Spectroscopic Investigation of Eu–EDTA Complexes*

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This spectroscopic investigation of Eu–EDTA (EDTA ethylene diamine tetraacetic acid, $(HCOOCH_2)_2N-CH_2-CH_2-N(CH_2COOH)_2$ noted H_4Y) complexes has been undertaken in a special experimental device using an optical fiber as light guide for both the exciting and emitted radiations. This way of working proves to be particularly well suited for exciting fluorescence with a laser beam (continuous or pulsed). It has permitted us to collect fluorescence spectra of Eu^{3+} aqueous solutions between 273 and 373 K and of frozen solutions at 77 K.

Within the literature reports on Eu–EDTA complexes, up to seven species have been suspected [1–5]: $[EuHY]^0$, $[EuY]^-$, $[Eu(YOH)]^{2-}$ for the 1/1 composition; $[Eu(HY)_2]^{3-}$, $[Eu(HY)Y]^{4-}$, $[EuY_2]^{5-}$ for the 1/2 composition; and $X[Eu_2Y_3]^{6-}$ for the 2/3 composition.

In the 1/1 complexes several water molecules are linked to the europium central ion. Several authors [2, 3, 6] have interpreted the evolution of europium absorption spectra with temperature as demonstrating the transition from four to three H_2O molecules in the first coordination shell. In the other Eu/EDTA ratios there is no water in the first coordination shell [5].

We have studied the modification of Eu^{3+} optical characteristics in Eu–EDTA aqueous solutions with respect to three parameters: temperature, pH and Eu/EDTA ratio, in order to try to identify the species present.

Experimental

The two starting 0.4 M solutions were obtained by dissolving $EuCl_3 \cdot nH_2O$ (99.9% Johnson Mathey) and EDTA (Prolabo) in water. In order to achieve complete dissolution of EDTA at room temperature, NH_4OH was added so that the pH of the EDTA solution was about 10. Different Eu/EDTA ratios were obtained by mixing in adequate proportions the two starting solutions; pH values ranging from 6 to 11 were adjusted by adding amounts of ammonia. More acidic solutions were made by heating EDTA in water at 80 °C until complete dissolution and then admixture of the Eu^{3+} solution. The resulting pH was 1.3.

The fiber optic device has been described in full detail [7]; the versatile coupler permitted the use of either plastic clad silica fibers (FOI, core diameter 600 μm) for temperatures from 0 to 100 °C or all silica (FOI, core diameter 200 μm) for liquid nitrogen temperature measurements. The solution under investigation was introduced in a glass capillary or a small plastic tube. The optical fiber end was guided into the solution by the capillary or by a medical needle, depending on the respective dimensions of the fiber and the container, the whole being immersed in a thermostated liquid (water, liquid nitrogen or other).

The spectroscopic apparatus was made of several components permitting a number of complementary investigations. As exciting source we used either a continuous argon ion laser (Spectra Physics 164) or a pulsed nitrogen laser (Jobin–Yvon LA04/E1T). Two spectrographs have been used, a Jarrel–Ash 78460 equipped with R374 Hamamatsu photomultiplier, and a Coderg PHO with R446 PM. The continuous emission was measured by a Keithley multimeter acting as amplifier, and pulsed fluorescence by a digital oscilloscope Tektronix 2430. Data were collected and processed by either a Commodore 3032 or a BFM 187 microcomputer.

Results

General Aspects of the Eu^{3+} Emission Spectra

All the spectra present the following characteristics: two narrow $^5D_0 \rightarrow {}^7F_0$ components, three wide $^5D_0 \rightarrow {}^7F_1$ lines and four ill-resolved $^5D_0 \rightarrow {}^7F_2$ lines with a small overall splitting. The appearance of two lines in the $^5D_0 \rightarrow {}^7F_0$ region shows the presence of two species and we have investigated the evolution of their intensities under various conditions. In the following we will refer to the higher energy component (17 251 cm^{-1}, 5796.8 Å at 0 °C) as C_1 and to the lower energy component (17 237 cm^{-1}, 5801.5 Å at 0 °C) as C_2.

Relative Evolution of the Two $^5D_0 \rightarrow {}^7F_0$ Emissions

In Fig. 1 are reported the $^5D_0 \rightarrow {}^7F_0$ emission spectra of a solution (1 Eu/1 EDTA, 0.2 M, pH = 6) under direct $^5D_2$ excitation of Eu^{3+} by one of the argon ion laser lines (4658 Å) for three temperatures. The same observation at 15 temperatures between 0

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TABLE I. Evolution of the $^5D_0 \rightarrow {}^7F_0$ Positions with Temperature

Temp.	100 °C/377 K	50 °C/320 K	30 °C/300 K	0 °C/273 K	−196 °C/77 K
λ (C_1) (Å)	5792.9	5795	5795.4	5796.8	5801
λ (C_2) (Å)	5798.7	5799.9	5800.3	5801.5	5805.5
$\Delta\lambda$ (Å)	5.8	4.9	4.9	4.7	4.5

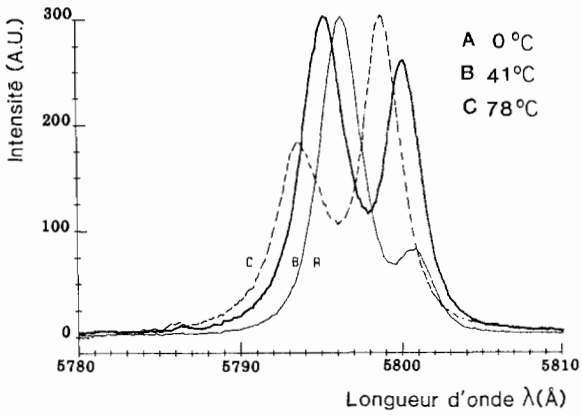

Fig. 1. Evolution of the fluorescence with temperature ($^5D_0 \rightarrow {}^7F_0$ transition). Solution 1Eu/1EDTA, pH = 6, excitation 4658 Å.

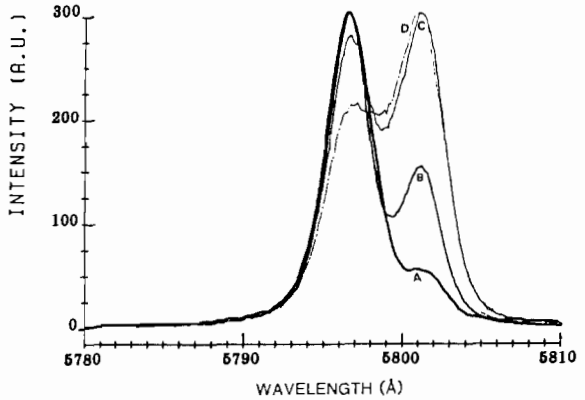

Fig. 2. Evolution of the fluorescence with pH ($^5D_0 \rightarrow {}^7F_0$ transition). Solutions 1Eu/1EDTA, 0.15 M, T = 273 K, excitation 4658 Å: (A) pH = 1.3, (B) 7.5, (C) 10.8, (D) 11.3.

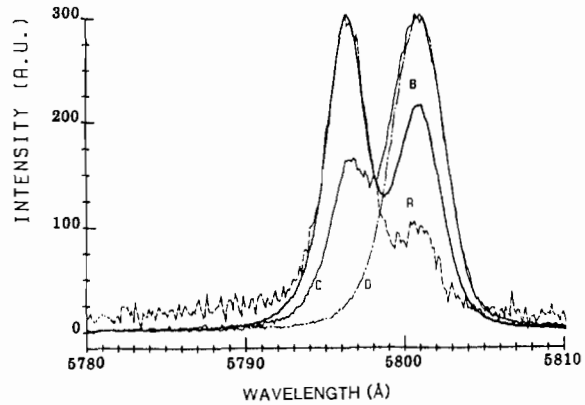

Fig. 3. Evolution of the fluorescence with Eu/EDTA ratio, [Eu] = 0.04 M, T = 273 K, excitation 4658 Å: (A) Eu/EDTA = 2, (B) 1, (C) 1/2, (D) 1/9.

and 100 °C shows that the maximum intensities ratio C_1/C_2 changes continuously from nearly 4 at 0 °C to 0.5 at 78 °C. at the same time the positions of the two lines exhibit a continuous shift, keeping almost the same energy difference, as reported in Table I.

In Fig. 2 are displayed the $^5D_0 \rightarrow {}^7F_0$ emission spectra observed at a given temperature under 4658 Å excitation for solutions with different pHs, and on Fig. 3 for different Eu/EDTA ratios. The two C_1 and C_2 lines always appear at 5796.8 and 5801.5 Å, respectively, but their relative intensities show a continuous evolution either with the pH or with the composition of the solution. Further information may be extracted from the $^5D_0 \rightarrow {}^7F_{1,2}$ transition. Although badly resolved, these lines show some features such as a characteristic line at 6175 Å (16 194 cm^{-1}) that may be unambiguously attributed to C_2 emission.

From this first series of experiments it appears that only two species are characterized by their fluorescence spectra in Eu–EDTA solutions. Their relative proportion varies with physical (temperature) or chemical (pH, composition) parameters. The ratio C_1/C_2 of their maximum intensities decreases when the temperature, the pH or the EDTA/Eu ratio increases. At this stage we can assert that the C_2 species is richer in EDTA than the C_1 one. Complementary and pertinent information has been obtained by means of time-resolved fluorescence measurements of these solutions in the liquid and in the frozen state, as will be detailed in the next paragraph.

Time-resolved Fluorescence of the Frozen and Liquid Solutions

The solution investigated was 1Eu/1EDTA, 0.2 M, pH = 9.5. Excitation in the $^5D_2$ level was achieved with a coumarin dye. The fluorescence spectrum of the frozen solution observed under 4656 Å excitation (maximum efficiency at 77 K), Fig. 4B, is comparable to the one recorded on the liquid at 273 K under 4653 Å excitation (maximum efficiency at this temperature), Fig. 4A. Although narrower and slightly better resolved at 77 K, the same lines are observed, with the same relative intensities, so that it seems to us justified to extend the information

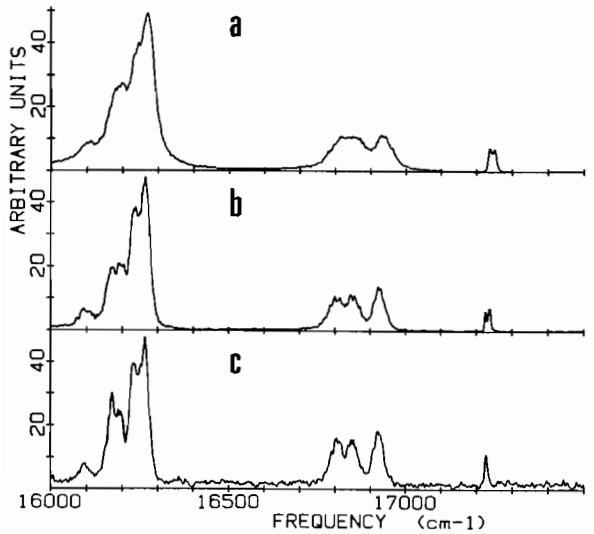

Fig. 4. Fluorescence spectra under $^5D_2$ selective excitation. Solution 1Eu/1EDTA, pH = 9.5: (A) T = 273 K, excitation 4653 Å; (B) T = 77 K, excitation 4656 Å; (C) T = 77 K, excitation 4665 Å.

deduced from the low temperature investigation to the liquid state.

The detailed $^5D_0 \rightarrow {}^7F_0$ emission at 77 K at various delay- and integration-times is shown in Fig. 5B. Three components may be isolated: one shorter-lived line at 5801 Å (17 238 cm^{-1}) and one longer-lived at 5805.5 Å (17 225 cm^{-1}). These two are attributed to C_1 and C_2 respectively, their energy positions following the evolution observed for higher temperatures (Table I). The third component at 5802.7 Å (17 233 cm^{-1}) was not isolated in liquid solutions; although appearing at an energy very close to C_1 its lifetime is rather similar to that of C_2. The fluorescence decays of C_1 and C_2 at 77 K are reported on Fig. 6B and C. The C_2 emission shows an exponential decay of 1/e lifetime 1300 ± 20 μs. The C_1 fluorescence exhibits a faster decay with a lifetime of 450 ± 20 μs, followed by a slower component probably due to spectral overlapping with the 17 233 cm^{-1} line. Due to the low emission intensities, observation during the first 50–70 μs following the pulse is distorted by the tail of the exciting light. The $^5D_0 \rightarrow {}^7F_0$ spectrum observed at 273 K shows practically no time evolution. The fluorescence measured at C_1 and C_2 positions exhibits the same exponential decay with 670 ± 20 μs 1/e lifetime (Fig. 6A).

Excitation spectra within the $^5D_2$ level recorded at 77 K when monitoring either C_1 or C_2 exhibit characteristic features: a common absorption line at 4656 Å, as shown by the above experiments, and a selective 'C_2' line at 4665 Å. Excitation at this last value actually led to C_2 emission alone in the $^5D_0 \rightarrow {}^7F_0$ region (see Fig. 5C). In $^5D_0 \rightarrow {}^7F_2$ the 6184 Å (16 160 cm^{-1}) line corresponds well to the characteristic C_2 emission already identified at 0 °C (seen at 16 175 cm^{-1}). Another narrow component appears at 6150 Å (16 260 cm^{-1}) but presents a time evolution different from C_2 and may rather be attributed to C_1 slightly excited by the laser. It thus appears that the $^7F_1$ and $^7F_2$ splittings of species C_1 and C_2 are rather similar and that several emission lines are still too wide at 77 K to permit identification of the individual spectra. The $(^5D_0 \rightarrow {}^7F_1)/(^5D_0 \rightarrow {}^7F_2)$ intensity ratio is greater for C_2 than for C_1 complexes.

Up to now our attempts to observe fluorescence under selective $^5D_0$ excitation at 77 K were unsuccessful due to the weakness of emission. On the contrary, at 273 K, as we used greater core diameter optical fibers, valuable $^5D_0 \rightarrow {}^7F_{1,2}$ signals were observed but the spectra did not show any selectivity. This last observation, combined with that of the same lifetime for the two emissions in the liquid state, has to be

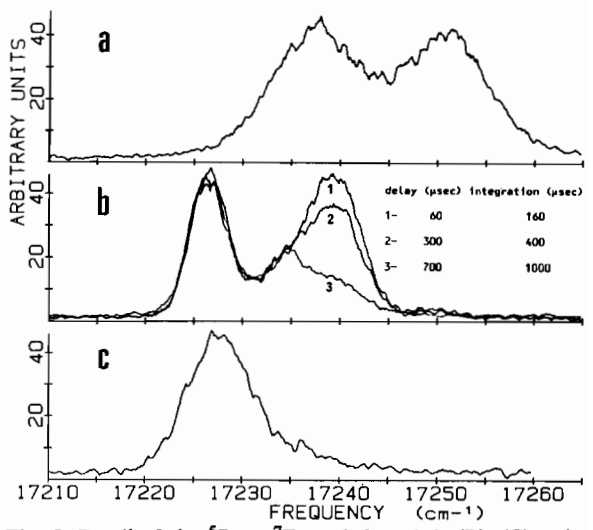

Fig. 5. Detail of the $^5D_0 \rightarrow {}^7F_0$ emission: (A), (B), (C) as in Fig. 4.

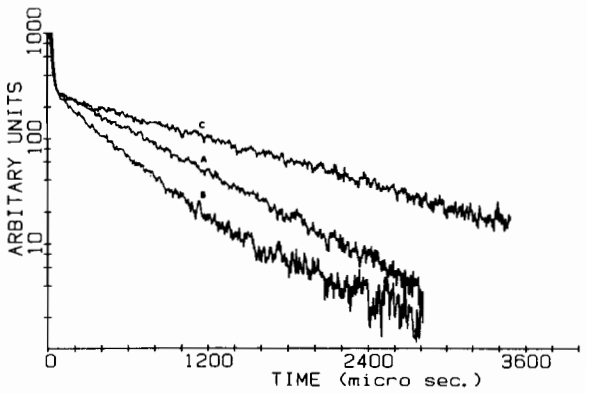

Fig. 6. Fluorescence decays: (A) T = 273 K, excitation 4653 Å, frequency monitored = 17 237 cm^{-1}; (B) T = 77 K, excitation 4656 Å, frequency monitored = 17 238 cm^{-1}; (C) T = 77 K, excitation 4656 Å, frequency monitored = 17 227 cm^{-1}.

attributed to the rapid exchange between the two C_1 and C_2 species in the dynamic equilibrium. The lifetime of each of them being by far shorter than the Eu^{3+} emission characteristics.

Discussion and Conclusion

In ref. 7 we concluded from our observations of Eu–EDTA emission spectra at different temperatures, pH and composition that only two species were identified in the solution, the first one with 1Eu–1EDTA·nH_2O, the second one with formula 1Eu–2EDTA, labelled respectively C_1 and C_2.

A strong new argument favoring our assignment arises from low temperature lifetime measurements. Since the 1/e lifetimes are 450 ± 20 μs for C_1 and 1.3 ± 0.02 ms for C_2, this confirms that the two complexes are very different in the number of coordinated water molecules. In the solid $Na[Ln(H_2O)_3(EDTA)]\cdot 5H_2O$ with 3 water molecules as europium first neighbors, the lifetime measured by W. de Horrocks *et al.* [8] was very near to that of C_1, whereas the much longer C_2 lifetime is comparable to reported observations on $Na_3[Ln(dipicolinate)_3]\cdot 15H_2O$ complex with zero water molecules in the lanthanide immediate neighbors.

In this interpretation all the species cited in the introduction for the 1/1 composition and existing at different pH would give rise to the C_1 spectrum, and in the same way all the 1/2 species would give the C_2 spectrum. This contradicts previous interpretations of absorption spectra, as in refs. 3 and 4, in which two different spectra were attributed to two 1/1 complexes, differing either by the *n* value for H_2O or by the ligand denticity, whereas in the same description two species of 1/1 and 1/2 compositions would fortuitously have the same optical spectra. It seems to us much more probable that the Eu^{3+} level dispositions are more sensitive to the variation in the number of coordinated EDTA than to more subtle modifications in the number of coordinated water molecules or the ligand denticity.

Finally we have to point out that the third $^5D_0 \rightarrow {}^7F_0$ emission observed at 77 K is a non-hydrated species because of its long lifetime; as shown by the time-resolved spectra (Fig. 5B), it should be due to the 2/3 complex.

From the comparison of observations recorded at 77 and 273 K on Eu–EDTA aqueous solutions it appears that spectroscopic information about the liquid state may well be deduced from experiments performed on the frozen state. The use of low temperature presents two advantages, which are to narrow the Eu^{3+} emission lines and to prevent the exchange between species in solution, thus permitting one to acquire site-selective, time-resolved emission spectra. The use of optical fibers as guides for the exciting and emitted light proves to be a convenient and relatively simple way to make such determinations.

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