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Optical Activity Induced in Terbium(III) Tris(pyridine-2,6-dicarboxylate) through Association with Certain Chiral Amino Acids

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Pfeiffer effect optical activity has been detected in $Tb(DPA)_3^{3-}$ (DPA = pyridine-2,6-dicarboxylate) upon the addition of L-histidine (low pH), L-proline (high pH), L-azetidine-2-carboxylic acid (high pH), L-pipecolic acid (high pH), L-thioproline (low pH), and L-2-pyrrolidone-5-carboxylic acid (mid pH). No optical activity was found at any pH when L-alanine, L-valine, L-leucine, L-isoleucine, or L-phenylalanine were added. The presence of chirality in the title Tb(III) complex was detected with use of circularly polarized luminescence (CPL) spectroscopy. Detailed examinations of the pH dependence of the induced CPL spectra led to the conclusion that association of the $Tb(DPA)_3^{3-}$ complex and the chiral substrates (probably through a hydrogen-bonding mechanism) was necessary to observe the Pfeiffer effect, and variations of the amount of added substrate permitted the calculation of association constants for the adducts in certain cases. Limiting CPL intensities and repeating CPL line shapes for various substrate systems suggest that the reported spectra are characteristic of configurational optical activity in a D_3 Tb(III) complex.

Introduction

The induction of optical activity in a solution of a labile racemic mixture by the addition of a secondary chiral substance was first discovered by Pfeiffer, and the effect has subsequently been termed the "Pfeiffer Effect" in honor of its discovered.[2] The scope of transition-metal complex systems which exhibit the effect has been reviewed many times,[3-5] and considerable discussion has been made regarding the molecular origins of the effect.[6] Most of the experimental evidence supports a mechanism by which a shift in the equilibrium between complex enantiomers occurs as a result of association with a chiral substance, but some evidence has been presented which favors an equilibrium shift without association.[7]

Almost all of the work carried out so far has dealt with complexes whose holohedrized symmetry is octahedral, although some studies have been carried out on tetrahedral compounds.[8] As part of our continuing investigation of the f–f optical activity associated with lanthanide compounds, we have begun a systematic study of the Pfeiffer optical activity associated with 9-coordinate lanthanide complexes in solution. Our previous efforts have focused on the $Tb(DPA)_3^{3-}$ system, where DPA is the anion of pyridine-2,6-dicarboxylic acid. This complex is ideal to study for a variety of reasons: (1) the high luminescence quantum yield of the Tb(III) ion when sensitized through DPA excitation permits the recording of circularly polarized luminescence (CPL) spectra; (2) the large association constants of Tb(III) with DPA ligands ensures that the complex will be fully formed at all pH values and that relatively few other ligands will be able to complete for coordination positions at the Tb(III) ion;[9] (3) the complex is one of the few lanthanide complexes whose solution symmetry is known with a fair degree of certainty (NMR studies have shown that the symmetry is approximately D_3 in aqueous solution[10]).

The $Tb(DPA)_3^{3-}$ complex therefore falls into the category of potentially resolvable metal complexes which happen to be too labile for the successful resolution of enantiomers. We have succeeded in inducing optical activity in the $Tb(DPA)_3^{3-}$ complex through outer-sphere association with L-ascorbic acid[11] and resolved tris(ethylenediamine)chromium(III)[12] and have studied the optical activity by means of CPL spectroscopy. CPL is an ideal method for the study of chiral lanthanide complexes, since the low absorptivity of these ions in the visible region makes measurement of CD difficult at the low concentrations necessary to prevent polynuclear association of the complexes. These problems are circumvented when the emission technique is used, and one has the additional advantage that the luminescence bands can be easily assigned and are well separated from each other.

In the present report, we detail the induced optical activity that results in the $Tb(DPA)_3^{3-}$ complex when it interacts with several amino acids. Most of the common amino acids do not induce optical activity in the $Tb(DPA)_3^{3-}$ complex, but in certain pH regions it was found that several amino acids would induce large degrees of chirality. Detailed examination of the pH variation of the CPL spectra reveals interesting features of the association process and provides evidence for the mechanism responsible for this type of Pfeiffer effect. Weak optical activity was detected upon addition of two other chiral ligands; the structures of the ligands which led to detectable optical activity may be found in Figure 1.

Experimental Section

$Na_3Tb(DPA)_3 \cdot 15H_2O$ was prepared by mixing Tb(III) and pyridine-2,6-dicarboxylic acid in a 1:3 ratio, setting the solution pH at 9.0, and then letting the solution slowly evaporate. Tb(III) was obtained by dissolving the 99.9% pure oxide (Kerr-McGee) in the minimum amount of $HClO_4$ and subsequently neutralizing to pH 3 with NaOH, while the DPA ligand was used as received from Aldrich. The $Na_3Tb(DPA)_3 \cdot 15H_2O$ crystals formed in large triclinic plates, and the crystal structure of the isomorphous Nd(III) compound has been reported previously.[13] An alternate series of studies was performed by using the initial 1:3 mixture of Tb(III) and DPA in the CPL work, and identical results were found in each case (within the experimental error).

Stock solutions prepared by either method were 14.5 mM for all studies. It was found that such a solution exhibited no detectable CPL, nor was any found when L-alanine, L-valine, L-leucine, L-isoleucine, or L-phenylalanine was added in large excess (these amino acids were all obtained from the Sigma Biochemical Co.). Weak optical activity was noted when L-2-pyrrolidone-5-carboxylc acid (Aldrich) and L-thioproline (Sigma) were added to a $Tb(DPA)_3^{3-}$ solution in excess amounts, and this induced optical activity was found

(1) Teacher-Scholar of the Camille and Henry Dreyfus Foundation.
(2) (a) Pfeiffer, P.; Quehl, K. *Ber. Dtsch. Chem. Ges.* **1931**, *61*, 2667; **1932**, *65*, 560. (b) Pfeiffer, P.; Nakatsuka, Y. *Ibid.* **1933**, *66*, 415.
(3) Kirschner, S.; Admad, N.; Magnell, K. *Coord. Chem. Rev.* **1968**, *3*, 201.
(4) Schipper, P. E. *Inorg. Chim. Acta* **1975**, *12*, 199.
(5) Kirschner, S.; Ahmad, N.; Munir, C.; Pollock, R. J. *Pure Appl. Chem.* **1979**, *51*, 913.
(6) Schipper, P. E. *J. Am. Chem. Soc.* **1978**, *100*, 1079.
(7) Gyarfas, E. C. *Rev. Pure Appl. Chem.* **1954**, *4*, 73.
(8) Pollock, R. J.; Kirschner, S.; Policec, S. *Inorg. Chem.* **1977**, *16*, 522.
(9) Grenthe, I. *J. Am. Chem. Soc.* **1961**, *83*, 360.
(10) Donato, H.; Martin, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 4129.
(11) Madaras, J. S.; Brittain, H. G. *Inorg. Chim. Acta* **1980**, *42*, 109.
(12) Madaras, J. S.; Brittain, H. G. *Inorg. Chem.* **1980**, *19*, 3841.
(13) Albertsson, J. *Acta Chem. Scand.* **1972**, *26*, 1023.

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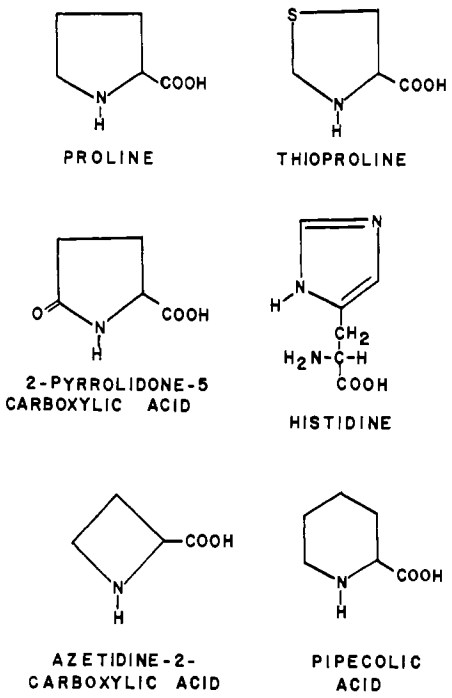


Figure 1. Structures of the chiral substrates that led to the observation of a Pfeiffer effect in $Tb(DPA)_3^{3-}$.

to be critically dependent on pH. Much stronger CPL was obtained when L-proline (Sigma), L-azetidine-2-carboxylic acid (Sigma), or L-pipecolic acid (Calbiochem) was added to the $Tb(DPA)_3^{3-}$ solution at high pH and also when L-histidine (Sigma) was added at low pH. The magnitude of these effects permitted a study of the induced optical activity as a function of amino acid concentration; detailed studies were carried out at ratios of amino acid/complex ranging from 0.75 to 6.0.

The optical activity of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition at 544 nm was monitored in all cases, and for very strong optical activity transitions from the $^5D_4$ to the $^7F_6$ (490 nm), $^7F_4$ (582 nm), and $^7F_3$ (622 nm) levels were also examined. All CPL and total luminescence (TL) data were obtained on an instrument constructed in this laboratory, whose operation has been recently described.[14] The Tb(III) complexes were excited at 295 nm (16-nm band-pass), and analyzed by a 0.5-m grating monochromator whose band-pass equaled 10 Å. Further increases in resolution of the analyzing monochromator did not yield any improvement of the spectral features, which is not unexpected since all measurements were made in fluid solution at room temperature.

The CPL and TL spectra were measured in proportional arbitrary units, with the TL being defined as $I = {}^1/_2(I_L + I_R)$ and the CPL defined as $\Delta I = I_L - I_R$); I_L and I_R stand for the emitted intensities of left and right circularly polarized light, respectively. The ratio of these quantities, $\Delta I/I$, is the luminescence dissymmetry factor (g_{lum}), and one may easily see that this quantity can run from zero to two and has no units. No other absolute quantal parameters were measured.

The pH of all solutions was obtained with use of an Orion Model 701A pH meter, and we employed a glass microcombination electrode which could be directly inserted into the fluorescence cuvette. The system was calibrated daily with phosphate buffers.

Results

Addition of L-histidine to an aqueous solution of $Tb(DPA)_3^{3-}$ at low pH results in the inducement of optical activity in the complex and to the observation of CPL spectra in each of the Tb(III) luminescence bands. These CPL spectra retain their basic line shape over the pH interval for which chirality can be detected, and representative examples of the CPL spectra associated with the $^5D_4 \rightarrow {}^7F_6$, $^7F_5$, $^7F_4$, $^7F_3$ Tb(III) transitions are found in Figures 2–5. The TL intensity of the 4–5

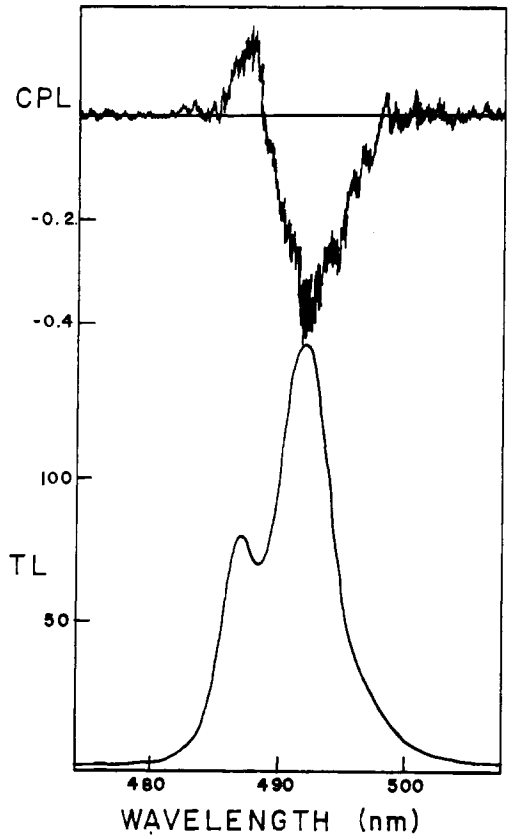


Figure 2. CPL and TL line shapes obtained in the $^5D_4 \rightarrow {}^7F_6$ Tb(III) transition when L-histine was used to induce optical activity in $Tb(DPA)_3^{3-}$. The spectra are shown in arbitrary units and were recorded after the addition of L-histidine at pH 2.0.

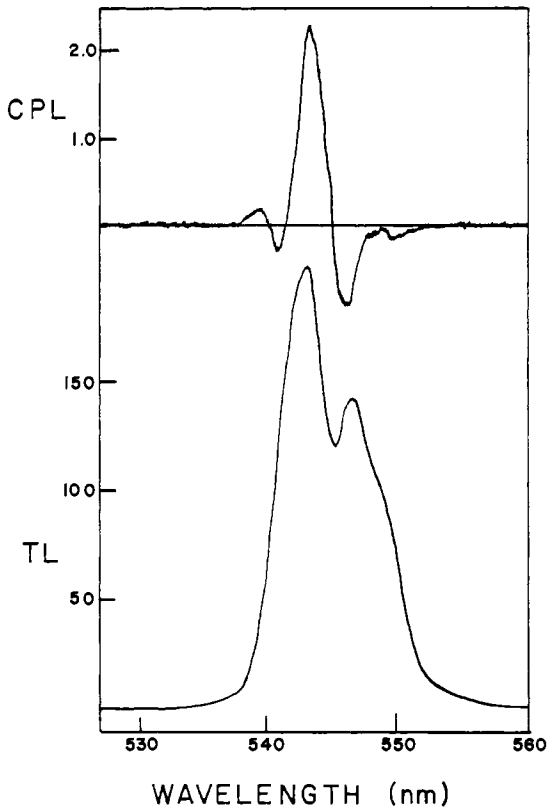


Figure 3. CPL and TL obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition, upon addition of L-histidine. The conditions and scales are as for Figure 2, but the scale factors are such that the figures may be directly compared.

(14) Brittain, H. G. *J. Am. Chem. Soc.* **1980**, *102*, 3693.

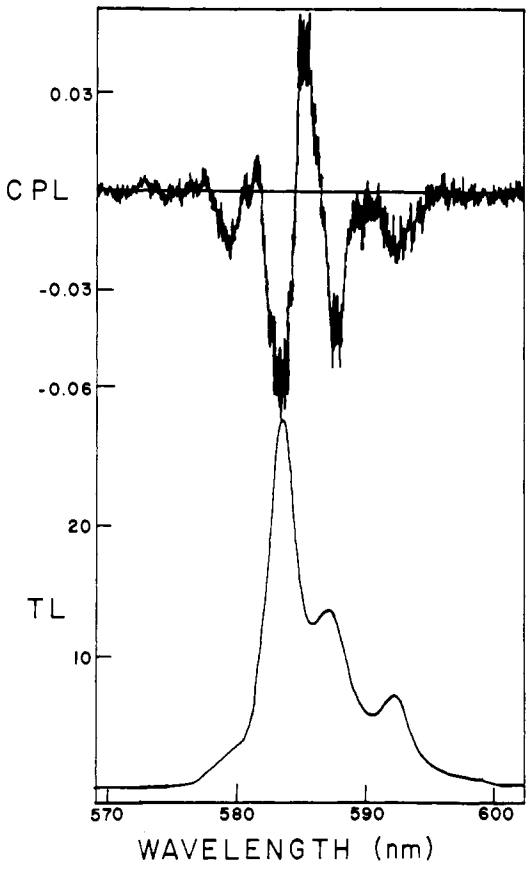


Figure 4. CPL and TL line shapes obtained for thee $^5D_4 \rightarrow {}^7F_4$ Tb(III) transition upon addition of L-histidine. Conditions are as for Figure 2.

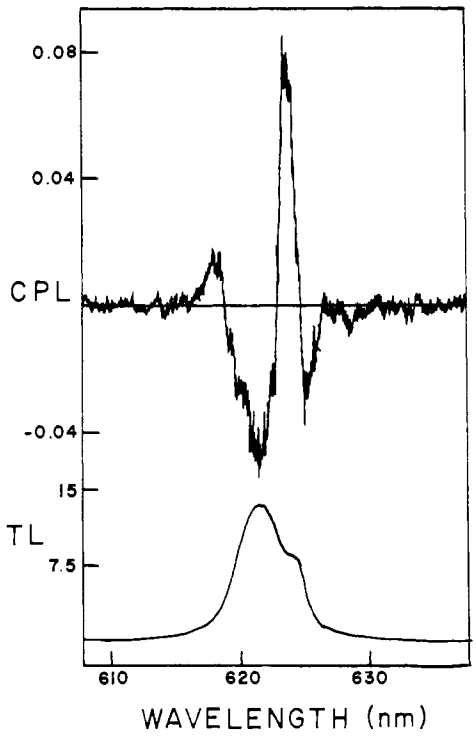


Figure 5. CPL and TL obtained within the $^5D_4 \rightarrow {}^7F_3$ Tb(III) transition upon addition of L-histidine. Conditions and scales are as for Figure 2.

transition is much greater than the corresponding intensities of the 4–4 and 4–3 transitions (we shall refer to the various emission bands by their J quantum numbers), and the CPL

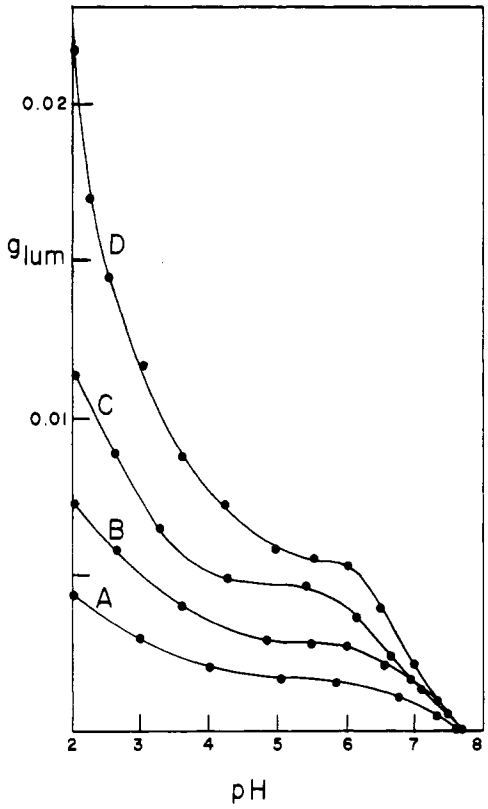


Figure 6. pH dependence of the luminescence dissymmetry factor of the 544-nm component of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition when L-histidine was used to induce optical activity in $Tb(DPA)_3^{3-}$. Data are shown for L-histidine/$Tb(DPA)_3^{3-}$ ratios of (A) 1.06, (B) 1.85, (C) 2.64, and (D) 5.28, with the initial Tb(III) concentration being 14.5 nM.

intensity of the 4–5 band is much higher than that of the 4–6 band; taken together, these results indicate that the 4–5 Tb(III) transition is the most useful for quantitative applications. However, the CPL of the other emission bands can be used as a qualitative estimate of the type of chirality experienced by the Tb(III) ion.

The CPL intensity was found to be a function of both pH and concentration of added L-histidine. The dependence of the luminescence dissymmetry factor on each of these parameters has been illustrated in Figures 6 and 7, and one may easily see that the strongest induced optical activity is found at pH 2. It did not prove possible to record data much below pH 2, since further increases in acidity tended to destroy the $Tb(DPA)_3^{3-}$ complex and precipitate the H_2DPA ligand. In Figure 7 it may be noticed that, at pH 2, the magnitude of the induced CPL is linear with the L-histidine concentration. Higher solution pH values display behavior that is much less linear, and one may also see that the limiting g_{lum} values are quite a bit smaller. These results strongly indicate that it is the most fully protonated form of L-histidine that is responsible for the inducement of optical activity.

Addition of L-proline to a solution of $Tb(DPA)_3^{3-}$ at low pH results in no detectable optical activity. However, if the pH is raised above neutral, CPL appears in all the Tb(III) bands, and this CPL is identical in line shape with the CPL curves of Figures 2–5. However, the degree of CPL obtained with L-proline is essentially 1 order of magnitude smaller than what was obtained with L-histidine at low pH. With L-proline, the maximum CPL was obtained at pH 11 and further increases in pH tended to hydrolyze the complex, resulting in the formation of various terbium(III) hydroxides. The CPL magntidues again depended critically on the solution pH and the quantity of L-proline present, as the results of Figures 8

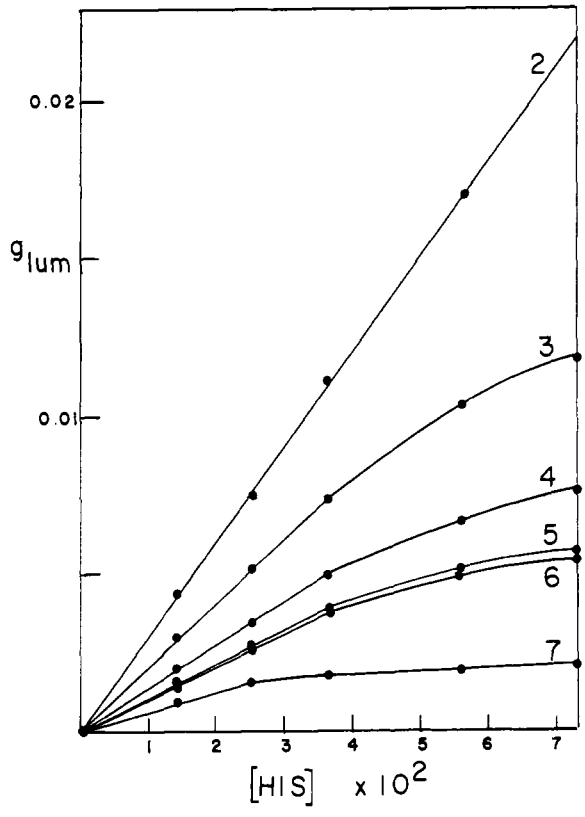


Figure 7. Dependence of the luminescence dissymmetry factor for the 544-nm component of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition with the molar concentration of L-histidine. The curves correspond to pH values of 2–7.

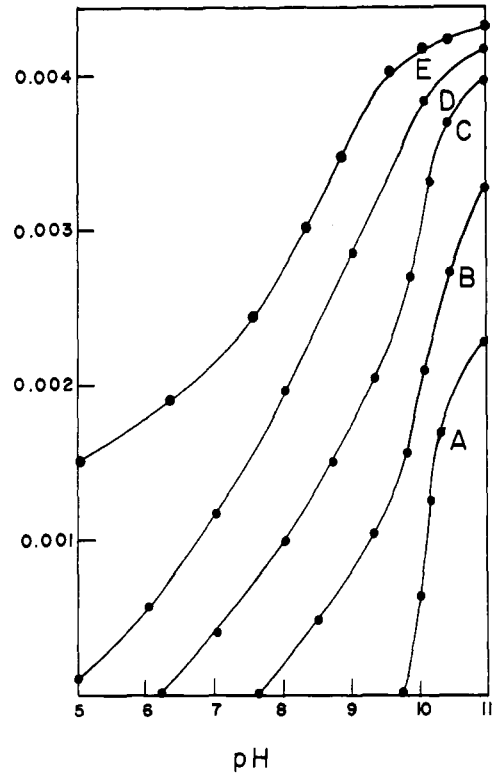


Figure 8. pH dependence of the luminescence dissymetry factor of the 544-nm component of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition when L-proline was used to induce optical activity in $Tb(DPA)_3^{3-}$. Data are shown for L-proline/$Tb(DPA)_3^{3-}$ ratios of (A) 0.73, (B) 1.51, (C) 3.02, (D) 4.75, and (E) 6.05.

and 9 clearly show. These studies clearly demonstrate that deprotonation of the ring nitrogen at position 1 is essential to the induction of chirality in $Tb(DPA)_3^{3-}$ by L-proline.

Analogous studies of induced optical activity were carried out with use of the closely related substrates L-azetidine-2-carboxylic acid and L-pipecolic acid. The data obtained during the course of these studies are essentially the same as were obtained during the L-proline studies, and the plots corresponding to Figure 8 and 9 are superimposable to within experimental error. It is quite clear that the steric nature of the chiral ligand plays no role in the inducement of optical activity in the $Tb(DPA)_3^{3-}$ complex.

We examined the L-proline situation further by examining the CPL induced by two proline analogues: L-2-pyrrolidone-5-carboxylic acid and L-thioproline. The pyrrolidonecarboxylic acid CPL was much weaker than the proline-induced CPL and exhibited a very different pH dependence. As may been seen in Figure 10, the CPL intensity is strongest between pH 8 and 8.5 and decreases rapidly outside of this region. The weak CPL can only be obtained with at least a 15-fold excess of chiral ligand relative to $Tb(DPA)_3^{3-}$, and as a result we were not able to document the pH dependence on the concentration of chiral substance. Thioproline also required large excesses of material (approximately 20-fold) to observe any CPL at all, and this CPL was only found at low pH. The CPL associated with the 4–5 transition was essentially the same as shown in Figure 3. g_{lum} values at the CPL extrema were calculated to be +0.001 55 and −0.000 73.

It was observed in essentially all the studies that the appearance of CPL in a $Tb(DPA)_3^{3-}$/substrate complex was accompanied by a small decrease in the TL intensity relative to uncomplexed $Tb(DPA)_3^{3-}$ at the same pH. For the L-histidine and L-proline complexes it was determined that this TL reduction reached a limiting value after the addition of approximately 1 equiv of substrate/mol of $Tb(DPA)_3^{3-}$ com-

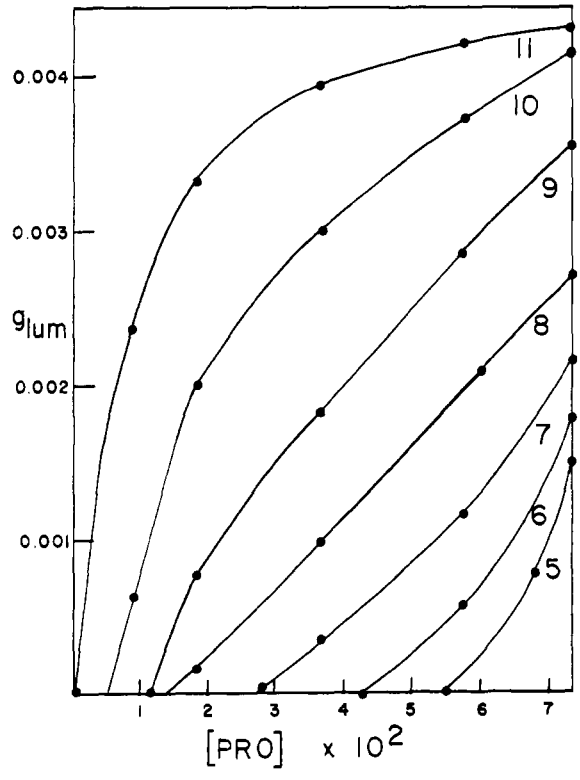


Figure 9. Dependence of the luminescence dissymetry factor for the 544-nm component of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) with the molar concentration of L-proline. The curves correspond to pH values of 5–11.

plex. This observation suggests that perhaps the CPL is due to the association of one molecule of chiral substrate to the $Tb(DPA)_3^{3-}$ complex and the dependence of g_{lum} on substrate

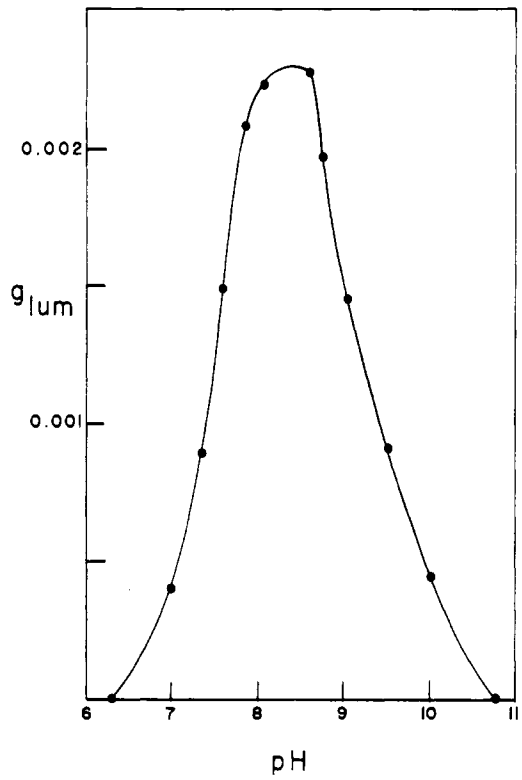


Figure 10. pH dependence of the luminescence dissymetry factor associated with the 544-nm component of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition when excess L-2-pyrrolidone-5-carboxylic acid was used to induce optical activity in $Tb(DPA)_3^{3-}$.

concentration is a reflection of the degree of complexation between complex and substrate.

If one then assumes a 1:1 stoichiometry for the $Tb(DPA)_3^{3-}$/substrate complex and that the induced CPL is a reflection of the degree of complexation, one should then be able to calculate a formation constant for the adduct. To do so, one would have to know what the g_{lum} value would be for a 100% resolved $Tb(DPA)_3^{3-}$ complex, but since the compound is so labile this value is not available. However, if one considers all the existing data on the $Tb(DPA)_3^{3-}$ Pfeiffer-active systems, one finds that a limiting value of g_{lum} does in fact appear to exist. For $Tb(DPA)_3^{3-}$/Λ-$Cr(en)_3^{3+}$ it was found that g_{lum} = +0.022,[12] for $Tb(DPA)_3^{3-}$/L-ascorbate g_{lum} reached a limiting value of +0.021,[11] and in our present work we have shown that for $Tb(DPA)_3^{3-}$/L-histidine the limiting value of g_{lum} is +0.022. If we therefore assume that a g_{lum} value of +0.022 corresponds to complete complexation of $Tb(DPA)_3^{3-}$ with substrate, then one can use the techniques we have outlined[15] to compute the association constants. The association constants obtained by these calculations were found to be a function of pH, and these have been collected in Table I for the L-proline and L-histidine adducts.

Discussion

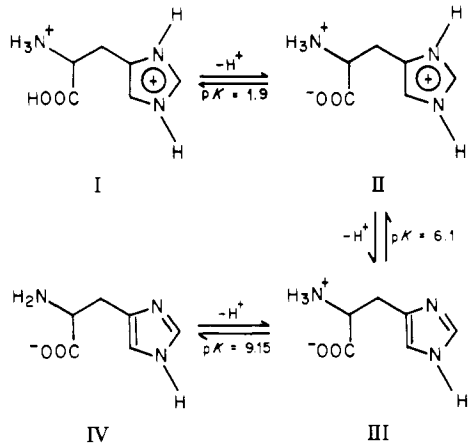
The results we have presented in the current work and those of our previous studies[11,12] are consistant with the associative mechanism of Pfeiffer optical activity. Were the equilibrium shift model to hold, one would predict that CPL would have been observed at all pH values, since no pH-dependent phenomena should exist without complexation. The very calculation of association constants (which are of reasonable precision) is in itself a support of the associative mechanism. The association between $Tb(DPA)_3^{3-}$ and the chiral substrates of our present study is quite selective in nature as evidenced by the inability of aliphatic amino acids to induce chirality in the Tb(III) complex.

Table I. Association Constants for the $Tb(DPA)_3^{3-}$/Substrate Adducts

pH	equilibrium const[a] L-histidine	L-proline[b]
2	22.4	
3	12.1	
4	7.7	
5	5.7	1.1
6	5.5	1.3
7	2.2	1.6
8		2.0
9		2.6
10		3.1
11		3.2

[a] The associated error with each constant is approximately 10%. [b] Essentially identical results were obtained for L-azetidine-2-carboxylic acid or L-pipecolic acid.

Scheme I



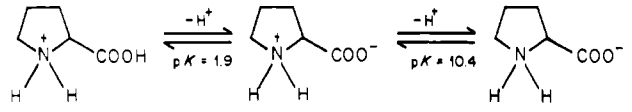
Insight into the nature of the $Tb(DPA)_3^{3-}$/substrate complex and determination of probable coordination positions on the chiral substrates can be obtained from considerations of the ionization equilibria of the substrates. The pH behavior of L-histidine has been documented by Sundberg and Martin,[16] with the ionization sequence in Scheme I being known. Since the CPL data are strongest at pH 2, we conclude that structures I and II bind most efficiently to the $Tb(DPA)_3^{3-}$ complex and thus provide the maximum perturbation of the enantiomer interconversion. This conclusion is not surprising when one considers the pure electrostatic attraction of the negative Tb(III) complex by the positive L-histidine ligand. We know immediately that the L-histidine cannot bind to the $Tb(DPA)_3^{3-}$ at the protonated ammonium group, since this sort of bonding would lead to Pfeiffer CPL in all protonated amino acids and we have determined that alanine, valine, leucine, isoleucine, and phenylalanine do not induce CPL at the Tb(III) complex.

It is clear, therefore, that the optical activity induced by structures I and II is due to binding of the positive imidazole ring to the Tb(III) complex. Binding of this type has been postulated in other Pfeiffer studies involving transition-metal ions and is thought to involve hydrogen bonding of the chiral substrate to the π-electron cloud of the aromatic rings of ligands attached to the metal ion (such as *o*-phenanthroline) in some cases.[5] Other situations are thought to involve a π–π charge-transfer complex being formed when the substrate and

(15) Brittain, H. G. *Inorg. Chem.* **1980**, *19*, 640.

(16) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471.

Scheme II

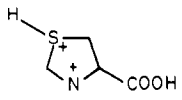


V VI VII

chelate ring both contain aromatic systems.[17] In the case of histidine/$Tb(DPA)_3^{3-}$ one or both of these effects is certainly taking place, with the electropositive imidazole ring taking part in hydrogen bonding to the pyridine π orbitals of the DPA ligands. As the pH is raised toward neutral, structure II converts to structure III and the imidazole ring loses its positive charge. At the same time, the CPL intensity decreases drastically as this process takes place, which supports binding of this ring to the Tb(III) complex at low pH. We notice that little change in CPL intensity takes place from pH 5 to 6, and it is precisely in this pH region that one would predict the presence of a II–III buffer system. The conversion of II to III should be complete by pH 8, and we notice that no CPL is seen beyond pH 7.75.

Induced CPL obtained with L-azetidine-2-carboxylic acid, L-pipecolic acid, or L-proline clearly represents a somewhat different type of mechanism, in that the degree of CPL is much smaller and the induced optical activity is found only at high pH. The ionization sequence in Scheme II is well established for proline.[18] Examination of the data in Figure 8 clearly demonstrate that maximum CPL is developed at pH 11 and that the magnitude of this induced optical activity appears to be leveling off above this value. It is therefore quite clear that structure VII must be responsible for the development of chirality in the $Tb(DPA)_3^{3-}$ complex when L-proline is added. Since VII contains a negative charge, one might anticipate that any bonding that takes place must be hydrophobic in nature (and we certainly have bonding, since it was possible to compute association constants). However, we note that, when VI is deprotonated to yield VII, the proline ring contains the same basic secondary amine functionality that led to hydrogen bonding to the DPA π orbitals. We believe that this hydrogen bonding is responsible for the formation of the $Tb(DPA)_3^{3-}$/VII adduct, and one can readily see the effect of decreasing positive charge on passing from VII to II. In addition, the proline ligand no longer contains an aromatic hererocycle, and the possibility of forming a π–π charge-transfer complex no longer exists. The magnitude of thee induced optical activity (as evidenced by the dissymmetry factors of Figures 6–9) and formation constants of the adducts (Table I) are greatly diminished when one compares the limiting situations for L-proline (pH 11) and L-histidine (pH 2). Analagous reaction schemes could be written for L-azetidine-2-carboxylic acid or L-pipecolic acid.

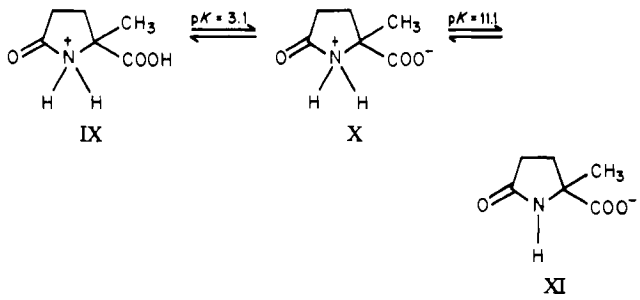
The very weak CPL induced by thioproline is an interesting case. At low pH, the amino acid probably has the structure



VIII

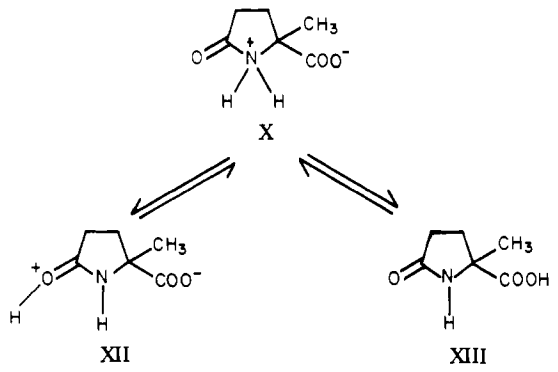
and we presume that the weak CPL of thioproline represents the hydrogen bonding of the SH group with the DPA ligands. The ionization constants of thioproline are not available, but it is possible that deprotonation of VIII to yield a structure analogous to VII takes place at pH values which are above those for which $Tb(DPA)_3^{3-}$ is stable.

Scheme III



IX X XI

Scheme IV



X XII XIII

The weak CPL exhibited in $Tb(DPA)_3^{3-}$/L-2-pyrrolidone-5-carboxylic acid solutions is different from either of the previous situations in that it is strongest at mid-pH values. While the ionization constants for this ligand are not available, data for the closely related system DL-5-methyl-2-pyrrolidone-5-carboxylic acid have been reported[19] (see Scheme III). Since the CPL is most fully established at pH 8–8.5, it would appear that structure X must be able to bond to the $Tb(DPA)_3^{3-}$ complex. It is not presently clear why this structure should interact favorably with the Tb(III) complex (although the degree of interaction is quite small), but one might imagine that the proton-transfer reactions in Scheme IV might be induced if structure X could bind to $Tb(DPA)_3^{3-}$. Either XII or XIII could interact weakly with the DPA π-orbital system, and formation of XI probably cannot interact in a similar fashion due to the negative charge on the substrate.

It is very interesting to note that all substrates used in the present study were of the S-configuration, and all induced CPL was of the same sign. This suggests that the sign of the optical activity induced upon adduct formation is a reliable indicator of the chirality of the inducing substrate. Since the substrates appear to bind on the second coordination sphere of the Tb(III) complex and since the DPA ligands contain no asymmetric atoms, we must conclude that all induced optical activity we have found is configurational in nature. The observation that we could reach a limiting CPL value in a number of different systems suggests that the CPL spectra of Figures 2–5 represent the spectra of a resolved $Tb(DPA)_3^{3-}$ complex. If this is so, then we have demonstrated how the Pfeiffer CPL may be used to study the chirality of Tb(III) complexes which are too labile to be resolved. It may be noted that the relative magnitudes of the CPL within the four Tb(III) emission bands we have examined are in accord with the recent theoretical predictions of Richardson.[20]

The Pfeiffer effects we have measured here appear to arise from definite association of the metal complex and the chiral substrates, and in certain cases the interaction was sufficiently

(17) Lee, C. C.; Hemmes, P. *Inorg. Chem.* **1980**, *19*, 485.
(18) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1977; Vol. I, p 69.
(19) Nyberg, M. N. T.; CeFola, M. *Arch. Biochem. Biophys.* **1965**, *111*, 321.
(20) Richardson, F. S. *Inorg. Chem.* **1980**, *19*, 2806.

strong to compute association constants. On an absolute scale, the degree of interaction is rather weak but is at least strong enough to permit the probing of f–f configurational optical activity. Our observation that hydrophobic amino acids to not lead to measurable Pfeiffer effects suggests that these do not bind to the $Tb(DPA)_3^{3-}$ complex. Other evidence we have acquired from NMR and luminescence quenching studies[21] has conclusively shown that essentially all amino acids will bind to the Tb(III) complex. We believe, therefore, that the CPL we have seen is due to (a) increased degrees of interaction between the amino acids possessing proper functionalities via these binding sites and (b) perturbation of the Δ–Λ equilibrium of the $Tb(DPA)_3^{3-}$ enantiomers by the relatively bulky side chains of the amino acids we have used.

The investigations of the present work and the results of our earlier studies have shown that the Pfeiffer effect is not limited to 6-coordinate transition-metal complexes but may be found in 9-coordinate lanthanide complexes as well.

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Registry No. $Tb(DPA)_3^{3-}$, 38682-37-0; L-histidine, 71-00-1; L-proline, 147-85-3; L-azetidine-2-carboxylic acid, 2133-34-8; L-pipecolic acid, 3105-95-1; L-thioproline, 2928-83-8; L-2-pyrrolidone-5-carboxylic acid, 98-79-3.

(21) Copeland, R.; Konteatis, Z.; Brittain, H. G., unpublished results.

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Single-Crystal Circular Dichroism of $[(+)_D\text{-}Cr(en)_3]^{3+}$

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Measurements of the axial single-crystal circular dichroism of $[(+)_D\text{-}Cr(en)_3]^{3+}$ doped in $2[Ir(en)_3Cl_3]\cdot KCl\cdot 6H_2O$ have been performed under high resolution at temperatures between 7 and 293 K. Transitions to the following excited states were observed: $^4T_2$, $^4T_1$, ^2E, $^2T_1$, $^2T_1$. Vibronically induced intensity carries little CD. For the $^4A_2 \rightarrow {}^4T_2$ transition the sign of the solution CD is determined by the sign of the axial component $^4A_2 \rightarrow {}^4E(T_2)$. The same is true for the electronic origins of transitions to ^2E and $^2T_1$. Spin–orbit coupling with $^4T_2$ induces both dipole and rotatory strength into the ^2E, $^2T_1$ transitions. The CD of the spin-forbidden transitions exhibits rich fine structure. The distribution of rotatory strength on the vibronic side bands is not the same as that of dipole strength.

1. Introduction

Circular dichroism (CD) spectroscopy has developed to an indispensable tool in coordination chemistry.[1] Quick structural information is obtainable without a full X-ray structure determination. Most of the spectra–structure relationships are empirical and have only a posteriori been rationalized by theory. Exceptions to the empirical rules do exist, and there is always a certain degree of uncertainty in assigning an absolute configuration to a new chiral complex on the basis of its solution CD spectrum.

There have been a large number of experimental and theoretical studies of the electronic origins of optical activity in coordination compounds.[2,3] Despite a wealth of information and undoubtable progress in the last two decades those mechanisms are not fully understood. On the one hand the theory is of a complexity which is frightening to the average coordination chemist, thus leaving it in the hands of a few specialists. On the other hand solution CD spectra hardly offer an adequate experimental basis for theoretical work. Single-crystal spectroscopy on carefully selected systems has been shown to be of high value.[4–9]

We have chosen $[Cr(en)_3]^{3+}$ (en = ethylenediamine), one of the most popular examples of complexes used to examine chiroptical properties,[10–16] as the object of a single-crystal study. Besides being chemically relatively stable and inert, $[Cr(en)_3]^{3+}$ offers the following advantages: uniaxial crystal lattices with high (trigonal) point symmetry;[17,18] absolute configuration of $[(+)_D\text{-}Cr(en)_3]^{3+}$ known to be Λ from anomalous X-ray scattering;[19] known optical absorption spectrum;[18] spin-allowed and spin-forbidden transitions observable;[18] luminescent.[18,20,21]

The solution CD spectrum of $[Cr(en)_3]^{3+}$ has been measured in the regions of both spin-allowed and spin-forbidden transitions.[13] The lowest energy transition $^4A_2 \leftrightarrow {}^2E$ has also been observed in luminescence (circularly polarized luminescence).[15] Single-crystal work has been confined to room temperature and to the first spin-allowed transition $^4A_2 \rightarrow {}^4T_2$. Mason and co-workers measured the axial CD of $[(+)_D\text{-}Cr(en)_3]^{3+}$ doped into $2[Rh(en)_3Cl_3]\cdot NaCl\cdot 6H_2O$,[22] while Jensen investigated the "active racemate" $[(+)_D\text{-}Cr(en)_3][(+)_D\text{-}Rh(en)_3]Cl_6\cdot 6H_2O$.[16] Theoretical calculations of rotatory strengths have been carried out for both spin-allowed[14,15] and spin-forbidden transitions.[13,15] The results are partly contradictory.

(1) For a recent review see, e.g.: Mason, S. F., Ed. "Optical Activity and Chiral Discrimination"; D. Reidel Publishing Co.: Dordrecht, Holland, 1979.
(2) Mason, S. F. Reference 1, Chapter VII, p 161.
(3) Richardson, F. S. *Chem. Rev.* **1979**, *79*, 17.
(4) McCaffery, A. S.; Mason, S. F. *Mol. Phys.* **1963**, *6*, 359.
(5) Mason, S. F.; Peart, B. J. *J. Chem. Soc., Dalton Trans.* **1977**, 937.
(6) Kuroda, R.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 433.
(7) Jensen, H. P.; Galsbøl, F. *Inorg. Chem.* **1977**, *16*, 1294.
(8) (a) Palmer, R. A.; Yang, M. C.-L. *Chem. Phys. Lett.* **1975**, *31*, 492. (b) Yang, M. C.-L.; Palmer, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 5390. (c) Palmer, R. A.; Yang, M. C.-L.; Hempel, J. C. *Inorg. Chem.* **1978**, *17*, 1200.
(9) Dubicki, L.; Ferguson, J.; Geue, R. J.; Sargeson, A. M. *Chem. Phys. Lett.* **1980**, *74*, 393.
(10) Mathieu, J. P. *J. Chim. Phys.* **1936**, *33*, 78.
(11) Kling, O.; Woldbye, F. *Acta Chem. Scand.* **1961**, *15*, 704.
(12) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1100.
(13) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Inorg. Chem.* **1973**, *12*, 142.
(14) Evans, R. S.; Schreiner, A. F.; Hauser, P. J. *Inorg. Chem.* **1974**, *13*, 2185.
(15) Hilmes, G. L.; Brittain, H. G.; Richardson, F. S. *Inorg. Chem.* **1977**, *16*, 528.
(16) Jensen, H. P. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 355.
(17) Whuler, A.; Brouty, C.; Spinat, P.; Herpin, P. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2069.
(18) McCarthy, P. J.; Vala, M. T. *Mol. Phys.* **1973**, *25*, 17.
(19) Whuler, A.; Brouty, C.; Spinat, P.; Herpin, P. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2877.
(20) Flint, C. D. *J. Chem. Phys.* **1970**, *52*, 168.
(21) Flint, C. D.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 579.
(22) Mason, S. F. In "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism"; Ciardelli, F.; Salvadori, P., Eds.; Heyden and Son Ltd.: New York, 1973; p 200.

0020-1669/81/1320-3013$01.25/0