

ENERGY TRANSFER IN COMPLEXES BETWEEN A CROWN ETHER AND VARIOUS LANTHANIDE SALTS

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Summary

The spectroscopic properties of complexes between benzo-15-crown-5 and europium and terbium nitrates, thiocyanates and perchlorates were investigated. The ligand fluorescence quantum yield in all the complexes is less than that of the uncomplexed crown ether, and in the complexes with terbium salts this quenching is accompanied by a sensitized emission from the metal ion. An intramolecular energy transfer from the excited singlet of the ligand to the metal ion is suggested to explain the emission from the metal ion. It is proposed that the charge transfer states associated with the lanthanide salts compete with the metal ion for the intramolecular transfer of excitation, and that this is important for the nitrate and thiocyanate complexes.

1. Introduction

The fluorescence quenching of organic molecules in solution by lanthanide ions is a well-established phenomenon and has recently been reviewed [1]. Triplet energy transfer from aromatic carbonyl compounds to Eu^{3+} and Tb^{3+} in rigid matrices results in phosphorescence quenching of the aromatic molecules and in sensitized fluorescence of the lanthanide metal ions [2].

However, it is still debatable whether the intramolecular sensitized rare earth emission in chelates involves exclusively triplet excitation transfer from the ligand to the rare earth metal ion, as originally suggested by Crosby *et al.* [3] and confirmed by El-Sayed and Bhaumik [4], or, as pointed out by Kleinermann [5], whether the singlet state can also participate in the electronic energy transfer in such chelates.

Recently, considerable interest has been aroused in macrocyclic polyethers because of their complexing properties and their potential significance in biological systems, particularly as model systems for studying ion trans-

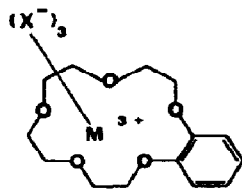


Fig. 1. The structure of the benzo-15-crown-5 (I) complexes: I(a), $M = \text{Tb}^{3+}$, $X = \text{NO}_3^-$; I(b), $M = \text{Eu}^{3+}$, $X = \text{NO}_3^-$; I(c), $M = \text{Tb}^{3+}$, $X = \text{SCN}^-$; I(d), $M = \text{Eu}^{3+}$, $X = \text{SCN}^-$; I(e), $M = \text{Tb}^{3+}$, $X = \text{ClO}_4^-$; I(f), $M = \text{Eu}^{3+}$, $X = \text{ClO}_4^-$; I(g), $M = \text{Gd}^{3+}$, $X = \text{NO}_3^-$.

port phenomena [6]. The complexation of naphtho-crown ethers with alkali metals has been found to affect their emission properties considerably [7].

We report some preliminary results of an investigation of the spectroscopic properties and the intramolecular energy transfer in complexes between a cyclic polyether and europium and terbium nitrates, thiocyanates and perchlorates (Fig. 1). The neutral ligand benzo-15-crown-5 was chosen because of the size of the hole in the polyether ring (1.7 - 2.2 Å) [8] compared with the ionic radii (1.03 Å and 1.00 Å respectively) of the Eu^{3+} and Tb^{3+} metal ions.

2. Experimental

Benzo-15-crown-5 was synthesized [8] by condensing catechol (from BDH Chemicals) with 1,11-dichloro-3,6,9-trioxoundecane. The rare earth salts were obtained from their respective oxides (from Fluka AG) using the standard methods [9] and the complexes between benzo-15-crown-5 and the lanthanide salts were obtained using the reported method [10].

Conductances were determined in 0.001 M acetonitrile solutions at room temperature using platinum electrodes and a Radiometer Copenhagen CDM 3 conductivity meter.

The absorption spectra were recorded in a Perkin-Elmer 124 spectrophotometer, and the emission and excitation spectra were obtained using an MPF-3 spectrofluorimeter with a phosphorescence attachment. Fluorescence measurements at 77 K were obtained using the phosphorescence accessory without the chopper. The fluorescence quantum yields were determined using the procedure described by Parker [11].

Proton nuclear magnetic resonance (NMR) spectra were recorded on a Jeol-P.S.-100 spectrometer at 100 MHz using acetone- d_6 solution with tetramethylsilane as an internal standard.

3. Results and discussion

The NMR spectra indicated a shift and a broadening of the aromatic and methylene ring proton resonances with respect to those of the uncom-

TABLE 1

Proton NMR spectral data

Compound	$C_6H_4^a$ (ppm)	CH_2^b (ppm)	CH_2^c (ppm)	CH_2^d (ppm)
I	6.92	4.11	3.84	3.68
I(a)	6.94	4.19	4.07	3.80
I(c)	6.88	3.99	3.58	3.41
I(e)	6.64	4.86	4.47	4.19

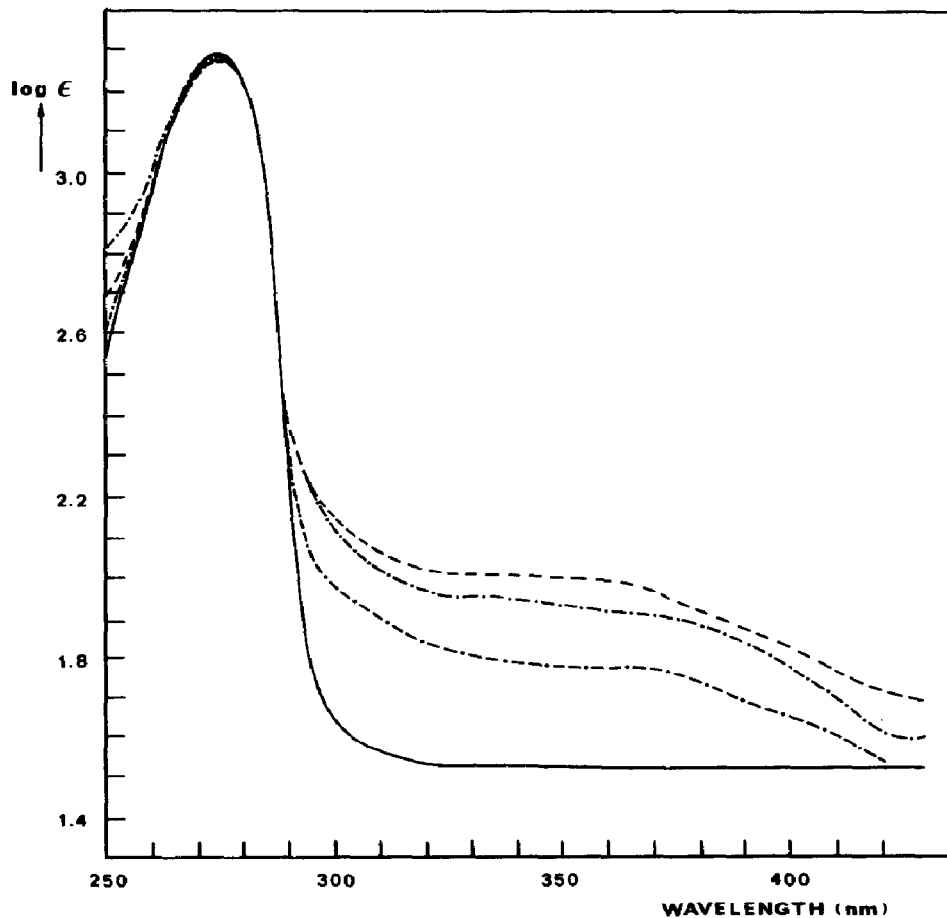
^aAromatic protons.^bThis resonance may be assigned to the four protons of the two methylene groups bonded to oxygen atoms also bonded to the benzene ring.^cThis resonance may be assigned to the two adjacent methylene groups.^dThis resonance may be assigned to the four methylene groups bonded to oxygen atoms only bonded to methylene groups.

Fig. 2. Absorption spectra in ethanol of complexes between benzo-15-crown-5 and lanthanide nitrates: —, I; ---, I(a); - · - ·, I(b); - - - -, I(g).

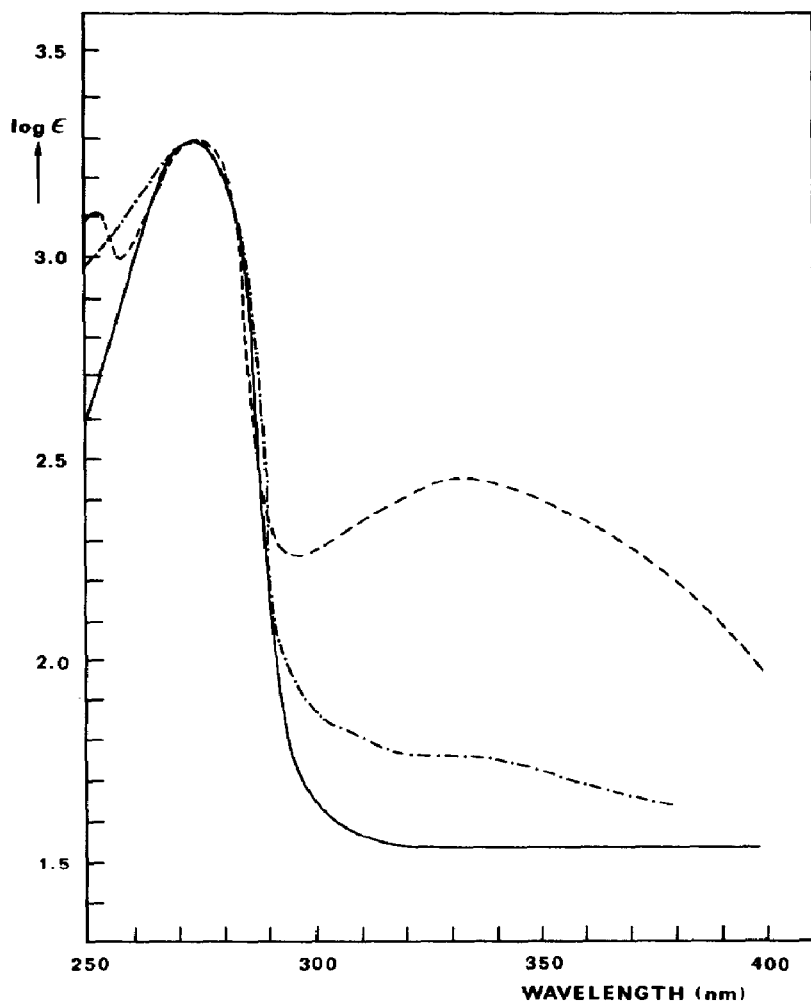


Fig. 3. Absorption spectra in ethanol of complexes between benzo-15-crown-5 and lanthanide thiocyanates: —, I; - · - · - ·, I(c); - - -, I(d).

plexed crown ether. The data obtained for the terbium complexes are shown in Table 1.

The absorption spectra in ethanol of the complexes between benzo-15-crown-5 and terbium, europium and gadolinium nitrates are shown in Fig. 2. In contrast with the results reported by Cassol *et al.* [10], no red shift is observed in the benzenoid band (275 nm) which has the same extinction coefficient as in the uncomplexed crown ether, indicating a very weak ion-dipole interaction in this solvent between the metal ion and the oxygen atoms of the polyether ring. The new structureless band centred at 340 nm is attributed to a charge transfer transition associated with the coordination of the metal ion with the bidentate nitrate [12]. The molar conductances of the complexes between the ligand and the lanthanide nitrates have values of $18 \pm 2 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$. These values, although higher than those previously

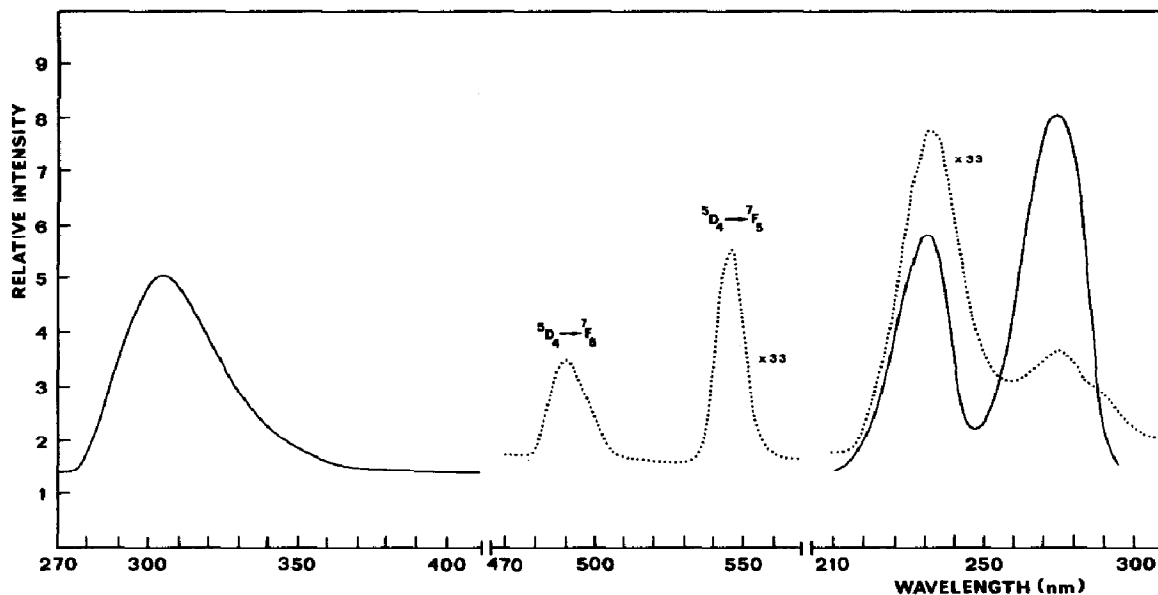


Fig. 4. Emission and excitation spectra of complex I(e) (concentration, 10^{-4} M) in acetonitrile at 298 K: —, ligand emission ($\lambda_{\text{ex}} = 286$ nm) and excitation ($\lambda_{\text{em}} = 305$ nm); . . ., sensitized Tb^{3+} emission ($\lambda_{\text{ex}} = 286$ nm) and excitation ($\lambda_{\text{em}} = 545$ nm).

reported [13], are identical with those found for the lanthanide salts, as would be expected for complexation with a neutral ligand.

The absorption spectra of the complexes between benzo-15-crown-5 and the lanthanide thiocyanates are presented in Fig. 3. They show a slight shift in the benzenoid band indicating that the interaction of the metal ion with the ring oxygen is stronger than that in the nitrates. The charge transfer transition at 335 nm, which is already present in the spectrum of $\text{Eu}(\text{SCN})_3$ [14], is intensified in compound I(d) suggesting that the crown ether is complexed with an ion pair [15]. $\text{Tb}(\text{SCN})_3$ does not have any absorption at 320 nm in solution, but its complex with benzo-15-crown-5 shows a very weak broad band at this wavelength which is assigned to a charge transfer transition. The molar conductances of the complexes with the lanthanide thiocyanates I(c) and I(d) are of the order of $23 \pm 2 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$.

The absorption spectra of complexes I(e) and I(f) are identical with that of the ligand (I). As expected the benzenoid band is unaffected; there is no evidence of a long wavelength band associated with the coordination of the metal ion with the perchlorate. The molar conductances of these complexes are $310 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$.

The fluorescence of the ligand (I) is quenched in all the terbium complexes and is accompanied by an emission of the metal ion associated with the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ (490 nm) and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ (545 nm) transitions [16], as shown in Fig. 4. This emission is only observed if the ligand is excited and it is not detected with direct excitation of the ${}^7\text{F}_6 \rightarrow {}^5\text{L}_{10}$ transition at 370 nm, as can be concluded from the excitation spectra. At 77 K in ethanol the

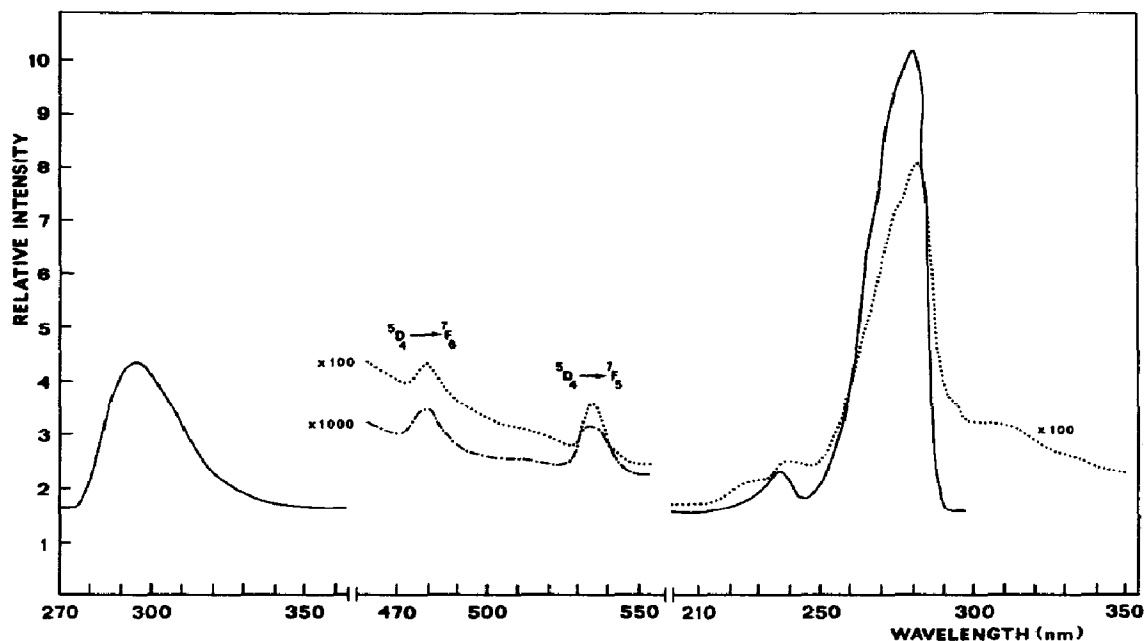


Fig. 5. Emission and excitation spectra of complex I(e) (concentration, 10^{-3} M) in ethanol at 77 K: —, ligand emission ($\lambda_{\text{ex}} = 281$ nm) and excitation ($\lambda_{\text{em}} = 305$ nm); . . . , sensitized Tb^{3+} emission ($\lambda_{\text{ex}} = 281$ nm) and excitation ($\lambda_{\text{em}} = 545$ nm); - , Tb^{3+} emission ($\lambda_{\text{ex}} = 370$ nm).

TABLE 2

Quantum yields of the ligand fluorescence ϕ_f and of the metal-ion-sensitized emission ϕ'_f for complexes between benzo-15-crown-5 and terbium salts in acetonitrile

Compound	ϕ_f	$\phi'_f \times 10^3$
I	0.42 0.34 ^a	—
I(a)	0.31 0.27 ^a	0.4
I(c)	0.29 0.24 ^a	0.3
I(e)	0.37 0.28 ^a	2.2 1.3 ^a

^a Aerated solutions.

excitation at 370 nm causes an emission, although it is much weaker than the emission obtained when the ligand is selectively excited (Fig. 5).

The absolute quantum yields of the ligand in the complexes and those of the sensitized emission of the terbium metal ion are shown in Table 2. The values obtained indicate a stronger quenching of the ligand fluorescence

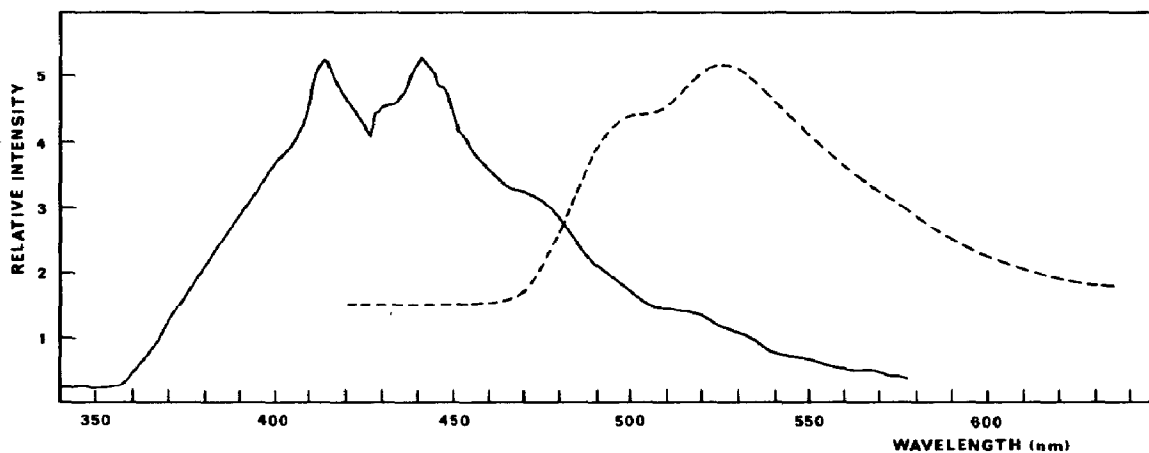


Fig. 6. Phosphorescence spectra in ethanol at 77 K: —, the ligand (I), $\lambda_{\text{ex}} = 286$ nm; - - -, complex I(b), $\lambda_{\text{ex}} = 354$ nm.

in the complexes with terbium nitrate and terbium thiocyanate than in those with terbium perchlorate, in agreement with the fact that the former counter-anions are more effective quenchers than the latter. Indeed the effect of quenching by oxygen is greater in the perchlorate complex than in the nitrate and thiocyanate complexes.

The apparent inefficiency of energy transfer in the thiocyanates and nitrates may be related to competition from the charge transfer states towards the ligand excitation which is known to increase in the following order: $\text{SCN}^- > \text{NO}_3^- > \text{ClO}_4^-$ [17]. At 77 K the emission from the metal ion increases, perhaps because of the decrease of non-radiative modes of decay [18].

The phosphorescence of the ligand (I) is given in Fig. 6 and shows two peaks at 415 nm and 440 nm with a vibrational progression characteristic of an emission from $T_1(\pi, \pi^*)$. This emission is not quenched in the complexes investigated which indicates that the transfer of excitation proceeds from the singlet state rather than from the triplet state. A new phosphorescence emission is observed following excitation of the charge transfer band, which is also observed in the Eu^{3+} and Gd^{3+} nitrate complexes suggesting that the energy level from which this emission originates is independent of the coordinated rare earth ion.

The complexation of the ligand (I) with the europium salts is still effective in quenching its fluorescence but to a much smaller extent than that observed in the terbium complexes. The quantum yield of fluorescence of the ligand in complex I(b) is 0.29 and hardly any quenching is observed in the perchlorates. The sensitized emission at room temperature is very weak in complex I(b) and is not observed in complexes I(d) and I(f).

It has been reported that SCN^- quenches the 5D_1 and 5D_0 states of europium(III) [19]; however, at 77 K the excitation of the charge transfer band (321 nm) in complex I(d) leads to the appearance of the emission

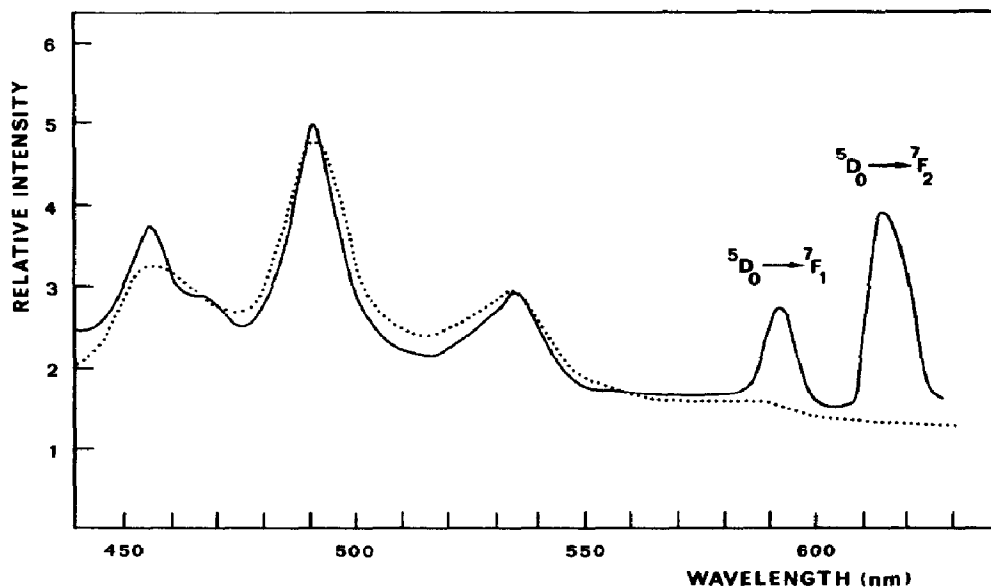


Fig. 7. Total emission spectra of complex I(d) (concentration, 10^{-3} M) in ethanol at 77 K and $\lambda_{\text{exc}} = 321$ nm: . . ., charge transfer emission; —, charge transfer and Eu^{3+} emission.

associated with the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (618 nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (592 nm) transitions [16] which is accompanied by the phosphorescence from the triplet charge transfer state (Fig. 7).

It is known that Tb^{3+} and Eu^{3+} chelates behave rather differently with respect to their roles as energy acceptors. For example, both metal ions quench the fluorescence of tryptophan but only the terbium-sensitized emission has been detected [20]. The extremely low efficiency of the intramolecular energy transfer process in europium acetylacetonate compared with the corresponding terbium analogue has been attributed to the presence of a charge transfer excited state lying below the ligand states [21]. Even in europium perchlorates the formation of a weakly bound ion pair in acetonitrile has been postulated [18]. We believe that in the compounds studied the charge transfer states also play an important role, competing with the metal ion for the intramolecular transfer of excitation.

The preliminary data reported for these systems indicate a sensitized metal ion emission via the singlet state. Further work is in progress to evaluate the importance of the ligand fluorescence quenching compared with the sensitized metal ion emission and to establish a quantitative relationship between these phenomena.

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