IV. Conclusion

Accurate heats of formation of $C_2H_5S^+$ and CH_2S^+ ions and the measured dissociation rates of energy-selected dimethyl disulfide ions are used to show that the dimethyl disulfide ion has a dihedral angle of 180° and that its energy is 1.6 eV more stable than the ion with a dihedral angle of 90°. The ionization energy of the dimethyl disulfide is calculated to be 7.4 eV on the basis of RRKM/QET calculations. This is 0.9 eV lower than the adiabatic ionization energy of 8.33 eV measured by PES.

Acknowledgment. We are greatful to the Department of Energy for the support of this work.

Registry No. CH_3SSCH_3, 624-92-0; CH_3SS^+, 12538-77-1; $C_2H_5S^+$, 20828-74-4; $CH_3SSCH_3{}^+$, 34628-72-3; CH_3SH^+, 53369-41-8; CH_3S^+, 20828-73-3; CH_2S^+, 61356-81-8.

Kinetic Parameters for a System at Equilibrium from the Time Course of Luminescence Emission: A New Probe of Equilibrium Dynamics. Excited-State Europium(III) as a Species Label

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Abstract: Forward and reverse rate constants for the equilibrium between the europium(III) complex of 1,2-diaminocyclohexanetetraacetate, $Eu(DCTA)^-$, and iminodiacetate, $IMDA^{2-}$, to form the ternary complex $Eu(DCTA)(IMDA)^{3-}$ are obtained from the time course of luminescence emission following selective laser excitation of the Eu(III)-containing species. This new method depends upon selective excitation of the $^7F_0 \rightarrow {}^5D_0$ electronic transition of a particular Eu(III) species while monitoring the time course of luminescence emission, either predominately from the same species or from one into which it is converted chemically, at a rate comparable to the reciprocal lifetime of the excited state of the species involved. Since excited state Eu(III) has the same reactivity in ligand-exchange reactions as the ground-state ion, the electronic excitation acts as a species label in a manner analogous to the use of nuclear spin saturation transfer as a nuclear label. Twelve different luminescence emission curves obtained at three different pH values (four permutations of λ_{ex} and λ_{em} at each pH) were fit with a total of five adjustable parameters. At 23.5 °C the following results were obtained: $k_f = 1.6 \times 10^7\ M^{-1}\ s^{-1}$, $k_r = 2.6 \times 10^3\ s^{-1}$, $K_{eq} = 6.3 \times 10^3\ M^{-1}$, $\tau_{Eu(DCTA)^-} = 0.320$ ms, $\tau_{Eu(DCTA)(IMDA)^{3-}} = 0.805$ ms. Other systems wherein chemical interconversion processes occur at rates much greater than (rapid exchange) or much slower than (slow exchange) the reciprocal excited-state lifetime of the Eu(III)-containing species are briefly examined. Eu(III) complexes of the ligands oxydiacetate and dipicolinate are examples of the former and latter, respectively.

Methods for obtaining kinetic information on systems at equilibrium rely on experiments that sample separate environments of interconverting species on a time scale comparable to that of the chemical rate process of the interconversion. Examples in current use include dynamic NMR methods,[1,2] nuclear spin saturation transfer,[3] EPR line broadening,[4] and fluctuation spectroscopy.[5] In dynamic NMR,[1,2] parameters are determined for processes that occur at rates comparable to the chemical shift difference (expressed in frequency units) between nuclei in interconverting environments. Nuclear spin saturation transfer[3] monitors rates comparable to the spin–lattice relaxation times of a nucleus shuttling between two environments. EPR line-broadening techniques[4] have proven useful particularly in the study of the rates of electron-transfer reactions. The fluctuation spectroscopic technique[5] of determining kinetic parameters is based on the principle that the rates of decay of spontaneous microscopic fluctuations are determined by the same rate constants as those for a macroscopic departure from equilibrium. The essence of most of these methods is the ability of an experiment to track a label, e.g., a chemical shift difference or degree of nuclear saturation, of interconverting chemical species on a time scale comparable to the interconversion rate. We report here a new method for obtaining kinetic information on a system at equilibrium where the label involved is the excited $^5D_0$ emissive state of Eu(III) and the kinetic process is monitored via the time course of luminescence emission.[6]

Experimental Section

The principal chemicals used were obtained from the suppliers indicated: 1,2-diaminocyclohexanetetraacetic acid, H_4DCTA (Aldrich); dipicolinic acid, H_2DPA (Eastman); iminodiacetic acid, H_2IMDA (Sigma); oxydiacetic acid, H_2ODA (Fluka AG); europium(III) chloride hexahydrate (Aldrich). All other chemicals were reagent grade or the purest commercially available.

The time course of luminescence emission was measured by using a pulsed nitrogen laser pumped dye laser apparatus described in detail elsewhere.[7,8] Individual emissions were recorded with the aid of a transient digitizer and signal averager. The data (1900 points per curve) were then computer fit by using every tenth or every fifth point to the theoretical expressions (vide infra) employing an IBM share program designated NLIN2, an algorithm for least-squares estimation of nonlinear parameters.[9]

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[1] Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982.

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[6] Kinetic information has, of course, been obtained from the fluorescence of organic molecules; however, excited-state organic molecules have a chemical reactivity different from their ground-state counterparts, and such systems are not in equilibrium following excitation. See: Weller, A. *Prog. React. Kinet.* **1961**, *1*, 187–214.

[7] Sudnick, D. R. Ph.D. Thesis, The Pennsylvania State University, 1979.

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Excitation spectra for the $^7F_0 \rightarrow {}^5D_0$ transition of Eu(III) were obtained by using the same pulsed dye laser equipped with a scan control unit. The laser was continuously scanned from 578.0 to 581.5 nm while monitoring the $^5D_0 \rightarrow {}^7F_2$ emission at 614.5 nm. The emission intensity was recorded with the aid of a boxcar integrator (PAR Model 162).

Emission spectra for the $^5D_0 \rightarrow {}^7F_2$ transition were obtained by using the same apparatus with the dye laser tuned to coincide with the $^7F_0 \rightarrow {}^5D_0$ transition. The emission monochromator (ISA DH20-VIR, 0.2-m double monochromator, band width 1.5 nm) was scanned continuously from 605 to 630 nm. the luminescence was again recorded with the aid of a boxcar integrator.

The acid dissociation constants of H_2IMDA were determined by using the potentiometric titration method of Chaberek and Martell[10] ($pK_1 = 2.66$, $pK_2 = 9.00$). All potentiometric measurements were carried out at 22.5 ± 0.2 °C on solutions adjusted to ionic strength 1.0 with KCl.

Theory

Our method monitors the chemical transfer of excited-state europium(III) ions between different coordination complexes in solution. The label in this experiment is the excitation of Eu(III) to the $^5D_0$ state using 578–581-nm light from a pulsed dye laser. Excited Eu(III) ions in chelate complexes in aqueous solution luminesce in the visible region with excited-state lifetimes in the 0.1–0.3-ms range. The $^7F_0 \rightarrow {}^5D_0$ excitation involves a transition within the $4f^6$ electronic configuration wherein two electrons are paired. The 4f orbitals of trivalent lanthanide ions are highly shielded, and the reactivity of excited lanthanide ions in ligand substitution reactions of the type of interest here is identical with that of ground-state ions. Owing to the nondegenerate nature of both the ground ($^7F_0$) and excited ($^5D_0$) states, it is generally possible to excite selectively different Eu(III)-containing species when they are present together in solution.

If two Eu(III) complexes, A and B, are present together in solution at equilibrium (eq 1) and are related by, say, a ligand-exchange reaction, there are three classes of behavior for the time course of luminescence emission following laser excitation.

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \tag{1}$$

(1) Slow Exchange. Selective excitation of A with a laser pulse is followed by an exponential decay of luminescence from A with a characteristic lifetime, τ_A. Likewise, selective excitation of B will be followed by an exponential decay of luminescence from B with a different lifetime, τ_B.

(2) Rapid Exchange. If the rate of chemical interchange of Eu(III) between A and B is rapid with respect to the deexcitation rates in the absence of interchange, τ_A^{-1} and τ_B^{-1}, it is still possible to excite selectively either A or B. The luminescence emission will decay exponentially, but with rate representative of a weighted average of τ_A^{-1} and τ_B^{-1}.

(3) Intermediate Exchange. If the chemical interchange process occurs at a rate comparable to the reciprocal excited-state lifetimes, τ_A^{-1} and τ_B^{-1}, the time course of luminescence emission is more complicated and is dependent on the chemical interconversion rate constants k_A and k_B as well as on the excited-state lifetimes. Equations 2–5 summarize the processes that can occur following selective excitation of A to form excited A*.

$$A^* \xrightarrow{\tau_A^{-1}} A + h\nu + \text{nonradiative loss} \tag{2}$$

$$A^* \xrightarrow{k_A} B^* \tag{3}$$

$$B^* \xrightarrow{\tau_B^{-1}} B + h\nu + \text{nonradiative loss} \tag{4}$$

$$B^* \xrightarrow{k_B} A^* \tag{5}$$

Equations 2 and 4 represent the radiative and nonradiative deexcitation of A* and B*, respectively. Equations 3 and 5 represent the chemical interconversion of A* into B* and vice versa with pseudo-first-order rate constants k_A and k_B, respectively. The differential equations describing these processes are given in eq 6 and 7 and their solutions in eq 8 and 9,

$$d[A^*]/dt = k_B[B^*] - (k_A + \tau_A^{-1})[A^*] \tag{6}$$

$$d[B^*]/dt = k_A[A^*] - (k_B + \tau_B^{-1})[B^*] \tag{7}$$

$$[A^*] = ([A^*]_0/2p)[(a_4 - a_2 + p)\exp(r_1 t) + (a_2 - a_4 + p)\exp(r_2 t)] \tag{8}$$

$$[B^*] = ([A^*]_0/p)k_A[\exp(r_1 t) - \exp(r_2 t)] \tag{9}$$

where $[A^*]_0$ is the initial ($t = 0$) concentration of excited complex A* and the remaining parameters are defined by the following relationships: $r_1 = {}^1/_2[p - a_2 - a_4]$; $r_2 = -{}^1/_2[p + a_2 + a_4]$; $a_2 = k_A + \tau_A^{-1}$; $a_4 = k_B + \tau_B^{-1}$; $p = [(a_2 - a_4)^2 + 4k_Ak_B]^{1/2}$.

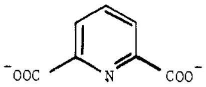
The luminescence intensity I, monitored at a particular wavelength, is given by eq 10, where Q_A and Q_B are the fractional luminescence emissions of species A and B at the wavelength in question.

$$I = Q_A[A^*]/[A^*]_0 + Q_B[B^*]/[A^*]_0 \tag{10}$$

For instance, if the emission monochromator is set at a wavelength where only B* emits ($Q_A = 0$, $Q_B = 1$), the time course of the luminescence emission following excitation of A will involve an increase in intensity as B* is formed chemically from A*, followed by an eventual decay by radiative, nonradiative, and chemical back-reaction pathways. On the other hand if emission from A* can be selectively detected (excluding any luminescence from species B*; $Q_A = 1$, $Q_B = 0$), the time course of luminescence will involve an initial rapid decrease in intensity owing to chemical conversion of A* into B*, followed by a longer lasting tail identical with that found in the case mentioned above. In the present experiments luminescence emission of the $^5D_0 \rightarrow {}^7F_2$ transition in the 600–630-nm range is monitored. While different Eu(III)-containing complexes in principle have different emission spectra, which reveal structure owing to ligand-field splitting of the $^7F_2$ level, as a practical matter it is often not possible to find a wavelength at which emission occurs exclusively from one species or the other. For this reason we employ Q_A and Q_B as parameters in our computer fitting procedure.

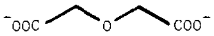
Results and Discussion

Eu(III) complex systems involving all three classes of behavior have been observed.[7] The $Eu(DPA)^+$–$Eu(DPA)_2^-$ (DPA = dipicolinate, **1**) system at millimolar concentrations is in the *slow exchange* limit. Each complex exhibits a characteristic peak in the $^7F_0 \rightarrow {}^5D_0$ excitation spectrum with an excited-state lifetime of its own. This information has been used to estimate the number of water molecules coordinated to the Eu(III) ion in each complex.[11] For systems in slow exchange the excitation spectra can be time resolved. Excitation spectra of systems containing more than one species recorded at successively greater time delays following the laser pulse will exhibit progressively less intensity due to the shorter lived species. Figure 1 shows the excitation spectra of a solution containing a 1:1.75 Eu(III):DPA ratio (1



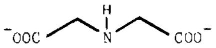
DPA

1



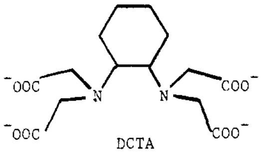
ODA

2



IMDA

3



DCTA

4

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[9] Marquardt, D. W. *J. Soc. Indust. Appl. Math.* **1963**, *11*, 431.

[10] Chaberek, S.; Martell, A. E. *J. Am. Chem. Soc.* **1952**, *74*, 5052.

[11] Horrocks, W. DeW., Jr.; Sudnick, D. R. *Science (Washington, D.C.)* **1979**, *206*, 1194–1196.

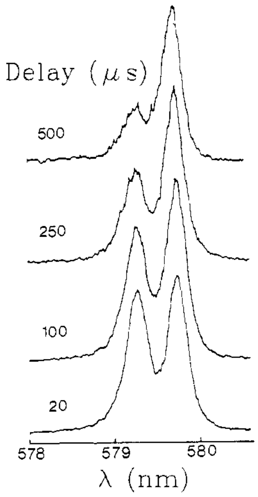

Figure 1. Time resolution of the excitation spectra of $Eu(DPA)^+$ and $Eu(DPA)_2^-$ for a 1 mM Eu(III) solution with a 1:1.75 molar ratio of Eu(III):DPA^{2-} at pH 6.6. The boxcar delay time (microseconds) following the laser pulse is indicated to the left of each spectrum.

mM in $EuCl_3$) at pH 6.6 at a series of delay times. As the delay time is increased, there is a progressive disappearance of the peak at 579.2 nm due to the shorter lived $Eu(DPA)^+$ complex (τ = 0.169 ms) relative to the peak (579.7 nm) for the longer lived $Eu(DPA)_2^-$ complex (τ = 0.304 ms). Such clean time resolution is impossible in cases where a chemical interconversion occurs at rates comparable to or greater than the reciprocal lifetimes of the species involved.

The $Eu(ODA)^+$–$Eu(ODA)_2^-$ (ODA = oxydiacetate, **2**) system is in the *rapid exchange* limit. The excitation spectrum of a solution containing a 1:1.75 Eu(III):ODA ratio (10 mM in $EuCl_3$) at pH 6.5 is shown in Figure 2. The peak at 579.1 nm is due to $Eu(ODA)^+$ while that at 579.5 nm corresponds to the absorption of $Eu(ODA)_2^-$. The τ values measured at either of these excitation wavelengths are identical at 0.248 ms. Moreover, an attempt to time resolve the spectrum analogous to that accomplished in the Eu(III)–DPA system fails to produce any change in the relative intensity of the two peaks as the delay time is increased (Figure 2). This behavior is that expected for the case where the excited-state Eu(III) shuttles between $Eu(ODA)^+$ and $Eu(ODA)_2^-$ with a rate in excess of the reciprocal lifetimes of the two species. Consistent with this interpretation is the fact that as the ratio of Eu(III) to ODA in solution is decreased, the observed reciprocal lifetime, τ_{obsd}^{-1}, decreases continuously owing to the increasing fraction of $Eu(ODA)_2^-$ in solution (top to bottom of Figure 3). This species has the higher quantum yield owing to exclusion of additional water molecules from its first coordination sphere by the second ODA ligand.[8,11,12]

For any such system wherein the chemical equilibrium between species A and B is established at a rate much greater than that of the normal luminescence decay of the two species, it is easily shown that the observed reciprocal lifetimes, τ_{obsd}^{-1}, for excitation into the absorption of either species is given by eq 11, where τ_A^{-1}

$$\tau_{obsd}^{-1} = \frac{[A]}{[A] + [B]}\tau_A^{-1} + \frac{[B]}{[A] + [B]}\tau_B^{-1} \qquad (11)$$

and τ_B^{-1} are the respective reciprocal lifetimes of excited states of A and B in the absence of chemical interconversion. The equilibrium concentration of species A, [A], is related to the intensity of the $^7F_0 \rightarrow {}^5D_0$ excitation peak for this species, I_A, by $[A] = \alpha_A I_A$, where α_A is a proportionality constant. If the total concentration of the two Eu(III)-containing species is C_{tot} = [A] + [B], eq 11 can be written as

$$\tau_{obsd}^{-1} = (\alpha_A I_A / C_{tot})(\tau_A^{-1} - \tau_B^{-1}) + \tau_B^{-1} \qquad (12)$$

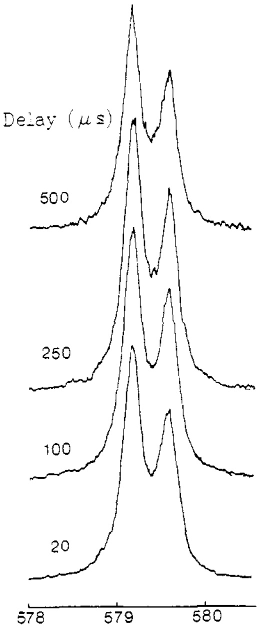

Figure 2. Attempted time resolution of the excitation spectra of $Eu(ODA)^+$ and $Eu(ODA)_2^-$ for a 10 mM Eu(III) solution with a 1:1.75 molar ratio of Eu(III):ODA^{2-} at pH 6.5. The boxcar delay time (microseconds) following the laser pulse is indicated to the left of each spectrum.

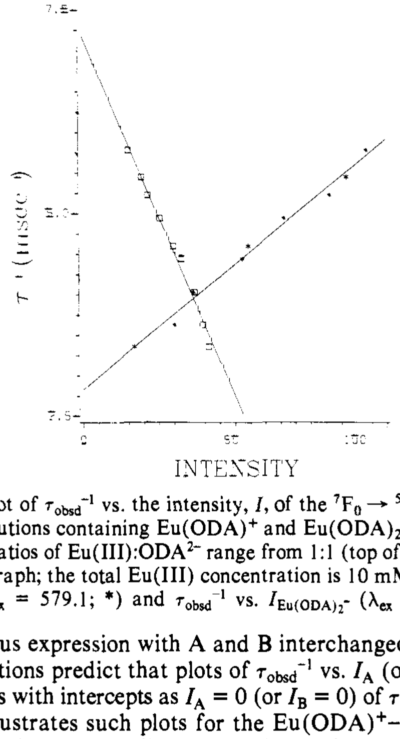

Figure 3. Plot of τ_{obsd}^{-1} vs. the intensity, I, of the $^7F_0 \rightarrow {}^5D_0$ excitation peaks for solutions containing $Eu(ODA)^+$ and $Eu(ODA)_2^-$ in equilibrium. Molar ratios of Eu(III):ODA^{2-} range from 1:1 (top of graph) to 1:2 (bottom of graph; the total Eu(III) concentration is 10 mM). τ_{obsd}^{-1} vs. $I_{Eu(ODA)^+}$ (λ_{ex} = 579.1; *) and τ_{obsd}^{-1} vs. $I_{Eu(ODA)_2^-}$ (λ_{ex} = 579.5; □).

An analogous expression with A and B interchanged also holds. These equations predict that plots of τ_{obsd}^{-1} vs. I_A (or I_B) will be straight lines with intercepts as $I_A = 0$ (or $I_B = 0$) of τ_B^{-1} (or τ_A^{-1}). Figure 3 illustrates such plots for the $Eu(ODA)^+$–$Eu(ODA)_2^-$ system and allows the individual lifetimes of the two interconverting species to be determined on solutions where both are present. The results are $\tau_{Eu(ODA)^+}^{-1}$ = 7.20 ms^{-1} and $\tau_{Eu(ODA)_2^-}^{-1}$ = 2.83 ms^{-1}. This method is a general one applicable to any two species in rapid equilibrium for which excitation spectra and lifetime data are available.

The *intermediate exchange* case, of particular interest here, is exemplified by the equilibrium between the binary and ternary complexes given in eq 13, although it has been observed[7] in several

$$Eu(DCTA)^- + IMDA^{2-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Eu(DCTA)(IMDA)^{3-} \qquad (13)$$

other ligand-exchange systems as well, where $IMDA^{2-}$ is iminodiacetate, **3**, and $DCTA^{4-}$ is 1,2-diaminocyclohexanetetraacetate,

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(12) Horrocks, W. DeW., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334–340.

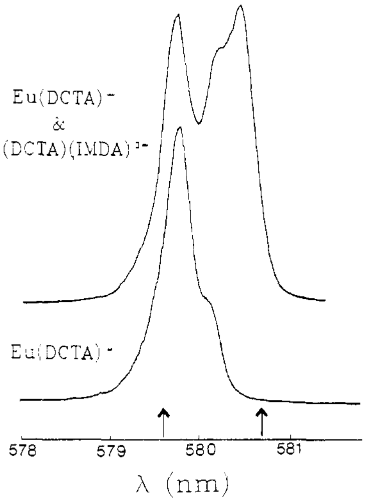

Figure 4. Excitation spectra of solutions containg (bottom) $Eu(DCTA)^-$, where the molar ratio of $Eu(III):DCTA^{4-}$ is 1:1 and the total Eu(III) concentration is 40 mM, and (top) $Eu(DCTA)^-$ and $Eu(DCTA)(IMDA)^{3-}$, where the molar ratio of $Eu(III):DCTA^{4-}:IMDA^{2-}$ is 1:1:3 and the total Eu(III) concentration is 40 mM at pH = 6.99. Arrows show λ_{ex} values used in the kinetic experiments.

4. It is data for this system that we here analyze in detail.

The experiments were carried out at room temperature (23.5 ± 0.5 °C) on solutions with total $EuCl_3$, H_4DCTA, and H_2IMDA concentrations of 0.04, 0.04, and 0.12 M, respectively, at pH values adjusted to the 6–9 range with NaOH and a total ionic strength of 1.0 attained by using KCl. Figure 4 shows the excitation spectra of solutions containing $Eu(DCTA)^-$ alone and both $Eu(DCTA)^-$ and $Eu(DCTA)(IMDA)^{3-}$. The spectrum of the former solution requires some comment in that it exhibits two peaks, indicative of the presence of two species. This phenomenon has been noted previously[13,14] in absorption and emission[15] spectral studies of concentrated $Eu(EDTA)^-$ solutions. The two species have been surmised to correspond to complexes differing by one in the number of coordinated water molecules and/or in the number of coordinated CH_2COO^- groups. In any case the lifetime is the same for excitation into either of the two peaks, and no time resolution is achievable.[15] The two $Eu(DCTA)^-$ species are clearly in the rapid exchange region and, for the present purposes, are considered to be one species. Examination of the excitation spectra of solutions containing both $Eu(DCTA)^-$ and $Eu(DCTA)(IMDA)^{3-}$ (Figure 4) reveals that the former can be selectively excited at 579.6 nm and the latter at 580.7 nm. These excitation wavelengths (λ_{ex}) were used in the experiments (arrows, Figure 4).

Emission spectra of the $^5D_0 \rightarrow {}^7F_2$ transition in the 605–628-nm region (Figure 5) show that at 610 nm most of the emission arises from $Eu(DCTA)^-$ while at 619.3 nm the majority of the luminescence comes from $Eu(DCTA)(IMDA)^{3-}$. These were the emission wavelengths (λ_{em}) employed in our experiments (arrows, Figure 5). Experiments were carried out at pH 6.58, 6.99, and 7.45, with use of a laser apparatus described elsewhere.[7,8] At each pH value, four experiments were performed (the permutations of two λ_{ex} and two λ_{em} values). The digitized data for pH 6.99 are compared, in the four parts of Figure 6, with the predicted curves on the basis of the final average parameters of best fit for all three solutions determined as described below. The qualitative features of the luminescence time courses in the intermediate exchange regime discussed above are quite evident in the curves (vide infra).

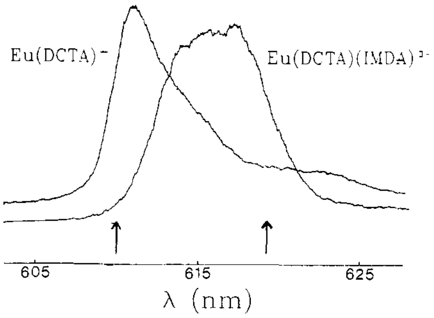

Figure 5. Emission spectra of $Eu(DCTA)^-$, where the molar ratio of $Eu(III):DCTA^{4-}$ is 1:1 and the total Eu(III) concentration is 40 mM, and $Eu(DCTA)(IMDA)^{3-}$, where the molar ratio of $Eu(III):DCTA^{4-}:IMDA^{2-}$ is 1:1:3 and the total Eu(III) concentration is 40 mM at pH 9.5. Arrows show λ_{em} values used in the kinetic experiments.

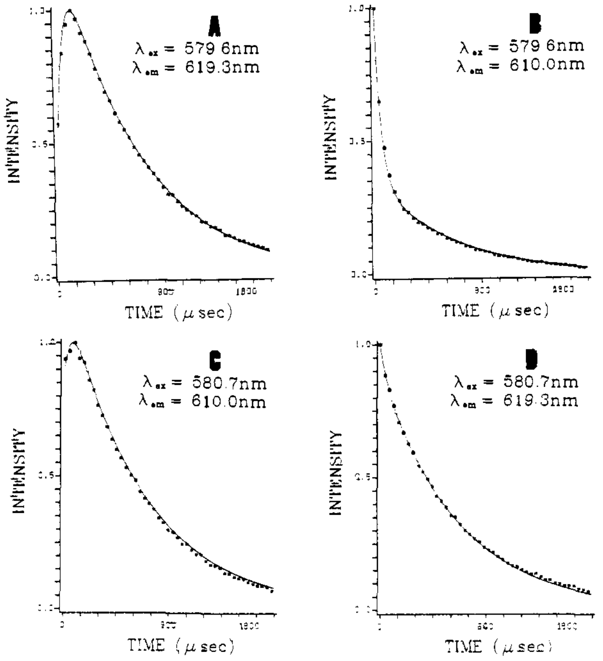

Figure 6. Luminescence decay curves for a solution containing $Eu(DCTA)^-$ and $Eu(DCTA)(IMDA)^{3-}$ at pH 6.99. The λ_{ex} and λ_{em} values used are indicated to the right of each curve. Every 30th digitized data point is plotted (asterisks). The curves are drawn from the predicted curves by using the final average parameters; $\tau_D = 0.320$ ms, $\tau_{DI} = 0.805$ ms, $k_f[IMDA^{2-}] = 13\ ms^{-1}$, and $k_r = 2.6\ ms^{-1}$.

The emission curves were analyzed by using eq 8–10 and a statistical nonlinear least-squares regression digital computer routine.[9] The subscripts D and DI are used to indicate the species $Eu(DCTA)^-$ and $Eu(DCTA)(IMDA)^{3-}$, respectively. The lifetime of the former, $\tau_D = 0.320$ ms, was measured on a solution devoid of $IMDA^{2-}$ and was held fixed in the analysis. The two independent sets of Q values (for λ_{em} = 610.0 and 619.3 nm) were varied by trial and error until internal consistency was achieved for the remaining parameters. The final values of Q_D/Q_{DI} were 0.790/0.210 and 0.175/0.825 at λ_{em} of 610.0 and 619.3 nm, respectively. The best-fit values for the remaining parameters are as follows: $\tau_{DI} = 0.805$ ms; $k_f = 1.6 \times 10^4\ ms^{-1}\ M^{-1}$; $k_r = 2.6\ ms^{-1}$. It was found to be possible to fit the 12 luminescence time-course curves at the three pH values with averaged values of these 5 adjustable parameters with an average standard error of 0.012.[16] The fits to the four experiments at pH 6.99 are shown in Figure 6. It should be noted that k_f, a second-order rate constant, is obtained from the pseudo-first-order constant k_A or k_B (depending on the experiment) of eq 6-9 by eq 14, where

$$k_{A\ \mathrm{or}\ B} = k_f[IMDA^{2-}] \qquad (14)$$

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[13] (a) Kostromina, N. A.; Ternovaya, T. V.; Yatsimirskii, K. B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1969**, *14*, 80–84. (b) Kostromina, N. A.; Tananaeva, N. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1971**, *16*, 1256–1259.

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[15] Bryden, C. C.; Reilley, C. N. *Anal. Chem.* **1982**, *54*, 610–615.

[16] Standard error = $[1/(n-2)(\sum_{i=1}^{n}(y_i - \hat{y}_i)^2)]^{1/2}$, when n is the number of data points, y_i is the observed intensity of the ith data point, and $\hat{y}_i$ is the predicted intensity of the ith data point.

[IMDA^{2-}] is calculated from a knowledge of the pH, the equilibrium constant for reaction eq 13, $K_{eq} = k_f/k_r = 6.3 \times 10^3$ M^{-1}, and the pK values of H$_2$IMDA obtained from a potentiometric titration (pK_1 = 2.66, pK_2 = 9.00).[17]

Average values of the pseudo-first-order rate constants for the forward reaction (eq 13), k_f[IMDA^{2-}], are 5.6, 13, and 36 ms^{-1} at pH 6.58, 6.99, and 7.45, respectively.

With these average parameters in hand it is possible to obtain a qualitative understanding of the luminescence emission time-course curves of the four experiments carried out on the same solution at pH 6.99 (Figure 6). In parts A and B, Eu(DCTA)$^-$ is being selectively excited while the emission monitored is predominantly from Eu(DCTA)(IMDA)$^{3-}$ in part A and from Eu(DCTA)$^-$ in part B. In part A the initial rapid rise in luminescence intensity comes from the rapid chemical conversion of excited Eu(DCTA)$^-$ to excited Eu(DCTA)(IMDA)$^{3-}$ species (pseudo-first-order rate constant 13 ms^{-1}) followed by a slower decay as the radiative and nonradiative deexcitation (τ_{DI}^{-1} = 1.24 ms^{-1}) and back chemical reaction (k_r = 2.6 ms^{-1}) processes become dominant. On the other hand when Eu(DCTA)$^-$ is selectively excited and the emission is monitored predominately for this species (part B), the luminescence emission initially falls very rapidly owing to rapid chemical conversion of Eu(DCTA)$^-$ into Eu(DCTA)(IMDA)$^{3-}$ followed again by a long-lived decay dominated by the smaller rate constants for the deexcitation and chemical back reactions.

Parts C and D present the results of the analogous experiments for selective excitation of Eu(DCTA)(IMDA)$^{3-}$ with luminescence emission sampled predominately from Eu(DCTA)$^-$ and Eu(DCTA)(IMDA)$^{3-}$, respectively. The initial rise in the curve in part C and the initial falloff in the curve of part D are less pronounced than in their respective part A and B counterparts owing to the fact that the rate constant for chemical conversion of Eu(DCTA)(IMDA)3$^-$ into Eu(DCTA)$^-$ is much smaller (k_r = 2.6 ms^{-1}) than the pseudo-first-order rate constant for the opposite interconversion (13 ms^{-1}) and is more on the order of magnitude of the parameters for deexcitation in the absence of chemical processes (τ_D = 3.13 ms^{-1}, τ_{DI} = 1.24 ms^{-1}). It should be emphasized that the four fits to experiment depicted in Figure 6 were obtained by using the *same* set of only five adjustable parameters, which also achieve comparably good fits to the eight additional curves (not shown) obtained at pH 6.58 and 7.45.

Finally, as proof that we are monitoring the kinetics of a ground-state equilibrium system, we carefully measured, at time t = 0, the intensity ratio of the excitation peak due to Eu(DCTA)(IMDA)$^{3-}$ to that of Eu(DCTA)$^-$, I_{DI}/I_D, at the series of pH values 6 58, 6.99, 7.45, and 7.67 with the following respective results: 0.487, 1.07, 3.12, and 4.68. Since [Eu(DCTA)(IMDA)$^{3-}$] = $\alpha_{DI}I_{DI}$ and [Eu(DCTA)] = $\alpha_D I_D$, where α_{DI} and α_D are proportionality constants, the equilibrium expression for the reaction (eq 13) can be written

$$\alpha_{DI}I_{DI}/(\alpha_D I_D[\mathrm{IMDA}^{2-}]) = K_{eq} \quad (15)$$

Thus, since α_{DI}/α_D is a constant $(I_{DI}/I_D)/[\mathrm{IMDA}^{2-}]$ should also be a constant. Dividing the above series of measured I_{DI}/I_D values by [IMDA^{2-}] yields the following numbers: 0.139, 0.128, 0.138, and 0.128, respectively. This result shows that the excited-state luminescence data accurately reflect the ground-state equilibrium and, by inference, the ground-state kinetic parameters.

While the equilibrium constant of the reaction (eq 13) has not been reported in the literature, log K_{eq} values of the analogous reaction with EDTA instead of DCTA of 4.23 and 4.28 have been reported based on potentiometric[18] and NMR[19] studies, respectively. These values can be compared with a log K_{eq} of 3.8 obtained by us on the present DCTA system. The lower value found in our study may be due in part to the much higher ionic strength employed in our study (1 vs. 0.1 M in the potentiometric study[18]). Forward and reverse rate constants in the analogous EDTA system were estimated roughly from NMR data and are each within an order of magnitude of the values found by us for the present system.

The present technique augments the arsenal of kinetic probes of systems at equilibrium. For the present Eu(III) examples the rate processes sampled occur on a time scale at or greater than the upper limit of the dynamic NMR range.[1,2] If selective excitation of other lanthanide ion complexes, which have even shorter excited-state lifetimes (e.g., Sm(III) or Dy(III)) proves possible, this method can be extended to the study of even faster processes.

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[17] The equilibrium concentration of LMDA^{2-}, [IMDA^{2-}] = Z, was obtained by solving the following quadratic equation:

$$Z^2K_{eq}A + Z(A + C - K_{eq}\mathrm{B}) - B = 0$$

where $A = ([\mathrm{H}^+]^2 + [\mathrm{H}^+]K_1 + K_1K_2)$ and $B = K_1K_2[\mathrm{H_2IMDA}]_{\mathrm{initl}}$, $C = K_1K_2K_{eq}[\mathrm{Eu(DCTA)}^-]_{\mathrm{initl}}$; K_1 and K_2 are the first and second acid dissociation constants of H$_2$IMDA, respectively.

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