(19) Calculations for over 200 reactions by MINDO/3, and about half that number by MNDO, have shown that the errors in the activation energies given by these procedures are no greater on average than those in the heats of formation calculated for stable species. Most of this work has been reported in previous papers of this series and in communications and papers not included in it. For references to the latter, see M. J. S. Dewar, *J. Faraday Discuss. Chem. Soc.*, **62**, 199 (1977); M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, **99**, 7439 (1977); M. J. S. Dewar and C. Doubleday, *ibid.*, **100**, 4935 (1978).

(20) The neglect of 3d AO's for chlorine does not seem to have significant consequences, judging by the results of MNDO calculations for a wide variety of chlorine compounds.[8] The same indeed seems to be true generally for third period elements in their group valence states (P^{III}, S^{II}, Cl^{I}).[5d]

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Fluorescence Spectra and Lifetime Measurements of Aqueous Solutions of Europium Nitrate and Perchlorate

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The relative intensities of the $^5D_0 \to {}^7F_J$ and $^5D_1 \to {}^7F_J$ ($J = 0, 1, 2$) transitions and the fluorescence lifetime of aqueous solutions of europium(III) perchlorate and nitrate are reported. For perchlorate solutions, these data are independent of both the salt (0.01–1 M) and the total perchlorate ($[ClO_4^-]/[Eu^{3+}]$ between 3 and 28) concentrations, reflecting an outer-sphere-type interaction between Eu^{3+} and ClO_4^-. A different situation is met for nitrate solutions: τ varies from 110 μs (salt concentration 0.004 M) to 121 μs (1 M) and to 138 μs ($[ClO_4^-]/[Eu^{3+}] = 53$), reflecting an inner-sphere interaction. The lifetime of $[Eu(NO_3)(H_2O)_n]^{2+}$ amounts to 159 μs and its formation constant is found to be 0.3 ± 0.1 M^{-1} in a 0.1 M aqueous solution of $Eu(NO_3)_3$.

The interaction between lanthanoid ions Ln(III) and NO_3^- in aqueous solutions has been studied by different techniques.[1-12] If the existence of inner-sphere complexes has been unambiguously demonstrated,[3,5,8,11,12] the overall Ln(III)/NO_3^- interaction probably results in the formation of both inner- and outer-sphere complexes.[2,6,7] Attempts have been made to calculate the corresponding association constants.[1,4,6-9] Outer-sphere complexation or ion-pair formation between ClO_4^- and Ln(III) is known,[1,13,14] but the existence of inner-sphere complexes is doubtful and remains controversial.[10,11,14,15] We are currently involved in a thorough investigation of the Ln(III) first coordination sphere in solids[16,17] and in both aqueous and strictly anhydrous solutions by means of spectrophotometric, fluorescence, conductometric, IR, and Raman measurements. A recent note in this journal about complex formation in dilute aqueous solutions of europium perchlorate[18] urges us to present some of the results that we have obtained from fluorescence and conductometric measurements of aqueous solutions of europium nitrate and perchlorate.

Experimental Section

$Eu(NO_3)_3 \cdot 6H_2O$ and $Eu(ClO_4)_3 \cdot 7H_2O$ were prepared from 99.99% Eu_2O_3 (Glucydur) and reagent grade acids (Merck). The europium salts were analyzed as described in ref 19. Solutions of Eu(III) were prepared using triply distilled water; the exact Eu(III) concentration was checked by complexometric titration with EDTA. The excess of NO_3^- or ClO_4^- was obtained by adding $(CH_3)_4NNO_3$ (Fluka, puriss) or $NaClO_4 \cdot H_2O$ (Merck). Degassing the solutions with N_2 or Ar did not influence the fluorescence lifetimes.

Fluorescence spectra were excited at 394 nm ($^7F_0 \to {}^5L_6$) by a Zeiss 450-W Xenon pressure lamp coupled with a Zeiss M-20 monochromator (band-pass used: 4 nm). Control runs of some spectra were recorded using excitation at 465 nm ($^7F_0 \to {}^5D_2$). The samples were put into 1-cm Spectrosil cells which were placed into a high-sensitivity, specially designed probe holder. The fluorescence light was analyzed at 90° with a 0.5-m Czerny-Turner monochromator from Spex Industries (Model 1870) equipped with a 1200 lines/mm grating blazed at 26°45′, with a maximum resolution of 0.02 nm. Light intensity was measured by a RCA 31034c photomultiplier with a cooled Ga–As photocathode (S-20 response, dark count <15 counts/s at 1920 V and −20 °C) coupled to an Ortec photon counting unit. The relative intensities of the $^5D_0 \to {}^7F_{0,1,2}$ transitions were obtained by direct planimetry of the spectra since the response of the spectrofluorimeter is almost constant between 570 and 630 nm; contributions from the $^5D_1$ level fluorescence were evaluated and substracted.

Fluorescence lifetimes were measured using two different setups. (i) The solutions were excited at 592.5 nm ($^7F_1 \to {}^5D_0$) by a flash lamp pumped CMX-4 dye laser from Chromatix containing rhodamine 6G. The pulse length was 1.3 μs with an average power of 30–40 mW at a repetition rate of 10 pulses/s (pps). Light from the $^5D_0 \to {}^7F_4$ transition at 695.0 nm was analyzed as above, except that the output of the PM was connected ($\tau_{RC} < 2$ μs) to a Bruker BC-104 transient recorder coupled to a DL-4000 signal averager from Datalab equipped with a DL-450 microprocessor. The lifetimes were calculated over at least 3 lifetimes after 512 or 1024 accumulations: $\tau = 1/s$, s being the slope of $\ln I = f(t)$. (ii) The Eu(III) ions were excited at ~395 nm ($^7F_0 \to {}^5L_6$) by a Xe flash lamp coupled to the M-20 monochromator. The pulse length was 2–5 μs with an estimated average power of 0.5 mW at 1 pps. The lifetimes obtained measuring the decay of the $^5D_0 \to {}^7F_1$, $^5D_0 \to {}^7F_2$, and $^5D_0 \to {}^7F_4$ transitions were identical with each other and to the lifetimes determined by method (i). All the data reported in the tables are averages of 2–6 determinations on at least two independent samples.

Conductometric measurements were performed at 25.6 ± 0.1 °C using an E-365 conductimeter from Metrohm.

Results and Discussion

The molar conductivity λ_M of 2×10^{-4} M aqueous solutions of $Eu(NO_3)_3$ and $Eu(ClO_4)_3$ are 423 and 435 Ω^{-1} mol^{-1} cm^{-1}, respectively. These data are in good agreement with the known values for the other lanthanoids,[20] which means that both salts are 3:1 electrolytes. When the concentration of the solutions is increased, λ_M decreases and amounts to 336 for 10^{-2} M $Eu(ClO_4)_3$ and 339 for 4×10^{-3} M $Eu(NO_3)_3$, reflecting the formation of outer- and possibly inner-sphere complexes.

Fluorescence spectra and fluorescence lifetimes are very sensitive to the first solvation sphere of the Eu(III) ion and they can be used to study the weak interaction between Eu(III) and different anions. Upon excitation to the $^5L_6$ level, the Eu(III) ions fluoresce mainly from the $^5D_0$ (92–94% of the total fluorescence intensity of europium perchlorate solutions) and from the $^5D_1$ (6–8%) excited states. Weak fluorescence from the $^5D_2$ level (<0.2%) is also observed. The fluorescence spectrum of europium perchlorate (see Figures 1 and 2 and Table I) shows that the aquo ion probably possesses a center

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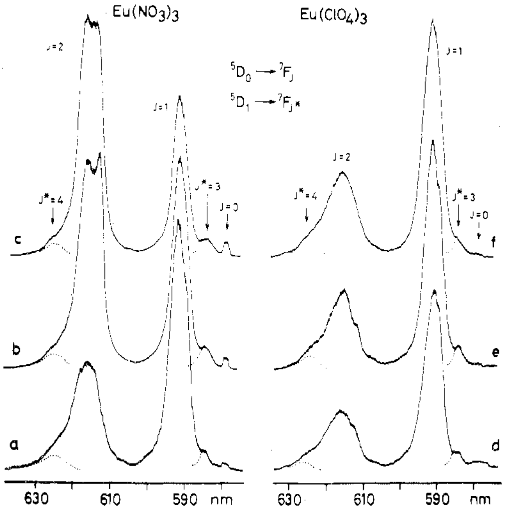

Figure 1. Part of the fluorescence spectra (λ_{exc} 392 nm) of $Eu(NO_3)_3$ and $Eu(ClO_4)_3$ in water: $Eu(NO_3)_3$, (a) 0.01 M, (b) 1 M, (c) 0.1 M + Me_4NNO_3 5 M; $Eu(ClO_4)_3$, (d) 0.01 M, (e) 1 M, (f) 0.05 M + $NaClO_4$ 0.5 M.

Table I. Fluorescence Lifetimes (λ_{exc} 592.5 nm, λ_{obsd} 695.0 nm) and Relative Intensities of the $^5D_0 \rightarrow {}^7F_{1,2}$ and $^5D_1 \rightarrow {}^7F_{0,1,2}$ Transitions (λ_{exc} 394 nm) for Aqueous Solutions of $Eu(ClO_4)_3$

$[Eu^{3+}]$, mol L^{-1}	$[ClO_4^-]$, mol L^{-1}	$^7F_2/{}^7F_1{}^a$ ± 0.05	$^7F_0/{}^7F_1{}^b$ ± 0.03	$^7F_2/{}^7F_1{}^b$ ± 0.3	τ ± 4, μs
0.01	0.03	0.50	0.30	3.0	105
0.02	0.06				107
0.05	0.15	0.57			110
0.10	0.30		0.33	3.0	
0.20	0.60	0.59	0.32	2.9	108
1.0	3.0	0.54			104
0.02	0.56	0.56			110
0.20	1.1	0.54			107
0.20	2.6				102

[a] $^5D_0$ fluorescence; the $^5D_0 \rightarrow {}^7F_0$ transition is not observed. [b] $^5D_1$ fluorescence.

of inversion:[21] the forced electric dipole transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ are not very intense and the forbidden magnetic dipole transition $^5D_0 \rightarrow {}^7F_0$ is indeed not observed;[22] moreover, the allowed magnetic dipole transitions $^5D_1 \rightarrow {}^7F_{0,1,2}$ are well observed. A closer look at the data reveals a more striking feature: the shape and the relative intensities of the fluorescence bands are independent of both the salt and the total ClO_4^- concentrations.[23] Contrary to recently reported results,[18] we did not observe significant changes of the fluorescence lifetimes when the concentrations were increased. Varying λ_{exc}, the excitation power, λ_{obsd}, the purity of the oxide used to prepare the solutions, and the pH by adding $HClO_4$ did not result in variations of the fluorescence lifetimes. This proves that the Eu(III)/ClO_4^- interaction is an outer-sphere type which does not influence the quenching of the excited

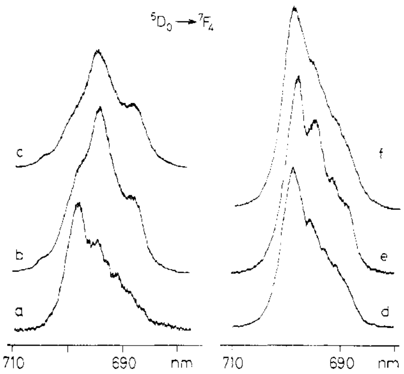

Figure 2. Part of the fluorescence spectra (λ_{exc} 392 nm) of $Eu(NO_3)_3$ and $Eu(ClO_4)_3$ in water. Same concentrations as in Figure 1.

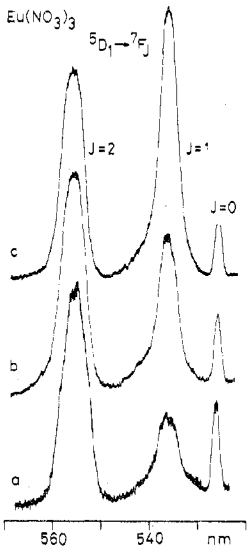

Figure 3. $^5D_1 \rightarrow {}^7F_{0,1,2}$ fluorescence bands of $Eu(NO_3)_3$ solutions in water: (a) 0.01 M, (b) 0.5 M, (c) 0.5 M + Me_4NNO_3 5 M.

Table II. Fluorescence Lifetimes (λ_{exc} 592.5 nm, λ_{obsd} 695.0 nm) and Relative Intensities of the $^5D_0 \rightarrow {}^7F_{0,1,2}$ and $^5D_1 \rightarrow {}^7F_{0,1,2}$ Transitions (λ_{exc} 394 nm) for Aqueous Solutions of $Eu(NO_3)_3$

$[Eu^{3+}]$, mol L^{-1}	$[NO_3^-]$, mol L^{-1}	$^7F_0/{}^7F_1{}^a \times 10^3$	$^7F_2/{}^7F_1{}^a$	$^7F_0/{}^7F_1{}^b$ ± 0.03	$^7F_2/{}^7F_1{}^b$ ± 0.2	τ ± 4, μs
0.004	0.012	4 ± 2	0.57 ± 0.05			110
0.01	0.03	4 ± 2	0.64 ± 0.05	0.31	2.7	108
0.03	0.09	6.5 ± 1.5	0.75 ± 0.05			110
0.05	0.15	7 ± 1.5	0.97 ± 0.08			111
0.10	0.30	8 ± 1.5	0.95 ± 0.08	0.28	2.0	114
0.18	0.54	8.5 ± 1.5	1.0 ± 0.1			114
0.50	1.5	12 ± 1.5	1.3 ± 0.1	0.13	1.8	120
1.0	3.0	15 ± 2	1.5 ± 0.1			121
0.10	0.40	8 ± 1.5	0.95 ± 0.08			114
0.10	0.80	11 ± 2	1.1 ± 0.1			117
0.10	1.3	12 ± 2	1.2 ± 0.1			120
0.10	2.8	20 ± 2	1.6 ± 0.1			130
0.10	5.3	30 ± 2	2.1 ± 0.2			138
0.50	2.5	16 ± 2	1.5 ± 0.1	0.10	1.5	124
0.50	3.5	19 ± 2.5	1.7 ± 0.1			128
0.50	6.5	31 ± 3	2.5 ± 0.1	0.06	0.8	140

[a] $^5D_0$ fluorescence. [b] $^5D_1$ fluorescence.

Eu(III) ions.[24]

A quite different situation is met for europium nitrate solutions. The fluorescence spectrum of the more dilute solutions (see Figures 1–3 and Table II) is similar to the spectra of $Eu(ClO_4)_3$ solutions, with minor changes: a weak band is always observed at 579.5 nm ($^5D_0 \rightarrow {}^7F_0$) and both the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ bands are differently shaped. When the salt concentration or the total NO_3^- concentration is increased above 0.01 M, all of the forced electric dipole transitions are enhanced.[25] The center of symmetry is removed because NO_3^- ions penetrate into the first coordination sphere. This results in a less effective quenching of the excited Eu(III) ions and the fluorescence lifetime increases from 108 μs to 140 μs for the more concentrated solution. The fluorescence lifetime of the mononitrato species $[Eu(NO_3)(H_2O)_n]^{2+}$ amounts to 159 μs,[26] and we can evaluate the association constant K for the inner-sphere process

$$[Eu(H_2O)_9]^{3+} + NO_3^- \rightleftarrows [Eu(NO_3)(H_2O)_n]^{2+} + (9 - n)H_2O$$

from the measured fluorescence lifetimes, if we make known assumptions.[18,26] K amounts to 0.3 ± 0.1 M^{-1} in a 0.1 M solution of $Eu(NO_3)_3$ and to 0.2 ± 0.1 in a 0.5 M solution. These values are in agreement with reported literature data for other inner-sphere $Ln(NO_3)^{2+}$ complexes: $K = 0.53$[4] and 0.54[8] for Ln = Dy; $K = 0.66$[9] for Ln = Pr. For comparison purposes, we should mention that the reported association constants which take into account both inner- and outer-sphere processes range between 2 and 4.[1,6,7]

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Registry No. $Eu(NO_3)_3$, 10138-01-9; $Eu(ClO_4)_3$, 13537-22-9; $Eu(NO_3)^{2+}$, 15974-15-9.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Trifluoromethyl Group 4 Compounds

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The carbon-13 chemical shifts and carbon–fluorine coupling constants for tetrakis(trifluoromethyl) compounds $(CF_3)_4M^{IV}$, where M = C, Ge, and Sn, and tris(trifluoromethyl)(difluoromethyl)methane are reported. The trends in the carbon-13 chemical shifts are the reverse of that expected on the basis of pure electronegativity effects. Correlations between carbon–fluorine coupling constants and both fluorine chemical shifts and the position in the periodic table of the substituents directly attached to the carbon atom are observed for trifluoromethyl derivatives of main-group elements.

Introduction

^{13}C NMR has proved to be a valuable technique for elucidating electronic and structural characteristics of numerous compounds.[1] However, a survey of the literature indicates that there is a paucity of carbon-13 spectral data for perfluorinated compounds and that the theoretical principles and molecular parameters affecting ^{13}C NMR coupling constants and chemical shifts of perfluorinated compounds are often not clearly understood. In an effort to provide new information we have recorded the ^{13}C spectra of the tetrakis(trifluoromethyl) derivatives of the group 4 elements and have compared their ^{13}C and ^{19}F NMR spectral data with that of other trifluoromethyl derivatives of main-group elements.

Experimental Section

The tetrakis(trifluoromethyl) compounds $(CF_3)_4C$,[2] $(CF_3)_4Ge$,[3] and $(CF_3)_4Sn$[4] were prepared by methods developed in our laboratory. $(CF_3)_3CCF_2H$ was obtained from the direct fluorination of $(CH_3)_4C$ and purified by gas chromatography on a SE-30 column.

The natural-abundance carbon-13 spectra were obtained on a Bruker WH-90 (FT mode) spectrometer operating at a resonance frequency of 22.615 MHz. The spectrum of $(CF_3)_3CCF_2H$ was determined with proton noise decoupling. In order to obtain the chemical shift of the central carbon of $(CF_3)_4C$, a fluorine-decoupled carbon-13 spectrum was measured on a Thompson Packard TPV-XLFT-100 (FT mode) spectrometer operating at 25.2 MHz.

The $(CF_3)_4Sn$ and $(CF_3)_4Ge$ compounds were sealed in 5-mm tubes as neat liquids, and the tubes were placed coaxially in 10-mm tubes containing $CDCl_3$, which served as an external lock. (Chemical shifts were converted to the Me_4Si scale by $\delta(Me_4Si) = \delta(CDCl_3) + 77.7$.) The $(CF_3)_4Sn$ ^{13}C NMR spectrum was recorded at 0 °C to prevent decomposition of the sample. The spectrum of $(CF_3)_4Ge$ was recorded at 23 °C. Both $C(CF_3)_4C$ and $(CF_3)_3CCF_2H$ were sealed in 8-mm tubes containing cyclohexane as an internal reference. (Chemical shifts were converted to the Me_4Si scale by $\delta(Me_4Si) = \delta(C_6H_{12}) + 27.8$.) The 8-mm tubes were placed coaxially in 10-mm tubes

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