

Figure 6. MoS<sub>2</sub> amorphous and poorly crystalline X-ray patterns.

In general there is an increasing tendency to stabilize lower crystallinity as one proceeds from group 4B to group 7B. Thus, MoS<sub>2</sub> is completely amorphous as prepared at room temperature and poorly crystalline when treated at 400 °C in H<sub>2</sub>/H<sub>2</sub>S. X-ray patterns are indicated schematically in Figures 5 and 6 for TiS<sub>2</sub> and MoS<sub>2</sub>. The poorly crystalline X-ray pattern is very similar to that reported by Wildervanck and Jellinek<sup>10</sup> for MoS<sub>2</sub> prepared via decomposition of MoS<sub>3</sub> at 400 °C. However, the structure of amorphous MoS<sub>2</sub> below 400 °C has not been studied and is the subject of a future report.<sup>11</sup> TiS<sub>2</sub> and VS<sub>2</sub> tended to show slightly less amorphous X-ray patterns at room temperature. TiS<sub>2</sub> was completely crystalline when treated at 400 °C but again extreme care had to be taken to exclude oxygen due to the high stability of TiO<sub>2</sub>.

### Conclusion

By combining chalcogenide reagents more reactive (ionic) than H<sub>2</sub>S (or by activating H<sub>2</sub>S with ammonia or amines) with transition-metal salts in nonhydroxylic medium under ambient conditions, it is possible to prepare a broad-ranging series of transition-metal chalcogenides. Since most of these compounds have heretofore only been accessible via high-temperature procedures, in addition to offering a decided economical

advantage due to rapid low-temperature procedures, this new route affords products showing distinctly different properties in many cases. These arise from surface area, crystallinity, particle size, phase, and stoichiometric characteristics resulting from the mild kinetic conditions of the preparation. Altogether new phenomena such as liquid and solid dispersions have also been observed, leading to many interesting avenues of future research for this group of materials. In addition, the structure and properties of the amorphous transition-metal disulfides will be the subject of intense investigation in the near future.

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**Registry No.** TiS<sub>2</sub>, 12039-13-3; ZrS<sub>2</sub>, 12039-15-5; HfS<sub>2</sub>, 18855-94-2; VS<sub>2</sub>, 12166-28-8; MoS<sub>2</sub>, 1317-33-5; NbS<sub>2</sub>, 12136-97-9; NH<sub>3</sub>, 7664-41-7; H<sub>2</sub>S, 7783-06-4; TiCl<sub>4</sub>, 7550-45-0; Li<sub>2</sub>S, 12136-58-2; NbCl<sub>5</sub>, 10026-12-7.

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## Intermolecular Energy Transfer between Lanthanide Complexes in Aqueous Solution. 1. Transfer from Terbium(III) to Europium(III) Complexes of Pyridinecarboxylic Acids

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Lanthanide complexes of picolinic, nicotinic, and dipicolinic acids have been studied using emission spectroscopy, lifetime of emission measurements, and pH titrations. In addition, energy transfer from Eu<sup>3+</sup> to Tb<sup>3+</sup> has been investigated. All of these measurements enable a description of the solution environment about the lanthanide ion when it is complexed to each of the pyridinecarboxylic acids. At high pH, the lanthanide complexes of dipicolinic acid are monomeric and discrete but probably are somewhat associated at low pH values. Complexes of picolinic acid are probably associated at all pH values. It was also concluded that picolinic acid can act as a bidentate ligand, that dipicolinic acid can act as a bidentate ligand at low pH and terdentate at high pH, and that nicotinic acid only functions as a monodentate ligand. The energy-transfer process was found to require the presence of mixed Tb<sup>3+</sup>-Eu<sup>3+</sup> complexes and polymeric formation.

### Introduction

Various lanthanide ions are finding widespread use as spectroscopic probes of calcium binding sites in proteins and enzymes, since the calcium ion itself does not possess any useful spectroscopic properties. For instance, Tb(III) has been found to substitute for Ca(II) in a wide variety of proteins and the resulting sensitized emission enables the determination of important molecular properties.<sup>1</sup> In an effort to gain more information regarding the binding of lanthanides by proteins, many workers have undertaken studies of the complexation of lanthanide ions by carboxylic and amino acids in solution. These studies have included pH titrations,<sup>2</sup> difference absorption spectroscopy,<sup>3</sup> circular dichroism spectroscopy,<sup>4</sup> and circularly polarized emission spectroscopy.<sup>5</sup> The formation

constants for lanthanide ions and a wide variety of carboxylic and amino acids have been reviewed,<sup>6</sup> as well as a number of solid-state crystal structures.<sup>7</sup>

It is well-known that energy may be transferred to and from lanthanide ions in solution.<sup>8</sup> Lanthanide ion emission is enhanced by organic molecules whose triplet levels lie just above those of the metal ion, and this emission enhancement seems to require some complexation of the lanthanide ion and the organic molecule.<sup>9-11</sup> Detailed studies have been made of the energy transfer between europium and terbium in dimethyl sulfoxide<sup>12</sup> and between europium and terbium β-diketonates in a variety of solvents.<sup>13</sup> Some energy-transfer studies involving lanthanide carboxylates have appeared,<sup>5a,b</sup> but these results have not received as full an interpretation as possible

due to the uncertain nature of the lanthanide stoichiometry.

In this report, the energy transfer from terbium to europium in the presence of different pyridinecarboxylic acids is studied. The acids used were picolinic acid (2-pyridinecarboxylic acid, or PIC), nicotinic acid (3-pyridinecarboxylic acid, or NIC), and dipicolinic acid (2,6-pyridinecarboxylic acid, or DPA). DPA complexes of lanthanides are unusual in that only very strong 3:1 ligand-to-metal complexes are formed,<sup>14</sup> the geometry of these complexes is well-known<sup>15</sup> (a nearly exact  $C_3$  axis is maintained both in solution and in the solid state), and the complexes are known to remain monomeric in solution.<sup>15</sup> The emission of  $Tb(DPA)_3$  complexes at room temperature in fluid solution is very strong compared to the emission of the free ion under similar conditions, and this enhanced emission forms the basis for a fluorometric determination of terbium at the nanomolar level.<sup>16</sup>

It is clear that the energy-transfer process must depend on the nature of the complexes in solution. For instance, Neilson and Shepherd found that dimeric complexes between europium and terbium acetylacetonates were required before energy could be transferred from the terbium to the europium.<sup>13a,b</sup> In this paper, the energy transfer in complexes of dipicolinic acid is contrasted with the energy transfer in the more labile picolinic acid complexes. No energy-transfer work was possible with nicotinic acid complexes, since neither terbium nor europium was found to emit when bound to nicotinic acid.

### Experimental Section

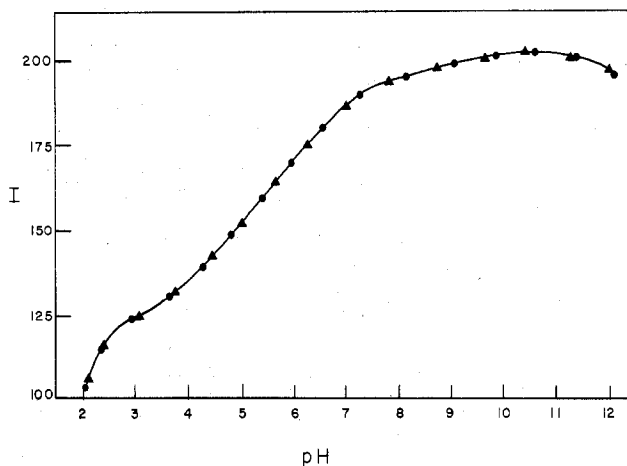
$TbCl_3 \cdot 6H_2O$  and  $EuCl_3 \cdot 6H_2O$ , 99.9% pure, were obtained from Alfa Inorganics, while picolinic, nicotinic, and dipicolinic acids were obtained from Eastman. All reagents were used as obtained. The concentration of  $Tb^{3+}$  in all solutions was held at  $2 \times 10^{-3}$  M, and ligand concentrations of  $1 \times 10^{-2}$  and  $2 \times 10^{-2}$  M (corresponding to 5:1 and 10:1 ligand-to-metal ratios) were used to determine the effect of changing the ligand concentration. The 1:5 and 1:10  $Eu^{3+}$ /ligand stock solutions were prepared having a europium concentration of  $2 \times 10^{-2}$  M, and these solutions were added in 10- $\mu$ L increments to 3.0 mL of the  $Tb^{3+}$ /ligand solution already in the fluorescence cuvette. In none of the cases was the final  $Eu^{3+}$  concentration greater than  $3 \times 10^{-4}$  M. The pH of all  $Tb^{3+}$ /ligand and  $Eu^{3+}$ /ligand solutions was adjusted with KOH.

All emission spectra were measured using an apparatus constructed in this laboratory. The excitation source was a 200-W high-pressure Hg-Xe lamp, whose output was filtered by a pair of Corning black-glass UV filters and a 0.1 M solution of  $CuSO_4$ . This filter arrangement passes all light having wavelengths between 300 and 390 nm. Light emitted by the sample is collected at  $90^\circ$  to the exciting beam and is passed immediately into the emission monochromator, which is a dual-prism device taken out of a Perkin-Elmer 4000A spectrophotometer. The detector is an EMI 9798B photomultiplier tube with S-20 response. The excitation beam was mechanically chopped at 30 Hz and the signal from the detector was processed by a Princeton Applied Research Model 128A lock-in amplifier and subsequently recorded on a strip-chart recorder.

All measurements were made at room temperature using an emission bandwidth of 5 nm. Most of the excitation energy was centered about 365 nm and it was found that a  $3 \times 10^{-4}$  M solution of  $Eu^{3+}$  did not show any measurable emission when complexed with any of the ligands in this study.  $Tb^{3+}$ /ligand solution emitted strongly, however, and  $Eu^{3+}$  emission was easily observed when  $Tb^{3+}$ - $Eu^{3+}$  energy transfer was found to take place. All of the solutions were optically dilute at 365 nm, which enabled Stern-Volmer calculations to be made.

Lifetime measurements were obtained by exciting the samples with a pulsed xenon flash lamp (Model FY-5D, EG & G, Inc.) and following the decay curves on a Techtronix 561-A oscilloscope. In all cases, the lifetime of the emitting species was confirmed using phase-resolved phosphorimetry.<sup>17</sup>

pH measurements were taken on a Fisher Accumet 144 pH meter using a standard glass combination electrode. The pH titrations were carried out by adding microliter quantities of a standard KOH solution to 3 mL of the  $Tb^{3+}$ /ligand solution (which was 0.1 M in KCl to ensure constant ionic strength) already in a fluorescence cuvette. PH de-



**Figure 1.** Emission intensity of the  ${}^5D_4 \rightarrow {}^7F_5$  transition of  $Tb^{3+}/DPA$  as a function of pH. Data for 1:5 (●) and 1:10 (▲)  $Tb^{3+}/DPA$  solutions are shown; the intensity units are arbitrary.

pendence of the emission was obtained by measuring the intensity of  $Tb^{3+}$  emission at 545 nm after each addition of KOH.

### Results

In aqueous media at room temperature, a  $2 \times 10^{-3}$  M solution of  $Tb^{3+}$  does not show measurable emission upon excitation at 365 nm. Addition of a fivefold or a tenfold excess of nicotinic acid does not induce any emission changes, but addition of either picolinic or dipicolinic acid results in greatly enhanced  $Tb^{3+}$  emission. For  $Tb^{3+}$  four distinct emission bands are observed, corresponding to the  ${}^5D_4 \rightarrow {}^7F_6$ ,  ${}^7F_5$ ,  ${}^7F_4$ , and  ${}^7F_3$  transitions. These are found at 491, 545, 585, and 621 nm, respectively. Only the  ${}^5D_4 \rightarrow {}^7F_6$  and  ${}^5D_4 \rightarrow {}^7F_5$  transitions have appreciable intensity, with the transition to the  ${}^7F_5$  level being the most intense.

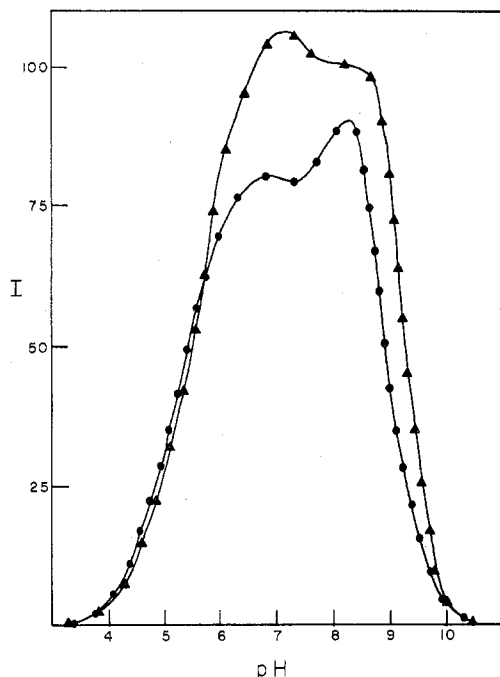
The emission intensities of the  $Tb^{3+}/DPA$  and  $Tb^{3+}/PIC$  complexes were also found to depend critically on the pH of the solution. In Figure 1, the intensity of  $Tb^{3+}$  emission in 1:5 and 1:10  $Tb^{3+}/DPA$  solutions is shown as a function of pH. No differences were found in emission intensity for the 1:5 and 1:10 terbium-to-DPA ratios, nor was any expected since it is known that  $Tb^{3+}$  will resist the addition of more than three molecules of DPA.<sup>14</sup> Strong emission is observed at all pH values with only a gradual rise in emission intensity being observed as the pH was raised. Strong emission is observed even at pH values greater than 12 which indicates that the  $Tb^{3+}/DPA$  complex is very resistant toward base hydrolysis.

The behavior of  $Tb^{3+}/PIC$  emission with pH was found to be very different from that of  $Tb^{3+}/DPA$ , as the results in Figure 2 illustrate. The emission intensity is at a maximum at pH values of 7 and 8.5, but the intensity ratio of these is very dependent on pH and changes in passing from the 1:5 to 1:10 ratio.

A second effect of ligand concentration is seen in comparison of the relative intensities of the 1:5 and 1:10  $Tb^{3+}/PIC$  solutions; doubling the picolinic acid concentration increases the  $Tb^{3+}$  emission by about 25% in the 7-9 pH region.

Terbium lifetime studies also provide information regarding the complexation of terbium ions in solution, and these have been summarized in Table I. No difference in  $Tb^{3+}$  lifetime was observed in the  $Tb^{3+}/DPA$  solutions upon changing the metal-to-ligand ratio from 1:5 to 1:10, but large differences were observed in lifetime as the pH of the solution was changed. An unusually long lifetime of 1725  $\mu$ s was found even at the very acidic pH of 2.5 and the lifetime rose very rapidly to 4200  $\mu$ s by the time a pH of 8.0 was reached.

The emission lifetime of terbium in  $Tb^{3+}/PIC$  complexes also exhibits a dependence on pH, but a dependence upon ligand concentration exists as well. As the data in Table I



**Figure 2.** Emission intensity of the  ${}^5D_4 \rightarrow {}^7F_5$  transition of  $Tb^{3+}/PIC$  as a function of pH. Data for 1:5 ( $\bullet$ ) and 1:10 ( $\blacktriangle$ ) solutions are shown. The intensity units are arbitrary but are on the same scale as Figure 1.

**Table I.** Terbium Emission Lifetimes<sup>a</sup> as a Function of Ligand and pH

pH	$Tb^{3+}/DPA$		$Tb^{3+}/PIC$	
	1:5	1:10	1:5	1:10
2.5	1725			
3.0	1940			
4.0	2300		510	510
5.0	2890		530	575
6.0	3520		545	640
7.0	4100		600	715
8.0	4200		720	810
9.0	4200		1050	1260
10.0	4200			
11.0	4175			
12.0	4150			

<sup>a</sup> All lifetimes are in  $\mu s$  and carry a deviation of  $\pm 25 \mu s$ .

show, lifetimes of the 1:5 solutions are always shorter than those of 1:10 solutions at corresponding pH values. As the pH is raised, the terbium lifetime becomes progressively longer until precipitation of insoluble terbium complexes begins at a pH of 10 and all emission is lost. At no point, however, did the lifetime of the  $Tb^{3+}/PIC$  complexes approach the values observed for the  $Tb^{3+}/DPA$  complexes.

To further aid the characterization of the  $Tb^{3+}/ligand$  complexes, pH titrations of these complexes were carried out at constant ionic strength. A very sharp and clear equivalence point was observed after the addition of 1 equiv of base (occurring at a pH of about 7.25) and no other inflections were noted. No difference in titration curves was found in titrating 1:5 and 1:10  $Tb^{3+}/DPA$  solutions with KOH. The pH titration of 1:5 and 1:10 solutions of  $Tb^{3+}/PIC$  yielded some important differences. An inflection point was again noted after the addition of 1 equiv of base, but unlike the DPA titration this equivalence point was preceded by a gradual rise in pH.

Shortly after this first inflection, a second was noted and this second rise in pH was accompanied by the beginning of terbium precipitation as the hydroxide (this process is complete by a pH of 11). The 1:10 solutions are slightly more resistant

**Table II.** Stern-Volmer Quenching Constants and Bimolecular Rate Quenching Constants for  $Tb^{3+}/PIC$  as a Function of pH<sup>a</sup>

pH	$K_{sv}^b$	$k_q^b$	$K_{sv}^c$	$k_q^c$
5.2	$1.0 \times 10^3$	$2.0 \times 10^6$	$3.9 \times 10^2$	$7.4 \times 10^5$
6.2	$1.6 \times 10^3$	$2.8 \times 10^6$	$4.9 \times 10^2$	$7.5 \times 10^5$
8.3	$2.4 \times 10^3$	$3.0 \times 10^6$	$2.5 \times 10^3$	$2.6 \times 10^6$
9.0	$1.2 \times 10^3$	$1.1 \times 10^6$	$7.7 \times 10^2$	$6.1 \times 10^5$

<sup>a</sup> All values of  $k_{sv}$  carry an error of  $0.2 \times 10^2$ . <sup>b</sup> Data are for 1:5  $Tb^{3+}/PIC$  solutions. <sup>c</sup> Data are for 1:10  $Tb^{3+}/PIC$  solutions.

toward hydrolysis than are the 1:5 solutions, since 1.3 equiv of base causes precipitation in a 1:5 solution, while 1.5 equiv is required for a 1:10 solution. No precipitation at any pH was noted in the DPA titrations.

At very low pH values, addition of  $Eu^{3+}/DPA$  to a solution of  $Tb^{3+}/DPA$  results in quenching of the  $Tb^{3+}$  emission intensity, a shortening of the  $Tb^{3+}$  emission lifetime, and the appearance of  $Eu^{3+}$  emission. The extent of quenching is very much less by the time a pH of 4.5 is reached (corresponding to the start of a new carboxylic acid proton ionization), and no transfer at all is observed at higher pH values. Stern-Volmer quenching constants may be obtained from the standard equation

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

where  $I_0$  is the light intensity in the absence of quencher,  $I$  is the intensity with quencher present,  $[Q]$  is the molar concentration of quencher, and  $K_{sv}$  is the Stern-Volmer quenching constant. Bimolecular rate constants for quenching are obtained from

$$k_q = K_{sv}/\tau_0 \quad (2)$$

At a pH of 2.5 the value of the Stern-Volmer constant was found to be  $4.3 \times 10^2$  (with  $k_q = 2.4 \times 10^5$ ), but by the time a pH of 4.5 was reached the value of  $K_{sv}$  had decreased to  $9.5 \times 10^1$  (having  $k_q = 3.7 \times 10^4$ ). Beyond this pH, no energy transfer was observed and all  $Eu^{3+}$  emission resulting from the transfer of energy by  $Tb^{3+}$  has also vanished.

The quenching of  $Tb^{3+}/PIC$  turned out to be very different from the DPA case. No quenching results could be obtained below a pH of 5 due to the low  $Tb^{3+}$  emission yield of the  $Tb^{3+}/PIC$  complex in this region. Values of  $K_{sv}$  and  $k_q$  at corresponding pH values for 1:5 and 1:10  $Tb^{3+}/PIC$  solutions are found in Table II and consistently indicated that energy transfer was less efficient in the solutions having the higher ligand-to-metal ratio. The energy transfer is less efficient at the low pH of 5 but becomes quite efficient immediately before and after the ionization of the carboxylic acid proton on the PIC ligand. In no cases, however, did the quenching approach the low values observed for the DPA ligand, and it is clear that energy transfer in the  $Tb^{3+}/PIC/Eu^{3+}$  system is much more efficient than in the  $Tb^{3+}/DPA/Eu^{3+}$  system.

## Discussion

Consideration of all the experimental details present in the titration curves, pH dependence of emission, and emission lifetime results enables certain conclusions to be drawn regarding the nature of  $Eu^{3+}$  and  $Tb^{3+}$  complexes of pyridinecarboxylic acids in solution. It has been established<sup>18</sup> that the predominant mode of quenching of the emission of lanthanide ions in solution is by the high-energy  $-OH$  vibrations of the solvent. Enhancement of  $Tb^{3+}$  emission therefore requires protection of the metal from the solvent, and the more effective the ligand is in insulating the metal the stronger the observed emission will be. This prediction has been verified for europium chelates of  $\beta$ -diketones.<sup>20</sup> Emission intensity measurements then afforded a probe into the inner coordination sphere of the  $Tb^{3+}$  and  $Eu^{3+}$  ions. If the solution environment about these lanthanide ions can be described with

reasonable certainty, then the energy-transfer data may also be interpreted and used as yet another probe of the extent of association among these and other lanthanide systems.

It is already known that  $Tb^{3+}$ /DPA complexes form in a 1:3 stoichiometry, the formation constants of these are large,<sup>14</sup> and the complexes remain monomeric in solution.<sup>15</sup> All of the data reported in this paper are in agreement with these previous conclusions. The titration curve of  $Tb^{3+}$ /DPA is indicative of very strong metal-ligand binding in that a single, well-defined equivalence point was observed. One would have expected to see an equivalence point after the addition of 2 equiv of base since DPA possesses two ionizable protons, but the inflection occurred after the addition of only 1 equiv. In Figure 1, it was noted that strong  $Tb^{3+}$  emission was observed in  $Tb^{3+}$ /DPA complexes even at a pH as low as 2. Since the aquo ion of  $Tb^{3+}$  does not emit measurably at the concentrations used here ( $2 \times 10^{-3}$  M), one is forced to conclude that the  $Tb^{3+}$  ion is *already* bound to one of the carboxylic acid groups of DPA even at the low pH of 2.

The lifetime data of Table I support this conclusion. It is known that in aqueous acidic solution, the emission lifetime of an uncomplexed  $Tb^{3+}$  ion is 400  $\mu$ s.<sup>18</sup> Complexation of a  $Tb^{3+}$  ion has been shown to result in an increased bath in the emission lifetime and in the emission intensity,<sup>19</sup> at a pH of 2.5 the lifetime of  $Tb^{3+}$  in  $Tb^{3+}$ /DPA was found to have increased to 1725  $\mu$ s and strong  $Tb^{3+}$  emission was observed. It therefore seems reasonable to assign the equivalence point of the pH titration to ionization of the *second* DPA carboxylic acid proton and not to the first. Since  $pK_{a1}$  of DPA is 4.53 and  $pK_{a2}$  is 2.09,<sup>21</sup> it is to be expected that both carboxylic acid protons will be ionized by the time a pH of 7 is reached. The emission intensity of  $Tb^{3+}$ /DPA in the pH region of 7-12 shows very little variation, and the  $Tb^{3+}$  emission lifetime also remains constant at 4200  $\mu$ s. The constant emission intensity and lifetime in this pH region indicate that little change takes place in the inner coordination sphere of the  $Tb^{3+}$  ion as the pH is raised.

Nothing exists in the literature regarding the extent of either ligation or molecular emission of  $Tb^{3+}$ /PIC complexes, but the data presented in this paper (with suitable comparison to  $Tb^{3+}$ /DPA complexes) allow some conclusions to be drawn. No emission is observed at low pH, but after a pH of 5 is passed strong  $Tb^{3+}$  emission is then seen. The titration curve indicates that a carboxylic acid proton is being ionized in this region and that this ionization is complete by the time a pH of 8.5 is reached. Immediately following this completion of ionization, hydrolysis of the complex begins and a precipitate of terbium hydroxide is observed (at a pH of 11). As seen in Figure 2, after a pH of 9 is reached the emission intensity drops rapidly and no emission is observed beyond a pH of 10, so it is apparent that hydrolysis of the  $Tb^{3+}$ /PIC complex destroys the environment necessary for strong  $Tb^{3+}$  emission.

The lifetime data of Table I are equally instructive. At a pH of 4 the PIC just begins to bind to the  $Tb^{3+}$  ion, and a 100- $\mu$ s increase in  $Tb^{3+}$  emission lifetime is seen. By the time a pH of 9 is reached, the lifetime has increased by about 600  $\mu$ s but never reaches the 4000- $\mu$ s lifetime associated with the DPA complexes. Throughout the study of lifetime dependence on pH, it was noted that longer lifetimes (and also more intense emission) were observed for 1:10  $Tb^{3+}$ /PIC solutions compared to corresponding 1:5 solutions, which indicates that a more favorable situation exists for metal-ligand binding at higher ligand ratios. This type of behavior may be contrasted with the  $Tb^{3+}$ /DPA results in which identical results for 1:5 and 1:10 metal-to-ligand ratios were obtained. It seems clear from these observations that  $Tb^{3+}$ /PIC complexes do not form with as definite metal-to-ligand ratios as do the  $Tb^{3+}$ /DPA complexes. This conclusion suggests that  $Tb^{3+}$ /PIC complexes

in solution are probably polymeric in nature unlike the discrete  $Tb^{3+}$ /DPA complexes.

It is also interesting to note that the  $Tb^{3+}$  emission lifetime in  $Tb^{3+}$ /PIC solutions at a pH of 9 is approaching the lifetime observed for  $Tb^{3+}$  in  $Tb^{3+}$ /DPA complexes at very low pH values. This observation suggests that the metal-ligand binding behavior is probably somewhat similar in both cases, a conclusion that is supported by the emission intensity data of Figures 1 and 2. In the DPA case it is believed that the  $Tb^{3+}$  ion is already bound to one carboxylic acid group even at a pH of 2, and by a pH of 9 the PIC ligand has had its sole carboxylic acid proton ionized providing therefore the same binding picture for the  $Tb^{3+}$  ion in each case.

It is concluded that bidentate binding by a pyridine-carboxylic acid ligand is probably necessary to observe strong  $Tb^{3+}$  emission (and  $Tb^{3+}$  binding) in these complexes, since nothing will prevent NIC from acting as a monodentate ligand and the data presented here show that mere monodentate binding does not provide the necessary environment for  $Tb^{3+}$  emission.  $Tb^{3+}$  emission is only found in  $Tb^{3+}$ /PIC complexes after the carboxylic acid proton is ionized and bidentate binding can take place. At low pH values,  $Tb^{3+}$  apparently is bound to DPA in a bidentate fashion, since both strong emission and a long  $Tb^{3+}$  lifetime are observed in  $Tb^{3+}$ /DPA complexes. After 1 equiv of base is added, the DPA ligand becomes terdentate, and greatly enhanced emission, very long  $Tb^{3+}$  lifetimes, and strong resistance toward hydrolysis are all observed.

Now that the solution environments of  $Tb^{3+}$  in the various pyridinecarboxylic acid complexes have been reasonably explained, it becomes possible to interpret the energy-transfer data and to refine this type of investigation into yet another probe of lanthanide solution chemistry. At low pH values, addition of  $Eu^{3+}$  to a solution of  $Tb^{3+}$ /DPA results in a quenching of  $Tb^{3+}$  emission as shown by the Stern-Volmer data. When the pH is raised, the extent of quenching drops rapidly and no energy is transferred in the pH region where the DPA ligand binds in a terdentate fashion. Since the energy transfer from terbium to europium does not take place at high pH where the DPA complexes are discrete and monomeric but does take place at low pH where the complexes are somewhat associated, it is probable that in these systems the energy-transfer process requires the presence of mixed  $Tb^{3+}$ - $Eu^{3+}$  complexes. This requirement has previously been noted in the energy transfer of acetylacetonate complexes.<sup>13a,b</sup>

Energy transfer in  $Tb^{3+}$ /PIC complexes depends both on pH and on the ligand-to-metal ratio, as was shown in Table II. The extent of energy transfer is greater in solutions having a 1:5  $Tb^{3+}$ /PIC composition compared to those having a 1:10 ratio. Since the data presented indicated that the PIC complexes are associated in solution, the energy-transfer data may be interpreted to show that a greater extent of mixed  $Tb^{3+}$ - $Eu^{3+}$  complexes exists in solutions having a lower ratio of ligand present.

It is dangerous in lanthanide solution chemistry to speak of one metal-ion geometry existing at a given pH. In any given solution several species may actually be present, although it is to be expected that one form might prevail over others for a set of conditions. Nevertheless, emission spectroscopy, lifetime studies, pH titrations, and energy-transfer studies can contribute to our meager knowledge of lanthanide solution chemistry. The energy-transfer studies appear promising in describing the nature of polymeric complexes in solution, since the energy-transfer process in these carboxylic acid complexes appears to require the presence of polymeric complexes containing  $Eu^{3+}$  and  $Tb^{3+}$  pairs. Further work along these lines is indicated and is being currently carried out in this laboratory.

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Registry No. PIC, 98-98-6; NIC, 59-67-6; DPA, 499-83-2; Eu, 7440-53-1; Tb, 7440-27-9.

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## Electron Transfer. 36. Reductions of Pentaamminecobalt(III) Derivatives of Dinitrophenols<sup>1</sup>

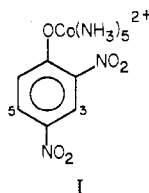
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The 2,4- and 2,5-dinitrophenylato complexes of  $(\text{NH}_3)_5\text{Co}^{\text{III}}$ , the first phenoxide derivatives of this type to be reported, are reduced by  $\text{Ru}(\text{NH}_3)_6^{2+}$  and by  $\text{V}^{2+}$  at the Co(III) center and by  $\text{Cr}^{2+}$  and  $\text{Eu}^{2+}$  both at the nitro substituents and at Co(III). The  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions are  $10^2$ – $10^4$  times as rapid as those of the carboxylato complexes of  $(\text{NH}_3)_5\text{Co}^{\text{III}}$ , a difference attributed to the relative ground-state instability of the nitro complexes, which is reflected also in the ease with which they undergo aquation. Specific rates for reduction by  $\text{V}^{2+}$  exceed the substitution-controlled limit for inner-sphere reactions with dipositive oxidants, indicating that a major path for these reductions is outer sphere. Reactions with  $\text{Eu}^{2+}$  and  $\text{Cr}^{2+}$  proceed at specific rates in excess of  $10^3 \text{ M}^{-1} \text{ s}^{-1}$ , with a ratio of ligand/cobalt(III) reduction about 3 and independent of the reductant used and isomer taken. The very rapid release of  $\text{Co}^{2+}$ , which continues after the nitro groups have been reduced to the nitroso and azo levels, points to a chemical mechanism in which one-electron reduction of a ring substituent to a radical-cation intermediate precedes internal electron transfer to cobalt(III). It is further suggested that the predominant path in each of these instances is initiated by inner-sphere attack at the 2 substituent. The ratio  $k_V/k_{\text{Ru}}$  for the 2,4 complex is approximately 3, in contrast to a ratio  $<0.4$  for "normal" outer-sphere oxidants.<sup>8a,9</sup> This reversal in reactivity is consistent with preliminary outer-sphere electron transfer from  $\text{V}^{2+}$  to a nitro group.

The array of varied organic ligands which have been reported to mediate electron transfer to bound cobalt(III) does not yet include substituted phenoxides,<sup>2</sup> an omission which can be attributed, in large part, to preparative difficulties. The ease with which phenols and their anions generally undergo oxidation complicates attempts to attach them to strongly oxidizing metal ions. Moreover, the high basicities of most phenoxides would be expected to lead to serious side reactions in ligation procedures involving those metals forming slightly soluble hydroxides.

These undesirable features can presumably be minimized by using phenols bearing strongly electron-withdrawing substituents. In 1974, Fan<sup>3</sup> described the preparation of the  $(\text{NH}_3)_5\text{Co}^{\text{III}}$  complex of 2,4-dinitrophenol, I, the first phe-



nol-coordinated derivative of this type reported. The present communication deals with the reactions of this complex, and those of its 2,5 isomer, with several dipositive reducing agents. As might be anticipated from earlier studies of the reductions of nitrobenzoato complexes,<sup>3,4</sup> reactions with  $\text{Cr}^{2+}$  and  $\text{Eu}^{2+}$  are complicated by reduction of the nitro group, but reactions with the more weakly reducing species  $\text{V}^{2+}$  and  $\text{Ru}(\text{NH}_3)_6^{2+}$  have been found to be more straightforward.

### Experimental Section

**Materials.** Lithium perchlorate,<sup>5</sup> carbonatopentaamminecobalt(III) perchlorate,<sup>3</sup> and solutions of chromium(II),<sup>6</sup> europium(II),<sup>7</sup> vanadium(II),<sup>8</sup> and hexaammineruthenium(II)<sup>9</sup> were prepared as described. Organic ligands (Aldrich products) were used as received.

**Preparation of the Complexes.** In a modification of the method of Fan,<sup>3</sup> 0.010 mol of the dinitrophenol was dissolved in 90 mL of absolute methanol, and to this mixture was added 400 mg of finely ground carbonatopentaamminecobalt(III) perchlorate. The mixture was refluxed for 2.5 h with stirring and then cooled to 0 °C. To the red solution was carefully added 1.2 mL of 12 M  $\text{HClO}_4$ , and the preparation was kept at 0 °C an additional 30 min. The mixture was then shaken with two 300-mL portions of ether, the precipitated complex filtered off, and the ether extracts discarded. The precipitate