

temperature, showing diamagnetism at low temperature.^{3,21} This can be understood in VB terms as metal-ligand anti-ferromagnetic exchange in the Cr(SQ)₃ systems. It is also consistent with the MO diagram above with a thermally accessible ³A₂ state, populated at room temperature, giving rise to residual paramagnetism.

While the use of the calculations carried out for the M-(bpy)₃ⁿ complexes will not be the final word on the electronic structure of the quinone complexes, it is interesting that the quinone complexes seem to conform to the results of these calculations better than the bipyridyl complexes. Also, the MO description of the Cr(quinone)₃ⁿ systems adds little to the conventional VB view of bonding contained in eq 1. In fact, it is easier to rationalize the diverse electrochemical behavior of these systems in terms of three noninteracting, essentially parallel ligand π* levels consistent with the localized view of ligand bonding expressed in this equation.

Experimental Section

Preparative routes to Cr(O₂C₆Cl₄)₃, Cr(O₂C₁₄H₈)₃, and Cr(O₂C₆H₂(*t*-Bu)₂)₃ have appeared.^{3,22} Cyclic voltammetric measurements were performed with a PAR Model 174A polarographic analyzer with platinum working and auxiliary electrodes. Potentials reported in Table I are referenced to a saturated calomel electrode. All runs were examined at scan rates ranging from 50 to 200 mV/s. Coulometry experiments were carried out with a PAR Model 179 digital coulometer positioned to potentials which were slightly more negative than the first reduction wave of the neutral complex.

Electron spin resonance spectra were recorded on a Varian V-4500 and on a Varian E-9 in the laboratory of Dr. Gareth Eaton, University of Denver. Spectra in Table II were recorded in dichloromethane solution at room temperature and referenced to DPPH.

Acknowledgment. This work was supported in part by Grant GM-23386 from the National Institutes of Health and by the NSF through a RIAS grant. We thank Professor Gareth Eaton of the University of Denver for his assistance with the EPR spectra.

Registry No. Cr(O₂C₆H₂(*t*-Bu)₂)₃³⁻, 70130-58-4; Cr(O₂C₆H₂(*t*-Bu)₂)₃²⁻, 68317-87-3; Cr(O₂C₆H₂(*t*-Bu)₂)₃⁻, 68317-86-2; Cr(O₂C₆H₂(*t*-Bu)₂)₃, 64020-84-4; Cr(O₂C₆H₂(*t*-Bu)₂)₃⁺, 70130-59-5; Cr(O₂C₆H₂(*t*-Bu)₂)₃²⁺, 70145-51-6; Cr(O₂C₁₄H₈)₃³⁻, 70130-60-8; Cr(O₂C₁₄H₈)₃²⁻, 70130-61-9; Cr(O₂C₁₄H₈)₃⁻, 70130-62-0; Cr(O₂C₁₄H₈)₃, 68846-34-4; Cr(O₂C₁₄H₈)₃⁺, 70130-63-1; Cr(O₂C₁₄H₈)₃²⁺, 70130-64-2; Cr(O₂C₁₄H₈)₃³⁺, 70145-49-2; Cr(O₂C₆Cl₄)₃³⁻, 70130-65-3; Cr(O₂C₆Cl₄)₃²⁻, 70130-66-4; Cr(O₂C₆Cl₄)₃⁻, 70130-65-3; Cr(O₂C₆Cl₄)₃, 60635-34-9; Cr(O₂C₆Cl₄)₃⁺, 70130-67-5.

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Intermolecular Energy Transfer between Lanthanide Complexes in Aqueous Solution. 4. Stereoselectivity in the Transfer from Terbium(III) to Europium(III) Complexes of Aspartic Acid

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Received August 31, 1978

Intermolecular energy transfer from Tb³⁺ to Eu³⁺, emission intensity and lifetime measurements, potentiometric titrations, and differential absorption spectroscopy were all used to study the bonding between Tb³⁺ and aspartic acid as a function of pH. At low pH (3.0–5.0), the Tb³⁺/Asp complexes are mononuclear, but once the pH is raised above 6.0, polynuclear association of complexes becomes important. Potentiometric, emission, and differential absorption titration curves were all superimposable for lanthanide complexes of L-Asp, D-Asp, and DL-Asp, but it was found that energy could be transferred from Tb³⁺ to Eu³⁺ more efficiently in associated complexes containing a racemic ligand than in polynuclear complexes containing resolved ligands. This effect represents the first observation of energy transfer characterized by stereoselectivity. All other types of measurement appear to be too insensitive to allow the detection of this effect.

Introduction

The stereoselective binding of metal ions by optically active α-amino acids is an area that has received attention lately and still is a matter of active research.¹ Stereoselectivity was not

found in the formation constants for the transition-metal complexes of asparagine, glutamine, aspartic acid, alanine, valine, and proline^{2,3} but has been detected in the Co²⁺, Ni²⁺, and Zn²⁺ complexes of histidine.^{4,5} While the stereoselective effect is largely lacking in the simple amino acid complexes of transition metals, it has been found in the metal complexes of a wide variety of substituted amino acid derivatives.^{6–10}

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Calorimetric studies involving transition-metal complexes of histidine have suggested that the stereoselective effect has its origin in enthalpy factors.¹¹

In this laboratory, work has been concentrated on the use of intermolecular energy transfer among lanthanide complexes as a probe of the solution chemistry of these compounds. Energy transfer from Tb^{3+} to Eu^{3+} has been used to study the complexes of various pyridinecarboxylic¹² and benzenecarboxylic¹³ acids. These studies have shown that the complexes are largely mononuclear at low pH and also that lanthanide carboxylates are extensively associated into polynuclear complexes at pH values much greater than 7 (where complex hydrolysis is also known to be taking place). At low pH values, the energy transfer arises mostly from collisional interactions, but at high pH the energy transfer becomes much more efficient due to the close proximity of associated donor-acceptor complexes.

In the present work, the first example of stereoselectivity involving lanthanide complexes is reported. The energy transfer from Tb^{3+} to Eu^{3+} complexes of aspartic acid (Asp) was examined in detail, and the effect of ligand chirality upon the energy-transfer process was also considered. Potentiometric titrations were carried out to learn the extent of ground-state stereoselectivity and its possible contribution to the excited-state stereoselectivity.

Aspartic acid is considered a "hard" ligand and stereoselectivity has not been detected in its binding of transition-metal ions.² However, the Cu^{2+} and Ni^{2+} complexes that are formed with *N*-(2-pyridylmethyl)- and *N*-(6-methyl-2-pyridinylmethyl)-*L*-aspartic acid have been shown to bind more tightly to the *L* isomers of alanine, phenylalanine, tryptophan, threonine, leucine, and valine than to the corresponding *D* isomers.⁸ Potentiometric titrations of lanthanide complexes of aspartic acid have shown that extensive association among complexes takes place in the hydrolysis region¹⁴ and that this association among complexes results in a rich and detailed circular dichroism spectrum in the region of the metal ion absorptions.¹⁵ Circularly polarized emission studies have provided evidence that reproducible complex geometries exist in the hydrolysis region in spite of the extensive association among the complexes.^{16,17} The present studies enable a further detailing of the very complex binding that takes place in solution when lanthanide ions coordinate to aspartic acid ligands and also provide new information regarding the energy-transfer process.

Experimental Section

$TbCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, and $HoCl_3 \cdot 6H_2O$, 99.9% pure, were obtained from Alfa Inorganics, *D*-aspartic acid (A grade) was obtained from Calbiochem, and *L*- and *DL*-aspartic acids were purchased from Eastman (98% minimum by titration). All reagents were used as received. The initial concentration of Tb^{3+} in all experiments was 2.0×10^{-3} M (verified by spectrophotometric determination with hydroxy naphthol blue¹⁸) and the initial concentration of aspartic acid was always adjusted to be 1.0×10^{-2} M (verified by titration with standardized KOH and thus corresponding to a 1:5 metal-to-ligand ratio).

The quenching experiments were carried out by adding microliter quantities of Eu^{3+} /Asp solution from a stock solution that was 2.0×10^{-2} M in the lanthanide ion and which contained the same ratio of metal to ligand. The pH of both solutions was adjusted to be the same at the start of each run with either KOH or HCl; then no variation in pH could occur during the addition of Eu^{3+} quencher. In none of the cases was the final Eu^{3+} concentration allowed to rise above 3×10^{-4} M. Quenching experiments were carried out by using both *D*- and *L*-aspartic acid as ligands, and two sets of experiments were performed with *DL*-aspartic acid as the ligand (one set used the commercial *DL* ligand and the other used a *DL* ligand prepared by mixing equimolar parts of *D*- and *L*-aspartic acid ligands). No difference was found in comparing results derived from the two sets of *DL* ligand data.

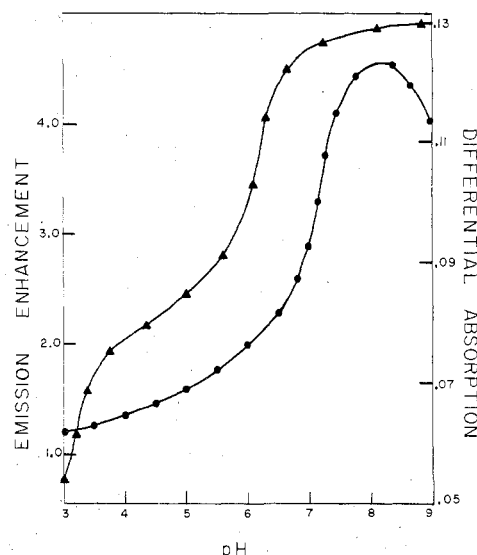


Figure 1. Emission intensity (●) of the ${}^5D_4 \rightarrow {}^7F_5$ transition of 1:5 Tb^{3+} /Asp as a function of pH; the intensity scale is relative to the emission of Tb^{3+}/H_2O . Differential absorption spectra (▲) are also shown as a function of pH for the ${}^5I_8 \rightarrow {}^5G_6$ transition of 1:5 Ho^{3+} /Asp.

All emission spectra were recorded on a medium-resolution emission spectrometer constructed in this laboratory and which has been previously described.¹² Emission intensities reported in this paper reflect integrated intensities and not merely peak heights; this precaution proved necessary since some splittings were observed within the Tb^{3+} ${}^5D_4 \rightarrow {}^7F_5$ transition that was monitored. It was found that the emission intensity of a 3×10^{-4} M solution of $EuCl_3$ was too weak to be measured on the apparatus under the conditions used. Tb^{3+} /Asp solutions emitted moderately, however, and it was possible to observe sensitized Eu^{3+} emission at high pH values where extensive energy transfer was found to take place. Lifetime measurements were made as before¹² by exciting the sample with a pulsed xenon flashlamp, photographing the emission decay as displayed on a storage oscilloscope, and fitting the decay curve with standard exponential-fitting methods.

Differential absorbance measurements were obtained on a Beckman 25 UV/VIS recording spectrophotometer operating on the 0.1 and 0.25 absorbance scales. The reference was a 0.03 M solution of Ho^{3+} at a pH of 5.0, and the sample was 0.03 M in Ho^{3+} and 0.15 M in aspartic acid. The pH of the sample was adjusted by adding either standard HCl or KOH and any volume changes in the sample were reproduced in the reference (by adding an equivalent amount of H_2O), thus ensuring that all difference spectra were the result of changes in metal-ligand interaction and were not due merely to dilution effects. The integrated absorbance of the ${}^5I_8 \rightarrow {}^5G_6$ Ho^{3+} transition was followed as the pH of the sample was varied. No differences in spectra or intensities were observed if the pH of the reference was varied between pH 2 and pH 5, but the pH of the reference could not be raised above 6.5 due to precipitation of lanthanide hydroxide.

pH measurements were taken on a Fisher Accumet Model 144 pH meter with a standard glass microcombination electrode and were usually made while inserting the electrode directly into the fluorescence cuvette. The glass electrode was calibrated each day by using phthalate and phosphate buffers. All measurements of emission intensity, differential absorption, and potentiometric titration were carried out at constant ionic strength (0.1 M KCl). Variations in solution pH were effected by the addition of microliter quantities of standardized KOH or HCl to the solutions. A metal-to-ligand ratio of 1:5 was used throughout the study.

Results

While the total emission of Tb^{3+} bound to aspartic acid is considerably weaker than the emission intensity observed when this ion was bound to either picolinic or dipicolinic acid¹² and somewhat weaker than observed in Tb^{3+} complexes of various benzenecarboxylic acids,¹³ it was easily measured on the apparatus used in this study. It was found that the emission

Table I. pH Dependence of Tb^{3+}/Asp Emission Lifetimes^a

pH	τ , μs	pH	τ , μs
3.0	455	6.5	730
3.5	485	7.0	795
4.0	515	7.5	880
4.5	550	8.0	1000
5.0	590	8.5	1160
5.5	630	9.0	1315
6.0	680		

^a All values carry an error of $\pm 20 \mu s$.

intensities at a given pH for $Tb^{3+}/L-Asp$, $Tb^{3+}/D-Asp$, and $Tb^{3+}/DL-Asp$ were all identical over the pH range studied. This pH dependence of Tb^{3+}/Asp emission relative to the emission of Tb^{3+}/H_2O is shown in Figure 1. Little intensity enhancement takes place up to a pH value of 6 but a large effect occurs at higher pH values. Above pH 8.5 the emission intensity drops somewhat and apparently reflects the effects of hydrolysis. With the metal-to-ligand ratio used in this study (1:5), precipitation of insoluble lanthanide complexes occurred above pH 9.

The use of differential absorption spectroscopy has proved useful in following environmental changes in neodymium complexes of several amino and carboxylic acids,¹⁹ so measurements of this type were made on the Asp complexes. The differential absorption spectra of 1:5 Ho^{3+}/Asp were measured in the region of the hypersensitive $^5I_8 \rightarrow ^5G_6$ Ho^{3+} transition (this transition of Ho^{3+} has been used in the spectrophotometric study of lanthanide shift reagent adducts²⁰). The chemical similarity of lanthanide elements will enable the Ho^{3+} absorption results to be compared directly with the Tb^{3+} emission results, and it was found that the differential intensity of Ho^{3+} absorbance was quite sensitive to the interaction between the Asp ligand and the lanthanide ion. The pH dependence of this differential absorption is also shown in Figure 1, and the data are somewhat different from the pH dependence of emission. The Ho^{3+} absorbance rises sharply in the 2–3 pH region but rises only gradually as the pH is increased from 3 to 6. After pH 6, another sharp rise in absorbance is seen, but once a pH of 7 is passed, the absorbance remains relatively constant up to the point of precipitation. No differences in the differential absorption spectra were seen when the ligand was either L-Asp, D-Asp, or DL-Asp.

The Tb^{3+} emission lifetimes of $Tb^{3+}/L-Asp$, $Tb^{3+}/D-Asp$, and $Tb^{3+}/DL-Asp$ were also found to be the same (within experimental error) at a given pH value. These results have been collected in Table I. Unlike the emission intensity data, the lifetime results show no dramatic increase in magnitude above pH 6. Instead, the Tb^{3+} emission lifetime increases in a fairly regular fashion up until the point of precipitation.

Potentiometric titrations for $Tb^{3+}/L-Asp$, $Tb^{3+}/D-Asp$, and $Tb^{3+}/DL-Asp$ indicated that the formation curves for each system were superimposable over the entire pH region. All of the curves show a gradual rise in pH until 5 equiv of base/mol of metal ion is added, with a rapid rise in pH being observed (this amount of base corresponds to deprotonation of the ligand and is complete by a pH of 5.5). A central portion of the curve follows next in which 2 equiv is titrated to an inflection near pH 8. Finally, the pH rises rapidly as more base is added, and a lanthanide complex precipitates once pH 9 is reached.

Titration curves may also be constructed by following the changes in emission intensity of Tb^{3+}/Asp or by following the changes in the differential absorption spectrum of Ho^{3+}/Asp . Representative curves for both types of measurement are shown in Figure 2, and identical results were found in all cases for L-Asp, D-Asp, and DL-Asp. The differential absorption shows a gradual rise until 5 equiv of base is added but rises rapidly as more base is added. The emission intensity hardly

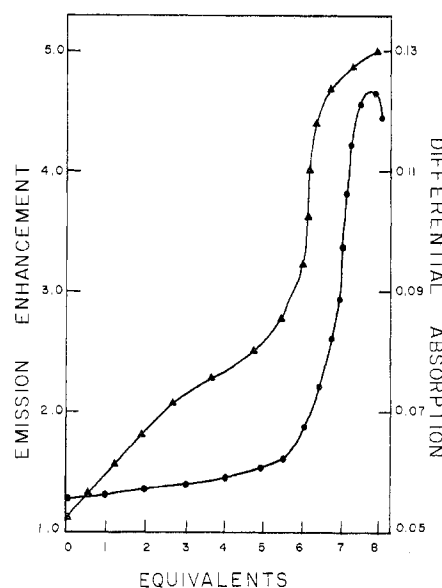


Figure 2. Emission intensity (●) and differential absorption (▲) titration curves for addition of standard base per mole of lanthanide in 1:5 solutions of Tb^{3+}/Asp and Ho^{3+}/Asp , respectively. The intensity scales are as for Figure 1.

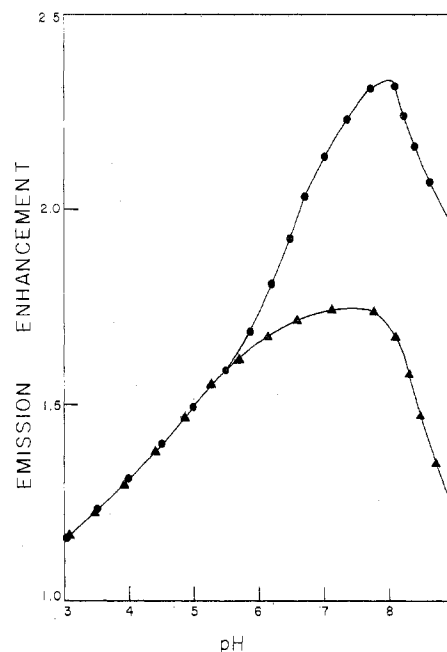


Figure 3. Emission intensity of the $^5D_4 \rightarrow ^7F_5$ Tb^{3+} transition of 1:5:0.145 $Tb^{3+}/D-Asp/Eu^{3+}$ (●) and of 1:5:0.145 $Tb^{3+}/DL-Asp/Eu^{3+}$ (▲) as a function of pH. The intensity scale is as for Figure 1.

changes at all until 6 equiv of base is added but rises very sharply as the next 1.5 equiv is added. Further addition of base results in a decrease in emission intensity, presumably as a result of complex hydrolysis.

Formation constants were not calculated from any of the titration curves since the presence of polynuclear complexes and extensive hydrolysis places any calculation on an uncertain basis.¹⁴ The potentiometric and differential absorption titrations would imply that stereoselectivity is absent in the ground states of the complexes, but it is probable that the measurements are simply not sensitive enough to pick up the effect.

Addition of Eu^{3+}/Asp to a solution of Tb^{3+}/Asp results in a decrease in Tb^{3+} emission intensity, in a shortening of the Tb^{3+} emission lifetime, and in the appearance of Eu^{3+} emission mostly at 615 nm (corresponding to the $^5D_0 \rightarrow ^7F_2$ transition).

Table II. Stern-Volmer Quenching Constants for the Quenching of $\text{Tb}^{3+}/\text{Asp}$ by $\text{Eu}^{3+}/\text{Asp}$ as a Function of pH^a

pH	$K_{sv}^{\phi} \times 10^{-3}{}^b$	$K_{sv}^{\phi} \times 10^{-3}{}^c$
3.0	0.99	0.99
3.5	1.01	1.00
4.0	1.11	1.08
4.5	1.18	1.17
5.0	1.46	1.45
5.5	1.62	1.70
6.0	1.77	1.80
6.5	2.25	2.44
7.0	3.79	4.44
7.5	5.47	6.87
8.0	6.72	8.60
8.5	7.50	10.71
9.0	7.64	12.33

^a All values are associated with an error of $\pm 0.03 \times 10^3$, and have the units of L/mol. ^b Data for D-Asp complexes. ^c Data for DL-Asp complexes.

In Figure 3, the pH dependence of 1:5:0.145 solutions of $\text{Tb}^{3+}/\text{D-Asp}/\text{Eu}^{3+}$ and $\text{Tb}^{3+}/\text{DL-Asp}/\text{Eu}^{3+}$ are shown (the pH dependence of a $\text{Tb}^{3+}/\text{L-Asp}/\text{Eu}^{3+}$ solution was identical with that of a $\text{Tb}^{3+}/\text{D-Asp}/\text{Eu}^{3+}$ solution). Below pH 6 both sets of Tb^{3+} emission intensities are the same, although somewhat less than for the intensity without Eu^{3+} present. Above pH 6 the Tb^{3+} emission intensity of the $\text{Tb}^{3+}/\text{DL-Asp}/\text{Eu}^{3+}$ solution is appreciably smaller than that of the Tb^{3+} solution containing the resolved ligand, indicating a greater degree of energy transfer from Tb^{3+} to Eu^{3+} in solutions that contain DL-Asp as the ligand than that containing either D-Asp or L-Asp. Identical results were obtained for the two sets of racemic acid determinations; so the difference between racemic and resolved ligands cannot be due to anything other than stereoselectivity.

To place the energy transfer results on a more quantitative basis, solutions of 1:5 $\text{Tb}^{3+}/\text{Asp}$ at a given pH were titrated with microliter quantities of a 1:5 $\text{Eu}^{3+}/\text{Asp}$ solution at the same pH. The decreases in Tb^{3+} emission intensity and lifetime at 545 nm were measured after each addition of Eu^{3+} quencher, with the data being analyzed by the standard Stern-Volmer equations for intensity quenching:

$$(I_0 - I)/I = K_{sv}^{\phi}[Q] \quad (1)$$

and lifetime quenching:

$$(\tau_0 - \tau)/\tau = K_{sv}^{\tau}[Q] \quad (2)$$

In eq 1 and 2, I_0 (or τ_0) is the Tb^{3+} emission intensity (or lifetime) in the absence of Eu^{3+} quencher, I (or τ) is the intensity (or lifetime) with quencher present, and $[Q]$ is the molar concentration of Eu^{3+} quencher. K_{sv}^{ϕ} and K_{sv}^{τ} are the respective Stern-Volmer quenching constants for intensity and lifetime quenching. For all solutions and all pH values K_{sv}^{τ} was found to be $(1.2 \pm 0.2) \times 10^3$ L/mol, while K_{sv}^{ϕ} was found to vary over a much larger range. Values for K_{sv}^{ϕ} have been tabulated in Table II.

It was found that the K_{sv}^{ϕ} values for $\text{Tb}^{3+}/\text{L-Asp}$ and $\text{Tb}^{3+}/\text{D-Asp}$ were equal within experimental error over the entire pH 3-9 interval. Below pH 6, the quenching of $\text{Tb}^{3+}/\text{DL-Asp}$ by $\text{Eu}^{3+}/\text{DL-Asp}$ was the same as for the quenching of $\text{Tb}^{3+}/\text{D-Asp}$ by $\text{Eu}^{3+}/\text{D-Asp}$. Above pH 6, it was found that the DL ligand led to a greater degree of quenching than did either of the resolved ligands. In all cases, the degree of quenching increases dramatically above pH 6.

The emission intensity of a 3×10^{-4} M solution of Eu^{3+} with a fivefold excess of aspartic acid was too weak to be measured under the conditions used in this study. However, in the presence of $\text{Tb}^{3+}/\text{Asp}$, weak Eu^{3+} emission could be measured. Above pH 6, this emission became much more intense and at pH 9 it was almost as intense as the emission from the Tb^{3+}

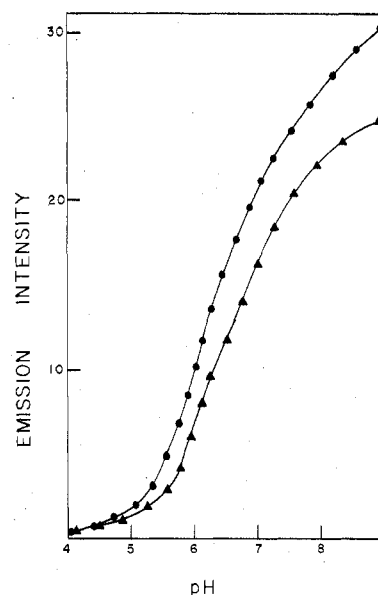


Figure 4. Sensitized emission intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of $\text{Eu}^{3+}/\text{D-Asp}$ (●) and $\text{Eu}^{3+}/\text{DL-Asp}$ (▲) as a result of energy transfer from the corresponding Tb^{3+} complexes. The intensity scale is completely arbitrary.

ion itself. The pH dependence of both $\text{Eu}^{3+}/\text{D-Asp}$ and $\text{Eu}^{3+}/\text{DL-Asp}$ in the high pH region is shown in Figure 4. It was found that the emission intensity of $\text{Eu}^{3+}/\text{DL-Asp}$ was measurably greater than either of these.

Discussion

Before a discussion of the stereoselective effects can be undertaken, a complete description (as complete as possible) of the binding between Tb^{3+} and aspartic acid must be made. Since it is known that the first dissociation constant (corresponding to the first carboxylic acid ionization) of aspartic acid has a $\text{p}K_1$ value of 1.94,² one would expect that in the very low pH region of 2-3, the Tb^{3+} ion is bound by the ligand in a monodentate fashion. Differential absorption spectra taken in this region indicate that little environmental changes have taken place and that the lanthanide ions are only weakly coordinated. Emission lifetime and intensity data also indicate that the Tb^{3+} ion is only slightly perturbed relative to that of $\text{Tb}^{3+}/\text{H}_2\text{O}$.

The next carboxylic acid proton has a $\text{p}K_2$ of 3.71.² Martin and co-workers¹⁴ have concluded from their titration curves that this second ionization is complete by the time a pH of 5.5 is reached. The intensity data of Figure 1 indicate that no real emission enhancements take place until pH 6, indicating that even bidentate attachment of Asp ligands is not sufficient to promote strongly enhanced Tb^{3+} emission. In addition, some enhancement is seen in the lifetime of $\text{Tb}^{3+}/\text{Asp}$ emission relative to that of $\text{Tb}^{3+}/\text{H}_2\text{O}$ (known to be $400 \mu\text{s}^{21}$), but the extent of enhancement is not great. The differential absorption experiments show that significant interaction between ligand and metal *does* take place as the pH is raised up to 6, however, since the intensity of Ho^{3+} absorption (the hypersensitive transition (whose intensity is very dependent on ligand binding) rises dramatically in the 3-5 pH interval.

Previous work on benzenecarboxylic acid complexes of Tb^{3+} had shown that simple bidentate binding was sufficient to induce very strong emission, but these studies involved the formation of five- and six-membered rings.^{12,22} When Asp binds in a bidentate fashion (using the two ionized carboxylic acid groups) only a seven-membered ring can be formed. Since enhanced $\text{Tb}^{3+}/\text{ligand}$ emission relative to the emission of $\text{Tb}^{3+}/\text{H}_2\text{O}$ is known to arise as a result of the ligand acting as an insulating agent²³ (protecting the metal ion from solvent

quenching via the -OH vibrational modes), it is concluded here that the formation of a seven-membered chelate ring does not provide the necessary environment that allows strong Tb^{3+} emission to be observed. This conclusion is further supported by the observation that the emission of Tb^{3+}/Asp complexes is much weaker than the emission of Tb^{3+} complexes of benzenecarboxylic and pyridinecarboxylic acids, all of which emit at least an order of magnitude greater than the Tb^{3+}/Asp complexes.

The lifetime data of Table I do indicate that a greater degree of metal-to-ligand binding is taking place as the pH is raised to 6, but the lack of detail in the data precludes any deeper interpretation. Circularly polarized emission¹⁷ and circular dichroism¹⁵ spectra have shown that no measurable metal ion chirality can be detected below a pH of 6, indicating that even bidentate binding of the Tb^{3+} by chiral Asp ligands will not induce optical activity into the electronic transitions of the lanthanide ion.

Once the pH of a Tb^{3+}/Asp solution reaches 6, the Tb^{3+} emission rises rapidly until pH 8, but apparently hydrolysis causes the intensity to drop at high pH. Potentiometric titration studies¹⁴ indicate that hydrolysis reactions and polynuclear complex formation become important in this pH region. The remaining ionization of the Asp ligand corresponds to deprotonation of the amino group and has a pK_3 of 9.63.² Since lanthanide ions bind weakly to amino groups, Martin and co-workers¹⁴ concluded that metal ion promoted deprotonation of and complexation with the amino group of aspartic acid would be unlikely. The Tb^{3+} emission enhancement observed in the pH 6-9 interval thus cannot be ascribed to the effects of terdentate Asp binding. Circularly polarized emission spectra¹⁷ observed in this pH region contain only one type of band shape for the ${}^5D_4 \rightarrow {}^7F_5$ transition, and this pattern merely changes in intensity as the pH is raised. In addition, the differential absorption spectra recorded in this region also show a rapid increase in intensity. It is clear that the lanthanide environment is changing in the 6-9 pH region *without* new chelating positions becoming available on the Asp ligands.

The Stern-Volmer quenching data provide additional information and enable a further description of the nature of the Tb^{3+}/Asp complex at different pH values. It is known²⁴ that quenching of an excited donor may take place by two means: collisional deactivation of the excited state (dynamic quenching) and associated donor-acceptor complex (static quenching). For the purposes of this discussion it is sufficient to note that dynamic quenching affects both the emission lifetime and intensity, while static quenching is only reflected in the intensity data. Thus, an equality of K_{sv}^{ϕ} and K_{sv}^{τ} demonstrates the absence of static quenching and associated donor-acceptor complexes. For the situation presented here, if K_{sv}^{ϕ} exceeds K_{sv}^{τ} at a given pH, one can conclude that association between Tb^{3+}/Asp donor and Eu^{3+}/Asp quencher is taking place. The quenching data then enable a precise determination of the point of onset when polynuclear formation begins and also provide an estimate of the extent of this association.

Examination of the Stern-Volmer quenching constants found in Table II show that below a pH of 5 a complete equality of K_{sv}^{ϕ} and K_{sv}^{τ} exists. This observation enables one to conclude that below this pH the Tb^{3+}/Asp complexes are all mononuclear in a pH region characterized by monodentate and bidentate ligand bonding. Once a pH of 5.5 is reached, however, K_{sv}^{ϕ} becomes measurably greater than K_{sv}^{τ} and the difference between the two grows as the pH is further raised. The Stern-Volmer data thus lead to the conclusion that polynuclear association of the complexes becomes more important as the pH is raised, as was concluded by Martin.¹⁴

The data of Figure 3 show that the sensitized Eu^{3+} emission rises sharply once the pH of 5.5 is passed. Since this emission cannot come from Eu^{3+}/Asp complexes alone (the emission of these being exceedingly weak even at high pH values), it is concluded that the Eu^{3+} emission must be due to the transfer of energy from an excited Tb^{3+} ion to an unexcited Eu^{3+} ion. Comparison of the Stern-Volmer results and the Eu^{3+} emission dependences clearly link a greater degree of polynuclear association with an increased Eu^{3+} emission quantum yield.

The data presented in Figure 2 and Table II show that, in the pH 3-5 region, energy is transferred from $Tb^{3+}/D-Asp$ (or $Tb^{3+}/L-Asp$) to $Eu^{3+}/D-Asp$ (or $Eu^{3+}/L-Asp$) just as effectively as it is transferred from $Tb^{3+}/DL-Asp$ to $Eu^{3+}/DL-Asp$. These results imply that no stereoselectivity in the energy transfer exists when the process takes place by purely collisional means. A similar conclusion was reached in a study of outer-sphere electron-transfer reactions, in which no stereoselectivity was noted in the electron-transfer reactions of racemic Cr^{2+} complexes with optically active Co^{3+} complexes.²⁵

Above pH 5.5, however, energy was transferred more effectively among the DL-Asp complexes than in either the D- or L-Asp complexes. This same pH interval (5.5-9.0) has been identified in this discussion as a region in which polynuclear association of complexes becomes more important. Therefore, stereoselectivity in Asp complexes only arises when the lanthanide complexes are associated and cannot occur before the onset of polynuclear formation.

The various titration curves reveal interesting features in the binding of lanthanide ions by aspartate. The potentiometric titration showed that the first inflection corresponds to the amount of aspartic acid present and that the second could be assigned to complex hydrolysis, in agreement with the results of Martin and co-workers.¹⁴ The differential absorption measurements demonstrated that the first 5 equiv of base does not alter the lanthanide absorption to a great extent but that the addition of 2 equiv more resulted in large spectral (and hence geometrical) changes. It is highly significant that the differential absorption titration curves leveled off somewhat after the addition of 7 equiv, since this would lead to the interpretation that a definite geometry has been established for the complexes. The energy-transfer data indicate that this new geometry is polymeric in nature. The emission titration data reveal that the metal-ion environment necessary for the observance of strong Tb^{3+} emission (where the metal is protected from the solvent by ligand molecules) begins to be formed after 6 equiv has been added and reaches a maximum when a total of 7.5 equiv of base/mol of metal ion has been added.

A common observation in other studies of stereoselectivity involving transition-metal complexes is that no effects are associated with the binding of the first amino acid ligand but that stereoselectivity occurs in the binding of the second.^{4,8,11} Since other lanthanide ions have been shown to bind two molecules of aspartic acid,²⁶ it seems probable that the stereoselectivity observed in the Tb^{3+}/Asp complexes reflects a greater stability of hydroxide-bridged $Tb^{3+}/L-Asp$ or $Tb^{3+}/(L-Asp)_2$ complexes. If the complexes are dimeric in nature, the titration would imply that two lanthanide complexes (each containing two molecules of Asp per metal ion) are linked by five hydroxide bridges. This arrangement would imply that the lanthanide ions would achieve a ninefold coordination state, which is not impossible.²⁷ The addition of a sixth hydroxide results in destruction of this arrangement and results in the formation of a lanthanide precipitate.

It is somewhat surprising that no trace of stereoselectivity was found in any of the ground-state measurements (potentiometric and differential absorption titrations). No stereoselectivity was found in the emission titration experiments

also, which indicates that the effect cannot arise solely in the excited state. Since the observation of stereoselectivity was found only in the energy-transfer results, it may be concluded that the other measurements are not sufficiently sensitive to detect the effect. Our previous work^{12,13} has shown that intermolecular energy transfer is the most sensitive technique for probing polynuclear association among lanthanide complexes in solution, and the present work indicates how effective the method can be. It is concluded here that a stereoselective association of lanthanide complexes derived from potentially chiral ligands exists in the hydrolysis region but that only sensitive emission measurements are able to detect this association. Further studies are under way to examine these stereoselective effects in greater detail.

Acknowledgment. This work was supported by a Cotrell grant from the Research Corp. which made possible the purchase of the luminescence apparatus.

Registry No. Tb^{3+} , 22541-20-4; Eu^{3+} , 22541-18-0; DL-Asp, 617-45-8; D-Asp, 1783-96-6; L-Asp, 56-84-8; Ho^{3+} , 22541-22-6.

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Polarized Crystal Spectrum of Bis(methylphenethylammonium) Tetrachlorocuprate(II): Analysis of the Energies, Vibrational Fine Structure, and Temperature Dependence of the "d-d" Transitions of the Planar $CuCl_4^{2-}$ Ion

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Received December 27, 1978

The electronic spectra of two crystal faces of bis(methylphenethylammonium) tetrachlorocuprate(II) are reported. The polarization properties of the transitions suggest the d-orbital energy sequence $d_{x^2-y^2} \gg d_{xy} > d_{xz} > d_{yz} > d_{z^2}$ for the planar, centrosymmetric $CuCl_4^{2-}$ ion present in this compound. The d-orbital energies are in agreement with a simple angular-overlap treatment of the bonding in a square-planar complex, except that the d_{z^2} orbital is $\sim 5000\text{ cm}^{-1}$ lower in energy than expected. This depression is rationalized in terms of configuration interaction with the copper 4s orbital. At low temperature, each band in the electronic spectrum exhibits considerable vibrational fine structure. The three lower energy transitions each consist of a single progression, and this is assigned to the a_{1g} stretching mode. The spacing is in each case $\sim 272\text{ cm}^{-1}$, and the half-widths of the components are $\sim 140\text{ cm}^{-1}$. The relative intensities of the components in y polarization imply a lengthening of the Cu-Cl bonds of $\sim 8.9 \pm 0.3\text{ pm}$ in these excited states, while the overall temperature dependence of the bands suggests that the intensity in each case is probably induced largely by coupling with the out-of-plane bending mode of b_{2u} symmetry with this having an energy of $\sim 105\text{ cm}^{-1}$. The highest energy band in xy polarization consists of four progressions, three of these being much weaker and sharper (half-widths $\sim 30\text{ cm}^{-1}$) than the fourth (half-width $\sim 120\text{ cm}^{-1}$). Each of these progressions is also assigned to the a_{1g} mode with an energy of $\sim 267\text{ cm}^{-1}$. The relative intensities of the components imply a lengthening of the Cu-Cl bond of $\sim 10.3 \pm 0.3\text{ pm}$ in this excited state. The separations between the progressions suggest that the bulk of the intensity at 10 K is derived by coupling with the in-plane stretching mode of e_u symmetry (energy 188 cm^{-1}), with the three weaker progressions being assigned to coupling with lattice modes of energy 108, 63, and $\sim 20\text{ cm}^{-1}$. The overall temperature dependence of the band is consistent with this interpretation. The three sharper progressions show a marked broadening of their components as the energy of the peaks increases, and this is rationalized in terms of the different vibrational frequencies expected for the various isotopic isomers expected for the $CuCl_4^{2-}$ ion. Although the energies of the a_{1g} mode are lower in the excited electronic states than those in the ground state (276 cm^{-1}), the difference is not as large as might be expected from the changes in the Cu-Cl bond lengths. It is possible that this results from a distortion toward a tetrahedral geometry in the excited electronic states.

Introduction

The tetrachlorocuprate(II) ion generally has either a flattened tetrahedral geometry or a tetragonally distorted octahedral arrangement of chloride ions about the copper(II).¹ Recently, however, it was found that the compound $(C_6H_5CH_2CH_2NH_2CH_3)_2CuCl_4$, (nmph)₂CuCl₄, contains discrete, planar $CuCl_4^{2-}$ ions in which no axial ligation is present.² The assignment of the energy levels in this complex is particularly

important, first because there are widely conflicting theoretical predictions³⁻⁷ concerning the d-orbital energies in this ion and second because a comparison with the energy levels of chlorocuprate(II) complexes having other geometries should provide a useful test of the self-consistency of simple models used to describe the bonding in transition-metal complexes.^{8,9}

The complex (nmph)₂CuCl₄ is also unusual in that preliminary investigations of the low-temperature electronic