pares favorably with the value of 6.16 mdyn/Å calculated in this study for the similar motion in the adduct. The slightly smaller value for the adduct is expected on the basis of a slight elongation of the N–H bond with complex formation. Likewise the Ga–C stretching force constant of 2.14 mdyn/Å is very similar to the value of 2.15 mdyn/Å calculated for the corresponding force constant in the study of $(CH_3)_3Ga \cdot PH_3$.[3]

In support of the proposed assignment, Teller–Redlich product rule calculations were carried out. The A_1 symmetry block gave essential agreement between the theoretical and experimental values, while the E symmetry block contained an error of 1.91% between the calculated and observed ratios. The values for the calculated and observed ratios respectively are 1.976 and 1.995 for the A_1 species and 2.674 and 2.623

for the E symmetry block; a change of only one wavenumber in the values of the frequencies assigned to GaC_3 symmetric deformations reduces the observed ratio to 1.975 for the A_1 species. The excellent agreement between the experimental and theoretical values adds support to the assignment proposed herein.

Further studies on other gallium–nitrogen complexes should be carried out to check the range of the force constants associated with the Ga–N bond. With such studies it should be possible to ascertain whether there is a direct correlation of the bond strength with the force constant. Additionally it should also be possible to clearly define the frequency range expected for the Ga–N stretching motion.

(17) Herzberg, G. "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand-Reinhold: Princeton, NJ, 1945.

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FT IR and Fluorometric Investigation of Rare-Earth and Metallic Ion Solvation. 1. Europium Perchlorate in Anhydrous Acetonitrile[1]

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The composition of the species in equilibrium in dilute and anhydrous solutions of $Eu(ClO_4)_3$ in acetonitrile is investigated by means of FT IR and fluorometric measurements. $Eu(ClO_4)_3$ is a 2:1 electrolyte in CH_3CN; fluorescence spectra and lifetimes reflect an inner-sphere interaction between ClO_4^- and Eu^{3+}. FT IR difference spectra show the simultaneous presence of ionic, monodentate, and bidentate perchlorates. A quantitative determination indicates that, in 0.05 M solutions, $71 \pm 2\%$ of the perchlorates are ionic; of the remaining 29%, two-thirds are monodentate and one-third are bidentate. A high-resolution analysis of the $^5D_0 \rightarrow {}^7F_0$ emission band reveals the presence of two main Eu-containing species. The concentration variations of the different perchlorate species vs. $[ClO_4^-]_t$ and various comparisons with methanolic solutions indicate that monodentate perchlorate, $ClO_4^-(m)$, is probably involved in inner-sphere association, whereas bidentate perchlorate, $ClO_4^-(b)$, is probably involved in outer-sphere interaction. One Eu–O vibration is observed at 217 cm^{-1}. Bonded acetonitrile molecules can also be evidenced; the Eu–N vibration occurs at 168 cm^{-1}. The average number of coordinated CH_3CN molecules per Eu^{3+} ion is 8.5 ± 0.3, as determined by quantitative measurements of the $\nu_3 + \nu_4$ absorption and by comparison with $Eu(NO_3)_3$ solutions. The average coordination number of the europium ion is therefore 9.1 ± 0.3. The reported data are consistent with the presence of two main nonacoordinated species in equilibrium in 0.05 M solutions of $Eu(ClO_4)_3$ in acetonitrile: $[(EuClO_4(m))(CH_3CN)_8]^{2+}$ ($\sim$60 %) and $[Eu(CH_3CN)_9]^{3+}(ClO_4^-(b))^-$ ($\sim$30 %). Silver perchlorate solutions contain ionic ClO_4^- only, whereas sodium perchlorate solutions also contain some nonionic ClO_4^- groups. Acetonitrile molecules bonded to these ions can be evidenced by FT IR.

Introduction

The coordinative properties of Ln(III) ions are different from those of d-transition ions because of the 4f electron shielding. The stabilization due to crystal field effects is only of the order of a few hundred cm^{-1}, and the bonding of Ln(III) ions to oxygen and nitrogen atoms remains essentially electrostatic. The number of ligands in the first coordination sphere and their geometrical arrangements will thus be largely determined by steric requirements. Large coordination numbers (N) are common, and their determination in solution is expected to be difficult since the following situations may occur: (i) equilibrium between species differing in constitution by one, or more, ligated solvent molecules[2,3] and (ii) equilibrium between species having the same N but different coordination polyhedra and thus different spectroscopic properties.

Moreover, the solvated ion is surrounded by an outer-coordination sphere and rapid exchange usually takes place between the bulk and coordinated solvent molecules.

A number of estimates for N have been made by a wealth of different techniques, including absorption and emission spectra,[4] vibrational spectra,[5] NMR,[6] ultrasonic measurements,[7] and X-ray crystallography. Using this latter technique, Habenschuss and Spedding have unambiguously demonstrated a change in N across the rare-earth series: in concentrated aqueous chloride solutions, $N = 9$ for La^{3+}–Nd^{3+}[8] and $N = 8$ for Tb^{3+}–Lu^{3+},[9] whereas Sm^{3+}, Eu^{3+}, and Gd^{3+} are transitional, with N between 8 and 9.[10]

(1) Abstracted, in part, from the Ph.D. thesis of C.M.
(2) Jørgensen, C. K. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr., Eyring, LeRoy, Eds.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. 3, Chapter 23.
(3) Geier, G.; Jørgensen, C. K. *Chem. Phys. Lett.* **1971**, *9*, 263.

(4) Carnall, W. T. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr., Eyring, LeRoy, Eds.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. 3, Chapter 24.
(5) Nelson, D. L.; Irish, D. E. *J. Chem. Phys.* **1971**, *54*, 4479.
(6) Reuben, J.; Fiat, D. *J. Chem. Phys.* **1969**, *51*, 4909.
(7) Jezowska-Trzebiatowska, B.; Ernst, S.; Legendziewicz, J.; Oczko, G. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1978**, *26*, 805.
(8) Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1979**, *70*, 2797.
(9) Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1979**, *70*, 3758.
(10) Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1980**, *73*, 442.

Few studies refer to nonaqueous solvents, and they are usually less systematic than those dealing with aqueous solvents. We have therefore initiated a systematic investigation of the solvation of Ln(III) ions in organic solvents, devoting a special attention to their complexation with perchlorate and nitrate ions.[11] Outer-sphere interaction between ClO_4^- and Ln(III) is known, but the existence of inner-sphere complexes remains controversial.[11] In this paper, we discuss the solvation of the Eu(III) ion in dilute anhydrous solutions of $Eu(ClO_4)_3$ in acetonitrile, as determined by fluorometric and FT IR measurements. Since $AgClO_4$ and $NaClO_4$ were used to add an excess of perchlorate to these solutions, we also briefly discuss the solvation of the Ag^+ and Na^+ ions.

Experimental Section

FT IR Measurements. In this (and following) work we extract quantitative data on metallic ion solvation using FT IR difference spectra. Under our experimental conditions, some of the absorption bands we discuss are very weak, with absorbances of a few hundredths only. We have therefore thoroughly tested the photometric accuracy of our interferometer since no data exist for this particular type of instrument and since the observed absorbance in FT IR spectra depends on many experimental factors.[12,13]

The spectra were recorded on a Bruker IFS-113c vacuum spectrometer, covering the spectral range 10–5000 cm^{-1}, with a maximum resolution of 0.06 cm^{-1}, an automatic beam-splitter changer, and two pyroelectric TGS detectors. The data acquisition and handling system includes a 15-bit converter, a 48K–24-bit ASPECT 2000 computer and a 7.8 Mbyte double-drive DIABLO 4044B disk unit. The signal to noise ratios, measured on 100% lines without apodization, are 1.2% (1 scan) and 0.07% (256 scans) between 800 and 2800 cm^{-1} and 1.7% (32 scans) and 0.6% (256 scans) between 150 and 600 cm^{-1}.

Measurements on benzonitrile solutions in CCl_4 (0.025–2.8 M) yield perfectly linear Lambert–Beer plots up to an absorbance of 0.8 (resolution R = 2 cm^{-1}, 64 scans, triangular apodization). The influence of apodization was tested on the 2231-cm^{-1} band (fwhh 7.5 cm^{-1}) of benzonitrile (6.45 g in 93.55 g of CCl_4). Boxcar apodization gives A^{max} values which increase by 1.7% when R is varied from 7.92 to 0.48 cm^{-1}; triangular apodization gives smaller A^{max} values: $\Delta A = A^{max}_{true} - A^{max}_{obsd}$ = 27%, 8%, and 1.5% for R = 7.92, 1.93, and 0.48 cm^{-1}, respectively, in good agreement with published data.[12] A 55.3-μm path length and KBr windows were used. The influence of $\rho = R/fwhh$[13] on the absorbance was determined for six bands of benzonitrile (1.05 M solution in CCl_4, 153-μm cell) and six to seven settings of R, between 30.86 and 0.48 cm^{-1}. For boxcar apodization and $A^{max} > 1$, A^{max} remains constant as long as $\rho < 0.2$. When ρ becomes larger, a variation of A^{max} similar to that reported by Anderson and Griffiths is observed.[13] With triangular apodization, A^{max} is always a decreasing function of ρ.[14] From this study, we conclude that quantitative measurements must be performed with $\rho < 0.2$ and $A^{max} < 0.5$; triangular apodization can only be used for relative measurements.

The absolute photometric accuracy of the interferometer was checked with acetonitrile, with use of a 26.94-μm cell with KBr windows. The mean deviation from the ϵ^{max} values reported by Jones et al.,[15] for 11 bands with $\epsilon^{max} > 1.5$, was ± 2.6% (R = 1 cm^{-1}, 68 scans, 4 points/resolution element, boxcar apodization).

The mid-IR spectra of perchlorate solutions were recorded under the following conditions: nitrogen purge, R = 1 cm^{-1} ($\rho < 0.2$), 4 points/resolution element, trapezoidal (4-point) apodization, which is intermediate between boxcar and triangular truncations, 64–500 scans. The cell thickness was determined before each measurement by the method of interference fringes.[16] Silver chloride windows (42 × 23 × 2.7 mm) were used: (i) perchlorate adsorbs so easily on KBr windows that repolishing is needed after every measurement and (ii)

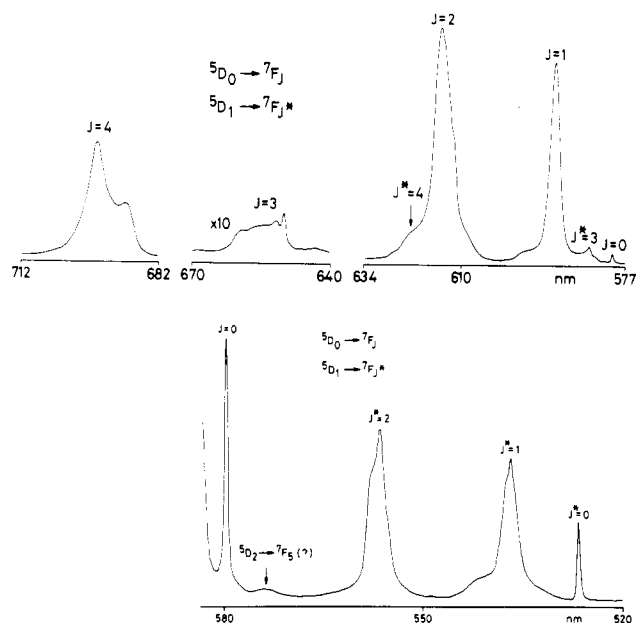(11) Bünzli, J.-C. G.; Yersin, J.-R. *Inorg. Chem.* **1979**, *18*, 605 and references therein.
(12) Anderson, R. J.; Griffiths, P. R. *Anal. Chem.* **1975**, *47*, 2239.
(13) Anderson, R. J.; Griffiths, P. R. *Anal. Chem.* **1978**, *50*, 1804.
(14) Detailed data are available as supplementary material.
(15) Goplen, T. G.; Cameron, D. G.; Jones, R. N. *Appl. Spectrosc.* **1980**, *34*, 657.
(16) Smith, A. L. In "Applied Infrared Spectroscopy, Chemical Analysis"; Elving, P. J., Winefordner, J. D., Kolthoff, I. M., Eds.; Wiley: New York, 1979, Vol. 54, p 117.

Figure 1. Fluorescence spectrum of $Eu(ClO_4)_3$ 0.1 M in CH_3CN: λ_{exc} = 395.5 nm, band pass = 0.2 nm; vertical scale, emission intensity in arbitrary units.

$AgClO_4$, which was used to add an excess of perchlorate to the solutions, reacts with KBr. The disadvantage of AgCl windows, namely, a large modulation of the spectrum by interference fringes,[17] is more than balanced by the elimination of these two problems, which caused our preliminary measurements to be poorly reproducible. The overall reproducibility we routinely achieve on difference spectra, taking into account the preparation of the highly hygroscopic perchlorate solutions, is less than 5% for bands the absorption of which is $0.01A$. Difference spectra were obtained in the following way. The solvent and solution spectra were recorded separately, ratioed against the background, and transformed in absorbance units. The solvent spectrum was then numerically substrated from the solution spectra with a different coefficient for each band.[13] Far-IR spectra were recorded at 8-cm^{-1} resolution (500 or 2000 scans) with a 30-μm cell and polyethylene windows. For quantitative data, at least two independently prepared solutions were measured, and each solution was measured twice.

Preparation of the Solutions. Europium perchlorate was prepared from 99.99% Eu_2O_3 (Glucydur) and reagent grade $HClO_4$ (Merck). Complete dehydration of the salt was performed at 60–110 °C, under high vacuum (10^{-5} mmHg, 10–12 days). Analytical grade $AgClO_4$, $AgNO_3$, and $NaClO_4$ (Merck) were used after being dried at 90–110 °C; CH_3CN (Fluka) and CD_3CN (99.98%, Ciba-Geigy) were treated by CaH_2 and P_2O_5 and distilled twice; they contained less than 0.1 molecule of H_2O/Eu^{3+} ion. Deuterated acetonitrile was used because it offers better windows in some regions of the IR spectra. Since $Eu(ClO_4)_3$ is highly hygroscopic, the solutions were prepared under strictly controlled atmosphere (N_2, containing less than 5 ppm of H_2O). The Eu concentration was determined by complexometric titration with EDTA (Titriplex III, Merck) in the presence of urotropine and xylene orange. The IR cells were also filled in the glovebox and immediately transferred into the spectrometer. The absence of water was checked by inspection of the 3500-cm^{-1} region of the spectrum.

Other experimental details are described elsewhere.[11]

Europium Ion Solvation

The molar conductivities of 0.01 and 0.0025 M solutions of $Eu(ClO_4)_3$ in anhydrous CH_3CN are 214 and 281 Ω^{-1} mol^{-1} cm^2, respectively. These values are in the range accepted for 2:1 electrolytes,[18] and they reflect a substantial ClO_4^-/Eu^{3+} interaction. The absorption spectra[19] of 0.05 M solutions also

(17) Elimination of these fringes by removing the corresponding frequency in the interferogram was not performed to avoid any distortion of the spectrum. We are now trying to solve this problem using a technique involving polarized light.
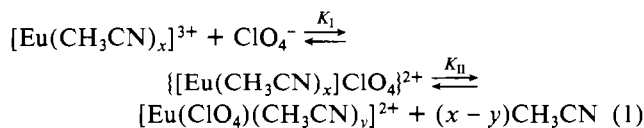(18) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table I. Fluorescence Lifetimes (λ_{exc} = 593 nm, λ_{anal} = 618 nm) and Relative Corrected Intensities of the $^5D_0 \to ^7F_{0,1,2,4}$ and $^5D_1 \to ^7F_{1,2}$ Transitions (λ_{exc} = 395 nm) vs. the Ratio R = $[ClO_4^-]/[Eu^{3+}]^a$

R	$\tau_f/\tau_f^{0\ c}$	$10^2 \times$ $(^7F_0/^7F_1)^c$	$^7F_2/$ $^7F_1^{\ d}$	$^7F_4/$ $^7F_1^{\ c}$	$^7F_2/$ $^7F_1^{\ b,c}$
3	1.00	1.0	1.7	0.8	0.9
7	0.89	1.1	2.0	0.8	0.9
11	0.88	1.2	2.1	0.9	1.0
28	0.68	1.5	2.2	1.0	1.1

^{a} [Eu^{3+}] = 0.05 M in anhydrous acetonitrile. ^{b} $^5D_1$ fluorescence. ^{c} ±0.1. ^{d} ±0.2.

point to such an interpretation: ϵ^{max} ($^7F_0 \to ^5L_6$) decreases from 5.1 L mol^{-1} cm^{-1} to 3.8 when R_t = $[ClO_4^-]_t/[Eu^{3+}]_t$ is increased from 3 to 28. However, the intensity of the hypersensitive $^7F_0 \to ^5D_2$ transitions remains constant (ϵ^{max} 0.28). Fluorescence intensities and lifetimes being very sensitive to the composition of the first coordination sphere, we have used them to try to determine whether the ClO_4^-/Eu^{3+} interaction is an outer- or inner-sphere one. Upon excitation to the $^5L_6$ level (395.5 nm), the Eu^{3+} ions fluoresce from the $^5D_0$ (96.7% of the total corrected fluorescence intensity) and from the $^5D_1$ (3.2%) excited states. Weak fluorescence from the $^5D_2$ level is also observed[20] (cf. Figure 1). With respect to the spectrum of Eu(ClO$_4$)$_3$ in water,[11] the main changes are the presence of a weak $^5D_0 \to ^7F_0$ transition and a more intense hypersensitive, ΔJ = 2, transition ($^7F_2/^7F_1$ = 1.7)[21] in acetonitrile as compared to 0.5 in water. That is, the solvated species in CH$_3$CN solutions certainly does not possess an inversion center, contrary to what is usually inferred from the spectrum in water.[11,23] The fluorescence lifetimes we measured for the $^5D_0$ level were independent of the excitation mode[11] and of the observed transition. Perfectly anhydrous solutions in CH$_3$CN have τ_f = 2.10 ms, a value much larger than the lifetime reported previously: 0.78 ms for 0.01–0.05 M solutions.[24] The energetic vibrations of the ligands, C–H and O–H stretches for instance, quench the Ln(III) ion fluorescence and shorten dramatically τ_f.[25] The addition of 1 molecule of H$_2$O/europium ion reduces τ_f to 1.7 ms. The measure of τ_f is therefore an excellent analytical test to detect traces of water in europium solutions. The addition of an excess perchlorate induces changes in both the fluorescence intensities and lifetimes (cf. Table I): the intensities of the $^5D_0 \to ^7F_0$ and $^5D_0 \to ^7F_2$ transitions increase and τ_f decreases. These changes are of the same order of magnitude as those induced by the addition of an excess of nitrate to Eu(NO$_3$)$_3$ solutions in water,[11] and we interpret them as reflecting an inner-sphere interaction between ClO$_4^-$ and Eu^{3+}. However, the extent of this interaction could not be evaluated from these data. The formation of inner-sphere perchlorate complexes may be described by the following equilibria where step I corresponds to the diffusion-controlled formation of an outer-sphere complex.[26]

$$[Eu(CH_3CN)_x]^{3+} + ClO_4^- \overset{K_I}{\rightleftharpoons}$$

$$\{[Eu(CH_3CN)_x]ClO_4\}^{2+} \overset{K_{II}}{\rightleftharpoons}$$

$$[Eu(ClO_4)(CH_3CN)_y]^{2+} + (x - y)CH_3CN \quad (1)$$

(19) A listing of 16 absorption bands (315–595 nm), along with their assignments and ϵ^{max} values, is available as supplementary material.
(20) A listing of 22 emission bands (525–820 nm), along with their assignments and their relative corrected intensities, is available as supplementary material.
(21) The magnetic dipole transition $^5D_0 \to ^7F_1$ may be used as internal standard for intensity comparison since it is not much affected by the environment of the fluorescent ion.[22]
(22) Porcher, P.; Caro, P. *J. Lumin.* **1980**, *21*, 207.
(23) Miller, D. G. *J. Am. Chem. Soc.* **1958**, *80*, 3576.
(24) Haas, Y.; Stein, G. *J. Phys. Chem.* **1971**, *75*, 3668.
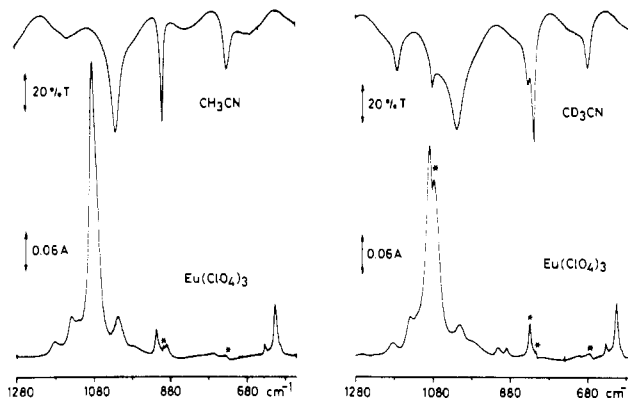(25) Haas, Y.; Stein, G. *J. Phys. Chem.* **1971**, *75*, 3677.

Figure 2. FT IR difference spectra of Eu(ClO$_4$)$_3$, 0.05 M in CH$_3$CN and CD$_3$CN, along with the transmission spectra of the solvents. Stars denote solvent absorptions which are not completely compensated.

Table II. IR Data (cm^{-1}) for ClO$_4^-$ in 0.05 M Solutions of Eu(ClO$_4$)$_3$ in Acetonitrile

monodentate (C_{3v})	ionic (T_d)	bidentate (C_{2v})
ν_6 (E)^a ←	ν_2 (E) IR inactive	ν_4 (A$_1$)^a / ν_5 (A$_2$) IR inactive
ν_5 (E)^b	ν_4 (T$_2$) 625	ν_9 (B$_2$) 612 sh / ν_7 (B$_1$)^b
ν_3 (A$_1$) 653		ν_3 (A$_1$) 650 sh
ν_2 (A$_1$) 933 ←	ν_1 (A$_1$) IR inactive	ν_2 (A$_1$) 909
ν_1 (A$_1$) 1031	ν_3 (T$_2$) 1101	ν_1 (A$_1$) 1000 sh / ν_6 (B$_1$) 1140 sh
ν_4 (E) 1158		ν_8 (B$_2$) 1202

^{a} Not observed. ^{b} Masked by the strong absorption of ν_4 (T$_2$).

We have turned to FT IR spectrometry to investigate further this interaction. Part of the difference spectrum of Eu(ClO$_4$)$_3$, 0.05 M in acetonitrile, is displayed in Figure 2, along with the spectrum of the solvent. Beside the two IR-active modes of ionic perchlorate (i, symmetry T_d), one clearly observes small absorption bands which can be assigned to monodentate (m, C_{3v}) and to bidentate (b, C_{2v}) perchlorate groups. All the IR-active vibrations of these two coordinated species could be found, except ν_6(m) and ν_4(b), which cannot be observed around 450–480 cm^{-1} with AgCl windows and which are probably too weak to be observed in the far-IR portion of the spectrum (vide infra). The two vibrational modes ν_5(m) and ν_7(b) absorb roughly at the same wavenumber as ν_4(i), which causes this latter absorption to deviate from Beer's law when an excess of perchlorate is added to the solution. The IR data are listed in Table II, along with the assignment of the vibrational modes.[27]

The high photometric accuracy of the FT IR spectrometer allows the determination of the concentrations of the different perchlorate species. We have first determined the molar absorption coefficients of ClO$_4^-$(i) using AgClO$_4$ solutions (0.01–0.6 M). These solutions contain ionic perchlorates only, contrary to NaClO$_4$ solutions (cf. Figure 3). Plotting $A^{max}_{\nu_3}$ (1100 cm^{-1}) vs. [ClO$_4^-$] results in a perfectly linear correlation

(26) Silber, J. B.; Pezzica, A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 2053.
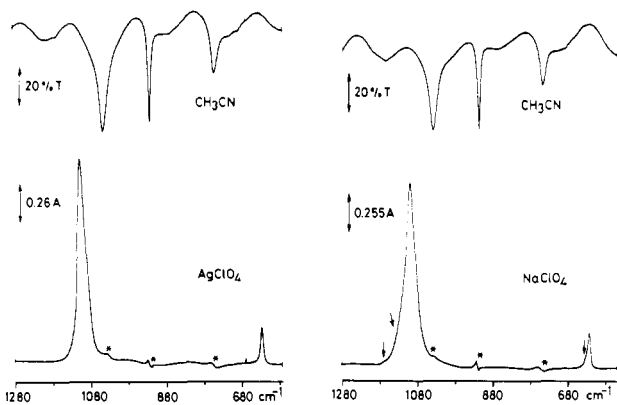(27) Scholer, R. P.; Merbach, A. E. *Inorg. Chim. Acta* **1975**, *15*, 15.

Figure 3. FT IR difference spectra of $AgClO_4$, 0.2 M, and $NaClO_4$, 0.5 M in CH_3CN, along with the transmission spectra of the solvent. Stars denote artefacts due to uncomplete solvent compensation. Arrows point to broadenings and weak absorptions due to ClO_4^- interacting with Na^+.

Table III. Acetonitrile Vibrations (cm^{-1}) in $Eu(ClO_4)_3$ (0.05 M)

assignt[a]	CH₃CN bulk	CH₃CN bonded	Δ	CD₃CN bulk	CD₃CN bonded	Δ
$\nu_3 + \nu_4$	2293	2311	18			
ν_2	2253	2283	30	2263	2295	32
ν_4	918	932	14	832	b	
ν_8	378	398	20	348	369	21

[a] According to: Evans, J. C.; Bernstein, H. J. *Can. J. Chem.* 1955, *33*, 1746. [b] Masked by another vibration.

(coefficient 0.9999) up to an absorbance of 0.7; this linear portion (cf. Figure 4) yields $\epsilon^{max}_{\nu_3} = 1720 \pm 40$ L mol^{-1} cm^{-1}. We can therefore calculate $R_i = [ClO_4^-(i)]/[Eu^{3+}]_t$. Two independent determinations on solutions with $[Eu^{3+}]_t = 0.0516$ and 0.0545 M give $R_i = 2.14 \pm 0.04$. The plot of $A^{max}_{\nu_4}$ (625 cm^{-1}) vs. $[ClO_4^-]$ is also perfectly linear (correlation coefficient 0.9997), with $\epsilon^{max}_{\nu_4}(i) = 258 \pm 5$ L mol^{-1} cm^{-1}. The absorbance of $Eu(ClO_4)_3$ solutions is slightly larger because of interferences with $\nu_5(m)$ and $\nu_7(b)$. The investigated solutions contain therefore 0.86 ± 0.04 nonionic ClO_4^-/Eu^{3+} ion, which nicely confirms the conclusions we made on the basis of conductometric and fluorometric measurements. An estimate of the concentrations of the mono- and bidentate perchlorates may be done with Koenig's method of internal standard.[28] This method was applied to two pairs of solutions in CH_3CN and CD_3CN having different compositions: $[Eu^{3+}]_t = 0.051$ M, $R_t = 3$ and 4. The total concentrations of nonionic perchlorates are first calculated as described above. To evaluate $[ClO_4^-(m)]$ and $[ClO_4^-(b)]$, we use the IR absorptions at 1202 (ν_8, b) and 653 cm^{-1} (ν_3, m) in CH_3CN, and at 909 (ν_2, b) and 933 cm^{-1} (ν_2, m) in CD_3CN. The two estimates give a proportion of monodentate perchlorate of 70% and 60%, respectively, and molar absorption coefficients of ~ 230, ~ 700, ~ 270, and ~ 360 L mol^{-1} cm^{-1} for $\nu_3(m)$, $\nu_8(b)$, $\nu_2(m)$, and $\nu_2(b)$, respectively. The absorbance of $\nu_3(i)$ being far larger than the absorbances of the nonionic species (~ 0.5 A, as compared to 0.01–0.02 A), and the base-line problems we have, did not allow better reproducibility. However, we can conclude that in anhydrous solutions of $Eu(ClO_4)_3$, ~ 0.05 M in acetonitrile, $(71 \pm 2)\%$ of the perchlorate groups are ionic; of the remaining 29%, approximately two-thirds are monodentate and one-third are bidentate.

Regarding the interaction between ClO_4^- and Eu^{3+}, we have to discuss whether perchlorate complexes are inner or outer sphere and whether species containing more than one perchlorate are formed. The presence of inner-sphere complexes is evidenced by the far-IR spectra of the solutions. In the spectral range 150–250 cm^{-1}, at least two absorptions are expected, corresponding to Eu–O[29,30] and Eu–N[31] vibrations. Indeed, the Eu–O(ClO_3) vibration is observed at 217 cm^{-1}, and the Eu–N(CCH_3) vibration, which corresponds to the motion of the cation inside the solvent cage,[31] occurs at 168

cm^{-1}. A slight red shift of 4 cm^{-1} of this latter vibration for solutions in CD_3CN, and the appearance of an additional Eu–O vibration at 231 cm^{-1} upon addition of the more strongly bonding anion NO_3^- confirm these assignements. In Figure 5, the absorbances of four IR bands of $ClO_4^-(m)$ and $ClO_4^-(b)$ are reported vs. $[ClO_4^-]_t$, at constant Eu concentration. The ratio $([ClO_4^-(m)] + [ClO_4^-(b)])/[Eu^{3+}]_t$ amounts to 0.9, 1.0, 1.2, and 1.5 for $R_t = 3, 4, 6$, and 12, respectively, which implies the existence of bis complexes for $R_t > 4$. From Figure 5, one sees that the concentration of $ClO_4^-(m)$ increases slightly more rapidly than the concentration of bidentate perchlorate. Strictly speaking, these quantitative data do not allow one to distinguish between different possible situations regarding which perchlorate species is in the inner or in the outer solvation sphere. We however think that monodentate perchlorate is essentially involved in inner-sphere interaction, whereas bidentate perchlorate is essentially involved in outer-sphere interaction because of the following considerations.

(i) When nitrate is added to $Eu(ClO_4)_3$ solutions, it is quantitatively complexed to the Eu^{3+} ion[32] and $[ClO_4^-(b)]$ decreases more rapidly than $[ClO_4^-(m)]$: the former species disappears completely when $R = [NO_3^-]/[Eu^{3+}]$ is equal to 2, whereas some $ClO^{4-}(m)$ is still present for $R = 3$. Moreover, the concentration of bound CH_3CN molecules decreases linearly with R, which means that these molecules are replaced first. (ii) The simultaneous presence of inner- and outer-sphere perchlorate complexes has been reported for Nd^{3+}, Gd^{3+}, and Er^{3+} in a more polar solvent, methanol, on the basis of ultrasonic data.[26] IR spectra of similar solutions (0.1 M) also display absorption bands arising from ionic, mono-, and bidentate perchlorates (Figure 6). The drastic change of $[ClO_4^-(m)]/[ClO_4^-(b)]$ in going from Nd^{3+} to Er^{3+} can be interpreted as reflecting the formation of more stable inner-sphere complexes with the smaller ions that have a larger charge density. This stronger interaction is reflected by a hypsochromic shift of the absorption bands corresponding to the $\nu_2(m)$ vibration: 928.1, 929.0, and 929.5 cm^{-1} for Ln = Nd, Eu, Er, respectively. Simultaneously there is a bathochromic shift of the $\nu_2(b)$ vibration: 913.5, 913.0, and 907.7 cm^{-1} for Ln = Nd, Eu, Er, respectively. The large difference between the data for Ln = Eu and Er may reflect the formation of the less stable ion pair $[Er(ClO_4)]^{2+}ClO_4^-$. (iii) If both perchlorates of bis complexes were inner sphere, we would expect a larger influence of $[ClO^{4-}]_t$ on the fluorescence lifetimes and intensities (cf. Table I). (iv) We have recorded the $^5D_0 \rightarrow {}^7F_0$ transition under high resolution[33] to determine the number of Eu-containing species in equilibrium in the excited state. Figure 7 reveals the presence of two main species emitting at 5798.5 and 5797.0 Å, respectively. For $R_t = 3$, there is an additional shoulder at ca. 5793 Å, which seems to disappear upon addition of perchlorate. For $R_t = 6$, the relative intensity of the slightly broadened bands is inverted.

(28) Koenig, J. L.; Kormos, D. *Appl. Spectrosc.* 1979, *33*, 349.
(29) Ferraro, J. R. "Low-frequency Vibrations of Inorganic and Coordination Compounds"; Plenum Press: New York, 1971.
(30) Bünzli, J.-C. G.; Moret, E.; Yersin, J.-R. *Helv. Chim. Acta* 1978, *61*, 762.
(31) Roche, J.-P.; Huong, P. V. *Bull. Soc. Chim. Fr.* 1972, 4521.

(32) Mabillard, C.; Yersin, J.-R., unpublished results.
(33) Ar laser excitation 465.8 nm, 40 mW; band pass 0.3–0.4 Å.
(34) Assuming the concentration of inner-sphere complexes is the same in the excited state as in the ground state, we find relative partial quantum yields $Q(EuClO_4^{2+})/Q(Eu^{3+})$ equal to 0.6 ± 0.2 and 0.35 ± 0.15 for $R_t = 3$ and 6, respectively.
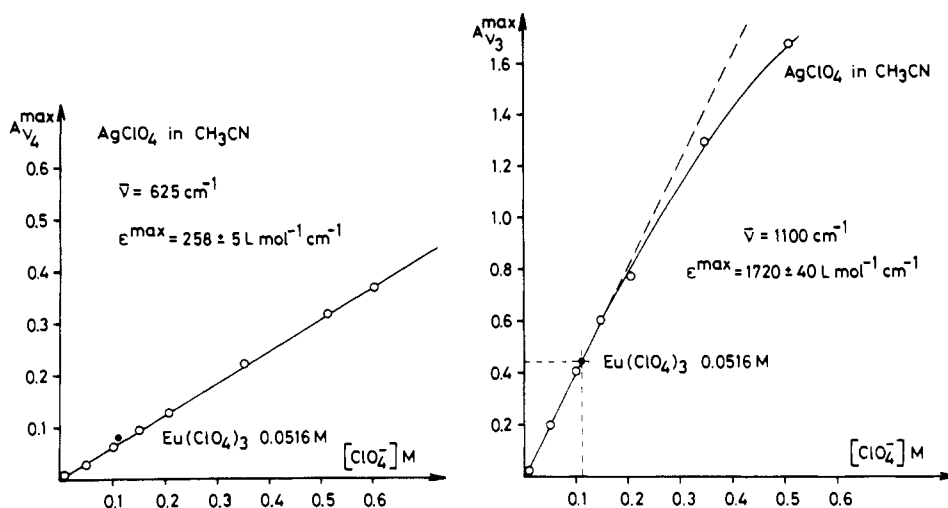
Figure 4. Determination of the molar absorption coefficients of ionic ClO_4^- with $AgClO_4$ in CH_3CN. Black dots represent the absorbances of $Eu(ClO_4)_3$, 0.0516 M in CH_3CN.
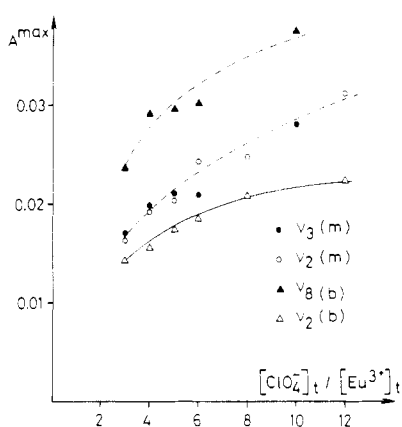

Figure 5. Absorbances of vibrations of $ClO_4^-(m)$ (m, $\bar{\nu}_2 = 933$, $\bar{\nu}_8 = 653$ cm^{-1}) and $ClO_4^-(b)$ (b, $\bar{\nu}_2 = 909$, $\bar{\nu}_8 = 1202$ cm^{-1}) vs. $[ClO_4^-]_t/[Eu^{3+}]_t$; $[Eu^{3+}]_t = 0.0516$ M.

Figure 7. High-resolution fluorescence spectra of the $^5D_0 \rightarrow {}^7F_0$ transition for $Eu(ClO_4)_3$ solutions in CH_3CN vs. $R_t = [ClO_4^-]_t/[Eu^{3+}]_t$; $[Eu^{3+}]_t = 0.05$ M.

Figure 6. Part of the IR spectra of $Ln(ClO_4)_3$ 0.1 M in CH_3OH, showing the simultaneous presence of mono- and bidentate perchlorates.
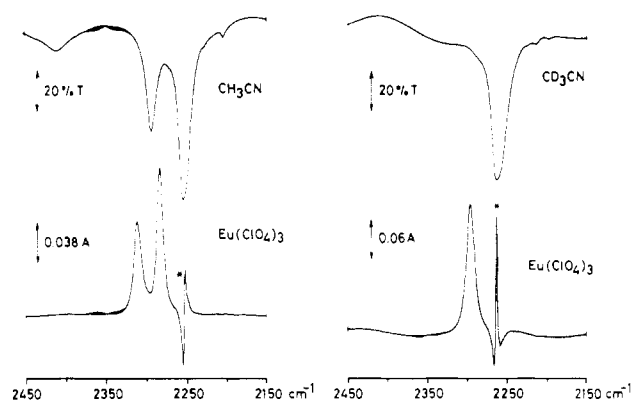

Figure 8. FT IR difference spectra of $Eu(ClO_4)_3$ solutions, 0.05 M in CH_3CN and CD_3CN, showing the $\nu(CN)$ region, along with the transmission spectra of the solvents. Stars denote solvent absorptions that are not completely compensated.

We therefore assign the transition at 5797.0 Å to the inner-sphere complex $[Eu*ClO_4]^{2+}$ and the less energetic transition to the ion pair or to solvated $Eu*^{3+}$ ions since the former may undergo dissociation, the excitation to the $^5D_2$ level corre-

sponding to an energy of 257 kJ mol^{-1}.

Acetonitrile molecules bonded in the inner sphere also give rise to distinct IR absorptions that are shifted toward higher wavenumbers (Table III, Figure 8). The $\nu_3 + \nu_4$ absorption of CH_3CN is particularly well suited for a quantitative determination of the average number of bonded CH_3CN molecules. However, the absorption coefficient cannot be determined directly. We have attempted to estimate $\epsilon(\nu_3 + \nu_4) = \epsilon$ and the average coordination number $\bar{N}$ of the europium ion by measuring $A^{max}(\nu_3 + \nu_4) = A^{35}$ for $Eu(ClO_4)_3$ and
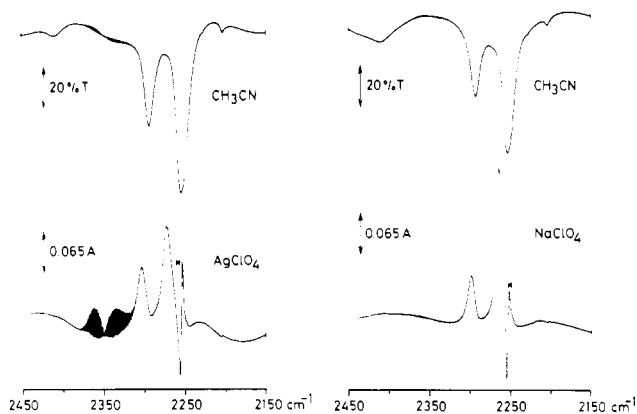
Figure 9. FT IR difference spectra of $AgClO_4$, 0.2 M, and $NaClO_4$, 0.5 M in CH_3CN, showing the $\nu(CN)$ region, along with the transmission spectra of the solvent. Stars denote solvent absorptions that are not completely compensated. The feature around 2350 cm^{-1} arises from traces of CO_2 in the spectrometer.

$Eu(NO_3)_3$ solutions having different total Eu concentrations ($0.05 < c < 0.14$ M). Assuming that $\bar{N}$ and ϵ^{36} are the same for the two systems, we have $A = (\bar{N} - 0.6)\epsilon lc$ for ClO_4^- and $A' = (\bar{N} - 6)\epsilon l'c'$ for NO_3^- since on average 0.6 and 6 coordination sites are occupied by $ClO^{4-}(m)$ and NO_3^-,[37] respectively.[38] The mean values we get are $\bar{N} = 9.1 \pm 0.3$ and $\epsilon = 82 \pm 3$ L mol^{-1} cm^{-1}.[39]

The experimental data reported in this paper are therefore consistent with the presence of nonacoordinated europium ions

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(35) Corrected for slight differences in widths at half-height.

(36) This assumption seems to be reasonable since ($\nu_3 + \nu_4$) of bound acetonitrile molecules is little affected when ClO_4^- is replaced by NO_3^-: it appears at 2311.3 ± 0.5 cm^{-1} (fwhh = 12.0 ± 0.5 cm^{-1}) and at 2309.1 ± 0.8 cm^{-1} (fwhh = 10.5 ± 1 cm^{-1}) in perchlorate and nitrate solutions, respectively. Moreover, the energy difference with respect to ν_2 is constant: 28.1 ± 0.8 and 28.8 ± 0.5 cm^{-1} for $Eu(ClO_4)_3$ and $Eu(NO_3)_3$ solutions, respectively.

(37) The three nitrates are bidentate.[32]

(38) The solvation of NO_3^- does not interfere with the calculation: [(CH_3)_4N]NO_3$ solutions do not exhibit IR bands from bonded acetonitrile molecules.

(39) If all the perchlorate were inner sphere, these values would become $\bar{N}$ = 8.8 ± 0.3 and ϵ 93 $\pm$ 4; the conclusion regarding the average coordination number would not be altered.

in dilute and anhydrous solutions of $Eu(ClO_4)_3$ in acetonitrile. At 0.05 M concentration, the two main species in equilibrium are $[EuClO_4(m)(CH_3CN)_8]^{2+}$ ($\sim 60\%$) and $[Eu(CH_3CN)_9]^{3+} \cdot ClO_4^-(b)$ ($\sim 30\%$). Small amounts of other species are certainly present, but our quantitative data are not precise enough to determine their composition. It does not seem, however, that nonacoordination is general for the Eu(III) ion since we have experimental evidences for the existence of decacoordinated species in other anhydrous solutions.[32]

IR absorptions of CH_3CN molecules bonded to Ag^+ are observed at 928 (ν_4), 2271 (ν_2), and 2303 ($\nu_3 + \nu_4$) cm^{-1}, which correspond to shifts with respect to bulk CH_3CN of 10, 18, and 10 cm^{-1}, respectively. The corresponding absorptions of the sodium solvate are less shifted; they occur at 924, 2265, and 2299 cm^{-1}, respectively. Again, the $\nu_3 + \nu_4$ absorption is best suited for quantitative determinations (cf. Figure 9). The structure of the silver solvate has been recently determined by EPR as being $[Ag(CH_3CN)_4]^+$,[40] which allows us to calculate $\epsilon^{max}(\nu_3 + \nu_4) = 25 \pm 1$ L mol^{-1} cm^{-1}. A similar value of 28 ± 1 is obtained for the sodium solvate (after correction for differences in the width of the bands), which is also comprised of four CH_3CN molecules.[41] These absorption coefficients are roughly 3 times smaller than the coefficient determined above for the trivalent Eu^{3+} ion.

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(40) Alesbury, C. K.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 244.

(41) Perelygin, I. S.; Klimchuk, M. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1973**, *47*, 1138.