BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2404—2409 (1970)

Effect of Halogenation on Intramolecular Energy Transfer in Rare Earth Chelates

Makoto Morita[*1] and Shigeo Shionoya

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo

(Received February 27, 1970)

Using tris-dibenzoylmethanates of terbium(III) and other rare earths(III) we investigated the effect of halogenation of the central hydrogen of a 1,3-diketonate ligand on the luminescence properties of these chelates in rigid media. As a result of halogenation, all chelates display blue shift of the ligand phosphorescence, the intensity of the rare earth emission I_{RE} relative to that of the phosphorescence I_{ph} is markedly decreased in the order of H→Cl→Br, and the lifetime of the phosphorescence τ_{ph} decreases in the same order. These facts provide the evidence that the intramolecular energy transfer takes place *via* the triplet state of the ligand. In halogenated and nonhalogenated terbium chelates the ratio of the probability of energy transfer P_t estimated from the quantity $I_{\mathrm{RE}}/I_{ph}\tau_{ph}$ to the overlap integral S between the phosphorescence spectrum and the terbium absorption spectrum is found to be roughly constant. These results lead us to the conclusion that intramolecular energy transfer is governed by the resonance mechanism due to exchange interaction.

For the intramolecular energy transfer from the ligand to the central metal ion in rare earth chelates, Crosby's proposal[1,2] has been generally accepted. This states that excitation energy is transferred from the triplet state of the ligand to the resonance level of the rare earth ion. In our previous paper,[3] we reported perturbation effects on the triplet states, such as oxygen effect and external heavy atom effect usually known in organic molecules, and gave some facts which strongly suggest Crosby's mechanism. Some other investigators[4-6] used the technique of triplet quencher to study this problem and presented some useful information.

Recently we have studied[7] this energy transfer process under the excitation of the triplet state of europium chelates by utilizing intermolecular triplet-triplet energy transfer from lanthanum chelates, and have presented evidence for Crosby's proposal. Further, we have investigated[8] the correlation between the energy transfer probability and the stretching vibration frequency of the chelate bond as obtained from infrared absorption measurements, and have concluded, according to an approximated treatment of Dexter's theory,[9] that the energy transfer process is dominated by the exchange interaction of the π electron system of the ligand triplet state with the f electron system of the central rare earth ion.

In parallel with these studies, we have continued the study of heavy atom effect on this intramolecular energy transfer with the purpose of investigating the transfer mechanism. Substitution of a halogen atom for 2-hydrogen of 1,3-β-diketonate as the ligand is expected to give an internal heavy atom effect, because this should change the probability of the transition from the triplet state to the ground singlet state and consequently influence the luminescence process of chelates. One may expect that this internal heavy atom effect is much more strongly observed than the external heavy atom effect. In the present paper, the luminescence properties of various halogenated tris-dibenzoylmethanates are reported. Exchange interaction has

---

[*1] Present address: Department of Industrial Chemistry, College of Technology, Seikei University, Kichijoji, Musashino-shi, Tokyo.

1) G. A. Crosby, R. E. Whan and R. M. Alire, *J. Chem. Phys.*, **34**, 743 (1961).

2) G. A. Crosby and R. E. Whan, *J. Mol. Spectry.*, **8**, 315 (1962).

3) S. Shionoya, Y. Matsuda, M. Morita and S. Makishima, Proc. Internatl. Conf. Luminescence (Budapest, 1966), p. 1709 (1968).

4) M. L. Bhaumik and M. A. Elsayed, *J. Chem. Phys.*, **43**, 787 (1965).

5) V. L. Ermolaev, V. G. Aleshin and E. A. Saenko, *Dokl. Akad. Nauk SSSR*, **165**, 1048 (1965); *Sov. Phys. Dokl.*, **10**, 1186 (1966).

6) V. L. Ermolaev, E. A. Saenko, G. A. Domrachev, Yu. K. Khundenski and V. G. Aleshin, *Opt. Spectry.*, **22**, 466 (1967).

7) Y. Matsuda, S. Makishima and S. Shionoya, This Bulletin, **41**, 1513 (1968).

8) Y. Matsuda, S. Makishima and S. Shionoya, *ibid.*, **42**, 356 (1969).

9) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

been further confirmed to dominate the intramolecular energy transfer process.

Experimental

1) **Samples.** Tris-dibenzoylmethanates of rare earth ions were prepared by the usual procedures.[2] Halogenated chelates were obtained by the direct substitution method similar to that used by Collman *et al.*[10] for transition metal chelates. Chlorinated chelates were also prepared by the indirect method, *i. e.* by treating rare earth nitrates or acetates with 3-chloro-3-dibenzoylmethane prepared by the method reported by Kochetkov *et al.*[11] The two different methods were found to give the same chlorinated products. However, the former method was mostly employed to obtain halogenated compounds in this paper. We have synthesized various samples of $Ln[(C_6H_5CO)_2CX]_3 \cdot H_2O$ in which Ln stands for Eu, Sm, Tb, Dy, Gd and La, and X is H, Cl or Br (abbreviated hereafter as LnD, LnDCl or LnDBr). Chemical analysis of rare earth content as well as measurement of infrared absorption spectra were carried out in order to identify the obtained products.

2) **Spectroscopic Measurements.** Infrared absorption spectra were measured by means of the KBr disk method with a Hitachi EPI-2 infrared spectrophotometer attached with an NaCl or KBr prism (for NaCl or KBr region, respectively). Ultraviolet and visible absorption spectra were obtained at room temperature using a Cary model 14 spectrophotometer for both alcohol and chloroform solutions with chelate concentrations 5×10^{-5} mol/*l*.

Measurement of emission spectra was made at liquid nitrogen temperature by using a Kipp and Zonen prism double monochromator for ether-toluene (4 : 1) solutions with chelate concentration 5×10^{-4} mol/*l*. For the reference, powder samples of chelates were also measured. The 254 nm line obtained from the combination of a 100 W high pressure mercury lamp and an appropriate set of filters were used as the exciting source, and the response of an EMI 9558QB photomultiplier was fed to a millivolt recorder.

In the measurements of time-resolved emission spectra and emission lifetime, an Edgerton xenon flash lamp of type FX-3 attached with ultraviolet pass filters was used as the exciting light source. Chelate solutions of ether-toluene (4 : 1) with the concentration 5×10^{-3} mol/*l* were irradiated at liquid nitrogen temperature by pulse light from the flash lamp having a half-width of 2 μsec and frequency of 25 Hz. The response of an RCA 931A photomultiplier gated for 1 μsec was recorded with delay times ranging from zero to 100 μsec. Lifetime was obtained directly from the decay characteristics of the time-resolved emission spectra.

Results and Discussion

Infrared absorption spectra of halogenated rare earth chelates were found not to involve the absorption of 1200 cm^{-1} region which is due to the C–H in-plane bending mode. The carbonyl stretching bands in 1500 and 1600 cm^{-1} region are simplified in the halogenated products and the absorption band due to the M–O bond stretching does not change appreciably upon halogenation. These facts are considered to give structural evidence for the halogenation as was done for chromium

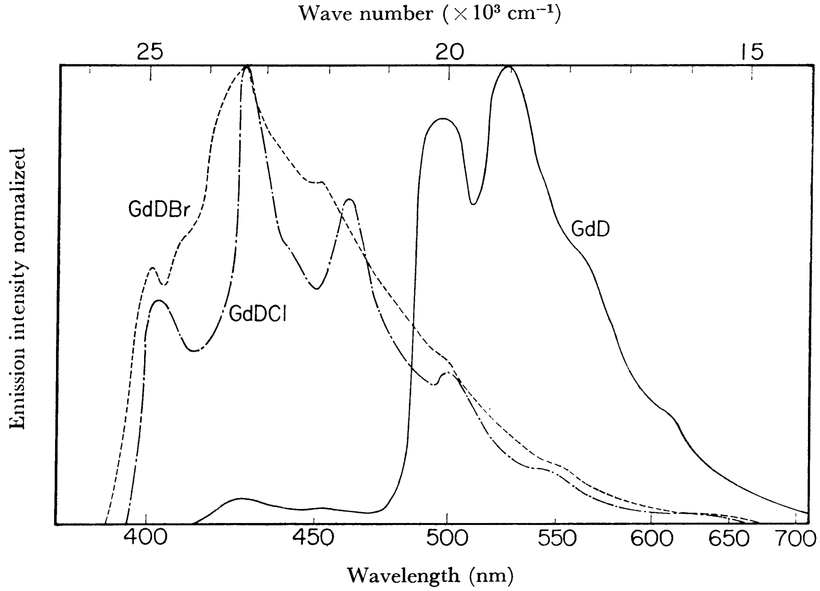

Fig. 1. Emission spectra of GdD, GdDCl and GdDBr in ether-toluene solutions (4 : 1) at 77°K under steady excitation by the 254 nm mercury line.

---

[10] J. P. Collman, R. A. Moss, H. Maltz and C. C. Heidel, *J. Amer. Chem. Soc.*, **83**, 531 (1961).

[11] N. K. Kochetkov, S. D. Sololov, N. M. Vagustova and E. E. Nifarten, *Dokl. Akad. Nauk SSSR*, **133**, 598 (1960).

chelates.[12]

The ultraviolet absorption spectra of LnD involve two broad bands at about 250 nm and 350 nm, respectively.[1] As a result of halogenation the 250 nm band strongly increases its absorbance and slightly shifts to longer wavelengths, while the 350 nm band almost disappears. We therefore used the mercury line of 254 nm as the exciting source in this study.

The emission spectra of ether-toluene solutions of GdD, GdDCl and GdDBr under steady excitation at 77°K are shown in Fig. 1. These spectra demonstrate how the ligand emission changes as a result of halogenation. If these spectra under steady excitation are compared with time-resolved emission spectra with a delay time of about 60 μsec, it turns out that in the GdD spectrum the weak band at about 430 nm is that of fluorescence while the strong band ranging from 480 to 600 nm is that of phosphorescence, and

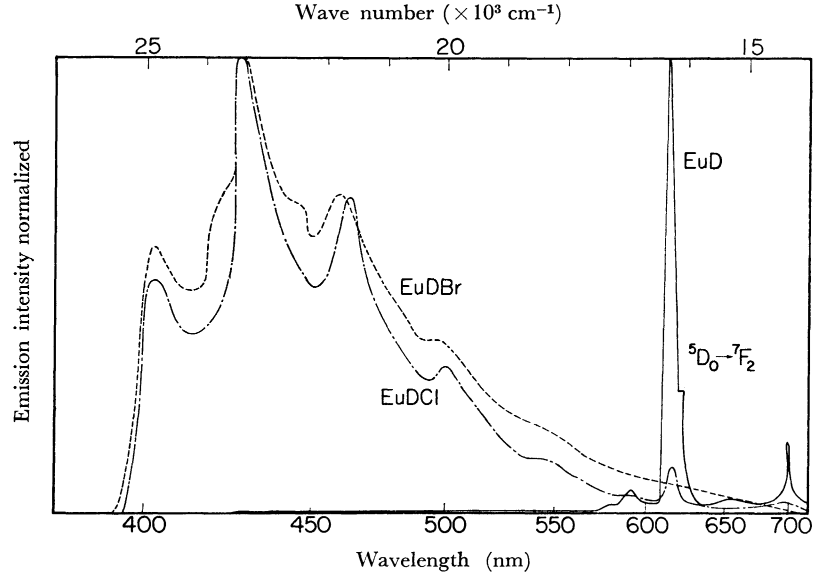

Fig. 2. Emission spectra of EuD, EuDCl and EuDBr in ether-toluene solutions (4 : 1) at 77°K under steady excitation by the 254 nm mercury line.

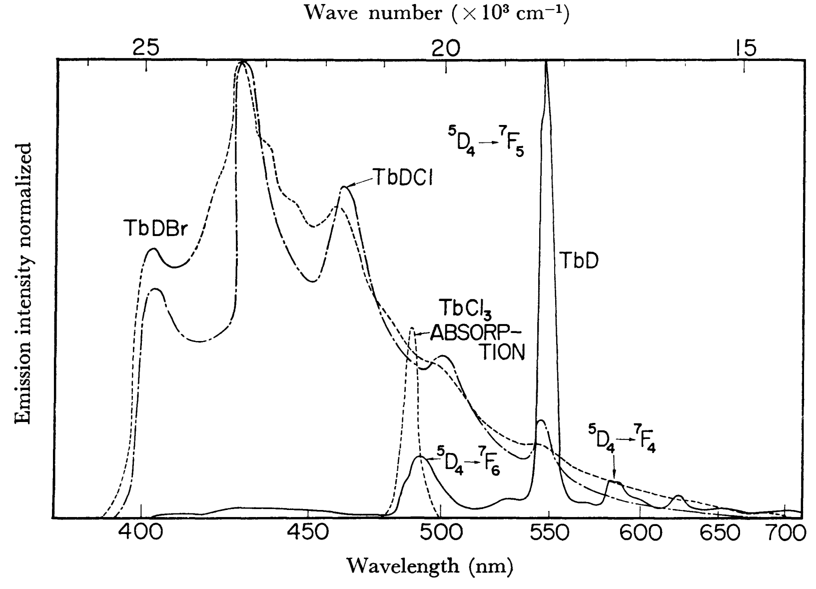

Fig. 3. Emission spectra of TbD, TbDCl and TbDBr in ether-toluene solutions (4 : 1) at 77°K under steady excitation by the 254 nm mercury line.

---

[12] P. R. Singn and R. Sahai, *Aust. J. Chem.*, **20**, 639 (1967).

that in the case of GdDCl and GdDBr the spectra observed under steady excitation are only those of phosphorescence. It is noted that as a result of halogenation the phosphorescence spectrum is markedly blue-shifted, but the shape and peak position of the spectrum are nearly the same among the halogenated chelates.

The results of the emission spectrum measurements for a series of LaD, EuD, TbD, SmD and DyD and their halogenated derivatives are as follows. Lanthanum chelates show broad band emission of the ligand which is analogous to gadolinium chelates. Other chelates show sharp line emissions due to central rare earth ions in addition to the ligand emission. As examples, the emission spectra of europium chelates and terbium chelates are given in Figs. 2 and 3, respectively. It was found that in all cases the ligand emission spectra are quite similar to those of gadolinium chelates.

However, it should be noted, as is observed from these figures, that the intensity of the ligand emission relative to that of rare earth emission strongly increases as a result of halogenation. For example, although EuD shows hardly any ligand emission, EuDCl and EuDBr exhibit pronounced ligand phosphorescence. In the case of EuDCl the emission lines due to $^5D_0 \rightarrow ^7F_J$ transition of Eu^{3+} ion are found only weakly at the tail of the strong ligand phosphorescence without the detectable change in the positions of the lines. In the case of EuDBr, the emission lines of Eu^{3+} ion are much more weakened. They are scarcely observed in glassy solutions as shown in this figure, although they are clearly found in a powder sample in which phosphorescence is completely quenched.

As in the case of europium chelates, terbium chelates have similar features of the halogenation effect. The variations of the emission intensity of rare earth ion as well as of the ligand are more clearly found in terbium chelates than in europium chelates. The emission spectra of samarium chelates, although not shown here, are also characterized by the halogenation effect. SmD has emissions of both ligand and rare earth ion with nearly equal intensities. However, in SmDCl and SmDBr the emission of ligand appears strongly and the emission of Sm^{3+} ion is almost quenched just as in the case of europium chelates. In the case of dysprosium chelates, the effect of halogenation is somewhat different. Namely, although DyD does not show Dy^{3+} emission, it becomes observable at around 500 nm in powder samples of DyDCl and DyDBr. This is interpreted as a result of the increase of the matching between the energies of the triplet state and the Dy^{3+} resonance levels caused by the blue shift of phosphorescence.

The decay time was obtained from time-resolved emission spectra. It was found that phosphorescence lifetime of GdD is 610 μsec while that of GdDCl and GdDBr decreases to 5.6 μsec and 4.1 μsec, respectively.

The results of the spectral measurements are summarized as follows. 1) The phosphorescence spectra of halogenated chelates are apparently blue-shifted in comparison with non-halogenated chelates, and chlorinated and brominated chelates have similar spectral features. 2) As a result of halogenation, the intensity of the ligand emission increases markedly, and instead the intensity of the rare earth emission lines decreases in the order H→Cl→Br. 3) The phosphorescence lifetime of gadolinium chelates decreases in the same order H→Cl→Br.

From these facts, one is led to the conclusion that the substitution of halogen atoms for hydrogen, *i.e.* the internal halogen effect, gives influences quite similar to the case of the external heavy atom effect.[3]

Let us next consider this substitution effect. In the case of naphthalene and its halogenated derivatives, relative decrease of the phosphorescence lifetime is H(1.0)→Cl(0.126)→Br(0.0078) against the relative increase of molecular weight of H(1.0)→Cl(1.27)→Br(1.62).[13] The internal heavy atom effect is known to depend predominantly on the weight of heavy atoms. Therefore, if we assume that for the phosphorescence lifetime of rare earth chelates the change of the same order of magnitude with halogenation as in the case of naphthalene and its derivatives is obtained, the lifetime of halogenated gadolinium chelates is estimated to fall into an order of magnitude of 10 μ to 100 μsec. The observed lifetime is comparable in magnitude with this value. However, since the peak position and shape of phosphorescence spectra change as a result of halogenation in rare earth chelates, it is inferred that the substitution effect in rare earth chelates is a pseudo-internal heavy atom effect. Hence, this substitution effect is considered to give the same conclusion as derived from the external heavy atom effect.[3] This then presents further evidence for Crosby's proposal that the intramolecular energy transfer takes place *via* the triplet states.[1,2]

Let us discuss the precise mechanism of the intramolecular energy transfer from the results obtained above. The theory of intermolecular energy transfer due to the resonance mechanism in condensed systems developed by Dexter[9] could be considered to be applicable to our present case of rare earth chelates.[5,6,8] Since intramolecular energy transfer takes place *via* the triplet state, the probability of the transfer P_t is given by the emission efficientcy of rare earth ion η divided by the lifetime of the ligand phosphorescence τ_{ph} as

$$P_t = \eta/\tau_{ph} \qquad (1)$$

Here η is expressed by the intensity ratio of the rare earth emission to the ligand phosphorescence I_{RE}/I_{ph}. We have to estimate the overlapping of the

---

[13] V. L. Ermolaev, *Opt. Spectry.*, **11**, 266 (1961).

phosphorescence spectrum of the ligand with the absorption spectrum of the rare earth ion. The overlap integral S is given by

$$S=\int I_{ph}(E)A(E)\mathrm{d}E, \tag{2}$$

where $I_{ph}(E)$ represents the phosphorescence spectrum and $A(E)$ the absorption spectrum of rare earth ion, both being normalized to unit area.

In order to obtain the values of P_t with Eq. (1), those rare earth chelates which display appreciably both ligand phosphorescence and rare earth ion emission when halogenated must be used. Although we have examined various rare earth chelates as mentioned above, only terbium chelates were found to be appropriate for this purpose. In the case of europium and samarium chelates, the rare earth emission are almost quenched in brominated chelates in rigid media. We have further investigated the use of chelates with different ligands, but it was found that chelates with many other ligands commercially available are not so easily halogenated according to the direct substitution method. Therefore, we have to confine our discussion to terbium(III) tris-dibenzoylmethanate and its chlorinated and brominated ones in this paper.

Let us discuss the mechanism of intramolecular energy transfer in terbium chelates. The quantities of P_t, S, η and τ_{ph} are estimated as shown in Table 1. In obtaining S, the absorption spectra of rare earth ion were substituted by those of terbium(III) chloride in aqueous solution, because the absorption in chelate solutions is too weak to be measured. Since the ligand emission of TbD is very weak, the lifetime τ_{ph} could not be measured. Then, the relative τ_{ph} values for terbium chelates were substituted by those observed for gadolinium chelates. This substitution is allowed because only the relative value of the lifetime is important in our present analysis.

The transfer probability P_t due to exchange interaction is approximately given by[9)]

$$P_t(\text{exch}) = \text{const.}\ S\exp(-2R/L), \tag{3}$$

where R is, in the case of rare earth chelates, the bond distance between the metal ion and the ligand, and L is the effective Bohr radius for the excited and unexcited states of energy donor and acceptor.

On the other hand, the transfer probability P_t due to electric multipole interaction is given by

$$P_t(\text{multipole}) = \text{const.}\ S/R^s\tau_{ph}\tau_{\mathrm{RE}} \tag{4}$$

Here, s is 6, 8 or 10 corresponding to dipole-dipole, dipole-quadrupole or quadrupole-quadrupole interaction, respectively.

The magnitude of the spacial overlap of the wavefunctions of the rare earth ion and the oxygen atom of the ligand, expressed by $\exp(-2R/L)$ in Eq. (3), is nearly independent of halogenation, because the frequency of the metal-oxygen vibration as obtained by infrared absorption measurement remains nearly unchanged as a result of halogenation so that the value of R is regarded as not changing. Therfore, if the energy transfer in rare earth chelates under discussion is dominated by exchange interaction, the P_t/S values must be constant among chelates in the table. In the case of multipole interaction, since the lifetime of rare earth ion τ_{RE} is not usually affected by the kinds of ligands, the value of $P_t\tau_{ph}/S$ in Eq. (4), which is equal to η/S, must be constant. Therefore, the values of P_t/S and η/S were calculated and are shown in the table to examine which of these mechanisms is responsible.

It is noted that the values of η/S change in two orders of magnitude while those of P_t/S are in the same order. By taking account of the experimental error in estimating the shape of phsphorescence spectrum in TbD, we might be allowed to conclude that P_t/S is kept nearly constant among three compounds, although η/S changes appreciably.

Although only poor data are available for the moment, we may conclude that the intramolecular energy transfer in rare earth chelates is governed by the resonance mechanism due to exchange interaction, but not to electric multipole interaction, between the ligand triplet state and central rare earth ion. In fact, this conclusion is in agreement

TABLE 1. RELATIVE VALUES OF THE QUANTITIES CONCERNING ENERGY TRANSFER PROCESS FOR HALOGENATED TERBIUM CHELATES IN ETHER-TOLUENE SOLUTIONS AT 77°K

The meaning of the symbols is given in the text.

Compound	TbD	TbDCl	TbDBr
Overlap integral S	1.0 ±0.1	0.34 ±0.03	0.29 ±0.03
Emission efficiency η	1.00±0.03	0.0039±0.0003	0.0018±0.0002
Phosphorescence lifetime τ_{ph}	1.00±0.00	0.0092±0.0002	0.007 ±0.001
Transfer probability P_t	1.00±0.03	0.43 ±0.10	0.26 ±0.09
η/s	1.0 ±0.1	0.012 ±0.002	0.006 ±0.001
P_t/S	1.0 ±0.1	1.3 ±0.5	0.9 ±0.4

with that obtained by our previous investigation[8] in which the measurement of the infrared absorption spectra was used as the tool.

Conclusion

The substitution of chlorine and bromine atoms for the central hydrogen of the ligand has been performed in a number of dibenzoylmethanates of rare earth ions such as Eu, Tb, Sm, Dy, Gd and La. The changes of luminescence properties due to halogenation have been found to be remarkable. The intensity of the rare earth ion emission decreases in the order H→Cl→Br, while the phosphorescence spectra are blue-shifted and the intensity is strongly enhanced accompanied by the decrease of the lifetime. This is understood as being due to a pseudo-internal heavy atom effect, and provides evidence that intramolecular energy transfer takes place *via* the triplet state of the ligand. Luminescence features were examined further according to the theory of resonance energy transfer. In the case of terbium chelates, the ratio of the transfer probability to the overlap integral between the phosphorescence spectra and the rare earth absorption spectra has been found to remain nearly unchanged under halogenation. These facts lead us to the conclusion that the intramolecular energy transfer is caused by the resonance mechanism due to exchange interaction.

The authors would like to thank Dr. Y. Matsuda for his discussion. They are also indebted to Mr. S. Tamura and Miss F. Miyazawa of this Institute for the analysis of rare earth chelates.