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Optical Activity Induced in the Terbium(III) and Europium(III) Tris Complexes of Pyridine-2,6-dicarboxylate through Association with Monoamino- and Diaminocarboxylic Acids

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Optical activity has been induced in $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ (DPA = pyridine-2,6-dicarboxylate) through outer-sphere coordination with a series of chiral monoamino- and diaminocarboxylic acids (a Pfeiffer effect). The induced optical activity was studied by means of circularly polarized luminescence (CPL) spectroscopy. It was found that the CPL spectra were strongest with the simple amino acids from pH 4 to pH 7 and that the chirality of the lanthanide complexes disappeared with deprotonation of the ammonium group. However, with certain of the diaminocarboxylic acids, the CPL sign patterns inverted upon deprotonation of the ammonium group and thus indicate a new mode of bonding that predominates at high pH (most likely at the terminal amino group opposite to the aminocarboxylic acid functionality). From a comparison to solid-phase work, we assign the absolute configuration of a D_3 $Tb(DPA)_3^{3-}$ or $Eu(DPA)_3^{3-}$ complex as being the Δ isomer if the CPL of the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(III) or the $^5D_0 \rightarrow {}^7F_1$ transition of Eu(III) is negative in sign.

Introduction

While the optical activity associated with the d–d bands of chiral transition-metal complexes has been extensively studied and is reasonably well understood,[2] analogous studies regarding f–f optical activity have received much less attention. One of the basic problems involving studies of chiral lanthanide complexes is their extremely fast racemization rates, and this feature precludes the resolution of these complexes by classical methods. While circular dichroism (CD) and circularly polarized luminescence (CPL) experiments have been carried out on a variety of systems,[3] there presently exists no experimental method by which absolute configurations about the metal centers can be inferred from the chiroptical data (as is commonly done with transition-metal complexes).

One of the ways by which the chiroptical spectra of a racemic mixture consisting of labile enantiomers may be obtained is through perturbation of the enantiomer interconversion. This can be done if the racemic complex is capable of complexing with added chiral material, and this effect has been termed the Pfeiffer effect.[4,5] The wide range of studies that have been carried out on transition-metal complexes have shown that the chiroptical spectra obtained in this manner are identical with those obtained after classical resolution of the complex in question.

We have recently begun to investigate the optical activity induced in lanthanide complexes through outer-sphere association with chiral substrates. Our investigations have centered on the lanthanide tris complexes of dipicolinic acid (DPA, or pyridine-2,6-dicarboxylic acid) since the association constants for formation of the tris complex are very large,[6] and since the complex is known to possess approximately D_3 symmetry in aqueous solution.[7] In addition, we have chosen to investigate the chiroptical properties of the $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ complexes in particular, since the emission intensity associated with these ions is extremely intense if excitation energy is channeled through the DPA ligands. One can then measure optical activity through CPL spectroscopy with very favorable signal-to-noise characteristics (measurements of CD spectra require abnormally high concentrations of complex to detect usuable signals due to the low absorptivity of lanthanide complexes in the f–f region).

A previous paper detailed the optical activity induced in $Tb(DPA)_3^{3-}$ by L-histidine and L-proline, and by several chiral amino acids that serve as analogues for proline.[8] The pH dependence of the optical activity varied considerably with the nature of the amino acid, and association constants calculated from the CPL spectra aided in a determination of the mode of bonding existing between the $Tb(DPA)_3^{3-}$ complex and the amino acid. Previously, we had noted that optical activity could be induced in $Tb(DPA)_3^{3-}$ when L-ascorbic acid[9] or resolved tris(ethylenediamine)chromium(III)[10] was allowed to complex. All these studies established that chirality could be induced in the Tb(III) complex either by a pure electrostatic attraction of oppositely charged complexes or by hydrogen bonding between the chiral substrates and the aromatic rings of the DPA ligands.

In the present work, we present results detailing the optical activity induced in $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ upon outer-sphere complexation with a series of aminocarboxylic and diaminocarboxylic acids. Previously[8] we had noted that no CPL spectra could be obtained when simple amino acids (such as alanine) were complexed to $Tb(DPA)_3^{3-}$ even though NMR studies showed that complexation could take place. We have since learned that the association constants are very small, and we have used much higher ratios of chiral substrate to lanthanide complex in order to obtain the results that are to follow. One basic question regarding any Pfeiffer optical activity is whether the sign of the induced chirality is a reliable measure of abolute configuration, and the studies carried out in the present work will show that only limited correlations are possible.

Experimental Section

$Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ complexes were prepared by mixing stoichiometric amounts of metal ion and DPA ligand solutions. The lanthanide solutions were prepared by dissolving the 99.9% pure metal oxide (Kerr-McGee) in a minimal amount of 70% $HClO_4$ and neutralizing to pH 3 with NaOH. The DPA ligand was used as received from Aldrich. Isolation of the $Tb(DPA)_3^{3-}$ or $Eu(DPA)_3^{3-}$ complexes

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was not performed, since our earlier studies using $Na_3Tb(DPA)_3 \cdot 15H_2O$ as the starting material yielded identical results when compared to studies using the starting material prepared in the above fashion.[8]

The 1:3 $Ln(DPA)_3^{3-}$ solutions thusly prepared were 13 mM in lanthanide ion, and such a solution was found to exhibit no CPL under any conditions. Addition of large excesses of aminocarboxylic or diaminocarboxylic acids to a $Ln(DPA)_3^{3-}$ solution led to measurable CPL if sufficient amounts of chiral substrate were present. The chiral acids used in the investigations were obtained from Sigma, Aldrich, or Eastman and were all used as received. These ligands were L-alanine (ALA), D-aminobutyric acid (ABA), L-norvaline (NVAL), L-valine (VAL), L-norleucine (NLEU), L-leucine (LEU), L-isoleucine (ILEU), L-2,4-diaminobutyric acid (DAB), L-asparagine (ASG), L-ornithine (ORN), L-glutamine (GLM), L-lysine (LYS), L-arginine (ARG), L-citrulline (CIT), and L-canavanine (CAN).

For $Tb(DPA)_3^{3-}$, the $^5D_4 \rightarrow {}^7F_5$ Tb(III) luminescence transition at 544 nm was monitored for most work, although spot-checks of the other Tb(III) emission bands were made when necessary. The optical activity of the $Eu(DPA)_3^{3-}$ complex was studied by examination of the $^5D_0 \rightarrow {}^7F_1$ (595-nm) and $^5D_0 \rightarrow {}^7F_2$ (615-nm) transitions. In no situation could a band be found corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition at 580 nm, which attests to the presence of axial symmetry in the $Eu(DPA)_3^{3-}$ complex and in its outer-sphere complexes.

All CPL and total luminescence (TL) spectra were obtained on an instrument constructed in our laboratory, whose operation has been described.[11] The lanthanide complexes were excited at 295 nm (16-nm bandpass), a wavelength that corresponds to an absorption band of the DPA ligand. Our previous work on DPA complexes[9-12] has shown that large sensitization of Tb(III) emission can be effected in this fashion, and the present work will show that Eu(III) emission can also be sensitized (although at a significantly lower degree of efficiency). The emission was analyzed by a 0.5-m grating monochromator at a band-pass of 1 nm and detected by a photomultiplier tube having S-20 enhanced-red response. All measurements were obtained in fluid aqueous solution at room temperature.

The CPL and TL spectra were obtained in proportional arbitrary units, with the TL being defined as $I = {}^1/_2(I_L + I_R)$ and the CPL as $\Delta I = (I_L - I_R)$, I_L and I_R referring to the emitted intensities of left and right circularly polarized light, respectively. The ratio $\Delta I/I$ is termed the luminescence dissymmetry factor,[3] and one may easily see that this dimensionless quantity can range from zero to two (as well as be either positive or negative). No other absolute quantal parameters were measured.

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

Proton magnetic resonance experiments were carried out with a Varian T-60A NMR spectrometer, with all data being obtained at ambient probe temperature and in D_2O solvent. Solid $Na_3Eu(DPA)_3 \cdot 15D_2O$ was added to the NMR tubes in varying weighed amounts and then dissolved in a stock solution of the various amino acids. In this fashion, the quantity of amino acid could be kept constant while continually increasing the amount of $Eu(DPA)_3^{3-}$. Since the Eu(III) complex can function as an aqueous shift reagent, it was found that the proton resonances of the amino acids shifted to higher fields. The data could not be internally referenced against any common standard, since the $Eu(DPA)_3^{3-}$ was also observed to bind the sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) reference and shift its resonance to higher fields. As a result, we were forced to standardize the instrument with DSS–amino acid and to compare $Eu(DPA)_3^{3-}$/amino acid solutions assuming no instrumental drift. However, it was found that the lanthanide-induced shifts were linear with the concentration of added $Eu(DPA)_3^{3-}$ over the concentration ranges studied, so any drift of the zero point was probably minimal.

Results

Addition of any one of the monoaminocarboxylic acids whose structures are shown in Figure 1 to a solution of either $Tb(DPA)_3^{3-}$ or $Eu(DPA)_3^{3-}$ results in the appearance of CPL in the lanthanide emission bands. For the Tb(III) complex, the strongest degree of optical activity was noted in the $^5D_4 \rightarrow {}^7F_5$ emission band at 545 nm, and the CPL associated with this transition remained invariant in line shape as the different amino acids were examined. An example of the TL and CPL associated with the formation of the outer-sphere complex is shown in Figure 2, where representative spectra obtained for $Tb(DPA)_3^{3-}$/L-norvaline are shown. The spectra for this transition and all other Tb(III) emission bands greatly resemble the line shapes previously reported.[8]

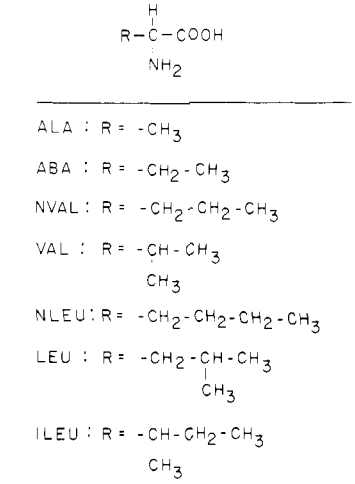

Figure 1. Structures of the monoaminocarboxylic acid substrates.

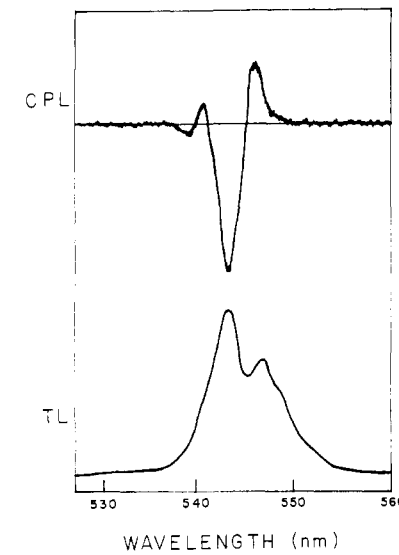

Figure 2. Total luminescence (TL, lower trace) and circularly polarized luminescence (CPL, upper trace) spectra of the $Tb(DPA)_3^{3-}$/L-norvaline complex at pH 5.0. The spectra shown are recorded in purely arbitrary units for the $^5D_4 \rightarrow {}^7F_5$ transition.

Pfeiffer-effect CPL has never been reported for $Eu(DPA)_3^{3-}$ complexes, but the representative spectra shown in Figures 3 and 4 (corresponding to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emission bands, respectively) show that this complex is also capable of forming outer-sphere complexes. As in the case of the Tb(III) complex, the sign of the induced CPL reflects the absolute configuration of the added amino acid. As long as the amino acid is of the *S* configuration (L isomer), the CPL of the $^5D_4 \rightarrow {}^7F_5$ transition (Tb(III) complex) and the $^5D_0 \rightarrow {}^7F_1$ transition (Eu(III) complex) are both negative in sign. At the same time, the CPL of the $^5D_0 \rightarrow {}^7F_2$ transition (Eu(III) complex) is always positive in sign. No CPL was ever associated with the very weak $^5D_0 \rightarrow {}^7F_0$ transition.

No variation in CPL line shape was noted when the pH of the adduct solutions was varied from 2.0 to 8.5, and the CPL intensity exhibited limited variability. The CPL intensity generally rose as the pH was raised from 2.0 to 3.0 (quanti-

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Table I. Association Constants[a] for the $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ Outer-Sphere Complexes with Monoaminocarboxylic Acids

substrate	$K_1(Tb(DPA)_3^{3-})$	$K_1(Eu(DPA)_3^{3-})$	substrate	$K_1(Tb(DPA)_3^{3-})$	$K_1(Eu(DPA)_3^{3-})$
alanine	0.506	0.476	valine	0.326	0.306
2-aminobutyric acid	1.734	1.630	norleucine	5.588	5.253
norvaline	4.122	3.875	leucine	1.495	1.405
			isoleucine	0.638	0.600

[a] The error associated with each constant ranges from 5 to 7%.

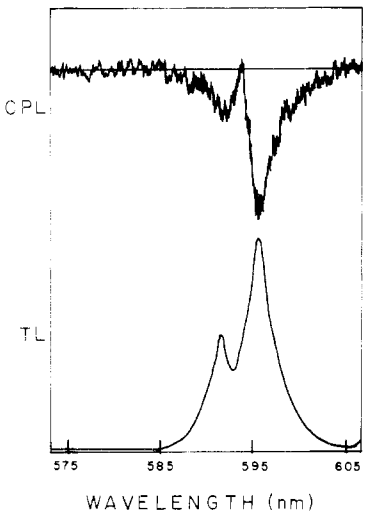

Figure 3. TL (lower) and CPL (upper) spectra obtained for the $Eu(DPA)_3^{3-}$/L-norvaline complex at pH 5.0 within the $^5D_0 \rightarrow {}^7F_1$ transition.

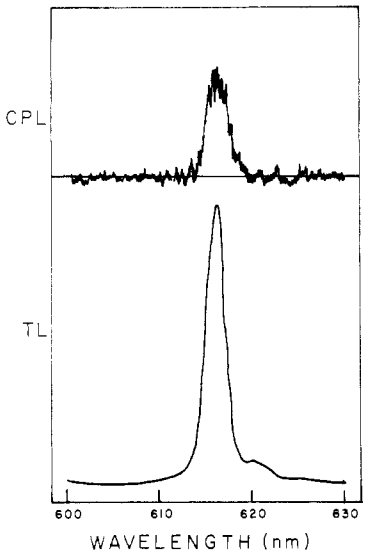

Figure 4. TL (lower) and CPL (upper) spectra obtained for the $Eu(DPA)_3^{3-}$/L-norvaline complex at pH 5.0 within the $^5D_0 \rightarrow {}^7F_2$ transition.

tative examination of TL intensities verified that three DPA ligands were still attached to the lanthanide ion over this pH range) and remained relatively constant until pH 7.0. Within the 7.0–8.5 pH region, the CPL intensity dropped rapidly, and no CPL was observed above pH 8.5 for any of the monoaminocarboxylate substrates.

The CPL intensity was found to depend critically on the concentration of added amino acid substrate, as may be seen in Figure 5. Application of the method of continuous variations revealed that only 1:1 complexes were formed between the $Ln(DPA)_3^{3-}$ complexes and the amino acid substrates. It is therefore possible to compute association constants for the reaction

$$Ln(DPA)_3^{3-} + AA \rightleftharpoons Ln(DPA)_3^{3-}/AA \qquad (1)$$

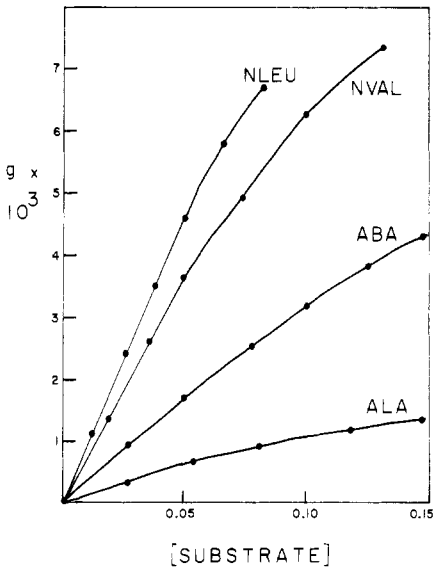

Figure 5. Dependence of optical activity (as measured by the luminescence dissymmetry factor) of $Tb(DPA)_3^{3-}$ with the concentration of added amino acid. Data are shown for L-alanine (ALA), D-2-aminobutyric acid (ABA), L-norvaline (NVAL), and L-norleucine (NLEU).

since the luminescence dissymmetry factor is clearly proportional to the concentration of adduct species formed (this will be true as long as the TL intensity is not affected by the amino acid substrate, and this is found to be the case). In that case, it is easy to show that the mole fraction of uncomplexed $Ln(DPA)_3^{3-}$ is given by

$$X_{Ln(i)} = \frac{g_f - g_i}{g_f} \qquad (2)$$

Knowledge of this mole fraction and all starting concentrations permits the calculation of the formation constant for the $Ln(DPA)_3^{3-}$/AA complex. In eq 2, g_f represents the dissymmetry factor of the fully formed complex. We have previously shown that for $Tb(DPA)_3^{3-}$, this quantity equals 0.022 within the $^5D_4 \rightarrow {}^7F_5$ transition.[8] Using similar procedures, we have found in the course of our present work that for $Eu(DPA)_3^{3-}$ the limiting dissymmetry factor within the $^5D_0 \rightarrow {}^7F_1$ band is 0.017 and is 0.0052 for the $^5D_0 \rightarrow {}^7F_2$ emission band.

Values for the formation constants calculated in this manner are found in Table I. One may note that the Eu(III) complex adducts are approximately 6% less stable than the corresponding Tb(III) adducts. It is significant to note that the degree of stability increases with chain length, as long as the hydrocarbon chain is unbranched. Branching of the chain is found to exert the strongest influence when the side chain is attached immediately next to the aminocarboxylic acid functionality.

Further proof that association does take place between the $Ln(DPA)_3^{3-}$ complexes and the amino acid substrates (thus demonstrating that the induced CPL is not due to the creation of a dissymmetric environment) was provided by using the $Eu(DPA)_3^{3-}$ complex to induce upfield shifts in the amino acid proton resonances. While most lantanide-induced shifts caused by Eu(III) are to lower applied fields, shifts to higher fields

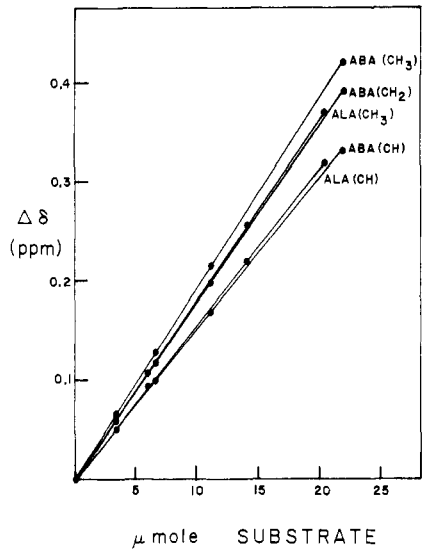

Figure 6. Dependence of lanthanide-induced shifts caused by the complexation of $Eu(DPA)_3^{3-}$ to L-alanine and D-2-aminobutyric acid. The shifts shown are in ppm relative to the resonance positions of the free amino acids and are plotted against the number of micromoles of $Eu(DPA)_3^{3-}$ actually added to the NMR tube.

Table II. Association Constants[a] for the $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ Outer-Sphere Complexes with Diaminocarboxylic Acids

substrate	$K_1(Tb(EPA)_3^{3-})$ low pH	$K_1(Tb(EPA)_3^{3-})$ high pH	$K_1(Eu(DPA)_3^{3-})$ low pH	$K_1(Eu(DPA)_3^{3-})$ high pH
2,4-diaminobutyric acid	0.189		0.178	
asparagine	0.335		0.315	
ornithine	1.164		1.094	
glutamine	1.809		1.701	
lysine	2.079	4.998	1.954	4.698
arginine	4.167	7.345	3.857	6.904
citrulline	4.096	7.162	3.850	6.732
canavanine	4.133	7.130	3.885	6.702

[a] Each constant carries an approximate 5-7% error.

are not unknown.[13] As may be seen Figure 6, an approximate linear shift in proton resonance with $Eu(DPA)_3^{3-}$ concentration is noted. The magnitude of this shift varies with the nature of the amino acid (reflecting the degree of complexation) and with the particular proton resonance being studied. In general, protons furthest from the ammonium group are shifted to the greatest degree, suggesting that these protons are closest to the Eu(III) ion. This situation could exist if the hydrocarbon tail of the amino acid substrate were to fit between the DPA ligand rings.

Several diaminocarboxylic acid substrates exhibited bonding characteristics similar to those just described for the monoaminocarboxylic acids. L-2,4-Diaminobutyric acid, L-asparagine, L-ornithine, and L-glutamine all lead to induced CPL in the $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ complexes, which becomes fully developed by pH 4.0 and which disappears when the solution pH is raised to 8.5. The association constants for these substrates and the $Ln(DPA)_3^{3-}$ complexes may be found in Table II.

As may be seen from the diaminocarboxylic acid structures shown in Figure 7, L-2,4-diaminobutyric acid and L-asparagine may be thought of as substituted analogues of the D-2-aminobutyric acid substrate. Additionally, L-ornithine and L-glutamine are seen to be substituted L-norvaline analogues. One would the expect that the formation constants of the

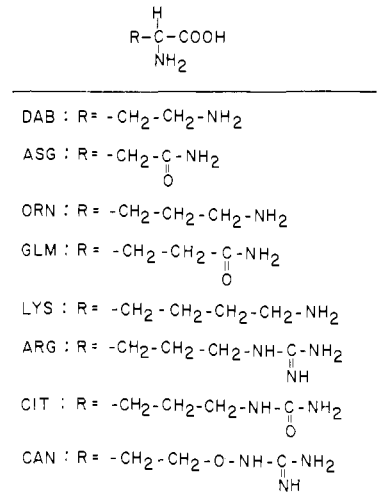

Figure 7. Structures of the diaminocarboxylic acid substrates.

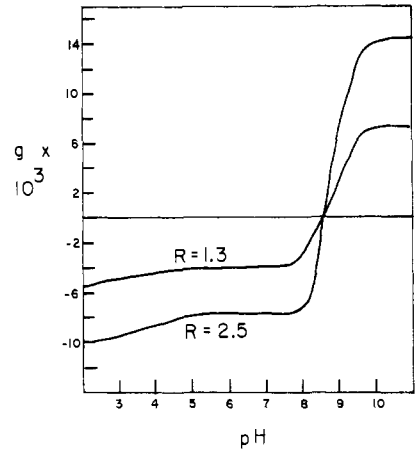

Figure 8. pH dependence of the luminescence dissymmetry factor associated with various $Tb(DPA)_3^{3-}$/L-citrulline solutions. The ratio of metal/substrate is shown for each curve.

corresponding systems would be similar in value, but a comparison of the data in Tables I and II clearly shows that this is not the case. Subsitution of a terminal hydrogen by the second amino group decreases the association constant by nearly 1 order of magnitude. Further substitution of the hydrocarbon portion of the chiral amino acid substrates (yielding an amide functionality) raises the degree of association, but the formation constants of the diaminocarboxylic acid substrates still remain significantly lower than those of the monoaminocarboxylic acids.

Further increase in the chain length of the diaminocarboxylic acid substrates results in the appearance of new behavior. L-Lysine, L-arginine, L-citrulline, and L-canavanine (whose structures are also shown in Figure 7) all exhibit the characteristics already described as the solution pH is raised from 2.0 to 8.5. As the pH is raised above 8.5, however, the CPL does not merely vanish. Instead the mirror image of the low-pH CPL associated with $Tb(DPA)_3^{3-}$/L-arginine appears, as is illustrated in Figure 8. The fact that the line shapes are identical (except for the sign change) is evidence that the other diastereomer of the $Ln(DPA)_3^{3-}$ complexes has been produced as a result of some bonding change between the lanthanide complex and the amino acid. Formation constants calculated from the CPL results are found in Table II.

It may be seen that the high-pH complex is essentially twice as stable as the low-pH complexes. In addition, comparison of the formation constants associated with L-lysine and its unsubstituted analogue, L-norleucine, reveals that the substitution has again decreased the degree of interaction. No

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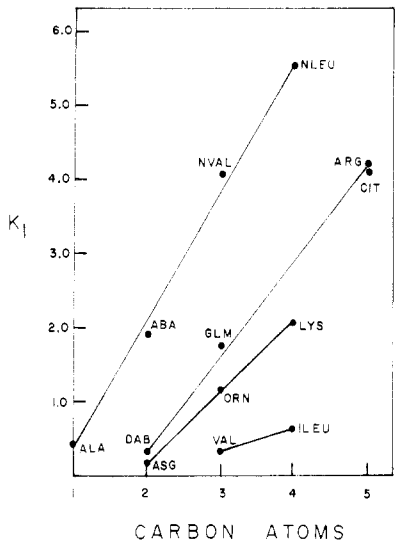

Figure 9. Variation of adduct formation constants with the number of carbon atoms in the amino acid side chains.

analogue could be obtained for the arginine-type ligands, but the association constants of these substrates are still significantly smaller than those of L-lysine. The slight structural modifications associated with the different substitution patterns of arginine, citrulline, and canavanine (see Figure 7) clearly do not have a significant effect on the interaction of these substrates with the $Ln(DPA)_3^{3-}$ complexes.

Discussion

The results of the present study agree with those of our earlier works[8-10] in establishing the associative mechanism as the source of the induced optical activity. In the previous study involving amino acids as the environmental substances inducing the chirality, we concluded that a positive nitrogen in a ring system was required to perturb the enantiomeric conversion

$$\Lambda\text{-}Ln(DPA)_3^{3-} \rightleftarrows \Delta\text{-}Ln(DPA)_3^{3-}$$

As has been postulated in Pfeiffer-active transition-metal complexes,[5] some sort of hydrogen bonding between the chiral substrate and the lanthanide complex appears to be necessary.

A very fascinating result is the dependence of the association constants with the length of hydrocarbon backbone of the amino acids. Examination of the ligand structures in Figures 1 and 7 reveals that several series of structurally related amino acid ligands are included among the substrates used in the present study. In Figure 9 we have plotted the association constants for the $Tb(DPA)_3^{3-}$ adducts against the number of carbon atoms in the aliphatic side chains. In the three series consisting of a least three members excellent linearity is observed. It is therefore a general conclusion that the stability of a particular adduct complex increases with the length of the hydrocarbon chain. Such as conclusion is in accord with the NMR results, which indicated that the aliphatic portion of the amino acid substrate protudes between the DPA rings. This conclusion effectively argues that hydrophobic forces between the amino acid side chains and the lanthanide complexes must be very important. The data also suggest that straight chains are the most effective in promoting this binding, as the adducts with branched chains are much less stable. Finally, we explain the lower stability of the diaminocarboxylic acid adducts (relative to the analogous monoaminocarboxylic acid adduct) as a reflection of placing a polar head group into the hydrophobic cavity, which clearly is not a favorable process.

Several pieces of evidence indicate that below pH 8, all the monoamino- and diaminocarboxylic acids coordinate to the $Ln(DPA)_3^{3-}$ complexes in the same fashion. The NMR studies indicate that protons closest to the aminocarboxylic acid functionality are shifted to the greatest degree when these amino acids are bound to the $Eu(DPA)_3^{3-}$ complex. In addition, if one examines the association constants of the norleucine–leucine–isoleucine sequence, one finds that as the branching methyl group moves closer to the aminocarboxylic acid group, the association constant of the adduct decreases dramatically.

Below pH 8.5, the ammonium groups of all amino acid substrates are protonated, and centers of positive charge exist at this site. Since the $Ln(DPA)_3^{3-}$ complex is of opposite charge, it is not difficult to see how electrostatics could assist the adduct formation. For the monoaminocarboxylic acids, the CPL (and presumably the outer-sphere adduct) disappears at pH 8.5 and it is certain that ionization of the ammonium proton is associated with this spectral change. It is clear that the amino acid anion cannot bind to the $Ln(DPA)_3^{3-}$ complexes.

With certain of the diaminocarboxylic acids, however, a new mode of bonding is indicated by the CPL sign inversion at high pH. These ligands present two positively charged ammonium groups, but at low pH it would appear that only the amino group α to the carboxyl group participates in the bonding. This observation would suggest that the carboxylic acid functional group plays some role in stabilizing bonding at this site. Examination of the ligand ionization constants (where these are known[14]) reveals an interesting feature: for 2,4-diaminobutyric acid, asparagine, ornithine, and glutamine the ionization constants for the two ammonium groups are sufficiently close in magnitude as to require that they titrate together. However, for the longer chain diaminocarboxylic acids the two ionization constants are sufficiently different that they titrate separately. It is also known that the amino group α to the carboxyl group is deprotonated at the lower pH.

We therefore believe that the sign change observed in the CPL spectra reflects the following situation: as the α-amino group of the substrate is deprotonated, the molecule switches its mode of attachment to the lanthanide complex and binds at the still protonated ammonium group on the other end of the ligand. Such a bonding change does not take place with the shorter chain diaminocarboxylic acids since both ammonium groups deprotonate over the same pH range and no driving force exists for a change. For a reason yet to be explained, binding at the terminal ammonium group leads to stabilization of the opposite enantiomer of the $Ln(DPA)_3^{3-}$ complex.

In any study of Pfeiffer optical activity, it is important to establish the absolute configuration of the preferred enantiomer that is actually observed. This has not been possible previously, since no one had correlated the absolute configuration of a chiral lanthanide complex with either the CD or CPL of the particular complex. However, quite recently the solid-state optical activity of lanthanide tris(oxydiacetate) complexes has been studied by several groups.[15-17] While this complex (which also has D_3 molecular symmetry) cannot be resolved in fluid solution, it happens to crystallize in an optically active space group ($R32$).[18] Schwartz and co-workers have determined the absolute configuration of the $Eu(ODA)_3^{3-}$ complex in $Na_3Eu(C_4H_4O_5)_3 \cdot 2NabF_4 \cdot 6H_2O$ and have determined that the CD associated with the $^7F_0 \rightarrow {}^5D_1$ transition is negative in sign for the Δ isomer.[16] In a similar vein, Richardson and co-workers have examined the CPL of the same Eu(III)

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complex and have determined that the CPL associated with the Δ isomer is negative in sign for the $^5D_0 \rightarrow {}^7F_1$ Eu(III) transition.[17]

These results indicate that as long as the immediate symmetry of a Eu(III) complex is D_3, a negative CPL band within the $^5D_0 \rightarrow {}^7F_1$ luminescence transition implies that the complex is the Δ isomer. We find that in the D_3 $Eu(DPA)_3^{3-}$ complexes (assuming that the outer-sphere complexation does not greatly change the site symmetry about the lanthanide ion), a negative peak is observed at low pH. We now interpret these results to imply that the Δ isomer of the $Eu(DPA)_3^{3-}$ complex is obtained in greater excess as a result of the Pfeiffer effects. One would naturally assume that the same isomer would be preferred in the analagous $Tb(DPA)_3^{3-}$ complexes, and we therefore conclude that if the CPL of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition is predominately negative, then one is observing the Δ isomer as well. For the few diaminocarboxylic acids that display the oppositely signed CPL at high pH, we conclude that it is the Λ isomer that is being produced in greater excess as a result of the outer-sphere complexation.

These conclusions enable a reevaluation of our previous results, which were presented elsewhere. We had previously found that addition of Λ-$Cr(en)_3^{3+}$ to $Tb(DPA)_3^{3-}$ led to the CPL having a predominantly negative sign.[10] From the correlations just described, we now conclude that for this Pfeiffer-active system, the Λ enantiomer of the environmental substance enriches the Δ isomer of the Tb(III) complex. This observation provides further evidence that the Pfeiffer effect is not always a reliable means to determine the absolute configuration of a labile metal complex.[19] In our study involving Pfeiffer optical activity induced by L-ascorbic acid,[9] only negatively signed CPL was found, and we take this to imply that the Δ isomer was produced in this system. On the other hand, the CPL produced when positive nitrogen atoms are incorporated in ring systems was always positive in sign,[8] and this result implies that the Λ isomer was enriched in this system.

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Conclusions

The work described in this paper has produced further evidence that Pfeiffer-type optical activity may be induced in 9-coordinate complexes of lanthanide ions, as well as in the better known 6-coordinate transition-metal complexes. The nature of the outer-sphere complexation is complex, but the bonding between the chelate and the chiral substrate appears to consist of a combination of hydrophobic and hydrogen-bonding forces. All the evidence presented in this and earlier works indicates that only the associative mechanism for the Pfeiffer effect can explain the experimental trends, and we have been able to use the CPL data in a quantitative manner as to obtain association constants for the outer-sphere complexes.

The variability in CPL sign patterns even for a single chiral substrate clearly demonstrates that general absolute configuration correlations must be made with extreme caution. We have found that the Δ isomer of $Ln(DPA)_3^{3-}$ is enriched if bonding takes place at the aminocarboxylic functionality but the Λ enantiomer is preferred if bonding takes place elsewhere. The origins of these preferences are not presently clear, and further investigations are currently under way to attempt more general correlation rules.

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Kinetics of the Chelate Effect. Ring-Closing Reactions of *trans*-Dichloroammine[(2-aminoethyl)ammonium]platinum(II) Chloride and the (3-Aminopropyl)ammonium and (4-Aminobutyl)ammonium Analogues

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The kinetics of the ring-closing reaction of *trans*-$[PtCl_2(NH_3)(N\text{–}NH)]^+$ [(N–NH) = (2-aminoethyl)ammonium (enH), (3-aminopropyl)ammonium (tnH), and (4-aminobutyl)ammonium (bnH)] have been studied in aqueous solution over a range of pH and temperature. The reaction takes the usual form

$$trans\text{-}[PtCl_2(NH_3)(N\text{–}NH)]^+ \overset{K_a'}{\rightleftharpoons} trans\text{-}[PtCl_2(NH_3)(N\text{–}N)] + H^+ \xrightarrow{k^f_{Cl}} [Pt(N\text{–}N)(NH_3)Cl]^+ + Cl^-$$

and the rate contants and activation parameters (k_{Cl}^f at 30.0 °C/s^{-1}, $\Delta H^\ddagger$ (kcal mol^{-1}), $\Delta S^\ddagger$/(cal K^{-1} mol^{-1})) for the en, tn, and bn complexes are 8.17, 12.1, −15; 0.62, 13.5, −15; and 0.0041, 16.1, −16, respectively. The acid dissociation constants, K_a' are 2.6×10^{-9}, 1.8×10^{-10}, and 3.9×10^{-11} mol dm^{-3}, respectively, at 30.0 °C, μ = 2.0. The marked dependence of rate constant on ring size arises from differences in $\Delta H^\ddagger$ rather than in $\Delta S^\ddagger$ whereas in analogous organic systems both contribute to the effect.

Introduction

In our studies of the effect of ring size on the kinetics of chelation we have used complexes containing the moderately strong trans-effect ligand, dimethyl sulfoxide, in order to facilitate ring opening.[1,2] However, this also enhances the rate of ring closing, and in the case of the smaller rings, we were unable to measure this rate unless the major part of the uncoordinated end of the diamine was rendered inactive by protonation. As a result it was not possible to separate the rate constant for ring closing (k^f_{Cl}) from the acid dissociation

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