Magnetic and Luminescence Characteristics of Dinuclear Complexes of Lanthanides and a Phenolic Schiff Base Macrocyclic Ligand

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Abstract

The magnetic and luminescence characteristics of trimorphic homodinuclear macrocyclic complexes of lanthanides and a 2:2 phenolate Schiff's base L, derived from 2,6-diformyl-*p*-cresol and triethylenetetramine were determined. The complexes of Pr^{3+} exhibit non-Curie–Weiss temperature dependent magnetic susceptibilities for which satisfactory fits to an axial relationship depends on crystal field splitting and a weak binuclear Pr^{3+}–Pr^{3+} antiferromagnetic interaction. The exchange interaction parameters are $zJ' = -2.2$, -4.4 and -7.0 cm^{-1} for 'off-white' Pr_2L-$(NO_3)_4 \cdot 2H_2O$, 'yellow' $Pr_2L(NO_3)_4$, and 'orange' $Pr_2L(NO_3)_2(OH)_2$, respectively. In contrast, magnetic susceptibilities of the $Ln_2L(NO_3)_3(OH)$ complexes (Ln = Dy, Ho) follow Curie–Weiss behavior over the entire temperature range (6 K to 300 K). The complexes of closed shell ions La^{3+}, Lu^{3+}, Y^{3+} and those of the half filled shell ion Gd^{3+} exhibit a strong ligand fluorescence in the 450 nm to 650 nm range with decay times at 77 K of 5–8 ns for $Ln \neq Gd$ or 2–4 ns for Ln = Gd. The complexes of Gd^{3+} also exhibit a phosphorescence at 600 nm (decay time ~ 200 μs). The complexes containing Ce^{3+}, Eu^{3+}, Pr^{3+}, Tb^{3+} and Er^{3+} show very weak ligand luminescence indicative of effective quenching processes. Sensitized emission from the lanthanide ion is observed only with the Eu^{3+} complexes ($^5D_o \rightarrow {}^7F_j$ transitions). The emisson lifetimes are on the order of 250 μs in the pure Eu^{3+} complexes. The emission decay curves from dilute samples of Eu^{3+} in 'off-white' $La_2L(NO_3)_{4n}H_2O$ show a noticeable rise time as well as a biphasic decay (fast component ~ 400 μs; slow component ~ 2500 μs). The luminescing states of L and Eu^{3+} have a common excitation spectrum which is similar to the electronic absorption spectrum of L indicating that ligand-to-metal ion energy transfer processes are dominant. Overall the results of this study suggest that the spectral properties of the complexes are determined by the coordination mode of the lanthanide ions to the Schiff base portion of macrocyclic ligand.

Introduction

The first examples of homodinuclear lanthanide (Ln) complexes of a 2:2 macrocyclic Schiff's base, L, were recently reported [1, 2]. These complexes are
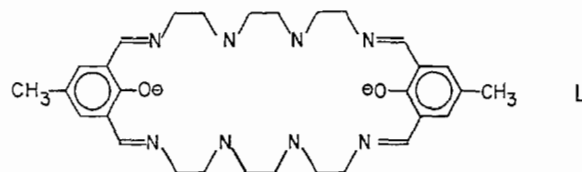
trimorphic, occurring in off-white, yellow and orange forms depending on lanthanide and counter anion, but more importantly, on preparation procedure [1]. The thrust of our synthetic effort was directed towards the preparation of isolated Ln^{3+}–Ln^{3+} pairs from which important coordination information and cooperative magnetic and spectroscopic properties may be derived. Attempts to obtain the various forms of complexes of L in crystalline states suitable for single crystal X-ray diffraction have not been successful; however, investigations of the magnetic and luminescence characteristics of the materials provide considerable insight.

Magnetic and luminescence studies of coupled Ln^{3+}–Ln^{3+} pairs are scientifically and technologically important as their collective characteristics are opening new applications in the laser and lighting industries [3–6]. Furthermore, luminescence of Ln^{3+}

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and the coordinated ligands as well as Ln^{3+}-to-ligand (and ligand-to-Ln^{3+}) energy transfer processes are pervasively making important advances in quantitative analysis of Ln^{3+} down to subpicomolar levels and in the characterization of biological [7] and other coordination sites of biochemical or chemical interest such as antibiotics [7, 8] and organometallics [9]. Magnetic and luminescence studies of the above homodinuclear lanthanide complexes are therefore of considerable relevance to these Ln^{3+} applications and the science on which the applications are based.

We herein report the magnetic characteristics of $Ln_2L(NO_3)_{4-n}(OH)_n \cdot xH_2O$, $n = 0,1,2$; Ln = Pr, Dy, Ho, and the luminescence properties of pure diamagnetic complexes of La^{3+}, Lu^{3+}, Y^{3+} and paramagnetic Gd^{3+} and Eu^{3+} complexes, as well as dilute Eu^{3+} complexes obtained by doping Eu^{3+} in diamagnetic La^{3+} and Y^{3+} complexes. For comparative purposes we have also included results of luminescence studies of a well defined chromophore, L', which is related to chromophoric centers of L.
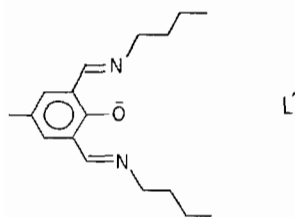
Experimental

Magnetic Susceptibility

The solid complexes used for magnetic susceptibility studies were the same as those reported earlier [1]. The superconducting quantum interference device (SQUID) susceptometer used in these studies has been described previously [10].

Electron Paramagnetic Resonance

A Varian E-line Century Series spectrometer equipped with accessories for variable temperature measurements was used to obtain X-band spectra of solid complexes of Gd^{3+} diluted in complexes of La^{3+}, Y^{3+}, Lu^{3+}.

Luminescence Experiments

The steady state emission and excitation spectra of powdered samples were recorded at room and liquid nitrogen temperature on a Spex Fluorolog spectrofluorimeter. Pulsed excitation at 337 nm for time resolved experiments was provided by a PRA LN-100 'Nitromite' N_2 laser. Sample emissions were collected at right angles through a McPherson model EU 700 monochrometer with a Hamamatsu R 928 phototube. Data for long lifetimes ($\tau > 100$ ns) were collected using a 10-bit 60 MHz Tektronix/Sony 390 AD

transient digitizer. Data were transferred to a series 200 Hewlett Packard 9826 microcomputer for averaging, storage and analysis. Typical data sets represents the average of 100 transients. Fast decays ($\tau < 100$ ns) were recorded on a PAR model 162 boxcar averager by scanning the time channel. Data were handled on the same system as those from the slow decays. The emission spectrum from the 'orange' $Gd_2L(ClO_4)_2(OH)_2$ complex observed at 100 μs after the excitation pulse was recorded using the boxcar averager with a gated integrator (0.5 μs gate). The laser was fired at a constant rate while slowly scanning the wavelength at the monochrometer. In all of the time resolved experiments the samples were maintained at 77 K in a quartz dewar (finger type).

Sample Preparation

(a) Ln_2L-complexes

The off-white, yellow and orange forms of the lanthanide complexes with the macrocyclic ligand, L, were prepared according to previously described procedures [1].

(b) Eu^{3+} doped La_2L- and Y_2L-complexes (orange form)

To a sample of yttrium or lanthanum nitrate in methanol (volume = 10 ml per mmol of Ln^{3+}), an equimolar amount of 2,6-diformyl-p-cresol was added followed by an equimolar amount of triethylenetetramine in methanol (5 ml per mmol). An appropriate sample of $Eu(NO_3)_3$ was similarly prepared and then the Ln^{3+} and Eu^{3+} samples were mixed and kept at ambient temperature. After 1–2 days the orange precipitate formed was filtered off, washed with methanol and air dried. The above procedure was repeated with the double component salt (Y, Eu)-$(NO_3)_3$ instead of the individual $Y(NO_3)_3$ and $Eu(NO_3)_3$ salts. This is to minimize the occurrence of Eu^{3+}–Eu^{3+} pairs and increase the relative concentration of heteronuclear sites, Eu^{3+}–Y^{3+}.

(c) Eu^{3+} doped La_2L-complex (off-white form)

The off-white complexes $(La_{1-x}Eu_x)_2L(NO_3)_4 \cdot nH_2O$, were prepared as above except for the use of much larger volumes of solvent and a two-fold excess of triethylenetetramine needed to ensure high yields of the pure off-white complexes [1]. However, since the pure off-white complex of Eu^{3+} is obtained in lower yields compared to that of La^{3+}, the levels of Eu^{3+} in the doped samples is most likely to be lower than expected on the basis of the ratios of La^{3+}:Eu^{3+} used in the reactant mixture.

(d) Preparation of Schiff's base L'

To 1 mmol of 2,6-diformyl-p-cresol in 20 ml of ethanol an excess of n-butylamine (3 mmol) in 10 ml of ethanol was added. The mixture was refluxed for
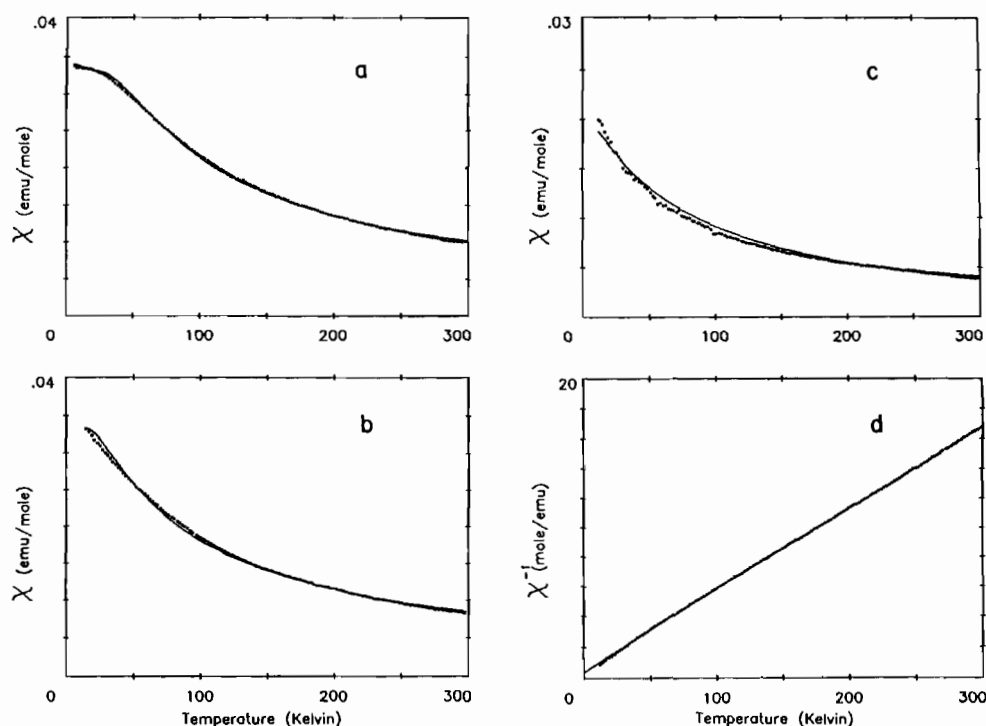
Fig. 1. Plots of molar magnetic susceptibility, χ, *versus* temperature for $Pr_2L(NO_3)_4 \cdot 2H_2O$ off-white form (curve a), $Pr_2L(NO_3)_4$ yellow form (curve b), and $Pr_2L(NO_3)_2(OH)_2$ orange form (curve c). The dots reflect the experimental data while the solid curves were obtained from least-squares fits of the data to eqns. (1)–(4). Curve d shows a plot of reciprocal susceptibility *versus* temperature for $Dy_2L(NO_3)_3(OH)$ orange form. The experimental data are indicated by dots while the solid line shows the least-squares fit to the Curie–Weiss law.

3 h and then rotavaporized to give an orange oil which was dissolved in ether and dried over $MgSO_4$. After filtration ether was removed and the remaining oil gave the expected simple NMR spectrum consisting of: a triplet at 0.94 ppm (alkyl-CH_3) (6), complex multiplet at 1.2–1.8 ppm (C-CH_2-C) (8), singlet at 2.29 ppm (aromatic-CH_3) (3), triplet at 3.62 ppm (CH_2–N) (4), singlet at 7.43 ppm (aromatic-H) (2), a singlet at 8.52 ppm (HC=N) (2) and a broad singlet at 14.17 ppm (OH) (1).

Results

Magnetic Properties

The temperature dependent magnetic susceptibilities between 6–300 K of $Pr_2L(NO_3)_4 \cdot 2H_2O$ (off-

white), $Pr_2L(NO_3)_4$ (yellow), $Pr_2L(NO_3)_2(OH)_2$ (orange), and $Dy_2L(NO_3)_3(OH)$ (orange) are given in Fig. 1. The temperature dependence of Pr^{3+} complexes do not follow the Curie–Weiss relationship but instead may be described by a model that depends on zero field splitting of LS coupled magnetic energy levels, as well as a weak binuclear exchange between the rare earth ions.

When dealing with the electronic energy levels of rare earth ions, spin orbit coupling dominates and J is a good quantum number. The Pr^{3+} ion has a $^3H_4$ ground term ($J = 4$). In an axial crystal field, the Pr^{3+} ion may exhibit a splitting of the m_J energy levels ($\hat{H} = \Delta L_z^2$) resulting in a magnetic susceptibility expression as shown in eqns. (1)–(3). These equations were derived according to the general procedure outlined in ref. 10.

$$\chi_\parallel = \frac{Ng^2\mu_B^2}{kT} \frac{2e^{-\Delta/kT} + 8e^{-4\Delta/kT} + 18e^{-9\Delta/kT} + 32e^{-16\Delta/kT}}{1 + 2e^{-\Delta/kT} + 2e^{-4\Delta/kT} + 2e^{-9\Delta/kT} + 2e^{-16\Delta/kT}} \tag{1}$$

$$\chi_\perp = \frac{Ng^2\mu_B^2}{\Delta} \frac{10(1 - e^{-\Delta/kT}) + 3(e^{-\Delta/kT} - e^{-4\Delta/kT}) + 7/5(e^{-4\Delta/kT} - e^{-9\Delta/kT})}{1 + 2e^{-\Delta/kT} + 2e^{-4\Delta/kT} + 2e^{-9\Delta/kT} + 2e^{-16\Delta/kT}}$$

$$+ \frac{4/7(e^{-9\Delta/kT} - e^{-16\Delta/kT})}{1 + 2e^{-\Delta/kT} + 2e^{-4\Delta/kT} + 2e^{-9\Delta/kT} + 2e^{-16\Delta/kT}} \tag{2}$$

$$\chi_p = \frac{\chi_\parallel + 2\chi_\perp}{3} + TIP \tag{3}$$

TABLE I. Magnetic Parameters

Property	$Pr_2L(NO_3)_4 \cdot 2H_2O$	$Pr_2L(NO_3)_4$	$PrL(NO_3)_2(OH)_2$
Pr Complexes[a]			
Color form	off-white	yellow	orange
Ground state	$^3H_4$	$^3H_4$	$^3H_4$
$\mu_{\text{free ion}}$	3.58	3.58	3.58
μ_{obs} (300 K)	3.43	3.11	2.62
Δ (cm^{-1})	93	52	22
zJ' (cm^{-1})	−2.2	−4.4	−7.0
TIP (emu/mol)	1.53×10^{-3}	1.1×10^{-3}	0
g	1.51	1.46	1.13

Property	$Dy_2L(NO_3)_3(OH)$	$Ho_2L(NO_3)_3(OH)$	
Dy and Ho Complexes[b]			
Color form	orange	orange	
Ground state	$^6H_{15/2}$	$^5I_8$	
$\mu_{\text{free ion}}$	10.65	10.61	
μ_{obs} (300 K)	8.49	8.49	
C (emu/mol K)	17.13	17.13	
θ (K)	−3.2	−3.2	
TIP (emu/mol)	3.9×10^{-3}	3.9×10^{-3}	

[a]Calculated according to eqns. (1–4).   [b]Calculated according to the Curie–Weiss law: $\chi = C/(T + \theta) + TIP$.

In these expressions, Δ is the zero field splitting parameter, TIP is the temperature independent paramagnetism and all of the other parameters have their usual meaning. Because of the close proximity of the two Pr^{3+} ions in the binuclear molecule, this expression (eqns. (1)–(3)) must also be corrected for the magnetic exchange that occurs between the two Pr^{3+} ions. The molecular field approximation may be used for this purpose [10] and is illustrated in eqn.

$$\chi' = \frac{\chi}{1 - (2zJ'/Ng^2\mu B^2)\chi} \tag{4}$$

(4) where χ' is the exchange coupled magnetic susceptibility actually measured, χ is the magnetic susceptibility in the absence of the exchange field (eqns. (1)–(3)), zJ' is the exchange parameter ($z = 1$ for one interacting neighbor) and the rest of the parameters have their usual meanings.

Using eqns. (1)–(4), least-squares fits to the magnetic susceptibility data (agreement between calculated and observed being better than 95%) yielded the values shown in Table I. The temperature dependence of the magnetic susceptibilities of $Ln_2L(NO)_3)_3(OH)$, Ln = Dy and Ho, follow the Curie–Weiss law from which the parameters shown in Table I were derived.

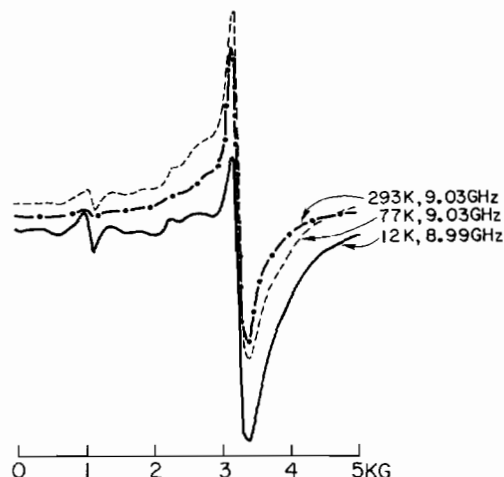The electron paramagnetic resonance spectra of $Gd_2L(NO_3)_4 \cdot 2H_2O$ (off-white and orange complexes)

Fig. 2. EPR spectra of Gd^{3+} doped (~2%) $Y_2L(NO_3)_4 \cdot 2H_2O$ (orange form) recorded at several temperatures.

are broad and featureless. But those of the dilute samples of $(Ln, Gd)_2L(NO_3)_4 \cdot nH_2O$ (Ln = La, Lu and Y) at 1–2% Gd^{3+} doping levels in the reaction mixtures have structured spectra (see Fig. 2) that are difficult to quantitatively interpret. Qualitatively, however, it is clear that the features reflect the fine structure of Gd^{3+} ions in low symmetry sites. For example, the orange complexes exhibit similar features to those seen for Gd^{3+} in sodium silicate [11] and $Tl_2SeAs_2Se_3$ [12] glasses.

Luminescence Properties of the Dinuclear Complexes and Schiff's Base L'

The luminescence and absorption characteristics of the ligand in the dinuclear complexes studied appear to define three categories: orange, yellow and off-white complexes. The orange complexes $Y_2L(NO_3)_4 \cdot 2H_2O$, $Ln_2(NO_3)_2(OH)_2$ (Ln = La, Gd), and $Gd_2L(ClO_4)_2(OH)_2$ exhibit a strong fluorescence at 590 nm and a weaker fluorescence at 510 nm (see Fig. 3). The gadolinium complexes exhibit a phosphorescence at about 600 nm in addition to the two fluorescences. The excitation spectrum shown in Fig. 4 is typical of the orange complexes and is qualitatively similar to the absorption spectra reported previously [1]. The emission lifetimes for the lanthanum and yttrium
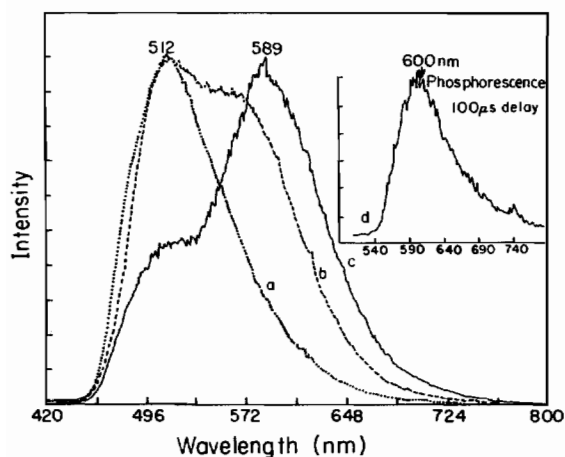
Fig. 4. Excitation spectrum of $Y_2L(NO_3)_4 \cdot 2H_2O$ recorded at 77 K while monitoring the emission at 590 nm.

Fig. 3. Luminescence spectra recorded at 77 K of La_2L-$(NO_3)_4$ off-white form (curve a), $La_2L(NO_3)_4$ yellow form (curve b) and $Y_2L(NO_3)_4 \cdot 2H_2O$ orange form (curve c). The inset (curve d) shows the emission from $Gd_2L(ClO_4)_2(OH)_2$ recorded under pulsed excitation with a delay of 100 μs.
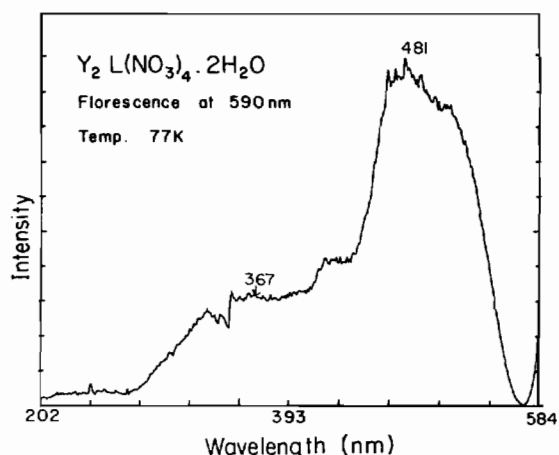
complexes at 77 K are roughly 8 ns for the 590 nm fluorescence and 5 ns for the 510 nm fluorescence (see Table II). The fluorescence lifetimes are noticeably shorter in the gadolinium complexes, about 4 ns at 590 nm and less than 3 ns at 510 nm. The phosphorescence lifetime is approximately 200 μs at 77 K.

Yellow complexes have two equally intense fluorescence peaks at about 510 and 590 nm (see Fig. 3) which appear partially resolved in yellow $La_2L(NO_3)_4$ or as a broad unresolved envelope centered at about 530 nm in $Y_2L(ClO_4)_3(OH)$. At room temperature, a broad envelope centered at about 530 nm is also obtained for yellow La_2L-$(NO_3)_4$. The excitation spectra based on ligand luminescence are similar to that shown in Fig. 4, but blue shifted by about 20 nm. The ligand electronic absorption spectra in yellow complexes have intense

TABLE II. Luminescence Lifetimes for Ligand Chromophore Emissions at 77 K

Complex	Color form	Lifetime, τ[a]	
		fluorescence (ns)	phosphorescence (μs)
$La_2L(NO_3)_4 \cdot 2H_2O$	off-white	7 (510 nm)	
$La_2L(NO_3)_4$	yellow	6 (530 nm)	
$Y_2L(ClO_4)_3OH$	yellow	8 (530 nm)	
$La_2L(NO_3)_2(OH)_2$	orange	5 (510 nm), 8 (590 nm)	
$La_2L(NO_3)_2(OH)_2$ (1% Eu^{3+})	orange	3 (510 nm), 7 (590 nm)	
$Gd_2L(ClO_4)_2(OH)_2$	orange	<3 (510 nm), 4 (590 nm)	200 (650 nm)
$Gd_2L(NO_3)_2(OH)_2$	orange	– –	200 (650 nm)
Schiff base analog			
HL' (neat)	–	6 (560 nm)	
HL' (ether)	–	6 (515 nm)	
KL' (ether)	–	8 (490 nm)	
$(CH_3)_4NL'(H_2O)$	–	6 (510 nm)	

[a] Numbers in parentheses represent the wavelengths at which the emission decays were monitored.

bands at 430–440 and 350–370 nm [1, 2]. The ligand luminescence lifetimes monitored at 530 nm are 6 and 8 ns for $La_2L(NO_3)_4$ and $Y_2L(ClO_4)_3(OH)$ respectively.

Off-white $La_2L(NO_3)_4$ and $Gd_2L(NO_3)_4 \cdot 2H_2O$ complexes exhibit a strong fluorescence at 510 nm (see Fig. 3). The excitation spectrum shows a strong peak at roughly 375 nm which corresponds to a prominent feature observed in the absorption spectrum [1]. The ligand fluorescence lifetime of $La_2L(NO_3)_4$ is 7 ns at 77 K.

Analogous complexes containing Ce^{3+}, Eu^{3+}, Pr^{3+}, Tb^{3+}, and Er^{3+} exhibit little or no ligand emission which indicates an efficient quenching process. It seems certain that ligand to lanthanide energy transfer accounts for the fluorescence quenching, however, sensitized lanthanide emission is observed only in complexes containing Eu^{3+}. The sharp-line highly structured emission is readily assigned to the $^5D_0 \rightarrow {}^7F_j$ ($j = 0, 1, 2, 3, 4, 5$) transitions of Eu^{3+} [4, 5, 13–16]. The excitation spectra obtained while monitoring the Er^{3+} emission are very similar to those observed for the ligand fluorescence in the complexes of the closed shell lanthanides. The ligand to Eu^{3+} energy transfer was further investigated by examining the properties of mixed $[La_{1-x}Eu_x]_2L(NO_3)_4$ (off-white and yellow) and $[Y_{1-x}Eu_x]_2L(NO_3)_4 \cdot 2H_2O$ (orange) complexes containing various amounts of Eu^{3+} (see Fig. 5). As expected the intensities of the $^5D_0 \rightarrow {}^7F_j$ emissions diminish with decreasing Eu^{3+} concentration while the ligand fluorescence gains intensity. The lifetime of the $^5D_0 \rightarrow {}^7F_j$ emissions in the $[Y_{1-x}Eu_x]_2L(NO_3)_4 \cdot 2H_2O$ (orange) complexes which range from 240 to 260 μs appear to be independent of Eu^{3+} concentration (see Table III). In the $[La_{1-x}Eu_x]_2L(NO_3)_4$ (off-white) complexes, however, there are noticeable concentration effects. At low Eu^{3+} concentrations the luminescence decay

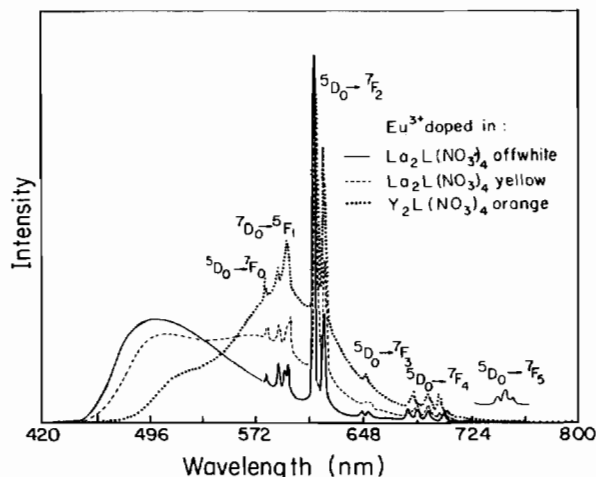Fig. 5. Luminescence spectra from three complexes doped with Eu^{3+} (1–2%) recorded at 77 K.

TABLE III. Luminescence Lifetimes for Eu^{3+} Emissions at 77 K

Complex	Color form	Lifetime (μs), $^5D_0$ state
$(La_{1-x}Eu_x)_2L(NO_3)_4 \cdot nH_2O$	off-white	
$x = 0.01$		400 (2500)[a]
$x = 0.25$		290 (1600)[a]
$x = 0.50$		300
$x = 0.75$		290
$x = 1.00$		270
$(Y_{1-x}Eu_x)L(NO_3)_4 \cdot 2H_2O$	orange	
$x = 0.02$		260
$x = 0.25$		240
$x = 0.32$		240
$x = 0.50$		250
$x = 0.56$		250
$x = 1.00$		240

[a]Biexponential decay, slow component in parentheses.
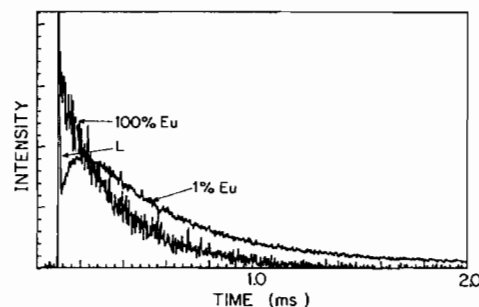

Fig. 6. Luminescence decay curves at 77 K for the $^5D_0 \rightarrow {}^7F_j$ transition of Eu^{3+} recorded at 620 nm for $Eu_2L(NO_3)_2 \cdot 2H_2O$ (off-white form) and 1% Eu^{3+} in $La_2(NO_3)_4$ (off-white form). The sharp rise and fall marked by L results from ligand fluorescence.

curves for the $^5D_0 \rightarrow {}^7F_j$ emission are distinctly biphasic and exhibit a well defined rise time (see Fig. 6).

The luminescence spectra of the Schiff's base L′ were recorded at 77 K on frozen samples of the neat oil HL′, a dilute solution of the oil HL′ in ether (12 mmol/l), the oil HL′ dissolved in aqueous tetraethylammonium hydroxide and the dilute ether solution shaken on potassium hydroxide pellets (see Fig. 7). The major fluorescence maximum shifts to higher energy in the order: neat oil < dilute solution < tetraethylammonium phenolate < potassium phenolate. No phosphorescence was observed. The fluorescence lifetimes at 77 K are 6 to 7 ns. The excitation spectra of L′ resembles that shown in Fig. 4 with peaks at about 350 nm and 455 nm. The absorption spectrum has a moderately strong peak at 447 nm and a strong peak at 350 nm.
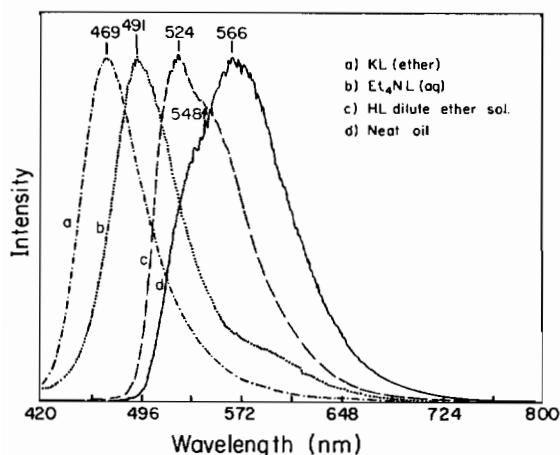
Fig. 7. Luminescence spectra of frozen samples of the Schiff base analog, L', in various media recorded at 77 K.

Discussion

It seems reasonably certain from the earlier studies that the lanthanide complexes of the macrocyclic ligand, L, are dinuclear [1], although the exact structural details are not available. The magnetic susceptibility measurements suggest that coupling between lanthanide ions is significant, at least in the case of the praesodymium complexes. The exchange terms required to give reasonable fits of the experimental data indicate relatively strong antiferromagnetic coupling between Pr^{3+} ions. It should be noted, however, that the theoretical expression used to treat the data contains a number of assumptions. One assumption, that of axial symmetry, seems particularly questionable so that the conclusions drawn from the analysis cannot be considered absolutely definitive. Similarly, the EPR spectra of the gadolinium complexes give an indication but not conclusive proof of coupling between lanthanide ions. The observation of a single unstructured resonance for the pure Gd^{3+} complexes and a highly structured resonance in 'diluted' complexes is certainly consistent with weak interactions between Gd^{3+} ions.

The luminescence properties provide considerably more detailed insight into the nature of the complexes. The luminescence from the La^{3+}, Y^{3+} and Gd^{3+} complexes are clearly attributable to emissions from the chromophoric (Schiff base) portion of the macrocyclic ligand. The Schiff base L', a monomeric analog of the chromophoric group L, exhibits an intense emission similar in appearance and lifetime to that from the complexes. The energy of the emission is strongly red shifted when the phenolate ion is protonated. In addition there is a sizable red shift going from a dilute solution of HL' to the neat oil. These observations suggest that the energy of the emissive excited state is significantly affected by

bonding (coordination) at the phenolate ion and by intermolecular aggregation. There are two distinct emissions (~590 nm and ~510 nm) in the luminescence from both the yellow and orange forms of the complexes while the luminescence from the off-white form seems to contain only one emission (~510 nm). It seems clear that there are two decidedly different environments for the Schiff base chromophore. Based on the observed behavior of L', the 510 nm emission looks more or less like a free phenolate ion (environment 'a') while the 590 nm emission can be attributed to a protonated or tightly coordinated phenolate (environment 'b'). The off-white complexes appear to contain only the free phenolate, environment 'b'. The fact that the gadolinium complexes exhibit phosphorescence as well as fluorescence is not unexpected since similar behavior has been reported in porphyrin complexes containing gadolinium [17–19]. The presence of the paramagnetic heavy metal ion enhances intersystem crossing as well as radiative relaxation of the triplet state.

Rapid energy transfer would be expected in complexes where the macrocyclic ligand is bound to lanthanide ions which possess excited states energetically near the emissive levels of L. The spectroscopic properties of L and several emissive lanthanide ions are summarized in Fig. 8. The energy levels of Eu^{3+}, Pr^{3+} and Er^{3+} seem particularly well placed for energy transfer. Not unexpectedly the ligand emissions in complexes of these ions are almost completely quenched. Surprisingly, however, sensitized lanthanide emission is observed only in the complexes containing Eu^{3+}. This is not typical behavior. For example, in diketonate complexes sensitized luminescence is observed with any lanthanide ion which has an emissive state below the T_1 state of the
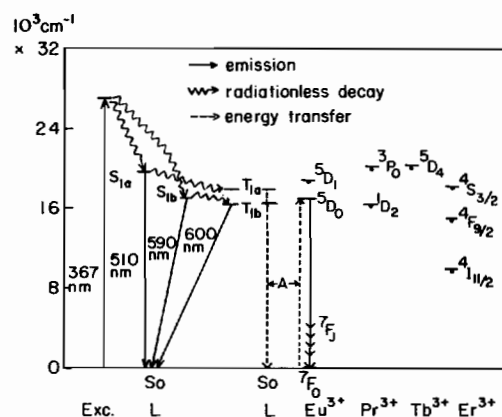

Fig. 8. Energy level diagram showing the estimated positions of the excited states (singlet and triplet) for the chromophoric portion of the macrocyclic ligand (environments a and b). Emissive levels of Eu^{3+}, Pr^{3+}, Tb^{3+} and Er^{3+} are also included. Solid arrows indicate observed radiative transitions while dotted lines indicate energy transfer.

diketonate ligand [20]. We have no explanation for the nonemissive behavior of the complexes of L containing Pr^{3+}, Tb^{3+} and Er^{3+}. The sensitized emission from Eu^{3+} ion which arises from the $^5D_0$ state shows measurable intensity in the $^5D_0 \rightarrow {}^7F_0$ transition suggesting that the lanthanide ions in these complexes do not occupy centrosymmetric sites [4, 5, 13–16]. The luminescence lifetimes of 200 μs to 300 μs for the $^5D_0$ state in the pure complexes are somewhat shorter than expected for a single Eu^{3+} ion and may reflect some pairwise coupling. Dilution of the Eu^{3+} in the orange complexes, however, has little effect on the $^5D_0$ lifetimes. In contrast, when Eu^{3+} is diluted in the off-white form of complexes a longer lived component (between 2 ms and 3 ms in very dilute samples) is observed in the luminescence decay. This slow decay component may arise from 'isolated' Eu^{3+} ions. The observation of a rise time on the Eu^{3+} emission in these dilute off-white samples suggests that the energy transfer may involve excited state migration through the solid via a long lived ligand excited state, presumably T_{1a}.

In summary, the lanthanide complexes with the macrocyclic ligand L exhibit a number of interesting magnetic and spectroscopic properties. The luminescence from these materials is particularly fascinating. In general the spectroscopy of the complexes is explainable in terms of chromophoric or Schiff base portion of the macrocyclic ligand. The different colored forms are attributable to different environments for the chromophoric group. Although there are a number of indications of significant interactions between the lanthanide ions in the dinuclear complexes, the experimental data are not definitive.

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