

of the V^{3+} ions. Such effects have been reported for $PbCu(NO_2)_6$ and other Cu^{2+} compounds.⁶

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Registry No. Potassium vanadium fluoride, 55957-20-5.

Contribution from the Department of Chemistry,
Seton Hall University, South Orange, New Jersey 07079

Solvent Dependence of the Circularly Polarized Luminescence of the Terbium(III) Chelate of 3-Acetyl-*d*-camphor

HARRY G. BRITTAİN

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The circularly polarized luminescence (CPL) spectra of $Tb(atc)_3$ have been obtained in 18 different amine solvents. Different CPL line shapes were obtained, which was interpreted to imply that certain diastereomers were preferred at the expense of others. It is proposed that the formation of a chelate adduct forces the chiral β -diketone ligands to interact and that they do so in a stereoselective fashion. The steric nature of the alkyl side chains of the amines was found to influence the degree of CPL observed and also determined the sign of the observed optical activity.

Introduction

The direct determination of enantiomeric compositions using optically active lanthanide shift reagents has been well documented,^{1,2} with the $Eu(III)$ and $Pr(III)$ β -diketone complexes derived from *d*-camphor having received the widest actual use. These ligands are prepared from 3-bromo-*d*-camphor, and the absolute configuration of this material is well-known.³ The most common ligands used have $R = CF_3$ (3-trifluoroacetyl-*d*-camphor or *facam*) or $R = C_3F_7$ (3-heptafluoropropylhydroxymethylene-*d*-camphor or *hfpc*). The most successful use of these shift reagents in NMR spectroscopy requires a complete knowledge of their solution bonding and steric requirements, and in addition one also needs to know about solution stereochemistries in order to perform meaningful theoretical calculations. In this laboratory, we have been quite interested in this problem and have determined binding ratios and formation constants for the complexes formed when $Eu(facam)_3$ and $Eu(hfpc)_3$ are titrated with simple alkylamines.⁴

While crystal-structure determinations of chiral shift reagent-substrate complexes yield maximum information,⁵ important information can be gathered by employing chiroptical methods such as circular dichroism (CD). Unfortunately, CD of lanthanide complexes is difficult to obtain except at very high concentrations of complex due to the very low molar absorptivities of the lanthanide $f-f$ transitions and hence has not been widely used. However, several of the lanthanide ions are known to emit in fluid solution at room temperature, and it is thus possible to record the circularly polarized luminescence (CPL) spectrum of these complexes.

The theory of the CPL effect has been described by Riehl and Richardson.⁶

The CPL of $Eu(facam)_3$ and $Eu(hfpc)_3$ has been reported in a variety of chiral and achiral solvents,⁷ where it was found that the strongest CPL was obtained when $Eu(facam)_3$ was dissolved in dimethyl sulfoxide. It was also found that CPL was only obtained for this chelate in 7 out of 28 neat solvents.^{7a} That CPL should be observed at all is rather striking, since it is known that tris chelates of chiral β -diketonates are capable of existing in a total of four diastereomers and that when one starts with an equal mixture of all four isomers, no net CD is obtained.⁸ Our previous work with $Eu(facam)_3$ and $Eu(hfpc)_3$ indicated that two molecules of alkylamine could be bound by each chelate but that they did so in a cooperative manner.⁴ This observation was interpreted to imply that some sort of reorganization of the β -diketone ligands took place upon binding, and we used this conclusion to infer that when CPL was obtained in the $Eu(III)$ chelates the geometry change was of a stereoselective type.⁴

In the present work, the CPL spectra are reported for a new chiral lanthanide β -diketone complex in a variety of solvents. The chelate, $Tb(atc)_3$ ($atc = 3$ -acetyl-*d*-camphor, where $R = CH_3$), differs in its behavior from that of $Eu(facam)_3$ in that CPL was observed in every solvent used. A definite stereoselective behavior was found, however, and CPL of different line shape could be obtained by varying the steric nature of the solvent. The previous work involving luminescence titrations⁴ indicated that "pockets" exist on the lanthanide ion coordination sphere and that the steric nature of the complexed substrates governs the extent of interaction. The present work demonstrates that in these labile complexes, the steric nature

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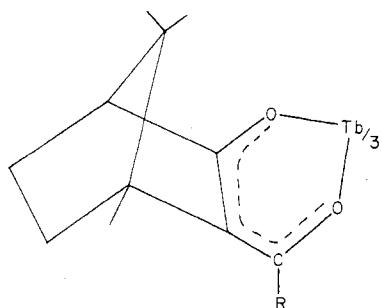


Figure 1.

of an achiral substrate can place a substantial demand on the coordination sphere of the metal ion.

Experimental Section

$Tb(acac)_3$ was synthesized according to a published method¹ and was analyzed by igniting weighed chelate samples to Tb_4O_7 . The complex could be obtained anhydrous after drying over P_4O_{10} in a vacuum desiccator; % Tb = 21.48 (21.51 theory), % C = 58.47 (58.53 theory), and % H = 6.90 (6.96 theory). Tb(III) ions were obtained from dissolution of Tb_4O_7 in the minimum amount of $HClO_4$, and acetylcamphor was kindly supplied by Professor G. W. Everett.

Spectra were obtained by dissolving approximately 10 mg of solid chelate in 3 mL of the neat solvent in a fluorescence cuvette, which corresponds to a chelate concentration of 0.005 M. All luminescence spectra were obtained on a high-resolution CPL spectrometer constructed in this laboratory, which has been described previously.⁹ An excitation wavelength of 290 nm was used for all studies (from a 200-W Hg-Xe arc lamp source), and the emission was collected at 180° to the exciting beam and analyzed by a $1/2$ -meter monochromator (Spex 1870) at 10-Å resolution. Higher resolution studies were carried out but failed to reveal any improvement in spectral features.

The CPL experiment measures two observables: total luminescence intensity (TL) given by $I = 1/2(I_L + I_R)$ and the differential luminescence intensity (CPL) given by $\Delta I = I_L - I_R$, where I_L and I_R refer to the intensities of left- and right-circularly polarized light, respectively. While the TL and CPL are measured in terms of relative units only, an absolute quantity may be obtained by taking the ratio of the two. The quantity is termed the luminescence dissymmetry factor and is given by $g_{lum} = \Delta I/I$.⁶

It was found that the $Tb(acac)_3$ chelate was not completely stable in the amine solvents used in this work and that the products of this thermal decomposition were totally nonluminescent. TL values for $Tb(acac)_3$ in various solvents could not therefore be compared, but since TL and CPL are recorded simultaneously, the values of g_{lum} are meaningful. In addition, the CPL line shapes did not depend on the extent of decomposition and hence make the most meaningful comparison.

Results

Previous work¹⁰ has demonstrated that lanthanide complexes of β -diketones bind most strongly to amine solvents and less strongly to alcohol donors. In these studies it proved possible to calculate formation constants from substrate-induced enhancements of luminescence intensities, and it was found in the present work that amine solvents bond most efficiently to $Tb(acac)_3$. In fact, very little enhancement at all was noted when attempting to study the luminescent behavior of $Tb(acac)_3$ in any oxygen-donor solvent, which led us to concentrate all work on the amine solvents.

After dissolution into primary, secondary, and tertiary amine solvents, it was found that CPL could always be measured in the $Tb(acac)_3$ emission bands. Four Tb(III) transitions were detected corresponding to the $^5D_4 \rightarrow ^7F_J$ emissions (where $J = 3, 4, 5, 6$), and it was always found that the transition to $J = 5$ was at least an order of magnitude stronger than the

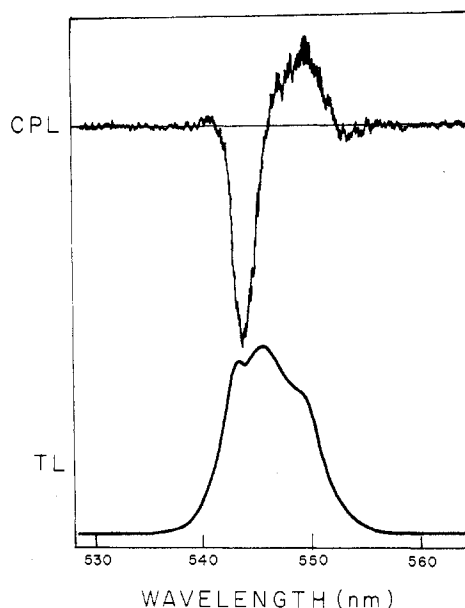


Figure 2. CPL (upper) and TL (lower) spectra for $Tb(acac)_3$ dissolved in *n*-propylamine. Both intensity scales are completely arbitrary.

Table I. Luminescence Dissymmetry Factors for $Tb(acac)_3$ Dissolved in Amine Solvents Leading to Type A Behavior

solvent	g_{lum}	
	543 nm	549 nm
<i>n</i> -propylamine	-0.019	+0.012
isopropylamine	-0.018	+0.013
<i>sec</i> -butylamine	-0.019	+0.011
ethylpropylamine	-0.019	+0.014
<i>tert</i> -butylamine	-0.031	+0.017
diethylamine	-0.021	+0.0089
methylbutylamine	-0.015	+0.0068
methylhexylamine	-0.012	+0.0063
methyloctylamine	-0.0093	+0.0049

Table II. Luminescence Dissymmetry Factors for $Tb(acac)_3$ Dissolved in Amine Solvents Leading to Type B Behavior

solvent	g_{lum}	
	543 nm	549 nm
<i>n</i> -butylamine	+0.0036	-0.0036
benzylamine	+0.010	-0.0023
triethylamine	+0.013	-0.028
tripropylamine	+0.016	-0.020
tributylamine	+0.020	-0.012
trihexylamine	+0.021	-0.010

others. We have concentrated our efforts on this transition. Under high resolution, three bands are noted in the total luminescence (TL) spectrum; these are found at approximately 543, 545, and 549 nm and correspond to various crystal field components of the $^5D_4 \rightarrow ^7F_5$ transition. CPL was found to be associated with the peaks at 543 and 549 nm, but no CPL was noted for the central transition at 545 nm.

When $Tb(acac)_3$ was dissolved in most of the amine solvents used in this study, it was found that the CPL of the 543-nm band was negative in sign and the CPL of the 549-nm band was positive. In most of these cases, the observed TL and CPL band shapes were identical, and a typical example is shown in Figure 2 where the spectra obtained for $Tb(acac)_3$ -*n*-propylamine are shown. Values for g_{lum} were calculated at both 543 and 549 nm, and these have been tabulated in Table I. A most interesting TL spectrum was recorded in diethylamine solvent, as is shown in Figure 3 with its associated CPL, and it was found here that the 545-nm band was quite reduced in intensity relative to the more normal spectral behavior.

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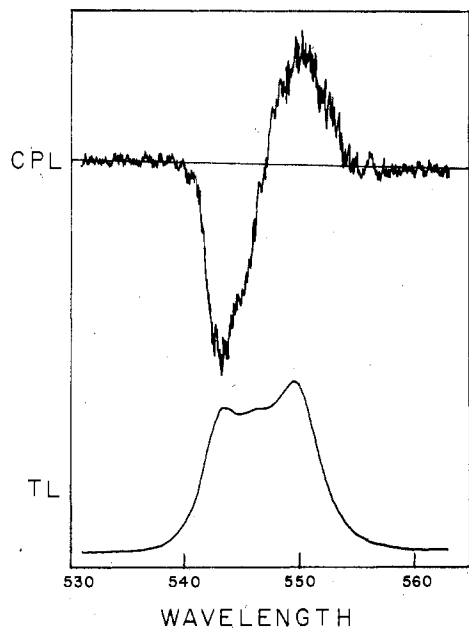


Figure 3. CPL (upper) and TL (lower) spectra for $\text{Tb}(\text{atc})_3$ -diethylamine.

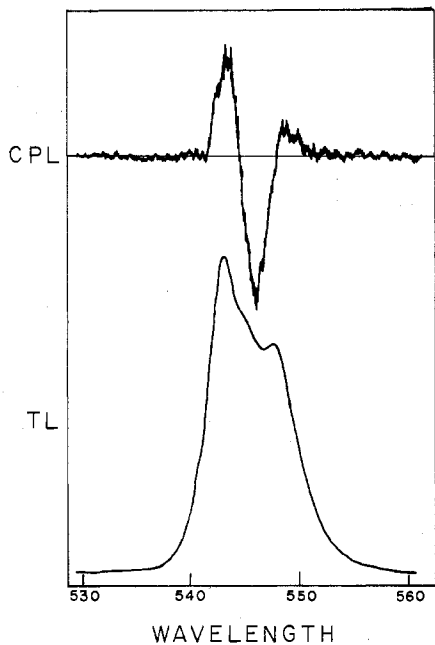


Figure 4. CPL (upper) and TL (lower) spectra for $\text{Tb}(\text{atc})_3$ -triethylamine.

It was found, however, that other CPL line shapes could be obtained in amine solvents not listed in Table I. A second type of line shape was found in six other solvents, and for this reason we have chosen to classify the solvents used as belonging to either class A (Table I) or class B (Table II). Class B solvents lead to positive CPL at 543 nm and negative CPL at 549 nm, with the CPL of the class B solvents appearing to be the mirror image of the CPL obtained with the class A solvents. An example of class B CPL is shown in Figure 4, where the spectra for $\text{Tb}(\text{atc})_3$ -triethylamine are shown. The g_{lum} values for class B solvents are collected in Table II, and one may note that most of the solvents leading to this type of CPL line shape are found to be tertiary amines.

Two solvents were found in which the observed CPL appeared to consist of a mixture of class A and class B behavior. The CPL spectrum of $\text{Tb}(\text{atc})_3$ in pyridine (Figure 5) and isobutylamine (Figure 6) consists of quite a few peaks which

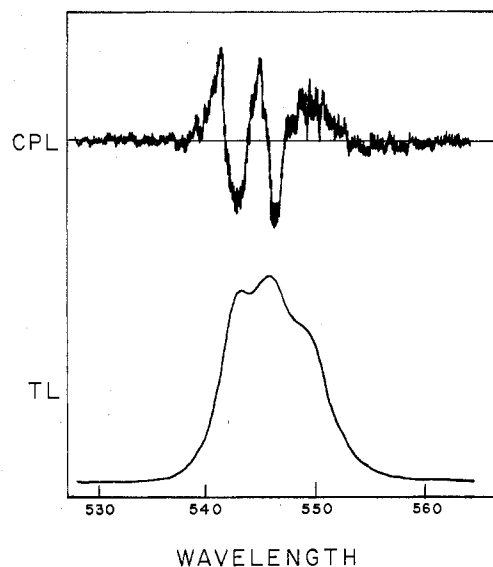


Figure 5. CPL (upper) and TL (lower) spectra for $\text{Tb}(\text{atc})_3$ -pyridine.

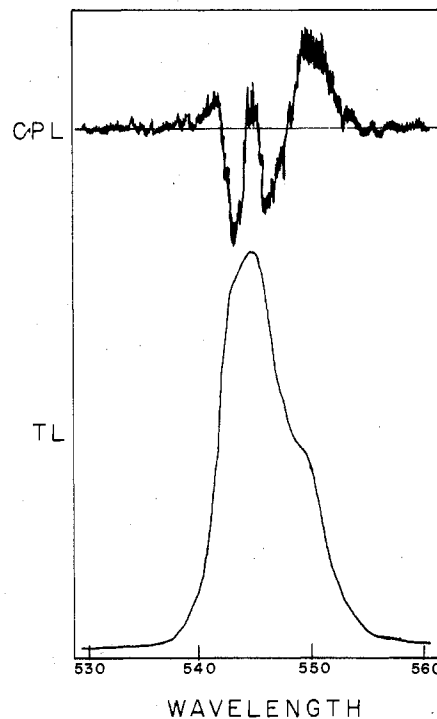


Figure 6. CPL (upper) and TL (lower) spectra for $\text{Tb}(\text{atc})_3$ -isobutylamine.

appear to have no correspondent peak in the TL spectrum. One can rationalize this behavior quite readily by realizing that the superimposition of the two types of line shape in nonequal amounts would lead to quite complicated spectra.

The nature of the $\text{Tb}(\text{atc})_3$ -substrate adducts was determined by applying Job's method of continuous variations to the emission spectra. The degree of luminescence intensity variations was not great enough to allow an accurate determination of formation constants, but it was possible to show that only 1:1 stoichiometry could be obtained for the $\text{Tb}(\text{atc})_3$ -substrate adducts of the present study.

Discussion

The CPL spectra presented in this work clearly demonstrate that the sense of chirality felt by the central Tb(III) changes with the nature of the solvent, even though almost all of the amine solvents used here are inherently achiral. It is well-known that 1:3 transition-metal complexes with atc and related

ligands form a series of four diastereomers, which are denoted Δ -cis, Δ -cis, Δ -trans, and Δ -trans.⁸ Experimentally, it is found that the CD spectra of the Δ -cis and Δ -trans forms are the same and that the CD of the Δ -cis and Δ -trans are opposite in sign and equal in magnitude.⁸ These four diastereomers cannot be separated when one prepares $\text{Tb}(\text{atc})_3$ since the analogous rare-earth complexes are exceedingly labile, and in solution phase one would expect that the four isomers would rapidly interconvert. As a result, if equal amounts of the four diastereomers were present in $\text{Tb}(\text{atc})_3$, one would predict that no CPL should be observed.

However, it is well-known that six-coordinate lanthanide complexes are rare in solution and that much higher coordination numbers are possible.¹¹ In the present work, evidence has been obtained which points toward seven-coordination for the $\text{Tb}(\text{III})$ ion in the atc-substrate complexes. The atc ligands would be expected to have a large degree of steric bulkiness due to the presence of the camphor group, and solvent coordination to the metal would force the three ligands to interact more with each other than in the absence of the solvent. Since the ligands are inherently chiral, one would expect, therefore, to observe a stereospecific preference for a particular conformation that would minimize the interactions between the chelate rings. Such a preference would perturb the diastereomer interconversion and would result in the enrichment of one form over another; this would in turn lead to observable CPL.

The magnitude of the CPL suggests that the effects found in the present work are configurational in nature since the g_{lum} values are nearly an order of magnitude higher than values obtained in another work where the optical activity was due solely to conformational and vicinal effects.⁹ This would then suggest that the sign of the CPL is related to the absolute configuration of the dominant diastereomer and that the class A and class B CPL line shapes represent the dominance of opposite configurations. We have recently observed that the sign of the CPL induced in the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission of $\text{Tb}(\text{thd})_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) by chiral solvents correlates nicely with the absolute configuration of those solvents.¹²

We conclude, therefore, that the different CPL line shapes that have been obtained during the course of this work reflect increased steric interactions among ligands in the $\text{Tb}(\text{III})$ coordinative environment when one forms the adduct. In

uncomplexed $\text{Tb}(\text{atc})_3$ (obtainable, for example, in CCl_4), there is little need for extensive interligand interaction to take place while the $\text{Tb}(\text{III})$ ion remains six-coordinate. The expansion of the coordination number that takes place upon adduct formation must force the chelate to choose one stereoisomer over others, and in the cases of the pyridine and isobutylamine chelate adducts there may be two possible structures of comparable energy available. The superimposition of CPL of each of these does not lead to net cancellation, although the reason for this is not yet clear. Presumably, the lack of observed CPL for $\text{Eu}(\text{facam})_3$ in a wide variety of solvents is a reflection of a lower degree of diastereomer preference.^{7a} While the chirality due to the asymmetric atoms of the ligands cannot be altered in any way, it is certainly possible that the configurational isomerism of the chelate adduct will be able to dominate the observed CPL.

A few trends are observed in the g_{lum} values which indicate that the steric nature of the solvent plays an important role in the diastereomer perturbation. In the secondary amines, one notes a decrease in g_{lum} values as the size of one of the alkyl side chains increases, and one may conclude that the amine is binding less efficiently and therefore inducing less of a change at the $\text{Tb}(\text{III})$ ion. It is interesting to note that the largest effects are found with the most sterically bulky amines; tertiary amines make up almost all the class B solvents, and *tert*-butylamine led to the largest value of g_{lum} in the class A group.

Exactly why different diastereomers of $\text{Tb}(\text{atc})_3$ should be enriched by the achiral solvents is not clear at the present time. In the case of $\text{Eu}(\text{facam})_3$, only one CPL line shape was obtained when CPL could be detected,^{7a} and these observations indicate that the process is more complicated than we have indicated. Further investigations are now under way to probe these effects in greater detail.

Acknowledgment. We are greatly indebted to Professor G. W. Everett, Jr. (University of Kansas), for providing the sample of acetylcamphor used to synthesize the $\text{Tb}(\text{III})$ chelate. Financial assistance by the Research Corp. (Cottrell Grant 8926) and the National Science Foundation (Grant CHE78-03402) is also gratefully acknowledged.

Registry No. $\text{Tb}(\text{atc})_3$, 73663-66-8; *n*-propylamine, 107-10-8; isopropylamine, 75-31-0; *sec*-butylamine, 13952-84-6; ethylpropylamine, 20193-20-8; *tert*-butylamine, 75-64-9; diethylamine, 109-89-7; methylbutylamine, 110-68-9; methylhexylamine, 35161-70-7; methyl-octylamine, 2439-54-5; *n*-butylamine, 109-73-9; benzylamine, 100-46-9; triethylamine, 121-44-8; tripropylamine, 102-69-2; tributylamine, 102-82-9; trihexylamine, 102-86-3.

Contribution from the Department of Chemistry, Tel-Aviv University, Ramat Aviv, Tel-Aviv, Israel

Optical Spectrum of Hexa-aquoruthenium(III) Ion and Its Conjugate Base

ZVI HARZION and GIL NAVON*

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The spectrum of $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ was measured and fitted to the Tanabe and Sugano matrices. The parameters obtained, $Dq = 2860 \pm 40 \text{ cm}^{-1}$ and $B = 640 \pm 40 \text{ cm}^{-1}$ assuming $C/B = 4$, were compared with a systematic survey of analogous ruthenium(III) and rhodium(III) complexes. The pK for the formation of $\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}$ was found to be 2.4 ± 0.2 at 20°C and $I = 1.0 \text{ M}$ by a spectrophotometric titration. The charge-transfer bands of $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ and $\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}$ were interpreted in terms of the optical electronegativities of H_2O and OH^- .

Introduction

There are various reports in the literature containing data on optical spectra of ruthenium(III) complexes.¹⁻⁷ In most

of these spectra the d-d transitions are obscured by strong charge-transfer ones. In ligands with high electronegativity,

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