Complexes containing Ferrocenyl Groups as Redox Spectators; Synthesis, Molecular Structure and Co-ordination Behaviour of 4'-Ferrocenyl-2,2':6',2''-terpyridine†

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The new ligand 4'-ferrocenyl-2,2':6',2''-terpyridine L has been prepared in good yield from ferrocenecarbaldehyde by two different routes. The crystal and molecular structure of L has been determined [monoclinic, space group $P2_1/c$, $a = 7.905(2)$, $b = 22.045(4)$, $c = 11.394(2)$ Å, $\beta = 107.10(3)°$, $Z = 4$, $R = 0.034$ for 2486 independent reflections]. The co-ordination behaviour of L has been studied and the homoleptic complexes $[ML_2][PF_6]_2$ (M = Co, Fe or Ru) prepared and characterised. In addition, the heteroleptic complex $[RuL(terpy)][PF_6]_2$ (terpy = 2,2':6',2''-terpyridine) has been prepared. All of these complexes are redox active.

Supramolecular systems containing a number of electronically coupled photo- or redox-active centres are of considerable current interest.[1,2] Particular emphasis has been placed upon the preparation of multinuclear systems which exhibit intermetallic energy- or electron-transfer processes.[2,3] Although metallocenes have been used as redox-active sites in molecular[4] and supramolecular[5–7] systems and oligopyridine complexes are widely used as both redox- and photo-active sites in supramolecular arrays,[8,9] very few examples have been reported in which such centres are covalently coupled.[5,6] The development of such covalently coupled systems is of interest, since electron transfer processes are usually facilitated if through-bond pathways are available.[1] As a part of our study of redox-active metallosupramolecular systems[9,10] we have developed ligands in which redox-active ferrocenyl substituents are covalently attached to a metal-binding oligopyridine domain. In this paper we describe the preparation, structural characterisation and co-ordination behaviour of a 2,2':6',2''-terpyridine ligand bearing a ferrocene group directly attached at the 4' position.

Experimental

Infrared spectra were recorded on a Philips PU9624 Fourier transform spectrophotometer at a resolution of 4 cm^{-1}, with the samples in compressed KBr discs. Proton NMR spectra were recorded on a Brüker WM250 spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix. Electrochemical measurements were performed using an AMEL model 553 potentiostat, model 567 function generator and model 721 integrator connected to an X-Y recorder *via* an AMEL model 560/A interface. A conventional three-electrode configuration was used, with platinum bead working and auxiliary electrodes and an Ag–AgCl reference. Acetonitrile, freshly distilled from CaH_2 and then P_4O_{10}, was used as solvent in all cases. The base electrolyte was 0.1 mol dm^{-3} $[NBu_4][BF_4]$, recrystallised twice from ethanol–water and rigorously dried. Potentials are quoted *vs.* the ferrocene–ferrocenium couple, and all potentials were referenced to internal ferrocene added at the end of each experiment. Elemental analyses were performed at the University Chemical Laboratory, Cambridge.

N-[2-Oxo-2-(2-pyridyl)ethyl]pyridinium iodide[11] and $[Ru(terpy)Cl_3]$[12] (terpy = 2,2':6',2''-terpyridine) were prepared according to the literature methods; ferrocenecarbaldehyde was used as supplied by Aldrich. Ammonium acetate was stored over P_2O_5 until required.

Preparations.—2-[3-(*Ferrocenyl*)-1-*oxoprop*-2-*enyl*]*pyridine*, **I**. 2-Acetylpyridine (0.12 cm^3, 1 mmol) was added to a solution of ferrocenecarbaldehyde (0.214 g, 1 mmol) in ethanol (20 cm^3). After 2 min, aqueous sodium hydroxide (3 cm^3, 2 mol dm^{-3}) was added and the mixture was stirred for 30 min. After the addition of distilled water (4 cm^3) a deep red precipitate was obtained which was collected by filtration, washed with a mixture of water and ethanol and dried *in vacuo* to give the desired enone (0.282 g, 89%) (Found: C, 67.3; H, 4.6; N, 4.1. Calc. for $C_{18}H_{15}FeNO$: C, 68.1; H, 4.7; N, 4.4%). IR (KBr): 1661s, 1595s, 1576s, 1357m, 1320s, 1222m, 1105m, 1025s, 987s, 745m and 481m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.1 (br, 5 H, C_5H_5), 4.5 (br, 2 H, C_5H_4), 4.6 (br, 2 H, C_5H_4) and 7.2–8.6 (br, 6 H, C_5H_4N and CH=CH). Mass spectrum (FAB): *m*/*z* 317 (M^+).

3-*Ferrocenyl*-1,5-*bis*(2-*pyridyl*)*pentane*-1,5-*dione*, **II**. Ferrocenecarbaldehyde (0.214 g, 1 mmol) and 2-acetylpyridine (0.3 cm^3, 2.5 mmol) were added to a mixture of ethanol (15 cm^3) and aqueous sodium hydroxide (3 cm^3, 2 mol dm^{-3}) and the solution was stirred for 22 h. After this period, a pale orange precipitate had been obtained; this was collected by filtration, washed with water and ethanol and dried *in vacuo* to give the dione (0.33 g, 80%) (Found: C, 67.9; H, 4.9; N, 6.3. Calc. for $C_{23}H_{21}FeN_2O_2$ C, 66.8; H, 5.1; N, 6.8%). IR (KBr): 1694s, 1584m, 1434m, 1355m, 1317m, 1281m, 1105m, 996m, 810m, 774m, 607m and 480m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.49 (dd, 2 H, CH_2), 3.75 (dd, 2 H, CH_2), 3.90 (m, 1 H, CH), 4.04 (s, 2 H, C_5H_4), 4.17 (s, 2 H, C_5H_4), 4.17 (s, 5 H, C_5H_5), 7.25 (br, 2 H, $H^{5,5''}$), 7.8 (br, 2 H, $H^{4,4''}$), 8.0 (br, 2 H, $H^{3,3''}$) and 8.6 (br, 2 H, $H^{6,6''}$). Mass spectrum (FAB): *m*/*z* 438 (M^+).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

4′-Ferrocenyl-2,2′:6′,2″-terpyridine, L. *Method* 1. A solution of **I** (0.317 g, 1 mmol), *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (0.326 g, 1 mmol) and ammonium acetate (5 g) in ethanol (10 cm^3) was heated to reflux for 2 h. After this period, cooling the reaction mixture resulted in the precipitation of the desired compound as a crystalline orange solid. This was collected by filtration, washed with ethanol and large amounts of distilled water and then dried *in vacuo* to give pure L (0.216 g, 52%).

Method 2. A solution of **II** (0.300 g, 0.73 mmol) and ammonium acetate (5 g) in ethanol (10 cm^3) was heated to reflux for 2 h. The product was isolated as described above (0.167 g, 55%) (Found: C, 70.6; H, 4.5; N, 9.7. Calc. for $C_{25}H_{19}FeN_3{\cdot}0.5H_2O$: C, 70.4; H, 4.7; N, 9.9%). IR (KBr): 1605s, 1585s, 1567m, 1548m, 1467m, 1434s, 1104m, 821m, 790m and 501m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.09 (s, 5 H, C_5H_5), 4.46 (t, 2 H, C_5H_4), 5.01 (t, 2 H, C_5H_4), 7.35 (dt, 2 H, $H^{5,5''}$), 7.87 (dt, 2 H, $H^{4,4''}$), 8.51 (s, 2 H, $H^{3',5'}$), 8.65 (d, 2 H, $H^{3,3''}$) and 8.74 (d, 2 H, $H^{6,6''}$). Mass spectrum (FAB): *m*/*z* 418 (M^+).

$[FeL_2][PF_6]_2$. A solution of $FeCl_2{\cdot}4H_2O$ (0.100 g, 0.5 mmol) in methanol (5 cm^3) was added to a stirred solution of L (0.419 g, 1 mmol) in methanol–chloroform (1:4, 5 cm^3). After stirring for a few minutes, an excess of $[NH_4][PF_6]$ was added to the dark coloured solution to give a violet precipitate. The violet solid was recrystallised from acetone–methanol, washed well with methanol and dried *in vacuo* to give $[FeL_2][PF_6]_2$ (0.442 g, 75%) (Found: C, 50.9; H, 3.4; N, 7.0. Calc. for $C_{50}H_{38}F_{12}Fe_3N_6P_2$: C, 50.85; H, 3.2; N, 7.1%). IR (KBr): 1612m, 1496m, 1435m, 1402m, 1105m, 842s, 790m, 757m, 558m and 490m cm^{-1}. ^1H NMR (CD_3CN): δ 4.39 (s, 10 H, C_5H_5), 4.84 (s, 4 H, C_5H_4), 5.44 (s, 4 H, C_5H_4), 7.09 (dt, 4 H, $H^{5,5''}$), 7.17 (d, 4 H, $H^{6,6''}$), 7.90 (dt, 4 H, $H^{4,4''}$), 8.58 (d, 4 H, $H^{3,3''}$), 8.89 (s, 4 H, $H^{3',5'}$). Mass spectrum (FAB): *m*/*z* 1036 {$[FeL_2][PF_6]$} and 890 {$[FeL_2]$}.

$[CoL_2][PF_6]_2$. A solution of $Co(O_2CMe)_2{\cdot}4H_2O$ (0.125 g, 0.5 mmol) in methanol (5 cm^3) was added to a stirred solution of L (0.419 g, 1 mmol) in methanol–chloroform (1:4, 5 cm^3). After stirring for a few minutes, an excess of $[NH_4][PF_6]$ was added to the dark coloured solution to give a red precipitate. The red solid was recrystallised from acetone–methanol, washed well with methanol and dried *in vacuo* to give $[CoL_2][PF_6]_2$ (0.414 g, 70%) (Found: C, 49.1; H, 3.3; N, 7.0. Calc. for $C_{50}H_{38}CoF_{12}Fe_2N_6P_2{\cdot}2H_2O$: C, 49.25; H, 3.5; N, 6.9%). IR (KBr): 1612m, 1498m, 1474m, 1435m, 1253m, 1106m, 1032m, 840s, 790m, 558m and 477m cm^{-1}. ^1H NMR (CD_3CN): δ 7.2 (s, C_5H_5), 7.9 (s, C_5H_4), 8.5 (s, C_5H_4), 11.9 (br), 32.2 (br), 52.1 (br), 58.3 (br) and 96.3 (br) (H of terpy fragment). Mass spectrum (FAB): *m*/*z* 1183 {$[CoL_2][PF_6]_2$}, 1039 {$[CoL_2][PF_6]$} and 893 {$[CoL_2]$}.

$[RuL_2][PF_6]_2$. A solution of L (0.419 g, 1 mmol) and $RuCl_3{\cdot}3H_2O$ (0.104 g, 0.4 mmol) was heated to reflux in ethane-1,2-diol (10 cm^3) for 30 min. After cooling the reaction mixture, water and $[NH_4][PF_6]$ were added to give a red precipitate which was collected by filtration. This solid was extracted with acetonitrile, and the red extract was chromatographed over silica using a 14:2:1 mixture of acetonitrile, saturated aqueous KNO_3 solution and distilled water as the mobile phase. The major red band was collected, and the complex was obtained as its red hexafluorophosphate salt by the addition of water and an excess of $[NH_4][PF_6]$ (0.181 g, 37%) (Found: C, 48.7; H, 3.1; N, 6.8. Calc. for $C_{50}H_{38}F_{12}Fe_2N_6P_2Ru$: C, 49.0; H, 3.1; N, 6.9%). IR (KBr): 1636m, 1496m, 1471m, 1433m, 1398m, 1385m, 1106m, 1028m, 844s, 558m and 422m cm^{-1}. ^1H NMR (CD_3CN): δ 4.34 (s, 10 H, C_5H_5), 4.78 (t, 4 H, C_5H_4), 5.35 (t, 4 H, C_5H_4), 7.18 (ddd, 4 H, $H^{5,5''}$), 7.42 (d, 4 H, $H^{6,6''}$), 7.94 (dt, 4 H, $H^{4,4''}$), 8.62 (d, 4 H, $H^{3,3''}$) and 8.73 (s, 4 H, $H^{3',5'}$). Mass spectrum (FAB): *m*/*z* 1226 {$[RuL_2][PF_6]_2$}, 1082 {$[RuL_2][PF_6]$} and 936 {$[RuL_2]$}.

[RuL(terpy)]$[PF_6]_2$. A suspension of [Ru(terpy)Cl_3] (0.100 g, 0.22 mmol) and L (0.95 g, 0.22 mmol) in methanol (10 cm^3) was treated with *N*-ethylmorpholine (0.2 cm^3) and the reaction mixture heated to reflux for 2 h. After cooling, the reaction mixture was treated with an excess of $[NH_4][PF_6]$ to give a dark red precipitate, which was collected by filtration. This crude material was dissolved in acetonitrile and chromatographed over silica using a 14:2:1 mixture of acetonitrile, saturated aqueous KNO_3 solution and water. The third major red fraction was collected and treated with water and $[NH_4][PF_6]$. The solution was then concentrated *in vacuo* until a deep red precipitate formed. This was collected by filtration, washed with water and dried *in vacuo* to yield [RuL(terpy)]$[PF_6]_2$ as a red solid (0.077 g, 34%) (Found: C, 45.35; H, 2.9; N, 7.9. Calc. for $C_{40}H_{30}F_{12}FeN_6Ru{\cdot}H_2O$: C, 45.3; H, 3.0; N, 7.9%). IR (KBr): 1612m, 1496m, 1451m, 1433m, 1387m, 1247m, 1109m, 1029m, 848s, 767m, and 558m cm^{-1}. ^1H NMR (CD_3CN): δ 4.34 (s, 5 H, C_5H_5), 4.78 (t, 2 H, C_5H_4), 5.34 (t, 2 H, C_5H_4), 7.14 (ddd, 2 H, $H^{5,5''}$ of terpy), 7.19 (ddd, 2 H, $H^{5,5''}$ of L), 7.30 (d, 2 H, $H^{6,6''}$ of terpy), 7.44 (d, 2 H, $H^{6,6''}$ of L), 7.92 (dt, 2 H, $H^{4,4''}$ of terpy), 7.93 (dt, 2 H, $H^{4,4''}$ of L), 8.42 (t, 1 H, $H^{4'}$ of terpy), 8.49 (d, 2 H, $H^{3,3''}$ of terpy), 8.62 (d, 2 H, $H^{3,3''}$ of L), 8.73 (s, 2 H, $H^{3',5'}$ of L) and 8.74 (d, $H^{3',5'}$ of terpy). Mass spectrum (FAB): *m*/*z* 1043 {[RuL(terpy)]$[PF_6]_2$}, 897 {[RuL(terpy)]$[PF_6]$} and 752 {[RuL(terpy)]}.

Structure Determination of L.—*Crystal data.* $C_{25}H_{19}FeN_3$, $M = 417.29$, monoclinic, space group $P2_1/c$, $a = 7.905(2)$, $b = 22.045(2)$, $c = 11.394(2)$ Å, $\beta = 107.10(3)°$, $Z = 4$, $U = 1897.8(7)$ Å^3, $F(000) = 864$, $D_c = 1.460$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, crystal size 0.37 × 0.29 × 0.28 mm, $T = 293$ K, μ(Mo-Kα) = 8.11 cm^{-1}.

Data collection and refinement. Data were collected on a Rigaku AFC7 four-circle diffractometer coupled to a molybdenum target rotating anode X-ray source, using a crystal of dimensions 0.37 × 0.29 × 0.28 mm by the 2θ–ω method ($5 < 2\theta = 45°$). Of 5299 reflections collected, 2486 were unique. The structure was solved by direct methods (SHELXTL PLUS[13]) and refined by full-matrix least-squares analysis on F^2 (SHELX 92[14]) with all data to R and R' values of 0.034 and 0.093 respectively $\{R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|,\ R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}\}$. Largest peak and hole in the final difference map +0.45, −0.29 e Å^{-3}. Final atomic coordinates for non-

Table 1 Atomic coordinates (× 10^4) for all non-hydrogen atoms in L

Atom	*x*	*y*	*z*
Fe	1879(1)	6154(1)	5640(1)
C(1)	3359(3)	5628(1)	4823(2)
C(2)	2297(4)	5258(1)	5340(3)
C(3)	2752(4)	5378(1)	6612(3)
C(4)	4089(4)	5822(2)	6890(3)
C(5)	4465(4)	5978(1)	5788(2)
C(6)	393(4)	6751(1)	4389(3)
C(7)	−707(4)	6365(2)	4797(3)
C(8)	−331(4)	6429(2)	6064(3)
C(9)	1000(4)	6863(1)	6449(3)
C(10)	1474(4)	7066(1)	5412(3)
N(11)	1238(3)	4155(1)	1240(2)
C(12)	556(3)	3685(1)	512(3)
C(13)	548(4)	3641(1)	−690(3)
C(14)	1307(4)	4095(1)	−1166(3)
C(15)	2025(4)	4585(1)	−441(3)
C(16)	1961(3)	4603(1)	757(2)
N(21)	3377(3)	5581(1)	1077(2)
C(22)	2677(3)	5128(1)	1567(2)
C(23)	2624(3)	5140(1)	2775(2)
C(24)	3335(3)	5625(1)	3526(2)
C(25)	4062(4)	6098(1)	3015(3)
C(26)	4039(3)	6059(1)	1794(2)
N(31)	5758(3)	6975(1)	1951(2)
C(32)	4768(3)	6556(1)	1205(2)
C(33)	4427(4)	6580(1)	−57(3)
C(34)	5167(4)	7042(1)	−561(3)
C(35)	6220(4)	7460(1)	192(3)
C(36)	6464(4)	7412(1)	1432(3)

Table 2 Selected bond lengths (Å) and bond angles (°) in L

Fe–C(5)	2.039(3)	Fe–C(10)	2.040(3)
Fe–C(8)	2.037(3)	Fe–C(9)	2.038(3)
Fe–C(7)	2.040(3)	Fe–C(6)	2.040(3)
Fe–C(4)	2.038(3)	Fe–C(3)	2.044(3)
Fe–C(2)	2.048(3)	Fe–C(1)	2.055(2)
C(1)–C(24)	1.472(4)	C(26)–C(32)	1.486(4)
C(16)–C(22)	1.484(4)		
C(16)–N(11)–C(12)	117.4(3)	C(22)–N(21)–C(26)	117.8(2)
C(36)–N(31)–C(32)	117.3(2)	C(23)–C(24)–C(25)	117.4(2)

hydrogen atoms and relevant bond lengths and bond angles are presented in Tables 1 and 2.

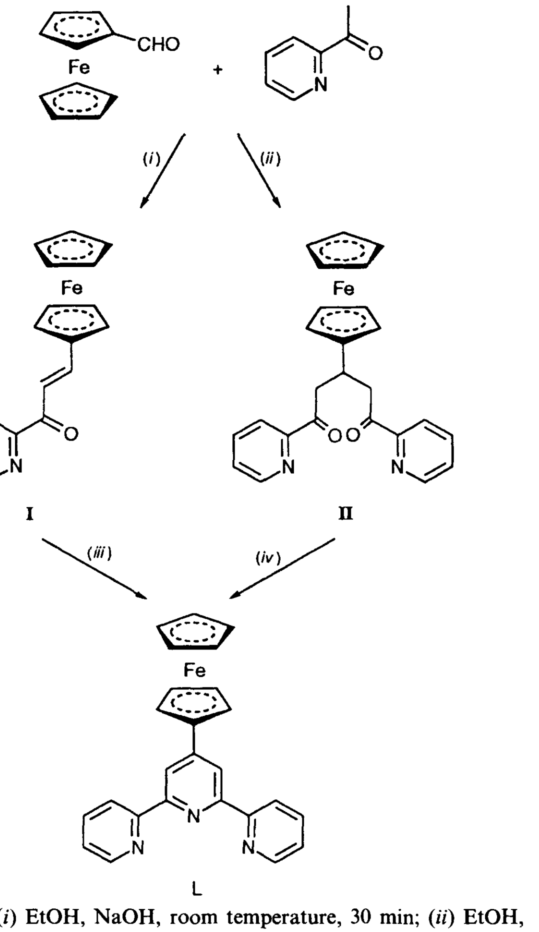
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The new ligand L was prepared by two different methods. The first is based upon the Kröhnke methodology[11] *via* an isolated enone, whilst the second utilises a classical route[15] *via* a 1,5-dione intermediate. The conditions under which the reaction of ferrocenecarbaldehyde and 2-acetylpyridine is performed determine which of the two intermediates is isolated. Short reaction times at low temperatures (Cambridge ambient) and a 1 : 1 stoichiometric ratio of ferrocenecarbaldehyde to 2-acetylpyridine afford the enone, 2-[3-(ferrocenyl)-1-oxoprop-2-enyl]pyridine I, as an orange solid in good (89%) yield. However, at room temperature with prolonged reaction times and an excess of 2-acetylpyridine the product of the reaction is the 2 : 1 adduct, 3-ferrocenyl-1,5-bis(2-pyridyl)pentane-1,5-dione **II**, which is isolated in 80% yield as an orange solid. These reactions are summarised in Scheme 1.

Analytical and spectroscopic data are in agreement with the proposed formulations of **I** and **II**. The IR spectrum of **I** exhibits a ν(C=O) stretching mode at 1661 cm^{-1} whereas the corresponding carbonyl mode is found at 1694 cm^{-1} for **II**. These values are characteristic of enones and 1,5-diketones, respectively, and compare well with the carbonyl modes of 2-[1-oxo-3-(phenyl)prop-2-enyl]pyridine and 3-phenylpentane-1,5-dione.[15] Both compounds also display absorptions characteristic of a monosubstituted ferrocene; FAB mass spectrometry showed molecular ion peaks at *m*/*z* 317 and 438 for **I** and **II** respectively. The ^{1}H NMR spectrum of **I** exhibits broad signals for all the proton resonances. Ferrocene resonances were observed at δ 4.1 (C_5H_5) and δ 4.5, 4.6 (C_5H_4 protons), whereas the pyridyl and vinyl signals appear in the region δ 7.2–8.6. The ^{1}H NMR spectrum of **II** displays similar chemical shifts for the pyridyl and ferrocenyl protons, with the only feature of note being that the C_5H_5 singlet resonance is coincident with one of the C_5H_4 signals. The spectrum also shows the expected, complex, AA'BB'M pattern for the CH_2CHCH_2 spin system.

Both compounds **I** and **II** can be used as starting materials for the preparation of the terpyridine derivative, 4'-ferrocenyl-2,2' : 6',2"-terpyridine L. The reaction of **I** with the Kröhnke reagent[11] *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide in ethanol in the presence of ammonium acetate, and the direct reaction of **II** with ammonium acetate in ethanol both gave dark blue solutions from which the orange compound L precipitated as a crystalline solid in 50–55% yield. The absence of any ν(C=O) stretching vibrations in the IR spectrum of L indicate that cyclisation has occurred. The ^{1}H NMR spectrum of L is characteristic. The ferrocenyl substituent gives rise to a five proton singlet for the unsubstituted cyclopentadienyl ring (δ 4.09) and two apparent triplets corresponding to the AA'MM' pattern for the monosubstituted ring (δ 4.46 and 5.01). The remainder of the spectrum is characteristic of a 4'-aryl-2,2' : 6',2"-terpyridine, with the resonance assigned to H^6 at lowest field.[12,15] The mass spectrum shows a molecular peak for L at *m*/*z* 418. Compound L is indefinitely stable in the solid state, but is somewhat air-sensitive in solution. Yellow solutions of L become blue after several days' exposure to air, probably as a result of the oxidation of the ferrocenyl group.



Scheme 1 (*i*) EtOH, NaOH, room temperature, 30 min; (*ii*) EtOH, NaOH, room temperature, 24 h, excess 2-acetylpyridine; (*iii*) EtOH, *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide, [NH$_4$][O$_2$CMe], 2 h, 80 °C; (*iv*) EtOH, [NH$_4$][O$_2$CMe], 2 h, 80 °C

Compounds **I**, **II** and L are all redox active and exhibit reversible processes in their cyclic voltammograms (MeCN for **I** and **II** and 1 : 1 w/w MeCN–CH$_2$Cl$_2$ for L; potentials quoted *vs.* internal ferrocene–ferrocenium reference; [NBu$_4$][BF$_4$] as supporting electrolyte) at +0.12, +0.08 and +0.12 V respectively, with ΔE_p values close to that obtained for ferrocene, and an anodic–cathodic intensity ratio equal to unity. Table 3 summarises the electrochemical data for these compounds. The oxidation processes correspond to the formation of the appropriate ferrocenium salts. For compounds **I** and **II** an irreversible cathodic wave was also found at about −2 V, but no such process was detected for L within the solvent window. When compared with ferrocene the oxidation wave of L is anodically shifted by 120 mV. Such an anodic shifting has also been observed in the electrochemical behaviour of the related ferrocene-containing ligand 4'-(4-ferrocenylphenyl)-2,2' : 6',2"-terpyridine and was attributed to the conjugation of the ferrocenyl unit to the electron deficient terpyridine group.[5] The conjugation of the ferrocenyl and 2,2' : 6',2"-terpyridine fragments through a 1,4-phenylene bridge increases the ferrocenyl oxidation potential by 60 mV whereas in L the direct linking of the groups results in a greater anodic shift of 120 mV.

In order further to understand the interactions between the 2,2' : 6',2"-terpyridine and the ferrocenyl group, we have undertaken a single crystal structural determination of L.

Table 3 Electrochemical data

Compound	M^{II}–M^{III}	*	Reductions
I		0.12	−1.94
II		0.08	−2.13
L		0.12	
$[FeL_2][PF_6]_2$	0.81	0.20	−1.69, −1.83
$[CoL_2][PF_6]_2$	−0.18	0.30	−1.14, −1.24
$[RuL_2][PF_6]_2$	0.90	0.22	−1.73, −1.97
$[RuL(terpy)][PF_6]_2$	0.87	0.18	−1.73, −1.99

* Ferrocene–ferrocenium for ferrocenyl moieties.

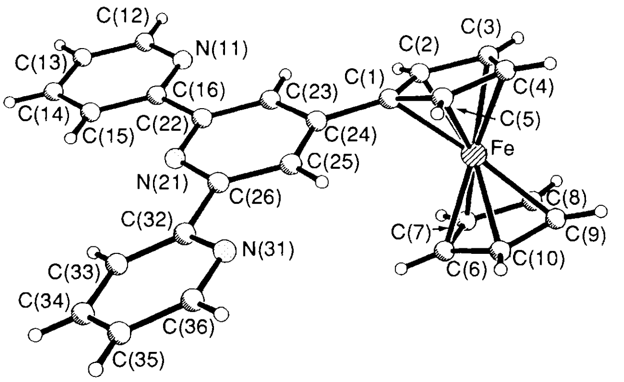


Fig. 1 Crystal and molecular structure of L showing the numbering scheme adopted

A view of the molecule is presented in Fig. 1, and confirms the molecular structure with the ferrocenyl group directly linked to the 4′ position of the 2,2′:6′,2″-terpyridine. Final atomic coordinates for non-hydrogen atoms and selected bond lengths and angles are listed in Tables 1 and 2 respectively. The 2,2′:6′,2″-terpyridine group adopts the expected *trans–trans* conformation about the interannular C–C bonds, as found in all other structurally characterised 2,2′:6′,2″-terpyridines.[12,15,16] The 2,2′:6′,2″-terpyridine group is not completely planar, and exhibits torsion angles between the N(11)–C(16) and N(21)–C(26) planes, and between the N(21)–C(26) and N(31)–C(36) planes of 1.1 and 13.5° respectively. The directly bonded cyclopentadienyl ring of the ferrocenyl group is not coplanar with the central ring of the 2,2′:6′,2″-terpyridine, but is slightly twisted with a torsion angle between N(21)–C(26) and C(1)–C(5) of 19.0°. This degree of non-planarity is within the range expected for crystal packing effects, and represents no significant loss of conjugation between the two rings.

We have also investigated the co-ordination behaviour of this novel ligand, which is expected to show behaviour similar to that of 2,2′:6′,2″-terpyridine. The reaction of L with iron(II) chloride in a chloroform–methanol solution gave a dark coloured solution, from which the complex $[FeL_2][PF_6]_2$ was precipitated as a violet-blue solid by the addition of $[NH_4][PF_6]$. It is reasonable to assume that this complex contains the substituted analogue of the six-co-ordinate $[Fe(terpy)_2]^{2+}$ cation.[17] The most notable features in the IR spectrum of $[FeL_2][PF_6]_2$ are a strong band at 842 cm^{-1} (P–F stretching vibration of hexafluorophosphate) and typical ferrocene and pyridine absorptions. The complex is diamagnetic {as is $[Fe(terpy)_2][PF_6]_2$[17] but not some other complexes with substituted 2,2′:6′,2″-terpyridine ligands} and exhibits a very slightly broadened, but unshifted ^1H NMR spectrum. The ^1H NMR spectrum of a CD_3CN solution of the complex exhibits three resonances for the ferrocenyl moiety; the unsubstituted cyclopentadienyl ring is observed as a 10 H singlet at δ 4.39 and the substituted cyclopentadienyl ring protons as two broadened 4 H apparent singlets at δ 4.84 and 5.44. These observations indicate that the two ferrocenyl substituents are equivalent on the NMR time-scale. Further confirmation of the symmetrical solution structure comes from the observation of only five resonances for the pyridine rings. The chemical shifts are typical of diamagnetic $[Fe(X\text{-}terpy)_2]^{2+}$ (X = substituent) complexes.[18] The FAB mass spectrum of $[FeL_2][PF_6]_2$ exhibits peaks at *m/z* 1036 and 890 corresponding to $\{[FeL_2][PF_6]\}$ and $[FeL_2]$ fragments respectively.

The corresponding cobalt(II) complex may be prepared in a similar manner to the iron(II) complex by the reaction of L with $Co(O_2CMe)_2{\cdot}4H_2O$ in methanol–chloroform solution. After the addition of $[NH_4][PF_6]$, the complex $[CoL_2][PF_6]_2$ was obtained as a deep red solid. The analytical and spectroscopic data are in good agreement with the proposed structure. The IR spectrum is extremely similar to that of the iron complex with a strong band at 840 cm^{-1}. The cobalt complex exhibits peaks in its FAB mass spectrum corresponding to the fragments $\{[CoL_2][PF_6]_2\}$, $\{[CoL_2][PF_6]\}$ and $[CoL_2]$ at *m/z* 1183, 1039 and 893 respectively. The complex is paramagnetic, and the ^1H NMR spectrum of a CD_3CN solution of $[CoL_2][PF_6]_2$ is characteristically shifted. All of the resonances are broadened and shifted downfield with respect to the diamagnetic iron(II) complex. The ferrocenyl protons are readily assigned as a 10 H singlet at δ 7.19 (C_5H_5) and two 4 H signals at δ 7.9 and 8.5 (C_5H_4). The observation of a single C_5H_5 resonance is strongly indicative of the expected symmetrical pseudo-octahedral structure on the NMR time-scale. The remaining 2,2′:6′,2″-terpyridine protons are observed as five broadened and shifted resonances, showing no resolved coupling, at δ 11.9, 32.2, 52.1, 58.3 and 96.3. This is also in accord with a symmetrical solution structure. Although we have had some success in assigning the spectra of paramagnetic cobalt(II) complexes of 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridines,[19] similar approaches to those of paramagnetic $[Co(X\text{-}terpy)_2]^{2+}$ have been unsuccessful.[20] This is almost certainly due to major changes in the magnetic behaviour of the complexes with even minor changes of ligand structure; this is in accord with the observation that $[Co(terpy)_2]^{2+}$ salts are spin-crossover species which exhibit high, low or intermediate spin states depending upon the anion.[17]

The iron(II) complex $[FeL_2][PF_6]_2$ shows two reversible oxidation processes on sweeping at anodic potentials, corresponding to the sequential oxidation of the ferrocenyl moiety and the iron(II)–iron(III) process associated with the $\{Fe(terpy)_2\}$ core at +0.20 and +0.81 V respectively. As expected, the intensity of the first wave is twice that of the second, as well as twice the intensity of the two consecutive reduction waves attributed to the formal reduction of the $\{Fe(terpy)_2\}$ core at −1.69 and −1.83 V. The shift of the central iron(II)–iron(III) process to more positive potential than that observed for $[Fe(terpy)_2]^{2+}$ (0.74 V)[18] is as expected on the basis of the charge build-up after the generation of the two positively charged ligands by the ferrocene–ferrocenium oxidation process. Similar effects are observed in iron complexes of other positively charged 2,2′:6′,2″-terpyridine ligands.[18] It is perhaps surprising that the two ferrocenyl substituents are oxidised at the same potential, and this suggests that there is little electronic interaction between the two substituents in the metal complexes. The reductive processes are undoubtedly ligand-based.[17] The cobalt(II) complex $[CoL_2][PF_6]_2$ shows similar behaviour, but with the one-electron cobalt(II)–cobalt(III) process at −0.18 V and the two-electron ferrocene–ferrocenium process at +0.30 V; 2,2′:6′,2″-terpyridine ligand-centred reduction waves are observed at −1.14 and −1.24 V. The cobalt(II)–cobalt(III) process compares favourably with those observed for $[Co(terpy)_2]^{2+}$ salts (−0.09 V).[15,17] The shift to more negative potential with L is in accord with the electron-releasing character of the ferrocenyl group (σ^+, −0.65).[21]

We have also prepared ruthenium(II) complexes of L. The reaction of ruthenium trichloride with L in boiling ethane-1,2-

diol gives a dark coloured solution, from which a solid is precipitated with $[NH_4][PF_6]$. Column chromatography (SiO_2, 14:2:1 MeCN, saturated aqueous KNO_3, water) allowed a red band to be isolated, and precipitation with $[NH_4][PF_6]$ gives the homoleptic complex $[RuL_2][PF_6]_2$. The FAB mass spectrum of this complex exhibits ions at *m/z* 1226, 1082 and 936 which correspond to the fragments $\{[RuL_2][PF_6]_2\}$, $\{[RuL_2][PF_6]\}$ and $[RuL_2]$, respectively. The IR spectrum is very similar to that found for the iron and cobalt complexes and is in agreement with the proposed formulation. The ^1H NMR spectrum of a CD_3CN solution of the complex shows a 10 H singlet at δ 4.34 for the C_5H_5 rings and two apparent 4 H triplets δ 4.78 and 5.35 for the AA'MM' system of the C_5H_4 rings of the ferrocenyl substituents. The remaining resonances of the 2,2′:6′,2″-terpyridine are similar to those observed for other $[Ru(X\text{-terpy})]_2]^{2+}$ complexes.[12]

This complex shows similar electrochemical behaviour to the iron complex, with three one-electron processes involving the $\{Ru(terpy)_2\}$ core at -1.97, -1.73 and $+0.90$ V and a single two electron process involving the ferrocenyl group at $+0.22$ V. It is worthy of note that the ruthenium(II)–ruthenium(III) process is little shifted with respect to $[Ru(terpy)_2]^{2+}$ (0.92 V[12]) salts even after oxidation of the two ferrocenyl substituents. This reflects the conversion of the electron-releasing ferrocenyl substituent[21] to the essentially innocent cationic form. Using the correlation methods that we have previously established,[12,22] we can now define a σ^+ parameter for the ferrocenium substituent of -0.18.

For the homoleptic cobalt(II), iron(II) and ruthenium(II) complexes the peak assigned to the oxidation of the ferrocenyl moiety shows in all cases a peak-to-peak separation close to that found for the ferrocene reference, a further indication that there is no electronic coupling of the two ferrocenyl groups across the $\{M(terpy)_2\}$ core.

Finally, we prepared a heteroleptic ruthenium(II) complex. The reaction of the ruthenium(III) complex $[Ru(terpy)Cl_3]$ with stoichiometric amounts of L in methanol in the presence of *N*-ethylmorpholine as a reducing agent allowed us to obtain, after chromatographic work-up, the mixed ligand ruthenium(II) complex $[RuL(terpy)][PF_6]_2$. Small amounts of the homoleptic complexes $[Ru(terpy)_2][PF_6]_2$ and $[RuL_2][PF_6]_2$ were also isolated by chromatography. The IR spectrum and analytical data are in full agreement with the proposed formulation. The FAB mass spectrum shows peaks centred at *m/z* 1043 $\{[RuL(terpy)][PF_6]_2\}$, 897 $\{[RuL(terpy)][PF_6]\}$ and 752 $\{RuL(terpy)\}$ each exhibiting the expected isotopomeric distribution. The ^1H NMR spectrum of a CD_3CN solution of the complex shows the three characteristic resonances for the ferrocenyl group (5 H, δ 4.34; 2 H, δ 4.78; 2 H, δ 5.34) essentially unshifted from the homoleptic species $[RuL_2]^{2+}$ (δ 4.34, 4.78 and 5.35) and a total of eight groups of signals in the aromatic region corresponding to the overlap of the L and terpy ligands. We have previously commented upon the transferability of chemical shift data from $[Ru(X\text{-terpy})_2]^{2+}$ and $[Ru(Y\text{-terpy})_2]^{2+}$ complexes to assign the spectra of $[Ru(X\text{-terpy})(Y\text{-terpy})]^{2+}$ species,[12,22] and the full assignment of the spectrum has been made by comparison with the spectra of the homoleptic $[RuL_2][PF_6]_2$ and $[Ru(terpy)_2][PF_6]_2$ complexes. All of the resonances of L are shifted to low field compared to those of the terpy ligand, in accord with the electron-withdrawing character of the ferrocenyl group in L.

The heteroleptic complex $[RuL(terpy)][PF_6]_2$ is redox active and exhibits two reduction process at -1.73 and -1.99 V assigned to the reduction of the bis(terpyridine) metal core, and two oxidation peaks at $+0.18$ and $+0.87$ V related to the ferrocene–ferrocenium and the ruthenium(II)–ruthenium(III) processes respectively. However, although the former is fully reversible if the oxidation sweep only extends to $+0.6$ V, it is not reversible after scanning through the ruthenium-based process. These electrochemical results are consistent with those previously reported for complexes in which a ferrocene was attached more remotely to a terpy unit.[5]

We are currently using the basic information we have collected regarding this ligand in an investigation of the coordination behaviour of helicating ferrocenyl-derivatised 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridines and 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2‴‴-sexipyridines.

Acknowledgements

We should like to thank the SERC for a studentship (to A. M. W. C. T.) and for a grant enabling the purchase of the Rigaku diffractometer. We should also like to thank the Cambridge Crystallographic Data Centre (A. J. E.), the Royal Society of Great Britain (E. C. C.) and the Isaac Newton Trust (E. C. C.) for support. R. M.-M. thanks the Comisíon Interministerial de Ciencia y Technologia (PB91-0807-CO2) and also the Ministerio de Educación y Ciencia for support.

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Received 6th October 1993; *Paper* 3/05989H