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Examination of Photophysics in Rare Earth Chelates by Laser-Excited Luminescence

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We report time-resolved and spectrally resolved luminescence investigations for several chelates of Eu(III) and Tb(III) as well as for the Eu^{2+} ion in glass-forming solvents. For those Eu(III) chelates in which the lowest ligand triplet state lies above the $^5D_1$ term of Eu(III), luminescence is observed from both $^5D_1$ and $^5D_0$. The $^5D_1$ level is observed to decay exponentially in time, while luminescence from $^5D_0$ shows a rapid rise followed by a slower rise and then a very slow decay. The characteristics of these luminescence decays are examined as a function of ligand, temperature, and solvent. The results are discussed in terms of a simple kinetic scheme. In the Tb(III) complexes studied, no emission other than that from the $^5D_4$ term was observed. It is proposed that ligand singlet–triplet energy transfer can occur by a spin-allowed process involving electronic levels of the rare earth complex. The 200-nsec lifetime of emission from Eu^{2+} near 4020 Å suggests that an interconfigurational transition may be involved.

I. Introduction

The mechanisms by which electronic energy, initially fed into spin-allowed absorption bands of numerous rare earth complexes, is funnelled into luminescing states, often with high efficiency, have been the subjects of extensive experimental and theoretical investigation. Understanding energy transfer in rare earth complexes is of immediate interest both to the fundamental theory of inorganic photophysical processes and to the very pragmatic development of better rare earth photosensitive and laser materials. In the first instance, rare earth complexes offer the possibility for modification of one part of the molecular system without drastically changing the other part. This opportunity does not exist, for instance, in most transition metal complexes where the ligand field is extremely important for the determination of the energy level structure. In the second instance, if we understand how energy is transferred from the ligand to the ion, we should be able better to predict changes that will yield higher quantum yields and more efficient sensitization.

Our knowledge of the dynamic photophysics of coordination complexes has been largely confined to the radiative and nonradiative processes between the lowest energy excited states and the ground states of the electronic manifolds. The pathways between *different* excited states can be partially mapped by quantum yield studies but little dynamic information has been available for these important processes. Eu(III) chelates demand particular attention in this regard because the steady-state luminescence in some cases arises from two neighboring states in the $4f^6$ configuration, suggesting the possibility for defining explicitly energy-transfer processes directly from the time-resolved emission characteristics of both the initial and terminal states.

In the present work, we have investigated the rates of nonradiative processes involving excited states in some Eu(III) and Tb(III) chelates with the aid of the tunable dye laser. Similar work on some Cr(III) complexes has been reported elsewhere.[1] Some observations of luminescence from the Eu^{2+} ion are reported here also.

A typical energy level diagram for the important electronic states of the Eu(III) chelates studied is shown in Figure 1. The positions of low-energy ligand-centered singlet (S_1) and triplet (T_1) levels vary with the ligand. For Tb(III) the energy level structure is similar, although the energy ordering of levels defined by the subscript J is reversed. The radiative transitions of interest in this work are Laporte forbidden and spin forbidden.[2] The energies of ligand-localized states are, of course, strongly dependent on the ligands.

II. Experimental Section

Piperidinium tetrakis(dibenzoylmethido)europate(III), $[Eu(dbm)_4]Hpip$, tris(8-hydroxyquinolato)europium(III), $[Eu(8\text{-}hq)_3]\cdot H_2O$, tris(acetylacetonato)europium(III), $[Eu(acac)_3]\cdot H_2O$, and piperidinium tetrakis(dibenzoylmethido)terbate(III), $[Tb(dbm)_3]Hpip$, were isolated from ethanolic solutions of anhydrous $EuCl_3$ or $TbCl_3$, piperidine, and the appropriate ligand and were recrystallized. Tris(dibenzoylmethido)europium(III), $[Eu(dbm)_3]$, was formed on high-vacuum pumping of $[Eu(dbm)_4]Hpip$ at 145°C for 36 hr. Tris(dipivaloylmethido)europium(II), $[Eu(thd)_3]$, was obtained from Aldrich Chemical Co. Tris(dipivaloylmethido)(1,10-phenanthroline)europium(III), $[Eu(thd)_3phen]$, was prepared by Dr. F. Kaufman.[3] Tris(acetylacetonato)terbium(III), $[Tb(acac)_3]\cdot H_2O$, was prepared by adapting the method of Lyle and Witts.[4] Elemental analyses confirmed the identity of the complexes obtained.[1a]

The complexes were dissolved in appropriate glass-forming solvents, including (equal parts by volume) diethyl ether–2-methylbutane (EP), diethyl ether–2-methylbutane–ethanol (EPA), methanol–ethanol (ME), and methylcyclohexane–2-methylbutane (MCHIP). Approximately 1-ml samples were filtered through fritted glass and were introduced into 18-mm Pyrex ampoules. These were repeatedly degassed by freeze (77 K)–pump (10^{-6} Torr)–thaw cycles and sealed off. During luminescence experiments, these ampoules were completely

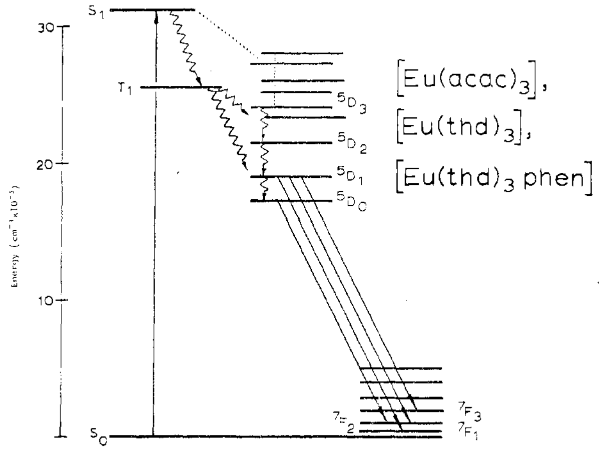

Figure 1. Energy level diagram for typical Eu(III) complexes.

immersed in the cryogenic liquid within the sample dewar. The dewar was equipped with quartz windows on both inner and outer walls for incoming exciting light and outgoing luminescence. When data were obtained at temperatures above 77 K, the sample dewar was fitted with a coil of copper tubing and filled with 2-methylbutane or ethanol. Nitrogen gas was cooled in a second coil immersed in a dewar of liquid nitrogen and fed into the sample dewar's coil at a controlled rate sufficient to maintain the sample at the temperature desired. The sample temperature was continuously monitored by a thermocouple.

A Xe lamp coupled with a monochromator (band-pass = 22 nm) was used in obtaining steady-state emission spectra. Exciting light for time-resolved experiments were provided by one of two pulsed laser systems. An AVCO nitrogen laser generated 337.1-nm (29,665-cm^{-1}) radiation in pulses of 5-nsec duration. This wavelength was found to be particularly convenient for the excitation of ligand-localized singlet states in several β-diketonate complexes. The tunable dye laser, utilizing the nitrogen laser as pumping source, consisted of a 1-cm dye cell, Littrow-configuration grating, and a dielectric output mirror and could be tuned to any wavelength in the range 350–620 nm with an appropriate series of dye solutions.[5]

Both steady-state and time-resolved work utilized an RCA C31034A photomultiplier tube in a cooled housing to detect luminescence from the samples. This tube has relatively flat response from 400 nm to beyond 860 nm. In obtaining steady-state emission spectra, a $^3/_4$-m monochromator scanned the wavelength region of interest. In time-resolved experiments, a $^1/_4$-m monochromator and appropriate Corning glass or dielectric filters provided the wavelength discrimination. The observation direction was at a 90° angle to the exciting light. Steady-state spectra were recorded with the aid of a conventional electrometer and recorder. In time-resolved experiments, the data were obtained by digitization and storage of the output signal in a Biomation 610 transient recorder, signal averaging over 128 laser pulses in a PDP8/e minicomputer, and subsequent analysis on a larger computer.[1a]

III. Results

A. Europium(III) Tris- and Tetrakis(dibenzoylmethides). The steady-state luminescence from these Eu(III) complexes generally consists of transitions originating from both the $^5D_0$ and $^5D_1$ terms and terminating in various ^7F terms for the parent metal.[1a] In our time-resolved experiments three bands assigned to $^5D_1$ emission and one band assigned to $^5D_0$ emission were clearly distinguished. For the purposes of analysis, it is most convenient to work with the predominant [$^5D_0 \rightarrow {}^7F_2$] and [$^5D_1 \rightarrow {}^7F_1$] transitions. The time behavior of the [$^5D_1 \rightarrow {}^7F_2$] and [$^5D_1 \rightarrow {}^7F_3$] bands was found to behave quantitatively like the [$^5D_1 \rightarrow {}^7F_1$] transition. In each sample of [Eu(dbm)$_4$]Hpip and [Eu(dbm)$_3$] the $^5D_0$ emission was observed to *rise* exponentially from an apparent initial intensity to a maximum within several microseconds and to *decay* exponentially on a much longer (millisecond) time scale. A typical intensity–time curve for the first few microseconds is shown in Figure 2. On the other hand, emission of the $^5D_1$ level was found to decay exponentially on a microsecond time scale. Figure 3 shows the observed lifetime for this decay as a function of temperature. Also shown is the *rise time* of the $^5D_0$ emission. Results at 77 K are tabulated in Table I. It may be seen that the rise time of $^5D_0$ emission is virtually identical with the decay time of $^5D_1$ emission.

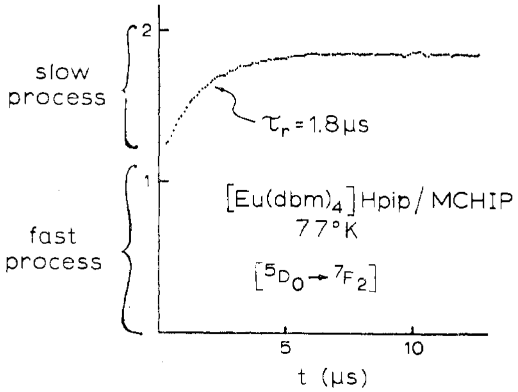

Figure 2. Typical plot of intensity against time for luminescence from $^5D_0$ levels of certain complexes on microsecond time scale.

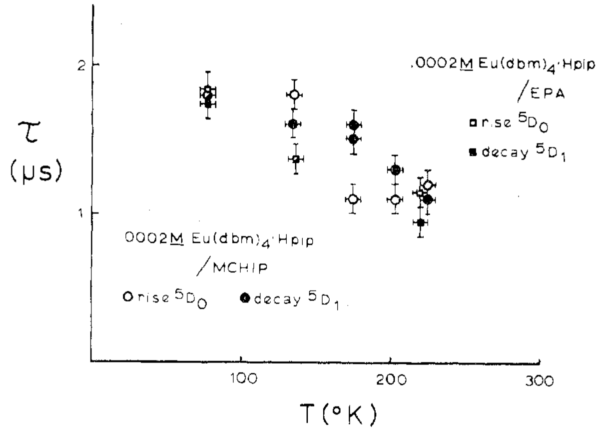

Figure 3. Observed temperature dependence of the observed rise times for $^5D_0$ emission and decay times for $^5D_1$ emission in [Eu(dbm)$_4$]Hpip in the solvents MCHIP and EPA.

Table I. Time-Resolved Data for [Eu(dbm)$_4$]Hpip and [Eu(dbm)$_3$] at 77 K

Solvent	Concn, *M*	$\tau_d(^5D_0)$, μsec	$\tau_r(^5D_0)$, μsec	$\tau_r(^5D_1)$, μsec	B_0/B_{tot}
		[Eu(dbm)$_4$]Hpip			
EPA	0.001	475 ± 50	1.9 ± 0.1	1.8 ± 0.1	0.7 ± 0.1
	0.0002	475 ± 50	1.8 ± 0.1	1.7 ± 0.1	0.8 ± 0.1
EPA[a]		442 ± 40	1.8 ± 0.3		
Crystal[a]		488 ± 40	1.8 ± 0.3	1.9 ± 0.3	
EP	Satd	670 ± 10	1.9 ± 0.1	1.7 ± 0.1	0.8 ± 0.05
MCHIP	0.0002	570 ± 20	1.8 ± 0.1	1.8 ± 0.1	0.45 ± 0.1
		[Eu(dbm)$_3$]			
EPA	0.0002	350 ± 20	1.8 ± 0.1	1.6 ± 0.1	0.8 ± 0.05
EP	Satd	320 ± 20	1.6 ± 0.2	1.7 ± 0.2	0.6 ± 0.2
MCHIP	0.0002	450 ± 20	2 ± 1	1.9 ± 0.1	0.1 ± 0.05

[a] Reference 7.

The $^5D_0$ lifetime τ_d = 475 μsec of [Eu(dbm)$_4$]Hpip–EPA at 77 K agrees well with previous reports[6] and within the error limits is concentration independent in the range of 0.01–0.002 *M*. The $^5D_0$ lifetime τ_d = 360 μsec of [Eu(dbm)$_3$]–EPA is consistent with a previous report in methanol solution.[7] For each complex, changing the solvent from EPA to the less polar MCHIP *increases* the lifetime. Simply removing the ethanol from EPA to form EP, however, *increases* the $^5D_0$ lifetime in the tetrakis complex while it decreases the lifetime in the tris complex.

The temperature dependence of the $^5D_0$ lifetime has been

Table II. Parameters and Observations for Eu(III) Complexes with High-Energy Ligand Triplet States

Complex	Ligand triplet energy, cm^{-1}	Solvent	Concn, *M*	$\tau_d(^5D_0)$, μ_{sec}	$\tau_r(^5D_0)$, μ_{sec}	$\tau_r(^5D_0)$, μ_{sec}	B_0/B_{tot}
$[Eu(acac)_3]$	25,300–26,000[a]	EPA	2×10^{-4}	550 ± 50	1.9 ± 0.1	2.0 ± 0.1	0.4 ± 0.1
$[Eu(thd)_3]$	25,500[b]	EPA	2×10^{-4}	580 ± 20	1.7 ± 0.1	1.7 ± 0.1	0.7 ± 0.1
$[Eu(thd)_3phen]$		EPA	$\sim10^{-3}$	885 ± 30	1.2 ± 0.1	1.2 ± 0.1	0.8 ± 0.1

[a] Reference 10. [b] Reference 11.

followed from room temperature to liquid nitrogen temperature for both compounds in two solvents. Results are presented graphically in Figure 4. It appears that $^5D_0$ lifetimes obtained at 77 K are well onto a "limiting lifetime plateau". It is interesting that, for a given solvent, tris $^5D_0$ lifetimes are consistently shorter than tetrakis lifetimes at 77 K but that this effect is reversed at room temperature. This is true in the solvents EPA, MCHIP, and EP used here.

The $^5D_1$ lifetimes at 77 K for both the $[Eu(dbm)_4]Hpip$ and the $[Eu(dbm)_3]$ complexes in various solvents cluster around the value of 1.8 μsec, which is consistent with the value of 1.9 μsec reported for $[Eu(dbm)_4]Hpip$ solid.[6b] It appears that here, also, substitution of the less polar MCHIP for EPA *increases* the lifetime but the increases are not as pronounced as in the longer $^5D_0$ lifetimes.

The rise times, τ_r, of the $^5D_0$ phosphorescence of several systems are also presented in Table I. These values are seen to correlate with the $^5D_1$ decay times, also shown. Furthermore, the temperature dependence of $\tau_r(^5D_0)$ mirrors rather closely the temperature dependence of $\tau_r(^5D_1)$ (see Figure 3). This is good evidence that the fraction of luminescing molecules which has come into the $^5D_0$ state via the "slow" mechanism has arrived by internal conversion from the $^5D_1$ state. We have observed that the $^5D_0$ phosphorescence has an initial intensity which is reached within the resolution time of our experiments. Under the best circumstances ($[Eu(dbm)_4]Hpip$–EPA), that resolution is ~20 nsec.

B. Europium(III) 8-Hydroxyquinolate. Crosby, Whan, and Alire[8] proposed, on the basis of steady-state emission studies, that sensitization of ion luminescence in rare earth complexes after ligand-localized excitation occurred through the ligand-localized triplet, T_1. Their evidence was the absence of $^5D_1$ emission from two complexes with T_1 states lower in energy than $^5D_1$ while other Eu(III) complexes displayed both $^5D_0$ and $^5D_1$ phosphorescence. The first excited triplet, T_1, of $[Eu(8\text{-}hq)_3]$ lies near 17,760 ± 50 cm^{-1},[8] above the $^5D_0$ state at 17,260 cm^{-1} but below the $^5D_1$ state at 19,020 cm^{-1}. The $S_0 \rightarrow S_1$ absorption band of 0.002 *M* $[Eu(hq)_3]$–ME apparently has a broad maximum near 370 nm (27,000 cm^{-1})[8] and $^5D_0$ emission was observed to be about equally strong on excitation with the nitrogen laser (337 nm) or the nitrogen-laser-pumped 2,5-dibiphenyl-1,3,4-oxadiazole (BBD) dye laser (~370 nm).

The observed $^5D_0$ lifetime of $[Eu(8\text{-}hq)_3]$–ME is 650 ± 30 μsec at 77 K. This observation was made on the $[^5D_0 \rightarrow {}^7F_2]$ band at 612 nm (16,400 cm^{-1}); the $[^5D_0 \rightarrow {}^7F_3]$ band at 595 nm (16,800 cm^{-1}) is barely observable on single-pulse observation. The rise time of all $^5D_0$ emission intensity was faster than 100 nsec. No short-lived phosphorescence in the 537-, 557-, or 595-nm bands typical of $^5D_1$ phosphorescence could be detected.

C. Europium(III) Acetylacetonate and Tetramethylheptanedionates. We have examined the time-resolved luminescence of $[Eu(acac)_3]$, $[Eu(thd)_3]$, and $[Eu(thd)_3phen]$ in an attempt to elucidate further the processes which were observed to populate the $^5D_0$ state on at least two time scales. These three complexes should have ligand-localized triplets which are of high enough energy to populate the metal-localized $^5D_3$ and $^5D_2$ states directly. Triplet energies are imprecisely known but available information is given in Table II.

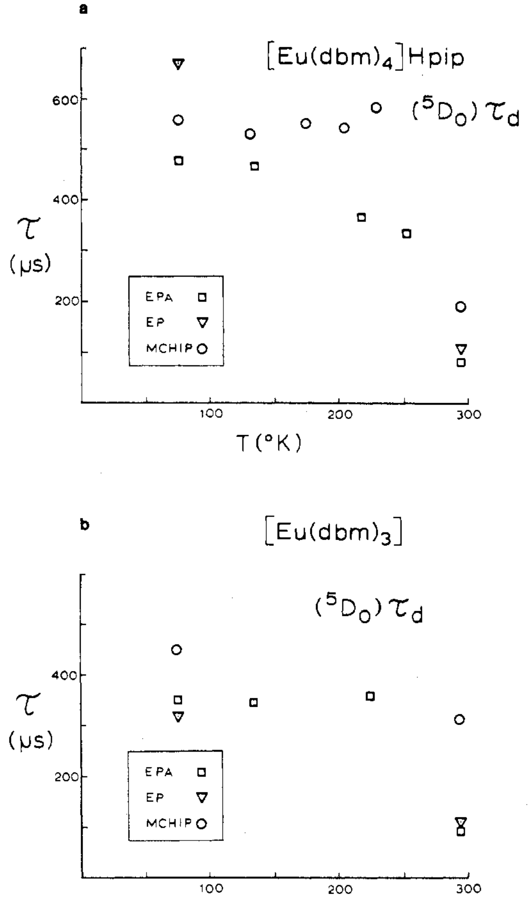

Figure 4. Temperature dependence of the long decay time for $^5D_0$ emission: (a) $[Eu(dbm)_4]Hpip$; (b) $[Eu(dbm)_3]$.

The lifetimes and rise times of $[Eu(acac)_3]$–EPA and $[Eu(thd)_3]$–EPA at 77 K, shown in Table II, are not dramatically different from those of $[Eu(dbm)_3]$–EPA. The large changes on adding the 1,10-phenanthroline ligand to $[Eu(thd)_3]$ are noteworthy. The lengthening of the $^5D_0$ lifetime follows the customary trend of decreasing $^5D_0$ nonradiative loss with a more protective ligand sphere.[9] For this mixed-ligand complex, the 1.2-μsec rise time of the $^5D_0$ state matches the 1.2-μsec decay of the $^5D_1$ state once again but this value is significantly shorter than the 1.6–2.0-μsec range for the $[^5D_1 \rightarrow {}^5D_0]$ process obtained in all other complexes studied here.

D. Terbium(III) Dibenzoylmethide and Acetylacetonate. That $[^5D_1 \rightarrow {}^5D_0]$ internal conversion might be slow relative to the other $[^5D \rightarrow {}^5D]$ nonradiative processes is an observation which begs theoretical interpretation. Peterson and Bridenbaugh[12] have observed a slow rise time to the $^5D_4$ phosphorescence of $KLa_{0.98}Tb_{0.02}W_2O_8$ crystals on direct excitation of $^5D_3$. If the appropriate terbium complex could be made to show this behavior, it could provide an important clue as to why certain internal conversions within the ^5D manifold are relatively slow.

We have obtained $^5D_4$ lifetimes for two complexes with T_1 below $^5D_3$ which are analogous to the results obtained from

[Eu(8-hq)$_3$]. For [Tb(dbm)$_4$]Hpip (10^{-3} *M*) in EPA at 77 K, the observed τ_d was 343 ± 10 μsec whereas for [Tb(acac)$_3$] (10^{-3} *M*) in EPA at 77 K, τ_d = 950 ± 50 μsec was determined. These results were obtained by pulsed nitrogen laser excitation at 337.1 nm (29,665 cm^{-1}) with 22-nm detection bandwidth. Five observed emission bands of [Tb(acac)$_3$] at 77°K were shown to display the same lifetime within the experimental uncertainty.

The [Tb(dbm)$_4$]Hpip complex has a ligand-localized T_1 state which is only approximately 100 cm^{-1} above the metal-localized $^5D_4$ state. At 77 K only $^5D_4$ phosphorescence is observed, and it is a single exponential decay which has risen to its maximum intensity within the resolution of the experiment, ~50 nsec. In contrast to all other Eu(III) and Tb(III) complexes in this work, [Tb(dbm)$_4$]Hpip does not luminesce sufficiently at room temperature on excitation with our nitrogen laser to be visible to the eye. This may be an effect of rapid thermal quenching of the $^5D_4$ state through the ligand-localized triplet.[13]

The [Tb(acac)$_3$] complex is a very strong emitter, even at room temperature, and displays a $^5D_4$ lifetime at 77 K that is longer than any $^5D_0$ lifetimes of Eu(III) chelates that have been reported here or in the literature. Although the acac$^-$ ligand-localized T_1 state should be nearly as high in energy as the metal-localized $^5D_3$ state, we were unable to observe short-lived emission at any of the calculated [$^5D_3 \rightarrow {}^7F_J$, J = 0–6] band wavelengths. In addition, the $^5D_4$ phosphorescence reached its maximum intensity within the resolution time of the experiment, ~20 nsec.

E. Dynamics of Eu^{2+} Luminescence. The Eu^{2+} ion is readily oxidized and this has hindered the investigation of its photophysical and photochemical properties. Calculations indicate that the lowest lying electronic transitions should be of the interconfigurational type [$4f^7 \leftrightarrow 4f^65d^1$].[2] In the doped-crystal environment, Eu^{2+} luminescence has been observed and the Zeeman splitting of this emission indicates that the terminal state is $^8S_{7/2}$,[14] the predicted ground state of the ion.

In the fluorescence spectrum obtained from either solid EuCl$_2$ or EuCl$_2$ dissolved in degassed EPA under illumination at 340 nm (29,400 cm^{-1}) we observe a broad peak centered at 402 nm. The luminescence decay of solid EuCl$_2$ excited directly by the pulsed N$_2$ laser appears to be exponential with a lifetime of 283 nsec at 77 K and 143 nsec at 298 K. Qualitatively, the quantum yield follows a consistent temperature dependence, increasing in intensity roughly by a factor of 2 from room to liquid nitrogen temperature.

These lifetimes are roughly 3 orders of magnitude shorter than comparable lifetimes, examined in this work and elsewhere, for strongly forbidden intraconfigurational [$4f^i \leftrightarrow 4f^i$] transitions in Eu(III), Tb(III), and other trivalent rare earths. This dynamical information lends support to the notion that an allowed *interconfigurational* transition, possibly [$4f^65d^1 \rightarrow 4f^7$], is involved.[2] Since both the lifetime and the quantum yield display a consistent temperature dependence in the temperature interval studied, we may assume that we are principally examining the rate of radiationless deactivation of the upper state. If the absorption spectrum of the $4f^65d^1$ term states could be resolved with respect to the particular term (or terms) responsible for the luminescence, absorption coefficients could lead to an estimate of the radiative lifetime. One would then be in a better position to speculate to what extent the violet emission of Eu^{2+} represents a spin-forbidden, or perhaps Laporte- or symmetry-forbidden, transition. Recently luminescence at 368 nm in doped crystals containing Eu^{2+} has been reported and assigned as an intraconfigurational $4f^7(^6I \rightarrow {}^8S)$ transition.[15] An anomalously high oscillator strength was found, with a fluorescence "delay time" of ~80 psec. Such luminescence would have been masked by the scattered exciting light and by the limited time resolution of our apparatus.

IV. Discussion

A. Kinetic Scheme. For the glasses containing the complex [Eu(8-hq)$_3$]·H$_2$O, in which the lowest energy excited triplet (T_1) of the ligand lies *below* the $^5D_1$ term of Eu, no emission from the $^5D_1$ level is observed upon excitation into S_1 at 77 K. The luminescence from the $^5D_0$ level rises rapidly (within the time resolution of the apparatus) and decays at a slow rate characteristic of the $^5D_0$ level. In contrast, in the complexes [Eu(dbm)$_4$]Hpip and [Eu(dbm)$_3$] for which the energy of T_1 exceeds that of the $^5D_1$ term of Eu, luminescence from the $^5D_1$ term is observed to rise within the time resolution of the apparatus and to decay on a time scale of ~2 μsec. Furthermore, the $^5D_0$ emission shows an initial rapid rise, followed by an additional increase on a time scale of ~2 μsec and then the characteristic slow (~500 μsec) $^5D_0$ decay. Additionally, at 77 K the number of molecules initially formed in $^5D_0$ relative to the total number formed at all times varies from ~0.1 to ~0.8 depending on the solvent. No emission from the terms $^5D_2$ or $^5D_3$ was observed in [Eu(acac)$_3$], [Eu(thd)$_3$], and [Eu(thd)$_3$phen] under the excitation conditions employed, in spite of the fact that these ligands have triplet levels with sufficient energy for excitation of the $^5D_2$ or $^5D_3$ terms.

The above observations suggest the following first-order kinetic scheme, where a and b refer to $^5D_1$ and $^5D_0$ terms, respectively. Subsequent to excitation into ligand-localized singlet bands, energy is transferred rapidly ($\tau < 10^{-8}$ sec) to *both* $^5D_1$ and $^5D_0$ levels with rate constants k_{ta} and k_{tb}. Energy transfer may also by-pass both levels with rate constant k_t. The $^5D_1$ level may decay to the ground state with radiative rate constant k_a'' and nonradiative rate constant k_a', or it may decay to $^5D_0$ with rate constant k_{ab}. Similarly, $^5D_0$ may decay radiatively or nonradiatively with rate constants k_b'' and k_b'. In this scheme our observed quantities τ_r and τ_d are related to the rate constants by $\tau_r^{-1} = k_a' + k_a'' + k_{ab}$ and $\tau_d^{-1} = k_b' + k_b''$. In addition, experimental measurements of I_0, the initial observed $^5D_0$ emission intensity, and I_0', the signal at t = 0 extrapolated from the long (millisecond), decay are related to the ratio of the number of molecules initially formed in $^5D_0$ (denoted B_0) to the total number of $^5D_0$ molecules formed at all times (denoted B_{tot}) by the relation $B_0/B_{tot} = I_0\tau_d[I_0'\tau_d - (I_0' - I_0)\tau_r]^{-1}$. Some representative values for this ratio at 77 K are shown in Tables I and II. It may be seen that this number varies from 0.1 to 0.8 and is highly solvent dependent.

From the kinetic model, it may be seen that our experiments yield no information concerning k_t and cannot unambiguously separate k_a', k_a'', and k_{ab} nor can they explicitly separate k_b' and k_b''. For Eu(8-hq)$_3$, where the ligand triplet lies below the $^5D_1$ term, k_{ta} is apparently zero or very small, suggesting energy transfer from the ligand triplet. For [Eu(acac)$_3$], [Eu(thd)$_3$], and [Eu(thd)$_3$phen] it is not clear whether the $^5D_2$ and $^5D_3$ terms act as intermediaries or not, but the excitation rapidly appears in the $^5D_1$ and $^5D_0$ terms. If it is assumed that $k_{ab} >> k_a' + k_a''$ (i.e., that there is negligible loss of excitation directly from $^5D_1$), then $B_0/B_{tot} \simeq k_{ta}(k_{ta} + k_{tb})^{-1}$ and B_0/B_{tot} would give the amount of transfer into $^5D_1$ relative to the total amount of transfer into $^5D_0$ and $^5D_1$. In this case the results in Tables I and II would suggest that the solvent can influence the relative amounts of energy transfer into $^5D_1$ and $^5D_0$. An alternative explanation for the variation of B_0/B_{tot} with solvent is that a solvent such as MCHIP can accelerate k_1', relative to k_2 as compared to EP or EPA. This would appear unlikely, since such an acceleration should show up in τ_r measurements, contrary to the observations. It is also interesting to note that B_0/B_{tot} differs for [Eu(acac)$_3$] and

[Eu(thd)$_3$] even though the ligand triplets are thought to lie at roughly the same energy.

B. Mechanisms of Energy Transfer in Rare Earth Complexes. Several workers[7,8,17,18] have pursued the role of [$S_1 \rightarrow T_1$] intersystem crossing in luminescence sensitization and have shown that for numerous six- and eight-coordinate rare earth complexes, only those metal-localized states which lie below the ligand-localized T_1 state will luminesce under steady-state excitation of the S_1 state. The effect is best documented for Eu(III) systems like the [Eu(8-hq)$_3$] complex investigated in this work. This has been interpreted as good evidence that the predominant energy-transfer pathway goes through the triplet: [$S_1 \rightarrow T_1$], then [$T_1 \rightarrow$ rare earth]. Kleinerman[19] has pointed out that it might equally be inferred that the triplet quenches those metal-localized states above it, extinguishing any luminescence from those states. Bhaumik and coworkers,[18a–c] however, have shown that organic triplet quenchers which were shown not able to affect excited singlets did quench ligand-localized T_1 states of several Eu(III) complexes as evidenced by the lack of the normal $^5D_1$ and $^5D_0$ luminescence. The complete pathway involves the spin-forbidden intersystem crossing within the ligand-localized states and intramolecular energy transfer from the triplet to metal-localized states of comparable energy. Kleinerman has pointed out that this latter step probably occurs by the short-range exchange interaction. If this is the case, the transfer is *spin-allowed* since exchange interactions of the sort $S_1 + S_2 \rightarrow S_3 + S_4$ proceed by the selection rule[20]

$$\{|S_1 + S_2|, |S_1 + S_2 - 1|, \ldots, |S_1 - S_2|\} \cup \{|S_3 + S_4|, |S_3 + S_4 - 1|, \ldots, |S_3 - S_4|\} \neq 0$$

where S_j's correspond to appropriate spin angular momenta. In this case, we have $S(T_1) = 1$, $S(^7F_0) = 3$, $S(S_0) = 0$ and $S(^5D_j) = 2$. Hence, $|1 - 3| = |2 + 0|$.

Kleinerman has investigated the direct population of the metal-localized manifold of states from the S_1 state without the participation of the triplet. The strength of his argument lay in two experimental observations. The first was the observation of $^5D_4$ luminescence from the three Tb(III) complexes which have T_1 states below $^5D_4$. The second was the lower relative quantum yield for ligand fluorescence [$S_1 \rightarrow S_0$] from the rare earth ions Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+}, which have metal-localized states adjacent to S_1 in energy, compared with the ions La^{3+}, Gd^{3+}, and Lu^{3+}, which have metal-localized states above S_1 only. He has shown this effect for a large number of ligands. This is good evidence that [$S_1 \rightarrow$ rare earth] intramolecular energy transfer does actually occur. It must, however, be noted that both types of Kleinerman's experiments were performed on solutions containing a large excess of rare earth cations compared to ligand anions and it is not at all clear what "complexes" he was observing or whether those observations can be appropriately extrapolated to the six- and eight-coordinate complexes. Kleinerman believed the [$S_1 \rightarrow$ rare earth] transition is essentially a dipole–quadrupole interaction. However, this transition is spin forbidden in at least these two systems. It is also spin forbidden as an exchange interaction[21] and the multipole rate constant of Dexter,[22] cited by Kleinerman as evidence of fast transfer, is in serious doubt.

To this conflicting and confusing testimony, we would add yet another transition from the ligand-localized S_1 state which should be considered. Both [$S_1 \rightarrow T_1$] intersystem crossing and [$S_1 \rightarrow$ rare earth] via multipole interaction are spin-forbidden processes but one can envision an *exchange interaction* between the ligand-localized and metal-localized orbitals which is spin allowed. In Eu(III) and Tb(III) complexes, for instance, [$S_1\ {}^7F_J \rightarrow T_1\ {}^7F_{J'}$] where $J = 0$ for Eu(III) and $J = 6$ for Tb(III) can be made spin allowed since $S(S_1) = 0$, $S(^7F_J) = 3$, $S(T_1) = 1$, and $|0 + 3| = |1 + (3 - 1)|$. This process is intersystem crossing in disguise, enhanced now by the juxtaposition of six unpaired electrons. In addition, for Eu^{3+} nearly 5000 cm^{-1} and for Tb^{3+} over 5800 cm^{-1} of energy can be absorbed by the ^7F manifold so that the process does not need to dissipate the whole $S_1 - T_1$ energy difference into vibrational modes. The $^7F_{J'}$ state so populated may be expected to decay to the respective ground states very rapidly by internal conversion. If the triplet now populates the ^5D manifolds of Eu^{3+} and Tb^{3+}, again by exchange interaction, a complete pathway which is *spin allowed* has been created. The exchange interaction[21] is effective only at short range but may be applicable here since the division of the molecular orbitals into metal localized and ligand localized was artificial at the outset.

V. Conclusions

The application of pulsed laser excitation to the luminescence studies of several rare earth chelates has expanded the time resolution of our photophysical interest in the rare earth ions to the nanosecond range. In time-resolved, wavelength-resolved investigations of some Eu(III) syystems, we have shown that the $^5D_0$ state is populated by both "fast" and "slow" processes. By systematically correlating $^5D_1$ decay times and $^5D_0$ rise times, the "slow" process has been definitively identified as [$^5D_1 \rightarrow {}^5D_0$] internal conversion. Efforts to understand the nature of [$^5D_J \rightarrow {}^5D_{J'}$] transitions by studying the [$^5D_3 \rightarrow {}^5D_4$] process in Tb(III) complexes have not been fruitful.

We have proposed a spin-allowed, enhanced intersystem crossing mechanism for relaxation of the ligand-localized S_1 state. This implies a predominant pathway of electronic relaxation involving the ligand-localized T_1 state. Further elaboration of the nonradiative mechanisms at work in these rare earth chelates probably awaits the application of fast-pulsed, tunable lasers capable of more adequately exciting the metal-localized states directly and the more effective techniques for eliminating stray light from cryogenic samples.

The lifetime of metal-localized Eu^{2+} emission from $EuCl_2$ is temperature dependent in our operating range and is approximately 200 nsec, indicating that an interconfigurational transition is likely to be involved.

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Registry No. [Eu(dbm)$_4$]Hpip, 17856-06-3; [Eu(8-hq)$_3$], 21301-33-7; [Eu(acac)$_3$], 14284-86-7; [Tb(dbm)$_4$]Hpip, 19478-56-9; [Eu(dbm)$_3$], 14552-07-9; [Eu(thd)$_3$], 15522-71-1; [Eu(thd)$_3$phen], 33134-15-5; [Tb(acac)$_3$], 14284-95-8; Eu^{2+}, 16910-54-6.

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Organolanthanides and Organoactinides. XV. Synthesis and Properties of New σ-Bonded Organolanthanide Complexes

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A series of new organolanthanide complexes containing σ bonds has been synthesized. The complexes are of the type $(\eta^5\text{-}C_5H_5)_2LnR$ (R = methyl, phenyl, and phenylacetylide) and are synthesized by the reaction of the appropriate RLi compound with $(\eta^5\text{-}C_5H_5)_2LnCl$ complexes. The new complexes have been characterized by vibrational and visible spectroscopy, as well as by magnetic susceptibility. The infrared data support the presence of ligands which are σ bonded to the metal. The magnetic data and, to a lesser extent, the visible data indicate that there is enhanced covalency in the lanthanide–carbon σ bond. The nature of this covalency and possible f-orbital involvement in the bonding are discussed.

Beginning with the preparation of uranocene in 1968 and the subsequent claim that the f orbitals were involved in the bonding,[3] there has been a dramatic resurgence of interest in the organometallic chemistry of the lanthanides and actinides. However, until the last three years, most of the work has been concerned with complexes which contained only π-bonded ligands.[4-10] Although σ-bonded organometallic compounds are well documented for the d-block transition metals,[11] they have been relatively unknown for the lanthanides and actinides. Consequently, much of the significant recent progress in the cheimstry of the f transition elements involves the synthesis and elucidation of properties of σ-bonded organoactinide complexes.[12-14] By contrast though, σ-bonded organolanthanide complexes have escaped the close scrutiny which their actinide analogs have undergone. Recently though, we communicated our preliminary results in synthesizing alkynyl,[15] alkyl, and aryl derivatives[16] for the lanthanides of the type $(\eta^5\text{-}C_5H_5)_2LnR$.[17] Generally, the complexes represent the first and only well characterized examples of compounds containing lanthanide–carbon σ bonds. These complexes also seemed to possess some degree of covalency (and possible 4f orbital involvement) in the σ bond. We now wish to present a detailed account of the synthesis and properties of these unique and unusual compounds.

Experimental Section

All operations of these organolanthanide complexes were performed in an atmosphere of prepurified argon using Schlenk techniques or in a drybox. Benzene and hexane were degassed, refluxed over finely divided $LiAlH_4$, and distilled under argon just prior to use. THF and toluene were distilled from blue sodium–benzophenone under argon immediately prior to use. Methyllithium was purchased from Alfa-Ventron, while anhydrous lanthanide trichlorides were obtained from Research Organic/Inorganic Chemical Corp. The Cp_2LnCl complexes (Cp = $\eta^5\text{-}C_5H_5$) were prepared by the method of Dubeck et al.[18] Melting points were determined in sealed argon-filled capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. We list below the syntheses for several of the new σ-bonded organolanthanide complexes, which are representative of all the complexes which were prepared. All the complexes not described below gave satisfactory elemental analyses.

Bis(η^5-cyclopentadienyl)gadolinium Phenylacetylide. Into a centrifuge Schlenk tube was placed 1.5 g (4.53 mmol) of Cp_2GdCl. Then, 60 ml of THF containing 4.65 mmol of freshly prepared lithium phenylacetylide[15] cooled to −78° was added to the Cp_2GdCl. With stirring, the solution was allowed to warm to room temperature over the course of several hours. By −50°, all of the solid material had dissolved, and by 0°, the solution (originally colorless) had begun to get darker until it had become dark red-orange. The reaction was allowed to stir overnight. At this time, the volume of THF was reduced in vacuo to about 5 ml. Then, 50 ml of toluene was added and an orange oil separated from the solution. The volume of the toluene–THF mixture was reduced in vacuo to 10 ml. During this time, the red-orange color disappeared, the solution becoming tan. Next, 50 ml of hexane was added. At this point, the mixture contained a tan solid and a tannish solution. The Schlenk tube was centrifuged and the solution was transferred away from the solid which was then dried. The crude material was purified by continuous extraction with benzene. The apparatus used was a Schlenk–Soxhlet extractor equipped with a coarse frit. About 60 ml of extractant (benzene in this case) was distilled into a centrifuge Schlenk tube and then used in the purification process. When the extraction began, the solution took on a yellow color, and after 1 hr, a yellow solid began to appear in the benzene. After the extraction was complete (as noted by the disappearance of the yellow color of the solid on the frit), the volume of benzene was reduced in vacuo to 10 ml, and 50 ml of hexane was added. After centrifugation of the Schlenk tube, the benzene–hexane was decanted from the pale yellow solid which was dried to give 0.7 g (40%) of $Cp_2GdC{\equiv}CPh$ (Ph = phenyl), mp 279–282° dec. Anal. Calcd for $C_{18}H_{15}Gd$: Gd, 40.47. Found: Gd, 40.56. Ir data (cm^{-1}): 3103 (m), 3075 (m), 3039 (m), 2047 (vs), 1483 (s), 1440 (vs), 1331 (w), 1308 (w), 1256 (w), 1184 (w), 1155 (w), 1113 (w), 1093 (w), 1066 (w), 1008 (vs), 919 (w), 773 (vs), 758 (vs), 692 (s).

Bis(η^5-cyclopentadienyl)ytterbium Methyl. Into a centrifuge Schlenk tube was placed 1.5 g (4.42 mmol) of Cp_2YbCl. THF (60 ml) was added and the resulting orange-red solution was cooled to −78°. Then, 2.4 ml (4.5 mmol) of methyllithium in diethyl ether was syringed into the Schlenk tube. The solution instantly became wine red. The reaction was allowed to warm to room temperature with stirring during a 4-hr period and then to proceed overnight. The volume of THF was reduced to 10 ml in vacuo and 50 ml of toluene was added causing a white solid to precipitate from solution. The volume of the THF–toluene mixture was reduced (to 5 ml) during which time the color of the solution gradually changed from burgundy to orange. At this point, 50 ml of hexane was added which precipitated an orange solid. The crude material was extracted with benzene, this being completed in 1 hr. The volume of benzene was reduced and hexane was added to precipitate out the product. The orange solid was isolated,