

was raised above 7. In those cases, the large changes were attributed to the onset of *terdentate* chelation by at least one or two of the bound malate ligands (via two carboxylate groups *plus* the α -OH, or hydroxylate, group). The change from bidentate to terdentate chelation by the malate ligands would be expected to significantly alter the ligand field sensed by the Ln^{3+} 4f electrons and, thereby, induce major changes in the 4f \rightarrow 4f optical spectra (especially in transition regions known to exhibit hypersensitive behavior).

Conclusions

The experimental results reported here clearly demonstrate the hypersensitive behavior of the $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ transitions of Nd(III), and it is shown how the absorption spectra associated with these transitions can be used to elicit information about complex formation (as a function of solution pH). Furthermore, it was shown how the *relative* $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ absorption intensities observed for the various systems could be rationalized (at least qualitatively) in terms of specific ligand structural features such as (1) the nature and number of donor groups, (2) the nature and number of

nonligating substituent groups, and (3) chelate-ring conformational properties. Our direct calculations of transition oscillator strengths (for model structures presumed to be similar to the real structures present in solution at pH > 7) met with mixed success. Agreement between the calculated vs. experimentally determined oscillator strengths was good (in some cases, excellent) for the tris terdentate chelate structures 2-5. However, our calculations grossly underestimated the oscillator strengths for the $\text{NdCl}_3(\text{aq})$ system (modeled as a 9-coordinate $\text{Nd}(\text{H}_2\text{O})_9^{3+}$ complex with exact D_{3h} symmetry). This led to significant overestimates of f - (complex): f ($\text{NdCl}_3(\text{aq})$) ratios and hypersensitive behavior. It is likely that this problem can be attributed primarily to the inappropriateness of using our idealized structure 1 to model the complexes present in the $\text{NdCl}_3(\text{aq})$ system.

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Registry No. $\text{Nd}(\text{ODA})_3^{3-}$, 43030-80-4; $\text{Nd}(\text{DPA})_3^{3-}$, 38721-35-6; $\text{Nd}(\text{IDA})_3^{3-}$, 12561-55-6; $\text{Nd}(\text{MIDA})_3^{3-}$, 89746-87-2; $\text{Nd}(\text{MAL})_3^{3-}$, 89773-17-1; NdEHPG^- , 89746-88-3.

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802

Europium(III) Luminescence Excitation Spectroscopy. A Species-Specific Method for the Quantitation of Lanthanide Ion Binding to Chelating Agents. Complexes of (1,2-Ethanediyldioxy)diacetate

MICHAEL ALBIN, GREGORY K. FARBER, and WILLIAM DEW. HORROCKS, JR.*

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Laser excitation spectroscopy was used to monitor the complexation of (1,2-ethanediyldioxy)diacetate (EDA^{2-}) with lanthanide(III) ions. Relative formation constants for the 1:1 species were determined in competition experiments that monitor the decrease in the excitation maximum due to $\text{Eu}(\text{EDA})^+$ as $\text{Ln}(\text{EDA})^+$ is formed. The formation constant, K_2 , for the bis complex, $\text{Eu}(\text{EDA})_2^-$, was evaluated by following the changes in the $^7F_0 \rightarrow ^5D_0$ excitation spectrum as a function of the concentration of added EDA^{2-} . Excited-state lifetime measurements in H_2O and D_2O solution provided the number of coordinated water molecules in the two complexes (7 and 3 for the mono and bis complexes, respectively). Structural comparisons between solid-state and solution species were made from the excitation spectra.

Introduction

Classical methods for the determination of the binding constants of metal ions to chelating ligands generally involve fitting the results of potentiometric titrations of the ligand in the presence and absence of metal ion to a sometimes complex scheme requiring the knowledge of multiple proton dissociation constants.¹ These methods are necessarily indirect, and their validity depends upon the correctness of assumptions made concerning the species present in solution. Work in this laboratory has involved the exploitation of laser-excited europium(III) luminescence to monitor the binding of this ion to specific sites in proteins or individual complexes in solution. Our experiment involves excitation of the $^7F_0 \rightarrow ^5D_0$ transition of Eu(III) by scanning a pulsed dye laser through the transition region (577-581 nm) while emission corresponding to the relatively intense $^5D_0 \rightarrow ^7F_2$ transition (~ 614 nm) is monitored. Since the absorptive transition is between nondegenerate levels, the observation of more than one peak in the excitation spectrum implies the presence of more than one Eu(III) environment. These methods have been employed in this laboratory to quantitate Eu(III) ion binding to proteins,²⁻⁸ iono-

phoric ligands,⁹ and monodentate anions¹⁰ as well as to monitor ligand-exchange kinetic processes in chelate systems.¹¹ In addition, from measurements of excited-state lifetimes made separately in H_2O and D_2O solution, it is possible to determine the number of water molecules coordinated to the Eu(III) ion in any given species.^{2,12}

The present research illustrates the application of these species-specific methods to obtain two additional classes of

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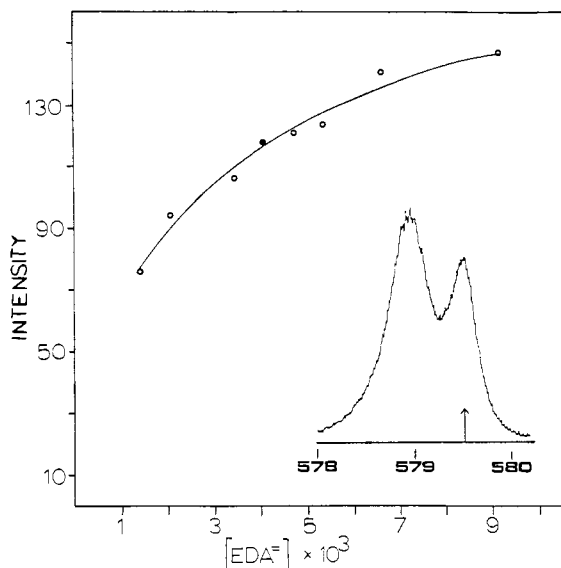
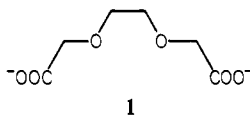
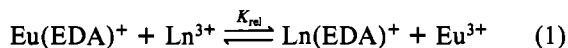


Figure 1. Plot of intensity ($\lambda_{\text{ex}} = 579.50 \text{ nm}$, $\gamma_{\text{em}} = 614 \text{ nm}$) vs. $[\text{EDA}^{2-}]$ ($[\text{Eu}]_i = 1.27 \text{ mM}$): circles, experimental points; solid line, best fit for $\log K_2 = 2.50$. The excitation spectrum at $[\text{EDA}^{2-}] = 3.44 \text{ mM}$ (solid circle) is shown in the insert.

information. The first is the measurement of relative (to Eu^{3+}) constants for the binding of various ions to a chelating ligand under conditions where complex formation is essentially quantitative (e.g., an equimolar mixture of metal ion and ligand contains no unbound species). The ligand (1,2-ethanediyldioxy)diacetate, EDA (1), has been chosen as the

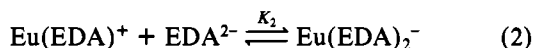


object of this study. Relative binding constants, K_{rel} , corresponding to the equilibrium of eq 1 (Ln^{3+} represents any



aquated ion of the lanthanide series other than Eu^{3+}), are obtained by monitoring the concentration of $\text{Eu}(\text{EDA})^+$ with laser excitation spectroscopy.

The second class of experiment exemplified here involves the measurement of the formation constant, K_2 , of the bis-(ligand) complex, according to eq 2. This is accomplished



by monitoring the concentrations of $\text{Eu}(\text{EDA})^+$ and $\text{Eu}(\text{EDA})_2^-$ as a function of solution composition by means of their two distinct excitation spectral peaks (see insert, Figure 1).

Experimental Section

(1,2-Ethanediyldioxy)diacetic acid (H_2EDA) was prepared by oxidizing triethylene glycol with nitric acid.¹³ Europium chloride solutions were prepared in doubly distilled deionized water with $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich Chemical Co.) and standardized by titration with EDTA, using arsenazo as indicator.¹⁴ H_2EDA stock solutions were standardized by titration with a sodium hydroxide solution standardized with potassium hydrogen phthalate. All laser experiments were performed at $25 \pm 0.1 \text{ }^\circ\text{C}$ on solutions with the ionic strength adjusted to 0.10 with sodium perchlorate, pH 5.5–6.0, and a total $\text{Eu}(\text{III})$ concentration of 1.27 mM. Excitation spectra and lifetime

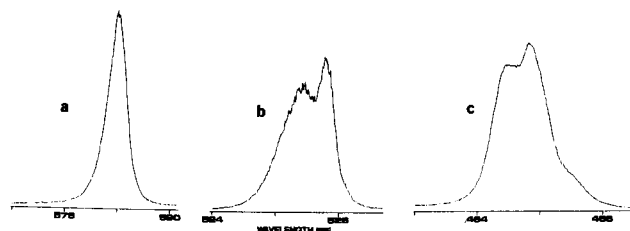


Figure 2. Excitation spectra of $\text{Eu}(\text{EDA})^+$ ($[\text{EDA}^{2-}]/[\text{Eu}] = 0.8$; pH 6): (a) ${}^7F_0 \rightarrow {}^5D_0$; (b) ${}^7F_0 \rightarrow {}^5D_1$; (c) ${}^7F_0 \rightarrow {}^5D_2$.

measurements were obtained by using a previously described nitrogen laser-pumped pulsed dye laser system.^{2,15} All intensities were recorded in a ratio mode with a photodyode used to monitor laser power fluctuations.

Determination of Relative Binding Constant, K_{rel} . These correspond to the equilibrium of eq 1 and are defined by eq 3. Experimentally

$$K_{\text{rel}} = \frac{[\text{Ln}(\text{EDA})^+][\text{Eu}^{3+}]}{[\text{Eu}(\text{EDA})^+][\text{Ln}^{3+}]} \quad (3)$$

$[\text{Eu}(\text{EDA})^+]$ is measured by recording the intensity, I , of the excitation peak at 579.00 nm (Figure 2), where

$$I = k[\text{Eu}(\text{EDA})^+] \quad (4)$$

and k is a proportionality constant determined from a plot of I vs. $[\text{Eu}(\text{EDA})^+]$ over the 1–10 mM concentration range. Equation 4, in conjunction with relationships 5–7, reduces the equilibrium ex-

$$[\text{Eu}^{3+}]_i = [\text{Eu}^{3+}] + [\text{Eu}(\text{EDA})^+] \quad (5)$$

$$[\text{Ln}^{3+}]_i = [\text{Ln}^{3+}] + [\text{Ln}(\text{EDA})^+] \quad (6)$$

$$[\text{EDA}^{2-}]_i = [\text{Ln}(\text{EDA})^+] + [\text{Eu}(\text{EDA})^+] \quad (7)$$

pression (eq 3) to a function of I , k , and initial concentrations (eq 8), where the subscript i denotes the initial concentration of the species

$$K_{\text{rel}} = \frac{([\text{EDA}^{2-}]_i - (I/k))([\text{Eu}^{3+}]_i - (I/k))}{(I/k)([\text{Ln}^{3+}]_i - [\text{EDA}^{2-}]_i + (I/k))} \quad (8)$$

indicated. Under the conditions employed (pH 5.5–6.0, $[\text{Ln}^{3+}]_i = [\text{Eu}^{3+}]_i = [\text{EDA}^{2-}]_i = 1.27 \text{ mM}$), the contribution from H_2EDA , H_2EDA and $\text{Ln}(\text{EDA})_2^-$ are negligible and are not considered in eq 5–7. Equation 8 is further reduced to eq 9 in the case where the initial concentrations of EDA^{2-} , Eu^{3+} , and competing ion, Ln^{3+} , are equal.

$$K_{\text{rel}} = \frac{([\text{Eu}^{3+}]_i - (I/k))^2}{(I/k)^2} \quad (9)$$

Determination of the Formation Constant of $\text{Eu}(\text{EDA})_2^-$, K_2 . This value was determined by monitoring changes in the ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra as a function of $[\text{EDA}^{2-}]_i$, while $[\text{Eu}^{3+}]_i$ was held constant. Only two excitation peaks are detected (Figure 1, insert), one due to $\text{Eu}(\text{EDA})^+$ and the other due to $\text{Eu}(\text{EDA})_2^-$ (no free Eu^{3+} , $\text{Eu}(\text{EDA})_3^{3-}$, or other $\text{Eu}(\text{III})$ -containing species were observed under our conditions). K_2 was obtained from intensity measurements at 579.50 nm, the excitation maximum for $\text{Eu}(\text{EDA})_2^-$. At this wavelength, $\text{Eu}(\text{EDA})^+$ makes a nonnegligible contribution to the intensity, I , so one must express I as a sum of terms: $I = k'[\text{Eu}(\text{EDA})^+] + k''[\text{Eu}(\text{EDA})_2^-]$. In a manner analogous to the procedure previously employed in this laboratory,¹⁰ this intensity relationship can be expressed as a function of k' , k'' , K_2 , and the initial concentrations of EDA^{2-} and Eu^{3+}

$$I = k'[\text{Eu}^{3+}]_i - \frac{k'P}{2} + \frac{k''P}{2} \quad (10)$$

where

$$P = [\text{Eu}^{3+}]_i + [\text{EDA}^{2-}]_i + K_2^{-1} - ([\text{Eu}^{3+}]_i^2 - 2[\text{Eu}^{3+}]_i[\text{EDA}^{2-}]_i + 2[\text{Eu}^{3+}]_iK_2^{-1} + [\text{EDA}^{2-}]_i^2 + 2[\text{EDA}^{2-}]_iK_2^{-1} + K_2^{-2})^{1/2} \quad (11)$$

By the use of a nonlinear regression analysis with k' , k'' , and K_2 as

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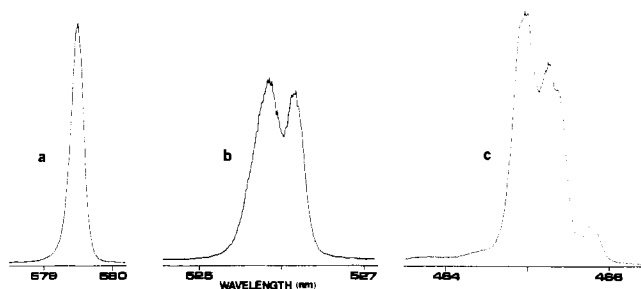


Figure 3. Excitation spectra of $\text{Eu}(\text{EDA})_2^-$ ($[\text{EDA}^{2-}]/[\text{Eu}] = 30$; pH 6). Transitions are as in Figure 2.

Table I. Frequencies of Electronic Transitions

transition	freq, cm^{-1}	
	$\text{Eu}(\text{EDA})^+$	$\text{Eu}(\text{EDA})_2^-$
${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$	17 272	17 257
${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$	19 032	19 016
	19 019	19 005
${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$	21 528	21 507
	21 512	21 494
	21 500 (sh)	21 469

adjustable parameters, the "best fit" value of K_2 was obtained for eight data points (see Figure 1).

Results and Discussion

Characterization of $\text{Eu}(\text{EDA})^+$ and $\text{Eu}(\text{EDA})_2^-$. Figures 2 and 3 show ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ excitation spectra of $\text{Eu}(\text{EDA})^+$ and $\text{Eu}(\text{EDA})_2^-$, respectively. The composition of the solution was so adjusted (see captions to Figures 2 and 3) that the complexes indicated were the only detectable Eu(III)-containing species present. In each case the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ region contains only a single peak indicative of a single Eu(III) species in solution. This transition occurs at 15 cm^{-1} lower energy in $\text{Eu}(\text{EDA})_2^-$ compared with $\text{Eu}(\text{EDA})^+$ (Table I). This is in accord with a previously noted trend^{15,16} wherein this transition occurs at lower energy the greater the negative charge on a complex in a homologous series. The peak width for the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ transition of $\text{Eu}(\text{EDA})^+$ is 13.1 cm^{-1} fwhm while that of $\text{Eu}(\text{EDA})_2^-$ is 6.3 cm^{-1} fwhm. For both complexes the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transitions (Figures 2 and 3) show structure owing to ligand field splittings of the excited states. Fewer than the maximum possible number of transitions (three in the case of ${}^5\text{D}_1$ and five in the case of ${}^5\text{D}_2$) are observed in all cases. The transitions for $\text{Eu}(\text{EDA})_2^-$ again tend to occur at slightly lower energies than those of $\text{Eu}(\text{EDA})^+$.

The number of water molecules coordinated to Eu(III) in the two complexes was determined by measuring the reciprocal excited-state lifetimes, τ^{-1} , separately in H_2O and D_2O solution.¹² The results were as follows: $\text{Eu}(\text{EDA})^+$, $\tau_{\text{H}_2\text{O}}^{-1} = 7.72 \text{ ms}^{-1}$, $\tau_{\text{D}_2\text{O}}^{-1} = 0.51 \text{ ms}^{-1}$; $\text{Eu}(\text{EDA})_2^-$, $\tau_{\text{H}_2\text{O}}^{-1} = 4.37 \text{ ms}^{-1}$, $\tau_{\text{D}_2\text{O}}^{-1} = 1.30 \text{ ms}^{-1}$. From the previously determined linear correlation between $\tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1}$ and the number of coordinated water molecules it is indicated that 7 ± 0.5 water molecules are coordinated in $\text{Eu}(\text{EDA})^+$ and 3 ± 0.5 in $\text{Eu}(\text{EDA})_2^-$. Four water molecules are apparently displaced when a second EDA^{2-} ligand binds to $\text{Eu}(\text{EDA})^+$, consistent with its potential tetradentate nature (vide infra). Reciprocal lifetime measurements on a crystalline solid of composition $\text{Na}[\text{Eu}(\text{EDA})_2(\text{H}_2\text{O})_2]$ isolated separately from H_2O and D_2O solution ($\tau_{\text{H}_2\text{O}}^{-1} = 3.55 \text{ ms}^{-1}$ and $\tau_{\text{D}_2\text{O}}^{-1} = 1.20 \text{ ms}^{-1}$) suggest the presence of two coordinated water molecules in the solid state, consistent with the X-ray structure of sodium diaqua-bis((1,2-phenylenedioxy)diacetato)lanthanate(III) tetra-

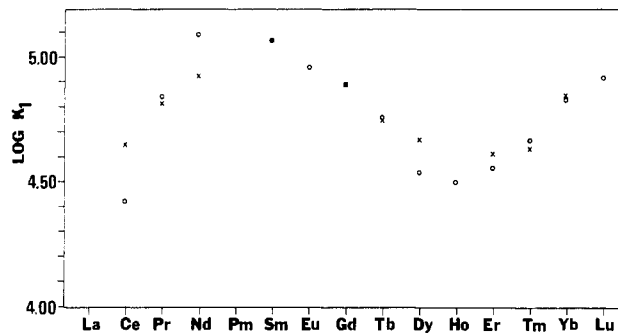


Figure 4. Relative formation constants for $\text{Ln}(\text{EDA})^+$: (O) laser results; (X) literature titration data.¹³

Table II. $\log K_1$ Values Obtained from Competition Studies^a

Ln	$\log K_1$	σ^b	Ln	$\log K_1$	σ^b
Ce	4.38	0.16	Dy	4.54	0.02
Pr	4.89	0.15	Ho	4.51	0.02
Nd	5.10	0.13	Er	4.53	0.09
Sm	5.07		Tm	4.69	0.06
Eu	4.94	0.15	Yb	4.83	0.05
Gd	4.84	0.23	Lu	4.84	0.02
Tb	4.77	0.01			

^a Numbers are relative to literature value for Sm.¹³ ^b σ is the standard deviation for six K_1 determinations.

hydrate,¹⁷ where the total coordination number of the lanthanide ion is 10. In solution the first coordination sphere apparently expands to a coordination number of 11, which is not unknown in lanthanide ion structural chemistry.¹⁸

Formation Constants for $\text{Ln}(\text{EDA})^+$ across the Lanthanide Series. Relative formation constants for $\text{Ln}(\text{EDA})^+$ complexes with respect to $\text{Eu}(\text{EDA})^+$ were obtained from experiments wherein equimolar concentrations of Eu^{3+} and another Ln^{3+} ion compete for EDA^{2-} ligand while the concentration of $\text{Eu}(\text{EDA})^+$ is monitored via laser methods (see Experimental Section). The logarithms of the formation constants, K_1 , for the entire series, based on the measured relative constants, are given in Table II and plotted in Figure 4. The relative formation constants were placed on an absolute scale by using the literature value¹³ for $\text{Sm}(\text{EDA})^+$. It was not possible for us to obtain an absolute value of K_1 for $\text{Eu}(\text{EDA})^+$ by directly using laser methods owing to the detection limits of our current apparatus and interference from the signal due to $\text{Eu}_{\text{aq}}^{3+}$ under the necessary conditions of the experiment. It can be seen in Figure 4 that good agreement between the direct spectroscopic results of this study (O) and the potentiometric titration data in the literature (X) is obtained. The errors in the observed $\log K_1$'s quoted in Table II are based on a minimum of six separate runs for each Ln^{3+} ion.

A variety of trends in complex formation constants across the lanthanide series have been observed for chelating ligands.^{19,20} Sinha¹⁹ has compiled data for many systems and discussed the factors that are involved in the variation of K across the lanthanide series. No simple relationship is observed between ionic radii, which decrease monotonically, and formation constants. Contributing factors include ionic size in relation to ligand cavity size or bite constraints and changes in total coordination number at a certain point in the series, as well as entropy and enthalpy effects. Depicted graphically in Figure 5 (literature values from ref 13, 23–26) are the formation constant (K_1) trends for the series of chelating lig-

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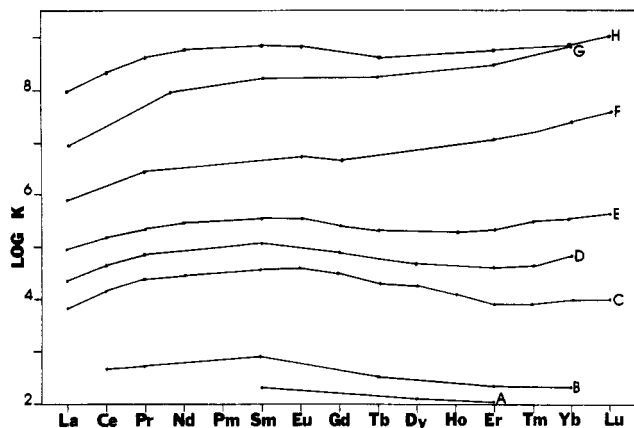
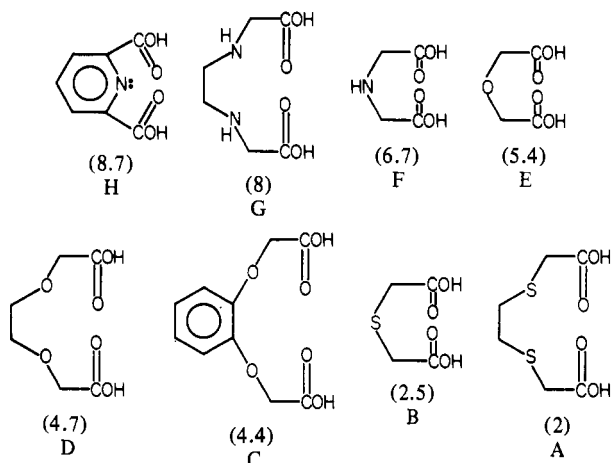
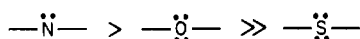


Figure 5. Trends in lanthanide ion formation constants with dicarboxylate ligands.

ands, A–H, all of which have carboxylate groups separated by one or two potentially liganding atoms (average $\log K_1$ values are indicated in parentheses under the structures). The



trend observed for H_2EDTA (ligand D) is clearly not exactly matched by any of the others, although those of ligands C and E are fairly similar. Several aspects of the interaction of $Ln(III)$ ions and these dicarboxylate ligands are apparent from the trend in average formation constant. Assuming a strong interaction with the two carboxylate moieties, the trend in preference for donor groups is



Perusal of a compendium²¹ of chelate stability constants for $Ln(III)$ ions reveals that $\log K_1$ values are typically in the ranges 2–4 for bidentate ligands, 5–7 for tridentates, and 8–10 for tetradentates. According to this correlation, ligands A and

B appear to be bidentate with no sulfur coordination. Ligands E and F fall in the tridentate range, while G appears to be tetradentate. Ligands C and D have formation constant values intermediate between those usually observed for bi- and tridentate ligands. With seven coordinated water molecules indicated from our lifetime data, bidentate coordination by D is not unreasonable (a total coordination number of 9); however, an analysis of the paramagnetically shifted 1H and ^{13}C nuclear resonances of C shows²² that this ligand coordinates in a tetradentate fashion. Additionally, our finding that upon coordination of a second EDA^{2-} ligand to Eu^{3+} four water molecules are displaced suggests tetradentate binding by ligand D. Clearly, a variety of factors contribute to the magnitude of a stability constant, and simplified interpretations of any particular result or trend must be viewed with caution.

Direct Spectroscopic Determination of the Formation Constant of $Eu(EDA)_2^-$, K_2 . $^7F_0 \rightarrow ^5D_0$ excitation spectra of solutions containing EDA^{2-} to Eu^{3+} ratios greater than 1 exhibit two distinct excitation peaks due to $Eu(EDA)^+$ and $Eu(EDA)_2^-$ (Figure 1, insert). By monitoring the intensity of the excitation spectra at 579.5 nm (where $Eu(EDA)_2^-$ is the principal absorber) as a function of the concentration of added EDA^{2-} and fitting the results to eq 10 and 11 (see Experimental Section), we obtained a value for $\log K_2$ of 2.50 ± 0.71 . The theoretical curve obtained from this value of K_2 and $k' = 2.76 \times 10^4$ and $k'' = 1.50 \times 10^5$ is compared with the experimental data points in Figure 1. The $\log K_2$ value found by us for the Eu^{3+}/EDA^{2-} system compares well with that obtained by means of potentiometric titration for the corresponding Sm^{3+} (2.91) and Gd^{3+} (2.98) systems as well as for the $Eu^{3+}/(1,2\text{-phenylenedioxy})diacetate$ (C) complex equilibrium (2.85).

Conclusions

We have demonstrated the utility of Eu^{3+} excitation spectroscopy of the $^7F_0 \rightarrow ^5D_0$ transition in determining relative formation constants by means of metal ion competition experiments in the case of very tight binding and an absolute formation constant in a more weakly binding situation. The advantage over other methods is that the present experiment measures a quantity that is species-specific and directly proportional to concentration. Extension of quantitative binding constant studies to more tightly binding systems should be possible by using a more intense laser source (e.g., a Nd-YAG laser-pumped dye laser), thus increasing the general applicability of the method.

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