

Synthesis and near-IR luminescence properties of neodymium(III) and ytterbium(III) complexes with poly(pyrazolyl)borate ligands

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We have prepared neodymium(III) and ytterbium(III) complexes from a range of poly(pyrazolyl)borate ligands and studied their near-IR luminescence properties, in particular using solution lifetimes obtained in protonated and deuterated methanol to determine the extent of solvation of the complexes. For the neodymium complexes, the luminescence lifetime in methanolic solutions increases as solvent is excluded from the inner coordination sphere. However, for a given inner sphere coordination number, these complexes have longer luminescence lifetimes than complexes with aminocarboxylate ligands: there are fewer proximate C–H oscillators in the pyrazolylborate complexes compared to the aminocarboxylate complexes, and non-radiative quenching is therefore reduced. This bears out earlier suggestions that long luminescence lifetimes can be obtained by minimising the number of close diffusing X–H oscillators.

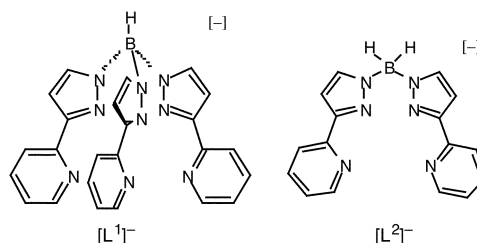
Introduction

Sensitised luminescence from lanthanide ions is becoming ever more important to the development of time-resolved imaging¹ and assay² techniques, chiefly due to the ease with which the metal-centred luminescence can be separated from short-lived background fluorescence. Historically, these studies have used europium and terbium complexes,^{3–5} which are emissive in the visible region and have long luminescence lifetimes (ms scale). However, the choice of sensitising chromophore is considerably restricted by the large energy gaps between the emissive state of these lanthanide ions and their respective acceptor states.^{6,7} As a result, interest has grown in the luminescence from lanthanide ions which are emissive in the near infrared region of the spectrum, particularly ytterbium^{8–10} and neodymium.^{11–14}

While the behaviour of ytterbium complexes is dependent on the local solvation environment to the same extent as other lanthanide complexes,¹⁵ neodymium has a manifold of intermediate excited states, making it considerably more sensitive to its local environment. In particular this means that significant non-radiative quenching of the metal-centred excited state occurs through C–H oscillators as well as O–H and N–H oscillators: C–H mediated non-radiative decay from complexes of Eu, Tb and Yb tends to be almost insignificant. As a result of this, unusually long luminescence lifetimes have been observed for complexes with few C–H oscillators close to the metal centre, especially those with β -diketonates and the Lehn cryptand.^{16,17}

We now report the synthesis and near IR luminescence properties of a range of ytterbium and neodymium complexes containing poly(pyrazolylborate) ligands (L^1 and L^2), which are hexadentate and tetradentate respectively. Photophysical studies on complexes of these ligands with Eu(III) and Tb(III) have been described recently. We found that some of the complexes, of Tb in particular, had particularly high emission quantum yields (up to 0.5) due to a combination of (i) efficient sensitisation of metal luminescence by energy-transfer from the

aromatic ligand chromophores, and (ii) limited access of solvent molecules to the protected metal centres.¹⁸ These ligands are therefore good candidates for study of near-IR emission from Yb and Nd; the presence of few C–H oscillators close to the metal centre make them suitable for use with neodymium in particular.



Experimental

Syntheses

All Yb and Nd complexes were made by the previously described methods used for the Eu or Tb analogues. Thus, $[M(L^1)(NO_3)_2]$ was prepared by reaction of the hydrated $M(NO_3)_3$ with $K(L^1)$ (1 : 1 proportions) in MeOH at room temperature, which resulted in precipitation of the product;^{4c} $[M(L^1)_2][BPh_4]$ was prepared by reaction of hydrated MCl_3 with two equivalents of $K(L^1)$ in MeOH, followed by precipitation with aqueous $NaBPh_4$;^{4c} $[M(L^2)_2(NO_3)_3]$ were prepared by reaction of the hydrated $M(NO_3)_3$ with two equivalents of $K(L^2)$ in MeOH, which resulted in precipitation of the product.^{4b} $[M(L^1)(dbm)_2]$ (Hdbm = dibenzoylmethane) was prepared by reaction of the hydrated metal chloride, $K(L^1)$, and dibenzoylmethane in a 1 : 1 : 2 ratio, in MeOH to which a few drops of Et_3N were added; the product precipitated on trituration with water.¹⁹ After vacuum filtration and washing with water, all complexes were then dried thoroughly and recrystallised from

Table 1 Characterisation data for the new complexes

Complex	FAB-MS ^a (<i>m/z</i>)		Analysis ^b			UV/Vis spectrum ^c $\lambda_{\max}/10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$
			%C	%H	%N	
[Nd(L ¹)(NO ₃) ₂]	587 (30) 650 (40)	{Nd(L ¹)} ⁺ {Nd(L ¹)(NO ₃) ₂ } ⁺	<i>f</i>			244 (28), 282 (23)
[Nd(L ¹) ₂][BPh ₄]	1032 (100)	{Nd(L ¹) ₂ } ⁺	<i>f</i>			243 (65), 290 (36)
[Nd(L ¹)(dbm) ₂]	811 (100)	{Nd(L ¹)(dbm) ₂ } ⁺	61.8 (62.7)	3.9 (4.0)	12.2 (12.2)	248 (43), 287 (25), 351 (32)
[Nd(L ²) ₂ (NO ₃) ₂]	746 (100)	{Nd(L ²) ₂ } ⁺	<i>f</i>			252 (29), 290 (24)
[Yb(L ¹)(NO ₃) ₂] ^d	618 (40) 680 (100)	{Yb(L ¹) ₂ } ⁺ {Yb(L ¹)(NO ₃) ₂ } ⁺	35.4 (36.3)	2.2 (2.6)	18.9 (18.6)	244 (34), 284 (29)
[Yb(L ¹) ₂][BPh ₄] ^e	1061 (100)	{Yb(L ¹) ₂ } ⁺	61.8 (62.7)	4.4 (4.7)	16.6 (17.3)	243 (64), 288 (57)
[Yb(L ¹)(dbm) ₂]	841 (100)	{Yb(L ¹)(dbm) ₂ } ⁺	60.7 (61.0)	3.7 (3.9)	11.9 (11.8)	246 (37), 288 (27), 353 (24)
[Yb(L ²) ₂ (NO ₃) ₂]	776 (40)	{Yb(L ²) ₂ } ⁺	<i>f</i>			252 (16), 289 (16)

^a Matrix: 3-nitrobenzyl alcohol. ^b Calculated values in parentheses. ^c MeOH, room temperature. ^d Elemental analysis requires one CH₂Cl₂ solvate. ^e Elemental analysis requires one Et₂O solvate. ^f Good analytical data could not be obtained; see text.

Table 2 Crystallographic data^a

Compound	[Nd(L ¹)(NO ₃) ₂] ^b ·Et ₂ O	[Nd(L ¹) ₂][BPh ₄] ^b ·0.6(Et ₂ O)·0.4(Me ₂ CO)	[Nd(L ²) ₂ (NO ₃) ₂] ^b ·2dmf
Empirical formula	C ₂₈ H ₂₉ BN ₁₁ NdO ₇	C _{75.6} H _{66.4} B ₃ N ₁₈ NdO	C ₃₈ H ₄₂ B ₂ N ₁₅ NdO ₅
<i>M</i>	786.67	1419.86	954.73
Crystal dimensions/mm	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.2	0.2 × 0.1 × 0.1
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> /Å	10.4274(11)	12.0803(14)	10.3989(12)
<i>b</i> /Å	13.4278(14)	24.827(3)	14.3209(15)
<i>c</i> /Å	14.5271(15)	22.673(3)	15.8589(15)
<i>a</i> ^o	113.062(2)	90	112.795(11)
<i>β</i> ^o	95.236(2)	97.707(2)	91.777(7)
<i>γ</i> ^o	105.849(2)	90	98.120(8)
<i>V</i> /Å ³	1754.6(3)	6738.5(13)	2145.9(4)
<i>Z</i>	2	4	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.489	1.400	1.478
Absorption coefficient/mm ⁻¹	1.538	0.832	1.271
Reflections collected: total/independent/ <i>R</i> _{int}	15113, 6170, 0.0438	43400, 15407, 0.0437	11976, 9184, 0.0334
Data/restraints/parameters	6170/0/433	15407/3/918	9184/0/584
Final <i>R</i> ₁ , <i>wR</i> ₂ ^{b,c}	0.0543, 0.1456	0.0329, 0.0919	0.0455, 0.0845

^a Data in common: $\lambda = 0.71073 \text{ \AA}$; Bruker SMART-CCD diffractometer; *T* = 173(2) K. ^b Structure was refined on F_o^2 using all data; the value of *R*₁ is given for comparison with older refinements based on F_o with a typical threshold of $F \geq 4\sigma(F)$. ^c $wR_2 = [\sum(w(F_o^2 - F_c^2))^2 / \sum w(F_o^2)]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

acetone–ether, dmf–ether or CH₂Cl₂–hexane mixtures *via* layering of the second solvent on a concentrated solution of the complex in the first solvent. Their formulations were confirmed from FAB mass spectroscopic data and partial elemental analytical data (collected in Table 1).

As we have found previously with lanthanide/pyrazolylborate complexes, elemental analytical data were poor.^{4c} Repeated attempts using two different analyzers gave in many cases low and highly variable %C and %N values, indicative of incomplete combustion, even when using burning aids such as V₂O₅. Those results that were acceptable are included in Table 1. All four types of complex have however been structurally characterised, and gave mass spectra consistent with their formulations. In the light of the analytical problems, only crystalline samples were used for solution state studies. Before these were used, the unit cell dimensions of representative crystals from each batch were checked to ensure homogeneity.

Crystallography

The crystal structures of three of the complexes, *viz.* [Nd(L¹)(NO₃)₂]^b·Et₂O, [Nd(L¹)₂][BPh₄]^b·0.6(Et₂O)·0.4(Me₂CO), and [Nd(L²)₂(NO₃)₂]^b·2dmf, have been determined. Suitable crystals were mounted on a Siemens SMART-CCD diffractometer under a stream of cold N₂ at –100 °C and all subsequent crystallographic studies were carried out at this temperature. The software used was SHELXS-97^{20a} for structure solution; SHELXL-97^{20b} for structure refinement, and SADABS^{20c} for the absorption correction. Details of the crystal parameters, data collection and refinement are collected in Table 2, and

selected metric parameters are in Table 3. None of the structural determinations presented any significant problems and all gave satisfactory refinements. In the unit cell of [Nd(L¹)₂][BPh₄]^b·0.6(Et₂O)·0.4(Me₂CO), there are two crystallographically independent complex units which both lie astride inversion centres with both metal ions in special positions. Each asymmetric unit therefore contains two independent halves of the complex cation and one anion, in addition to a region containing disordered solvent molecules which were successfully approximated as 0.6 ether and 0.4 acetone molecules superimposed. In [Nd(L²)₂(NO₃)₂]^b·2dmf, one of the dmf molecules was disordered over two positions with fractional occupancies of 0.67 and 0.33. In [Nd(L¹)(NO₃)₂]^b·Et₂O the two largest residual electron-densities, of intensity *ca.* 3 e Å⁻³, are both within 1 Å of the metal centre and located either side of it, indicating that they arise from absorption effects and are not chemically significant.

CCDC reference numbers 177766–177768.

See <http://www.rsc.org/suppdata/dt/b2/b200519k/> for crystallographic data in CIF or other electronic format.

Steady state luminescence measurements

The sample under study was illuminated by the fourth harmonic (266 nm) of a Nd:YAG laser (Spectra Physics DCR-11). Luminescence perpendicular to the laser excitation was collected, collimated and focused onto the entrance slits of a monochromator (Spex Triax 320), with the bandpass set to 2.5 nm. The emission intensity at the selected wavelength was recorded using a liquid nitrogen cooled germanium photodiode (North

Table 3 Selected bond distances (Å) for the crystallographically characterised molecules

[Nd(L ¹)(NO ₃) ₂] ⁺ ·Et ₂ O			
Nd(1)–N(31)	2.520(5)	Nd(1)–O(3)	2.586(4)
Nd(1)–N(11)	2.563(4)	Nd(1)–O(4)	2.541(4)
Nd(1)–N(51)	2.564(5)	Nd(1)–N(61)	2.705(5)
Nd(1)–O(6)	2.567(4)	Nd(1)–N(41)	2.707(4)
Nd(1)–O(7)	2.581(4)	Nd(1)–N(21)	2.726(5)
[Nd(L ²) ₂][BPh ₄] ⁺ ·0.6(Et ₂ O)·0.4(Me ₂ CO)			
Nd(1)–N(32)	2.664(2)	Nd(2)–N(112)	2.662(2)
Nd(1)–N(52)	2.680(2)	Nd(2)–N(152)	2.672(3)
Nd(1)–N(12)	2.702(2)	Nd(2)–N(132)	2.693(2)
Nd(1)–N(41)	2.924(2)	Nd(2)–N(121)	2.899(3)
Nd(1)–N(61)	2.945(2)	Nd(2)–N(141)	2.970(2)
Nd(1)–N(21)	2.963(3)	Nd(2)–N(161)	2.970(3)
[Nd(L ²) ₂ (NO ₃) ₂] ⁺ ·2dmf			
Nd(1)–N(71)	2.578(3)	Nd(1)–O(1)	2.633(3)
Nd(1)–N(11)	2.586(3)	Nd(1)–N(21)	2.711(4)
Nd(1)–O(2)	2.590(3)	Nd(1)–N(81)	2.711(3)
Nd(1)–N(51)	2.622(3)	Nd(1)–N(41)	2.712(4)
Nd(1)–N(31)	2.624(3)	Nd(1)–N(61)	2.729(3)

Coast EI817-P). The average of 10–25 laser shots was captured by digital oscilloscope (Tektronix TDS-320), generating a record of 1000 data points. The data were transferred to a PC for analysis. The emission spectra were obtained by recording the luminescence decay at each wavelength, and stepping the monochromator over the spectral window; typically a step of 2.5 nm was used. The total emission spectrum was obtained by the integration of each decay and plotting this as a function of wavelength. The shot-to-shot stability of the laser, coupled with the signal averaging, gave a reproducibility of *ca.* 1% in the recorded intensity.

Time-resolved luminescence measurements

The fourth harmonic of a Q-switched Nd:YAG laser (Spectra Physics GCR-150–10) operating at 10 Hz was used to excite the sensitising chromophore. Interference from stray 532 nm and 1064 nm radiation in the excitation beam was avoided by the use of optical filters. The luminescence was collected at 90° to the excitation beam and focused onto the entrance slits of a Spex TRIAX 320 monochromator; the bandpass was set to 5 nm. The selected radiation was detected by a liquid nitrogen cooled germanium photodiode/amplifier (North Coast EO-817P) operating in high sensitivity mode. The signal was captured and averaged by a digital storage oscilloscope (Tektronix TDS-320) and transferred to a PC for analysis. Typical decays were recorded as the average of eight laser shots. Instrument response functions were obtained using the fluorescence from a solution of a red laser dye (DCM), $\tau_f = 2.2$ ns. The luminescence lifetime was obtained by iterative reconvolution of the decay with the detector response to obtain the best fit (as judged by minimisation of residuals and reduced χ^2). The details of this approach have been discussed elsewhere.^{11,12} A typical fitted decay is shown in Fig. 1. Unless otherwise stated fitting to a double exponential decay did not yield significant improvements in the fit. Where double exponentials did yield a better fit, the longer exponential was estimated by fitting the tail of the decay conventionally, then using iterative reconvolution with two exponential decay components to obtain the best fit by variation of both decay components. The values obtained are the results of repeated convergence.

Results and discussion

Syntheses and structural characterisation of complexes

Four types of complex were used for this work, with M = Nd and Yb. These are [M(L¹)(NO₃)₂] (ten-coordinate, based on the hexadentate podand ligand L¹ and two bidentate nitrates);^{4c,18b}

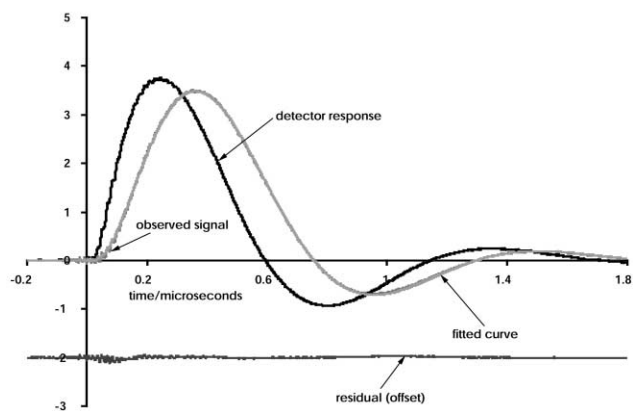


Fig. 1 A typical fitted decay showing the time-resolved profile of the luminescence of [M(L¹)(NO₃)₂] in methanol.

[M(L²)₂(NO₃)₂] (ten-coordinate, based on two tetradentate ligands L² and one bidentate nitrate),^{4b,18a} [M(L¹)₂][BPh₄]⁺, which have 12-coordinate metal centres from two interpenetrating hexadentate podand ligands L^{1,4c,18b} and [M(L¹)(dbm)₂], which are eight-coordinate from two bidentate dibenzoylmethane anions and a tetradentate L¹ (one bidentate arm is pendant).¹⁹

The crystal structures of [Nd(L¹)(NO₃)₂], [Nd(L¹)₂][BPh₄]⁺ and [Nd(L²)₂(NO₃)₂], which illustrate three of the four structural types under investigation, have been determined and are shown in Figs. 2–4 respectively (see also Tables 2 and 3). These are

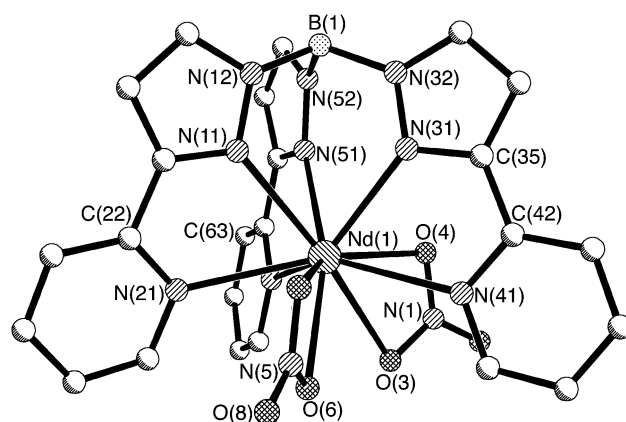


Fig. 2 View of [Nd(L¹)(NO₃)₂] derived from structural data.

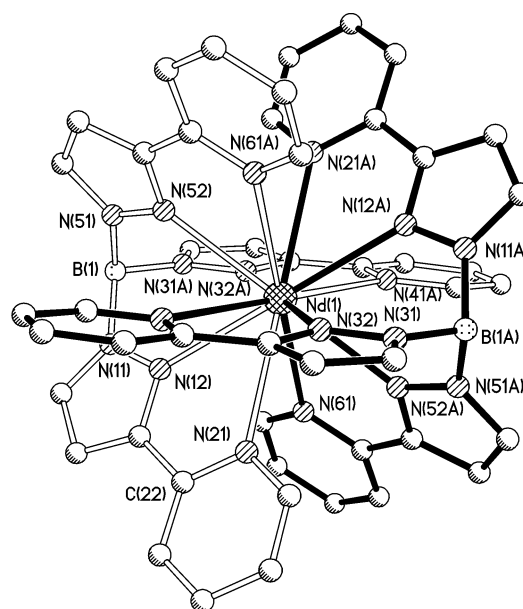


Fig. 3 View of the complex cation of [Nd(L²)₂][BPh₄]⁺ derived from structural data, with the two ligands shaded differently for clarity.

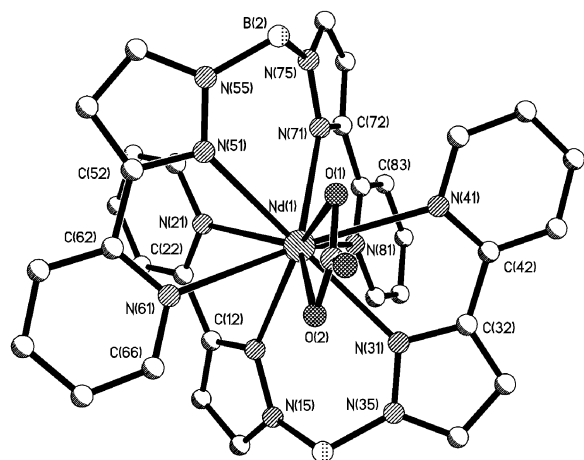


Fig. 4 View of $[\text{Nd}(\text{L}^2)_2(\text{NO}_3)_2]$ derived from structural data.

similar to the structures of the same type with other members of the lanthanide series which have already been published^{4b,c} and therefore do not need any detailed discussion other than to point out that in conjunction with the mass spectral data they confirm the nature of each complex. It is noticeable that the M–N(pyridine) bonds are significantly longer than the M–N(pyrazolyl) bonds because of the divergent geometry of the ligand, an effect which is particularly obvious in the more crowded icosahedral 12-coordinate complex $[\text{Nd}(\text{L}^1)_2][\text{BPh}_4]$ where there is an equatorial ‘belt’ of six pyridyl ligands close together, resulting in M–N(pyridine) distances that are considerably longer than those in $[\text{Nd}(\text{L}^1)(\text{NO}_3)_2]$.

Luminescence properties

Luminescence spectroscopy revealed that all of the complexes under study were luminescent in the near-IR region. The steady state emission spectra of the Nd(III) complexes are in Fig. 5;

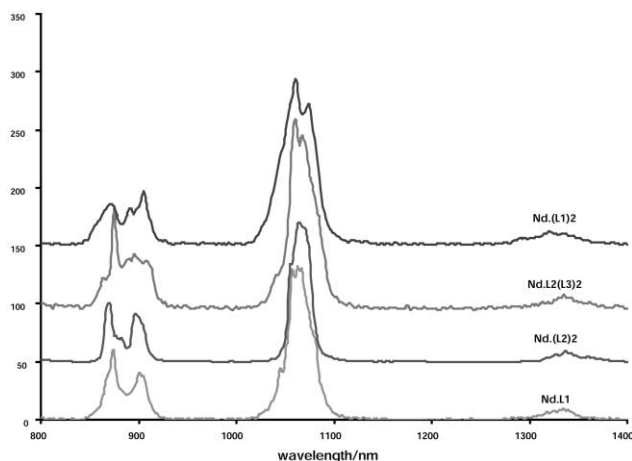


Fig. 5 Steady state emission spectra of the Nd(III) complexes. Spectra are offset for clarity.

those of the Yb(III) complexes are in Fig. 6. The spectra contain peaks which correspond to the transitions expected for these ions,^{8,11} however, they also show differences in their fine structure, which may be attributed to differences in local site symmetry around the metal. This is particularly evident for the Yb(III) complexes, which all have a major peak at around 970 nm (corresponding to ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$), with additional weaker peaks at the red end of the spectrum which differ from one complex to another. The presence of the peak at 970 nm implies that the site has approximately threefold symmetry in solution in all cases. The spectra are very similar to that of Yb(dbm)₃,⁸ but noticeably different from those obtained with azamacrocyclic

Table 4 Luminescence lifetimes (error, $\pm 10\%$) and inner sphere hydration numbers for the complexes under study

Complex	$\tau_{\text{CH}_3\text{OH}}/\mu\text{s}$	$\tau_{\text{CD}_3\text{OD}}/\mu\text{s}$	q_{calc}
$[\text{Nd}(\text{L}^1)(\text{NO}_3)_2]$	0.16, 1.20 ^a	0.56, 1.62 ^a	0.9, 0
$[\text{Nd}(\text{L}^2)_2(\text{NO}_3)_2]$	0.23	0.83	0.5
$[\text{Nd}(\text{L}^1)(\text{dbm})_2]$	0.15	0.58	1.0
$[\text{Nd}(\text{L}^1)_2][\text{BPh}_4]$	1.61	1.76	0
$[\text{Yb}(\text{L}^1)(\text{NO}_3)_2]$	1.58	14.86	0.9
$[\text{Yb}(\text{L}^2)_2(\text{NO}_3)_2]$	0.45, 1.36 ^a	4.72, 17.2 ^a	3.8, 1.2
$[\text{Yb}(\text{L}^1)(\text{dbm})_2]$	2.94	12.5	0.3
$[\text{Yb}(\text{L}^1)_2][\text{BPh}_4]$	2.01	12.9	0.6

^a Lifetimes obtained by fitting the tail of the luminescence decay rather than by deconvolution.

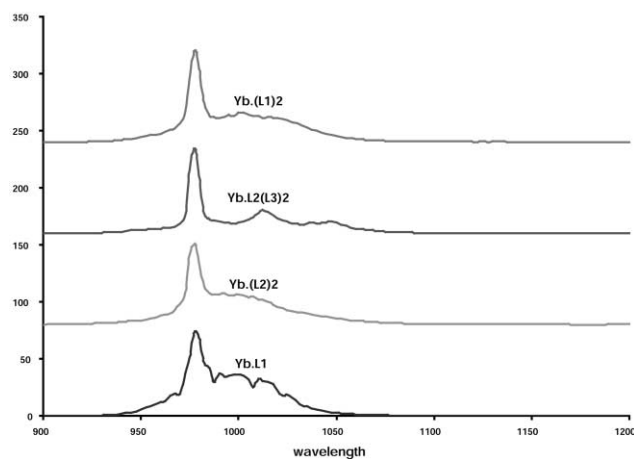


Fig. 6 Steady state emission spectra of the Yb(III) complexes. Spectra are offset for clarity.

complexes in which the 970 nm peak appears as a shoulder on the rest of the band which occurs at lower energy.

Time resolved spectra were measured to determine the luminescence lifetimes of the complexes; these were obtained by iterative reconvolution with the detector response using conventional methodologies. In all cases the growth of the luminescence signal was rapid ($\tau < 30$ ns), suggesting that energy transfer is efficient and that the luminescence itself is the rate-determining step. Luminescence lifetimes for the complexes are shown in Table 4. It may be seen that most of the luminescence profiles can be fitted to a single exponential decay, although the two complexes $[\text{Yb}(\text{L}^2)_2(\text{NO}_3)_2]$ and $[\text{Nd}(\text{L}^1)(\text{NO}_3)_2]$ give poor fits to a single exponential decay. In these cases, a dual exponential decay of the emission was observed, with the lifetime of the longer-lived component estimated by tail fitting. Such double exponential behaviour has been noted before for Yb(III) complexes, and has been assigned to exchange of coordinated solvent molecules on a timescale slower than that of the luminescence,²¹ a situation which can arise for Yb(III) because of the particularly slow rate of solvent exchange and the relatively short luminescence timescale.²² Such a model may apply to $[\text{Yb}(\text{L}^2)_2(\text{NO}_3)_2]$, where the disparity in lifetimes between the two components is sufficiently great to suggest that two species with quite different solvation numbers are present and interconverting slowly on the luminescence timescale.

The behaviour of $[\text{Nd}(\text{L}^1)(\text{NO}_3)_2]$ is more difficult to assess, since the second component of the decay has a relatively small weighting (around 15%). The most likely explanation is that some rearrangement of the ligands is occurring in solution to give $[\text{Nd}(\text{L}^1)_2]^+$ in which the metal ion is almost completely shielded from its surroundings (in the solid state the metal is 12-coordinate). In agreement with this, we measured separately the lifetime of $[\text{Nd}(\text{L}^1)_2][\text{BPh}_4]$, and found it to be similar to the longer-lived component of the dual emission observed

for $[\text{Nd}(\text{L}^1)(\text{NO}_3)_2]$ (1.76 vs. 1.62 μs , Table 4). (Note that the FAB mass spectrum of the initial crystalline sample of $[\text{Nd}(\text{L}^1)(\text{NO}_3)_2]$ showed that it was free of this impurity, which gives an intense and characteristic signal).

For the Yb(III) complexes, the luminescence lifetimes may be used to calculate q , the inner sphere hydration number, using the equation

$$q = A_{\text{Ln}} \cdot \Delta k^{\text{corr}} \quad (1)$$

where A_{Ln} is an experimentally determined coefficient, and $\Delta k^{\text{corr}} = k_{\text{CH}_3\text{OH}} - k_{\text{CD}_3\text{OD}} - B$ (where $k_{\text{CH}_3\text{OH}}$ and $k_{\text{CD}_3\text{OD}}$ are the luminescence decay rate constants in methanol- H_4 and methanol- D_4 respectively, and B is a correction factor taking outer sphere contributions into account).¹⁵ For Yb(III) in methanol, $A_{\text{Ln}} = 2.0 \mu\text{s}^{-1}$ and $B = 0.1 \mu\text{s}^{-1}$.¹⁵ The value of q obtained for $[\text{Yb}(\text{L}^1)(\text{NO}_3)_2]$ in this way (0.9) is significantly smaller than the values obtained for the analogous Eu(III) and Tb(III) complexes, for which q values of 2.3 and 1.4 respectively were obtained in MeOH. This difference may be ascribed to the smaller ionic radius of Yb(III), which is the penultimate member of the Ln(III) series; it is well established that across the lanthanide(III) series a reduction in coordination number can occur at some point because of the steadily decreasing size of the metal ion.

For $[\text{Yb}(\text{L}^2)_2(\text{NO}_3)_3]$, the q values obtained for the two different luminescent species which appear to be present are 1.2 and 3.8. The smaller of these values is in good agreement with our earlier findings for the Eu(III) and Tb(III) analogues ($q = 1.5$ and 0.6, respectively) which we suggested as arising from dissociation of the nitrate ligand and its replacement by *ca.* one solvent molecule. The larger q value of 3.8 for the other component cannot be explained if we assume that both tetradentate ligands $[\text{L}^2]^-$ remain fully coordinated. We suggest therefore that the component with the shorter luminescence and higher degree of solvation arises from partial displacement of the bidentate arms of $[\text{L}^2]^-$ by solvent molecules; detachment of one bidentate arm would approximately account for the higher q value. The remaining two Yb(III) complexes, $[\text{Yb}(\text{L}^1)(\text{dbm})_2]$ and $[\text{Yb}(\text{L}^1)_2][\text{BPh}_4]$, have low q values consistent with their crowded structures. The non-zero value of q may therefore arise as a result of the separation between the solvent molecules and the metal centre being greater than the 'ideal' value assumed by the equation above, which will introduce an error into the calculation of the second-sphere quenching contribution.¹⁵ Dissociation of a dibenzoylmethane ligand in solution may also be partly responsible for the non-zero q value.

The luminescence lifetimes observed for our Nd(III) complexes are long compared to those observed for other Nd(III) complexes, being in the microsecond domain. Analysis of their behaviour is however more difficult. The relation

$$q = 130(k_{\text{H}_2\text{O}} - k_{\text{D}_2\text{O}}) - 0.4 \quad (2)$$

works well for aminocarboxylate complexes of Nd(III) in water where the luminescence lifetimes are in the nanosecond domain.¹⁷ To adapt this for use in CH_3OH and CD_3OD it is not just a question of doubling the A value to account for the reduced number of OH oscillators [which works satisfactorily for Tb(III) and Eu(III)] because this ignores the effect of replacing the C–H oscillators of the solvent by C–D which is significant for Nd(III).^{11–17} The hydrated Nd(III) ion has a luminescence lifetime of 30 ns while the deuterated analogue has a lifetime of 150 ns;¹¹ in methanol the emission lifetimes of 'free' Nd(III) are around 65 ns and 290 ns for CH_3OH and CD_3OD respectively.¹¹ Assuming that the methanolic and aqueous species have the same stoichiometry, we may suggest that the A factor will change with the ratio of Δk , *i.e.* this gives

$$q = 290(k_{\text{CH}_3\text{OH}} - k_{\text{CD}_3\text{OD}}) - 0.4 \quad (3)$$

as an equation to take into account deuteration of the C–H oscillators of the solvent as well as the O–H oscillators.

This remains a very crude approximation, but does give reasonably sensible q values (Table 4), though variations between the calculated and crystallographic values for q arise from the relative absence of C–H oscillators from the ligands around the metal. Such an influence on the environment cannot be ignored, though we would suggest that further adjustment to this equation represents unnecessary effort when q values are readily determined with other lanthanides. Any attempt to develop a robust formula for calculating q for neodymium complexes from luminescence data would have to take account of the distribution of distances between quenching X–H oscillators and the metal centre, since the efficiency of the quenching process decreases with separation.

The absence of C–H oscillators around the metal centre also makes the luminescence lifetimes much longer than those of analogous complexes based on carbon containing backbones (≈ 150 ns for a typical complex with $q = 1$).^{11,12,17} The lifetime of $[\text{Nd}(\text{L}^1)_2][\text{BPh}_4]$ is exceptionally long, and is similar to that of neodymium and its complexes in dmsu.^{9,11} This argues that, as with dmsu, there is minimal coupling between the bound metal and the ligand X–H oscillators. The observation of such a lifetime in protic solvents confirm that the solvent is excluded from the coordination sphere in this complex. It is also worth noting that $[\text{Nd}(\text{L}^1)(\text{dbm})_2]$ has a shorter luminescence lifetime than the complexes derived solely from pyrazolylborate ligands, presumably as a result of the increased number of C–H oscillators in the skeleton of the ligated dbm. This is borne out by the fact that fluorinated β -diketonates exhibit longer lifetimes than their counterparts containing C–H oscillators.¹⁶ This observation of unusually long luminescence for some of the neodymium complexes is interesting and potentially valuable, since it simplifies the application of time-gating techniques to observation of luminescence from neodymium complexes in protic solvents.

Conclusions

Near-IR emission has been detected from these pyrazolylborate-derived complexes of Nd(III) and Yb(III). The chief advantage of such systems lies in their relative lack of C–H oscillators close to the metal centre, which causes the lifetimes of the Nd(III) complexes in particular to be particularly long compared to the luminescence lifetimes of complexes with aminocarboxylate ligands. We intend to concentrate on the synthesis of kinetically stable systems which incorporate these functionalities and their desirable luminescence properties.

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