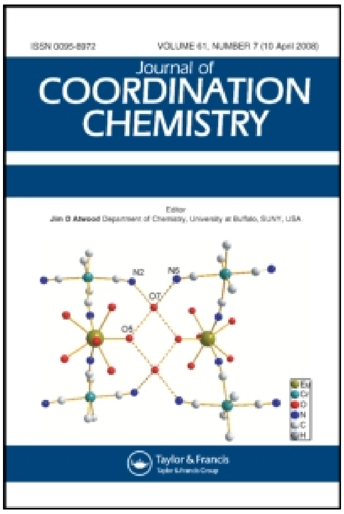

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Harry G. Brittain[a]
[a] The Squibb Institute for Medical Research, New Brunswick, NJ

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CIRCULARLY POLARIZED LUMINESCENCE STUDIES OF CHIRAL LANTHANIDE COMPLEXES

HARRY G. BRITTAIN

The Squibb Institute for Medical Research, 1 Squibb Drive, New Brunswick, NJ 08903

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The utility of circularly polarized luminescence (CPL) spectroscopy in the study of lanthanide ion coordination chemistry has been described. A variety of optically active Tb(III) and Eu(III) compounds have been considered, containing chiral carboxylic acids, chiral amino acids, chiral aminopolycarboxylic acids, achiral β-diketones and chiral substrates, and chiral β-diketones and achiral substrates. In addition, studies of the Pfeiffer effect in lanthanide compounds have also been discussed. CPL spectroscopy has been found to be the chiroptical technique of choice for lanthanide compounds, and a considerable amount of structural and stereochemical information has been obtained from these investigations.

Keywords: Circularly polarized luminescence, chiroptical spectroscopy, lanthanide complexes, carboxylic acid complexes, aminopolycarboxylic acid complexes, beta-diketone complexes, lanthanide

1. INTRODUCTION

Studies of optical activity have figured prominently in the development of inorganic chemistry, and such work began with Werner himself.[1] In terms of chiral transition metal complexes, the field is fairly mature and still exceedingly active. The absolute configurations of many complexes have been established by X-ray diffraction methods,[2] and correlation of these observations with chiroptical spectroscopic studies has led to more detailed probings of the optical activity associated with the d–d transitions of transition metal compounds.[3] One may use a variety of procedures to theoretically model the complex chirality, and these calculations can reach high degrees of accuracy.[4]

The field of f-element optical activity has not yet reached this sophisticated state. Several important differences exist when comparing transition metal and lanthanide chemistries, and these differences have important implications for chiroptical work. Lanthanide–ligand bonding is almost entirely ionic in nature, and hence one must abandon the concept of directed valence in lanthanide compounds. The complexes are normally labile and fluxional on spectroscopic time scales, and therefore complexes cannot be produced in solution whose chirality is due exclusively to a dissymmetric arrangement of chelate ligands. Finally, the intensities of f–f absorption bands are feeble, and consequently the use of circular dichroism (CD) as a chiroptical probe is usually inappropriate. While CD spectra may be obtained in solutions of high complex concentration,[5] spectra–structure correlations under these conditions are not possible due to possible oligomerization of the complexes.[6]

These difficulties may be circumvented by using circularly polarized luminescence (CPL) spectroscopy as the chiroptical probe. Of the members of the lanthanide

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*Author for correspondence.

series, Tb(III) and Eu(III) can exhibit quite large quantum yields for photoluminescence and are exceedingly useful as emissive bioinorganic probes.[7] CPL spectroscopy combines the instrumental sensitivity of luminescence techniques with the structural selectivity of CD spectroscopy. By employing CPL spectroscopy, chiroptical data may be obtained at low concentrations of lanthanide complex, thus avoiding questions of polynuclear self-association. Careful design of ligation systems may also produce molecular chirality which may be directly related to observable CPL phenomena, and such work has proven to be useful in the study of lanthanide ion coordination chemistry.[8] In the following sections, work will be described in which CPL spectroscopy has been used to obtain new and significant details of lanthanide ion complexation and molecular stereochemistries.

2. INSTRUMENTATION FOR THE MEASUREMENT OF CIRCULARLY POLARIZED LUMINESCENCE SPECTRA

Circularly polarized luminescence is the spontaneous emission of left- or right-circularly polarized light by a chiral, luminescent molecule. No commercial instrumentation is available for the detection of this effect, but suitable apparatus has been assembled by several groups. Several descriptions of analog spectrometers have been provided,[9-11] and more recently the design of a digital instrument has been described.[12]

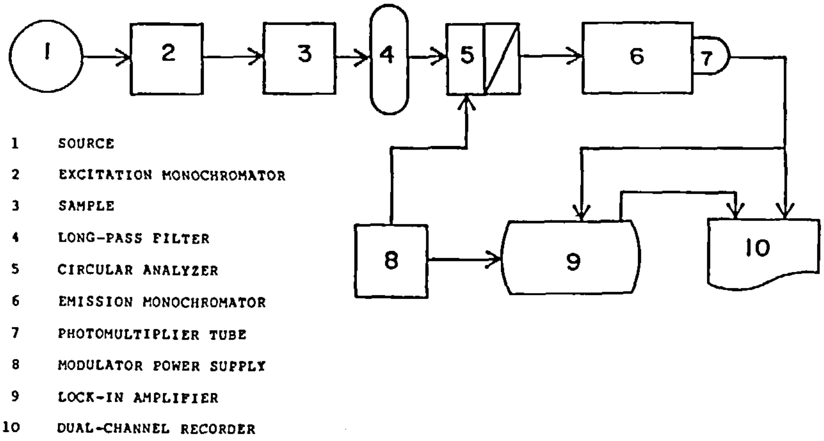

FIGURE 1 Block diagram of a typical CPL spectrometer, configured to acquire data in the analog mode.

The first working CPL spectrometers were all based on essentially the same analog design, for which a typical block diagram is shown in Figure 1. The excitation source can be either a laser or an arc lamp, but to avoid spectral artifacts the excitation energy should be completely depolarized. Either monochromators or filters can be used to isolate the desired exciting wavelengths. The sample itself can be a fluid solution contained in a fluorescence cuvette, or a single crystal mounted in a suitable holder. Naturally optically active compounds will spontaneously emit left- or right-circularly polarized light, but chirality may also be induced in an achiral sample by placing the material in a longitudinal magnetic field. One normally collects the resulting luminescence at 0° to the excitation beam to avoid complications due to the possible presence of linear polarization in the emission. Other small artifacts may arise due to imperfections in the optical train, but techniques exist whereby these may be minimized.[13]

The emission is then passed through a circular analyzer, which consists of a dynamically driven guarter-wave retardation element followed by a linear polarization element. Essentially all CPL spectrometers employ a photoelastic modulator as the retardation element since its wide acceptance angle is well suited for luminescent work. The working element of the modulator is isotropic silica (for visible wavelengths) which is rendered anisotropic by the application of a periodic external stress. The modulator induces polarization phase shifts of $\pm 90°$, and thus transforms the small quantity of circular polarization in the emission beam into periodically interconverting orthogonal planes of linearly polarized light. The linear polarizer following the modulator extinguishes one of the linear components and thus produces an AC ripple (proportional to the CPL intensity) on top of a large DC background (proportional to the total luminescence, or TL). A major loss of CPL signal can arise from depolarization effects originating with imperfect optical elements, and consequently it is advisable to reduce the number of optical components preceding the modulator to the absolute minimum.

The emission is then analyzed in the conventional manner by an emission monochromator. The light is detected by a photomultiplier tube (cooled so as to reduce noise), whose current output is converted to voltage and divided. One component can be displayed directly as the TL spectrum. The other signal is directed to a lock-in amplifier, and phase-sensitive detection is used to detect only the high-frequency AC signal proportional to the CPL intensity. The output of the lock-in can either be observed directly, or one can take the analog ratio of the CPL and TL signal and display this quantity.

A digital instrument suitable for the measurement of circularly polarized luminescence has been described.[12] The optical design is basically the same as for the analog version, but the method of detection is quite different. In the digital device, photon counting detection is used to measure the number of photopulses originating from right-circularly polarized emission separately from the photopulses associated with left-circularly polarized emission. These pulse counts may be subtracted and averaged to yield the luminescence dissymmetry factor. When measured in this fashion, the CPL magnitudes are obtained on an absolute scale, particularly well suited for calibration purposes. The advantages of the digital approach over the conventional method are flat stable baselines, and improved signal-to-noise ratios. The sensitivity of the instrument exceeds 1×10^{-5}, which is comparable to the sensitivity of circular dichroism measurements. The digital instrument is particularly suited for the detection of small degrees of circular polarization.

Regardless whether the circularly polarized luminescence is obtained by means of the analog or digital method, two observable quantities are produced. The total luminescence (TL) intensity is given by:

$$\mathrm{I} = (\mathrm{I}_L + \mathrm{I}_R)/2$$

and the CPL intensity is given by:

$$\mathrm{dI} = \mathrm{I}_L - \mathrm{I}_R$$

In these equations, I_L and I_R represent the emitted intensities of left- and right-circularly polarized light. It should be stressed that in conventional CPL spectroscopy, the differential emission arises from the dissymmetry of the sample itself. Alternate methods to obtain CPL spectra consist of placing the compound in a longitudinal magnetic field,[10] or by exciting the sample with pure circularly polarized light.[14,15] As in most luminescence measurements, the values of **I** and **dI** are obtained in arbitrary units. This unit dependence may be removed by taking the ratio of these quantitites, thus obtaining the luminescence dissymmetry factor:

$$g_{lum} = dI/I$$

The luminescence dissymmetry factor is to be considered exactly analogous to the Kuhn anisotropy factor associated with CD spectroscopy.[11] In suitable circumstances, the dissymmetry factor may be related to the rotational strength of the luminescent transition.

Richardson has developed a series of selection rules for the electronic factors which govern the magnitudes of the chiroptical properties of f–f transitions in chiral lanthanide compounds.[16] These rules were based on the S, L, and J quantum numbers of lanthanide 4f-electron states, as perturbed by spin–orbit coupling and crystal field interactions. The theory predicts that for Tb(III), the largest optical activity should be observed within the $^5D_4 \rightarrow {}^7F_5$, $^7F_4$, and $^7F_3$ transitions. For Eu(III) the largest CPL should be noted within the $^5D_0 \rightarrow {}^7F_1$ transition, and the theory indicates that this band system contains the most favorable combination of factors leading to the largest rotational strengths. All of the predictions made on the basis of these selection rules have been verified in many CPL investigations.[8]

As mentioned earlier, lanthanide complexes are far too labile to permit resolution of compounds whose chirality is due solely to a dissymmetric arrangement of ligands. However, these configurational effects have been measured in compounds where the dissymmetric arrangement was stabilized by outer-sphere association phenomena (Pfeiffer Effects). Two other possible sources of lanthanide ion chirality exist, and these have been found to be very common in solution phase chemistry. One of these is the vicinal effect, where the metal ion experiences dissymmetry when a ligand contains an asymmetric carbon atom. The other is the conformational effect, and this contribution requires that the asymmetric carbon be bound as part of the chelate ring. In this latter effect, the mirror images of the entire chelate ring are non-superimposible and a much larger chirality is experienced by the metal ion.

3. CIRCULARLY POLARIZED LUMINESCENCE STUDIES OF CHIRAL LANTHANIDE COMPLEXES

3.1 Lanthanide Complexes with Chiral Carboxylic Acids

In aqueous solutions, the interactions between lanthanide ions and ligands capable of binding in a multidentate fashion are normally quite strong, and this binding strength is maximal when a significant portion of the ligation groups consists of carboxylates. Hydroxy carboxylic acids represent a class of ligands which are known to bind lanthanide ions with great efficiency,[17] and which may be obtained enantiomerically pure without much difficulty. As a result, early chiroptical studies were carried out on such complexes using CD spectroscopy.[18–20]

As part of the first CPL studies performed at the University of Virginia, Luk and Richardson studied the chirality of Tb(III) and Eu(III) complexes containing a variety of chiral amino and carboxylic acids.[21,22] In these and subsequent works of that period,[23] quite large ligand/metal ratios were used. It was subsequently learned[24] that many of the compounds studied during this series of investigations actually existed as part of polynuclear assemblies, and thus the derived spectra–structure correlations required further refinement.

In an attempt to simplify the solution equilibria to a manageable level, a series of CPL investigations involving ternary lanthanide complexes was begun. With this approach, a complex is first formed in which the lanthanide ion (Tb(III) for the most part) is partially coordinated by an achiral ligand:

$$Tb^{3+} + AL^{n-} \longleftrightarrow Tb(AL)^{(3-n)+}$$

The achiral ligand is invariably a multidentate coordinator of high binding strength: ethylenediamine tetraacetate, nitrilotriacetate, and dipicolinate are a few of the ligands which have been used. The $Tb(AL)^{(3-n)+}$ complex is then allowed to bind the chiral ligand of interest:

$$Tb(AL)^{(3-n)+} + CL^{m-} \longleftrightarrow Tb(AL)(CL)^{(3-n-m)+}$$

thus producing a ternary complex in the process. Several advantages result from this approach: (1) the Tb(III)/chiral ligand stoichiometry can be limited to that of 1:1 complexes, (2) the presence of polymeric Tb(III) compounds can be eliminated, and (3) normally insoluble Tb–ligand complexes can be rendered soluble over all pH values. Through the use of ternary complexes, systematic structure–spectra correlations useful for describing the nature of Tb(III) interactions with a variety of chiral ligands may be obtained.

In these ternary complexes, it was possible to differentiate between the situations where Tb(III) chirality was due to the presence of vicinal or vicinal/conformational effects. When the chiral ligand could bind Tb(III) merely in a monodentate fashion, only vicinal effects could yield Tb(III) optical activity. It was determined that for 13 chiral ligands, the Tb(III) optical activity within the $^5D_4 \rightarrow {}^7F_5$ band system was exceedingly weak and of one sign only.[25] The sign of this CPL correlated with the absolute configuration of the chiral ligand; substrates of the (S)-configuration led to the observation of positive CPL. On the other hand, simple *alpha*-hydroxycarboxylic acids were known to bind lanthanides in a bidentate fashion, and the chirality induced in the Tb(III) emission bands by these ligands would be dominated by conformational effects. Double-signed CPL spectra of much higher magnitude were observed in that case.[26] The two types of CPL spectra have been compared in Figure 2.

It was thus concluded that CPL spectroscopy was an ideal technique for the study of lanthanide–ligand interactions. In a series of studies in which the nature of the chiral *alpha*-hydroxycarboxylic acid and the achiral ligand fillers were varied, it was determined that a particular CPL lineshape could be identified with this simple mode of coordination.[25–28] These results were confirmed by the observations of Das Gupta and Richardson.[29] Changes in the fashion by which a given ligand could bind lanthanide ions would, of course, alter the nature of the conformational effect experienced by the Tb(III) ion. This effect was observed most dramatically for Tb(dipicolinate) complexes of (S)-malic acid: the CPL spectra inverted at neutral pH

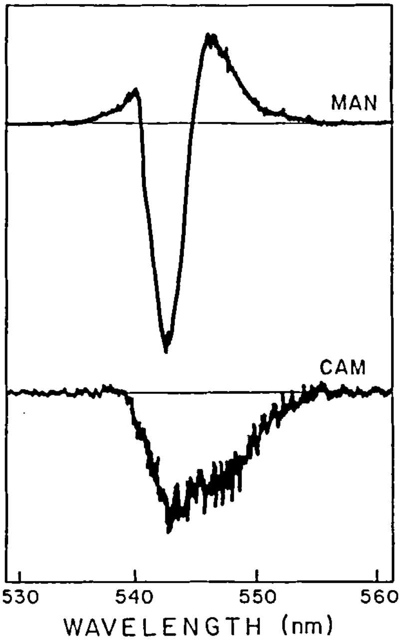

FIGURE 2 CPL spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) band system for the Tb(DPA) complexes of L-camphoric acid (lower trace) and L-mandelic acid (upper trace). The CPL intensity of the camphorate complex is approximately 20 times less than that of the mandelate complex.

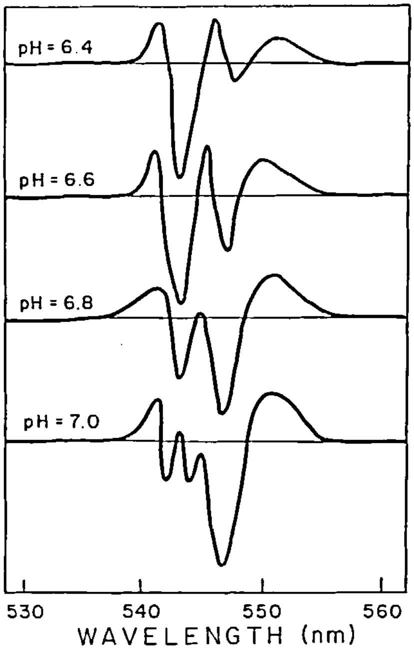

FIGURE 3 CPL spectra obtained as a function of pH within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) band system for the Tb(NTA) complex of L-malic acid.

values as the coordination mode change from bidentate to tridentate.[30] An example of this phenomenon is shown in Figure 3.

The correlation of CPL lineshapes with plausible solution phase structures has enabled the deduction of coordination modes in multi-functional ligands. The exact ligating groups employed by (R,R)-tartaric acid was found to vary with the nature of the achiral ligand used to fill the Tb(III) coordination sphere,[31] thus providing evidence that steric interactions in the Tb(III) coordination sphere could be studied by CPL spectroscopy. It has also been observed through CPL studies that D-isocitric and (S)-carboxymethoxy succinnic acids[32] exhibit a multitude of coordinative possibilities, but that these may be deduced through comparisons with CPL spectra obtained in known situations.

Through these studies on simple carboxylic acids, the CPL technique has been calibrated to the point where unknown coordination possibilities can be confirmed or discounted after comparison with the existing library of spectra–structure correlations. The ability to differentiate between monodentate and multidentate ligand bonding is extremely useful, as will be seen in succeeding sections.

3.2 Lanthanide Complexes with Chiral Amino Acids

The family of (S)-amino acids forms another sequence of chiral substrate ligands for which a large variety of coordination possibilities exist. When in the zwitterionic form, the aliphatic amino acids bind only as monodentate ligands. Raising the solution pH to sufficiently high values so as to form the anionic ligand results in precipitation of highly insoluble hydroxide compounds, and thus all previous work involved amino acids containing additional functional groups.[33] It was shown that potentially terdentate amino acids would exhibit a variety of CPL lineshapes,[34] but with the identity of the complexes being in doubt further work was again required.

Since it had been established that strong CPL could be obtained in Tb(III) complexes of (S)-aspartic acid[22] and that the ligand bound Tb(III) between the two carboxylate groups, the first mixed-ligand CPL work focused on this ligand system. CPL spectra obtained for these complexes did indeed reflect the presence of conformational effects,[35] but it was also learned that the conformational effect could be perturbed by the nature of the achiral portion of the Tb(III) coordination sphere.[36] It has now become established that hexadentate achiral filler ligands will alter the conformation of coordinated aspartic acid, but that pentadentate or tetradentate filler ligands will not.[37] Interestingly, two dipicolinate ligands (equating a broken hexadentate ligand) do not perturb the conformation of aspartic acid, thus implying that bound ligands will attain their most favorable conformations if sufficient flexibility exists in the achiral portion of the coordination sphere.

Proof that lanthanide ions can form chelate rings with *alpha*-amino carboxylates (after deprotonation of the ammonium group) was obtained through studies of ternary complexes.[38] CPL studies were carried out on the Tb(EDTA) complexes of 27 amino acids, and the transition from vicinal (monodentate binding) to conformational (implying formation of a chelate ring) chirality was observed for all substrates. The presence of other functional groups on the amino acid ligands led to different CPL lineshapes when these could be involved in Tb(III) binding. Extremely similar spectra were observed once both terminal ligating groups were ionized in the case of (S)-aspartic acid, (S)-asparagine, and (S)-diaminobutyric acid, implying bidentate coordination modes for each. Exactly the same result was observed for (S)-cysteine, indicating for the first time that an ionized sulfhydryl group could bind lanthanide ions in aqueous solution. This interaction was found to be even stronger than the interactions of (S)-serine or (S)-threonine with Tb(EDTA). Evidence that the imidazole portion of (S)-histidine could also bind directly to Tb(III) was also obtained from the CPL studies. Examples of the various CPL spectra observed for amino acid substrates are shown in Figure 4.

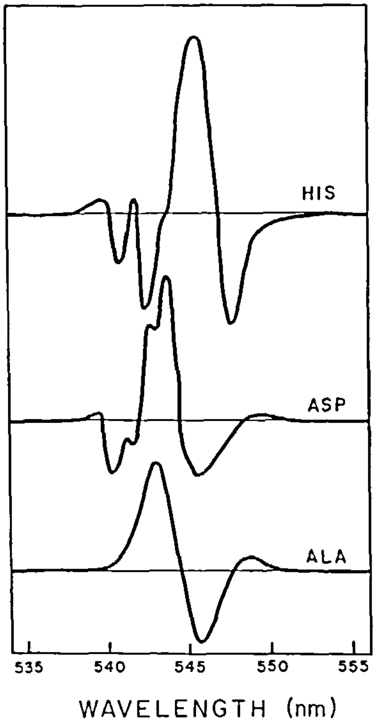

FIGURE 4 CPL spectra obtained at pH 9 within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) band system for Tb(EDTA) complexes with L-amino acids. Data are shown for L-alanine (lowest trace), L-aspartic acid (middle trace), and L-histidine (upper trace).

3.3 Lanthanide Complexes with Chiral Aminopolycarboxylic Acids

The first chiroptical studies of lanthanide compounds concerned CD investigations of complexes containing (R)-1,2-propylenediamine tetraacetic acid (PDTA),[39,40] or (S,S-ethylenediamine disuccinic acid (EDDS).[41] Pearson and coworkers subsequently used (R)-PDTA[42] or (R,R)-trans-1,2-cyclohexanediamine tetraacetic acid (CDTA)[43] as reagents in the spectropolarimetric titration of lanthanide ions. Given the large stability constants for lanthanide aminopolycarboxylate complexes, CPL investigations of complexes containing chiral ligands were of high interest.

The first CPL investigations concentrated on the Tb(III) and Eu(III) complexes containing (R)-PDTA and (R,R)-CDTA.[44] It was found that the CPL spectra remained invariant between pH 4 and 10, and underwent drastic changes above pH 10. This behaviour could be readily understood in light of energy transfer studies[45] which demonstrated that the complexes experienced significant degrees of polynuclear self-association above pH 10. In a subsequent work, the lanthanide complexes of (S,S)-EDDS were studied, and the complexation chemistry was found to be considerably more complicated. For the 1:1 complexes, the low pH regions were characterized by self-association, but the oligomers were broken up at high pH values.[46]

Since earlier work had shown that steric interactions could exist in ternary complexes containing hexadentate aminopolycarboxylate ligands, CPL studies were used to study these phenomena for compounds containing chiral aminopolycarboxylates and achiral substrate ligands. For Tb(PDTA) and Tb(CDTA), it was found that only relatively large ligands (particularly those capable of binding in a terdentate manner) could perturb the Tb(III) stereochemistry.[47] Flexible ligands (such as succinic acid) were evidently more prone to adjust their own conformation (rather than perturb the aminopolycarboxylate stereochemistry) in order to fit in the available space in the Tb(III) coordination sphere. At high pH, most ligands were expelled from the Tb(III) coordination sphere; only the most strongly binding ligands could interfere with the formation of oligomeric compounds. In the case of Tb(EDDS) compounds, the low pH oligomers proved to be almost impossible to break apart with the common substrates used.[48] The EDDS ligand evidently took up less space on the Tb(III) ion than did either PDTA or CDTA, since only the most sterically demanding ligands were found to perturb the EDDS stereochemistry.

3.4 Lanthanide Complexes with Achiral beta-*Diketones and Chiral Substrates*

Lanthanide derivatives of *beta*-diketones have found extensive use as NMR shift reagents, with the principal applications being spectral clarification and relaxation time perturbation.[49] The lanthanide complexes function as Lewis acids, and will form adduct complexes with virtually any compound capable of acting as a Lewis base:

$$\mathrm{Ln(DK)_3} + \mathrm{S} \longleftrightarrow \mathrm{Ln(DK)_3(S)}$$

DK signifies a *beta*-diketone ligand which is inherently achiral. When the substrate, S, is chiral, the adduct complex will be optically active and CD spectroscopy could be used as a means to determine absolute configurations and enantiomeric purities of substrates.[50,51]

Optical activity can be induced in the f–f emission bands of $\mathrm{Eu(DK)_3}$ compounds upon adduct formation with chiral substrates, and the resulting CPL has been characterized by exceedingly large dissymmetry factors.[52] It was shown that the CPL spectra induced in Tb(III) derivatives of dipivaloylmethane (DPM) could be directly related to the absolute configuration of the chiral substrate.[53] This correlation of CPL signs with absolute configuration enabled a determination of the substrate binding sites which led to adduct formation between several cinchona alkaloids and the Eu(III) derivative of theonyltrifluoroacetone (TTFA).[54]

A systematic study of the CPL induced by ten chiral phenylalkylamines and pheylalkylamino alcohols in two $\mathrm{Eu(DK)_3}$ compounds was undertaken to establish whether one could differentiate between vicinal and conformational effects.[55] Simple amines did indeed yield the lowest dissymmetry factors, and one could count the number of chelate rings bound to the Eu(III) ion by the intensity of CPL. It was established that terdentate substrates could bind $\mathrm{Eu(DK)_3}$ using all functionalities, thus forming a 9-coordinate adduct complex. Verification of these binding modes was possible through determination of adduct formation constants, which could be calculated from concentration dependencies of CPL intensities. In further work, the CPL induced in Eu(TTFA)$_3$[56] and Eu(FOD)$_3$[57] was used to study the effects of substrate stereochemistry on the adduct formation process. As long as the chiral substrates contained only a single asymmetric atom, correlation of CPL signs with absolute configurations was possible. However, when the substrates contained more than one asymmetric centre, then the empirical correlations became more complicated.

Evidence that formation of adduct complexes is not always a simple phenomenon was obtained from CPL investigations. When titrating non-fluorinated Eu(DK)$_3$ compounds with amino alcohols, it was found that the CPL spectra were concentration dependent.[58] Examples of this behaviour are shown in Figure 5. Examination of infrared spectra of isolated adducts revealed that the amino alcohol and *beta*-diketone ligand had condensed to form Schiff bases even though the *beta*-diketone was coordinated to the Eu(III) ion. This process does not take place effectively with fluorinated *beta*-diketones, as the resulting Schiff base ligands are prone toward hydrolysis. When adduct complexes were formed with amines incapable of forming Schiff bases, the CPL and IR spectra were indicative of well-defined adducts.[59]

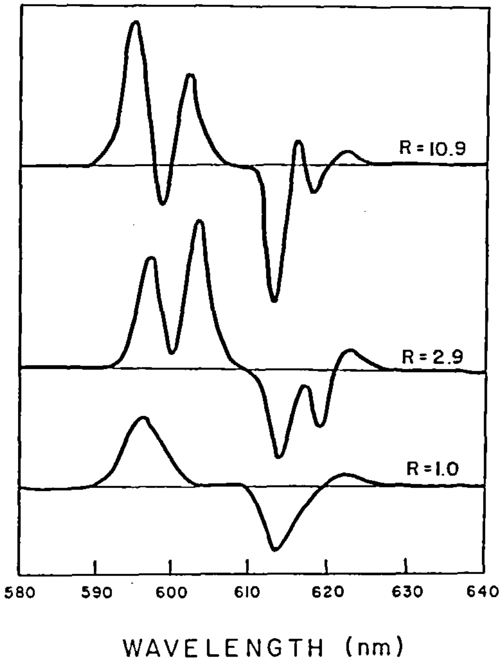

FIGURE 5 CPL spectra obtained within the $^5D_0 \rightarrow {}^7F_1, {}^7F_2$ Eu(III) band systems during the titration of Eu(DBM)$_3$ with D-phenylglycinol. The ratio of substrate to complex is given with its corresponding CPL spectrum.

A systematic study of the ternary complexes formed by ten Eu(DK)$_3$ compounds with (R)-methyl p-tolyl sulfoxide has been reported.[60] Adduct complexes having 1:1 and 1:2 chelate/substrate stoichiometries were formed, depending on the degree of fluorination in the *beta*-diketone chelate rings. Enhancements in Eu(III) luminescence intensities and lifetimes were used to obtain formation constants for the adduct species. In the 1:1 adducts, the Eu(III) chirality appeared to be dictated pimarily by vicinal effects. For the 1:2 complexes, the presence of weak configurational effects (probably due to some geometrical isomerism) was deduced in addition to the vicinal effects.

3.5 *Lanthanide Complexes with Chiral* beta-*diketones and Achiral Substrates*

Lanthanide derivatives of chiral *beta*-diketone ligands (containing camphorato groups) were developed as reagents suitable for NMR determinations of enantiomeric purity.[61,62] The adduct formation processes associated with these compounds would be similar to those of the $Eu(DK)_3$ compounds, but the resulting adducts could exist in a variety of diasteromeric forms:

$$Ln(CDK)_3 + S \longleftrightarrow Ln(CDK)_3(S)$$

CDK now signifies a *beta*-diketone ligand which is inherently chiral. It was found that no CPL could be detected in non-coordinating solvents, but that upon formation of adduct complexes exceedingly strong CPL could be observed.[52,63]

Through earlier studies on inert transition metal compounds of the same chiral *beta*-diketone ligands, Everett and coworkers demonstrated that a $M(CDK)_3$ complex would exist as a mixture of four diasteromers. The CD of the two *delta* and two *lambda* isomers was found to be equal and opposite in sign, and that a mixture containing equal amounts of all diastereomers would exhibit no optical activity.[64-66] In a highly labile $Ln(CDK)_3$ complex, all possible diasteromers should be present in equal amounts, since there should be no steric reason for a 6-coordinate Ln(III) ion to exhibit stereoselectivity. However, upon formation of the adduct complexes, steric crowding of the bulky camphorato ligands would be expected to take place. This crowding would cause stabilization of the isomers which minimize the interactions among the chelate rings, and thus one would effectively resolve the $Ln(CDK)_3(S)$ compound to the extent that stereoselectivity would permit.

These stereoselective processes were studied in great detail for the Eu(III) derivatives of (+)-3-trifluoroacetylcamphorate (FACAM) and (+)-3-heptafluorobutyrylcamphorate (HFBC). Large degrees of stereoselectivity were noted in the adducts containing sulfoxides, sulfones, and phosphate esters,[67] as well as a series of formamide and acetamide derivatives.[68] In most cases, the preferred diastereomer of $Eu(FACAM)_3$ was opposite to that preferred by $Eu(HFBC)_3$ indicating that the replacement of $-CF_3$ by $-C_3F_7$ on the *beta*-diketone ring profoundly altered the steric nature of that substrate binding site. It was also noted that the largest stereoselectivities were obtained when the substrate was exceedingly bulky, or when a 1:2 $Eu(CDK)_3(S)_2$ adduct could be formed. These observations support the conclusion that steric interactions among the coordinated *beta*-diketones and substrates are responsible for the stereoselective effects observed.

In a subsequent work, the CPL spectrum of tris(D,D-dicampholy methanato) Eu(III) was obtained in 40 different solvent systems.[69] Once again, CPL was obtained only in the solvents which were strongly coordinative toward the $Eu(DCM)_3$ complex. The highest degrees of stereoselectivity were observed for bulky substrates, or for substrates capable of forming 1:2 adduct complexes. Stereoselectivity in adduct formation is a general feature of $Ln(CDK)_3$ compounds, and was also observed in Tb(III) derivatives of 3-acetyl-d-camphor when these formed adducts with amine substrates.[70]

Further study of the stereoselective process was achieved through the synthesis and characterization of $Eu(DK)_2$ (CDK) and Eu(DK) $(CDK)_2$ mixed-ligand compounds. In non-coordinating solvents, the observed CPL spectra were consistent with the existence of weak vicinal effects.[71] Formation of the dimethyl sulfoxide or N,N-dimethyl formamide adducts of these mixed-ligand compounds did lead to alterations in the CPL spectra, but these changes were infinitely smaller than those observed for the $Eu(CDK)_3$ compounds.[72] These observations indicate that the steric requirements of DK ligands are far less than those of the CDK ligands, and that formation of adducts in compounds containing less than three CDK ligands takes place with stereoselectivity.

3.6 *Pfeiffer Effects in Trigonal Lanthanide Complexes*

The observation of optical activity in a racemic mixture of a labile metal complex upon addition of a chiral substance was first observed by Pfeiffer.[73,74] In many cases, the mechanism entails formation of an outer-sphere complex after addition of the chiral material, forming diastereomers of unequal stability. This process shifts the position of enantiomeric equilibrium, and observable optical activity results. While CD studies have been used to study Pfeiffer effects in a wide variety of transition metal complexes,[75] analogous studies on lanthanide compounds have received far less attention. Pfeiffer optical activity normally represents one way to study the chirality of metal complexes too labile to be resolved by conventional means.

Since it had been established that the tris(pyridine-2,6-dicarboxylate) salts of lanthanide ions exhibited D_3 symmetry in solution,[76] all Pfeiffer effects reported to date have concerned this trigonal system. That the enantiomeric interconversion of $Tb(DPA)_3^{3-}$ could be upset was first demonstrated using resolved tris(ethylenediamine)Cr(III) as the chiral environment substance.[77] The resulting CPL was found to be extremely strong, and the signs of the lineshapes were determined by the absolute configuration of the Cr(III) complex used to induce the CPL. This work also served to identify electrostatic forces as being the major driving force leading to Pfeiffer effects in lanthanide complexes.

Although the electrostatic effect played a major role in promoting the outer-sphere association, it was found that a hydrophobic contribution could augment the observed effects. Quite strong Pfeiffer effects were obtained when using L-ascorbic acid with $Tb(DPA)_3^{3-}$, but these effects were eliminated upon breakage of the ascorbate lactone ring.[78] Further evidence that the presence of a ring system on the environment substance led to enhanced Pfeiffer effects came from a study of the interaction of $Tb(DPA)_3^{3-}$ with several analogues of L-proline.[79]

The existence of a hydrophobic pocket on the outer-sphere of $Tb(DPA)_3^{3-}$ was established separately through studies of monoamino- and diaminocarboxylic acids,[80] and phenylalkylamines, phenylalkylamino alcohols, and phenylalkylamino acids.[30] It was found that while electrostatic effects were required for the existence of strong outer-sphere association, when the substrate contained a hydrophobic side-chain enhancement of the association took place. Further verification of these principles was obtained through studies of the Pfeiffer effects induced by tartrate substrates,[81] monosaccharide aldose sugars,[82] amino sugars,[83] and histidine derivatives.[84]

In many of these works, it was found that limiting values for Tb(III) dissymmetry factors were reached at high levels of chiral substrate, and that these values were always independent of the identity of the substrate used. This observation was taken to imply that this value corresponded to the fully formed $Tb(DPA)_3^{3-}$ substrate complex. With knowledge of this limiting dissymmetry factor, systematic studies of the concentration dependence of induced CPL can be used to obtain the association constants corresponding to the outer-sphere processes. These were usually found to be fairly weak, and generally less than 100 litre/mol. However, the data were always interpretable with the assumption of 1:1 stoichiometry, and indicated that actual complexation between $Tb(DPA)_3{}^{3-}$ and the chiral substrate was required for the observance of a Pfeiffer effect.

It happens that the tris(oxydiacetate) lanthanide complexes crystallize in an optically active space group (R32), and consequently Richardson and coworkers were able to relate CPL lineshapes with absolute configurations.[85] Since similar lineshapes were obtained during the Pfeiffer studies, correlation of induced CPL lineshapes with absolute configurations was possible. No simple correlation between substrate stereochemistry and the preferred Ln(III) enantiomer could be established, and in several cases when the association mechanism changed so did the identity of the preferred $Tb(DPA)_3{}^{3-}$ enantiomer.[80] These results could always be rationalized in terms of known substrate behaviour, however.

Proof that the Pfeiffer CPL is intrinsic of the trigonal $Tb(DPA)_3{}^{3-}$ complex itself has been provided by Riehl and coworkers.[15,86] Racemic $Tb(DPA)_3{}^{3-}$ was excited with circularly polarized light, and photoselected CPL was observed. The CPL lineshapes obtained for all Tb(III) emission bands were completely identical to those observed in the Pfeiffer CPL experiments, thus establishing the CPL lineshapes as being characteristic of lanthanide ions experiencing trigonal optical activity.

Riehl and coworkers have also studied the Pfeiffer effects as these exist in DPA complexes not containing Tb(III). CPL spectra were obtained from $Eu(DPA)_3{}^{3-}$ and $Dy(DPA)_3{}^{3-}$ after these formed outer-sphere complexes with (+)-dimethyl-L-tartrate.[86] As mentioned above, comparison of the CPL lineshapes with those obtained from optically active crystals of tris(oxydiacetate) Eu(III)[85] enabled deductions to be made regarding the absolute configuration of the preferred enantiomer. Riehl and coworkers reached the same conclusion as had been obtained previously,[80] and also have provided a spectra–structure correlation useful for Dy(III) Pfeiffer effects. This same group has also studied the Pfeiffer chirality induced in $Dy(DPA)_3{}^{3-}$ upon complexation with L-histidine.[87] Similar conclusions to those previously reported for Pfeiffer effects induced in $Tb(DPA)_3{}^{3-}$ by histidine[79,85] were reached in this study involving Dy(III) analogues.

All of the results obtained to date indicate that when a centre of positive charge exists on the chiral substrate, Pfeiffer CPL may be induced in the anionic $Tb(DPA)_3{}^{3-}$ complex. Whenever the substrate also contained a hydrophobic side-group, additional binding strengths were observed. Analysis of NMR data[80] indicated that these groups preferred to become oriented between the dipicolinate chelate rings, and that a hydrophobic pocket therefore existed in the lanthanide complexes. However, it was also established that this hydrophobic binding was insufficient by itself to yield measurable Pfeiffer optical activity.

3.7 *CPL studies of Other Chiral Lanthanide Compounds*

More recently, several new types of chiral lanthanide complexes have been investigated by means of CPL spectroscopy. Chiral macrocycles form compounds for which spectra–structure correlations ought to be easily obtained, although this is not always the case. In the solution phase, the Tb(III) and Eu(III) complexes with [1(R)-[1(R*),4(R*),7(R*),10(R*)]]-tetramethyl-1,4,7,10-tetraazacyclododecane-1,4,7,10-

tetraacetic acid (DOTMA) were found to exist as a mixture of axially and non-axially symmetric forms.[88] Unfortunately, the CPL seemed to be associated with the poorly defined non-axially symmetric compound.

Palmer and coworkers have carried out extensive studies of the chirality of lanthanide derivatives of chiral macrocycle complexes, and CPL spectroscopy has proven to be of major importance in their work.[89] In their first work, Palmer and coworkers studied the CPL obtained from the Tb(III) and Eu(III) complexes of (2R, 3R, 11R, 12R)-2,3,11,12-tetramethyl-18-crown-6.[90] The complex was also found not to be axially symmetric, and the authors concluded that the optical activity was predominantly configurational in nature. The CPL of complexes of (2R, 3R, 11R, 12R)-2,3,11,12-tetramethyl-1,4,7,10,13,16-hexaoxacyclooctadecane with Eu(III) nitrate and perchlorate has been used to study the solution phase behaviour as a function of solvent.[91] Evidence was obtained during these studies which indicated the formation of inner-sphere nitrate complexes with the lanthanide macrocycle complexes. In a subsequent work, the chirality of these complexes (as existing in trifluoroethanol) was detailed with regard to the nature the configurational effects.[92] It was deduced that the chirality of the nitrate complexes contained a contribution arising from the presence of a dissymmetric, two-bladed propeller formed by opposing bidentate nitrate groups. The chirality of the analogous chloride complexes was concluded to be due solely to the configurational and conformational effects of the chiral ligand.

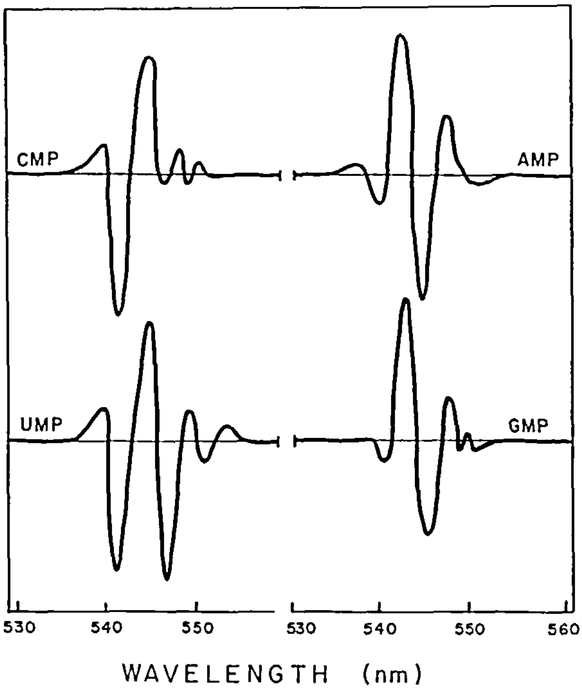

FIGURE 6 CPL spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) band system for the Tb(EDTA) complexes of nucleotides. Data are illustrated for pyramidine-based nucleotides (cytidine 5′-monophosphate and uridine 5′-monophosphate), and for purine-based nucleotides (adenosine 5′-monophosphate), and for purine-based nucleotides (adenosine 5′-monophosphate and guanosine 5′-monophosphate).

CPL spectroscopy has been used recently to study the chirality of Tb(III) complexes of nucleosides and nucleotides. Davis and Richardson[93] determined that the lanthanide ion binding capability of nucleosides required terdentate chelation, using two adjacent hydroxyls (of the ribose group) and one carbonyl (of the base moiety). The optical activity of Tb(EDTA) complexes with nucleotides was found to depend on the identity of the aromatic base: purine based nucleotides yield one type of CPL spectrum, and pyramidine based nucleotides yield a mirror image spectrum.[94] Examples of the CPL spectra are shown in Figure 6. The CPL in these complexes actually results from interactions between a partially dissociated EDTA ligand and the base residue, and the chirality is due to a stabilization of a particular chiral EDTA conformation. Replacement of hexacoordinate ligands by pentacoordinate ligands results in the loss of all CPL.

Metal ion binding by ionic polysaccharides has also been studied by means of CPL spectroscopy.[95] Non-specific Tb(III) binding leads to luminescence intensity enhancements, but no CPL is observed within the emission bands. When working with carboxylated polysaccharides (carboxymethyl cellulose, alginate, polygalacturonic acid, etc.), one observes strong CPL characteristic of configurational effects. With these materials, well defined Tb(III) binding sites exist and these sites are highly chiral. The CPL spectra were found to be sensitive to the gelation processes, and therefore CPL spectroscopy will be a useful probe technique for the characterization of gels.

4. CONCLUDING REMARKS

CPL spectroscopy has been shown to be the chiroptical technique of choice for the study of chiral lanthanide compounds. The emission spectra of Tb(III) and Eu(III) consist of a series of easily identified and non-overlapping series of bands, and the measurement of CPL within these bands is normally not a difficult matter. Through careful design of experimental protocol, it is possible to relate the CPL spectra with plausible solution phase chemistry. Since the theory of f–f optical activity is still in an active state of development, much of the work has been of an empirical nature. However, this situation will change with future developments. In well defined crystalline environments, relation of theory and experiment has already been shown to be possible.[85]

The CPL investigations carried out to date indicate the potential of these methods for the systematic characterization of lanthanide coordination chemistry. The solution phase is certainly the most important medium for lanthanide bioinorganic chemistry, but also represents a difficult medium for study. While NMR techniques are extremely valuable in this regard, quantification of the results normally entails the use of assumptions which may or may not be valid. In CPL spectroscopy one makes direct observations, and the conclusions obtained from these studies can be used to validate the assumptions required for an NMR analysis. The validity of this approach has been demonstrated,[88] and further investigations along these lines may be anticipated. It may be concluded that CPL investigations would aid any characterization of lanthanide compounds containing centres of chirality.

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