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The Amine Sensitization of the Fluorescence of Tris(dibenzoylmethano)europium(III)

Tadashi FUKUZAWA and Nozomu EBARA
College of General Education, The University of Tokyo, Tokyo

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The effect of amines on the efficiency of fluorescence of tris(dibenzoylmethano)europium(III) has been investigated in a methanol solution. Amines with low pK_b values seem to form 1:1 complexes with the chelate, and the change in the fluorescence intensity of the chelate is due exclusively to the formation of a complex, which fluoresces more strongly than the chelate itself. It seems that the sensitization of the fluorescence is due to the change in the relaxation lifetime. In the case of amines with aromatic moieties, sensitization through energy transfer may also take place, but this never occurs unless the amine molecule is present in the complex. The structure of the complex and the mechanism of sensitization are discussed.

Fluorescence in rare-earth chelates has been a subject of extensive study[1-5] because of its prospective applicability in laser devices. The excitation of the chelates in a wavelength region where only the ligands absorb light results in high yields of a sharp emission characteristic of the rare-earth metal ions. The intramolecular energy-transfer process has been investigated by Crosby, Whan, and Alire,[6] who compared the fluorescence of several rare-earth chelates and concluded that the transfer of energy from the ligands to resonance levels of metals took place *via* the triplet states of the ligands. Bhaumik and El-Sayed[7] have studied the sensitization of the fluorescence of the chelates by benzophenone and supported the above mechanism.

On the other hand, the third-body effect on the fluorescence efficiency of chelates has been investigated by

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[1] N. E. Wolff and R. J. Pressley, *Appl. Phys. Lett.*, **2**, 152 (1963).

[2] A. Lempicki and H. Samelson, *ibid.*, **2**, 159 (1963); *J. Chem. Phys.*, **39**, 110 (1963); *ibid.*, **40**, 2547 (1964); A. Lempicki, H. Samelson and C. Brecher, *Appl. Optics*, Suppl. on Chemical Lasers, 205 (1965).

[3] E. J. Schimitschek, *Appl. Phys. Lett.*, **3**, 117 (1963).

[4] H. Winston, O. J. Marsh, C. K. Suzuki, and C. L. Telk, *J. Chem. Phys.*, **39**, 267 (1963).

[5] V. A. Brophy and C. Brecher, *ibid.*, **40**, 2553 (1965).

[6] G. A. Crosby, R. E. Whan, and R. M. Alire, *ibid.*, **34**, 743 (1961).

[7] M. L. Bhaumik and M. A. El-Sayed, *J. Phys. Chem.*, **69**, 275 (1965); see Y. Matsuda, S. Makishima, and S. Shionoya, This Bulletin, **41**, 1513 (1968).

several authors,[8,9] in the expectation that an increase in the fluorescence quantum yield might favor its laser activity. These authors found that the addition of several amines or alkylphosphine oxides greatly affected the quantum yields of the europium resonance fluorescence in the solid state. These investigations, however, lacked quantitative treatment and involved no apposite mechanism of sensitization. Systematic studies are required to account for the sensitization scheme in the fluorescence of europium chelates. The present paper will deal with the effect of several amines on the fluorescence yield of tris(dibenzoylmethano)europium(III) (EuD_3) in a methanol solution.

Experimental

Materials. Tris(dibenzoylmethano)europium(III) was prepared from europium oxide and dibenzoylmethane according to the method of Charles and Perrotto.[10] Yellow prisms, mp 231°C.

Tris(dibenzoylmethano)cobalt(III) was prepared from cobalt oxide and dibenzoylmethane according to the method of Ginestra and Marucci.[11] Green prisms, mp 232°C.

The amines used were G. R.-grade triethylamine, piperidine, octylamine, benzylamine, 4-aminopyridine, *N*-1-naphthylethylenediamine, 9-aminoacridine, pyridine, aniline, *N*-methylaniline, *N,N*-dimethylaniline, acridine, 1-naphthylamine, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, and 2,5-diphenyloxazole; they were purified repeatedly by vacuum distilation or by recystallization.

Commercially-available spectrograde methanol, chloroform, and tetrahydrofuran were used as solvents without further purification.

Methods of Measurements. The absorption spectra were measured with a Hitachi EPS-2 type spectrophotometer, using 10 mm×10 mm quartz cells. It is very important to note that the difference spectrum exhibited a marked irregularity when both the reference and sample solutions showed large extinctions. Therefore, care was taken to avoid this wavelength range.

The fluorescence excitation spectra were measured as follows. The sample solutions contained in a 1 mm×10 mm quartz cell were excited with a 500 W Xenon arc through a Beckmann monochrometer. The radiation from the light source was modulated with a sector and was focused by a quartz lens at a normal incidence on the 10-mm surface of the cell. The fluorescence radiation emitted through the 1-mm surface of the cell was led into a photomultiplier, HTV 374, through several filters. The output of the photomultiplier was amplified with a PAR 122 Lock-in amplifier and displayed on a Toa EPR-2T recorder.

Results and Discussion

Complex Formation. Tris(dibenzoylmethano)europium(III) (EuD_3) and triethylamine were mixed at 15°C in a methanol solution, the concentration of the former being kept constant (7.67×10^{-5} mol/*l*), while that of the latter was varied. The solutions were left standing for more than 30 min, and then the difference spectra of the solutions were measured against a EuD_3 reference solution of the same concentration as that of the sample solutions (Fig. 1). A new peak appeared near 390 mμ, at which the amine did not absorb light, and the chelate absorption peak at 352 mμ seemed to shift gradually towards a shorter wavelength. The spectrum showed isosbestic points and indicated that a single complex was formed.

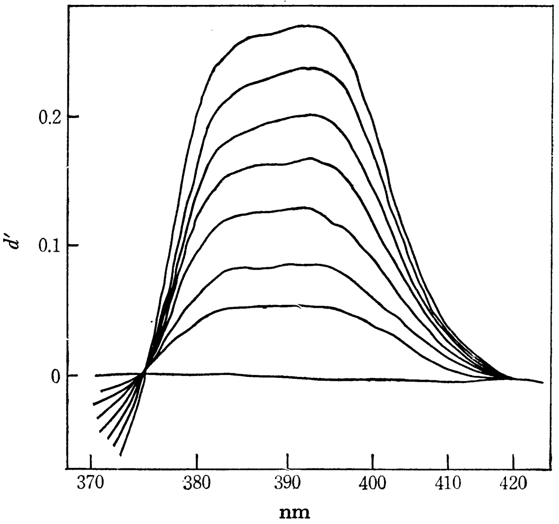

Fig. 1. Difference spectra of the mixtures of EuD_3 and triethylamine (reference EuD_3 solution)
EuD_3: 7.67×10^{-5} mol/*l*, amine: 3.37, 1.69, 0.843, 0.422, 0.211, 0.105 and 0.0527×10^{-2} mol/*l*

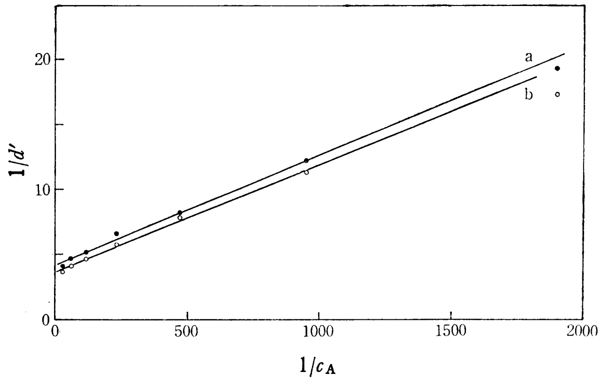

Fig. 2. Plot of $1/d'$ against $1/c_A$ for the mixtures of EuD_3 and triethylamine
a. at 384 mμ, b. at 396 mμ

The plot of $1/d'$ at several wavelengths against $1/c_A$ according to the following equation gave straight lines (Fig. 2), which showed that an equilibrium was reached between the chelate and the triethylamine to form a 1 : 1 complex[12];

$$1/d' = (1+1/c_E K)/(\varepsilon_C-\varepsilon_E)c_A + 1/(\varepsilon_C-\varepsilon_E)c_E$$

where d' is the optical density of the difference spectrum; c_E and c_A, the initial concentrations of the chelate and

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[8] R. G. Charles and R. C. Ohlmann, *J. Chem. Phys.*, **40**, 3131 (1964); *J. Inorg. Nucl. Chem.*, **27**, 119 (1965).

[9] F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.* **41**, 157 (1964).

[10] R. G. Charles and A. Perrotto, *J. Inorg. Chem.*, **26**, 373 (1964).

[11] A. L. Ginestra and G. Marucci, *Ann. Chim.*, (Rome), **54**, 891 (1964).

[12] A 1 : 2 complex may as well be conceived provided no 1 : 1 complex is formed at all. However this is unlikely in a methanol solution.

amine respectively; ε_E and ε_C the molar extinction coefficients of the chelate and the complex respectively, and K, the equilibrium constant.

Similar plots gave similar straight lines when piperidine, octylamine, benzylamine, 4-aminopyridine, and *N*-1-naphthylethylenediamine were used instead of triethylamine (Fig. 3). The calculated equilibrium constants are listed in Table 1. In the case of 9-aminoacridine, the regular change in the spectrum indicated that a complex was formed, but the change was too small to allow an evaluation of the equilibrium constant.

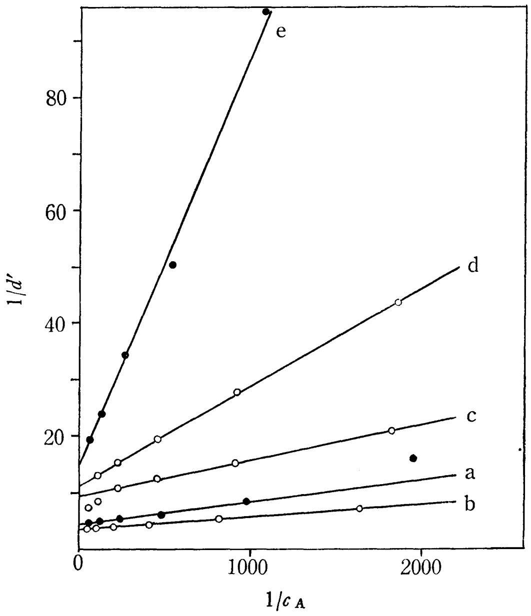

Fig. 3. Plots of $1/d'$ against $1/c_A$ for
a. piperidine: EuD_3 5.86×10^{-5} mol/l, c_A 1.64×10^{-2}—5.12×10^{-4} mol/l, b. octylamine: EuD_3 6.93×10^{-5} mol/l, c_A 1.95×10^{-2}—6.10×10^{-4} mol/l, c. benzylamine: EuD_3 5.06×10^{-5} mol/l, c_A 1.75×10^{-2}—5.48×10^{-4} mol/l, d. 4-aminopyridine: EuD_3 4.73×10^{-5} mol/l, c_A 8.95×10^{-3}—5.37×10^{-4} mol/l, e. N-1-naphthylethylenediamine: EuD_3 4.73×10^{-5} mol/l, c_A 1.48×10^{-3}—2.32×10^{-5} mol/l

TABLE 1. EQUILIBRIUM CONSTANTS AND FLUORESCENCE INTENSITY RATIOS OF EUROPIUM CHELATE-AMINE COMPLEXES

	Amine	pK_b	K	F(C)[a)]/F(E)
I	triethylamine	3.13	480	11.4
	piperidine	2.88	510	12.6
	octylamine	3.35	1760	10.0
	benzylamine	4.65	1680	5.97
	aminopyridine	4.82	650	4.76
	naphthyl-ethylenediamine	4.04[b)]	2020	5.28
	aminoacridine	4.55	+	
II	pryidine	8.82		
	aniline	9.40		
	methylaniline	9.30		
	dimethylaniline	8.94		
	acridine	8.50		
	naphthylamine	10.08		
	tetramethyl-phenylenediamine	6.76		
	diphenyloxazole	—		

a) F(C): calculated fluorescence intensity of the complex
b) value of ethylenediamine

On the other hand, aromatic amines such as pyridine, aniline, *N*-methylaniline, *N,N*-dimethylaniline, acridine, 1-naphthylamine, *N,N,N',N'*-tetramethylphenylenediamine, and 3,5-dipehnyloxazole showed no evidence of forming complexes.

An inspection of Table 1 suggests that the ease with which the complex is formed is determined mainly by the following two factors:

1) Only amines with low pK_b values (lower than 5 in the present case) tend to form complexes. This parallelism is not consistent with the other properties of amines, such as the ionization potentials and the dipole moments.

2) The steric factor affects the equilibrium constant. The equilibrium constant is greater for primary amines and smaller for secondary or tertiary amines. In the case of 9-aminoacridine the equilibrium constant seems to be small, probably because of the dense steric disposition in the proximity of ring nitrogen.

Charles and Ohlmann[8)] have prepared solid 1 : 2 complexes of EuD_3 with several amines involving pyridine and aniline (a 1 : 1 complex in the latter case) and have suggested that the amine is attached directly to the europium atom. This assumption has been supported by later workers[13–15)] because of its consistency with current theory and with the experimental results, as exemplified by an X-ray analysis of a hydrated EDTA complex of lanthanum $LaAH_4\cdot7H_2O$ (AH_4 means the acidic form of EDTA) by Hoard *et al.*,[16)] who showed that four of seven water molecules in the crystal were bonded directly to the La atom. They nevertheless did not reject the possibility that some of the complexes were formed by a van der Waals force (or a charge-transfer force) between the amine and the ligand. It is evident that the present result conforms to the assumption of Charles, in which a dative bond is formed between europium and nitrogen by the intrusion of amine molecules into the ligands.

To confirm the assumption more directly, we have prepared tris(dibenzoylmethano)cobalt(III) (CoD_3) and examined whether it could form complexes with amines in tetrahydrofuran or in chloroform. As the coordination number of Co(III) is six, and since it never exceeds six, the formation of a complex, if ever, must involve interaction between the amine and the ligand. Our experiment showed that CoD_3 formed no complex with triethylamine. It is hoped that the NMR chemical shift measurement of the NH proton in a complex of EuD_3 with a primary or secondary amine will reveal unambiguously the bonding aspect.[17–19)]

The present experiment differed from that of Charles

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13) L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris *J. Amer. Chem. Soc.*, **86**, 5117 (1964).

14) H. Bauer, J. Blanc, and D. L. Ross, *ibid.*, **86**, 5125 (1964).

15) E. L. Muetterties and C. M. Wright, *ibid.*, **87**, 4706 (1965).

16) J. L. Hoard, M. D. Lind, and B. Lee, *ibid.*, **87**, 1612 (1965).

17) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, **1970**, 422.

18) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *ibid.*, **1970**, 749.

19) G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, **92**, 6979 (1970).

in that the complex was 1 : 1 rather than 1 : 2 and in that pyridine and aniline formed no complex: this is not surprising, because the amine molecule had to replace the already-bonded solvent molecule to form a complex in the solution. In fact, the spectra of the mixture solutions of EuD_3 and aliphatic amines turned out to change within a short time after mixing, with the above consideration. The details of the time dependence will be presented elsewhere.

Fluorescence. The above mixed solutions of EuD_3 and amines have been subjected to the measurement of their fluorescence excitation spectrum. The excitation of the chelate in the ultraviolet region gave rise to a sharp red emission which peaked at 612 mμ; this was identified with the europium resonance fluorescence from $^5D_0$ to $^7F_2$.2) In the case of amine which did not fluoresce, such as triethylamine, piperidine, or octylamine, the excitation spectra of the mixed solutions were measured with this emission peak alone. When amine itself fluoresced, as in 1-naphthylamine, the excitation spectra of a chelate solution (E), amine solutions (A) of various concentrations, and mixed solutions (M) in which the concentrations of the solutes were the same as in E and A were measured either with a 612 mμ emission (e) using Toshiba filters VR-60 and UV-39 or with an appropriate wavelength range (a) in which the amine fluorescence had an appreciable oscillator strength, but neither the amine nor chelate absorbed radiation. In the cases of 1-naphthylamine and *N*-1-naphthylethylenediamine, for example, the 422—520 mμ region using a combination of filters, UV-39, VV-42, and VY-44, was found to be appropriate.

For the sake of conciseness and clarification, the following notations are adopted:

F(A) and F(E)
fluorescence intensities of the amine solution and the chelate solution respectively

F(M)
fluorescence intensity of the mixed solution

F_A(M) and F_E(M)
parts of F(M) due to amine and europium respectively, so that $F_A(M)+F_E(M)=F(M)$

F^e and F^a as in F^e(A)
fluorescence intensities measured at 612 mμ (e) and at (a)

The excitation wavelength and the concentration of the amine are not specified.

The intensities were corrected for absorption and the emission of the partner molecules as follows:

1) The fluorescence of amine occasionally had a nonvanishing intensity, even at 612 mμ, at which point the europium fluorescence was to be measured (perhaps due to the low resolution of the filters). To obtain the intensity of the europium fluorescence at this wavelength in the mixture, $F_E{}^e$(M), the portion of the intensity due to amine, $F_A{}^e$(M), must be subtracted from the observed value, F^e(M). As the amine fluorescence was found to be affected strongly by the presence of a chelate, as will be shown later, $F_A{}^e$(M) can not be equated with F^e(A), but is obtained by:

$$F_A{}^e(M) = F^e(A) \times F^a(M)/F^a(A)$$

It is to be recalled that the effect of absorption on the above values has already been eliminated.

On the contrary, the observed fluorescence intensity, F^a(M), can be ascribed solely to amine, so that only the succeeding correction applies in this case.

2) The amine and chelate absorbed radiation at the same time in the exciting wavelength range, thereby reducing mutually the number of photons which, otherwise, were to be absorbed by the partner molecules. This was taken into account by multiplying the respective intensity values, F_E(M) or F_A(M), by:

$$f = (c\varepsilon+c'\varepsilon')[1-\exp(-c\varepsilon l)]/c\varepsilon[1-\exp\{-(c\varepsilon+c'\varepsilon')l\}]$$

where l is the cell length (0.1 cm). The other notations, c, c', ε, and ε', require some comment; c (c') represents the concentration, and ε (ε'), the extinction coefficient, at the exciting wavelength. When the fluorescence of the amine is going to be modified, the unprimed numbers, c and ε, refer to the chelate and the primed numbers, c' and ε', to the amine. Inversely, when the fluorescence of the chelate is going to be modified, the former refer to the amine, and the latter, to the chelate. In what follows, the intensity values, F_E(M) and F_A(M), are to be understood as already corrected for this factor.

3) The amine fluorescence was partly absorbed by the chelate. The extent of this factor could not be evaluated, but it seemed to be small and was disregarded.

A) Amines Which Do Not Form Complexes: Amines of the second group in Table 1 did not form complexes. The excitation spectrum of the EuD_3 solution $F_E{}^e$(E or M) did not change on the addition of these amines over the whole range of excitation wavelengths covering 370 mμ. In the case of 1-naphthylamine, for example, the radiation of 300 mμ excited the amine molecule almost exclusively, and $F_E{}^e$(M) was very weak. An increase in the amine concentration did not seem to affect the intensity, indicating that no transfer of energy from the amine to chelate took place. This also the case for aniline and pyridine, which were excited at 280 and 260 mμ respectively. It is concluded that free amine molecules, excited or unexcited, do not affect the fluorescence of the EuD_3 in solution.

B) Amines Which Form Complexes: Amines of the first group in Table 1 formed complexes. When these amines were added to the solution of EuD_3, the $F_E{}^e$(M) increased markedly on excitation at 370 mμ as the concentrations of amines increased. As most of the amines involved did not absorb any exciting radiation, excitation transfer from the amine molecule to the chelate molecule did not account for the sensitization. Moreover, the dielectric behavior of the solvent, which might affect the fluorescence intensity, did not change noticeably upon the addition of amine of such low concentrations. This is consistent with the fact that the addition of ketones, such as acetone or cyclohexanone, to a similar extent affected neither the absorption spectrum nor the fluorescence quantum yield.20)

The fluorescence intensities, $F_E{}^e(M)/F^e(E)$, were plotted against the optical densities, d', of the difference spectra of the solutions near the peak of the band of the EuD_3-amine complex; they gave straight lines (Figs. 4

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20) Unpublished data.

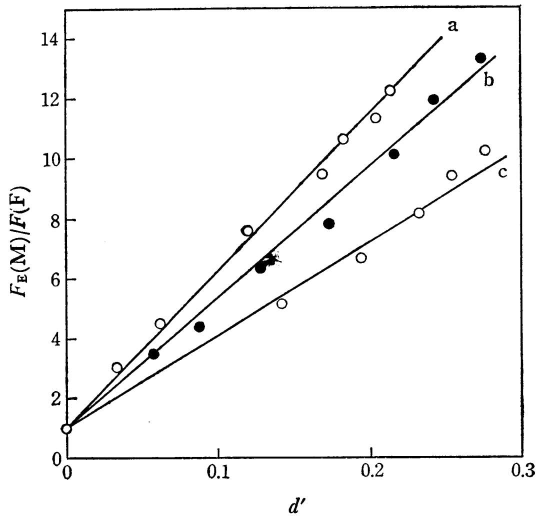

Fig. 4. Plots of $F_E(M)/F(E)$ against the optical density of the difference spectrum a. piperidine, b. triethylamine, c. octylamine concentrations are the same as in Figs. 1—3.

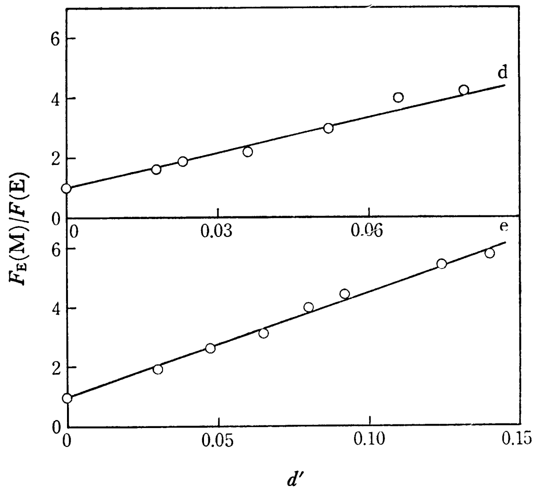

Fig. 5. Plots of $F_E(M)/F(E)$ against the optical density of the difference spectrum. The concentrations are the same as in Fig. 3. d. 4-aminopyridine, e. benzylamine

and 5). As d' is proportional to the concentration of the complex, as can be shown easily, the change in the fluorescence intensity, which is also proportional to it, should be attributed solely to the complex formation. The sensitization mechanism involving long-range interaction can again be ruled out. It follows, from our knowledge of the equilibrium constants and the intensity-optical density plits, that the fluorescence efficiencies of the complexes in a methanol solution are 4 to 12 times as high as that of the uncomplexed chelate (Table 1).

In the case of *N*-1-naphthylethylenediamine, the $F_E^e(M)/F^e(E)$ ratio was plotted at each of these excitation wavelengths, 370, 330, and 290 mμ. These wavelengths, were chosen for the following reasons. The radiation of 370 mμ excited almost exclusively the ligand of the chelate, the radiation of 290 mμ excited mainly the amine, and that of 330 mμ, excited both the chelate and amine. All of the plots showed a good linearity, but the slope was the greatest for the last plot (Fig. 6). As the slope of the plot for 370 mμ is a measure of the increase in the quantum yield of the fluorescence of the chelate by complex formation, it must be invariant under a change in the excitation wavelength, provided only that the ligand is excited at its first absorption band, as was the case for aliphatic amine complexes. Therefore, the increase in the slope should be attributed to the cooperative excitation-transfer process which took place from the amine to the chelate.

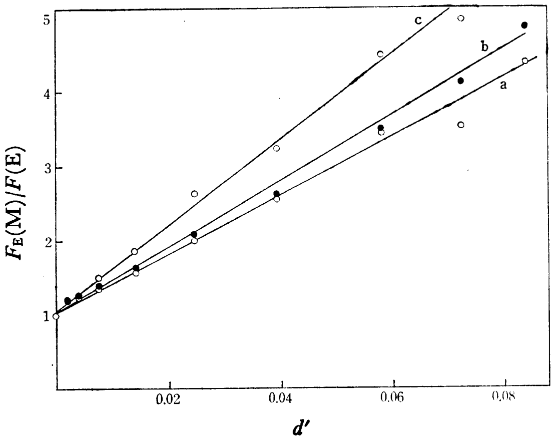

Fig. 6. Plots of $F_E(M)/F(E)$ for *N*-1-naphthylethylenediamine against the optical density of the difference spectrum.
a: excited at 370 mμ, b: 330 mμ, c: 290 mμ.

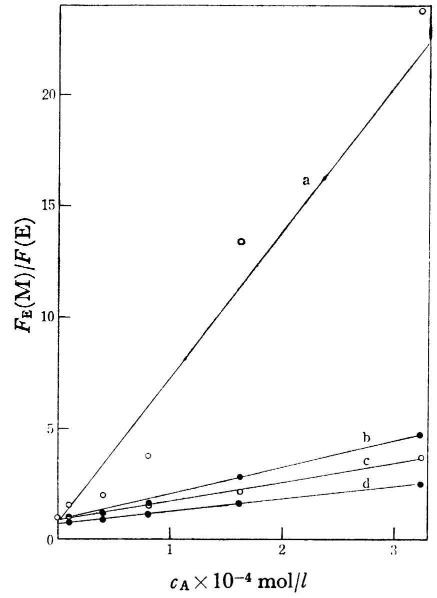

Fig. 7. Plots of $F_E(M)/F(E)$ for 9-aminoacridine against the concentration of amine.
a: excited at 410 mμ, b: 390 mμ, c: 370 mμ, d: 340 mμ

This was also the case for 9-aminoacridine. In Fig. 7, $F_E^e(M)/F^e(E)$ is plotted against the concentration of amine, as the optical density is not available because of the superposition of the amine absorption. The radiation of 370 or 340 mμ mainly excites the chelate, but that of 390 or 410 mμ mainly excites the amine. The latter two plots have larger slopes than the former.

The linearity of the $F_E^e(M)/F^e(E)$ ratio of *N*-1-naphthylethylenediamine against d', and the fact that naphthylamine, which failed to form a complex, did not affect the $F_E^e(M)$, suggest that the energy transfer takes place only from the amine molecule which is attached to europium. Here again, the long-range or collisional-transfer mechanism can be discarded.

On the other hand, the excitation spectrum of the complex with benzylamine or aminopyridine fell to zero intensity near 260 mμ, although the amine absorbed radiation at this wavelength. It seemed, therefore, that the energy transfer did not take place in these complexes.

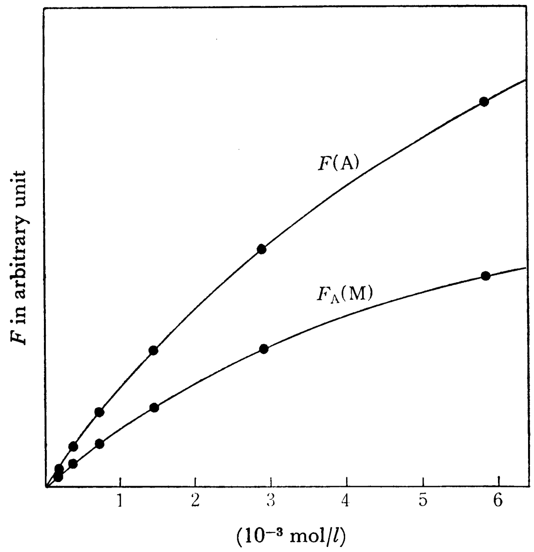

Fig. 8. Plots of F_A(M) and F(A) for aniline against the concentration of amine.

C) Fluorescence of Amine: Figure 8 shows the effect of the concentration on the fluorescence intensity of aniline, both in the absence and in the presence of the chelate, F^a(A) and $F_A{}^a$(M), on the excitation at 280 mμ, the peak of the excitation spectrum of aniline. Their ratio, $F_A{}^a(M)/F^a(A)$, is almost constant irrespective of the concentration of aniline: it amounts to 0.58. This suggests that the encounter-quenching mechanism accounts for the effect. The same is the case for tetramethylphenylenediamine on excitation at 330 mμ, the intensity ratio of which is 0.55 (Fig. 9).

When the amine forms a complex, the encounter-quenching mechanism applies only to free amine molecules and the $F_A{}^a(M)/F^a(A)$ ratio is expected to depend upon the concentration of amine, because the amount of the complex is most proportional to the latter. Unfortunately, in the cases of *N*-1-naphthylethylenediamine and 9-aminoacridine, both of which formed complexes, the expected concentration dependence could not be ascertained. Probably, the absorption of amine trailed into the transmission range of the filter with which the fluorescence was measured, and this precluded any exact determination of the fluorescence intensity. However, a comparison of 1-naphthylamine and *N*-1-naphthylethylenediamine showed that the fluorescence of naphthylamine was quenched to a somewhat smaller extent when the amine molecule was attached to the chelate.

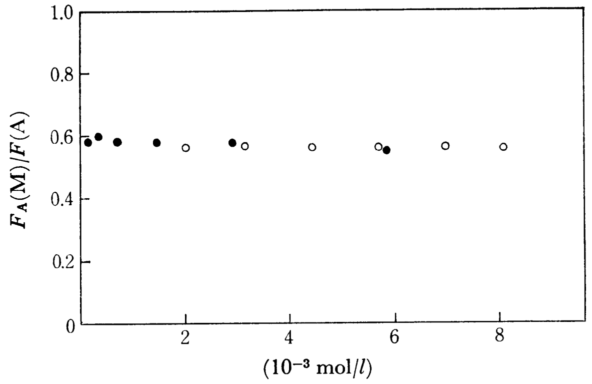

Fig. 9. Plots of $F_A(M)/F(A)$ against the concentration of amine.
●: aniline, ○: tetraemthylphenylenediamine

D) Mechanism of Sensitization: It seems to be established that the sensitization of the fluorescence of EuD_3 with amine take place solely by way of complex formation, and that two processes compete in the sensitization: sensitization involving energy transfer, and that not involving energy transfer. The following mechanisms are likely to hold.

1) Sensitization involving no energy transfer: There seem to be two concerted mechanisms; both serve to increase the relaxation lifetime of the chelate. Sensitization in the solid state, in which there is no participation of a solvent, suggests that the piling up of ligand molecules is responsible for it. The intrusion of amine molecules may restrict the free arrangement of ligand molecules so that the equilibrium structures of the ground state and the excited state of the complex become alike. This may reduce the Franck-Condon factor and suppress the radiationless process.

In solution, the fluorescence intensity of EuD_3 is a function of the nature of the solvent.20) The solvent molecules seem to attach to the europium atom and exchange easily with other free solvent molecules. This may favor a radiationless transition by providing an energy continuum like that of predissociation near the energy levels of the chelate, thus invoking Fano configuration interaction,21,22) or by bringing anharmonicity to the vibrational wavefunctions. Amines form comparatively rigid bonds and may interrupt this process.

2) Sensitization involving energy transfer: Excitation transfer takes place only from the ligand amine molecule, not from the free amine molecule. The collision of the free amine and the chelate only results in the quenching of the fluorescence of amine (but not of the fluorescence of the chelate). This suggests that the amine excitation energy is transferred directly to the europium atom, not through the ligand dibenzoylmethane molecule. This was strongly supported by the fact that 9-aminoacridine, the triplet and singlet levels of which lie below the corresponding levels of the ligand of the chelate, transfers its energy to the chelate, while the reverse process does not occur. This, in turn, gives support to the assumption that the complex is formed by an amine-europium bond.

The absence of energy transfer in benzylamine and in 4-aminopyridine still remains a problem. It may be due either to the intensity of the light source being too low to excite the amine to a detectable amount or to the energy separation being too large for crossing over to occur in the transfer process.

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21) U. Fano, *Phys. Rev.*, **124**, 1866 (1961).
22) M. Bixon and J. Jortner, *J. Chem. Phys.*, **48**, 715 (1968).