

Synthesis and Crystal Structures of Mono-Helical Complexes of Zinc(II) and Europium(III) with 1,2-Bis{[3-(2-pyridyl)pyrazol-1-yl]ethoxy}ethane

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A new multidentate ligand L, 1,2-bis{[3-(2-pyridyl)pyrazol-1-yl]ethoxy}ethane, has been synthesized by linking two 3-(pyridin-2-yl)pyrazoles with a 1,2-bis(ethoxy)ethyl spacer. Coordination of L with zinc(II) and europium(III) centres has led to mononuclear complexes of [Zn(L)](ClO₄)₂ (**1**) and [Eu(L)Cl₂](ClO₄) (**2**). X-ray crystal structures of both complexes have shown that L adopted a helical coordination geo-

metry around both metal centres. The spectroscopic properties of both complexes have also been determined. In **1**, photoluminescence was dominated by ligand centred ¹(π-π*) fluorescence. In **2**, ligand-to-metal energy transfer leading to ⁵D₀ → ⁷F_n luminescence at the europium(III) centre was observed.

Introduction

Molecular architecture showing helical arrangement of multidentate ligands around one or more metal centres has long been one of the goals in the field of supramolecular chemistry.^[1] Besides their structural elegance, molecular helices are emblems of synthetic chemists' ability to make use of the various steric and electronic interactions within/among molecular units to engineer preferred molecular structures. While double-helical and triple-helical multinuclear (most often dinuclear) coordination complexes are the most common classes of supramolecular helix,^[2,3] mononuclear molecular helices are believed to offer better control over the assembly of molecular units into desirable crystal lattices.^[4] Among the various ligand systems that are capable of promoting self-assembly of mononuclear and multinuclear helical coordination complexes, oligopyridine^[1b,2c-2e,2g] is the most famous and thoroughly studied one. Other ligands such as substituted bis(benzimidazolyl)pyridines,^[3b,3g] substituted pyridine-2,6-dicarboxamide and pyridine-2,6-dicarboxylate,^[3f,4c] as well as bis- and tris-catechol^[5] are also known to induce helical coordination configurations. Recently, Ward et al.^[6] has demonstrated the versatile coordination chemistry of the ligand 3-(pyridin-2-yl)pyrazole. The ease of substitution at the pyrazolyl-*N*¹ position provides convenient access to multidentate pyridyl-pyrazolyl ligands with the potential to induce high nuclearity supramolecular assemblies. In fact, a dicopper(I) double helicate with ligands containing two pyridyl-pyrazolyl units joined by an *o*-CH₂C₆H₄CH₂ spacer has been synthesized.^[6h] We are particularly interested in link-

ing two 3-(pyridin-2-yl)pyrazoles through the pyrazolyl-*N*¹ by a flexible carbon chain containing additional donor atoms. In this way, multidentate ligands capable of wrapping around metal centres with much greater flexibility can be formed. Compared with oligopyridine ligands, where helical configuration has to be achieved by the twisting of interannular C–C bonds between adjacent pyridine rings, the new ligand system is expected to be more energetically and sterically favourable for a helical coordination geometry. In this work we report a new, potentially hexadentate ligand formed by the linkage of two 3-(pyridin-2-yl)pyrazoles by a 1,2-ethoxyethane spacer – the 1,2-bis{[3-(2-pyridyl)pyrazol-1-yl]ethoxy}ethane (L) (Figure 1) – and its mononuclear helical complexes [Zn(L)](ClO₄)₂ (**1**) and [Eu(L)Cl₂](ClO₄) (**2**).

Results and Discussion

Formation of the polyether-linked pyridyl-pyrazole ligand L is straightforward. Deprotonation of the pyrazolyl-

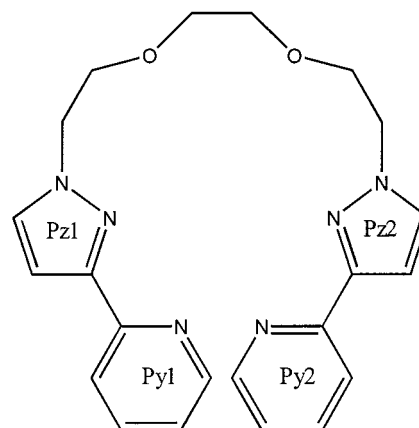
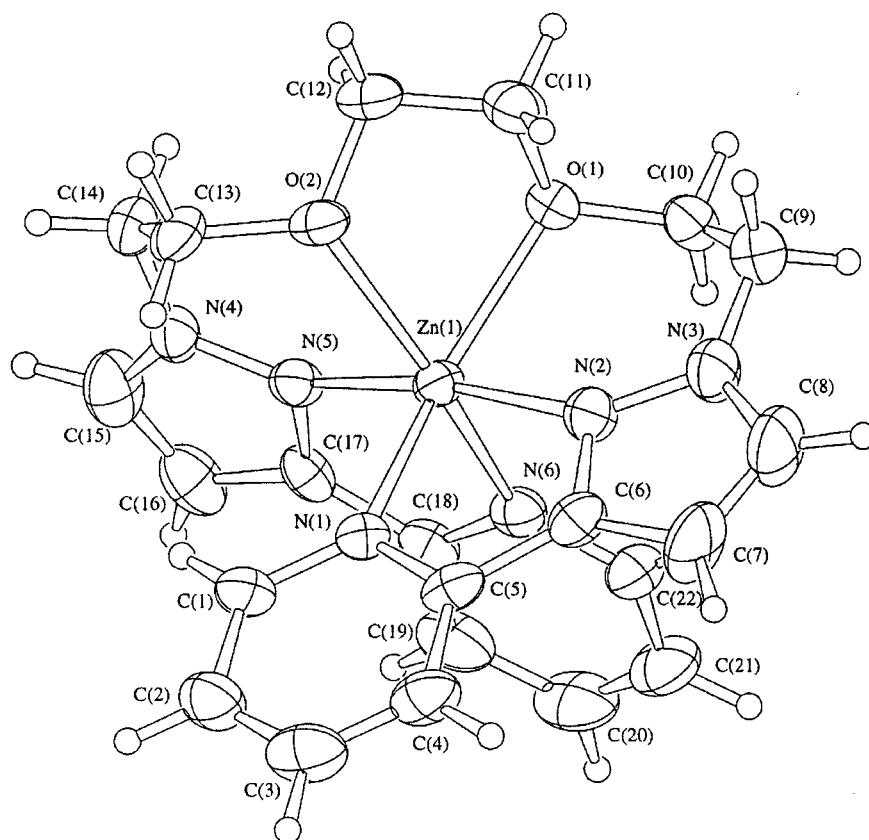


Figure 1. 1,2-Bis{[3-(2-pyridyl)pyrazol-1-yl]ethoxy}ethane (L)

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Figure 2. Perspective view of $[\text{Zn}(\text{L})](\text{ClO}_4)_2$ (**1**)Table 1. Selected bond lengths (Å) and angles (°) of $[\text{Zn}(\text{L})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**· H_2O)

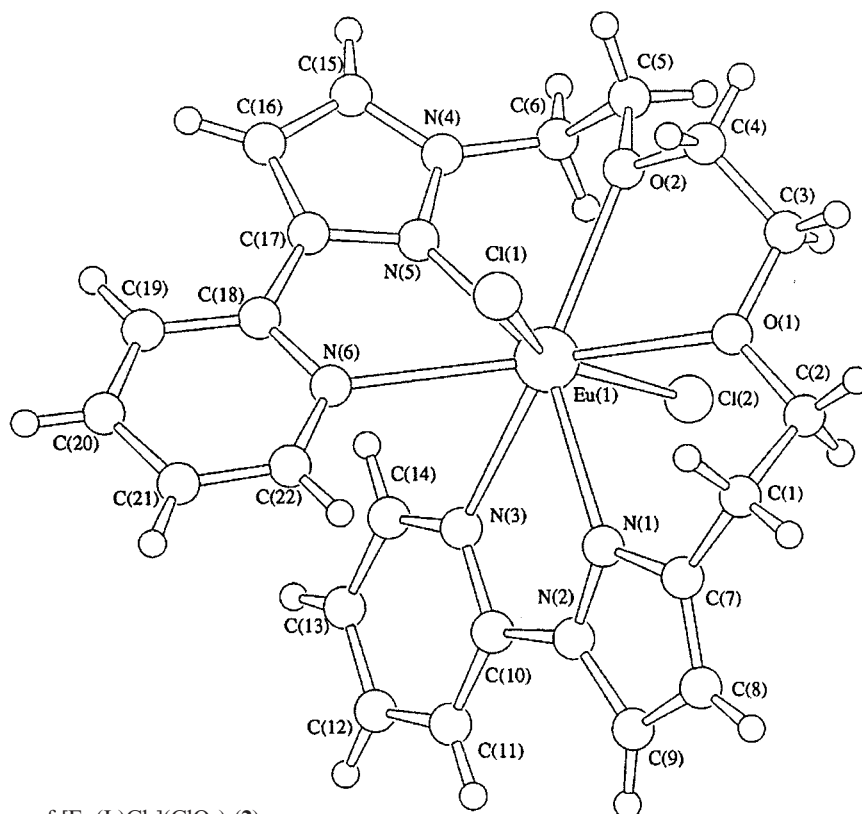
Zn(1)–O(1)	2.203(5)	Zn(1)–O(2)	2.211(5)
Zn(1)–N(1)	2.146(7)	Zn(1)–N(2)	2.081(7)
Zn(1)–N(5)	2.071(7)	Zn(1)–N(6)	2.163(7)
O(1)–Zn(1)–O(2)	74.6(2)	O(1)–Zn(1)–N(1)	153.3(2)
O(1)–Zn(1)–N(2)	80.7(2)	O(1)–Zn(1)–N(5)	104.9(2)
O(1)–Zn(1)–N(6)	101.2(2)	O(2)–Zn(1)–N(1)	97.3(2)
O(2)–Zn(1)–N(2)	106.9(2)	O(2)–Zn(1)–N(5)	82.1(2)
O(2)–Zn(1)–N(6)	156.9(2)	N(1)–Zn(1)–N(2)	77.4(3)
N(1)–Zn(1)–N(5)	99.0(3)	N(1)–Zn(1)–N(6)	95.7(2)
N(2)–Zn(1)–N(5)	170.5(3)	N(2)–Zn(1)–N(6)	94.4(3)
N(5)–Zn(1)–N(6)	77.1(3)	Zn(1)–O(1)–C(11)	115.3(5)
Zn(1)–O(1)–C(11)	109.5(5)	Zn(1)–O(2)–C(13)	116.9(5)
Zn(1)–O(2)–C(12)	113.2(5)	Zn(1)–N(1)–C(1)	127.2(6)
Zn(1)–N(1)–C(5)	113.0(6)	Zn(1)–N(2)–C(6)	114.5(6)
Zn(1)–N(2)–N(3)	135.7(6)	Zn(1)–N(5)–N(4)	136.0(6)
Zn(1)–N(5)–C(17)	115.6(6)	Zn(1)–N(6)–C(22)	128.7(6)
Zn(1)–N(6)–C(18)	112.9(6)		

N^1 of 3-(pyridin-2-yl)pyrazole by NaH followed by alkylation by 1,2-bis(chloroethoxy)ethane affords **L** in good yield. The coordination chemistry of 3-(pyridin-2-yl)pyrazole has been thoroughly explored by Ward et al.,^[6] who have also applied a similar approach to link two 3-(pyridin-2-yl)pyrazoles by *o*-CH₂C₆H₄CH₂ and propyl spacers.^[6h,15] In the former case, the dinuclear double helicate with copper(I) was obtained while no helical coordination geometry was observed in Fe^{II}, Cu^{II}, Zn^{II}, Ag^I and Pb^{II} complexes containing the latter, relatively more-flexible ligand. In our

case, reacting the polyether linked **L** with ZnCl₂ or EuCl₃·6H₂O in refluxing absolute ethanol gives the hygroscopic mononuclear complexes $[\text{Zn}(\text{L})](\text{ClO}_4)_2$ (**1**) or $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)_2$ (**2**), where the two ether oxygens also participate in metal coordination. In both complexes, **L** acts as a hexadentate ligand resulting in a helical coordination geometry around the metal centres. The hygroscopic nature of both complexes prevented accurate elemental analysis. Therefore, the characterization relied on FAB-MS and an X-ray crystal analysis.

Perspective views of the crystal structures of complexes **1** and **2**, with atom numbering, are shown in Figure 2 and Figure 3, respectively. Selected bond lengths and angles of the two complexes are tabulated in Table 1 and Table 2. In both complexes, each symmetric unit contains one complex molecule. In $[\text{Zn}(\text{L})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**· H_2O), the 22-electron zinc(II) centre is coordinated to two pyridyl-*N*, two pyrazolyl-*N* and two ether-*O* donors. The bond lengths between Zn(1)–N(1)-pyridyl and Zn(1)–N(6)-pyridyl are 2.146(7) and 2.163(7) Å, respectively. The bond lengths between Zn(1)–N(2)-pyrazolyl and Zn(1)–N(5)-pyrazolyl are 2.081(7) and 2.071(7) Å, respectively. These bond lengths are typical for zinc(II) polypyridyl and pyridyl-pyrazolyl complexes.^[15] The bond lengths between Zn(1)–O(1)-ether and Zn(1)–O(2)-ether are 2.203(5) and 2.211(5) Å, respectively.

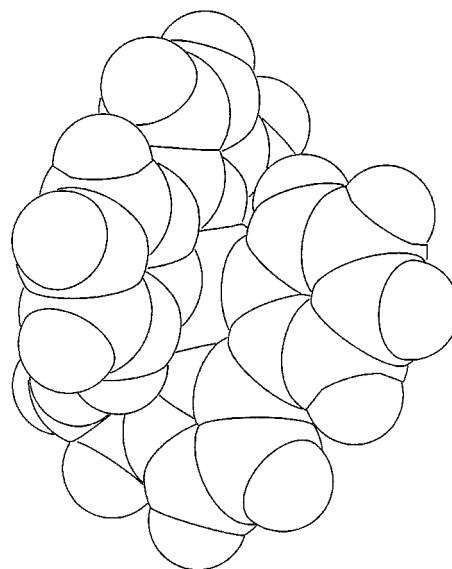
The coordination geometry at Zn(1) is a distorted octahedron with **L** helically wrapped around the metal centre.

Figure 3. Perspective view of $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)$ (**2**)Table 2. Selected bond lengths (Å) and angles (°) of $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)$ (**2**)

Eu(1)–Cl(1)	2.678(1)	Eu(1)–Cl(2)	2.661(1)
Eu(1)–O(1)	2.530(3)	Eu(1)–O(2)	2.507(3)
Eu(1)–N(1)	2.497(4)	Eu(1)–N(3)	2.623(4)
Eu(1)–N(5)	2.496(4)	Eu(1)–N(6)	2.648(4)
Cl(1)–Eu(1)–Cl(2)	152.30(4)	Cl(1)–Eu(1)–O(1)	74.84(8)
Cl(1)–Eu(1)–O(2)	86.13(8)	Cl(1)–Eu(1)–N(1)	91.00(9)
Cl(1)–Eu(1)–N(3)	126.18(8)	Cl(1)–Eu(1)–N(5)	101.61(9)
Cl(1)–Eu(1)–N(6)	72.35(9)	Cl(2)–Eu(1)–O(1)	77.63(8)
Cl(2)–Eu(1)–O(2)	80.42(9)	Cl(2)–Eu(1)–N(1)	84.45(10)
Cl(2)–Eu(1)–N(3)	75.73(8)	Cl(2)–Eu(1)–N(5)	95.81(9)
Cl(2)–Eu(1)–N(6)	135.28(9)	O(1)–Eu(1)–O(2)	67.3(1)
O(1)–Eu(1)–N(1)	74.1(1)	O(1)–Eu(1)–N(3)	131.5(1)
O(1)–Eu(1)–N(5)	135.7(1)	O(2)–Eu(1)–N(6)	145.7(1)
O(2)–Eu(1)–N(1)	140.7(1)	O(2)–Eu(1)–N(3)	143.6(1)
O(2)–Eu(1)–N(5)	68.4(1)	O(2)–Eu(1)–N(6)	119.6(1)
N(1)–Eu(1)–N(3)	63.6(1)	N(1)–Eu(1)–N(5)	149.7(1)
N(1)–Eu(1)–N(6)	96.5(1)	N(3)–Eu(1)–N(5)	86.9(1)
N(3)–Eu(1)–N(6)	65.3(1)	N(5)–Eu(1)–N(6)	62.3(1)
Eu(1)–O(1)–C(2)	129.2(3)	Eu(1)–O(1)–C(3)	113.7(3)
Eu(1)–O(2)–C(5)	132.4(3)	Eu(1)–O(2)–C(4)	111.1(3)
Eu(1)–N(1)–C(7)	122.3(3)	Eu(1)–N(1)–C(8)	130.9(3)
Eu(1)–N(3)–C(10)	118.9(3)	Eu(1)–N(3)–C(14)	123.1(3)
Eu(1)–N(5)–C(17)	129.4(3)	Eu(1)–N(5)–C(18)	123.6(3)
Eu(1)–N(6)–C(22)	122.2(3)	Eu(1)–N(6)–C(18)	119.7(3)

The dihedral angles between Py1/Py2 and Pz1/Pz2 are 80.64° and 79.64°, respectively.

Figure 4 shows the space filling representation of the $[\text{Zn}(\text{L})]^{2+}$ core. The pyridine and pyrazole rings in **L** are nearly coplanar with interannular angles in Py1/Pz1 and Py2/Pz2 of 1.14° and 0.74°, respectively. The degree of interannular twisting is much smaller than that in found in

Figure 4. Space filling representation of $[\text{Zn}(\text{L})]^{2+}$ cation with counter anions omitted

oligopyridyl helices, which normally range from 5 to 20°. [1b,16b] Presumably this is due to the presence of a flexible polyether chain in **L** that eases the requirement for twisting of the aromatic rings from a co-planar configuration to achieve the helical conformation.

In $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)$ (**2**), the coordination number of the europium(III) centre is eight. The ligand **L** adopts a helical twist about the equatorial plane of the complex while the two coordinated chlorides occupy the apparent axial posi-

tions, although they are not exactly at 180° to each other. The bond lengths between Eu(1)–N(3)-pyridyl and Eu(1)–N(6)-pyridyl are 2.623(4) and 2.648(4) Å, respectively, and those between Eu(1)–N(1)-pyrazolyl and Eu(1)–N(5)-pyrazolyl are 2.497(4) and 2.496(4) Å, respectively. These bond lengths are typical for europium(III) pyridyl complexes.^[16] The bond lengths between Eu(1)–O(1)-ether and Eu(1)–O(2)-ether are 2.530(3) and 2.507(3) Å, respectively, and those between Eu(1)–Cl(1) and Eu(1)–Cl(2) are 2.678(1) and 2.661(1) Å, respectively. The angle Cl(1)–Eu(1)–Cl(2) is $152.30(4)^\circ$ and the two chlorides are evidently bent away from the two pyridine rings, probably because of steric interactions. The helical arrangement of the coordinated ligand L is more clearly demonstrated in complex **2** than in complex **1**. In **2**, the dihedral angles between Py1/Py2 and Pz1/Pz2 are 60.42° and 69.35° , respectively; the interannular angles in Py1/Pz1 and Py2/Pz2 are 7.83° and 8.58° , respectively. The degree of interannular twisting is significantly larger than that of complex **1** and is moderate compared to that found in oligopyridyl helices. Figure 5 shows the space filling representation of the $[\text{Eu}(\text{L})\text{Cl}_2]^+$ core.

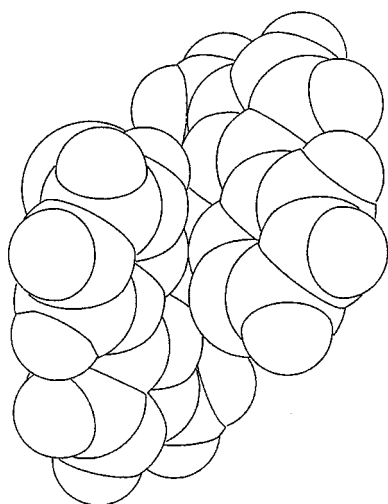


Figure 5. Space filling representation of $[\text{Eu}(\text{L})\text{Cl}_2]^+$ cation with chlorides and counter anion omitted for clarity

Table 3. Spectroscopic and emission properties of $[\text{Zn}(\text{L})](\text{ClO}_4)_2$ (**1**) and $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)$ (**2**)

Ligand L	UV/Vis λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) ^[a]	Emission λ/nm ^{[a],[b]}
	252 (2.4×10^4) 282 (1.3×10^4)	— —
$[\text{Zn}(\text{L})](\text{ClO}_4)_2$ (1)	245 (1.27×10^4) 289 (1.35×10^4)	357
$[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)$ (2)	250 (5.3×10^4) 290 (4.4×10^4)	595 616 655 696

^[a] In acetonitrile. — ^[b] At 298 K.

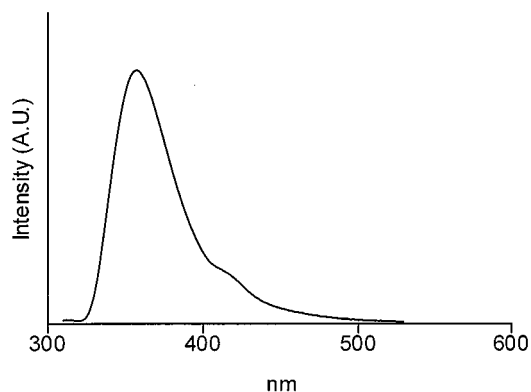


Figure 6. Room temperature emission spectra of $[\text{Zn}(\text{L})](\text{ClO}_4)_2$ (**1**) in acetonitrile; excitation at 300 nm

Table 3 tabulates the solution spectroscopic and emission properties of complexes **1** and **2**. The UV/Visible absorption bands of both complexes are attributable to intraligand transitions. Complex **1** gives violet-blue photoluminescence in acetonitrile at room temperature (Figure 6) due to the $^1(\pi-\pi^*)$ fluorescence of the ligand. On the other hand, complex **2** produces an intense red emission in acetonitrile at room temperature. Figure 7 shows the room-temperature solution emission spectrum of **2** upon excitation at 300 nm. Emission peaks in the range 595–750 nm are characteristic of $^5\text{D}_0 \rightarrow ^7\text{F}_n$ ($n = 0$ to 4) transitions at the Eu^{III} centre.^[17] The observation of Eu^{III} -centred emission indicates the occurrence of energy transfer from the ligand to the metal centre **2**.

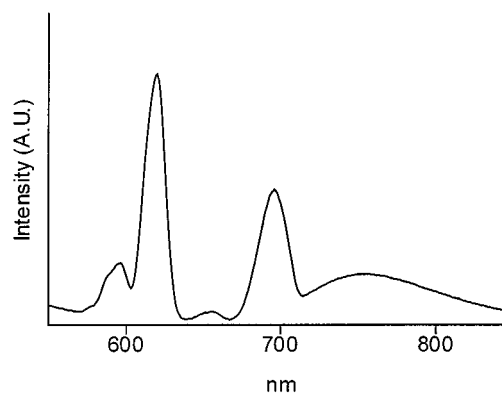


Figure 7. Room temperature emission spectra of $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)$ (**2**) in acetonitrile; excitation at 300 nm

Conclusion

The strategy of linking two bidentate polypyridyl/pyrazolyl moieties by a flexible alkyl chain containing additional donor atoms has led to helical coordination architectures. With a 1,2-bis(ethoxy)ethyl linker, mononuclear helical complexes of $[\text{Zn}(\text{L})]^{2+}$ and $[\text{Eu}(\text{L})\text{Cl}_2]^+$ are obtained. Induction of a helical coordination geometry is probably assisted by the affinity of both metals for oxygen donors. An efficient ligand-to-metal energy transfer is observed in $[\text{Eu}(\text{L})\text{Cl}_2]^+$ which leads to intense Eu^{III} centred lumines-

cence in the region 595–750 nm. This makes $[\text{Eu}(\text{L})\text{Cl}_2]^+$ a potentially useful luminescent material in organic electroluminescent devices. Work on induction of higher nuclearity helices by L is in progress. The synthesis of analogous ligands with donor atoms other than oxygen in the linker is also being pursued.

Experimental Section

General Remarks: Europium(III) chloride hexahydrate, anhydrous zinc(II) chloride, sodium hydride (60% in mineral oil) and 1,2-bis(chloroethoxy)ethane were obtained from Aldrich. All solvents used were of analytical reagent grade (Riedel-de Haën and BDH). UV/vis spectra were measured by a Hewlett–Packard 8452A ultraviolet visible diode array spectrophotometer. Emission spectra were measured on an SFM 4800C spectrofluorometer and Perkin–Elmer LS-50B luminescence spectrometer. ^1H NMR spectra were measured on a Varian YH300 300 MHz NMR spectrometer. All manipulations were carried out under an N_2 atmosphere with standard Schlenk vacuum line techniques.

1,2-Bis[3-(2-pyridyl)pyrazol-1-yl]ethoxyethane (L): 3-(Pyridin-2-yl)pyrazole^[6a] (2.03 g, 14.0 mmol) was added to a suspension of NaH (60%, 0.56 g, 14.0 mmol) in 30 mL THF. The mixture was stirred at room temperature for 15 min. 1,2-Bis(chloroethoxy)ethane (1.31 g, 7.0 mmol) was then added to the resultant reddish brown solution and the mixture was refluxed for 12 h. After cooling to room temperature, the mixture was filtered and the filtrate evaporated in vacuo to yield L as a light brown oil [1.9 g, 67% based on 1,2-bis(chloroethoxy)ethane]. The product was pure enough for further reaction. – ^1H NMR (CDCl_3 , 300 MHz): δ = 8.61 (d, J = 4.2 Hz, 2 H, pyridyl- H^6), 7.87 (d, J = 8.1 Hz, 2 H, pyridyl- H^3), 7.69 (td, J = 8.5, 7.5 Hz, 2 H, pyridyl- H^4), 7.51 (d, J = 2.1 Hz, 2 H, pyrazolyl- H^4 or H^5), 7.18 (m, 2 H, pyridyl- H^5), 6.84 (d, J = 2.1 Hz, 2 H, pyrazolyl- H^4 or H^5), 4.33 (t, J = 5.5 Hz, 4 H, CH_2), 3.82 (t, J = 5.3 Hz, 4 H, CH_2), 3.49 (t, J = 6.3 Hz, 4 H, CH_2).

$[\text{Zn}(\text{L})](\text{ClO}_4)_2$ (1): A mixture of anhydrous ZnCl_2 (0.14 g, 1.0 mmol) and L (0.40 g, 1.0 mmol) in 30 mL of absolute ethanol

was refluxed for 24 h. $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.31 g, 2.2 mmol) was then added and the mixture was refluxed for a further 30 mins. The resultant mixture was evaporated in vacuo and the white residue was dissolved in DMF. The DMF solution was filtered into a Schlenk tube and a layer of diethyl ether was carefully laid on top of the DMF solution. The whole assembly was allowed to stand at -10°C for two days to yield colourless crystalline $[\text{Zn}(\text{L})](\text{ClO}_4)_2$ (1) (0.42 g, 62%). – MS (FAB^+ , m -NBA): m/z = 569 $[\text{M}(\text{ClO}_4)^+]$. – ^1H NMR ($[\text{D}_6]\text{DMSO}$, 300 MHz): δ = 8.32 (d, J = 4.1 Hz, 2 H, pyridyl- H^6), 7.7 (m, 6 H, pyridyl- H^3 & H^4 and pyrazolyl- H^4 or H^5), 7.2 (m, 2 H, pyridyl- H^5), 6.6 (m, 2 H, pyrazolyl- H^4 or H^5), 4.1 (t, J = 5.4 Hz, 4 H, CH_2), 3.6 (t, J = 5.5 Hz, 4 H, CH_2), 1.98 (t, J = 6.0 Hz, 4 H, CH_2).

X-ray quality crystals of $[\text{ZnN}_6\text{O}_2\text{C}_{22}\text{H}_{24}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ were obtained by repeated recrystallization from DMF/ Et_2O .

$[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)_2$ (2): The synthesis was similar to 1 except $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1.0 mmol) was used. Layering of diethyl ether on top of a DMF solution of the reaction mixture and standing at -10°C for three days gave colourless crystals of $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)_2$ (2) (0.55 g, 76%). – MS (FAB^+ , m -NBA): m/z = 627 $[\text{M}^+]$. The crystals obtained were already of a quality suitable for an X-ray crystal structure determination.

X-ray Crystallographic Study: Crystal structures of 1 and 2 were determined by X-ray diffraction using a Rigaku AFC 7R diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation and a 12-kW rotating anode generator. To avoid loss of solvent, the crystals were sealed in a layer of paraffin. Crystal data and details of measurements for complexes $[\text{Zn}(\text{L})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (1· H_2O) and $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)_2$ (2) are summarized in Table 4. Absorption correction was applied using Lorentz and polarization effects, and for absorption effects by an empirical method based on azimuthal scans of several reflections.

The structures were solved by heavy-atom Patterson Methods^[7] (for 1) and Direct Methods^[8] (for 2) and expanded using Fourier techniques.^[9] Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically by full-matrix least-squares calculations. Reliability factors were defined as $R = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. Neutral

Table 4. Crystal data for $[\text{Zn}(\text{L})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (1· H_2O) and $[\text{Eu}(\text{L})\text{Cl}_2](\text{ClO}_4)_2$ (2)

	1· H_2O	2
Formula	$\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{N}_6\text{O}_{11}\text{Zn}$	$\text{C}_{22}\text{H}_{23}\text{Cl}_3\text{EuN}_6\text{O}_6$
M	686.77	726.79
Crystal colour, habit	Colourless	colourless, block
Crystal system	Triclinic	triclinic
Space Group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
$a/\text{\AA}$	12.527(3)	7.564(1)
$b/\text{\AA}$	13.008(3)	13.184(1)
$c/\text{\AA}$	10.193(3)	14.286(1)
$\alpha/^\circ$	108.91(2)	76.24(1)
$\beta/^\circ$	108.39(2)	89.34(1)
$\gamma/^\circ$	98.84(2)	81.31(1)
$U/\text{\AA}^3$	1429.3(8)	1367.4(2)
Z	2	2
Crystal dimensions/mm	$0.27 \times 0.34 \times 0.38$	$0.24 \times 0.25 \times 0.25$
$F(000)$	704.00	720.00
$D_{\text{calc}}/\text{g cm}^{-3}$	1.596	1.765
μ (Mo- $K\alpha$) cm^{-1}	11.14	26.29
Reflection measured: total, unique	3936, 3729	4731, 4150
Maximum peak in final difference map/ e \AA^{-3}	0.75	0.78
Minimum peak in final difference map/ e \AA^{-3}	−0.61	−1.47
R	0.060	0.035
R_w	0.068	0.033

atom scattering factors were taken from Cromer and Waber.^[10] Anomalous dispersion effects were included in F_{calc} ,^[11] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.^[12] The values for the mass attenuation coefficients were those of Creagh and Hubbel.^[13] All calculations were performed using the teXsan^[14] crystallographic software package of Molecular Structure Corporation.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138696 (2) and CCDC-138697 (1). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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