

Synthesis and coordination chemistry of boron-functionalized poly(pyrazolylpyridyl)borate with Ln(III) metals

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ABSTRACT: A new family of lanthanide/boron-based complexes have been synthesized from the novel substituted poly(pyrazolylpyridyl)borate ligand containing phenyl substituents on the boron atom Ph₂Bp^{py} (L). The complexes have been fully characterized by analytical and spectroscopic methods. The single crystal X-ray structure and mass spectroscopy reveal the isostructural dinuclear complexes: [Ln₂(L)₂(NO₃)₂(OH)₂] where Ln = Eu, Gd or Tb. Upon excitation of the Ln(III) complexes in DCM, their luminescence spectra display narrow f-f transitions. It is found that the ligand can efficiently sensitize the Tb(III) complex because of the better triplet state energy match to the Tb(III)-⁵D₀ excited states.

Keywords: Boron; europium(III); terbium(III); crystal structure; emission.

التركيب والخصائص الكيميائية لمركبات البورون مع بايروزول بيريدين وفلزات اللانثانات

نوال الراسبي و مايكل د. وورد

الملخص: تم تكوين عائلة جديدة لمركبات اللانثانات/بورون من ليجند البورون مع بايروزول بيريدين والذي يحتوي على مجموعتي فينول ملتصقة بذرة البورون Ph₂Bp^{py} (L). كما أثبت التركيب البلوري المعقد ثنائي الفلز: [Ln₂(L)₂(NO₃)₂(OH)₂] حيث Ln = Eu, Gd or Tb. ولقد دل الطيف الضوئي للمركبات ف محاليلها على انتقالات ضوئية بطبيعة f-f. وجدنا بأن الليجند يستطيع أن ينحسض ضوئيا لمركب التيربيوم بفعالية وذلك لأقتراب مستويات الطاقة بينهما.

الكلمات المفتاحية: بورون، يوربيوم(III)، تيربيوم(III)، تركيب بلوري، طيف ضوئي.

1. Introduction

Boron, the only non-metal of Group 13, displays a unique structural diversity in its combinations with transition metals [1]. The enormous diversity of boron chemistry ranges from polyboranes [2] to carboranes [3] to metallaboranes [4] and metal complexes of organoboron ligands [5]. In 1966, poly(pyrazolyl)borates were first reported by S. Trofimenko [6]. The poly(pyrazolyl)borate ligands have been proven to be extremely popular amongst coordination chemists for a wide range of applications because of their ease of synthesis, ease of functionalisation, and the steric protection which they afford to metal centres [7].

Over the years poly(pyrazolyl)borates such as bidentate Bp ligands have been compared to β-diketonates (Chart 1) [5]. These 'first-generation' ligands are labile, rich in electron density and their coordination behavior is strongly dependent on the coordinating metal [8-11]. In subsequent years, a new class of C³-substituted poly(pyrazolyl)borate ligands were developed in which additional coordinating groups have been attached to the pyrazolyl rings, completely changing the character of the simple first-generation ligands. Constituents such as pyridine [12]. (Bp^{py} in Chart 1), bipyridyl, [13] thioanisyl, [14] pyrazinyl, [15] and carboxamide [16] units have

been appended to the pyrazolyl C³ positions of poly(pyrazolyl)borates, converting the ligands to polydentate chelates.

The Ward group prepared new ligands by the attachment of a 2-pyridyl substituent to each pyrazolyl ring at the C³ position converting each 'arm' of the ligand to a tridentate chelate [17-18]. Substitution of poly(pyrazolyl)borates is also confined largely to the boron atom [5]. The potentially reactive B–H bonds in **Bp**^{py}, may be replaced with either alkyl or aryl groups. Suitably sized ligand substituents can help to prevent agostic interaction through steric blocking of the space above and below the poly(pyrazolyl)borate ligands [19-20]. Substituents on the boron atom of Bp ligands have shown great stability such as on [(Ph₂Bp)₂Ni]. [21] Whilst the complex [(H₂Bp)Ag] is air-sensitive, the analogue [(Ph₂Bp)Ag] is very stable, [22] suggesting that the stability of these complexes result from a combination of steric effects and not just solely from the aromatic substituents on the pyrazolyl rings.

As part of our interest in luminescent lanthanide complexes, we describe the synthesis, crystal structure and luminescence behavior of a series of lanthanide complexes with the boron-substituted bis(pyrazolylpyridyl)borate ligand: Ph₂Bp^{py} (**L**) (Chart 1) in which two bidentate arms are connected to a boron centre. The incorporation of two phenyl units at the boron centre has altered its sensitization properties to Eu(III) and Tb(III) ions. The X-ray crystal structure confirmed the general formulae of the complexes to be: [Ln₂(L)₂(NO₃)₂(OH)₂] where Ln = Eu, Gd or Tb.

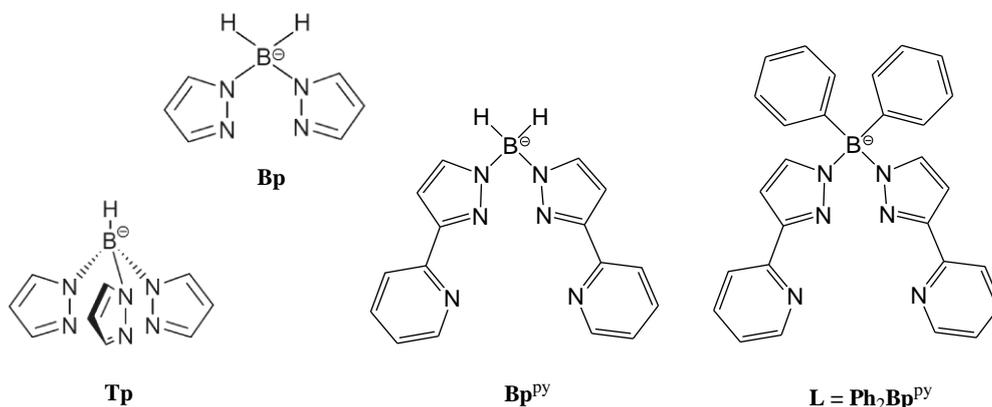


Chart 1: The structures of the poly(pyrazolyl)borates: Bp, Tp, Bp^{py} and Ph₂Bp^{py} (**L**).

2. Experimental

The Boron ligand was prepared according to the method described by Trofimenko [19].

L (Na[Ph₂Bp^{py}]): 3-(2-pyridyl)pyrazole (0.6 g, 4.14 mmol) and NaBPh₄ (0.58 g, 1.70 mmol) were ground together finely and heated gradually to 190 °C for 4 hrs under N₂. During this time, H₂ gas was evolved at 150 °C and then benzene was evolved at 190 °C. Any unreacted 3-(2-pyridyl)pyrazole sublimed at the top of the flask. After cooling to r.t.; the melt was washed with hot toluene (15 mL) and hexane (15 mL) and finally dissolved in CH₂Cl₂ and concentrated in vacuum to yield 0.50 g of white powder (60%). Positive-ion electrospray MS: *m/z* 477 [M⁺]. IR(KBr) 1021 cm⁻¹ (B–C). ¹¹B NMR (CDCl₃): δ –0.819. Found: C, 70.61; H, 5.09; N, 17.49. Required for C₂₈H₂₂N₆BNa: C, 70.63; H, 4.62; N, 17.65%.

Synthesis of the complexes

The complexes were prepared by combining equimolar quantities of Eu(NO₃)₃, Gd(NO₃)₃ or Tb(NO₃)₃ with the ligand in MeOH and left to stand for 1 hr during which time a precipitate was formed. The precipitate was filtered off and washed with MeOH to give a powder. Characterization data for the complexes are as follows:

[Eu₂(L)₂(OH)₂(NO₃)₂]. Yield 70 %. ES-MS: *m/z* 1310 {[Eu₂(Ph₂Bp^{py})₂(OH)₂(NO₃)₂]}⁺. IR(KBr) 1001 cm⁻¹ (B–C).

[Gd₂(L)₂(OH)₂(NO₃)₂]. Yield 72 %. ES-MS: *m/z* 1253 {[Gd₂(Ph₂Bp^{py})₂(OH)₂]}²⁺ and 1316 {[Gd₂(Ph₂Bp^{py})₂(OH)₂(NO₃)₂]}⁺. IR(KBr) 1003 cm⁻¹ (B–C). X-ray quality crystals were grown by slow evaporation of a DCM solution of the complex in air.

[Tb₂(L)₂(OH)₂(NO₃)₂]. Yield 70 %. ES-MS: *m/z* 1318 {[Tb₂(Ph₂Bp^{py})₂(OH)₂(NO₃)₂]}⁺. IR(KBr) 1001 cm⁻¹ (B–C).

Spectro-fluorimetric measurements

UV-visible spectra were recorded on a Varian Cary 50 conc UV-visible spectrophotometer in range 250-800 nm. Quartz cuvettes of 1 cm path length were used and solvent background corrections were applied. Steady state fluorescence spectra in solid and solution states were recorded on an Edinbrough FS5 fluorimeter. The solid state

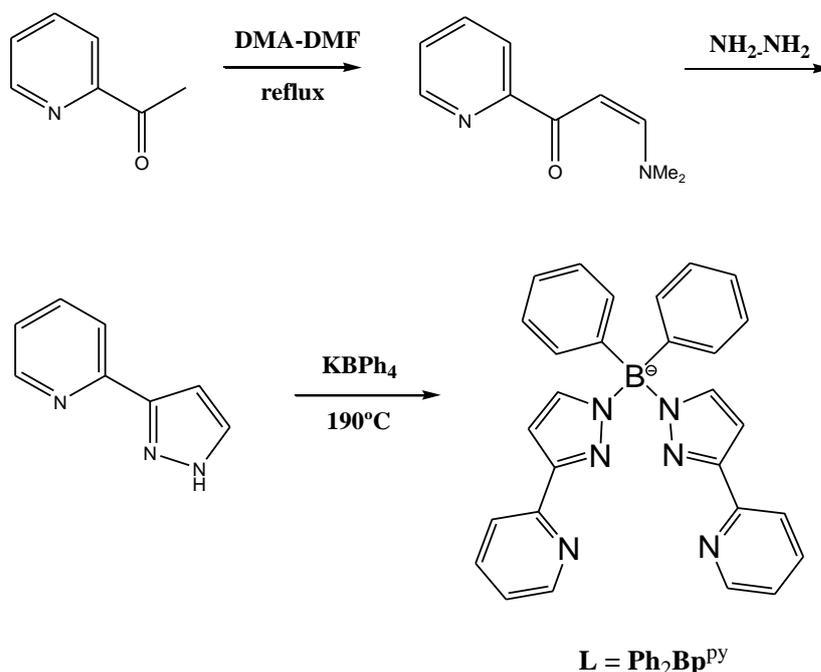
phosphorescence lifetime measurements for the Ln(III) complexes were measured on Perkin-Elmer LS50B Fluorimeter at RT and 77 K.

Crystallography

Single crystals of the complex **GdL** was obtained as detailed above. Data was collected at 100 K, using Bruker APEX-II CCD diffractometer equipped with Mo-K α radiation. Absorption corrections were applied in each case using SADABS. [28] The structures were solved by direct methods or heavy atom Patterson methods and refined by full matrix least squares methods on F^2 using SHELXL-97. [29] The hydrogen atoms were generated geometrically with isotropic thermal parameters. Crystallography data (excluding the structure factors) for the reported structure have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

The synthesis of the new bi(pyrazolylpyridyl)borate ligand: Ph₂Bp^{py} (**L**) is outlined in Scheme 1. The key intermediates for formation of the ligand is 3-(2-pyridyl)pyrazole, which is prepared from 2-acetylpyridine, in the usual two-step procedure for conversion of acetyl groups to pyrazole groups. [23] Then, **L** was prepared by reaction of 3-(2-pyridyl)pyrazole with KBPh₄ in a melt at 190 °C until benzene vapour is no more evolved. [24] Satisfactory elemental analysis, FAB mass spectra, [11] B NMR and ¹H NMR spectra confirmed the formulation of the ligand.



Scheme 1. Schematic route for the synthesis of Ph₂Bp.

Reaction of **L** with nitrate salts of Eu(III), Gd(III) or Tb(III) in MeOH afforded white precipitates respectively. X-ray quality crystals were grown by slow evaporation of their solutions in dichloromethane, DCM. The complexes were satisfactorily characterised by FAB mass spectrometry. For example, the fragment: $\{[M_2(L)_2(OH)_2(NO_3)]\}^{2+}$ was observed at m/z 1310, 1316 and 1318 respectively for Eu(III), Gd(III) or Tb(III) complexes. The crystal structure of $[Gd_2(L)_2(NO_3)_2(OH)_2] \cdot CH_2Cl_2$ (**GdL**) in Figure 1 has proved to be a dinuclear complex in which each ligand donates two bidentate sites to one metal ion, with the two metal centres bridged through two hydroxyl groups. The coordination environment about each metal centre is 8-coordinate and best described as a square antiprismatic, having an equatorial belt of four N atoms from [L]⁻ with two bridging hydroxyl groups and one bidentate chelating (NO₃⁻) in the ‘axial’ positions on either side of the MN₄ plane. The four N-donor atoms from each [L]⁻ ligand form a plane, with the Gd(III) centre lying 0.33 Å out of the N₄ plane. The angle between the two Gd(NN) planes is 14.3°. The metal–ligand bond distances exhibit a Gd–N(py) bonds are on average significantly longer than the Gd–N(pz) bonds and are comparable to previously reported complexes. [12–13] Selected bond distances and angles are listed in Table 1.

It is also worth noting that replacement of the hydrogen atoms in Bp by two phenyl rings in Ph₂Bp^{py} (**L**) changes the coordination behaviour of the ligand compared to functionalized Bp which yielded mononuclear

complexes with Ln(III) ions. [12] The steric effects caused by the phenyl rings play a big role in the new structure. Intra-molecular O–H $\cdots\pi$ hydrogen-bonding interactions (~ 2.9 Å) are observed, involving one phenyl ring and the coordinating hydroxyl group, which clearly plays an important role in stabilising this complex. The steric interactions within the Gd(III) complex are shown in Figure 1 (Bottom). Other $\pi\cdots\pi$ and $\pi\cdots\text{CH}$ stacking interactions between the aromatic rings and the solvent molecules, were observed in the molecular packing.

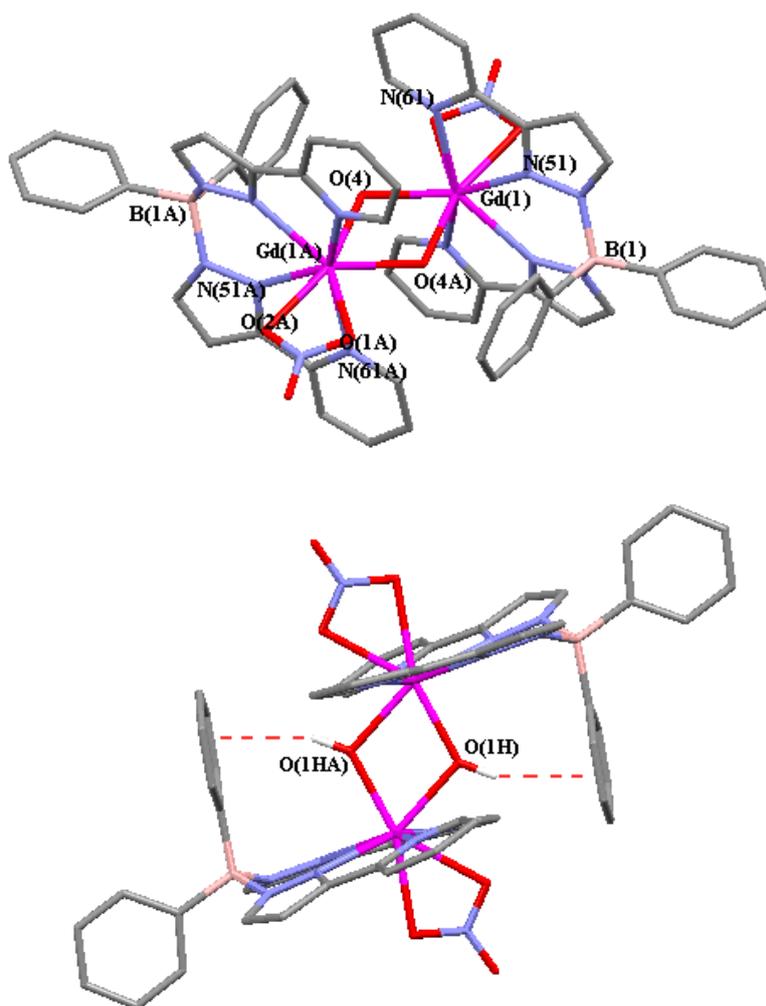


Figure 1 Top: The crystal structure of **GdL** showing the two hydroxyl bridges. Bottom: The π -interactions within the molecule.

Table 1. Selected bond lengths (Å) and angles ($^\circ$) for GdL.

Gd(1)-O(1H)#1 ^[a]	2.253(5)	Gd(1)-N(11)	2.496(6)
Gd(1)-O(1H)	2.284(5)	Gd(1)-N(31)	2.554(6)
Gd(1)-O(1)	2.481(5)	Gd(1)-N(1)	2.560(6)
Gd(1)-N(21)	2.488(6)	Gd(1)-Gd(1)#1 ^[a]	3.7240(15)
Gd(1)-O(2)	2.491(5)		
O(1H)#1-Gd(1)-O(1H) ^[a]	69.9(2)	O(1H)-Gd(1)-O(2)	77.26(18)
O(1H)#1-Gd(1)-O(1) ^[a]	161.09(17)	O(1)-Gd(1)-O(2)	51.43(17)
O(1H)-Gd(1)-O(1)	128.68(17)	N(21)-Gd(1)-O(2)	119.06(18)
O(1H)#1-Gd(1)-N(21) ^[a]	85.19(18)	O(1H)#1-Gd(1)-N(11) ^[a]	87.62(18)
O(1H)-Gd(1)-N(21)	137.24(19)	O(1H)-Gd(1)-N(11)	135.33(18)
O(1)-Gd(1)-N(21)	77.82(19)	O(1)-Gd(1)-N(11)	79.98(18)
O(1H)#1-Gd(1)-O(2) ^[a]	147.09(17)	N(21)-Gd(1)-N(11)	74.63(18)

^[a] Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1.

Photo-physical properties

The absorption spectrum of **L** in DCM is shown in Figure 2. It shows two strong transitions at 250 and 285 nm which can be attributed to ligand-centred $\pi \rightarrow \pi^*$ transitions from (pyrazolyl/pyridine) units [25].

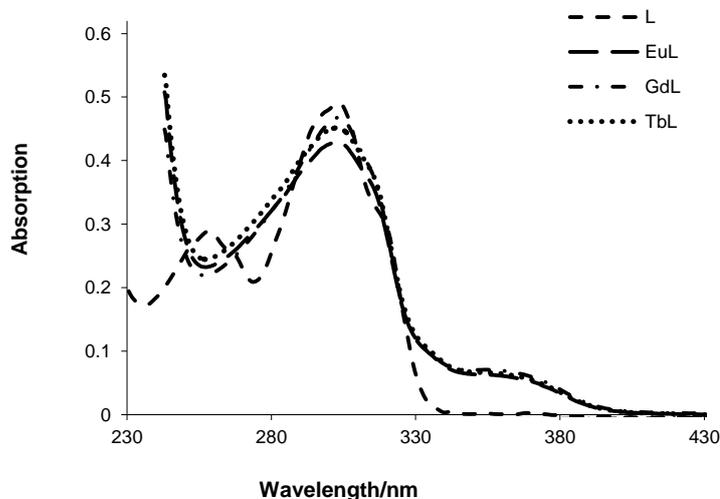


Figure 2. The absorption spectra of **L** and its Ln(III) complexes (1×10^{-5} M) in DCM solutions at room temperature.

Metal-centred luminescence

The triplet state energy (${}^3\pi\pi^*$) of **L** can be determined from the phosphorescence spectrum of its Gd(III) complex recorded in a mixture of ethanol/methanol solution at 77K. Gd(III) ion lacks a low lying electronic acceptor level ($>30,000$ cm^{-1}), so its luminescence features are associated with those of the coordinated ligand. From this emission spectrum, the ligand-based triplet state energy of **GdL** is $28,800$ cm^{-1} (347 nm). The luminescence from the Eu(III) and Tb(III) complexes in DCM solution are presented in Figure 3. Excitation of the **EuL** at 345 nm in DCM results in intense red luminescence of Eu(III) showing characteristic peaks from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transitions of Eu(III) at 558, 603, 626, 662 and 711 nm. This implies that energy-transfer from the ligand triplet state to the emissive ${}^5\text{D}_0$ level of Eu(III) (*ca.* $17,500$ cm^{-1}) is favourable. The presence of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition proves the presence of the Eu(III) centres in a non-centrosymmetric site in **EuL** which agrees with the X-ray crystal structures. [26] Upon excitation of the Tb(III) complex, **TbL**, at 345 nm in CH_2Cl_2 , its luminescence spectrum displays strong green emission from the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_{6-2}$ transitions at 632, 592, 550 and 496 nm. The energy difference between the triplet state energy of **L** and the ${}^5\text{D}_4$ level ($20,500$ cm^{-1}) of Tb(III) is equal to *ca.* $8,300$ cm^{-1} . According to Latva's empirical rule, optimal sensitization for the Tb(III) luminescence requires an energy gap $\Delta E({}^3\pi\pi^* - {}^5\text{D}_4)$ more than $1,850$ cm^{-1} . [27] Therefore, **L** can sensitise the Tb(III) centre efficiently. By comparison to the Eu(III) complex, the situation is different. According to Latva's empirical rule, for optimal ligand to Eu(III) energy transfer, the energy gap should be no more than $2,500$ cm^{-1} . In fact the calculated energy difference $\Delta E({}^3\pi\pi^* - {}^5\text{D}_0)$ is higher than this at around $11,300$ cm^{-1} . Therefore, the ligands can poorly transfer energy to the ${}^5\text{D}_0$ excited states and hence the luminescence from Eu(III) is weak. This result is in agreement with their observed lifetime (τ_{obs}) measurements. The phosphorescence decays of the Eu(III) and Tb(III) complexes with **L** in DCM are mono-exponential. The luminescence lifetime of Tb(III) is longer than that from Eu(III).

Table 2. Summary of the photophysical data for **L** and its Ln(III) complexes.

Compd	λ_{max} (nm) [ϵ (10^3 $\text{M}^{-1}\text{cm}^{-1}$) in MeCN]	Lifetime at $f-f$ (ms) ^[a]
L	296(65), 248 (29)	–
EuL	293(36), 345 (sh)	0.56
GdL	294(45), 345 (sh)	–
TbL	294(43), 345 (sh)	0.84

^[a] τ in dry DCM, the estimated standard error < 1%.

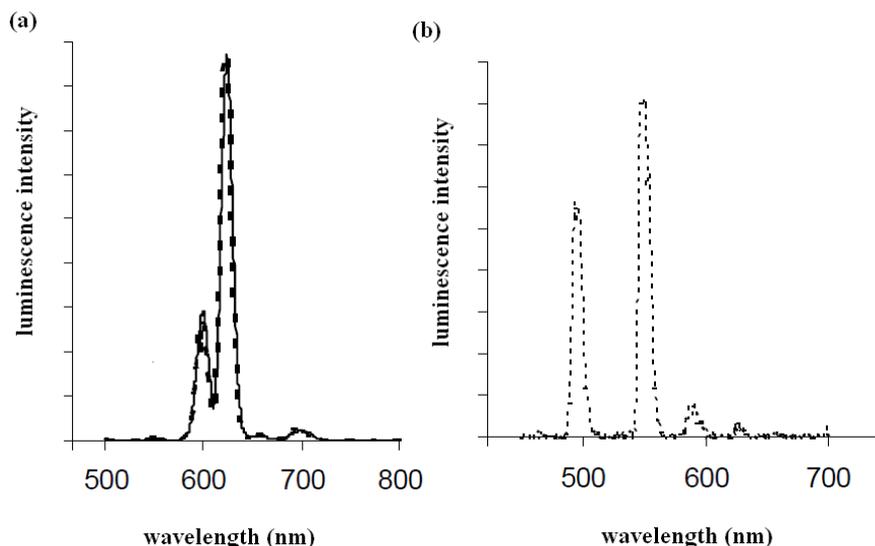


Figure 3. Luminescence spectra of the Ln(III) complexes: (a) $[\text{Eu}_2(\text{L})_2(\text{NO}_3)_2(\text{OH})_2]$ (EuL) and (b) $[\text{Tb}_2(\text{L})_2(\text{NO}_3)_2(\text{OH})_2]$ (TbL) in (1×10^{-5} M) DCM solutions at room temperature.

4. Conclusion

The new boron-based ligand, **L**, which is derived from the well-known bis(pyrazolyl)borate core, has been synthesised and fully characterised. The X-ray crystal structure and MS analysis revealed the isostructural dinuclear complexes: $[\text{Ln}_2(\text{L})_2(\text{NO}_3)_2(\text{OH})_2]$, Ln = Eu, Gd and Tb. The metal centres are bridged through two hydroxyl groups. The steric effects caused by the aromatic substituents on the boron centre has played a big role in stabilizing the structures, through intra-molecular O–H $\cdots\pi$ hydrogen-bonding interactions. The photophysical investigations in DCM gave evidence that **L** is able to achieve ligand to metal energy transfer and intense red emission from Eu(III) and green emission from Tb(III) centres are observed in the visible region.

Table 3. Crystallographic data for GdL.

Formula	$\text{C}_{29}\text{H}_{25}\text{BCl}_2\text{GdN}_7\text{O}_4$
Formula weight	774.52
T (K)	100(2) K
Crystal system	Triclinic, P1
a (Å)	11.430(4)
b (Å)	12.063(4)
c (Å)	12.255(4)
α (°)	85.638(17)
β (°)	80.838(18)
γ (°)	63.208(17)
V (Å ³)	1489.1(8)
Z	2
D_{calc}	1.727
μ (mm ⁻¹)	2.455
Crystal size (mm)	0.16 x 0.08 x 0.04
Reflections collected	24005
Independent reflections	6845 [R(int) = 0.0887]
Data / restraints / parameters	6845 / 4 / 392
Goodness-of-fit on F^2	0.976
Final R indices ^a	R1 = 0.0580, wR2 = 0.1419
Largest diff. peak and hole (e.Å ⁻³)	3.722 and -1.756

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Appendix

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center. A copy of the data can be obtained free of charge from the Director, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1222-336033; email: deposit@ccdc.cam.ac.uk.

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