

## Absorption and Fluorescence of Sm(III) Complexes with some Terdentate Ligands

Jong Goo Kim

Chemistry and Chemical Analysis Division, Korea Atomic Energy Research Institute, Taejeon 302-353

Soo Kyung Yoon, Sock Sung Yun, and Jun-Gill Kang\*

Department of Chemistry, Chungnam National University, Taejeon 305-764. Received September 9, 1991

Spectroscopic measurements and theoretical calculations are performed for the four 1:3 Sm(III):ligand solutions. The ligands included in this study are oxidiacetate, iminodiacetate, methyliminodiacetate and dipicolinate. The oscillator strengths for the  $4f \rightarrow 4f$  multiplet-to-multiplet transitions are empirically determined from the absorption spectra. The intensity parameters  $\Omega_\lambda$  ( $\lambda=2, 4, 6$ ) of  $\text{Sm}^{3+}$  (aquo) and  $\text{SmL}_3^{3-}$  complexes are also evaluated by applying the Judd-Ofelt theorem to the observed oscillator strengths. The values of the intensity parameters are compared and discussed in term of structural properties of the complexes. In addition, the fluorescence spectra are reported for the Sm(III) complex systems under mild alkaline condition. The excitation from the  ${}^6\text{H}_{5/2}$  ground state to any excited states lying above the emitting energy level ( ${}^4\text{G}_{5/2}$ ) produces four fluorescence bands, following nonradiative transitions from a certain excited state to the  ${}^4\text{G}_{5/2}$  state. The ratios of oscillator strengths of  $\text{SmL}_3^{3-}$  complexes to that of  $\text{Sm}^{3+}$  (aquo) are also evaluated from the fluorescence spectra and compared to the results obtained from the absorption bands.

### Introduction

Lanthanide ions show very characteristic  $f \rightarrow f$  absorption spectra which correspond to transitions from the ground multiplet to the excited multiplet.<sup>1,2</sup> The oscillator strengths of these multiplet-to-multiplet transitions have been successfully described by the Judd-Ofelt theory.<sup>3,4</sup> According to the Judd-Ofelt theory, mixing between  $4f^n$  configuration and another configuration having opposite parity may be occurred by the crystal-field potential and cause the  $4f \rightarrow 4f$  transitions to be allowed by the induced electric dipole. On the basis of the intermediate coupling scheme, the oscillator strength of the transition from the initial  $\psi J$  state to the final  $\psi' J'$  state is expressed as

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

where  $\chi$  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  $\text{cm}^{-1}$ , and  $2J+1$  is the degeneracy of the initial state with the assumption that all the Stark levels may be equally populated in the solution state, and  $U^{(\lambda)}$  is a unit tensor operator of rank  $\lambda$ , the sum running over the three values  $\lambda=2, 4, 6$ . In the equation, the  $\Omega_\lambda$  quantities, called as the Judd-Ofelt intensity parameters, are phenomenologically obtained from the experimental oscillator strengths. It has been shown that among the three intensity parameters the  $\Omega_2$  is very sensitive to the structural details and chemical nature of the ligand environment.<sup>5-7</sup> When the ion is complexed, oscillator strengths of certain bands increase markedly, compared with the cases in the correspon-

ding aquo ion. Such bands have been labelled hypersensitive. It has been pointed out that hypersensitivity is strongly correlated with those transition having large matrix elements of  $U^{(2)}$  and that accordingly it is rationalized as the peculiar sensitivity of the  $\Omega_2$  to the environment.<sup>8</sup>

Recently, for Nd(III), Ho(III) and Er(III) complexes in aqueous solution the Judd-Ofelt intensity parameters were empirically determined<sup>6,7</sup> and also theoretically interpreted in terms of the lanthanide-ligand-radiation field interaction.<sup>9</sup> The successful rationalization of the  $\Omega_2$  sensitivity for those complexes could be due to the fact that those ions show the hypersensitive transitions in accessible spectral region. No attempts for Sm(III) complexes, however, have been made to rationalize  $\Omega_2$  sensitivity to the minor changes in the coordination environment. Contrary to those ions, Sm(III) ion does not have large value of  $U^{(2)}$  for transitions from the ground state to any observable excited-states except the transition  ${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{1/2}, {}^4\text{F}_{3/2}$  peaking at  $6,400 \text{ cm}^{-1}$ . It is very difficult to scan the absorption spectrum down to this wavenumber because of uprising absorbance below  $7,000 \text{ cm}^{-1}$  due to water. In the present paper, we evaluate empirical oscillator strengths from the UV/visible absorption spectra for a series of Sm(III) complexes in aqueous solution. The primary interest here is to determine the Judd-Ofelt intensity parameters from the oscillator strengths and to examine how the  $\Omega_2$  intensity parameters can respond to the minor changes in the ligand environment, although no hypersensitivity are observed. The ligands used in this study are oxidiacetate (ODA), dipicolinate (DPA), iminodiacetate (IDA) and methyliminodiacetate (MIDA). The similarity in these ligands is that the central atom of each ligand acts as an electron-pair donor along two carboxylate groups as terminals. Likely, it is that the major species in the 1:3 Ln(III):ligand is tris (terdentate) complex under the mild

\*To whom all correspondence should be addressed.

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

transition region		$\langle    U^{(\lambda)}    \rangle^2$			
label	transition	$\bar{\nu}(\text{cm}^{-1})$	$\lambda=2$	$\lambda=4$	$\lambda=6$
(a)	${}^6H_{5/2} \rightarrow {}^4I_{9/2}$	20,619	0.0022	0.0005	0.0014
(b)	${}^6H_{5/2} \rightarrow {}^4I_{11/2}, {}^4M_{15/2}$	20,942	0	0	0.0415
(c)	${}^6H_{5/2} \rightarrow {}^4I_{13/2}$	21,505	0	0.0030	0.0228
(d)	${}^6H_{5/2} \rightarrow {}^4F_{7/2}, {}^4L_{13/2}$	24,570	0.0002	0.0093	0.0099
(e)	${}^6H_{5/2} \rightarrow ({}^4K_{11/2}), {}^6P_{3/2}$	24,814	0	0.1688	0.0027
(f)	${}^6H_{5/2} \rightarrow ({}^4K_{13/2}), {}^6P_{7/2}$	26,631	0	0.0021	0.0762
(g)	${}^6H_{5/2} \rightarrow {}^4D_{7/2}, ({}^4H_{9/2})$	28,986	0.0001	0.0007	0.0381

<sup>a</sup> The peak position observed in the absorption spectra of the 1 : 3 Sm(III) : ODA solutions. The term symbols given in the parentheses indicate the electronic state contributing a very weak transition probability to the observed band.

alkaline solution.

In addition, we also measured fluorescence spectra of the complexes to investigate how the variation of the complex environment alters the oscillator strength of the fluorescence, in conjunction with that of the absorption.

### Experimentals

$\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  (99.99%) was purchased from Aldrich and was used without further purification. Oxydiacetic acid (ODAH<sub>2</sub>), dipicolinic acid (DPAH<sub>2</sub>), iminodiacetic acid (IDAH<sub>2</sub>) and methyliminodiacetic acid (MIDAH<sub>2</sub>) were also obtained from Aldrich and were used without further purification. The pH of the 1 : 3 Sm<sup>3+</sup> : ligand solution was adjusted with NH<sub>4</sub>OH aqueous solution. All absorption spectra were carried out on aqueous solution in which the concentrations of Sm<sup>3+</sup> and the ligand were held at 0.04 M and 0.12 M, respectively. Absorption spectra of the samples were recorded on a Beckman 5260 UV/visible Spectrophotometer at room temperature and fluorescence spectra were measured using a SLM AMINCO 4880 Spectrofluorometer.

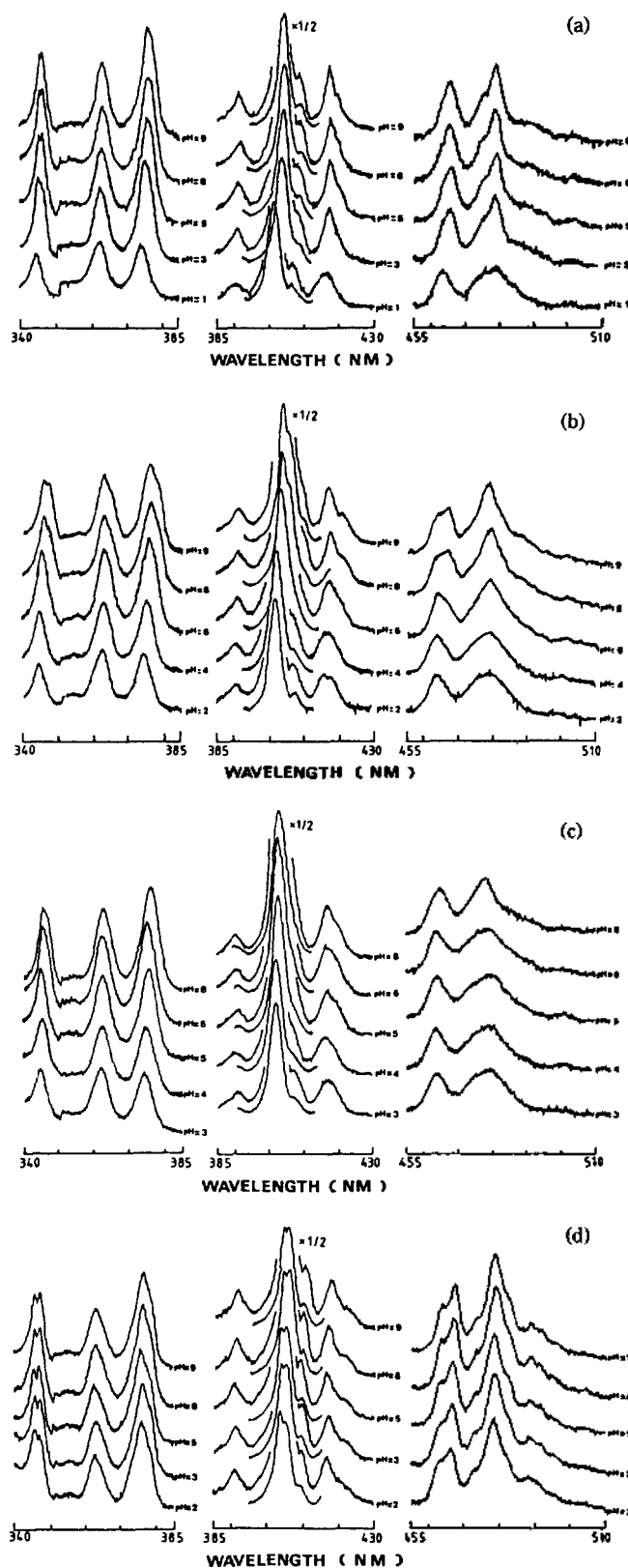
The oscillator strength defined as Eq. (1) can be expressed by the measured intensity of an absorption band in an aqueous medium as follows:

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

where  $\epsilon(\bar{\nu})$  is the molar absorption coefficient at the energy  $\bar{\nu}$  and the integral corresponds to the area of the absorption band for a certain transition. The combination of Eq. (1) and (2) can express the integration over the entire  $\psi_f \rightarrow \psi_i$  absorption band as:

$$I(\psi_f) = \int \epsilon(\bar{\nu}) d\bar{\nu} \\ = (2.98 \times 10^{19}) \bar{\nu} (2f+1)^{-1} \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle \psi_f || U^{(\lambda)} || \psi_i \rangle^2 \quad (3)$$

where  $2f+1=6$ , since the initial multiplet state of Sm<sup>3+</sup> is  ${}^6H_{5/2}$ . The resolution of the observed band and the integration of the resolved band were made by employing the modified Gaussian-Lorentzian function<sup>10</sup> to the observed datum points. The seven transitions of interest in this study are



**Figure 1.** Absorption spectra of  $\text{SmL}_3^{3-}$  complex solutions under various pH conditions: L=(a) ODA, (b) IDA, (c) MIDA and (d) DPA.

identified according to the term symbol and are listed in Table 1.

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

complex	$\Omega_\lambda \times 10^{20} \text{ (cm}^2\text{)}$		
	$\lambda=2$	$\lambda=4$	$\lambda=6$
Sm <sup>3+</sup> (aquo)	5.84 ( $\pm 33.55$ )	4.06 ( $\pm 0.36$ )	2.86 ( $\pm 0.60$ )
Sm <sup>3+</sup> /ODA	30.17 ( $\pm 24.99$ )	4.37 ( $\pm 0.27$ )	5.96 ( $\pm 0.45$ )
Sm <sup>3+</sup> /IDA	33.10 ( $\pm 77.84$ )	4.57 ( $\pm 0.85$ )	6.58 ( $\pm 1.45$ )
Sm <sup>3+</sup> /MIDA	33.91 ( $\pm 70.97$ )	5.14 ( $\pm 0.77$ )	7.02 ( $\pm 1.28$ )
Sm <sup>3+</sup> /DPA	44.16 ( $\pm 56.11$ )	4.28 ( $\pm 0.61$ )	5.79 ( $\pm 1.01$ )

## Results and Discussion

Absorption spectra of the 1:3 Sm(III):ligand solutions were measured under various pH conditions to investigate the effect of the pH in the solution on the coordination environment. Figure 1 shows the absorption spectra as a function of pH, in which the transitions labelled as (e) and (g) are certainly affected by the pH among the transitions measured in this study. For the 1:3 Sm(III):DPA solution, the absorbances and the structures of these two bands are nearly independent of the pH. Under very acidic condition splitting of the bands by the ligand field takes place. There is no appearance of the pH effect on the absorbance and the structure of the bands under the condition of pH>2. Similarly, in the case of the 1:3 Sm<sup>3+</sup>:ODA solution, the ligand effect on the absorbance and the band structure were observed under the condition of pH>3. These results indicate that the DPA and ODA ligands can form tris(terdentate) complexes with Sm(III) under the acidic condition. Contrary, the absorbance and the structure of the bands for the 1:3 Sm(III):IDA and Sm(III):MIDA solutions are very dependent on the pH under acidic condition. It is also found that the peak position of the transition (e) shifts to the low energy with increasing value of pH under the acidic condition. Reasonably, the absorption spectra of the four systems measured under the mild alkaline condition were chosen for the intensity analysis.

The three Judd-Ofelt intensity were obtained from the empirically determined oscillator strengths by the multiple regression analysis method, in which the  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  quantities were treated as adjustable parameters. The  $\Omega_\lambda$  values yielding optimal fits are listed in Table 2. The large root-mean-square deviations appeared in the  $\Omega_2$  parameters. It

could be due to that most of matrix elements of  $\Omega^{(2)}$  are zero or very small, compared with those of  $\Omega^{(4)}$  and  $\Omega^{(6)}$ . Experimental and fitted oscillator strengths are listed in Table 3: the latter were calculated from Eq. (3) by using the  $\Omega_\lambda$  parameters. The very good agreements between the experimental and the calculated oscillator strengths were found in the transitions labeled as (a) and (e): the latter yields the largest value of the oscillator strength among the transitions examined in this study. It may arise from the fact that the matrix element of  $\Omega^{(4)}$  for this transition is exceptionally large, compared with the others. It should be noted that for the transition labeled as (d) the exceptional increase in oscillator strength were observed in the 1:3 Sm(III):IDA and Sm(III):MIDA solutions. This phenomenon remains questionable.

It has been recognized that  $\Omega_2$  is a parameter exhibiting the relative coordination-abilities of the various ligands, if and only if at least one or two transitions have large  $\Omega^{(2)}$  element. We shall first examine whether  $\Omega_2$  of Sm(III) complexes can reflect the ligand effect, although the electronic character arisen from Sm(III) with  $f^6$  electronic configuration exhibits small matrix elements of  $\Omega^{(2)}$ . Among the transition regions examined in this study, it can be found that the transitions labeled as (a), (d) and (g) show the large variations in oscillator strength from complex to complex. It could be due to that these transitions have nonzero matrix elements of  $\Omega^{(2)}$  (see Table 1). Specially, the transition (a) exhibits the largest variation. One can find that the experimentally determined oscillator strength of the transition (a) shows somewhat the hypersensitivity. It may result from that in the case of the transition (a)  $\Omega^{(2)}$  is not only the largest value among those of the three transitions, but also is of suitable, compared with  $\Omega^{(4)}$  and  $\Omega^{(6)}$ . Clearly, one can find it from ratios of  $\Omega_\lambda(\text{complex})$  to  $\Omega_\lambda(\text{aquo})$  listed in Table 4 that  $\Omega_2$  is much more sensitive to the coordination environment than  $\Omega_4$  and  $\Omega_6$ . It should be noted that among the ligands examined here the DPA complexes shows the largest  $\Omega_2(\text{complex})/\Omega_2(\text{aquo})$ . The similar results can be seen in series of Nd(III), Ho(III) and Er(III) complexes.<sup>6,7</sup>

The ratios of  $\Omega_2(\text{complex})/\Omega_2(\text{aquo})$  have been considered to discuss the relative binding abilities of the various ligands in terms of structural differences between the complexes. According to the structures of the Ln(III) complexes described previously,<sup>7</sup> the tris(terdentate) complexes of ODA, IDA, MIDA and DPA forming the tricapped trigonal prism are classified to two isomer groups. The ODA and DPA complex-

**Table 3.** Experimental and Calculated Oscillator Strengths\* for The Sm(III) Systems in The Neutral pH Condition

transition	AQUO		ODA		IDA		MIDA		DPA	
	exptl.	fit	exptl.	fit	exptl.	fit	exptl.	fit	exptl.	fit
(a)	0.085	0.083	0.343	0.340	0.225	0.373	0.232	0.385	0.498	0.475
(b)	1.074	0.533	1.445	1.111	1.761	1.226	1.479	1.308	2.016	1.079
(c)	0.607	0.357	0.812	0.687	0.846	0.755	0.758	0.809	1.039	0.668
(d)	0.350	0.354	0.416	0.557	1.965	0.602	1.994	0.654	0.437	0.558
(e)	3.721	3.690	4.025	4.011	4.134	4.200	4.669	4.718	3.934	3.928
(f)	1.017	1.293	2.404	2.646	2.521	2.918	2.837	3.117	2.194	2.571
(g)	0.688	0.699	1.628	1.459	1.605	1.600	1.843	1.706	1.238	1.417

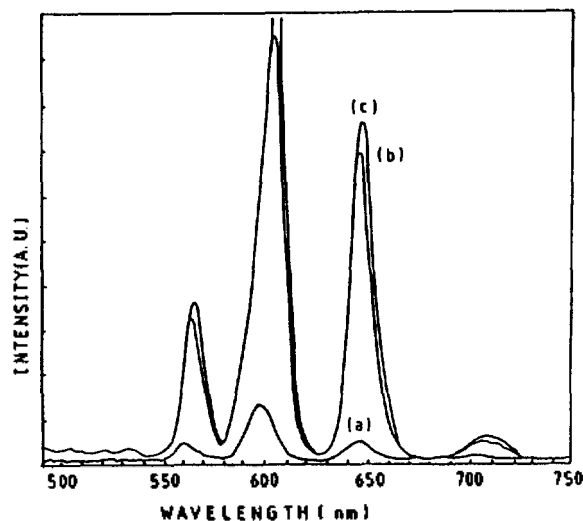
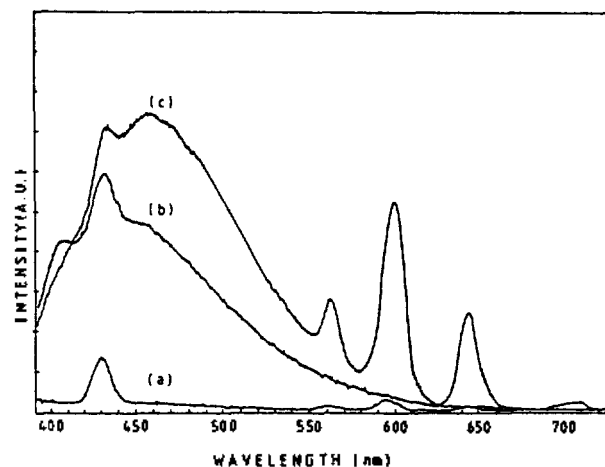
\*Oscillator strength values are given as  $P/10^{-6}$ .

**Table 4.** Ratios of the Judd-Ofelt Intensity Parameters

ligand	$\Omega_\lambda$ (complex)/ $\Omega_\lambda$ (aquo)		
	$\lambda=2$	$\lambda=4$	$\lambda=6$
ODA	5.17	1.08	2.08
IDA	5.67	1.13	2.30
MIDA	5.81	1.27	2.45
DPA	7.56	1.05	2.02

**Table 5.** Assignments for Fluorescence Spectra of Sm(III) Complexes

peak position (nm)	transition
706 (v w)	$^4G_{5/2} \rightarrow ^6H_{11/2}$
647 (s)	$^4G_{5/2} \rightarrow ^6H_{9/2}$
605 (v s)	$^4G_{5/2} \rightarrow ^6H_{7/2}$
565 (w)	$^4G_{5/2} \rightarrow ^6H_{6/2}$

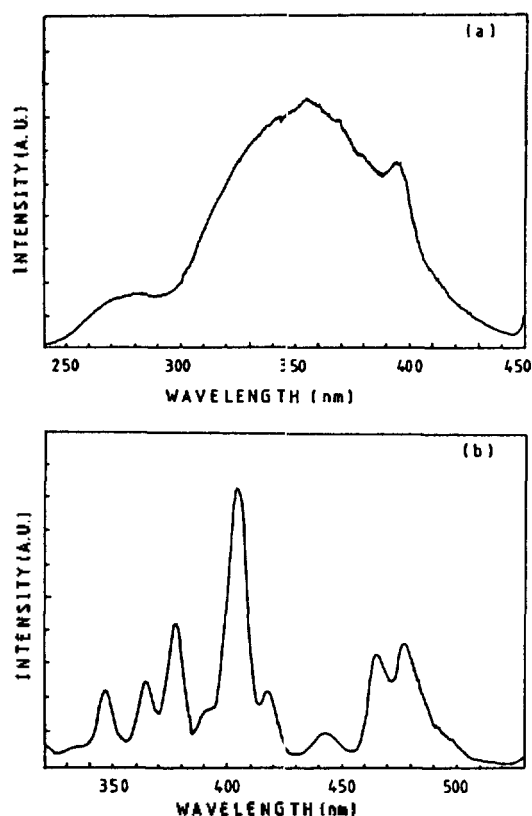
**Figure 2.** Fluorescence spectra of: (a)  $\text{Sm}^{3+}$ (aquo) at pH=7, and  $\text{Sm}(\text{DPA})_3^{3-}$  solution at (b) pH=3 and (c) pH=6. The excitation wavelengths are 401 nm for  $\text{Sm}^{3+}$ (aquo) and 406 nm for  $\text{Sm}(\text{DPA})_3^{3-}$ , respectively.**Figure 3.** Fluorescence spectra of: (a)  $\text{Sm}^{3+}$ (aquo), (b) ODA ligand and (c)  $\text{Sm}(\text{ODA})_3^{3-}$  under mild alkaline solutions, excited at 376 nm.

es have so-called meridional isomeric structure of  $D_3$  symmetry, in which the chelate rings are planar and they stretch diagonally across the rectangular faces of the prism. On the other hand, the IDA and MIDA complexes have facial configurations of  $C_{3h}$  symmetry, in which the ligands are presumed to be wrap up the prism. According to the structural similarity, the comparisons of ligand environments can be made on between ODA and DPA and also between IDA and MIDA. The ratios of  $\Omega_2(\text{complex})/\Omega_2(\text{aquo})$  show that  $\text{ODA} < \text{DPA}$  and  $\text{IDA} \leq \text{MIDA}$ . In addition, taking into account the sum of  $P_{obs}$  given in Table 3, it can be also seen that  $\text{ODA} < \text{DPA}$  and  $\text{IDA} \leq \text{MIDA}$ . The large difference in  $\Omega_2$  is found between  $\text{Sm}(\text{ODA})_3^{3-}$  and  $\text{Sm}(\text{DPA})_3^{3-}$ . It has been suggested that the differences in  $\text{Er}^{3+}$ -carboxylate interactive strengths may not affect the  $f \rightarrow f$  transition intensities significantly.<sup>7</sup> Assuming that it is also applicable to Sm(III) systems, the differences in  $\Omega_2$  could account for the differences in binding abilities of the central donor atoms of the respective ligands. The N atom in pyridine ring has denser electronic charge 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 comparison with binding abilities of IDA and MIDA ligands, it can be expected that at the central nitrogen atom methyl group substitution is more effective than hydrogen. In the case of  $\text{Sm}(\text{IDA})_3^{3-}$  and  $\text{Sm}(\text{MIDA})_3^{3-}$  complexes, however, the substitution effect appear

to only a small extent in the variation of  $\Omega_2$  and oscillator strengths. A similar feature for binding abilities of the four ligands with  $\text{Sm}^{3+}$  ions can be found from stability constants, *i.e.*,  $\text{DPA} > \text{MIDA} \geq \text{IDA} > \text{ODA}$ .<sup>11</sup>

Figure 2 shows the fluorescence spectra of  $\text{Sm}^{3+}$ (aquo) and  $\text{Sm}(\text{DPA})_3^{3-}$ , respectively, excited at 401 nm and 406 nm.  $\text{Sm}^{3+}$  ion produces four fluorescence bands peaking at 706 nm, 647 nm, 605 nm and 565 nm. The assignment of these four bands is given in Table 5. In the case of  $\text{Sm}(\text{ODA})_3^{3-}$ ,  $\text{Sm}(\text{IDA})_3^{3-}$  and  $\text{Sm}(\text{MIDA})_3^{3-}$  complexes, a strong and very broad fluorescence band was accompanied to the four principal bands at the high-energy side. Figure 3 shows fluorescence spectra of  $\text{Sm}^{3+}$ (aquo),  $\text{Sm}(\text{ODA})_3^{3-}$  and ODA. Excitation spectra of the 458 nm and the 600 nm bands were also measured. As shown in Figure 4, the uncharacteristic high-energy band arises from the ligand itself. The 430 nm band can be attributed to Stock's shift of the excitation wavelength.

The characteristic feature shown in Figure 2 is that the fluorescence intensity of the complex increased markedly, compared with that of  $\text{Sm}^{3+}$ (aquo). Similarly to the absorption, the relative oscillator-strengths of the fluorescences have been also considered to examine the ligand strength. For the 647 nm, 605 nm and 565 nm bands, the ratios of oscillator strengths of the complexes to those of  $\text{Sm}^{3+}$ (aquo) are listed in Table 6. Independently of the excited state, the ratios for the three bands indicate that  $\text{ODA} < \text{DPA}$  and  $\text{IDA} > \text{MIDA}$ . The coincidence of the relative binding ability of the ligands between ODA and DPA occurs between the absorption and the fluorescence. Contrary to absorption, the oscillator strength of the fluorescence of  $\text{Sm}(\text{IDA})_3^{3-}$  is much stronger than that



**Figure 4.** Excitation spectra of: (a) 458 nm emission for the ODA solution and (b) 600 nm emission for the  $\text{Sm}(\text{ODA})_3^{3-}$  solution.

of  $\text{Sm}(\text{MIDA})_3^{3-}$ . It could be due to the substitution effect on the fluorescence, *i.e.*, the substitution of methyl group at the central nitrogen atom may quench the fluorescence.

### Conclusion

The Judd-Ofelt intensity parameters  $\Omega_\lambda$  ( $\lambda=2, 4, 6$ ) for Ln (III) complexes have been extensively studied to demonstrate the sensitivity of these intensity parameters to ligand effects. Among the  $\Omega_\lambda$  parameters  $\Omega_2$  shows the most sensitivity to minor changes in the ligand environment if a certain transition has large element of  $\text{U}^{(2)}$ . Unfortunately, for Sm(III) ion,  $\text{U}^{(2)}$  matrix elements for most of transitions are very small. A series of Sm(III) complexes in aqueous solution, however, were investigated to examine how to a certain extent these parameters are sensitive to the coordination environment. Among the ligands examined in this study, the  $\Omega_2(\text{complex})/\Omega_2(\text{aquo})$  ratios varied by as much as a factor of 5.1. Although  $\text{U}^{(4)}$  matrix element for the transition  ${}^6H_{5/2} \rightarrow ({}^4K_{11/2}, {}^6P_{3/2})$  is very large,  $\Omega_4$  was found to be insensitive to ligand effect. The results obtained from oscillator strengths of absorption bands clearly show that among the  $\Omega_\lambda$  parameters  $\Omega_2$  is the most sensitive to the ligand environment. 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  $\Omega_2$  values between  $\text{Sm}(\text{ODA})_3^{3-}$  and  $\text{Sm}(\text{DPA})_3^{3-}$  complexes could be attributed to electron densities at the central atoms of each ligand. Contrary to expectation,  $\Omega_2$  values of  $\text{Sm}(\text{IDA})_3^{3-}$  was

**Table 6.** Ratios of Oscillator Strengths of the Three Fluorescence Bands of  $\text{SmL}_3^{3-}$  to Those of  $\text{Sm}^{3+}$  (aquo)

(a) 647 nm band

ligand	excited state				
	${}^4M_{15/2} + {}^4I_{11/2}$	${}^4I_{13/2}$	${}^4L_{13/2} + {}^4F_{7/2}$	${}^4P_{5/2}$	${}^6P_{3/2}$
ODA	7.81	8.46	7.39	8.24	7.04
IDA	12.26	11.58	10.63	10.95	9.20
MIDA	5.87	5.31	10.27	8.62	9.95
DPA	20.26	16.69	12.12	13.67	13.03

(b) 605 nm band

ligand	excited state				
	${}^4M_{15/2} + {}^4I_{11/2}$	${}^4I_{13/2}$	${}^4L_{13/2} + {}^4F_{7/2}$	${}^4P_{5/2}$	${}^6P_{3/2}$
ODA	6.06	7.25	5.99	8.56	6.76
IDA	8.40	9.09	8.08	12.02	7.53
MIDA	4.67	4.64	6.66	6.67	6.50
DPA	12.16	12.01	8.38	10.10	8.48

(c) 565 nm band

ligand	excited state				
	${}^4M_{15/2} + {}^4I_{11/2}$	${}^4I_{13/2}$	${}^4L_{13/2} + {}^4F_{7/2}$	${}^4P_{5/2}$	${}^6P_{3/2}$
ODA	2.24	1.98	5.30	6.29	4.80
IDA	3.45	1.75	9.55	19.29	8.56
MIDA	1.69	1.37	5.75	5.35	5.15
DPA	4.14	2.60	7.60	7.24	7.89

found to be almost equal to that of  $\text{Sm}(\text{MIDA})_3^{3-}$ , although at central nitrogen atom electron density of MIDA is denser than that of IDA. The ligand effects on complexation with Sm(III) ion were also investigated in terms of oscillator strength of fluorescence band. Similar results were obtained on  $\text{Sm}(\text{ODA})_3^{3-}$  and  $\text{Sm}(\text{DPA})_3^{3-}$ . In the case of  $\text{Sm}(\text{IDA})_3^{3-}$  and  $\text{Sm}(\text{MIDA})_3^{3-}$ , however, the fluorescence of Sm(III) was much more intensified by coordinating with IDA than with MIDA. It could be due to that the substitution of methyl group at the central nitrogen atom quenches the fluorescence possibly.

Furthermore, we are carrying out the extensive study on the Sm(III) complexes in acetonitrile media for various transitions including the transition  ${}^6H_{5/2} \rightarrow {}^4F_{1/2}, {}^4F_{3/2}$  peaking at  $6400 \text{ cm}^{-1}$ , which shows large value of  $\text{U}^{(2)}$ . It may allow us to present the sensitivity of the intensity parameters to ligand effects in detail.

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## An Explanation of the Contrasting Reactivities of *meso*- and *d,l*- $D_3$ -Trishomocubylidene- $D_3$ -trishomocubane towards Electrophiles

Oh Seuk Lee\* and Eiji Ōsawa†

Department of Chemistry, Andong National University, Kyongbuk 760-749

†Department of Knowledge-Based Information Engineering,

Toyohashi University of Technology, Toyohashi 441, Japan. Received September 24, 1991

The contrasting behaviour of *meso*- and *d,l*- $D_3$ -trishomocubylidene- $D_3$ -trishomocubane (**1** and **2**) in the electrophilic addition reaction, the former giving rearranged spiro compound (**1a** and **1b**) and the latter giving 1,2-adduct (**2a** and **2b**), has been explained as arising from the secondary steric effects based on computational evidence. As the degree of out-of-plane deformation of the olefinic carbon atoms increases with reaction progress, the resulting internal congestion in the region behind the double bond becomes unbearably large in *meso*-**1**. The absence of symmetry plane across the double bond of *d,l*-**2** helps for the closing fragments to adjust themselves.

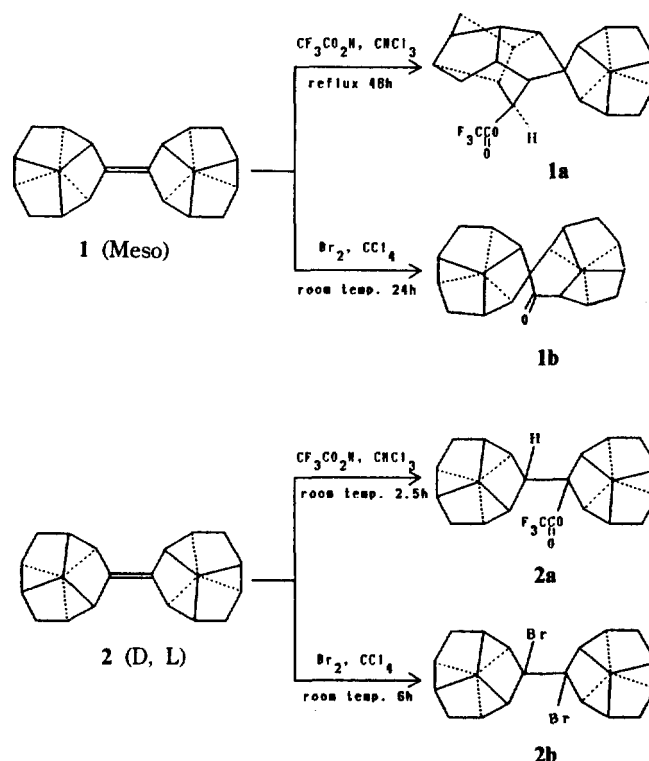
### Introduction

The reaction of a mixture of *meso*-dimer (**1**) of  $D_3$ -trishomocubane and corresponding *d,l*-dimer (**2**)<sup>1</sup> with trifluoroacetic acid in chloroform at room temperature afforded a single adduct, **2a**, which arose solely from the *d,l*-dimer, leaving unreacted *meso*-dimer behind, which could be recovered in nearly pure form. When a solution of isomerically pure **1** in trifluoroacetic acid-chloroform was refluxed, a spiro compound, **1a**, was produced (Scheme 1). Electrophilic bromination of **2** also was studied. When isomerically pure **2** was reacted with excess  $\text{Br}_2\text{-CCl}_4$  solution at room temperature, a single adduct, **2b**, was isolated. The *meso*-dimer, **1**, also reacted with excess  $\text{Br}_2\text{-CCl}_4$  solution at room temperature, and the product obtained was not a 1,2-addition product but instead was found to be rearranged spiroketone **1b** (Scheme 1).<sup>2</sup>

The observation is remarkable in that the two stereoisomers, differing only in the axial chirality, showed such contrasting behaviours towards electrophiles. Since the stereoelectronic effect is apparently absent, we sought a steric explanation, using MM2<sup>3</sup> and AM1<sup>4</sup> methods.

### Computational Techniques

MM2 calculations were performed by using a packaged program, BIGSTRN-3.<sup>5</sup> MM2-parameters for carbocation were taken from the work of Müller and Mareda.<sup>6</sup> A locally



Scheme 1.