a related Cu^{2+}-catalyzed ester hydrolysis using various nucleophiles[15] suggested that external OH^- attack (eq 10) was the more likely of the mechanisms.

Correlation of CuL^{2+} Complex Stability with Ester Hydrolysis. Overall rates of the Cu(II)-complex-catalyzed hydrolysis of MeGly are dependent upon both the degree of ester coordination (K_X) and the rate of hydrolysis (k_{OH}) of the coordinated ester (see eq 9). As has been noted previously[8] the degree of ester coordination (K_X) depends upon the coordinating ability of the ligand L on the Cu(II). It was found that ester coordination (i.e., K_X) decreases as the coordination of L (i.e., K_l) increases. This trend can be seen in Table II (columns 3 and 4) which includes results reported earlier[8] as well as those reported herein. From these data, it is clear that CuL^{2+} complexes with the most strongly coordinating L ligands bind the amino acid ester substrate most weakly. This trend is reasonable if one considers that the most strongly binding L groups will most effectively neutralize the Lewis acid character of the Cu(II) making it a less effective Lewis acid toward the ester.

The second step (k_{OH}) in the overall hydrolysis (eq 9) is the rate-determining hydrolysis of the coordinated amino acid ester. Although the mechanism for this step could be one or more of those given in eq 10, 11, or 12, it will be assumed that mechanism 10 is the primary route for the purpose of this discussion. It should be noted, however, that the observed trends can be rationalized in terms of mechanisms 11 and 12 also.

In mechanism 10, the rate of hydrolysis depends on the extent of chelation by the ester group as well as on the subsequent rate of attack of OH^- on the ester carbonyl carbon center. The OH^- attack step, and possibly the rapid equilibrium chelation step, will be favored by CuL^{2+} complexes of high Lewis acidity. As described above, a measure of the Lewis acidity of the CuL^{2+} complexes is K_X. Therefore the rate of the second step (k_{OH}) of eq 9 should decrease as K_X decreases. This trend can be seen in Table II.

Since the Lewis acidities (K_X) of the CuL^{2+} complexes decrease as the formation constant (K_L) for CuL^{2+} increases, k_{OH} should decrease as K_L increases; this trend can be seen in Table II. Since the trend includes data for the two additional complexes, $Cu(terpy)^{2+}$ and $Cu(tren)^{2+}$, reported in this paper, it is evident that the rigidity of the terpy ligand has no major effect on the catalytic activity of its complex.

In summary, it should be noted that the new data reported here follow trends that were observed previously[8] for CuL^{2+} complexes. They indicate that the catalytic activities of the CuL^{2+} complexes in the hydrolysis of amino acid esters depend upon the strength of the binding of L to Cu^{2+}—the more strongly binding the L ligand, the less catalytic the CuL^{2+} complex.

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Registry No. MeGly, 616-34-2; tren, 4097-89-6; terpy, 1148-79-4; IMDA, 28528-43-0; Cu, 7440-50-8.

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Contribution from the Laser Physics Branch,
Naval Research Laboratory, Washington, D.C. 20375

Complex Formation in Dilute Aqueous Solutions of Europium Perchlorate Detected through Fluorescence Lifetime Measurements

J. F. Giuliani and T. Donohue*

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The interaction between lanthanide ions (Ln^{3+}) and simple inorganic anions in aqueous solution is generally weak and difficult to quantify.[1] Absorption spectrophotometry is a method commonly used for this purpose, but it has several major disadvantages.[1-3] Of the transitions that exhibit some sensitivity to the environment of Ln^{3+}, charge-transfer and f–d transitions lie at energies too close to or higher than the water cutoff (except cerium(III) complexes and europium(III) complexed by sulfate or thiocyanate).[4] Furthermore, only a few lanthanides have f–f transitions in the near-UV to near-IR spectral regions that are hypersensitive.[5] Europium has a convenient hypersensitive transition at 465 nm, but it is very weak ($\epsilon \sim 0.05\ M^{-1}\ cm^{-1}$) and thus is of limited use in studies at concentrations much less than 0.1 M. Fortunately, Eu^{3+} fluoresces strongly from the $^5D_0$ level to several states within the ground state (^7F) multiplet ($\lambda \sim 600$ nm),[6,7] and changes in the local environment influence relaxation rates by interactions too small to be observable spectroscopically.[8] Thus the local environment can be probed with high sensitivity by an examination of the fluorescence decay characteristics of the aqueous Ln^{3+} solution.

Chelation has been demonstrated to cause dramatic changes in fluorescence lifetimes,[8-10] and in addition, small changes in Eu(III) lifetimes have been observed while varying nitrate concentrations in H_2O and D_2O and were ascribed to complex formation,[11] but calculation of a formation constant was not possible due to the limited range of concentrations used. The same authors saw no change in lifetime upon variations of perchlorate concentrations.

In this note, we show that substantial changes in the lifetime of Eu^{3+} ($^5D_0$) fluorescence can be observed when perchlorate concentration is varied at levels significantly lower than those used in previous work. This effect is hypothesized to be due to a weakly bound complex, and a formation constant (K) for this species is estimated.

Experimental Section

Two sets of solutions were examined containing Eu^{3+} at various concentrations. In the first, Eu^{3+} was dissolved directly as the perchlorate salt, so that $[ClO_4^-] = 3[Eu^{3+}]$. In the second set, excess $NaClO_4$ was added so that $[ClO_4^-] \equiv 0.50$ M. Samples were placed in 1-cm Suprasil fluorescence cells and excited by a pulsed nitrogen pumped dye laser, using the dye α-NPO dissolved in cyclohexane.[12] The dye laser output was grating tuned to the $^7F_0$–$^5L_6$ transition at 393.7 nm. Laser energy was about 100 μJ and pulse length 10 ns. Fluorescence was detected at right angles to the pump beam with a photomultiplier through a cutoff filter, which rejected wavelengths less than 500 nm. No fluorescence was detectable from the $^5D_1$ level. Quantum yields were not measured here but have been observed by

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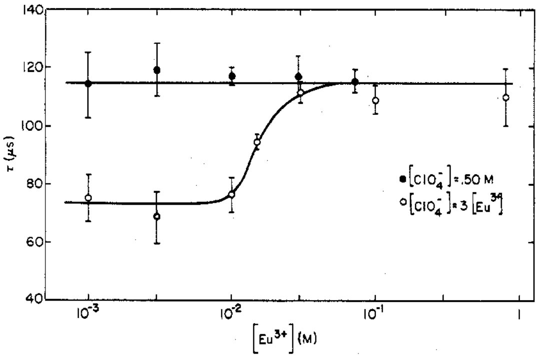

Figure 1. Fluorescent lifetimes (τ) of Eu^{3+} ($^5D_0$) at various concentrations. Error bars give single standard deviation limits. Points are joined by smooth curves for clarity.

others[11] to be about 0.6% under similar conditions. Signals were displayed on an oscilloscope and photographed for subsequent analysis.

Results and Discussion

Fluorescence decays were found to be first order, such that $I(t) = I(t = 0) \exp(-t/\tau)$. $I(t = 0)$ was linear in $[Eu^{3+}]$ for concentrations less than 0.03 M and independent of $[ClO_4^-]$. Experimental results are summarized in Figure 1. Each point represents an average of 4–8 runs. It is immediately evident that the observed lifetimes (τ) fall into two regions. Long lifetimes, 110–120 μs, are found for all solutions where $[ClO_4^-] \geq 0.09$ M and shorter τ's, of 70–75 μs, for solutions where $[ClO_4^-] < 0.03$ M.

These results can be explained in terms of two distinct fluorescing species in solution which are in equilibrium:

$$Eu^{3+}(H_2O)_n + ClO_4^- \overset{K}{\rightleftharpoons} EuClO_4^{2+}(H_2O)_m \tag{1}$$

The shorter lifetime (τ_1) arises from the peraquo species and the longer (τ_2) from a europium perchlorate ion pair. The data do not permit us to invoke a more detailed mechanism involving various intermediate hydrated species[13] or specify whether the complex is inner or outer sphere in character.[14–16] The rate at which the equilibrium between the two species is established is very likely much more rapid than τ,[11,13] so an expression for intermediate lifetimes can be derived[11] as in

$$\tau = \frac{k_1 + K[ClO_4^-]k_2}{1 + K[ClO_4^-]} \tag{2}$$

where $k_i = 1/\tau_i$. At the average value of τ, $\bar{\tau} = {}^1/_2(\tau_1 + \tau_2)$, $[Eu^{3+}(H_2O)_n] = [EuClO_4^{2+}(H_2O)_m]$ and $K = [ClO_4^-]^{-1}$. Thus K can be calculated at this particular concentration and is found to be approximately 24 M^{-1} in our experiments.[17]

Since formation constants for other ion-pair complexes (chloride,[18] bromide,[18] and nitrate[14]) of Eu(III) are about the same as those for Ce(III), this value for K can be compared with an earlier one determined for $CeClO_4^{2+}$ by Heidt and Berestecki,[19] using changes in absorption spectra. Using their values for K as a function of ionic strength and temperature, under our conditions at $\tau = \bar{\tau}$, a value of 25 M^{-1} is obtained. While it should be emphasized that the comparison between equilibrium constants determined by the two different methods is valid only at one concentration, the agreement is excellent and gives independent verification of complex formation in very dilute aqueous solution.

Comparison of the lifetimes reported herein with ones determined in earlier work allows some interesting conclusions to be made. Virtually all lifetimes measured for Eu^{3+} in aqueous solution have been around 110–120 μs,[7,11,21,22] as found for τ_2, but no previous work has attempted lifetime measurements at Eu^{3+} concentrations less than 0.04 M. Apparently in all cases, the accompanying anion must complex or associate with Eu^{3+} to a large enough extent to form a species with a lifetime of 110–120 μs. Only in extreme dilute solution does the peraquo species predominate. The situation is even more extreme when anions other than perchlorate are involved, since perchlorate is generally accepted as displaying the weakest complexing powers of common inorganic anions.[3,11] The implication is that when other anions, such as Cl^- or NO_3^- are involved, concentrations much less than 0.01 M would be necessary to remove any effect of ion-pairing in lifetime measurements.

There is other evidence for short lifetimes in very dilute nonaqueous europium solutions. Halverson and co-workers measured lifetimes of many Eu(III) complexes in methanol,[8] and in a few instances, they found lifetimes in the 65–70-μs range, similar to our τ_1. Their concentrations were $\leq 10^{-3}$ M and they explained their short τ's as due to complete dissociation of the complexes, thus allowing the unprotected Eu^{3+} to be quenched by the solvent. The situation appears to be similar in aqueous solution, assuming that the –OH groups in methanol and water are similarly effective at quenching electronically excited Eu^{3+}.

The difference in lifetimes between the two types of complexes must be due to a change in coordination number or strength of interaction by the molecules surrounding the lanthanide ion. Previous studies on perchlorate complexing cerium(III)[19] and americium(III)[3] (similar to Eu^{3+}) indicate that the interactions should be the outer-sphere type, where some disruption of the hydration sphere is expected.[14] This effect is apparently sufficient to change the environment of Eu^{3+} to a great enough extent to affect the lifetime.

In conclusion, our results clearly demonstrate that ion-pair formation is significant at concentrations much lower than have previously been assumed. For this reason, the method of fluorescence lifetime determination appears to have several advantages over conventional techniques used for detection of complex formation. Besides being relatively easy, concentrations much lower than are possible with other spectral techniques can be used. The type of species present and their nature (e.g., inner or outer sphere) cannot be determined directly, but formation constants can be estimated with reasonable accuracy.

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