# Luminescence and Potentiometric Studies on the Complexation of Europium(III) by Picolinate in an Aqueous Solution

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**Abstract:** The complexation of $Eu^{3+}$ aquo ions by picolinic acid in an aqueous solution was investigated to describe the formation of polynuclear complexes that are uncommon for trivalent lanthanides. Potentiometric titration indicated that no polynuclear complexes formed *via* hydroxide bridges, even at high pH, and that the monomeric form $[Eu(Pic)_4 \cdot (H_2O)]^-$ was present when a large excess of a picolinate ligand was used. In addition, lifetime analysis of $Eu^{3+}$ luminescence *via* time-resolved laser-induced fluorescence spectroscopy was performed under conditions where $Eu(pic)^{2+}$ appears as the secondary dominant species. Strong quenching of the luminescence was detected, suggesting that polymeric complexes $([Eu(Pic)]_m^{2m+})$ form, even at low pH, owing to a vicinal Eu–Eu interaction.

**Keywords:** $Eu^{3+}$ complex, picolinic acid, polynuclear complex, TRLFS.

## INTRODUCTION

Understanding of the coordination chemistry for lanthanide(III)–organic ligand complexes in an aqueous solution plays a significant role in the current design and synthesis of fascinating hybrid materials, such as porous coordination polymers, metal organic frameworks, and supramolecular polymetallic assemblies of lanthanides [1-3]. The analytical methods used for investigating such materials, for example, time-resolved laser-induced fluorescence spectroscopy (TRLFS) at low concentration, are also useful for examining chemical speciation under the wide-ranging experimental conditions assumed to be present in the terrestrial environment [4-6].

In particular, the chemical behavior of these complexes has attracted much attention with respect to nuclear waste management. This is because natural organic ligands are generated as a result of microbiological degradation of organic materials, and thus, their complexation with lanthanide(III) species significantly contributes to the transport phenomena of radionuclides. Note that lanthanide(III) is considered a chemical analogue of trivalent actinides in this case.

A few studies have described the determination of the stoichiometry and stability constants for lanthanide

and actinide complexes with organic ligands using TRLFS. These studies mainly treated simple binary M–L systems upon complexation, where M and L denote the metal ions and ligands, respectively [7-9]. However, a more complicated complexation is expected under practical conditions, *e.g.,* in the neutral to high pH region.

Recent studies have revealed the polynuclear complex formation of tetravalent actinide and trivalent lanthanide–glycolate ($HO-CH_2-COO^-$) and 5-sulfosalicylate ($HO-C_6H_3SO_3-COO^-$) systems in aqueous solutions [10-12] as metal-OH-ligand-type ternary complexes. Both the glycolate and 5-sulfosalicylate ligands form chelate complexes *via* -OH and -COOH functional groups. Thus, a similar reaction would be expected in the presence of other functional groups.

According to Zheng [10], even a highly stable ligand such as ethylenediaminetetraacetic acid (EDTA; a typical N/O-type ligand) can form polymetallic complexes with -OH- ($\mu$-hydroxo) bridging donors in the solid state. Moreover, a number of polymeric complexes have been reported in the solid state. An N/O-type ligand would actually favor polynuclear complex formation. We, therefore, investigated the complexation behavior of $Eu^{3+}$ with picolinate as a representative system for trivalent lanthanide-N/O-type donor group systems and explored the possibility of polynuclear complex formation in aqueous solutions.

In previous studies with glycolate and 5-sulfosalicylate as ligands, polymerization in an aqueous

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system was driven by two different controlling factors: metal cation hydrolysis and ligand bridging. The hydrolytic -OH group can act as a strong bridging donor between the metals in the case of glycolate and 5-sulfosalicylate. On the other hand, the heterogeneous N atom on the six-membered ring in the picolinate system cannot play the same role without carboxylate coordination. Therefore, polymeric complex formation may take place *via* only two mechanisms: 1) bridging *via* hydroxide caused by hydrolysis and 2) bridging *via* the N/O atoms of the picolinate. Brittain [13] suggested the polynuclear complex formation of the $Tb^{3+}$–picolinate system based on the pH dependence of its luminescence quenching behavior. In his study, while the 1:1 complex $Tb(Pic)^{2+}$ may exist in a polymeric conformation, no evidence for such a polymeric form was obtained. To confirm the formation of the polymetallic form using TRLFS, we conducted two experimental series in which the predominant chemical species was different.

## 2. EXPERIMENTAL

### 2.1. Materials

A stock solution of 0.218 M $EuClO_4$ was prepared by dissolving $Eu_2O_3$ (Kanto Chemical Co., Ltd.) in perchloric acid followed by determination of the $Eu^{3+}$ concentration using inductively coupled plasma-atomic emission spectroscopy. Analytical grade picolinic acid was used as received to prepare a stock solution of sodium picolinate and picolinic acid. A sodium perchlorate solution was prepared from analytical grade $NaClO_4 \cdot H_2O$ (Merck p.a.) and analyzed by weighing samples dried at 393 K. All aqueous solutions were obtained using degassed ultrapure water (Milliore, Milli-Q plus).

### 2.2. Apparatus

$Eu^{3+}$–piconilnate complexes were excited at $\lambda_{ex}$ = 394 nm *via* second harmonic generation at 788 nm derived from a Ti:sapphire oscillator connected to a regenerative amplifier. A streak camera (Hamamatsu C5680) with a Czerney-Turner spectrograph (Chromex 250is) and 300 g $mm^{-1}$ grating was used to collect the emission light. Detailed information on the instrumental setup is described elsewhere [6,8-9].

### 2.3. Experimental Procedures

#### a. Potentiometry: Complexation in the Alkaline Region with a Large Excess of Ligand

Standard potentiometric titration and TRLFS were employed in the present study, because the former

gives information on the number of released protons due to hydrolysis and the latter reveals polymeric complex formation as luminescence quenching (*vide infra*). The reaction in the system can generally be described as follows:

$$pM^{3+}(aq) + qL^- \rightleftarrows M_pL_q(OH)_r^{3p-q-r} + rH^+. \tag{1}$$
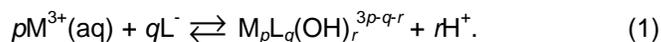
The average number of dissociated protons $n_H$ in the complex is determined using potentiometric titration as follows:

$$n_H = \frac{C_{OH} - K_w/[H^+] + [HL]}{C_M} = \frac{C_{OH} - K_w/[H^+] + [H^+] \cdot C_L / K_a}{C_M}, \tag{2}$$

where $C_{OH}$ and $C_M$ denote the total concentrations of the NaOH and metal ions, respectively, and $K_a$ represents the deprotonation constant for HL.

The formation constants for binary $Eu^{3+}$–picolinate have been reported as $\log\beta_{1,1}$ = 3.61, $\log\beta_{1,2}$ = 6.75, $\log\beta_{1,3}$ = 9.16, and $\log\beta_{1,4}$ = 11.16 [18, 19]. Therefore, in the presence of a large excess of ligand, e.g., $C_{Eu,tot} \approx$ 1 mM and $C_{L,tot}$ = 1.5 M, *eq.* (1) can safely be reduced to *eq.* (3) under neutral to alkaline conditions, where the complexation of $EuL_4^-$ is complete:

$$pEuL_4^-(aq) \rightleftarrows Eu_pL_{q'}(OH)_r^{3p-q'-r} + (4p-q')L^- + rH^+. \tag{3}$$
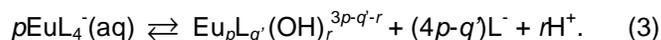
The number "$r$" in *eq.* (3) can directly be determined by standard potentiometric titration. Therefore, based on the reactions of *eq.* (1) and *eq.* (2), titration curves of $r/p$ (=$n_H$) against $-\log[H^+]$ yield the average number of dissociated protons per metal ion. Hydrolysis in an aqueous solution containing $Eu^{3+}$ ion concentration of several millimolar typically occurs at pH > 7 [14]. Therefore, polynuclear complex formation *via* hydroxide bridges may be expected in neutral to alkaline conditions. It should be noted, however, that at high pH, hydroxide precipitates such as insoluble $Eu(OH)_3(s)$ are typically formed. In fact, the formation of hydroxide precipitates was observed when $C_{Eu,tot}$ = 0.563 mM and $C_{L,tot}$ = 258.1 mM at pH = 10.98. Note that hereafter $C_{Eu,tot}$ and $C_{L,tot}$ represent the total concentrations of $Eu^{3+}$ and picolinate in the system, respectively. Nevertheless the formation of hydroxide could be avoided by using a large excess of picolinate, thus allowing the exploration of further complexation behavior, such as polymerization, at higher pH.

Hence, standard potentiometric titration at $C_{Eu,tot}$ = 6.84 mM and $C_{Eu,tot}$ = 710 mM was performed. All measurements were performed at a constant sodium

ion concentration ([Na$^+$] = 1.50 M) *via* addition of NaClO$_4$. All electromotive force measurements were performed at room temperature using the combined Orion pH electrode (Thermo Fisher Scientific K. K.). The inner solution for the electrode was replaced with 1.00 M NaCl in order to avoid precipitation of insoluble KClO$_4$. The electrode slope was calibrated using an acid–base titration, and E$_0$ was determined before each titration using Gran's method. Ar gas passed through the water was purged during the titration to avoid contamination by CO$_2$. In the titration curves, the measured pH is plotted against the amount of OH added to the system.

### b. TRLFS: Evaluation of the Hydration Number

TRLFS was also employed to determine the coordination structure of the complexes and to examine the possibility of polynuclear complex formation. A detailed description of the procedure is available in the literature [5, 14-17], and thus, only a brief summary is provided here.

In general, the rate of decay of the apparent luminescence of Eu$^{III}$ ($^5D_0$) from the excited state to the ground state without any quencher, $k_{app}$, is written as follows:

$$k_{app} = k_{rad} + k_{nr} + k_{H_2O}, \tag{4}$$

where $k_{rad}$, $k_{nr}$, and $k_{H_2O}$ are the rate constants of the de-excitation caused by radiation, nonradiative decay, and vibrational excitation of the water molecules surrounding the Eu$^{3+}$. Because of the third term, $k_{H_2O}$, the apparent luminescence lifetime of Eu$^{3+}$ is related to its hydration number. Horrocks Jr. [15] and lately Kimura [14] reported the empirical relationship between the apparent lifetime in an H$_2$O solvent and the hydration number, $q$, of Eu$^{3+}$ as follows:

$$q = 1.05 \cdot k_{app} - 0.44. \tag{5}$$

Beeby *et al.* [17] also reported an empirical relationship for *q'*:

$$q' = A'(k_{app(H_2O)} - k_{app(D_2O)} + k_{corr}'), \tag{6}$$

where $k_{app(H_2O)}$ and $k_{app(D_2O)}$ are the apparent luminescent lifetimes in H$_2$O and D$_2$O solvents, respectively. The coefficient *A'* is the improved factor, and $k_{corr}'$ is the correction factor for the effect due to water diffusion. Relationship (6) is obtained using the same approach as that for *eq.* (5); therefore, in principle, *eq.* (5) and *eq.* (6) may give an identical result. Only in the two following exceptional cases will *eqs.* (5) and (6) lead to different results: 1) the effect of water diffusion (water molecules beyond the second coordination sphere) is not strong and 2) the nonradiative de-excitation pathway, $k_{nr}$, is strongly different from that for the free Eu$^{3+}$ ion. It is known that the former sometimes causes problems for complexes with highly hydrophilic ligands, and both *eq.* (5) and *eq.* (6) provide incorrect results in this case. In fact, the factor *A'* and correction term $k_{corr}'$ were proposed by Beeby *et al.* [16] for highly hydrophilic ligand systems in order to avoid this problem. The latter is caused by the appearance of other de-excitation processes, *e.g.*, intramolecular metal-to-ligand charge transfer or metal–metal charge transfer in polynuclear complexes, and thus, *eq.* (5) leads to "overestimation" of the hydration number. Moreover, *eq.* (6) may give the correct result because the subtraction of $k_{app(D_2O)}$ from $k_{app(H_2O)}$ cancels out the effect in the $k_{nr}$ term. Accordingly, a comparison of the results for the two different empirical relationships may allow a discussion of the possibility of polymerization.

**Table 1:  Hydration State *q* in the First Hydration Sphere of Eu(Pic)$_4^-$**

| pH | $t_{H2O}$ / ms | S.D. | $k_{H2O}$ / ms$^{-1}$ | $t_{D2O}$ /ms | S.D. | $k_{D2O}$ / ms$^{-1}$ | $q$ | $q'$ |
|---|---|---|---|---|---|---|---|---|
| 6.135 | 0.577 | 0.016 | 1.733 | 1.833 | 0.055 | 0.568 | 1.379 | 1.097 |
| 6.539 | 0.573 | 0.011 | 1.746 | 1.527 | 0.059 | 0.635 | 1.393 | 1.033 |
| 7.090 | 0.589 | 0.025 | 1.698 | 1.552 | 0.035 | 0.6568 | 1.342 | 0.949 |
| 8.184 | 0.572 | 0.008 | 1.749 | 1.525 | 0.089 | 0.698 | 1.397 | 0.961 |
| 8.581 | 0.577 | 0.001 | 1.733 | 1.621 | 0.086 | 0.670 | 1.379 | 0.974 |
| 9.300 | 0.592 | 0.028 | 1.689 | 1.635 | 0.096 | 0.654 | 1.333 | 0.942 |
| 10.180 | 0.599 | 0.028 | 1.669 | 1.620 | 0.095 | 0.657 | 1.312 | 0.914 |

The variable $\tau_{H2O}$ is the apparent lifetime of the transition moment owing to the electric dipole ($^5D_0 \rightarrow ^7F_1$) in H$_2$O, $\tau_{D2O}$ is the lifetime in D$_2$O, $k_{H2O}$ and $k_{D2O}$ are the rate constants in H$_2$O and D$_2$O solutions, respectively, and S. D. stands for standard deviation.

The TRLFS measurements were performed at $C_{Eu,tot}$ = 6.84 mM and $C_{L,tot}$ = 710 mM at pH (and pD) values varying from 6.33 to 10.88. All measurements were performed at a constant sodium ion concentration of $[Na^+]$ = 1.50 M (adjusted with $NaClO_4$) at 293 K. Each measurement was repeated three times in order to evaluate the standard deviation of the lifetime. Typical luminescence spectra are shown in Figure **2**. All of the decay curves were found to be mono-exponential. The evaluated lifetimes and the hydration numbers calculated using *eqs.* (5) and (6) are listed in Table **1**.

### c. Complexation in the Acidic Region—Dependence on the Total Concentration of the Complexes

This series of experiments was performed to examine whether polymeric complex formation takes place *via* a bridging carboxylate group. TRLFS measurements were performed under conditions where $Eu(Pic)^{2+}$ and $Eu^{3+}$ coexist, and the formation of polymeric complexes was confirmed from the spectral analysis of the quenching behavior. The total concentration of $Eu^{3+}$ and picolinate in the samples was adjusted to 1.0–100 mM and 0.33–33.3 mM, respectively. Note that the $C_{Eu,tot}$ to $C_{L,tot}$ ratio was kept constant at 3:1. The pH of all samples was adjusted to 5.50 ± 0.01, where the $[Eu^{3+}]:[Eu(pic)^{2+}]$ ratio is nearly constant at 8:2 over a wide concentration range. The distribution diagram for the present experimental conditions was calculated using stability constants reported in the literature [18,19].

## 3. RESULTS AND DISCUSSION

### 3.1. Complexation in the Alkaline Region with a Large Excess of Ligand

The titration curves are shown in Figure **1**. The solution at $C_{L,tot}$ = 1.00 M was neutralized by the addition of 10.0 ml of a 2.00 M NaOH solution, although the system contained 8.12 mM $Eu^{3+}$. If hydrolytic reaction had occurred, *eq.* (3) would apply, and the total amount of added 2.00 M NaOH would vary from 10.08–10.16 to 10.24 ml, corresponding to r = 1, 2, and 3, respectively. This result consequently supports the conclusion that no hydrolysis took place under the present conditions. Strong buffering was observed at pH ≈ 11, presumably indicating the formation of a binary hydroxide. A white precipitate was observed indeed at pH = 11.68.

The luminescence spectra and lifetime analysis seem to indicate that hydrolysis is not promoted. It is often stated that a change in the shape of the luminescence spectrum occurs when the hydrolytic reaction of $Eu^{3+}$(aq) proceeds [20]. However, as shown in Figure **2**, no major difference in the luminescence spectra was observed with changing pH. The hydration number calculated by the empirical relationship modified by Beeby *et al.* [16] showed no change and remained constant at approximately $q'$ = 1.00 within negligible standard uncertainties. It is generally thought that the most common hydration number for $Eu^{3+}$ is between eight and nine in aqueous solutions. In this case, the hydration number implies the formation of bi-
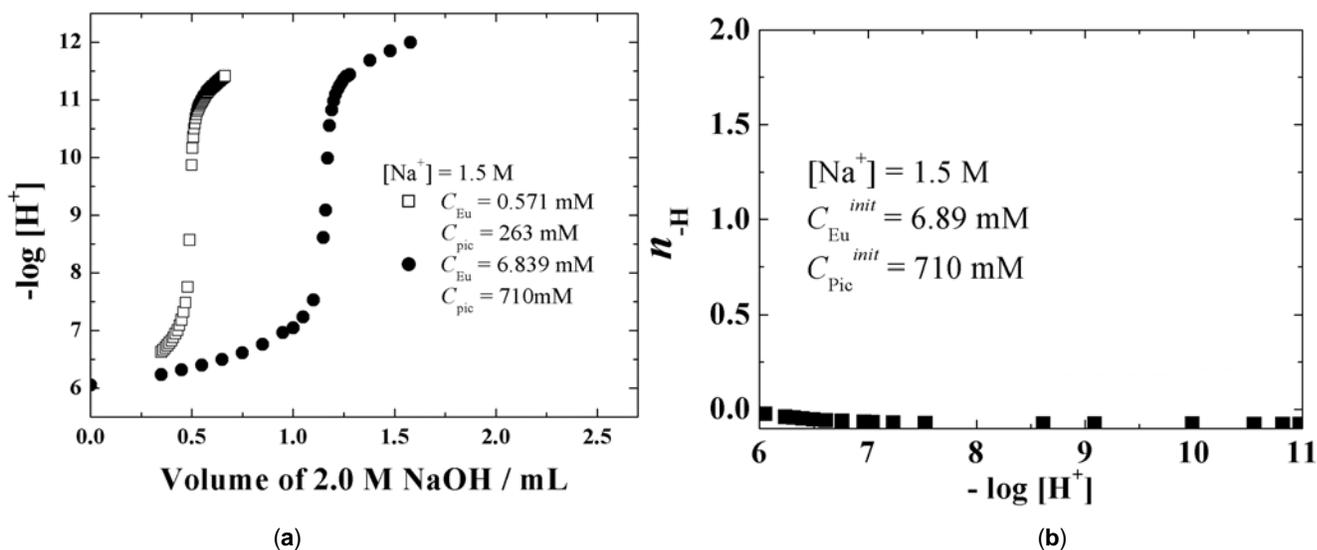


(a)                                                    (b)

**Figure 1:** Titration curves for the Eu(III)–picolinate system. (**a**) Total concentration of europium is 0.57 mM (□) and 6.83 mM (●), and the total concentration of picolinate is 263 mM (□) and 710 mM (●). (**b**) Average number of protons dissociated per europium in the presence of a large excess of ligand plotted against −log[H$^+$].

dentate ligands with a hydrated water molecule, $EuL_4 \cdot H_2O$, which corresponds to the potentiometric result; even at relatively high pH, hydrolysis does not take place (Figure **1b**). This finding is noteworthy; although hydration water remains, further hydrolytic reaction does not take place, even under highly alkaline conditions, *e.g.*, pH = 10. It should be mentioned that other chemical species in the system may provide a quenching effect, which could lead to an incorrect estimation of the luminescence lifetime. According to the report by Kimura *et al.* [14], the apparent luminescence lifetime value can be variable in a condensed ionic solution. In this study, perchlorate ions may cause luminescence quenching. In ionic media composed of 0.5 M $NaClO_4$, the effect was found to be negligible as a matter of fact.
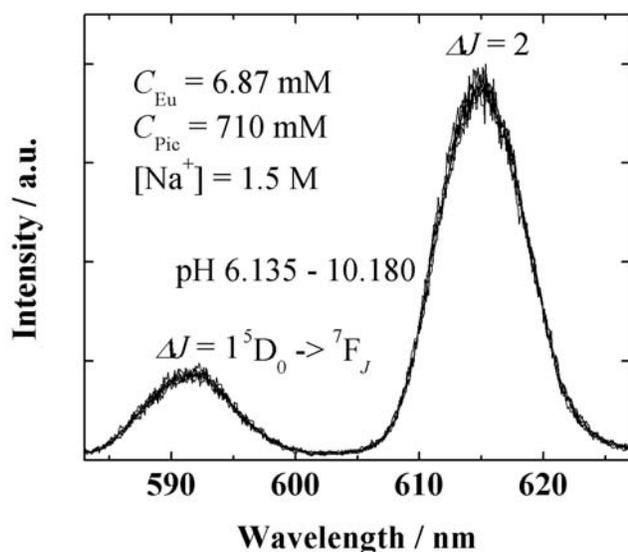


**Figure 2:** Luminescence spectra of Eu–picolinate complexes as a function of pH (from near neutral to alkaline conditions: 6.135, 6.539, 7.090, 8.184, 8.581, 9.300, and 10.180).

## 3.2. Complexation in the Acidic Region—Dependence on the Total Concentration of the Complexes

Typical luminescence spectra of $Eu^{3+}$–picolinate complexes as a function of the total concentration are shown in Figure **3**. The peak height ratio of 615/592 remained constant at approximately 0.5 in the series. Because the emission intensity of $Eu^{3+}$ ions is far weaker than that of $Eu(Pic)^{2+}$, one cannot determine the precise quantitative change in chemical speciation. However, a plausible assumption was made based on the speciation calculated from the potentiometry measurements, and the results indicated that the molar ratio of $Eu^{3+}$ aquo ions and $Eu(Pic)^{2+}$ ions was nearly constant, as mentioned above, within meaningful

deviations. The lifetimes are plotted against $C_{Eu,tot}$ in Figure **4**. Interestingly, the lifetime in $D_2O$ was reduced as the total $C_{Eu}$ concentration increased. If a mononuclear species was dominant, the lifetime would be constant. Therefore, the change in the lifetime suggests the formation of a new chemical component in the system, although the previously reported stability constants gave the dominant species as $[Eu(Pic)]^{2+}$ under all experimental conditions. This observation can be explained by considering the kinetics of the luminescence lifetime analysis.
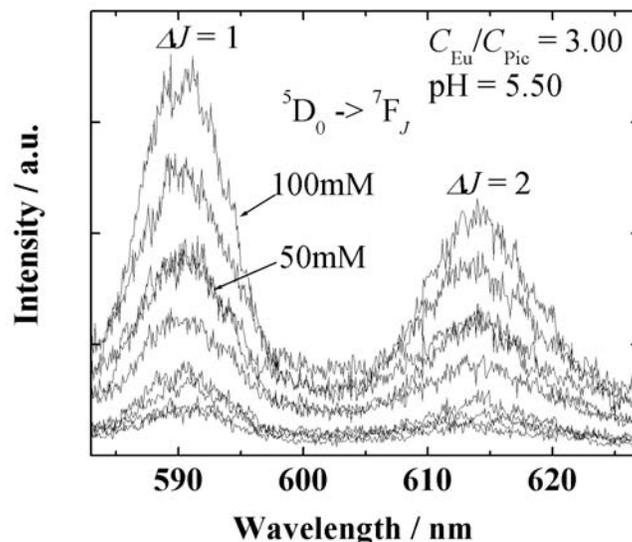


**Figure 3:** Luminescence spectra of Eu–picolinate complexes as a function of the increasing total Eu(III) concentration (1.00 mM, 3.33 mM, 5.00 mM, 7.50 mM, 10.0 mM, 33.3 mM, 50.0 mM, 75.0 mM, and 100 mM). The arrows in the graph indicate the different concentrations.
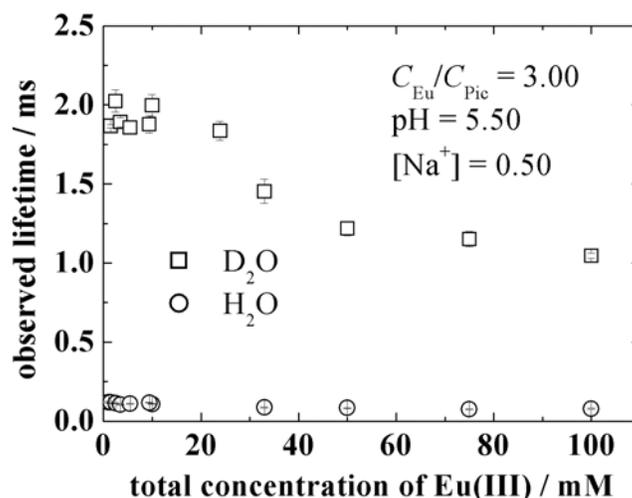


**Figure 4:** Apparent lifetimes in $H_2O$ and $D_2O$ solutions as a function of the total Eu(III) concentration. The ratio of the total Eu(III) concentration to that of picolinate was kept constant at $C_{Eu}/C_{Pic} = 3.00$.

Horrocks *et al.* [15] found that the following approximation varies if the chemical exchange between the chemical components is rapid in comparison with the de-excitation process, and the decay shows mono-exponential behavior:

$$k_{app} = \sum_i k_i \cdot \frac{[ML_i]}{C_{M,tot}}, \tag{7}$$

where $k_{app}$ is the apparent rate constant of the luminescence decay, $k_i$ is the rate of luminescence decay of the *i*th chemical component containing $M^{3+}$, and $[ML_i]$ is the concentration of the *i*th component. Billard and Lüthenkirchen reported that the approximation varies for lanthanide(III) ions based on the so-called "lanthanide approximation," where the rate of chemical exchange between the components is the same in the ground and photoexcited states [21]. In the present case, *eq.* (7) is expressed explicitly as follows:

$$k_{app} = k_0 \cdot \frac{[Eu^{3+}]}{C_{Eu,tot,}} + k_1 \cdot \frac{[EuL^{2+}]}{C_{Eu,tot}}. \tag{8}$$

We preliminarily confirmed $k_0 = 8.84 \pm 0.20$ ms$^{-1}$ (H$_2$O) in the absence of a ligand. In addition, the concentrations of $[Eu^{3+}]$ and $[EuL^{2+}]$ can be directly determined from the formation constant $\log\beta_{1,1} = 3.61$ reported in [19]. Consequently, measurement of the luminescence lifetime enables the calculation of the value of $k_1$. The calculated $k_1$ values were nearly constant up to $C_{Eu,tot} = 5.00$ mM. The mean value of the rate constants, $k_1 = 8.35 \pm 0.10$ ms$^{-1}$, provides a hydration number for the [Eu(Pic)]$^{2+}$ component of $q' = 7.0$, indicating that the [Eu(Pic)]$^{2+}$ component is a monomer favoring the constitution [Eu(Pic)·(H$_2$O)$_7$]$^{2+}$. A discrepancy was found for the $k_1$ values when $C_{Eu,tot} > 5.00$ mM, which is where the apparent lifetime was reduced in contrast. This result is due to the formation of polymeric complexes. The rate constant for the de-excitation process from the photoexcited state is given as in *eq.* (4). With polymer formation, the Eu$^{3+}$ ions become vicinal to one another, and thus, the back transfer rate of energy between them can be higher. The rate constant defined in *eq.* (5) then becomes

$$k_{app} = k_{rad} + k_{nr} + k_{H_2O} + k_{M\text{-}M}, \tag{9}$$

where $k_{M\text{-}M}$ is the rate of the energy transfer process between the Eu$^{3+}$ ions. If the measurement of the luminescence is performed in a D$_2$O solvent, the third term is substituted for $k_{D2O}$,

$$k_{app} = k_{rad} + k_{nr} + k_{D_2O} + k_{M\text{-}M}. \tag{10}$$

The term $k_{M\text{-}M}$ causes a decrease in the observed lifetime. Note that $k_{M\text{-}M}$ is derived from the Eu$^{3+}$–Eu$^{3+}$ interaction in a single complex. Kahwa *et al.* [22, 23] reported that a shorter luminescence lifetime is observed in homo-dinuclear complexes of lanthanides with a phenolic Schiff base macrocyclic ligand than that observed for mononuclear complexes. Thus, the Ln–Ln interaction has not been well-elucidated in either a theoretical or experimental manner. On the other hand, in the present case, the decrease in the apparent luminescence lifetime is caused by the formation of polymetallic complexes in which Ln ions exist as neighbors.

Other factors may also contribute to the shorter luminescence lifetime. One possibility is concentration quenching [24], which was confirmed in a preliminary test. It was found that at higher concentrations, such as ~200 mM, quenching behavior was meaningful for the free Eu$^{3+}$ aquo ions. It is also possible that the change in the luminescence lifetimes is caused by condensed ionic media. However, sodium perchlorate does not affect the lifetime at low concentrations of approximately 0.5 M. It can be, therefore, concluded that the formation of polynuclear complexes is plausible at ~50 mM. On the contrary, it is difficult to isolate the target species from coexisting complexes at the concentration investigated. The square plots in Figure **4** seem to have two plateaus in the D$_2$O system. The similar trend is also found in the H$_2$O system which is not apparent due to the scale: from ca. 115 μs to 63 μs at $C_{Eu} = 3.3$ mM to 100 mM, respectively. The species present in the solution are Eu$^{3+}$, Eu(Pic)$^{2+}$ (up to several millimolar), and [Eu(Pic)]$_m^{2m+}$ (beyond 50 mM). Here, *m* is the number of monomeric units. Based on this lifetime analysis, it can be concluded that mononuclear Eu$^{3+}$–picolinate polymetallic complexes can form in aqueous solutions *via* ligand bridges, even when the ligand is a soft N/O donor and coordinates as a bidentate structure. This type of polynuclear complex is not well known in aqueous solutions; however, the Ln$^{3+}$–EDTA complex favors a hydroxo core bridge in the solid state. Further luminescence studies are required to determine the number of monomeric units *m* for complexes having metal–metal interactions and to explore the self-assembly of lanthanide complexes and their photophysical properties.

## 4. CONCLUSION

The complexation of Eu$^{3+}$ by picolinate in aqueous solutions was studied to investigate the formation of

polynuclear complexes. In the presence of a large excess of ligand, no polynuclear complex formation *via* hydroxide bridges takes place, even at very high pH. In addition, the monomeric form $[Eu(Pic)_4(H_2O)]^-$ is favored. The lifetime analysis of $Eu^{3+}$ luminescence where $Eu(Pic)^{2+}$ is the secondary dominant species showed strong quenching of the luminescence emission, implying the formation of polymeric complexes of the type $[Eu(Pic)]_m^{2m+}$, even at low pH. This result was confirmed through several experiments with different total concentrations of the chemical components and using $H_2O$ and $D_2O$ solvents. An effective interaction between the $Eu^{3+}$ ions was observed in the TRLFS measurements and was explained as back transfer.

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