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# Synthesis, Characterization, and Properties of $V^{IV}O$-Ln(III) (Ln=La, Pr, Eu, Gd, Tb) Complexes of *N*,*N'*-Bis(3-carboxysalicylidene)ethylenediamine

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Mononuclear oxovanadium(IV) and europium(III) complexes, $[VO(H_2fsaen)]\cdot 2H_2O$ and $[Eu(H_2fsaen)(NO_3)(H_2O)_n]\cdot(5-n)H_2O$, and dinuclear oxovanadium(IV)–rare earth(III) complexes, $[VOLn(fsaen)(NO_3)(H_2O)_n]\cdot(m-n)H_2O$ (Ln=La, Pr, Eu, Gd, Tb), of *N*,*N'*-bis(3-carboxysalicylidene)ethylenediamine ($H_4fsaen$) have been synthesized. Oxovanadium(IV) ion and europium(III) ion in the respective mononuclear complexes is bound at the $O_4$-site of ligand, whereas in the $V^{IV}O$–Ln(III) complexes $V^{IV}O$ ion is bound at the $N_2O_2$-site and Ln(III) ion at the $O_4$-site. Based on the absorption and CD spectra, it is suggested that amino alcohols are specifically bound at the $V^{IV}O$–Ln(III) heterometal center, through the nitrogen to the $V^{IV}O$ and through the oxygen to the Ln(III). The fluorescent spectral measurements reveal that the fluorescent bands of Eu(III) for the mononuclear Eu(III) complex are significantly quenched in the dinuclear $V^{IV}O$–Eu(III) complex.

Heteronuclear metal complexes give many useful informations on the active sites of some metalloenzymes,[1] the magnetic spin-exchange mechanisms between paramagnetic ions,[2] and the development of catalyses.[3] In order to obtain discrete heterodinuclear complexes, some dinucleating ligands with dissimilar coordination sites have been developed so far.[4] However, efforts have been mainly devoted to the synthesis of dinuclear complexes comprising d-transition metal ions and very few reports[5] are available on d-f heterodinuclear complexes comprising a d-transition metal ion and a rare earth ion (f-transition metal ion). For the design of ligand which can afford d-f heterodinuclear complexes, it should be taken into consideration that rare earth ions are generally hard in the HSAB sense and large in ionic radii compared with d-transition metal ions.

Recently we have found that *N*,*N'*-bis(3-carboxysalicylidene)ethylenediamine ($H_4fsaen$) and bis [2-(3-carboxysalicylidene)aminoethyl] amine ($H_4fsadien$) afford discrete M(II)–Ln(III) dinuclear complexes (M=Cu, Co and Ln=rare earths), where copper(II) or cobalt(II) ion is bound at the inside coordination site ($N_2O_2$- or $N_3O_2$-site) and rare earth(III) ion at the outside coordination site ($O_4$-site) (Fig. 1).[6–8] These dinuclear complexes show unique "selective solvation" associated with the copper or rare earth center depending upon the nature of solvents.[6] That is, in nitrogen-containing solvent like pyridine the solvation occurs preferentially at the copper center, whereas in oxygen-containing solvent like *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) the solvation occurs exclusively at the rare earth center. This selective solvation has been extended to specific binding of substrates, which contain both nitrogenous and oxygenous donating groups, on the Cu(II)–Ln(III) or Co(II)–Ln(III) heterometal center.[7–9] Furthermore, it was found that the fluorescent properties of europium(III) are significantly affected on forming dinuclear Cu(II)–Eu(III) or Ni(II)–Eu(III) complex.[10,11]

In this work we have prepared and characterized the mononuclear oxovanadium(IV) complex $[VO(H_2fsaen)]\cdot 2H_2O$, mononuclear europium(III) complex [Eu-

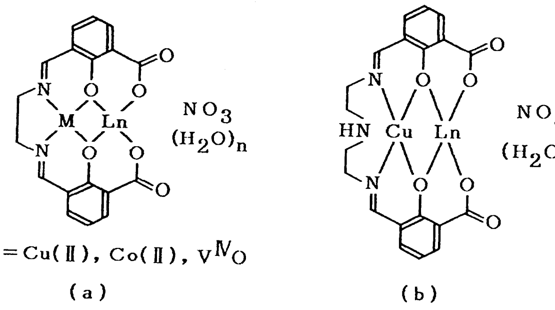

Fig. 1. Chemical structures of $[MLn(fsaen)(NO_3)(H_2O)_n]\cdot(m-n)H_2O$ (a) and $[CuLn(fsadien)(NO_3)(H_2O)_n]\cdot(5-n)H_2O$ (b).

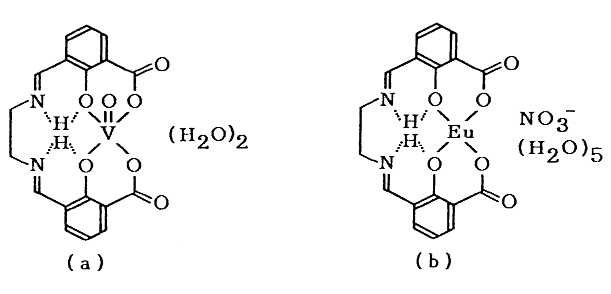

Fig. 2. Chemical structures of $[VO(H_2fsaen)]\cdot 2H_2O$ (a) and $[Eu(H_2fsaen)(NO_3)(H_2O)_n]\cdot(5-n)H_2O$ (b).

$(\mathrm{H_2fsaen})(\mathrm{NO_3})(\mathrm{H_2O})_n]\cdot(5-n)\mathrm{H_2O}$, and dinuclear oxovanadium(IV)-rare earth(III) complexes $[\mathrm{VOLn(fsaen)}(\mathrm{NO_3})(\mathrm{H_2O})_n]\cdot(m-n)\mathrm{H_2O}$ (Figs. 1 and 2). The electronic spectra of the $\mathrm{V^{IV}O}$-Ln(III) complexes in DMF and DMSO are studied in view of selective solvation and the specific binding of amino alcohols on the $\mathrm{V^{IV}O}$-Ln(III) center is discussed based on electronic and circular dichroism (CD) spectra. Furthermore, the fluorescence spectra of the mononuclear Eu(III) and dinuclear $\mathrm{V^{IV}O}$-Eu(III) complexes have been compared, in order to investigate the effect of the $\mathrm{V^{IV}O}$ ion upon the fluorescent property of the Eu(III) ion.

## Experimental

**Syntheses.** 3-Formylsalicylic acid was prepared after the method of Duff and Bills.[12] The ligand, *N*,*N*′-bis(3-carboxysalicylidene)ethylenediamine ($\mathrm{H_4fsaen}$), was obtained by the condensation of 3-formylsalicylic acid and ethylenediamine in the 2 : 1 molar ratio in ethanol.

**$[\mathrm{VO(H_2fsaen)}]\cdot 2\mathrm{H_2O}$:** To a suspension of $\mathrm{H_4fsaen}$ (10 mmol) in water (30 $\mathrm{cm^3}$) was added sodium carbonate (10 mmol) under stirring. To the resulting clear solution was added oxovanadium sulfate trihydrate (10 mmol) in water (30 $\mathrm{cm^3}$). Soon yellowish green needle crystals were precipitated. After the mixture was stirred for 30 min at room temperature, the crystals were collected on a glass filter, washed successively with water, methanol, and diethyl ether, and dried in the open air. The yield was 65.5%.

**$[\mathrm{Eu(H_2fsaen)(NO_3)(H_2O)}_n]\cdot(5-n)\mathrm{H_2O}$:** A methanolic solution (30 $\mathrm{cm^3}$) of lithium hydroxide monohydrate (8 mmol) was added to a suspension of $\mathrm{H_4fsaen}$ (4 mmol) in methanol (30 $\mathrm{cm^3}$). To the resulting clear solution was added europium(III) nitrate hexahydrate (4 mmol) in methanol (10 $\mathrm{cm^3}$). Yellowish crystals were soon precipitated. After the mixture was heated under stirring for 2 h, the crystals were collected on a glass filter, washed with methanol and then diethyl ether, and dried in the open air. The yield was almost quantitative.

**$[\mathrm{VOLn(fsaen)(NO_3)(H_2O)}_n]\cdot(m-n)\mathrm{H_2O}$ (Ln=La, Pr, Eu, Gd, or Tb):** A methanolic solution (50 $\mathrm{cm^3}$) of lithium hydroxide monohydrate (2 mmol) was added to a suspension of $[\mathrm{VO(H_2fsaen)}]\cdot 2\mathrm{H_2O}$ (1 mmol) in methanol (50 $\mathrm{cm^3}$). To the resulting clear solution was added a methanolic solution (10 $\mathrm{cm^3}$) of a rare earth(III) nitrate hexahydrate (1 mmol). Soon greenish crystals were precipitated. After the mixture was refluxed under stirring for 2 h, the crystals were collected on a glass filter, washed with methanol and then diethyl ether, and dried in the open air. The yields were 50—75%.

Analytical results are given in Table 1.

Table 1. Elemental Analyses of Complexes

| Complex | Found/% (Calcd/%) | | |
|---|---|---|---|
| | C | H | N |
| $\mathrm{VO(H_2fsaen)(H_2O)_2}$ | 47.65<br>(47.28) | 3.70<br>(3.97) | 6.18<br>(6.13) |
| $\mathrm{Eu(H_2fsaen)(NO_3)(H_2O)_5}$ | 32.24<br>(32.84) | 3.39<br>(3.67) | 6.22<br>(6.38) |
| $\mathrm{VOLa(fsaen)(NO_3)(H_2O)_4}$ | 30.89<br>(31.23) | 2.92<br>(2.91) | 6.28<br>(6.07) |
| $\mathrm{VOPr(fsaen)(NO_3)(H_2O)_4}$ | 30.74<br>(31.14) | 2.81<br>(2.90) | 6.01<br>(6.05) |
| $\mathrm{VOEu(fsaen)(NO_3)(H_2O)_4}$ | 30.98<br>(30.65) | 2.97<br>(2.86) | 5.98<br>(5.96) |
| $\mathrm{VOGd(fsaen)(NO_3)(H_2O)_5}$ | 29.75<br>(29.67) | 3.01<br>(3.04) | 5.67<br>(5.77) |
| $\mathrm{VOTb(fsaen)(NO_3)(H_2O)_5}$ | 29.68<br>(29.61) | 3.29<br>(3.04) | 5.55<br>(5.75) |

**Measurements.** Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University. Infrared spectra were measured with a JASCO IR-G Spectrometer on KBr disks. Absorption spectra were obtained with Hitachi 320 Spectrophotometer. The CD and fluorescence spectra were measured with a JASCO J-20 Automatic Recording Spectropolarimeter and a Shimadzu RF-540 Fluorospectrophotometer, respectively.

## Results and Discussion

Infrared spectra of ligand, $\mathrm{H_4fsaen}$, and mononuclear copper(II) complex, $[\mathrm{Cu(H_2fsaen)}]\cdot 1/2\mathrm{H_2O}$,[13] show the strong band due to the $\nu$ (C=O) of the uncoordinating carboxyl group at 1700 and 1705 $\mathrm{cm^{-1}}$, respectively, in addition to the broad bands characteristic of the $\nu$ (OH) of the chelated carboxyl group in the range of 2800 to 2000 $\mathrm{cm^{-1}}$. These bands, however, disappeared in the spectrum of $[\mathrm{VO(H_2fsaen)}]\cdot 2\mathrm{H_2O}$, suggesting that in $[\mathrm{VO(H_2fsaen)}]\cdot 2\mathrm{H_2O}$ the $\mathrm{V^{IV}O}$ ion is located at the $\mathrm{O_4}$-site as illustrated in Fig. 2(a). It appears that hard $\mathrm{V^{IV}O}$ ion prefers the $\mathrm{O_4}$-site to the $\mathrm{N_2O_2}$-site in view of HSAB sense, though the binding of $\mathrm{V^{IV}O}$ ion to the $\mathrm{N_2O_2}$-site of *N*,*N*′-disalicylideneethylenediamine and related Schiff bases has been demonstrated.[14,15]

In the $\mathrm{V^{IV}O}$-Ln(III) complexes the $\nu$ (C=N) vibration was observed at 1620 $\mathrm{cm^{-1}}$, whereas the $\nu$ (C=N) vibration was observed at 1640 $\mathrm{cm^{-1}}$ in $[\mathrm{VO(H_2fsaen)}]\cdot 2\mathrm{H_2O}$, indicating the coordination of the azomethine nitrogens to a metal ion, V(IV) or Ln(III). Despite the lack of direct evidence we presume that the $\mathrm{V^{IV}O}$ ion shifts to the $\mathrm{N_2O_2}$-site and Ln(III) is bound to the $\mathrm{O_4}$-site, because Ln(III) ion that is more hard than $\mathrm{V^{IV}O}$ ion strongly prefers oxygen donor atoms. Indeed, the mononuclear Eu(III) complex $[\mathrm{Eu(H_2fsaen)(NO_3)(H_2O)}_n]\cdot(5-n)\mathrm{H_2O}$ does not show any band around 1700 $\mathrm{cm^{-1}}$ and in the 2800—2000 $\mathrm{cm^{-1}}$ region. Instead a strong band assigned to the coordinated carboxylate group was observed at 1540 $\mathrm{cm^{-1}}$, suggesting that in $[\mathrm{Eu(H_2fsaen)(NO_3)(H_2O)}_n]\cdot(5-n)\mathrm{H_2O}$ the Eu(III) ion is bound to the $\mathrm{O_4}$-site as expected.

The absorption spectra of the $\mathrm{V^{IV}O}$-La(III), $\mathrm{V^{IV}O}$-Eu(III), and $\mathrm{V^{IV}O}$-Gd(III) complexes were measured in DMF and DMSO, in order to examine the solvent effect. The spectra are shown in Fig. 3 and the numerical data are summarized in Table 2, together with the tentative band assignments.[14,15] For each complex, the third d-d band near 19000 $\mathrm{cm^{-1}}$ attributable to the $\mathrm{d_{xy}(b_2)}\rightarrow\mathrm{d_{z^2}(a_1^*)}$ transition shifts apparently to the lower energy on changing the solvent from DMF to DMSO. This seems strange, since DMSO molecule is a stronger donor than

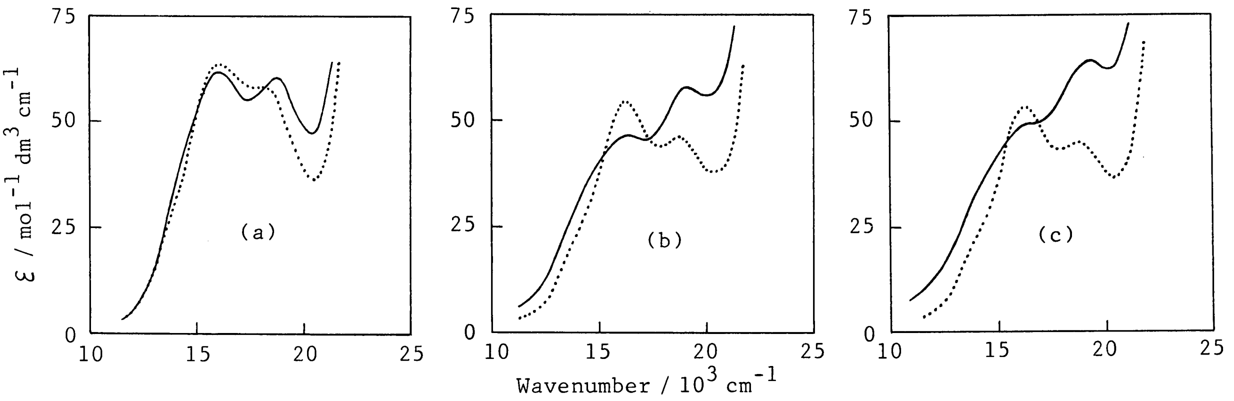

Fig. 3. Absorption spectra of dinuclear V$^{IV}$O-La(III) (a), V$^{IV}$O-Eu(III) (b), and V$^{IV}$O-Gd(III) (c) complexes in DMF (——) and DMSO (·····). Concentration of complex is 5×10$^{-3}$ mol dm$^{-3}$.

Table 2. The d–d Band Absorption Maxima of Dinuclear V$^{IV}$O–Ln(III) Complexes in DMF or DMSO

| Complex | $\nu_{max}/10^3$ cm$^{-1}$ in DMF | | | $\nu_{max}/10^3$ cm$^{-1}$ in DMSO | | |
|---|---|---|---|---|---|---|
| | $d_{xy}\rightarrow d_{yz},d_{zx}$ | $d_{xy}\rightarrow d_{x^2-y^2}$ | $d_{xy}\rightarrow d_{z^2}$ | $d_{xy}\rightarrow d_{yz},d_{zx}$ | $d_{xy}\rightarrow d_{x^2-y^2}$ | $d_{xy}\rightarrow d_{z^2}$ |
| VOLa(fsaen)($NO_3$)($H_2O$)$_4$ | ca. 14.1 | 16.00 | 18.66 | ca. 14.1 | 16.08 | ca. 18.3 |
| | (sh, 37) | (62) | (61) | (sh, 33) | (64) | (sh, 58) |
| VOEu(fsaen)($NO_3$)($H_2O$)$_4$ | ca. 14.1 | 16.26 | 19.19 | ca. 14.1 | 16.26 | 18.76 |
| | (sh, 32) | (46) | (58) | (sh, 25) | (55) | (47) |
| VOGd(fsaen)($NO_3$)($H_2O$)$_5$ | ca. 14.1 | ca. 16.4 | 19.31 | ca. 14.1 | 16.31 | 18.76 |
| | (sh, 34) | (sh, 49) | (64) | (sh, 24) | (53) | (45) |

Values in parentheses are molar extinction coefficients and sh stands for shoulder.

DMF so that the $d_{xy}{\rightarrow}d_{z}2$ transition should shift to higher energy in DMSO. The spectral change observed may be explained in terms of selective solvation as follows. If solvent molecules preferentially coordinate to the rare earth ion to afford a high coordination number around the rare earth ion, then the bound molecules may sterically hinder the approach of a solvent molecule to the sixth position of the adjacent V$^{IV}$O ion. Such a steric shielding must be more effective in DMSO than in DMF, because DMSO molecule is believed to have a higher affinity to a rare earth ion compared with DMF molecule. As a result, the energy level of $d_{z}2$ orbital is lowered in DMSO compared with in DMF, giving rise to the red-shift of the third d–d band in DMSO. Such a unique "selective solvation" was also observed for the Cu(II)-Ln(III) complexes of $H_4$ fsaen.[6]

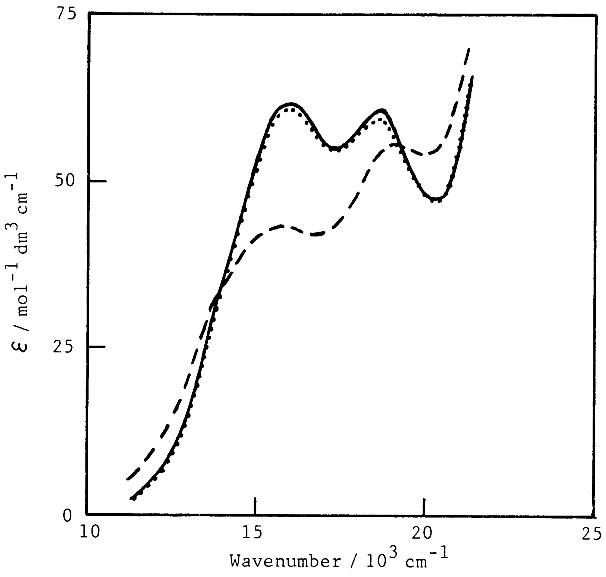

Fig. 4. Absorption spectra of dinuclear V$^{IV}$O-La(III) complex in DMF. Concentration of complex is 5×10$^{-3}$ mol dm$^{-3}$. (——): without additive; (·····): with 1,2-ethanediol (5×10$^{-2}$ mol dm$^{-3}$); (– – –): with 2-aminoethanol (5×10$^{-2}$ mol dm$^{-3}$).

The absorption spectra of the V$^{IV}$O-La(III) complex in DMF were measured by adding 1,2-ethanediol or 2-aminoethanol as a substrate, in order to examine if "specific binding of substrates" observed previously for the Co(II)-Ln(III)[7] and Cu(II)-Ln(III)[8,9] complexes is also the case for the present V$^{IV}$O-Ln(III) complexes or not (see Fig. 4). The spectral data are given in Table 3. When 2-aminoethanol was added as a substrate, the third d-d band was affected most remarkably and shifted to the higher energy, whereas all of the d-d bands were little affected by adding 1,2-ethanediol. This suggests the coordination of the amino nitrogen to V$^{IV}$O center. However, it is unclear if the alcoholic oxygen of 2-aminoethanol is associated with the coordination to the La(III) center. The CD spectral investigations using chiral amino alcohols, alcohols or diol as the substrate have been made to see the ligating interaction of alcoholic

Table 3. The d–d Band Absorption Maxima of Dinuclear $V^{IV}O$-La(III) Complex in DMF Solution of 1,2-Ethanediol or 2-Aminoethanol

| | $\nu_{max}/10^3\ cm^{-1}$ | | |
|---|---|---|---|
| | $d_{xy} \rightarrow d_{yz}, d_{zx}$ | $d_{xy} \rightarrow d_{x^2-y^2}$ | $d_{xy} \rightarrow d_{z^2}$ |
| Without additive | ca. 14.1 | 16.00 | 18.66 |
| | (sh, 37) | (62) | (61) |
| With 1,2-ethanediol | ca. 14.1 | 16.00 | 18.66 |
| | (sh, 35) | (61) | (59) |
| With 2-aminoethanol | ca. 14.1 | 15.87 | 19.05 |
| | (sh, 36) | (43) | (56) |

Concentration of complex is $5\times10^{-3}$ mol dm$^{-3}$. Concentration of additives is $5\times10^{-2}$ mol dm$^{-3}$. Values in parentheses are molar extinction coefficients and sh stands for shoulder.

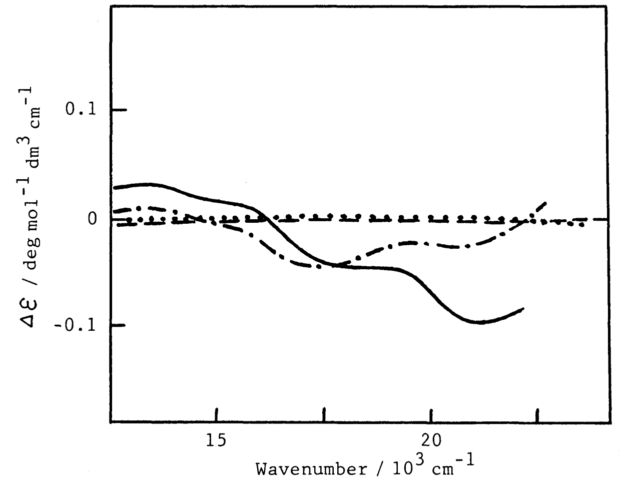

Fig. 5. The CD spectra of dinuclear $V^{IV}O$-La(III) complex in DMF. Concentration of complex is $5\times10^{-3}$ mol dm$^{-3}$. (——): with *R*-(−)-2-amino-1-propanol ($5\times10^{-2}$ mol dm$^{-3}$); (—•—): with *R*-(−)-2-amino-1-butanol ($5\times10^{-2}$ mol dm$^{-3}$); (– – –): with *S*-(+)-2-butanol ($5\times10^{-2}$ mol dm$^{-3}$); (•••••): with *S*-(+)-1,2-propanediol ($5\times10^{-2}$ mol dm$^{-3}$).

oxygen with the La(III) center (Fig. 5). When *R*-(−)-2-amino-1-propanol or *R*-(−)-2-amino-1-butanol was added as the substrate, significant circular dichroism was induced at the d–d band region of $V^{IV}O$. This clearly indicates that the free rotation of the amino alcohols with respect to the $V^{IV}O$–N bond is fixed, because of (i) direct coordination of the hydroxyl group of the amino alcohol to the lanthanum(III) ion or (ii) interaction of the hydroxyl group with lanthanum(III) center, through the hydrogen bonding of the hydroxyl group to DMF or $H_2O$ molecules coordinated to the lanthanum(III) ion.[7,8] Such a CD activity was not observed in the d–d band region when *S*-(+)-2-butanol or *S*-(+)-1,2-propanediol was added as the substrate (Fig. 5). These substrates may be captured on the La(III) center as a unidentate or a bidentate ligand.

The fluorescence spectra of the mononuclear Eu(III) and dinuclear $V^{IV}O$–Eu(III) complexes in DMF are shown in Fig. 6, where the exciting wavelength is 394 nm. The mononuclear Eu(III) complex shows the fluorescent bands attributable to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions at 580, 593, 615, 653, and 700 nm, respectively. The intensities of these bands are significantly decreased in the dinuclear $V^{IV}O$–Eu(III) complex. The fluorescence decrease may be due to the energy loss from the excited Eu(III) to the $V^{IV}O$ center through the phenolic oxygen bridges, as proposed previously.[10,11] However, we cannot rule out the possibility that the fluoreacence decrease results from the absorption of exciting light by the $V^{IV}O$–Eu(III) complex itself because the dinuclear $V^{IV}O$–Eu(III) complex shows a significant absorption at 394 nm (see Fig. 7). In order to gain an insight into the diminished fluorescence in the $V^{IV}O$–Eu(III) complex, the fluorescence spectra were

Fig. 6. Fluorescence spectra of mononuclear Eu(III) (a) and dinuclear $V^{IV}O$–Eu(III) (b) complexes in DMF. Concentration of complex is $5\times10^{-3}$ mol dm$^{-3}$. Exciting wavelength is 394 nm. Slit widths(nm) of (excitation and emission sides) are (5 and 2) for (a) and (20 and 10) for (b). Ordinate scales are ×64 for (a) and ×128 for (b).

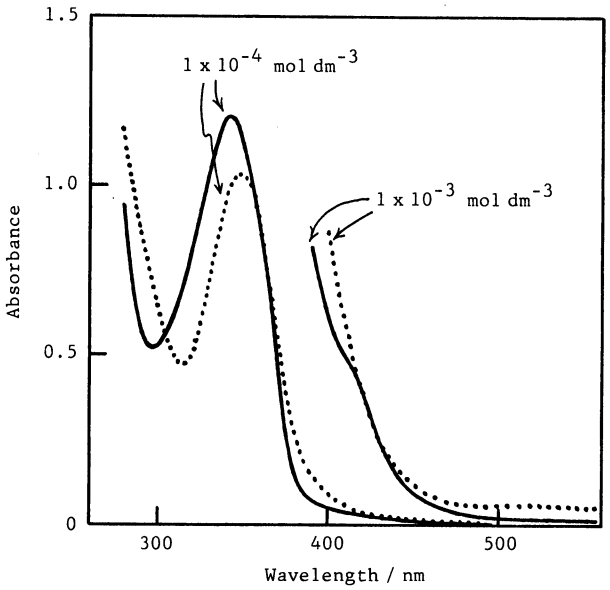

Fig. 7. Absorption spectra of mononuclear Eu(III) (——) and dinuclear $V^{IV}O$–Eu(III) (·····) complexes in DMF.

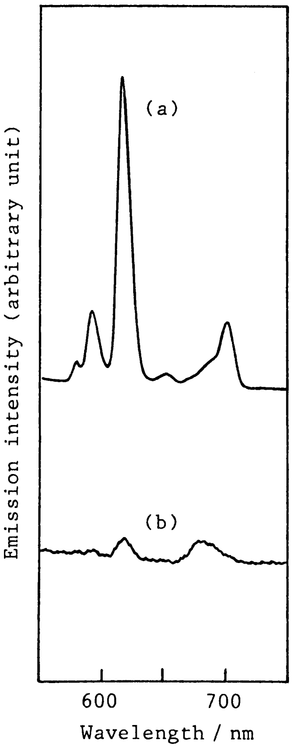

Fig. 8. Fluorescence spectra of mononuclear Eu(III) (a) and dinuclear $V^{IV}O$–Eu(III) (b) complexes in DMF. Concentration of complex is $5\times10^{-3}$ mol dm$^{-3}$. Exciting wavelength is 342 nm. Slit widths (nm) of (excitation and emission sides) are (10 and 5). Ordinate scales are ×512 for (a) and ×1024 for (b).

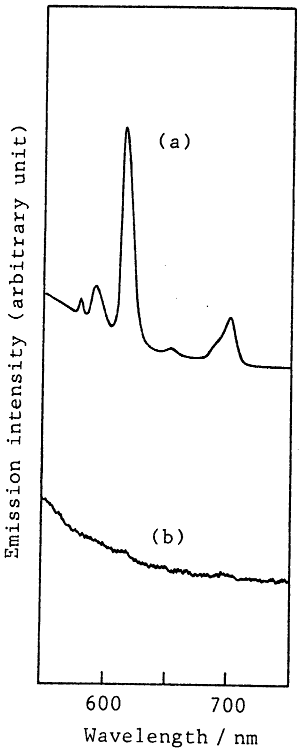

Fig. 9. Fluorescence spectra of mononuclear Eu(III) (a) and dinuclear $V^{IV}O$–Eu(III) (b) complexes in DMF. Concentration of complex is $5\times10^{-3}$ mol dm$^{-3}$. Exciting wavelength is 464 nm. Slit widths (nm) of (excitation and emission sides) are (5 and 2). Ordinate scales are ×128 for (a) and ×1024 for (b).

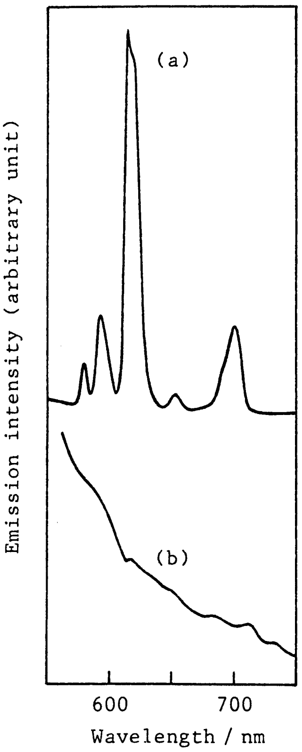

Fig. 10. Fluorescence spectra of mononuclear Eu(III) (a) and dinuclear $V^{IV}O$–Eu(III) (b) complexes in solid state. Exciting wavelength is 394 nm. Slit widths (nm) of (excitation and emission sides) are (2 and 2) for (a) and (10 and 5) for (b). Ordinate scale is ×64.

measured by excitations at 342 and 464 nm. We have chosen these two wavelengths for excitation because the absorption of the mononuclear Eu(III) complex is more intense at 342 nm than the dinuclear $V^{IV}O$–Eu(III) complex and the absorption at 464 nm, at which Eu(III) ion exhibits the absorption attributed to the $^7F_0 \rightarrow {}^5D_2$ transition, is weak for both the mononuclear Eu(III) and dinuclear $V^{IV}O$–Eu(III) complexes (Fig. 7). As seen in Figs. 8 and 9, the drastic decrease in intensities is also observed in the dinuclear complex. Such a fluorescence decrease in the $V^{IV}O$–Eu(III) complex is observed also in solid state (Fig. 10). Thus, it may be concluded that the fluorescence of Eu(III) is effectively quenched by the energy loss from the excited Eu(III) to the $V^{IV}O$ center (intramolecular energy transfer), though the fluorescence quenching by the intermolecular energy transfer should not be neglected.

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