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Competition between Intraligand Triplet Excited State and LMCT on the Thermal Quenching in β-Diketonate Complexes of Europium(III)

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Luminescence lifetime measurements of Eu(fod)$_3$ solutions in carbon tetrachloride, benzene, and acetonitrile were performed at temperatures between 5 and 75 °C. Ligand to metal charge transfer involving Eu(II) formation upon 300 nm steady state irradiations of Eu(fod)$_3$ solutions, besides the dependence of the difference in energy of the emitting $^5D_0$ and the upper level support, photoinduced electron transfer as the main deactivation mechanism in the thermal quenching of the Eu(III) chelate.

1. Introduction

The complexes of lanthanide ions have characteristic luminescence properties due to the intra- and intermolecular energy-transfer processes. Because of their narrow-band, long-lifetime emission they are widely applied in fluoroimmunoassays, as luminescent probes or as luminescent display materials, etc.[1] It has been shown that the emitting excited states can be populated by directly irradiating at the f−f absorption bands or by intersystem crossing from the triplet intraligand excited state.[2,3] In several cases a temperature effect on the luminescence lifetime and intensity has been observed. For compounds such as Eu(NO$_3$)$_3$ or Eu(ClO$_4$)$_3$ the temperature quenching has been attributed to the depopulation of the emitting $^5D_0$ excited state via the upper $^5D_1$ excited state.[2,4] On the other hand, many europium macrocyclic complexes showed intramolecular quenching due to the thermal population of a ligand to metal charge-transfer excited state from the emitting state.[5,6] Besides, in β-diketonates complexes of Tb(III) and Eu(III) a third mechanism of thermal deactivation seems to be operative. In those cases, the energy difference between the intraligand triplet and the $^5D_0$ excited state has been considered as the deciding factor for observing a temperature effect.[3,7−9] However, although the reduction potential of Eu(III) ion makes it easily reducible, not much attention has been paid to the photochemical reduction as a possible quenching pathway, even though a charge-tranfer state has been made responsible for the thermal quenching in Eu(thd)$_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate).[10] In this paper evidence on the temperature effect upon the emission of an europium(III) β-diketonate complex is reported and a rationale of that behavior is given on the basis of the photoinduced electron transfer as the main deactivation mechanism.

2. Experimental Details

2.1. Materials, Equipment, and Procedures. The Eu(fod)$_3$ (fod = 1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octandionato) complex from Aldrich Chemical Co. was used as received. Acetonitrile (J. T. Baker), benzene (Merck), carbon tetrachloride (Merck), chloroform (Merck), ethanol (Merck), methanol (Mallinckrodt), and 2-propanol (Merck) were used without further purification.

UV−visible spectra were recorded on a CARY 3 spectrophotometer. Luminescence spectra at temperatures between 10 and 70 °C were taken with an SLM 4800 (Aminco) spectrofluorometer coupled to a PC computer.

A laser flash photolysis setup used for performing time-resolved luminescence measurements has been described elsewhere.[11] Lifetime measurements were made at temperatures between 5 and 75 °C using a thermostatized Pyrex cell coupled to a Lauda thermostat and to an Ultra Kryomat TK30D cryostat using a pulsed nitrogen laser with excitation at 337 nm and monitoring the signal at 610, 615, and 620 nm for the europium(III) compound. A modified 1P28 photomultiplier tube circuit with ca. 1 ns response time was used as the detector for the red emission dispersed through a monochromator. The signal was directly measured on a fast digitizing oscilloscope (Hewlett-Packard Instruments), and the temporal resolution of the overall system was ca. 2 μs.

Lifetime measurements were carried out on fresh solutions of the europium(III) compound ([Eu(fod)$_3$] = (1−2) × 10^{-4} M) without deaereation. No differences were observed when lifetime measurements were carried out on solutions which had been deaereated by bubbling O$_2$−free N$_2$.

Eu(fod)$_3$ dimerization has been reported to occur in CCl$_4$ and CHCl$_3$ with overall aggregation constants β_2 being 100 and 1.6, respectively.[12] In our experimental conditions such aggregates were meaningless. For intance, the fraction of dimer complex present in CCl$_4$ solutions should be less than 2%.

Steady-state irradiations at 300 and 350 nm were carried out in an irradiator with appropriate Rayonet lamps for quasi monochromatic photolysis, i.e., the bandwidth of the excitation light of 20 nm. The concentration of the photolyte was adjusted to absorb more than 99.9% of the incident light. The homogeneity of the reaction medium was maintained during irradiation by stirring with magnetic bars.

3. Results

3.1. Emission Spectra. When solutions of Eu(fod)$_3$ were irradiated with UV light (λ_{ex} = 337 nm), an intense red

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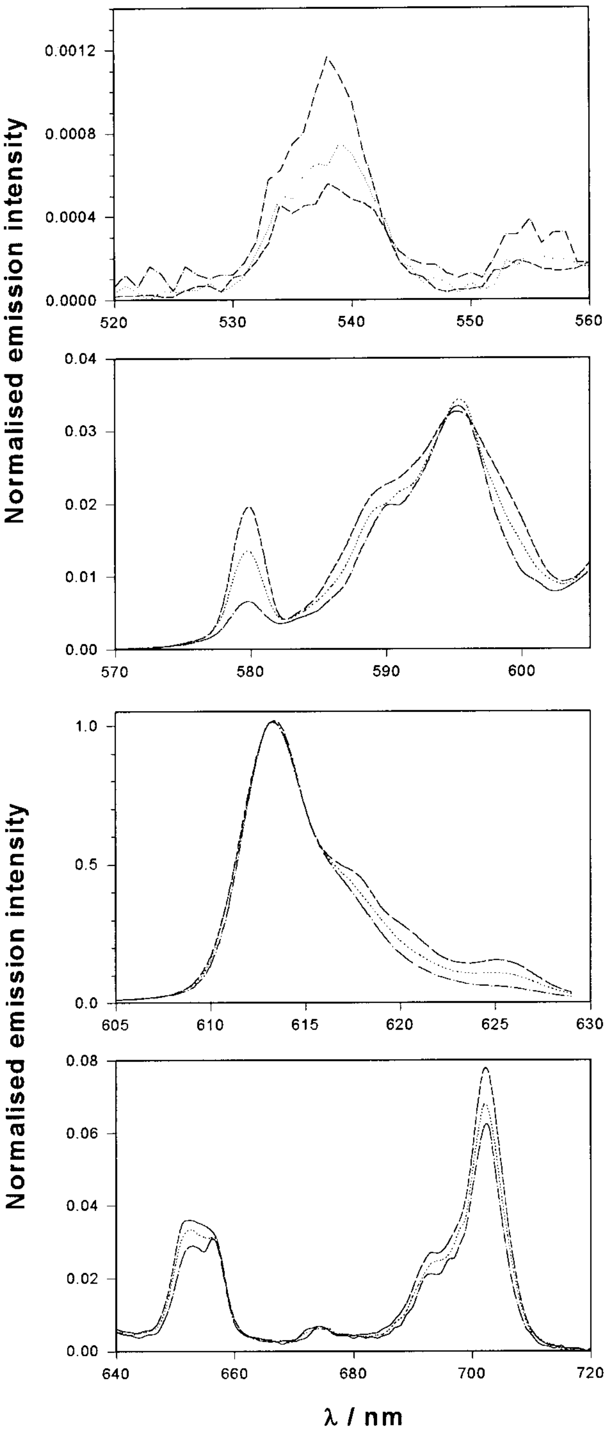


Figure 1. Emission spectra of Eu(fod)$_3$ in acetonitrile taken at different temperatures: (- -) $t = 15$ °C, (···) $t = 42$ °C, and (— · —) $t = 65$ °C.

luminescence could be seen. The emission spectra taken in acetonitrile and carbon tetrachloride at different temperatures are shown in Figures 1 and 2. They were normalized to unity at $\lambda_{em} = 613$ nm, where changes are minimal, for comparison. In every case, as temperature increases, the emission intensity corresponding to the $^5D_0 \rightarrow {}^7F_j$ transitions, band maxima at 580, 595, 652, and 702 nm, decrease relative to the band at 613 nm. The latter band experiences a narrowing as temperature increases. However, the emissions at $\lambda_{em} = 535$ and 555 nm corresponding to the transition $^5D_1 \rightarrow {}^5F_1$ and $^5F_2$ increase their intensities relative to the band at 613 nm as temperature is raised.

3.2. Lifetime Measurements. *Carbon Tetrachloride. F*or the whole range of temperatures studied the emission decay,

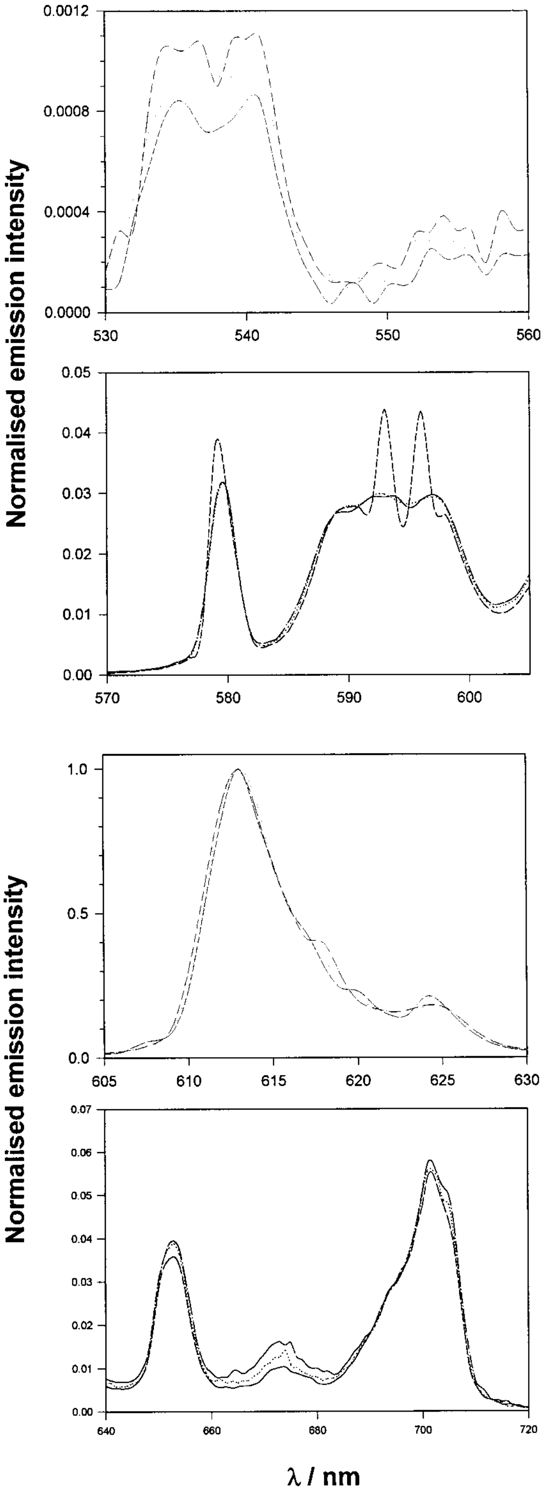


Figure 2. Emission spectra of Eu(fod)$_3$ in carbon tetrachloride taken at different temperatures: (- -) $t = 35$ °C, (···) $t = 45$ °C, and (— · —) $t = 55$ °C.

followed at 610, 615, and 620 nm, can be fitted, without appreciable deviations, to a single exponential, eq 1, where $I(\lambda)$

$$I(\lambda) = I_0(\lambda) \exp(-t/\tau) \quad (1)$$

represents the emission intensity at time t monitored at λ, after the laser pulse, $I_0(\lambda)$ represents the emission intensity at time $t = 0$ monitored at the same wavelength, and τ is the observed lifetime for the luminesence decay. The observed lifetime is nearly temperature independent between 5 and 25 °C. At higher

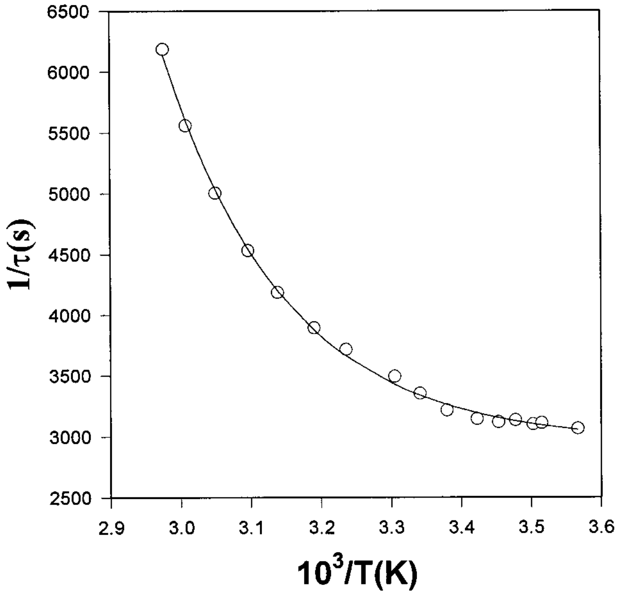


Figure 3. Temperature dependence of observed lifetimes of Eu(fod)$_3$ in carbon tetrachloride. Experimental lifetimes (○) were plotted against 1/*T* and fitted according to eq 2 (—). See text for details.

TABLE 1: Parameters *k*, *k*′, and Δ*E* Obtained by Fitting to Equation 2 Experimental Lifetime Dependence on Temperature of Eu(fod)$_3$ Solutions in Carbon Tetrachloride, Benzene, and Acetonitrile (See Text for Details)

solvent	Δ*E*/cm^{-1}	*k*/s^{-1}	*k*′/s^{-1}
carbon tetrachloride	4000 ± 100	(2.95 ± 0.03) × 10^3	(8 ± 4) × 10^{10}
benzene	4438 ± 6	(3.05 ± 0.04) × 10^3	(6.5 ± 0.1) × 10^{11}
acetonitrile	4954 ± 3	(1.29 ± 0.06) × 10^3	(1.000 ± 0.001) × 10^{13}

temperatures the lifetime begins to decrease. The observed lifetimes (τ) vary with temperature, as can be seen in Figure 3, in which the filled curve was obtained by fitting the experimental data according to eq 2, where *k* is the decay rate constant in the

$$1/\tau = k + k' \exp(-\Delta E/RT) \qquad (2)$$

absence of temperature dependent quenching processes and can be determined from the constant lifetime at lower temperature and where dτ/d*T* is almost zero. As thermal population of an upper level from a lower emitting level will result in quenching of fluorescence, Δ*E* can be identified as the difference in energy of the two levels and *k*′ as a measure of the frequency factor for the deactivation of the upper level. Values obtained for *k*, *k*′, and Δ*E* are shown in Table 1.

Acetonitrile and Benzene. For temperatures below 35 °C emission decays in acetonitrile can be fitted, without appreciable deviations, to a single exponential, eq 1. Emission decays in benzene solutions, however, were biexponential even at lower temperatures. For temperatures above 40 °C emission decays were biexponential in both solvents and were fitted according to eq 3. The two lifetimes obtained by curve fit analysis, namely,

$$I(\lambda) = I_{01}(\lambda) \exp(-t/\tau_1) + I_{02}(\lambda) \exp(-t/\tau_2) \qquad (3)$$

τ_1 and τ_2, present similar behavior in both solvents. τ_2 (the longer one) is temperature independent, and τ_1 (the shorter one) decreases when temperature increases. The experimental τ_1 values obtained in these conditions were fitted according to eq 2 (see Figures 4 and 5). The τ_2 values are almost the same as those observed at room temperature when no thermal deactivation is present.

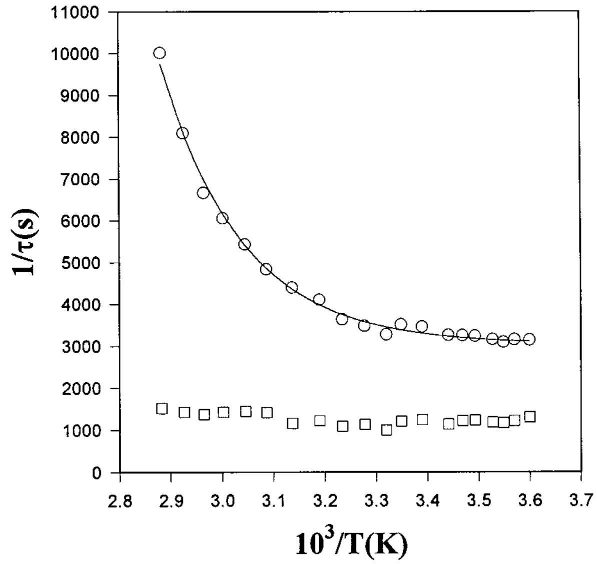


Figure 4. Temperature dependence of observed lifetimes of Eu(fod)$_3$ in benzene. Experimental lifetimes τ_1 (○) and τ_2 (□) were plotted against 1/*T*. τ_1 values were fitted according to eq 2 (—). See text for details.

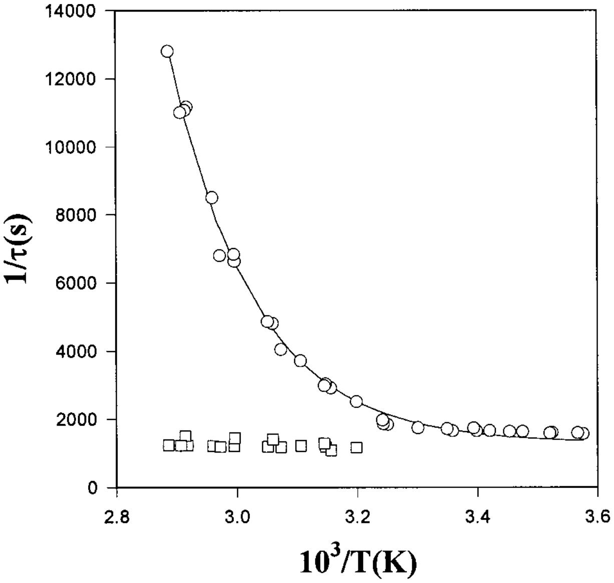


Figure 5. Temperature dependence of observed lifetimes of Eu(fod)$_3$ in acetonitrile. Experimental lifetimes τ_1 (○) and τ_2 (□) were plotted against 1/*T*. τ_1 values were fitted according to eq 2 (—). See text for details.

The *k* values and Δ*E*’s are shown in Table 1.

Steady-State Photolysis. When solutions of Eu(fod)$_3$, being the solvents CCl$_4$, CCl$_3$H, CH$_2$Cl$_2$, 2-propanol, ethanol, and methanol, were irradiated at 300 nm, the absorption band peaking at 290 nm (intraligand transitions) decreased as photolysis went on. At 275 nm an isosbestic point could be observed, and around 260 nm the absorption grew (see Figure 6a). Differential spectra in this region showed a growing peaking at $\lambda_{max} \sim 260$ nm (see Figure 6b). This new band can be attributed to some species of Eu(II).[13] The absorption spectrum of Eu^{2+}(aq)[14] consists of a long-wavelength band, $\lambda_{max} = 320$ nm ($\epsilon = 602$ cm^{-1} M^{-1}), and an overlapping band in the UV centered at 250 nm ($\epsilon = 1778$ cm^{-1} M^{-1}). These bands have been caracterized as 4f → 5d transitions. On the other hand, the absorption depletion could indicate that the ligand undergoes

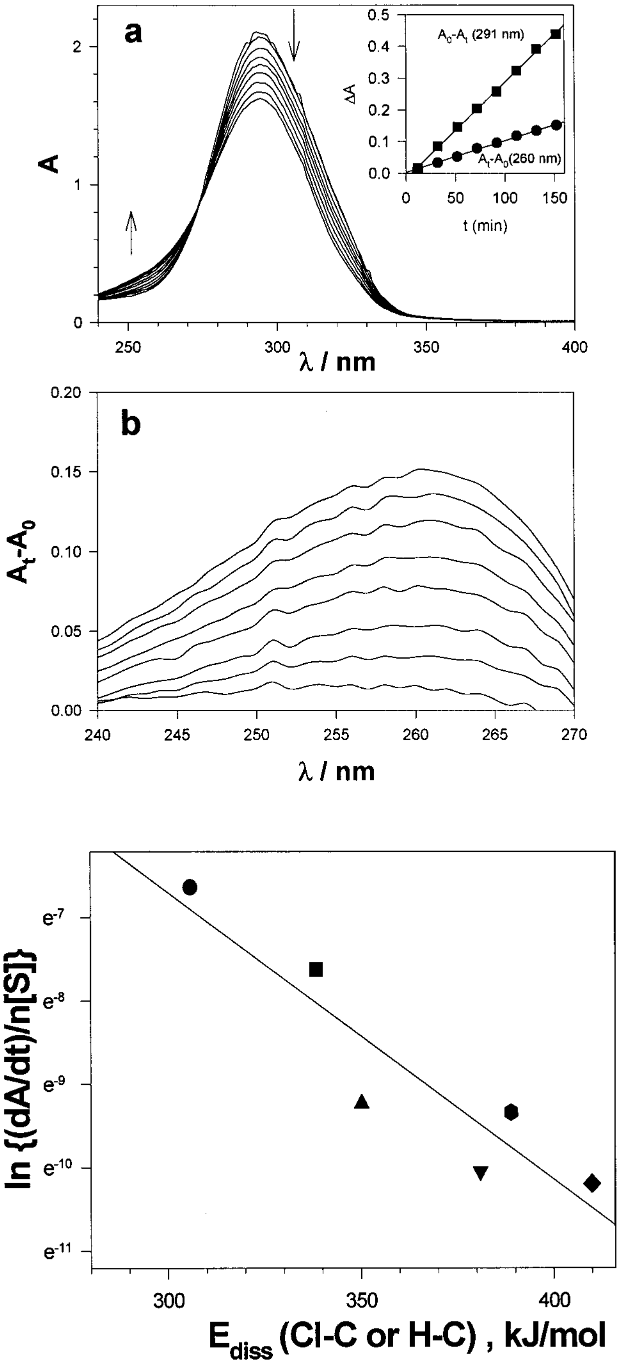


Figure 6. Photochemistry of Eu(fod)$_3$. (a) Spectral changes upon 300 nm irradiation of Eu(fod)$_3$ solutions in CH_2Cl_2 are shown. The inset to this figure shows changes in absorbance (Δ*A*) vs irradiation time at 291 nm (depletion) and at 260 nm (growth). (b) The differential spectrum in the spectral region between 240 and 270 nm is shown. (c) Solvent effects on the conversion rate are shown. In this figure, d*A*/d*t* at 260 nm measured in CCl_4 (●), CCl_3H (■), CH_2Cl_2 (▲) 2-propanol (▼), methanol (◆) and ethanol (⬢) were divided by solvent concentration [S] and by the number of bonds C−Cl or C−H (*n*) present in the solvent molecule and plotted against C−Cl (for CCl_4, CCl_3H, and CH_2Cl_2) and C−H (for 2-propanol, methanol, and ethanol) dissociation energies.

a transformation leading to a product of lower conjugation. On the entire period of photolysis (150 min) the rate remains constant, showing no secondary photolysis. However, when the irradiation wavelength was 350 nm, no Eu(II) was observed and the ligand absorption decrease (at λ_{obs} = 330 nm in chloroform solutions) was similar than that under irradiation at 300 nm, being

TABLE 2: Data of Thermal Quenching Attributed to the Thermally Activated Process $^5D_0 \rightarrow {}^5D_1$

compd	Δ*E*/cm^{-1}	*k*′/s^{-1}	solvent
Eu(NO$_3$)$_3$^{a}	2000	1.3×10^6	CH_3OD or CD_3OD
EuCl$_3$^{a}	1700	4×10^5	D_2O
Eu(ClO$_4$)$_3$^{b}	2500		mixtures H_2O/CH_3CN
Eu(ClO$_4$)$_3$^{c}	2500		CD_3CN

[a] Data taken from reference 2. [b] Data taken from reference 4a. [c] Data taken from reference 4b.

$$\phi_{300\ \mathrm{nm}}/\phi_{350\ \mathrm{nm}} = 1.03$$

When the photolysis was performed in acetonitrile solutions (λ_{irr} = 300 nm), similar absorption changes at 290 nm were observed. However, absorption growth at 260 nm was absent.

Highly concentrated Eu(fod)$_3$ (i.e. 1×10^{-2} M) chloroform solutions showed an absorption band at 464 nm attributed to the $^7F_0 \rightarrow {}^5D_2$ Eu(III) transition. As the photolysis occurs (λ_{irr} = 300 nm), this band decreases, showing that Eu(III) is disappearing. Since in this spectral region that band is the only feature present, the quantum yield of Eu(III) consumption could be determined, being $\phi = 1.0 \times 10^{-3}$. Taking into account that Eu(III) only can disappear by generating Eu(II) that is further support for the assumption that during the photolysis Eu(II) is generated. Changes on the ligand enviroment would affect the intensity of the Laporte forbbiden transitions. However, any ligand modification would lead to a lower symmetry situation, producing an absorption augment as the photolysis progresses.[15]

4. Discussion

The effect of the temperature upon the emission lifetime of Eu(III) ion in solution has been reported in early works (see Table 2). It has been attributed to the thermal population of the $^5D_1$ state, the lifetime of which is of the order of 10^{-6} s. As the rate constant for the process $^5D_1 \rightarrow {}^5D_0$ is 100 s^{-1} [2,4b] thermal population of $^5D_1$ from $^5D_0$ produces the shortening of the lifetime of the latter. Δ*E* values obtained ranging between 1700 and 2500 cm^{-1} are in agreement with the energy gap between both levels involved, which was reported[2,4a,b] as being 1740 cm^{-1}, supporting that deactivation mechanism. However, when macrocyclic or bidentate ligands (chelates) are coordinated to the ion, the thermal quenching observed seems to be produced by different mechanisms.

Europium cryptate,[16] *aza*-macrocycle,[17] or calixarene[18] absorption spectra usually showed features originated in ligand to metal charge-transfer (LMCT) transitions. Though no systematic studies were available, the observed decrease of the emission lifetime when the temperature is raised[19] or the lack of emission[18] at room temperature has been attributed to the thermal population of the close LMCT excited state. For complexes of lanthanide ions with β-diketonate ligand thermal deactivation of the metal centered emitting state has been attributed to the intraligand triplet excited state.[3,7,8] A unique case, involving Eu(thd)$_3$ where the thermal quenching was attributed to a charge-transfer state has been reported.[10]

No features attributable to a charge-transfer transition can be observed in the absorption spectrum of Eu(fod)$_3$. Nevertheless, in other lanthanide complexes[17] the extinction coefficients for charge-transfer transition have been of the order of 10^2 or lower. Moreover, the existence, in Eu(fod)$_3$, of charge transfer from the C=O to the metal center has been reported.[16] Although, the temperature dependent quenching mechanism involving LMCT excited states has been considered unlikely for Schiff base complexes of europium because no apparent LMCT band was observed,[20] actually, low extintion coefficients make it possible for such absorptions to be hidden under the stronger intraligand absorption bands.

Despite that, the observed photochemistry in Eu(fod)$_3$ leading to Eu(II) formation strongly supports the existence of a LMCT excited state playing an important role. Similar photoreduction of Eu(III) has been reported as a consequence of exciting the charge tranfer to the solvent band in alcoholic[13] and aqueous[21] solutions.

The solvent effect on the conversion rate (Figure 6c) can be rationalized by considering the atom abstraction (Cl$^\bullet$ or H$^\bullet$) for the β-diketonate radical, formed during the photolysis, as being the determining step

$$\mathrm{Eu^{(II)}(fod)_2fod^\bullet + Cl_4C \rightarrow Eu^{(II)}(fod)_2fod{-}Cl + Cl_3C^\bullet} \quad (4)$$

The conversion rate is proportional to the number of C−Cl or C−H bonds present in the solvent molecule, following the trapping of Eu^{II}(fod)$_2$fod$^\bullet$, an expected trend of reactivity. Those bond numbers would be as follows: 4 in CCl$_4$, 3 in CCl$_3$H, 2 in CH$_2$Cl$_2$, 1 in CH$_3$CH(OH)CH$_3$, 3 in CH$_3$OH, and 2 in CH$_3$CH$_2$OH, as any other numbers would involve higher dissociation energies. To understand the role of bond dissociation energy upon conversion rate, dA/dt must be divided by solvent concentration and the number of bonds C−Cl or C−H, as can be seen in Figure 6c. The fact that, in acetonitrile solutions, no photoreduction was observed adds support to this mechanism since this solvent is unable to trap the photogenerated radical.

Studying the temperature effect on compounds of the type TbL$_3$,[3] where L = trifluoroacetylacetonate, hexafluoroacetylacetonate and benzoylacetonate, the frequency factor for the deactivation of triplet excited state (k') has been found to be of the order of 10^9 and ΔE of the order of the energy difference between the emitting level, $\nu(^5D_4)$, and the triplet state, ν(T). The same k' value was found for toluene or ethanol solvents. Actually, ΔE values were systematically higher than $[\nu(\mathrm{T}) - \nu(^5D_0)]$. In this case charge transfer could be discarded because the high reduction potential for Tb(III)/Tb(II) would bring the energy of such a state too high. No thermal quenching was observed for the europium complexes, which is attributed to the resonant level $^5D_0$ energy being 3100 cm^{-1} lower than that $^5D_4$ for the terbium ion. However, it is worthy to note that the highest temperature used in those studies was only 23 °C. Nevertheless, an early work[8] showed that with increase in temperature up to 70 °C the complex Eu(thenoyltrifluoroacetate)$_3$ exhibits thermal deactivation of $\Delta E = 4700$ cm^{-1} (no k$'$ value was reported). Though this value was reported to be the same for the three solvents used, it is possible to see from those data that, actually, ΔE is solvent dependent. Curiously, the gap is 1500 cm^{-1} higher than $[\nu(\mathrm{T}) - \nu(^5D_0)]$. This mismatch was related to a temperature effect on the triplet lifetime or thermal population of higher-lying ^{5}D levels.[3]

For Eu(fod)$_3$ ΔE and k' are clearly solvent dependent. That charge-transfer excited states (CT) have sensitivity to solvent properties[22] arises from the significant change in dipole moment that accompanies CT excitation. Then, as solvent polarity increases, ΔE should decrease. However, in this case ΔE takes higher values as solvent polarity increases. It can be understood by taking into account that when charge is transferred from the β-diketonate to the Eu(III), the dipole moment should decrease. The dependence of the energy difference between the LMCT and the $^5D_0$ excited states (ΔE) with solvent polarity can be seen in Figure 7. The charge-transfer excited state thermally populated might lead to a fast electron transfer with k' being the rate constant for that process. The current theories for electron transfer[23] led us to express k' as follows:

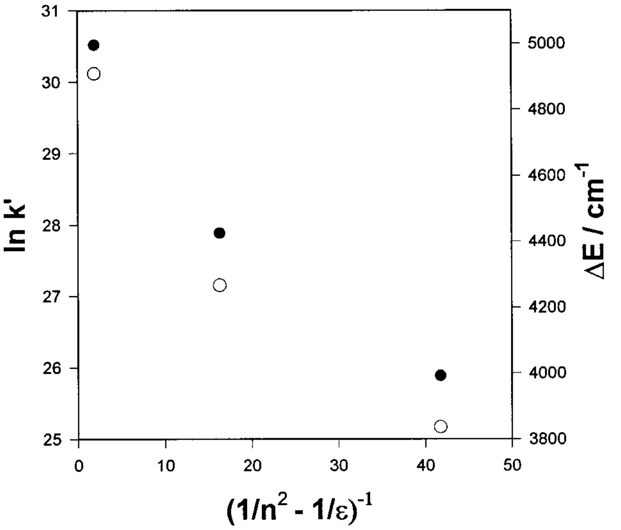


Figure 7. Solvent effects upon parameters k' (○) and ΔE (●).

TABLE 3: Triplet Energies of Selected Eu(chelate)$_3$

chelate	triplet energy[a]/cm^{-1}
thenoyltrifluoroacetone	20 450
trifluoroacetylacetonate	23 000
hexafluoroacetylacetonate	22 000
acetylacetonate	25 300−26 000
benzoylacetone	21 460

[a] Data taken from references 3 and 23.

$$k' = 2\pi/\mathrm{h}|V_{\mathrm{PR}}|^2(\pi/\lambda k_{\mathrm{b}}T)^{1/2}\exp[-\Delta G^{\ddagger}/k_{\mathrm{b}}T] \quad (5)$$

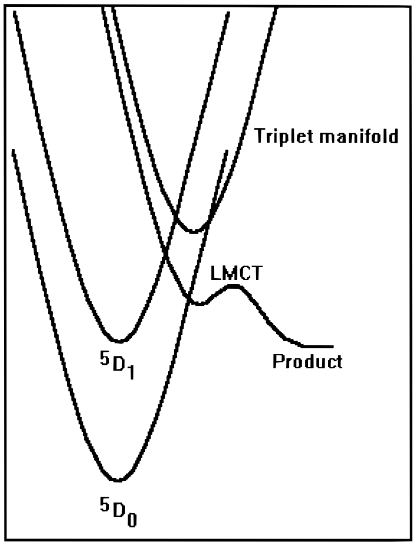
where

$$\Delta G^{\ddagger} = (\Delta G^\circ + \lambda)^2/4\lambda \quad (6)$$

V_{PR} is the effective electronic coupling element, λ accounts for the complex and the solvent reorganizational energy ($\lambda = \lambda_{\mathrm{i}} + \lambda_{\mathrm{o}}$), and ΔG° is the difference between the reactant and product free energy. The other parameters have the usual meaning. It is obvious that the solvent effect on k' must be complex. In Figure 7 a graph of ln k' vs $(1/n^2 - 1/\epsilon)^{-1}$ is shown. Here n is the solvent refraction index and ϵ its dielectric constant, and the factor $(1/n^2 - 1/\epsilon)^{-1}$ is proportional to $1/\lambda_{\mathrm{o}}$. This linear-like behavior indicates a predominance of the solvent effect on the activation free energy of the electron-transfer process in agreement with an adiabatic reaction.

Some values for the energy triplet excited state in β-diketonates complexes have been reported (see Table 3). Taking into account structural similarities the fod triplet energy could be between 22 000 and 23 000 cm^{-1}. This put $[\nu(\mathrm{T}) - \nu(^5D_0)]$ between 4500 and 5500 cm^{-1}. This energy gap is close to the experimental ΔE, and the triplet role on the deactivation process should not be meaningless. However, solvent effects are not significant on intraligand excited states. The predominance of the LMCT excited state as the quenching path can be rationalized assuming that both states are in equilibrium, and the fastest decay way is the electron transfer since k' is 1−3 orders of magnitude higher than that attributed to the triplet decay.[3] In Chart 1 a diagram for a cut (along a distortion coordinate) of Eu(fod)$_3$ electronic state potential surfaces is depicted. Moreover, a ΔE value of 5300 cm^{-1} found by Dao et al.[9] is 300 cm^{-1} higher than our highest value obtained in acetonitrile. They

CHART 1



attributed this barrier to the triplet state. However, in the gas phase, the higher temperatures used can change the nonradiative rate constants for the triplet and the charge-transfer states on a different extension, making deactivation via triplet state more important.

For Eu(thd)$_3$, in solid state a $\Delta E = 4120$ cm^{-1} and a $k' = 1.2 \times 10^{13}$ s^{-1} were found. It was assumed that thermal quenching[10] occurs via a CT state. A $k' = 2.2 \times 10^{11}$ s^{-1} for gas phase was calculated, by Berry et al.,[10] from ref 9, and the difference was attributed to dimer formation[25] in the solid state. Nevertheless, the data used consisted of few scattered points, making the comparison doubtful. On the other hand, as the gas-phase energy barrier found was 4100 cm^{-1}, ΔE appears to not be enviromentally dependent. However, both studies were carried out on quite different temperature ranges (-10 to $+80$ °C and $+190$ to $+220$ °C), and the deactivation mechanism could change because the temperature is affecting the vibronic states population and nonradiative rate constants. Besides, a higher k' value in the solid state due to acceptor traps outside the complex cannot be completely discarded. However, those results and deactivation via CT in β-diketonate complexes deserve further experimental tests.

A last point remains, the temperature independent lifetime. Although we were not able to get any spectroscopic evidence of complex dissociation, it is probably happening. Nevertheless, no complete release of ligands would occur because the emitting state is still populated via nonradiative relaxation from the ligand triplet excited state. The lack of thermal deactivation could be explained whether ligands, becoming monodentate, let that process go on, making the rate constants for electron transfer or energy transfer smaller as a consequence of a weaker effective electronic coupling through the mono oxo-bridge.[26,27] On the other hand, both complex species would not be in equilibrium; otherwise just one lifetime should be observed.

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