formation, since sparteine is incapable of forming Schiff bases with β-diketone ligands. All evidence which exists indicates that when DK = FOD, TTFA, or DFHD, sparteine and amino alcohols bind to the Eu(III) ion as simple bidentate ligands.

In the earlier works, it was found that simple bidentate ligands exhibit a correlation of CPL signs with ligand absolute configurations [5–7]. In particular, should the substrate be of the S-absolute configuration, then the sign of the 0–1 CPL would be totally positive and the 0–2 CPL would be totally negative. Referring to the numbering system given in Fig. 1, the absolute configuration of (–)-sparteine is 6R, 7S, 9S, 11S [16]. The CPL observed with this substrate is consistent with (–)-sparteine behaving as if it were a substrate of the S-configuration. Since the chiralities of positions 6 and 11 oppose each other, we conclude that the observed Eu(III) chirality represents that induced by the dissymmetry of positions 7 and 9.

Eu(III) Complexes Containing Chiral β-Diketone Ligands

The phenomena associated with the $Eu(CDK)_3$ complexes are more complicated than those associated with the $Eu(DK)_3$ compounds. Since the CDK ligands are inherently chiral, preparation of the $Eu(CDK)_3$ compounds results in the formation of four diastereomers. In $CHCl_3$ solution one would anticipate that these would be formed in roughly equivalent amounts, since these compounds are exceedingly labile. The analogous diastereomers of inert transition metal complexes have been resolved [17, 18], and it has been found that the chirality of the Δ isomers is essentially equal in magnitude and opposite in sign to that of the Λ isomers. Thus, in a solution containing equal amounts of the various stereoisomers, one should not be able to observe any optical activity. This has been found to be the case [19], indicating that in non-coordinating solvents the camphorato ligands do not sterically crowd each other. Upon formation of the adduct complexes:

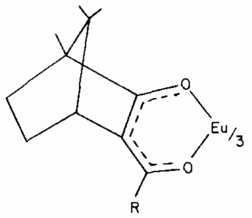
$$Eu(CDK)_3 + S \rightleftharpoons Eu(CDK)_3(S) \tag{6}$$

$$Eu(CDK)_3 + 2S \rightleftharpoons Eu(CDK)_3(S)_2 \tag{7}$$

one would anticipate that the bulky camphorato ligands would be forced to interact more in the adduct complexes, and the complexes ought to adopt the configurations of lower energy. This process would effectively constitute a partial resolution, and should result in the observation of optical activity within the f–f bands. Such predictions have been verified [20–22]. As with the $Eu(DK)_3$ compounds, it is most likely that with the bulky sparteine ligand only 1:1 adducts would be formed.

The optical activity resulting when achiral substrates were used to form adducts with $Eu(TFAC)_3$ or $Eu(HFBC)_3$ results primarily from the dissymmetric arrangement of the chelate ligands, and hence is a configurational effect. With (–)-sparteine as the substrate, then one might anticipate that the observed chirality could contain an additional contribution from conformational effects. It appears that the magnitude of a configurational effect is much larger than a conformational effect [4], and thus such a mechanism would be evident in the data.

Formation of $Eu(CDK)_3$(sparteine) adducts resulted in the generation of extremely strong optical activity within the Eu(III) emission bands. The TL and CPL spectra obtained for the sparteine adduct of $Eu(TFAC)_3$ may be found in Fig. 5, while the analogous spectra obtained with $Eu(HFBC)_3$ are located in Fig. 6. One may immediately note that the CPL lineshapes obtained with the two complex systems



R = CF_3 , TFAC

R = C_3F_7 , HFBC

Fig. 4. Structures of the chiral β-diketone ligands used in the present work.

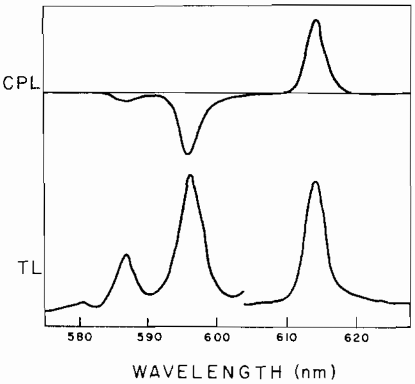


Fig. 5. Total luminescence (lower trace) and circularly polarized luminescence (upper trace) spectra obtained for the $Eu(TFAC)_3$(sparteine) adduct complex. The intensity of the 0–2 TL spectrum has been reduced by a factor of 10; no such reduction has been applied to the CPL spectrum.

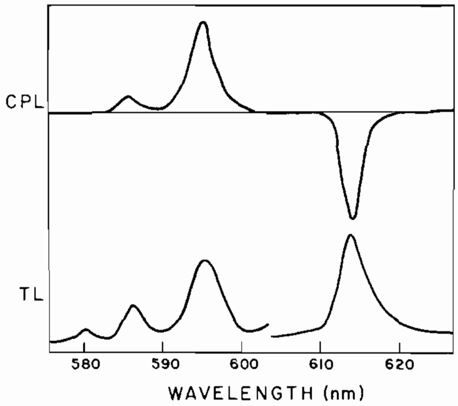


Fig. 6. Total luminescence (lower trace) and circularly polarized luminescence (upper trace) spectra obtained for the $Eu(HFBC)_3$(sparteine) adduct complex. The intensity of the 0–2 TL spectrum has been reduced by a factor of 10; no such reduction has been applied to the CPL spectrum.

appear to be mirror images of each other. This behavior has been noted in other studies contrasting the behavior of $Eu(TFAC)_3$ and $Eu(HFBC)_3$ [20, 21].

The luminescence dissymmetry factors provide insight into this situation. As one may note from the values shown in Table I, the degree of optical activity associated with the $Eu(CDK)_3$ compounds is significantly greater than that noted with the $Eu(DK)_3$ compounds. In fact, the second 0–1 Eu(III) band appears to be *totally* circularly polarized. CPL intensities of this magnitude are certainly connected with the existence of configurational effects. It is quite clear, therefore, that the differing lineshapes observed for the $Eu(CDK)_3$ compounds represent the generation of opposite enantiomers. This conclusion is supported by the observation that the CPL peaks obtained for the two $Eu(CDK)_3$ compounds are located at exactly the same wavelengths, and that the dissymmetry factors of these are numerically equal but opposite in sign.

In $CHCl_3$ solution, the three β-diketone ligands present in the $Eu(CDK)_3$ complex do not interact sterically, and in this non-coordinating solvent no CPL can be observed. Formation of the adduct complex causes the CDK ligands to become crowded, and to adopt the configuration of lowest energy. This process leads to the observation of optical activity, since the conformer present to the greatest extent will be optically active. It is interesting to note that the chirality of the sparteine appears not to play any role in determining the favored $Eu(CDK)_3$ diastereomer. The most stable $Eu(TFAC)_3$ and $Eu(HFBC)_3$ adduct complexes are of opposite absolute configuration. This observation indicates that the primary role played by the sparteine ligand in the $Eu(CDK)_3$ complexes is steric, and that its own chirality does not affect the stereoselective processes.

Conclusions

Several trends have emerged from studies of the adduct formation of (–)-sparteine with Eu(III) β-diketone complexes. When the β-diketone ligands lack fluorinated groups, the acidity of the Eu(III) is too low for adduct formation to take place. The presence of even a single perfluoro group makes the Eu(III) ion sufficiently acidic as to permit adduct formation with the bulky sparteine substrate. Apparently the steric bulk associated with the various β-diketone ligands plays only a minor role, as strong adducts can be formed even with the very bulky camphorato ligands.

The chirality resulting when the $Eu(DK)_3$ compounds form adducts with (–)-sparteine is largely due to a sum of vicinal and conformational effects. Here, the optical activity is premarily determined by the Eu(III)–sparteine dissymmetry, and the remainder of the Eu(III) coordination sphere plays little or no role in determining the overall optical activity. This conclusion is reasonable since the presence of only one chiral ligand in the inner coordination sphere of the Eu(III) ion should not lead to the existence of any configuration effects.

With the $Eu(CDK)_3$ compounds, the configurational effect completely determines the chirality experienced by the lanthanide ion. The binding of a bulky sparteine ligand merely serves as the steric perturbation necessary to induce a stereoselective rearrangement of the CDK ligands, and it is this process which yields CPL in the $Eu(CDK)_3$ compounds. The magnitude of this configurational effect is far greater than any possible conformational effect, and hence the observed chirality is dominated by configurational effects.

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