

# Synergistic Coordination in Ternary Complexes of $\text{Eu}^{3+}$ with Aromatic $\beta$ -Diketone Ligands and 1,10-Phenanthroline

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Ternary  $\text{Eu}^{3+}$  complexes with aromatic  $\beta$ -diketone ligands and 1,10-phenanthroline are observed in aqueous solution by  $\text{Eu}^{3+}$  luminescence spectroscopy, as revealed by a large shift in the position of the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition as well as a large increase in intensity. Formation of the ternary complexes also results in a dramatic increase in the sensitized emission of  $\text{Eu}^{3+}$  as well as a change in the excitation band profile from that of the parent  $\text{Eu}^{3+}$   $\beta$ -diketone complex. These complexes are unusual in light of the fact that  $\beta$ -diketone ligands bind  $\text{Eu}^{3+}$  only weakly, and 1,10-phenanthroline does not coordinate  $\text{Eu}^{3+}$  at all in aqueous solution by itself. The  $\beta$ -diketone ligands that were observed to form these ternary complexes are 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Hbtfa), and 1,3-diphenyl-1,3-propanedione (Hdbm). Several other  $\beta$ -diketone ligands did not form ternary complexes with 1,10-phenanthroline including 2,4-pentanedione (Hacac), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfacac), and 1-phenyl-1,3-butanedione (Hba). Likewise, when 2,2'-dipyridyl or 1,7-phenanthroline was substituted for 1,10-phenanthroline, the ternary complex was not observed to form. The  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  excitation band of the ternary complexes can be resolved into two component bands, revealing two distinct  $\text{Eu}^{3+}$  environments. Likewise, the lifetime recorded at the peak maximum is a double exponential with lifetimes much longer than the parent  $\text{Eu}^{3+}$   $\beta$ -diketone complex. The observation of energy transfer from  $\text{Eu}^{3+}$  to  $\text{Nd}^{3+}$  in the ternary complexes shows that they are multinuclear with respect to the metal ion. The stoichiometries of the complexes were determined by monitoring the intensity of  $\text{Eu}^{3+}$  luminescence as a function of added ligand.

## Introduction

Most often the stability of a metal complex is governed solely by the strength of the interaction between the metal ion and the coordinating atoms. However, in special cases intramolecular noncovalent interactions between ligands can contribute a significant portion of the binding energy. These interactions include hydrogen bonding,<sup>1,2</sup> hydrophobic interactions,<sup>3,4</sup> and stacking interactions.<sup>5,6</sup> Typically these interactions are revealed by deviations from the predicted stability of metal complexes based on the  $\text{p}K_a$  values of their ligands.<sup>1–6</sup> In this paper we present evidence for the synergistic coordination of  $\beta$ -diketone ligands and 1,10-phenanthroline to  $\text{Eu}^{3+}$  in aqueous solution. This coordination is quite remarkable in light of the fact that 1,10-phenanthroline does not coordinate  $\text{Eu}^{3+}$  in aqueous solution in the absence of the  $\beta$ -diketone ligands, which themselves bind  $\text{Eu}^{3+}$  only weakly in this solvent. The observed formation of ternary  $\text{Eu}^{3+}$  complexes with  $\beta$ -diketone ligands and 1,10-phenanthroline must therefore be attributed to strong intracomplex ligand–ligand interactions.

Ternary  $\text{Eu}^{3+}$  complexes with  $\beta$ -diketone ligands and 1,10-phenanthroline have been characterized extensively both in the solid state and in organic solution.<sup>7–12</sup> The luminescence of

complexes of this type is much stronger than that of the parent hydrate,  $(\text{Eu}(\text{H}_2\text{O})_9)^{3+}$ , especially when  $\beta$ -diketones with aromatic or fluorine substituents are present.<sup>7</sup> Suspensions of complexes of this type in aqueous solution have also been observed to form when  $\text{Eu}^{3+}$ , 1,10-phenanthroline, and certain  $\beta$ -diketones are mixed at high micromolar concentrations.<sup>13,14</sup> The  $\text{Eu}^{3+}$  luminescence intensity of these suspensions is found to vary a great deal when other  $\text{Ln}^{3+}$  ions are present.  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Lu}^{3+}$  are found to enhance the luminescence emission of  $\text{Eu}^{3+}$  in these suspensions, while  $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Er}^{3+}$  quench it.<sup>13</sup> Dissolving the suspensions in organic solvents such as benzene eliminates the effect that the other ions have on the  $\text{Eu}^{3+}$  luminescence.

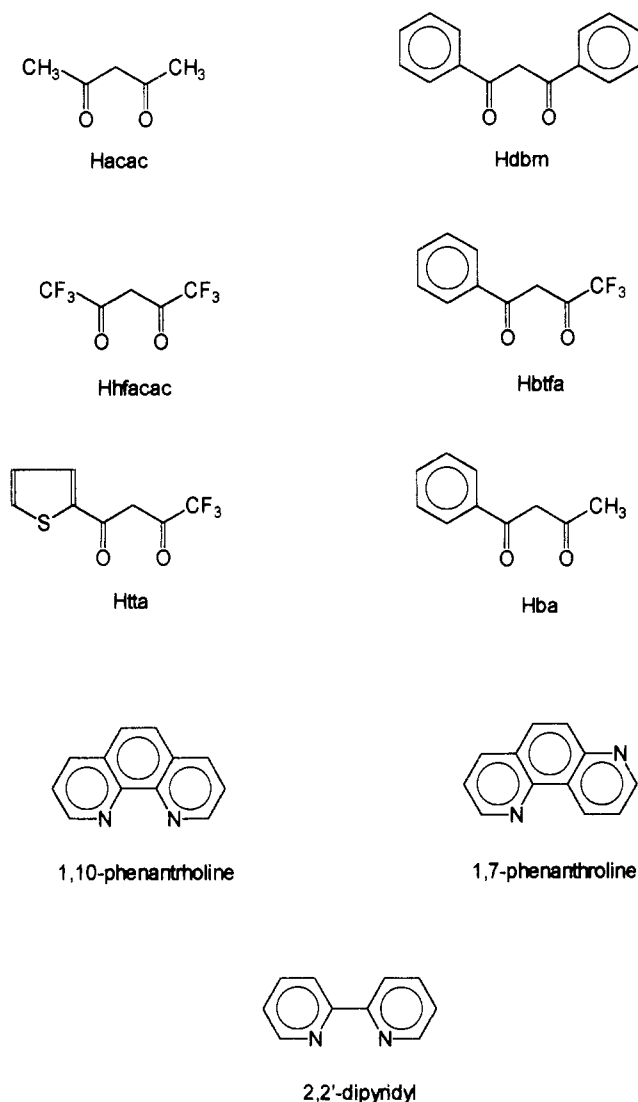
The possible application of these ternary complexes in the manufacture of luminescent materials has prompted recent interest in their properties.<sup>15,16</sup> Complexes of this type are currently being used as “fluorescent additives” in the preparation of photofluorescent high-polymer materials which emit visible fluorescence under UV radiation at room temperature.<sup>15</sup> Luminescent ternary complexes are also of potential interest to the enzyme assay and DNA hybridization assay fields.<sup>17,18</sup> For example, the DNA template-mediated formation of a ternary  $\text{Tb}^{3+}$  complex between oligonucleotide-tethered diethylenetriaminepentaacetic acid (dtpa) and 4-aminosalicylic acid has been used as a luminescent label in a DNA hybridization assay.<sup>17</sup>

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**Chart 1.**  $\beta$ -Diketone- and Pyridine-Based Ligands Used in This Study

Our ability to probe the solution structure of  $\text{Eu}^{3+}$  complexes by laser-induced  $\text{Eu}^{3+}$  luminescence spectroscopy and our interest in the aqueous chemistry of lanthanide complexes led us to investigate the interaction of  $\text{Eu}^{3+}$  ion with  $\beta$ -diketones and 1,10-phenanthroline in aqueous solution. Chart 1 diagrams each of the ligands investigated in this study. Not surprisingly, we find that 1,10-phenanthroline does not react with  $\text{Eu}^{3+}$  ion in aqueous solution, and  $\beta$ -diketones form only weak complexes with  $\text{Eu}^{3+}$ . However, to our astonishment, when 1,10-phenanthroline is added to a solution containing certain  $\beta$ -diketones and the  $\text{Eu}^{3+}$  ion, highly luminescent complexes are formed. Herein we describe the  $\text{Eu}^{3+}$  luminescence studies used to characterize the interaction of this ion with 1,10-phenanthroline and several  $\beta$ -diketones, Htta, Hbtfa, Hdbm, Hacac, Hhfacac, and Hba. Both direct, laser-induced excitation and sensitized emission spectroscopies were employed during these studies.

### Experimental Section

**Materials.** Hydrated  $\text{EuCl}_3$  (99.9%),  $\text{D}_2\text{O}$  (99.8 atom %), Htta, Hbtfa, Hacac, Hhfacac, Hba, 2,2'-dipyridyl, and 1,7-phenanthroline were purchased from Aldrich Chemical Co. 1,10-Phenanthroline was obtained from J. T. Baker Chemical Co. N-(2-Hydroxyethyl)piperazine-N'-ethanesulfonic acid (HEPES) was purchased from Sigma Chemical Co. Rhodamine 590 and 610 laser dyes were obtained from the Exciton Co. and Kodak Co. respectively. The  $\text{H}_2\text{O}$  used was deionized and doubly distilled.

**Methods.** A 15 mM stock solution of  $\text{EuCl}_3$  in doubly distilled water was prepared and standardized by and edta titration with arsenazo as an

**Table 1.** Protonation and Stability Constants for Hacac, Hba, and Hdbm

ligand	$\log K_{\text{H}}$	$\log K^1_{\text{Eu}^{3+}}$	$\log K^2_{\text{Eu}^{3+}}$	$\log K^3_{\text{Eu}^{3+}}$
Hacac <sup>a</sup>	8.80	5.94	4.43	3.33
Hba <sup>a</sup>	8.89	6.89	6.48	6.23
Hdbm <sup>b</sup>	10.06	7.58	6.67	6.45

<sup>a</sup> Reference 22. <sup>b</sup> Reference 23.

indicator.<sup>19</sup> Stock solutions 1–2 mM in the individual ligands were prepared in doubly distilled water (pH  $\sim$ 8) with the exception of hdbm which had to be made up in a 1/1 mixture of  $\text{H}_2\text{O}$  and absolute ethanol due to solubility problems.

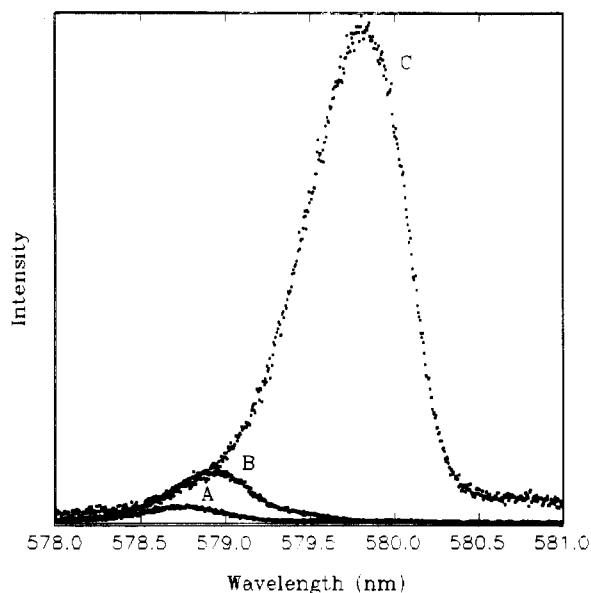
Excitation spectra, lifetimes, and intensity measurements were carried out with a Continuum Series YG581C pulsed (10 Hz) Nd:YAG laser pumped tunable dye laser, Model TDL-50, as an excitation source. The data collection apparatus and instrumentation has been described elsewhere.<sup>20</sup> In a typical experiment, the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition of  $\text{Eu}^{3+}$  was accessed ( $\sim$ 580 nm) using a mixture of rhodamine-590 and -610 dyes while the hypersensitive  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  emission band was monitored at 614 nm. Excitation spectra were recorded by tuning the dye laser through the range of 578–581 nm while monitoring the emission intensity at 614 nm.  $\text{Eu}^{3+}$   ${}^5\text{D}_0$  excited state lifetimes were recorded at static excitation wavelengths by monitoring the intensity at 614 nm as a function of time following a laser pulse. Successive pulses were summed for 2–3 min in order to increase the signal to noise ratio. Intensity measurements were made by monitoring the emission intensity at 614 nm for several minutes while exciting at a specific wavelength. The  $\text{Eu}^{3+}$  concentration for these experiments was 5  $\mu\text{M}$  while the amounts of individual ligands varied from 1 to 75  $\mu\text{M}$ . Concentrations much higher than this resulted in precipitation. During titrations it was necessary to allow 5–20 min for equilibration between each point. All of the experiments were carried out in 50 mM HEPES at pH 7, 25  $^\circ\text{C}$ . Spectral peak fitting and lifetime analysis were achieved using the program PeakFit (Jandel Scientific). This program employs a nonlinear regression based on the Marquadt algorithm. Excitation spectra were fit to a Lorentzian–Gaussian product function discussed elsewhere.<sup>21</sup>

Emission spectra were recorded on a Spex Fluorolog 2 fluorescence spectrometer with excitation wavelengths around 360 nm corresponding to the absorption of the ligands. These measurements were made on 5  $\mu\text{M}$  solutions of  $\text{Eu}^{3+}$  in 50 mM HEPES, pH 7, with varying amounts of ligand. An equilibration time of 30 min was allowed after mixing the components ( $\text{Eu}^{3+}$ ,  $\beta$ -diketone, 1,10-phenanthroline) before the emission spectra were recorded.

### Results and Discussion

**$\beta$ -Diketone Ligands.** The interaction of  $\beta$ -diketone ligands with  $\text{Eu}^{3+}$  ion in aqueous solution is difficult to monitor for a several reasons. First, they bind only weakly. Table 1 lists the logarithms of literature values<sup>22,23</sup> for the protonation constant and stepwise stability constants for several of the  $\beta$ -diketone ligands that are considered in this study. A solution containing 5  $\mu\text{M}$   $\text{Eu}^{3+}$  and 20  $\mu\text{M}$   $\beta$ -diketone at pH 7 will have <70% of the europium present as  $\text{Eu}(\beta\text{-diketonate})^{2+}$  and negligible amounts of  $\text{Eu}(\beta\text{-diketonate})_2^{+}$  and  $\text{Eu}(\beta\text{-diketonate})_3$ . Second, the  $\text{Eu}^{3+}$  luminescence of the  $\text{Eu}(\beta\text{-diketonate})^{2+}$  complex is feeble with the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition shifted only slightly to longer wavelength than that of  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$ . Figure 1 shows the  $\text{Eu}^{3+}$   ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  spectra of  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$  and  $\text{Eu}^{3+}$  in the presence of 4 equiv of Htta at pH 7. The band shifts from 578.7 nm for  $\text{Eu}^{3+}(\text{aq})$  to 578.9 nm in the complex with a slight increase in intensity. Identical behavior is observed for Hbtfa. The spectrum of 5  $\mu\text{M}$   $\text{Eu}^{3+}$  with 4 equiv of Hdbm exhibits a broad band ranging from

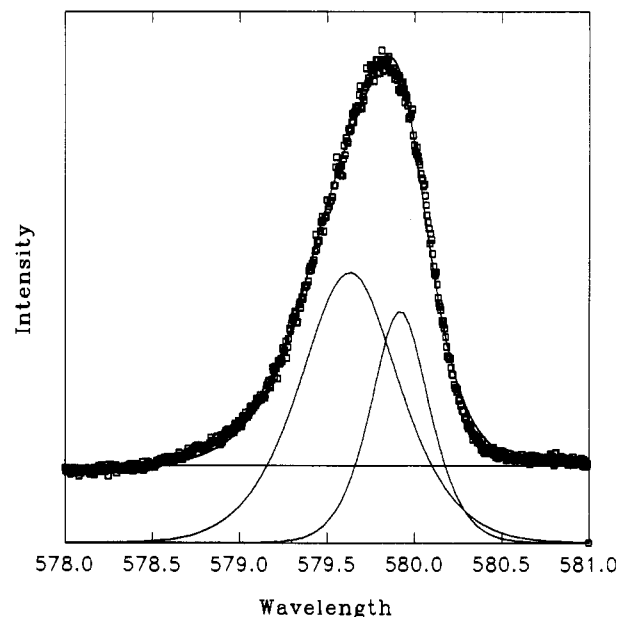
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**Figure 1.**  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  excitation spectra of  $5 \mu\text{M}$   $\text{Eu}(\text{H}_2\text{O})_9^{3+}$  (A),  $5 \mu\text{M}$   $\text{Eu}^{3+}$  and  $20 \mu\text{M}$  Htta (B), and  $5 \mu\text{M}$   $\text{Eu}^{3+}$ ,  $20 \mu\text{M}$  Htta, and  $10 \mu\text{M}$  1,10-phenanthroline (C), all recorded in  $50 \text{ mM}$  HEPES pH 7.0.

578 nm that tails off at wavelengths beyond 579.4 nm. This broad band is composed of several component bands, most likely due to  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$ ,  $\text{Eu}(\text{Hdbm})_2^{2+}$ , and  $\text{Eu}(\text{Hdbm})_2^{1+}$ . Finally, the  $\text{Eu}^{3+} {}^5\text{D}_0$  excited state lifetime for each of the 1:1,  $\text{Eu}^{3+}$ : $\beta$ -diketone complexes studied is remarkably short (Htta =  $90 \mu\text{s}$ , Hbtfa =  $30 \mu\text{s}$ , Hdbm =  $50 \mu\text{s}$ ). All of these lifetimes are shorter than that of  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$  ( $110 \mu\text{s}$ ). This is surprising in light of the fact that  $\text{H}_2\text{O}$  provides an efficient pathway for deexcitation of the  ${}^5\text{D}_0$  state of  $\text{Eu}^{3+}$  by means of energy transfer to the O–H vibration manifold. In virtually all complexes that we have studied to date, excitation lifetimes are longer than  $110 \mu\text{s}$  due to exclusion of water molecules in the complex. We conclude that the  $\beta$ -diketones provide their own pathway for deexcitation. It is well known that ligand-sensitized emission can occur when a ligand triplet level lies above the emitting level of a rare earth ion.<sup>24</sup> Sensitized emission has been observed for  $\beta$ -diketone chelates of  $\text{Eu}^{3+}$ .<sup>7,24,25</sup> Perhaps some degree of quenching of the  $\text{Eu}^{3+} {}^5\text{D}_0$  excited state level occurs in these systems from a ligand triplet level that lies below or in close proximity above the emitting level of the rare earth ion. The short excited state lifetimes and subtle spectral differences from  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$  are nonetheless observable, revealing the formation of weak complexes between the  $\text{Eu}^{3+}$  ion and  $\beta$ -diketones in aqueous solution.

**1,10-Phenanthroline.** 1,10-Phenanthroline is a neutral, bidentate, nitrogen donor ligand. It has been shown to form strong complexes with many transition metals in organic and aqueous solutions.<sup>26</sup> It has also been shown to form complexes with trivalent lanthanides in solvents such as alcohols.<sup>27</sup> However, in aqueous solution the coordinating ability of 1,10-phenanthroline is obscured by the strong interaction of  $\text{Ln}^{3+}$  with aqua ligands. We have titrated 1,10-phenanthroline into solutions of  $5 \mu\text{M}$   $\text{Eu}^{3+}$ , pH 7, and have not observed any change in the  $\text{Eu}^{3+}$  luminescence spectrum or excited state lifetime from that of  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$ . This implies that there is no interaction of  $\text{Eu}^{3+}$  with 1,10-phenanthroline by itself in aqueous solution at micromolar concentrations. The low solubility of 1,10-phenanthroline in aqueous solution prevents our studying this interaction at higher concentrations of ligand.



**Figure 2.** Resolved  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$   $\text{Eu}^{3+}$  excitation spectrum of  $5 \mu\text{M}$   $\text{Eu}^{3+}$ ,  $20 \mu\text{M}$  Htta, and  $10 \mu\text{M}$  1,10-phenanthroline with peak maxima at 579.6 and 579.9 nm.

**Table 2.**  $\text{Eu}^{3+} {}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  Resolved Peak Maxima,  $\text{Eu}^{3+}$  Lifetimes in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , and the Calculated Number of Bound Water Molecules ( $\pm 0.5$  Water Molecule) for Solutions of  $5 \mu\text{M}$   $\text{Eu}^{3+}$ ,  $10 \mu\text{M}$  1,10-Phenanthroline, and  $20 \mu\text{M}$  Htta, Hbtfa, or Hdbm

$\beta$ -diketone	resolved peak maxima, nm	$\tau_{\text{H}_2\text{O}}$ , ms	$\tau_{\text{D}_2\text{O}}$ , ms	$q^a$
Htta	579.63	0.249	0.307	0.8
	579.92	0.598	0.601	0.0
Hbtfa	579.59	0.234	0.310	1.1
	579.89	0.586	0.717	0.3
Hdbm	579.53	0.231	0.285	0.9
	579.90	0.482	0.526	0.2

<sup>a</sup>  $q$  (The number of coordinated water molecules) =  $1.05(\tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1})$

**Ternary Complexes.** Much to our surprise, when 1 equiv of 1,10-phenanthroline is added to a solution containing  $5 \mu\text{M}$   $\text{Eu}^{3+}$  and 3 equiv of Htta, there is a marked increase in the intensity of the  $\text{Eu}^{3+} {}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  excitation signal (8-fold), as well as a large shift in the wavelength of the peak maximum (1 nm) towards higher wavelength. Figure 1 shows the excitation spectra of  $\text{Eu}(\text{H}_2\text{O})_9^{3+}$ ,  $\text{Eu}^{3+}$  in the presence of 3 equiv of Htta, and  $\text{Eu}^{3+}$  with 3 equiv of Htta and 1 equiv of 1,10-phenanthroline. Similar behavior is observed when Hbtfa or Hdbm is substituted for Htta in the above experiment. The excitation band appears to be asymmetric and can be fit as the sum of two bands, one at 579.6 nm and one at 579.9 nm (Figure 2). Since both the ground ( ${}^7\text{F}_0$ ) and excited ( ${}^5\text{D}_0$ ) states are nondegenerate, a single  $\text{Eu}^{3+}$  environment gives rise to a single excitation band. It is therefore evident that more than one  $\text{Eu}^{3+}$  environment exists in this solution. The resolved peak positions for each of the ternary complexes are listed in Table 2.

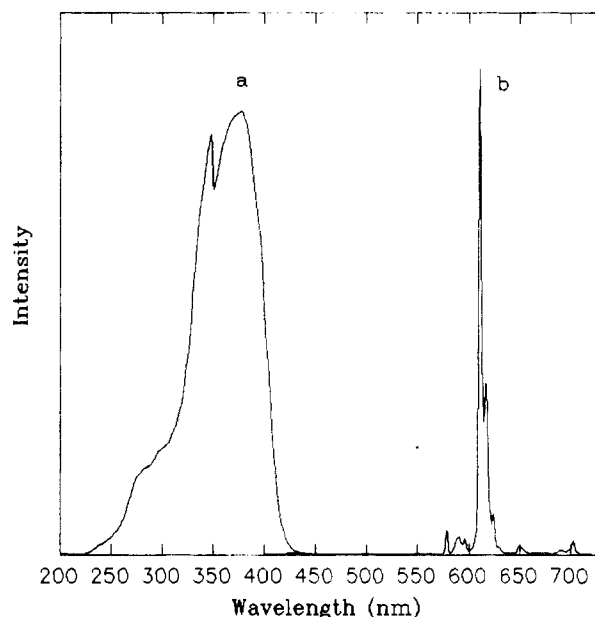
**Luminescence from Sensitized Emission.** The sensitized emission of  $\text{Eu}^{3+}$  increases markedly when the ternary complexes are formed. Figure 3 shows the excitation and emission spectra of  $5 \mu\text{M}$   $\text{Eu}^{3+}$  and  $15 \mu\text{M}$  Hdbm in presence of  $5 \mu\text{M}$  of 1,10-phenanthroline. There is a strong increase in the intensity of the  $\text{Eu}^{3+}$  emission at 614 nm upon the addition of the 1,10-phenanthroline. Perhaps more interestingly, the excitation spectrum (200–400 nm) reveals that the strong  $\text{Eu}^{3+}$  emission is due to a sensitization process and not to direct excitation of the  $\text{Eu}^{3+}$  ion. The features of the excitation spectrum show components from 1,10-phenanthroline absorption ( $\sim 280 \text{ nm}$ ) and Hdbm absorption ( $\sim 350 \text{ nm}$ ). This data implies that both

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**Figure 3.** Excitation and sensitized  $\text{Eu}^{3+}$  emission spectrum of  $5 \mu\text{M}$   $\text{Eu}^{3+}$ ,  $20 \mu\text{M}$  Hdbm, and  $10 \mu\text{M}$  1,10-phenanthroline in 50 mM HEPES pH 7.0.

**Table 3.** Excitation Band Positions and  $\text{Eu}^{3+}$ -Sensitized Emission Intensities for Solutions Containing  $5 \mu\text{M}$   $\text{Eu}^{3+}$  and  $20 \mu\text{M}$   $\beta$ -Diketone, in the Absence and Presence of  $10 \mu\text{M}$  1,10-Phenanthroline.

$\beta$ -diketone	ex max, nm (em = 614 nm)	rel em intens at 614 nm (ex $\lambda$ )
Htta	350	1.3 (350 nm)
+ phen	288, 370	400 (370 nm)
Hbtfa	340	1.0 (340 nm)
+ phen	287, 345	200 (345 nm)
Hdbm	360	10.7 (360 nm)
+ phen	287, 365	800 (365 nm)

Hdbm and 1,10-phenanthroline are binding to the  $\text{Eu}^{3+}$  ion and that their presence together affords a strong sensitization of the  $\text{Eu}^{3+}$  emission. This type of behavior is also observed in complexes of Hbtfa and Htta. Table 3 lists the excitation band maxima and emission intensities in the absence and presence of 1,10-phenanthroline for each of the ternary complexes.

**Luminescence Lifetimes.** There is also a drastic change in the excited state lifetime upon addition of the 1,10-phenanthroline. For  $5 \mu\text{M}$   $\text{Eu}^{3+}$  in the presence of 3 equiv of Htta, the excited state lifetime measured at 578.9 nm is 81  $\mu\text{s}$ . When 1 equiv of 1,10-phenanthroline is added, the lifetime data measured at 579.9 nm fit to a double exponential with  $\tau$ -values of 250 and 600  $\mu\text{s}$ , revealing that the two  $\text{Eu}^{3+}$  environments are not in "fast exchange" on the time scale of the luminescence. Very similar lifetime values are observed when Hbtfa or Hdbm is substituted for Htta. Measurement of the excited state lifetime in  $\text{D}_2\text{O}$  affords the number of coordinated water molecules,  $q$ , by the application of the following equation:

$$q = 1.05(\tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1}) \quad (1)$$

Table 2 lists the resolved lifetime values for each of the complexes in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  as well as the calculated number of coordinated water molecules,  $q$ . Lifetimes were assigned to a particular band on the basis of their intensities at time = 0,  $I_0$ , recorded at various wavelengths. In each case, the conclusion is that a single coordinated water molecule is found for the  $\text{Eu}^{3+}$  environment

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**Table 4.**  $\text{Eu}^{3+}$  Lifetimes in the Absence ( $\tau_0$ ) and Presence ( $\tau$ ) of  $\text{Nd}^{3+}$  as well as the Efficiency of Energy Transfer ( $E$ ) for Solutions Containing  $5 \mu\text{M}$   $\text{Ln}^{3+}$ ,  $10 \mu\text{M}$  1,10-Phenanthroline, and  $40 \mu\text{M}$   $\beta$ -Diketone

$\beta$ -diketone	$\tau_0$ , ms	$\tau$ , ms	$E = 1 - (\tau/\tau_0)$
Htta	0.249	0.039	0.84
	0.598	0.096	0.84
Hbtfa	0.234	0.023	0.90
	0.586	0.081	0.86
Hdbm	0.231	0.036	0.84
	0.482	0.078	0.84

corresponding to the shorter wavelength band, while no coordinated water molecules are present in the  $\text{Eu}^{3+}$  environment corresponding to the longer wavelength band.

**Energy Transfer.** Since two distinct  $\text{Eu}^{3+}$  environments exist when ternary complex formation is accomplished, we set out to investigate whether dinuclear or multinuclear complexes were forming in solution. Dimers, trimers, and other structural aggregates of  $\beta$ -diketone complexes are well-known and have been documented in detail.<sup>29–31</sup> The crystal structure of a  $\text{Pr}^{3+}$  dimer complex with 2,2,6,6-tetramethyl-3,5-heptanedione (thd) was reported with the formula  $\text{Pr}_2(\text{thd})_6$ .<sup>29</sup> In this complex, each  $\text{Pr}^{3+}$  ion binds three thd ligands in a bidentate fashion and shares one oxygen atom from a bridging thd with the other  $\text{Pr}^{3+}$  ion. Several modes of bridging have been described for  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  complexes of 2,2,6,6-tetramethylheptane-3,5-dione (tmhd).<sup>30</sup> The  $[\text{Ba}_5(\text{OH})(\text{tmhd})_9(\text{H}_2\text{O})_3]$  species has been obtained from aqueous media.<sup>31</sup>

Previous work has shown that energy transfer from a bound  $\text{Eu}^{3+}$  ion to a bound acceptor ion, such as  $\text{Nd}^{3+}$ , is diagnostic of multimetallic complexes.<sup>20</sup> The experimental efficiency of energy transfer is related to the lifetime of  $\text{Eu}^{3+}$  in the absence of a neighboring acceptor ion,  $\tau_0$ , and the lifetime,  $\tau$ , in the presence of such an acceptor by eq 2. In a typical experiment, a solution

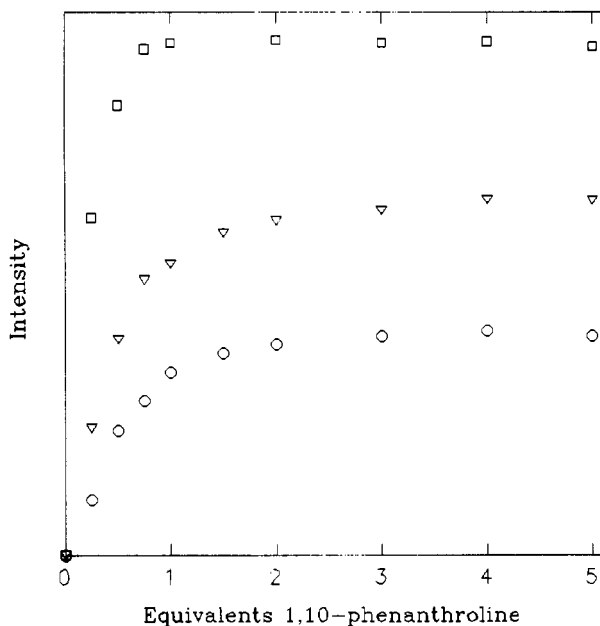
$$E = 1 - (\tau/\tau_0) \quad (2)$$

containing  $1 \mu\text{M}$   $\text{Eu}^{3+}$ ,  $4 \mu\text{M}$   $\text{Nd}^{3+}$ ,  $10 \mu\text{M}$  1,10-phenanthroline, and  $40 \mu\text{M}$   $\beta$ -diketone (Htta, Hbtfa, or Hdbm) was prepared in 50 mM HEPES buffer at pH 7, and the excited state lifetime was measured at an excitation wavelength of 579.9 nm. A ratio of 1:4,  $\text{Eu}^{3+}:\text{Nd}^{3+}$  was used to minimize the occurrence of species with more than a single  $\text{Eu}^{3+}$  ion. In each case, the lifetimes were observed to drop drastically in the presence of  $\text{Nd}^{3+}$  ion. For the case of Htta, the 249- $\mu\text{s}$  lifetime dropped to 40  $\mu\text{s}$  and the 598- $\mu\text{s}$  lifetime dropped to 96  $\mu\text{s}$ . This corresponds to an 84% efficiency of energy transfer. Table 4 lists the lifetimes for all of the ternary complexes in the presence and absence of  $\text{Nd}^{3+}$  as well as the derived efficiencies of energy transfer. It is important to note that, in each case, the efficiency of energy transfer that is derived from both observable excited state lifetimes is identical. This indicates that energy transfer occurs at both environments giving rise to those lifetimes and suggest that the energy transfer is between these two environments. According to the Förster dipole-dipole theory of energy transfer, the distance separating the metal ions can be calculated from the efficiency of energy transfer. Unfortunately in cases such as this where the metal ions are very close (<7 Å), other mechanisms of energy transfer become operative, causing calculated distances to be much shorter than actual distances. However, the present purpose is to use the observation of energy transfer to detect the presence of dinuclear or polynuclear species, rather than to measure distances.

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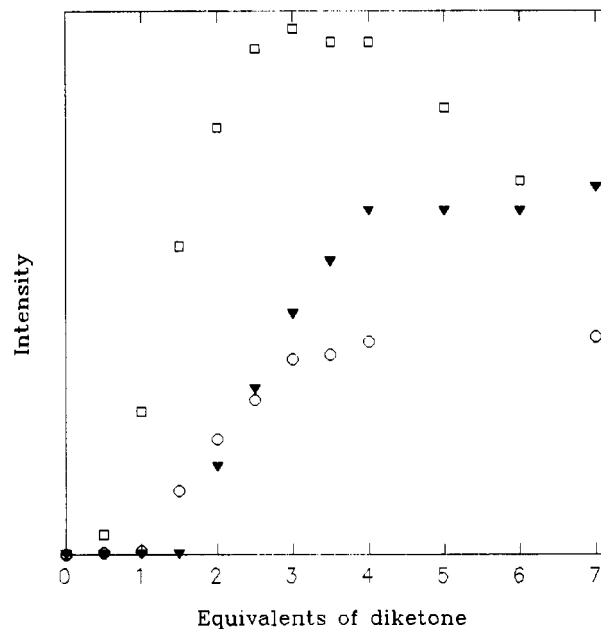
(31) Turnipseed, S. B.; Barkley, R. M.; Sievers, R. *Inorg. Chem.* **1991**, *30*, 1164–1170.



**Figure 4.** Titration curves of  $5 \mu\text{M}$   $\text{Eu}^{3+}$  and  $20 \mu\text{M}$  Htta (triangles), Hbtfa (circles), or Hdbm (squares) with varying amounts of 1,10-phenanthroline in 50 mM HEPES, pH 7.0.

As stated earlier, energy transfer from  $\text{Eu}^{3+}$  to  $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$ , or  $\text{Er}^{3+}$  has been observed for aqueous suspensions of ternary  $\text{Eu}^{3+}$  complexes with 1,10-phenanthroline and certain  $\beta$ -diketone ligands.<sup>14</sup> This energy transfer has been attributed to a coprecipitation of  $[\text{Eu}(1,10\text{-phenanthroline})(\beta\text{-diketone})_3]$  and  $[\text{Ln}(1,10\text{-phenanthroline})(\beta\text{-diketone})_3]$  complexes, since dissolving the suspension in organic solvent causes the energy transfer to disappear.<sup>14</sup> However, the present study demonstrates the existence of at least two distinct  $\text{Eu}^{3+}$  environments with energy transfer from  $\text{Eu}^{3+}$  to  $\text{Nd}^{3+}$ . This is proof that multinuclear species exist in homogeneous aqueous solution. It is therefore suggested that the complexes studied in aqueous suspension are multinuclear in nature, and that they convert to mononuclear forms upon dissolution in organic solvent, where complexes of the stoichiometry  $[\text{Ln}(1,10\text{-phenanthroline})(\beta\text{-diketone})_3]$  are well established.

**Complex Stoichiometries.** In order to determine the stoichiometries of the complexes formed, titrations were carried out where the concentration of one of the component ligands and  $\text{Eu}^{3+}$  ion were held constant, while that of the other ligand was varied. These titrations were carried out by monitoring the intensity of the  $\text{Eu}^{3+} {}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition as a function of added ligand. Figure 4 shows the plots obtained for the titration of 1,10-phenanthroline into solutions  $5 \mu\text{M}$  in  $\text{Eu}^{3+}$  and  $20 \mu\text{M}$  in  $\beta$ -diketone (htta, hbtfa, or hdbm). In each case, the plots show nearly quantitative binding, with the intensity rising sharply to 1 equiv and then leveling off. There is an apparent tightening of binding in the order of  $\text{Htta} < \text{Hbtfa} < \text{Hdbm}$ . It thus appears that the ternary complexes involve a single 1,10-phenanthroline ligand per metal ion. Figure 5 shows the titration plots of Htta, Hbtfa, and Hdbm into solutions of  $5 \mu\text{M}$   $\text{Eu}^{3+}$  with 2 equiv of 1,10-phenanthroline. For the cases of Htta and Hbtfa, there is a lag in the intensity rise until 2 equiv of  $\beta$ -diketone has been added followed by a sharp rise until between 3 and 4 equiv has been added, after which the plots level off. Precipitation occurs after  $\sim 10$  equivalents of Htta or Hbtfa have been added. For Hdbm, a much shorter intensity lag is observed (to about 0.5 equiv), followed by a sharp intensity rise until approximately 3 equiv have been added, after which the intensity steadily drops. The drop in intensity after 3 equiv of Hdbm is attributed to formation of a precipitation observable in the sample. From these titrations we conclude that the complexes formed, whatever their structure, involve three  $\beta$ -diketone ligands per metal ion. Since



**Figure 5.** Titration curves of  $5 \mu\text{M}$   $\text{Eu}^{3+}$  and  $10 \mu\text{M}$  1,10-phenanthroline with varying amounts of Htta (solid triangles), Hbtfa (open circles), or Hdbm (open squares) in 50 mM HEPES, pH 7.0.

one  $\text{Eu}^{3+}$  environment was found to coordinate a single water molecule while the other coordinates none, the simplest formula, providing one species is formed, is  $[\text{Eu}_2(1,10\text{-phenanthroline})_2(\beta\text{-diketonate})_6(\text{H}_2\text{O})]$ .

**Ligand Substitutions.** In order better to understand the factors that contribute to the synergistic binding in the  $\text{Eu}^{3+}$ - $\beta$ -diketone-1,10-phenanthroline complexes, we carried out experiments in which other aromatic nitrogen donor ligands were substituted for 1,10-phenanthroline. Initially 1,7-phenanthroline was investigated. This compound was chosen since it can only bind in a monodentate fashion (see Chart 1). We reasoned that by diminishing the coordinating ability of the phenanthroline that we could ascertain whether the phenanthroline was able to cause the spectroscopic changes previously discussed, without actually binding to the  $\text{Eu}^{3+}$  ion. Upon titration of 1,7-phenanthroline into a solution of  $5 \mu\text{M}$   $\text{Eu}^{3+}$  containing  $20 \mu\text{M}$  Htta, no changes in the  $\text{Eu}^{3+}$  luminescence were detected. Likewise, when 2,2'-dipyridyl was substituted for 1,10-phenanthroline, no luminescence changes were observed, implying that ternary complex formation did not take place. This we find somewhat unusual since 1,10-phenanthroline and 2,2'-dipyridyl are so similar. In fact,  $\text{Eu}(\beta\text{-diketone})_3(2,2'\text{-dipyridyl})$  complexes have been synthesized in the past.<sup>7,8</sup> Nevertheless, in aqueous solution, they do not appear to exist. Perhaps the 2,2'-dipyridyl does not provide a large enough aromatic framework for  $\pi$ -stacking interactions to take place.

Experiments involving substitutions of the  $\beta$ -diketone ligand were also carried out. Since the  $\beta$ -diketones that we observed to form ternary complexes (Htta, Hbtfa, and Hdbm) contain aromatic moieties, it seems likely that  $\pi$ -stacking interactions may be responsible for the synergistic coordination of the complexes. We attempted to vary the substituents of the  $\beta$ -diketone ligands by substituting Hacac, Hba, and Hhfacac (see Chart 1) for Htta, Hbtfa, and Hdbm. When 1,10-phenanthroline is titrated into a solution containing  $5 \mu\text{M}$   $\text{Eu}^{3+}$  and  $20 \mu\text{M}$  Hacac (two methyl substituents), Hba (one phenyl and one methyl substituent), or Hhfacac (two trifluoromethyl substituents), there is no detectable change in the luminescent signal. In the case of Hacac, this is understandable since the substituents do not provide any means of forming ligand-ligand attractions except perhaps hydrophobic interactions. In the case of Hhfacac, it appears that hydrogen bonding substituents alone are not enough to allow ternary complex formation. The case of

Hba is somewhat surprising, since Hbtfa (one phenyl and one trifluoromethyl substituent) is effective in forming ternary complexes. From these experiments, we conclude that the presence of at least one aromatic  $\beta$ -diketone substituent is critical to the formation of these ternary complexes in aqueous solution.

### Conclusions

The interaction of the  $\beta$ -diketonate ligands with  $\text{Eu}^{3+}$  ion in aqueous solution is very weak. Furthermore, 1,10-phenanthroline is not observed to bind  $\text{Eu}^{3+}$  at all in aqueous solution. Remarkably however, when 3 equiv of Htta, Hbtfa, or Hdbm is present with 1 equiv of 1,10-phenanthroline and 1 equiv of  $\text{Eu}^{3+}$  in aqueous solution, a relatively strong, highly luminescent ternary complex is formed, as evidenced by both direct excitation of the  $\text{Eu}^{3+}$  ion by laser spectroscopy and sensitized emission of the  $\text{Eu}^{3+}$  ion observed by fluorescence spectrometry.

Two distinct  $\text{Eu}^{3+}$  environments are detected for each of the ternary systems from the resolution of two bands from the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  spectrum of  $\text{Eu}^{3+}$  and the observation of two lifetimes in the decays of the  ${}^5\text{D}_0$  excited states. Energy transfer from  $\text{Eu}^{3+}$

to  $\text{Nd}^{3+}$  is proof that these distinct environments arise from the formation of dinuclear or polynuclear complexes. The measurement of coordinated water molecules reveals that one  $\text{Eu}^{3+}$  environment binds a single water molecule while the other binds none. Titrations of the individual ligands affords a stoichiometry of 1 1,10-phenanthroline and 3  $\beta$ -diketone ligands per metal ion.

Ligand substitutions for 1,10-phenanthroline reveal that the 1,10-phenanthroline must coordinate the  $\text{Eu}^{3+}$  and that the extensive aromatic platform of the 1,10-phenanthroline is probably responsible for the strong ligand–ligand interaction that must take place in order to allow these complexes to form. A survey of results for a variety of  $\beta$ -diketone ligands reveals that at least one substituent must be aromatic, and the other either aromatic or electronegative, in order for the complex to form. We therefore believe that intracomplex ligand  $\pi$ -stacking has the strongest influence on the formation of the complexes.

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