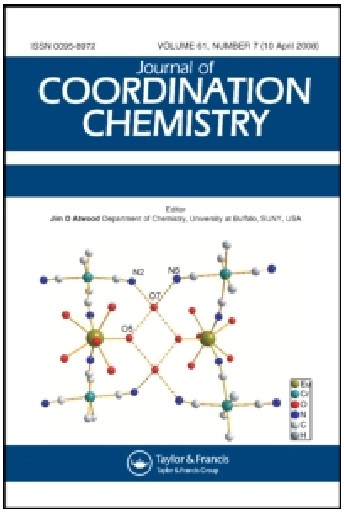

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SOLUTION STRUCTURES OF EUROPIUM(III) COMPLEXES OF ETHYLENEDIAMINETETRAACETIC ACID

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To cite this Article Latva, Martti , Kankare, Jouko and Haapakka, Keijo(1996) 'SOLUTION STRUCTURES OF EUROPIUM(III) COMPLEXES OF ETHYLENEDIAMINETETRAACETIC ACID', Journal of Coordination Chemistry, 38: 1, 85 — 99

To link to this Article: DOI: 10.1080/00958979608022693

URL: http://dx.doi.org/10.1080/00958979608022693

J. Coord. Chem., 1996, Vol 38, pp. 85–99
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SOLUTION STRUCTURES OF EUROPIUM(III) COMPLEXES OF ETHYLENEDIAMINETETRAACETIC ACID

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(Received May 10, 1995)

Coordination of ethylenediaminetetraacetic acid (EDTA) with europium(III) has been studied at different concentrations in solution using $^7F_0 \rightarrow {}^5D_0$ excitation spectroscopy and excited-state lifetime measurements. EDTA forms with Eu(III) ion three different species in equimolar solutions at room temperature. At low pH values EuEDTAH is formed and at higher pH values than 1.5 two $EuEDTA^-$ complexes, which differ from each other with one water molecule in the first coordination sphere of the Eu(III) ion, total coordination number and coordination geometry, are also formed. When the concentration of EDTA is higher than the concentration of Eu(III), an $EuEDTA(EDTAH)^{4-}$ species where the second EDTA is weakly coordinated to $EuEDTA^-$, is formed. If the concentration of Eu(III) ion is higher than EDTA, the extra Eu(III) ions associate with $EuEDTA^-$ and link to one of the carboxylate groups of EDTA thus causing a shortening of the excited-state lifetime of the $EuEDTA^-$ complex.

KEYWORDS: Lanthanides, europium, luminescence, ethylenediaminetetraacetic acid.

INTRODUCTION

In recent years, a great deal of synthetic work has been done with lanthanide chelates.[1–5] There are various reasons for such growing interest, such as the excellent luminescence properties of the complexes, which make them good candidates for use as spectroscopic probes and labels for a variety of chemical and biological applications,[6–8] their use as paramagnetic shift reagents or relaxation agents in NMR spectroscopy and imaging,[9–11] and the valuable catalytic properties of some lanthanides in organic synthesis.[12]

However, structures of lanthanide chelates in solution are not well known. Luminescence excitation spectroscopy of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu(III) using a pulsed dye laser light source has proved to be a valuable method in characterizing Eu(III) ion environments, particularly in solution.[13–16] The Eu(III) ion is especially useful in this regard as it has non-degenerate ground ($^7F_0$) and emitting ($^5D_0$) states, neither of which can be split by a ligand field of any symmetry. Thus the number of peaks in the excitation spectrum corresponds with the number of distinct Eu(III) ion environments. The $^7F_0 \rightarrow {}^5D_0$ transition corresponds to the pairing of two of

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the six unpaired electrons found in the ground state of Eu(III). It is forbidden as a magnetic dipole transition by the free ion selection rules $\Delta J \neq 0$ when $J = 0$ and is allowed by the electric dipole selection rules for ligand field symmetries of the point groups C_{1h}, C_n and $C_{n'v}$, where $n = 1,2,3,\ldots$ and $n' = 2,3,4,\ldots$[17] The energy of $^7F_0 \rightarrow {}^5D_0$ transition will therefore be a function of the interelectronic repulsion parameters of the ion, and any change in the energy can be regarded as a "nephelauxetic" effect. On the basis of the magnitude of this "nephelauxetic" effect, Horrocks and co-workers have discovered correlation between the overall formal charge on the ligands and the energy of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu(III) chelates.[18] Lately they have developed the theory further and found the correlation between the sum of partial charges of the coordinated atoms and the energy of the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu(III) chelate.[19]

In order to obtain more information on the complexation and solution structures of europium complexes of polyaminopolycarboxylate ligands, we studied the complexation of ethylenediaminetetraacetic acid (EDTA) with Eu(III) ion. Although EDTA is the most widely studied polyaminopolycarboxylate ligand complexed with lanthanides there are still some unresolved questions. Several research groups have studied the $^7F_0 \rightarrow {}^5D_0$ absorption, excitation or emission spectra of Eu(III)-EDTA-system.[14,15,20-22] Two distinct peaks at wavelengths 5796 Å and 5801 Å have always been found, thus indicating that there are two different complexes. These two peaks and consequently two different complexes are present together in solution at equilibrium and are related to ligand-exchange. The rate of interconversion is much greater than the characteristic de-excitation rate for each species and therefore the luminescence emission decays exponentially with a rate representative of a weighted average of the decay constants of both species.[14,23,24] The peak at 5796 Å is assigned to the complex with equimolar composition and the peak at 5801 Å is suggested to be due to a 1:2 complex, a 1:1 complex or both. Two 1:1 complexes at different wavelengths are thought to differ from each other because of different numbers of coordinated water molecules[22,25] or because of one carboxylate group with concomitant change in total coordination number.[21-23,25] In this work we have used luminescence spectroscopy in order to provide more detailed information about the structures of Eu(III)-EDTA complexes in different solutions and under different circumstances.

EXPERIMENTAL

Materials

The disodium salt of EDTA (99%), $EDTAH_4$ (99.5%), $CaCl_2$ (99.5%), H_3BO_3 (99.8%), CH_3COOH and NaCl (99.5%), were purchased from Merck. Europium(III) oxide (Eu_2O_3, 99.95%), 3-cyclohexylamino-1-propanesulfonic acid (CAPS, 99%), 4-morpholinepropanesulfonic acid (MOPS, 98%), 4-morpholineethanesulfonic acid (MES, 98%) and $TbCl_3$ (99.999%) were purchased from the Aldrich Chemical Co. LiCl (99.7%) was received from J.T. Baker Chemical Co. Gadolinium(III) oxide (Gd_2O_3, 99.9%) was obtained from Koch-Light Laboratories Ltd; sodium perchlorate ($NaClO_4$, 99.5%) and $(CH_3)_4N(Cl)$ (98%) from Fluka AG and CH_3CN (99.9%) from Lab-Scan Analytical Sciences.

A 0.1 M stock solutions of Eu(III) and Gd(III) were prepared by dissolving Eu_2O_3 or Gd_2O_3, respectively, in perchloric acid and a stock solution of 0.1 M Tb(III) by dissolving $TbCl_3$ in triply distilled water. These solutions were standardized using complexometric titrations with xylenol orange as indicator. A 0.1 M solution of EDTA was prepared by dissolving a weighed amount of Na_2H_2EDTA in triply distilled water. Buffer solutions (0.05 M) were prepared by dissolving either CAPS, H_3BO_3, MOPS, MES, CH_3COOH in triply distilled water and adjusting the pH with NaOH or HCl. The experimental solutions were then prepared by mixing appropriate volumes of Eu(III) and EDTA stock solutions and diluting to the required concentration with buffer solution of desired pH.

Instrumentation

Luminescence measurements were made using a pulsed nitrogen-pumped tunable dye laser apparatus. The nitrogen laser (model LN 1000, Photochemical Research Associates) operated at a repetition rate of 5 Hz. Rhodamine 6-G was used as a laser dye in the tunable dye laser (model LN 107, Photochemical Research Associates), which was controlled *via* a digital drive unit (model L-SCAN, Photochemical Research Associates). The bandwidth of the dye lasers was 0.04 nm and the pulse width 500 ps. The pulsed output of the dye laser was focused on the sample cell and luminescence emissions were collected and detected at 90° after passing through a spectrometer (model SPEX 1702, SPEX industries, inc.) by a photomultiplier tube (model R928, Hamamatsu Photonics, K.K.). The spectrometer has a 0.01 nm resolution, 0.75 m focal length and 0.1 nm accuracy. It was controlled *via* a unit (model SPEX Compudrive CD2A, SPEX industries, inc.) linked to a personal computer. The signal from the photomultiplier tube was transferred to the computer after integration on a gated integrator and boxcar averager module (model SR 250, Standford Research System), where the gate width was 150 μs and the delay of the gate after trigger pulse was changed by a control program, *via* computer interface (model SR 245, Stanford Research System). When measuring the excited-state lifetime the signal from the photomultiplier tube was monitored after amplification by a digitizing oscilloscope (Hewlett-Packard 54503A). The computer interface, digitizing oscilloscope and digital drive unit were connected to a personal computer *via* a GPIB bus. The measurement system was controlled by the personal computer and all data acquisition was carried out using the ASYST language programming package (Version 1.56, Macmillan Software Company).

The $^7F_0 \rightarrow {}^5D_0$ excitation spectra were obtained by scanning the dye laser through the $^7F_0 \rightarrow {}^5D_0$ absorption band from 5785 Å to 5815 Å whilst the luminescence intensity of the intense $^5D_0 \rightarrow {}^7F_2$ transition was monitored at 6150 Å. The excited-state lifetimes were determined by exciting the sample at a chosen wavelength and monitoring the emission profile on an oscilloscope at 6150 Å. The number of water molecules in the first coordination sphere of Eu(III) ion is obtained by recording the luminescence decay curves in both H_2O and D_2O, from which the reciprocal excited-state lifetimes, $\tau^{-1}_{H_2O}$ and $\tau^{-1}_{D_2O}$, were determined. The number of coordinated water molecules in the case of europium can be calculated from the equation given below.[26]

$$q = 1.05(\tau^{-1}_{H_2O} - \tau^{-1}_{D_2O})$$

Luminescence excitation spectra were resolved into their components using a curve fitting program, which was written using ASYST. The peak shapes are Lorentzian-Gaussian in aqueous solutions.[27] We used product function

$$I = I_{max}*\exp\{-0.30[(x-a)/b]^2\}/\{1+[(x-a)/b]^2\}$$

where I_{max} is the maximum intensity of the peak, a is the wavelength of the peak maximum and b is the half-width where $I = I_{max}*[\exp(-0.30)]/2$.

RESULTS AND DISCUSSION

Equimolar solutions

$^7F_0 \rightarrow {}^5D_0$ excitation spectra and excited-state lifetimes were measured as a function of pH in solutions, where Eu(III) ion and EDTA concentrations were 0.01 M. In our studies there were in almost every solution two major peaks centred at 5796.3 Å and at 5801.1 Å. The observed luminescence decay curves were always single exponentials and excited-state lifetimes were independent of the excitation wavelength. Maximum intensities of the two major peaks of Eu(III)-EDTA complex as a function of pH are plotted in Figure 1a and observed excited-state lifetimes at different pHs are plotted in Figure 2. Luminescence intensities of the two major peaks 5796.3 Å and 5801.1 Å were constant in pH range from 3.5 at 10.0. At low pH values the intensity of the 5796.3 Å peak reaches its maximum at about pH 2.5 and above that pH its intensity decreases, until it reaches a constant value after pH 3.5. The intensity of 5801.1 Å peak reaches its maximum at about pH 3.5 and

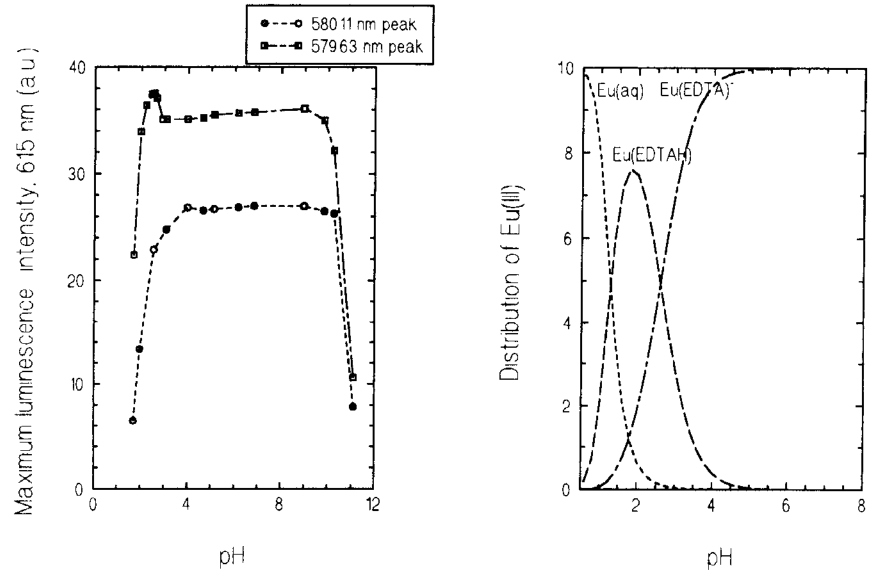

Figure 1 (a) The maximum intensities of the two major peaks of the $EuEDTA^-$ complexes at wavelengths 5796.3 Å and 5801.1 Å as a function of pH and (b) a distribution diagram based on the existing stability constants of different Eu(III)-EDTA species.[28] The concentrations of Eu(III) and EDTA were both 0.01 M.

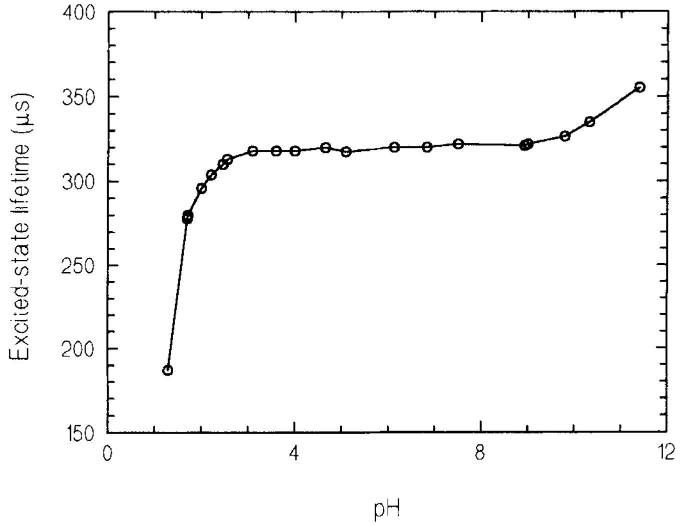

Figure 2 The observed excited-state lifetimes as a function of pH. The concentrations of Eu(III) and EDTA were both 0.01 M.

remains constant. In Figure 1b is shown a distribution diagram based on the existing stability constants of different Eu(III)-EDTA species.[28] According to this the intensity of the 5796.3 Å peak coincides well with the existence of both EuEDTAH and $EuEDTA^-$ chelates and because the position of this peak did not change and no new peaks were seen in the spectra in the pH range from 1.3 to 3.5 the first coordination sphere of Eu(III) ion must be quite similar in EuEDTAH and $EuEDTA^-$ chelates (chelates Ia and Ib). The intensity of 5801.1 Å peak, however, coincides only with the existence of $EuEDTA^-$ (chelate II). The excited-state lifetimes changed from 160 μs at pH 1.0 to 320 μs at pH 3.0 and remained constant until pH 10, after which the excited-state lifetimes became longer, probably due to formation of hydroxy complexes. Excited-state lifetimes shorter than 320 μs, which correspond quite well with six-coordination of EDTA if the total coordination number of Eu(III) ion is 9, were observed in equimolar solutions at pHs below 3 and also at pH 5.5 in solutions where concentration of Eu(III) ion was higher than the concentration of EDTA. In those solutions there were, besides EuEDTA chelates, $Eu(H_2O)_9{}^{3+}$ ions. $Eu(H_2O)_9{}^{3+}$ has an excited-state lifetime of ~105 μs but its peak were not seen in ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra due to the low luminescence quantum yield and high symmetry around the Eu(III) ion. These $Eu(H_2O)_9{}^{3+}$ ions have an influence on EuEDTA chelates because it is reported that in neutral media the exchange between $Ce(EDTA)^-$ and La(III), Gd(III), Pr(III), Sm(III) and Er(III) ions proceeds by association between the complex and Ln(III).[29] It is assumed that the dinuclear intermediate $Ce(EDTA)Ln^{2+}$ is formed on collision and the Ln(III) is linked to one of the carboxylate groups of EDTA. In order to see if these shorter excited-state lifetimes are due to association of excess Eu(III) ions with $EuEDTA^-$, we carried out an experiment where different amounts of either 0.05 M Eu(III) or 0.05 M Gd(III) solution were added to a 0.001 M solution of $EuEDTA^-$ at pH 5.5.

The lowest excited state of Gd(III) ion ($^6P_{7/2}$) is at a much higher energy level than the excited $^5D_0$ state of $EuEDTA^-$, making energy transfer from $EuEDTA^-$ to Gd(III) ions impossible. Stability constants of $GdEDTA^-$ and $EuEDTA^-$ are almost equal.[30] The excited-state lifetimes in both cases were measured as a function of concentration of excess of ions. These curves are plotted in Figure 3. In the case of Eu(III) ion the excited-state lifetime decreased from 325 μs to 155 μs when concentration of added Eu(III) ions was increased to 0.008 M but in the case of Gd(III) ion the shortening of excited-state lifetime was much smaller (from 325 μs to 255 μs). In the case of Gd(III) the shortening of the excited-state lifetime indicates the loosening of one coordination group of EDTA and binding of one water molecule in the first coordination sphere of Eu(III). Because the coordination properties of Eu(III) are much like those of Gd(III), in both cases the extra Ln(III) ions associate with $EuEDTA^-$ and coordinate to one of the carboxylate groups of EDTA rapidly. The difference in excited-state lifetimes between added Gd(III) ions and Eu(III) ions is probably due to energy transfer from $EuEDTA^-$ to associated or weakly coordinated Eu(III) ions. According to NMR-studies, the Ln(III)-O bond breaks and reforms very quickly.[29] Thus the exchange of the extra Ln(III) ions, which are coordinated with one group of the $EuEDTA^-$ complex or are associated with the $EuEDTA^-$ complex, is very rapid, causing the observed luminescence decay curve in solutions, where the concentration of Eu(III) is higher than the concentration of EDTA, to be single exponential and the excited-state lifetime to be independent of excitation wavelength (and dependent on the concentration of excess Eu(III) ions).

The peaks at 5796.3 Å and 5801.1 Å exists at the same time in equimolar solutions of Eu(III) and EDTA in the pH range from 3.5 to 10, and the rate of chemical interchange between these species is rapid, causing the observed excited-state lifetimes to be weighted averages of these species. For this reason it is difficult

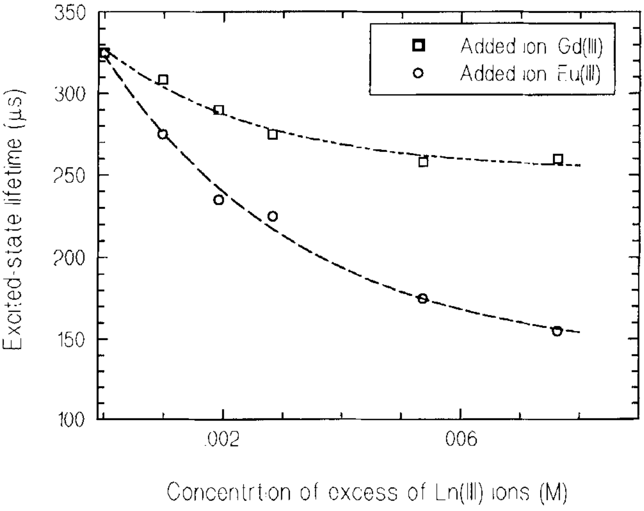

Figure 3 The excited-state lifetimes as a function of concentration of Ln(III) ions added to 0.001 M solution of Eu(III) and EDTA at pH 5.5.

to separate and identify them. According to published results[14,15,22] and our data we consider that in solutions where the concentration of Eu(III) is equal or higher than the concentration of EDTA, both peaks in the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III) are due to 1:1 complexes. In order to identify these peaks we undertook several different studies in equimolar solutions of Eu(III) and EDTA.

We added to solutions, where concentrations of both Eu(III) and EDTA were 0.002 M and pH was buffered to 5.8 with MES, either LiCl, $CaCl_2$, NaCl or $(CH_3)_4NCl$, in order to investigate the effect of added cations and ionic strength. Results are plotted in Figure 4. In the case of Na^+, Li^+ and Ca^{2+}, the added ions changed the spectra so that the intensity of the peak at 5796.3 Å increased relative to the intensity of the peak at 5801.1 Å, but the positions of the peaks did not change. The effect of $(CH_3)_4NCl$ was opposite, as 5801.1 Å peak gained intensity relative to 5796.3 Å peak. The reason for this behaviour is the increase of the ionic strength, favouring the formation of chelate II; in the case of NaCl, $CaCl_2$ and LiCl the small cations are associated with EuEDTA, as reported by Elglavish and Reuben[25,31] and this association clearly favours the formation of chelate Ia or Ib.

It has been previously reported by Geier and Jorgensen[21] that as temperature is increased, the intensity of the 5801.1 Å peak is increased and the intensity of 5796.3 Å peak is decreased. At the same time both peaks were slightly shifted to lower wavelengths. Because the 5801.1 Å peak was favoured at high temperatures and the 5796.3 Å peak at low temperatures, we attempted to crystallize these different species at different temperatures. From a solution where the concentrations of Eu(III) ion and EDTA were 0.02 M, pH was 3.0 and temperature 20 °C, we crystallized the Eu-EDTA complex and the measured $^7F_0 \rightarrow {}^5D_0$ excitation spectrum is shown in Figure 5a. Only one peak, which coincides well with the lower

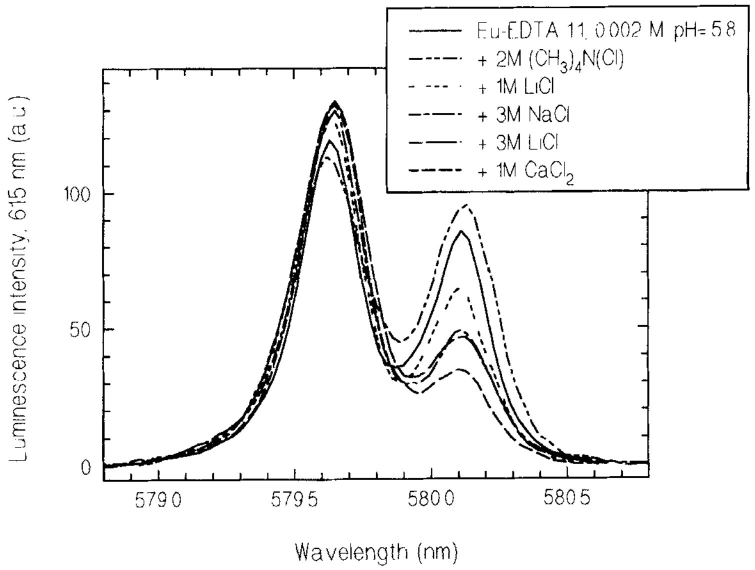

Figure 4 The effect of added cations and ionic strength on $^7F_0 \rightarrow {}^5D_0$ excitation spectra of 0.002 M $EuEDTA^-$ at pH 5.8.

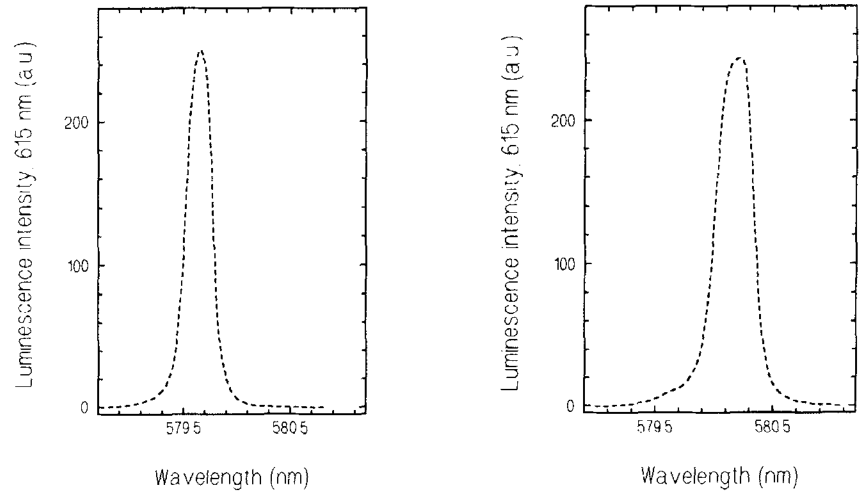

Figure 5 The $^7F_0 \rightarrow {}^5D_0$ excitation spectra of crystallized products from equimolar Eu-EDTA-solutions, (a) crystallized in 20°C and (b) crystallized from hot solution.

wavelength peak in Eu(III)-EDTA solutions at 5796.4 Å, was seen and the measured excited-state lifetime was 367 μs. The crystal structure was confirmed using X-ray studies and is $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$, which agrees with the structure reported by Hoard *et al.*[32] In this structure, Na^+ is simultaneously coordinated to one carboxylic acid oxygen of coordinated EDTA and to one coordinated H_2O molecule. From hot solutions of Eu_2O_3 and $EDTAH_4$, which was known on the basis of temperature measurements to favour the formation of chelate II, we obtained different crystals. In the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of these crystals there was also only one peak at 5802.0 Å. The spectrum is shown in Figure 5b. The observed excited-state lifetime was 1550 μs, indicating that there are no water molecules in the first coordination sphere of Eu(III). Unfortunately we were not able to solve the crystal structure of this compound, but the data obtained led us to conclude that Eu-EDTA complexes form some kind of a polymeric structure.

The $^7F_0 \rightarrow {}^5D_0$ excitation spectra and the excited-state lifetimes were measured in solutions where the concentration of $EuEDTA^-$ changed from 0.02 M to 0.0001 M at pH 7.1 (buffered with 0.1 M MOPS). The ratio between the intensity of the 5796.3 Å peak and the intensity of the 5801.1 Å peak together with the observed excited-state lifetimes are plotted as a function of $EuEDTA^-$ concentration in Figure 6. We found that the ratio between the intensity of the 5796.3 Å peak and the intensity of the 5801.1 Å peak slightly decreased when the concentration of $EuEDTA^-$ decreased. Simultaneously the excited-state lifetime increased from 320 μs to 380 μs probably because of the smaller number of water molecules in the first coordination sphere of Eu(III) in chelate II. This indicates that in solutions at 20 °C the 5801.1 Å peak cannot be from a polymeric structure because the proportion of this peak increased as the concentration of $EuEDTA^-$ chelate decreased.

The composition of solution was changed in such a way that instead of water we used acetonitrile-water mixtures. As we increased the proportion of CH_3CN relative

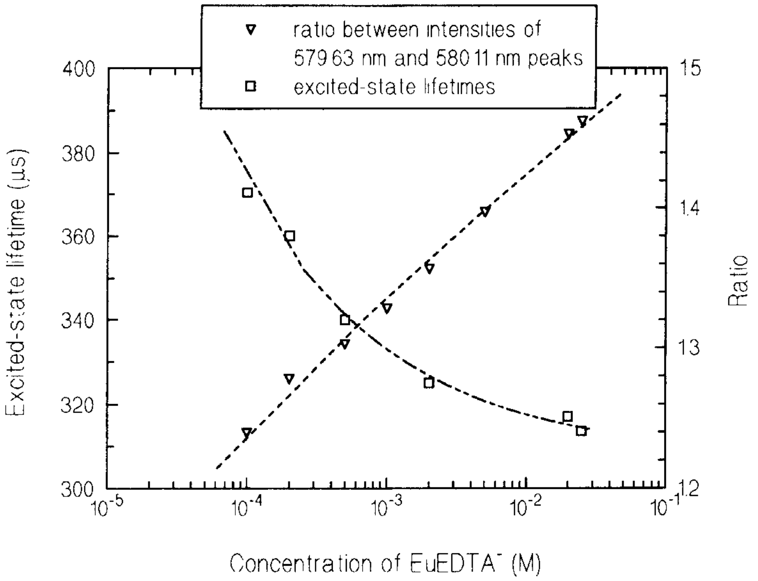

Figure 6 The ratio between the intensity of 5796.3 Å peak and the intensity of 5801.1 Å peak (dashed line) and the observed excited-state lifetimes (solid line) as a function of concentration of $EuEDTA^-$ at pH 7.1.

to H_2O, the intensity of the peak at 5801.1 Å increased referring also to smaller number of water molecules in chelate II.

Dexpert-Ghys and co-workers[15] have examined the EuEDTA-system in frozen solutions, where the exchange process becomes slow. They have observed in an equimolar solution three different peaks, one shorter-lived at 5801 Å and two longer-lived at wavelengths 5802.7 and 5805.5 Å. As the peaks in $^7F_0 \rightarrow {}^5D_0$ excitation spectra seem to shift to longer wavelengths as the temperature decreases, it is possible to interpret this peak at 5801 Å in a frozen solution as arising from the same structure as the 5796.3 Å peak in solution at 25 °C and at pHs higher than four. This structure around Eu(III) ion in solution is most likely the same as obtained from X-ray studies of $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$. At pH values lower than 4 the peak at 5796.3 Å is formed by both this $EuEDTA^-$ structure and the EuEDTAH structure and at pH values lower than 2.5, mostly by EuEDTAH. This conclusion was supported by the results obtained when adding into $Eu\text{-}EDTA^-$ solution either Ca^{2+}, Li^+ or Na^+ ions; association or coordination increased the intensity of this peak. Chelate II exists in equimolar solutions above pH 3 and its $^7F_0 \rightarrow {}^5D_0$ excitation peak is at longer wavelengths than the peak of chelates Ia and Ib. In aqueous solutions of Eu(III) ion the change in the "nephelauxetic" effect after Eu(III) is complexed is due to the compensation of water molecules with different ligating groups and atoms in the first coordination sphere of Eu(III). The magnitude of the "nephelauxetic" effect can then be thought to be the sum of several factors such as the type of coordinating atoms, the charge of the coordinating groups, the geometry of the ligand and the distance of different groups and coordinating atoms from the Eu(III) ion. To better understand the shifts of the $^7F_0 \rightarrow {}^5D_0$ transition

Frey *et al.*[19] have created a new model, where the energy of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu(III) chelate is dependent on the sum of partial (negative) charges on the ligating atoms. According to this model a partial charge of H_2O molecule is -0.834[19] and calculated sum of the partial negative charges of the eight-coordinated structure (six coordinating groups of EDTA and two water molecules) is -5.0. This value corresponds to an energy of 17238 cm^{-1} and a wavelength of 5801.1 Å, indicating that the difference in the energies of the $^7F_0 \rightarrow {}^5D_0$ transitions of chelates I_a and I_b and chelate II is due to exclusion of one water molecule in the first coordination sphere of the Eu(III) ion. Our observations from experiments, where the ionic strength was increased with $(CH_3)_4N(Cl)$ and the proportion of water was reduced with CH_3CN, support the conclusion that the chelate II is a complex where less than three water molecules are in the first coordination sphere of Eu(III). Chelate II is thus most likely eight-coordinate by six coordinating groups of EDTA and two water molecules. From hot solutions, a structure where two or more $EuEDTA^-$ complexes are linked together is crystallized, but the concentration of this species is probably quite small in aqueous solutions.

Solutions of Excess of EDTA

$^7F_0 \rightarrow {}^5D_0$ excitation spectra, maximum intensities, I_0, and excited-state lifetimes of the individual exponential components, resolved from the luminescence decay curves, were measured as a function of concentration of EDTA at pH 6.1. The solutions were buffered with MES. Maximum intensities of 5796.3 Å and 5801.1 Å peaks are plotted in Figure 7a and observed excited-state lifetimes in Figure 7b. The concentration of Eu(III) was 0.01 M. Luminescence decay curves were also always

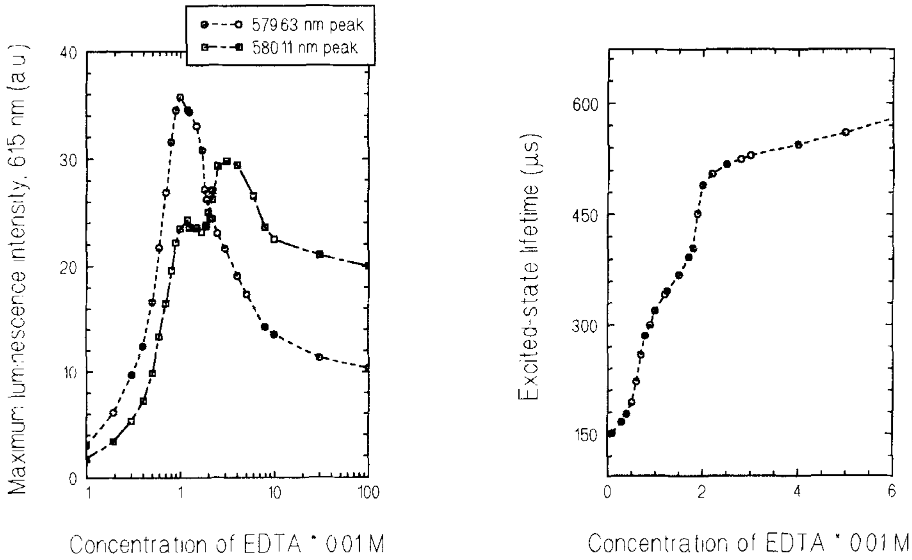

Figure 7 The maximum intensities of 5796.3 Å peak and 5801.1 Å peak (a) and the observed excited-state lifetimes (b) as a function of concentration of EDTA at pH 6.1. The concentration of Eu(III) was 0.01 M.

single exponentials and the excited-state lifetimes were independent of the excitation wavelength. In these measurements, when the EDTA-Eu(III) ratio was greater than 1, besides the peaks at 5796.3 and 5801.1 Å, there a new peak centred at 5800.2 Å was seen. The measured $^7F_0 \rightarrow {}^5D_0$ excitation spectrum, resolved components and calculated sum spectrum of the components from solutions where the EDTA-Eu(III) ratio is 10 are illustrated in Figure 8. In Figure 7a it is seen that the intensity of the 5796.3 Å peak reaches a maximum at ratio 1, when the EDTA-Eu(III) ratio changes from 0.1 to 10.0 at pH 6.1. The 5801.1 Å peak also reaches its first maximum at this same ratio and reaches a second and higher maximum at ratio 2 because of the formation of the 5800.2 Å peak. In Figure 7b, when the EDTA-Eu(III) ratio changes from 0.1 to 10.0, the observed excited-state lifetime is changed from 160 μs to 770 μs. There are also two plateaus in this Figure at ratios 1 and 2. Because the excited-state lifetime is clearly longer than 320 μs at EDTA-Eu(III) ratios greater than 1.5, it can be deduced that these species have less than three water molecules in the first coordination sphere of Eu(III). The $^7F_0 \rightarrow {}^5D_0$ excitation spectra is shown as a function of EDTA-Eu ratio in Figure 9. The combination 5800.2 and 5801.1 Å peak shifts to lower wavelengths, because of the growth of the 5800.2 Å peak and decrease of the 5801.1 Å peak. When the concentration of Eu(III) was 0.001 M and the concentration of EDTA was 0.1 M at pH 10.0, only this 5800.2 Å peak existed and the observed excited-state lifetime was 1080 μs. According to this data the 5800.2 Å peak is due to the formation of a chelate where one Eu(III) ion is coordinated to two EDTAs. The shift from 5796.3 Å to 5800.2 Å in $^7F_0 \rightarrow {}^5D_0$ excitation spectra occurs because the extra coordinating groups of EDTA exclude water molecules from the first coordination sphere of

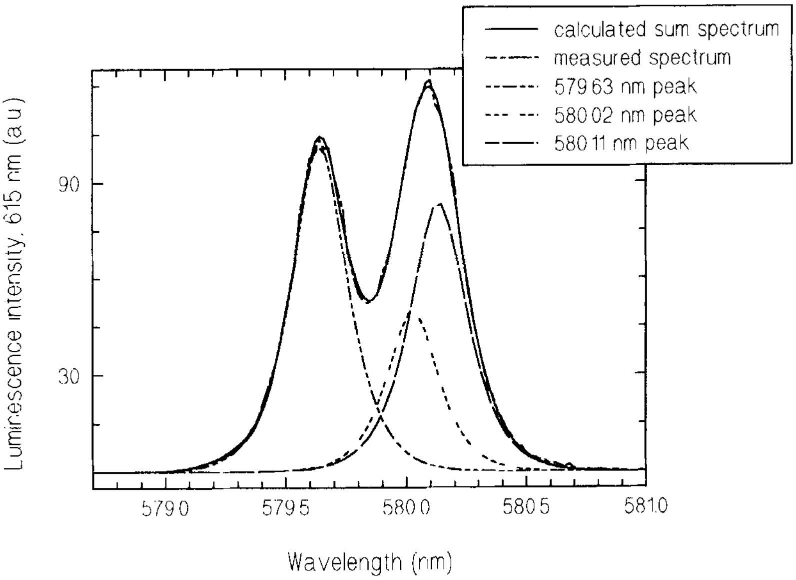

Figure 8 The measured $^7F_0 \rightarrow {}^5D_0$ excitation spectrum, resolved components and calculated sum spectrum of the components from solutions where the concentration of EDTA was 0.1 M, the concentration of Eu(III) 0.01 M and pH 6.1.

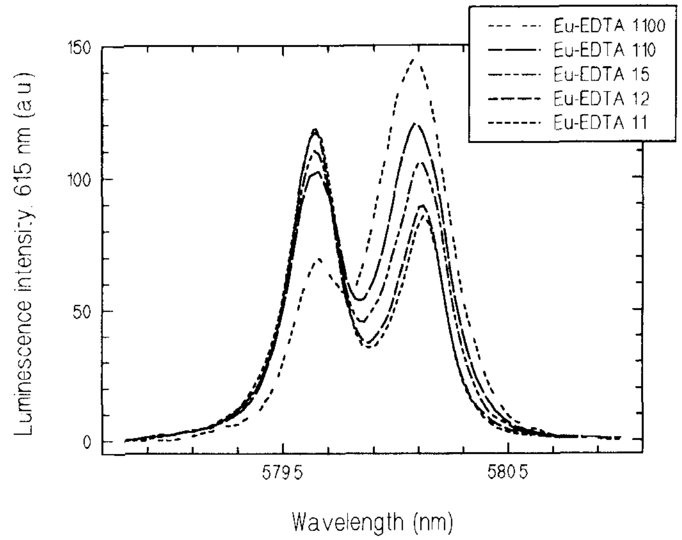

Figure 9 The $^7F_0 \rightarrow {}^5D_0$ excitation spectra as a function of Eu(III):EDTA ratio at pH 7.0. The concentration of Eu(III) was 0.001 M.

the Eu(III) ion. To obtain further information on this chelate we measured $^7F_0 \rightarrow {}^5D_0$ excitation spectra of solutions in which the concentration of Eu(III) ion was 0.01 M and the concentration of EDTA 0.02 M as a function of pH. In Figure 10 the ratio between the intensity of the 5796.3 Å peak and the sum of intensities of 5800.2 and 5801.1 Å peaks is plotted as a function of pH. The ratio between intensities of 5796.3 and 5801.1 Å peaks as a function of pH from equimolar solutions of Eu(III) and EDTA is shown in the same Figure. According to this it seems to be that at lower pH values only 1:1 complexes exist, because the ratio between the intensity of this unresolved peak and the intensity of the 5796.3 Å peak is equal for equimolar solutions, and when pH > 5 formation of the 1:2 complex starts. It also seems to be that the formation of this 1:2-complex correlates with deprotonation of the third carboxylic acid group of EDTA (pK_a 6.18). This means that this chelate is formed when there are EDTAH^{3-} ions in solution and the concentration of EDTA is higher than the concentration of Eu(III) ion. In this case the excited-state lifetimes were also independent of excitation wavelength, which means that excitation at wavelengths of 5796.3, 5800.2 and 5801.1 Å led to the same excited-state lifetime. This is not possible unless there are energy transfer processes between 1:2 and 1:1 -chelates or unless the coordination sphere around excited Eu(III) is able to change from 1:2 to 1:1 chelates or *vice versa*, faster than the observed excited-state lifetime. In this case the existence of energy transfer is not probable, because both chelates are negatively charged. Taking into account that in the case of the ternary Eu(EDTA)(IMDA) complex, where IMDA is iminodiacetic acid, the observed excited-state lifetime of Eu-EDTA-IMDA solutions is dependent on excitation wavelength, we suppose that in the 1:2-chelate the second EDTA is weakly coordinated through two groups to EuEDTA$^-$ and is able to bind reversibly and faster than the observed excited-state lifetime. The ligating atoms of the second

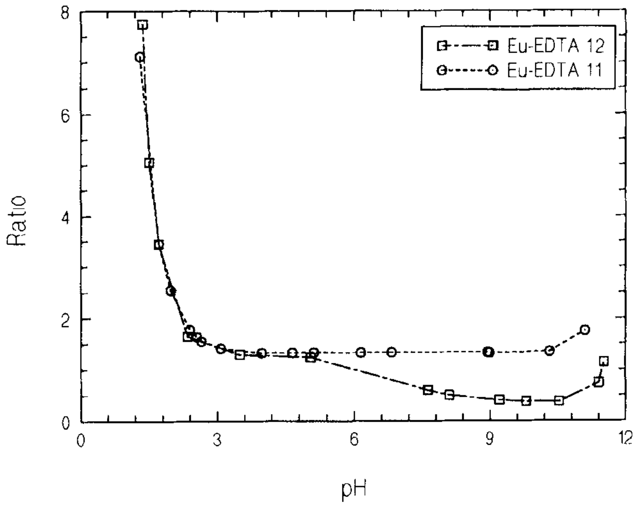

Figure 10 The ratio between the intensity of the 5796.3 Å peak and the sum of intensities of peaks at 5801.1 and 5800.2 Å when Eu:EDTA ratio is either 1:1 or 1:2 as a function of pH. The concentration of Eu(III) was 0.01 M.

EDTA may be the carboxylate oxygens of one of the iminodiacetic acid groups of EDTA, because according to Figure 9 the formation of the 1:2 chelate starts after deprotonation of the third carboxylic acid group of EDTA, thus enabling the one of the iminodiacetic acid groups of EDTA be totally deprotonated. This peak at 5800.2 Å is at shorter wavelengths than in the ternary complex Eu(EDTA)(IMDA),[33] indicating also that the second EDTA is coordinated to $EuEDTA^-$ with a smaller number of coordinating groups than IMDA; there is probably still one water molecule left in the first coordination sphere of the Eu(III) ion in this chelate. We thus interpret this chelate to be $Eu(EDTA)(EDTAH)^{4-}$.

It is rather difficult to obtain exact information on the coordination of Eu(III) with polyaminopolycarboxylate ligands in solution. With luminescence measurements, especially with measured excited-state lifetimes and $^7F_0 \rightarrow {}^5D_0$ – spectroscopy, it is possible to get good estimates of the coordination around the Eu(III) ion. There are often different species present, which are together at equilibrium, and the rate of chemical interchange of different species is rapid or there are energy transfer processes between them. In these cases we are able to observe different peaks in $^7F_0 \rightarrow {}^5D_0$ spectra but only a single exponential decay curve. In addition it is not possible to obtain exact information about concentrations of certain species, because the intensity of the peak in the $^7F_0 \rightarrow {}^5D_0$ spectrum depends on the concentration of the species, the symmetry of the chelate and on its luminescence quantum yield.

EDTA forms both 1:1 and 1:2 complexes with Eu(III) ion. In $^7F_0 \rightarrow {}^5D_0$-spectroscopy three different 1:1 complexes were isolated, one EuEDTAH and two $EuEDTA^-$ complexes, which differ from each other by one water molecule, total coordination number and coordination geometry. The $EuEDTA^-$ complex, whose peak in the $^7F_0 \rightarrow {}^5D_0$ excitation spectra is at 5796.3 Å, is nine coordinate (six ligand groups of EDTA and three water molecules). The peak at 5801.1 Å is then due to a structure where Eu(III) ion is eight coordinate (six ligand groups of EDTA and two water molecules). The formation of a 1:2 complex, which is most probably Eu(EDTA)(EDTAH)$^{4-}$, starts when the concentration of EDTA is higher than the concentration of Eu(III) and the $^7F_0 \rightarrow {}^5D_0$ peak of this complex is at wavelength 5800.2 Å. An interesting feature is the crystallization of a polymeric structure from hot solutions of 0.025 M Eu_2O_3 and 0.05 M H_4EDTA. This probably exists only in crystals or at high temperatures and in concentrated solutions. When the concentration of Eu(III) ion is higher than the concentration of EDTA, the extra Eu(III) ions are associated with EuEDTA$^-$ complex and linked to one of the carboxylate groups of EDTA, leading to shortening of excited-state lifetime. This is possible, because the difference in energies of $^5D_0$ states of the chelated Eu(III) ion and the weakly bonded Eu(III) ion is small and Eu(III) ion is capable to accepting energy from the excited complex.

Acknowledgements

The author would like to thank Reijo Sillanpää for the measurements of X-ray crystal structures. The research was supported by the Emil Aaltonen Foundation.

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