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Structural and luminescence study of europium and terbium nitrate hexahydrates

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Abstract

The crystal structure of $Tb(NO_3)_3 \cdot 6H_2O$ is determined at 295 K from X-ray diffraction measurements. The compound crystallizes in the triclinic space group $P1$ (ITC No. 2) with $Z=2$. Cell parameters are $a=9.095(7)$, $b=11.600(6)$, $c=6.705(4)$ Å, $\alpha=91.14(4)$, $\beta=110.79(5)$, $\gamma=70.14(5)°$, $V=617.9(6)$ Å^3, $D_{calc}=2.44$ g cm^{-1}, $D_{meas}=2.41$ g cm^{-1}. The final R_F was 0.036 for 2165 unique reflections. The Tb(III) is decacoordinated, being bonded to four water molecules and three bidentate nitrate ions. The coordination polyhedron is a distorted 4A,6B-extended dodecahedron. One nitrate ion is asymmetrically bonded, with one Tb–O distance 0.22 Å longer than the other. The luminescent properties of Eu(III) and Tb(III) in $[Ln(NO_3)_3(X_2O)_4] \cdot 2X_2O$, X = H, D are reported. The number of water molecules directly coordinated to the metal ion are estimated from lifetime measurements. These numbers largely exceed the expected value of 4. This fact, together with analogous results reported for the chloride hexahydrates, tend to demonstrate that this method should be used with care.

Introduction

The unique spectroscopic properties of the trivalent lanthanide ions make them ideal candidates as luminescent probes, especially Eu(III) and Tb(III) [1]. In particular, luminescence lifetime determinations allow one to evaluate the number n of water molecules directly bonded to these ions. Indeed, vibronic coupling of the Ln(III) ion excited states with OH oscillators provides an easy path for radiationless deexcitation and all experimental observations tend to demonstrate that the OH oscillators act independently [2]. Since radiationless deexcitation exhibits a large isotopic effect, the study of systems in the presence of H_2O and D_2O leads to an estimate of n. Several hydrated crystalline solids and solutions have been investigated by this method and the following relationship between n and Δk_{obs} was proposed [3]

$$n = c\Delta k_{obs} = c[k_{obs}(H_2O) - k_{obs}(D_2O)] \qquad (1)$$

$c = 1.05$ for Eu(III) and 4.2 for Tb(III)

The radiative deexcitation rate constants (k_{obs}) are simply the inverses of the measured luminescence lifetimes. This method is increasingly being used both in coordination chemistry [1, 4] and biochemistry [1]. However, disparities are sometimes observed between n values determined by different methods, e.g. hydration numbers of the Ln(III) ions in aqueous solutions [5–7].

In this communication, we report a spectroscopic study of the solvates $[Ln(NO_3)_3(X_2O)_4] \cdot 2X_2O$, Ln = Eu, Tb, and X = H, D, along with the crystal structure determination of the Tb hydrate. The validity of the luminescence lifetime method for the determination of the number of bonded water molecules is discussed.

Experimental

Synthesis and characterization of the salts

The hydrated nitrates were prepared from the oxides (Glucydur 99.99%) as previously described [8]. The substitution of the H_2O molecules by D_2O (Glaser AG, 99.95%) was achieved through 4 to 5 dissolution/evaporation cycles; care was exercised to prevent contamination by air moisture. The crystals

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were grown from saturated solutions, by slow evaporation at room temperature in a dessicator containing P_4O_{10}. They were filtered and washed with 1,2-dichloroethane (Fluka, puriss p.a.). All samples containing heavy water were handled in water-free atmosphere (dry N_2 or Ar). The Ln content, and therefore the H_2O:Ln or D_2O:Ln ratios, were determined by complexometric titrations with EDTA. The X_2O:Ln ratios obtained are 6.0 ± 0.1 for X/Ln = H/Eu, H/Tb, D/Eu and 5.9 ± 0.1 for X/Ln = D/Tb, respectively. The purity of the compounds was checked by IR spectroscopy (Alpha Centaury FT-IR spectrometer from Mattson). Taking the $\nu_2(NO_3)$ vibration at c. 1040 cm^{-1} as internal reference, the relative integrated intensity of the OH vibration at c. 3400 cm^{-1} was used to evaluate the contamination of the deuterated salts by H_2O: all the deuterated samples contained less than 0.03 H_2O molecule per Ln(III) ion.

Crystal structure determination

A colourless crystal of $Tb(NO_3)_3 \cdot 6H_2O$ with dimensions $0.5 \times 0.2 \times 0.2$ mm was mounted on an automatic four-circle diffractometer. Cell dimensions were refined from 17 accurately centered reflections with $5° < 2\theta < 30°$. The reflections were corrected for absorption and for Lorentz–polarization effects, and the intensity of 3 reference reflections were periodically monitored. The crystal data and intensity measurements are summarized in Table 1. The structure was solved by the heavy atom method and successive difference-Fourier syntheses. The refinement was carried out in space group $P\bar{1}$ by a full-matrix least-squares technique minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. The computational work was carried out with the XRAY-72 system [9] and the Figures were drawn by means of the ORTEP program [10]. Atomic positions and equivalent isotropic displacement parameters are reported in Table 2, while Table 3 displays selected bond lengths and angles.

TABLE 1. Crystal data and intensity measurements of $H_{12}N_3O_{15}Tb$

Crystal data	
Formula	$H_{12}N_3O_{15}Tb$
Crystal class	triclinic
Space group	$P\bar{1}$
Cell parameters at 293 K	
a (Å)	9.095(7)
b (Å)	11.600(6)
c (Å)	6.705(4)
α (°)	91.14(4)
β (°)	110.79(5)
γ (°)	70.14(5)
V (Å^3)	617.9(6)
Z	2
μ(Mo Kα) (cm^{-1})	58.71
D_{calc} (g cm^{-3})	2.44
D_{meas} (g cm^{-3})	2.41
Molecular weight	453.07
Parameters and results pertinent to the data collection	
Diffractometer	Nicolet R3m
Diffraction geometry	equatorial
Radiation	Mo Kα, graphite monochromatized ($\lambda = 0.71069$ Å)
Scan width	$((K\alpha_2 + 0.8) - (K\alpha_1 - 0.8))°$
Scan speed	$8 - 15°$ min^{-1}
Scan type	$2\theta:\omega$
Background	stationary
Reflections collected	$\pm h \pm k \pm l$ 2165 unique reflections, of which 2086 observed
Observation criterion	$I(h) > 3$ e.s.d. $(I(h))$
Agreement between equivalent reflections	$R_{int} = 0.022$
2θ range	0–50°
sin $(\theta/\lambda)_{max}$	0.67
No. variables	172
Final agreement factors	
R_F	0.036
R_w	0.042
GOF	4.6
Maximal shift/e.s.d.	0.30

Luminescence measurements

The luminescence spectra and lifetimes of microcrystalline powders were measured at 77 and 295 K on a previously described instrumental setup [11]. The Eu(III) ion was excited at 395 nm ($^5L_6$ level) by a Zeiss XBO-450 xenon lamp or at c. 580 nm ($^5D_0$ level) by a Coherent 599 dye laser (200 mW, Rhodamine 6G, 0.03 nm bandpass) pumped by a Coherent Innova-90 8-watt argon laser. The Tb(III) ion was excited at 377 nm ($^5D_3$ level) by the xenon lamp or at 488 nm ($^5D_4$ level) by a line from the argon laser. Selective pulsed excitations were achieved with a tunable dye laser (Lambda Physik FL-3002) pumped with a Xe-Cl exciplex laser (Lambda Physik EMG 101 MSC). Coumarin 102 was used for exciting the Tb(III) ion at 489.00 nm and Rhodamine 6G for exciting the Eu(III) ion at 579.55 nm. The signal was averaged with a W&W SMR memory recorder (20 MHz, 8 bits) and the decay curves were mathematically treated on an IBM PS/2-80 computer.

Results and discussion

Structure of the Tb hydrate

Structural investigations have been published for some polyhydrated lanthanide nitrates. Both La [12] and Ce [13] give rise to undecacoordinate species

TABLE 2. Fractional atomic coordinates of $[Tb(NO_3)_3(H_2O)_4]\cdot 2H_2O$

Atom	x	y	z	U_{eq}
Tb	0.59627(4)	0.72555(3)	0.19855(4)	0.0227(2)
O(1)	0.5608(7)	0.9280(5)	0.3043(8)	0.033(2)
O(2)	0.5527(7)	0.5445(5)	0.2815(7)	0.033(2)
O(3)	0.7616(6)	0.6772(6)	0.5728(7)	0.039(2)
O(4)	0.3950(7)	0.7787(5)	0.3609(9)	0.041(3)
O(5)	0.1968(7)	1.0158(6)	0.3696(8)	0.040(2)
O(6)	0.7794(7)	0.3621(5)	0.5936(8)	0.039(2)
N(1)	0.2780(8)	0.8117(7)	−0.1708(9)	0.034(3)
O(11)	0.3432(8)	0.8870(6)	−0.0743(9)	0.049(3)
O(12)	0.3563(7)	0.7002(5)	−0.0981(8)	0.046(2)
O(13)	0.1469(7)	0.8466(6)	−0.3262(8)	0.052(3)
N(2)	0.8336(8)	0.4985(6)	0.0855(9)	0.031(3)
O(21)	0.6950(7)	0.5745(5)	−0.0439(8)	0.037(2)
O(22)	0.8796(7)	0.5198(7)	0.2751(8)	0.053(3)
O(23)	0.9172(7)	0.4104(6)	0.023(1)	0.053(3)
N(3)	0.8227(8)	0.8202(6)	0.085(1)	0.035(3)
O(31)	0.8633(7)	0.7646(6)	0.2613(8)	0.045(3)
O(32)	0.6813(7)	0.8295(5)	−0.0549(8)	0.042(3)
O(33)	0.9169(8)	0.8596(7)	0.043(1)	0.055(3)

TABLE 3. Bond distances (Å) and angles (°) in $[Tb(NO_3)_3(H_2O)_4]\cdot 2H_2O$

Tb–O(1)	2.388(6)	Tb–O(31)	2.508(8)
Tb–O(2)	2.376(7)	Tb–O(32)	2.567(8)
Tb–O(3)	2.38(1)	Tb···N(1)	2.92(2)
Tb–O(4)	2.35(1)	Tb···N(2)	3.064(8)
Tb–O(11)	2.52(1)	Tb···N(3)	2.95(1)
Tb–O(12)	2.48(1)	Tb···O(5)	4.51(1)
Tb–O(21)	2.524(7)	Tb···O(6)	4.48(1)
Tb–O(22)	2.744(7)	Tb···Tb	6.705(4)
N(1)–O(11)	1.26(1)	N(2)–O(23)	1.22(1)
N(1)–O(12)	1.25(1)	N(3)–O(31)	1.23(1)
N(1)–O(13)	1.22(1)	N(3)–O(32)	1.26(1)
N(2)–O(21)	1.27(1)	N(3)–O(33)	1.21(1)
N(2)–O(22)	1.24(1)		
O(1)–Tb–O(2)	139.7(2)	O(11)–N(1)–O(12)	116.3(5)
O(1)–Tb–O(3)	79.5(2)	O(11)–N(1)–O(13)	121.1(7)
O(1)–Tb–O(4)	71.2(2)	O(12)–N(1)–O(13)	122.6(8)
O(2)–Tb–O(3)	78.3(2)	O(21)–N(2)–O(22)	116.9(6)
O(2)–Tb–O(4)	71.1(2)	O(21)–N(2)–O(23)	120.8(6)
O(3)–Tb–O(4)	76.3(2)	O(22)–N(2)–O(23)	122.2(5)
O(11)–Tb–O(12)	50.6(2)	O(31)–N(3)–O(32)	117.1(8)
O(21)–Tb–O(22)	47.7(2)	O(31)–N(3)–O(33)	121.6(7)
O(31)–Tb–O(32)	49.6(2)	O(32)–N(3)–O(33)	121.2(7)

$[Ln(NO_3)_3(H_2O)_5]\cdot H_2O$ while Pr [14] and Y [17] yield decacoordinate complexes $[Ln(NO_3)_3(H_2O)_4]\cdot 2H_2O$. Powder diffraction data point to Nd and Sm salts having the same structure as the Pr compound [15], a statement also true for the Eu salt [16]. A vibrational and powder diffraction study concluded that terbium nitrate crystallizes preferentially as the pentahydrate and not the hexahydrate [18]. Our analytical data are at variance with this conclusion, and are confirmed by the results of the crystallographic determination.

Terbium nitrate hexahydrate crystallizes in the $P\bar{1}$ triclinic space group. A view of the unit cell is presented in Fig. 1. The structure consists of isolated decacoordinated complex molecules $[Tb(NO_3)_3(H_2O)_4]$ with two additional water molecules bonded to the hydrate through H bonds. The three nitrate groups are tied on the same side of the Tb ion (Fig. 2(a)), while the water molecules are located on the other side. A similar arrangement was observed for the Pr compound [14]. The coordination polyhedron (Fig. 2(b)) is a distorted 4A,6B-extended dodecahedron close to possessing a mirror plane determined by O(3), O(4) and N(1). The average Ln–O distance is 2.48 ± 0.11 Å, the water O atoms being at shorter distances (average 2.37 ± 0.01 Å) than the nitrate O atoms (average 2.56 ± 0.09 Å). A noteworthy feature, however, is that one nitrate ion, N(2), is asymmetrically bonded, the Tb–O(22) distance being 0.22 Å longer than the other Tb–O distance. For the two remaining nitrates, N(1) and N(3), this difference Δd(Tb–O) amounts only to 0.04 and 0.06 Å, respectively. Such an asymmetry does not occur in the undecacoordinate La compound [12], but was observed both in the Pr salt [14] (Δd(Pr–O) = 0.03, 0.04 and 0.10 Å) and in the Y salt [17] (Δd(Y–O) = 0.06, 0.09 and 0.33 Å) for the three coordinated nitrates, respectively. The increasing asymmetry in the binding mode of one nitrate group in going from Pr to Tb and Y is related to the decrease in the effective ionic radius of the ten-coordinate metallic ions, from 1.23 Å to 1.15 and 1.13 Å, respectively.

With respect to the mean N–O distance of 1.245 Å observed for symmetrical ionic nitrate groups, the three terminal N–O bonds are shortened (mean value 1.216 Å), and the six N–O bonds involving chelating O atoms are lengthened (mean value 1.252 Å). The O–N–O angles involving both coordinated O atoms are smaller than the regular 120° angle (mean value 116.8°) while the other angles are larger (mean value 121.6°), but no deviation from planarity is observed for either the symmetrically or the asymmetrically bonded nitrate groups.

Luminescence study

Non-selective excitation of the Eu($^5L_6$) level (395 nm) results in the spectrum reported in Fig. 3. Emission bands originating from the $^5D_0$ and $^5D_1$ excited levels are observed. The $^5D_0 \rightarrow {}^7F_0$ transition is clearly visible at 77 K, indicating that the slight coordination change postulated by Blasse *et al.* [16] takes place below this temperature. With respect to

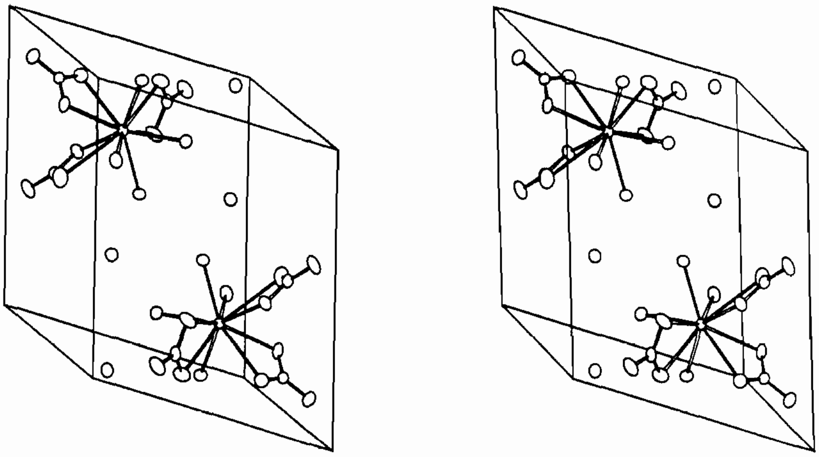

Fig. 1. Stereoscopic view of the crystal packing in [Tb$(NO_3)_3(H_2O)_4$]·$2H_2O$.

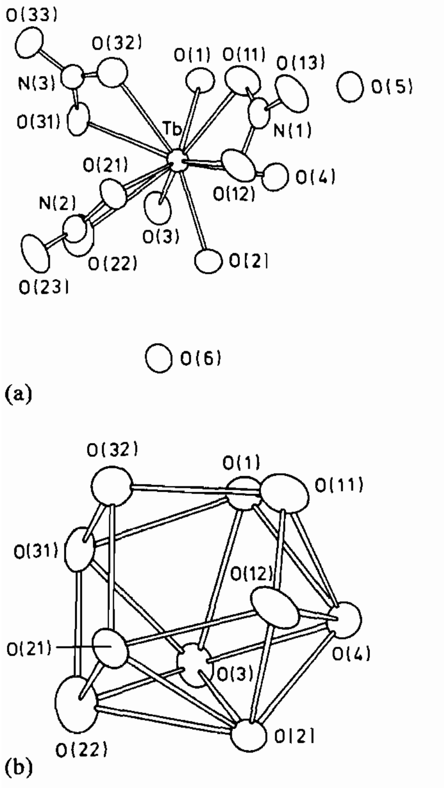

Fig. 2. (a) ORTEP drawing of [Tb$(NO_3)_3(H_2O)_4$·$2H_2O$ showing the atomic-numbering scheme. (b) Coordination polyhedron around Tb(III).

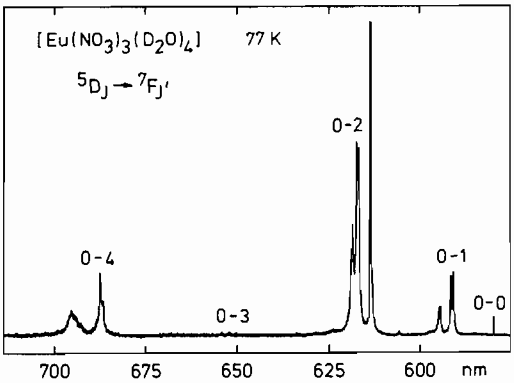

Fig. 3. Emission spectrum of [Eu$(NO_3)_3(D_2O)_4$]·$2D_2O$ at 77 K under non-selective excitation of the $^5L_6$ level (395 nm).

the data for [Eu$(NO_3)_3(H_2O)_4$], the spectrum of the deuterated solvate displays an increase in the intensity of the transitions originating from the $^5D_0$ level, relative to those originating from $^5D_1$. This is attributed to the large decrease in the quenching of the luminescence from the long-lived $^5D_0$ state. The excitation spectrum of the $^5D_0 \leftarrow {}^7F_0$ transition displays a single sharp band (width at half height 1.6 cm^{-1}) centered at 17255 cm^{-1} and pointing to the presence of a single Eu(III) site. A comparison with the measurements reported at 295 K [19] illustrates the expected red shift (8 cm^{-1}) and narrowing of this 0–0 transition consecutive to the temperature lowering.

Selective excitation of the $^5D_0$ level results in the emission spectra reported in Fig. 4. The $^5D_0 \rightarrow {}^7F_J$ transitions display a maximum number of $(2J+1)$ components, reflecting a low symmetry around the Eu(III) ion. The integrated and corrected relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 0.03, 1.0, 4.9, 0.01, 1.8, 0.05 and 0.4 for $J=0$, 1, 2, 3, 4, 5 and 6, respectively. In addition to the electronic transitions, additional bands are observed and ascribed to cooperative vibronic processes [16] involving both Eu–O and nitrate vibrations (Table 4).

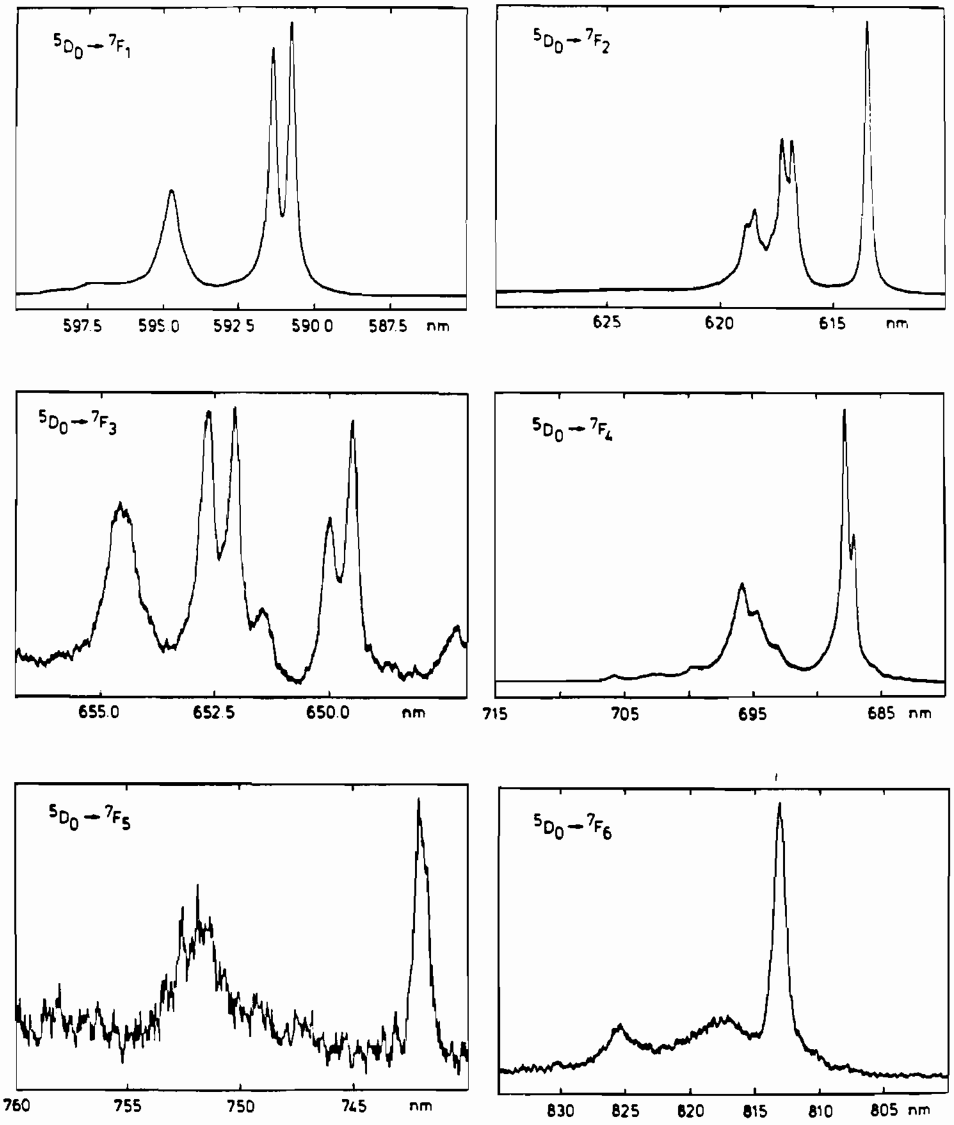

Fig. 4. Emission spectra of $[Eu(NO_3)_3(D_2O)_4]\cdot 2D_2O$ at 77 K under selective laser excitation of the $^5D_0$ level (579.55 nm).

TABLE 4. Cooperative vibronic transitions observed in the emission spectrum of $[Eu(NO_3)_3(D_2O)_4]\cdot 2D_2O$

E_0 (cm^{-1})	Assignment		ν_{IR} (cm^{-1})
511	$^5D_0 \to {}^7F_1 + \nu(M\text{-}O)$	[345 + 166]	167
745	$^5D_0 \to {}^7F_0 + \nu(NO_3)$		746
1042	$^5D_0 \to {}^7F_0 + \nu(NO_3)$		1041
1078	$^5D_0 \to {}^7F_1 + \nu(NO_3)$	[327 + 751]	746

The luminescence lifetimes measured for the Eu($^5D_0$) level in both the hydrate and the deuterated solvate are reported in Table 5 along with the estimation of n, the number of water molecules directly bonded to Eu(III). The τ value measured for the $[Eu(NO_3)_3(D_2O)_4]\cdot 2D_2O$ species is twice as large as the estimation of Blasse *et al.* [16] for the pure radiative decay time. Absence of a radiative energy transfer process which could affect the lifetime of $[Eu(NO_3)_3(D_2O)_4]\cdot 2D_2O$ was established by measuring a $[Gd(NO_3)_3(D_2O)_4]\cdot 2D_2O$ sample doped with 3% Eu: the obtained τ values (1.85 ± 0.04 ms at 77 K and 1.76 ± 0.04 ms at 295 K) are identical with the lifetimes of the pure Eu salt, within experimental error. These results leads to a n value of 5.5, which no longer corresponds to the stoichiometry of the solvate ($n = 4$). A similar discrepancy is observed for $EuCl_3\cdot 6X_2O$ (X = H, D) [3, 5], suggesting that the

TABLE 5. Radiative lifetimes (ms) of the Eu($^5D_0$) and Tb($^5D_4$) levels in $[Ln(NO_3)_3(X_2O)_n](X_2O)_m$ (X = H, D) and calculated number of water molecules directly coordinated to Ln(III)

Ln	Temperature (K)	τ_{H_2O}	τ_{D_2O}	n_{H_2O}
Eu	77	0.177 ± 0.002	1.90 ± 0.01	5.4 ± 0.5
Eu	295	0.171 ± 0.004	1.76 ± 0.02	5.5 ± 0.5
Tb	77	0.661 ± 0.005	2.22 ± 0.03	4.5 ± 0.5
Tb	295	0.653 ± 0.004	2.20 ± 0.02	4.5 ± 0.5

value of the constant c proposed for Eu(III) in relationship (1) is not valid in these cases.

The luminescence spectra of the Tb(III) compounds provide less structural information because of the large degeneracy of the $^5D_4$ level. The luminescence lifetimes can however be used to estimate n (Table 4). The calculated values of n are again too large, but the deviation is in the uncertainty range proposed in ref. 3: ±0.5 water molecule.

Conclusions

The two compounds $Ln(NO_3)_3 \cdot 6H_2O$, Ln = Pr, Tb, have similar structures featuring decacoordinate Ln(III) ions. However, the effect of the lanthanide contraction is seen in the asymmetric binding of one nitrate ion which has the tendency to become coordinated to Tb(III) in a monodentate fashion. The determination of the number of water molecules directly coordinated to Ln(III), using the lifetime method described by eqn. (1) is at variance with the stoichiometry derived from the crystal structure determination. This suggests that the c values used in eqn. (1) cannot be considered as constant for any hydrated species in solution or in the solid state, especially for Eu compounds. The quenching efficiency of the OH oscillators is related to several parameters, e.g. the water–lanthanide distances, the polarizability of the water molecules, and the effective charge on the Ln(III) ion. All these parameters may differ substantially from one compound to another, which affects the Ln–OH interaction, as was pointed out in the discussion of the vibronic transitions [20]. This phenomenon is now being systematically investigated in our laboratory [5].

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