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Effect of heptadentate (N_4O_3) tripodal Schiff base ligand and its yttrium(III) complex on the luminescence and extraction of tris(β -diketonato)europium(III)

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Abstract

In order to learn the effect of a Schiff base and the complex of Y^{III} on the extraction of Eu^{III} with β -diketones and on the luminescence of the extracted species, the extraction of Eu^{III} with 2-thenoyltrifluoroacetone (Htta) and/or these Schiff bases, tris(5-*t*-butyl)salicylidenaminoethyl amine (H₃L¹), and its Y^{III} complex ([YL¹]) prepared, into CHCl₃ was examined. Further, the luminescence and excited spectra of CHCl₃ phases extracted Eu^{III} complexes and the solutions containing tris(β -diketonato)Eu^{III} and/or the Schiff bases were measured. On the measurement of the luminescence spectra, tris(pivaloyltrifluoroacetonato)Eu^{III} (Eu(pta)₃) as well as Eu(tta)₃ was used. Synergistic effect with Htta and these Schiff bases was observed. However, proper effect of Y^{III} was not observed. The luminescence intensity of Eu(tta)₃ at 613 nm decreased with increasing concentration of H₃L¹ or [YL¹], whereas that of Eu(pta)₃ increased with increasing concentration of the ligands, but no difference between both Schiff bases was observed, because of picking up of Y^{III} from [YL¹] with the interaction between [YL¹] and water. © 2007 Elsevier B.V. All rights reserved.

Keywords: Europium(III); 2-Thenoyltrifluoroacetone; Pivaloyltrifluoroacetone; Tris(5-t-butyl)salicylidenaminoethyl amine; Luminescence enhancement

1. Introduction

Since lanthanoid(III) complexes with β -diketone and Lewis base such as 1,10-phenanthroline show much stronger luminescence than the tris(β -diketonato)Ln itself, the ternary complexes can be used for micro-analysis [1]. The ternary complexes consisting of lanthanoids(III), β -diketones, and Lewis bases are mostly accepted as the extracted species in the synergistic extraction of lanthanoids(III) with β -diketones and Lewis bases.

In the present paper, the effect of a Schiff base and the complex of Y^{III} on the luminescence of tris(β -diketonato)Eu^{III} and the extraction of Eu^{III} with β -diketone into CHCl₃ has been examined. As a Schiff base, tris(5-*t*-butyl)salicylidenaminoethyl amine was used to neutralize the charge of Y^{III}. Yttrium(III) was chosen because Y^{III} would be expected to function as sensitizer, since luminescence enhancement is observed in aqueous solutions, e.g., the luminescence of Eu^{III} β -diketonate in the presence of Y^{III} was enhanced in the micellar environment [2,3]. It was

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expected to obtain the dinuclear complexes consisting of Eu^{III} and Y^{III} as the extracted species in the synergistic extraction of Eu^{III} with β -diketone and the Lewis base [4].

2. Experimental

Reagents: The β -diketones and the Schiff bases used in the present work are shown in Scheme 1. Tris(β -diketonato)Eu^{III} was prepared in a similar way described elsewhere [5]. The purity was checked with elemental analysis—For C₂₄H₃₀F₉EuO₆ (Eu(pta)₃): Anal. Calcd. C 39.1, H 4.10; found: C 37.1, H 4.20. C₂₄H₁₂S₃F₉EuO₆ (Eu(tta)₃·H₂O): Anal. Calcd. C 34.6, H 1.69; found: C 37.0, H 1.62.

Tris[4-(2-hydroxy-5-*tert*-butylphenyl)-3-aza-3-butenyl]amine (H_3L^1) : A solution of 5-*tert*-butylsalicylaldehyde (2.68 g, 15.0 mmol) in methanol (20 cm³) was added to a hot solution of tris(2-aminoethyl)amine (tren) (0.73 g, 5.0 mmol) in methanol (40 cm³). The solution was stirred at 50–60 °C for 10 min. After cooling, the precipitate was filtered and dried in vacuo to leave a yellow powder (2.44 g, 78%). Anal. Calcd. for C₃₉H₅₄N₄O₃: C, 74.72%; H, 8.68%; N, 8.94%; found: C, 75.06%; H, 8.72%; N, 8.89%.

[YL¹]: A solution of tren (1.46 g, 10.0 mmol) in methanol (5 cm³) was added to a hot solution of Y(CF₃SO₃)₃ (2.68 g, 5.0 mmol) in methanol (40 cm³). The reaction solution was stirred at 50–60 °C for 2 min. Then, a solution of 5*tert*-butylsalicylaldehyde (2.68 g, 15.0 mmol) in methanol (5 cm³) was added and stirred at 50–60 °C for 2 min. After cooling, the precipitate was filtered and dried in vacuo to leave a yellow powder (3.01 g, 83%). Anal. Calcd. for

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tris[4-(2-hydroxyl-5-t-butylphenyl)-3-aza-3-butenyl]amine

Scheme 1.

 $\begin{array}{l} C_{39}H_{51}N_4O_3Y\cdot 0.5H_2O; C, 64.90\%; H, 7.26\%; N, 7.76\%; found: C, 65.00\%; H, 7.19\%; N, 7.73\%. ESI-MS; m/z (\%): 735 (100) <math display="inline">[YL^1+Na^+]. \ IR: \nu_{C=N} \ (cm^{-1}) \ (KBr): 1630. \end{array}$

Europium(III) aqueous solution was prepared by dissolving the oxide into perchloric acid. The total ionic solution was adjusted to 0.10 M ($1 \text{ M} = 1 \text{ mol } \text{dm}^{-3}$) with sodium perchlorate. The hydrogen ion concentration was measured potentiometrically using 0.0100 M perchloric acid and 0.09 M sodium perchlorate as a standard of pC_H = 2.00 (pC_H = $-\log[\text{H}^+]$).

Procedures: $Tris(\beta$ -diketonato)Eu^{III} chloroform solution and a Lewis base solution were mixed at different molar ratio. The excitation and emission spectra were measured with a Hitachi-F4500 spectrofluorometer. Synergistic extraction of Eu^{III} was performed by using Htta and the Lewis bases according to the procedures reported previously [6]. The concentration of Eu^{III} and Y^{III} was determined by ICP/AES (inductively coupled plasma atomic emission spectrometry; Hitachi P-4000).

3. Results and discussion

3.1. Preparation and properties of $[YL^1]$

The complex of $[YL^1]$ prepared exhibited an IR band at 1630 cm^{-1} due to C=N stretching vibration, but the IR bands corresponding to a primary amine or a trifluoromethanesulfonate anion were not observed. Since the complex does not contain a counter anion, it is concluded that the ligand (H_3L^1) forms an inner-complex in which it functions as a trivalent anionic heptadentate ligand.

Concerning the complexes with tripodal heptadentate ligands, one of the authors (M.K.) reported the syntheses and crystallographic studies of yttrium(III) and lanthanoid(III) complexes of tris[4-(2-hydroxy-3-*tert*-butylphenyl)-3-aza-3butenyl]amine (H₃L²) [7]. Although attempts to obtain a single crystal of [YL¹] suitable for X-ray structure analysis were unsuccessful, the tripodal heptadentate Schiff-base ligand H₃L¹ seems to effectively encapsulate the metal ion and enforce a sevencoordinate geometry in the same manner as H₃L² because the difference between [YL¹] and [YL²] is the only position of the *tert*-butyl group of the salicylidene group of the ligands.

3.2. Photochemical properties of Eu^{III} complexes

Fig. 1 shows the excitation and emission spectra of [Eu(tta)₃] (a) and $[Eu(pta)_3]$ (b). The shape of the emission spectrum of [Eu(tta)₃] is quite similar to that of [Eu(pta)₃], although the intensity is quite different, that is, the former is much larger by a factor of 160 times than that of the latter; both spectra show a sharp peak at 613 nm. However, the excitation spectra are different to each other; at around 394 nm the intensity of $[Eu(tta)_3]$ is larger than that of $[Eu(pta)_3]$ (the intensity of the former is by a factor of 130 than the latter at the same concentration. In Figs. 1–3, the initial concentration of Eu(tta)₃ was used 5×10^{-5} M while that of Eu(pta)₃ was 1×10^{-4} M. The intensity of Eu(pta)₃ was linear to the concentration at least till 5×10^{-4} M. The UV spectra of [Eu(pta)₃] and [Eu(tta)₃] show the peak at 290 and 350 nm, respectively, and at longer than 340 nm, [Eu(pta)₃] slightly shows absorbance (the molar absorptivity is 20 at 394 nm), but [Eu(tta)₃] still shows somewhat absorbance (the molar absorptivity is 600 at 394 nm). The much smaller absorbance of $[Eu(pta)_3]$ than that of $[Eu(tta)_3]$ at 394 nm would give rise to the much weaker luminescence of $[Eu(pta)_3].$

In spite of low excitation intensity and molar absorptivity at 394 nm, Eu^{III} was excited at 394 nm in the present work. The reason is as follows: it has been reported that the excitation to ${}^{5}L_{6}$ electronic level resulted mainly in emission from the first excited energy level of ${}^{5}D_{0}$ situated at ${\sim}17300 \text{ cm}^{-1}$ (around 578 nm) above the ground level ${}^{7}F_{0}$ [8,9]. For the fluorescence spectra measured in all cases, the intense peak was observed at 613 nm. Due to the large Stokes shift, the fluorescence of Eu^{III} was measured without the influence of ligands. Further, it has been reported that since the energy gap between Htta sin-



Fig. 1. Excitation and emission spectra of tris(β -diketonato)Eu^{III} in CHCl₃: (---) excitation spectra at emission wavelength, 613 nm; (--) emission spectra at excitation wavelength, 394 nm ((a) Eu(tta)₃ and (b) Eu(pta)₃).

glet (26107 cm^{-1}) and ${}^{5}\text{L}_{6}$ (25300 cm^{-1}) is small, the energy transfer from tta to Eu^{III} is efficient [10].

Fig. 2 shows the effect of $[YL^1]$ on the excitation and emission spectra of $[Eu(tta)_3]$ (a) and $[Eu(pta)_3]$ (b). The spectrum of $[YL^1]$ itself (chain curve) shows a strong peak at around 470 nm, although it is not sharp as shown in Fig. 2(a). The intensity at 613 nm and at 470 nm in the solution containing $[Eu(tta)_3]$ and $[YL^1]$ (solid curve) is remarkably smaller than that observed in the spectra of the respective solution of $[Eu(tta)_3]$ and $[YL^1]$, though their concentration is similar to each other. On the other hand, as shown in Fig. 2(b), in the solution containing $[YL^1]$ and $Eu(pta)_3$ (solid curve), the intensity at 613 nm is enhanced to that of $[Eu(pta)_3]$ itself (broken curve) and the intensity at 470 nm assigned to $[YL^1]$ decreases to that of $[YL^1]$ itself (chain curve).

Fig. 3 shows the emission intensity at 613 nm against $[H_3L^1]$ or $[YL^1]$ concentration at a given Eu^{III} concentration and at λ^{ex} 394 nm. As seen from Fig. 3(a), the intensity of $[Eu(tta)_3]$ decreases with increase in the Schiff base concentration, while that of $[Eu(pta)_3]$, as shown in Fig. 3(b), increases along with the increasing concentration. We cannot explain the different behavior with these β -diketones up to now. From the comparison of



Fig. 2. Effect of concentration of $[YL^1]$ on the luminescence spectra of tris(β -diketonato)Eu^{III} in CHCl₃ at the excited wavelength 394 nm and excited spectra at the emission wavelength 613 nm. (a) Eu(tta)₃: (---) [Eu(tta)₃]_T = 5.0 \times 10^{-5} M, (---) $[YL^1]_T = 5.0 \times 10^{-5}$ M, (---) mixed solution [Eu(tta)₃]_T (5.0 \times 10^{-5} M), $[YL^1]_T$ (5.0 $\times 10^{-5}$ M). (b) Eu(pta)₃: (---) [Eu(pta)₃]_T = 1.0 $\times 10^{-4}$ M, (---) [YL¹]_T = 1.0 $\times 10^{-4}$ M, (---) mixed solution [Eu(pta)₃]_T (1.0 $\times 10^{-4}$ M) and [YL¹]_T (1.0 $\times 10^{-4}$ M).

the spectra in Fig. 2, it was found that the luminescence intensity ratio at 613 nm between [Eu(tta)₃] and [Eu(pta)₃] is almost equivalent to that of the excitation intensity ratio at 394 nm (for the former the ratio is 80 and for the latter it is 70), and also the luminescence intensity ratio in the solution containing [YL¹] complex and $[Eu(tta)_3]$ to that containing $[YL^1]$ and $[Eu(pta)_3]$ is almost equivalent to that of the excitation intensity ratio (the ratio for the former 7.0 and also that for the latter 6.6), that is, the intensity ratio, either in luminescence or in the excitation, of the $[YL^1]$ complex with the tris(β -diketonato)Eu^{III} is almost one tenth smaller than that of tris(β -diketonato)Eu^{III} themselves. However, the result of UV spectra which was separately measured showed that the ratio of the absorbance at 394 nm between the solution containing the $[YL^1]$ complex and $[Eu(tta)_3]$ and that containing the $[YL^1]$ complex and $[Eu(pta)_3]$ (the value is almost 1) is much smaller compared to the intensity ratio between [Eu(tta)₃] and [Eu(pta)₃] (20). It may suggest that the energy absorbed at 394 nm would be much smaller in [Eu(tta)₃] complex with $[YL^1]$ than the pta complex. Accordingly, it would



Fig. 3. Emission intensity at 613 nm ($\lambda^{ex} = 394$ nm) of tris(β -diketonato)Eu^{III} in CHCl₃ as a function of [YL¹]_T (\bigcirc) or [H₃L¹]_T (\bigcirc): (a) Eu(tta)₃ (6.25 × 10⁻⁵ M) and (b) Eu(pta)₃ (1.25 × 10⁻⁴ M).

be related that the energy absorbed with the complex between $[Eu(tta)_3]$ and $[YL^1]$ is reduced.

As seen from Fig. 3, any different effect is not recognized between H_3L^1 and $[YL^1]$. Although the structural interaction between $[YL^1]$ and $Eu(pta)_3$ or $[YL^1]$ and $Eu(tta)_3$ is still uncertain, Y^{III} encapsulated into H_3L^1 through the bonding to three hydroxyl groups and the coordination with four N donor atoms would not be involved in the photochemical process to Eu^{III} .

Tris(β -diketonato) Eu^{III} seems to be influenced to the luminescence of Y^{III} in [YL¹], that is, as seen in Fig. 2, in the mixed solution of [Eu(pta)₃] or [Eu(tta)₃] with [YL¹], the intensity derived from Y^{III} at around 470 nm decreases with the presence of tris(β -diketonato)Eu^{III}. It is suggested that [YL¹] forms dinuclear complex with Eu^{III} like as [Eu(pta)₃·YL¹] but the Y^{III} in [YL¹] does not influence to the luminescence of Eu^{III}.

3.3. Synergistic extraction of Eu^{III} with Htta and H_3L^1 or $[YL^1]$ and the emission intensity of the organic phases

When Eu ion is extracted with Htta and H_3L^1 or $[YL^1]$ (in this section, to simplify, Htta is described as HA and H_3L^1 or $[YL^1]$, Lewis base, is represented as B), the extracted species



Fig. 4. Change in the distribution ratio of Eu^{III} as a function of concentration of YL^1 and H_3L^1 when Eu^{III} was extracted with Htta and YL^1 (\bigcirc) and H_3L^1 (\bullet).

are the ternary complexes consisting of $[EuA_3]$ and H_3L^1 or $[EuA_3]$ and $[YL^1]$ in addition to EuA_3 , and the species of Eu^{III} in aqueous phase is only Eu^{3+} , the distribution ratio (*D*) defined by the total concentration ratio of Eu^{III} between the organic and aqueous phases is represented as

$$D = \frac{[\text{EuA}_3]_{\text{o}} + [\text{EuA}_3\text{B}]_{\text{o}} + \cdots}{[\text{Eu}^{3+}]}$$

The extraction equilibria can be represented as

 $\mathrm{Eu}^{3+} + 3\mathrm{HA}_{(\mathrm{o})} + n\mathrm{B}_{(\mathrm{o})} \rightleftharpoons \mathrm{EuA}_3 \cdot n\mathrm{B}_{(\mathrm{o})} + 3\mathrm{H}^+$

or

$$Eu^{3+} + 3HA_{(o)} \rightleftharpoons EuA_{3(o)} + 3H^{+}$$

$$(K_{ex0} = [EuA_{3}]_{o}[H^{+}]^{3}[Eu^{3+}]^{-1}[HA]_{o}^{-3});$$

$$EuA_{3(o)} + nB_{(o)} \rightleftharpoons EuA_{3} \cdot nB_{(o)}$$

$$(\beta_{n} = [EuA_{3} \cdot nB]_{o}[EuA_{3}]_{o}^{-1}[B]_{o}^{-n})$$

Then D is rewritten as

$$D = K_{\text{ex0}}[\text{HA}]_{0}^{3}[\text{H}^{+}]^{-3}(1 + \Sigma \beta_{n}[\text{B}]_{0}^{n})$$

where $\log K_{ex0}$ was -8.28 ± 0.05 .

Fig. 4 shows the plot of $\log D - 3 \log [\text{HA}]_o - 3pC_H$ against the total concentration of $[\text{YL}^1]$ (\bigcirc) and H_3L^1 (\bigcirc) ($\log [\text{B}]_T$). Although the reproducibility is not good, the value at *Y*-axis approaches to $\log K_{ex0}$ along with decreasing Schiff base concentration, and also any difference is not observed between both Schiff bases. When the concentration of Y^{III} in the organic and the aqueous phases was measured, it was found that most Y^{III} was in aqueous phases. This result suggests that $[YL^1]$ easily interacts with water to be Y^{III} and H_3L^1 . The H_3L^1 forms a complex with tris(β -diketonato)Eu^{III} and the complex makes better extraction of Eu^{III}. Since Y ion as well as lanthanoid ions is typical Lewis hard acid, Y ion has strong affinity to O donor atoms so that water interacts with $[\text{YL}^1]$ and pulls out Y^{III} of $[\text{YL}^1]$.



Fig. 5. Luminescence intensity at 613 nm in the CHCl₃ into which Eu^{III} was extracted with 0.10 M Htta and 1.25×10^{-3} M [YL¹] (\bigcirc) or H₃L¹ in the presence of Y^{III} in aqueous phase (\bullet) as a function of Y^{III} concentration in the CHCl₃ at equilibrium.

The luminescence spectra in the extracted organic phase were also measured. The luminescence intensity at 613 nm in the CHCl₃ phase into which Eu^{III} was extracted with 0.10 M Htta and $1.25 \times 10^{-3} \text{ M} \text{ [YL}^1 \text{]}$ was measured and compared with the luminescence in the CHCl₃ into which Eu^{III} was extracted with 0.10 M Htta and 1.25×10^{-3} M H₃L¹ from the aqueous solution containing Eu^{III} and 1.25×10^{-3} M Y^{III}. Fig. 5 shows the intensity as a function of Y^{III} concentration in the CHCl₃ at equilibrium. Either in the extraction with $[YL^1]$ and Htta (\bigcirc) or in the extraction with H_3L^1 and Htta in the presence of Y^{III} in the aqueous solution (\bullet), the intensity at peak wavelength similarly decreases along with increasing the Y^{III} concentration. Yttrium(III) released from [YL¹] may form a chelate with Htta which is present in a large excess of Y^{III}. The energy transfer may occur from $[Eu(tta)_3]$ to $Y(tta)_3$. The extraction constant of [Y(tta)₃] was separately determined to be $\log K_{\rm ex} = -8.12 \pm 0.05$. Strong luminescence is generally observed when Eu^{III} was doped in yttrium oxide and the system is widely used as phosphor, as already described [2,3].

The co-luminescence is also observed in a dinuclear complexes consisting of Eu^{III} and Y^{III} with salicylic acid and 1, 10-phenanthroline [11] or the Eu^{III} and Ln^{III} such as Nd³⁺, Gd³⁺ and Tb³⁺ with dibenzoylmethide and phenanthroline [12]. However, the presence of Y^{III} in CHCl₃ does not show the co-luminescence.

4. Conclusion

In CHCl₃, the luminescence of Eu^{III} was enhanced with the interaction between tris(pivaloyltrifluoroacetonato)Eu and H_3L^1 or [Eu(pta)₃] and [YL¹], while that of [Eu(tta)₃] decreased in the presence of H_3L^1 or [YL¹]. The difference between H_3L^1 and [YL¹] was not observed. This is due to Y^{III} encapsulated into the Schiff base. The extraction of Eu ion with Htta and H_3L^1 or [YL¹] increased with increasing ligand concentration, whereas the luminescence intensity decreased with increasing Y^{III} concentration in organic phases. The co-luminescence with Eu^{III} and Y^{III} can not be observed.

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