The Mechanism of Amine Sensitization of the Emission of Tris(dibenzoylmethano)europium(III)

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(Received April 14, 1975)

The mechanism of enhancement of emission quantum yield of the methanol solution of tris(dibenzoylmethano)europium(III) by triethylamine has been investigated. Lifetime of Eu^{3+} resonance emission of the chelate did not change remarkably when triethylamine was added. The aspect of temperature dependence of the emission intensity was similar for both the chelate itself and the chelate-amine adduct under direct excitation of the metal level, but differed under excitation of the ligand. It was suggested that the sensitization is mainly due to a suppression of nonradiative process in the ligand triplet state.

Intramolecular energy transfer process in rare earth metal chelate has been studied by many investigators since Crosby *et al.*[1] suggested that the transfer of energy from ligands to excited electronic levels of metal takes place *via* the lowest triplet state of ligands. Their assumption was supported by Matsuda *et al.*[2] who observed a sensitized emission of Eu chelate in the presence of La chelate, in which an energy transfer, if any, was allowed only from the ligand triplet of the latter to the ligand triplet of the former. The time constant of energy transfer from the triplet state to the rare earth level was determined by Tanaka *et al.* to be of the order of 10 ns.[3] Their observation proved to be in good coincidence with the cascade mechanism of Crosby *et al.*[1]

On the other hand, a number of mechanisms have been proposed for the sensitization and quenching effect of the emission of rare earth metal compound.[4–6] It is well-known that there are several rare earth metals, such as europium and terbium, which give narrow emission in solutions. Their quantum yields are generally low, varying with ligand, solvent, or temperature.

In order to study the energy loss due to the solvent or other added components, it is convenient to consider the three separate processes, (I) quenching in the ligand level, (II) quenching in the upper levels of the ions, and (III) quenching in the emitting levels of the metal. Weissman[7] assumed that process (I) is important but no experimental confirmation was given. Kropp and Dawson[8] showed that process (II) is effective in methanol solution of $Eu(NO_3)$. Contribution of quenching process (III) was investigated by Dawson *et al.*[9] who showed that for terbium chelate strong temperature dependence of the emission intensity can be explained in terms of quenching of the emitting level *via* thermal excitation to the lowest triplet state of the ligand.

Sato and Wada[10] also reported that the yield of the emission of europium chelate in several solutions depends upon the energy difference between the triplet level of ligand and the emitting level of europium ion, a maximum yield being observed at a certain value of the energy difference. They interpreted the change of the quantum yield as due to the thermal deactivation process from the emitting level of rare earth ions.

In a preceeding paper[11] the effect of several amines on the yield of the emission of tris(dibenzoylmethano) europium(III) (EuD_3) was reported with emphasis on the effect of triethylamine. It was shown that the yield of the emission of EuD_3 in methanol solution increased by a factor of 11 when triethylamine was added. It was suggested that the enhancement of the yield can be ascribed to the suppression of some deactivation process in which the solvent may take part. The present paper deals with the mechanism of the sensitization of the emission of EuD_3 by triethylamine molecule.

Experimental

Materials. Tris(dibenzoylmethano)europium(III) was prepared from europium oxide and dibenzoylmethane according to the method of Charles and Perroto.[12] Mp 231 °C. Elemental analysis; found: C, 65.73; H, 3.87%; calcd for C, 65.78; H, 3.87%. Triethylamine was used after fractional distillation. Commercial fluorescence spectrograde methanol was used as a solvent without further purification.

Method of Measurement. EuD_3-triethylamine were dissolved in methanol at a concentration of 10^{-4} mol/l. Emission and excitation spectra were observed with a Hitachi MPF II fluorescence spectrometer. The emission lifetimes of the EuD_3 and EuD_3-triethylamine complex in methanol were measured as follows. Fresh solutions of the sample were introduced into 3 mm diameter quartz tube and immersed in a liquid nitrogen or other coolants in a transparent quartz dewar. An exciting light pulse from Gellar coaxial nitrogen laser,[13] 10 kW peak power with 20 ns pulse width, was focussed on the sample through an aqueous $CuSO_4$ filter solution. The emission was focused on a Canon optical fiber guide (6 mm diameter, 1000 mm length) after transmission of Toshiba filters UV-39 and VR-60, and detected by HTV-R500 red sensitive and short transit time photomultiplier placed in an electric shield room. In order to minimize stray capacitance, an output resister of the photomultiplier was directly connected with the BNC receptacle of a vertical amplifier 7A11 plug-in-unit of Tektronix oscilloscope 7904. The apparatus had overall rise time of less than 10 ns. The measurement of the temperature dependence was carried out with the same sample tube and Dewar as was used in the lifetime measurement. After being cooled with liquid nitrogen, the sample was left standing to allow the temperature to rise gradually, and the emission intensity and the temperature were measured simultaneously. The tem-

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** Present address: Naka Works, Hitachi Ltd. Katsuta, Ibaraki, perature was measured with a Cu-constantan thermocouple placed in the sample solution just above the excitation volume.

First, the samples were excited by 365 nm radiation of a high pressure Hg-Xe lamp filtered through a $CuSO_4$ aqueous solution and a Toshiba UV-DIC filter, or by 465.8 nm line of an Ar ion laser Coherent Radiation model CR52G. The former radiation excited the ligand level efficiently. According to our observation of the excitation spectra of Eu^{3+} ion, 465.8 nm line of Ar laser coincides with one of the absorbing lines of Eu^{3+} ion ($^7F_0$-$^5D_2$). Since the ligand has no absorption at 465.8 nm, we can directly excite the ion which forms the chelate.

The temperature dependence of the emission intensity under 365 nm and 465.8 nm excitation was measured at 538 nm ($^5D_1$-$^7F_1$) and 612 nm ($^5D_0$-$^7F_2$), respectively. For the measurement of intensity, it is important to note that the magnetic field of Ar laser seriously affects the photomultiplier. In order to eliminate the effect, we used a long optical fiber between a monochrometer and HTV photomultiplier R 306 placed in a shield room. The output of photomultiplier and thermocouple was led into the x axis and y axis of a x-y recorder.

Results

Emission and Excitation Spectra. EuD_3 and triethylamine were mixed at 15 °C in methanol solution. The concentration of the former was kept constant (7.67×10^{-5} mol/l), and that of the latter was varied from 5.27×10^{-4} to 3.37×10^{-2} mol/l. The solutions were left standing more than 30 min, and the emission and excitation spectra were observed. At room temperature, there was no difference between the excitation and emission spectra of EuD_3 solution and those of EuD_3–amine complex solution. Even at 77 K the difference was slight.

The change of absorption spectrum of the EuD_3 solution by addition of the amine was also slight. Thus, the enhancement of emission intensity is not due to an increase in the photon uptake in the excitation process.

Lifetime of the Emission. The solution contains 4.72×10^{-4} mol/l EuD_3 and 4.25×10^{-1} mol/l triethylamine. Because of the weak intensities, lifetime measurements were made only for the strongest transition of $^5D_0$–$^7F_2$. The measured lifetimes of EuD_3 and EuD_3–triethylamine complex at several temperature are listed in Table I. Charles and Ohlman[4] showed that the lifetime of EuD_3–amine complex is 8 times as long as that of EuD_3. However, our measurement showed no remarkable difference between the lifetimes of EuD_3 and amine complex in methanol solutions.

The efficiency of the emission of the complex in methanol solution is 11 times as large as that of EuD_3. Such a striking enhancement can hardly be considered to be due to a decrease in the radiative lifetime. As the quantum yield of emission is low (0.005 in methanol)[9] it is also impossible that an increase in the radiationless lifetime of the emitting level causes the enhancement without affecting the overall lifetime. The effect should be attributed to the change in the radiationless process in the ligand levels.

Table 1. Emission lifetimes of EuD_3 and EuD_3-triethylamine complex

Materials	Lifetime		
	77 K	273 K	289 K
EuD_3 in MeOH	440 μs	384 μs	140 μs
EuD_3-TA in MeOH	439	394	136

Temperature Dependence of Emission Intensity. The solution contains 4.72×10^{14} mol/l EuD_3 and 4.25×10^{-1} mol/l triethylamine. Figure 1 shows the temperature dependence of the emission intensity at 538 nm ($^5D_1$–$^7E_1$) of EuD_3 and amine complex in methanol solution when only Eu^{3+} ions were excited by 465.8 nm of Ar ion laser. Both curves are normalized at the maximum intensities. With a rise in temperature they show sharp decrease at the temperature of phase change, presumably because of inhomogeneity of solid solution.

When the ligand was excited by 365 nm radiation, the emission intensities changed with temperature as shown in Fig. 2. In contrast to the 465.8 nm excitation, the intensity still decreased gradually with the rise of temperature in the liquid state, after a sharp decrease at melting point. This strongly suggests that the deactivation in the ligand level plays a dominant

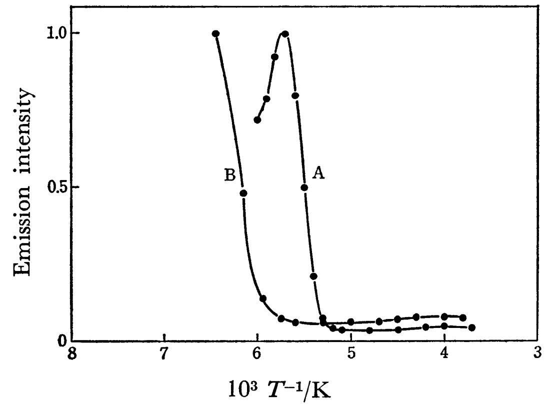

Fig. 1. Temperature dependence of the emission intensities excited by Ar ion laser. A; EuD_3, B; EuD_3-amine complex. Wave length; 538 nm ($^5D_1-{}^7F_1$).

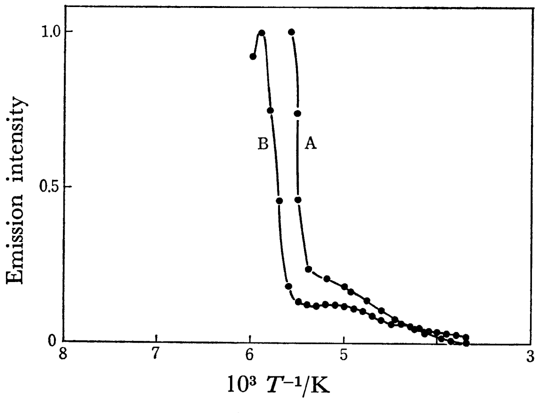

Fig. 2. Temperature dependence of the emission intensities excited by 365 nm radiation. A; EuD_3, B; EuD_2-amine complex. Wave length; 538 nm ($^5D_1-{}^7F_1$).

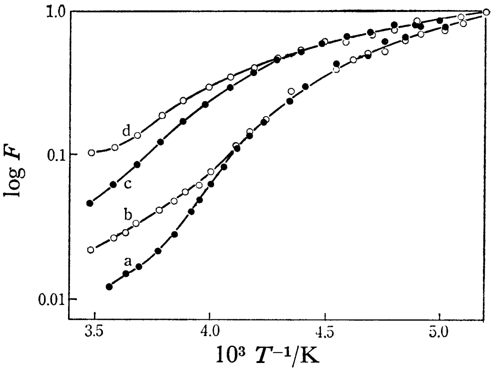

Fig. 3. Logarithm of the emission intensities measured at 612 nm and 538 nm versus $1/T$ in the case of excitation by 365 nm radiation. a; EuD_3, 612 nm, b; EuD_3, 538 nm, c; EuD_3-TA, 612 nm, d; EuD_3-TA, 538 nm.

role in the intensity change. Figure 3 shows the relation between $1/T$ and the emission intensities of 612 nm and 538 nm in logarithmic scale in the temperature range 192—294 K for both EuD_3 and the amine complex when the ligand was excited. All the curves are normalized at the value of 192 K.

The change of intensity of EuD_3 with temperature was larger than that of the complex. The intensity of 612 nm decreased much faster than that of the 538 nm radiation at temperatures above 240 K. Since the difference between a and b is similar to that between c and d (Fig. 3), the differences can be ascribed to the phonon process in $^5D_0$ level of EuD_3 in which triethylamine takes no part. The formation of EuD_3–amine complex causes the difference between a and c as well as that between b and d. It should be noted that these differences appeared only in the case of ligand excitation.

Mechanism of Thermal Quenching

Figure 4 shows the energy levels of EuD_3 and the processes involved in the excitation of emission from Eu^{3+} ion. Here, n_T, n_A and n_B denote deactivation rates from ligand triplet T and from metal levels A ($^5D_0$) and B ($^5D_1$), respectively, r_A and r_B the corresponding radiative rate constants and k_A, k_B, k_C, k_{TA}, k_{TB} and k_{BT} the internal transition rates from A to B, B to A, C to B, T to A, T to B and B to T, respectively.

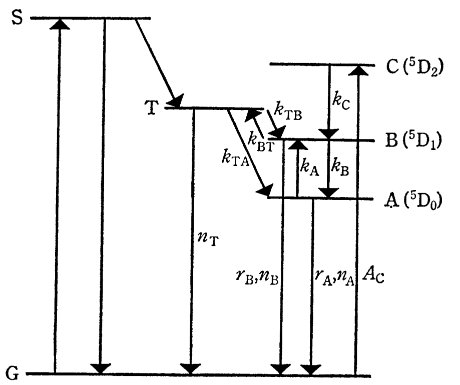

Fig. 4. Energy diagram of chelate. S and T are singlet and triplet of chelate, A, B and C are the excited states of europium ion.

To account for the thermal property of emission, the temperature dependence of radiationless process should be taken into consideration. Since the internal rates k_B, k_{TA} and k_{TB} can be regarded as temperature independent, we can assume that k_{BT}, k_A, n_A and n_T depend on temperature, because the former two are endothermic processes and the latter two are slow processes liable to external deactivation. n_A can be regarded as constant below 260 K, as the emission lifetime becomes constant. For k_{BT} and k_A, we assume that the transfer takes place *via* Boltzmann distribution, so that

$$k_{BT} = k_{TB}\exp(-E_{TB}/kT),$$

and

$$k_A = k_B\exp(-E_{BA}/kT),$$

where E_{TB} and E_{BA} are the energy differences between level T and level B and between level B and level A, respectively. Since both the values of E_{TB} and E_{BA} are nearly 1600 cm^{-1}, the Boltzmann factors amount to as 10^{-4} at room temperature.

As for the rate constant n_T, we assume that the deactivation of the triplet levels takes place by a thermalization which is established by the interaction between the vibronic levels of the triplet state of the ligand and the phonon levels of the solvent molecules; n_T is then expressed approximately as

$$n_T = k_n\exp(-E/kT),$$

where E is the average energy difference between the triplet state and some dissipative state which might be provided by weak bonded solvent molecules, and k_n is the density factor in the dissipative process in the triplet state.

The intensity of 538 nm emission ($^5D_1$-$^7F_1$) at temperature T under ligand excitation is expressed, after some manipulation, by

$$I = \frac{\alpha k_{TB}}{k_{TB}+k_{TA}+k_n\exp(-E/kT)},$$

where $\alpha = I_0 r_B/(r_B+n_B+k_B)$ and I_0 is the pumping intensity to the ligand triplet. This equation is rewritten as

$$\ln F = -E/kT + \ln(k_n/k_{TB}), \qquad (1)$$

where $F = 1/I - 1/I'$ and $I' = k_{TB}/(k_{TA}+k_{TB})$. Since I' can be assumed to be constant, we can plot in F *versus* T^{-1} by selecting an appropriate value of I' in order to obtain a straight line. The Arrhenius plots of 538 nm emissions of EuD_3 and amine complex are shown in Fig. 5, with best values of $1/I'$, 4.0 for the former and 4.5 for the latter (intensity scale is the same as in Fig. 2), from which the values of energy difference E are obtained: 2300 cm^{-1} for EuD_3 and 1400 cm^{-1} for the complex. It is to be noted that the energy values are not sensitive to the values of I'. Next, we define the radiative ratio R by

$$R = (k_{TB}+k_{TA})/k_n,$$

which can be obtained from the emission intensity ratio

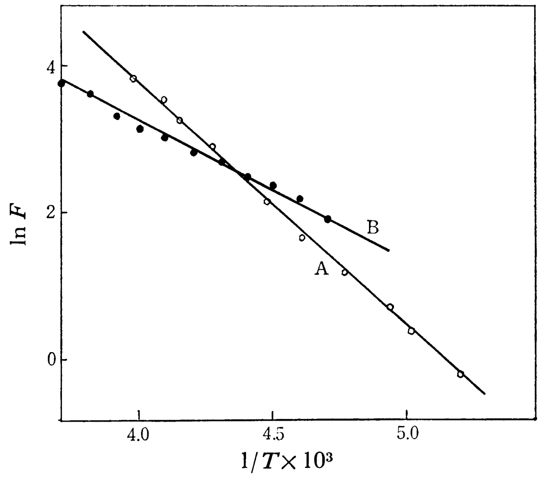

Fig. 5. Arrhenius plot of thermal quenching of emission measured at 538 nm. A; EuD_3, B; EuD_3-amine complex.

$$I_2/I_1 = \frac{k_{TB}+k_{TA}+k_n \exp(-E/kT_1)}{k_{TB}+k_{TA}+k_n \exp(-E/kT_2)} = \frac{R+\exp(-E/kT_1)}{R+\exp(-E/kT_2)}, \tag{2}$$

where I_1 and I_2 are the intensities observed at T_1 and T_2. The ratio R can be obtained from Eq. (2). Any pair of temperature T_1 and T_2 gives consistent R values, which indicates that the assumed mechanism is appropriate.

In the same way, the emission intensity of 612 nm ($^5D_0$-$^7F_2$) is represented by

$$I = \frac{(k_{TA}+\beta k_{TB})\gamma}{k_{TA}+k_{TB}+k_n \exp(-E/kT)} \tag{3}$$

where $\beta = k_B/(k_B+r_B+n_B)$ and $\gamma = I_0 r_A/(r_A+n_A)$, both of which can be assumed constant. Arrhenius plots are obtained from Eq. (3) in a similar way and we get energy difference E and the ratio R. The values of E and R for EuD_3 and amine complex calculated from both 538 and 612 nm emission are listed in Table 2.

TABLE 2. ENERGY DIFFERENCE BETWEEN THE LIGAND TRIPLET LEVEL AND QUENCHING LEVEL AND THE RATIO OF THE RADIATIVE TO NONRADIATIVE PROCESSES

Materials	Emission Wave length	E		R
EuD_3	538 nm	2270 cm^{-1}		2×10^{-7}
			av. 2225 cm^{-1}	
EuD_3	612	2180		3×10^{-7}
EuD_3-TA complex	538	1390		8×10^{-4}
			av. 1507	
EuD_3-TA complex	612	1624		4×10^{-5}

Mechanism of Amine Sensitization

We have shown that the enhancement of emission intensity from Eu^{3+} ion is traceable to the change in the processes in the ligand levels. The values of I' for EuD_3 and the complex differ only by about 10%, which seems to circumscribe the range of the changes in k_{TB} and k_B (and possibly in k_{TA}). Table 2 shows that the ratio R of the complex is hundred to thousand times as large as that of EuD_3, although the value of E is somewhat smaller. The enhancement of the intensity in the amine complex seems to be entirely due to the large value of R, which is brought about by a marked decrease in the value of k_n. If we assume that the dissipative channel is provided by an interaction with solvent phonon state, weak bonds formed between the solvent molecules and chelate produce dense energy state near the vibronic band of the ligand to facilitate deactivation. Triethylamine forms a comparatively rigid bond with the chelate and replaces the solvent molecules, thus reducing the state density for deactivation.

It was found that at higher temperature the emission intensity of the amine complex decreased more rapidly than that of the chelate. This is presumably due to the fact that the amine molecule dissociates and is replaced by a solvent molecule. The lifetime of the 612 nm emission decrease abruptly above 273 K. This may be ascribed to the quenching in the $^5D_1$ and $^5D_0$ levels of EuD^{3+} ion.

We are grateful to Dr. A. Kuboyama of the National Chemical Laboratory for Industry of Tokyo for his stimulating discussion.

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