250. Spectroscopic Investigation of Anhydrous Solutions of Europium Perchlorate and Europium Nitrate in *N*, *N*-Dimethylformamide[1])

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Summary

Anhydrous solutions of $Eu(ClO_4)_3$ and $Eu(NO_3)_3$ 0.05 M in *N*,*N*-dimethylformamide (DMF) are investigated by means of conductometric measurements, vibrational spectroscopy, electronic absorption and emission spectra, and fluorescence lifetime determinations. $Eu(ClO_4)_3$ is completely dissociated and no inner-sphere interaction takes place between ClO_4^- and Eu^{3+} ions. The solvated species $Eu(DMF)_x^{3+}$ has a C_{2v}-symmetry and x is probably equal to 8.

A more complicated situation occurs for $Eu(NO_3)_3$, the solutions of which contain at least three different solvates; the predominant species is $[Eu(NO_3)_2(DMF)_{x-4}]^+$ ($\approx$80% of the total Eu-concentration) and it is more stable than the mononitrato complex $[Eu(NO_3)(DMF)_{x-2}]^{2+}$; the neutral complex $Eu(NO_3)_3(DMF)_{x-6}$ is also present, as can be inferred from a high-resolution analysis of the $^5D_0 \rightarrow {}^7F_0$ emission band. The absence of emission from the excited $^5D_1$-level can be rationalized in terms of an efficient non-radiative deexcitation path through a vibrational mode of the DMF-molecules bonded to the central metal ion.

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1. Introduction. – The interaction between rare-earth nitrates and *N*,*N*-dimethylformamide (DMF) was first investigated by *Krishnamurthy & Soundararajan* [3] who isolated the solvates $Ln(NO_3)_3(DMF)_4$ (Ln = La, Pr, Nd, Sm) and found that they are uni-univalent electrolytes in DMF-solutions. These authors suggested that a further DMF-molecule may replace one nitrate ion in the first coordination sphere to form $[Ln(NO_3)_2(DMF)_5]^+$-cations. *Abrahamer & Marcus* concluded later, on the basis of a spectrophotometric investigation of nine Ln(III)-ions, that *i*) the affinity sequence of ligands and solvents for Ln(III)-ions in DMF is: DMF > $(C_4H_9O)_3PO > NO_3^- \approx H_2O > C_2H_5OH >$ dioxane, and *ii*) the nitrate ions in the

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above-mentioned cationic species are present in the outer, and not in the inner coordination sphere [4]. Recent data on the electronic and ultrasonic absorption spectra of neodymium nitrate in both methylformamide and DMF [5], and on the absorption and emission spectra of $Ln(NO_3)_3$ in DMF (Ln = Nd, Eu, Tb) [6] [7] are, however, at variance with this latter conclusion; they are indeed consistent with an inner-sphere interaction between the lanthanide and the nitrate ions.

As part of a systematic study of the solvation of trivalent rare-earth ions in both aqueous [8] and strictly anhydrous solutions [1] [2] [6] [7] we present here the results of an investigation of $Eu(ClO_4)_3$ and $Eu(NO_3)_3$ in dilute and anhydrous solutions containing DMF. Molar conductances, vibrational spectra, electronic absorption and emission spectra, and fluorescence lifetimes are reported. The number of differently solvated species is obtained by inspection, under high resolution, of the $^5D_0 \rightarrow {}^7F_0$ transition, and their composition and structure are discussed.

2. Experimental. – 2.1 *Preparation of the solutions.* Anh. $Eu(ClO_4)_3$ was prepared by dissolving 5 mmol Eu_2O_3 (99.99%, *Research Chemicals*) in 28–29 mmol of concentrated reagent-grade $HClO_4$ (*Merck*). The mixture was heated at 50° for 2–3 h. The excess of oxide was filtered off and the solution was evaporated to dryness. The perchlorate was dried over KOH during 1 week and the resulting crystalline hydrate $Eu(ClO_4)_3 \cdot n\,H_2O$, n = 6–7, was transferred into a pyrex tube. Dehydration was performed *i.v.* (10^{-2} Torr) by stepwise heating: 2 days/50°, 2 days/80°, 5 days/100°, and 6 days/150°. The pyrex tube was then sealed off and was only opened under controlled atmosphere. (*Any impurities such as acid traces or grease must be carefully avoided to prevent an explosion!*) Dehydration under high vacuum (10^{-5} Torr, 60–110°, 10 days) is also possible. Complexometric analyses yielded an Eu-content of 34.0% (calc. 33.75%).

Anh. $Eu(NO_3)_3$ was prepared as previously described [9]. CH_3CN (*puriss, Fluka*), DMF (*puriss, Fluka*) and $(CH_3)_4NNO_3$ (*purum, Fluka*) were carefully dried before use. Since the anh. salts are extremely hygroscopic, the solutions were prepared in a glovebox containing less than 10 ppm water and, whenever possible, with use of the corresponding solvates $Eu(ClO_4)_3 \cdot n$ DMF and $Eu(NO_3)_3 \cdot m$ DMF. In principle, n = 8 [10] [11] and m = 4 [3]; however, treatment of these solvates *i.v.* leads to the loss of one DMF-molecule.

The absence of water in the solutions could be checked on their IR. spectra and by measuring their fluorescence lifetimes [1], which amount to 1.44 and 1.47 ms for $Eu(ClO_4)_3$ and $Eu(NO_3)_3$ 0.05 M in anh. DMF, respectively. The Eu-content of the solutions was determined after completion of the measurements by means of complexometric titrations with EDTA.

2.2. *Spectroscopic measurements.* Absorption spectra were recorded on a *Perkin-Elmer-Hitachi* Model *340* spectrophotometer; FT.-IR. measurements were performed with a *Bruker IFS-113c* interferometer [1]; fluorescence spectra (band-pass 0.08 nm) and lifetimes were measured with use of the instrumentation previously described [1] [8]. The different components of the $^5D_0 \rightarrow {}^7F_0$ transition were resolved by numerical deconvolutions: *Lorentzian* instrumental functions were fitted by a general least-squares procedure on a *Nord 10-S* computer from *Norsk Data*. The quantum yield, Q, of a $Eu(NO_3)_3$-solution 0.05 M in DMF was determined taking $Eu(NO_3)_3 \cdot 6\,H_2O$ 0.1 M in CH_3OH as reference (Q = 5.0% [12]): it amounts to 20.3% upon excitation to the $^5L_6$-level.

3. Results and discussion. – 3.1 *Properties of* $Eu(ClO_4)_3$ *in DMF-solution.* The molar conductivity at 25°, Λ_M, of a 0.001 M solution in anh. DMF is equal to 200 $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$ and it is typical of a 3:1 electrolyte [13], at higher concentrations, Λ_M decreases to 146 $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$ for a 0.05 M solution, which reflects that some interaction takes place between Eu^{3+} and ClO_4^-: the accepted range for 2:1 electrolytes is 140–170 $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$ [13]. Since both the absorption and the emission spectra are concentration-independent in the range 0.04–0.2 M, this interaction is not expected to correspond to the formation of contact ion-pairs, but rather to an outer-sphere complexation, contrary to what was observed in CH_3CN [1] Supporting evidence for this conclusion comes from the narrow ^{35}Cl-NMR. line-widths measured for anh. solutions of $La(ClO_4)_3$ in DMF: 1.6–2.0 Hz, as compared to 206–261 Hz for solutions in CH_3CN [11].

The absorption spectra of $Ln(ClO_4)_3$ (Ln=Nd, Ho, Er) in DMF have been interpreted as arising from nonaccordinated species of D_{3h}-symmetry [14]. The absorption spectrum of $Eu(ClO_4)_3$ *(Table 1)* is clearly at variance with this conclusion since the hypersensitive transition $^5D_2 \leftarrow {}^7F_0$ is comprised of at least three components. According to the selection rules on symmetry [15], this is only feasible if the point group of the absorbing species is D_2, C_{3v}, or C_3. The emission spectrum *(Table 2, Fig. 1)* displays transitions from the $^5D_0$-level only. The observation of a single, symmetric although broad, band (full width at half height, FWHH. = 6.7 cm^{-1}) corresponding to the transition to the $^7F_0$-level indicates the presence of only *one* solvated species. This transition is allowed in lower and in axial symmetries (C_s, C_n, C_{nv} point groups)[4]). The number of transitions observed to J = 0, 1, 2, and 4 is 1, 3, 4, and 5, respectively *(Table 2)*; in C_{3v}-symmetry 1, 2, 3, and 5 transitions to these sublevels are active, respectively, and in C_{2v}-symmetry 1, 3, 4, and 7 transitions are allowed, respectively. Therefore, we think the emission spectrum is consistent with the presence of a solvated species of C_{2v}-symmetry. The absence of an inversion centre is confirmed by the larger intensities of the transitions to the J = 2 and J = 4 sublevels, with respect to the intensity of the magnetic dipole transition to the J = 1 sublevel.

Table 1. *Part of the absorption spectra of $Eu(ClO_4)_3$ 0.045 M and $Eu(NO_3)_3$ 0.045 M in anh. DMF, at 22°*

Assignment[a])	$Eu(ClO_4)_3$		$Eu(NO_3)_3$	
	λ [nm]	ε_{max} [$l \cdot mol^{-1} \cdot cm^{-1}$]	λ (nm)	ε_{max} [$l \cdot mol^{-1} \cdot cm^{-1}$]
$^5D_4 \leftarrow {}^7F_0$	362	1.50	362	1.1
$^5D_4 \leftarrow {}^7F_1$			367	0.1
	374	0.2		
$^5G_{3,4,5,6}$	376.5	0.7	375.5	0.7
$\leftarrow {}^7F_{0,1}$	380.5	0.4	381	0.55
$^5L_7 \leftarrow {}^7F_{0,1}$	384	0.5	385.5	0.5
$^5L_6 \leftarrow {}^7F_0$	393.8	7.4	394.4	4.0
	396.2	0.5	396	Shoulder
	398.0	0.3	398.4	0.6
$^5L_6 \leftarrow {}^7F_1$	399.8	0.2	399.4	0.5
$^5D_3 \leftarrow {}^7F_1$	415	0.08	415	0.05
	417	0.08	417	0.1
$^5D_2 \leftarrow {}^7F_0$	464.1	0.28	464.6	0.4
	464.8	0.20	465.1	0.6
	465.6	0.09	465.5	1.0
$^5D_1 \leftarrow {}^7F_0$	526	0.1	526	0.1
$^5D_1 \leftarrow {}^7F_1$	534.5	0.03		
	537	0.02	536	0.1

[a]) According to [16].

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[4]) This transition is forbidden by both *Laporte's* and the spin-orbit selection rules. Its intensity arises through J-mixing with the $^7F_2$- and $^7F_4$-states [17].

Table 2. *Emission spectra of* $Eu(ClO_4)_3$ *0.042*M *and of* $Eu(NO_3)_3$ *0.047*M *in anhydrous DMF, at 22°* (λ_{exc} = 393.5 nm; analyzing band-pass = 0.3 nm; I_{rel} represents the corrected, integrated emission intensities of all the components of the transition, relative to the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition taken as internal reference [17])

Lower sublevel	$Eu(ClO_4)_3$ λ [nm]	I_{rel}	$Eu(NO_3)_3$ a) λ [nm]	I_{rel}
Emission from the $^5D_1$-level				
$^7F_0$	b)		526.7	0.02
$^7F_1$	b)		537.3	0.5
$^7F_2$	b)		555.0, 556.2, 557.5	0.2
$^7F_3$	b)		585.8	c)
$^7F_4$	b)		627.0	3.3
$^7F_5$	b)		673.5	d)
Emission from the $^5D_0$-level				
$^7F_0$	579.35	0.4	579.45e), 579.8, 580.1e)	2.5
$^7F_1$	588.9e), 590.3, 593.0	100	592.5	100
$^7F_2$	612.2, 613.5e), 618.2, 623e)	260	615e), 618.2	590
$^7F_3$	645e), 650.6, 654.3	7	650, 653, 659	15
$^7F_4$	682e), 689.5e), 691.3, 696.5e), 699.6	220	689e), 691.5e), 693.3	150
$^7F_5$	750	d)	752	d)
$^7F_6$	807	d)	814	9

a) For $Eu(NO_3)_3$, $^5D_2 \rightarrow {}^7F_5$ is observed at 574.2 nm (I_{rel} = 0.2) b) Not observed. c) Doubtful assignment. d) Very weak. e) Shoulder.

This C_{2v}-symmetry is compatible with both octacoordination and nonacoordination since there is a C_{2v}-reaction path between the capped square antiprism with C_{4v}-symmetry and the tricapped trigonal prism with D_{3h}-symmetry [18]. Octacoordination is more probable since the emission spectrum ressembles closely that of the solid adduct $Eu(PF_6)_3 \cdot 8\,DMF$ [19]; moreover, ^{1}H-NMR. data on the $Tm(ClO_4)_3 \cdot 8\,DMF/DMF/CD_2Cl_2$ system yielded an average coordination number of 7.7 ± 0.2 at 185 K [11].

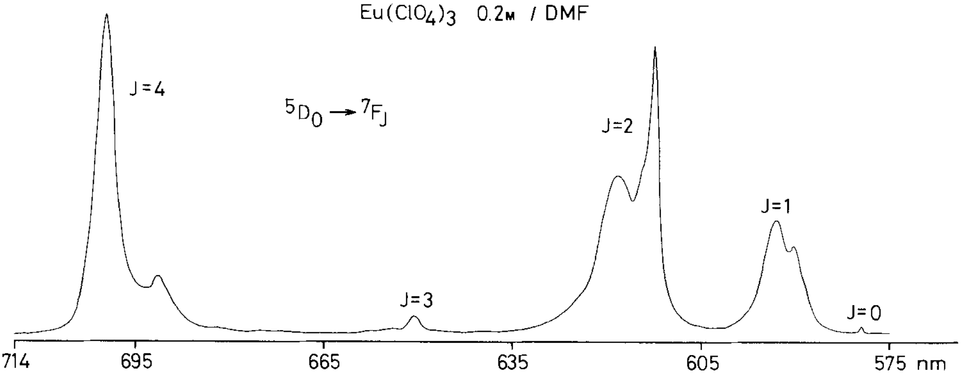

Fig. 1. *Emission spectrum of* $Eu(ClO_4)_3$ *in DMF;* λ_{exc} *= 393 nm* (Vertical scale: arbitrary units)

3.2. *Properties of $Eu(NO_3)_3$ in DMF-solution.* – The molar conductivities of 0.0002, 0.0005, 0.001, 0.002, and 0.01 M solutions of $Eu(NO_3)_3$ in anhydrous DMF are 198, 165, 123, 102, and 65 $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$, respectively. These values are in the range accepted for 2:1 (140–170 $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$) and 1:1 ($<85$) electrolytes, respectively. They reflect a substantial interaction between Eu^{3+} and NO_3^-. A similar result was obtained for a 0.0008 M $Nd(NO_3)_3$-solution: $\Lambda_M = 126.9$ $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$ [5].

FT.-IR. and *Raman* spectra of 0.04–0.3 M solutions reflect the presence of two different nitrates; vibrations of ionic NO_3^- appear at 831 (ν_2) and 1344 (ν_3) cm^{-1}, whereas bonded NO_3^- absorb at 739, 742 (*Raman:* 741, depolarized), 818, 1034 (1037, polarized), 1305, and 1490 (1495, polarized) cm^{-1}. Both the energy of these latter vibrations and their *Raman* polarizations point to the presence of bidentate nitrates with C_{2v} local symmetry [9]. Therefore, there is no doubt that nitrate ions are present in the inner coordination sphere of the metal ion.

Contrary to an earlier report [4], we find that the electronic absorption spectra also reflect this inner-sphere interaction. Large intensity variations are observed for the bands of nitrate solutions, compared to those of perchlorate solutions *(Table 1);* namely, the $^5D_2 \leftarrow {}^7F_0$ transition is 3–4 times more intense and its intensity, relative to that of the $^5D_1 \leftarrow {}^7F_0$ transition, increases when $[NO_3^-]$ is increased. Evidences for an inner-sphere interaction also come from the emission data *(Table 2, Fig. 2):*

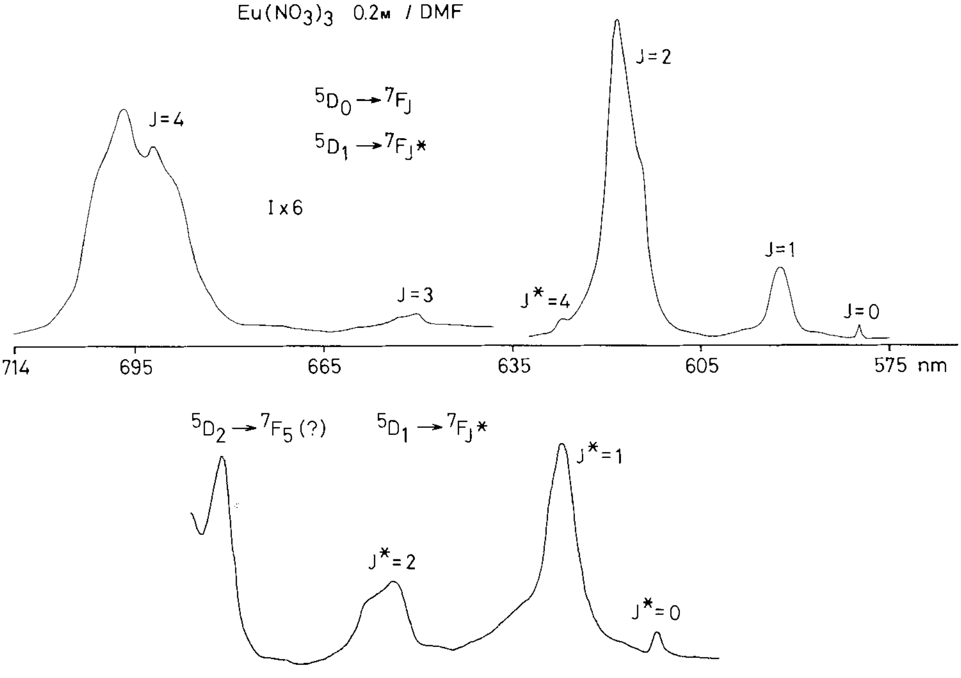

Fig. 2. *Emission spectrum of $Eu(NO_3)_3$ in DMF; $\lambda_{exc} = 393$ nm* (Vertical scale: arbitrary units)

compared to the spectrum of $Eu(ClO_4)_3$, the relative intensities of the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 2, 4) transitions are enhanced, and emissions from the $^5D_1$-level are also observed, and they amount to 1% of the total emitted light. Moreover, the $^5D_0 \rightarrow {}^7F_0$ transition is comprised of three components, which reflects the presence of at least three different species in equilibrium *(Fig. 3 c)*.

To assign these components to specific solvated species, we have added increasing quantities of $(CH_3)_4NNO_3$ to solutions of $Eu(ClO_4)_3$ in DMF. The fluorescence data of such solutions are presented in *Table 3*, along with the results of the deconvolution of the 0–0 transition. The formation of different nitrato complexes is reflected by the numerous components of this transition, the relative intensities of which vary considerably with the ratio $R = [NO_3^-]_t/[Eu^{3+}]_t$ *(Fig. 3)*. These components are assigned as follows, assuming that one nitrate replaces y

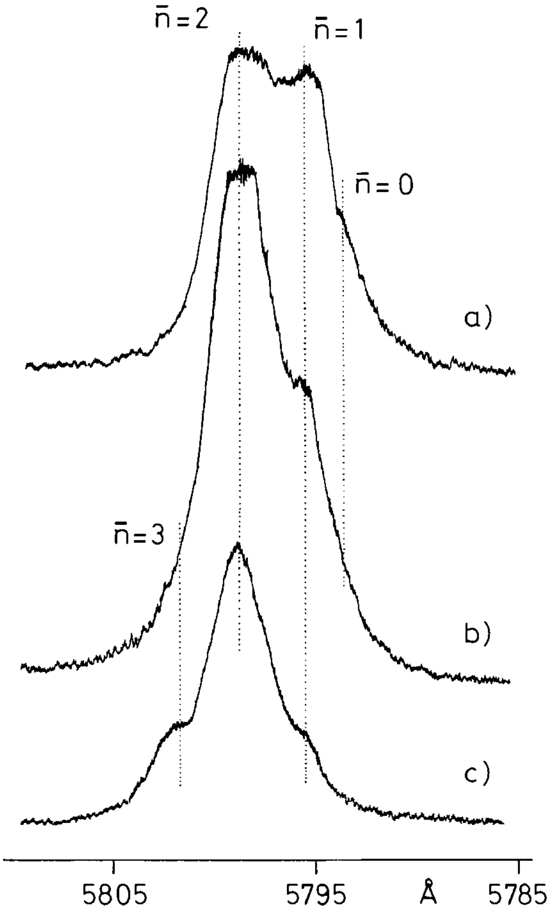

Fig. 3. *High-resolution fluorescence spectra of the $^5D_0 \rightarrow {}^7F_0$ transition for $Eu(NO_3)_3$-solutions in DMF* ($[Eu^{3+}] = 0.047$ M in DMF; *a)* $R = [NO_3^-]_t/[Eu^{3+}]_t = 1$, *b)* R = 2, *c)* R = 3; m indicates the number of bonded NO_3^--ions in $[Eu(NO_3)_m(DMF)_{x-2m}]^{(3-n)+}$ Vertical scale: arbitrary units)

Table 3. *Fluorescence data for solutions with different ratios $R = [NO_3^-]_t/[Eu^{3+}]_t$* ($\lambda_{exc} = 395$ nm or 593 nm (lifetimes); $[Eu^{3+}] = 0.045$ M in DMF)

R	τ_f[ms] ± 0.03	$^5D_0 \rightarrow {}^7F_2$ a) ± 0.1	$^5D_0 \rightarrow {}^7F_0$ b) Eu^{3+}	$[Eu(NO_3)]^{2+}$	$[Eu(NO_3)_2]^+$	$Eu(NO_3)_3$
0	1.47	2.7	100	–	–	–
1	1.45	4.0	10	41	49	–
2	1.41	4.4	6	27	67	–
2.5	1.39	4.9	c)	12	88	c)
3	1.37	5.7	–	7	87	6
4	1.36	6.3	–	5	85	10

a) Relative intensity, *cf. Table 2.*

b) Relative band area after deconvolution (in % of total area); DMF-molecules are omitted in the formula; Eu^{3+}: $\lambda_{max} = 579.35$ nm, FWHH. = 0.4 nm; $[Eu(NO_3)]^{2+}$: 579.55(2), 3.1(1); $[Eu(NO_3)_2]^+$: 579.83(1), 3.4(3); $Eu(NO_3)_3$: 580.07(2), 2.4(1).

c) Too weak to be included in the deconvolution.

DMF-molecules5)): 579.35 nm (shoulder), $Eu(DMF)_x^{3+}$; 579.50 nm, $[Eu(NO_3)(DMF)_{x-y}]^{2+}$; 579.83 nm, $[Eu(NO_3)_2(DMF)_{x-2y}]^+$; 580.07 nm, $Eu(NO_3)_3(DMF)_{x-3y}$. Both the mono- and the dinitrato species are predominant in the solutions with $R < 3$. In more concentrated solutions, > 0.15 M and with $R = 3$, di- and trinitrato complexes are predominant. Solubility problems prevented us to investigate whether tetra- and pentanitrato species are also formed in DMF as in CH_3CN [21]. Moreover, the area of the deconvoluted components could not be used directly for quantitative estimations: the quantum yields of different solvates may be quite different, and our data are not precise enough to calculate both these and the stability constants.

Qualitatively, however, one sees that the dinitrato complex is more stable than the mononitrato one. This confirms the trend observed by *Airoldi et al.* who found, in dimethylacetamide, that K_1 and K_2 are equal to 17 and 16 $l \cdot mol^{-1}$, and to 25 and 92 $l \cdot mol^{-1}$ for the corresponding La- and Nd-salt solutions, respectively [22]. For Nd(III)-solutions in DMF, K_1 was estimated to be of the order of 110 $l \cdot mol^{-1}$ and K_2 to be at least of the same order of magnitude [6].

The average number of coordinated NO_3^- per Eu^{3+}, $\bar{n}$, could be determined by use of an unexpected property of the $^5D_0 \rightarrow {}^7F_2$ transition. As already observed in CH_3CN [21], its intensity increases linearly with $\bar{n}$, regardless of the solvate structure. In a series of experiments, we have added increasing amounts of nitrate to an $Eu(ClO_4)_3$-solution 0.05 M in CH_3CN and containing 0.35 M of DMF. When $R > 1.5$, the relationship is indeed linear and the extrapolation to $R = 0$ exactly matches the value for $Eu(ClO_4)_3$ in DMF. The deviation for $R < 1.5$ can be explained by the presence of CH_3CN- and/or ClO_4^--moieties in the inner coordination sphere [1]. From *Figure 4*, one gets $\bar{n} = 1.8$ for a 0.047 M solution of $Eu(NO_3)_3$ in DMF, a value quite consistent with the conductometric data.

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5) The number y is greater than 1 since $x = 8$ [10] [11] and the maximum number of NO_3^--ions that can enter the inner coordination sphere is 5 in solution [20] [21]. We think y is equal to 2.

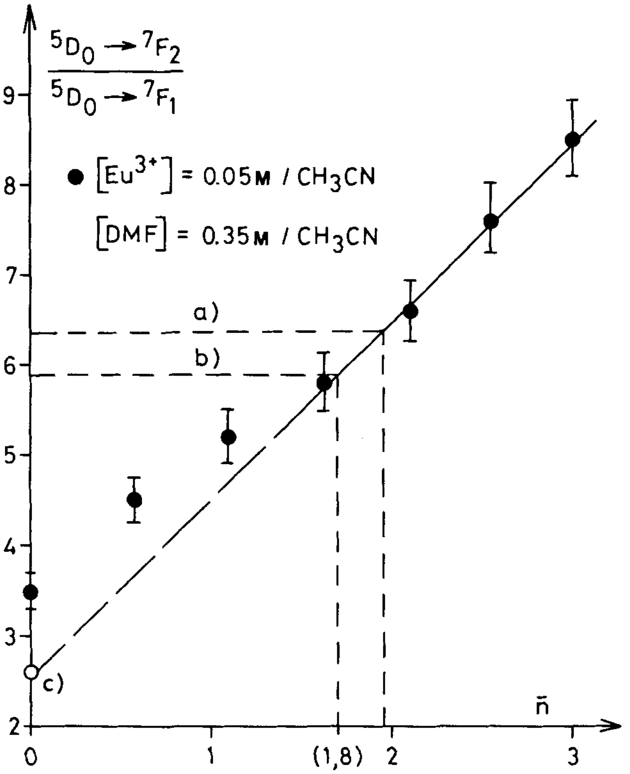

Fig. 4. *Relative intensity of the $^5D_0 \to {}^7F_2$ transition with respect to the $^5D_0 \to {}^7F_1$ transition,* vs. *the number of coordinated NO_3^--ions per Eu^{3+}-ion,* $\bar{n}$ (Particular values: *a)* $Eu(NO_3)_3$ 0.18M/DMF; *b)* $Eu(NO_3)_3$ 0.047M/DMF; *c)* $Eu(ClO_4)_3$ 0.05M/DMF)

4. Conclusions. – It has been shown that in DMF-solutions, $Eu(ClO_4)_3$ is completely dissociated and yields $Eu(DMF)_x^{3+}$-ions with C_{2v}-symmetry; x is probably equal to 8. A more complex situation prevails for $Eu(NO_3)_3$: the predominant species in solution is $[Eu(NO_3)_2(DMF)_{x-4}]^+$ ($\approx$80% of the total Eu-concentration), and it is in equilibrium with both $[Eu(NO_3)(DMF)_{x-2}]^{2+}$ and with $Eu(NO_3)_3(DMF)_{x-6}$. The dinitrato solvate appears to be more stable than the mononitrato complex, as observed for Nd(III) in DMF-solutions [22].

The luminescence spectra of the two solvates, $Eu(DMF)_x^{3+}$ and $[Eu(NO_3)_2(DMF)_{x-4}]^+$, reveal an interesting feature. Emission from the $^5D_1$-level occurs only for the latter species and it is weak. That is, the non-radiative transfer $^5D_1 \to {}^5D_0$ is very important and it can be explained by the presence of an intense and broad IR. absorption band at 1650 cm^{-1} arising from the bonded DMF-molecules, whereas the energy gap between these two electronic levels is *ca.* 1700 cm^{-1}. Efficient quenching through this vibration [23] can then easily occur.

We are presently investigating frozen DMF-solutions by both FT.-IR. and laser-excited, time-resolved spectrofluorimetry in order to gain more information on the structure of the different nitrato solvates.

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