

Absorption and Fluorescence Spectra of Dy(III) Complexes with Some Terdentate Ligands

Seung Hee Jung, Soo Kyung Yoon, Jong Goo Kim[†], and Jun-Gill Kang*

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

[†]Chemistry and Chemical Analysis Division, Korea Atomic Energy Research Institute, Taejeon 302-353. Received June 15, 1992

Absorption and fluorescence spectra are reported for four different 1 : 3 Dy³⁺ : ligand systems in aqueous solution under mild alkaline pH conditions. The ligands included in this study are oxidiacetate, dipicolinate, iminodiacetate and methyliminodiacetate. The oscillator strengths for the 4*f*→4*f* multiplet-to-multiplet transitions are empirically determined from the absorption spectra and the intensity parameters Ω_λ ($\lambda=2, 4, 6$) for the systems are also obtained by applying the Judd-Ofelt theorem to the observed oscillator strengths. The values of the intensity parameters for the systems are compared and discussed in terms of ligand structural properties to investigate how the intensity parameters can respond to the minor changes in the ligand environment. In addition, the relative oscillator strengths for fluorescence are evaluated and compared to the results obtained from absorption spectra.

Introduction

Lanthanide ions with 4*f*^{*n*} electron configuration show very characteristic *f*→*f* absorption spectra, of which transitions are forbidden in principle by the electric dipole. Judd¹ and Ofelt² proved individually that mixing between 4*f* configuration and another configuration having opposite parity may be occurred by the crystal-field potential and the transitions from the ground multiplet to the excited multiplet be allowed by the induced electric dipole. According to the Judd-Ofelt theorem, the oscillator strength of the transition from the initial Ψ^J state to the final $\Psi'^{J'}$ state in the intermediate coupling scheme is expressed as

$$P_{ED} = \chi \left[\frac{8\pi^2 m c}{3h} \right] \bar{\nu} (2J+1)^{-1} \sum_{\lambda=2,4,6} \Omega_\lambda \langle \Psi^J || U^{(\lambda)} || \Psi'^{J'} \rangle^2 \quad (1)$$

where χ is the Lorentz field correction for the refractivity of the sample, m is the mass of an electron, $\bar{\nu}$ 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 unit tensor operators and the bracket is the reduced matrix element of the $U^{(\lambda)}$. In the equation, the three intensity parameters, Ω_λ ($\lambda=2, 4, 6$), are phenomenologically determined from the experimental oscillator strengths. Among the three intensity parameters, the Ω_2 draws a special attention since it is very sensitive to the structural details and chemical nature of the ligand environment.³⁻⁵ In the case of that more than one transition with a large value of the $U^{(2)}$ matrix element is included, oscillator strengths of those transitions increase markedly when the ion is complexed. Such transitions have been labelled hypersensitive and rationalized as the peculiar sensitivity of the Ω_2 to the environment. The successful rationalization of the Ω_2 sensitivity have been found for Nd³⁺, Ho³⁺ and Er³⁺ complexes showing the hypersensitive transitions in accessible spectral region.^{4,5}

Previously,⁶ we reported the absorption and fluorescence spectra of Sm³⁺ complexes in aqueous state. The ligands used in that study were oxidiacetate (ODA), dipicolinate

(DPA), iminodiacetate (IDA) and methyliminodiacetate (MIDA), each of which has the central atom as an electron-pair donor along two carboxylate groups as terminals. The oscillator strengths for transitions from the ground multiplet ⁶H_{5/2} state to the excited multiplet states and the Judd-Ofelt intensity parameters were determined from the absorption spectrum. Although Sm³⁺ ion has very small value of $U^{(2)}$ matrix element for most of transitions, it was found that among Ω parameters the Ω_2 shows somewhat the sensitivity to the coordination environment. The ratios of oscillator strengths of Sm³⁺ complexes to that of Sm³⁺ (aquo) were also evaluated from the fluorescence spectra and compared to the results obtained from the absorption bands.

In this study, we have attempted to extend the series for the rationalization of the Ω_2 sensitivity to Dy³⁺ complexes. Similarly to Sm³⁺ ion, Dy³⁺ ion with *f*⁹ electronic configuration does not have large value of $U^{(2)}$ for transitions from the ground state to any observable excited states except the transition ⁶H_{15/2}→⁶F_{11/2} peaking at 7848 cm⁻¹. In the present paper, we evaluate empirical oscillator strengths from visible-near IR absorption spectra, including the ⁶H_{15/2}→⁶F_{11/2} transition which may show the hypersensitivity, for a series of the four 1 : 3 Dy³⁺ : ligand solutions and also determine the intensity parameters by applying the Judd-Ofelt theorem to the empirical oscillator strengths. The principal objective here is to examine how the Ω_2 intensity parameters can respond to the minor changes in the ligand environment. In addition, we also measure the fluorescence spectra and evaluate the ratios of fluorescing oscillator strengths of the Dy³⁺ complexes to that of Dy³⁺ (aquo). These ratios are discussed in conjunction with absorption to investigate how ligand environment alters the intensity of fluorescence.

Experimentals

DyCl₃·6H₂O (99.99%) was purchased from Aldrich and was used without further purification. Oxidiacetic acid (ODAH₂), dipicolinic acid (DPAH₂), iminodiacetic acid (IDAH₂) and methyliminodiacetic acid (MIDAH₂) were also purchased from Aldrich and were used without further purification. All spec-

*To whom all correspondence should be addressed.

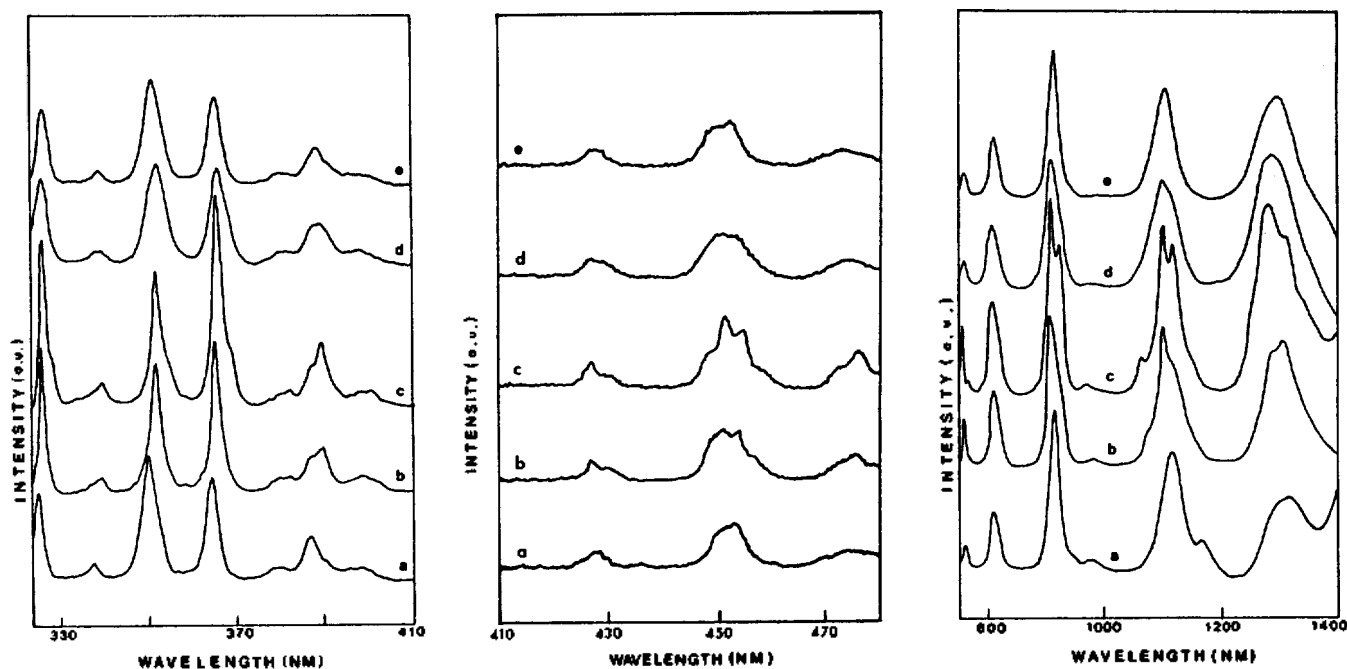


Figure 1. Absorption spectra of (a) Dy³⁺(aquo) and the 1:3 Dy³⁺:ligand solutions under mild alkaline conditions: (b) ODA, (c) DPA, (d) IDA and (e) MIDA.

troscopic measurements performed in this study were carried out on aqueous solution samples in which the concentrations of Dy³⁺ was 0.040 M and of which pH was fixed at about 8.0. Solution pH was adjusted with NH₄OH solution. Absorption and fluorescence spectra of the samples were recorded on a Cary 5 spectrophotometer and a JASCO FP-770 spectrofluorometer, respectively.

The oscillator strength, defined as Eq. (1), can be rewritten in terms of the measured intensity of an absorption band in an aqueous media as follows:

$$P_{\text{obs}} = 4.318 \times 10^{-9} \int \varepsilon(\bar{\nu}) d\bar{\nu} \quad (2)$$

where $\varepsilon(\bar{\nu})$ is the molar absorption coefficient at the $\bar{\nu}$ wave-number and the integral corresponds to the area of the band for a certain transition $\Psi f \rightarrow \Psi' f'$. A detailed description of the experimental section has been presented in the previous work.⁶

Results and Discussion

Figure 1 shows the absorption spectra of Dy³⁺(aquo) and the four 1:3 Dy³⁺:ligand solutions under the mild alkaline condition. The observed absorption bands can be identified by the energy-level diagram reported by Carnal *et al.*⁷ One of characteristic features of the absorption spectrum is that Dy³⁺ ion does not have any electronic states in the wide range of energy from 13,400 to 21,000 cm⁻¹. The fitting of absorption spectrum over whole range from UV to near IR with the large energy gap between ⁶F_{3/2} and ⁴F_{9/2} states shows the poor standard deviation. Accordingly, we shall focus our attention on the near IR spectral region (750-1400 nm). The five transitions observed in this spectral range were identified according to the term symbol and are listed in Table 1. Among the solutions, the 1:3 Dy³⁺:DPA solution produced characteristic band structures for the transi-

Table 1. Transition Regions and Matrix Elements* of $U^{(\lambda)}$ Used in the Intensity Analysis

Label	Transition region	$\nu(\text{cm}^{-1})$	$\langle U^{(\lambda)} \rangle^2$		
			$\lambda=2$	$\lambda=4$	$\lambda=6$
(a)	⁶ H _{15/2} → ⁶ H _{9/2} , ⁶ F _{11/2}	7,760	0.9387	0.8468	0.4033
(b)	⁶ H _{15/2} → ⁶ F _{9/2} , ⁶ H _{7/2}	9,010	0	0.5743	0.7605
(c)	⁶ H _{15/2} → ⁶ H _{5/2} , ⁶ F _{7/2}	10,910	0	0.1360	0.7168
(d)	⁶ H _{15/2} → ⁶ F _{5/2}	12,370	0	0	0.3452
(e)	⁶ H _{15/2} → ⁶ F _{3/2}	13,150	0	0	0.0610

*Values of matrix elements are cited from ref. 7.

Table 2. The Judd-Ofelt Intensity Parameters Evaluated from Experimental Data

Complex	$\Omega_{\lambda} \times 10^{20} (\text{cm}^2)$		
	$\lambda=2$	$\lambda=4$	$\lambda=6$
Dy ³⁺ (aquo)	0.772 (± 0.337)	-0.171 (± 0.380)	1.195 (± 0.181)
Dy ³⁺ /ODA	1.030 (± 0.235)	0.271 (± 0.265)	1.211 (± 0.127)
Dy ³⁺ /DPA	1.767 (± 0.216)	0.735 (± 0.243)	1.402 (± 0.116)
Dy ³⁺ /IDA	1.298 (± 0.250)	0.177 (± 0.282)	1.192 (± 0.135)
Dy ³⁺ /MIDA	1.292 (± 0.338)	-0.333 (± 0.381)	1.277 (± 0.182)

tions labelled as (b) and (c). It indicates that DPA may give a very strong ligand field on the electronic states inducing the band splitting, compared with the other ligands.

The resolution of the observed band and the integration of the resolved band were made by employing the modified Gaussian-Lorentzian function to the observed datum points with background subtracted. The three Judd-Ofelt intensity parameters were obtained from the empirically determined oscillator strengths by the multiple regression analysis method, in which the Ω_2 , Ω_4 and Ω_6 quantities were treated

Table 3. Experimental and Calculated Oscillator Strength* for the Dy(III) Systems under Mild Alkaline Condition

Transition	AQUO		ODA		DPA		IDA		MIDA	
	Exptl.	Fit	Exptl.	Fit	Exptl.	Fit	Exptl.	Fit	Exptl.	Fit
(a)	177.3	177.3	283.8	283.8	475.0	475.0	308.4	308.4	241.2	241.2
(b)	150.7	157.1	210.5	214.5	285.8	288.4	191.1	195.3	144.6	151.1
(c)	218.2	195.6	233.1	219.0	268.3	259.2	220.6	206.1	226.6	204.0
(d)	81.2	109.8	98.9	114.9	120.4	128.7	92.9	109.4	88.9	117.2
(e)	7.7	20.6	4.9	21.6	2.4	24.2	2.0	20.6	7.9	22.0

*Oscillator strength values are given as $P/10^{-6}$

as adjustable parameters. The three parameters yielding the optimal fit are listed in Table 2. In general, the weight of each Ω in fitting procedure is associated with the value of the reduced matrix element of U . Among the five transitions examined in this study, three transitions have nonzero values of $U^{(0)}$ matrix elements, and those are not very small, compared with the others. The large root-mean-deviations, however, appeared in the Ω_4 parameters. In the case of Dy^{3+} (aquo) and the Dy^{3+} :MIDA solution, even negative values of Ω_4 were obtained, which is not expectable within the Judd-Ofelt theorem. These evidences have been often observed in the Ω_2 parameters in the case of that no transitions have large values of the $U^{(2)}$. Applying the three Judd-Ofelt parameters to Eq. (1), we evaluated oscillator strengths. Experimental and fitted oscillator strengths are listed in Table 3. The very good agreements between the experimental and the fitted oscillator strengths were found in the transitions labelled as (a) and (b). Among the transition regions examined in this study, the transition (a) shows the large variation in oscillator strength from complex to complex. It could be due to that not only the transition (a) has nonzero matrix element of the $U^{(2)}$, but also the element has relatively large value. Clearly, one can find for the Dy^{3+} complexes that the Ω_2 is much more sensitive to the coordination environment than the Ω_6 , if the Ω_4 is ruled out because of its large uncertainty. The ratios of Ω_2 (complex) to Ω_2 (aquo) have been considered to discuss the relative binding abilities of the various ligands. The ratios are 1.334 for the ODA system, 2.29 for the DPA system, 1.68 for the IDA system, and 1.67 for the MIDA system. It was found that among the ligands examined in this study the DPA complex gives the largest Ω_2 (complex) to Ω_2 (aquo) ratio.

According to model structures⁵ for the ODA, DPA, IDA and MIDA complexes under mild alkaline pH conditions, the major species are tris(terdentate) complexes certainly for the 1:3 Ln^{3+} :ODA and Ln^{3+} :DPA systems, and likely for the 1:3 Ln^{3+} :IDA and the 1:3 Ln^{3+} :MIDA systems. The tris(terdentate) complexes of ODA, DPA, IDA and MIDA forming the tricapped trigonal prism are classified to two isomers: the types $Dy(ODA)_3^{3-}$ and $Dy(DPA)_3^{3-}$ have a meridional structure of D_3 symmetry, and the types $Dy(IDA)_3^{3-}$ and $Dy(MIDA)_3^{3-}$ have a facial structure of C_{3h} symmetry. According to the structural similarity, the comparison of binding abilities of the ligands can be made on between ODA and DPA, and also between IDA and MIDA. The ratios of Ω_2 (complex) to Ω_2 (aquo) show:

$$ODA < DPA \quad \text{and} \quad IDA \cong MIDA$$

The large variation in the Ω_2 (complex) to Ω_2 (aquo) ratio is found between $Dy(ODA)_3^{3-}$ and $Dy(DPA)_3^{3-}$. The similar results can be seen in series of Nd^{3+} , Ho^{3+} and Er^{3+} showing hypersensitive transitions,^{4,5} and also found in Sm^{3+} system⁶ showing no hypersensitivity. The large difference in Ω_2 value between these two systems with identical coordination geometries must be attribute to the distinctive differences in binding abilities of the central atoms of the ODA and DPA ligands. The nitrogen atom in pyridine ring has denser electron density than the oxygen atom in ether bonding, so that the pyridine may act as more reliable electron-donor group than the ether do. In the case of $Dy(IDA)_3^{3-}$ and $Dy(MIDA)_3^{3-}$, taking into account binding abilities of IDA and MIDA ligands, one can expect that at the central nitrogen atom methyl group substitution is more effective than hydrogen. The Ω_2 (complex) to Ω_2 (aquo) ratios for both $Dy(IDA)_3^{3-}$ and $Dy(MIDA)_3^{3-}$, however, were obtained to be almost the same. It indicates that the substitution effect in complexations of Dy^{3+} with IDA and MIDA ligands may not affect the $f \rightarrow f$ transition intensities. A similar feature for binding abilities of the four ligands with Dy^{3+} ions can be found from the critical stability constants.⁸ The constants for complexation of DyL_n type show that the values for $Dy(DPA)_n$ are much larger than those for $Dy(ODA)_n$ ($n=1, 2$ and 3). In the case of the IDA and MIDA complexes, the stability constants for $Dy(IDA)_3^{3-}$ and $Dy(MIDA)_3^{3-}$ have not been reported. We, however, suppose from the values of $\log K$ for DyL_2 (12.31 for IDA and 12.86 for MIDA) that the values for these $n=3$ complexes may not very differ.

Figure 2 shows the fluorescence spectra of the 1:3 Dy^{3+} :ODA solution under various pH conditions, excited at 383 nm and 451 nm. These excitations are attributed to transitions from the ground state ($^6H_{15/2}$) to $^4H_{7/2}$ and $^4I_{13/2}$, respectively. As shown in the figure, one can find that independently of the excitation energy, the solution under the pH condition ranged from 4 to 8 produced very strong intensities of the two fluorescence bands, peaking at 480 nm and 573 nm, respectively. It indicates that the stable complex are formed under mild alkaline condition. The 480 nm and 573 nm bands have been attributed to transitions from $^4F_{9/2}$ to $^6H_{13/2}$ and $^6H_{15/2}$, respectively.

The fluorescence spectra of the four Dy:ligand solutions were also measured under mild alkaline condition to investigate the effect of the concentration ratio of Dy^{3+} to the ligand on the fluorescence: Dy^{3+} concentration is fixed at 0.04 M and the ligand concentration was varied. As shown in Figure 3, the fluorescence intensity of the 1:3 Dy^{3+} :ligand solution was more intensified than the 1:2 solution and

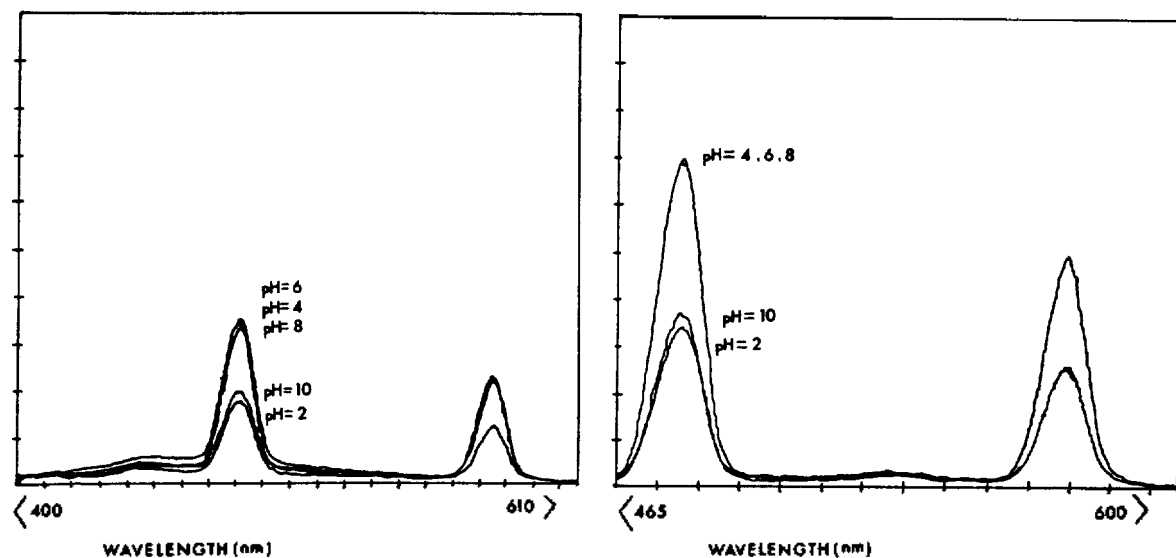


Figure 2. Fluorescence spectrum of the 1:3 Dy³⁺:ODA solution under various pH conditions, excited at (a) 383 nm and (b) 451 nm.

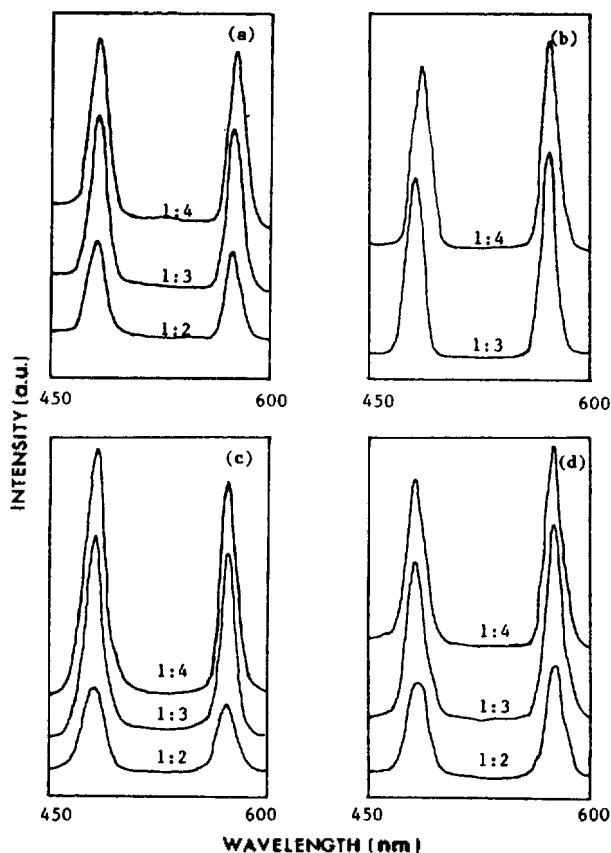


Figure 3. Fluorescence spectra of the Dy³⁺:ligand solutions under mild alkaline condition as a function of ligand concentration ([Dy³⁺]=0.040 M, λ_{exc} =387 nm); (a) ODA, (b) DPA, (c) IDA and (d) MIDA.

those of the 1:3 and the 1:4 Dy³⁺:ligand solutions are the same. This result indicates that the ODA, DPA, IDA and MIDA ligands may form tris (terdentate) complexes with Dy³⁺ ion under mild alkaline condition.

The characteristic feature of the 1:3 Dy³⁺:ligand solution

Table 4. Ratios of Oscillator Strengths of The Two Fluorescence Bands of DyL₃³⁻ to Those of Dy³⁺(aquo)

	$P_{flu}(\text{complex})/P_{flu}(\text{aquo})$			
	ODA	DPA	IDA	MIDA
$\lambda_{exc} = 387 \text{ nm}$				
${}^4F_{9/2} \rightarrow {}^6H_{15/2}$	127.0	240.3	104.4	51.0
${}^4F_{9/2} \rightarrow {}^6H_{13/2}$	126.5	330.5	131.0	59.9
$\lambda_{exc} = 452 \text{ nm}$				
${}^4F_{9/2} \rightarrow {}^6H_{15/2}$	99.4	232.0	88.4	36.3
${}^4F_{9/2} \rightarrow {}^6H_{13/2}$	118.9	311.0	121.6	49.0

under mild alkaline condition is that the fluorescence intensity of the complex increased markedly, compared with that of Dy³⁺(aquo). The oscillator strengths of the two fluorescence bands were also calculated by employing the modified Gaussian-Lorentzian function to the observed datum points with background substrated. The ratios of the fluorescing oscillator strengths of the complexes to that of Dy³⁺(aquo) are listed in Table 4. The ratios show that fluorescing oscillator strengths for Dy³⁺ complexes increased markedly. Compared with Dy³⁺(aquo), the fluorescing oscillator strengths of Dy(ODA)₃³⁻, Dy(DPA)₃³⁻ and Dy(IDA)₃³⁻ increased about 100-300 times, and that of Dy(MIDA)₃³⁻ increased approximately 50 times. This result shows that for Dy³⁺ systems, the transitions ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ are hyper-sensitive to ligand environment.

Similarly to the absorption, the relative oscillator strengths of the fluorescences have been also considered to examine the ligand strength. According to the results listed in Table 4, independently of the excited state, the ratios of the two bands show that ODA < DPA and IDA > MIDA. The coincidence of the relative binding ability of the ligands between ODA and DPA occurs between the absorption and the fluorescence. Contrary to the absorption, the fluorescing oscillator strength of Dy(MIDA)₃³⁻ is much smaller than that of Dy(IDA)₃³⁻. It could be due to that the substitution of methyl

group at the central nitrogen atom may quench the fluorescence. This substitution effect on the fluorescence was also appeared in Sm^{3+} complexes.⁶

Conclusions

The Judd-Ofelt intensity parameters Ω_λ ($\lambda=2, 4, 6$) for Dy^{3+} complexes with terdentate ligands have been determined to demonstrate the sensitivity of these intensity parameters to ligand environment. For Dy^{3+} ion, $U^{(2)}$ matrix elements for most of transitions in an UV-near IR spectral range are very small except only one transition ${}^6H_{15/2} \rightarrow {}^6F_{11/2}$, peaking at 7760 cm^{-1} . It was found that the evaluation of the three intensity parameters running over the full UV-near IR spectral range accompanied large uncertainty in regression analysis. Hence, the five transitions in the near IR spectral range have been considered in this study. Among the three Ω parameters Ω_2 shows the most sensitivity to minor changes in the ligand environment. Although $U^{(6)}$ matrix elements for most of the transitions are large, Ω_6 was found to be insensitive to ligand effect. Contrary to Ω_2 and Ω_6 values, the large root-mean-deviations appeared in the Ω_4 parameters and even negative values of Ω_4 was obtained for $\text{Dy}^{3+}(\text{aquo})$ and the $\text{Dy}^{3+}:\text{MIDA}$ solution. It shows that Ω_4 may behave as a fitting parameter. The $\Omega_2(\text{complex})/\Omega_2(\text{aquo})$ ratios were used to discuss the ligand effect according to coordination geometry. The large difference in the ratio was found between $\text{Dy}(\text{ODA})_3^{3-}$ and $\text{Dy}(\text{DPA})_3^{3-}$. It could be attributable to differences in electron densities at the central atoms of each ligand. Consequently, pyridyl donor group interacts with the f electrons of Dy^{3+} more than ether oxygen donor group does. Contrary to expectation, the Ω_2 ratio for $\text{Dy}(\text{MIDA})_3^{3-}$ was found to be equal to that for $\text{Dy}(\text{IDA})_3^{3-}$.

It suggests that methyl *vs.* hydrogen substitution at the central nitrogen donor atom of the ligands may not significantly affect their complexation with Dy^{3+} ion.

The ligand effects on complexation with Dy^{3+} ion were also investigated in terms of fluorescing oscillator strengths for the transitions ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, which are hypersensitive to ligand environment. Similar results were obtained on $\text{Dy}(\text{ODA})_3^{3-}$ and $\text{Dy}(\text{DPA})_3^{3-}$. For $\text{Dy}(\text{IDA})_3^{3-}$ and $\text{Dy}(\text{MIDA})_3^{3-}$, the fluorescence of Dy^{3+} was much more intensified by coordinating with IDA than with MIDA. It could be attributed to that the substitution of methyl group at the central nitrogen atom quenches the fluorescence possibly.

Acknowledgement. This work was supported by the Korean Research Foundation.

References

1. B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).
2. G. S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).
3. R. D. Peacock, *Struct. Bonding*, Vol. 22, p. 83, edited by J. D. Dunitz, Springer-Verlag, Berlin, Heidelberg and New York, 1975.
4. E. M. Stephenes, S. Davis, M. F. Reid and F. S. Richardson, *Inorg. Chem.*, **23**, 4607 (1984).
5. M. T. Devlin, E. M. Stephens, F. S. Richardson, T. C. Van Cott, and S. A. Davis, *Inorg. Chem.*, **26**, 1204 (1987).
6. J. G. Kim, S. K. Yoon, S. S. Yun, and J.-G. Kang, *Bull. Korean Chem. Soc.*, **13**, 54 (1992).
7. W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49**, 4424 (1968).
8. A. E. Martell and R. M. Smith, *Critical Stability Constant*, Vol. 1-3, Plenum Press, New York and London (1977).

Photochemistry of Conjugated Polyacetylenes: Photoaddition Reactions of 1-Phenyl-1,3,5-hexatriynes to Tetrahydrofuran

Sang Chul Shim*, Cheon Seok Lee, and Seong Taek Lee

Department of Chemistry, The Korea Advanced Institute of Science and Technology, Taejon 305-701

Received August 8, 1992.

Photolysis of 1-phenyl-1,3,5-hexatriynes in deaerated tetrahydrofuran gave photoreduction and photoaddition products, while photolysis of 1-phenyl-1,3,5-hexatriynes in deaerated alcoholic solvents (methanol, *i*-propanol) yielded dark red products, probably oligomers or decomposition products of reactants, as exclusive major products. A plausible mechanism for the reaction is proposed.

Introduction

In photoaddition reactions of alkynes, proton or hydrogen abstraction by alkynes from substrates or solvents is the initial step. Radical photoaddition reaction to acetylenes oc-

curs with cyclic ethers such as tetrahydrofuran¹, and saturated hydrocarbons such as cyclohexane.² Although the reaction with tetrahydrofuran does not require a triplet sensitizer, efficient addition of tetrahydropyran or dioxan is only achieved when a ketone is added to promote the formation