

Absorption and Luminescence Spectra of Eu(III) Complexes with Oxydiacetate and Dipicolinate in Aqueous Solution

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Absorption and luminescence spectra of Eu³⁺ (aquo) and the two different 1:3 Eu³⁺:ligand systems in aqueous solutions are measured under mild acidic pH condition. The oxydiacetate (ODA) and dipicolinate (DPA) ligands, forming the similar geometric complexes, are used in this work. The three intensity parameters, Ω_λ ($\lambda=2, 4, \text{ and } 6$) are empirically determined by applying the Judd-Ofelt theorem to the oscillator strengths of the six absorption bands arising from the ground 7F_0 state. Among the three intensity parameters, the Ω_2 is found to respond markedly to a minor change in the ligand environment *via* the ${}^7F_0 \rightarrow {}^5D_0$ transition. In addition, the relative oscillator strengths of the four luminescence bands in the visible region, assigned to the ${}^5D_0 \rightarrow {}^7F_J$ ($J=1, 2, 3 \text{ and } 4$) transitions are obtained to investigate their sensitivity to the ligand environment. Among the four bands, the 610 nm band, attributed to the ${}^5D_0 \rightarrow {}^7F_2$ transition, shows hypersensitivity in the luminescence.

Introduction

Electronic transitions of lanthanide ions have been well characterized by the Judd-Ofelt theorem.^{1,2} Oscillator strength of the transitions from the initial $|\Psi J\rangle$ state to the final $|\Psi' J'\rangle$ state is described by

$$P_{ED} = 1.08 \times 10^{11} \chi \bar{\nu} \sum_{\lambda=2,4,6} \Omega_\lambda \langle \Psi J || U^{(\lambda)} || \Psi' J' \rangle (2J+1)^{-1}$$

where χ is the Lorentz field correction for the refractivity of the sample, $\bar{\nu}$ is the transition energy given in cm^{-1} and $2J+1$ is the degeneracy of the initial state. $U^{(\lambda)}$ of rank λ is a sum of the unit tensor operator and the bracket is the reduced matrix element of $U^{(\lambda)}$. These reduced matrix elements are simply determined from the eigenstates of the free ion state. The intensity parameters, Ω_λ ($\lambda=2, 4, 6$), contain the perturbation terms resulting from the mixing between $4f$ orbital and another orbitals having opposite parity by the crystal-field potential. These intensity parameters reflect the variation in oscillator strength from complex to complex for a given lanthanide ion. Among the intensity parameters, the Ω_2 has been found to be very sensitive to the ligand environment if the matrix elements of $U^{(2)}$ are not very small compared with the values of $U^{(4)}$ and $U^{(6)}$. The binding abilities and structural details of lanthanide complexes have been discussed in terms of the relative value of Ω_2 .³⁻⁵

Previously, we reported the absorption and luminescence spectra of Sm(III)⁶ and Dy(III)⁷ complexes in aqueous solution. In those studies, oxydiacetate (ODA), dipicolinate (DPA), iminodiacetate (IDA) and methyliminodiacetate (MIDA) were used as ligand. In the crystalline state, all of these complexes form the tricapped trigonal prisms. According to x-ray structure analyses reported by Albertsson, Ln(ODA)₃³⁻,⁸ and Ln(DPA)₃³⁻,⁹ complexes in crystalline states reveal the meridional structure with D_3 symmetry. However, Ln(IDA)₃³⁻ and Ln(MIDA)₃³⁻ complexes in crystalline states form the facial isomeric structure with C_{3V} symmetry. The

complexes in solution state are found to have identical structures with those formed in crystals. These ligands, having a structural similarity, are very useful for investigating the sensitivity of the Ω_2 intensity parameter to minor change in ligand environment.

For Sm(III) and Dy(III), the increase oscillator strength due to complexation was found to be very small in the absorption spectra. The oscillator strengths of the luminescence bands, however, are markedly increased by 2-20 times for Sm(III)⁶ and by 30-330 times for Dy(III)⁶ by the complexation. This suggests that the luminescence may provide a more useful probe to monitor a minor change in the chemical environment.

Luminescence properties of Eu(III) complexes in aqueous and solid states have been extensively studied owing to the nondegeneracy of the emitting level (5D_0). The ${}^5D_0 \rightarrow {}^7F_2$ emission and the excitation of the ${}^5D_0 \rightarrow {}^7F_0$ emission have drawn special attention since the hypersensitivity and the site selectivity have been occasionally observed in these two transitions, respectively.¹⁰ The variation in the oscillator strength of the absorption bands of the Eu(III) complexes have not been previously related to the binding abilities of ligands. Contrary to most of lanthanide ions, Eu(III) shows a complexity in its absorption spectrum because the transitions from the first excited 7F_1 state overlap to the transitions from the ground 7F_0 state in the UV and visible regions. Furthermore, as in the case of Sm(III), Eu(III) with an f^6 electronic configuration does not have a large $U^{(2)}$ matrix element for the transitions from the ground state to any observable excited states in the UV and visible region.

In this study, we have investigated the variation in the oscillator strength with complexation of Eu(III) by ODA and DPA ligands and attempted to rationalize the sensitivity of the Ω_2 to a minor change in the ligand environment. In addition, we also measured the luminescence spectra and evaluated the ratio of oscillator strengths of the complexes to that of Eu³⁺ (aquo). The chemical stability of the complexes studied in this work is discussed in terms of Ω_2 in the absorption spectra and the ratio of the oscillator strength for

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the luminescence spectra.

Experimentals

$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%) was purchased from Aldrich and oxidiacetic acid and dipicolic acid were also purchased from Aldrich. These chemicals were used without further purification. All spectroscopic measurements in this work were carried out on aqueous solution samples (where pH is kept at 5.0 to prevent hydrolysis), in which the concentration of Eu^{3+} ion was 0.075 M and the $[\text{Eu}^{3+}] : [\text{L}]$ ratio was maintained at 1:3. The absorption and luminescence spectra were recorded on a Cary 5 spectrophotometer and an Edinburgh FS-900 spectrofluorometer, respectively.

Results and Discussion

Figure 1 shows the absorption spectra of $\text{Eu}^{3+}(\text{aq})$ and 1:3 $[\text{Eu}^{3+}] : [\text{L}]$ solutions. $\text{Eu}(\text{III})$ undergoes electronic transitions not only from the 7F_0 ground state but also from the first excited 7F_1 state. A complicated absorption bands appeared in the near UV region. Carnall *et al.*¹¹ reported the detailed assignments for $\text{Eu}^{3+}(\text{aq})$. Among the observed bands, the strongest band, peaking at 393.7 nm, can be attributed to the ${}^7F_0 \rightarrow {}^5L_6$ transition and the sharp band, peaking at 361.4 nm, can be attributed to the ${}^7F_0 \rightarrow {}^5D_4$ transition. In this study, we shall confine our attention to the transitions from the 7F_0 state. The five absorption bands which were distinctively observed in the visible region are listed in Table 1.

The deconvolution of the observed band, followed by the integration of the resolved bands were carried out by fitting the experimental data points with the background subtracted. The experimental oscillator strengths are listed in Table 2. As shown in Figure 1 and listed in Table 2, the characteristic feature in the absorption spectrum can be found in the ${}^7F_0 \rightarrow {}^5D_2$ transition. The oscillator strength of this transition is markedly increased by the complexation. Relative to $\text{Eu}^{3+}(\text{aq})$, it increased by a factor of 27 for $\text{Eu}(\text{ODA})_3^{3-}$ and 114 for $\text{Eu}(\text{DPA})_3^{3-}$. This transition can be labelled hyper-sensitive to the ligand environment. Most of the transitions

in the UV and visible region have $U^{(2)}$ matrix elements that are zero or very small. Among the three transitions with non-zero $U^{(2)}$ matrix element, the oscillator strength for the ${}^7F_0 \rightarrow {}^5G_2$ ($\lambda_{\text{obs}} = 380$ nm) and ${}^7F_0 \rightarrow {}^5F_2$ ($\lambda_{\text{obs}} = 301$ nm) transitions are somewhat difficult to evaluate, owing to the overlap with other transitions. Only the ${}^7F_0 \rightarrow {}^5D_2$ transition with the largest value among the transitions with non-zero $U^{(2)}$ matrix elements can be definitely isolated from other transitions. The three Judd-Ofelt intensity parameters were obtained from the empirically determined oscillator strengths, in which the Ω_2 , Ω_4 and Ω_6 were treated as adjustable parameters.

Table 1. Selected Transition Regions and U Matrix Elements¹¹ for the Eu^{3+}

Transition	Barycenter (cm^{-1})	$\langle \parallel U^{(\lambda)} \parallel \rangle^2$		
		$\lambda=2$	$\lambda=4$	$\lambda=6$
(a) ${}^7F_0 \rightarrow {}^5D_2$	21,520	0.0008	0	0
(b) ${}^7F_0 \rightarrow {}^5L_6$	25,400	0	0	0.0155
(c) ${}^7F_0 \rightarrow {}^5G_6 + {}^5G_4$	26,670	0	0.0030	0.0038
(d) ${}^7F_0 \rightarrow {}^5D_4$	27,670	0	0.0011	0
(e) ${}^7F_0 \rightarrow {}^5H_4$	31,250	0	0.0013	0
(f) ${}^7F_0 \rightarrow {}^5H_6$	31,520	0	0	0.0056

Table 2. Experimental and Calculated Oscillator Strengths for the $\text{Eu}(\text{III})$ Systems*

Transi- tion	aquo		ODA		DPA	
	P_{obs}	P_{ED}	P_{obs}	P_{ED}	P_{obs}	P_{ED}
(a)	0.0000753	0.0000753	0.00202	0.00202	0.00859	0.00859
(b)	1010	1010	982.4	982.2	1361	1361.1
(c)	260.1	261.1	252.9	254.0	350.3	352.4
(d)	0.325	0.418	0.337	0.433	0.586	0.754
(e)	0.681	0.557	0.707	0.579	1.23	1.006
(f)	452.9	452.9	440.4	440.4	610.0	610.2

*Oscillator strength values are given as $P/10^{-10}$.

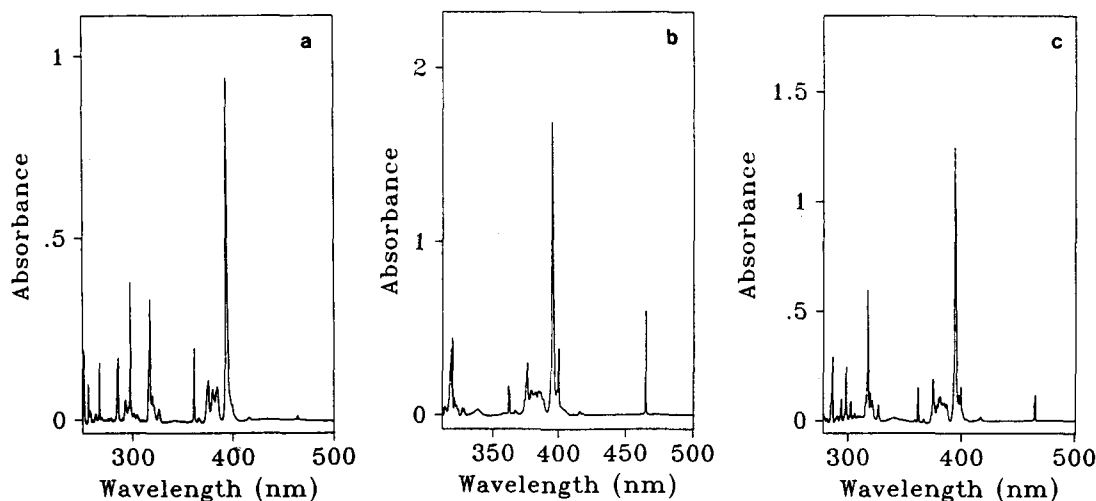


Figure 1. Absorption spectra of: a; $\text{Eu}^{3+}(\text{aq})$, b; $\text{Eu}(\text{DPA})_3^{3-}$ and c; $\text{Eu}(\text{ODA})_3^{3-}$, where $[\text{Eu}^{3+}] = 0.075$ M and $\text{pH} = 5.0$.

Table 3. Intensity Parameters Calculated from Experimental Data for the Eu(III) System

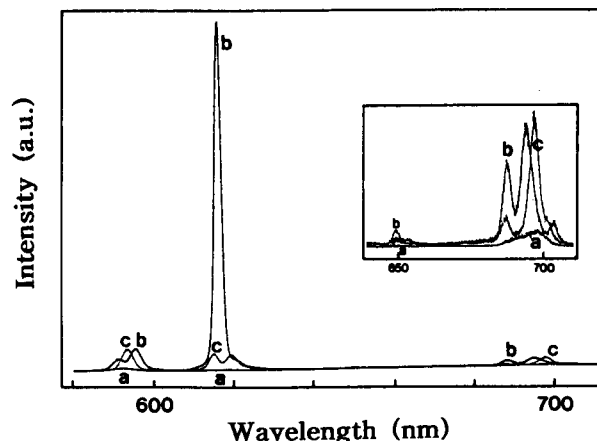
Complex	$\Omega_\lambda \times 10^{-20}$ (cm ²)			$\Omega_\lambda(\text{complex})/\Omega_\lambda(\text{aquo})$		
	$\lambda=2$	$\lambda=4$	$\lambda=6$	$\lambda=2$	$\lambda=4$	$\lambda=6$
Eu ³⁺ (aquo)	3.391×10^{-5}	0.106	19.89			
Eu ³⁺ /ODA (1:3)	9.096×10^{-4}	0.110	19.34	26.82	1.038	0.968
Eu ³⁺ /DPA (1:3)	3.868×10^{-3}	0.192	26.80	114.07	1.805	1.341

ters. The three intensity parameters yielding the optimal fit are listed in Table 3. Using these three parameters, we calculated the oscillator strengths of the bands. As listed in Table 2, there is good agreement between the calculated and the observed oscillator strengths for all transitions studied in this work.

As listed in Table 3, the largest variation from complex to complex is found in Ω_2 . Clearly, it indicates that Ω_2 is much more sensitive to the ligand environment than Ω_4 and Ω_6 . The ratios of Ω_λ (complex) to Ω_λ (aquo) are very indicative of the relative binding abilities of complexes. As listed in Table 3, the Ω_λ (complex)/ Ω_λ (aquo) ratios are seen to be much larger for DPA than that for ODA. Although these two complexes have identical coordination geometries, large variation in Ω_2 are found in them. It could arise from minor difference in the central atoms of the ODA and DPA ligands. The nitrogen atom in the pyridine ring acts as more reliable electron donor than the oxygen atom in the ether bond.

Previously, the $\Omega_\lambda(\text{complex})/\Omega_\lambda(\text{aquo})$ ratios were reported for Nd³⁺,⁴ Sm³⁺,⁶ Dy³⁺,⁷ Ho³⁺,⁴ and Er³⁺,⁵ complexes. The similar binding abilities of ODA, DPA, IDA and MIDA have been also found in all complexes, no matter whether they showed the hypersensitive transitions. Compared with the results for those complexes, the Eu³⁺ ion produces an exceptionally large variation in Ω_2 from complex to complex. It suggests that the ${}^7F_0 \rightarrow {}^5D_0$ band of Eu³⁺ can be used as a very effective probe in examining minor changes in the ligand environment.

Luminescence spectra of Eu³⁺(aquo) and the aqueous Eu³⁺ complexes excited within the ${}^7F_0 \rightarrow {}^5L_6$ absorption band were also measured in the 570–720 nm region. Figure 2(a) shows the luminescence spectra of the solutions with four distinctive bands in the region. These four bands have been attributed to the ${}^5D_0 \rightarrow {}^7F_j$ ($j=1, 2, 3$ and 4) transitions. For some cases, an additional band responsible for the ${}^5D_1 \rightarrow {}^7F_3$ transition may appear as a trace at the high energy side of the ${}^5D_0 \rightarrow {}^7F_1$ band. This additional band, however, does not appear in the spectra (see the extended intensity scale in Figure 2(b)). The bands, which appeared very broaden and weakly in Eu³⁺(aquo), were markedly changed in the band structure and intensity by the complexation. Band splittings were apparently induced in the ${}^5D_0 \rightarrow {}^7F_{1,2,4}$ transitions. It has been found for Eu(ODA)₃³⁻ and Eu(DPA)₃³⁻ in single crystalline states that the band splittings are strongly correlated with the site symmetry of the Eu³⁺ ion under the crystal field potential.¹² It is especially notable that the crystal field induced by the ligands enhances markedly the luminescence

**Figure 2.** Luminescence spectra of: a; Eu³⁺(aquo), b; Eu(DPA)₃³⁻ and c; Eu(ODA)₃³⁻ excited within ${}^7F_0 \rightarrow {}^5L_7$ band (room temperature).**Table 4.** Ratios of Oscillator Strengths of the Emission Band for EuL₃³⁻ to that for Eu³⁺(aquo), Observed within the ${}^5D_0 \rightarrow {}^7F_j$ ($j=1, 2, 3$ and 4) transitions

Complex	$P_{ems}(\text{complex})/P_{ems}(\text{aquo})$			
	590 nm (7F_1)	610 nm (7F_2)	650 nm (7F_3)	695 nm (7F_4)
Eu ³⁺ /ODA (1:3)	4.21	10.74	3.65	4.54
Eu ³⁺ /DPA (1:3)	6.07	66.64	5.60	6.09

intensity. For the four luminescence bands, the ratios of the oscillator strengths of the complexes to those of Eu³⁺(aquo), $P_{ems}(\text{complex})/P_{ems}(\text{aquo})$, are listed in Table 4. In general, the ${}^5D_0 \rightarrow {}^7F_0$ transition is forbidden in principle by the J quantum number selection rule, but may gain the emission intensity *via* the mixing of the 7F_0 state to other states by a lowered crystal field symmetry. For Eu(ODA)₃³⁻ and Eu(DPA)₃³⁻ complexes, however, the emission band responsible for this transition appeared only as a trace. Similarly, the ${}^5D_0 \rightarrow {}^7F_3$ transitions appeared very weakly peaking around the 650 nm region. This transition may gain intensity by mixing to other states under a lowered crystal field symmetry. The 590 nm emission band responsible for the ${}^5D_0 \rightarrow {}^7F_1$ transition, strongly observed in most of Eu³⁺ complexes, has been known to be mainly allowed by the magnetic dipole moment. This selection rule suggests that its intensity would be almost independent of the environment. However, it was found that the intensity of the 590 nm band shows a slight dependency on the ligand that was comparable to the observed for the 695 nm emission band. The latter, that is assigned to the ${}^5D_0 \rightarrow {}^7F_4$ transition, has been characterized as having a moderate sensitivity to the ligand environment.¹⁰

As listed in Table 4, the most striking characteristic feature in the luminescence of the Eu(III) is found in the ${}^5D_0 \rightarrow {}^7F_2$ transition. The oscillator strength of the 610 nm emission band increased by 11 times for the Eu(ODA)₃³⁻ and 67 times for the Eu(DPA)₃³⁻ relative to the Eu³⁺(aquo). The variation in the oscillator strength from complex to complex is very large. Although there is only a minor difference in the cent-

ral atoms between the ODA and DPA ligands, the DPA ligands enhanced the oscillator strength of the 610 nm emission band 6 times as much as the ODA. Accordingly, the 610 nm emission band shows hypersensitivity to minor changes in the Eu^{3+} environment. This band can provide a useful probe for monitoring Eu^{3+} complexation.

Conclusion

The ${}^7F_0 \rightarrow {}^5D_2$ transition in absorption and the ${}^5D_0 \rightarrow {}^7F_2$ transition in emission have been found to be very sensitive to minor changes in the ligand environment. Though $\text{Eu}(\text{ODA})_3^{3-}$ and $\text{Eu}(\text{DPA})_3^{3-}$ show a similarity in coordination geometry, there is a large difference in the oscillator strengths for these two transitions. These two transitions could provide a very useful and versatile probe in the investigation of the $\text{Eu}(\text{II})$ environment.

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