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# Spectroscopic Investigation of Europium(III) Nitrato Complexes in Anhydrous and Aqueous Acetonitrile*

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*Electronic absorption and emission spectra, along with lifetime measurements and vibrational spectra, are used to investigate the interaction between nitrate and trivalent europium ions in dilute solutions in anhydrous and aqueous acetonitrile. Upon addition of increasing quantities of nitrate, the complexes* $[Eu(NO_3)_n]^{(3-n)+}$*, with* $n = 1-5$*, form quantitatively in anhydrous acetonitrile. In solution, the pentanitrato species is not further solvated and its spectroscopic properties are similar to those of solid samples, indicating a similar structure with five bidentate nitrates bonded to the 10-coordinate Eu(III) ion. The lifetimes of the* $^5D_0$ *level are 1.35(5) and 1.25(5) ms for* $Eu(NO_3)_3$ *and* $(Me_4N)_2Eu(NO_3)_5$ *0.05* M *in* $CH_3CN$*. The quantum yield of* $Eu(NO_3)_3$ *in* $CH_3CN$ *is 27.4%.*

*The addition of small quantities of water to* $Eu(NO_3)_3$ *solutions does not result in the dissociation of the nitrate ions, provided* $R_w = [H_2O]_t/[Eu^{3+}]_t$ *is smaller than 8; the apparent equilibrium ratios for* $[Eu(NO_3)_3(H_2O)_n]$ *are* $K_3 = 40 \pm 15$ $M^{-1}$ *and* $K_4 = 9 \pm 3$ $M^{-1}$*;* $K_1$ *and* $K_2$ *are too large to be determined. The formation of nitrato complexes is studied in mixtures containing increasing amounts of water and nitrate. Deconvolution of the different components of the* $^5D_0 \rightarrow {}^7F_0$ *transition allows a semi-quantitative estimate of the relative concentration of the nitrato complexes. The total number of coordinated nitrate ions per europium ion can be determined on the basis of fluorescence lifetime measurements. The apparent equilibrium ratios for the formation of the mono- and dinitrato species amount to* $K_1 = 23 \pm 3$, $15 \pm 5$ *and* $5 \pm 1$ *for* $R_w = 44$, $94$ *and* $304$*, respectively, and to* $K_2 = 17 \pm 8$ *for* $R_w = 44$ *and 94.*

## Introduction

Spectrofluorimetric and lifetime measurements have established that the interaction between trivalent europium and nitrate ions leads to the formation of inner-sphere complexes in both water [3–6] and organic solvents [7–10]. In previous papers, we have investigated the solvation of europium nitrate and perchlorate in anhydrous dimethylsulfoxide [9] and dimethylformamide [10], and of europium perchlorate in anhydrous acetonitrile [11]. As part of a systematic investigation of the coordinative properties of trivalent lanthanide ions, both in the solid state [12, 13] and in organic solutions, we present here a study of europium(III) nitrato complexes in anhydrous acetonitrile and in acetonitrile/water mixtures. Emission spectra and lifetimes are measured as a function of the total nitrate concentration; deconvolution of the $^5D_0 \rightarrow {}^7F_0$ transition allows a quantitative estimate of the concentration of the different species in equilibrium. Electronic absorption and vibrational spectra are also reported and discussed.

## Experimental

### *Preparation of the Solutions*

Anhydrous $Eu(NO_3)_3$ [14] and $(Me_4N)_2[Eu(NO_3)_5]$ [12] were prepared as previously described. $(Me_4N)NO_3$ (Merck, p.a.) was dehydrated under vacuum ($10^{-2}$ mmHg/80 °C). $CH_3CN$ (Fluka, puriss) and $CD_3CN$ (Ciba-Geigy, 99.98%) were treated by $CaH_2$ and $P_2O_5$ and distilled twice; they contained less than 0.1 molecule of water per europium ion. Since europium nitrate is hygroscopic, the anhydrous solutions were prepared under a strictly controlled atmosphere of $N_2$, containing less than 5 ppm of water. The Eu-concentration was determined by complexometric titration with EDTA (Titriplex III, Merck) after completion of the measurements.

### *Spectroscopic measurements*

Emission spectra and lifetimes were measured as previously described [5]. Relative intensities of the emission bands were determined by planimetry and manually corrected for the mean instrumental function at the barycentre of the transition. The wavelength accuracy is ±2 Å and the wavelength

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repeatability is ± 0.1 Å. The components of the $^5D_0 \rightarrow {}^7F_0$ transition were resolved by numerical deconvolution using Lorentzian band shapes and a general least-squares procedure. Electronic absorption spectra were recorded with a Perkin-Elmer-Hitachi 340 spectrometer. IR spectra were performed with a Bruker IFS-113c interferometer and Raman spectra were measured with a Ramalog-4 spectrometer from Spex Industries.

## Results and Discussion

### *Anhydrous Solutions in Acetonitrile*

The molar conductivities of 0.0004 and 0.01 *M* solutions of $Eu(NO_3)_3$ in anhydrous $CH_3CN$ are 21 and 15 $\Omega^{-1}$ $mol^{-1}$ $cm^2$ at 25 °C, respectively. These values are clearly in the range for non-electrolytes [15], which means the three nitrate ions remain in the inner coordination sphere of the metal ion upon solvation. This is readily confirmed by vibrational data (Table I) since at least five of the six modes of the coordinated nitrate ion are observed whereas no band from ionic nitrate appears in the FT IR and Raman spectra. Moreover, the polarization of the Raman emission bands (Fig. 1) allows us to conclude that the anions are bidentate, with a $C_{2v}$ local symmetry [16]. The assignment of the vibrational modes made in Table I differs from our previous one [14]: contrary to our original report, the band at 745 $cm^{-1}$, which interferes with the $2\nu_8$ vibration of $CH_3CN$ at 748 $cm^{-1}$ [17], is polarized and has to be assigned to $\nu_3(A_1)$. As often observed [14, 18], the $\nu_6(B_1)$ mode at 815 $cm^{-1}$ is not present in the Raman spectrum so that its polarization could not be measured. Another feature of the Raman spectrum is the splitting of the $\nu_2(A_1)$ band, which points to slightly inequivalent nitrate groups.

TABLE I. Vibrations of the Nitrato Groups [$cm^{-1}$] in Anhydrous Solutions of $Eu(NO_3)_3$ 0.05 *M* (FT IR) and 0.3 *M* (Raman) in Acetonitrile.

| Assignment[a] | IR | Raman[b] |
|---|---|---|
| $\nu_5$ ($B_2$) | – | 710 vw (d)? |
| $\nu_3$ ($A_1$) | 741 m | 745 m[c] (p) |
| $\nu_6$ ($B_1$) | 815 m | – |
| $\nu_2$ ($A_1$) | 1026 m | 1023 s (p) |
|  |  | 1030 s (p) |
| $\nu_4$ ($B_2$) | 1290 s | [c] |
| $\nu_1$ ($A_1$) | 1495 s | 1515 m (p) |
| $2\nu_6$ ($A_1$) | 1647 w | – |
| $\nu_2 + \nu_3$ ($A_1$) | 1768 w | – |

[a] Labels according to $C_{2v}$ local symmetry. [b] (d) = depolarized, (p) = polarized. [c] Masked by a solvent band.

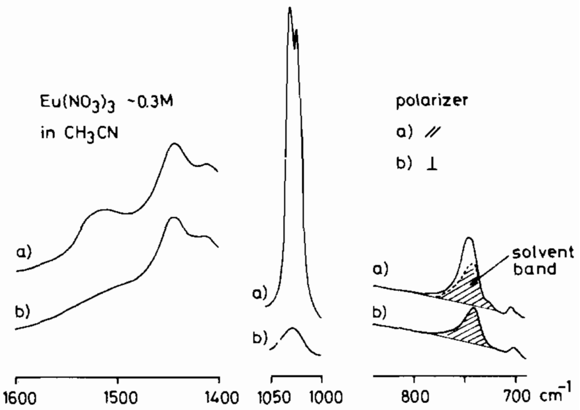

Fig. 1. Raman spectra of $Eu(NO_3)_3$ 0.3 *M* in $CH_3CN$ showing the polarization of the bands.

TABLE II. Absorption Spectra (360–470 nm) of Solutions of Eu(III) 0.05 *M* in Anhydrous $CH_3CN$, *vs.* the Ratio R = $[NO_3^-]_t/[Eu^{3+}]_t$; $\lambda_{max}$ in nm and $\epsilon_{max}$ in l $mol^{-1}$ $cm^{-1}$.

| Assignment | R = 0 |  | 1.05 |  | 3.01 |  | 4.05 |  | 5.0 |  | 5.9 |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | λ | ε | λ | ε | λ | ε | λ | ε | λ | ε | λ | ε |
| $^5D_4 \leftarrow {}^7F_0$ | 361.6 | 0.81 | 361.6 | 0.75 | 361.8 | 0.54 | 361.2 | 0.6 | 361.5 | 0.6 | 361.6 | 0.5 |
| $^5L_8 \leftarrow {}^7F_0$ | 366.5 | [a] | 366.5 | [a] | 366.5 | [a] | 366.5 | [a] | 366.5 | [a] | 366.5 | [a] |
| $^5G_{6,5} \leftarrow {}^7F_0$ | 374.6 | 1.15 | 374.8 | 1.15 | 375.6 | 0.7 | 375.5 | 0.65 | 375.6 | 0.45 | 375.6 | 0.4 |
| $^5L_7 \leftarrow {}^7F_0$ | 380.2 | 0.74 | 380.0 | 0.8 | 379.6 | 0.4 | 381 | 0.5 | 382 | 0.35 | 382 | 0.35 |
| $^5G_6 \leftarrow {}^7F_0$ | – | – | 385.5 | 0.85 | 384 | 0.6 | 384 | 0.55 | 384.8 | 0.4 | 384.8 | 0.35 |
| $^5L_6 \leftarrow {}^7F_0$ | 394.8 | 5.1 | 394.9 | 4.83 | 395.6 | 2.48 | 395.6 | 1.87 | 396.0 | 1.52 | 396 | 1.5 |
|  |  |  |  |  | 399.0 | 0.85 | 398.8 | 1.14 | 399.6 | 0.80 | 399.4 | 0.80 |
| $^5D_2 \leftarrow {}^7F_0$ | 466 | 0.28 | 464.8 | 0.75 | 465.0 | 1.01 | 465.0 | 1.52 | 465.0 | 2.82 | 465.0 | 2.7 |

[a] Weak shoulder.

TABLE III. Wavelengths (nm, $^5D_{J'} \rightarrow {}^7F_J$ Transitions) and Relative Intensities ($S_{rel}$, Arbitrary Units) of the Emission Bands of Anhydrous Solutions of $Eu(NO_3)_3$ and $(Me_4N)_2[Eu(NO_3)_5]$ 0.05 *M* in Acetonitrile (Excitation: 395 nm).

| J' | J | $Eu(NO_3)_3$[a] | | $(Me_4N)_2[Eu(NO_3)_5]$ | |
|---|---|---|---|---|---|
| | | λ | $S_{rel}$ | λ | $S_{rel}$ |
| 2 | 5 | 373.5 | 0.05 | 573.5 | 0.03 |
| 1 | 0 | 526.8 | 0.02 | 527.5 | 0.02 |
| | 1 | 538 | 1.5 | 537.2, 538.2 | 1 |
| | 2 | 557 | 0.5 | 555, 557, 558 | 0.3 |
| | 3 | 587.5 | [b] | 586.5 | [b] |
| | 4 | 626.5 | [b] | 627.8 | [b] |
| | 5 | 670 | 3.9 | 666, 670 | [c] |
| 0 | 0 | 579sh, 580.1 | 9.6 | 580.2 | 1.1 |
| | 1 | 590.2, 590.9,<br>594.5 | 96 | 590.5, 593.2,<br>594.5 | 56 |
| | 2 | 617.2 | 714 | 617.7 | 641 |
| | 3 | 649, 650.5,<br>657 | 20 | 648, 650.5,<br>657 | [b] |
| | 4 | 687, 694, 700 | 19 | 682sh, 685.3,<br>702.5, 708.5 | 57 |
| | 5 | 749 | [d] | 745.5, 749 | [d] |
| | 6 | 815 | [d] | 819.5, 825 | [d] |

[a] The quantum yield of the $^5D_0$ level (upon excitation to the $^5L_6$ level) amounts to 27.4% as measured taking $Eu(NO_3)_3 \cdot 6H_2O$ 0.1 *M* in $CH_3OH$ as standard (Q = 5% [19]). [b] Shoulder. [c] Very weak. [d] Not determined.

TABLE IV. Relative Intensities of the $^5D_0 \rightarrow {}^7F_{0,1,2,4}$ and $^5D_1 \rightarrow {}^7F_{1,2}$ Transitions ($\lambda_{exc}$ = 395 nm) and Fluorescence Lifetimes (ms) of the $^5D_0$ Level ($\lambda_{exc}$ = 591 nm, $\lambda_{anal}$ = 694 nm) of Eu(III) Solutions 0.05 *M* in Acetonitrile Versus R = $[NO_3^-]_t/[Eu^{3+}]_t$.

| R | $100F_0/F_1$[a] | $F_2/F_1$[a] | $F_4/F_2$[a] | $F_1/F_2$[b] | $\tau_f$ |
|---|---|---|---|---|---|
| 0 | 1.0 ± 0.1 | 1.8 ± 0.2 | 1.4 ± 0.1 | 0.90 ± 0.05 | 2.1 ± 0.1 |
| 0.97 | 16.2 ± 0.8 | 4.0 ± 0.2 | 1.4 ± 0.1 | – | 1.7 ± 0.1 |
| 1.05 | 15.3 ± 0.8 | 4.0 ± 0.2 | 1.5 ± 0.1 | 1.7 ± 0.1 | – |
| 1.94 | 13.2 ± 0.7 | 5.6 ± 0.3 | 1.4 ± 0.1 | 2.2 ± 0.1 | 1.47 ± 0.06 |
| 3.0 | 10.0 ± 0.5 | 7.6 ± 0.4 | 1.3 ± 0.1 | 2.7 ± 0.2 | 1.35 ± 0.05 |
| 3.04 | 9.8 ± 0.5 | 7.1 ± 0.4 | 1.3 ± 0.1 | 2.6 ± 0.2 | 1.31 ± 0.05 |
| 3.88 | 4.6 ± 0.2 | 9.8 ± 0.5 | 1.3 ± 0.1 | – | 1.27 ± 0.05 |
| 4.06 | 4.6 ± 0.2 | 10.1 ± 0.5 | 1.2 ± 0.1 | 3.1 ± 0.1 | – |
| 5.0 | 1.9 ± 0.2 | 11.8 ± 0.5 | 1.1 ± 0.1 | 3.6 ± 0.2 | 1.25 ± 0.05 |
| 6.0 | 1.8 ± 0.2 | 12.2 ± 0.5 | 1.1 ± 0.1 | 3.6 ± 0.2 | 1.25 ± 0.05 |

[a] Emission from $^5D_0$. [b] Emission from $^5D_1$.

To study the interaction between the nitrate and the europium ions, we have prepared $Eu(ClO_4)_3$ solutions containing increasing amounts of $(Me_4N)NO_3$. Their spectroscopic properties were monitored as a function of R = $[NO_3^-]_t/[Eu^{3+}]_t$. Both the absorption (Table II) and the emission spectra (Tables III and IV, Fig. 2) undergo significant changes up to R = 5. Further addition of nitrate, the maximum concentration of which is limited by the solubility of $(Me_4N)NO_3$ in acetonitrile, does not modify the spectra. This is especially well demonstrated by the hypersensitive transitions $^5D_2 \leftarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$, the intensities of which increase by a factor of 10 between R = 0 and R = 5. The IR spectra do not show the presence of ionic nitrate for R $\leqslant$ 5, so that we can conclude the quantitative formation of $[Eu(NO_3)_5]^{2-}$. High resolution spectra of the $^5D_0 \rightarrow {}^7F_0$ transition reveal the presence of shoulders for R = 0 to 3 or 4. This was expected, since the starting solution contains two main species, $[EuClO_4(m)(CH_3CN)_8]^{2+}$ (~60%) and $[Eu(CH_3CN)_9]^{3+}ClO_4^-$ (b) (~30%) [9], where m and b stand for mono- and bidentate, respectively. Upon addition of nitrate, the $ClO_4^-(m)$ ion remains in the inner sphere up to R = 4

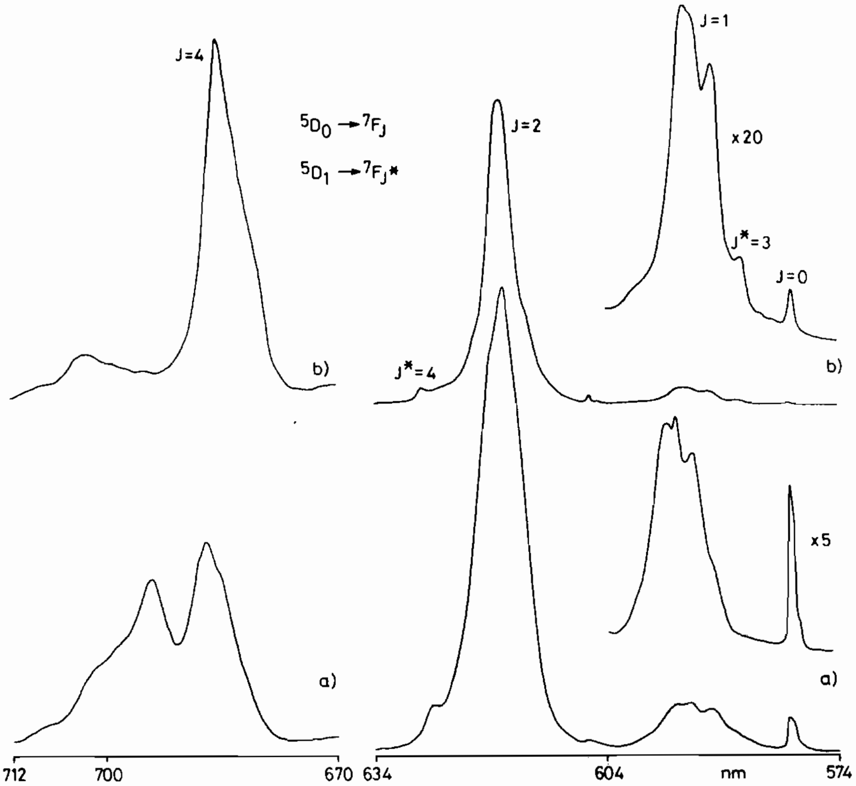

Fig. 2. Part of the emission spectra of $Eu(NO_3)_3$ (a) and $(Me_4N)_2Eu(NO_3)_5$ (b) 0.05 *M* in $CH_3CN$ (excitation: 395 nm).

[20], so that at least two nitrato species are present, $[EuClO_4(m)NO_3]^+_{solv}$ and $[EuNO_3]^{2+}_{solv}$, for instance. A detailed analysis of the transition was not possible, even under very high resolution conditions, because (i) the different components have a width at half height comparable to or larger than the wavelength shifts between them (from 579.8 nm for R = 0 to 580.2 nm for R = 5), and (ii) large intensity differences occur, *i.e.* for R = 0 both components account for 1% with respect to the magnetic dipole allowed transition $^5D_0 \rightarrow {}^7F_1$ [21], whereas the addition of one nitrate ion per Eu(III) ion causes this intensity to increase to 16% (Fig. 3). Information on the nitrato complexes that form for $R < 5$ can therefore not be obtained. It is also interesting to note that the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition increases linearly with R [2], as observed in dimethylformamide [10], despite the presence of different nitrato species, especially for small values of R.

The pentanitrato species does not contain additional solvent molecules in the inner coordination sphere of the metal, which is therefore 10-coordinate. Indeed, the FT IR spectra do not present bands from coordinated $CH_3CN$ molecules when $R \geqslant 5$. Moreover, the fluorescence lifetimes of solutions containing 0.9 molecule $H_2O$ per Eu(III) ion provide additional proof; they amount to 0.66, 0.53, 1.23, and 1.24 ms for R = 3, 4, 5, and 6, respectively.

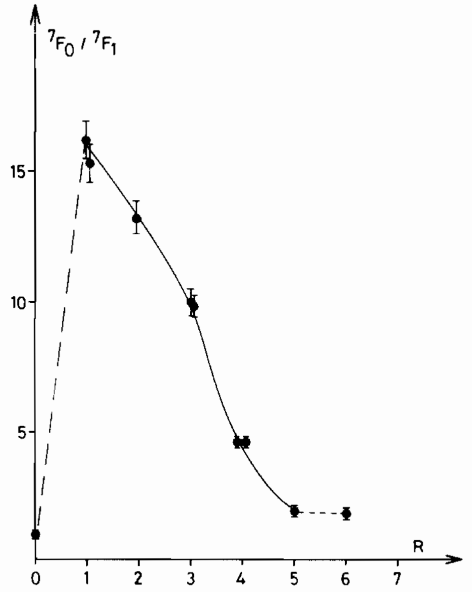

Fig. 3. Variation of the relative integrated and corrected intensity of the $^5D_0 \rightarrow {}^7F_0$ transition as a function of the ratio $[NO_3^-]_t/[Eu^{3+}]_t$.

These two latter values are exactly the same as the lifetimes observed for the corresponding anhydrous solutions, which means that the water molecule is expelled from the inner coordination sphere upon addition of the fifth nitrate. Finally, both the vibrational and the emission spectra of the pentanitrato solutions resemble those reported for the solid samples [12], so that a similar structure [22] is expected.

### *Solutions in Water/Acetonitrile Mixtures*

Water is expected to replace the acetonitrile molecules in the Eu(III) first coordination sphere and, possibly, when the ratio $R_w = [H_2O]_t/[Eu^{3+}]_t$ is large enough, the nitrate ions. The molar conductivity of $Eu(NO_3)_3 \cdot 6H_2O$ 0.0005 and 0.01 *M* in $CH_3CN$ are 26 and 17.5 $\Omega^{-1}$ mol$^{-1}$ cm$^2$ at 25 °C, respectively, which corresponds to non-electrolyte solutions. Moreover, FT IR spectra clearly reflect the absence of ionic nitrate up to $R_w = 18$, which means the three $NO_3^-$ ions remain in the inner coordination sphere. Upon addition of water, both the fluorescence spectra and lifetimes undergo considerable changes (Table V) due to the large quenching effect of the $H_2O$ molecules [23]. The Stern-Völmer plot [1, 24] of the latter is only linear up to $R_w = 2$ (Fig. 4), with a quenching rate constant $k(\tau)$ [1] equal to $25.5 \pm 1.0$ l mol$^{-1}$. The two asymptotic straight lines of the plot intersect at $R_w = 4.0 \pm 0.5$. The curvature of the plot is indicative of the presence of the following equilibria:

$$[Eu(NO_3)_3(CH_3CN)_{m-n+1}(H_2O)_{n-1}] + H_2O \xrightarrow{K_n} [Eu(NO_3)_3(CH_3CN)_{m-n}(H_2O)_n] + CH_3CN$$

$$K_n = \frac{[Eu(NO_3)_3(CH_3CN)_{m-n}(H_2O)_n]}{[Eu(NO_3)_3(CH_3CN)_{m-n+1}(H_2O)_{n-1}]\,[H_2O]} = \frac{X_n}{X_{n-1} \cdot [H_2O]}$$

The first two apparent equilibrium ratios, $K_1$ and $K_2$, are large and cannot be estimated from our data whereas $K_3$ and $K_4$ can be calculated as follows. When $X_n = X_{n-1}$, $K_n = 1/[H_2O]$, the lifetime will be equal to the average lifetime of the species with n = n − 1 and n = n. These latter can be obtained from extrapolation of the straight line between $R_w = 0$ and 2 (dotted line in Fig. 4) so that $[H_2O]$ can be easily calculated. We find $K_3 = 40 \pm 15$ *M*$^{-1}$ and $K_4 = 9 \pm 3$ *M*$^{-1}$. A similar procedure was used by Gruzdev and Ermolaev [8], who investigated the formation of hydrates in $Eu(NO_3)_3$ solutions in acetone and who report the following apparent equilibrium ratios: $K_1 = (1.3 \pm 0.2) \cdot 10^3$ *M*$^{-1}$, $K_2 = 44 \pm 5$ *M*$^{-1}$, $K_3 = 7.9 \pm 1.3$ *M*$^{-1}$, and $K_4 = 1.3 \pm 0.2$ *M*$^{-1}$. The larger formation constants found in acetonitrile reflect the smaller donor number of this solvent, 14.1, as compared to 17.0 for acetone.

TABLE V. Relative Intensities of the $^5D_0 \rightarrow {}^7F_{0,1,2}$ and $^5D_1 \rightarrow {}^7F_{1,2}$ Transitions ($\lambda_{exc}$ = 395 nm) and Fluorescence Lifetimes (ms) of the $^5D_0$ Level ($\lambda_{exc}$ = 593 nm, $\lambda_{anal}$ = 694 (nm) for $Eu(NO_3)_3$ Solutions 0.05 *M* in $CH_3CN$ *versus* $R_w = [H_2O]_t/[Eu^{3+}]_t$.

| $R_w$ | $F_0/F_1$ [a] | $F_2/F_1$ [a] | $F_1/F_2$ [b] | $\tau_f$ |
|---|---|---|---|---|
| 0 | 0.10 | 7.6 | 2.7 | $1.35 \pm 0.05$ |
| 0.6 | c | c | c | $0.73 \pm 0.03$ |
| 1.1 | c | c | c | $0.57 \pm 0.02$ |
| 6.1 | 0.05 | 6.6[d] | 2.4 | $0.26 \pm 0.01$ |
| 8.0 | 0.05 | 6.4 | 2.4 | c |
| 20 | 0.06 | 6.1 | c | c |
| 31 | 0.06 | 5.7 | c | $0.23 \pm 0.01$ |
| 55 | c | c | c | $0.20 \pm 0.01$ |

[a] Emission from $^5D_0$. [b] Emission from $^5D_1$. [c] Not measured. [d] This value remains constant for $0.01 \leq [Eu^{3+}]_t \leq 0.2$ *M*.

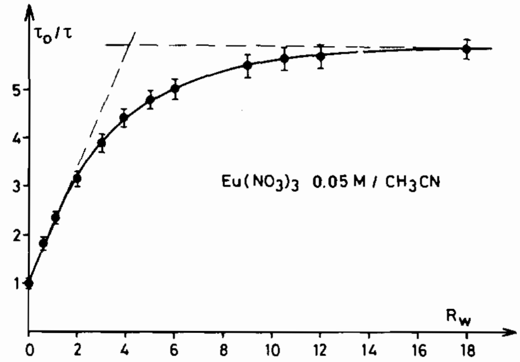

Fig. 4. Stern–Völmer plot for $Eu(NO_3)_3$ 0.05 *M* in $CH_3CN$, *vs.* $R_w = [H_2O]_t/[Eu^{3+}]_t$.

The formation of the 10-coordinate species $[Eu(NO_3)_3(H_2O)_4]$ in both acetone and acetonitrile is consistent with X-ray crystal structure determinations of $Ln(NO_3)_3 \cdot 6H_2O$. For Ln = La [25] and Ce [26], the metal ion is 11-coordinate, with five water molecules bonded in the inner coordination sphere; for Ln = Pr–Sm, the hexahydrates are isostructural [27] and four water molecules are bonded to the 10-coordinate metal ion. A similar experiment with $Tb(NO_3)_3$ [1] led to the conclusion that the main species formed under comparable conditions is probably $[Tb(NO_3)_3(H_2O)_3]$. Although not unexpected since both ions belong to this part of the lanthanide series where a change in coordination number often occurs, for instance in water [28], these results have to be interpreted with care; the determination of the number of bonded water molecules by the above technique is subject to a large uncertainty (±0.5) and, moreover, in the terbium study the hypothesis on which Stern–Völmer plots are based may not have been valid [1].

TABLE VI. Relative Intensities after Deconvolution (in % of Total Area, ±5) of the $^5D_0 \rightarrow {}^7F_0$ Components; $Eu(ClO_4)_3$ Solutions 0.047 *M* in Acetonitrile Containing Various Amounts of Nitrate and Water. Solvent Molecules are Omitted in the Formula; $R = [NO_3^-]_t/[Eu^{3+}]_t$, $R_w = [H_2O]_t/[Eu^{3+}]_t$; n stands for 3, 4, and 5.

| $R_w$ | R | $[Eu(NO_3)]^{2+}$ $\lambda_{max} = 579.49$ nm | $[Eu(NO_3)_2]^+$ $\lambda_{max} = 579.79$ nm | $[Eu(NO_3)_n]^{(3-n)+}$ $\lambda_{max} = 580.09$ nm |
|---|---|---|---|---|
| 8 | 1.0 | 88 | 12 | – |
| | 1.5 | 61 | 39 | – |
| | 1.75 | 47 | 53 | – |
| | 2.0 | 38 | 62 | a |
| | 2.25 | 29 | 59 | 12 |
| | 2.5 | 18 | 68 | 14 |
| | 3.0 | 10 | 64 | 32 |
| 44 | 0.5 | 100 | a | – |
| | 1.0 | 81 | 19 | – |
| | 1.5 | 63 | 37 | a |
| | 2.0 | 37 | 59 | 4 |
| | 3.0 | 16 | 60 | 23 |
| | 4.0 | 8 | 62 | 30 |
| 94 | 0.5 | 100 | a | – |
| | 1.0 | 83 | 17 | – |
| | 1.5 | 62 | 38 | – |
| | 2.0 | 44 | 56 | a |
| | 3.0 | 31 | 61 | 8 |
| | 4.0 | 28 | 60 | 13 |
| 304 | b | 100 | – | – |

[a] Too weak to be included in the deconvolution. [b] $0.5 \leqslant R \leqslant 5$, only one component is observed.

In another series of experiments, the formation of the nitrato species $[Eu(NO_3)_n(H_2O)_m]^{(3-n)+}$ upon addition of nitrate to $Eu(ClO_4)_3 \cdot 8H_2O$ solutions 0.047 *M* in acetonitrile* was followed by monitoring the changes in the $^5D_0 \rightarrow {}^7F_0$ emission band (Table VI) and the fluorescence lifetimes (Table VII). The component which appears at 579.49 nm is assigned to the mononitrato complex. For $R \geqslant 1$, a second component is present, the relative intensity of which reaches a maximum for R = 2.5; it corresponds to the dinitrato complex which therefore forms simultaneously to the mononitrato species, as observed in dimethylformamide solutions [10]. The component assigned to the trinitrato species appears for $R \geqslant 2.25$. According to the vibrational data, no ionic nitrate is present in these solutions, so that the ratio of the partial quantum yields of the mono- and dinitrato complexes can be calculated from the data for $R \leqslant 1.5$; it amounts to 1.65. Using these data to calculate the average number of coordinated nitrate ions per europium ion, $\bar{n}$, one finds 1.75 and 1.95 for R = 1.75 and 2.0 respectively, which demonstrates the consistency of the data. The estimation of $\bar{n}$ with this method is, however, limited since upon further addition of nitrate (R > 3), no additional component appears for the $^5D_0 \rightarrow {}^7F_0$ transition. That is, the species $[Eu(NO_3)_n]^{(3-n)}$ with $\bar{n}$ = 3, 4, and 5 give rise to undistinguishable 0–0 transitions. Moreover, the variations of the total band area (see previous Section) may induce large errors in the estimated intensities of the different components. The formation of the tetra- and pentanitrato species is evidenced by the fluorescence lifetimes (Table VII); for R = 6, $\tau$ is only slightly smaller than for anhydrous solutions of $(Me_4N)_2Eu(NO_3)_5$: 1.18 ± 0.02 ms, as compared to 1.25 ± 0.05 ms. The $\tau/\tau_0$ *vs.* R plot exhibits a complex behaviour (Fig. 5), $\tau_0$ being taken as the lifetime of perchlorate solutions in water [5]. A closer inspection reveals that the points between R = 1.5 and R = 3.0 fall on a straight line (correlation coefficient: 0.986), the intercept of which is close to one (0.92); including the (1.0; 0.0) point into the linear regression increases the correlation coefficient to 0.995. This linear correlation can conveniently be used to estimate $\bar{n}$:

$$\bar{n} = 1.89(\tau/\tau_0) - 1.85$$

For R = 2, $\tau/\tau_0$ = 2.0, and n = 1.93, in good agreement with the value calculated previously from the intensities of the $^5D_0 \rightarrow {}^7F_0$ components.

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*The ionic strength of the resulting solutions does not vary much since $(Me_4N)ClO_4$ precipitates upon addition of $(Me_4N)NO_3$.

TABLE VII. Relative Corrected Intensities (±6%) of the Hypersensitive $^5D_0 \rightarrow {}^7F_2$ Transition and Fluorescence Lifetimes (μs, ±2%) *Versus* $R = [NO_3^-]_t/[Eu^{3+}]_t$ and $R_w = [H_2O]_t/[Eu^{3+}]_t$; $Eu(ClO_4)_3$ Solutions 0.047 *M* in $CH_3CN$; $\lambda_{exc}$ = 595 nm ($\tau$) or 395 nm, $\lambda_{anal}$ = 618 nm.

| $R_w$ | R | $F_2/F_1$ | $\tau_f$ | $R_w$ | R | $F_2/F_1$ | $\tau_f$ |
|---|---|---|---|---|---|---|---|
| 8 | 0.0 | 1.0 | 150 | 44 | 0.0 | 0.75 | 104 |
| | 0.5 | 1.8 | 161 | | 0.5 | – | 114 |
| | 1.0 | 2.8 | 174 | | 1.0 | – | 129 |
| | 1.25 | – | 180 | | 1.5 | 3.0 | 144 |
| | 1.5 | 3.7 | 188 | | 2.0 | 3.8 | 158 |
| | 1.75 | 4.1 | 196 | | 2.5 | – | 181 |
| | 2.0 | 4.5 | 208 | | 3.0 | 6.1 | 203 |
| | 2.25 | 4.9 | 224 | | 3.5 | – | 237 |
| | 2.5 | 5.2 | 239 | | 4.0 | 6.9 | 277 |
| | 3.0 | 6.4 | 274 | | 4.5 | – | 315 |
| | 3.25 | – | 312 | | 5.0 | 7.3 | 345 |
| | 3.5 | 7.5 | 341 | 94 | 0.0 | 0.7 | 104 |
| | 3.75 | – | 402 | | 0.5 | – | 112 |
| | 4.0 | 8.8 | 456 | | 1.0 | 2.0 | 123 |
| | 4.25 | – | 550 | | 1.5 | 2.7 | 136 |
| | 4.5 | – | 667 | | 2.0 | 3.1 | 149 |
| | 4.75 | – | 865 | | 3.0 | 4.1 | 171 |
| | 5.0 | 9.4 | 1070 | | 4.0 | 4.6 | 190 |
| | 5.25 | – | 1150 | | 5.0 | 5.5 | 205 |
| | 5.50 | – | 1180 | 304[a] | 0.0 | [b] | 103 |
| | 5.75 | – | 1190 | | 1.5 | [b] | 110 |
| | 6.0 | 11.4 | 1180 | | 2.0 | [b] | 116 |
| | | | | | 3.0 | [b] | 120 |
| | | | | | 4.0 | [b] | 122 |

[a] $[Eu^{3+}]_t$ = 0.045 *M*. [b] Not determined.

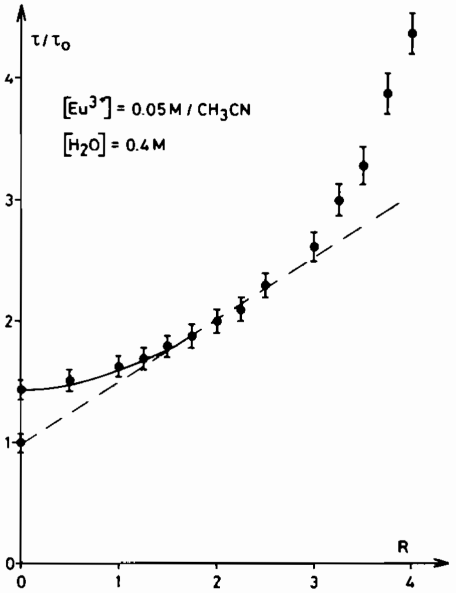

Fig. 5. Influence of the nitrate concentration upon the ratio $\tau/\tau_0$ ($\tau_0$ = 104 μs); $R = [NO_3^-]_t/[Eu^{3+}]_t$.

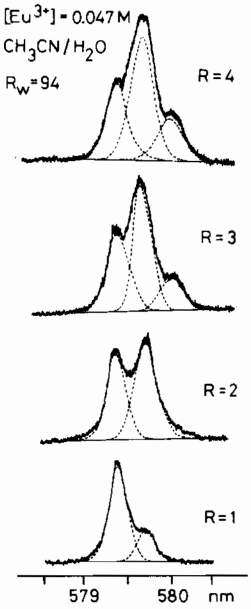

Fig. 6. High resolution spectra of the $^5D_0 \rightarrow {}^7F_0$ transition; $Eu(ClO_4)_3$ 0.047 *M* in $CH_3CN$; $R = [NO_3^-]_t/[Eu^{3+}]_t$, $R_w = [H_2O]_t/[Eu^{3+}]_t$.

The influence of the mole water fraction on the formation of the nitrato complexes was also studied for $R_w$ = 44, 94, and 304. Again, both the $^5D_0 \rightarrow {}^7F_0$ (Table VI, Fig. 6) and $^5D_0 \rightarrow {}^7F_2$ (Table VII) transitions undergo large changes upon addition of nitrate. The intensity of the latter increases linearly with R for $R_w$ = 8 and 44, but no more for larger $R_w$'s. This

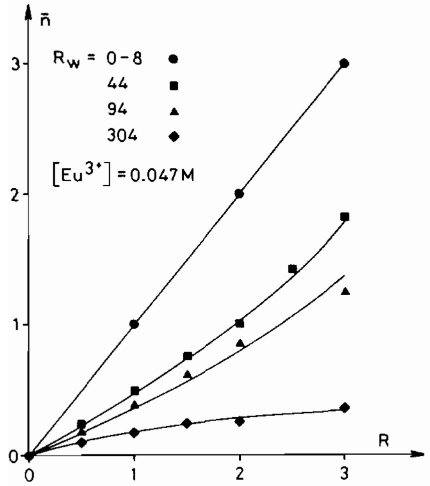

Fig. 7. Average number of coordinated nitrate ions per europium ion, n̄, as a function of water and nitrate concentrations; $R = [NO_3^-]_t/[Eu^{3+}]_t$, $R_w = [H_2O]_t/[Eu^{3+}]_t$.

may be due to substantial changes in the dielectric constant of the solvent when the water mole fraction is increased; this transition therefore cannot be used to estimate n̄ [10]. The different components of the 0–0 transition appear at the same wavelengths as for $R_w$ = 8 and they are assigned similarly. The number n̄ can be estimated from the lifetime measurements with the help of the above relationship, which is valid up to R = 3 (Fig. 7). The apparent equilibrium ratios:

$$K_n = \frac{[Eu(NO_3)_n]_{solv}^{(3-n)+}}{[Eu(NO_3)_{n-1}]_{solv}^{(4-n)+}[NO_3^-]}$$

may be extracted from both these data and the deconvolutions of the $^5D_0 \rightarrow {}^7F_0$ transition. Considering the uncertainties involved in the intensities of the 0–0 components and in the n̄ determinations, the following numbers have to be taken as indicative. We find $K_1 = 23 \pm 3, 15 \pm 5$, and $5 \pm 1\ M^{-1}$ for $R_w$ = 44, 94 and 304, respectively, and $K_2 = 17 \pm 10\ M^{-1}$ for $R_w$ = 44 and 94. The equilibrium ratios for $n \geqslant 3$ cannot be estimated. The trend in $K_1$ is consistent with the reported values in pure water, which range from $0.3 \pm 0.1$ [5] to $1.6 \pm 0.7\ M^{-1}$ [7].

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