

Spectroscopic Studies of Eu(III) Complexes with Iminodiacetic and Methyliminodiacetic Acids

Dong-Cheul Kim, Soo-Kyung Yoon, Jun-Hyun Bae[†], Jong-Goo Kim[†],
Youn-Doo Kim, and Jun-Gill Kang*

Department of Chemistry, Chungnam National University, Taejeon 305-764, Korea

[†]Department of Environmental Engineering, Anyang University, Kyungki-Do 430-714, Korea

[‡]Korea Atomic Energy Research Institute, Taejeon 302-353, Korea

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The luminescence spectra of Eu(III) complexes have been measured as a function of molar metal-to-ligand ratio and pH. The ligands used in this study are tridentate iminodiacetate (IDA) and methyliminodiacetate (MIDA). The 620 nm emission band, attributed to the ${}^5D_0 \rightarrow {}^7F_2$ transition, is monitored to investigate the optimum condition for EuL_3^{3-} complex formation in aqueous state. In addition, the sensitivity of the 465 nm absorption band, attributed to the ${}^7F_0 \rightarrow {}^5D_2$ transition, to the ligand environment has been also investigated.

Introduction

The trivalent lanthanide ions, Ln(III), with f^N electronic configuration show very characteristic multiplet-to-multiplet transitions.¹ These transitions are basically forbidden by an electric dipole moment, but allowed by an induced electric dipole due to a crystal field potential. When Ln(III) ion is placed under a ligand environment with low symmetry, some absorption or luminescence transitions gain their intensities markedly. These transitions are labelled as the hypersensitivity. Among trivalent lanthanide ions, Eu(III) and Tb(III) ions have drawn much attention.² Characteristic features in luminescence have been observed in the ${}^5D_0 \rightarrow {}^7F_J$ transitions for Eu(III) and the ${}^5D_4 \rightarrow {}^7F_J$ transitions for Tb(III). The luminescence features of these ions have been used to obtain some informations on the composition, the chemical ability and the structure of the chemical system.

Previously, we reported the absorption and luminescence spectra of Eu(III) complexes with oxydiacetate (ODA) and dipicolinate (DPA) in aqueous state.³ It has been found that the ${}^7F_0 \rightarrow {}^5D_2$ transition in absorption and the ${}^5D_0 \rightarrow {}^7F_2$ transition in emission show the sensitivity to minor changes in the ligand environment. Though $\text{Eu}(\text{ODA})_3^{3-}$ and $\text{Eu}(\text{DPA})_3^{3-}$ complexes are isomorphous, the DPA ligand enhanced the oscillator strength of the both transitions more than 5 times as much as the ODA.

This paper is a continuation of our earlier studies on absorption and luminescence of Eu(III) complexes with ODA and DPA. In this work, iminodiacetate (IDA) and methyliminodiacetate (MIDA) are selected, in which two carboxyl groups and one central nitrogen atom are included. All of the ODA, DPA, IDA and MIDA are potentially tridentate ligands forming LnL_3^{3-} of the tricapped trigonal prism. They are classified to two isomer groups. The ODA and DPA complexes have meridional isomeric structures and the IDA and MIDA complexes have facial configurations.⁴

According to the previous works, the ODA and DPA ligands form tris (tridentate) complexes with $\text{Sm}(\text{III})$,⁵ $\text{Dy}(\text{III})$ ⁶ and $\text{Eu}(\text{III})$ ⁷ independently of the pH under the condition of

pH > 3. The complexes with IDA and MIDA ligands, however, are very dependent on the pH. The luminescence lifetimes of Eu(III) and Tb(III) complexes with IDA and MIDA show the similar pH dependency.^{7,8}

In this work, we have measured the luminescence spectrum of Eu(III) ion in complexes with IDA and MIDA as a function of pH and molar metal-to-ligand ratio. The luminescence properties will reveal the optimum condition for tris(tridentate) Eu(III) complexes. In addition, we have also investigated the absorption spectra of Eu(III) ion under the optimum solution and attempted to rationalize the sensitivity of the ${}^7F_0 \rightarrow {}^5D_2$ transition.

Experimentals

$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), iminodiacetic acid (99%) and methyliminodiacetic acid (99%) were purchased from Aldrich and used without further purification. The 0.10 M and 0.50 M stock solutions of Eu(III) for luminescence and absorption measurements, respectively were prepared at pH 3 to prevent hydrolysis. The 0.10 M stock solutions of IDA and MIDA were prepared at pH 10. All spectroscopic measurements in this work were carried out on aqueous solution samples, in which the concentration of Eu(III) was fixed at 0.010 M for the luminescence and 0.10 M for the absorption. The pH was controlled with a combination of 0.10 M NaOH and 0.10 M HCl solutions.

Absorption and luminescence spectra were recorded on a Cary 5 spectrophotometer and an Edinburghs FS-900 spectrofluorometer, respectively.

Results and Discussion

Luminescence spectra of Eu^{3+} (aquo) and the Eu(III) aqueous complexes excited within the ${}^7F_0 \rightarrow {}^5L_6$ absorption band ($\lambda_{\text{exc}} = 384 \text{ nm}$) were measured in the 570-720 nm region. Figure 1 shows the luminescence spectra of Eu^{3+} (aquo) and 1:3 Eu(III):L solutions under mild alkaline condition. Four distinctive bands in the region were observed. These bands have been attributed to the ${}^5D_0 \rightarrow {}^7F_J$ ($J=1, 2, 3$ and 4) transitions. It can be found that the ${}^5D_0 \rightarrow {}^7F_2$ transition peaking

*To whom correspondence should be addressed.

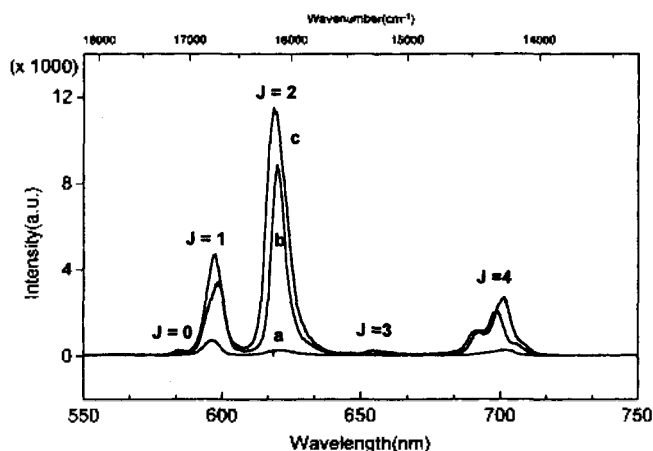


Figure 1. Luminescence spectra of a; Eu^{3+} (aquo) at pH 3, b; the 1:3 Eu(III):IDA and c; the 1:3 Eu(III):MIDA solutions under a mild alkaline condition ($[\text{Eu}^{3+}] = 0.010 \text{ M}$ and $\lambda_{\text{exc}} = 384 \text{ nm}$).

at 620 nm gained the intensity markedly by the complexation. This band was chosen to monitor the effect of pH and molar ratio on the complexation.

Figure 2 shows the dependence of the 620 nm luminescence band intensity on pH for the molar 1:4 and the molar 1:5 Eu(III):IDA ratios. For the molar 1:4 ratio, the intensity of the 620 nm emission band increase gradually with increasing pH up to 10. The 1:5 Eu(III):IDA solutions shows somewhat a different pH dependency. The great increase in the 620 nm emission is observed from pH 4 to 9. Above pH 9, the intensity is changed slightly. At pH 10, the dependence of the 620 nm emission intensity on molar ratio was also investigated. As shown in Figure 2, the intensity increases with increasing the molar metal-to-ligand ratio and gains the maximum at the 1:5 molar ratio. The 1:6 Eu(III):IDA ratio gives the slightly decreased value but almost the same to the 1:4 ratio. This result indicates that the optimum condition for the complexation of Eu(III) ion with IDA is the molar 1:5 ratio at pH 10. However, it does not suggest that the complex formed under this condition is Eu(IDA)_5^{7-} species. The possible species formed between Ln(III) and tridentate IDA ligand could be ML^+ , ML_2^- and ML_3^{3-} under a mild pH condition. The theoretical calculation was made on the contribution of the forms of complexes as a function of pH for the 1:3 and

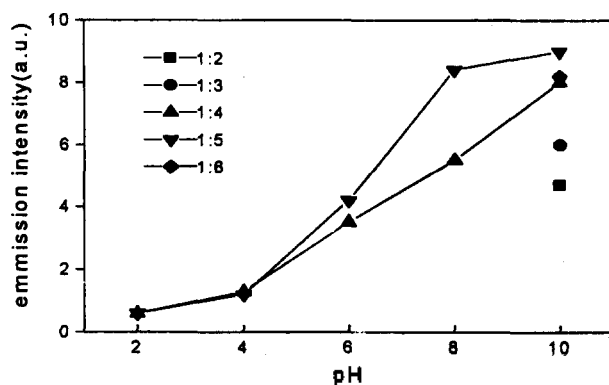


Figure 2. Luminescence intensity of Eu(III) ions in the Eu(III)/IDA system vs. pH ($\lambda_{\text{em}} = 619.7 \text{ nm}$).

the 1:5 Eu(III):IDA solutions using the reported equilibrium constants.⁹ In real solution, other species such as M(OH)_n , MLH , $\text{M(H}_2\text{O)}_n$ may compete with ML_n species. However, because of a lack of data, only M , ML , ML_2 and ML_3 species were considered. As shown in Figure 3, the 1:5 Eu(III):IDA molar ratio is able to favour the formation of the ML_3 species, compared with the case of the 1:3 ratio. According to the luminescence lifetimes of Eu(III) in complex with IDA reported by Lis and Choppin,⁷ the contribution of the EuL_3 species formed in the 1:4 Eu(III):IDA solution at pH 11.09 is 89.4%. The contribution of EuL_3 will be more increased for the 1:5 molar ratio. Unlikely, the intensity of the 620 nm emission decreased, compared with the case of the 1:4 solution. It could be due to the energy transfer from Eu(IDA)_3^{3-} species to the free IDA ligand via the collision in the solution.

The dependence of the 620 nm emission on pH was also investigated on the 1:2 and the 1:4 Eu(III):MIDA solutions up to pH 8. As shown in Figure 4, the great increase in the 620 nm emission is observed from pH 6 to 8 for the 1:4 Eu(III):MIDA solution. The measurement was limited up to pH 8, because of the hydrolysis above pH 8. The pH dependency of Eu(III) in complex with MIDA is very similar to the case with IDA . At pH 8, the luminescence spectrum was measured as a function of molar metal-to-ligand ratio. As shown in Figure 4, the intensity of the 620 nm emission increases with increasing the molar ratio of ligand. The maximum intensity was obtained in the 1:4 ratio. Likely to IDA , the excess ligand concentration decreases the luminescence intensity. It is very difficult to predict the contribution of the species formed in the Eu(III):MIDA solution since the equilibrium constants are known for only ML

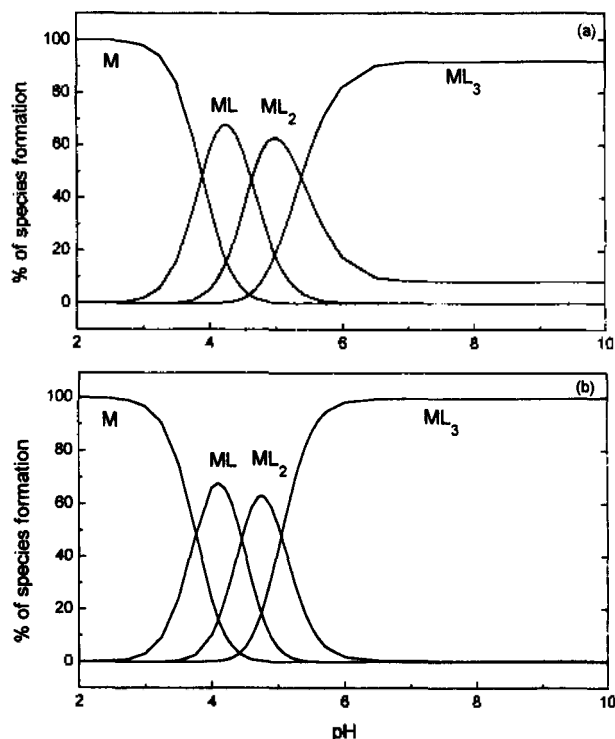


Figure 3. Plots of the % contribution of species formation, appearing in the Eu(III)/IDA system for metal-to ligand ratios: (a) 1:3 and (b) 1:5, vs. pH.

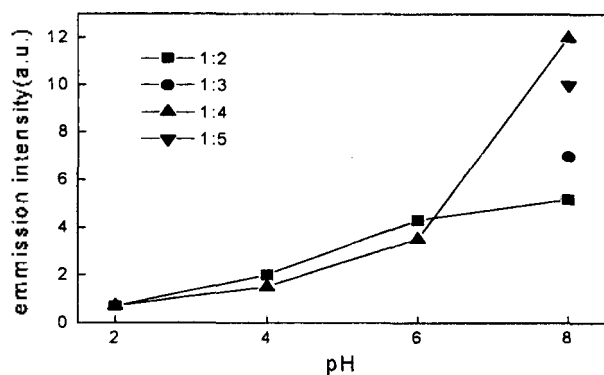


Figure 4. Luminescence intensity of Eu(III) ions in the Eu(III)/MIDA system vs. pH ($\lambda_{\text{exc}}=619.7$ nm).

and ML_2 species. However, this result may prove that EuL_3 complex is most probably formed in the 1:4 Eu(III):L solution for MIDA ligand.

The oscillator strength ratios of the complexes to those of $\text{Eu}^{3+}(\text{aquo})$, $P_{\text{emis}}(\text{complex})/P_{\text{emis}}(\text{aquo})$ were evaluated from the observed luminescence bands of the 1:5 Eu(III):IDA and the 1:4 Eu(III):MIDA solutions. As listed in Table 1, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition reveals the most striking features in the luminescence of Eu(III) ion. At pH 8, the oscillator strength of the 620 nm emission band increased by 22 times for the 1:5 Eu(III):IDA and 38 times for the Eu(III):MIDA relative to $\text{Eu}^{3+}(\text{aquo})$. Although these two complexes are isomorphous, the variation in the oscillator strength is very large. It could arise from minor difference in the environment of the central nitrogen atom. At the central nitrogen atom the methyl group substitution is more effective than hydrogen atom as an electron donor. Accordingly, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition provides very useful versatility in the comparison of binding abilities of the ligands.

Previously, we have determined the Judd-Ofelt intensity parameters, Ω_λ ($\lambda=2, 4, 6$), from the UV/visible absorption spectra for some lanthanide complexes.³⁻⁵ For

Table 1. Ratios of oscillator strengths of the luminescence bands from EuL_3 to those for $\text{Eu}^{3+}(\text{aquo})$ under different pH conditions, observed within the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($J=0, 1, 2$ and $3, 4$) transitions

pH	$P_{\text{emis}}(\text{complex})/P_{\text{emis}}(\text{aquo})^*$				
	560 nm (${}^7\text{F}_0$)	595 nm (${}^7\text{F}_1$)	620 nm (${}^7\text{F}_2$)	654 nm (${}^7\text{F}_3$)	699 nm (${}^7\text{F}_4$)
Eu(III)/IDA (1:5)					
2	2.4340	1.4823	2.4471	2.3832	1.4246
4	1.4602	1.6009	4.6438	2.5108	1.7568
6	0.8576	2.9425	12.905	5.6973	4.0665
8	1.2770	4.7856	21.652	10.473	7.6462
10	1.1533	5.0527	22.288	10.644	7.7777
Eu(III)/MIDA (1:4)					
2	1.3776	1.4652	2.3172	1.609	1.3632
4	0.9670	1.5611	3.7480	1.7866	1.6206
6	0.5241	2.4029	10.906	4.7811	3.3690
8	0.5558	6.1685	37.858	9.8828	9.4994

*Maximum intensities of each bands for $\text{Eu}^{3+}(\text{aquo})$ are 102 for $J=0$, 1895 for $J=1$, 712 for $J=3$ and 770 for $J=4$.

aqueous solutions, the oscillator strength of the transitions from the initial $|\Psi^J\rangle$ state to the final $|\Psi'^{J'}\rangle$ state is described by^{10,11}

$$P_{ED} = 1.29 \times 10^{11} \bar{\nu} (2J+1)^{-1} \sum_{\lambda=2,4,6} \Omega_\lambda \times \langle f^N; \Psi^J || U^{(\lambda)} || f^N; \Psi'^{J'} \rangle^2$$

where $\bar{\nu}$ is the transition energy given in cm^{-1} , $(2J+1)$ is the degeneracy of the initial state, $U^{(\lambda)}$ is a sum of the unit tensor operator and the bracket represents the reduced matrix element of $U^{(\lambda)}$. Among the three intensity parameters, the Ω_2 has been proved its sensitivity to the minor changes in the coordination environment.¹² For Eu(III) complexes with ODA and DPA,³ the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition in absorption has been found to response markedly to a minor change in the ligand environment via the Ω_2 . The f^6 configuration does not have large value of $U^{(2)}$ for the transitions from the ground state in the accessible spectral range. Only the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition has the nonzero $U^{(2)}$ matrix element among the distinctive transitions. Furthermore, for this transition, the other two $U^{(4)}$ and $U^{(6)}$ matrix elements are zero.

The absorption spectra of $\text{Eu}^{3+}(\text{aquo})$, the 1:5 Eu(III):IDA and the 1:4 Eu(III):MIDA solutions at the optimum solution condition for EuL_3 species were also measured. Among the observed absorption bands, the 465 nm absorption band, corresponding to the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition, shows the remarkable hypersensitivity to the ligand environment as shown in Figure 5. Using the above equation, the Ω_2 's were experimentally determined as $9.11 \times 10^{21} \text{ cm}^2$ for $\text{Eu}^{3+}(\text{aquo})$, $42.1 \times 10^{21} \text{ cm}^2$ for the 1:5 Eu(III):IDA solution and $58.1 \times 10^{21} \text{ cm}^2$ for the 1:4 Eu(III):MIDA solution. The ratios of $\Omega_2(\text{complex})/\Omega_2(\text{aquo})$ have been assumed to be very indicative of the relative binding abilities of complexes. The ratios are 4.6 for the 1:5 Eu(III):IDA solution and 6.4 for the 1:4 Eu(III):MIDA solution. These variation in the ratios of $\Omega_2(\text{complex})/\Omega_2(\text{aquo})$ could arise from only a minor change in the central nitrogen atom of the ligands. Accordingly, the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition shows the responsibility to a minor change in the ligand environment, although its oscillator strength is fundamentally small.

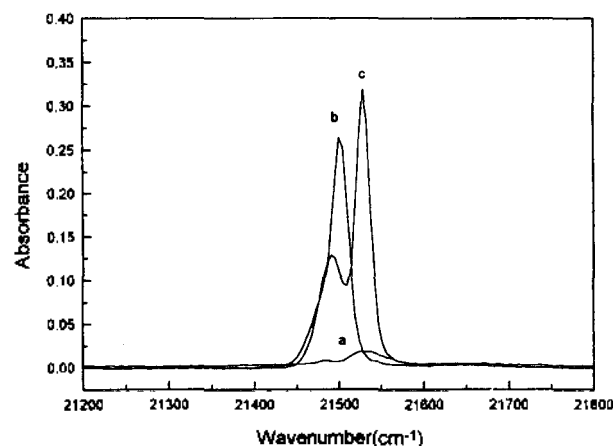


Figure 5. Absorption band of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition of a; $\text{Eu}^{3+}(\text{aquo})$ at pH 3, b; the 1:5 Eu(III):IDA and c; the 1:4 Eu(III):MIDA solutions under mild alkaline condition.

Conclusion

The optimum solution conditions for Eu(III) complexes with tridentate iminodiacetate (IDA) and methyliminodiacetate (MIDA) ligands were determined from the luminescence spectra. The maximum contribution of EuL_3^{3-} species to the species formation could be attained when the molar metal-to-ligand ratios are 1:5 for the Eu(III)/IDA solution and 1:4 for the Eu(III)/MIDA solution under mild alkaline condition. Though $\text{Eu}(\text{IDA})_3^{3-}$ and $\text{Eu}(\text{MIDA})_3^{3-}$ show a similarity in coordination geometry, a large difference in the oscillator strength was found for the ${}^5D_0 \rightarrow {}^7F_2$ transition in luminescence and the ${}^7F_0 \rightarrow {}^5D_2$ transition in absorption.

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Preparation and Photophysical Properties of 4-(9-Anthrylethenyl)-4'-methyl-2,2'-bipyridine and Its Ruthenium Bipyridyl Complex $[\text{Ru}(\text{bpy})_2(\text{t-aemb})](\text{PF}_6)_2^\dagger$

Eun Young Bae and Eun Ju Shin*

Department of Chemistry, Sunchon National University, Sunchon 540-742, Korea

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Trans-4-(9-anthrylethenyl)-4'-methyl-2,2'-bipyridine(t-aemb) and its bipyridyl Ru complex $[\text{Ru}(\text{bpy})_2(\text{t-aemb})](\text{PF}_6)_2$ (bpy=2,2'-bipyridine) **1** have been prepared and their excited state properties have been studied. t-Aemb exhibits solvent-dependent fluorescence and efficient *trans* \rightarrow *cis* photoisomerization. **1** shows very weak fluorescence and is photochemically reactive. Fluorescence is wavelength-dependent. While the excitation into the MLCT band makes the complex fluorescent, direct absorption by the t-aemb ligand leads to the photoreaction of t-aemb ligand and no fluorescence is observed. **1** is considered to behave in part as bichromophoric molecule in which $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and anthryl group are covalently linked by ethenyl linkage. Because anthryl moiety is not effectively conjugated with bipyridylethenyl moiety due to steric hindrance, weak fluorescence can be explained due to the efficient energy or electron transfer.

Introduction

Polypyridine ruthenium(II) complexes have been of considerable interest because of their photophysical, photochemical and electrochemical properties.¹⁻³ The excited state properties and redox behavior of polypyridine ruthenium(II)

complexes are controlled by low-lying electronic levels which are ligand-dependent.⁴⁻⁶ Therefore, the rational design of the ligand is required for them.⁴⁻⁹ Red shift of the metal-to-ligand charge transfer (MLCT) bands can be obtained by using ligands with lower π^* levels, but nonradiative decay rate constants increases as the energy gap between the ground and excited states decreases.^{7,8} Because of this effect, complexes with low energy visible absorption bands are weak emitters and have short-lived excited states. The decreased lifetimes limit their use as sensitizers in pho-

*To whom correspondence should be addressed.

[†]Dedicated to Prof. Sang Chul Shim at Korea Advanced Institute of Science and Technology on the occasion of his 60th birthday.