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Fluorescence Quenching of Europium(III) by the Interaction with Copper(II) or Nickel(II) Complex of N,N'-Disalicylidene-1,3-propanediamine

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Effect of the co-existence of the titled copper(II) or nickel(II) complex upon the fluorescence of europium(III) has been investigated in methanol. Intensities of the fluorescent bands at 580, 593, 618, 687, and 696 nm are significantly quenched by the addition of the copper(II) or nickel(II) complex but not by a simple metal salt, copper (II) nitrate trihydrate or nickel(II) nitrate hexahydrate.

Some lanthanoid ions and their complexes exhibit a characteristic fluorescence of each lanthanoid, and it is well known that these fluorescent properties are very often sensitive to the adduct formations with "synergic agents" such as trioctylphosphine oxide and trialkylphosphates and the complex formations with various organic molecules.[1-6] However, there are few studies on the effect of the co-existing metal ions or metal complexes upon the fluorescence of lanthanoid ions.[2,7,8] In the present work the fluorescent properties of europium(III) were investigated in methanol at room temperature by adding copper(Ⅱ) nitrate trihydrate, nickel(Ⅱ) nitrate hexahydrate, or copper(Ⅱ) or nickel (Ⅱ) complex of N,N'-disalicylidene-1,3-propanediamine (H_2saltn).

Some typical spectra are shown in Fig. 1. Fluorescent spectrum of europium(Ⅲ) nitrate hexahydrate shows the bands attributed to the $^5D_0 \longrightarrow {}^7F_J$ transitions at 580, 593, 618, 687, and 696 nm (trace a). These bands were not almost affected when copper(Ⅱ) nitrate trihydrate or nickel(Ⅱ) nitrate hexahydrate was added to the solution (traces b and c). On the other hand, the addition of Cu(saltn) or Ni(saltn) significantly quenched the fluorescence (traces d and e).

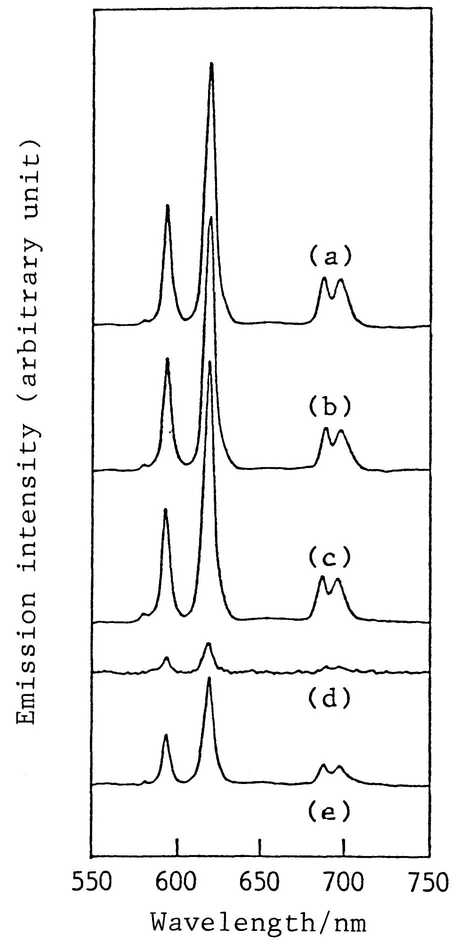

Fig. 1. Typical fluorescent spectra of Eu(Ⅲ) in methanol. Exciting wavelength is 394 nm. Ordinate scales are x 128 for (a), (b), (c),and (e), and x 256 for (d). [Eu(Ⅲ)] = 5 x 10^{-3} mol dm^{-3}. (a) without additive; (b) with $Cu(NO_3)_2 \cdot 3H_2O$ (5 x 10^{-3} mol dm^{-3}); (c) with $Ni(NO_3)_2 \cdot 6H_2O$ (5 x 10^{-3} mol dm^{-3}); (d) with Cu(saltn) (1 x 10^{-3} mol dm^{-3}); (e) with Ni(saltn) (1 x 10^{-3} mol dm^{-3}).

It is generally accepted that the luminescent intensity decreases by the radiationless energy loss through the excited state of other molecules, which are near the exciting species.6) It is well known that M(saltn) (M = Cu, Ni) and related complexes of tetradentate Schiff bases function as bidentate ligands through the two phenolic oxygens.9) Giuffrida et al. reported the bi- and trinuclear complexes Ln[M(saltn)]$_n \cdot$ $X_3(H_2O)_m$ (M = Cu(Ⅱ) or Ni(Ⅱ); X = NO_3^-, NCS^-, ClO_4^-, or Cl^-; n = 1 or

2).[10,11] Furthermore, Gatteschi et al. determined the crystal structures of $[\{Cu(saltn)\}_2Gd(NO_3)_2(H_2O)](NO_3)\cdot 2C_2H_5NO_2$, and $[\{Cu(salen)\}_2Gd(H_2O)_3](ClO_4)_3\cdot 2Cu(salen)\cdot 0.5C_2H_5NO_2$ (H_2salen = N,N'-disalicylideneethylenediamine), in which the copper(II) and gadolinium(III) ions are indeed bridged by two phenolic oxygen atoms.[12,13] From the above discussions, we presume that the decrease of fluorescent intensity of europium(III) is attributable to the formation of a M(II)-Eu(III) (M = Cu, Ni) binuclear species bridged by the phenolic oxygen atoms (see Fig. 2). In relation to this, it should be pointed out that the fluorescent intensity of tris(1,3-diketonato)europium(III) complexes is quenched in the dimeric species.[14] Figure 3 shows the relationships between the relative intensities (the sum of the five fluorescent bands) and the concentration ratios of M(saltn) to europium(III). Cu(saltn) is more effective for the fluorescence quenching than Ni(saltn). This may relate to the different electronic structures of copper(II) and nickel(II) ions. Further studies using various types of metal complexes are in progress in our laboratories.

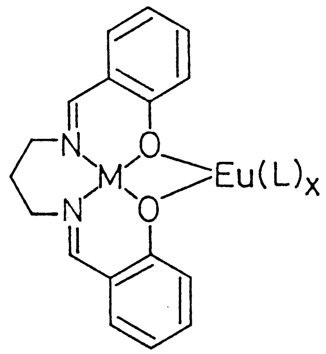

Fig. 2. Schematical representation of M(saltn)-Eu(III) bonding. L denotes the coordinated nitrate ion, water, or methanol molecule.

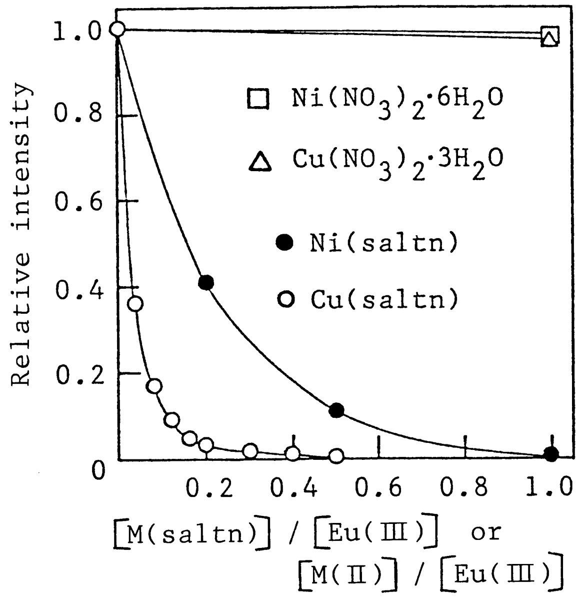

Fig. 3. Relationships between relative intensities and concentration ratios of M(saltn) or M(II) to Eu(III). The intensity for [M(saltn)] = [M(II)] = 0 is taken as an unit. [Eu(III)] = 5×10^{-3} mol dm^{-3}.

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