Luminescence Spectroscopic Study of Europium(III) and Terbium(III) with Ethylenediamine in Dimethyl Sulfoxide

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The luminescence excitation and emission spectra of europium(III) and terbium(III) complexes of ethylenediamine (en) in dimethyl sulfoxide have been studied. The $^7F_0 \rightarrow {}^5D_0$ spectra of Eu^{III} and the values of the luminescence decay constant confirmed that trivalent lanthanides form 1:1, 1:2 and 1:3 inner-sphere complexes with en. The quenching of the luminescence of Eu^{III} and Tb^{III} are linearly proportional to the number of N–H groups attached to the metal ions. The equations are k_{obs} (Eu) = 0.759 n_{N-H} + 0.416 and k_{obs}(Tb) = 0.073 n_{N-H} +0.299. The quenching mechanism is assumed to be the same as that of the O–H group, i.e. it involves coupling between the electronic transition energy of Eu^{III} or Tb^{III} and the vibrational overtones of N–H. Luminescence spectra and decay contents measured between 15 and 80 °C indicate decreased stability of the complexes with increased temperature, in agreement with the reported enthalpies of complexation.

Trivalent lanthanides (Ln), typical hard acids, preferentially bind to hard bases, such as fluoride, oxygen and nitrogen donor ligands. In comparison with studies of complexation of Ln^{III} by O-donor ligands, those involving ligands with only N donors are quite limited.[1–4] Complexation of lanthanide(III) cations with aliphatic amines has been shown to depend on the solvent.[4–6] In aqueous solution protonation of the amine nitrogens and hydrolysis of the lanthanide(III) ions prevent complexation. In non-aqueous solvents the strength of complexation varies; e.g., in acetonitrile, complexes with ethylenediamine (en) as high as 1:4 species form with log β_4 ca. 25.[5] By contrast, in dimethyl sulfoxide (dmso) the 1:3 complex is the highest complex observed and log β_3 has a value of only 4–5.[6]

Most of the trivalent lanthanide cations exhibit luminescence in which both the spectra and the lifetimes are sensitive to the co-ordination environment of the metal ion. The luminescent properties of Eu^{III} and Tb^{III}, in particular, have been used to study lanthanide complexes.[7–11] Owing to the chemical and physical similarity between Ln^{III} and Ca^{II}, Eu^{III} and Tb^{III} have been used as luminescent probes to investigate calcium binding sites in biological systems.

Horrocks and Sudnick[10] established a quantitative relation between the number of water molecules co-ordinated to their inner sphere and the luminescent lifetimes of Eu^{III} and Tb^{III}. Complexed N–H groups can, like their O–H analogues, decrease the luminescent lifetimes. Since in many biological systems, N–H groups directly co-ordinate to Eu^{III} and Tb^{III}, quantitative knowledge of the quenching effect of the N–H group would be very useful in using lanthanide(III) luminescence to define the ligand binding site.

Ethylenediamine introduces four N–H oscillators into the inner sphere of Eu^{III} and Tb^{III} upon co-ordination and therefore can be used as a sensitive ligand for the study of the N–H quenching effect. Previously, lanthanide(III) complexes of aliphatic amines have been studied by potentiometry,[6] NMR spectroscopy[4] and calorimetry.[4] In this paper we report the results of a study of the luminescence properties of complexes of Eu^{III} and Tb^{III} with ethylenediamine.

Experimental

Reagents.—Ethylenediamine (99 + %) and anhydrous dimethyl sulfoxide (99 + %) were purchased from Aldrich and used as received. The salts Eu(ClO$_4$)$_3$·7.5dmso and Tb(ClO$_4$)$_3$·7.5dmso were prepared from the corresponding oxides (99.99%, Aldrich) according to procedures described elsewhere.[6]

[^{2}H$_4$]Ethylenediamine, [^{2}H$_4$]en, was prepared using a modification of the procedure of Sabatini and Califano.[12] Ethylenediamine dihydrochloride (10 g) was dissolved in D$_2$O (25 cm^3) and refluxed for 12 h, to ensure isotopic equilibrium, and the residual solvent removed by vacuum pumping. This procedure was repeated five times. Following the final removal of D$_2$O, anhydrous BaO (98%, Aldrich) was added to the amine hydrochloride. The [^{2}H$_4$]en was vacuum distilled at 200 °C and collected in a solid CO$_2$–acetone trap. The final traces of D$_2$O were removed by distillation over an excess of anhydrous BaO. The completeness of isotope exchange was confirmed by the lack of absorption peaks above 3000 cm^{-1} in the IR spectrum. The en and [^{2}H$_4$]en were stored over molecular sieves (Fisher) of 4 Å diameter. Europium and terbium perchlorate solutions in dmso were prepared by dissolving weighed amounts of the solvated salts in dmso. Solutions of en and [^{2}H$_4$]en were prepared by dissolving a calculated volume of the amine in dmso. Solutions of the europium and terbium amine complexes were prepared by mixing aliquots of the solutions of the metal ions and the ligands.

All reagents and solutions were stored and all manipulations were performed in a glove box with a dry nitrogen atmosphere in the presence of powdered P$_2$O$_5$. Except during manipulations, the box was kept dark to protect the reagents and solutions from possible photolytic effects.

Spectroscopic Measurements.—Luminescence measurements of the solutions were performed with a standard 1 cm fluorimeter cell sealed with a Teflon stopper. The excitation and emission spectra of the europium(III) and terbium(III) complexes were recorded using a modified Perkin Elmer

MPF — 2A spectrophotometer equipped with a Hamamatsu R928 photomultiplier tube and a temperature controlling unit. The excitation spectra for Tb^{III} were obtained by monitoring the emission intensity of the $^5D_4$ ⟶ $^7F_5$ band at 545 nm while the emission spectra were obtained from excitation of the $^7F_6$ ⟶ $^5D_3$ band at 368 nm. For Eu^{III}, the excitation spectra were obtained by monitoring the intensity of the $^5D_0$ ⟶ $^7F_2$ band at 616 nm. The emission spectra resulted from excitation of the $^7F_0$ ⟶ $^5L_6$ band at 394 nm.

The selective excitation spectra of the $^7F_0$ ⟶ $^5D_0$ band of Eu^{III} were obtained with a system described elsewhere[11] with a few modifications. The pulsed (10 Hz) 532 nm output of a Quanta Ray DCR 2A Nd-YAG laser was used to pump a 50 : 50 (v/v) mixture of Rhodamine 590 and Rhodamine 610 (Exciton Chemical) in methanolic solution in Quanta Ray PDL2 equipment. The $^7F_0$ ⟶ $^5D_0$ excitation spectra were recorded by scanning the dye laser continuously through the absorption band with a computer-controlled stepping motor while monitoring the emission at 616 nm. The light emitted was collected at 90° by an optic cable and detected by a Hamamatsu R1527 photomultiplier tube after passing through a low-fluorescence filter (cut-off wavelength 520 nm). After amplification in a Lecroy 6103 amplifier, the signal was fed into a Lecroy TR 8828C transient recorder that connected the GPIB interface to an IBM PC computer in which the signal was gated, summed, averaged and stored.

The luminescence lifetimes of samples of Eu^{III} and Tb^{III} were obtained with the same system used to record the europium(III) $^7F_0$ ⟶ $^5D_0$ excitation spectra. In the case of terbium(III) complexes, a laser beam at 368 nm was used and the amplifier (Lecroy 6103) and digitizer (Lecroy TR8828C) were replaced by a Lecroy 9401 oscilloscope. The pulsed (10 Hz) 368 nm laser beam was obtained by mixing the output of the dye laser (Rhodamine 590 in methanol) beam at 562 nm with the 1064 nm fundamental of a Nd-YAG laser in a Quanta Ray WEX-1 wavelength extender.

The laser pulse energy at 580 nm was ca. 30 mJ, while that at 368 nm was typically 3 mJ. The pulse width was in the nanosecond range.

The programs used for the deconvolution of spectra and data processing of the exponential luminescence decays were written in this laboratory using the Marquardt non-linear regression and Simplex procedures.[10,13,14] The deconvolution of the spectra was also checked by the program SQUAD[15] when applicable. High resolution of the monochromator (0.3 cm^{-1}) and signal to noise ratio ensure the precision of the deconvolution of the spectra ($\leqslant$ 1 cm^{-1}).

Results and Discussion

Excitation and Emission Spectra.—Both Eu^{III} and Tb^{III} have forbidden f ⟶ f absorption bands in the UV region and well resolved emission bands in the visible region with molar absorption coefficients less than 3 dm^3 mol^{-1} cm^{-1}. The maximum absorption of Eu^{III} is at ca. 394 nm ($\varepsilon \approx 2.75$) and that of Tb^{III} is at 368 nm ($\varepsilon \approx 0.36$ dm^3 mol^{-1} cm^{-1}). The emission bands of Eu^{III} originate from electronic transitions from the lowest excited state, $^5D_0$, to the ground state manifold, ^7F_J ($J = 0$–6) and those of Tb^{III} from the lowest excited state, $^5D_4$, to the ground state manifold, ^7F_J ($J = 6$–0). Terbium(III) has two f ⟶ d absorption bands located at 217 nm (allowed) and 263 nm (spin forbidden).[16,17] The allowed f ⟶ d band is not observable in the excitation spectrum of the free metal ion but appears in complexes with the maximum of the manifold shifting to lower energies.[18] These features are observed in the excitation and emission spectra of Eu^{III} and Tb^{III} complexes with en.

As shown in Figs. 1 and 2 and Table 1, addition of en to a solution of Eu^{III} and Tb^{III} in dmso causes significant reduction of the luminescence intensity of the metal ions. This reflects the effect of en in the inner sphere of the Ln^{III} to form rather strong Ln^{III}-en complexes. For Eu^{III}, as the ligand concentration
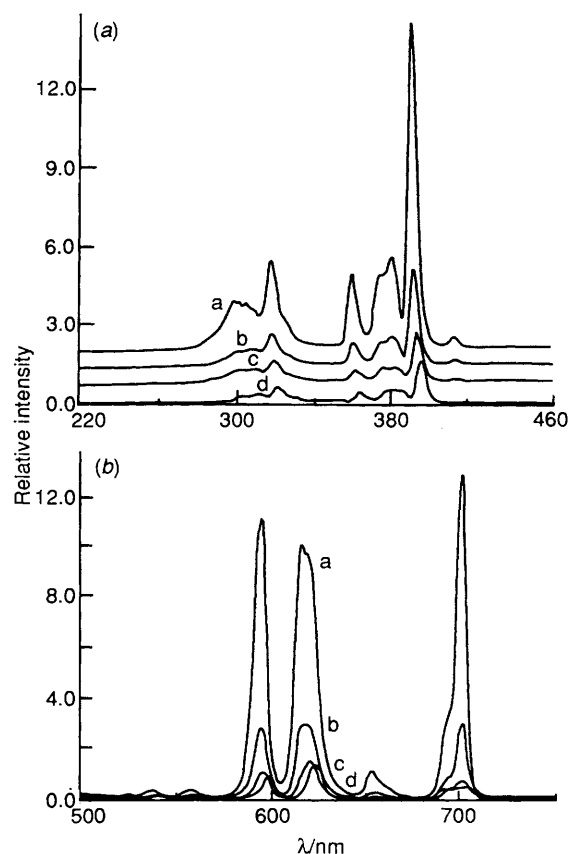

Fig. 1 Excitation (*a*) and emission spectra (*b*) of europium(III) complexes with en in dmso at different Eu^{III}: en ratios. [Eu^{III}] = 0.0167 mol dm^{-3}. [Eu^{III}]:[en] 1:0 (a) 1:1 (b); 1:7 (c), 1:25 (d). λ_{ex} = 394.0, λ_{em} = 616.0 nm. Offset to the intensity in (*a*): 2.0 (a), 1.4 (b), 0.8 (c), 0.0 (d)

increases the relative intensity of the transitions $^5D_0$ ⟶ $^7F_2$ at 616 nm and $^5D_0$ ⟶ $^7F_1$ at 592 nm is reversed. This is associated with the change of Eu^{III} from a weaker ligand field of pure solvent to a stronger ligand field of en.[19] For Tb^{III}, while the intensities of the f ⟶ f transitions are reduced by complexation, the intensity of the forbidden f ⟶ d band at 261 nm is greatly increased as is that of the allowed f ⟶ d band which is shifted to 297 nm.[18–20] Although the 4f orbitals are shielded from direct interaction with the ligand orbitals, the 5 d orbitals are more extended and can overlap with the ligand orbitals.[21] Therefore the changes in the f ⟶ f and f ⟶ d bands provide evidence of the strong interaction of Eu^{III} and Tb^{III} with en.

Selective Excitation Spectra of $^7F_0$ ⟶ $^5D_0$ *of* Eu^{III}.—The $^7F_0$ ⟶ $^5D_0$ excitation spectra of Eu^{III} are unique since both the ground state and the excited state are non-degenerate. Since these states cannot be further split by the ligand field, only a single electronic transition is allowed for each europium(III) environment. The $^7F_0$ ⟶ $^5D_0$ excitation spectra are shown in Fig. 3 for solutions of Eu(ClO$_4$)$_3$ alone and with en at different molar ratios. As the ligand concentration increases more peaks appear at lower energies. Deconvolution of the spectra shows four distinct peaks with maxima at 579.20, 579.37, 579.64 and 579.94 nm, respectively, corresponding to the four species, Eu^{III}, Eu(en), Eu(en)$_2$ and Eu(en)$_3$. This assignment is in agreement with the results of potentiometric and calorimetric titrations.[6]

The shift of the electronic transition $^7F_0$ ⟶ $^5D_0$ to lower energies in the excitation spectra upon complex formation has been studied by several workers[22–24] and can be attributed to a nephelauxetic effect.[25] Such a shift has been interpreted as related to an increase of the metal–ligand bond covalency.[22,25]

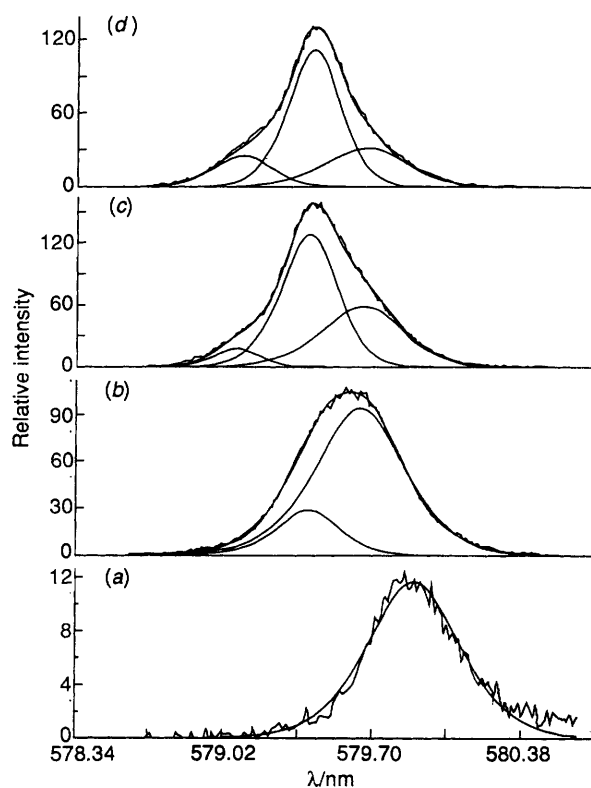**Table 1** Luminescence data of en complexes of Eu^{III} and Tb^{III} at 25 °C

	[M]:[en]	$I_{complex}/I_{free}$ (297 nm)	$I_{complex}/I_{free}$ (261 nm)	$\lambda_{max,ex}$/nm	$\lambda_{max,em}$/nm	$\lambda_{max,ex}$/nm	$\lambda_{max,em}$/nm	I_{616}/I_{592}
			Tb^{III}				Eu^{III}	
1	1:0	1.000	1.000	368.0	544.5	392.6	615.0	0.902
2	1:1	2.754	1.435	368.0	544.5	393.0	618.6	1.051
3	1:3	2.876	2.720	368.0	544.5	393.1	618.9	1.280
4	1:5	3.311	3.643	368.0	544.5	394.4	619.7	1.442
5	1:7	3.526	4.792	368.0	544.5	394.6	619.9	1.519
6	1:10	3.751	5.792	368.0	544.5	395.4	622.0	1.525
7	1:13	3.620	6.072	368.0	544.5	395.6	622.5	1.573
8	1:25	3.757	7.389	368.0	544.5	396.6	623.9	1.617

* $[Tb^{III}] = 0.0179$, $[Eu^{III}] = 0.0167$ mol dm^{-3}.
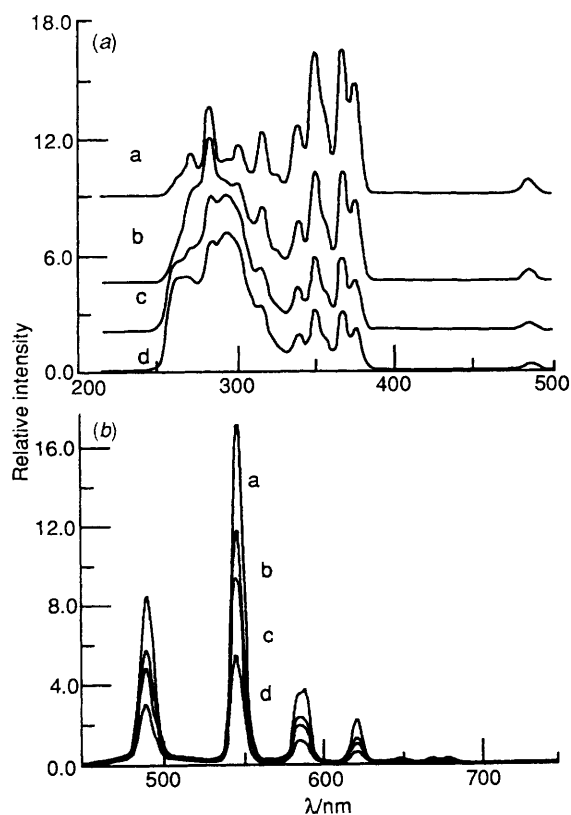
Fig. 2 Excitation (a) and emission spectra (b) of terbium(III) complexes with en in dmso at different Tb^{III}: en ratios. $[Tb^{III}] = 0.0179$ mol dm^{-3}. $[Tb^{III}]$:[en] = 1:0 (a), 1:2.5 (b), 1:10 (c), 1:25 (d). $\lambda_{ex} = 368.0$ nm, $\lambda_{em} = 544.5$ nm. Offset to the intensity in (a):9.0 (a), 4.5 (b), 2.0 (c), 0.0 (d)

Fig. 3 The $^7F_0 \rightarrow {}^5D_0$ selective excitation spectra of Eu^{III} at various $[Eu^{III}]$:[en] ratios and its deconvolution into Gaussian–Lorentzian product type functions. $[Eu^{III}] = 0.0167$ mol dm^{-3}. $[Eu^{III}]$:[en] = 1:0 (a) 1:2, (b), 1:9 (c), 1:15 (d). $\lambda_{em} = 616.0$ nm

However, this study has not provided a sufficient basis to confirm such an interpretation.

Luminescence Quenching Effect of N–H.—The luminescence decay of complexes of Eu^{III} and Tb^{III} in dmso for different metal to ligand ratios could be analysed by a single exponential in every case. This indicates that if different species are present, they are in a dynamic equilibrium with a fast exchange rate.[26]

Using the program SPECIES[27] with the reported stability constants[6] for complexation of Eu^{III} and Tb^{III} with en, the mole fractions of Eu^{III}, Eu(en), Eu(en)$_2$ and Eu(en)$_3$, f_0–f_3, in each sample were calculated. Since each en introduces four N–H groups, the weighted average number of N–H groups coordinated to the metal ion, n_{N-H}, can be calculated from these mole fractions. The total concentrations of the metal ion and ligand of each solution, the mole fractions f_n of the species present, the values of n_{N-H} and the measured decay constants, k_{obs}, are listed in Tables 2 and 3.

Data on the luminescence decay constants of complexes of Eu^{III} and Tb^{III} with $[^2H_4]$en in $[^2H_6]$dmso are listed in Table 4. The decay constants show no significant variation for complexes of Eu^{III} or Tb^{III} as the number of N–D groups coordinated to the metal ion is varied and are only negligibly different from the decay constants obtained in dmso of the non-complexed metal ions.

The observed decay constants of complexed Eu^{III} and Tb^{III} are plotted in Fig. 4 against the weighted average number of bonded N–H groups. The linearity of this plot is evidence that each bonded N–H vibrator unit acts independently in the luminescence quenching process. Least-squares regression of the data in Table 3 gives equations (1) and (2) for Eu^{III} and Tb^{III}

$$k_{obs} = 0.759 n_{N-H} + 0.416 \quad (1)$$

$$k_{obs} = 0.073 n_{N-H} + 0.299 \quad (2)$$

respectively.

Salama and Richardson[28] determined the relative quenching

Table 2 Concentrations, mole fractions and decay constants of en complexes of Eu^{III} at 25 °C

	$[Eu]_{total}$/mol dm^{-3}	$[en]_{total}$/mol dm^{-3}	Molar fraction at equilibrium		
			f_0	f_1	f_2	f_3	n_{N-H}	k_{obs}/ms^{-1}
1	0.0167	0.0000	1.0000	0.0000	0.0000	0.0000	0.000	0.530
2	0.0167	0.0167	0.5496	0.3798	0.0636	0.0072	2.114	2.174
3	0.0167	0.0333	0.3084	0.4722	0.1752	0.0444	3.823	3.551
4	0.0167	0.0500	0.1794	0.4446	0.2670	0.1092	5.225	4.114
5	0.0167	0.0667	0.1080	0.3798	0.3240	0.1884	6.372	5.481
6	0.0167	0.0833	0.0672	0.3120	0.3156	0.2964	7.006	5.908
7	0.0167	0.1167	0.0288	0.2052	0.3528	0.4128	8.597	6.900
8	0.0167	0.1500	0.0144	0.1380	0.3258	0.5220	9.422	7.337
9	0.0167	0.1667	0.0102	0.1152	0.3090	0.5652	9.715	7.506
10	0.0167	0.2167	0.0048	0.0714	0.2618	0.6612	10.322	8.154
11	0.0167	0.2500	0.0024	0.0540	0.2370	0.7062	10.586	8.682
12	0.0167	0.4166	0.0006	0.0198	0.1542	0.8256	11.220	9.287
13	0.1000	0.1500	0.1990	0.4550	0.2511	0.0944	4.720	3.650
14	0.1000	1.0000	0.0000	0.0058	0.0881	0.9060	11.600	8.801
15	0.0600	0.2460	0.0157	0.1463	0.3302	0.5078	9.321	6.800

Table 3 Concentrations, mole fractions and decay constants of en complexes of Tb^{III} at 25 °C

	$[Tb]_{total}$/mol dm^{-3}	$[en]_{total}$/mol dm^{-3}	Molar fraction at equilibrium		
			f_0	f_1	f_2	f_3	n_{N-H}	k_{obs}/ms^{-1}
1	0.0179	0.0000	1.0000	0.0000	0.0000	0.0000	0.000	0.352
2	0.0179	0.0143	0.5247	0.3942	0.0734	0.0078	2.250	0.484
3	0.0179	0.0446	0.1260	0.4060	0.3242	0.1445	5.951	0.758
4	0.0179	0.0804	0.0269	0.2027	0.3780	0.3926	8.546	0.904
5	0.0179	0.1250	0.0062	0.0862	0.3052	0.6026	10.018	0.981
6	0.0179	0.1786	0.0017	0.0398	0.2279	0.7314	10.759	1.083
7	0.0179	0.2321	0.0006	0.0218	0.1781	0.7991	11.101	1.152
8	0.0179	0.4464	0.0000	0.0006	0.0930	0.9016	11.556	1.241
9	0.0294	0.0706	0.0918	0.3618	0.3536	0.1928	6.590	0.718
10	0.0474	0.0526	0.3152	0.4727	0.1756	0.0363	3.731	0.536
11	0.0556	0.2222	0.0056	0.0828	0.3011	0.6106	10.068	0.982
12	0.0250	0.3750	0.0000	0.0088	0.1172	0.8740	11.461	1.165
13	0.0200	0.0200	0.4310	0.4415	0.1120	0.0160	2.854	0.497
14	0.0200	0.0500	0.1145	0.3930	0.3345	0.1585	6.150	0.736
15	0.0143	0.0714	0.0287	0.2086	0.3794	0.3843	8.481	0.865
16	0.0083	0.4167	0.0000	0.0048	0.0936	0.9012	11.582	1.107

Table 4 Luminescence decay constants of [$^2H_4$]en complexes of Eu^{III} and Tb^{III} in [$^2H_6$]dmso at 25 °C *

\multicolumn{2}{c}{Eu^{III}}	\multicolumn{2}{c}{Tb^{III}}
[Eu]:[($^2H_4$)en]	k_{obs}/ms^{-1}	[Tb]:[($^2H_4$)en]	k_{obs}/ms^{-1}
1:1	0.461	1:1	0.280
1:3	0.430	1:3	0.312
1:5	0.497	1:5	0.323

* [Eu^{III}], [Tb^{III}] = 0.01 mol dm^{-3}.

efficiencies of N–H to be about two-thirds that of O–H on Tb^{III} luminescence of complexes of iminodiacetate in aqueous solution. For a decay constant of aquated Tb^{III} of 2.3 ms^{-1} (ref. 26) and assuming binding of eight water molecules to Tb^{III},[29] the decay constant associated with a single O–H group is 0.144 ms^{-1}. The decay constant of the N–H group from the present work is 0.0759 ms^{-1}, indicating about 52% of the quenching effect relative to that of O–H. The present value is considered more reliable since the earlier study had mixed OH and NH quenching.

For europium(III) complexes of a substituted 1,4,7,10-tetraazacyclododecane ligand, Anelli et al.[30] estimated that the quenching effects of N–H and O–H groups is about the same. If the decay constant of aquated Eu^{III} is 9.0 ms^{-1}[11,26] and assuming a formulation [Eu(H$_2$O)$_9$]$^{3+}$ (ref. 29), the decay

constant due to each O–H group is calculated to be about 0.50 ms^{-1}. Thus the luminescence quenching effect of an N–H group on Eu^{III} from the present work is 150% of that of an O–H group, a result much higher than that obtained by Anelli et al.[30] There are probably relatively large uncertainties in the measurements in ref. 30 as only one N–H group is present in the ligand they studied.

The mechanism of quenching by O–H of the luminescence of Eu^{III} and Tb^{III} has been investigated often[31–34] and involves radiationless de-excitation by O–H by coupling of the electronic transition energy of the metal ion and the vibrational overtones of the O–H oscillator. For Eu^{III}, the fourth vibrational level of the O–H and the fifth level of the O–D oscillators are involved; while for Tb^{III}, it is the fifth and sixth vibrational levels, respectively, of the two oscillators. Coupling to a higher overtone of an oscillator provides less efficient quenching, so for both Eu^{III} and Tb^{III} the lower quenching by O–D oscillators can be explained by the involvement of higher overtone levels. Since the vibrational energies of N–H and N–D oscillators are close to those of O–H and O–D,[12] it is reasonable to assume N–H and N–D groups have the same quenching mechanism as OH and OD.

Temperature Dependence of the Complex Equilibrium.— Experiments were carried out between 15 and 80 °C to study the effect on the complexation equilibrium. Fig. 5 shows the spectral profile of the $^5F_0 \longrightarrow ^5D_0$ excitation spectra of the europium(III) complexes at various temperatures. Upon
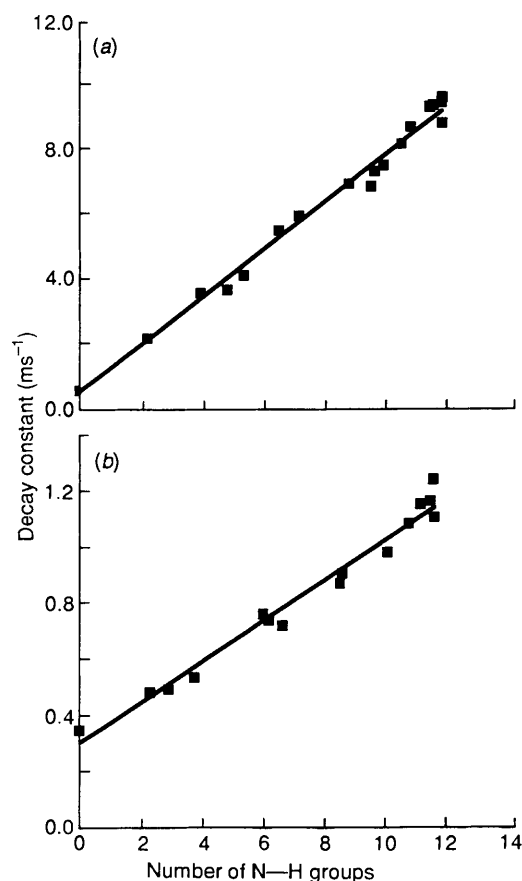
Fig. 4 Plots of observed decay constants *vs.* the weighted average number of N–H groups in the inner sphere of complexes of en with Eu^{III} (*a*) and Tb^{III} (*b*), in dmso at 25 °C

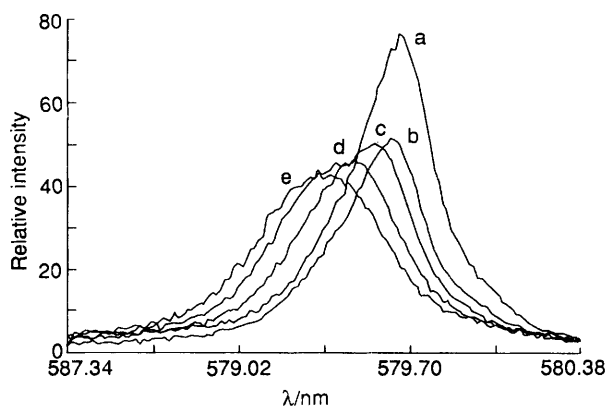**Fig. 5** Temperature dependence of the $^7F_0 \rightarrow {}^5D_0$ selective excitation spectra of europium(III) complexes of en in dmso. [Eu^{III}] = 0.0167 mol dm^{-3}; [en] = 0.167 mol dm^{-3}. λ_{em} = 616.0 nm; 12.5 (a), 25.0 (b), 40.0 (c), 60.0 (d) and 80.0 °C (e)

increasing the temperature, the maxima of the spectra shift to higher frequencies, reflecting decreased complexation because the enthalpy change of complexation is exothermic.[6] The same trend was observed in the excitation spectra of complexed Tb^{III} (Fig. 6). Increasing the temperature results in a decrease of intensity of the f———→ d bands of Tb^{III} which also indicates increased dissociation. Associated with the decreased complexation a monotonic decrease in the luminescence decay constants was also observed. Usually luminescence decay constants of Eu^{III} and Tb^{III} increase with increased temperatures because of thermal quenching.[35] Apparently, complexation is sufficiently decreased in the en systems that the decrease of luminescence
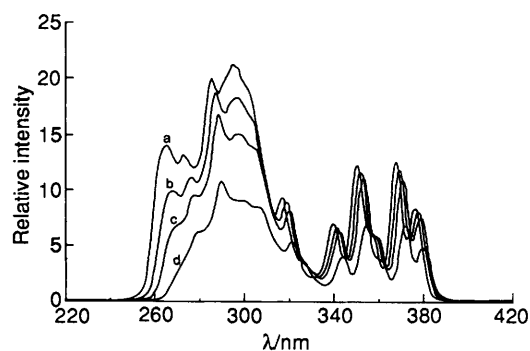

Fig. 6 Temperature dependence of excitation spectra of terbium(III) complexes of en in dmso. [Tb^{III}] = 0.0179 mol dm^{-3}, [en] = 0.179 mol dm^{-3}. λ_{ex} = 368.0 nm, λ_{em} = 544.5 nm; 16.2 (a), 36.4 (b), 55.7 (c) and 80.7 °C (d)

decay constants due to loss of N–H groups from the inner co-ordination sphere surpasses the increase caused by thermal quenching.

In summary, from the luminescence decay constants of the 1:1, 1:2 and 1:3 complexes of ethylenediamine with Eu^{III} and Tb^{III} in dmso, we are able to assign quenching factors for the bonded N–H groups. The quenching effect of a bonded N–H vibrator is 150% that of the O–H vibrator for Eu^{III} and 52% for Tb^{III}.

Acknowledgements

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