A Study of Fluorescence in Some Tris- and Tetrakis-diketonates of Europium(III) by Examination of Absorption and Excitation Spectra

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From a spectroscopic study of tris- and tetrakis-diketonate complexes of europium(III) information on the mechanism by which radiation absorption in the ligand produces fluorescence characteristic of the metal ion has been obtained. Excitation and absorption spectra of the complexes in the solid state and in solution are used to show that energy transfer takes place wholly, or predominantly, from one level of the first excited singlet state to the triplet manifold of the ligand from which excitation of the europium(III) occurs. Problems in obtaining excitation spectra free from distortion are discussed.

DIKETONATES of europium(III) are known to emit orange-red fluorescence characteristic of the *f–f* transitions in the europium when they are irradiated with light in the near-u.v. region of the spectrum. Crosby [1,2] has proposed a mechanism for the process whereby energy is transferred from the triplet state of the ligand to the ^5D manifold of the europium(III) with subsequent radiative decay to the ^7F state. This outline mechanism has been further supplemented by information from time-resolved spectroscopy [3-6] and fine-structure in the emission spectra has been used to suggest stereochemical arrangements for europium(III) in the chelates.[7,8]

Published work of a mechanistic nature has been based on studies of the emission process or processes. However, although excitation spectra have been examined in photochemical studies of organic substances [9] their use in work on europium(III) diketonate systems appears to have been neglected. The only report [10] to our knowledge referring to europium excitation in such chelates deals but briefly with some studies carried out on solutions.

In the work to be described, fluorescence excitation spectra are examined for the europium(III) diketonates which are listed in Table 1. While the emphasis has been placed on measurements in the solid state, aspects of several systems have also been studied in solution in organic solvents. Reflectance spectra for the solid substances and, where required, absorption spectra of solutions have been obtained in the wavelength range (240—500 nm) covered in the excitation measurements.

TABLE 1

Diketone	Abbreviation used [a]	Europium chelate
1,3-Diphenylpropane-1,3-dione	Hdbm	$[Eu(dbm)_4]PIP$ [b] $Eu(dbm)_3$
1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione	Hpta	$[Eu(pta)_4]Na$
1,1,1-Trifluoro-4-(2-thienyl)-butane-2,4-dione	Htta	$[Eu(tta)_4]PY$ [c]
1-Phenylbutane-1,3-dione	Hba	$[Eu(ba)_4]PIP$ $Eu(ba)_3,2H_2O$
1,1,1-Trifluoro-4-phenylbutane-2,4-dione	Hbta	$[Eu(bta)_4PIP]$ $Eu(bta)_3,2H_2O$
1,1,1-Trifluoropentane-2,4-dione	Htfa	$[Eu(tfa)_4]PIP$ $Eu(tfa)_3,2H_2O$
1,1,1,5,5,5-Hexafluoropentane-2,4-dione	Hhfa	$[Eu(hfa)_4]PIP$ $Eu(hfa)_3,2H_2O$

[a] The ligand is considered to be derived from the diketone by removal of a hydrogen ion. [b] PIP Is the piperidinium ion. [c] PY Is the pyridinium ion.

Problems relating to the elimination of spectral distortion are considered. Practical implications of the results and some aspects of energy transfer leading to europium(III) excitation in the molecule are discussed.

EXPERIMENTAL

The europium(III) diketonates (Table 1) were prepared and purified as previously described.[11]

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

[2] G. A. Crosby, *Mol. Crystals*, 1966, **1**, 37.

[3] M. L. Bhaumik, G. L. Clark, J. Snell, and L. Ferder, *Rev. Sci. Instr.*, 1965, **36**, 37.

[4] M. L. Bhaumik and L. J. Nugent, *J. Chem. Phys.*, 1965, **43**, 1680.

[5] S. Sato and M. Wada, *Bull. Chem. Soc. Japan*, 1970, **43**, 1955.

[6] M. Tanaka, G. Yamaguchi, J. Shiokawa, and C. Yamanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 549.

[7] K. Kreher, E. Butter, and W. Siefert, *Z. Naturforsch.*, 1967, **22b**, 242.

[8] S. Björklund, N. Filipescu, N. McAvoy, and J. Degnan, *J. Phys. Chem.*, 1968, **72**, 970.

[9] C. A. Parker, 'Photoluminescence of Solutions,' Elsevier, London, 1968.

[10] Y. Matsukda, S. Makishima, and S. Shionoya, *Bull. Chem. Soc. Japan*, 1968, **41**, 1513.

[11] S. J. Lyle and A. D. Witts, *Inorg. Chim. Acta*, 1971, **5**, 481.

Spectra.—Electronic reflectance spectra were obtained using a Pye–Unicam SP 500-2 spectrophotometer fitted with a reflectance attachment having a magnesium oxide reference surface. The diketonates were diluted with potassium bromide (5 μM to 1·00 g of potassium bromide). It was confirmed that fluorescence of the europium(III) was not augmenting the reflected light by making a comparison with the corresponding (non-fluorescent) lanthanum complex. Solution spectra were taken in hexane with cells of 1 cm path-length using a Hitachi–Perkin-Elmer 139 spectrophotometer.

A standard Aminco–Bowman spectrophotofluorimeter was employed to obtain the fluorescence excitation spectra. The emission monochromator was set to pass light from the $^5D_0 \longrightarrow {}^7F_2$ transition (*ca.* 613 nm)[2] in europium(III). Frontal illumination and detection were used in examination of the solid samples (held in a de-mountable silica cell) and the thin films. The latter were prepared by controlled evaporation of ethanol or benzene solutions of a diketonate on a silica surface. On examination with a microscope (450×) ' film ' produced from ethanolic solutions turned out to consist of very small but discrete crystals covering approximately one third of the surface area of the silica. Benzene gave a continuous and therefore more uniform deposit with evidence for crystallinity only at the edges of the preparation. Unfortunately this solvent only appears to be suitable for those chelates containing phenyl groups.

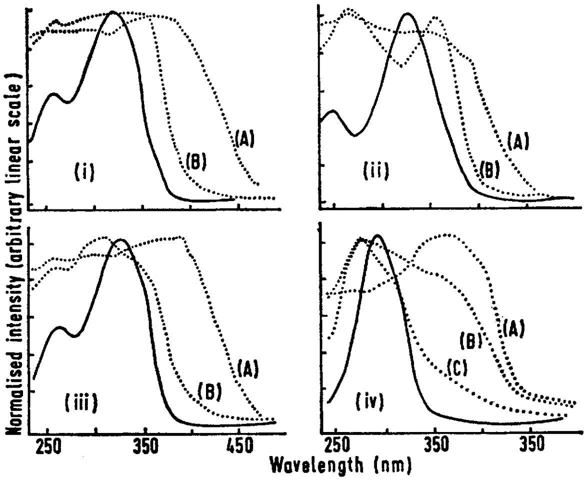

FIGURE 1 Fluorescence excitation and u.v. reflectance spectra of solid samples of various europium(III) diketonates; (i)—(iv) the solid line represents the u.v. reflectance spectrum of a KBr mixture and curve (A) represents the fluorescence excitation spectrum of the neat compound; (i) [Eu(bta)$_4$]PIP, curve (B) is the excitation spectrum of the solid diluted with KBr in the ratio 1 : 100 (wt/wt); (ii) [Eu(ba)$_4$]PIP, curve (B) is the excitation spectrum of the solid diluted with KBr in the ratio 1 : 540; (iii) Eu(bta)$_3$,2H$_2$O, curve (B) is the excitation spectrum of the solid diluted with KBr in the ratio 1 : 100; (iv) Eu(tfa)$_3$,2H$_2$O, curves (B) and (C) are the excitation spectra of the solid diluted with KBr in the ratios 1 : 5 and 1 : 50 respectively

Excitation spectra from hexane solution were examined using right angled illumination–detection geometry[9] in a cell of 8 mm × 8 mm cross-section.

Corrections to Excitation Spectra.—(*a*) The light intensity–wavelength relation for the Xenon arc source (Mazda type XE/D, ref. no. 98-0352) was determined experimentally by monitoring the output at 2 nm intervals between 240 and 500 nm using a photomultiplier tube of known response (E.M.I. 9665B). A computer programme was written to use this data to correct excitation spectra to constant light intensity.

(*b*) Excitation spectra from solutions were corrected for inner filter effects[12] by assuming the validity of the Beer–Lambert law at all wavelengths and using the measured molecular extinction coefficients.

(*c*) A ' spike ' at 307 nm, due to second order diffraction at the excitation monochromator, was eliminated graphically from each spectrum.

RESULTS

Figure 1 provides a range of uncorrected spectra taken using solid samples. It is seen that there are considerable differences in shape between the absorption spectrum obtained by reflectance measurement and the excitation spectrum for the same chelate–potassium bromide mixture. Further, in most instances, excitation spectra appear to change considerably with change in chelate ' concentration ' in the potassium bromide ' diluent.' A major problem in obtaining excitation spectra in solution is known to arise from so-called inner filter effects.[12] It is reasonable to assume that similar problems will be encountered in measurements on solids.

The inner filter effect was therefore examined in solution where it can be arranged to arise from attenuation of the incident light beam by the chelate substance. (Fluorescence radiation is readily shown to be transmitted efficiently through the solution.) The results in Table 2 show how the apparent wavelength for maximum excitation can change with solute concentration for a europium diketonate.

TABLE 2

The apparent wavelength for maximum excitation, $\lambda_{\text{max.}}$, at various concentrations of [Eu(ba)$_4$]PIP in hexane

Concn. (10^6M)	230	60	30	15	8	4
$\lambda_{\text{max.}}$ (nm)	368	357	350	340	332	330

If a correction is made for absorption of incident radiation then for some but not all systems reasonable agreement is obtained between the solution absorption spectrum and the excitation spectrum at the same concentration in the common solvent (Figure 2). There is also agreement

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[12] Ref. 9, p. 220.

between the corrected excitation spectra for the solutions and the reflectance spectrum although one might anticipate some minor discrepancies attributable to matrix differences between the samples. Hence for solutions from which excitation spectra are recorded by the method described here essentially undistorted spectra are obtained (see for example Figure 2) by taking proper account of inner filter effects. Exceptions can, however, arise if, as is not uncommon for this class of substance, the chelate is partly decomposed in solution. The example quoted in Table 2 is a case in point. The corrected excitation spectra for solutions of 15 × 10^{-6} and 4 × 10^{-6}M were found to be coincident and to be in reasonable agreement with the reflectance spectrum but not with the absorption spectrum from the corresponding solution. Decomposition was confirmed by the eventual spontaneous deposition of a white substance from the solution.

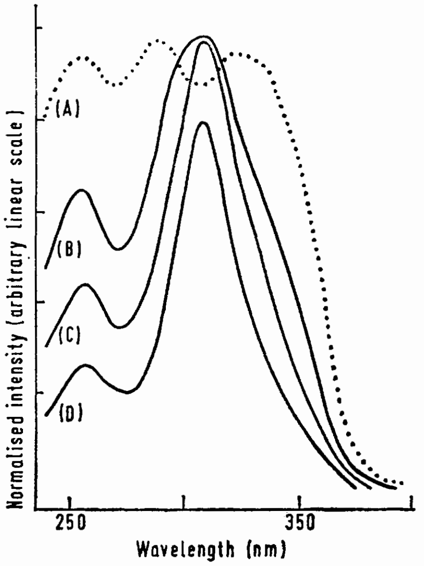

FIGURE 2 Fluorescence excitation and u.v. absorption spectra of [Eu(bta)$_4$]PIP in hexane solution; (A), excitation spectrum (concentration 15 × 10^{-6}M) uncorrected for the internal filter effect (i.f.e.); (B), excitation spectrum (concentration 6 × 10^{-6}M) uncorrected for the i.f.e.; (C), excitation spectrum (concentration 15 × 10^{-6}M) corrected for the i.f.e.; (D), absorption spectrum (concentration 6 × 10^{-6}M)

It was concluded from the work on solutions that an examination of solid samples under conditions whereby this particular filter effect could be accounted for or eliminated was required. This decision was reinforced by a comparison of spectra in Figure 1. It will be seen that some of the broad excitation spectra have minima in the wavelength region of maximum light absorption. Spectra from solutions are, however, much more easily corrected than those from solids because the sample is homogeneous and the incident light–sample–detector geometry better defined. Means were therefore sought whereby filter effects in the solid samples could be eliminated. To this end methods for the production of very thin layers of sample were investigated.

Silica plates were lightly dusted with finely divided chelate in initial experiments. A typical spectrum is recorded in Figure 3. Comparison of it with spectra in Figure 1 for the same substance would suggest that filter effects are present in the former. The microcrystalline 'film' produced from ethanol solution gave much broader excitation spectra than the more uniform 'film' derived from benzene solution (see Figure 3). The latter gave excitation spectra coincident with the absorption spectra within the precision of the instruments employed (Figure 3).

DISCUSSION

It is now generally accepted that light absorption in the europium diketonates results initially in a singlet ⟶ singlet ($S_0 \longrightarrow S_1$) transition in the ligand. As might be expected on general theoretical grounds direct population of triplet levels from S_0 has been shown[10] to have a negligible probability. There is now, however, an appreciable body of evidence[13] to show that energy in the S_1 manifold is transferred by radiationless processes (inter-systems crossing) to one or more triplet manifolds, T, which in turn pass on all or part of their energy to the europium(III). Thus there may be more than one channel for energy transfer from the S_1 levels to the ^5D manifold of the europium(III). For the efficiency of fluorescence to be independent of the wavelength of excitation all transfers from S_1 to T should occur from one particular vibrational level (probably the lowest) in the S_1 manifold.

In the family of substances under consideration it is not obvious that this condition will be fulfilled. Since triplet states are involved, the ligands might be expected to have features characteristic of organic substances exhibiting phosphorescence. From work on such sub-

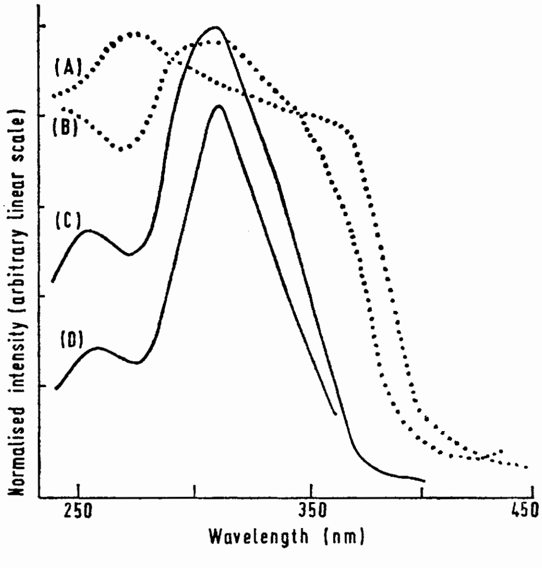

FIGURE 3 Fluorescence excitation and u.v. absorption spectra of [Eu(bta)$_4$]PIP in the form of thin films. Curves (A)—(C) are fluorescence excitation spectra; (A), a thin sprinkling of solid complex; (B), an 'alcohol' film; (C), a 'benzene' film; (D), absorption spectrum of a 'benzene' film (for further details see text)

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[13] A. P. B. Sinha in 'Spectroscopy in Inorganic Chemistry,' eds. C. N. R. Rao and J. R. Ferraro, Academic Press, London, 1971, vol. II, p. 255.

stances there is some evidence[14,15] for direct intersystems crossing from an upper, as well as from the lowest, vibrational level of the excited singlet state giving rise to a wavelength dependent efficiency of phosphorescence.

Formerly it was estimated[16] that energy transfer from the triplet to the europium(III) occurred in a time of the order of 10^{-10} s but more recent work[6] has resulted in this time being revised to 10^{-8} s. It would thus appear that de-excitation to the lowest vibrational level of the particular triplet state is probable before europium(III) excitation occurs.

From the experiments carried out on solid and liquid samples of europium(III) diketonates we consider that the excitation spectrum and corresponding absorption spectrum are coincident for the tris- and tetrakis-complexes. The fluorescence efficiency for a given europium(III) diketonate is therefore essentially constant and independent of the wavelength of the exciting radiation. This constancy, in turn, may be taken as evidence for the predominance of energy transfer from one level of the first excited singlet of the ligand to the triplet manifold from which excitation of the europium(III) occurs.

Excitation at the wavelength of maximum absorption of the chelate or, as is prevalent, by using a single line in the mercury emission spectrum need not result in the optimum yield of fluorescence radiation from a given sample. This will be particularly true for solid preparations as is readily seen from Figure 1.

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[16] M. L. Bhaumik and M. A. El-Sayed, *J. Chem. Phys.*, 1965, **42**, 787.