

The rate constants for reactions with $(^2E) Cr(bpy)_3^{3+}$ show that $Ni(13-At)^+$ is a better redox quencher than $Ni([13]dieneN_4)^{2+}$. The back-electron-transfer reactions between the oxidation products and $Cr(bpy)_3^{2+}$ show the opposite tendency. Indeed, the oxidation product of $Ni([13]dieneN_4)^{2+}$ reacts faster than the one of $Ni(13-At)^+$ with $Cr(bpy)_3^{2+}$. This behavior can be related, in part, with the expected differences in the redox potentials of the two nickel complexes.

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Appendix

The formula of the product of the sensitized oxidation of $Ni([14]aneN_4)^{2+}$ was investigated by combining the results of the apparent molecular weight, determined by measurements of osmotic pressure, and conductometric determinations. A formula X_nD was assigned to the complex in the mathematical treatment described below. Such a compound will dissociate in $n X^-$ anions, $X^- = Cl^-$ or ClO_4^- , and D^{n+} cations. The apparent molecular weight, $M^{ap}_{X_nD}$, can be expressed according to the molecular weight of the corresponding ions, namely, M_x and M_D in eq 14.

$$M^{ap}_{X_nD} = (n/(n+1))M_x + (1/(n+1))M_D \quad (14)$$

The expression for the molar conductance of the chloride or perchlorate salts of the compound, eq 15, contains the

$$\Lambda_{X_nD} = K_{X_nD} \frac{1000}{w_{X_nD}} M^{T}_{X_nD} = K_{X_nD} \frac{1000}{w_{X_nD}} (nM_x + M_D) \quad (15)$$

molecular weight of the salt, $M^{T}_{X_nD}$, which can be replaced by the molecular weight of the ions. Combination of eq 14 and 15 for $X = Cl^-$ and ClO_4^- gave eq 16 and 17 for the molar

$$\Lambda_{(ClO_4)_nD} = K_{(ClO_4)_nD} \frac{1000}{w_{(ClO_4)_nD}} (n+1) M^{ap}_{(ClO_4)_nD} \quad (16)$$

$$\Lambda_{Cl_nD} = K_{Cl_nD} \frac{1000}{w_{Cl_nD}} [(n+1) M^{ap}_{(ClO_4)_nD} - 64n] \quad (17)$$

conductance of the chloride and perchlorate salts. We used $w_{(ClO_4)_nD} = w_{Cl_nD} = w$ in our experiments. Moreover, conductance measurements were carried out with various concentrations of complexes, $[X_nD] \leq 2.7 \times 10^{-4}$ M, and extrapolated to infinite dilution. Such conditions allowed to express the molar conductance in terms of the independent conductances of the ions (eq 18). The combination of eq

$$\lambda^{\infty}_{X_nD} = \lambda^0_D + n\lambda^0_x \quad (18)$$

16-18 gave an explicit expression for n (eq 19). An average $n =$

$$n = \frac{M^{ap}_{(ClO_4)_nD}(K_{(ClO_4)_nD} - K_{Cl_nD})}{(\lambda^0_{ClO_4} - \lambda^0_{Cl}) \frac{w}{1000} - M^{ap}_{(ClO_4)_nD}(K_{(ClO_4)_nD} - K_{Cl_nD}) - 64K_{Cl_nD}} \quad (19)$$

value $n = 3.9 \pm 0.1$ is consistent with a dimeric structure of the $Ni(II)$ product. Substitution of the n value in eq 14 and use of the expression of $M^{T}_{X_nD}$, in terms of M_D and M_x , gave $M^{T}_{(ClO_4)_nD} = 1301$.

Registry No. $[Ni(13-At)]^+$, 79135-14-1; $[Ni([14]aneN_4)]^{2+}$, 18444-42-3; fluorenone, 486-25-9; $Cr(bpy)_3^{3+}$, 15276-15-0; $[Cu([14]aneN_4)]^{2+}$, 33727-14-9; benzophenone, 119-61-9.

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Optical Activity in Mixed-Ligand Terbium Complexes Containing Pyridine-2,6-dicarboxylic Acid and Chiral Hydroxycarboxylic Acids

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The optical activity associated with the $f-f$ emission bands of $Tb(III)$ complexes which contain chiral hydroxycarboxylic acids has been studied by means of circularly polarized luminescence (CPL) spectroscopy. Complexes having the general formulas $Tb(DPA)(L)$ and $Tb(DPA)_2(L)$ were studied (where DPA signifies pyridine-2,6-dicarboxylate), with the chiral L ligand being L-lactic acid, L- α -hydroxyisocaproic acid, L-argininic acid, L-mandelic acid, L-phenyllactic acid, L-malic acid, L-hydroxyglutaric acid, and D-isocitric acid. The CPL spectra were found to be sensitive to the mode of bonding existing between the metal and the chiral ligand and therefore enabled predictions to be made regarding how the hydroxycarboxylic acid ligands attach to the $Tb(III)$ ion. In addition, the degree of optical activity varied systematically with the concentration of chiral ligand, and we have used this dependence to calculate formation constants for the addition of a hydroxycarboxylic acid ligand to the Tb/DPA complexes. Finally, the line shapes and magnitudes of the CPL spectra provide information regarding the type of chirality experienced by the $Tb(III)$ ion.

Introduction

The lanthanide complexes of α -hydroxycarboxylic acids have been of interest since the early observations that these ligands could be used in the ion-exchange separation of the rare-earth cations.^{2,3} The formation constants of these complexes have been extensively studied by potentiometric means, although there has been some dispute regarding which particular hydroxycarboxylic acid ligand yields the most stable complex.⁴

More recently, a variety of NMR techniques have been used to study the dynamics of aqueous solutions this class of lanthanide complexes.⁵

Much less is known about the mixed-ligand complexes of lanthanide ions with hydroxycarboxylic acids and about the influence of other ligands on the binding of the hydroxycarboxylic acid ligands by lanthanide ions. In one recent study, the potentiometric method has been used to study the complexation phenomena associated with mixed lanthanide com-

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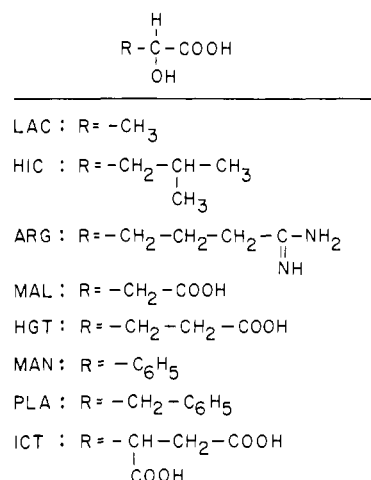


Figure 1. Structures of the α -hydroxycarboxylic acid ligands used in the present study.

plexes of hydroxycarboxylic acids and 1,2-diaminocyclohexanetetraacetic acid.⁶ Mixed-ligand complexes which contain one or more strongly bound ligands are particularly attractive to study in that they permit one to restrict equilibria associated with more weakly bound ligands to a desired level. For instance, if the aminopoly(carboxylate) ligand is hexacoordinate, then only one hydroxycarboxylic ligand could be bound by the lanthanide ion.

Other than glycolic acid (hydroxyacetic acid), all α -hydroxycarboxylic acids can be resolved into optical isomers, and one would anticipate that the interaction between lanthanide ions and these ligands could be best studied by chiroptical techniques. Circular dichroism studies revealed that the spectra associated with Pr(III) complexes were complicated and that the overlapping nature of the f-f absorptions prevented effectual use of the data.⁷ More recently, we have begun to study these complexes by examining the circularly polarized luminescence (CPL) associated with the highly emissive Tb(III) complexes and recently reported studies involving pure and mixed-ligand chelates of L-lactic, L-mandelic, and L-phenyllactic acids.⁸ CPL spectroscopy is particularly attractive to use in that it combines the instrumental sensitivity of luminescence spectroscopy with the stereochemical selectivity chiroptical methods. In addition, the Tb(III) emission bands are well separated and characterized, and this feature makes data interpretation much simpler. We have also reported a detailed study of the pH dependence of mixed-ligand Tb(III) complexes containing L-malic acid,⁹ and this study demonstrated the extreme usefulness of the CPL method.

In the present work, we have studied mixed-ligand Tb(III) complexes containing pyridine-2,6-dicarboxylic acid (dipicolinic acid, or DPA), since our past experience^{8,9} has shown that the DPA ligand is a most efficient channel by which excitation energy may be pumped into the Tb(III) ion. DPA also binds very strongly to lanthanide ions in a terdentate manner¹⁰ and thus permits a filling of the Tb(III) coordination sphere to a desired level. The remaining coordination positions are filled by the hydroxycarboxylic acids, and the structures of the ligands used in this work are shown in Figure 1. We now have developed methods whereby the equilibria associated with the mixed-ligand complexes may be evaluated from the CPL results and as a result have included extensions of the earlier

work^{8,9} with data on new hydroxycarboxylic acid systems as part of the current investigation.

Experimental Section

Tb(III) solutions were prepared by dissolving a weighed amount of Tb₄O₇ (99.9% pure, Kerr-McGee) in the minimum amount of 70% HClO₄, neutralizing to pH 3 with NaOH, and then diluting to the desired volume. A sufficient amount of NaClO₄ was then added to insure that the final total ionic strength was 0.1 M. L-lactic acid (LAC, 1) was obtained from Sigma as the 98–100% pure crystalline free acid, as were L- α -hydroxyisocaproic acid (HIC, 2), L-argininic acid (ARG, 3), L-hydroxyglutaric acid (HGT, 7), and *threo*-D-isocitric acid (ICT, 8). In addition, L-mandelic (MAN, 4) and L-malic (MAL, 6) acids were purchased from Eastman, while L-phenyllactic (PLA, 5) and pyridine-2,6-dicarboxylic (DPA) acids were obtained from Aldrich. All materials were used as received.

Solutions containing a 1:1 and 1:2 ratio of Tb(III) and DPA were prepared from concentrated stock solutions, with the final Tb(III) concentration being 15 mM. The very large formation constants associated with the Tb(DPA)⁺ and Tb(DPA)₂⁻ complexes insure that these materials form completely and instantly under our conditions.¹⁰ For each system, varying amounts of each hydroxycarboxylic acid was added in turn, with ratios of Tb(III):carboxylic acid ranging from 1:1 to 1:20. Eventually for all systems the CPL intensity was observed to level off and to remain constant at higher ratios. No attempts were made to isolate the complexes in solid form.

All CPL spectra were recorded on a high-resolution luminescence spectrometer constructed in our laboratory, whose operation and features have recently been described in detail.¹¹ All samples were excited at 295 nm (obtained from a 200 W Hg-Xe arc lamp and selected by a 0.1-m grating monochromator), corresponding to irradiation of the DPA ligand. Very strong Tb(III) emission was observed, and CPL spectra could be recorded for several Tb(III) luminescence bands. An emission bandpass of 10 Å was used for all work, and further increases in resolution did not lead to any improvement of the spectral features. All studies were obtained in fluid aqueous solution at room temperature.

pH adjustment of the solutions was carried out by adding microliter amounts of standard NaOH or HClO₄ directly to the fluorescence cuvette, with the pH being read on an Orion 701A pH meter. The pH was obtained by inserting a glass microcombination electrode directly into the cuvette, and this electrode was calibrated daily with phosphate buffers.

Results

The luminescence spectrum of the Tb(III) ion shows no dependence on excitation wavelength and consists of a series of well-resolved emission bands in the visible region of the spectrum, and the wavelength of these bands is essentially unaffected by the nature of the ligands attached to the Tb(III) ion. All emissions originate in the ⁵D₄ excited state, and transitions to the ⁷F₆ (490 nm), ⁷F₅ (545 nm), ⁷F₄ (580 nm), and ⁷F₃ (620 nm) *J* levels of the ground state are commonly observed. Of these, the 4 → 5 transition (we shall label the transitions by their *J* quantum numbers) is the most intense and also exhibits the largest degree of CPL. While CPL spectra were obtained for all complexes in all bands, the strong intensity of the 4 → 5 transition insured that most attention would be focused on this band.

Simple mixing of 1:1 or 1:2 mol ratios of Tb(III) and DPA results in the formation of Tb(DPA)⁺ and Tb(DPA)₂⁻, respectively, since the formation constants associated with the addition of each ligand are log *K*₁ = 8.68 and log *K*₂ = 7.43.¹⁰ Williams and co-workers have studied these same complexes via NMR spectroscopy and have independently verified the stoichiometry of the complexes and have shown that the remaining coordination positions left unfilled on the Tb(III) ion are occupied by solvent molecules.¹² Our previous work has shown that these coordinated water molecules may be replaced

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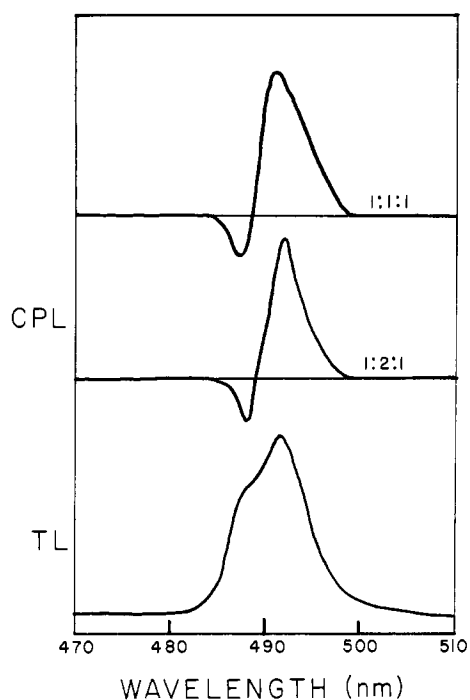


Figure 2. Total luminescence (lower) and circularly polarized luminescence associated with the $^5D_4 \rightarrow ^7F_6$ Tb(III) transition in Tb-(DPA)₂(MAN) (middle) and Tb(DPA)(MAN) (upper). The spectra shown were obtained at pH 4.5, and the intensity scales are completely arbitrary. The TL spectra of each complex is the same.

by a variety of chiral ligands (thus yielding CPL as an observable), ranging from monodentate carboxylic acids¹³ and monodentate amino acids to bidentate amino acids¹¹ and bidentate α -hydroxycarboxylic acids.⁸ In every situation, the CPL spectra of the mixed-ligand complexes were diagnostic of the nature of bonding existing between the Tb(III) ion and the chiral ligand. In addition, our past work has shown that the Tb(III) complexes of DPA are monomeric at all pH ranges and that the DPA ligand binds to the Tb(III) ion as low as pH 1.75.^{14,15}

Addition of any one of the simple hydroxycarboxylic acids, 1–5, led to the observation of strong CPL in each of the Tb(III) emission bands associated with the 1:1 or 1:2 Tb^{III}/DPA complexes. No CPL was observed between pH 1.75 and 2.5, which we take to imply that no bonding exists between the Tb^{III}/DPA complexes and the chiral ligands in this pH region. CPL develops as the pH is raised to 4.0, and while its intensity increases steadily with pH, the line shape remains invariant. Between pH 4.0 and 7.0, the CPL intensity and line shape remain constant. Above pH 7.0, the CPL intensity decreases rapidly until the formation of a precipitate occurs at pH 7.5. This insoluble material has analyzed as a complex mixture of Tb(III) complexes containing hydroxide ion, DPA, and the hydroxycarboxylic acid. Representative examples of CPL spectra associated with the 4–6 (Figure 2), 4–5 (Figure 3), 4–4 (Figure 4), and 4–3 (Figure 5) Tb(III) luminescence bands are shown for Tb(DPA)₂(MAN) and Tb(DPA)(MAN).

We generate two observables during the course of a CPL determination. One of these is the total luminescence (TL) intensity, given by eq 1, and the other is the CPL intensity,

$$I = \frac{1}{2}(I_L + I_R) \quad (1)$$

given in eq 2, where I_L and I_R represent the emitted intensities

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

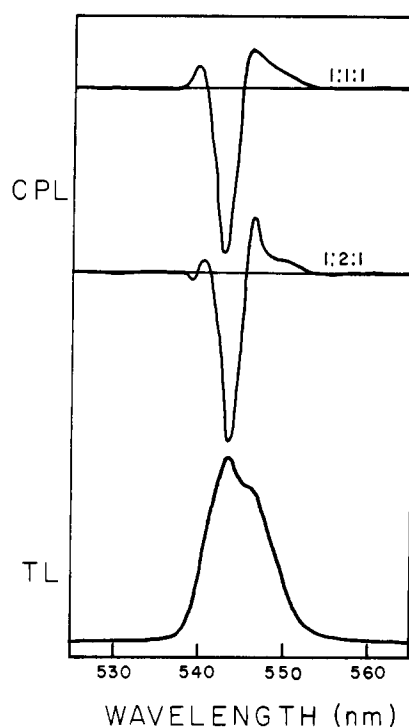


Figure 3. TL (lower) and CPL spectra associated with the $^5D_4 \rightarrow ^7F_5$ transition of Tb(DPA)₂(MAN) (middle) and Tb(DPA)(MAN) (upper).

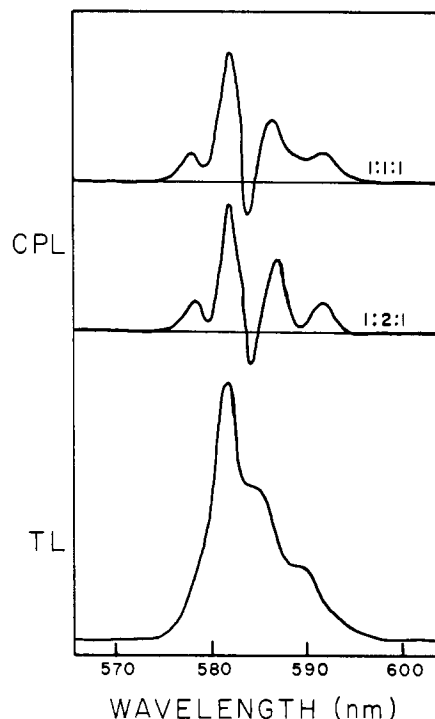


Figure 4. TL (lower) and CPL spectra associated with the $^5D_4 \rightarrow ^7F_4$ transition of Tb(DPA)₂(MAN) (middle) and Tb(DPA)(MAN) (upper).

of left- and right-circularly polarized light, respectively. It is possible to eliminate the unit dependence associated with these two quantities by taking their ratio; this results in a parameter which is termed the luminescence dissymmetry factor (eq 3). This dissymmetry factor has theoretical as well

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

as experimental significance, as it may be related to the rotational strength of the transition.¹⁶

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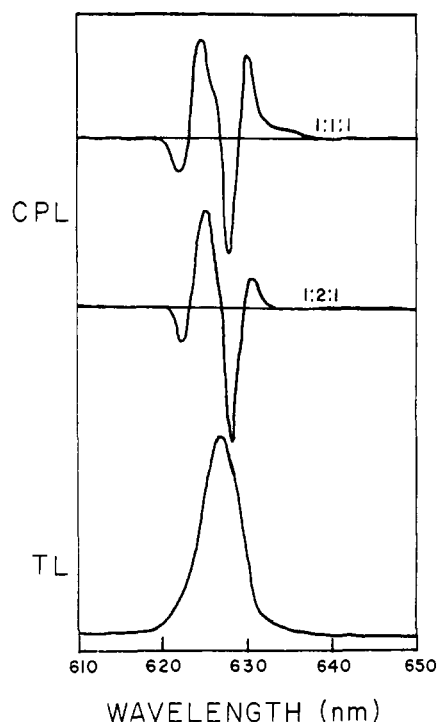


Figure 5. TL (lower) and CPL spectra associated with the $^5D_4 \rightarrow ^7F_3$ transition of $Tb(DPA)_2(MAN)$ (middle) and $Tb(DPA)(MAN)$ (upper).

Table I. Luminescence Dissymmetry Factors for the Various $Tb(III)$ Emission Bands in the $Tb(DPA)(L\text{-mandelic acid})$ Complexes

transition	wavelength, nm	$10^2 g_{lum}$	
		Tb-(DPA)(MAN)	Tb-(DPA) ₂ (MAN)
4-6	491	+1.1	+0.88
4-5	544	-8.3	-6.4
4-4	583	+1.1	+0.87
4-3	619, 623	+6.6, -4.6	+5.1, -3.5

Values of g_{lum} were calculated at each of the main extrema for each Tb^{III}/DPA complex. In Table I, we present results obtained for $Tb(DPA)(MAN)$ and $Tb(DPA)_2(MAN)$ within each of the four $Tb(III)$ emission bands, and this table illustrates the degree of optical activity associated with each band system. One notes that the 4-5 and 4-3 bands display the strongest CPL, with the CPL of the 4-6 and 4-4 bands being much weaker. This relation holds for all other chiral ligands, and in addition, the ratios of the dissymmetry factors for a given pair of bands are generally insensitive to the identity of the ligand. In Table II, we illustrate the degree of optical activity that is induced by the various ligands. Since all bands exhibit the same relationships, only data for the 4-5 band are shown in Table II. In general, the ligands which have the greatest steric bulk appear to induce the largest degrees of optical activity. The results presented were calculated in the low-pH region (where the CPL intensity remained constant), and each value represents the average of at least six spectra. In addition, the reported dissymmetry factors were obtained under conditions where the Tb^{III}/DPA complexes were as fully saturated with the hydroxycarboxylic acid as possible. Further addition of chiral ligand did not lead to more intense CPL.

In a previous work,⁹ it was noted that the CPL spectrum of $Tb(DPA)_2(MAL)$ and $Tb(DPA)(MAL)$ inverted above pH 7 and that no precipitate was formed. We had studied only the 4-5 transition in this work and noted that in the low-pH

Table II. Luminescence Dissymmetry Factors for the $^5D_4 \rightarrow ^7F_5$ $Tb(III)$ Emission Band in the Various $Tb(DPA)(ligand)$ Complexes^a

ligand	$10^2 g_{lum}$	
	Tb-(DPA)(L)	Tb-(DPA) ₂ (L)
L-lactic acid	-5.7	-4.2
L- α -hydroxyisocaproic acid	-9.5	-9.7
L-argininic acid	-6.2	-5.9
L-mandelic acid	-8.3	-6.4
L-phenyllactic acid	-11.0	-9.1
L-malic acid (low pH)	-3.3	-3.2
L-hydroxyglutaric acid	-3.5	-3.4

^a All data were obtained at 544 nm.

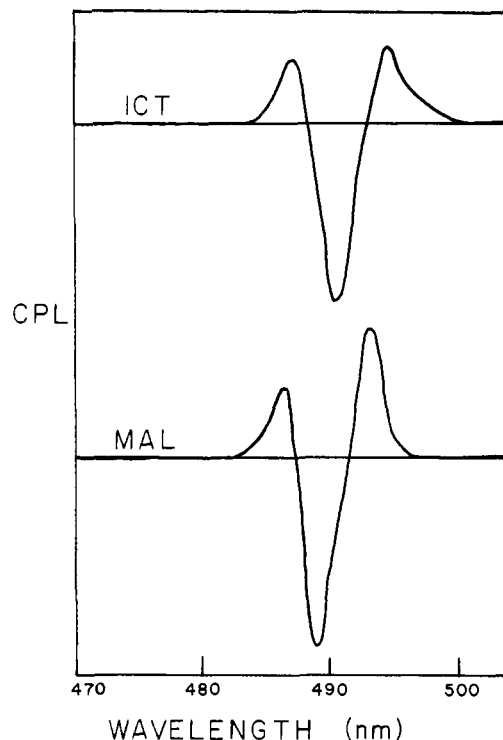


Figure 6. CPL spectra associated with $Tb(DPA)$ complexes of potentially terdentate ligands. Data are shown for the $^5D_4 \rightarrow ^7F_5$ $Tb(III)$ emission bands of $Tb(DPA)(MAL)$ (lower, at pH 7.5) and $Tb(DPA)(ICT)$ (upper, at pH 5.0).

region (below pH 7) that the CPL spectra of MAL complexes were identical in both line shape and magnitude with the spectra obtained for the LAC complexes. We concluded that the bonding between $Tb(III)$ and these two ligands must be through the same α -hydroxycarboxyl functionality at low pH and that the CPL sign inversion involved attachment of the second carboxyl group of the MAL ligand to the metal ion. Study of the CPL associated with the other $Tb(III)$ emission bands was part of the present study, and we find that our original conclusion is supported: the CPL of all $Tb(DPA)(MAL)$ low-pH emission bands is the same as shown in Figures 2-5, and the dissymmetry factors are also quite close in magnitude. The high-pH CPL spectra of the MAL complexes may be seen in Figures 6-9.

To examine this behavior further, we studied the CPL of two other potentially terdentate hydroxycarboxylic acids, HGT and ICT. In a previous study,¹¹ we established that while aspartic acid could form a bidentate chelate with $Tb(III)$, glutamic acid could not. Presumably, the extra methylene group of the glutamate ligand makes the resulting chelate ring too large to be stable. It is clear, then, that the HGT ligand should not form a terdentate chelate system and that any bonding should be via the α -hydroxycarboxyl functionality.

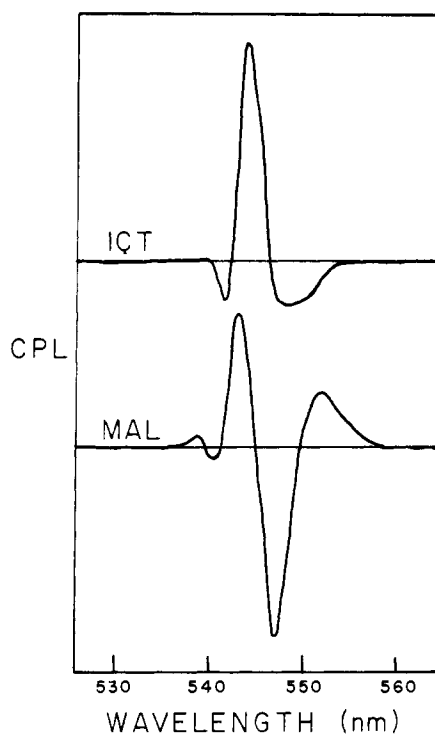


Figure 7. CPL spectra associated with the ${}^5D_4 \rightarrow {}^7F_5$ transition of Tb(DPA)(MAL) (lower) and Tb(DPA)(ICT) (upper), with both ligands in the terdentate bonding mode.

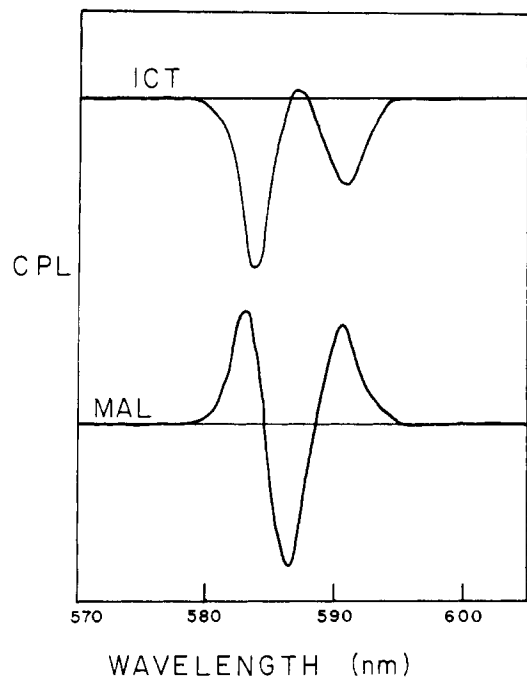


Figure 8. CPL spectra associated with the ${}^5D_4 \rightarrow {}^7F_4$ transition of Tb(DPA)(MAL) (lower) and Tb(DPA)(ICT) (upper).

The low-pH spectra of HGT complexes are identical with the MAL spectra (as well as being the same as those for compounds 1-5), and the HGT complexes are found to undergo *no* CPL sign inversion above pH 7. We feel that this observation further solidifies our description of the bonding changes that take place for the MAL ligand systems.

The ICT ligand offers several possibilities for multidentate bonding. In Figures 6-9, we show the CPL spectra obtained with Tb(DPA)(ICT), and one can immediately note that the spectra are somewhat different from the line shapes shown in Figures 2-5 (characteristic of pure bidentate ligand bonding)

Table III. Luminescence Dissymmetry Factors for the Various Emission Bands in Tb(DPA) Complexes with Potentially Terdentate Hydroxycarboxylic Acid Ligands

transition	Tb(DPA)(ICT)		Tb(DPA)(MAL) ^a	
	wave-length, nm	$10^3 g_{lum}$	wave-length, nm	$10^3 g_{lum}$
4-6	487	+2.4	486	+1.3
	490	+4.0	489	-2.2
	494	+2.9	493	+0.95
4-5	544	+30.3	543	+10.3
			547	-15.8
4-4	584	-5.7	583	+1.26
			586	-3.0
4-3	590	-7.3	590	+3.9
	617	-27.0	618	-16.3
	619	+12.8	620	+7.4
	623	-23.1	622	-11.7

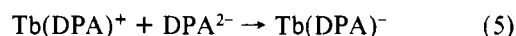
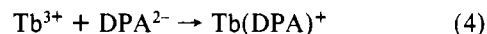
^a Data for Tb(DPA)(MAL) were taken at pH 7.7.

Table IV. Formation Constants of the Mixed-Ligand Complexes Formed between the Tb(DPA) Species and Various α -Hydroxycarboxylate Ligands

ligand	Tb(DPA)(L)		Tb-(DPA) ₂ (L)
	K_1	K_2	K_1
L-lactic	175	19	50
L- α -hydroxyisocaproic acid	192		81
L-argininic acid	184		55
L-mandelic acid	210	22	60
L-phenyllactic acid	255	27	89
L-malic acid (low pH)	120		30
L-hydroxyglutaric acid	110		30
D-isocitric acid	380	50	165

and very different from the high-pH spectra of the corresponding MAL complexes. ICT presents an additional interpretational problem in that this ligand contains two asymmetric atoms, with the material being obtained as the three isomer. The configuration at the α -hydroxycarboxyl carbon is *R*,¹⁹ and we find that the CPL spectra do appear to be mirror images of the spectra shown in Figures 2-5. The slight line shape differences we see are probably due to some small degree of terdentate bonding. We shall return to these points in the Discussion section.

Complete understanding of the complexation phenomena associated with the mixed-ligand chelates requires that the equilibria between the Tb(III) ion and the various ligands be understood. Given the large values that are known for the association constants of Tb(III) and DPA,¹⁰ one would predict that reactions 4 and 5 would be complete at Tb^{III}:DPA ratios



of 1:1 and 1:2, respectively. It is known that the association constants for Tb(III) and α -hydroxycarboxylic acid ligands range from 300 to 800,¹⁷ and we conclude that none of the chiral ligands we have used will be able to displace a DPA ligand.

It is clear, therefore, that the magnitude of the CPL will be proportional to the degree of complexation existing between the Tb/DPA complexes and the hydroxycarboxylic acid ligands. Since the unbound Tb/DPA complexes cannot show any CPL, it is a trivial matter to show that if one molecule of chiral ligand is bound per molecule of complex, then the mole fraction of free Tb/DPA complex is given by eq 6 where

$$X_{L,n} = (g_F - g_i)/g_i \quad (6)$$

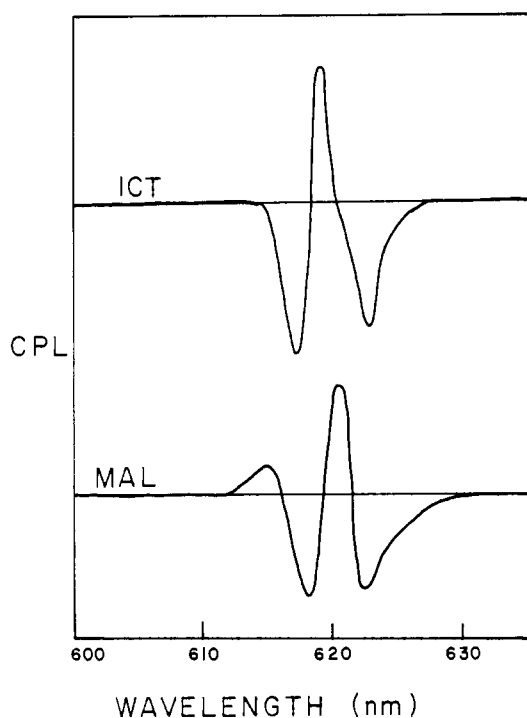
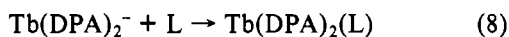
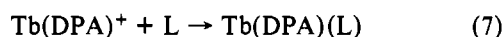
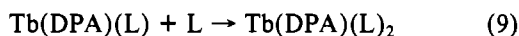


Figure 9. CPL spectra associated with the ${}^5D_4 \rightarrow {}^7F_3$ transition of $Tb(DPA)(MAL)$ (lower) and $Tb(DPA)(ICT)$ (upper).

g_F is the dissymmetry factor reached after addition of excess hydroxycarboxylic acid (values from Tables I–IV) and g_i is the dissymmetry factor at the concentration of interest. With this mole fraction known, and with a knowledge of all starting concentrations, we can easily calculate association constants for reactions 7 and 8.



Formation constants for these 1:1 complexes were calculated by these means, and the results have been tabulated in Table VI. Calculations for the $Tb(DPA)^+$ complexes are complicated by the possibility that a second reaction, reaction 9, might take



place. Examination of the limiting dissymmetry factors provides a method whereby this problem can be addressed. One commonly finds that optical activity due to conformational or vicinal effects is usually additive,¹⁸ and this would imply that the g_{lum} value of a $Tb(DPA)(L)_2$ complex should be twice that of a $Tb(DPA)(L)$ complex. If we approximate the g_{lum} value of the $Tb(DPA)(L)$ complex as being the same as that of the analogous $Tb(DPA)_2(L)$ complex, then an examination of Table II shows that only when $L = LAC, MAN, PLA,$ or ICT is the limiting dissymmetry factor of $Tb(DPA)_2(L)$ exceeded for the $Tb(DPA)(L)$ complex. We conclude, therefore, that $MAL, HGT, HIC,$ and ARG do not form a $Tb(DPA)(L)_2$ complex. For the ligands where the $Tb(DPA)(L)_2$ complex does form, one can compute K_1 at low concentrations of L and K_2 at high concentrations, and all these values are found in Table IV.

One very interesting observation was made when attempting to obtain the association constants for the terdentate ligands. With ICT , the usual behavior was noted: the degree of CPL increased with ICT concentration until a limiting value was reached. The K_1 and K_2 constants we calculated were sig-

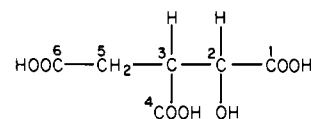
nificantly higher than for any other ligand system, which we attribute to the presence of some terdentate ligand bonding. For the MAL complexes, however, excessive amounts of MAL ligand actually hindered the formation of the high-pH CPL. This hindrance is certainly associated with the presence of the DPA ligand, since additional CPL enhancement could be obtained with the $Tb(DPA)$ system relative to the $Tb(DPA)_2$ system. At very high concentrations of MAL (ratio of $MAL:Tb = 10:1$), the spectra are exclusively of the bidentate complex. One would then infer that dissociation of the MAL ligand is required for the bonding change to take place and that at high concentrations of MAL another MAL ligand takes the place of the departing ligand before the original ligand can reattach at three coordinating positions.

Discussion

In our previous work on mixed-ligand hydroxycarboxylic acid complexes, we established that the observed optical activity was due to a mixture of vicinal (chirality due to the presence of an asymmetric atom bound to a metal ion) and conformational (chirality due to the presence of an asymmetric atom in a chelate ring bound to a metal ion) effects.⁸ Configurational optical activity (chirality due to an asymmetric placement of ligands about a metal ion) was found in this study to be considerably stronger than chirality due to either vicinal or conformational effects, and a comparison of the g_{lum} factors of our present work with the earlier⁸ reveals that under no conditions have we found configurational optical activity in any of the complexes examined in the course of the present work.

We have now presented ample evidence that the α -hydroxycarboxylic acids are capable of forming bidentate chelates with lanthanide ions. Malic acid is able to form a terdentate ligating system once both carboxylic acid groups become fully deprotonated, but it is clear that the unionized hydroxyl group remains involved in the bonding. We have discounted the possibility that the CPL change reflects a change from bidentate bonding between hydroxyl and the α -carboxyl group to bidentate bonding between the two carboxyl groups, since the CPL spectrum of $Tb(DPA)(Asp)$ and $Tb(DPA)_2(Asp)$ (aspartic acid) is radically different than either of the CPL spectra of the MAL complexes.¹¹ The aspartic acid complexes form a useful class of complexes for the study of the hydroxycarboxylic acid complexes, in that we have established that aspartic acid does form only a bidentate chelate through its two carboxyl groups.¹¹

The bonding situation exhibited by the ICT ligand is radically different from any we have seen before, but a careful examination of related data leads to a prediction of the most probable mode. For purposes of discussion, it is useful to number the carbon atoms in the ICT ligand:



It is known that D-isocitric acid exists as the threo isomer, with carbon 2 being of the R configuration and carbon 3 having a S configuration.¹⁹ The possible modes of complexation are (a) bidentate via the 2-OH group and the 1-COOH group, (b) bidentate via the 1-COOH and 4-COOH groups, (c) bidentate via the 4-COOH and 6-COOH groups, (d) terdentate via the 1-COOH, 2-OH, and 4-COOH groups, and (e) terdentate via the 1-COOH, 4-COOH, and 6-COOH groups.

While the situation may appear to be complicated, it turns out that we have studied a number of the postulated bonding

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systems in detail. Possibility (a) represents the α -hydroxycarboxyl mode of attachment associated with LAC, HIC, ARG, MAN, and PLA ligands. Comparison of Figures 2-5 and 6-9 shows that the band shapes are very similar, with the ICT spectra being the mirror image of the illustrated MAN spectra. However, the absolute configuration of the MAN ligand is *S* and the analogous carbon in the ICT ligand is *R*, so this difference would be expected if the mode of bonding were the same. In addition, if one compares the dissymmetry factors of the Tables, one finds that the degree of optical activity is roughly equivalent. Possibilities b and c represent a similar bonding mode as already shown for the aspartic acid complexes, and an examination of our published spectra and g_{lum} values for the 4-5 emission band¹¹ (and unpublished data for the 4-6, 4-4, and 4-3 bands) shows that no similarities exist. Possibility d reflects the bonding situation presented by MAL at high pH, and a simple examination of Figures 6-9 demonstrates a clear difference. We can discount possibility e since this would require the existence of two seven-membered rings, and we have already shown that these are unstable.¹¹ We therefore believe that the ICT ligand binds predominately in a bidentate manner through the α -hydroxycarboxyl functionality and that any CPL line shapes that do exist must be a reflection of a small amount of terdentate bonding through participation of the carboxyl group at carbon 4.

The formation constants of Table IV represent trends that one would predict from simple arguments. We have already mentioned that the K_1 constants of Tb^{3+}/α -hydroxycarboxylic acid complexes range from 300 to 800.¹⁷ The binding of one DPA ligand by $Tb(III)$ reduces the overall positive charge of the complex as $Tb(DPA)^+$ is formed, and we now find that the K_1 constants range from 110 to 255. The effect on K_2 is even more pronounced; while for Tb^{3+} , K_2 is usually almost equal to K_1 , for $Tb(DPA)^+$ we find that K_2 (if a second ligand is bound at all!) is only one-tenth that of K_1 . Finally, a further decrease in positive charge must occur with formation of the $Tb(DPA)_2^-$ species, and now one finds that the association constants range from 30 to 90.

The data we have presented in the present study permit a critical evaluation of the selection rules for lanthanide optical activity recently proposed by Richardson.²⁰ In this work, Richardson developed predictions for the electric dipole strengths, rotatory strengths, and dissymmetry factor magnitudes solely on the basis of the *S*, *L*, and *J* quantum numbers of the states involved in the transitions. Details of the lanthanide crystal field were omitted in this treatment, but the conclusions should be good estimates of the relative magnitudes of the various properties. Richardson predicts that the 4-5, 4-4, and 4-3 transitions should all have approximately equal degrees of optical activity and the dissymmetry factors associated with the 4-6 transition ought to be much smaller. In fact, we find that while the 4-5 and 4-3 transitions do have approximately the same degree of CPL, the 4-4 transition actually has the same order of magnitude as the 4-6. Our observations simply point out the necessity for including the crystal field in the optical activity calculations, which shows that crystal field effects in lanthanide complexes are perhaps more significant than is generally thought.

The results presented in our present work demonstrate the usefulness of CPL spectroscopy as a probe of lanthanide ion stereochemistry. Given the current state of existing CPL theory as applied as lanthanide ions, our discussions have remained qualitative in nature. Nevertheless, by a systematic variation of functionality on the chiral ligands, one can deduce a fair amount of stereochemical information from a study of the CPL spectra of a chiral lanthanide complex.

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Optical Activity Induced in the Europium(III) Complexes of β -Diketones through Association with Phenylalkylamines and Phenylalkylamino Alcohols

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The optical activity induced in the $Eu(III)$ chelates of two fluorinated β -diketones upon complexation with two chiral phenylalkylamines and six phenylalkylamino alcohols was studied by means of circularly polarized luminescence (CPL) spectroscopy. In addition, association constants for the adducts were computed from emission titrations of the chelates with substrates. These results were used to deduce the manner in which the substrate bound to the chelate, and arguments are presented regarding the major type of chirality experienced by the $Eu(III)$ ion. Depending on the nature of the substrate, the chiral ligands could function as mono-, bi-, or terdentate chelators. The optical activity was found to arise solely from vicinal or vicinal/conformational effects, with no evidence being obtained to indicate the presence of configurational optical activity.

Introduction

The use of paramagnetic lanthanide complexes of β -diketones as shift reagents in NMR spectroscopy is a well-known phenomenon, with literally hundreds of articles having been published regarding applications of these materials. In general,

most of the interest has been focused on questions of spectral resolution and simplification or of structure elucidation.²⁻⁴ Structural aspects of the shift reagent adducts have been probed by means of X-ray crystallography, and it has been

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