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Effect of pH on the Emission Properties of Aqueous Tris(2,6-dipicolinato)terbium(III) Complexes*

T. K. TROUT**, J. M. BELLAMA

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, U.S.A.

R. A. FALTYNEK, E. J. PARKS and F. E. BRINCKMAN

Ceramics and Polymers Divisions, National Bureau of Standards, Gaithersburg, MD 20899, U.S.A.

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There have been many documented applications of lanthanide (Ln^{3+}) ion complexes which incorporate luminophores, such as pyridine-2,6-dicarboxylic acid, to studies in both chemical and biological systems [1–4]. The use of Ln^{3+} ions as structural probes in various matrices has necessitated a greater understanding of the properties and structural features of these complexes under dissimilar conditions. In general, these complexes are considered labile [5, 6]. In the specific case of pyridine-2,6-dicarboxylic acid (dipicolinic acid, H_2DPA), the nature of the association between a lanthanide ion and the tridentate ligand can be expected to vary with pH, since the free ligand can exist as a neutral (H_2DPA), monoanionic ($HDPA^-$) or dianionic (DPA^{2-}) species. In this work, the lability of these complexes is demonstrated by correlating changes noted in the photostability of the luminescence of aquated tris-(2,6-dipicolinato)terbium complexes upon variation of solution pH to the pK_a values of both the free and metal-coordinated ligand.

Experimental†

Materials

Aqueous solutions of the complexes ($[Tb^{3+}] = 1.0 \times 10^{-3}$ M) were prepared by combining stock solutions of $Tb(NO_3)_3 \cdot 5H_2O$ (Alfa Products, Morton Thiokol, as received) with stock solutions of DPA^{2-} (Aldrich Chemical Co., as received) to control the molar ratios of the ligand and metal. The DPA^{2-} stock solution was prepared by dissolving H_2DPA in aqueous sodium hydroxide solutions and adjusting the pH to about 9 with 6 M HNO_3. After combining the Tb^{3+} with the DPA^{2-}, the pH of each sample was initially adjusted to the 6.4–8.0 range.

Procedure

All emission data were obtained using a Zeiss Universal epifluorescence microscope [7] equipped with a high pressure mercury arc lamp as the excitation source, excitation and emission monochromators with 1 nm resolution capabilities and a PMT detector for intensity measurements. The reader is directed to ref. 8 for a thorough description of the microspectrofluorimeter. Luminescence intensities of the aqueous solutions were measured with the samples in an essentially fixed position, using a depression slide with an optical quartz cover slip as the sample holder. The depression slide was placed under a quartz objective (magnification 10X) through which passed the excitation beam of the high pressure mercury lampsource. Photostabilities of the emissions of solutions were measured during 30-s exposure to an excitation beam of 272 nm, with a bandpass of 20 nm. All relative emission intensity measurements were made at the approximate emission maximum for the complex, 545 nm. The pH of samples was adjusted between intensity measurements by addition of NaOH and HNO_3. The pH was monitored using a Fisher Model 640A pH meter. pK_a values of the complex and the free ligand were obtained by titrating HNO_3 into aqueous solutions of $Tb(DPA)_3{}^{3-}$ and DPA^{2-}.

Results and Discussion

The effect of variation of the molar ratio of ligand to metal ([L]:[M]) on the emission intensities of Tb^{3+}–DPA^{2-} complexes is large. A Job's plot [9] analysis verified [10] that the 3:1 [L]:[M] stoichiometry is the most emissive stoichiometry in aqueous solution. It can be assumed that a tris-complex will form between Tb^{3+} and DPA^{2-} when the [L]:[M] ratio is greater than or equal to 3:1.

Acid titration of aqueous solutions of Na_2DPA and $Na_3Tb(DPA)_3$ allowed for the determination of pK_a values for these compounds. Titration curves (Fig. 1) generated for non-coordinated DPA^{2-} and $Tb(DPA)_3{}^{3-}$ indicated that the free ligand, DPA^{2-}, accepts the first proton by pH 5.6, and the second proton by pH 1.9. Titration of the tris-complex clearly showed only two of the expected three endpoints, corresponding to addition of the first proton by pH 2.8, and addition of the third proton by

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**Author to whom correspondence should be addressed.

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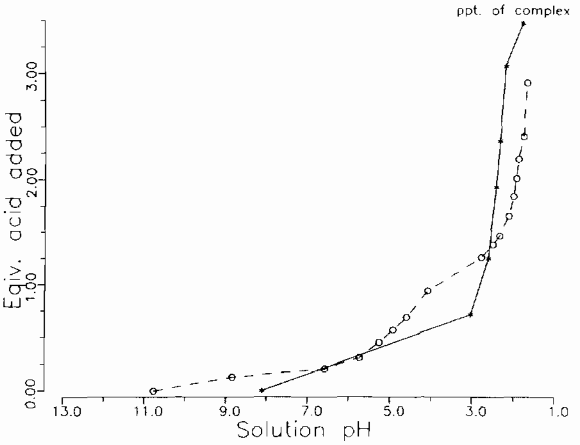

Fig. 1. Titration curves for the free 2,6-DPA^{2-} ligand (○, dashed line) and for the 3:1 DPA:Tb complex (*, solid line) in aqueous solution.

pH 1.6, at which point precipitation of what we believe to be the neutral, tris-protonated complex occurs. Elemental analysis of an HNO_3 washed precipitate of $Na_3Tb(DPA)_3 \cdot 6H_2O$ verified that the acid-treated complex has a stoichiometry of $Tb(H_2DPA)_3 \cdot 2H_2O$ in the solid state. It is clear that the pK_a values of the free ligand are strongly affected by coordination to the metal. Qualitative evidence of strong interaction between metal and ligand in aqueous solution is provided by the observation that precipitation of $Tb(OH)_3$ from a 0.050 M $Tb(DPA)_3^{3-}$ solution remains negligible up to at least pH 10.5, whereas in the absence of such a strongly coordinating ligand $Tb(OH)_3$ is precipitated by a pH of 5.2.

A direct correlation exists between the pK_a values of the free ligand and the complex and the solution luminescence characteristics of the Tb^{3+}–chelate. Figures 2 and 3 are comprised of data obtained from two different [L]:[M] ratios, which display the effect of variation of pH on both the initial emission intensities of the samples and their photostabilities of emission, *i.e.* the retention of the luminescence of the samples after 30 s of exposure to the UV source. Figure 2 presents data using an 8:1 molar ratio of ligand to metal as a representative case where the [L]:[M] ratio exceeds the stoichiometric 3:1 ratio. Above pH 11, the luminescence is diminished, presumably due to hydroxide ion entering the coordination sphere of terbium, but remains stable from pH 11 down to about 6.4. In the pH range 6.41 to 5.76, the photodegradation is markedly rapid. As the pH is lowered further, the initial intensities of luminescence decrease. By a pH of 3.97, however, the decrease in luminescence measured 30 s after exposure to UV light begins to taper off, and by pH 3.51 the diminished luminescence intensity remains unchanged 30 s after exposure to the excitation source.

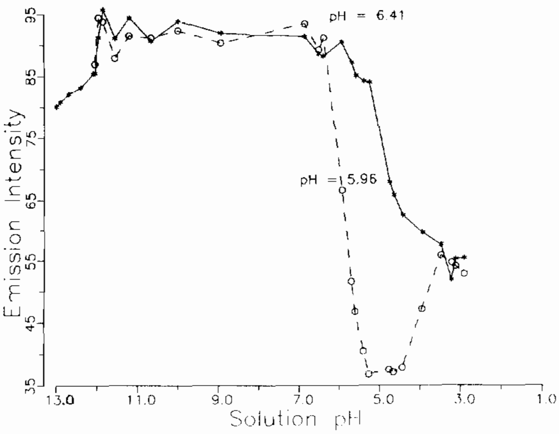

Fig. 2. Emission intensity measurements (545 nm) recorded upon initial exposure to 272 nm excitation (solid line) and after 30 s of exposure to the excitation source (dashed line) of an aqueous solution comprised of an 8:1 molar ratio of DPA:Tb. Emission intensities were measured as a function of pH.

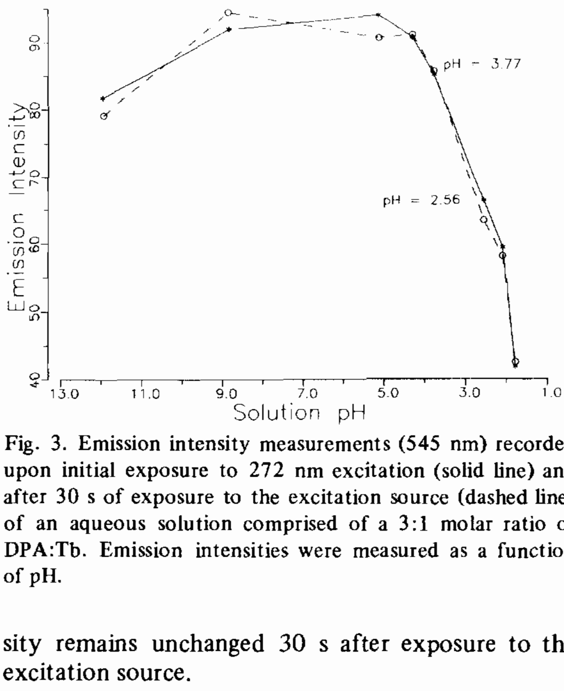

Fig. 3. Emission intensity measurements (545 nm) recorded upon initial exposure to 272 nm excitation (solid line) and after 30 s of exposure to the excitation source (dashed line) of an aqueous solution comprised of a 3:1 molar ratio of DPA:Tb. Emission intensities were measured as a function of pH.

Figure 2 data suggest that the probable mechanism for the observed decreased photostability of the emission of the complex is due to substitution of mono-protonated ligand within a labile Tb^{3+} coordination sphere. It is not likely that direct protonation of coordinated ligand would be significant at a pH as high as about 6 to have such large effects on the emission of the complex. Literature values [11] as well as the experimental values noted above for the pK_{a2} of the free ligand match the pH region where photoinstability of emissions became apparent during acid addition (pH ~ 6). Upon further addition of acid, mono-protonated ligand eventually becomes the predominant species in solution. At that point, photostability of the complexes improves. The observed decrease in luminescence intensity *versus* time of exposure to the excitation source can be explained by a two-step process of ligand substitution where: (i) protonation of free ligand in solution preceeds (ii) substitution of mono-protonated ligand into a labile Tb^{3+} coordination sphere.

A process of direct protonation of dianionic ligands coordinated to the metal in the presence of free ligands in solution would not account for the differences in photostabilities described in Figs. 2 and 3. One sees in Fig. 3 that in the case of a 3:1 [L]:[M] complex, stable emission is noted in the pH 6.4 to 4 region since no free ligand is available to substitute into the coordination sphere of the Ln^{3+}. The emissions remains stable throughout the pH range at which free DPA^{2-} would have been protonated. At a pH of 2.56 and below, the emissions are still photostable, but diminished, presumably due to direct protonation of coordinated ligands.

References

1 H. G. Brittain, *J. Am. Chem. Soc., 102* (1980) 3693.
2 T. D. Barela and A. D. Sherry, *Anal. Biochem., 71* (1976) 351.
3 F. W. Dahlquist, J. W. Long and W. L. Bigbee, *Biochemistry, 15* (1976) 1103.
4 W. DeW. Horrocks, Jr. and D. R. Sudnick, *Acc. Chem. Res., 14* (1981) 384.
5 J. Reidler and H. Silber, *J. Phys. Chem., 77* (1973) 1275.
6 S. Salama and F. S. Richardson, *Inorg. Chem., 19* (1980) 629.
7 J. I. Siegel, *Am. Lab., 14(4)* (1982) 65.
8 W. R. Blair, E. J. Parks, G. J. Olson, F. E. Brinckman, M. C. Valeiras-Price and J. M. Bellama, *J. Chromatogr., 410* (1987) 383.
9 P. Job, *Ann. Chim., 9* (1928) 113.
10 Unpublished results.
11 J. A. Dean (ed.), *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 1979, 12th edn., pp. 5–38.