

Effects of Zinc(II) on the Luminescence of Europium(III) in Complexes Containing β -Diketone and Schiff Bases

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Dedicated to Professor Jean-Claude Bünzli on the occasion of his 65th birthday

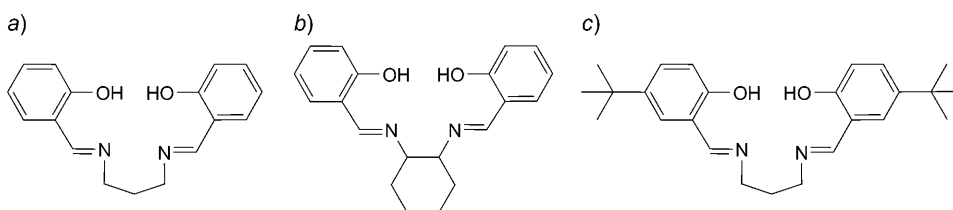
The UV, excitation, and luminescence spectra of tris(pivaloyltrifluoroacetato)europium(III) ($[\text{Eu}(\text{pta})_3]$; Hpta = 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione = HA) were measured in the presence of bis(salicylidene)trimethylenediamine (H_2saltn), bis[5-(*tert*-butyl)salicylidene]trimethylenediamine ($\text{H}_2(\text{Bu})\text{saltn}$), or bis(salicylidene)cyclohexane-1,2-diylidiamine (H_2salchn), and the corresponding Zn^{II} complexes $[\text{ZnB}]$ ($\text{B} = \text{Schiff}$ base). The excitation and luminescence spectra of the solution containing $[\text{Eu}(\text{pta})_3]$ and $[\text{Zn}(\text{salchn})]$ exhibited much stronger intensities than those of solutions containing the other $[\text{ZnB}]$ complexes. The introduction of a *t*Bu group into the Schiff base was not effective in sensitizing the luminescence of $[\text{Eu}(\text{pta})_3]$. The luminescence spectrum of $[\text{ZnB}]$ showed a band around 450 nm. The intensity decreased in the presence of $[\text{Eu}(\text{pta})_3]$, reflecting complexation between $[\text{Eu}(\text{pta})_3]$ and $[\text{ZnB}]$. On the basis of the change in intensity against the concentration of $[\text{ZnB}]$, stability constants were determined for $[\text{Eu}(\text{pta})_3\text{Zn}(\text{saltn})]$, $[\text{Eu}(\text{pta})_3\text{Zn}(\text{Bu})\text{saltn}]$, and $[\text{Eu}(\text{pta})_3\text{Zn}(\text{salchn})]$ as 4.13, 4.9 and 5.56, respectively ($\log \bar{\beta}$, where $\bar{\beta} = \frac{[\text{Eu}(\text{pta})_3\text{ZnB}]}{([\text{Eu}(\text{pta})_3][\text{ZnB}]^{-1})}$). The quantum yields of these binuclear complexes were determined as 0.15, 0.11, and 0.035, although $[\text{Eu}(\text{pta})_3\text{Zn}(\text{salchn})]$ revealed the strongest luminescence at 613 nm. The results of X-ray diffraction analysis for $[\text{Eu}(\text{pta})_3\text{Zn}(\text{saltn})]$ showed that Zn^{II} had a coordination number of five and was bridged with Eu^{III} by three donor O-atoms, *i.e.*, two from the salicylidene moieties and one from the ketonato group pta.

Introduction. – It is well-known that most ternary complexes consisting of Eu^{III} , a β -diketone (HA), and a strong Lewis base (B), $[\text{EuA}_3\text{B}]$, show intense luminescence [1–6]. For such complexes of lanthanides(III) (Ln^{III}), if a metal ion is introduced into the Lewis base and it is still operating as a Lewis base, the binuclear molecule formed between $[\text{LnA}_3]$ and the metal-containing Lewis base is expected to have new functions induced by the interaction between Ln^{III} and the metal ion as well as the properties of the respective metal ions. For this purpose, the Lewis base should be multidentate; and from this point of view, the use of Schiff bases is preferred. An example of this is a complex produced by Ramade *et al.* [7] consisting of tris(β -diketonato)gadolinium(III) and $[\text{Cu}(\text{salen})]$, where salen is the bis(salicylidene)ethylenediamine dianion (= {2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]bis[phenolato]}(2-)). Their interest was to improve the magnetic properties of Ln^{III} . There are many reports of complexes containing Ln^{III} and Schiff bases [8–17]; however, these are not always concerned with luminescence in binuclear complexes or complexes involving β -diketones. Apart from Ln^{III} complexes containing Schiff bases and β -diketones, there have also been several

reports that the luminescence of Ln^{III} is enhanced by the formation of heterodinuclear complexes – e.g., Ln^{III} and Y^{III} – which is referred to as co-luminescence [18–20].

In the course of our study on the effects of metal(II) incorporated into *Schiff* bases [21][22] on the luminescence of tris(β -diketonato)europium(III) complexes, we found that the presence of most metal(II) results in quenching of the luminescence of Eu^{III} , e.g., in the presence of Cu^{II} [8][10][21] or Pd^{II} [21]. Only Zn^{II} was effective in enhancing luminescence [16][17][21]. Although the reason for this was not clear, there have been several reports of Zn^{II} -based sensitive luminescence sensors [23][24]. Thus, the present study was focused on investigating how and why the luminescence of Eu^{III} is enhanced by the presence of Zn^{II} .

Experimental. – *Reagents.* All reagents were of anal. grade. CHCl_3 purchased from *Kanto Chemical Co.* was washed three times with deionized H_2O just prior to use. All other reagents were used without purification. Tris(2,2'-bipyridine)dichlororuthenium(II) hexahydrate (99.95%) and quinine sulfate dihydrate (98.0%) were purchased from *Aldrich*, USA, and *Wako Pure Chemical Industries*, Japan, respectively. Bis(salicylidene)trimethylenediamine (=2,2'-[propane-1,3-diylbis(nitrilomethylidyne)]bis[phenol]; H_2saltn), bis[5-(*tert*-butyl)salicylidene]trimethylenediamine (=2,2'-[propane-1,3-diylbis(nitrilomethylidyne)]bis[4-(1,1-dimethylethyl)phenol]; $\text{H}_2(\text{tBu})\text{saltn}$), or bis(salicylidene)cyclohexane-1,2-diylidiamine (=2,2'-[cyclohexane-1,2-diylbis(nitrilomethylidyne)]bis[phenol]; H_2salchn) (*Fig. 1*), and the corresponding Zn^{II} complexes [ZnB] were used as *Schiff* bases. Tris(pivaloyltrifluoroacetato)europium(III) ($[\text{EuA}_3] = [\text{Eu}(\text{pta})_3]$); $\text{Hpta} = \text{Me}_3\text{CC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CF}_3 = \text{HA} = 1,1,1\text{-trifluoro-5,5-dimethylhexane-2,4-dione}$), the binuclear complexes consisting of $[\text{EuA}_3]$ and *Schiff* bases containing Zn^{II} , the *Schiff*-base complexes with Zn^{II} ($[\text{ZnB}]$), and several *Schiff* bases themselves were prepared by *Shimada Chemical Research*, Tokyo.



*Fig. 1. Chemical structure of the Schiff bases: a) bis(salicylidene)trimethylenediamine (H_2saltn), b) bis(salicylidene)cyclohexane-1,2-diylidiamine (H_2salchn) and c) bis[5-(*tert*-butyl)salicylidene]trimethylenediamine ($\text{H}_2(\text{tBu})\text{saltn}$)*

Excitation and Luminescence Spectra and Quantum Yields. A soln. of $[\text{Eu}(\text{pta})_3]$ in CHCl_3 was mixed with [ZnB] solutions in different molar ratios. Excitation and luminescence spectra were recorded with a *Hitachi-F4500* spectrofluorometer equipped with a *Hamamatsu* photomultiplier tube. UV Spectra: *Hitachi-U3500* spectrophotometer.

Before determining the quantum yield, the refractive indexes were measured with an *Abbe* refractometer (*Atago*, model *NAR-IT*). The quantum efficiencies of luminescence from [ZnB] and from the complexes formed from $[\text{EuA}_3]$ and [ZnB] were calculated with the formula $\Phi_{\text{Eu}} = \left[\int I_{\text{Eu}}(\lambda) d\lambda A_S n_{\text{Eu}}^2 / \int I_S(\lambda) d\lambda A_S n_S^2 \right] \Phi_S$, where the subscripts Eu and S refer to the Eu^{III} complex and the standard (mostly $[\text{Ru}(\text{bpy})_3]^{2+}$; to determine the quantum yield of [ZnB], quinine sulfate was sometimes used); Φ is the quantum yield, $\int I(\lambda) d\lambda$ is the area under the luminescence curve (expressed in numbers of photons) from 390 to 725 nm; A is the absorbance at 370 nm; n is the refractive index. The refractive indexes in CHCl_3 (n_{Eu}), H_2O (solvent for $[\text{Ru}(\text{bpy})_3]^{2+}$; n_S) and 0.5M sulfuric acid (n_S) were 1.444, 1.333, and 1.338, resp. $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and quinine sulfate were chosen because they show bands

similar to Eu^{III} (at around 600 nm) and Zn^{II} (around 460 nm), resp., although the bands are broad. For the luminescence references, the quantum yield value $\Phi_s = 0.042 \pm 0.002$ ($[\text{Ru}(\text{bpy})_3]^{2+}$) [25] and 0.55 ± 0.04 (quinine sulfate) [26] in aq. soln. at 25° were used. The standard aq. solns. were prepared by dissolving $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in H_2O and quinine sulfate in 0.5M sulfuric acid ($1 \cdot 10^{-5}$ M) in every experiment to determine the quantum yield.

X-Ray Diffraction Analysis. A single crystal used for X-ray diffraction analysis was prepared by recrystallization of the synthesized complex $[\text{EuA}_3\text{Zn}(\text{saltn})]$ from CHCl_3 at r.t. The experiments for analysis were performed as follows: Crystal data: crystal dimensions, $0.45 \times 0.22 \times 0.17$ mm; $\text{C}_{41}\text{H}_{46}\text{EuF}_9\text{N}_2\text{O}_8\text{Zn}$, M_r 1083.13; triclinic, space group $P-1(\#2)$; $a = 10.0253(19)$ Å, $b = 12.637(3)$ Å, $c = 19.624(4)$ Å, $\alpha = 97.958(4)^\circ$, $\beta = 91.879(4)^\circ$, $\gamma = 112.286(3)^\circ$, $V = 2268.3(8)$ Å³, $Z = 2$; $F(000) = 1088$, $D_{\text{calc}} = 1.586$ g cm⁻³; $\mu(\text{MoK}_\alpha) = 0.1986$ cm⁻¹, T 273 K, λ 0.71073 Å; $R_1 = 0.0563$ for $I > 2.0 \sigma(I)$, $\omega R_2 = 0.1447$ for all data (9807 reflections), g.o.f. = 0.806 (568 parameters); maximum and minimum peaks for the highest and lowest electron density in the final differential map, 1.115 and -1.099 e⁻/Å³, resp. The single crystal was mounted on a glass fiber, and diffraction data were measured with a *Bruker-APEX-CCD*-detector X-ray diffractometer with monochromated MoK_α radiation from a rotating-anode-source apparatus. Data reduction, structure solution, and refinement, and all the necessary computational data processes were performed with the APEX, SAINT, and SHELXTL programs. CCDC-738726 contains the supplementary crystallographic data for $[\text{EuA}_3\text{Zn}(\text{saltn})]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion. – *Excitation and Luminescence Spectra of $[\text{EuA}_3]$ in the Presence of Schiff Bases and the Corresponding Complexes with Zn^{II} .* To check the effect of Zn^{II} on the spectra of $[\text{EuA}_3]$, the excitation and luminescence spectra of $[\text{EuA}_3]$ and H_2saltn , $\text{H}_2(\text{Bu})\text{saltn}$, or H_2salchn in CHCl_3 solution were measured and compared with those of the corresponding *Schiff* bases complexed with Zn^{II} ($[\text{ZnB}]$). The free ligands H_2saltn and $\text{H}_2(\text{Bu})\text{saltn}$ were chosen to investigate the effects of lateral groups in *Schiff* bases on the spectra of $[\text{EuA}_3]$, while H_2saltn and H_2salchn were used to investigate the effect of the linking group connecting the two *Schiff*-base moieties. The excitation spectra were monitored at a luminescence wavelength of 612 nm, which was chosen because Eu^{III} shows a strong and narrow luminescence at 612 nm in most complexes. *Fig. 2, a* shows the excitation spectra of CHCl_3 solutions containing $[\text{EuA}_3]$ and the *Schiff* bases at a molar ratio of 1:1.7 as well as that of $[\text{EuA}_3]$ itself. The spectrum of $[\text{EuA}_3]$ shows a strong band at around 320 nm, while in the presence of the *Schiff* bases, the intensity is diminished, and a broad and weak band appears at 370–400 nm depending on the *Schiff* base used, although the difference is not clear. Based on the expanded spectra (*Fig. 2, a*, inset), the order of intensity appears to be $\text{H}_2(\text{Bu})\text{saltn} > \text{H}_2\text{saltn} > \text{H}_2\text{salchn}$. However, as shown in *Fig. 2, b*, the order of intensity in the presence of the *Schiff*-base complexes containing Zn^{II} is exactly the opposite: $[\text{Zn}(\text{Bu})\text{saltn}] < [\text{Zn}(\text{saltn})] < [\text{Zn}(\text{salchn})]$. In addition, in the presence of Zn^{II} , the bands shift to shorter wavelength, i.e., to ca. 350 nm, and the intensities of the bands are much stronger than those of the corresponding *Schiff* bases, although the band wavelength around 320 nm (originating from pta) does not change. As pointed out in a previous paper [2], the small enhancement of intensity of the complex between $[\text{EuA}_3]$ and *Schiff* bases is due to the formation of intramolecular H-bonding. When the *Schiff* base is complexed with Zn^{II} , the H-bonding is loosened, allowing for an easier electron transfer. The different place of H_2salchn and $[\text{Zn}(\text{salchn})]$ in the orders of intensity may be due to the fact that H_2salchn has the strongest intramolecular H-bonding among these *Schiff* bases. The enhancement of the excitation intensity at

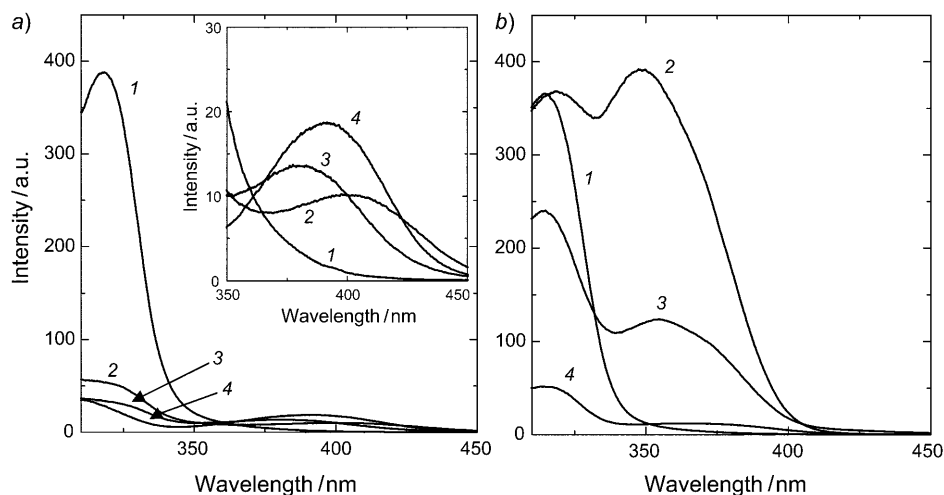


Fig. 2. Excitation spectra of CHCl_3 solutions containing a) $[\text{EuA}_3]$ and Schiff bases (1, $[\text{EuA}_3]$; 2, $\text{H}_2\text{salchn}/[\text{EuA}_3]$; 3, $\text{H}_2\text{saltn}/[\text{EuA}_3]$; 4, $\text{H}_2(\text{tBu})\text{saltn}/[\text{EuA}_3]$; $[[\text{H}_2\text{B}]/[[\text{EuA}_3]] = 1.7$, $[[\text{EuA}_3]] = 1.1 \cdot 10^{-4}$ M, inset drawn on an expanded scale) and b) $[\text{EuA}_3]$ and Schiff bases incorporating Zn^{II} at a molar ratio of 1:1, monitored at a luminescence wavelength of 612 nm (1, $[\text{EuA}_3]$; 2, $[\text{Zn}(\text{salchn})]/[\text{EuA}_3]$; 3, $[\text{Zn}(\text{saltn})]/[\text{EuA}_3]$; 4, $[\text{Zn}(\text{tBu})\text{saltn}]/[\text{EuA}_3]$; $[[\text{EuA}_3]]/[[\text{ZnB}]] = 1.0$, $[[\text{EuA}_3]] = 7.5 \cdot 10^{-5}$ M).

around 350 nm is thought to be caused by complexation between $[\text{EuA}_3]$ and $[\text{ZnB}]$. The presence of a tBu functional group in the salicylidene moieties results in a reduction in intensity over all wavelengths. Most of the energy absorbed at 612 nm by the Schiff base with the tBu substituents will not effectively be spent on excitation of Eu^{III} .

Fig. 3 shows the luminescence spectra monitored at an excitation wavelength of 370 nm. A strong band appears at 612 nm regardless of the absence or presence of Zn^{II} (Figs. 3, a and b), although the degree of enhancement of intensity is much greater in the presence of Zn^{II} . The luminescence spectra in the presence of Zn^{II} also showed a band at 430–460 nm, depending on the Schiff base used. The intensity at 612 nm is strongest for $[\text{Zn}(\text{salchn})]$; however, the intensity at around 450 nm is the weakest. This observation supports the assertion that $[\text{EuA}_3]$ and Schiff bases incorporating Zn^{II} form complexes with different stability, depending on the Schiff base used.

To treat the data quantitatively, it was necessary to acquire the luminescence spectra of $[\text{ZnB}]$ in the absence of $[\text{EuA}_3]$. Fig. 4, a shows the luminescence spectrum of $[\text{Zn}(\text{saltn})]$ at $\lambda_{\text{ex}} 370$ nm, while Fig. 4, b shows that obtained in the presence of $[\text{EuA}_3]$. A comparison between the two figures shows that although both wavelengths of the band are at around 450 nm, the intensity of the band is much stronger in the absence of $[\text{EuA}_3]$. This observation may be utilized to determine the stability constants of complexes of $[\text{EuA}_3]$ and Schiff bases containing Zn^{II} .

Stability Constants of Complexes between $[\text{EuA}_3]$ and $[\text{ZnB}]$. When the intensities of the bands at 450 nm (Figs. 4, a and b) are plotted as a function of the $[\text{Zn}(\text{saltn})]$ concentration in the presence and absence of $[\text{EuA}_3]$, both plots show straight lines,

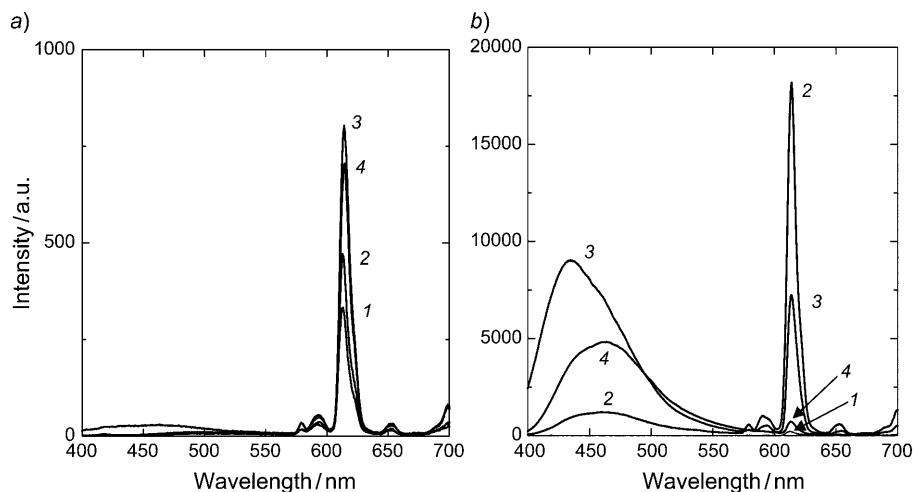


Fig. 3. Luminescence spectra of a) $[EuA_3]$ and Schiff bases and b) $[EuA_3]$ and Schiff bases incorporating Zn^{II} in $CHCl_3$ solution, monitored at an excitation wavelength of 370 nm. For experimental conditions and the numbering system, see Fig. 2.

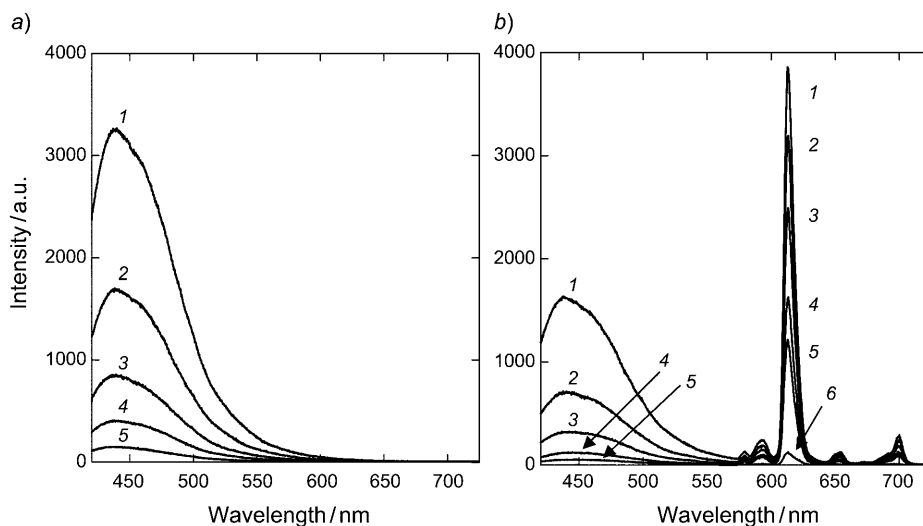


Fig. 4. Luminescence spectra of a) $[Zn(saltn)]$ and of b) $1.3 \cdot 10^{-4} M [EuA_3]$ in the presence of $[Zn(saltn)]$. $[Zn(saltn)]$: 1, $1.3 \cdot 10^{-4} M$; 2, $6.5 \cdot 10^{-5} M$; 3, $3.7 \cdot 10^{-5} M$; 4, $1.9 \cdot 10^{-5} M$; 5, $9.3 \cdot 10^{-6} M$; 6, 0.0M.

although the slope of the graph for the complex without $[EuA_3]$ is greater than that of the complex containing $[EuA_3]$. Assuming that the intensities at the specified wavelengths originate from $[ZnB]$, the intensity obtained from the $[ZnB]$ solution

(i.e., without $[\text{EuA}_3]$) is I_0 , while that of a mixed solution is I_s . Thus, Eqn. 1 and 2 can be formulated, where the subscript T refers to the total concentration and no subscript refers to the concentration at equilibrium, and ε_{ZnB} represents the intensity per 1M $[\text{ZnB}]$ in CHCl_3 . Introducing Eqns. 1 and 2 into Eqn. 3 furnishes Eqn. 4. The mass balance of Eu^{III} can be also represented by Eqn. 5. Introducing Eqn. 4 into Eqn. 5 gives Eqn. 6. Accordingly, the stability constant $\bar{\beta}$, which is defined by Eqn. 7, can be obtained with Eqns. 2, 4, and 6 from each intensity point measured. To determine the stability constants as systematically as possible, the value of ε_{ZnB} was also treated as an unknown number, that is as defined in Eqn. 8.

$$I_0 = \varepsilon_{\text{ZnB}}[[\text{ZnB}]]_{\text{T}} \quad (1)$$

$$I_s = \varepsilon_{\text{ZnB}}[[\text{ZnB}]] \quad (2)$$

$$[[\text{ZnB}]]_{\text{T}} = [[\text{ZnB}]] + [[\text{EuA}_3\text{ZnB}]]. \quad (3)$$

$$[[\text{EuA}_3\text{ZnB}]] = (I_0 - I_s)/\varepsilon_{\text{ZnB}}. \quad (4)$$

$$[[\text{EuA}_3]]_{\text{T}} = [[\text{EuA}_3]] + [[\text{EuA}_3\text{ZnB}]] \quad (5)$$

$$[[\text{EuA}_3]] = [[\text{EuA}_3]]_{\text{T}} - (I_0 - I_s)/\varepsilon_{\text{ZnB}} \quad (6)$$

$$\bar{\beta} = [[\text{EuA}_3\text{ZnB}]] [[\text{EuA}_3]]^{-1} [[\text{ZnB}]]^{-1} \quad (7)$$

$$\frac{I_0 - I_s}{I_s} \cdot \frac{1}{[[\text{EuA}_3]]_{\text{T}}} = \bar{\beta} - \frac{\bar{\beta}}{\varepsilon_{\text{ZnB}}} \frac{(I_0 - I_s)}{[[\text{EuA}_3]]_{\text{T}}} \quad (8)$$

An $1.0 \cdot 10^{-4}$ M $[\text{EuA}_3]$ solution and $[\text{Zn}(\text{saltn})]$ solution of various concentrations were mixed and the luminescence spectra measured, together with that of $[\text{ZnB}]$. From these data, $(I_0 - I_s)[[\text{EuA}_3]]_{\text{T}}^{-1} I_s^{-1}$ was plotted as a function of $(I_0 - I_s)/[[\text{EuA}_3]]_{\text{T}}$: the plot showed a straight line with an intercept at $1.5 \cdot 10^4$ and a slope of $-5 \cdot 10^{-4}$. The stability constant $\bar{\beta}$ was calculated as $10^{4.16}$, and ε_{ZnB} as $2.9 \cdot 10^7$. Since the molar intensity ε_{ZnB} , obtained directly from the relation between the $[\text{ZnB}]$ concentration and the intensity was $2.7 \cdot 10^7$, the method proposed for determining the stability constants will be reasonable. Actually the stability constant ($\log \bar{\beta}$) obtained from Eqn. 7 was 4.13 ± 0.05 and agrees well with that obtained from the plots. A method of determining the stability constants of Eu^{III} complexes in aqueous solutions from luminescence data was reported previously, but the data were treated with a quite different approach [22]. The stability constants for other complexes obtained in the present study are listed in Table I.

Since H_2B has no clear excitation or luminescence band over the wavelength range measured, the stability constant of $[\text{EuA}_3(\text{H}_2\text{B})]$ cannot be determined in a similar way. However, the stability constant for $[\text{EuA}_3(\text{H}_2\text{saltn})]$ has been calculated on the basis of solvent extraction data and reported to be 2.95 ± 0.06 ($\log \bar{\beta}$) [2]. If the phenomenon observed in solvent extraction is similar to that for luminescence, it may be concluded that $[\text{Zn}(\text{saltn})]$ forms a more stable complex with $[\text{EuA}_3]$ than H_2saltn . It is suggested that when a solution of $[\text{EuA}_3]$ is mixed with $[\text{Zn}(\text{saltn})]$, a greater

Table 1. Stability Constants of $[EuA_3]$ Complex with Schiff Bases Incorporating Zn^{II} , and Luminescence Intensity Ratios of $[EuA_3ZnB]$ and $[EuA_3]$ Monitored at an Excitation Wavelength of 370 nm

$[EuA_3ZnB]$	$\log \bar{\beta}^a)$	I_{EuA_3ZnB}/I_{EuA_3}
$[EuA_3Zn(saltn)]$	4.13 ± 0.05	34
$[EuA_3Zn('Bu)saltn]$	4.9 ± 0.2	3.4
$[EuA_3Zn(salchn)]$	5.56 ± 0.17	86

$$^a) \bar{\beta} = \frac{[EuA_3ZnB]}{[EuA_3][ZnB]}^{-1}$$

number of complexes will be formed than with H_2saltn ; this may be one of the reasons why the $[Zn(saltn)]$ complex shows stronger luminescence intensity.

From the results described above, it was concluded that the introduction of a 'Bu group into the salicylidene moieties leads to enhancement of luminescence at the wavelength of Zn^{II} ; however, it is not effective as a sensitizer for $[EuA_3]$ luminescence. When two Schiff-base moieties are linked *via* a cyclohexane-1,2-diyl group instead of a propane-1,3-diyl group, however, the luminescence of $[EuA_3]$ is effectively sensitized, and a stable complex is formed. In the next stage of the experiment, the luminescence quantum yields were measured and compared to determine the relationship between ligand–metal ion energy transfer and nonradiative decay.

UV Spectra and Quantum Yields. Fig. 5 shows the UV spectra of $[EuA_3]$ and $[Zn(saltn)]$ (Fig. 5,a), or $[Zn(salchn)]$ (Fig. 5,b), and a solution containing both $[EuA_3]$ and $[ZnB]$. Although the UV spectrum of $[EuA_3]$ shows a band at 290 nm, there is scarcely any absorbance at wavelengths longer than 350 nm. The UV spectrum of the solution containing $[Zn(saltn)]$ and $[EuA_3]$ is very similar to that of $[Zn('Bu)saltn]$ and $[EuA_3]$; however, the spectrum of the $CHCl_3$ solution containing $[Zn(saltn)]$ is slightly different from that of $[Zn(salchn)]$. The band due to $[Zn(saltn)]$

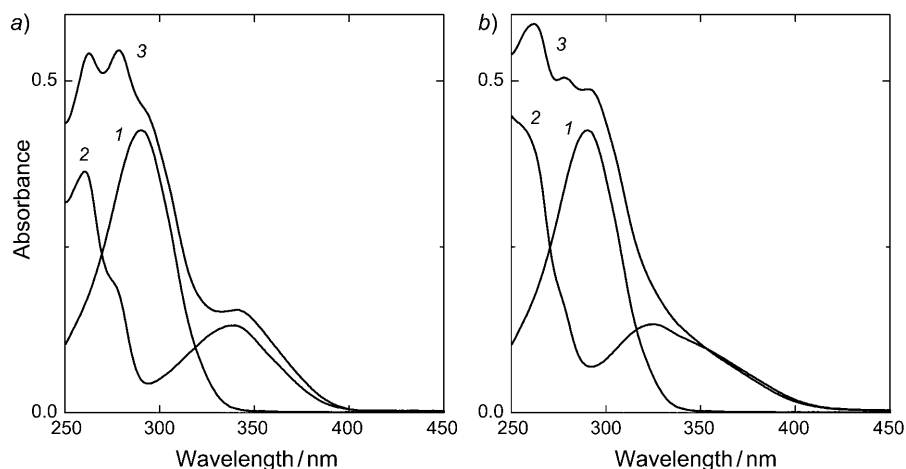


Fig. 5. UV Spectra of $[EuA_3]$ and/or $[ZnB]$: a) $[EuA_3]$ and $[Zn(saltn)]$ and b) $[EuA_3]$ and $[Zn(salchn)]$. Initial concentration $[EuA_3] = [ZnB] = 2 \cdot 10^{-5}$ M. 1, $[EuA_3]$; 2, $[ZnB]$; 3, $[EuA_3]$ and $[ZnB]$.

at 340 nm shifts to a slightly shorter wavelength in the solution containing [Zn(salchn)] (ca. 330 nm), which may imply stronger enhancement of the excitation intensity in the presence of [Zn(salchn)] (see Fig. 2, b).

The quantum yield Φ of the binuclear complex [EuA₃Zn(saltn)] obtained from the synthesized complex was 0.12 (Entry 1, Table 2). The quantum yield was also measured for a mixed solution of [EuA₃] and [Zn(saltn)] and $\Phi = 0.15$ was obtained (Entry 2). These two Φ_s agree with each other within the limits of experimental accuracy, which suggests that the quantum yield can be determined with mixed solutions of [EuA₃]/[ZnB] instead of synthesized complexes [EuA₃ZnB]. Hence, the yields for other [EuA₃ZnB] complexes were determined with mixed solutions of [EuA₃]/[ZnB] in a molar ratio of 1:1. The values obtained are listed in Table 2, along with those of the [ZnB] themselves. As can be seen in Fig. 3, b, and Table 2, the quantum yield of [EuA₃Zn(salchn)] is much smaller than those of [EuA₃Zn(saltn)] or [EuA₃Zn{(‘Bu)-saltn)]; nevertheless, [Zn(salchn)] has the greatest sensitizing effect on the luminescence of [EuA₃]. The large enhancement of [EuA₃] luminescence in the presence of [ZnB] cannot reasonably be interpreted in terms of the quantum yield. It may be related to the area occupied in the complex by the [ZnB] portion, i.e., the smaller quantum yield of [EuA₃Zn(salchn)] may be caused by the smaller contribution of [Zn(salchn)] to the area compared to [Zn(saltn)] or [Zn{(‘Bu)saltn)]. The ratio of the areas of [ZnB] (Fig. 4, a) and [EuA₃ZnB] (Fig. 4, b) in the range 390–550 nm was obtained aiming at the elucidation of the contribution of the Schiff base to sensitize the

Table 2. Quantum Yields Φ of [EuA₃] Complexes with [ZnB] and of [ZnB] Complexes

Determination of Φ for [EuA ₃ ZnB]				
	[[Zn ^{II}]]/M	Absorbance at 370 nm	Area <i>S</i> (390–725 nm)	Quantum yield Φ^a)
[EuA ₃ Zn(saltn)] ^{b)}	$1.0 \cdot 10^{-5}$	0.036	122600	0.12 ± 0.03
[EuA ₃]/[Zn(saltn)] ^{c)}	$2.3 \cdot 10^{-5}$	0.068	264000	0.15 ± 0.02
[EuA ₃]/[Zn{(‘Bu)saltn)] ^{c)}	$2.3 \cdot 10^{-5}$	0.104	312340	0.11 ± 0.01
[EuA ₃]/[Zn(salchn)] ^{c)}	$2.2 \cdot 10^{-5}$	0.064	60665	0.035 ± 0.002
Determination of Φ for [ZnB]				
	[[ZnB]]/M	Absorbance at 370 nm	Area <i>S</i> (390–725 nm)	Quantum yield Φ
[Zn(saltn)]	$2.3 \cdot 10^{-5}$	0.051	283600	$0.20 \pm 0.08^a)$ $0.12^d)$
[Zn{(‘Bu)saltn)]	$2.3 \cdot 10^{-5}$	0.071	473600	$0.25 \pm 0.006^a)$ $0.15^d)$
[Zn(salchn)]	$2.2 \cdot 10^{-5}$	0.068	91863	$0.050 \pm 0.005^a)$ $0.03^d)$

^{a)} Data for the standard [Ru(bpy)₃]Cl₂: $1 \cdot 10^{-5}$ M, $\Phi = 0.042$, $I(\lambda_{\text{ex}} 370 \text{ nm}) = 562.4$ at $\lambda_{\text{em}} 612 \text{ nm}$, Abs = 0.033 at 370 nm, $S(390-725 \text{ nm}) = 4399$. ^{b)} A solution of [EuA₃Zn(saltn)] was prepared by dissolving the synthesized complex in CHCl₃. ^{c)} A mixed solution containing [ZnB] and $2.1 \cdot 10^{-5}$ M [EuA₃] was used. ^{d)} Data for the standard quinine sulfate: $8.5 \cdot 10^{-6}$ M, $\Phi = 0.55$, $I(\lambda_{\text{ex}} 370 \text{ nm}) = 1341$ at 460 nm, Abs = 0.005/cm (actually a 5.00 cm cell was used for the measurement) at 370 nm, $S(390-725 \text{ nm}) = 13446$.

luminescence of $[\text{EuA}_3]$. The ratios for $[\text{Zn}(\text{saltn})]$, $[\text{Zn}\{(\text{tBu})\text{saltn}\}]$, and $[\text{Zn}(\text{salchn})]$ were 0.55, 0.65, and 0.20, respectively, which means that 45%, 35%, and 80% of all photons absorbed by these complexes are spent on sensitizing the luminescence of $[\text{EuA}_3]$.

From these observations, it may be concluded that when a cyclic hydrocarbon linker rather than a saturated hydrocarbon linker connects the two *Schiff* base moieties of ligand B, the energy of the photons is efficiently converted into Eu^{III} luminescence. Other useful information for interpreting the effect of $[\text{ZnB}]$ on the luminescence of Eu^{III} is the intensity ratio of the luminescence bands at 592 and 612 nm, which correspond to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions, respectively. Since the transition to ${}^7\text{F}_1$ is almost independent of the coordination environment, the intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (I_{612}) normalized to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (I_{592}), described as $\eta = I_{612}/I_{592}$, has been utilized to discuss the hypersensitivity and asymmetry of Eu^{III} complexes [3]. The ratio has been reported to be 11.0 ± 0.1 for $[\text{EuA}_3]$ and 15.3 ± 0.2 for $[\text{EuA}_3(\text{H}_2\text{saltn})]$ [22]. The values for $[\text{EuA}_3(\text{H}_2\text{salchn})]$ and $[\text{EuA}_3(\text{H}_2\{(\text{tBu})\text{saltn}\})]$ obtained in this work were similar to that of $[\text{EuA}_3(\text{H}_2\text{saltn})]$. The value for $[\text{EuA}_3\text{Zn}(\text{salchn})]$ was 18.0 ± 0.1 , while for $[\text{EuA}_3\text{Zn}(\text{saltn})]$, the value was similar to that for $[\text{EuA}_3]$. For $[\text{EuA}_3\text{Zn}\{(\text{tBu})\text{saltn}\}]$, a clear value could not be obtained because of the strong intensity effect of Zn^{II} . These results suggest that the presence of a cyclohexane-1,2-diyl group has the effect of changing the structure asymmetrically.

As the next step in the examination of the effect of Zn^{II} on the luminescence of $[\text{EuA}_3]$, X-ray diffraction was performed with a single crystal of $[\text{EuA}_3\text{Zn}(\text{saltn})]$.

Structural Properties of the Binuclear Complex Formed between $[\text{EuA}_3]$ and $[\text{Zn}(\text{saltn})]$. Fig. 6 shows the ORTEP view of the $[\text{EuA}_3\text{Zn}(\text{saltn})]$ complex. Fig. 7 also

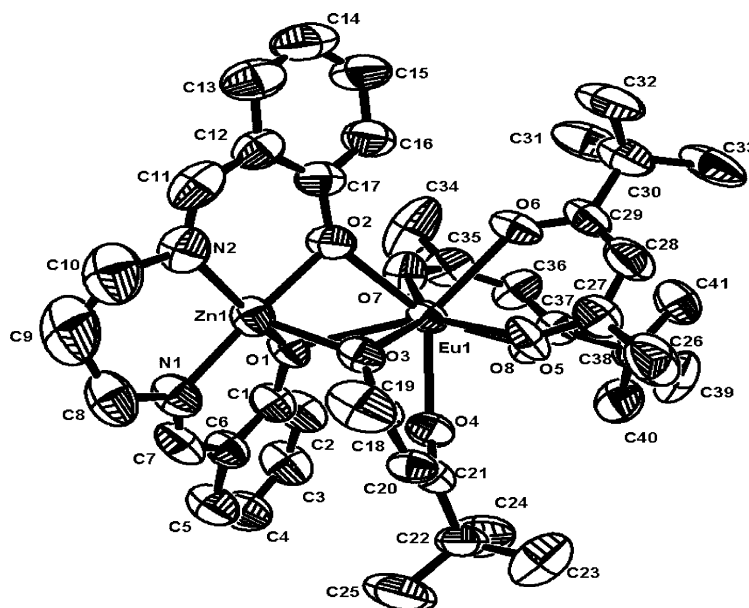


Fig. 6. Molecular structure of $[\text{EuA}_3\text{Zn}(\text{saltn})]$, determined by X-ray diffraction analysis

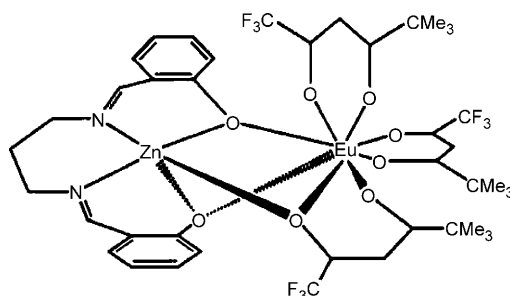


Fig. 7. Schematic representation of the molecular structure of $[\text{EuA}_3\text{Zn}(\text{saltn})]$

shows a schematic representation of the molecular structure of $[\text{EuA}_3\text{Zn}(\text{saltn})]$. The Zn(1) ion of $[\text{EuA}_3\text{Zn}(\text{saltn})]$ has a five-coordinate structure with a slightly distorted square pyramidal shape, which is formed by coordination of the two phenolato O-atoms (O(1) and O(2)) of the saltn^{2-} ligand and two =N– moieties (N(1) and N(2)) in the basal positions, and the O(3) atom of the pta^- ligand in the apical position (Zn(1)–O(1) = 2.012(5) Å, Zn(1)–O(2) = 2.088(5) Å, Zn(1)–N(1) = 2.043(7) Å, Zn(1)–N(2) = 2.023(8) Å, and Zn(1)–O(3) = 2.081(5) Å). In contrast, the Eu(1) ion has an eight-coordinate structure, with six O-atoms (O(3), O(4), O(5), O(6), O(7), and O(8)) from the three pta^- ligands, and in the vacant space, two phenolato O-atoms (O(1) and O(2)) from the $[\text{Zn}(\text{saltn})]$ (Eu(1)–O(1) = 2.488(5) Å, Eu(1)–O(2) = 2.365(5) Å, Eu(1)–O(3) = 2.494(5) Å, Eu(1)–O(4) = 2.369(5) Å, Eu(1)–O(5) = 2.326(5) Å, Eu(1)–O(6) = 2.393(5) Å, Eu(1)–O(7) = 2.352(5) Å, and Eu(1)–O(8) = 2.363(5) Å). Thus, the Zn(1) and Eu(1) ions are bridged by three O-atoms, O(1) and O(2) from saltn^{2-} and O(3) from pta^- , thus forming a hetero-binuclear complex ($\angle \text{Zn(1)–O(1)–Eu(1)} = 90.71(17)^\circ$, $\angle \text{Zn(1)–O(2)–Eu(1)} = 92.4(2)^\circ$, $\angle \text{Zn(1)–O(3)–Eu(1)} = 88.96(19)^\circ$, and Zn(1)–Eu(1) = 3.2188(11) Å). Since the bond angles between Zn(1), Eu(1), and the bridging O-atoms are approximately 90° , Zn(1) and Eu(1) can be relatively close.

It was reported previously, based on crystallographic data from $[\text{Gd}(\text{hfa})_3\text{Cu}(\text{salen})]$, that Cu^{II} forms a plane with two N- and two O-atoms of salen^{2-} , and Gd^{III} and Cu^{II} are doubly bridged by the O-atoms of the salen^{2-} ligand [7]. It was also estimated, from experimental data such as from IR, UV, and elemental analysis [16], that in the binuclear complexes $[\text{Eu}(\text{acac})_3\text{Zn}(\text{salen})]$ and $[\text{Eu}(\text{tfa})_3\text{Zn}(\text{salen})]$, Eu^{III} and Zn^{II} are bridged by the two O-atoms of salen^{2-} (acac^- = acetylacetonato anion, tfa^- = trifluoroacetato anion). Our finding that Zn^{II} adopts a five-coordinate geometry in the binuclear complex $[\text{EuA}_3\text{Zn}(\text{saltn})]$ is a plausible reason for its effectiveness in sensitizing the luminescence of binuclear complexes consisting of $[\text{EuA}_3]$ and Schiff bases incorporating Zn^{II} .

Conclusions. – From the results of a study of the photophysical properties (UV, excitation and luminescence spectra, and quantum yields) of complexes consisting of $[\text{EuA}_3]$ and $[\text{Zn}(\text{saltn})]$, $[\text{Zn}\{(\text{tBu})\text{saltn}\}]$, or $[\text{Zn}(\text{salchn})]$, it was found that $[\text{EuA}_3\text{Zn}(\text{salchn})]$ is the most stable and has the strongest luminescence among these binuclear complexes and also in comparison to the corresponding complexes

[EuA₃(H₂B)]. The introduction of a cyclic hydrocarbon linker between two *Schiff*-base moieties is effective in enhancing the luminescence of [EuA₃] by incorporating Zn^{II} into the *Schiff* base. Due to the strong sensitization of [EuA₃] by Zn^{II} – which is thought to be caused by the five-coordinate structure of Zn^{II} resulting from the bridging between Zn^{II} and Eu^{III} through the O-atoms of the β-diketonato and the *Schiff* base ligands – energy transfer takes place more smoothly.

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