Circularly Polarized Luminescence Studies of the Eu(III) Bis(pyridine-2,6-Dicarboxylate) Complexes with Chiral α-Hydroxycarboxylic Acids

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Received May 7, 1982

Considerable interest has focused on the lanthanide complexes of α-hydroxycarboxylic acids since it was learned that these ligands could be useful in the ion-exchange separation of the members of the series [1, 2]. The potentiometric titration method has been used to obtain the formation constants corresponding to 1.1 and 1:2 metal/ligand stoichiometries [3], and it is also known that the 1:3 complexes are quite insoluble in most cases. The formation constant associated with the metal/hydroxycarboxylate complex is known to be affected by the presence of other ligands in a mixed-ligand complex, as was shown for lanthanide complexes of 1,2-diaminocyclohexanetetraacetic and hydroxycarboxylic acids [4].

We have recently used circularly polarized luminescence (CPL) spectroscopy to probe the dynamics of ternary complexes containing Tb(III), 2,6-pyridinedicarboxylic acid (DPA, or dipicolinic acid), and a series of hydroxycarboxylic acids [5, 6], and similar studies have been carried out by Das Gupta and Richardson [8]. In these studies, it has been established that the α-hydroxycarboxylic acids bind the Tb(III) ion in a bidentate manner [6], with the exceptions of L-malic [5] and L-tartaric acids [8] which appear capable of exhibiting multidentate modes of binding. Systematic variation of the concentration of chiral material has enabled the calculation of association constants for the Tb(III)/hydroxycarboxylate complexes (as modified by the presence of the other achiral ligands), and in general these are much smaller than those measured by potentiometric means in the absence of the extra ligands [7].

It is known that the formation constants of the hydroxycarboxylic acid complexes of the lanthanide elements vary across the series, although the degree of variation is not great [3]. It therefore is of importance to determine how the formation constants vary in the ternary complexes in order to evaluate how pertinent to the entire series is the information obtained from chiroptical studies on one particular metal ion.

Besides Tb(III), only Eu(III) displays strong luminescence in aqueous solution at room temperature, however, and it is found that the luminescence of Eu(III) complexes is usually an order or magnitude weaker than that of the corresponding Tb(III) complexes. Nevertheless, we have been able to measure CPL spectra for several mixed-ligand complexes of Eu(III), DPA, and chiral α-hydroxycarboxylic acids, and to determine the association constants accompanying the formation of the Eu(III)/hydroxycarboxylate portion of the complex.

Experimental

Eu(III) stock solutions were prepared by dissolving weighed amounts of Eu_2O_3 (Kerr-McGee, 99.9% pure) in the stoichiometric amount of $HClO_4$ with gentle heating, adjusting the pH to 3 with NaOH, and then diluting to the desired volume. L-lactic (LAC) acid was obtained as the 98–100% pure crystalline free acid from Sigma Biochemicals, with L-arginic acid (ARG, or L-α-hydroxy-δ-guanidino valeric acid) being obtained from the same source. L-mandelic acid was obtained from Eastman, and L-malic and dipicolinic acids were purchased from Aldrich; all materials were used as received.

Solutions having a 1:2 ratio of Eu(III) and DPA were prepared from concentrated stock solutions, with the final Eu(III) concentration being 15.5 m*M*. A number of solutions were prepared for each chiral ligand in which the concentration of hydroxycarboxylic acid was systematically varied, and the CPL spectrum recorded for each at intervals of 0.5 pH units. The pH of each solution was obtained on an Orion 701 pH meter, after insertion of a glass microcombination electrode directly into the cuvette. pH adjustment was effected by the addition of standard NaOH or $HClO_4$ solutions.

All CPL spectra were obtained on instrumentation constructed in this laboratory [9]. An excitation wavelength of 295 nm was used, as it is possible to channel energy into the Eu(III) ion by means of ligand sensitization. While the degree of sensitization was not as dramatic as observed for the analogous Tb(III) complexes, sufficient intensity could be obtained in this manner. An emission bandpass of 16A was used for all work, as further increases in resolution did not yield any improvement of the spectral features.

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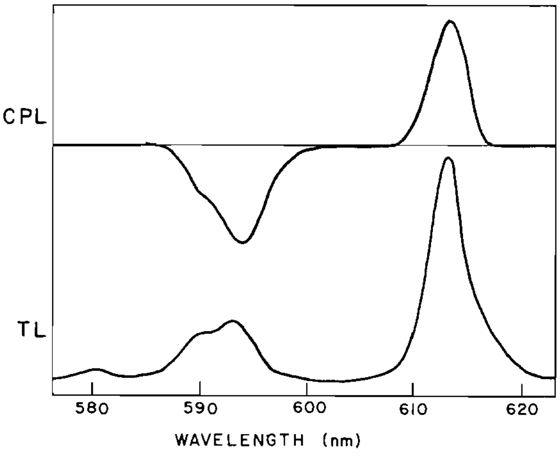

Fig. 1. CPL (upper) and TL (lower) spectra obtained within the 0-1 and 0-2 emission bands of Eu(DPA)$_2$(MAN) at pH 5.0. The ratio used for this study was 1.2:10, and all spectra are shown in arbitrary units. The weak feature at 580 nm is due to the 0-0 transition.

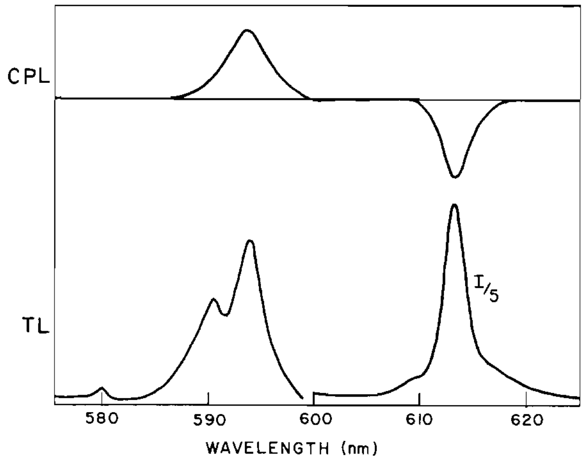

Fig. 2. CPL (upper) and TL (lower) spectra obtained within the 0-1 and 0-2 emission bands of Eu(DPA)$_2$(MAL) at pH 9.5. The molar ratios used were 1:2:5.

Results and Discussion

The addition of two molecules of DPA to a lanthanide ion:

$$Eu^{3+} + 2DPA^{2-} \rightleftharpoons Eu(DPA)_2^- \quad (1)$$

is known to be a very efficient process, as it has been determined that log K_1 = 8.84 and log K_2 = 7.14 [10]. Williams and coworkers have shown that these bis complexes exhibit fast fluxional behavior (with the DPA ligands moving rapidly about the metal ion), and that the vacant coordination positions are occupied by solvent molecules [11]. During the course of our previous work involving Tb(III)/DPA complexes [5, 7, 9], it became established that the coordinated solvent molecules could be displaced to yield a mixed-ligand complex. In the case of Eu(III), this equilibria may be written as:

$$Eu(DPA)_2^- + S^- \rightleftharpoons Eu(DPA)_2(S) \quad (2)$$

Accompanying the formation of this mixed-ligand complex is the appearance of CPL in the emission bands of the Eu(III) ion. The most intense luminescence bands correspond to the $^5D_0 \rightarrow {}^7F_1$ transition at 595 nm and the $^5D_0 \rightarrow {}^7F_2$ transition at 615 nm, although other transitions from the excited $^5D_0$ level to the $^7F_0$ (580 nm), $^7F_3$ (650 nm), and $^7F_4$ (690 nm) ground levels can be observed. We shall label these spectroscopic transitions by their J quantum numbers, and note that the most useful CPL is only obtained within the 0-1 and 0-2 bands.

The CPL obtained for the Eu(DPA)$_2$ complexes of L-lactic, L-mandelic, and L-argininic acids all turned out to be essentially of the same lineshape. No CPL could be observed below pH 2.5 but increasing the pH to 4.0 led to development of the spectral features. The spectra (representative examples are found in Fig. 1) remained invariant until pH 6.5, and above this pH value the CPL intensities decreased rapidly until the formation of a precipitate was observed at pH 7.0.

The results obtained for L-malic acid were somewhat different, as had been noted for the analogous Tb(III) complexes [5]. Below pH 7, the spectra were absolutely identical to those obtained for the other hydroxycarboxylate ligands, but above this pH value new behavior was observed. No precipitate was observed even when the pH was raised to 11.5, and the CPL spectra were found to undergo complete inversion (see Fig. 2). In addition, the total luminescence (TL) spectra were observed to change drastically in this pH region· the 0-1 TL system splits into two bands as the pH is raised, and the 0-2TL increases considerably at the same time. The identity of the low pH spectra with those of the other ligands identifies the α-hydroxycarboxyl functionality as the low pH binding site for all ligands, and we thus assign the CPL sign inversion as being due to the presence of terdentate bonding with the malic acid ligand. These conclusions are similar to those reached for the Tb(III) complexes [7].

The CPL and TL spectra were obtained in arbitrary units, with the TL intensity being defined by $I_L + I_R$, and the CPL intensity being given as $I_L - I_R$. The luminescence dissymmetry factor has been defined as twice the ratio of the CPL to the TL [12], and this dimensionless quantity may be related to the

TABLE I. Luminescence Dissymmetry Factors for $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Transitions of the Eu(DPA)$_2$(Hydroxycarboxylate) Complexes.

Ligand	0 - 1 $g_{lum} \times 10^2$	0 - 2 $g_{lum} \times 10^2$
L-lactic acid	−4.86	+1.66
L-mandelic acid	−8.02	+3.02
L-argininic acid	−7.20	+2.58
L-malic acid (low pH)	−3.30	+0.97
L-malic acid (high pH)	+2.21	−0.62

rotational strength of the transition. We have calculated the dissymmetry factors obtained after the Eu(DPA)$_2$ complexes have been saturated with chiral hydroxycarboxylic acid substrate, and these values may be found in Table I. The CPL of the 0-1 band is seen to be much more intense than that of the 0-2 band, as is usually the case.

It is clear that the optical activity at substrate concentrations less than the limiting values is proportional to the concentration of mixed-ligand complex. In that case, it is possible to calculate the mol fraction of free Eu(DPA)$_2$ by:

$$X_{Eu(DPA)_2} = \frac{g_f - g}{g} \tag{3}$$

where g_f is the limiting dissymmetry factor, and g is the dissymmetry factor of the solution in question. Since we know the stoichiometry of the Eu(DPA)$_2$ complexes (defined by equation 2) and all starting concentrations, it is a trivial matter to compute the association constant for the adduct:

$$K = \frac{[Eu(DPA)_2(S)]}{[Eu(DPA)2]\,[S]} \tag{4}$$

Values of these formation constants have been collected in Table II.

TABLE II. Formation Constants of the Mixed-Ligand Eu(DPA)$_2$ Hydroxycarboxylic Acid Complexes.[a]

Ligand	K_1
L-lactic acid	20
L-mandelic acid	28
L-argininic acid	25
L-malic acid (low pH)	13

[a]The error associated with each constant is approximately 6%.

The Eu(DPA)$_2$ formation constants are found to be only 45% those obtained for the analogous Tb(DPA)$_2$ complexes [7]. This difference in formation constants is considerably larger than that found for the Eu(III) and Tb(III) of the same hydroxycarboxylic acid ligands, were the stability constants of the Eu(III) complexes average 90% those of the Tb(III) complexes [3]. This difference in stability is due to a combination effect reflecting the larger size of the Eu(III) ion and the perturbed binding capabilities of the Eu(DPA)$_2$ complex which are affected by the presence of the DPA ligands.

One final note concerns the relative TL and CPL intensities of the 0-1 and 0-2 transitions. Richardson has developed a series of selection rules relating the relative chiroptical strengths associated with various transitions of lanthanide ions, and has noted that the predicted rotational strength of the 0-1 band ought to be much higher than that of the 0-2 band [13]. These predictions, based on considerations of the L, S, and J quantum numbers of the initial and final states, are found to be in complete agreement with the data obtained during the course of the present study.

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