

of the MCD of the visible band was made in the absence of single-crystal structural and spectroscopic data.

Both the off-resonance *and* RR scattering using visible laser excitation³ are weak and rather broad. One would expect that for the $\sigma^* \leftarrow \sigma$ transition, RR spectra would give a strong scattering with long overtone progressions in totally symmetric bridging vibrations. Instead, only a few weak bands have been assigned to overtones and combinations of the breathing ν_4 (a_1) and the stretching ν_2 (a_1) vibrations. The presence of a $\pi e' \leftarrow \delta e'$ ($e_g \leftarrow t_{2g}$) transition in the visible region can lead to a destructive interference between preresonant and RR scattering (see Appendix). This may explain not only the weak RR scattering but also the photochemical sensitivity³ of the trihalides to resonant laser excitation in the visible region.

Conclusions

Our assignments of the $\sigma^* \leftarrow \sigma$ and $\sigma^* \leftarrow \delta^*$ transitions associated with the ${}^1A_1 \times {}^2T_2$ multiplet agree with those of Hush et al.² However, the visible absorption must contain a number of electronic states, including ${}^2A_1'$ ($\sigma^* \leftarrow \sigma$). We suggest that one major component of the visible band is the ${}^2E''$ ($\pi e' \leftarrow \delta e'$) state, which is antibonding with respect to metal-ligand and bonding with respect to direct Ru-Ru interactions. The ${}^2E''$ state may be photochemically active, as is the ${}^4T_{2g}$ state²⁰ in Cr^{3+} . It could also give destructive interference in the RR spectra, which seems common for ligand field states involving $e_g \leftarrow t_{2g}$ one-electron excitations (see Appendix).

Further progress will probably require the preparation of single crystals suitable for an X-ray structure determination in order

to confirm the cofacial bioctahedral geometry of the pair. Single-crystal measurements will also allow a more precise analysis of the polarization properties of the visible absorption band.

Appendix

Interference between Resonance and Preresonance Scattering. Stein et al.² have reported the resonance Raman excitation profiles (RREP) for totally symmetric vibrations in $\text{Co}(\text{en})_3^{3+}$. A destructive interference was observed for excitation into the ligand field state 1T_1 ($e_g \leftarrow t_{2g}$). We have also observed the same effect in other cobalt(III) polyamines, e.g. cobalt(III) sepulchrate.²² Zgierski¹⁹ used the δ -approximation model²³ to interpret the RREP on the basis of an interference between resonance scattering with the 1T_1 state and preresonance scattering with a higher lying charge-transfer state. He deduced that the interference is destructive provided the displacements of the potential energy surfaces along the a_1 coordinate have opposite signs with respect to the ground state. Since the 1T_1 state in $\text{Co}(\text{III})$ is expanded along the a_1 coordinate, the charge-transfer state must in this analysis be contracted.

In contrast to Zgierski,¹⁹ we find that given the δ -approximation model²³ and two competing scattering amplitudes, the condition for destructive interference is that the two displacements have the *same* sign and hence the charge-transfer state must be expanded along the a_1 coordinate. This result can be obtained from eq 16 given in ref 23, but the analysis is somewhat lengthy²² and will not be reproduced here.

Registry No. $[\text{Ru}(\text{NH}_3)_3]_2\text{Br}_3^{2+}$, 98838-11-0; $[\text{Ru}(\text{NH}_3)_3]\text{Cl}_3^{2+}$, 98838-12-1.

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Contribution from the Departments of Chemistry, Seton Hall University, South Orange, New Jersey 07079, and Wayne State University, Detroit, Michigan 48202

Circularly Polarized Luminescence Studies of the Adduct Complexes Formed by (*R*)-Methyl *p*-Tolyl Sulfoxide with Various Europium(III) β -Diketonate Complexes

Harry G. Brittain*[†] and Carl R. Johnson[‡]

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Circularly polarized luminescence spectroscopy has been used to study the ternary complexes formed by europium(III) β -diketonate complexes and methyl *p*-tolyl sulfoxide. Adduct complexes having 1:1 and 1:2 chelate/substrate stoichiometries were formed, depending on the degree of fluorination in the β -diketone chelate rings. Enhancements in the Eu(III) luminescence intensities and lifetimes were used to evaluate the formation constants of the adduct complexes. In the 1:1 adduct complexes, the Eu(III) chirality was determined primarily by vicinal effects. In the 1:2 adduct complexes, evidence was obtained that indicated the presence of weak configurational effects due to geometrical isomerism.

Introduction

The use of lanthanide β -diketone complexes as nuclear magnetic resonance shift reagents is usually considered to be a mature field, and the deduction of conformational information from such work is often routine.¹ However, it is common practice to treat lanthanide-induced shift 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 Consequently, further probing of the adduct formation process is of great importance, and the acquisition of stereochemical information on the nature of the adduct complexes is vital to the further development of the theory.

Chiroptical techniques are ideally suited for studies of the stereochemistry of these adduct complexes, and circularly polarized luminescence (CPL) spectroscopic studies of Eu(III) derivatives

has yielded the largest amount of information.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

For the most part, these studies have employed chiral amines and amino alcohols as substrates inducing optical activity in Eu(III) complexes prepared from achiral β -diketone ligands. With non-fluorinated β -diketone ligands, formation of the adduct complex actually consisted of a chemical reaction that produced

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[†] Seton Hall University.

[‡] Wayne State University.

coordinated Schiff base ligands.⁸ This reactivity eliminated any deduction of structure–spectra correlations. Reliable studies of the adduct complexes require a total lack of chemical reaction between the substrate and the β -diketone ligands, and this situation was realized when (–)-sparteine was employed as the chiral substrate ligand.⁹

In the present work, we detail the results of chiroptical investigations probing the complexation of a chiral sulfoxide substrate, (*R*)-(+)-methyl *p*-tolyl sulfoxide (MTS), by a series of europium(III) β -diketone complexes. As no chemical reactions are possible between the coordinated ligands and the sulfoxide substrate, direct relation of observed CPL spectra and plausible complex structures should be possible.

Experimental Section

Eu(FOD)₃ (FOD = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione), Eu(DPM)₃ (DPM = 2,2,6,6-tetramethylheptane-3,5-dione), and Eu(DFHD)₃ (DFHD = 1,1,1,5,5,6,6,7,7-decafluoroheptane-2,4-dione) were all purchased from Aldrich and used as received. Eu(TTFA)₃ (TTFA = 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione) was prepared in the manner described by Melby et al.,¹⁰ Eu(Bzac)₃ (BZAC = benzoylacetone) was prepared according to the method of Charles,¹¹ and Eu(DBM)₃ (DBM = dibenzoylmethane) was prepared by a similar route.¹² Eu(ACAC)₃ (ACAC = pentane-2,4-dione) was prepared in the manner of Stites et al.,¹³ Eu(TFAC)₃ (TFAC = 1,1,1-trifluoropentane-2,4-dione) was synthesized according to the procedure of Sager et al.,¹⁴ Eu(HFAC)₃ (HFAC = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) was prepared as described by Richardson et al.,¹⁵ and Eu(TFBD)₃ (TFBD = 4,4,4-trifluoro-1-phenylbutane-1,3-dione) was prepared in the manner of Ismail et al.¹⁶ The β -diketone ligands used in the various syntheses were obtained from either Aldrich or Eastman and were used as received. After their synthesis, all compounds were dried to constant weight over P₂O₅. Dry, spectral quality chloroform was used as the solvent for all work.

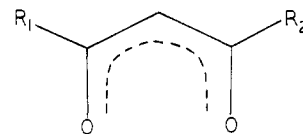
(*R*)-(+)-Methyl *p*-tolyl sulfoxide (MTS) was prepared by the method of Andersen.^{17b} The specific rotation of this material was found as $[\alpha]_D^{25} +145.7^\circ$ (lit.^{17a} $+145.5^\circ$), and the melting point was obtained as 74–76 °C (lit.^{17b} 73–74.5 °C).

Stock solutions of each europium(III) β -diketone complex were prepared in CHCl₃, with the complex concentration ranging between 0.1 and 0.8 mM. Due to the relatively weak complexation between the europium(III) β -diketone complexes and the MTS substrate, solid amounts of MTS were added to a CHCl₃ solution of the Eu(III) complexes. In a typical study, several 10-mg additions of MTS were required to produce limiting Eu(III) photophysical behavior. All measurements were performed in fluid chloroform solutions at room temperature.

All CPL and TL (total luminescence) measurements were obtained on apparatus constructed at Seton Hall University. In all cases, the 365-nm output of a 1000-W Xe arc lamp was used as the excitation source. This wavelength was selected by a combination of a 0.1-m grading monochromator and UV-transmitting filters. Measurements of the TL and CPL spectra were carried out simultaneously within the ³D₀ → 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 2-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 current.

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

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



	R ₁	R ₂
ACAC	CH ₃	CH ₃
TFAC	CF ₃	CF ₃
HFAC	CF ₃	CF ₃
DFHD	CF ₃	C ₂ F ₇
FOD	C(CH ₃) ₃	C ₂ F ₇
DPM	C(CH ₃) ₃	C(CH ₃) ₃
TTFA	CF ₃	C ₄ H ₉ S
TFBD	CF ₃	C ₆ H ₅
BZAC	C ₆ H ₅	C ₆ H ₅
DBM	C ₆ H ₅	C ₆ H ₅

Figure 1. Structures of the β -diketone ligand systems used to prepare the various Eu(DK)₃ complexes.

and the other is the circularly polarized luminescence (CPL) intensity, defined by

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

In eq 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:¹⁸

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

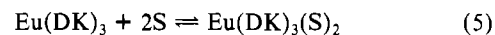
Emission lifetimes were obtained on a separate apparatus. Samples were excited by the 337-nm output of a pulsed nitrogen laser (PRA Associates, Model LN-1000). The transient currents developed upon pulsed excitation of the sample were converted into voltages by using a 220K load resistor, and these voltage pulses were captured for viewing on a storage oscilloscope. At the same time, the data were digitized at 4- μ s intervals via a homebuilt analog/digital converter, and the digitized data were fed directly into a Commodore PET 4032 microcomputer. The details of the transient digitizer have been described.¹⁹ Our program calculates the baseline from data points taken before the laser pulse and subtracts the baseline from the decay data. The corrected decay curves were then analyzed by using a linear-regression analysis of the $\ln I$ vs. time data points.

Results and Discussion

Structures for the β -diketone ligands (denoted generically by DK) are all shown in Figure 1. Although the ligands are themselves achiral, a Eu(DK)₃ compound is potentially optically active, since the tris(bidentate) complex could exhibit an ideal *D*₃ symmetry. However, the extreme lability of these compounds insures that the Eu(DK)₃ complexes will always exist as racemic mixtures. In noncoordinating 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



and 1:2 adducts



may be observed. When the substrate is optically active (as in the present system), 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 could come from a configurational effect, from which additional chirality would result if formation of the adduct complex was accompanied by the generation of a dissymmetric arrangement of the β -diketone

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Table I. Initial and Limiting Lifetimes and Formation Constants for the $\text{Eu}(\text{DK})_3(\text{S})$ Adduct Complexes

ligand	$\tau_0, \mu\text{s}$	$\tau_\infty, \mu\text{s}$	K_1
DPM	215	301	3.31
ACAC	332	377	5.43
TFBD	402	584	10.6
TTFA	223	459	39.4
TFAC	327	376	113.0

chelate rings. Such a stereoselective process could only take place when working with chiral substrate ligands. One would anticipate that the configurational effect would be greatly larger than the vicinal effect.

The rather low absorptivities of the $\text{Eu}(\text{III})$ 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 europium(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 $^5\text{D}_0$ level to the $^7\text{F}_j$ levels of the ground state. We shall henceforth label the spectroscopic transitions by their defining J quantum numbers, and observe the 0-0 (580 nm), 0-1 (595 nm), and 0-2 (615 nm) bands. The formation of adduct complexes is normally accompanied by a strong enhancement of the luminescence intensities 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. The $\text{Eu}(\text{III})$ emission lifetime is also found to undergo substantial increase upon adduct formation, and the lack of an increase in the lifetime is another indicator of the lack of chelate-substrate interaction. When the substrate is inherently chiral, the adduct formation process is also signified by the presence of measurable optical activity within the $\text{Eu}(\text{III})$ emission bands. CPL within the 0-0 transition is not permitted,¹⁸ but strong CPL was normally observed within the 0-1 and 0-2 transitions.

The stoichiometries of the adduct complexes formed by the various $\text{Eu}(\text{DK})_3$ compounds with MTS were found to vary with the nature of the DK ligand. Examples of 1:1 and 1:2 chelate/substrate adduct complexes were observed, and these will each be discussed in turn.

1:1 $\text{Eu}(\text{DK})_3(\text{S})$ Adduct Complexes. When DK = DPM, ACAC, TFBD, TTFA, or TFAC, it was found that only 1:1 chelate/substrate stoichiometry was possible. This conclusion was reached through the use of Job's method, where the dependence of emission intensities and lifetimes was used to determine the conditions corresponding to maximum formation of the adduct complex. For the β -diketone systems just mentioned, the break in the curves invariably occurred at mole fractions of 0.5. This observation may be taken as indicating the presence of only 1:1 adduct complexes, as was defined earlier in eq 4.

The $\text{Eu}(\text{III})$ luminescence intensity and lifetime were found to increase rapidly with small additions of MTS, but eventually each parameter was found to reach a constant level at high ratios of MTS/chelate. This behavior permits one to compute formation constants for the adduct complexes, since it is trivial to relate the enhancement in emission intensity (or lifetime) to the concentration of free and adduct $\text{Eu}(\text{DK})_3$ complexes.²⁰ It was found during the course of the present work that evaluation of intensity data yielded the same results as did evaluation of lifetime data, and hence only one data series need be reported. In Table I we have collected the lifetimes of the uncomplexed $\text{Eu}(\text{DK})_3$ compounds, the limiting lifetimes reached upon saturation of the complexes with MTS, and the apparent formation constant of the adduct complex. The formation constants are not thermodynamic in the sense that concentrations (and not activities) were used for the computations.

The formation constants were found to vary in a manner consistent with accepted ideals of Lewis acid/base behavior. It is known that increasing degrees of fluorination lead to enhanced

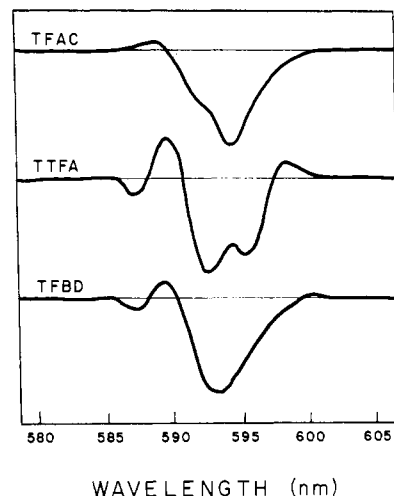


Figure 2. Circularly polarized luminescence spectra obtained within the 0-1 $\text{Eu}(\text{III})$ luminescence band system for 1:1 $\text{Eu}(\text{DK})_3(\text{MTS})$ complexes. The CPL lineshapes correspond to the limiting spectra obtained after complete formation of the adduct complexes. The data correspond to DK = TFAC (upper trace), TTFA (middle trace), and TFBD (lower trace).

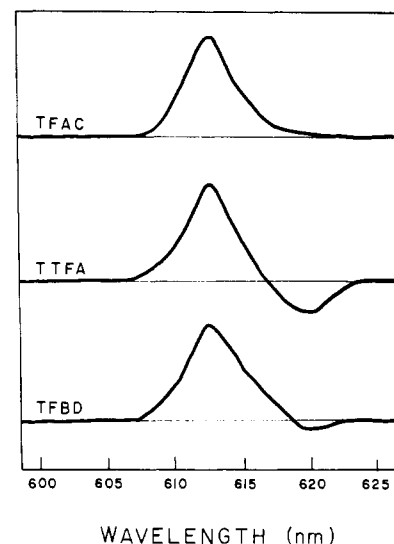


Figure 3. Circularly polarized luminescence spectra obtained within the 0-2 $\text{Eu}(\text{III})$ luminescence band system for 1:1 $\text{Eu}(\text{DK})_3(\text{MTS})$ complexes. The CPL lineshapes correspond to the limiting spectra obtained after complete formation of the adduct complexes. The data correspond to DK = TFAC (upper trace), TTFA (middle trace), and TFBD (lower trace).

acidity of $\text{Eu}(\text{DK})_3$ complexes.¹ The smallest formation constants were observed with the two β -diketone systems containing only aliphatic hydrocarbon side chains. Replacement of one CH_3 by a CF_3 group results in a 20-fold increase in the adduct formation constant, consistent with the greater acidity of the $\text{Eu}(\text{III})$ complex. Steric effects are also evident in the data, since the $\text{Eu}(\text{DPM})_3$ complex was found to form weaker complexes than did the $\text{Eu}(\text{ACAC})_3$ complex. In addition, in the TFBD and TTFA systems one keeps the CF_3 group, but replaces the other CH_3 by bulkier phenyl or thienyl groups. While the formation constants observed with these $\text{Eu}(\text{DK})_3$ compounds are larger than those observed for $\text{Eu}(\text{ACAC})_3$, they still are greatly reduced relative to those of $\text{Eu}(\text{TFAC})_3$.

Addition of MTS of $\text{Eu}(\text{ACAC})_3$ or $\text{Eu}(\text{DPM})_3$ solutions did not lead to measurable optical activity in the $\text{Eu}(\text{III})$ emission bands, but this situation is merely another reflection of the very weak complexation phenomena governing these adducts. With $\text{Eu}(\text{TFBD})_3$, $\text{Eu}(\text{TTFA})_3$, or $\text{Eu}(\text{TFAC})_3$, quite strong chirality was detectable in the $\text{Eu}(\text{III})$ 0-1 and 0-2 emission band systems. Examples of the CPL obtained within the 0-1 system for the limiting $\text{Eu}(\text{DK})_3(\text{MTS})$ compounds are shown in Figure 2, while

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Table II. Luminescence Dissymmetry Factors for the Major CPL Peaks in the $\text{Eu}(\text{DK})_3(\text{S})$ Adduct Complexes

ligand	wavelength, nm	g_{lum}
TFBD	593.3	-0.0153
	612.5	+0.00249
TTFA	592.5	-0.0148
	595.4	-0.0122
	612.3	+0.00405
TFAC	594.3	-0.0147
	612.4	+0.00307

Table III. Initial and Limiting Lifetimes and Formation Constants for the $\text{Eu}(\text{DK})_3(\text{S})_2$ Adduct Complexes

ligand	$\tau_0, \mu\text{s}$	$\tau_\infty, \mu\text{s}$	β_{12}
DBM	199	332	191
HFAC	328	582	4730
FOD	291	471	8330
DFHD	308	594	28875

the analogous 0-2 data are depicted in Figure 3.

Examination of the respective traces of Figures 2 and 3 reveals no gross differences, indicating that the overall complex stereochemistries are not greatly dependent on the nature of the β -diketone ligand system. The minor variations which are noted are an indication that the adduct complexes should be considered as being similar, not identical. The similarity of the complex species is further indicated by the dissymmetry factors associated with the major $\text{Eu}(\text{III})$ emission peaks. These have been collected in Table II. Again, there are minor differences between the various values, but all are within a restricted order of magnitude.

It is highly significant to note that these CPL line shapes and dissymmetry factors are extremely similar to the analogous values reported for $\text{Eu}(\text{DK})_3$ complexes with chiral primary amines.⁵ This observation is consistent with a mechanism in which only vicinal effects determine the chirality of the $\text{Eu}(\text{III})$ ion. The CPL magnitudes associated with configurational effects are at least 10 times greater than those of the vicinal effect,⁵ and clearly no such configurational contribution exists with the MTS substrate and the 1:1 adduct complexes. Thus, it is concluded that no stereoselectivity accompanies the binding of a single MTS substrate by a $\text{Eu}(\text{DK})_3$ complex.

Very different behavior was noted in the complexation of MTS by $\text{Eu}(\text{BZAC})_3$. No emission intensity or lifetime enhancements were noted in the titrations, and these quantities were actually found to decrease upon addition of MTS to a $\text{Eu}(\text{BZAC})_3$ solution. It was determined that the MTS substrate actually replaced the coordinated β -diketone ligands, yielding a weakly luminescent sulfoxide complex. No CPL could be measured due to the very low degree of $\text{Eu}(\text{III})$ emission, and the reaction was not probed further.

1:2 $\text{Eu}(\text{DK})_3(\text{S})_2$ Adduct Complexes. Application of Job's method to $\text{Eu}(\text{DK})_3$ complexes where $\text{DK} = \text{HFAC}$, FOD , or DFHD revealed that the dominant species were of the 1:2 chelate/substrate stoichiometry. This result is not surprising when one considers that these β -diketone ligands all are characterized by a higher degree of fluorination and hence would be expected to be more acidic than the compounds just considered.

When these $\text{Eu}(\text{DK})_3$ compounds are titrated with MTS, no inflection point could be detected in the concentration range for which 1:1 complexes ought to predominate. Instead, the emission intensities and lifetimes rose smoothly until reaching their limiting values. This behavior indicates that the two MTS substrate molecules are not bound in a cooperative manner. Such behavior is typical for the titration curves of $\text{Eu}(\text{DK})_3$ complexes containing achiral β -diketone ligands, but not for complexes where the β -diketone ligands are themselves chiral.²¹

Formation constants for the 1:2 adduct complexes were calculated from the emission intensity and lifetime data, and these parameters are all found in Table III. As before, one finds that

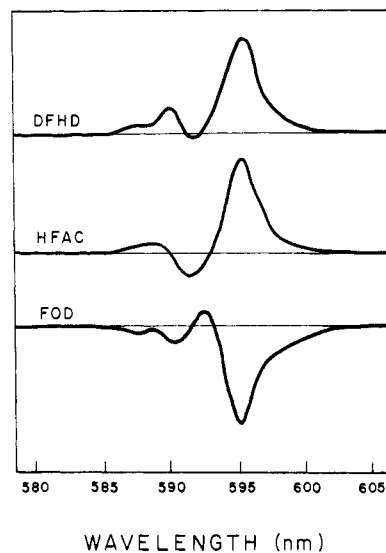


Figure 4. Circularly polarized luminescence spectra obtained within the 0-1 $\text{Eu}(\text{III})$ luminescence band system for 1:2 $\text{Eu}(\text{DK})_3(\text{MTS})_2$ complexes. The CPL lineshapes correspond to the limiting spectra obtained after complete formation of the adduct complexes. The data correspond to $\text{DK} = \text{DFHD}$ (upper trace), HFAC (middle trace), and FOD (lower trace).

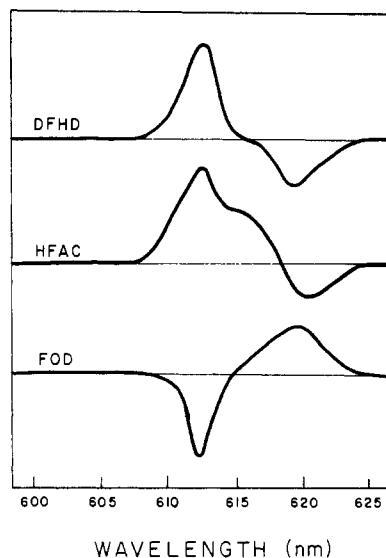


Figure 5. Circularly polarized luminescence spectra obtained within the 0-2 $\text{Eu}(\text{III})$ luminescence band system for 1:2 $\text{Eu}(\text{DK})_3(\text{MTS})_2$ complexes. The CPL lineshapes correspond to the limiting spectra obtained after complete formation of the adduct complexes. The data correspond to $\text{DK} = \text{DFHD}$ (upper trace), HFAC (middle trace), and FOD (lower trace).

the $\text{Eu}(\text{DK})_3$ complex acidity increases in a regular fashion with the degree of fluorination on the β -diketone ligands. When replacing *tert*-butyl (FOD) by perfluoromethyl (DFHD), one finds almost a 4-fold increase in complex acidity. This effect may also be related to the decreased steric bulk of the DFHD ligand.

Quite strong CPL spectra were also obtained within the 0-1 and 0-2 $\text{Eu}(\text{III})$ emission band systems, and these are shown in Figures 4 and 5. The spectra characteristic of the 1:2 adduct complexes were found to be very different from those of the 1:1 complexes and also exhibited differences with each other. While the DFHD and HFAC spectra greatly resemble each other, the FOD spectra are quite different. In fact, one observes that the FOD spectra are essentially mirror images of the DFHD spectra. Such an effect cannot be due to simple vicinal effects and must therefore represent a configurational effect.

Further probing of the configurational effects was possible through study of the luminescence dissymmetry factors, and these

Table IV. Luminescence Dissymmetry Factors for the Major CPL Peaks in the $\text{Eu}(\text{DK})_3(\text{S})_2$ Adduct Complexes

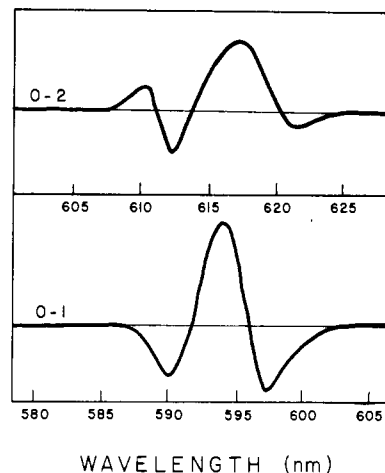
ligand	wavelength, nm	g_{lum}
DFHD	595.2	+0.020 2
	612.6	+0.001 79
	619.3	-0.002 78
HFAC	595.2	+0.019 6
	612.4	+0.002 14
	615.2	+0.001 93
	620.2	-0.003 37
FOD	595.2	-0.020 9
	612.3	-0.001 47
	619.4	+0.002 49

have been collected in Table IV. The 0-1 band system is most diagnostic for such considerations, since the lower degeneracy of the ${}^7\text{F}_1$ ground level leads to the simplest possible CPL spectra. The luminescence dissymmetry factors obtained for the 1:2 adduct complexes were approximately double those obtained for the 1:1 adducts. The dissymmetry factors calculated for the 0-2 band systems of the 1:2 adducts were actually reduced relative to those of the 1:1 adducts, but this observation is clearly a consequence of the band splitting that has taken place with the 1:2 compounds.

The approximate additivity of the 0-1 dissymmetry factors suggests an additive effect in the induced chirality. The configurational effect would therefore not consist of a dissymmetric arrangement of the β -diketone ligands induced by the stereoselective binding of two MTS ligands, but instead would represent varying $\text{Eu}(\text{DK})_3$ stereochemistries differing in the placement of the MTS ligands. One could obtain *cis* and *trans* $\text{Eu}(\text{DK})_3(\text{MTS})_2$ compounds, and the generation of either geometrical isomer would be determined by the steric constraints placed on the $\text{Eu}(\text{III})$ ion by the alkyl side chains of the β -diketone ligand.

$\text{Eu}(\text{DBM})_3(\text{S})$ Adduct Complexes. Unlike $\text{Eu}(\text{BZAC})_3$ (which was found to be decomposed by MTS), $\text{Eu}(\text{DBM})_3$ was found to form adduct complexes with the MTS substrate. This observation indicates that the formation constant of the $\text{Eu}(\text{DBM})_3$ compound is greater than that of the $\text{Eu}(\text{BZAC})_3$ compound. However, the CPL spectra were found to be a function of the chelate/substrate ratio and generally were quite different from the spectra shown for the well-defined 1:1 and 1:2 adduct complexes. In addition, the luminescence intensities and lifetimes could not be made to reach limiting values. These observations are consistent with complicated solution chemistry, in which 1:1 and 1:2 adduct complexes occur simultaneously at most chelate/substrate ratios.

At very low chelate/substrate ratios, the CPL spectra resembled those of the 1:1 complexes to a degree. Further additions of MTS (to concentration values which led to full formation of either 1:1 or 1:2 complexes) led to the generation of a new CPL pattern, not resembling any of the previous line shapes shown. Examples of the 0-1 and 0-2 CPL line shapes are shown in Figure 6. Even at MTS concentrations that led to limiting CPL line shapes, the luminescence lifetimes and intensities did not reach constant values. However, one can compute both the limiting value and formation constant through an iterative procedure in which the standard deviation in calculated constants was minimized. The assumption of 1:1 adducts did not lead to a minimum error (or even to reasonable errors), but the assumption of a 1:2 chelate/substrate stoichiometry permitted a calculation of formation constants precise to within 0.5%. This association constant is reported with those of the other 1:2 adduct complexes in Table III and is significantly smaller than any of the other values.

**Figure 6.** Circularly polarized luminescence spectra obtained within the 0-1 (lower trace) and 0-2 (upper trace) $\text{Eu}(\text{III})$ luminescence band systems of the $\text{Eu}(\text{DBM})_3$ adduct with MTS.

It is concluded, therefore, that the $\text{Eu}(\text{DBM})_3$ complex forms both 1:1 and 1:2 adduct complexes with MTS, but that these are rather weak in nature. The variability in the CPL spectra indicates the presence of multiple compounds in the solutions, an observation consistent with the weak nature of the interaction.

Conclusions

It has been shown that methyl *p*-tolyl sulfoxide is capable of forming 1:1 and 1:2 adduct complexes with $\text{Eu}(\text{DK})_3$ compounds, depending on details associated with the β -diketone ligand. Increasing degrees of ligand fluorination produce more acidic $\text{Eu}(\text{DK})_3$ complexes, and the 1:2 adduct stoichiometry is noted for the most acidic complexes. Formation constants for the adduct complexes can be calculated from trends in either luminescence intensity or lifetime data, and these values can be used to detail the relative acidities of the various $\text{Eu}(\text{DK})_3$ compounds.

The chirality experienced by the $\text{Eu}(\text{III})$ ion was found to result from either vicinal or vicinal/configurational effects. In the 1:1 adduct complexes, only vicinal effects were found to contribute to the $\text{Eu}(\text{III})$ optical activity. In the 1:2 adducts, weak configurational effects were found to yield the observed effects. The magnitudes of the chirality were found to be approximately additive, indicating that no stereoselectivity accompanied formation of the 1:2 adduct complexes. The configurational effects (as evidenced by variability in the CPL spectra) of the 1:2 complexes are undoubtedly due to geometrical isomerism. These should not be confused with chirality arising from a dissymmetric placement of the chelate rings, which would require the presence of stereoselective effects.

A combination of conventional and chiroptical spectroscopies can be used to study the details of $\text{Eu}(\text{DK})_3$ adduct formation. The results of the present and earlier studies have demonstrated that the adduct formation process is greatly complicated by a variety of geometrical constraints, most of which are normally ignored when the same $\text{Eu}(\text{DK})_3$ compounds are used as NMR shift reagents. Since the applicability of existing theory of LIS data requires knowledge of the adduct stereochemistries, further investigation into the process of adduct formation is required.

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