

Spectroscopic Properties of Anhydrous and Aqueous Solutions of Terbium Perchlorate and Nitrate: Coordination Numbers of the Tb(III) Ion*

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The fluorescent properties of $Tb(ClO_4)_3$, $Tb(NO_3)_3 \cdot 6H_2O$, and $Tb(NO_3)_3$ are reported. The lifetime of anhydrous $Tb(NO_3)_3$ depends strongly on its preparation mode. In $Tb(NO_3)_3 \cdot 6H_2O$, only three water molecules are directly bonded to the 9-coordinated Tb(III) ion. Aqueous solutions of TbX_3 have lifetimes of 0.467(3), 0.470(5), and 0.478(2) ms for $X = ClO_4^-$, Cl^- and NO_3^- , respectively. The nitrate solution is sensitive to light exposure and care must be exercised when Tb(III) is used as a spectrofluorimetric probe.

The excitation and emission spectra, lifetimes, and energy transfer efficiencies to Nd(III) ions of anhydrous solutions of $Tb(ClO_4)_3$ and $Tb(NO_3)_3$ in CH_3CN , $(CH_3)_2CO$, DMF, DMSO, TMSO, and isopropanol are reported. The following affinity sequence was found: $NO_3^- > DMSO > DMF \sim H_2O > (CH_3)_2CO > CH_3CN$. In the presence of an excess of nitrate, the 10-coordinated species $Tb(NO_3)_3^{2-}$ form in CH_3CN but not in DMF. The 9-coordinated complexes $Tb(NO_3)_3(DMSO)_3$ and $Tb(NO_3)_3(H_2O)_3$ have been evidenced in CH_3CN . The addition of water (or isopropanol) to $Tb(ClO_4)_3$ solutions in CH_3CN probably leads to the formation of 8-coordinated species. The coordinative properties of Ln(III) ions are governed by a delicate balance between electrostatic interactions and steric effects.

Introduction

For rare-earth ions high coordination numbers are common and, in solution, equilibria between

differently coordinated species can occur [3]. The problem of determining the coordination numbers of Ln(III) ions in solution has been addressed by many authors using a wealth of different techniques. However, due to the above-mentioned complex situation the problem has not yet received a definitive answer, except in the case of water for which a change in coordination number across the lanthanide series has been determined by X-ray crystallography [4]. Few studies refer to anhydrous solvents and we have therefore initiated a systematic investigation of the solvation of Ln(III) ions in these solvents by means of spectrofluorimetry, lifetime measurements and vibrational spectroscopy. In previous papers we have dealt with the solvation of the Eu(III) ion in acetonitrile [5], dimethylsulfoxide (DMSO) [6], and N,N-dimethylformamide (DMF) [1]. In the present communication we present a spectrofluorimetric study of strictly anhydrous solutions of terbium perchlorate and nitrate in acetonitrile, acetone, DMF, DMSO, tetramethylenesulfoxide (TMSO), and isopropanol. Fluorescence data for the anhydrous and hydrated salts and for their aqueous solutions are also included and discussed. The terbium ion was chosen because its coordinative properties are intermediate between those of the lighter and of the heavier lanthanide ions, and because it is often used as a spectroscopic probe in systems of biological interest [7]. Its ground state is 7F_6 and emission of light can arise from the transitions originating from the 5D_3 and 5D_4 excited states. In solution, the fluorescence from 5D_3 is usually weak because of a very efficient non-radiative de-excitation path between 5D_3 and 5D_4 , the energy difference being dissipated in the vibrations of the solvent [8]. The fluorescence spectra, quantum yields and lifetimes of Tb(III) solutions in aqueous CH_3CN , DMF, DMSO, pyridine, methanol, and n-propanol have been reported by several authors [9–12]. The inner- and outer-sphere complexes formed by terbium

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TABLE I. Fluorescence Lifetimes [ms] at Room Temperature of some Terbium Salts ($^5D_4 \rightarrow ^7F_5$ Transition; Excitation: 336–364 nm; Standard Deviation between Parentheses).

Salt	τ_f	Salt	τ_f
Tb(NO ₃) ₃ ·6H ₂ O	0.65(1)	A ₂ Tb(NO ₃) ₅ ^a	1.82(4)
Tb(NO ₃) ₃	1.28(3) ^b	TbCl ₃ ·6H ₂ O	0.48 [16]
	0.91(2) ^c	Tb(ClO ₄) ₃	2.99(7)

^aA = N(CH₃)₄⁺. ^bPrepared at 80 °C. ^cPrepared at 180 °C.

ions in non-aqueous solvents have been investigated by means of their fluorescence lifetimes [13]. These experiments lead to the establishment of an affinity sequence of the Tb(III) ion for various donors: acetonitrile < n-propanol < acetone < DMF < methanol ~ pyridine < water. In the present work we intended to determine the composition of the main solvated species in solution and, therefore, the coordination number of the Tb(III) ion.

Experimental

Preparation of the Solutions

Anhydrous Tb(ClO₄)₃, Tb(NO₃)₃, and Nd(ClO₄)₃ were prepared from the oxides (99.99%, Glucydur) as previously described for the europium salts [1, 14]. Dehydration was performed under high vacuum (10⁻⁵ mmHg) by heating stepwise to 80–180 °C. **Caution: any impurities such as traces of acid or grease must be carefully avoided to prevent an explosion while heating perchlorates.** The purity of the salts was controlled by complexometric analyses, by their IR spectra, and by their fluorescence lifetimes. The solvents CH₃CN, DMF, DMSO, TMSO and i-propanol (all from Fluka, either puriss or of spectroscopic quality) were carefully dried before use. NMe₄NO₃, NaNO₃, and NaClO₄ (Merck, p.a.) were dehydrated under vacuum (10⁻² mmHg/80 °C). All the solutions were prepared under a strictly controlled atmosphere (N₂ with less than 10 ppm water); their Ln-content was determined by complexometric analyses after completion of the measurements.

Spectroscopic Measurements

Fluorescence spectra and lifetimes were measured using the instrumentation previously described [5, 14]. For lifetime determinations a Xe-flash lamp coupled with a UG5 filter was used, resulting in an excitation spectral range of 336–364 nm. The relative intensities of the fluorescence bands were determined by planimetry and manually corrected

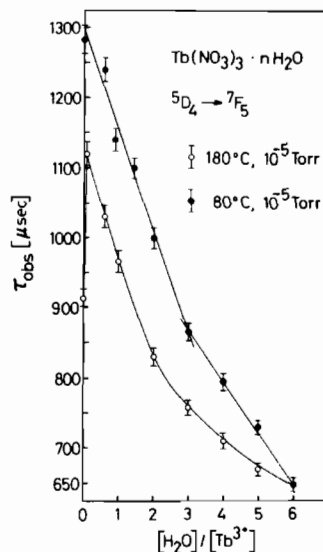


Fig. 1. Lifetimes, at room temperature, of Tb(NO₃)₃·nH₂O versus n and versus the heating temperature (excitation: 336–364 nm, analysis: 545 nm).

for the mean instrumental function of the spectrometer at the barycentre of the bands. IR spectra were performed with a Bruker IFS-113c interferometer and Raman spectra were recorded with a Ramalog-4 spectrometer from Spex Industries. The reported results are averages of measurements taken on at least two independently-prepared solutions.

Results and Discussion

Fluorescent Properties of Terbium Salts and of their Aqueous Solutions

The fluorescence of the lanthanide ions is readily quenched by the presence of water molecules in the first coordination sphere [15], so that fluorescence lifetimes provide an analytical test to detect the presence of water in solutions or salts under investigation [5]. We have found that the lifetime of Tb(NO₃)₃ depends strongly on its preparation mode (Table I). When heated under high vacuum Tb(NO₃)₃·6H₂O gradually loses its hydration molecules: τ_f increases strongly and its final value depends on the heating temperature (Fig. 1). The chemical analyses of samples prepared at various temperatures are identical; therefore, the explanation for the discrepancy must be sought in differences in their solid state structure, as the IR and Raman spectra indeed display substantial differences in the N–O stretch region. Both samples, however, yield aqueous solutions with identical optical properties. All the Tb(NO₃)₃ samples used for this work were produced using low-temperature heating. The break at n = 3 in the upper curve of Fig. 1 may indicate that only

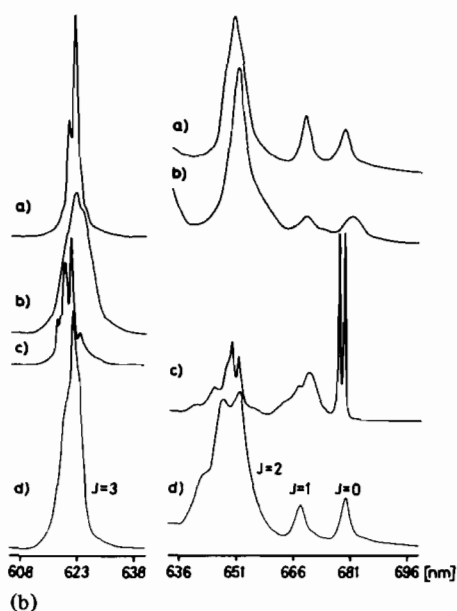
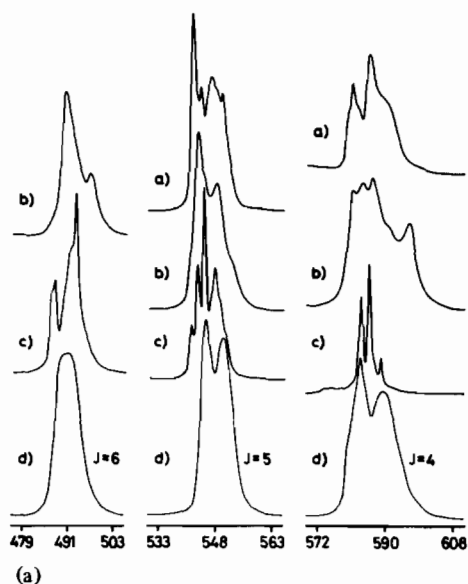


Fig. 2. Emission spectra, at room temperature, of solid samples of a) $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (excitation: 488 nm), b) $(\text{NMe}_4)_2\text{Tb}(\text{NO}_3)_5$, c) anh. $\text{Tb}(\text{ClO}_4)_3$, and d) anh. $\text{Tb}(\text{NO}_3)_3$ (excitation: 371 nm; vertical scale: arbitrary units).

three water molecules are bonded in the first coordination sphere of the Tb(III) ion in $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The quenching efficiency of these molecules is greater, as indicated by the larger slope of τ_f vs. n for $n < 3$. A plot of τ_f/τ_0 vs. n , where τ_0 is the fluorescence lifetime of the nonhydrate (0.42 ms [16]) also yields two straight lines which intersect at $n = 2.9$. Moreover, the lifetime of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is substantially longer than that of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$.

If we assume the presence of bidentate nitrates, the coordination number of the Tb(III) ion would be equal to 9. The crystal structures of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are known for $\text{Ln} = \text{La} - \text{Sm}$; for La and Ce, five water molecules are bonded to the metal ion which is 11-coordinated [17]; for $\text{Ln} = \text{Pr} - \text{Sm}$, the hexahydrates are isostructural [18] and four water molecules are bonded to the 10-coordinated rare-earth ions [19]. The lifetime of the anhydrous nitrate is shorter than that of the perchlorate since radiationless de-excitations occur through the nitrate vibrations; when the nitrate groups lie further apart, as it is the case in the pentanitrates, the efficiency of the quenching is reduced and the lifetime increases. The emission spectra of the salts are reported in Fig. 2. The lifetimes of diluted aqueous solutions of terbium salts reported in the literature span a range from 0.38 [20] to 0.48 ms [11]; these differences are clearly too large to be explained by the effect of the anion alone, especially when for the same anion quite different values are reported. At pH 2, we have observed reproducible lifetimes of 0.467(3), 0.470(5), and 0.478(2) ms for freshly prepared 0.1 M solutions of perchlorate, chloride, and nitrate respectively. At pH 5, the lifetime of the nitrate solution decreases with the aging of the solution. Moreover, the fluorescence is quenched upon exposure of the solution to UV-VIS light: an irradiation of 5 minutes by photons with $\lambda > 300$ nm results in a lifetime of 0.28 ms, while more energetic photons ($\lambda > 200$ nm) lead to the complete disappearance of the emission spectrum. A less severe quenching occurs if the solution is heated in the dark: $\tau_f = 410$ ms after 24 h at 60 °C. The original emission spectrum and lifetime are retrieved when the pH of the solution is lowered to 2. At pH 2 these phenomena also occur, but to a much lesser extent: a drop of only 6% is observed in τ_f after a one-hour irradiation by UV-VIS light. The addition of nitrate to the solutions increases the quenching, which means that this species is implied in the quenching mechanism. Indeed, it is known that in aqueous solutions, nitrate ions can be photochemically reduced to nitrite ions in the presence of a sensitizer [21], and that these latter ions quench the terbium fluorescence [22]. In our case, Tb(III) would serve as the sensitizer: the energy of its excited states $^5\text{D}_J$, $^5\text{G}_J$, and $^5\text{L}_J$ are, indeed, well above the one-electron reduction potential of nitrate [21]. Care must therefore be exercised when Tb(III) is used as a spectrofluorimetric probe in systems which may potentially contain nitrate groups.

Fluorescent Properties of $\text{Tb}(\text{ClO}_4)_3$ and $\text{Tb}(\text{NO}_3)_3$ in Anhydrous Solutions

The excitation and emission spectra, lifetimes, and energy transfer efficiencies of $\text{Tb}(\text{ClO}_4)_3$ and $\text{Tb}(\text{NO}_3)_3$ in various organic solvents were studied

TABLE II. Energy (cm^{-1}) of the Excited Levels of Tb(III) in Anhydrous Solutions of $\text{Tb}(\text{ClO}_4)_3$ and $\text{Tb}(\text{NO}_3)_3$ 0.1 M in Various Solvents, as Obtained from the Excitation Spectra at Room Temperature (analysis: 545 nm).

Level ^a	$\text{Tb}(\text{ClO}_4)_3$		$\text{Tb}(\text{NO}_3)_3$			
	CH_3CN	DMSO	CH_3CN	DMSO	TMSO	DMF
⁵ D ₄	20,491	20,491	20,576	20,533	20,491	20,491
⁵ D ₃	26,246	26,315	26,315	26,315	26,315	26,246
⁵ G ₆	26,385	26,455	b	26,455	26,385	26,385
⁵ L ₁₀	27,027	27,027	27,027	27,027	27,027	27,027
⁵ G ₅	27,777	27,855	b	27,885	27,777	27,777
⁵ D ₂	28,169	b	28,169	b	b	b
⁵ G ₄	28,248	28,248	b	b	b	28,248
⁵ L ₉	28,490	28,409	28,409	28,409	28,409	28,376
⁵ G ₃	28,901	b	b	b	b	28,901
⁵ L ₈	29,239	29,154	29,154	29,154	29,154	29,154
⁵ L ₇	29,411	29,411	b	b	b	b
⁵ L ₆ , ⁵ G ₂	b	29,673	b	b	b	b
⁵ D ₁	30,581	30,395	30,581	b	b	30,487

^aAssignment according to [23]. ^bNot observed.

TABLE III. Emission Wavelengths (nm, ⁵D₄–⁷F_J Transitions) of Anhydrous Solutions of Tb(III) 0.002–0.5 M in Various Solvents (excitation: 371 nm).

J	$\text{Tb}(\text{ClO}_4)_3$			$\text{Tb}(\text{NO}_3)_3$				
	CH_3CN	$\text{C}_3\text{H}_8\text{OH}$	DMSO	CH_3CN	$\text{C}_3\text{H}_8\text{OH}$	DMSO	TMSO	DMF
6	489.3	489.2	489.8	488.3 ^a	490.1	489.2	489.8	489.7
	494.4 ^a	495.5 ^a	495.8 ^a	490.2		494.6 ^a	494.3 ^a	491.8 ^a 492.3 ^a
5	543.8	543.6	546.2	541.7	543.3	543.2 ^a	543.2 ^a	542.9 ^a
	545.9	545.0 ^a	550.4	543.5	545.0	545.0	544.4	544.4
4		548.6 ^a	552.2 ^a	545.9 ^a	550.1 ^a	548.3 ^a	548.0 ^a	548.0 ^a
	583.4	584.6	575.6	583.1	584.6	575.3	582.8	575.0
3	588.5 ^a	588.5	582.8	584.6 ^a	589.4 ^a	582.5	588.8 ^a	582.8
			589.4	590.0 ^a		589.1		588.6
2	619.4	622.2	618.8	613.4 ^a	622.4	619.1 ^a	619.1 ^a	619.2 ^a
	620.4		621.8	617.6		621.2	621.6	621.9
1			627.2					623.1
	646.5	651.0	648.0	643.5 ^a	648.9	647.4	647.4	647.1
0			657.0 ^a	647.1		654.9 ^a	654.0 ^a	651.6 ^a
	666.0	669.6	663.0 ^a	664.9	668.7	669.6	664.8 ^a	668.2
0			670.0			669.6	669.6	
	676.5	682.9	677.4 ^a	675.0	679.2	678.1 ^a	678.0 ^a	678.9
	678.0 ^a		679.9			679.5	680.1	

^aShoulder.

in order to establish the affinity sequence of these donors for the Tb(III) ion under strictly anhydrous conditions. The excitation spectra are reported in Table II and an example is shown in Fig. 3. As expected, the energy shifts are small (70–85 cm^{-1}) when the perchlorate ion is replaced by the

nitrate ion. The fluorescence spectra show more substantial differences (Fig. 4, Table III). Emission from the ⁵D₄ level only was observed, and the relative intensities of the bands do not depend upon the excitation wavelength (Table IV). The weak transitions to the ⁷F₀ and ⁷F₁ levels are the most sensitive

TABLE IV. Relative Corrected Intensities of the $^5D_4-^7F_J$ Transitions for Anhydrous Solutions of Tb(III) 0.02–0.5 M in Various Solvents (excitation: 1 = 371 nm and 2 = 488 nm).

J	Tb(ClO ₄) ₃				Tb(NO ₃) ₃	
	DMSO		CH ₃ CN		DMSO	CH ₃ CN
	1	2	1	2	1	1
6	0.210	^a	0.270	^a	0.200	0.180
5	1.000	1.000	1.000	1.000	1.000	1.000
4	0.370	0.390	0.420	0.450	0.270	0.230
3	0.250	0.250	0.240	0.230	0.180	0.160
2	0.058	0.057	0.036	0.036	0.034	0.041
1	0.077	0.080	0.023	0.025	0.023	0.007
0	0.072	0.069	0.022	0.022	0.022	0.009

^aTransition not observed.

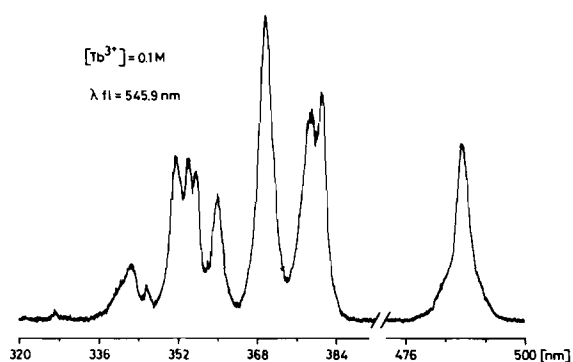


Fig. 3. Excitation spectrum of an anhydrous solution of Tb(ClO₄)₃ 0.1 M in CH₃CN (analysis: 545.9 nm; vertical scale: arbitrary units).

to changes in the first coordination sphere. A comparison of the data for the perchlorate and nitrate solutions clearly indicates that a strong interaction takes place between the nitrate and the Tb(III) ions in both CH₃CN and DMSO.

In order to study the relative affinity of the donors for the Tb(III) ion, we have measured the energy transfer to the Nd(III) ion [25]. The results are presented in Table V, along with the fluorescence lifetimes of the anhydrous terbium solutions. These do not vary with the excitation nor with the analysis wavelengths, and single exponential decays were always observed. The smaller fluorescence lifetimes of the nitrate solutions clearly reflect the presence of nitrate ions in the first coordination sphere. The energy transfer is also more efficient in the nitrate solutions: in such a process, the donor–acceptor distance is determinant and the solvated species can come in closer contact when their ionic charges are smaller. In acetonitrile, all the nitrate ions are coordi-

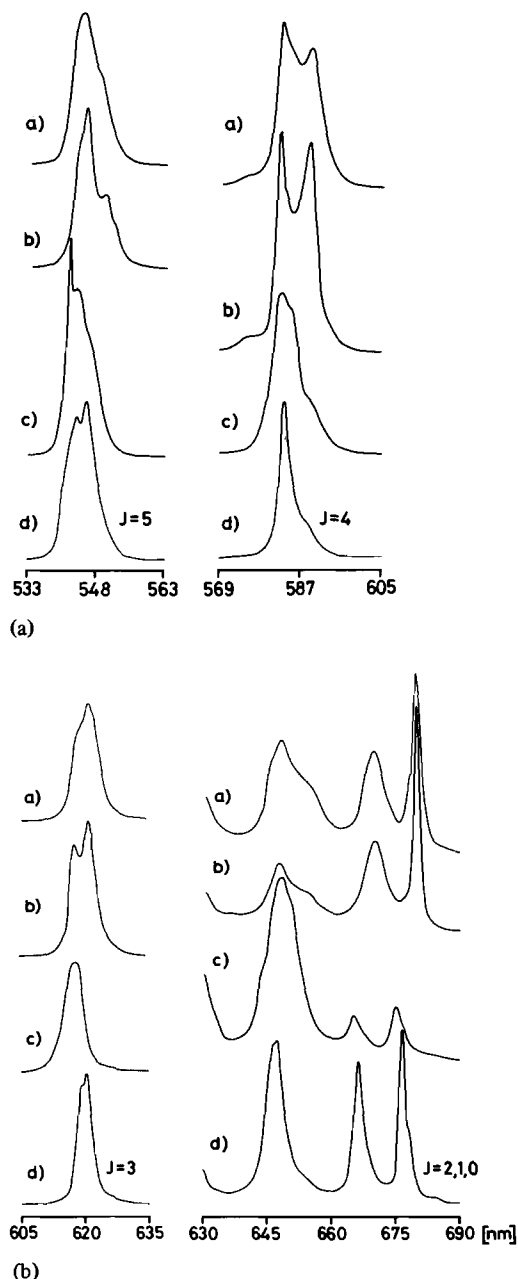


Fig. 4. $^5D_4-^7F_3$ transitions for anhydrous solutions of 0.02–0.05 M in DMSO (a: Tb(NO₃)₃, b: Tb(ClO₄)₃) and CH₃CN (c: Tb(NO₃)₃, d: Tb(ClO₄)₃); excitation: 371 nm; vertical scale: arbitrary units; the intensities of the spectra are not directly comparable).

nated (*vide infra*) and the energy-transfer yield is maximum. For the perchlorate solutions, no transfer occurs in DMSO and TMSO, while some transfer is observed in the other solvents, in agreement with the previously reported observation of inner- and outer-sphere interactions between the perchlorate and Eu(III) ions in CH₃CN [5] and DMF [1]. When the

TABLE V. Lifetimes [ms] and Yields of the Energy Transfer, η , between the Tb(III) and Nd(III) Ions for Various Anhydrous Solutions of Terbium Salts, at Room Temperature (excitation: 336–364 nm, analysis: 545 nm; [Tb] = 0.003–0.1 M; [Ln] = 0.75 [Tb] + 0.25 [Nd] = 0.02 M; $\eta = (1 - \tau_f/\tau_0)$ [24]; standard deviations between parentheses).

Solvent	Tb(ClO ₄) ₃	Ln(ClO ₄) ₃		Tb(NO ₃) ₃	Ln(NO ₃) ₃	
	τ_0	τ_f	η	τ_0	τ_f	η
CH ₃ CN	2.42(6)	2.00	0.17	1.87(5) ^a	0.29	0.84
(CH ₃) ₂ CO	2.13(5)	1.76	0.17	1.74(4)	0.94	0.46
DMSO	2.71(7)	2.64	0.03	2.61(7)	2.36	0.10
TMSO	1.48(4)	1.48	0	1.48(4)	1.29	0.13
DMF	2.35(6)	1.85	0.21	1.86(5)	1.26	0.32

^a0.003–0.04 M; a concentration quenching is observed: $\tau_0 = 1.60$ ms for a 0.1 M solution.

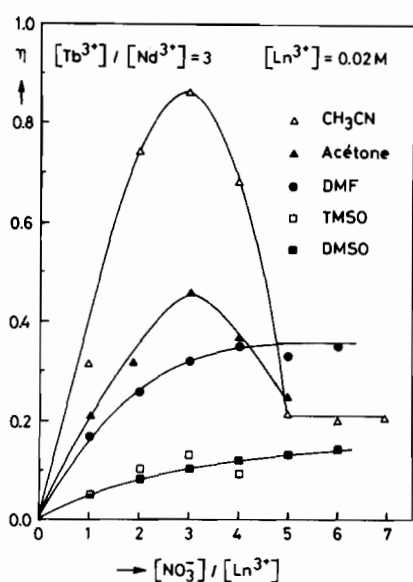


Fig. 5. Yields of the energy transfer between the Tb(III) and Nd(III) ions in anhydrous solutions of terbium salts, versus the nitrate concentration.

yield of the energy transfer is plotted versus the nitrate concentration (Fig. 5), one clearly observes maxima in the case of CH₃CN and acetone. There are no maxima for DMF and DMSO, which means that anionic nitrate complexes do not form easily in these solvents. From these results the following affinity sequence for the Tb(III) ion in anhydrous solutions can be inferred: DMSO > DMF > (CH₃)₂CO > CH₃CN. The affinity for DMSO and for TMSO seems to be about the same.

Solvation of the Tb(III) Ion in Anhydrous Acetonitrile and DMF

The molar conductivity, at 25 °C, Λ_M , of a 0.001 Tb(NO₃)₃ solution is equal to 11 ohm⁻¹·cm²·mol⁻¹

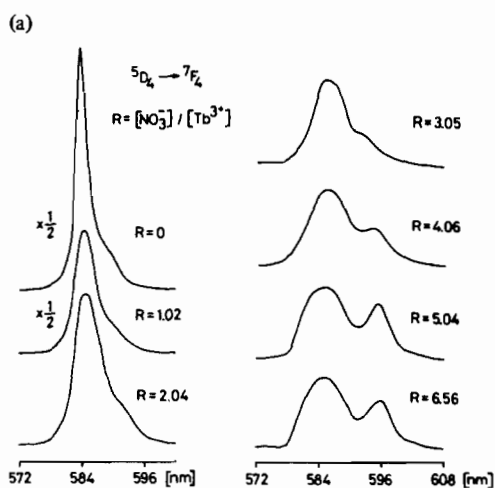
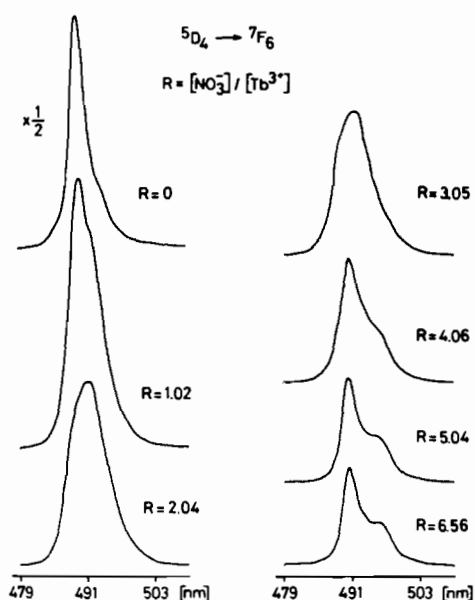


Fig. 6. Effect of the nitrate concentration on some emission bands of Tb(ClO₄)₃ 0.02 M in anhydrous CH₃CN ($R = [\text{NO}_3^-]/[\text{Tb(III)}]$, excitation: 371 nm).

TABLE VI. Relative Intensities of the $^5D_4-^7F_J$ Transitions and Fluorescence Lifetimes [ms] for $Tb(ClO_4)_3$ Solutions 0.02 M in Anhydrous CH_3CN versus the Ratio $R = [NO_3^-]/[Tb(III)]$ (excitation: 371 nm or 336–364 nm (lifetimes); standard deviations in parentheses).

R	Relative intensities, J =				τ_f
	6	5	4	3	
0	1.00	1.00	1.00	1.00	2.42(6)
1.02	1.17(6)	0.92(5)	1.33(7)	1.16(6)	2.05(5)
2.04	1.36(7)	0.91(5)	1.68(8)	1.38(7)	1.93(5)
3.05	1.89(8)	1.07(5)	2.5(1)	1.70(8)	1.81(5)
4.06	2.7(1)	1.36(7)	4.1(2)	2.3(1)	1.68(4)
5.04	3.6(2)	1.69(8)	5.9(3)	2.9(1)	1.68(4)
6.56	3.6(2)	1.81(9)	5.9(3)	3.4(2)	1.68(4)

and is typical of a non-electrolyte [26]; at lower concentration (0.0002 M), Λ_M increases to 20.5 $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. The vibrational data (FT-IR and Raman) are identical to those of similar Eu(III) solutions and imply the presence of bidentate nitrates [2]. The addition of up to 10 molecules of water per Tb(III) ion does not modify the conductivity of the solutions or the IR spectra, which means that no dissociation of the nitrates occurs and, consequently, that the affinity of Tb(III) is larger for the nitrate ion than for water. The changes in the emission spectra of a $Tb(ClO_4)_3$ solution have been monitored as a function of the ratio $R = [NO_3^-]/[Tb(III)]$ (Fig. 6, Table VI). All the emission bands experience an increase of intensity up to $R = 5$ and no significant change is observed when the nitrate concentration is further increased. The fluorescence lifetimes behave slightly differently: τ_f decreases up to $R = 4$ and then remains constant; a Stern-Völmer plot [27] yields an intersection at $R = 4.1 \pm 0.3$. This could be interpreted as resulting from an equilibrium between tetra- and penta-nitrato species. Infrared spectra, however, only show the presence of ionic nitrate when R is larger than 5, and the yield of the energy transfer to the Nd(III) ion (Fig. 5) remains constant for $R > 5$. We therefore conclude that these data demonstrate the formation of the 10-coordinated pentanitrato species $[Tb(NO_3)_5]^{2-}$.

The salt $(Me_4N)_2Tb(NO_3)_5$ can be readily crystallized out of the solutions with $R > 5$. The Stern-Völmer quenching rate constant* calculated using the lifetime data are consistent with the inner-sphere association [28] of the nitrate ions: $k(\tau) = 5.0(5) \text{ l}\cdot\text{mol}^{-1}$. We have tried to determine the number of solvent molecules bonded to the Tb(III) ion by

*This constant is the slope of the straight line: $(\tau_0 - \tau_f)/\tau_f = k(\tau)[Q]$, Q being the quenching molecule.

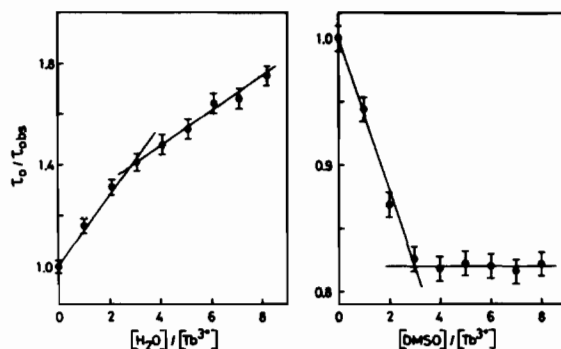


Fig. 7. Stern-Völmer plots for $Tb(NO_3)_3$ 0.02 M in CH_3CN , vs. water and DMSO concentrations (excitation: 336–364 nm; analysis: 545 nm).

substituting the CH_3CN molecules by DMSO and water which are better donors. The lifetime data are shown in Fig. 7. For DMSO they clearly indicate the formation of the non-coordinated species $Tb(NO_3)_3\cdot(DMSO)_3$, as in the case of the europium ion [6]; when the DMSO concentration is increased, the nitrate ions begin to be expelled from the inner coordination sphere and τ_f increases from 2.25(6) ms ($[DMSO]/[Tb(III)] = 15$) to 2.61 ms ($Tb(NO_3)_3$ in DMSO). The interpretation of the data obtained with water is less clear although a break in the Stern-Völmer plot is observed at $[H_2O]/[Tb(III)] = 3$: at higher water concentrations, the lifetime continues to decrease. This may be interpreted in three ways: (i) The additional water molecules penetrate in the outer coordination sphere of the metal ion and influence its fluorescent properties by the formation of hydrogen bonds with molecules or ions bonded in the first coordination sphere. (ii) The nitrate ions are substituted by the water molecules: both the IR and conductivity data reported above preclude such an explanation, at least as long as $[H_2O]/[Tb(III)] < 10$. (iii) The hypotheses on which Stern-Völmer plots are based are no more valid:

$$\tau_0 = (k_{rad} + k_{nrad})^{-1}$$

$$\tau_f = (k_{rad}^n + k_{nrad}^n + k_2[Q])^{-1},$$

and

$$\tau_0/\tau_f = (k_{rad}^n + k_{nrad}^n)/(k_{rad} + k_{nrad}) + k_2[Q]/(k_{rad} + k_{nrad})$$

n is the number of quenching molecules Q bonded to the metal ion, and τ_0 is the lifetime when $n = 0$. If $(k_{rad}^n + k_{nrad}^n)$ remains constant and does not depend on n , if all the molecules have the same quenching effect, and if the donor strength of Q is

TABLE VII. Relative Intensities of the $^5D_4-^7F_J$ Transitions and Fluorescence Lifetimes [ms] for $Tb(ClO_4)_3$ Solutions 0.05 M in Anhydrous DMF versus the Ratio $R = [NO_3^-]/[Tb(III)]$ (excitation: 371 nm or 336–364 nm (lifetimes); standard deviations in parentheses).

R	Relative intensities, J =				τ_f
	6	5	4	3	
0	1.00	1.00	1.00	1.00	2.33(6)
0.9	1.17(6)	1.07(5)	1.11(5)	1.11(5)	2.19(5)
1.8	1.26(6)	1.11(5)	1.26(6)	1.18(6)	2.07(5)
2.8			1.41(7)	1.31(6)	1.96(5)
3.8	1.41(7)	1.16(6)	1.53(8)	1.37(7)	1.89(5)
5.8	1.39(7)	1.14(6)	1.64(8)	1.37(7)	1.85(5)
9.6			1.77(9)	1.42(7)	1.85(5)

much larger than that of the substituted molecules, then τ_0/τ_f vs. $[Q]$ is comprised of two straight lines, one of which is horizontal. Their intersection gives the number of quenching molecules bonded in the inner coordination sphere. If one of the above-mentioned conditions is not valid, a curve is obtained. A similar experiment was performed on $Tb(ClO_4)_3$. Again, the Stern-Völmer plot does not present a clearcut break; the intersection of the two limiting straight lines occurs at $[H_2O]/[Tb(III)] \sim 8$, but the imprecision is too large to determine the coordination number with certainty. Part of the problem arises because perchlorate ions are bonded in the first coordination sphere [29]. An almost identical plot is obtained when *i*-propanol is added to the $Tb(ClO_4)_3$ solution, with a break around $[i\text{-prop}]/[Tb(III)]$ equal to 8.

The molar conductivity at 25 °C, Λ_M , of a 0.001 M solution of $Tb(ClO_4)_3$ in anhydrous DMF is $202 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ and is typical of a 3:1 electrolyte [26]. At higher concentration, Λ_M decreases to $135 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ for a 0.05 M solution, which reflects that some interaction takes place between the $Tb(III)$ and perchlorate ions: the accepted range for 2:1 electrolytes is $140\text{--}170 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ [26]. The emission spectra and lifetimes are independent of the added ClO_4^- concentration, so that this interaction is not expected to correspond to the formation of contact ion-pairs but rather to an outer-sphere complexation. The conductivity of 0.0002, 0.0005, 0.001, 0.002, 0.005, and 0.05 M solutions of $Tb(NO_3)_3$ are 163, 132, 107, 86, 66, and $29 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, respectively. The solutions we have investigated by emission spectroscopy were 0.05 M, that is, intermediate between 1:1 (accepted range: $65\text{--}90 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ [26]) and non-electrolytes. FT-IR spectra show the presence of both ionic (about 20%) and bidentate nitrate ions in these solutions. To study the inner-sphere interaction between

the $Tb(III)$ and nitrate ions we have added increasing quantities of nitrate to a $Tb(ClO_4)_3$ solution. The data are reported in Table VII. The quenching rate constant $k(\tau)$ is equal to $1.3(1) \text{ l} \cdot \text{mol}^{-1}$; it is smaller than in CH_3CN , in agreement with the stronger donor strength of DMF. Both the intensity and lifetime data indicate that pentanitrate species do not form in the solutions we studied. The Stern-Völmer plots point to the presence of an equilibrium between tri and tetranitrate species when $R > 4$. The $Tb(III)/NO_3^-$ interaction is stronger than the $Eu(III)/NO_3^-$ interaction [1], but our data do not allow a quantitative evaluation.

Conclusions

In water Habenschuss & Spedding found slightly different mean coordination numbers for $Eu(III)$ (8.3) and $Tb(III)$ (8.0) [4]. In anhydrous solvents, we have found smaller differences in the coordinative properties of these two ions. With a small bidentate ligand such as NO_3^- , 10-coordinated stable pentanitrate species can be formed with both ions, in acetonitrile; if two nitrates are replaced by larger, monodentate ligands, 9-coordinated species form: $Ln(NO_3)_3(DMSO)_3$ ($Ln = Eu$ [6], Tb), $Tb(NO_3)_3 \cdot (H_2O)_3$. The study of the $Ln(III)/NO_3^-$ interaction in anhydrous DMF points, however, to differences between Tb and Eu , this interaction being larger with the former. In the presence of water (or *isopropanol*) the coordination number of $Tb(III)$ seems to be lower (~ 8) than in anhydrous solvents, but outer-sphere effects are larger. This may be due to steric effects since water molecules very often form clusters through hydrogen bonding. Consequently, it appears that the coordinative properties of rare-earth ions are governed by a delicate balance between electrostatic interactions and steric effects, which act in opposite directions. The presence of nitrate complexes in both DMF and DMSO, and the non-displacement of NO_3^- by water in CH_3CN , indicate that the nitrate ions have a better affinity for the $Tb(III)$ ion than do these solvents. The affinity sequence for the $Tb(III)$ is therefore: $NO_3^- > DMSO > H_2O \sim DMF > (CH_3)_2CO > CH_3CN$.

We are currently extending this study to other $Ln(III)$ ions using FT-IR spectrometry in order to find out if a coordination change occurs along the $Ln(III)$ series in anhydrous solvents.

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