Table I. Concentrations and Equilibrium Constants of Low-Spin and High-Spin $[Co(bpy)_3]^{2+}$ Complexes in a K-Y Zeolite

	concn, 10^{19} molecules/g		
temp, K	low-spin complex	high-spin complex	equil const
77	4.40 (4.16)[a]	0	
82	2.65	1.75	0.66
96	2.23	2.17	0.97
107	1.81	2.59	1.43
121	1.49	2.91	1.95
139	1.43	2.97	2.08

[a] The value in parentheses indicates the concentration of cobalt as determined by atomic absorption.

spectrum is attributed to the low-spin $[Co^{II}(bpy)_3]^{2+}$ complex. When the temperature of the sample was increased to 100 K, the spectrum of the high-spin complex decreased in intensity by a factor of 50, whereas the intensity of the low-spin complex decreased by a factor of 3.

When the temperature of the zeolite sample was increased above 77 K, the EPR spectrum was reversibly reduced in intensity and the line width increased. The spectrum eventually disappeared at 298 K. If the concentration of the low-spin complex had remained unchanged, the second integral of the spectrum would have been proportional to the reciprocal of the sample temperature. The observation that the integral measured at 298 K was far less than 1/3.87 of that at 77 K indicates a decrease in concentration of the low-spin complex, due to a spin equilibrium of the type

$$\text{low-spin complex } ({}^6t_{2g}{}^1e_g) \overset{K}{\rightleftharpoons} \text{high-spin complex } ({}^5t_{2g}{}^2e_g) \quad (1)$$

A $[Co^{II}(bpy)_3]^{2+}$ complex was found to be in a high-spin state at room temperature, with a magnetic moment of 4.85 μ_b.[18] A short relaxation time at $T > 80$ K is probably responsible for the absence of its EPR spectrum in zeolites. Such was the case for $[Co^{II}(NH_3)_6]^{2+}$, $[Co^{II}(en)_3]^{2+}$, and $[Co^{II}(en)_2]^{2+}$ complexes in zeolites,[19,20] as well as for $[Co^{II}(bpy)_3]^{2+}$ in Me_2SO at $T > 100$ K.

The concentrations of the low-spin and high-spin complexes with a gross bpy/Co^{2+} ratio of 4.4 are tabulated in Table I, after taking into account the normal temperature dependence of the signal intensity. From these values the equilibrium constant, K, was calculated, with the assumption that all of the complex at 77 K was in the low-spin state (see Figure 2). From a plot of ln K vs. $1/T$, $\Delta H° = 0.5 \pm 0.2$ kcal/mol and $\Delta S° = 5 \pm 1$ eu were determined. K vs. $1/T$, $\Delta H° = -0.5 \pm 0.2$ kcal/mol and $\Delta S° = 5 \pm 1$ eu were determined. Enthalpy values of 0.8–1.4 kcal/mol have been obtained from the spin equilibrium of cobalt–terpyridine complexes.[9,11] These thermodynamic parameters suggest that the spin equilibrium of $[Co^{II}(bpy)_3]^{2+}$ in a zeolite is analogous to that of several cobalt complexes, in which a low-spin state is the one of lower energy, and the transition from a low-spin level to a high-spin level accompanies increases both in spin multiplicity and in molecular dimension.[7] Relative to $[Co^{II}(bpy)_3]^{2+}$ in more conventional solvents such as Me_2SO, the geometric limitations imposed by the zeolite may stabilized the low-spin state since the cavity and the complex have approximately the same dimensions (11–13 Å).

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Contribution from the Department of Chemistry,
Seton Hall University, South Orange, New Jersey 07079

Intermolecular Energy Transfer between Lanthanide Complexes. 9. Terbium(III) Donor and Europium(III) Acceptor Complexes of Amino Polycarboxylic Acids

Laura Spaulding and Harry G. Brittain*

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The commercial availability of separated lanthanide elements became possible through the use of ion-exchange chromatography, and the best methods employed amino polycarboxylic acids as complexing agents.[1] As a result, a great deal of work has focused on the study of lanthanide complexes with a wide variety of amino polycarboxylate ligands, and in many cases the association constants have been determined for all members of the series.[2,3] In addition, several lanthanide amino polycarboxylate complexes have been used as aqueous NMR shift reagents capable of functioning in alkaline solutions.[4,5] It is known that a ternary amino polycarboxylate hydroxo compound is formed above pH 10[6] and that formation of the hydroxy species interferes with the shift reagent functions of the complexes.[4]

Recently, we reported a series of investigations in which circularly polarized luminescence spectroscopy was employed to study the complexation between chiral amino polycarboxylate ligands and lanthanide ions.[7] At that time, it was noted that a wide variety of spectral changes could be observed when the solution pH was raised from 10 to 13 and that these modifications appeared to be associated with formation of the hydroxo species. In the present work, we have further investigated the complexation phenomena through an examination of the intermolecular transfer among lanthanide amino polycarboxylate complexes. With this spectroscopic technique, one may determine the conditions under which the formation of polynuclear species might take place. Such interactions were noted in several instances.

Experimental Section

Amino polycarboxylate ligands were generally obtained from Eastman or Aldrich and were used as received. The ligands examined were ethylenediaminetetraacetic acid (EDTA), 1,2-propanediaminetetraacetic acid (PDTA), (2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA), ethylenebis(oxyethylenenitrilo)tetraacetic acid (EGTA), and diethylenetriaminepentaacetic acid (DTPA). In addition, 1,3-propanediaminetetraacetic acid (trimethylenedinitrilotetraacetic acid, TMDTA) was furnished by Professor G. R. Choppin (Florida State University).

Stock solutions of Tb(III) and Eu(III) were prepared by dissolving the 99.9% oxides (Research Chemicals) in a stoichiometric amount of 70% $HClO_4$, neutralizing to pH 3.5 with NaOH, and then diluting to the desired volume. Stock solutions of Tb(III) and the amino polycarboxylate ligands were combined in such volumes as to yield an initial Tb(III) concentration of 15 mM and a final ligand:metal ratio of 1:1. In the energy-transfer experiments, microliter amounts of a stock Eu(III) solution were added to 3.0 mL of the Tb/amino polycarboxylate solution and extra ligand was also added to keep the

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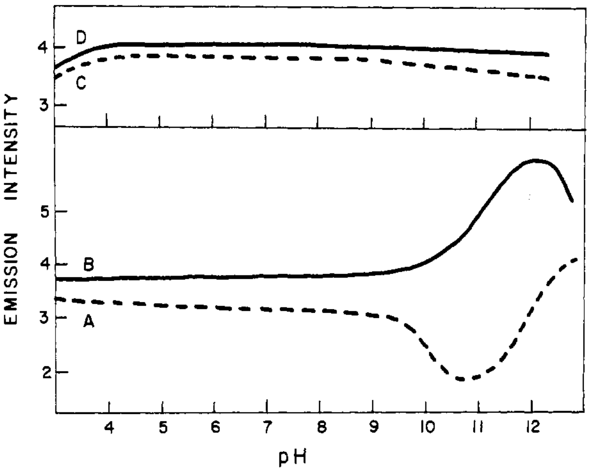

Figure 1. Luminescence intensity of the $^5D_4 \rightarrow {}^7F_5$ emission band system of 1:1 Tb(APC) complexes as a function of pH. Data are shown for a 15 mM Tb(PDTA) solution (trace B), a 15 mM Tb(PDTA) solution containing 1 mM Eu(PDTA) (trace A), a 15 mM Tb(EGTA) solution (trace D), and a 15 mM Tb(EGTA) solution containing 1 mM Eu(EGTA) (trace C). The emission intensity scale is arbitrary.

overall ratio of metal:ligand constant.

The pH of each solution was varied in an incremental fashion between 3.0 and 13.0 (at approximate pH intervals of 0.3), with the emission intensity associated with the $^5D_4 \rightarrow {}^7F_5$ band system (at 545 nm) being measured at each pH value. This band was employed since it exhibited the largest luminescence quantum yield of all the Tb(III) emission bands, but all of the trends to be discussed were obtainable for any of the other Tb(III) transitions. In this manner, plots of emission intenstiy vs. pH were produced for each ligand in the absence of and in the presence of Eu(III) quencher. Thus, it proved to be quite simple to obtain (by interpolation) the emission intensity at given pH values for the entire sequence of amino polycarboxylate ligands.

All emission spectra were recorded on a low-resolution fluorimeter constructed in our laboratory. Samples were excited by the 365-nm output of a 100-W Hg-Xe arc lamp, with this excitation wavelength being selected by a combination of a prism monochromator and UV-transmitting glass filters. This particular wavelength was chosen as we had previously determined that Tb(III) could be efficiently excited at 365 nm but that the efficiency for Eu(III) excitation was much less. The emission was analyzed by the monochromator of a Beckman DU spectrometer and detected by an EMI 9781R photomultiplier tube (S-5 response). All measurements were obtained at room temperature at an emission band-pass of approximately 5 nm. Day-to-day fluctuations in emission intensities were accounted for by referencing all emission intensities to that of a standard piece of uranyl glass.

pH variation in the solutions was effected by the addition of microliter amounts of standard $HClO_4$ or NaOH directly to the fluorescence cuvette. The pH was obtained by using a glass microcombination electrode that could be inserted into the cuvette and read on an Orion 701A pH meter. The system was calibrated daily with phosphate buffers.

Results and Discussion

It has been reported by us[7] and others[8] that the emission intensity of lanthanide amino polycarboxylate complexes (we shall use Ln(APC) as a generic name for these complexes) increases only slightly between pH 3.0 and 10.0. A much more substantial increase in luminescence intensity is noted between pH 10.0 and 12.0, and one generally observes a decrease in emission intensity between pH 12.0 and 13.0. An example of these trends is found in Figure 1. Essentially the same behavior was noted for Tb(EDTA), Tb(PDTA), Tb(HEDTA), and Tb(CDTA). We have concluded[7] that the rise in emission intensity above pH 10.0 is due to formation of ternary hydroxy complexes and that the intensity decrease observed above pH 12.0 is due to hydrolysis of the ternary complex.

On the other hand, the emission intensity of Tb(EGTA), Tb(DTPA), or Tb(TMDTA) exhibits no variation with solution pH, as is shown in Figure 1 for a representative example. Following our working hypothesis, one would predict that these complexes do not form ternary complexes. Such a conclusion is not unreasonable when one considers the steric requirements of these ligands. EGTA and TMDTA contain extra groups between the nitrogen atoms, enveloping the Tb(III) ion to a greater extent and preventing the formation of ternary complexes. DTPA also contains additional groups between the nitrogen atoms, but this ligand also contains extra carboxylate groups. These groups serve to occupy more coordination positions on the Tb(III) ion. That the Tb(EGTA) and Tb(DTPA) compounds do not form ternary complexes with L-aspartic acid has been shown.[9] It has been noted that Ln(TMDTA) compounds do form ternary aquo complexes,[10] and it is equally clear that these could be deprotonated to form a ternary hydroxo species. Nevertheless, the observation that EDTA and TMDTA complexes behave in different fashions indicates that the situation is more complicated than had been originally proposed.[7]

In the preceding papers of this series,[11] we have shown that intermolecular energy transfer from Tb(III) donor complexes to Eu(III) acceptor complexes can be used to determine conditions under which formation of a static donor/acceptor complex might take place. Addition of trace amounts of Eu(APC) to a solution of Tb(APC) generally resulted in quenching efficiencies that were dependent on pH and ligand type. Illustrations of the pH dependence of Tb(III) emission intensities for Tb(APC)/Eu(APC) solutions are also shown in Figure 1.

When APC = EDTA, PDTA, HEDTA, or CDTA, the degree of quenching is found to be quite low between pH 3.0 and 10.0 but very substantial between pH 10.0 and 12.5. On the other hand, the quenching efficiency noted when APC = EGTA, DTPA, or TMDTA is uniformly low at all pH values. To place the results on a more quantitative basis, the data were analyzed by the standard Stern-Volmer equation

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

In eq 1, I_0 is the Tb(III) emission intensity in the absence of Eu(III) quencher, I is the analogous intensity in the presence of Eu(III) quencher having the concentration [Q], and K_{sv}^{ϕ} is the Stern-Volmer quenching constant. Values for the quenching constants obtained from the luminescence data as a function of pH for all seven APC ligands have been collected in Table I.

Luminescence quenching may take place by dynamic (collisional in nature) or static (complex formation between donor and quencher) processes. These can be differentiated through a comparison of emission intensity and emission lifetime quenching studies.[12] We have carried out this procedure in a number of our earlier studies involving Tb(III) and Eu(III) compounds.[11] The Stern-Volmer quenching constants obtained from lifetime data (in a manner analogous to eq 1) are a measure of the dynamic quenching, as static quenching does not affect the observed emission lifetime. For monomeric compounds it follows that Stern-Volmer quenching

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Table I. pH Dependence of the Stern–Volmer Quenching Constants Obtained for the Ln(APC) Compounds

pH	EDTA	PDTA	HEDTA	CDTA	EGTA	DTPA	TMDTA
3.0	135	101	29	83	16	145	25
3.5	167	118	29	83	15	138	53
4.0	169	118	29	83	14	130	66
4.5	171	118	29	74	14	130	58
5.0	143	134	39	74	18	130	44
5.5	99	152	39	70	21	116	21
6.0	83	152	39	65	21	116	10
6.5	114	152	39	65	21	101	10
7.0	147	152	61	67	21	101	10
7.5	123	152	86	67	21	101	10
8.0	157	169	100	80	19	116	10
8.5	221	188	235	119	19	132	21
9.0	303	222	333	175	19	149	11
9.5	294	317	515	395	19	134	45
10.0	394	588	500	609	22	118	112
10.5	638	1204	474	972	22	103	*a*
11.0	1000	1424	410	1024	30	78	*a*
11.5	1340	1412	341	750	30	75	*a*
12.0	1070	858	390	380	30	75	*a*
12.5	706	493	341	195	28	70	*a*
13.0	421	333	302	185	25	65	*a*

[a] Data could not be obtained for the TMDTA complexes above pH 10.0 as a precipitate formed around pH 10.5.

Table II. Formation Constants (K_c) of the Tb(APC)/Eu(APC) Polynuclear Compounds

pH	EDTA	PDTA	HEDTA	CDTA
9.0	159	85	293	98
9.5	150	175	472	311
10.0	244	429	457	517
10.5	475	1005	431	667
11.0	816	1214	369	718
11.5	1137	1201	301	453
12.0	882	682	349	296
12.5	539	340	301	118
13.0	270	190	262	108

constants calculated from emission intensity and lifetime measurements must be equal. When these are not equal, the presence of static quenching is indicated.

It can easily be shown[13] that when both static and dynamic quenching mechanisms are operative, the formation constant of the donor/acceptor complex is calculable:

$$\frac{I_0 - I}{I} = (K_{sv}^{\tau} + K_c)[Q] + K_{sv}^{\tau}K_c[Q]^2 \qquad (2)$$

Formation constants were calculated in this manner for the EDTA, PDTA, CDTA, and HEDTA complexes in the pH regions where the presence of static quenching was indicated, and these results have been collected in Table II.

The results presented in the tables enable complexation trends to be discussed. Below pH 10.0, the quenching constants indicate that all Ln(APC) complexes are monomeric. When APC = EGTA, DTPA, or TMDTA, no evidence for the existence of polynuclear species exists. However, for APC = EDTA, PDTA, or CDTA the complexes become extensively associated between pH 10.0 and 11.5. Above these pH values, the degree of association is found to decrease. These trends are exhibited by the HEDTA complexes, but with this compound the association process begins at significantly lower pH values. One might have anticipated that the HEDTA complexes would have exhibited the largest degree of intermolecular association, as these complexes form neutral species when the ligand is fully deprotonated. Instead, the formation values of Table II indicate that the situation for Ln(HEDTA) complexes is closer to that of Ln(CDTA). One might then infer that the steric nature of the ligands (dictated by the cyclohexane ring of CDTA or the dangling hydroxylethyl group of HEDTA) plays an important role in determining the extent of polynuclear association.

Therefore, we conclude that the increase in luminescence intensity noted between pH 10.0 and 12.0 for certain APC ligands is due to the formation of polymeric species, undoubtably held together by μ-hydroxy bridges. These polynuclear species only form when the APC ligand cannot prevent the formation of ternary complexes, and this situation exists when the ligand is incapable of filling a sufficient amount of space on the lanthanide ion coordination sphere. These results imply that the failure as aqueous NMR shift reagents of certain lanthanide amino polycarboxylate complexes (under conditions of high pH) is a direct result of the polymeric nature of the species formed when the solution pH exceeds 10.0. These materials would be coordinatively saturated and hence unable to form adducts with other substrates.

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