Synthesis and Luminiscence Properties of Europium(III) and Terbium(III) Complexes with Polyacid Chelates Derived from 2,6-Bis(*N*-pyrazolyl)pyridine[1]

Modesto J. Remuiñán, Herminia Román, Maria Teresa Alonso and Juan C. Rodríguez-Ubis*
Departamento de Química, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

A short and efficient synthesis of *N,N,N',N'*-[2,6-bis(3-aminomethyl-1-pyrazolyl)pyridine]-tetrakis(acetic acid) (**6**), an analogue of terpyridine with additional chelating iminodiacetic groups, is described. Compound **6** forms stable complexes with Eu^{III} and Tb^{III} in water whose relative luminescence yields, excitation maxima and emission decay lifetimes have been measured. The number of water molecules in the first coordination sphere of the europium complex have also been determined. Comparison of data from the Eu^{III} and Tb^{III} complexes of **6** and of the parent trisheterocycle diacid 2,6-bis(3-carboxy-1-pyrazolyl)pyridine shows that the iminodiacetic subunits give extra stabilization to the complexes and are essential to protect the metal from the water environment.

The luminescence of lanthanide(III) compounds is widely applied in various fields. In particular, the luminescent lanthanide complexes have found applications in the analysis of the Ln^{3+} ions and in fluoroimmunoassays.[2] Schematically, a luminescent lanthanide(III) complex can be described as a system in which light is absorbed by the organic ligand, transferred to the metal centre and emitted by the cation. For such a system to have an efficient cation emission, the ligand should have a high molecular extinction coefficient and the ligand-to-metal energy transfer should be effective.[3] The latter condition is fulfilled by ligands which have excited states close in energy to those of the emitting Ln^{3+} ions. Most of the studies found in the literature are concerned with β-diketonato and aromatic ligands, which behave as good chromophores towards lanthanoid(III) cations.[4] However the photophysical properties of Eu^{3+} and Tb^{3+} ions markedly depend on their environment. In particular, their luminescence is strongly decreased by the inclusion of water molecules in the coordination shell.[5] Considerable efforts have thus been made to isolate the ion from their surroundings, *i.e.* designing cryptands,[6] calixarenes,[7] and cyclodextrins[8] as ligands but a detailed analysis of the structures showed that the cation was not entirely protected and still accessible to water molecules.

In the present paper we report the synthesis and luminescence study of lanthanide(III) complexes of new ligands derived from 2,6-bis(*N*-pyrazolyl)pyridine, a tridentate N_3 analogue to terpyridine ligand. The terpyridine-like ligands have added interest because their ruthenium complexes are potential catalysts for photochemical and redox reactions.[9] However, while the synthesis of substituted terpyridines is relatively difficult, the chemistry of the pyrazole ring in similar N_3 structures facilitates the variation in number and type of substitution.[10]

It is well known that 1,2-ethanediamine *N,N,N',N'*-tetraacetic acid (EDTA) and its analogues form quite strong complexes with metal ions. Iminodiacetic subunits have been recently included in different structures in order to study the luminescence properties of their lanthanide complexes.[11] Our interest in the properties of metal complexes, and especially in a good aqueous stability, led us to investigate the preparation of structures containing both subunits, 2,6-bis(*N*-pyrazolyl)pyridine and iminodiacetic acid. Besides, the geometry of the five-membered pyrazole ring and the spatial arrangement of the attached iminodiacetic subunits were expected to provide interesting spectral properties to its metal complexes.

Results and Discussion

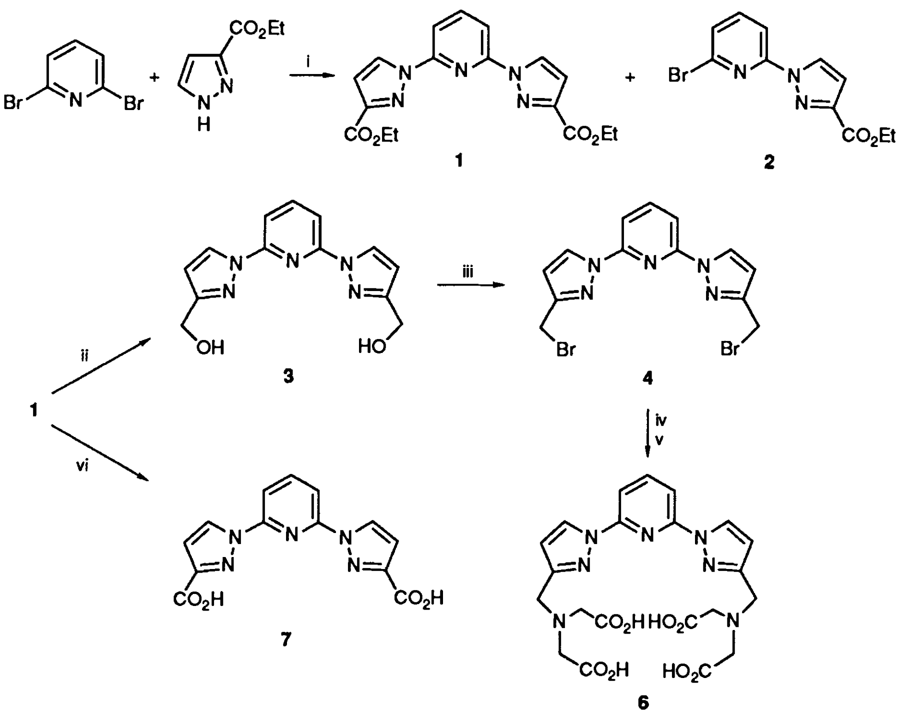
Synthesis and Characterization of the Ligands.—The parent trisheterocyclic ligand **1** was obtained by displacement of both bromides of 2,6-dibromopyridine by means of the potassium salt of 3-ethoxycarbonylpyrazole (see Scheme 1). Although three isomers can be obtained, steric and electronic factors seemed to control the reactivity towards the 1,3-disubstituted pyrazole **1** which was the only isomer detected.

The preparation of **1** was achieved under vigorous conditions and, since 3-ethoxycarbonylpyrazole was relatively unstable, a large excess of it was needed to complete the reaction. However, the yield of isolated **1** was never higher than 55% in those conditions and a considerable amount of the intermediate 2-bromo-6-(3-ethoxycarbonyl-1-pyrazolyl)pyridine **2** was isolated (37%). This product was treated with a second mole of pyrazole giving **1** and improving its overall yield. Moreover, this two-step procedure opened an entry to new unsymmetrically substituted pyridines with interesting properties. Namely, we have used monosubstituted bromopyridine **2** to prepare 2,2'-bipyridine analogues by Ni(0) coupling reactions.[12]

Reduction of diester **1** with lithium aluminium hydride and subsequent bromination (PBr_3/CH_3CN) of the resulting diol **3** produced the bis(bromomethyl) derivative **4**. The iminodiacetic subunits were introduced as *tert*-butyl esters because they can be easily cleaved by acid hydrolysis.[13] Trifluoroacetic acid reacted with tetraester **5** at room temperature for a short period (1–2 h) to give good yields of the tetraacid **6**. When base hydrolysis was used, a variable amount of mono- and di-salts of tetracarboxylic acid precipitated along with the desired product during acidification of the hydrolysed base material.

Finally we obtained the diacid **7** by hydrolysis of diester **1**. This product is also used in order to evaluate the influence of the iminodiacetic subunits on both the stability of the complexes and the photophysical properties of the trisheterocyclic chromophore responsible for the energy transfer to the lanthanide ion.

Luminescence.—Solutions of the complexes of Eu^{3+} and Tb^{3+} with **6** and **7** are very stable in aqueous solution exhibiting absorption spectra which did not change even after several weeks. Ligands formed 1:1 complexes with both lanthanide ions at pH = 7. The Tb(**7**)$^{3+}$ complex showed emission between pH = 4 and 9 and its maximum occurred at pH = 7, whereas for Eu(**7**)$^{3+}$ complex the maximum emission took place at



Scheme 1 *Reagents and conditions:* i, K/Diglyme (130 °C); ii, LAH; iii, PBr_3/CH_3CN; iv, Di-Bu^t-iminodiacetate/K_2CO_3; v, TFA; vi, KOH/ EtOH

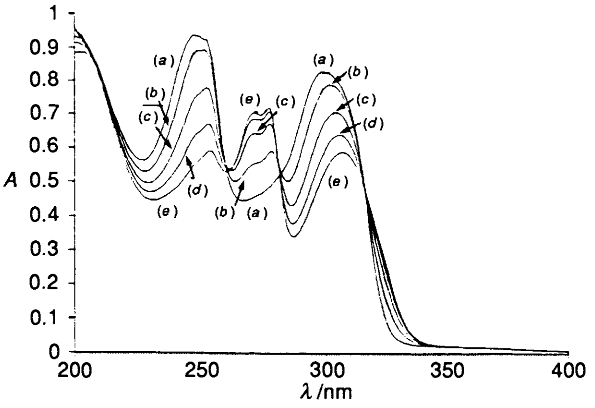


Fig. 1 Absorption spectra of **7** (*a*) with successive additions of $TbCl_3$ (*b*)–(*e*); conc. 4.2×10^{-5} mol dm^{-3}

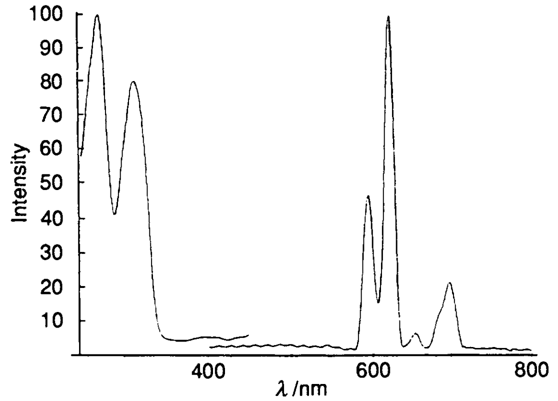


Fig. 2 Excitation and emission spectra of Eu(**6**)3^+; conc. 5.6×10^{-5} mol dm^{-3}

pH = 9 and no emission was observed at pH = 4. At the latter pH some precipitation of the ligand **7** was observed for both complexes. The emission observed for complexes of **6** was pH-independent in the range 4–9.

The UV spectra of all the studied complexes were very similar but different from those of the parent free ligands **6** and **7**. Compound **6** showed two maxima at 245 and 300 nm (ε = 17 650 and 12 200 dm^3 mol^{-1} cm^{-1} respectively) which were shifted to 270 (275 shoulder) and 313 nm (ε = 12 300 and 8100 dm^3 mol^{-1} cm^{-1}, respectively) in the corresponding Eu(**6**)$^{3+}$ complex. Similar shifts were observed for the Tb(**6**)$^{3+}$ complex.

In the spectra of **7** and its complexes, similar effects were observed but two maxima were resolved at 272 and 279 nm in the case of the complexes Eu(**7**)$^{3+}$ and Tb(**7**)$^{3+}$ (see Fig. 1). This splitting could be explained if one considers some degree of asymmetry in the latter complexes, where the coordination mode of the two pyrazole rings would be slightly different, leading to distinct π–π* transitions on each ring.

This shift of the absorption to lower energy from the free ligands to their complexes is indicative of a perturbation produced by the coordinated metal ion.[14] While the pyrazoles are presumably out of the pyridine plane in the free ligand, the almost planar meridional coordination of the metal to the three nitrogens expected for the complexes, in analogy to other N_3 ligands, should force the pyrazoles to planarity, therefore increasing conjugation.[15,16]

Excitation of the aqueous solutions of Eu^{3+} and Tb^{3+} into the lowest energy ligand-centred absorption band gave rise to the well known structured emission of the cations. This suggests that energy transfer did take place from ligand-centred (LC) to metal-centred (MC) levels. The Tb(**6**)$^{3+}$ complex presented $^5D_4$–^7F_J emissions at 491 (J = 6), 546 (J = 5), 586 (J = 4), 624 (J = 3), and 644 nm (J = 2) whereas the Eu(**6**)$^{3+}$ complex showed the $^5D_0$–^7F_J emissions at 593 (J = 1), 621 (J = 2), 654 (J = 3) and at 682 (shoulder), 696 nm (broad signals, J = 4). The excitation spectra were in perfect agreement with the absorption spectra (see Fig. 2). The Eu^{III} and Tb^{III} complexes of **7** exhibited very similar phosphorescence spectra to those of the corresponding complexes of **6**.

The absorption maxima corresponding to λ_{exc} used, luminescence lifetimes and quantum yields (φ) for Eu^{3+} and Tb^{3+} complexes, obtained under various experimental conditions are gathered in Table 1.

Table 1 Absorption and emission data for Eu^{3+} and Tb^{3+} complexes of **6** and **7**[a]

Complex[b]	Absorption max.[c]	Emission[d]	Lifetime τ/ms	φ
$Eu(\mathbf{6})^{3+}$	270, *313*	621	1.30 (2.45[e])	0.03
$Tb(\mathbf{6})^{3+}$	270,*314*	546	2.75	0.84
$Eu(\mathbf{7})^{3+}$	272, 278, *310*	623	0.27	—
$Tb(\mathbf{7})^{3+}$	272, 279, *307*	547	0.72	—

[a] Experimental uncertainties: lifetimes, < 10%; luminescence yields, *ca.* 30%. [b] The values described for complexes of **7** have been determined in buffer solution (pH = 8.5). [c] Italic wavelengths correspond to the λ_{exc} used in the emission study. [d] Assigned to the most intense emission band ($^5D_0$–$^7F_2$ and $^5D_4$–$^7F_5$ transitions for Eu^{3+} and Tb^{3+} complexes, respectively). [e] Decay emission lifetime calculated in D_2O; value used to obtain the number of coordinated water molecules of the Eu^{III} ion (see text).

The great similarity between the absorption and emission spectra of the complexes of **6** and **7** suggests that the coordination geometry should be very similar in both cases. However, complexes of **7** exhibited lower luminescence lifetimes and emission intensities compared to those of **6**, suggesting that the metal in the former complexes is less isolated from the solvent. Deactivation by coupling with the high-energy O–H vibrations is very efficient[17] and it appears to be more relevant in complexes of **7** than in those of **6**. This indicates that the additional iminodiacetic subunits may play two different roles: (i) they leave less room for the solvent to have access to the first coordination sphere and (ii) they improve complex stability. These factors are essential in designing efficient luminescent probes.[18]

The use of the empirical equation proposed by Horrocks[19] and the experimental lifetimes at 300 K in H_2O and D_2O solutions revealed the average number of water molecules (q) in the first coordination sphere of the metal ion to be $q = 0.4$ (± 0.5) for $Eu(\mathbf{6})^{3+}$. This showed that the Ln^{3+}ion is much better protected by **6** towards the interaction with water molecules. The decay curves of the remaining complexes in different H_2O:D_2O ratios were multiexponential and an accurate evaluation of τ in this solvent was not possible.

Finally, it should be noted that at similar concentrations, the φ value of the $Tb(\mathbf{6})^{3+}$ complex was much higher (*ca.* 30 times!) than that of the $Eu(\mathbf{6})^{3+}$ complex (*cf.* Table 1). The relatively small difference between the τ values of the Eu^{3+} and Tb^{3+} complexes (1.30 *vs.* 2.75 *cf.* Table 1), compared to their very dissimilar φ values, suggest that the radiationless deactivation pathways should not play a relevant role in making different to such an extent the aforementioned φ values. On the other hand, the close similarity between the excitation spectra of the Eu^{3+} and Tb^{3+} complexes, which fit their absorption spectra, strongly suggest that the energy transfer processes involve the same excited states of the ligand. Therefore it is quite reasonable in our opinion to assume that the big difference observed in the φ values arises from a significantly different efficiency in the ligand-to-metal energy transfer. Unfortunately, our instrument did not allow us to compute directly the energy transfer efficiencies.

Conclusions

The studied compounds showed a remarkable luminescence under UV excitation. Because of their broad and strong absorption in the UV region, their luminescence efficiencies (lifetimes and high quantum yields) and their stability in aqueous solution, these complexes could be excellent molecular devices, useful as 'antenna components'[20] for photosensitisation purposes and as luminescence labels, especially for biological applications.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer. Chemical shifts are given in ppm relative to TMS as the internal reference and J values are given in Hz. Mass spectra were obtained with a VG Autospec spectrometer in electronic impact mode. Absorption spectra were obtained with a Lambda 6 Perkin-Elmer spectrophotometer. Excitation and emission spectra were recorded with a LS50 Perkin-Elmer spectrofluorimeter. The excitation spectra were automatically corrected, and the emission spectra were corrected according to the instrument guidebook. The emission quantum yields were determined as previously described[5b] using two standards [9,10-diphenylanthracene in hexane ($\varphi_f = 1.0$) and quinine sulfate in 0.05 mol dm^{-3} H_2SO_4 ($\varphi_f = 0.52$)]. Analytical data were obtained from the *Servicio Interdepartamental de Investigación (SIdI) de la Universidad Autónoma de Madrid.* All solvents were purified prior to use by the standard methods.[21] Europium(III) and terbium(III) chlorides were purchased from Aldrich.

2-Bromo-6-(3-ethoxycarbonyl-1-pyrazolyl)pyridine (**2**) *and 2,6-Bis(3-ethoxycarbonyl-1-pyrazolyl)pyridine* (**1**).—Potassium (1.5 g, 0.038 mol) was added in small portions to a solution of 3(5)-ethoxycarbonylpyrazole (5 g, 36 mmol) in diglyme (50 cm^3) at 70 °C. When the metal was dissolved, freshly recrystallized 2,6-dibromopyridine (2.13 g, 9 mmol) was added in one portion. The mixture was stirred at 130 °C for 4 days. The solution was filtered and evaporated and the residue washed with water. The result was a mixture of compounds **1** and **2** which were separated by flash chromatography on silica gel (dichloromethane:methanol 9:1). Compound **2** in 37% yield as white crystals, m.p. 183–185 °C (Found: C, 44.45; H, 3.2; N, 14.35. $C_{11}H_{10}BrN_3O_2$ requires: C, 44.62; H, 3.40; N, 14.19%); δ_H(200 MHz; $CDCl_3$) 8.59 [1 H, d, J 2.6, Pz(5)H], 8.11 [1 H, d, J 8.5, Py(3)H], 7.71 [1 H, t, J 8.5, Py(4)H], 7.43 [1 H, d, J 8.5, Py(5)H], 6.97 [1 H, d, J 2.6, Pz(4)H], 4.44 (2 H, q, J 7.1, CH_2CH_3), 1.43 (3 H, q, J 7.1, CH_2CH_3); m/z 296 (M^+). Compound **1** (1.77 g, 55%) was obtained as white crystals, m.p. 163–165 °C (Found: C, 57.15; H, 4.6; N, 19.55. $C_{17}H_{17}N_5O_4$ requires: C, 57.46; H, 4.82; N, 19.71%); δ_H(200 MHz; $CDCl_3$) 8.60 [2 H, d, J 2.6, Pz(5)H], 8.13–7.93 (3 H, m, PyH), 7.02 [2 H, d, J 2.6, Pz(4)H], 4.46 (4 H, q, J 7.2, CH_2), 1.44 (6 H, t, J 7.2, Me); δ_C(50.3 MHz, $CDCl_3$) 161.8 (C=O), 149.2 (Pz-3), 146.3 (Py-2,6), 141.7 (Py-4), 128.2 (Pz-5), 111.2 (Py-3,5), 110.2 (Pz-4), 61.2 (CH_2), 14.2 (CH_3); m/z 355 (M^+).

2,6-Bis(3-hydroxymethyl-1-pyrazolyl)pyridine (**3**).—A suspension of lithium aluminium hydride (0.15 g, 4 mmol) in dry THF (10 cm^3) was added to a solution of diester **2** (0.36 g, 1 mmol) in THF (100 cm^3). After stirring for 3 h at room temperature, the mixture was treated with 0.15 cm^3 of water, 0.15 cm^3 of 15% aqueous sodium hydroxide and 0.45 cm^3 of water. The solution was filtered and the solvent evaporated to yield 0.24 g (89%) of **3** as a white powder, m.p. 209–211 °C (Found: C, 57.55; H, 4.65; N, 17.65. $C_{13}H_{13}N_5O_2$ requires: C, 57.56; H, 4.83; N, 17.82); δ_H(200 MHz, $CDCl_3$) 8.73 [2 H, d, J 2.6, Pz(5)H], 8.05–7.85 (3 H, m, PyH), 6.61 [2 H, d, J 2.6, Pz(4)H], 4.72 (4 H, s, CH_2); δ_C(50.3 MHz, CD_3OD) 155.1 (Pz-3), 149.2 (Py-2,6), 140.8 (Py-4), 127.5 (Pz-5), 107.9 (Py-3,5; Pz-4), 57.0 (CH_2); m/z 271 (M^+).

2,6-Bis(3-bromomethyl-1-pyrazolyl)pyridine (**4**).—Phosphorous tribromide (0.3 cm^3) was added to a solution of diol **3** (0.31 g, 1.14 mmol) in acetonitrile (50 cm^3). The solution was heated under reflux for 3 h. The solvent was removed and the residue treated with a solution of sodium carbonate. The aqueous solution was extracted with dichloromethane (3 × 50 cm^3). The organic phase was dried with sodium sulfate and evaporated *in vacuo*. The residue was recrystallized from dichloromethane : hexane. The yield was 0.32 g (70%); m.p. 203–204 °C (Found: C, 39.55; H, 2.65; N, 17.65. $C_{13}H_{11}N_5Br_2$ requires: C, 39.32; H, 2.79; N, 17.64%); δ_H(200 MHz; CDCl$_3$) 8.50 [2 H, d, *J* 2.5, Pz(5)H], 7.97–7.77 (3 H, m, PyH), 6.56 [2 H, d, *J* 2.5, Pz(4)H], 4.56 (4 H, s, CH$_2$); δ_C(50.3 MHz, CDCl$_3$) 152.0 (Pz-3), 149.6 (Py-2,6), 141.4 (Py-4), 128.3 (Pz-5), 109.7 (Py-3,5), 108.1 (Pz-4), 24.7 (CH$_2$); *m*/*z* 399 (M$^+$).

Tetra-tert-*butyl* N,N,N′,N′-[2,6-*Bis*(3-*aminomethyl*-1-*pyrazolyl*)*pyridine*] *tetrakis*(*acetate*) (**5**).—A solution of di-*tert*-butyl iminodiacetate (0.25 g, 0.2 mmol) in dry acetonitrile (5 cm^3) was added to a mixture of sodium carbonate (0.5 g) and dibromide **4** (0.2 g, 0.5 mmol) in acetonitrile (30 cm^3). The mixture was stirred for 24 h and then filtered. The filtrate was evaporated and redissolved in dichloromethane (50 cm^3) and this solution was washed with water (2 × 25 cm^3). The organic layer was dried with sodium sulfate and evaporated. The resulting oily residue was purified by chromatography on silica gel (dichloromethane : methanol 99 : 1) eluting **5** (0.2 g, 55%) as an oil; δ_H(200 MHz; CDCl$_3$) 8.48 [2 H, d, *J* 2.6, Pz(5)H], 7.93–7.73 (3 H, m, PyH), 6.56 [2 H, d, *J* 2.6, Pz(4)H], 4.04 (4 H, s, Pz–CH$_2$–N), 3.50 (8 H, s, N–CH$_2$–CO$_2$Bu^t), 1.46 [36 H, s, (CH$_3$)$_3$C]; *m*/*z* 725 (M$^+$).

N,N,N′,N′-[2,6-*Bis*(3-*aminomethyl*-1-*pyrazolyl*)*pyridine*] *tetrakis*(*acetic acid*) (**6**).—Trifluoroacetic acid (1 cm^3) was added to a solution of tetraester **5** (0.16 g, 0.2 mmol) in dichloromethane (2 cm^3). The mixture was stirred for 3 h. The solution was evaporated *in vacuo* and the resulting oil was vigorously stirred with diethyl ether (20 cm^3) and the resulting white solid filtered. The yield was 0.12 g (78%); m.p. 238–240 °C (Found: C, 50.0; H, 4.6; N, 19.3. $C_{21}H_{23}N_7O_8$ requires: C, 50.20; H, 4.62; N, 19.55%); δ_H(200 MHz, D$_2$O) 8.46 [2 H, d, *J* 2.6, Pz(5)H], 7.85–7.60 (3 H, m, PyH), 6.60 [2 H, d, *J* 2.6, Pz(4)H], 4.50 (4 H, s, Pz–CH$_2$N), 4.07 (8 H, s, N–CH$_2$–CO$_2$H); δ_C(50.3 MHz, D$_2$O) 170.7 (C=O), 150.9 (Pz-3), 146.0 (Py-4), 144.7 (Py-2,6), 132.2 (Pz-5), 112.9 (Py-3,5), 112.3 (Pz-4), 56.9 (NCH$_2$N), 53.9 (CH$_2$CO$_2$H).

2,6-*Bis*(3-*carboxy*-1-*pyrazolyl*)*pyridine* (**7**).—A solution of **1** (0.3 g, 0.85 mmol) and potassium hydroxide (1 g) in ethanol (20 cm^3) was heated at 60 °C for 24 h. The solution was acidified with 10% HCl and the resulting solid filtered and washed with water yielding **7** as a white powder (0.23 g, 92%); m.p. 279 °C (decomp.) (Found: C, 52.0; H, 3.0; N, 23.3. $C_{13}H_9N_5O_4$ requires: C, 52.18; H, 3.03; N, 23.40%); δ_H(200 MHz, CD$_3$OD) 8.83 [2 H, d, *J* 2.6, Pz(5)H], 8.18–8.05 (3 H, m, PyH), 6.99 [2 H, d, *J* 2.6, Pz(4)H]; *m*/*z* 299 (M$^+$).

Luminescence Measurements.—The luminescence properties of Eu^{3+} and Tb^{3+} chelates were measured using equimolecular mixtures of the ligand **6**, and EuCl$_3$ or TbCl$_3$ in water solution, and with ligand **7**, the same salts in borate buffer (pH 8.5). The concentrations used were between 10^{-5} and 10^{-6} mol dm^{-3}. In the case of Tb(**6**)$^{3+}$ complex we had to use a 2% attenuator in the emission path in order to avoid signal saturation, and to keep concentration of sample and standards in the same range.

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