of NH_3 to a mechanism which is basically *more associative* than that suggested above for the photosubstitution of X^-.

The associative character is furthermore in good agreement with the conclusions drawn[72,81] from the stereochemical effects generally observed in the photochemistry of chromium(III) ammine complexes. For a purely associative mechanism we would once again expect a $\Delta V^{\ddagger}_{A}$ value of approximately -16 $cm^3\ mol^{-1}$, which is more negative than our mean value of -10.9 ± 1.4 $cm^3\ mol^{-1}$ for $\Delta V^{\ddagger}_{r}$ (Φ_{NH_3}). The difference is ascribed to a counteracting dissociative contribution from the expulsion of the leaving group (NH_3). The dissociative character is in line with the theoretical foundations[82,83] for Adamson's first rules,[30] which in general correctly predict the leaving group in mixed-ligand complexes. Since no change in charge occurs during this process, $\Delta V^{\ddagger}_{D}$ is expected to be of the order of $+24.8$ $cm^3\ mol^{-1}$, i.e., the partial molar volume of NH_3. This is, however, substantially more positive than $\Delta V^{\ddagger}_{D}$ calculated for the release of X^-, with the result that a smaller dissociative contribution will cause the same effect. In an overall consideration the photoaquation of NH_3 is indeed more associative (less dissociative) in character than the corresponding photoaquation of X as mentioned above. Hydrogen bonding may partially stabilize the $Cr-NH_3$ bond in the transition state and account for the observed decrease in dissociative character for the photoaquation of NH_3. It follows that an I_a mechanism also described the photosubstitution of NH_3 in the studied complexes.

We conclude that the results of this first high-pressure mechanistic study of photosubstitution reactions are very encouraging. They can lead to a better understanding of the molecular nature of such photoreactions and enable us to make meaningful suggestions regarding the intimate mechanisms involved.

Acknowledgment. The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $Cr(NH_3)_5Br^{2+}$, 22289-65-2; $Cr(NH_3)_5NCS^{2+}$, 16884-60-9; $Cr(NH_3)_6^{3+}$, 14695-96-6.

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Circularly Polarized Luminescence Studies of Terbium(III) Complexes of Hydroxycarboxylic Acids

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Circularly polarized luminescence (CPL) spectroscopy has been used to study the binding of L-lactic (LAC), L-mandelic (MAN), and L-phenyllactic (PLA) acids by Tb(III). Complexes having the general formulas $Tb(L)_3$, $Tb(DPA)(L)_2$, and $Tb(DPA)_2(L)$ were studied (DPA = pyridine-2,6-dicarboxylate), and these complexes were used to evaluate the relative contributions of vicinal, conformational, and configurational effects to the overall chirality of the Tb(III) complex. It was found that both the line shape and magnitude of the CPL spectra could be used to deduce the major source of optical activity in the complexes and that the results could also be used to deduce modes of ligand bonding to the metal ion in these and other related complexes.

Introduction

Since the earliest work[1,2] involving the binding of trivalent lanthanide ions by proteins and enzymes, considerable effort has been expended in the development of these ions as structural probes.[3,4] One of the most useful methods that has been developed involves the use of Tb(III) as a luminescence probe, and it has been demonstrated that Tb(III) will substitute for Ca(II) almost without exception.[5] A considerable enhancement of Tb(III) emission is found when one irradiates the aromatic residues of phenylalanine, tyrosine, or tryptophan, and these in turn sensitize the Tb(III) luminescence by means of a radiationless energy transfer.

To obtain a higher degree of information regarding the stereochemistry of the Tb(III) site, various workers have employed circular polarization of luminescence (CPL) as a chiroptical tool.[5-10] Strong CPL was found in many cases, but it was found that CPL was not observed in a considerable fraction of Tb(III)-substituted proteins.[5] When CPL was observed, however, one generally obtained one mirror image or the other of a particular line shape. These features led to the suggestion that a dissymmetric arrangement of donor atoms about the Tb(III) ion (such as would exist at the interior of a protein chain) was responsible for the CPL and that binding at exterior protein sites might not lead to observable CPL.[4]

In order to understand these effects in greater detail, we have undertaken a study of model Tb(III) complexes which mimic the metal-binding site of a protein. Mixed-ligand complexes of Tb(III), pyridine-2,6-dicarboxylic acid (DPA), and an asymmetric ligand have proved especially useful, since the DPA ligand acts both as a luminescence sensitizer and as an achiral portion of the Tb(III) coordination sphere (thus enabling a study of isolated metal–ligand interactions). In an effort to understand the various mechanisms by which optical activity may be induced in a Tb(III) ion, we have examined the CPL spectra of mixed-ligand Tb/DPA complexes containing monodentate carboxylic acids,[11] α-amino acids,[12] and

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malic acid.[13] During the course of these studies, new modes of ligand bonding were uncovered as a result of CPL line-shape changes, and it was found that the magnitude of the CPL could be used to predict the major contribution to the molecular chirality.

In the present work, CPL spectroscopy has been used to study the Tb(III) complexes of three hydroxycarboxylic acids. Complexes having the general formulas $Tb(L)_3$ and $Tb(DPA)_2(L)$ were prepared, where L was L-lactic acid (LAC), L-mandelic acid (MAN), and L-phenyllactic acid (PLA). These studies form a highly interesting supplement to our earlier work, where $Tb(DPA)_2(MAL)$ and $Tb(DPA)(MAL)_2$ = L-malic acid) complexes were studied by the CPL method and a profound change in CPL line shape was observed when the MAL ligand changed its mode of bonding from bidentate to terdentate.[13]

Experimental Section

Tb(III) solutions were prepared by dissolving a weighed amount of Tb_4O_7 (99.9% pure, Ker McGee) in the minimum amount of 70% $HClO_4$, neutralizing to pH 3 with NaOH, and then diluting to the desired volume. A sufficient amount of $NaClO_4$ was also added to ensure a final ionic strength of 0.1 M. L-Lactic acid was obtained from Sigma as the 98–100% pure crystalline free acid, while L-mandelic, L-phenyllactic, and pyridine-2,6-dicarboxylic acids were purchased from Aldrich (all certified to be at least 98% pure).

Solutions containing an initial ratio of 1:2 of Tb(III) and DPA were prepared, and best results were obtained when a 2-fold excess of chiral ligand (L) was added to the solution. These mixed-ligand complexes were not actually isolated in solid form; slow evaporation of aqueous solutions tended to yield polymeric Tb(DPA), $Tb(L)_3$, and other mixtures of products. A similar mixture was obtained once the solution pH exceeded 8.0. Attempted precipitation with heavy metal cations also resulted in destruction of the complexes. In the absence of DPA, $Tb(L)_3$ complexes precipitated above pH 3, and these materials analyzed in a proper manner for a $Tb(L)_3$ complex.

All CPL spectra were recorded on a high-resolution spectrometer constructed in this laboratory, which has been described in detail.[12] The luminescence spectra were recorded at 180° to the exciting light, with a KNO_2 filter being used to remove any unabsorbed excitation from the emission train. CPL of the $Tb(L)_3$ complexes were obtained by suspending a small amount of the insoluble material in H_2O and placing of this suspension in a 2-mm cell; the CPL obtained in this way were somewhat irreproducible in magnitude, but not excessively so. Tb/LAC complexes were excited at 365 nm, Tb/MAN and Tb/PLA complexes were excited at 250 nm, and all mixed-ligand Tb/DPA/L complexes were excited at 295 nm. It was found that excitation of the aromatic portions of each complex resulted in greatly enhanced Tb(III) emission. In all cases, an excitation band-pass of 16 nm and an emission band-pass of 10 Å was used; further increase in resolution of the emission spectrum did not lead to an improvement of the spectral features.

All studies were carried out in aqueous solutions at room temperature. pH adjustment of each solution was carried out by adding microliter amounts of standard NaOH or $HClO_4$ directly to the complex in the fluorescence cuvette, and the pH was then read on an Orion 701A pH meter. In all cases, the pH was obtained by inserting a glass microcombination electrode (calibrated daily with phosphate buffers) into the cuvette.

Results

The luminescence spectrum of a Tb(III) complex consists of a series of sharp, well-resolved emission bands in the visible region of the spectrum. These correspond to transitions from the $^5D_4$ excited state to several components of the ^7F_J ground state, and it has been found in a wide variety of studies that emission to the $J = 5$ ground level is always the most intense and exhibits the largest degree of CPL in a chiral Tb(III) complex.[14] Our present work confirms this general trend and supports the selection rules recently proposed by Richardson.[15]

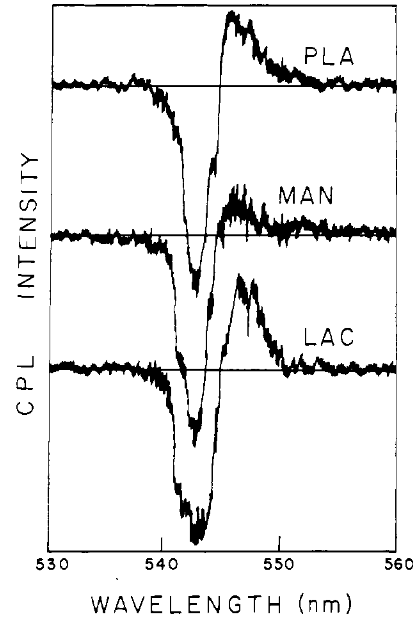

Figure 1. CPL spectra of the mixed-ligand $Tb(DPA)_2(L)$ complexes, where L = LAC (lower), MAN (middle), and PLA (upper). All spectra were obtained at pH 4.5, and all the intensity scales are completely arbitrary.

Two series of mixed-ligand complexes were examined, and these had the general formulas $Tb(DPA)_2(L)$ and $Tb(DPA)(L)_2$. The very large association constants of Tb(III) and DPA ensures that a simple mixing of 1:1 and 1:2 ratios of Tb(III) to DPA will result in the formation of Tb(DPA) and $Tb(DPA)_2$ complexes, respectively.[16] Williams and coworkers have formed these compounds in a similar fashion and have studied the conformations and hydration numbers by means of NMR spectroscopy.[17] These workers have demonstrated the presence of water molecules in the inner coordination sphere of the lanthanide ion, and our previous work[11-13] has demonstrated that these bound water molecules may be replaced by a chiral ligand. CPL spectra may be obtained as a result of this substitution, and the spectra thus enable a determination of metal–ligand bonding characteristics.

Addition of a slight excess of LAC, MAN, or PLA to a solution of $Tb(DPA)_2$ resulted in the appearance of CPL within the luminescence spectrum of the Tb(III) ion, and this CPL was taken to indicate the presence of a mixed-ligand complex. The line shapes of the CPL spectra were invarient to pH, and it was found that the CPL intensity increased through the 2.0–3.5 pH region. The CPL intensity remained essentially constant until pH 7.0 and declined sharply after that until a precipitate formed at pH 7.5. This insoluble material analyzed to be a mixture of Tb(DPA) and other Tb(III) complexes. Representative examples of the mixed-ligand CPL spectra are shown in Figure 1.

The CPL measurement actually results in the detection of two quantities. One is the total luminescence (TL) intensity, usually given by eq 1, and the other is the circularly polarized

$$I = \tfrac{1}{2}(I_L + I_R) \tag{1}$$

luminescence (CPL) intensity (eq 2). In eq 1 and 2, I_L and

$$\Delta I = I_L - I_R \tag{2}$$

I_R represent the emitted intensities of left and right circularly polarized light, respectively. Since I and ΔI are measured in

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Table I. Luminescence Dissymmetry Factors Found for Tb(III) Mixed-Ligand Complexes[a]

complex	$g_{\text{lum}} \times 10^2$ 543 nm	$g_{\text{lum}} \times 10^2$ 548 nm
$Tb(DPA)_2(LAC)$	−2.05	+1.18
$Tb(DPA)_2(MAN)$	−3.55	+1.44
$Tb(DPA)_2(PLA)$	−5.00	+2.42
$Tb(DPA)(LAC)_2$	−3.41	+1.59
$Tb(DPA)(MAN)_2$	−5.19	+3.05
$Tb(DPA)(PLA)_2$	−7.58	+4.33

[a] All g_{lum} values were obtained from the averaging of at least six spectra and have an associated error of approximately ±0.05.

arbitrary quantal units, it is common practice to calculate the luminescence dissymmetry factor, g_{lum}, by taking the ratio of these quantities and thus eliminating any unit dependence[14] (eq 3). The g_{lum} has theoretical as well as experimental

$$g_{\text{lum}} = \Delta I/I \tag{3}$$

significance, as it may be related to the rotational strength of the transition[14]

$$g_{\text{lum}} = 4R_{\text{ab}}/D_{\text{ab}} \tag{4}$$

where R_{ab} is the rotatory strength

$$R_{\text{ab}} = \text{Im}\langle\Psi_a|\hat{\mu}|\Psi_b\rangle\langle\Psi_b|\hat{m}|\Psi_a\rangle \tag{5}$$

and D_{ab} is the dipole strength

$$D_{\text{ab}} = \langle\Psi_a|\hat{\mu}|\Psi_b\rangle^2 \tag{6}$$

Equations 4–6 are valid for randomly oriented emitted systems in which the luminescent excited state is thermally equilibrated prior to emission. It should be noted that, while the value of g_{lum} has little theoretical significance without a detailed analysis of the CPL line shape, values of g_{lum} may be compared to each other to evaluate trends in the data that may be correlated with changes in complex structure.[14]

Values of g_{lum} were calculated at the maxima of the CPL peaks for all mixed-ligand systems, and the limiting values obtained in the 3.5–7.0 pH region have been collected in Table I. In all complexes, a negative peak was obtained at 543 nm and a positive peak was located at 548 nm. The electronic effect of the phenyl ring present in MAN and PLA is clearly evident from the magnitude of g_{lum} associated with these complexes (when compared to the LAC complexes). This effect cannot be due to increased association of $Tb(DPA)_2$ with MAN or PLA, since the first association constant of Tb(III) and all ligands is approximately the same (and LAC actually has the highest value).[18]

Addition of a 4-fold amount of either LAC, MAN, or PLA to a solution of Tb(DPA) also led to the observation of strong CPL. The line shape of this CPL strongly resembled that found for the $Tb(DPA)_2(L)$ complexes, but a weak positive peak was noted at 541 nm in the $Tb(DPA)(L)_2$ complexes. Examples of the CPL line shapes associated with the $Tb(DPA)(L)_2$ complexes may be found in Figure 2. It was found that the CPL intensity increased rapidly up to pH 3.0 and then remained relatively constant up to pH 7.0. Above this pH value, it was noted that formation of insoluble complexes was accompanied by a drastic decrease in CPL intensity. g_{lum} values were calculated for the main CPL peaks at 543 and 548 nm, and these have also been collected in Table I.

It may be seen that the CPL intensity is approximately doubled in the $Tb(DPA)(L)_2$ complexes relative to the $Tb(DPA)_2(L)$ complexes, and we take this observation to imply that the $Tb(DPA)(L)_2$ complex does exist in a reasonable concentration. The second association constant of Tb(III) for the hydroxycarboxylic acid ligands is almost as large as the first, so this conclusion is not unlikely.[18] Once again, the two chiral ligands containing a phenyl group induce considerably larger CPL than does the LAC ligand. It may also be noted that the total luminescence intensity associated with the $Tb(DPA)(L)_2$ complexes is approximately one-third that of the $Tb(DPA)_2(L)$ complexes, clearly demonstrating that a different complex exists in the former case (less DPA ligands in the inner coordination sphere of the Tb(III) ion must result in a lower degree of emission sensitization).

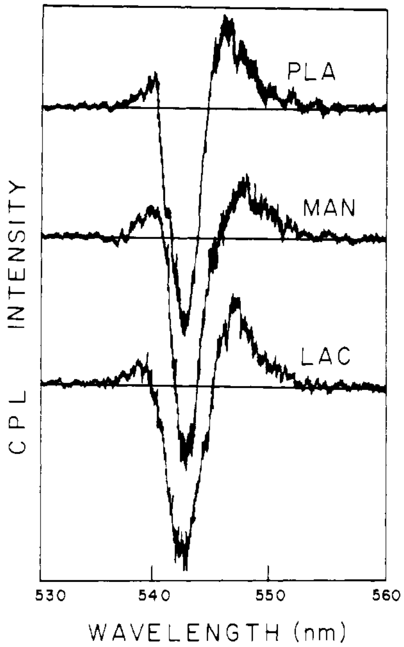

Figure 2. CPL spectra of the mixed-ligand $Tb(DPA)(L)_2$ complexes, where L = LAC (lower), MAN (middle), and PLA (upper). These spectra were obtained at pH 6.0.

Table II. Luminescence Dissymmetry Factors for Trischelated Hydroxycarboxylic Acid Complexes of Tb(III)[a]

complex	$g_{\text{lum}} \times 10$ 542 nm	$g_{\text{lum}} \times 10$ 545 nm	$g_{\text{lum}} \times 10$ 549 nm
$Tb(LAC)_3$	+0.9	−1.3	+0.8
$Tb(MAN)_3$	+1.5	−2.0	+1.6
$Tb(PLA)_3$	+1.4	−1.1	+0.7

[a] All g_{lum} values represent the averaging of 8–10 spectra, but the difficulty of obtaining reproducible suspensions of these insoluble materials increases the approximate error to ±0.1.

Solutions containing a 1:3 (or higher) ratio of Tb(III) to either LAC, MAN, or PLA invariably form a precipitate of $Tb(L)_3$ once the solution pH exceeds 3.0. We were able to record the CPL spectra of these precipitates by suspending the material in H_2O and irradiating a thin section. Some depolarization of the emitted light must result from scattering effects (therefore leading to lower g_{lum} values), but very strong CPL was observed. This CPL contained three strong peaks (found at 542, 545, and 549 nm), and representative spectra may be found in Figure 3. g_{lum} values were computed at each of the CPL maxima, and these are collected in Table II; reasonable reproducibility could be obtained by combining the results of many measurements. These dissymmetry factors average almost twice those of the $Tb(DPA)(L)_2$ complexes and would probably be even higher if all depolarization effects could be avoided.

Discussion

The overall optical activity exhibited by a lanthanide complex may be partitioned into three components:[19] (a) a vicinal

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[19] For an extremely lucid description of these effects, see: Richardson, F. S. *Chem. Rev.* **1979**, *79*, 17.

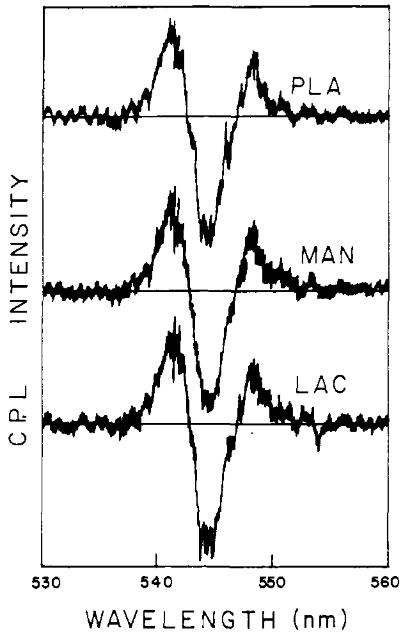

Figure 3. CPL spectra of $Tb(L)_3$ complexes obtained as suspensions in H_2O. Data for L = LAC (lower), MAN (middle), and PLA (upper) are shown.

effect (due to the presence of one or more asymmetric atoms within a bound ligand), (b) a conformational effect (due to the possible chiral conformations of coordinated ligand rings), and (c) a configurational effect (due to an asymmetric arrangement of ligands about the lanthanide ion). A fourth type of asymmetry (inherent dissymmetry, due to an asymmetric arrangement of monodentate ligands about a metal ion) is not expected to be of importance for lanthanide complexes, since all known derivatives of lanthanide ions are quite labile. In the absence of rigorous theoretical descriptions of f-f optical activity, one must presently be content with an evaluation of the type of optical activity exhibited by a lanthanide complex. This type of information can at least provide *some* description of the stereochemical nature of a lanthanide complex, and is useful for that reason.

Comparison of the CPL of mixed-ligand Tb/DPA complexes obtained during the course of the present study with the CPL of "pure" $Tb(L)_3$ complexes enables one to evaluate the empirical differences between conformational and configurational effects. A vicinal contribution will also be present in both situations, and its effect must be evaluated as well. In our previous studies,[12,13] it was demonstrated that the various effects led to characteristic CPL spectra (at least for the Tb(III) ion) and that each effect was also distinguished by having g_{lum} values within a certain range. We have also shown that the presence of a pure vicinal effect (obtained by forming $Tb(DPA)_2$ complexes with monodentate chiral carboxylic acids) let to the observation of CPL spectra having one sign only and g_{lum} values less than 10^{-4}.[11,12]

In the $Tb(DPA)_2(L)$ series of complexes, one would predict that only vicinal and conformational effects could contribute to the overall chirality, and the latter effect will only be present if the chiral L ligand (L = LAC, MAN, or PLA in the present work) is capable of forming a chelate ring. On the other hand, in the $Tb(L)_3$ complexes, one would anticipate that all three effects (vicinal, conformational, and configurational) could possibly be operative.

The CPL line shapes observed in the $Tb(DPA)_2(L)$ and $Tb(DPA)(L)_2$ complexes clearly demonstrate that a conformational effect is operative in addition to the vicinal effect. The double-signed CPL line shape and magnitude of the dissymmetry factors clearly indicate the presence of this effect, and a comparison to other mixed-ligand complexes where conformational effects were observed[13] indicates a close correspondence of CPL spectra. We therefore conclude that all three ligands used in our present work are capable of binding to a Tb(III) ion in a bidentate fashion. That this bidentate bonding is fully established at pH 3.0 suggests that the metal ion binds to an ionized carboxylic (p*K* = 3.2–3.6 for the hydroxycarboxylic acids[18]) and an unionized hydroxyl group (p*K* not reported, but is probably much higher).

The greater CPL intensities (as manifested by the g_{lum} values) observed in the study of the $Tb(DPA)(L)_2$ complexes indicates that a possible configurational effect is operational as well. The additional CPL peak at 541 nm does provide additional evidence for this effect, which we believe might come about from a stereoselective ligand configurational preference (having an origin in steric effects). The g_{lum} values associated with these complexes are approximately twice those found for the simple conformational effect and indicate that the effects are additative.

In the $Tb(L)_3$ complexes, the CPL line shapes and g_{lum} magnitudes are clearly different from the analogous data obtained on the mixed-ligand chelates, with changes being observed both in line shape and in wavelength maxima. In particular, the CPL line shape of Figure 3 is quite distinctive, and we believe that this particular form is indicative of a configurational effect. This last type of optical activity would be predicted to induce the largest degree of chirality,[19] and this is found to be the case for the $Tb(L)_3$ complexes. It is very noteworthy to compare the CPL spectra of the $Tb(L)_3$ complexes with the CPL of a Tb(III) ion bound by a calcium-binding protein,[5-10] the two are alike in both line shape and in magnitude. We therefore conclude that, when CPL is exhibited by a Tb(III) ion in a protein molecule, that ion is experiencing configurational optical activity. It would therefore appear that either vicinal or conformational effects are insufficient to induce CPL in the emission of a Tb(III)–protein complex. One could easily imagine a situation where many vicinal and conformational effects would add in a destructive fashion and lead to no net CPL. If the effects were to add in a constructive manner, CPL would then be observed (this, of course is the configurational effect).

In the earlier work involving $Tb(DPA)_2(MAL)$ and $Tb(DPA)(MAL)_2$ complexes (MAL = L-malic acid) it was noted that the CPL spectra provided dramatic evidence for a bidentate (at low pH) to terdentate (at high pH) bonding change within the MAL ligand. We had thought that the bidentate mode would involve both ionized carboxyl groups and the terdentate mode would include an unionized hydroxyl group as well. However, comparison with our present data does not support the earlier assignment. It may be noted that the sign patterns associated with the CPL of the Tb(DPA)(LAC) complexes match those of the Tb(DPA)(MAL) complexes at low pH, and the g_{lum} values of the $Tb(DPA)_2(L)$ complexes are essentially identical (the values for MAN and PLA ligands are quite a bit higher, but this must be due to an electronic effect of the phenyl group). In addition, the ratio of the g_{lum} values associated with the 543- and 548-nm CPL peaks is approximately the same in the MAL and LAC chelates, and we feel that these observations provide a strong impetus for proposing a common mode of ligand bonding in the two systems.

These assignments are further supported from a consideration of mixed-ligand CPL studies of complexes containing amino acids. $Tb(DPA)_2(ASP)$ also shows the same basic CPL line shape,[12] but here the g_{lum} values are a factor of 4 lower than the corresponding MAL and LAC complexes and the ratio of the 543- and 548-nm peaks is approximately 5 (instead of 2 as is the case for the MAL and LAC complexes). By comparison to simple amino acids (which only bind in a monodentate fashion), it was possible to prove that the ASP ligand must bind to the Tb(III) ion in a bidentate manner.[12] However, the ASP chelate ring contains seven members, while the LAC, MAN, and PLA chelate rings are five membered. A five-membered ring would have a different conformation than a seven-membered one (thus accounting for the difference in CPL line shape) and should also bring the asymmetric atom of the ligand closer to the metal (thus increasing the degree of CPL intensity).

It is our belief, therefore, that the mode of bonding (at low pH) existing at low pH is the same for MAL, LAC, MAN, and PLA complexes and involves bidentate attachment of the ligand to the metal via an ionized carboxyl and an unionized hydroxy group. In the case of the MAL complexes, a new terdentate mode of bonding becomes available once the solution pH exceeds 7.5, and one would assume that this mode would involve the other carboxyl group. Salama and Richardson[20] have demonstrated that MAL binds to Tb(III) in a bidentate fashion at low pH and in a terdentate fashion at high pH (this was done by examining solvent quenching of the Tb(III) ion and "counting" the number of coordinated water molecules) but had no evidence to suggest that the bidentate mode involved anything other than the two ionized carboxyl groups.

Conclusions

The studies reported in the present work clearly show the power of CPL spectroscopy when applied to studies of lanthanide complex stereochemistry. A careful analysis of line shape and dissymmetry factors may be used to assign the major contribution to the overall complex chirality and may also be used to deduce modes of ligand bonding. More detailed analysis must await further developments in theory and might be difficult to apply even after it is in place: the large number of crystal field components produced when the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition is placed in a low-symmetry crystal field makes resolution (in fluid solution at room temperature) of each component impossible. Nevertheless, CPL spectroscopy will remain a powerful tool to probe lanthanide ion stereochemistries. It shall be most powerful in the study of Tb(III)-substituted proteins, now that theoretically is possible to deduce the major contribution to the metal ion chirality from an examination of the CPL spectra.

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Registry No. Tb(DPA)$_2$(LAC), 76282-20-7; Tb(DPA)$_2$(MAN), 76282-21-8; Tb(DPA)$_2$(PLA), 76282-22-9; Tb(DPA)(LAC)$_2$, 76282-23-0; Tb(DPA)(MAN)$_2$, 76319-71-6; Tb(DPA)(PLA)$_2$, 76282-24-1; Tb(LAC)$_3$, 19042-17-2; Tb(MAN)$_3$, 37740-78-6; Tb(PLA)$_3$, 76282-25-2.

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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 21.[1] The Trisulfur Trinitride Anion

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Magnetic circular dichroism of the $S_3N_3^-$ anion shows a negative A term for the transition at 27 800 cm^{-1} and confirms the assignment to a $2e'' \rightarrow 2a''$ (HOMO–LUMO) excitation of the $\pi^* \rightarrow \pi^*$ type. Both the sign and the magnitude (0.98 β_e) of the excited-state magnetic moment are in perfect agreement with expectations based on the perimeter model. The general applicability of the model to inorganic ring systems derived from ($4N + 2$)-electron delocalized perimeters is pointed out.

Introduction

Magnetic circular dichroism (MCD) of molecules derived from ($4N + 2$)-electron cyclic conjugated perimeters with n identical atoms in a ring can be understood simply in terms of the perimeter model.[2-4] The highly symmetrical parent ($4N + 2$)-electron perimeters can be divided into three classes (Figure 1). The first comprises systems with only two π-electrons ($N = 0$), in which the highest occupied MO of π symmetry (HOMO) is not degenerate while the lowest unoccupied MO of π symmetry (LUMO) is degenerate. The second contains perimeters with only two π holes [$N = (n/2) - 1$], and is possible only for cycles with an even number of vertices. In this case, HOMO is degenerate while LUMO is not. In these two types of parent perimeters, the low-energy HOMO → LUMO transition is doubly degenerate and the excited state will be referred to as the B state. The MCD A term of the transition into this state is positive if $N = 0$ and negative if $N = (n/2) - 1$. Symmetry-lowering perturbations which cause the n centers to differ in electronegativity or substitution, which introduce cross-links, bridges, etc., may remove this degeneracy. If so, they lead to two nondegenerate transitions labeled B_1 and B_2 in the order of increasing energy. These are polarized in mutually perpendicular directions in the perimeter model approximation. If $N = 0$, the B_1 transition has a positive and the B_2 transition a negative B term. If $N = (n/2) - 1$, the signs are just the opposite.

The third class of ($4N + 2$)-electron [n]-center perimeters contains all other cases [$N \neq 0$, $N \neq (n/2) - 1$]. In this instance, both HOMO and LUMO are degenerate, and there are four possible single-electron promotions of the HOMO → LUMO type. In charged perimeters ($n \neq 4N + 2$), they give rise to two doubly degenerate excited states, L at lower energies and B at higher energies. In uncharged perimeters ($n = 4N + 2$), they lead to two nondegenerate excited states, L_b and L_a in the order of increasing energy, followed by a high-energy degenerate B state. Transitions into the states of the L type are forbidden by symmetry and appear in the experimental spectra only due to vibronic mixing. Transitions into the B state are allowed and have a small A term, whose sign and size are given by simple formulas given in ref 2. The MCD effect of both L and B transitions is usually complicated by

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[1] Part 20: S. L. Wallace and J. Michl, *Tetrahedron*, **36**, 1531 (1980).

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[3] J. Michl, *J. Am. Chem. Soc.*, **100**, 6812 (1978).

[4] J. Michl, *J. Am. Chem. Soc.*, **100**, 6819 (1978).

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