

## Circularly Polarized Luminescence Spectroscopy of Mixed-ligand Complexes of Europium(III) with 2,6-Pyridine-dicarboxylic acid and L-malic acid

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### Abstract

Circularly polarized luminescence (CPL) from solutions of Eu(III), 2,6-pyridine carboxylic acid (dipicolinic acid, DPA), and L-malic acid (L-mal) at differing concentration ratios have been measured. The magnitude and sign of the CPL under varying excitation polarizations are quite different indicating that the source of the emission under these conditions is not the same. Comparison of the CPL observed for a solution in which DPA and L-malic acid are present to that of pure Eu:DPA and Eu:L-mal under identical conditions suggests that most of the emission in the mixed-ligand system occurs from  $\text{Eu}(\text{DPA})_3^{3-}$ , and not from a species containing two DPA ligands and one L-mal.

### Introduction

The study of the solution structure and chemistry of aqueous lanthanide complexes has experienced significant growth in recent years primarily due to the increased use of a number of these species as luminescent probes of biomolecular structure [1, 2] and as NMR shift reagents [3]. Luminescence studies have been particularly successful in elucidating structural information concerning the generally complex aqueous lanthanide species. Of special importance have been the relatively new experimental techniques of selective excitation spectroscopy of europium(III) [4], and circularly polarized luminescence (CPL) spectroscopy [5], primarily involving Eu(III) and Tb(III).

Whereas wavelength selective excitation spectroscopy may be applied to a fairly wide class of lanthanide species, CPL spectroscopy is useful only if the emitting complex is optically active. Very recently, however, we have demonstrated that in certain lanthanide systems it is possible to measure

CPL from *racemic* mixtures if one uses as the excitation source a circularly polarized laser beam [6, 7]. The *racemic* lanthanide solutions from which CPL has been observed have involved the terdentate ligands 2,6-pyridine-dicarboxylic acid (dipicolinic acid, DPA) and oxydiacetic acid (ODA) which are presumed to exist in tris-enantiomeric structures. Use of circularly polarized excitation results in a preferential absorption by one enantiomer. This results in an emitting state population which is not *racemic*. These experiments are possible only if this differential excited state population remains intact during the lifetime of the emitting state [8]. These experiments can be considered to be another example of selective excitation spectroscopy, although the selectivity in this case is due to polarization differences not wavelength variations. In the work reported here we illustrate the fact that this type of experiment is not limited to *racemic* mixtures, and can provide useful information about the nature of lanthanide complexes that complements existing techniques.

The focus of this initial study is on lanthanide solutions in which more than one ligand has been added [5, 9]. In particular, we have studied solutions of Eu(III), DPA, and L-malic acid at varying molar ratios and pH conditions. Interest in these so-called mixed-ligand systems has been for the most part focussed on the relative effects of configurational *versus* vicinal optical activity, and in some cases on studies involving variations in the coordination properties of the lanthanide ions. A large number of these studies have been concerned with solutions of Tb(III) and Eu(III) with DPA and another ligand at varying ratios of lanthanide ion, DPA and the third component. The added ligand is usually chiral in order to generate a chiral emitting species so that the CPL technique can be applied. In a large portion of this work interpretation of the circularly polarized emission spectra has centered on the existence and structure of one dominant species in solution. In this work we show that in interpretations of CPL experiments on mixed-ligand lanthanide systems, important information concerning the nature of the

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emitting species can be obtained through circularly polarized excitation.

## Experimental

Three solutions were prepared. The first was 0.015 M in  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (99.9%, Aldrich) and 0.075 M in L-malic acid (Eastman) with the pH adjusted to 8.1 with 1 N NaOH. The second solution was also 0.015 M in  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.045 M in 2,6-pyridine-dicarboxylic acid (DPA) from Aldrich (99%) again with the pH adjusted to 8.1. A third solution was prepared by mixing a 1:2 (by volume) mixture of the first and second solution. CPL and total emission spectra were recorded on an instrument described previously [6].

## Results and Discussion

In Figs. 1 and 2 we show total luminescence spectra for the three solutions prepared as described

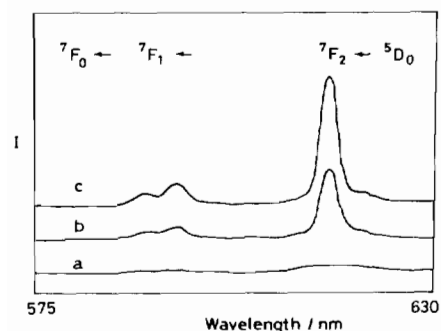


Fig. 1. Total luminescence ( $I$ ) from solutions of Eu(III), DPA, and L-mal in varying ratios at pH = 8.1. (a) Eu/L-mal = 1/3 and  $\lambda_{\text{exc}} = 476.5$  nm. (b) Eu/L-mal/DPA = 1/1.82/2  $\lambda_{\text{exc}} = 476.5$  nm. (c) Eu/DPA = 1/3  $\lambda_{\text{exc}} = 476.5$  nm.

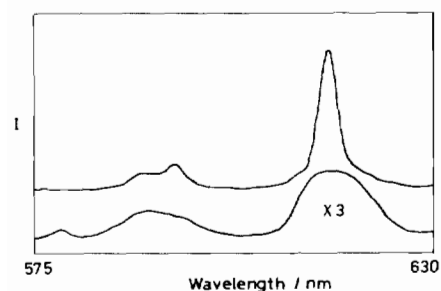


Fig. 2. Total luminescence ( $I$ ) from solutions of Eu(III), DPA, and L-mal in varying ratios at pH = 8.1. Lower spectrum corresponds to a ratio Eu/L-mal = 1/3 with  $\lambda_{\text{exc}} = 465.8$  nm. Upper spectrum corresponds to a ratio Eu/L-mal/DPA = 1/1.82/2 with  $\lambda_{\text{exc}} = 465.8$  nm.

above. The three spectra in Fig. 1 correspond to an excitation wavelength of 476.5 nm, and the two spectra in Fig. 2 to an excitation wavelength of 465.8 nm. As is evident in these figures, the total emission intensity is much less for the Eu(III):L-malic acid solutions as compared to solutions which contain DPA. Excitation at 476.5 nm corresponds to the absorption transition  ${}^7F_1 \rightarrow {}^5D_2$  and at 465.8 nm to the transition  ${}^7F_0 \rightarrow {}^5D_2$ . 465.8 nm excitation is slightly more efficient at exciting the Eu:L-mal complex. Also given in this figure are the spectral assignments for the emissive transitions. In the presumably low symmetry Eu:(L-mal) there is evidence for the  ${}^5D_0 \leftarrow {}^7F_0$  emission at approximately 580 nm, which is formally forbidden in the axially symmetrical  $\text{Eu}(\text{DPA})_3^{3-}$  complex.

In Figs. 3 and 4, the circularly polarized luminescence spectra for the three solutions are displayed. The two spectra in Fig. 3 correspond to experiments in which the excitation beam was circularly polarized. The lower spectrum is the result for pure  $\text{Eu}(\text{DPA})_3^{3-}$ , and the upper spectrum for the mixed ligand solution. The two spectra in Fig. 4 are for an experimental configuration in which the excita-

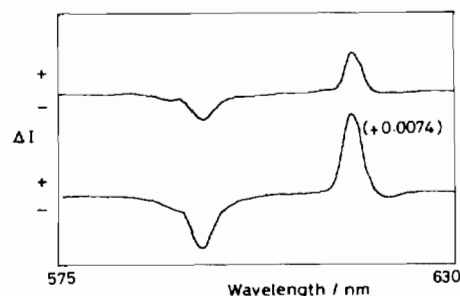


Fig. 3. Circularly polarized luminescence ( $\Delta I$ ) from solutions of Eu(III), DPA and L-mal in varying ratios at pH = 8.1 under circularly polarized excitation. Lower spectrum corresponds to a ratio of Eu/DPA = 1/3 with  $\lambda_{\text{exc}} = 476.5$  nm. Upper spectrum corresponds to a ratio of Eu/L-mal/DPA = 1/1.82/2 with  $\lambda_{\text{exc}} = 476.5$  nm.

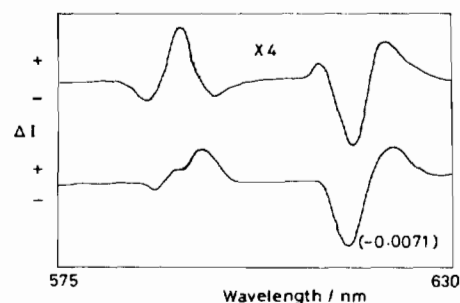


Fig. 4. Circularly polarized excitation ( $\Delta I$ ) from solutions of Eu(III), DPA, and L-mal in varying ratios at pH = 8.1 under linearly polarized excitation. Lower spectrum corresponds to a ratio of Eu/L-mal = 1/3 with  $\lambda_{\text{exc}} = 465.8$  nm. Upper spectrum corresponds to a ratio of Eu/L-mal/DPA = 1/1.82/2 with  $\lambda_{\text{exc}} = 465.8$  nm.

tion beam was unpolarized. The CPL results for the Eu:L-mal solution were independent of excitation polarization, and only the spectra for unpolarized excitation are shown in this Figure (lower). The upper spectrum in Fig. 4 again corresponds to the mixed-ligand solution. The CPL spectra of Eu:L-mal with unpolarized excitation has been reported previously [10], and our spectra are similar to that data. CPL spectra of similarly prepared mixed Eu:DPA-malic acid solutions at a range of pH values with unpolarized excitation have also been reported, and the results given in this work are consistent with these published spectra [9].

An interpretation of the emission spectra from this mixed-ligand system in terms of structural features of one dominant species is clearly very dangerous. If the emission originated from only a single species, then the shape of the CPL spectrum should be independent of excitation polarization. The only difference might be small intensity variations due to slightly different absorption probabilities for the different absorption polarizations. Comparison of the CPL results in Figs. 3 and 4 clearly show that circularly polarized excitation and unpolarized excitation result in very different CPL spectra. Experimentally reversing the incident circular polarization from left to right yields a completely inverted CPL spectrum for the pure Eu:DPA solution and for the mixed-ligand solution. Thus, there must exist in these solutions, species that have enantiomeric-like interactions with the circularly polarized excitation beam. We have already shown that in lanthanide:DPA solutions there exist enantiomeric tris-terdentate complexes.

One possible interpretation of the results from the mixed-ligand solution is that the presumed Eu:2:1 complex that might be formed exists in diastereomeric isomers. In this case excitation with circularly polarized light preferentially excites one of these isomers over the other resulting in large circular polarization in the emission, and excitation with unpolarized light excites the two isomers almost equally, so that a large amount of cancellation is present in the CPL spectra. We believe this conclusion is not correct. Comparison of the total emission and CPL spectra for pure  $\text{Eu}(\text{DPA})_3^{3-}$  with that of the mixture shows that the spectra are identical except for absolute intensity differences. One would expect a very different spectra for a complex composed of two DPA ligands with the other coordination sites occupied by malate,  $\text{H}_2\text{O}$ , etc. These results suggest strongly that in this mixed-ligand system most of the total emission originates from  $\text{Eu}(\text{DPA})_3^{3-}$

even though there is not sufficient quantity of this ligand to complex all of the available lanthanide ion. It should be noted that solutions with a 1:2 ratio of lanthanide:DPA are unstable at this pH as evidenced by precipitation.

Further confirmation of the existence of multiple emitting species is seen in a comparison of CPL results for the Eu:L-mal solution and the mixed-ligand system under unpolarized excitation as displayed in Fig. 4. These spectra, although not identical, are very similar. Under linearly polarized or unpolarized excitation there will be exact cancellation of CPL from the racemic  $\text{Eu}(\text{DPA})_3^{3-}$ , therefore although the total emission is almost exclusively from the  $\text{Eu}(\text{DPA})_3^{3-}$  complex, the weak CPL originates from a quite different source. This is just one example of the danger of simply calculating ratios of  $I/I$  for systems of this complexity, and interpreting the result in terms of structural characteristics of one predominant species in solution.

#### Acknowledgements

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