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Europium(III) Luminescence Excitation Spectroscopy. Inner-Sphere Complexation of Europium(III) by Chloride, Thiocyanate, and Nitrate Ions

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Luminescence excitation spectroscopy of the $^7F_0 \rightarrow {}^5D_0$ transition of europium(III) using a pulsed dye laser light source is shown to provide a direct measure of inner-sphere complexation of the Eu(III) ion by thiocyanate, chloride, and nitrate ions in aqueous solution. Formation constants, K_1, for the SCN^-, Cl^-, and NO_3^- mono complexes determined from the excitation spectra (5.96 ± 2.38, 0.13 ± 0.01, and 1.41 ± 0.2 M^{-1}, respectively) are in good agreement with those determined by indirect methods. In the case of the Eu(III)/SCN^- system the charge-transfer band at 292 nm is also used to quantitate inner-sphere complexation, with results ($K_1 = 5.43 \pm 2.17$ M^{-1}) in good agreement with the excitation spectrum method. Excited-state lifetime measurements on the Eu(III)/NO_3^- system in H_2O and D_2O solutions suggest that 6.8 ± 0.4 water molecules coordinate to the Eu(III) ion in the mono(nitrato) complex. No evidence for inner-sphere complex formation in the case of the perchlorate ion solutions is apparent, although lifetime changes suggest a possible effect on the equilibria between aqua ion species at high ClO_4^- concentrations.

Introduction

Luminescence excitation spectroscopy of the $^7F_0 \rightarrow {}^5D_0$ transition in Eu(III) using a pulsed dye laser light source is proving to be valuable in characterizing Eu(III) ion environments, particularly in biomolecular systems.[1,2] The dye laser is scanned continuously through the transition region (577-581 nm) while photons emitted from the relatively intense $^5D_0 \rightarrow {}^7F_2$ transition (~612 nm) are monitored. Since the absorptive transition is between nondegenerate levels, the observation of more than one peak in an excitation spectrum implies the presence of more than one Eu(III) environment. In addition, the lifetime, τ, of the $^5D_0$ excited state is environmentally sensitive, and the number of water molecules coordinated to Eu(III) can be determined from the measurement of τ values separately in H_2O and D_2O solutions.[2,3]

The present research applies these techniques to a more classical area of coordination chemistry, namely, the detection of anion binding to Eu(III) ions in aqueous solution and its quantitation in terms of stability constants. While there are numerous reports of the measurement of anion complexation to the Eu(III) ion and other tripositive lanthanide ions (symbolically, Ln(III)), virtually all of the stability constants were obtained by indirect, nonspectroscopic methods such as ion exchange and solvent extraction. These indirect techniques are unable to distinguish between inner-sphere and outer-sphere (solvent-separated ion pair) complexation, and there has been considerable speculation regarding the nature of the complexes formed. For instance, the chloride, nitrate, and thiocyanate ions are thought by some[4,5] to form predominantly outer-sphere complexes in aqueous solution although inner-sphere coordination of the nitrate ion has been suggested by others.[6-9] Since the Eu(III) excitation spectroscopic technique developed in this laboratory directly probes the first coordination sphere of this ion, we can straightforwardly address the question of inner- vs. outer-sphere complexation by anions and other ligands. Our study reveals that, in aqueous solution, chloride, nitrate, and thiocyanate ions form inner-sphere complexes with the Eu(III) ion, while the perchlorate ion does not.

Experimental Section

Luminescence measurements were made with a pulsed nitrogen laser-pumped dye laser apparatus described elsewhere.[2,11] The excitation spectra were recorded in a ratio mode with use of a beam splitter to divert a portion of the laser beam to a photodiode in order to correct for random fluctuation in the laser-beam intensity.

Excitation spectra were recorded at room temperature (22 ± 1 °C) on solutions prepared from doubly distilled deionized water approximately 10^{-2} M in $Eu(ClO_4)_3$ containing various concentrations of NaCl, $NaNO_3$, NaSCN, or $NaClO_4$. Constant ionic strengths of 0.1, 0.5, and 5.0 were maintained by using $NaClO_4$ for the SCN^-, NO_3^-, and Cl^- series of experiments, respectively.

Absorption spectra of the SCN^--containing solutions were recorded on a Cary 118 double-beam spectrophotometer with a solution of 10^{-2} M $Eu(ClO_4)_3$ in the reference beam for quantitation of the charge-transfer band.

Luminescence-decay lifetimes were signal averaged and were recorded on magnetic tape and analyzed with the aid of an interactive computer graphics program on a MODCOMP II computer. All observed luminescence decays are single exponentials.

Determination of Formation Constants, K_1. The relative intensities of the peaks in the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III) in the presence of the various anions were used to monitor inner-sphere complex formation and to evaluate the formation constant, K_1, for the equilibrium

$$Eu(H_2O)_x^{3+} + L^- \overset{K_1}{\rightleftharpoons} EuL(H_2O)_y^{2+} \qquad (1)$$

Treating the peak intensity, I, as directly proportional to the amount of complex in solution

$$kI = [EuL(H_2O)_y^{2+}] \qquad (2)$$

where k is the proportionality constant, we obtain

$$K_1 = \frac{kI}{([L^-]_i - kI)([Eu^{3+}]_i - kI)} \qquad (3)$$

which, upon rearrangement, gives

$$I = \frac{K_1[Eu^{3+}]_i + K_1[L^-]_i + 1 - Q^{1/2}}{2kK_1} \qquad (4)$$

where

$$Q = K_1(K_1[Eu^{3+}]_i^2 + 2[Eu^{3+}]_i + K_1[L^-]_i^2 + 2[L^-]_i - 2K_1[L^-]_i[Eu^{3+}]_i + 1) \qquad (5)$$

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Table I. Relative $^7F_0 \rightarrow {}^5D_0$ Excitation Peak Intensities, *I*, of Eu(III) (~10^{-2} M) as a Function of SCN^-, Cl^-, and NO_3^- Concentrations

ligand, L	[L], M	[$NaClO_4$], M	*I*
SCN^- [a]	0.000	0.100	0.0
	0.010	0.090	22.8
	0.015	0.085	33.7
	0.020	0.080	42.0
	0.025	0.075	51.0
	0.030	0.070	62.0
Cl^- [b]	0.00	5.00	12.4
	1.00	4.00	43.5
	1.50	3.50	58.2
	2.00	3.00	67.8
	2.50	2.50	80.0
	3.00	2.00	86.5
	3.50	1.50	96.2
	4.00	1.00	103.7
	4.50	0.50	112.0
	5.00	0.00	119.5
NO_3^- [a]	0.000	0.500	3.3
	0.025	0.475	11.8
	0.050	0.450	30.7
	0.075	0.425	48.0
	0.100	0.400	66.0
	0.125	0.375	85.5
	0.150	0.350	93.0
	0.200	0.300	116.0

[a] $\lambda_{exc} = 579.06$ nm. [b] $\lambda_{exc} = 579.04$ nm.

Table II. Stability Constants of $EuL(H_2O)_x^{2+}$ Complexes

ligand	K_1, M^{-1}	*T*, °C	μ [a]	ref
SCN^-	5.431 ± 2.174 [b]	22	0.1	this work
	5.955 ± 2.380 [c]	22	0.1	this work
	5.05 ± 0.72	25	1.01	12
Cl^-	0.13 ± 0.01 [c]	22	5.0	this work
	0.80 ± 0.12	25	1.00	15
	0.80 ± 0.05	26	1.00	14
	0.95 ± 0.15	20	1.00	16
	0.71 ± 0.10	25	4.00	17
	1.02 ± 0.04	30	1.00	18
NO_3^-	1.59 ± 0.72 [c]	22	0.50	this work
	1.41 ± 0.20 [c,d]	22	0.50	this work
	2.73 ± 0.15	25	0.50	13
	1.40 ± 0.15	26	1.0	14
	0.30 ± 0.10	25	0.6	9
	1.85 ± 1.05	30	1.0	18
	2.00 ± 1.30	22	1.0	19

[a] Ionic strength. [b] From charge-transfer absorption band measurements. [c] From $^7F_0 \rightarrow {}^5D_0$ excitation spectra. [d] Value obtained by using NaCl to maintain constant ionic strength instead of $NaClO_4$. Cl^- binding should be negligible at concentrations used (<0.5 M).

Table III. Absorption at 292 nm of the Eu(III)-SCN^- Complex as a Function of [NaSCN] [a]

[NaSCN], M	[$NaClO_4$], M	abs [b]	[NaSCN], M	[$NaClO_4$], M	abs [b]
0.000	0.100	0.000	0.020	0.080	0.034
0.005	0.095	0.010	0.025	0.075	0.042
0.010	0.090	0.019	0.030	0.070	0.051
0.015	0.085	0.027			

[a] [$Eu(ClO_4)_3$] = 0.01 M. [b] Relative to a reference cell containing 0.01 M $Eu(ClO_4)_3$.

Table IV. Excited-State Reciprocal Lifetimes, τ^{-1}, of Eu(III) (10^{-2} M) as a Function of NO_3^- and ClO_4^- Ion Concentrations

anion, A	[A], M	[$NaClO_4$], M	$\tau_{H_2O}^{-1}$, ms^{-1}	$\tau_{D_2O}^{-1}$, ms^{-1}	$\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}$, ms^{-1}
NO_3^- [a]	0.000	0.500	9.09	0.31	8.78
	0.025	0.475	9.08	0.30	8.78
	0.050	0.450	8.97	0.31	8.66
	0.100	0.400	8.89	0.29	8.60
	0.125	0.375	8.83	0.29	8.54
	0.150	0.350	8.72	0.30	8.42
	0.175	0.325	8.73	0.31	8.42
	0.200	0.300	8.70	0.30	8.40
ClO_4^- [b]	4.00		10.06	0.34	9.72
	3.00		9.60	0.32	9.27
	2.00		9.17	0.30	8.88
	1.00		9.16	0.28	8.87
	0.50		9.22	0.28	8.94
	0.03		9.09	0.28	8.81

[a] $\lambda_{exc} = 579.06$ nm. [b] $\lambda_{exc} = 578.8$ nm.

and where i denotes the initial concentration. K_1 and *k* were treated as adjustable parameters in a statistical nonlinear regression analysis. In the case of the Cl^- complexes the peak for the $EuCl(H_2O)_x^{2+}$ species was not far enough removed from that of the aqua ion to neglect the contribution from the latter, so an additional parameter, *k'*, was added in the regression analysis (eq 6).

$$I = k[EuCl(H_2O)_y^{2+}] + k'[Eu(H_2O)_x^{3+}] \qquad (6)$$

In the case of the SCN^- system a similar procedure, based on the intensity of the charge-transfer absorption band at 292 nm, was used to determine the formation constant.

Results

Figure 1 shows $^7F_0 \rightarrow {}^5D_0$ excitation spectra obtained for 10^{-2} M Eu(III) ion alone and in the presence of the indicated concentrations of added anions. Figure 2 shows the effect of increasing concentration of the NO_3^- ion on the $^7F_0 \rightarrow {}^5D_0$ excitation peak. The shoulder growing in at ~579.35 nm is attributed to the formation of $Eu(NO_3)_2(H_2O)_z^+$ at higher NO_3^- ion concentrations (>0.2 M). Table I gives the relative intensities (arbitrary scales) of the $^7F_0 \rightarrow {}^5D_0$ excitation peaks as a function of solution composition for the NO_3^-, Cl^-, and SCN^- systems. These data were used to evaluate the stability constants, K_1, for the 1:1 complexes, which are listed in Table II along with literature[9,12-19] values for these quantities.

Figure 3 shows the absorption spectrum of Eu(III) (10^{-2} M) in the presence of SCN^- (1.5×10^{-2} M), the principal broad feature being the charge-transfer band maximizing at 292 nm. Absorbance values at 292 nm used for the evaluation of the formation constant of the 1:1 Eu(III):SCN^- complex are given in Table III. The equilibrium constant evaluated from the absorption spectral data is $K_1 = 5.43 \pm 2.17\ M^{-1}$. The data used in this calculation were limited to SCN^- concentrations ≤0.03 M. This was done in order to avoid complications from the formation of the 1:2 Eu(III):SCN^- complex.

The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of Eu(III) showed no change in position, shape, or intensity as the ClO_4^- ion concentration was increased up to 6 M with $NaClO_4$ (Figure 1). The relative intensities of the two major bands in the $^7F_0 \rightarrow {}^5D_1$ excitation spectrum (Figure 4) change slightly over this ClO_4^- concentration range in accord with reported changes in the absorption spectrum.[20]

Table IV lists the $^5D_0$ excited-state reciprocal lifetimes, τ^{-1}, of Eu(III) in the presence of various concentrations of added

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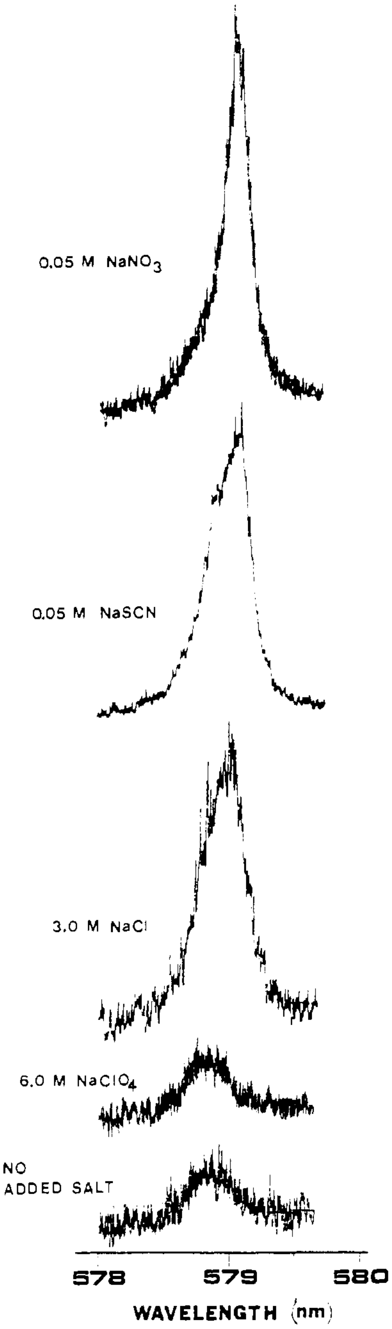

Figure 1. $^7F_0 \rightarrow {}^5D_0$ excitation spectra of $Eu(ClO_4)_3$ (~10^{-2} M) in the presence of several different salts. The $NaNO_3$ and NaSCN spectra have been reduced ~50% and 75%, respectively, relative to the other three spectra.

anions in both H_2O and D_2O solutions.

Discussion

Inner-Sphere Complexation by the Thiocyanate Ion. One of our objectives is to establish a firm experimental criterion by which to distinguish between inner- and outer-sphere complexation since there is considerable confusion in the literature in this regard. For this reason we begin our discussion with a consideration of the interaction of Eu(III) with the SCN^- ion in aqueous solution. In a 1965 solvent extraction study, Choppin and Ketels[12] concluded on the basis of a large negative entropy of formation that Ln(III) ions form outer-sphere complexes with the SCN^- ion, at least at SCN^- ion concentrations less than 1 M. On the other hand, Barnes[21]

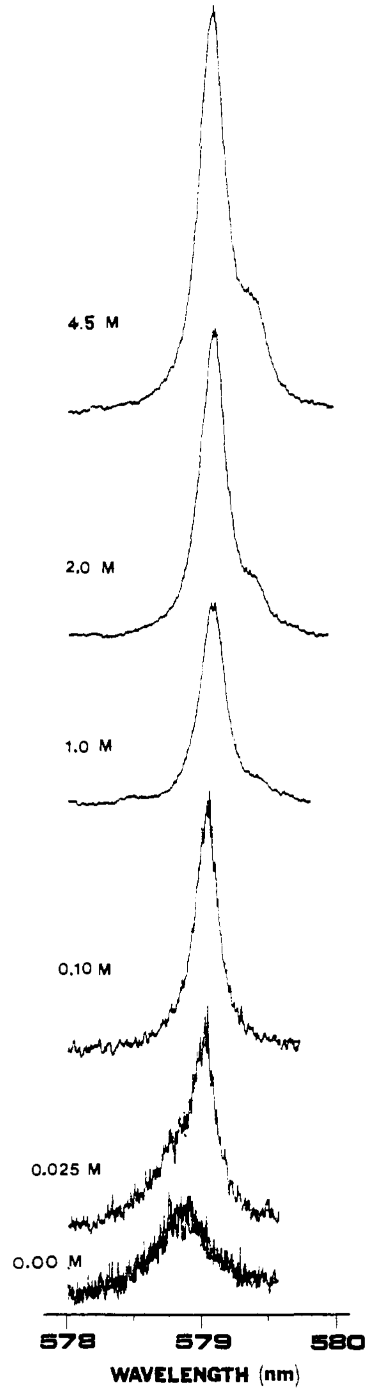

Figure 2. $^7F_0 \rightarrow {}^5D_0$ excitation spectra of $Eu(ClO_4)_3$ (~10^{-2} M) in the presence of varying amounts of $NaNO_3$.

and Barnes and Day[22] noted an excellent linear correlation between the energies of lowest energy charge-transfer bands in a series of Eu(III) complexes of reducing ligands, X^{n-}, including SCN^-, and the analogous transition in $[CoX(NH_3)_5]^{(3-n)+}$. This result implies that SCN^- forms inner-sphere complexes with Eu(III). A similar conclusion was researched by Gruzdev and Ermolaev.[23] By monitoring the absorbance of the charge-transfer band at its 292-nm maximum (Table III), we determined a formation constant, K_1, for Eu(III) with SCN^- of 5.43 ± 2.17 M^{-1}. We used only data for low added SCN^- concentrations (≤0.03 M) in order to minimize complications from the formation of $Eu(SCN)_2$-

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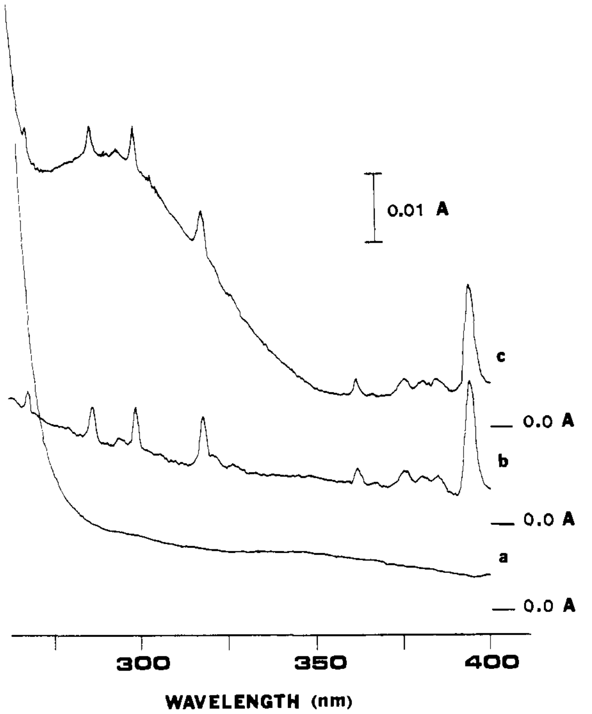

Figure 3. Absorption spectra of (a) 0.03 M NaSCN, (b) 0.01 M $Eu(ClO_4)_3$, and (c) 0.01 M $Eu(ClO_4)_3$ with 0.015 M NaSCN.

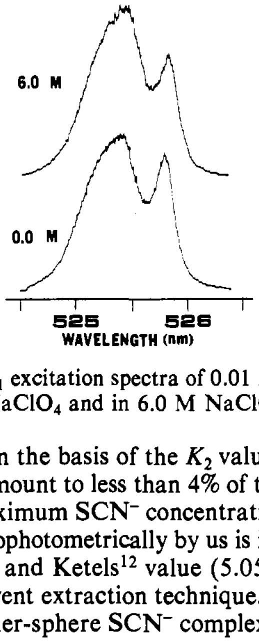

Figure 4. ${}^7F_0 \rightarrow {}^5D_1$ excitation spectra of 0.01 M $Eu(ClO_4)_3$ in the absence of added $NaClO_4$ and in 6.0 M $NaClO_4$.

$(H_2O)_x{}^+$ which, on the basis of the K_2 value of Choppin and Ketels,[12] should amount to less than 4% of the Eu(III)–SCN^- species at this maximum SCN^- concentration. The K_1 value determined spectrophotometrically by us is in good agreement with the Choppin and Ketels[12] value (5.05 ± 0.72 M^{-1}) determined by a solvent extraction technique. This finding implies that only inner-sphere SCN^- complexes of Eu(III) are formed.

Figure 1 shows a comparison of the ${}^7F_0 \rightarrow {}^5D_0$ excitation spectrum of the Eu(III) aqua ion with that obtained from the same concentration of Eu(III) in the presence of 0.05 M SCN^-. The Eu(III) aqua ion exhibits a weak peak centered at 578.8 nm while the much more intense feature due to $Eu(SCN)(H_2O)_x{}^{2+}$ is evident at 579.1 nm. The apparent shoulder to shorter wavelength of the main peak in the SCN^- spectrum is due to residual intensity from the aqua ion. With use of the intensities of the $Eu(SCN)(H_2O)_x{}^{2+}$ excitation peaks (Table I) to monitor complex formation, a value of 5.96 ± 2.38 M^{-1} was obtained for the formation constant, a value in good agreement with that determined by us from absorption spectra and with other values in the literature (Table II). This finding implies that the excitation spectra of SCN^- complexes of Eu(III) provide a direct measure of inner-sphere complex formation. In the case of Eu(III) interacting with SCN^- there is no direct evidence for, nor any need for the postulation of, outer-sphere complex formation. Other reasons must be sought to explain the apparent conflict of these direct spectroscopic results with the thermodynamic parameters based on indirect formation constant measurements.

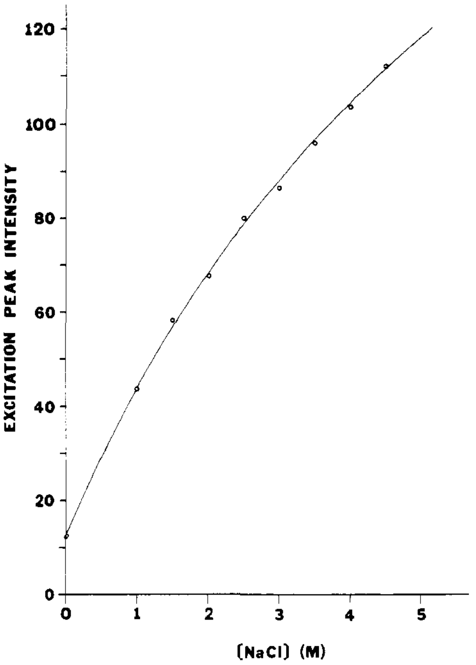

Figure 5. Experimental data (○) superimposed on the calculated theoretical curve (—) for peak intensities of 0.01 M $Eu(ClO_4)_3$ in the presence of varying amounts of NaCl. The nonzero intercept arises from the contribution of the Eu(III) aqua ion.

Inner-Sphere Coordination by the Chloride Ion. Having established that the ${}^7F_0 \rightarrow {}^5D_0$ Eu(III) luminescence excitation spectrum provides a direct and unambiguous measure of inner-sphere complex formation, we turn our attention to other anions. The Cl^- ion has generally been considered to form only outer-sphere complexes with Ln(III) ions, even in very concentrated solutions.[4,5,15,24] Indeed, low-angle X-ray diffraction data[25,26] on a concentrated (3.23 *m*) $EuCl_3$ solution and those of other Ln(III) ions as well have been interpreted to exclude inner-sphere Cl^- complexation. Figure 1 reveals, however, that a solution 0.01 M in Eu(III) and 3 M in NaCl exhibits an excitation peak centered at 579.04 nm, which is distinct from that of the aqua ion and which increases in intensity with increasing Cl^- ion concentration. We attribute this peak to the inner-sphere chloro complex $EuCl(H_2O)_x{}^{2+}$. From the variation in the intensity of this peak with increasing Cl^- ion concentration (Table I), a formation constant K_1 = 0.13 ± 0.01 M^{-1} was obtained. Figure 5 shows the variation of the excitation peak intensity (not corrected for the contribution from the aqua ion) as a function of added NaCl concentration superimposed on the curve calculated from the above formation constant. The value of K_1 obtained by us at very high ionic strength (μ = 5) is close to values reported for this quantity obtained by indirect means (Table II), but is somewhat smaller. This discrepancy may be due to the necessarily high ionic strength employed or, perhaps, to some outer-sphere complexation as well. Nevertheless, our results provide clear evidence for inner-sphere Cl^- complexation with Eu(III). Using our value of K_1, we calculate that one-third of the Eu(III) ions in the 3.23 *m* $EuCl_3$ solution used in the X-ray

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diffraction studies involve inner-sphere complexation by Cl^- ion. A reinterpretation of the X-ray diffraction data on this basis might be enlightening.

Inner-Sphere Complexation by the Nitrate Ion. The uppermost excitation spectrum of Figure 1 shows clear evidence for inner-sphere complexation of Eu(III) by the NO_3^- ion. This again contrasts with the prevailing view[4,5,27] that the NO_3^- ion forms largely outer-sphere complexes with the Ln(III) ions. Bukietynska and Choppin[27] estimate that there is only 2% inner-sphere character for Ln(III) mono(nitrato) species, although other authors at least tacitly assume inner-sphere complex formation with this ligand.[6-9] Taking the intensity of the $Eu(NO_3)(H_2O)_x^{2+}$ excitation peak at 579.06 nm (Table I, Figure 2) as a measure of the concentration of inner-sphere complex, we obtained a formation constant of $K_1 = 1.41 \pm 0.20\ M^{-1}$. This value is in excellent agreement with most of the values found in the literature obtained by indirect (nonspectroscopic) means (Table II). This finding again suggests that is is not necessary to postulate *any* outer-sphere complexation by the NO_3^- ion in order to account for the stability-constant data. In the case of the Eu(III)–NO_3^- system, excitation spectroscopy shows evidence for the formation of a bis(nitrato) complex, $Eu(NO_3)_2(H_2O)_y^+$, at concentrations of added NO_3^- greater than 1 M as shown in Figure 2. The excitation peak due to the bis(nitrato) species occurs on the long-wavelength side of that due to the mono(nitrato) complex, consistent with the previously noted[11] correlation of the energy of the $^7F_0 \rightarrow {}^5D_0$ transition with total charge on the complex. It was not possible to determine the value of K_2 from these data, however.

Eu(III) Lifetimes in the Presence of Nitrate Ion. The measured reciprocal lifetime of Eu(III) in H_2O, $\tau_{H_2O}^{-1}$, decreases from 9.09 ms^{-1} in the absence of added NO_3^- to 8.70 ms^{-1} at 0.2 M NO_3^- (Table IV). In D_2O solution the $\tau_{D_2O}^{-1}$ values are virtually independent to NO_3^- concentration and average 0.30 ms^{-1} (Table IV). Taking into account the fact that both water and NO_3^- ions exchange rapidly[10] with respect to the Eu(III) excited-state lifetime from the bulk solution to the first coordination sphere, it is possible, with a knowledge of K_1, to estimate[28] a $\tau_{H_2O}^{-1}$ value for the $Eu(NO_3)(H_2O)_x^{2+}$ complex of 6.75 ms^{-1}. This result leads, according to eq 7,[2]

$$q = 1.05(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}) \qquad (7)$$

to an estimate of the number of water molecules, q, coordinated to the Eu(III) ion in the mono(nitrato) complex of 6.8 ± 0.4. If the NO_3^- ion coordinates in a bidentate fashion, this result implies a total coordination number of 9 in the mono(nitrato) species, which is quite reasonable.

Interaction of Eu(III) with the Perchlorate Ion. Of the four mononegative ions examined in this study, the ClO_4^- is the least likely to participate in inner-sphere complex formation. Consistent with this expectation is the fact that the $^7F_0 \rightarrow {}^5D_0$ excitation spectrum remains unchanged in the presence of ClO_4^- ion concentrations as high as 6 M (Figure 1). The ClO_4^- is not, however, entirely without effect on the Eu(III) ion. Yatsimirskii and Davidenko[20] have reported an effect of high concentrations of ClO_4^- ion on the Eu(III) absorption spectra in the regions of the $^7F_0 \rightarrow {}^5D_1$ (524–527 nm) and $^7F_0 \rightarrow {}^5D_2$ (464–467 nm) transitions. Figure 4 gives a comparison of the excitation spectra of the former transition of Eu(III) (10^{-2} M) in the absence and in the presence of 6 M $NaClO_4$. A small change in the relative heights of the two principal peaks is the only notable change and is consistent with the absorption spectral results of Yatsimirskii and Davidenko.[20]

The most notable effect on Eu(III) of high concentrations of ClO_4^- is on the τ^{-1} values. Table IV reveals that both $\tau_{H_2O}^{-1}$ and $\tau_{D_2O}^{-1}$ increase with increasing ClO_4^- ion concentration. If ClO_4^- is displacing inner-sphere water molecules, $\tau_{H_2O}^{-1}$ should decrease with increasing ClO_4^- ion concentration. We propose the following explanation for this unusual trend. It is possible for an outer-sphere ClO_4^- interaction to affect $\tau_{H_2O}^{-1}$ by affecting the efficiency of energy transfer to the OH oscillators of water molecules in the first coordination sphere. Hydrogen bonding of ClO_4^- to coordinated water molecules[29] will affect the OH vibrational manifold and thereby the Eu(III) to H_2O energy transfer.[30-38] The significant effect of ClO_4^- ion concentration on $\tau_{D_2O}^{-1}$ must have another explanation since it is known that energy transfer to the OD vibrational manifold is markedly inefficient.[31-38] Changes in structure or in relative amounts of different species present in solution can, however, affect $\tau_{D_2O}^{-1}$ through changes in radiative and nonradiative rate processes. It should be noted (Table IV) that the ($\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}$) values increase from about 8.8 at low ClO_4^- ion concentrations to 9.7 at 4 M ClO_4^-. We offer the following tentative explanation of this observation that is consistent with earlier proposals that the Eu(III) aqua ion exists as an equilibrium mixture of complexes $Eu(H_2O)_n^{3+}$ where $n = 8$ and 9[39] or where $n = 9$ and 10.[3] If such an equilibrium exists, the presence of significant quantities of outer-sphere ClO_4^- ions could affect this equilibrium between aqua ion species such that high ClO_4^- concentrations favor the aqua ion with the higher number of coordinated water molecules. On the basis of Raman data other authors[40] have postulated a concentration-dependent change in the ratio of aqua ion species in the center of the $LnCl_3$ series, although inner-sphere chloro complexation was not considered.

The present experiments represent a generally applicable method for the detection and quantitation of complex formation by Eu(III) with potential applications to other anions, buffer systems, ionophoric ligands, and chelating agents. Studies in these areas are in progress in this laboratory.

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Registry No. Eu, 7440-53-1; SCN^-, 302-04-5; Cl^-, 16887-00-6; NO_3^-, 14797-55-8.

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