Assembly of [2 + 2] Bimetallic Macrocyclic Complexes from Bis(bipyridyl) Ligands and Metal Ions†

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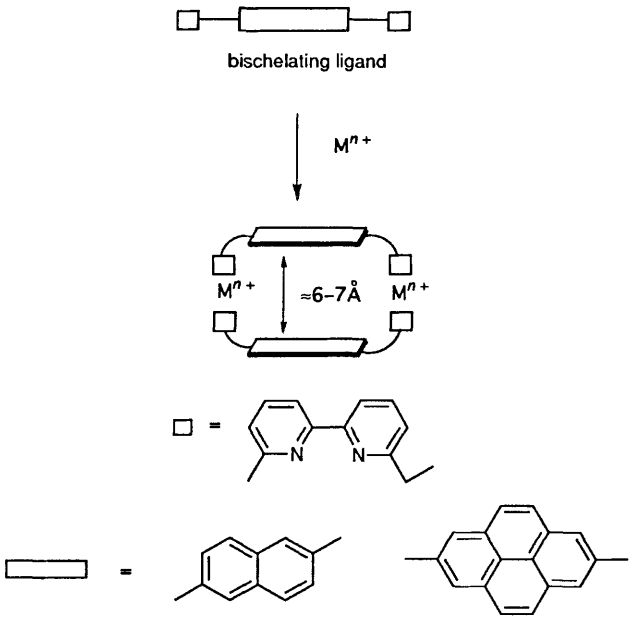
Two new ligands L^1 and L^2, in which 6,6'-dimethyl-2,2'-bipyridyl groups are attached at the 6-position to 2,6-naphthalene or 2,7-pyrene *via* ether bridges, have been synthesised. In the presence of Cu^I, L^1 forms equal amounts of two [2 + 2] complexes $[Cu_2L^1_2][PF_6]_2$, which have been assigned tentatively to helical (**1a**) and non-helical (**1b**) forms. With Zn^{II}, L^1 forms two complexes $[Zn_2L^1_2][CF_3SO_3]_4$, tentatively assigned to the helical (**3a**) and non-helical (**3b**) forms, in the ratio ≈7:4. The relative populations of **3a** and **3b** are temperature and solvent dependent. Ligand L^2 forms equal amounts of helical and non-helical complexes $[Cu_2L^2_2][PF_6]_2$ **2a**, **2b** with Cu^I. However, in the presence of Zn^{II}, L^2 forms exclusively one complex, which has been assigned as the non-helical species $[ZnL^2_2][CF_3SO_3]_4$ **4b**, on the basis of NMR data. In this complex, the pyrene rings are rotating rapidly on the NMR time-scale at 300 K. Molecular modelling suggests that the size and interior of the cavities of these macrocycles are ideal for encapsulation of charged aromatic substrates.

The use of metal ions in the efficient and elegant assembly of new materials with defined geometries and properties has resulted in impressive reports in recent years.[1-9] The appropriate choice of metal ion with carefully designed ligands has led to spontaneous assembly of double[2,3] and triple helices,[4,5] molecular cylinders,[6] catenanes[7] and boxes,[8,9] and established the importance of metal complexes as key building blocks that may be incorporated into supramolecular structures.[10,11]

Much synthetic effort has been directed towards the design and synthesis of macrocyclic structures with selective recognition properties.[12] Our approach in this area has been to develop efficient routes to macrocyclic structures of defined shape and size that assemble from bischelating ligands in the presence of metal ions (Scheme 1). Binuclear complexes of this type are rare, but clearly metal co-ordination provides an efficient route to formation of these rings compared to formation of similar structures by covalent bonds. Several recent examples have used a similar approach using metal ions[13-16] or organometallic complexes[17] to prepare cyclic structures.

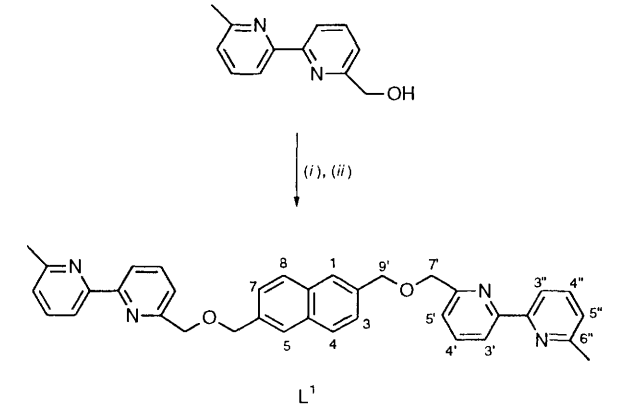
In this study, 2,2'-bipyridines were chosen in the design of the bischelating ligands, due to their well characterised co-ordination chemistry.[2,3,18] Aromatic spacer units were used to link the 2,2'-bipyridines as in the corresponding [2 + 2] complexes (Scheme 1) they provide sites for π stacking and hydrophobic interactions in the cavity.[19] In addition, molecular modelling suggested that a CH_2OCH_2 linker between the aromatic spacer and the 6-position of the 2,2'-bipyridine units provides the optimal separation (6.8–7.0 Å)[19] between the aromatic groups in the [2 + 2] complex to allow π interactions with a bound aromatic substrate. This paper reports the synthesis of ligands L^1 and L^2, in which 6,6'-dimethyl-2,2'-bipyridyl groups are attached at the 6-position to 2,6-naphthalene and 2,7-pyrene *via* ether bridges, and the spontaneous assembly of these ligands into [2 + 2] frameworks in the presence of copper(I) and zinc(II) metal ions.



Scheme 1

Results and Discussion

Synthesis of Ligands.—The ligands L^1 and L^2 were prepared as shown in Schemes 2 and 3. Ligand L^1 was prepared in 70%



L^1

Scheme 2 (*i*) KOBu^t, thf; (*ii*) 2,6-bis(bromomethyl)naphthalene, −30 °C

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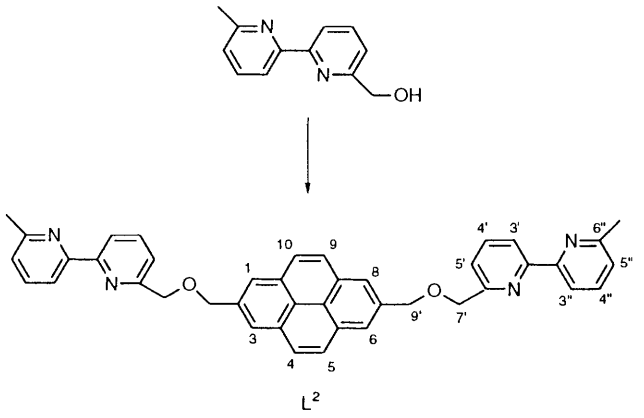

Scheme 3 (*i*) NaH, thf, room temperature; (*ii*) 2,7-bis(bromomethyl)-pyrene, 50 °C

yield by reaction of 2,6-bis(bromomethyl)naphthalene with 6-hydroxymethyl-6′-methyl-2,2′-bipyridine[20] in the presence of potassium *tert*-butoxide in tetrahydrofuran (thf) under standard Williamson reaction conditions. Ligand L^2 was prepared by a similar route in 65% yield from 2,7-bis-(bromomethyl)pyrene.[21] The new ligands were fully characterized by NMR, mass spectrometry and elemental analyses (see Experimental section).

Copper(I) *Complexation Studies with* L^1 *and* L^2.—Ligands L^1 and L^2 were treated with Cu^I and the resultant complexes were characterized by ^1H NMR spectroscopy and mass spectrometry. The general method for preparation of the copper(I) complexes involved addition of the ligand to a solution of copper(I) chloride in acetonitrile–water to give a deep red solution. Addition of ammonium hexafluorophosphate resulted in precipitation of the corresponding hexafluorophosphate salt which was collected and washed. The hexafluorophosphate salts are soluble in acetonitrile, nitromethane and dichloromethane, sparingly soluble in organic alcohols and chloroform, and insoluble in aqueous solutions. Alternatively, the hexafluorophosphate salt was prepared directly by using tetrakis(acetonitrile)copper(I) hexafluorophosphate.

Fast atom bombardment (FAB) and electrospray (ES) mass spectrometry were used to establish the stoichiometry of the complexes, and in each case, peaks corresponding to the presence of [2 + 2] complexes of formula $[Cu_2L^1{}_2][PF_6]_2$ **1** and $[Cu_2L^2{}_2][PF_6]_2$ **2** respectively were obtained. Thus, peaks with the correct isotopic distribution and mass expected for the molecular ions $[Cu_2L^1{}_2(PF_6)]^+$ and $[CuL^1{}_2]^+$ were observed in the FAB spectrum of **1**. The same fragment pattern was observed in the FAB spectrum of $[Cu_2L^2{}_2][PF_6]_2$ **2**. In the ES spectrum, the most abundant peak was detected at *m*/*z* 615 corresponding to the dipositive ion $[Cu_2L^2{}_2]^{2+}$.

The ^1H NMR spectra of **1** and **2** in CD_3CN contained only broad signals, suggesting ligand exchange in the co-ordinating solvent, CD_3CN. A variable-temperature NMR experiment confirmed this assignment, and at 235 K sharp spectra were obtained. In contrast, sharp spectra of **1** and **2** were obtained in the non-co-ordinating solvent CD_2Cl_2 at 298 K recorded with dilute samples [Figs. 1(*b*) and 2(*b*)]. Increasing the concentration of samples resulted in the gradual appearance of new broad signals in the spectra, superimposed on the sharp spectrum [*e.g.*, see starred peaks in Fig. 1(*b*)], which suggests some degree of intermolecular aggregation at high concentrations.

Due to the tetrahedral geometry of the copper(I) centre, four possible [2 + 2] complexes can be formed *i.e.*, (*R*,*R*)/(*S*,*S*) helical complexes and or (*R*,*S*)/(*S*,*R*) non-helical complexes

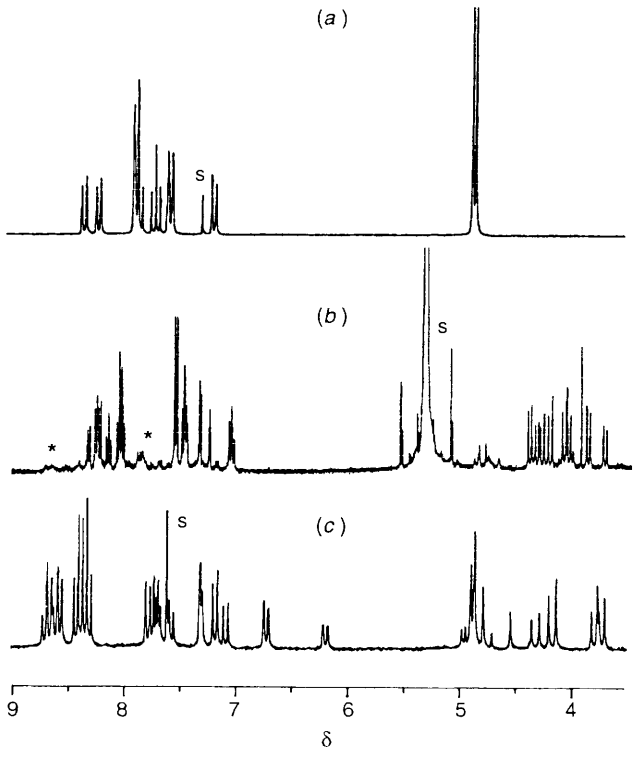

Fig. 1 Proton NMR spectra (298 K) of (*a*) ligand L^1 ($CDCl_3$, 200 MHz), (*b*) complex **1** (CD_2Cl_2, 400 MHz), (*c*) complex **3** (CD_3CN, 200 MHz); s indicates solvent peaks, * indicates peaks due to aggregation (see text)

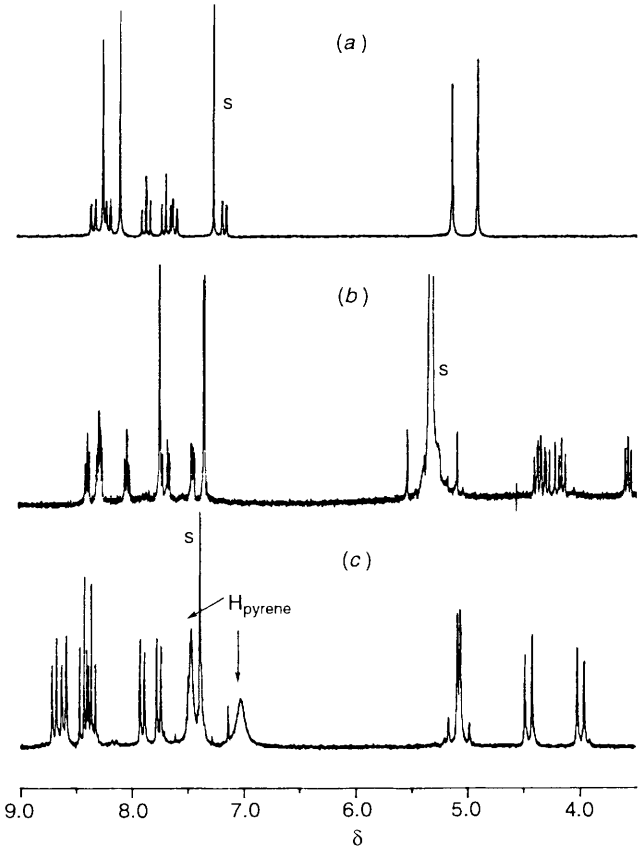

Fig. 2 Proton NMR spectra (298 K) of (*a*) ligand L^2 ($CDCl_3$, 200 MHz), (*b*) complex **2** (CD_2Cl_2, 400 MHz), (*c*) complex **4** (CD_3CN, 200 MHz); s indicates solvent peaks

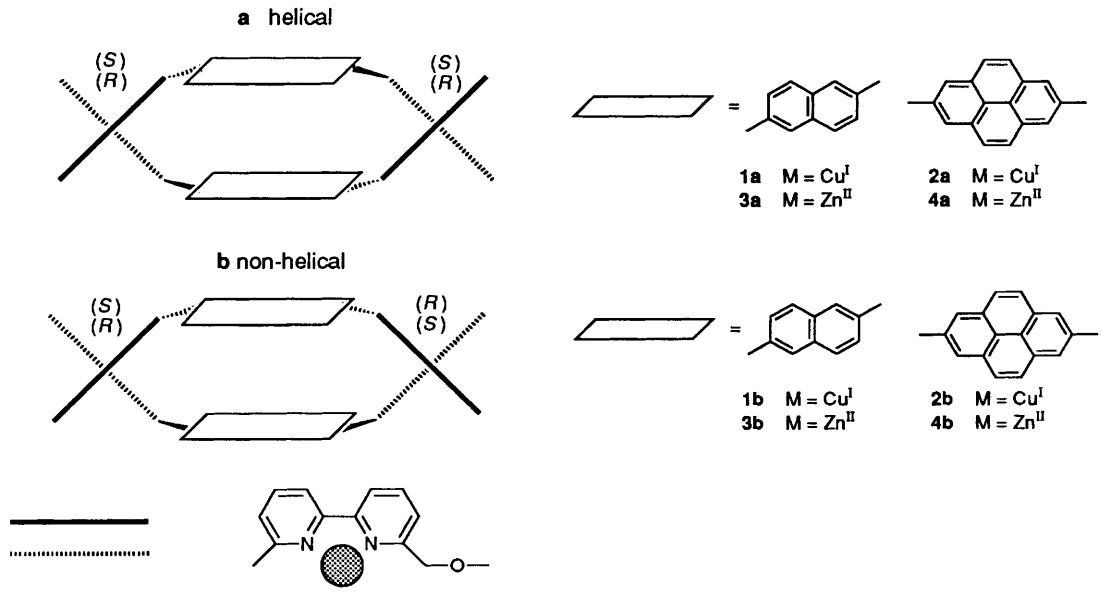

Fig. 3 Schematic representation of helical and non-helical complexes that may be formed with L^1 and L^2 and metal ions with tetrahedral co-ordination

(Fig. 3).* NMR spectroscopy was used to provide information about the number and type of complexes formed. Fig. 1(*b*) shows the NMR spectrum of the complex $[Cu_2L^1{}_2][PF_6]_2$ **1**. The most significant change in this spectrum compared to the free ligand L^1 [Fig. 1(*a*)] is the appearance of the methylene protons which change from two singlets in L^1 to four AX systems (eight doublets) in **1**. The diastereotopic nature of the methylene protons is entirely consistent with the formation of a [2 + 2] cyclic assembly and the upfield shift and signal multiplicity of these protons is reminiscent of the copper(I) helicates,[2] which also contain ether bridges. However, exclusive formation of the [2 + 2] chiral helical complex, as in the case of the helicates,[2] in which the central symmetry axis is maintained, would result in 2 AX (or AB) systems. The observed 4 AX systems may be explained by either (*i*) formation of equal amounts of helical and non-helical complexes, each of which would give rise to two AX systems, or (*ii*) one [2 + 2] complex which lacks two-fold symmetry, possibly due to the skewed substitution of the naphthalene linker. A similar spectrum was obtained for $[Cu_2L^2{}_2][PF_6]_2$ **2** [Fig. 2(*b*)]. In this complex, which contains the symmetrical pyrene linker, it is difficult to imagine formation of an unsymmetrical complex. Hence, the spectra of **1** and **2** seem to indicate that L^1 and L^2, in the presence of Cu^I spontaneously form 1 : 1 mixtures of the helical and non-helical complexes (Fig. 3).

In order to confirm this assignment, two titration experiments with complex **1** and the chiral shift reagents, tris[3-(heptafluoropropylhydroxymethylene-D-1,7,7-trimethylbicyclo[2.2.1]heptan-2-onato]europium(III) and *R*-(+)-*tert*-butylphenylphosphinothioic acid, were carried out. Only the signals due to the chiral [2 + 2] helical complex should be affected in the presence of these reagents,[22] and hence it was predicted that one set of resonances, due to the helical complex **1a**, would be affected by the shift reagent, while those due to the non-helical complex **1b** would remain unchanged. However, no changes in the signal multiplicities of any of the signals were observed in these titration experiments. This result does not exclude the existence of the helical chiral [2 + 2] complex, as this type of experiment is highly dependent on the nature of the shift reagent and it is possible that with another reagent changes in the NMR spectrum may occur.[22]

Beer *et al.*[13] have recently reported the synthesis and complexation of bis(bipyridyl) ligands linked by crown ethers. In the presence of Cu^I and Ag^I ions, multiple species including helical and non-helical complexes were observed by NMR spectroscopy and full assignment of the structures of the complexes was not possible. In the present study, we observe exclusive formation of [2 + 2] helical and non-helical complexes of L^1 and L^2 with Cu^I. The additional ligand rigidity provided by the aromatic linkers compared to the crown ethers,[13] and the 6,6′-substituents in L^1 and L^2 which favour tetrahedral co-ordination,[18] undoubtedly contributes to the formation of the complexes **1** and **2**.

Zinc(II) *Complexation Studies with* L^1 *and* L^2.—Zinc(II) metal ions generally form either six-co-ordinate octahedral or five-co-ordinate trigonal-pyramidal complexes.[23] The zinc(II) chelates $[Zn_2L^1{}_2][CF_3SO_3]_4$ **3** and $[Zn_2L^2{}_2][CF_3SO_3]_4$ **4** were prepared by treatment of ligands L^1 and L^2 respectively with 1 equivalent of $Zn(CF_3SO_3)_2$ in acetonitrile–chloroform. The solvent was removed and the remaining solid was refluxed in chloroform and filtered to give the pure complexes.

The ES mass spectra of complexes **3** and **4** confirmed the presence of cyclic [2 + 2] complexes. The spectrum of **3** contained peaks corresponding to $[Zn_2L^1{}_2(CF_3SO_3)_2]^{2+}$, $[Zn_2L^1{}_2(CF_3SO_3)]^{3+}$ and $[Zn_2L^1{}_2]^{4+}$. Similarly, FAB analysis of **4** showed a strong peak at 1682, assigned to $[Zn_2L^2{}_2(CF_3SO_3)_2]^{2+}$.

Relative to the copper(I) complexes **1** and **2**, the zinc(II) complexes **3** and **4** appear to be more stable. Sharp ^1H NMR spectra were obtained in all solvents, and there was no evidence for ligand exchange in co-ordinating solvents. The NMR spectra also remained unchanged with different concentrations of compound, thus indicating that aggregation is non-existent (or minimal) in these complexes.

The ^1H NMR spectra of **3** and **4** are presented in Fig. 1(*c*) and Fig. 2(*c*) respectively. For complex **3**, two species in the ratio 7 : 4 in CD_3CN at 300 K were present by integration of the spectrum [Fig. 1(*c*)]. The relative ratios of these two complexes were

* The stereochemistry of the four possible [2 + 2] complexes is defined by the chirality at the copper(I) centres. The (*S*,*S*) and (*R*,*R*) complexes are enantiomers and hence give identical NMR spectra. The (*R*,*S*) and (*S*,*R*) are superimposable *meso*-isomers. For simplicity, the complexes are referred to as helical and non-helical as defined in Fig. 3.

found to be solvent- and temperature-dependent. For example, in [$^2H_5$]nitrobenzene at 300 K two complexes were detected in the ratio 28:9, while increasing the temperature to 420 K changed the ratio to 7:5. Hence, it appears that an equilibrium exists between two interconvertible complexes with different relative energies. The appearance of the methylene protons and the mass spectra results are consistent with the presence of the helical and non-helical complexes, **3a** and **3b**, but on the basis of these data, the major complex cannot be assigned.

In contrast to the results obtained for the naphthalene bridged complex **3**, only one complex (> 98%) was observed in the ^1H NMR spectrum of $[Zn_2L^2{}_2][CF_3SO_3]_4$ **4** at 300 K [Fig. 2(*c*)]. The methylene protons appear as an AB and an AX system, with one set of methylene protons being shifted upfield compared to the ligand L^2. Of particular interest was the appearance of the pyrene protons as two broad peaks at room temperature in both CD_3CN and CD_3OD, which suggested rapid rotation of the pyrene rings on the NMR time-scale. This assignment was confirmed by a variable-temperature experiment (Fig. 4). When the sample was heated to 340 K the pyrene peaks sharpened to give two singlets at δ 7.01 and 7.48. On cooling the complex in CD_3OD, the pyrene peaks exchange broadened into the baseline (260 K), but at 220 K, four new resonances due to the 16 pyrene protons were observed [Fig. 4(*c*)]. At low temperature several minor resonances (< 5%) were also detected.

The NMR spectra of **4** are consistent with $[Zn_2L^2{}_2][CF_3SO_3]_4$ being either the helical complex **4a** or the non-helical complex **4b**. Addition of incremental amounts of the chiral shift reagent (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol to a solution of **4** did not result in splitting of the resonances due to formation of a diastereomeric salt with the shift reagent, which would be expected for **4a**. However, in the absence of any spectral changes, and as discussed above, this result is of limited use, and does not rule out the helical complex **4a**. Analysis of the low-temperature NMR spectra (Fig. 4), however, provided some structural information about complex **4**.

At low temperature, when rotation of the pyrene rings is slow on the NMR time-scale, the pyrene protons appear as four singlets at δ 8.30, 8.32, 6.84 and 5.87; the chemical shift differences of these peaks is quite dramatic. Careful comparison of molecular models of the helical and non-helical geometries suggests that the large differences in chemical shifts of the pyrene protrons arise from the non-helical complex **4b**. In this configuration (Fig. 5), the pyrene rings are offset with respect to one other, and H^4 and H^5 (and $H^{4'}$ and $H^{5'}$) which are shielded by the pyrene ring above (and below) the plane were assigned to the upfield singlet at δ 5.87. Protons H^3 and H^6, which are also slightly shielded appear as a singlet at δ 6.84, while H^1, H^8, H^9 and H^{10} appear in the aromatic region of the spectrum between δ 8.30 and 8.32.

In the helical conformation **4a**, the pyrene rings are 'crossed' and such dramatic changes in chemical shifts of the pyrene protons would not be expected. In addition, when the pyrene rings are slowly rotating at low temperature in **4a**, H^4/H^5 and H^9/H^{10} are not chemically equivalent and thus the pyrene protons in **4a** should appear as two singlets and an AB system.

Hence, the [2 + 2] zinc(II) chelate formed by ligand L^2 has been assigned to the non-helical complex **4b** on the basis of the appearance of the pyrene protons as four singlets in the range δ 5.9–8.3. In view of this assignment, it appears that complex **3** which contains the shorter naphthyl linker, exists as a mixture of helical and non-helical complexes **3a** and **3b**. In the absence of other data, it is not possible to assign the major complex to the helical or non-helical complex. However, assuming that our assignment of **4b** is correct, it is reasonable to expect that a similar structural relationship exists for formation of complex **3**. Hence the major [2 + 2] complex formed by ligand L^1 and Zn^{II} has been assigned tentatively to the non-helical form **3b**; this complex is more stable than the helical complex **3a** and predominates in most solvents.

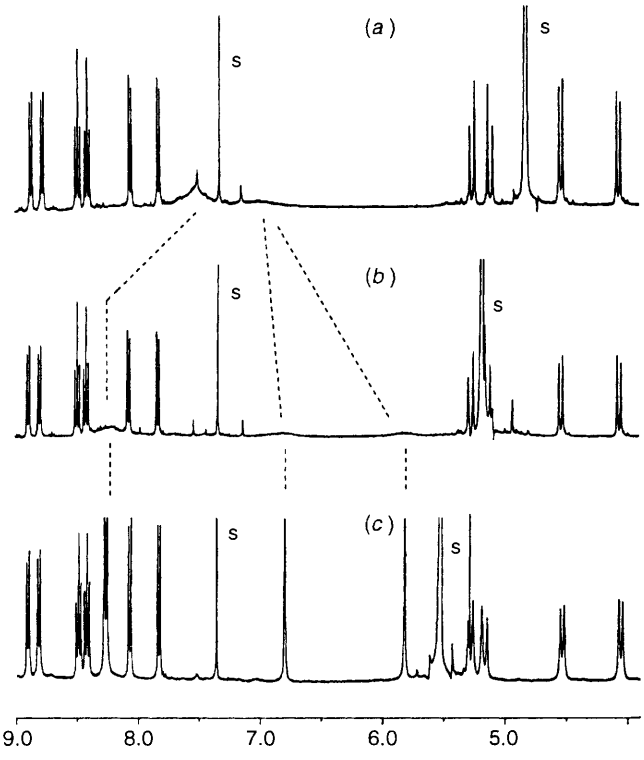

Fig. 4 Variable-temperature 200 MHz ^1H NMR spectra of complex **4** in CD_3OD at (*a*) 298, (*b*) 260 and (*c*) 220 K; s indicates solvent peaks

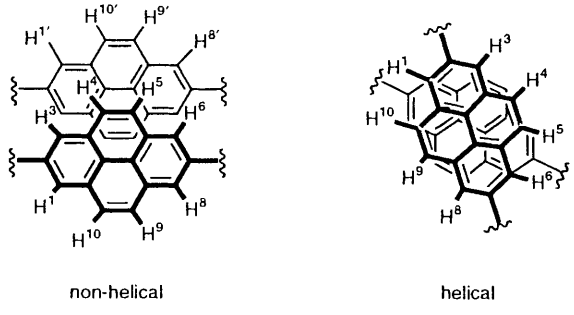

Fig. 5 Schematic view of the orientation of the pyrene rings with respect to one another in the helical complex **4a** and non-helical complex **4b**

In the case of the pyrene system **4**, minor amounts of a second complex were observed at low temperatures. These peaks most probably arise from the helical complex **4a**, but clearly this complex is much less stable than **4b** and is only detected at low temperatures. Thus, it appears that for zinc(II) the pyrene linker provides the optimal spacer length to allow exclusive formation of the non-helical complex **4b**. In contrast to these results, the helical and non-helical complexes of the corresponding copper(I) chelates have approximately the same relative stabilities. The larger size and co-ordination properties of zinc(II), in the present systems, appear to be ideal for preferential formation of non-helical complexes. X-Ray crystallography of **4** is essential to establish the molecular structure of this complex and to confirm our NMR assignments. However attempts to grow crystals suitable for diffraction have been unsuccessful to date.

Silver(I) Complexation Studies with L^1.—The silver(I) complex of L^1 was prepared, as silver is known to form tetrahedral complexes with bipyridyls, and silver(I) has been successfully used in the assembly of helicates[2] and cyclic structures.[13] Thus, treatment of L^1 with silver triflate afforded a pale yellow

complex tentatively assigned as $[Ag_2L^1{}_2][CF_3SO_3]_2$. Analysis of the complex by FAB mass spectrometry showed only peaks assigned to the free ligand HL^{1+}. However, with the softer technique of ES mass spectrometry, a molecular ion peak due to $[Ag_2L^1{}_2]^{2+}$ was observed. The mass spectral results suggest that the complex is quite weak, a result confirmed by NMR analysis of the product. In contrast to the results obtained with Cu^I and Zn^{II}, the methylene protons remained as broad singlets and only minor changes in the chemical shifts of the protons were observed. Due to the lability of this complex further detailed studies were not carried out.

Experimental

Melting points were determined on a Reichert heating stage and are uncorrected. Ultraviolet spectra were recorded on a Hitachi 150–20 spectrophotometer. NMR spectra were recorded on a Bruker AC200 or AMX400 spectrometer. The temperature of the spectrometer probe was calibrated by the shift difference of methanol resonances in the ^1H NMR spectrum.[24] Assignments follow the numbering given in Schemes 2 and 3. Spectra were recorded in the solvent indicated, locked on solvent deuterium and referenced to residual solvent protons. FAB mass spectra were recorded on a Finnigan/Mat TSQ-46 mass spectrometer (n-butyl alcohol matrix). Electrospray (ES) mass spectra were recorded at the University of Wollongong on a Vestec model M-200 electrospray mass spectrometer. Samples were introduced in $MeCN/H_2O$ at 3–5 μl min^{-1}. Flash column chromatography was carried out on Merck silica gel (type 9385, 230–400 mesh). 6-Hydroxymethyl-6′-methyl-2,2′-bipyridine[20] and 2,9-bis(bromomethyl)pyrene[21,25] were prepared according to the literature procedures.

2,6-Bis{3-(6′-methyl-2,2′-bipyridin-6-yl)-2-oxapropyl}naphthalene L^1. Potassium *tert*-butoxide (420 mg, 3.75 mmol) was added portionwise to a solution of 6-hydroxymethyl-6′-methyl-2,2′-bipyridine (725 mg, 3.6 mmol) and 2,6-bis(bromomethyl)naphthalene (565 mg, 1.8 mmol) in thf (60 cm^3) under nitrogen at −30 °C. The reaction was stirred at this temperature for 8 h, warmed to room temperature, stirred for 1 h, quenched with water (100 cm^3) and the solution extracted with $CHCl_3$ (4 × 60 cm^3). The combined organic extracts were washed with water (2 × 100 cm^3) and brine (100 cm^3), dried over magnesium sulfate and the solvent removed. The resultant solid was subjected to chromatography on silica ($CHCl_3$). The major band was collected, the solvent removed and the solid recrystallised from ethyl acetate to give ligand L^1 as colourless plates (700 mg, 70%): m.p. 167–169 °C (Found: C, 78.5; H, 5.7; N, 9.9. Calc. for $C_{36}H_{32}N_4O_2$: C, 78.2; H, 5.8; N, 10.1%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, CH_3), 4.87 (s, 7′-CH_2), 4.94 (s, 9′-CH_2), 7.19 (d, *J* 8.3, $H^{5''}$), 7.57 (dd, *J* 1.3, 8.5, H^3,H^7), 7.58 (d, *J* 8.3, $H^{5'}$), 7.72 (dd, *J* 8.3, $H^{4''}$), 7.85 (m, H^1,H^4,H^5,H^8,$H^{4'}$), 8.21 (d, *J* 8.3, $H^{3''}$) and 8.38 (d, *J* 8.3 Hz, $H^{3'}$). $\lambda_{max}(CHCl_3)$ (log ε/dm^3 mol^{-1} cm^{-1}: 289 (5.74) nm. FAB mass spectrum: *m/z* 553 ($M + H^+$), 427, 399, 329, 309, 275 and 273.

2,7-Bis{3-(6′-methyl-2,2′-bipyridin-6-yl)-2-oxapropyl}pyrene L^2. Sodium hydride (60% dispersion in oil, 48 mg, 1.2 mmol) was added to a solution of 6-hydroxymethyl-6′-methyl-2,2′-bipyridine (216 mg, 1.08 mmol) in thf (30 cm^3) under nitrogen. The mixture was heated at 50 °C for 1 h, cooled to room temperature and the 2,9-bis(bromomethyl)pyrene (210 mg, 0.54 mmol) was added. The reaction mixture was heated at 50 °C for 24 h, cooled to room temperature, poured onto brine and the product was extracted into chloroform (4 × 20 cm^3). The combined organic extracts were dried over sodium sulfate, the solvent removed and the resultant brown residue was chromatographed on silica (chloroform). The major band was collected, the solvent removed and recrystallization of the residue from chloroform–ethyl acetate afforded ligand L^2 as white flakes (220 mg, 65%): m.p. 213.5–215 °C (Found: C, 80.2; H, 5.5; N, 8.7. Calc. for $C_{42}H_{34}N_4O_2$: C, 80.5; H, 5.4; N, 9.0%). ^1H NMR (200 MHz, $CDCl_3$): δ 2.64 (s, CH_3), 4.91 (s, 7′-CH_2), 5.14 (s, 9′-CH_2), 7.16 (br d, $H^{5''}$), 7.60 (br d, $H^{5'}$), 7.68 (dd, *J* 7.8, $H^{4''}$), 7.87 (dd, *J* 7.7 Hz, $H^{4'}$), 8.09 (br s, H^4,H^5,H^9,H^{10}), 8.19 (br d, H^3), 8.24 (br s, H^1,H^3,H^6,H^7) and 8.32 (br d, $H^{3'}$). $\lambda_{max}(CHCl_3)$ (log ε/dm^3 mol^{-1} cm^{-1}): 268 (5.20), 280 (5.36), 325 (5.08) and 340 (5.23) nm. FAB mass spectrum: *m/z* 627 ($M + H^+$), 459 and 427.

Reactions of L^1.—*With* Cu^I. *Method* 1. Ligand L^1 (90 mg, 160 mmol) was added to a solution of copper(I) chloride (16 mg, 160 mmol) and hydrazine hydrate (1 μmol dm^{-3}) in acetonitrile–water (5 cm^3, 2:3). The mixture was stirred at room temperature for 3 h and ammonium hexafluorophosphate (100 mg, 610 mmol) in water (2 cm^3) was added to the red reaction mixture. The resultant red precipitate was collected, washed successively with water (10 cm^3) and chloroform (10 cm^3) and dried under high vacuum to give $[Cu_2L^1{}_2][PF_6]_2{\cdot}H_2O$ **1**·H_2O as a red orange powder (84 mg, 69%) (Found: C, 55.8; H, 4.3; N, 7.1. Calc. for $C_{72}H_{66}Cu_2F_{12}N_8O_5P_2$: C, 56.1; H, 4.3; N, 7.3%). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.13, 2.25 (2 s, CH_3), 3.74 and 4.34 (AX system, *J* 12.2, CH_2), 3.99 and 4.41 (AX system, *J* 12.4, CH_2), 4.06 and 4.26 (AX system, *J* 13.6, CH_2), 4.10 and 4.30 (AX system, *J* 13.6, CH_2); 7.04 (d, *J* 10.2), 7.06 (d, *J* 8.8), 7.24 (s), 7.34 (s), 7.60 (d, *J* 8.8) (H of naphthalene unit), 7.44–7.49 (m), 7.60 (d, *J* 8.4), 8.00–8.06 (m), 8.14 (dd, *J* 7.6), 8.21–8.26 (m) and 8.32 (d, *J* 8.1 Hz) (H of bipyridyl). λ_{max}(MeCN) (log ε/dm^3 mol^{-1} cm^{-1}): 229 (5.43) and 287 (4.92) nm. FAB mass spectrum: *m/z* 1377 $[M - PF_6]^+$ and 1168 $[M - Cu(PF_6)_2]^+$.

Method 2. Ligand L^1 (125 mg, 226 mmol) in chloroform (5 cm^3) was added to a solution of $[Cu(MeCN)_4]PF_6$ (82 mg, 220 mmol) in acetonitrile–chloroform (4 cm^3, 1:1). The red reaction mixture was stirred for 1 h and the solvent was removed. The residue was taken up in chloroform (10 cm^3) and the mixture was sonicated for 30 min. The mixture was filtered and the residue was washed with chloroform and dried under high vacuum to give $[Cu_2L^1{}_2][PF_6]_2$ **1** (110 mg, 64%) identical to the product obtained in method 1.

With $Zn(CF_3SO_3)_2$. Ligand L^1 (100 mg, 181 mmol) was added to a solution of zinc triflate (65 mg, 179 mmol) in acetonitrile–chloroform (5 cm^3, 4:1) and the solution was stirred for 3 h. The solvent was removed, chloroform (20 cm^3) was added and the mixture was heated at reflux for 5 h. The reaction mixture was filtered, the residue washed with hot chloroform (30 cm^3) and dried under high vacuum to give $[Zn_2L^1{}_2][CF_3SO_3]_4{\cdot}2H_2O$ **3**·$2H_2O$ as an off white solid (128 mg, 78%) (Found: C, 48.6; H, 3.9; N, 5.7. Calc. for $C_{76}H_{68}F_{12}N_8O_{18}S_4Zn_2$: C, 48.9; H, 3.6; N, 6.0%). ^1H NMR (400 MHz, CD_3CN): δ 2.02, 2.04 (2 s, CH_3), 3.77 and 4.20 (AX system, *J* 12.7, CH_2), 3.82 and 4.35 (AX system, *J* 13.9, CH_2), 4.78 and 4.92 (AX system, *J* 15.9, CH_2), 4.87 and 4.95 (AX system, *J* 15.9, CH_2), 6.23, 6.76 (2 dd, *J* 1.4, 8.4, H^3,H^7), 7.12, 7.21 (2 d, *J* 8.4, H^4,H^8), 7.33, 7.35 [2 br, s H^1,H^5 (H of naphthalene unit)], 7.61, 7.82 (2 d, *J* 8.0, $H^{5'}$), 7.71, 7.74 (2 d, *J* 8.0, $H^{5''}$), 8.37 (dd, *J* 8.0, $H^{4''}$), 8.44 (dd, *J* 8.0, $H^{4'}$), 8.60, 8.64 (2 d, *J* 8.0, $H^{3''}$), 8.69 and 8.74 (2 d, *J* 8.0 Hz, $H^{3'}$) (H of bipyridyl). λ_{max}(CN) (log ε/dm^3 mol^{-1} cm^{-1}): 229 (5.46), 289 (4.92), 301 (4.88) and 316 (4.72) nm. ES mass spectrum: *m/z* 767 $[M - 2(CF_3SO_3)]^+$, 553 $[L^1 + H]^+$, 461.5 $[M - 3\ CF_3SO_3]^+$, 309 $[M - 4CF_3SO_3]^+$ and 277 $[L^1 + 2H]^+$.

Reactions of L^2.—*With* Cu^I. Using method 2 described above, reaction of ligand L^2 (20 mg, 32 mmol) afforded $[Cu_2L^2{}_2][PF_6]_2{\cdot}2H_2O$ **2**·H_2O as a red solid (25 mg, 78%) (Found: C, 58.8; H, 4.4; N, 6.2. Calc. for $C_{84}H_{72}Cu_2F_{12}N_8O_6P_2$: C, 59.1; H, 4.2; N, 5.7%). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.00, 2.04 (2 s, CH_3), 3.47 (d, *J* 11.7, CH_2), 3.49 (d, *J* 11.7, CH_2), 4.15 (d, *J* 13.2, CH_2), 4.21 (d, *J* 13.2, CH_2), 4.29 (d, *J* 13.2, CH_2), 4.33 (d, *J* 11.7, CH_2), 4.37 (d, *J* 13.2, CH_2), 4.40 (d, *J* 13.2, CH_2), 7.24, 7.26, 7.65 (3 s, 1:1:2, H of pyrene unit), 7.35 (br d, *J* 7.8), 7.56 (d, *J* 4.8), 7.73 (d, *J* 7.8), 7.93 (br dd, *J* 7.8), 8.18 (m), 8.28 (br dd, *J* 7.8 Hz) (H of bipyridyl). λ_{max}(MeCN) (log ε/dm^3 mol^{-1} cm^{-1}): 240 (5.20), 249 (5.28), 266

(4.95), 278 (4.08), 322 (4.81) and 337 (4.96) nm. FAB mass spectrum: m/z 1525 $[M - PF_6]^+$ and 1316 $[M - Cu(PF_6)_2]^+$.

With $Zn(CF_3SO_3)_2$. Using the method described above, reaction of L^2 (50 mg, 80 mmol) afforded $[Zn_2L^2{}_2][CF_3SO_3]_4 \cdot 2H_2O$ **4**·$2H_2O$ as a light yellow solid (72 mg, 90%) (Found: C, 52.3; H, 4.0; N, 5.2. Calc. for $C_{88}H_{72}F_{12}N_8O_{18}S_4Zn_2$: C, 52.2; H, 3.6; N, 5.6%). ^{1}H NMR (200 MHz, CD_3CN): δ 2.08 (s, CH_3), 3.92 and 4.43 (AX system, J 12.2 Hz, $H^{9'}$), 5.04 (ABq, J 16.3, $H^{7'}$), 6.98 and 7.44 (2 br s, H of pyridine unit), 7.73 (d, J 7.9), 7.88 (d, J 7.9), 8.33 (dd, J 7.9), 8.89 (dd, J 7.9), 8.56 (d, J 7.9) and 8.65 (d, J 7.9 Hz) (H of bipyridyl). λ_{max}(MeCN) (log ε/dm^3 mol^{-1} cm^{-1}): 240 (5.11), 249 (6.3), 267 (4.92), 278 (5.04), 321 (4.80) and 337 (4.94) nm. FAB mass spectrum: m/z 1682 $[M - 2(CF_3SO_3)]^+$.

Molecular Modelling.—Modelling was carried out using MacroModel[26] (version 3.1X) on a Silicon Graphics Indigo. Complexes were constructed using X-ray coordinates for silver(I) and copper(I) complexes of 6,6-dimethyl-2,2′-bipyridine[27,28] to which were added aromatic linkers. The linker chains were subjected to a substructure minimisation using the MM2 force field resident within MacroModel.

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