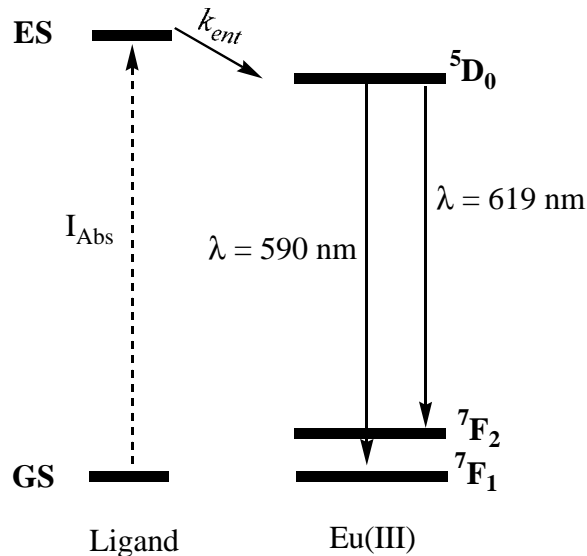


Experiment XI.

Chelate-Induced Enhancement of Lanthanide Photoluminescence

The term lanthanide generally refers to the elements lanthanum ($Z = 57$) to lutetium ($Z = 91$). The lanthanides plus yttrium are some times referred to as rare-earths since they are found in relatively low abundance as metal oxides in the earth's crust. The most prevalent oxidation state for the lanthanides is +3 and thus have electronic configurations denoted $[\text{Xe}]f^0$ to $[\text{Xe}]f^{14}$. The f orbitals are relatively uninvolved in bonding. However, these highly electropositive metals have a rich coordination chemistry and are strong Lewis acids. Because of their large size, lanthanides are known with coordination numbers as high as twelve. Lanthanides are commonly used as nmr shift reagents and may have applications in catalysis.¹ Perhaps their most important feature however, is their luminescence behavior that has been exploited in commercial phosphors for television and other display applications. In this experiment you will explore the spectroscopic properties of some highly luminescent Eu(III) complexes.^{1,2}

The visible absorption spectra of lanthanide compounds is generally dominated by $f-f$ transitions. Because the f orbitals are well shielded from the surroundings and are not involved in the bonding, the $f-f$ transitions are very sharp and essentially insensitive to the coordination environment.³ This behavior is quite different from the $d-d$ (or ligand field) transitions of transition metal compounds which display broad absorption bands whose color can be tuned by varying the ligand field, see Experiment VIII for example. Lanthanide complexes in the +3 oxidation state, Ln(III), derived from Terbium (Tb), Holmium (Ho), and Europium (Eu) all display $f-f$ luminescence when they are excited with light. Several years ago, it was discovered that complexation by certain chelating ligands enhances the Ln(III) photoluminescence.⁴ A simplified diagram that explains the enhanced photoluminescence is shown below in Scheme 1. The basic idea is that energy transfer occurs from ligand localized excited states, ES, to f orbitals of the lanthanide, Eu(III) shown here. The energy transfer products are an excited Ln(III) complex that then relaxes to the ground state by emission of a photon. In this lab you will utilize the chelating ligand 2,6-pyridinedicarboxylic acid (dipicolinic acid or DPA) to enhance the photoluminescence of Eu(III) solution.



Scheme 1.

Hazards

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Eu(NO₃)₃: Europium nitrate salts are nonvolatile, air stable materials. They are toxic if ingested orally. ORL-RAT LD50 > 5000 mg/kg.

DPA: No toxicity data is available. However, the corresponding methyl amide has an ORL-RAT LD50: 3400 mg/kg.

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Experimental Procedure.

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A. Synthesis of [Eu(DPA)₃]ⁿ⁻ Complexes

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Stock aqueous solutions of 1.00×10^{-3} M Eu(NO₃)₃ and 0.1 M DPA solutions will be provided. Then prepare a series of 10 mL solutions that have a 1:0, 1:1, 1:2, 1:3, 1:4, and 1:5 molar ratios of Eu:DPA. In these solutions make certain that the Eu(III) concentration is around 10^{-5} M and is *unchanged* through these series. If precipitation occurs, add a known amount of concentrated NaOH to all the solutions. You will be

comparing absolute PL intensities so it is important that the Eu(III) concentration is constant for all the solutions prepared.

B. Optical Characterization

Measure the absorption spectra of all six solutions in polystyrene cuvettes. You may use water as a reference. Calculate the extinction coefficient of the most intense bands if possible.

Take the 1:5 solution and record the PL spectrum from 500 – 700 nm with 395 nm excitation. You may then autoscale this solution and take the PL spectrum of the other solutions. When you have finished take the excitation spectra by monitoring the most intense PL band and scanning to higher energies until the polystyrene cuvette begins to absorb light.

Plot the PL intensity versus the molar ratio of DPA ligand. What is the likely identity of the Eu(III) complex at high DPA concentrations? What evidence is there for energy transfer from DPA → Eu(III)?

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References.

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1. a) Pitzer, K.S. *Acc. Chem. Res.* **1979**, *12*, 271. b) Kremers, H.E. *J. Chem. Ed.* **1985**, *62*, 665.

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2. Jenkins, A.L.; Murray, G.M. *J. Chem. Ed.* **1998**, *75*, 227.

3. The energy of f-f transitions is relatively unperurbed by ligand coordination but, the intensity can change dramatically. See for example, Richardson, F.S. *Inorg. Chem.* **1984**, *23*, 4607, 4611.

4. Crosby, G.A.; Whan, R.A.; Freeman, J.J. *J. Phys. Chem.* **1962**, *66*, 2493.