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Fluorescence Quenching of Europium(III) by Heteronuclear Complex Formation with Copper(II) or Nickel(II)

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Synopsis. Fluorescent spectra of the mononuclear europium(III) complex, Eu(H_2 fsaen) (NO_3)·$5H_2O$, and the heteronuclear complexes, MEu(fsaen)(NO_3)·nH_2O (n=4 for M=Cu(II) and n=6 for M=Ni(II)), were compared, where H_4 fsaen is a binucleating ligand, *N,N'*-bis (3-carboxysalicylidene) ethylenediamine. It was found that the fluorescent bands of Eu(III) observed for the mononuclear complex were significantly quenched on forming binuclear complexes.

Heteronuclear complexes comprising a d-transition metal ion and a rare earth ion are of recent interest1—10) to investigate the interaction between d- and f-metal ions. Recently we studied the effects of the copper(II) and nickel(II) complexes of *N,N'*-disalicylidene-1,3-propanediamine ([M(saltn)] (M=Cu, Ni)) upon the fluorescent properties of europium(III) in methanol and found that the fluorescent intensities decreased by the addition of the complexes whereas little affected by the addition of a metal salt such as Cu (NO_3)$_2$·$3H_3O$ or Ni (NO_3)$_2$·$6H_2O$.11) As the most probable reason for the quenching of fluorescence, we proposed that [M(saltn)] (M=Cu or Ni) coordinates to Eu(III) through the phenolic oxygens (see Fig. 1) and the radiationless energy loss occurs from the excited Eu(III) to the Cu(II) or Ni(II) through the phenolic oxygen bridges. In this work mononuclear Eu(III) complex and binuclear M(II)–Eu(III) (M=Cu, Ni) complexes of *N,N'*-bis (3-carboxysalicylidene)ethylenediamine (H_4fsaen), Eu (H_2fsaen) (NO_3)·$5H_2O$ and MEu (fsaen) (NO_3)·nH_2O (n=4 for M=Cu(II), n=6 for M=Ni(II)) (see Fig. 2), have been prepared and their fluorescent spectra were compared in solid state and in solution, in order to gain a further insight into the quenching mechanism of Eu(III) fluorescence.

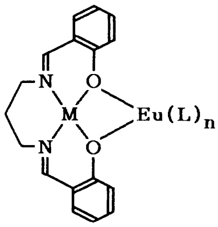
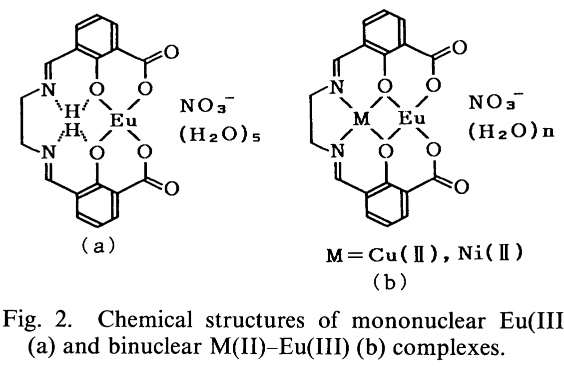


Fig. 1. Schematic representation of M(saltn)–Eu(III) bonding. L denotes the coordinated nitrate ion, water, or methanol molecule.



(a) (b)

Fig. 2. Chemical structures of mononuclear Eu(III) (a) and binuclear M(II)–Eu(III) (b) complexes.

Experimental

Syntheses. The binuclear complexes, MEu(fsaen) (NO_3)·nH_2O (n=4 for M=Cu (II), n=6 for M= Ni (II)), were synthesized by the previous method.7)

Mononuclear Complex, Eu(H_2fsaen)(NO_3)·$5H_2O$: To a methanolic solution (30 cm^3) of H_4fsaen (4 mmol) and LiOH·H_2O (8 mmol) was added a methanolic solution (10 cm^3) of Eu (NO_3)$_3$·$6H_2O$ (4 mmol). Yellowish microcrystals were immediately separated. After the reaction mixture was warmed 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 2.6 g (almost quantitative).

Found: C, 32.24; H, 3.39; N, 6.22; Eu, 22.96%. Calcd for $C_{18}H_{24}N_3O_{14}Eu$: C, 32.84; H, 3.67; N, 6.38; Eu, 23.08%.

Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University. Infrared spectra were recorded on KBr disks with a JASCO IR-G Spectrometer. Fluorescent spectra were obtained with a Shimadzu RF-540 Fluorospectrophotometer.

Results and Discussion

Although IR band assigned to the free carboxyl group was obseved at 1700—1730 cm^{-1} for the mononuclear Cu(II) and Ni(II) complexes as reported,12) no band was found in this region for the mononuclear Eu(III) complex. Instead a broad and strong band assigned to the coordinated carboxylate group was observed around 1540 cm^{-1}, suggesting that the Eu(III) ion is bound at the outside coordination site (O_4-site) as shown in Fig. 2 (a).

The fluorescent spectra in solid state and in *N,N*-dimethylformamide (DMF) are shown in Figs. 3 and 4, respectively, where exciting wavelength is 394 nm, at which the Eu(III) ion shows the absorption assigned to the $^7F_0 \rightarrow {}^5L_6$ transition. The mononuclear Eu(III) complex shows the fluorescent bands attributed to the $^5D_0 \rightarrow {}^7F_J$ transitions at 580, 593, 615, 653, and ca. 700 nm. The intensities of these bands decrease drastically in the binuclear complexes. These observations support our previous hypothesis11) that the decrease in fluorescent intensities is due to the energy transfer from

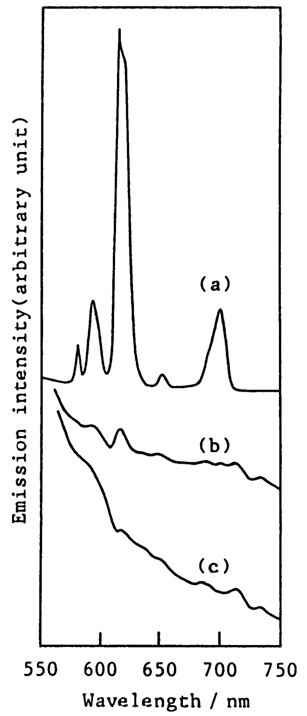


Fig. 3. Fluorescent spectra of mononuclear Eu(III) (trace a), binuclear Cu(II)-Eu(III) (trace b), and Ni(II)-Eu(III) (trace c) complexes in solid state. Exciting wavelength is 394 nm. Slit widths (nm) of (excitation and emission sides) are (2 and 2) for (a), and (10 and 5) for (b) and (c). Ordinate scale is ×64.

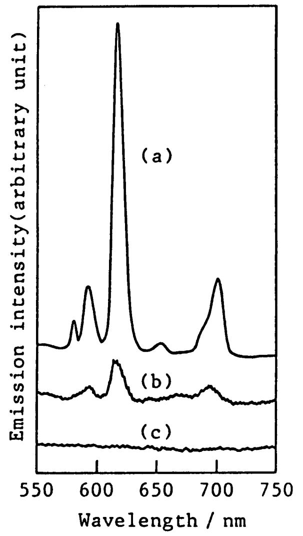


Fig. 4. Fluorescent spectra of mononuclear Eu(III) (trace a), binuclear Cu(II)-Eu(III) (trace b), and Ni(II)-Eu(III) (trace c) complexes in DMF solution. Exciting wavelength is 394 nm. Slit widths (nm) of (excitation and emission sides) are (5 and 2) for (a) and (20 and 10) for (b) and (c). Ordinate scales are ×64 for (a) and ×1024 for (b) and (c). Concentration of each complex is 5×10^{-3} mol dm^{-3}.

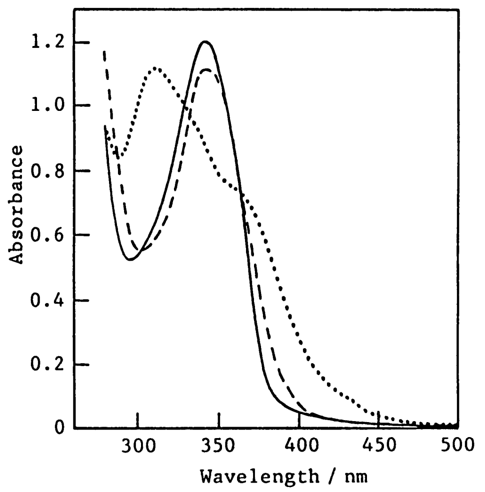


Fig. 5. Absorption spectra of mononuclear Eu(III) (——), binuclear Cu(II)-Eu(III) (----), and Ni(II)-Eu(III) (······) complexes in DMF solution. Concentration of each complex is 1×10^{-4} mol dm^{-3}.

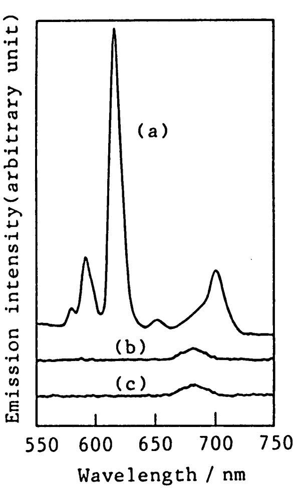


Fig. 6. Fluorescent spectra of mononuclear Eu(III) (trace a), binuclear Cu(II)-Eu(III) (trace b), and Ni(II)-Eu(III) (trace c) complexes in DMF solution. Exciting wavelength is 342 nm. Slit width (nm) of (excitation and emission sides) is (10 and 5). Ordinate scale is ×512. Concentration of each complex is 5×10^{-3} mol dm^{-3}.

the excited Eu(III) to the Cu(II) or Ni(II) center through the bridging phenolic oxygen atoms. However, from the absorption spectra shown in Fig. 5, it cannot be excluded that exciting light may be absorbed by the Cu(II) or Ni(II) complex moiety without exciting the Eu(III). In order to check this suspicion, we measured the fluorescent spectra using the exciting wavelength of 342 or 464 nm, since the absorption of the mononuclear Eu(III) complex is more intense at 342 nm compared with the binuclear Cu(II)-Eu(III) and Ni(II)-Eu(III) complexes, and the binuclear complexes show little absorption at 464 nm. Here again, as shown in Figs. 6 and 7, the drastic decrease in intensities is observed in the binuclear complexes.

Thus, the present study clearly demonstrates that fluorescence of Eu(III) is effectively quenched on forming a binuclear complex with a d-transition metal ion. The mechanistic studies on the fluorescence quenching of Eu(III) by neighbouring metal ions and their complexes are in progress in our laboratories.

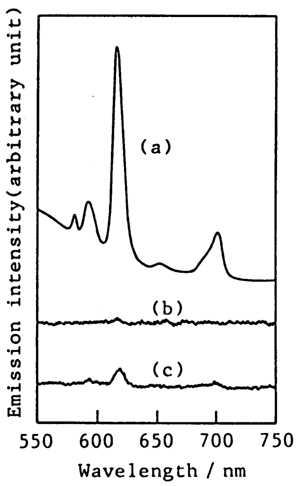


Fig. 7. Fluorescent spectra of mononuclear Eu(III) (trace a), binuclear Cu(II)-Eu(III) (trace b), and Ni(II)-Eu(III) (trace c) complexes in DMF solution. Exciting wavelength is 464 nm. Slit width (nm) of (excitation and emission sides) is (5 and 2). Ordinate scales are ×128 for (a) and ×1024 for (b) and (c). Concentration of each complex is 5×10^{-3} mol dm^{-3}.

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