Effect of Some d-Transition Metal Complexes of Salen-Type Ligands and Acetylacetone on Fluorescence of Europium(III) and Terbium(III)

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Fluorescence spectra of europium(III) and terbium(III) have been measured in methanolic solutions containing various amounts of [M(salen)] (M=Cu(II), Ni(II)), [Cr(salen)(H_2O)$_2$]Cl, [M(saltn)] (M=Cu(II), Ni(II)), [Cu(acacen)], [M(acac)$_2$] (M=Cu(II), $V^{IV}O$), [M(acac)$_3$] (M=Cr(III), Co(III)), or [Ni(acac)$_2$(H_2O)$_2$]. Our purpose was to investigate the influence of these metal complexes on the fluorescence of Eu(III) and Tb(III), where H_2salen, H_2saltn, H_2acacen, and Hacac stand for *N,N'*-bis(salicylidene)ethylenediamine, *N,N'*-bis(salicylidene)-1,3-propanediamine, *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine, and acetylacetone, respectively. The fluorescence intensities of both Eu(III) and Tb(III) decreased with increasing the concentration of [M(salen)] (M=Cu, Ni), [Cr(salen)(H_2O)$_2$]Cl, [M(saltn)] (M=Cu, Ni), [Cu(acacen)], and [M(acac)$_3$] (M=Cr, Co), whereas it was little affected by simple metal salts. The intensity of Tb(III) increased up to the addition of a given amount of [M(acac)$_2$] (M=Cu, VO) or [Ni(acac)$_2$(H_2O)$_2$] and then decreased on further addition, whereas the intensity of Eu(III) decreased gradually by the addition of these acetylacetonate complexes. These results are explained by the formation of heteronuclear complex species and by the stabilities of acetylacetonate complexes.

Some lanthanide ions and their complexes exhibit a characteristic fluorescence of each lanthanide and it is well known that these fluorescence properties are sensitive to the adduct formations with "synergic agents" such as trioctylphosphine oxides and trialkylphosphates, and the complex formations with various kinds of organic compounds.[1)] But there are few studies on the effect of the co-existing metal ions or their complexes upon the fluorescence of lanthanide ions.[1b,2—5)] Berner et al.[2)] reported that the fluorescence of Tb(III) is enhanced when two of the four Ca(II) in proteolytic enzyme, thermolysin, are replaced by Tb(III), whereas it decreases by further replacement of Zn(II) bound at the active site of the enzyme by Co(II). Recently, we investigated the effect of the copper(II) and nickel(II) complexes, [M(saltn)] (M = Cu, Ni), of *N,N'*-bis(salicylidene)-1,3-propanediamine (H_2saltn) upon the fluorescence of Eu(III)[6)] and Tb(III).[7)] We found that the fluorescence intensities of both Eu(III) and Tb(III) decrease markedly by the addition of the above complexes. These results were presumed to be partly due to the formations of M-Eu and M-Tb heteronuclear complex species bridged by the phenolic oxygen atoms of the ligand, saltn^{2-}. Such studies will give basic and useful information for the development of fluorescence materials, because the metal complexes reported so far are beyond enumeration and show a great variety of characteristic colors of the respective complexes.

In the present work, fluorescence spectra of Eu(III) and Tb(III) in methanol were measured by adding some d-transition metal complexes, [M(salen)] (M= Cu(II), Ni(II)), [Cr(salen)(H_2O)$_2$]Cl, [M(salen–OCH_3)] (M=Cu(II), Ni(II)), [Cu(acacen)], [M(acac)$_3$] (M=Cr(III), Co(III)), [M(acac)$_2$] (M=Cu(II), $V^{IV}O$), and [Ni(acac)$_2$(H_2O)$_2$]. The purpose was to get further information about the effect of metal complexes on the fluorescence of lanthanides, where H_2salen, H_2salen–OCH_3, H_2acacen, and Hacac stand for *N,N'*-bis(salicylidene)ethylenediamine, *N,N'*-bis(3-methoxysalicylidene)ethylenediamine, *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine, and acetylacetone, respectively.

Experimental

Materials. $Eu(NO_3)_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 6H_2O$ were prepared in the usual way by evaporating the solution almost to dryness after dissolving commercially obtained Eu_2O_3 (99.9% purity) and Tb_4O_7 (99.9% purity) in HNO_3. $Cr(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ were of special grade and were used as received.

Procedure. Various amounts of the metal nitrates or complexes were added to a methanolic solution of $Eu(NO_3)_3 \cdot 6H_2O$ or $Tb(NO_3)_3 \cdot 6H_2O$ and fluorescence spectra were recorded with a Shimadzu RF-540 fluorospectrophotometer. The exciting wave lengths were 394 and 355 nm for Eu(III) and Tb(III), respectively.

Results and Discussion

Typical fluorescence spectra are shown in Figs. 1 and 2. Fluorescence spectrum of $Eu(NO_3)_3 \cdot 6H_2O$ shows bands attributable to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$, and $^5D_0 \rightarrow {}^7F_4$, at 580, 593, 618, 650, 687, and 696 nm, respectively (spectrum (a) in Fig. 1). $Tb(NO_3)_3 \cdot 6H_2O$ gives bands attributable to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$, at 491, 546, 582, and 622 nm, respectively (spectrum (a) in Fig. 2). These band positions were not greatly changed by the addition of metal salts and complexes used in this work. Figures 3—8 show the relationships between the relative intensities and the concentration ratios of metal salts or complexes to Eu(III) or Tb(III), together with results previously reported for the

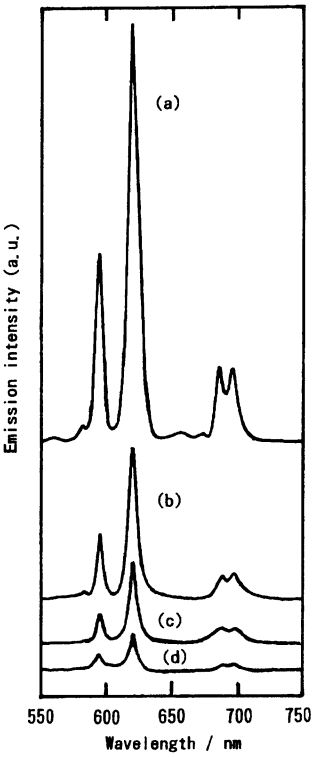

Fig. 1. Typical fluorescence spectra of Eu(III) in methanolic solutions of salen-complexes. Concentration of Eu(III) is 5×10^{-3} mol dm^{-3}. Concentration of each complex is 2×10^{-4} mol dm^{-3}. Ordinate scales are ×256 for (a), (b), and (c), and ×512 for (d). (a): without additive, (b): with $[Cr(salen)(H_2O)_2]Cl$, (c): with [Ni(salen)], (d): with [Cu(salen)].

Cu(II) and Ni(II) complexes of H_2saltn.[6,7] Here the intensity is the sum of the six bands for Eu(III) and the sum of the four bands for Tb(III), and is taken as an unit for the solution containing only $Eu(NO_3)_3\cdot6H_2O$ or $Tb(NO_3)_3\cdot6H_2O$. As can be seen from Figs. 3, 4, and 5, the fluorescence of Eu(III) and Tb(III) is significantly quenched by the addition of complexes of H_2salen, H_2saltn, and H_2acacen, whereas it is little affected by the addition of simple metal salts.

It is generally accepted that the luminescence intensity is decreased by the radiationless energy loss through the excited state of other molecules, which are near the exciting species.[1m] It is also known that [M(salen)] and [M(saltn)] (M=Cu(II), Ni(II)) function as bidentate ligands through the two phenolic oxygen atoms.[8] Giuffrida et al.[9,10] synthesized the di- and trinuclear complexes, $Ln[M(salen)]_nX_3(H_2O)_m$ and $Ln[M(saltn)]_nX_3(H_2O)_m$, where Ln is lanthanide ions, M is Cu or Ni, X is NO_3^-, NCS^-, ClO_4^-, or Cl^-, and n is one or two, and found that the di- or trinuclear structures are maintained in an usual organic solvent such as nitromethane, acetonitrile, nitrobenzene, methanol, or ethanol. Furthermore, Gatteschi et al.[11,12] determined the molecular structures of $[\{Cu(salen)\}_2Gd(H_2O)_3](ClO_4)_3\cdot2[Cu(salen)]\cdot0.5C_2H_5NO_2$ and $[\{Cu(saltn)\}_2Gd(NO_3)_2(H_2O)](NO_3)\cdot2C_2H_5NO_2$. According to their studies, the copper(II) and gadolinium(III) ions are indeed bridged by two phenolic oxygen atoms, forming the Cu_2Gd trinuclear complexes. From these discussions, we presume that the decrease in fluorescence intensity by the addition of complexes of H_2salen, H_2saltn, or H_2acacen may be due to the energy transfer from the excited Eu(III) or Tb(III) to the d-transition metal complex moieties through the phenolic oxygen atoms of H_2salen and H_2saltn and the exogenous oxygen atoms of H_2acacen. In order to examine whether such energy transfer contributes to the fluorescence decrease or not, we measured the fluorescence spectra of Eu(III) in methanolic solution of various concentrations of $[M(salen–OCH_3)]$ (M=Cu(II), Ni(II)), where H_2salen–OCH_3 denotes *N*,*N*′-bis(3-methoxysalicylidene)ethylenediamine. Because of the steric effect of two methoxy groups of this ligand, the formation of heteronuclear species bridged by the phenolic oxygen atoms is expected to become difficult. As shown in Fig. 6, $[Cu(salen–OCH_3)]$ and $[Ni(salen–OCH_3)]$ are less effective for the fluorescence quenching, compared with [Cu(salen)] and [Ni(salen)], respectively. From these results, we conclude that the fluorescence is effectively quenched by the energy transfer from the excited Eu(III) or Tb(III) to the Cu(II), Ni(II), or Cr(III) center through the bridging oxygen atoms, though the fluorescence decrease resulting from the absorption of ex-

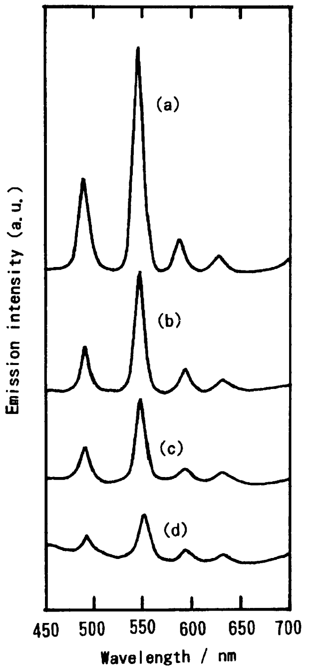

Fig. 2. Typical fluorescence spectra of Tb(III) in methanolic solutions of salen-complexes. Concentration of Tb(III) is 5×10^{-3} mol dm^{-3}. Concentration of each complex is 1×10^{-3} mol dm^{-3}. Ordinate scales are ×4 for (a), (b), and (c), and ×16 for (d). (a): without additive, (b): with $[Cr(salen)(H_2O_2]Cl$, (c): with [Ni(salen)], (d): with [Cu(salen)].

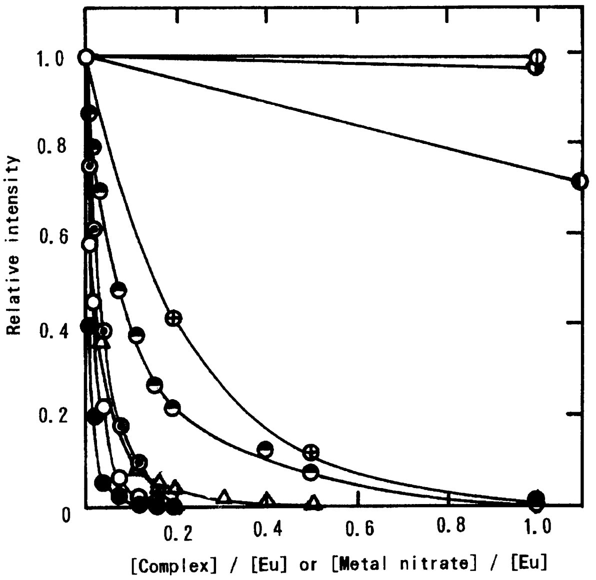

Fig. 3. Relationships between relative intensities of Eu(III) and concentration ratios of complexes or metal nitrates to Eu(III). Concentration of Eu(III) is 5×10^{-3} mol dm^{-3}. ⦶: $Cu(NO_3)_2\cdot3H_2O$, ◑: $Ni(NO_3)_2\cdot6H_2O$, ◐: $Cr(NO_3)_3\cdot9H_2O$, ●: [Cu(salen)], ○: [Ni(salen)], ◉: $[Cr(salen)(H_2O)_2]Cl$, △: [Cu(saltn)],[6] ⊕: [Ni(saltn)],[6] ◓: [Cu(acacen)].

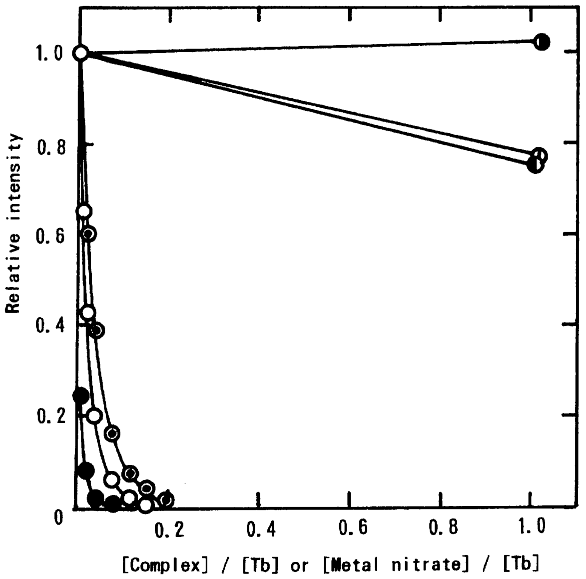

Fig. 4. Relationships between relative intensities of Tb(III) and concentration ratios of salen-complexes or metal nitrates to Tb(III). Concentration of Tb(III) is 5×10^{-3} mol dm^{-3}. ⦶: $Cu(NO_3)_2\cdot3H_2O$, ◑: $Ni(NO_3)_2\cdot6H_2O$, ◐: $Cr(NO_3)_3\cdot9H_2O$, ●: [Cu(salen)], ○: [Ni(salen)], ◉: $[Cr(salen)(H_2O)_2]Cl$.

citing light by the d-transition complexes themselves also cannot be ruled out. Our proposal will be supported by the fact previously reported that the mononuclear Eu(III) complex of H_4fsaen, Eu(H_2fsaen)(NO_3)(H_2O)$_5$, exhibits strong fluorescence in the 580—700 nm and the fluorescence is almost completely quenched on forming the dinuclear Cu–Eu, Ni–Eu, and VO–Eu complexes, where H_4fsaen is the dinucleating ligand, *N*,*N*′-bis(3-carboxysalicylidene)ethylenediamine which can accomodate a d-transition metal ion and a lanthanide ion at the endogenous (N_2O_2-site) and the exogenous (O_4-site) coordination sites, respectively.[13,14]

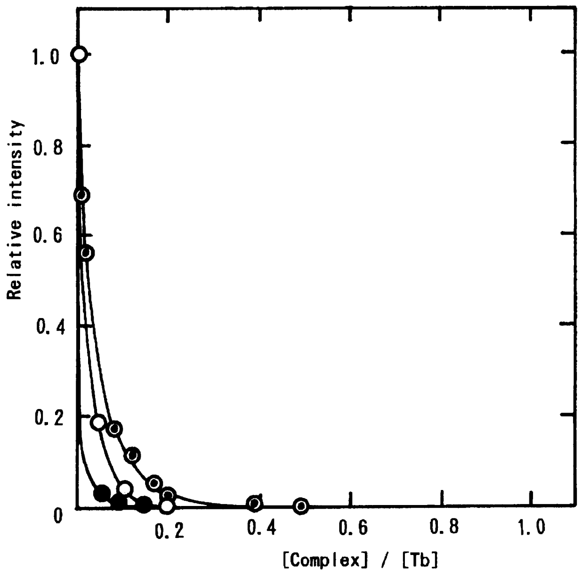

Fig. 5. Relationships between relative intensities of Tb(III) and concentration ratios of saltn-complexes or acacen-complex to Tb(III). Concentration of Tb(III) is 5×10^{-3} mol dm^{-3}. ○: [Ni(saltn)],[7] ●: [Cu(saltn)],[7] ◉: [Cu(acacen)].

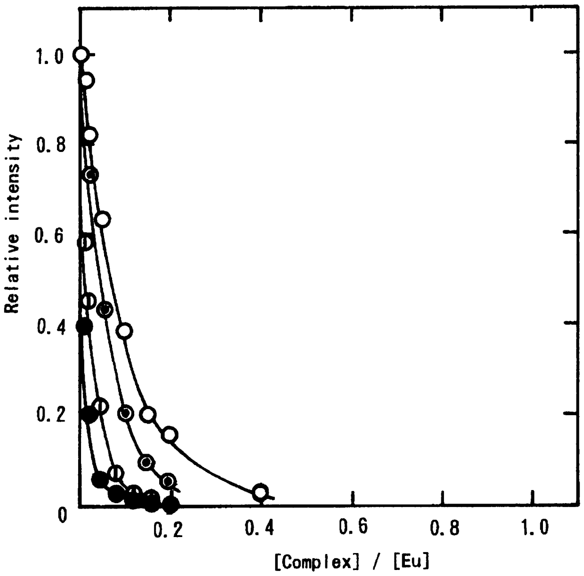

Fig. 6. Comparison of the effects of salen-complexes with those of salen–OCH_3-complexes on the fluorescence of Eu(III). Concentration of Eu(III) is 5×10^{-3} mol dm^{-3}. ●: [Cu(salen)], ○: [Cu(salen–OCH_3)], ⦶: [Ni(salen)], ◉: [Ni(salen–OCH_3)].

Effects of the complexes of Hacac are shown in Figs. 7

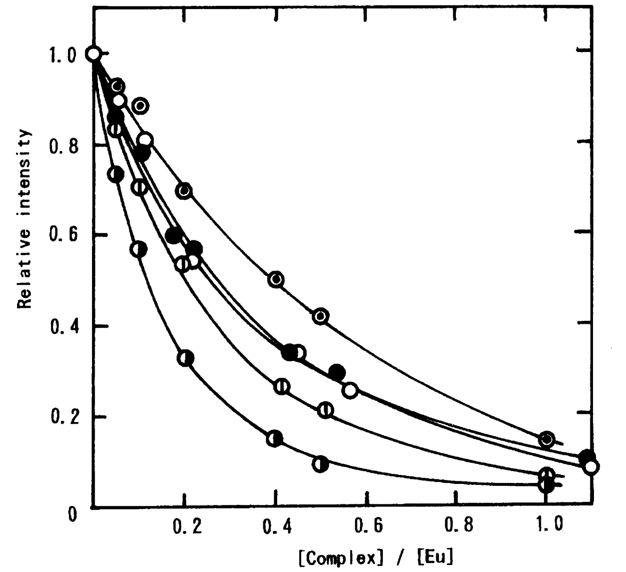

Fig. 7. Relationships between relative intensities of Eu(III) and concentration ratios of acac-complexes to Eu(III). Concentration of Eu(III) is 5×10^{-3} mol dm^{-3}. ○: $[VO(acac)_2]$, ◉: $[Ni(acac)_2(H_2O)_2]$, ●: $[Cu(acac)_2]$, ⦶: $[Cr(acac)_3]$, ◑: $[Co(acac)_3]$.

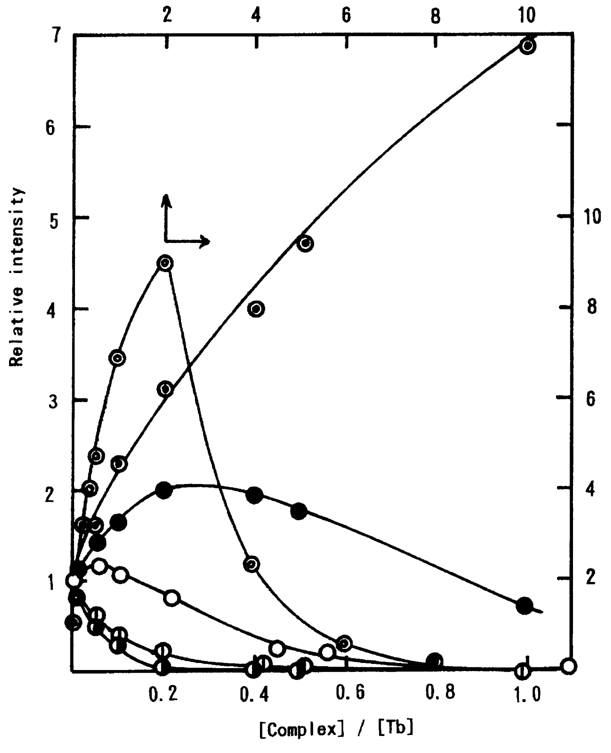

Fig. 8. Relationships between relative intensities of Tb(III) and concentration ratios of acac-complexes to Tb(III). Concentration of Tb(III) is 5×10^{-3} mol dm^{-3}. ○: $[VO(acac)_2]$, ◉◎: $[Ni(acac)_2(H_2O)_2]$, ●: $[Cu(acac)_2]$, ⦶: $[Cr(acac)_3]$, ◑: $[Co(acac)_3]$.

and 8. The fluorescence intensities of both Eu(III) and Tb(III) decrease monotonously with increasing the concentration of $[Cr(acac)_3]$ and $[Co(acac)_3]$. When $[VO(acac)_2]$, $[Ni(acac)_2(H_2O)_2]$, or $[Cu(acac)_2]$ are added, the intensity of Eu(III) decreases monotonously with increasing the concentration of complexes (Fig. 7), whereas the intensity of Tb(III) is enhanced in the lower concentration region of complexes added and then decreases gradually above a given concentration (Fig. 8). In order to explain these observations, the fluorescence spectra of $[Eu(acac)_3]$ and $[Tb(acac)_3]$ in methanol were compared with those of $Eu(NO_3)_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 6H_2O$, respectively, and it was found that the fluorescence of $[Eu(acac)_3]$ is weaker than that of $Eu(NO_3)_3 \cdot 6H_2O$ and the fluorescence of $[Tb(acac)_3]$ is more intense than that of $Tb(NO_3)_3 \cdot 6H_2O$. From these results, we explain the enhancement in fluorescence intensity of Tb(III) in the lower concentration region of $[M(acac)_2]$ (M=VO, Cu) and $[Ni(acac)_2(H_2O)_2]$ by the following reasoning: The metal-ligand dissociation may occur in the lower concentration region of these three complexes, since $V^{IV}O$, Ni(II), and Cu(II) ions are more labile for the ligand-substitution. Therefore, the complex species of terbium(III) with $acac^-$ may be formed, resulting in the fluorescence enhancement of Tb(III).

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