support the electron-transfer scheme shown in Figure 5. In the presence of 0.1 M Cl$^-$, the first reduction involves (P)InCl and [(P)InCl]$^-$ while the second reduction involves both [(P)InCl]$^-$ and (P)In(py)$_2$, which is formed after Cl$^-$ dissociation. This is illustrated by the voltammogram at 0.1 V/s. At 15 V/s, dissociation of Cl$^-$ does not occur during the time scale of the measurement and only the top set of electrode reactions in Figure 5 take place. At all other scan rates, intermediate behavior is observed, and between two and four oxidation peaks are obtained depending upon scan rate.

In conclusion, the electrochemical studies are consistent with the ligand-addition reactions reported earlier for the (P)InX system.[10] The formation of a mono- and bis(*N*-methylimidazole) adduct is observed by electrochemistry for all of the neutral compounds but the formation of bis(pyridine) adducts is observed only for the SO$_3$R$^-$ derivatives. The electrochemistry also provides information on nitrogenous base addition to the species formed after reduction by one or two electrons. In the presence of pyridine or *N*-MeIm the formation of [(P)InX(L)]$^-$ or (P)In(L)$_2$ is observed after reduction by one electron. The exact species formed is dependent upon both the nature of the axial ligand and the ligand concentration. However, after the addition of a second electron to [(P)InX(L)]$^-$ or (P)In(L)$_2$, a pentacoordinated indium porphyrin dianion is always formed.

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**Registry No.** *N*-MeIm, 616-47-7; (TPP)InSO$_3$Ph, 70619-92-0; (TPP)InSO$_3$CH$_3$, 70619-88-4; (TPP)InCl, 63128-70-1; (TPP)InOAc, 96150-61-7; (OEP)InSO$_3$Ph, 70619-98-6; (OEP)InSO$_3$CH$_3$, 70619-94-2; (OEP)InCl, 32125-07-8; (OEP)InOAC, 96150-60-6; (TPP)InSO$_3$Ph(*N*-MeIm), 102614-85-7; (TPP)InSO$_3$Me(*N*-MeIm), 102648-59-9; (OEP)InSO$_3$Ph(*N*-MeIm), 102614-86-8; (OEP)InSO$_3$Me(*N*-MeIm), 102630-10-4; [(TPP)In(*N*-MeIm)$_2$]$^+$, 102614-87-9; [(OEP)In(*N*-MeIm)$_2$]$^+$, 102614-88-0; pyridine, 110-86-1.

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# Circularly Polarized Luminescence from Racemic Lanthanide(III) Complexes with Achiral Ligands in Aqueous Solution Using Circularly Polarized Excitation

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The circularly polarized luminescence (CPL) and total luminescence (TL) spectra are reported for aqueous solutions of tris complexes of Tb(III), Eu(III), Sm(III), and Dy(III) with 2,6-pyridinedicarboxylic acid in basic media. The optical activity is generated from these *racemic* solutions by using as the excitation source circularly polarized Ar ion laser lines. No CPL was observed from similarly prepared solutions of Tb(III), Eu(III), and Sm(III) with oxydiacetic acid. CPL was measured for the aqueous complex of Dy(III) with oxydiacetic acid. These results are interpreted in terms of the kinetic stability of the complexes formed, and comparisons are made with other optical and with NMR measurements.

## Introduction

Spectroscopic interest in the study of complexes of lanthanide ions has increased significantly in the last 10 years primarily because of the use of a number of these species as NMR shift reagents[1] and as optical probes of biomolecular structure.[2,3] Several lanthanide ions have been shown, for example, to replace spectroscopically inert Ca(II) (and sometimes Mg(II)) in a number of important biomolecular systems, such as calcium-binding proteins, while retaining, at least partially, their associated biological activity.[2-4] The intraconfigurational 4f–4f electronic transitions of lanthanide ions are generally very sensitive to the coordination environment around the lanthanide ion. The optical spectroscopy of these f–f transitions may involve several different free-ion states that are well-separated in energy. In addition, each electronic band may be composed of a number of possible individual crystal field transitions. For these reasons, the lanthanide ions are considered to be potentially important tools for the study of biomolecular systems, particularly if theoretical formalisms or models relating the observed spectra to specific aspects of molecular structure can be developed. The present work is a contribution toward such an understanding. Almost all of the emission studies on lanthanides in solution have involved either Tb(III) or Eu(III), both of which emit strongly even in solution at room temperature, to a number of different well-resolved electronic states.[2] Generally, excitation of the lanthanide is achieved via absorption in the ultraviolet region by either the ligand or metal ion, but the 4f–4f absorption bands can also be excited directly by using visible region laser excitation.

The measurement of the circularly polarized luminescence (CPL) in the emission spectra of lanthanide ions has been shown to be a very important probe of the structure of lanthanide complexes.[5,6] The development of useful and reliable spectra–structure relationships in CPL from lanthanide(III) ions has to some extent been hindered by the lack of spectral measurements for systems in which the structure is known. In particular, much of the CPL work that has been reported on lanthanide complexes with *chiral* ligands yields only indirect and, in most cases, only speculative conclusions concerning the structure of these complexes in aqueous solution. One is never really able to separate completely effects due to the configuration of ligands about the central ion from effects due to chelate ring conformations or so-called vicinal effects. These latter effects arise from the existence of asymmetric centers on inherently chiral ligands. Very little CPL data exist for complexes that are chiral due solely to the configuration of *achiral* chelate rings about the lanthanide ion. There have been measurements of CPL from a limited number of *crystals* in which the lanthanide complexes crystallize in enantiomorphic space groups.[7,8] There has also been a fairly large amount of work reported on CPL from aqueous solutions of Tb(III) with 2,6-pyridinedicarboxylic acid (dipicolinic acid, DPA) in which a chiral species has been added or a chiral solvent used.[9] This complex has been shown to possess $D_3$ geometry in the solid state.[10-12] Much of the solution CPL work has been concerned with the nature of the coordination or perturbation caused by the additional chiral component. A considerable amount of this work has been described as examples of the so-called "Pfeiffer effect",[13,15] al-

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though it has not been completely clear in some of these studies whether the addition of a chiral substance to the solution is simply disturbing the lanthanide racemate equilibrium or if some other mechanism is operative. It is interesting to note that this effect has only been reported for complexes of Eu(III) and Tb(III) with DPA. The sources of geometry-dependent optical activity are clearly more limited and, certainly, better defined in racemic systems with achiral ligands than in situations in which chiral ligands are utilized or chiral species added. The lability of these complexes renders conventional optical activity methods useless, because the complexes racemize rapidly in solution and cannot be resolved. Little is, in fact, known about the lability of these multidentate ligands.

We have recently demonstrated that it is possible to measure the circularly polarized luminescence from aqueous solutions of 2,6-pyridinedicarboxylic acid and Tb(III) by using as the excitation source a circularly polarized 488-nm laser line.[15] The circularly polarized luminescence is generated by differential absorption of the circularly polarized excitation beam (i.e. CD at the excitation wavelength), resulting in preferential excitation of one of the two possible tris enantiomers over the other. This report was the first example of this kind of experiment using metal complexes. The first realization that CPL could be detected from racemic solutions with use of circularly polarized excitation was by Dekkers, Emeis, and Oosterhof.[16] Since then, the CPL spectra of a very small number of organic molecules have been measured from racemic solutions.[17,18] A complete theoretical treatment of this phenomenon including the effects due to racemization and energy transfer has recently been reported.[19]

In this work we report the measurement of CPL from aqueous solutions of Eu(III)–DPA, Sm(III)–DPA, and Dy(III)–DPA excited with circularly polarized light. The implications of these measurements with respect to the solution structure and lability of the aqueous $Ln(DPA)_3^{3-}$ complexes are discussed along with an analogous discussion concerning negative results (i.e. no CPL) for similarly prepared solutions of the Eu(III) and Sm(III) ions with oxydiacetic acid and iminodiacetic acid as ligands but positive results for the Dy(III)–oxydiacetic acid complex.

## Experimental Section

The excitation source in the work reported here was an argon ion laser (Coherent-CR6) operating in the visible region in the light regulation mode. Reflection from a dichroic mirror (CVI laser) removed most of the unwanted plasma lines in the region from 530 to 670 nm. The laser beam was rendered circularly polarized by a mica $^1/_4$-wave plate (Karl Lambrecht) carefully positioned in the laser beam. The extent of circular polarization was determined to be >90% by monitoring emission intensity while rotating a linear polarizer in the circularly polarized laser beam.

The circular analyzer was a photoelastic modulator (PEM, Hinds Int.) operating at 50 kHz for $\lambda/4$ retardation and 100 kHz for $\lambda/2$ retardation and a Glan-Thompson linear polarizer (Karl Lambrecht). The excitation beam was oriented perpendicular to the direction of emission detection. This arrangement requires an assessment of the relative magnitude of linearly polarized emission due to the small birefringence in the PEM. In all cases the $^1/_2$-wave, 100-kHz signal was very small and judged insignificant as a source of any artifact in the CPL spectra. This is the expected result due to the "spherical" nature of the metal ion chromophore. Stray excitation light was filtered by a 520-nm long-pass colored-glass filter. Fluorescence from the filter was not important since the excitation was at 90° to the direction of emission detection. The emission was focused by a lens into a 20-cm holographic-grating monochromator (H-20 Instruments SA). A cooled EMI 9558B photomultiplier tube was used for photodetection.

**Table I.** Spectroscopic Transitions for the Selected Lanthanide(III) Ions Observed in This Work

| Ln(III) ion | abs/em | transition | wavelength, nm[a] |
|---|---|---|---|
| Pr(III) | abs | $^3H_4 \rightarrow {}^3P_0$ | (476.5) |
| | em | $^3H_4 \leftarrow {}^1D_2$ | 585–630 |
| Sm(III) | abs | $^6H_{5/2} \rightarrow ?$ | (476.5) |
| | em | $^6H_{5/2} \leftarrow {}^4G_{5/2}$ | 550–565 |
| | | $^6H_{7/2} \leftarrow {}^4G_{5/2}$ | 580–620 |
| | | $^6H_{9/2} \leftarrow {}^4G_{5/2}$ | 630–660 |
| Eu(III) | abs | $^7F_0 \rightarrow {}^5D_2$ | (465.8) |
| | | $^7F_1 \rightarrow {}^5D_2$ | (472.7) |
| | | $^7F_2 \rightarrow {}^5D_2$ | (488.0) |
| | em | $^7F_1 \leftarrow {}^5D_0$ | 585–600 |
| | | $^7F_2 \leftarrow {}^5D_0$ | 610–625 |
| | | $^7F_3 \leftarrow {}^5D_0$ | 640–660 |
| | | $^7F_4 \leftarrow {}^5D_0$ | 685–710 |
| Tb(III) | abs | $^7F_6 \rightarrow {}^5D_4$ | (488.0) |
| | em | $^7F_5 \leftarrow {}^5D_4$ | 540–560 |
| | | $^7F_4 \leftarrow {}^5D_4$ | 575–600 |
| | | $^7F_3 \leftarrow {}^5D_4$ | 620–635 |
| Dy(III) | abs | $^6H_{15/2} \rightarrow {}^4F_{15/2}$ | (457.9) |
| | | $^6H_{15/2} \rightarrow {}^4F_{9/2}$ | (476.5) |
| | em | $^6H_{13/2} \leftarrow {}^4F_{9/2}$ | 560–585 |
| | | $^6H_{11/2} \leftarrow {}^4F_{9/2}$ | 630–680 |

[a] Values in parentheses indicate laser wavelength used for excitation.

The photomultiplier output was passed through a 50-kΩ output resistor and a custom-built 50-kHz active filter before entering a lock-in amplifier (PAR128A) referenced to the PEM. The signal measured at the lock-in amplifier is proportional to the differential emission intensity, $\Delta I$. The total emission, $I$, is proportional to the dc current, which was measured on an electrometer (General Radio 1230A). Both signals were appropriately amplified and input through 8-bit A/D ports of a Z-80 microcomputer (Horizon North Star) for calculating the dissymmetry ratios and for plotting and storing the spectra. Calibration was achieved by recording the $^7F_2 \leftarrow {}^5D_0$ emission from $Eu(facam)_3$ (Aldrich) in $Me_2SO$. This particular transition was chosen because the dissymmetry ratio is close to that of the transitions observed in this work. The 1:3.5 solutions of Tb(III) and Eu(III) with oxydiacetic acid (ODA) and DPA were prepared by neutralizing either oxydiacetic acid (Aldrich) or dipicolinic acid (Aldrich) with 1 N NaOH and then adding 99.9% pure $EuCl_3{\cdot}6H_2O$ or $TbCl_3{\cdot}6H_2O$ (both Aldrich). The final pH of all solutions was adjusted to 8.0. Solutions of Sm(III), Dy(III), and Pr(III) were prepared from the oxides (Alfa), which were dissolved in 60% $HClO_4$. These solutions were then adjusted to pH 3 with 6 N NaOH. Dipicolinic acid or oxydiacetic acid was added and the pH adjusted to 8.0 with 1 N NaOH. The metal ion concentration in each of these solutions was approximately 0.03 M.

The lanthanide–ODA solutions were used as prepared. The lanthanide–DPA solutions, however, were prepared by growing crystals of the lanthanide–DPA complex through slow evaporation, drying the crystals in an oven to remove some of the water of hydration, and then dissolving the complex in the minimum amount of $D_2O$. The reason for this procedure is the enhanced emission yield for lanthanide(III) ions in $D_2O$ solutions.

Total emission and circularly polarized emission were obtained by using right circularly polarized excitation. Authenticity of the CPL was checked by reversing the incident polarization by carefully rotating the $\lambda/4$ waveplate and noting an exactly inverted differential spectrum. The excitation wavelengths used were 465.8, 472.7, 476.5, and 488.0 nm for Eu(III) solutions, 488.0 nm for Tb(III) solutions, 476.5 nm for Sm(III) and Pr(III) solutions, and 457.9 nm for Dy(III) solutions. The emission band-pass was 2 nm in all cases. No correction was made for the wavelength-dependent response of the instrument. Emission lifetimes were measured by mechanically chopping the excitation beam and recording the decay of the emitted beam on a storage oscilloscope.

## Theoretical Considerations and Results

An abbreviated approximate energy level diagram for Pr(III) [$f^2$], Sm(III) [$f^5$], Eu(III) [$f^6$], Tb(III) [$f^8$], and Dy(III) [$f^9$] is presented in Figure 1.[20] Almost all of the emission spectroscopy for lanthanides in aqueous solution has involved emission from the $^5D_0$ state of Eu(III) or the $^5D_4$ state of Tb(III) to the manifold of $^7F_J$ states. It is generally observed that the emission from Tb(III) is much stronger than that from Eu(III) although considerably enhancement of the emission of both can be obtained if $D_2O$ is employed as the solvent. In the work reported here, we also report emission from aqueous solution complexes of Sm(III),

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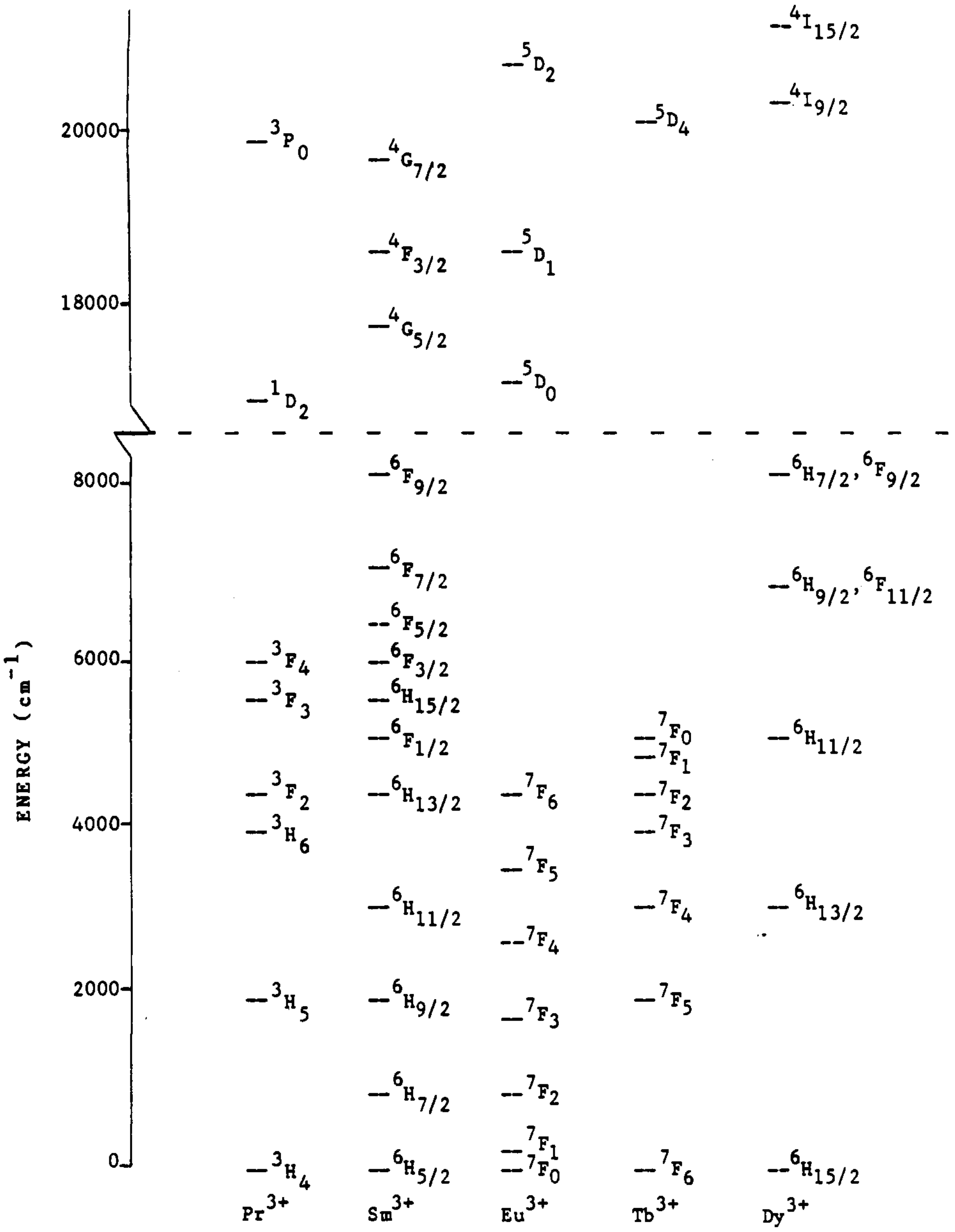

**Figure 1.** Approximate energy level diagram for low-energy electronic states of selected lanthanide(III) ions.

Pr(III), and Dy(III). These lanthanide ions were chosen because of their spectral accessibility both in regard to the ability to absorb Ar ion laser wavelengths and to emit at visible wavelengths. A summary of the absorption and emission transitions observed in this work is given in Table I.

In our previous note concerning the measurement of circularly polarized emission from racemic $Tb(DPA)_3^{3-}$ complexes, it was emphasized that in order for CPL to be observed it is necessary that *both* the absorption and emission processes be associated with relatively large enantiomeric discriminations. In CD and CPL spectroscopy, the common experimental quantities that yields this information are the absorption and emission disymmetry ratios, which are defined as

$$g_{abs} = (\epsilon_L - \epsilon_R)/[(\epsilon_L + \epsilon_R)/2] \qquad (1)$$

$$g_{em} = (I_L - I_R)/[(I_L + I_R)/2] \qquad (2)$$

In these equations the subscripts L and R refer respectively to left and right circularly polarized light, $\epsilon$ is the molar extinction coefficient, and $I$ denotes emitted light intensity. The emission dissymmetry ratio appropriate for CPL studies involving racemic mixtures can be related to the dissymmetry ratios for enantiomers given above as

$$g_{em}^{rac} = -g_{abs}g_{em}/2 \qquad (3)$$

This equation is appropriate only for situations in which the chiral distribution of excited species generated by the circularly polarized excitation beam remains intact during the lifetime of the excited state. If the species racemize partially before emission takes place, then the CPL will be less than that calculated from this equation. If racemization is fast compared to the emitting-state lifetime, then no CPL will be observed.

**A. Ln(III)–DPA Solutions.** Observation of CPL following circularly polarized excitation was first observed for a lanthanide complex with achiral ligands for a 3:1 mixture of DPA (0.06M) to Tb(III) (0.02 M) at a pH of 8.4. Excitation was achieved via the $^7F_6 \rightarrow {}^5D_4$ absorption, which overlaps the 488.0-nm line of the argon ion laser. Linear polarization was found to be negligible in all of these lanthanide systems. The CPL line shape and dissymmetry ratios were independent of pH in the range 7.0–8.8 and did not change appreciably after a 3:1 ligand:metal ratio was reached; i.e. additional ligand did not change the magnitude or line shape of the CPL. This result is consistent with previous reports on the total emission of this species.[21] The CPL and total luminescence (TL) spectra are plotted in Figure 2 for emission from 535 to 640 nm along with the electronic assignments derived

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[21] Brittain, H. G. *Inorg. Chem.* **1978**, *17*, 2762.

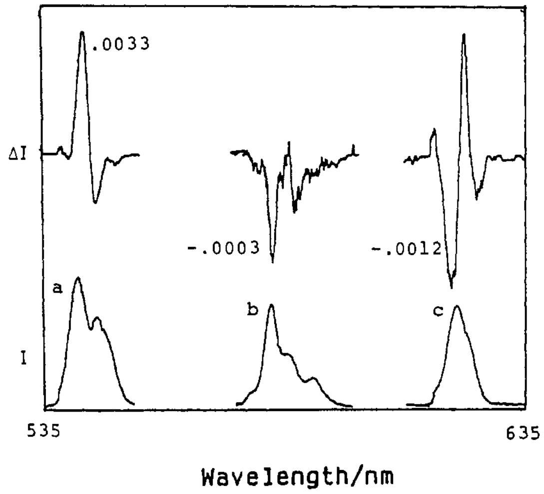

**Figure 2.** CPL (upper) and TL (lower) spectra for $Tb(DPA)_3^{3-}$ in $H_2O$ at pH 8.4: (a) $^7F_5 \leftarrow {}^5D_4$; (b) $^7F_4 \leftarrow {}^5D_4$; (c) $^7F_3 \leftarrow {}^5D_4$.

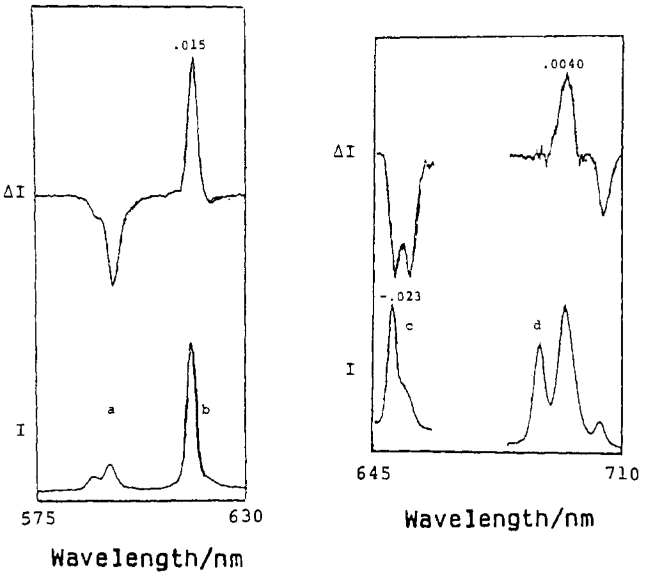

**Figure 3.** CPL (upper) and TL (lower) spectra for $Eu(DPA)_3^{3-}$ in $D_2O$: (a) $^7F_1 \leftarrow {}^5D_0$; (b) $^7F_2 \leftarrow {}^5D_0$; (c) $^7F_3 \leftarrow {}^5D_0$; (d) $^7F_4 \leftarrow {}^5D_0$.

from the free-ion states. Emission also occurs to the $^7F_2$, $^7F_1$, and $^7F_0$ states, but these transitions are much weaker and are not reported in this work because of signal to noise difficulties in this spectral region. Both the TL and CPL in this figure are given in arbitrary units; we have also given the associated sissymmetry ratios ($g_{em}^{rac}$) for the major peaks.

This observation is the first example of CPL from a racemic lanthanide ion complex. This is also the first measurement of CPL from a lanthanide complex in an aqueous system *without* an added chiral chemical perturbation. This species is optically active only because of the chiral configuration of the ligands around the central metal ion. This result indicates that an optically active species of Tb(III)–DPA exists in solution that is not labile on the time scale of Tb(III) emission from the $^5D_4$ state (~4.2 ms).[19] In addition, the lack of an increase in $g_{em}^{rac}$ or a change in CPL line shapes upon a 4-fold dilution implies that no polynuclear species are formed. More specific information about the solution structure of $Tb(DPA)_3^{3-}$ must be obtained from a consideration of the transitions occurring among crystal field states by comparison with theoretical calculations.

The $^5D_4$ state from which emission originates is at most 9-fold degenerate in the free ion. If a trigonal ($D_3$) complex is formed, the crystal field of the ligands will split this degeneracy into six crystal field states. Similarly, in this symmetry, the free-ion 11-fold degeneracy of the $^7F_5$ state is lifted, and the possibility of 7 energy-distinct crystal field states results. Clearly, the number of individual crystal field transitions is very large and prohibits a detailed assignment. This is true especially because of the line-broadening mechanisms that exist in solution.

**Table II.** Dissymmetry Ratios Measured at 616 nm ($^7F_2 \leftarrow {}^5D_0$) as a Function of Excitation Wavelength

| exc wavlength, nm | | $g_{em}^{rac}$ |
|---|---|---|
| 465.8 | $^7F_0 \rightarrow {}^5D_2$ | -0.0002 |
| 472.7 | $^7F_1 \rightarrow {}^5D_2$ | +0.015 |
| 476.5 | | -0.0074 |
| 488.0 | $^7F_2 \rightarrow {}^5D_2$ | +0.0030 |

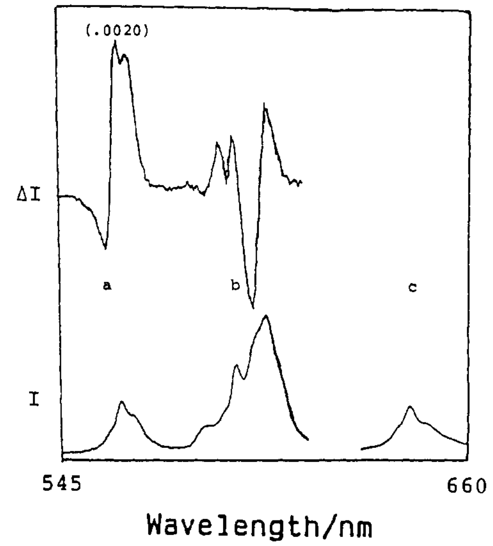

**Figure 4.** CPL (upper) and TL (lower) spectra for $Sm(DPA)_3^{3-}$ in $D_2O$: (a) $^6H_{5/2} \leftarrow {}^4G_{5/2}$; (b) $^6H_{7/2} \leftarrow {}^4G_{5/2}$; (c) $^6H_{9/2} \leftarrow {}^4G_{5/2}$.

Much of this complexity is reduced in the analogous europium(III) complex. In Figure 3 we display CPL and TL spectra for a solution 0.15 M in DPA and 0.05 M in Eu(III) at a pH of 7.5. The CPL was measured with use of circularly polarized 472.7-nm radiation. In this case the excitation process is via the "hot" electronic transition $^7F_1 \rightarrow {}^5D_2$. The $^7F_1$ state is estimated to have a thermal population of about 20% at 300 K. Emission is observed from the nondegenerate $^5D_0$ state to the $^7F_1$ (two crystal field levels) and to the $^7F_2$ (three crystal field levels) states. In the spectrum shown, two levels are evident in each of the multiplet transitions. No emission is seen to the $^7F_0$ level. This transition is formally forbidden in high-symmetry species. This spectrum is consistent with the approximate selection rules in $D_3$.[8] It is also evident that crystal field assignments are possible in the case of the $Eu(DPA)_3^{3-}$ spectrum, but specific crystal field calculations on this system have not been reported. It is important to note that, due to the free-ion magnetic dipole selection rules, the associated $g_{em}^{rac}$ values that are measured in the CPL of this trigonal species are unusually large. Several absorption transitions originating from hot electronic bands can be excited by using the available lines of the argon ion laser. This is illustrated in Table II. Note that the dissymmetry ratio is the largest in the case of the $^7F_1 \rightarrow {}^5D_2$ absorption and $^7F_1 \leftarrow {}^5D_0$ emission. Both of these transitions are magnetic dipole allowed in the free ion.

In Figure 4 is displayed the CPL and total emission spectra of a similarly prepared solution of Sm(III)–DPA. The absorption in this case is from the $^6H_{5/2}$ ground state to any one of a number of possible excited-state levels. In this spectral region there are a number of closely spaced states and an explicit assignment is not possible. A number of emissive transitions are observed. The two transitions with measurable dissymmetry ratios that are displayed in this figure both originate in the $^4G_{5/2}$ state. The emissive transitions that obey magnetic dipole selection rules again have the larger dissymmetry ratios. In Figure 5, we show similar results for a Dy(III)–DPA solution. Excitation in this case is via the 457.9-nm line of the Ar ion laser, which overlaps that $^6H_{15/2} \rightarrow {}^4F_{15/2}$ absorption. Excitation via the $^6H_{15/2} \rightarrow {}^4F_{9/2}$ transition

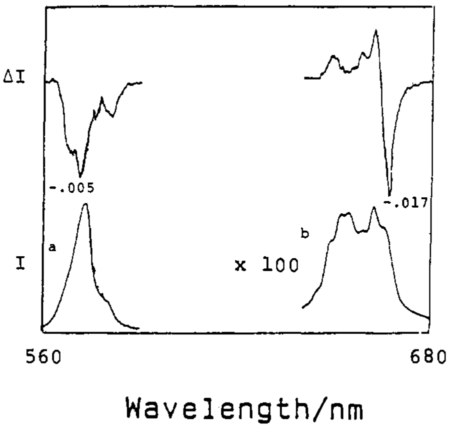

**Figure 5.** CPL (upper) and TL (lower) spectra for $Dy(DPA)_3^{3-}$ in $D_2O$: (a) ${}^6H_{13/2} \leftarrow {}^4F_{9/2}$; (b) ${}^6H_{11/2} \leftarrow {}^4F_{9/2}$.

using 476.5-nm radiation yields large emission intensity but no measurable CPL. Irradiation of a solution containing Pr(III) and DPA at 476.5 nm also yields large emission intensity between 585 and 630 nm but no measurable CPL.

**B. Ln(III)–ODA Solutions.** It has been demonstrated that, in single crystals of $Na_2Ln(ODA)_3{\cdot}ClO_4{\cdot}6H_2O$, the configuration of the terdentate ODA ligands is approximately $D_3$. The species crystallizes in the enantiomorphic space group $R^{32}$.[22,23] Strong CPL signals have been measured from resolved crystals containing Eu(III) and Tb(III).[7,8] Very large CD signals have also been reported for the europium crystal.[24] It is reasonable to expect that if these complexes retain the $D_3$ geometry in solution, then it should also be possible to measure CPL from these species in solutions excited by circularly polarized light. Previous reports of *total* emission spectra for aqueous solutions of $Tb(ODA)_3^{3-}$ and $Eu(ODA)_3^{3-}$ indicate that the spectra are very similar to the respective solid-state spectra, suggesting similar molecular geometries in the crystal and solution.[25]

Solutions of Tb(III), Eu(III), Sm(III), and Dy(III) and ODA were prepared as described above. No measurable CPL could be detected from the room-temperature solutions containing Tb(III), Eu(III), and Sm(III). The effective dissymmetry ratios must be <0.001 for $Eu(ODA)_3^{3-}$ excited at 472 nm, <0.0002 for $Tb(ODA)_3^{3-}$ excited at 488 nm, and <0.0007 for $Sm(ODA)_3^{3-}$ excited with 476.5-nm radiation. In Figure 6 we show the CPL and TL spectra for a solution of $Dy(ODA)_3^{3-}$ excited with circularly polarized 457.6-nm light in the spectral region corresponding to the ${}^6H_{13/2} \rightarrow {}^4F_{9/2}$ transition. Attempts at measuring the CPL of the ${}^6H_{11/2} \leftarrow {}^4F_{9/2}$ transition were unsuccessful due to the much lower quantum yield for this transition.

## Discussion

Although slight differences might be expected in the solution chemistry of the various lanthanide(III) ions studied in this work due to decreasing size as one progresses across the lanthanide series, for the most part one should expect similar chemical behavior. All of the Ln(III) ions studied here form optically active complexes with DPA that are intact during the lifetime of the emitted state. The lack of measurable CPL from the Pr(III) complex is most likely due to the lack of sufficient CD at the excitation wavelength. This problem has also hindered application of CD to solutions of this ion with optically active ligands.[26] It is well-known that complexes of DPA with lanthanide ions form stable complexes.[27] It has also been demonstrated that these complexes do not exchange with free ligands in solution on the NMR time scale.[28]

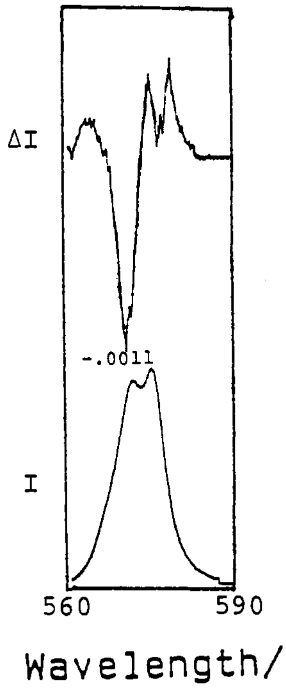

**Figure 6.** CPL (upper) and TL (lower) spectra for the ${}^6H_{13/2} \leftarrow {}^4F_{9/2}$ transition of $Dy(ODA)_3^{3-}$ in $D_2O$.

**Table III.** Emission Lifetimes for Aqueous Solutions of $Ln(ODA)_3^{3-}$

| complex | lifetime, ms | complex | lifetime, ms |
|---|---|---|---|
| $Eu(ODA)_3^{3-}$ ($D_2O$) | 1.00 | $Sm(ODA)_3^{3-}$ ($H_2O$) | 0.13 |
| $Sm(ODA)_3^{3-}$ ($D_2O$) | 0.15 | $Dy(ODA)_3^{3-}$ ($D_2O$) | 0.07 |

Albin, Farber, and Horrocks[29] have recently studied the thermodynamic stability of complexes of Eu(III) with ODA, DPA, and other multidentate ligands through selective excitation spectroscopy involving the ${}^5D_0 \rightarrow {}^7F_0$ transition. Although these results are for the association constant, $K_1$, and are not directly applicable to the stability of the tris complexes studied here, the general behavior should be the same. It was found that stability of the Eu(III)–ODA complexes is much less than that of the DPA complex. Preliminary NMR results obtained in this laboratory indicate that, unlike DPA, free ODA exchanges rapidly with complexed ligand on the NMR time scale. Although the binding constants for ODA with lanthanides are high, their kinetic stability with respect to ligand–ligand and ligand–solvent exchange is such that racemization of the chiral photoselected distribution occurs during the lifetime of the excited state for Eu(III), Tb(III), and Sm(III). The results presented here are also in agreement with the time-resolved emission experiments of Horrocks et al.,[30] who showed that the ligand exchange $Eu(ODA)^+ \leftrightarrow Eu(ODA)_2^-$ is rapid on the emission time scale, whereas the corresponding exchange with DPA is very slow.

In Table III we report the emission lifetimes for the various ODA complexes. This relatively large variation in lifetimes is due principally to the large differences in energy between the emitting state and the lower energy multiplet terms. Of the ions studied, Tb(III) has the longest lived emitting state and Dy(III) the shortest. It is only in the Dy(III)–ODA complex that we observe CPL, indicating that only in this complex is the photoselected chiral distribution maintained at least to some extent during the (relatively short) excited-state lifetime of this species.

Attempts to measure CPL from aqeuous solutions of these lanthanides with iminodiacetic acid were unsuccessful. This ligand is expected to have a binding constant somewhere between those of ODA and DPA. The lack of measurable CPL in these systems

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is consistent with previous total emission and magnetic circularly polarized emission results, which have suggested that this ligand binds to the central lanthanide ion in a facial geometry, as opposed to meridional geometry, in the nine-coordinate distorted tricapped prism.[26] This alternative method of terdentate binding does not result in enantiomeric structures, and therefore, no CPL would be observed.

## Summary

CPL from aqueous solutions of lanthanide ions with multidentate achiral ligands excited with circularly polarized light can provide important and unique information concerning the solution structure of the lanthanide complexes that are formed. In general, luminescence experiments yield information concerning the structure of the emitting species at the time of emission, but since in this experiment we are concerned only with the *differential* population in the excited state, our results reflect the kinetic stability of the chiral distribution photoprepared at the time of absorption. The variable emission lifetimes of the lanthanide(III) ions result in a relatively large time window for this type of study, assuming that the solution chemistries of the Ln(III) species are similar. In addition, shielding of Ln(III) by the terdentate ligands from water molecules leads to relatively high quantum yields. This allowed us to measure CPL from solutions of Sm(III) and Dy(III), which had not been reported previously.

Extensions of this work to include variable-wavelength excitation, temperature-controlled experiments, and comparison of our results with theoretical calculations of 4f–4f optical activity are in progress. It should be possible to obtain relative differential and total emission intensities for both absorptive and emissive transitions by these methods. In addition, an analysis of "mixed-ligand" systems and the effects due to the addition of *chiral* impurity compounds is under way.

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**Registry No.** Tb(DPA)$_3^{3-}$, 38682-37-0; Eu(DPA)$_3^{3-}$, 38721-36-7; Sm(DPA)$_3^{3-}$, 38682-36-9; Dy(DPA)$_3^{3-}$, 38721-96-9; Dy(ODA)$_3^{3-}$, 58855-72-4; Tb(ODA)$_3^{3-}$, 58855-80-4; Eu(ODA)$_3^{3-}$, 43030-81-5; Sm(ODA)$_3^{3-}$, 102538-37-4; Pr$^{3+}$, 22541-14-6; Sm$^{3+}$, 22541-17-9; Eu$^{3+}$, 22541-18-0; Tb$^{3+}$, 22541-20-4; Dy$^{3+}$, 22541-21-5.

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# Studies of Copper(I) Olefin Complexes. Formation Constants of Copper Olefin Complexes with 2,2′-Bipyridine, 1,10-Phenanthroline, and Their Derivatives

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Twenty-five new copper(I) olefin complexes, [Cu(biL)(olefin)]$^+$ (biL = the derivatives of 2,2′-bipyridine and 1,10-phenanthroline (phen); olefin = ethylene and derivatives), were synthesized, and the formation constants were determined spectrophotometrically in 0.3 and 0.5 M acetonitrile/ethanol. The influence of substitutents of the biL and olefin on the formation constants and the $^1$H NMR of the olefinic protons of coordinated ethylene was investigated. The formation constant for the copper ethylene complex ($\mathrm{Cu(biL)^+ + C_2H_4 \rightleftharpoons [Cu(biL)(C_2H_4)]^+}$) was found to increase with increasing p$K_a$ of biL; electron-donating substituents such as methyl on biL stabilize the ethylene complexes, whereas electron-withdrawing substituents such as Cl destabilize it. $^1$H NMR resonances of the olefinic protons of [Cu(biL)(C$_2$H$_4$)]$^+$ move upfield as the p$K_a$ value of biL increases, indicating an increase in the electron density around the olefinic protons. These findings demonstrate that the $\sigma$ donation from biL to copper(I) is enhanced as the basicity of biL increases and the resulting electron-rich copper(I) enhances $\pi$ back-donation in the copper(I)–ethylene bonding. The formation constants of [Cu(phen)(olefin)]$^+$ at 25 °C vary from 0.1 to 18 M$^{-1}$, although they are not as sensitive to the substituent groups on the double bond of the olefin as those of nickel(0) olefin complexes. There is no simple correlation of the formation constant with the Hammett $\sigma$, as is distinct from nickel(0) and silver(I) olefin complexes.

## Introduction

The binding of unsaturated hydrocarbons to transition metals has occupied a central position in organometallic chemistry[1] in connection with the C═C bond distance,[2-4] activation[5-8] coordination form (upright or in plane),[9] olefinic proton and carbon NMR of the coordinated olefin,[10,11] and the formation constant

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