Metallosupramolecular Complexes containing Ferrocenyl Groups as Redox Spectators; Synthesis and Co-ordination Behaviour of the Helicand 4′,4⁗-Bis(ferrocenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine

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The compound 4′,4⁗-bis(ferrocenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (L) has been prepared in two steps from ferrocenecarbaldehyde and 2,6-diacetylpyridine and its co-ordination behaviour investigated. Reaction with cobalt(II) and iron(II) salts gives the seven-co-ordinate complexes $[ML(H_2O)_2][PF_6]_2$ (M = Co or Fe). The presence of ferrocenyl groups in the ligand appears not to present a steric barrier to the formation of helicates, and the double-helical complexes $[Ni_2L_2(H_2O)_2][PF_6]_4$ and $[Cu_2L_2][PF_6]_3$ can be obtained by reaction with nickel(II) and copper(II) salts respectively. The compound L reacts with $[RuCl_3L']$ (L′ = 2,2′:6′,2″-terpyridine or its 4′-dimethylamino, -methylsulfonyl or -ferrocenyl derivatives) to give the heteroleptic ruthenium(II) complexes $[RuL(L')][PF_6]_2$. In these complexes L is acting as a tridentate hypodentate ligand leaving a non-co-ordinated didentate 2,2′-bipyridyl moiety. The latter may act as a didentate domain for an additional ruthenium centre, and the tetranuclear complexes $[L'RuLRuCl(L')][PF_6]_3$ with two ruthenium(II) centres in two different, N_6 and N_5Cl, donor environments have been prepared.

There is a considerable interest in the utilisation of transition-metal ions to control the assembly of organic molecules into defined supramolecular arrays.[1] We have developed a metallosupramolecular methodology for the specific and controlled formation of complexes in which the consequences of co-ordination are precisely determined by the acceptor properties of the metal(s) and the donor properties of the ligand(s).[2,3] This approach involves the matching of donor sets of ligands to the acceptor properties of metal ions, and a key feature is the partitioning of multidentate ligands into discrete metal-binding domains. As a consequence we have developed routes for the preparation of complexes containing hypodentate ligands which do not exhibit their maximum denticity to a single metal centre.[4] We and others have been particularly interested in the design of metallosupramolecular systems containing linked photo- and redox-active centres, and particular emphasis has been placed upon the preparation of multinuclear systems which exhibit intermetallic energy- or electron-transfer processes.[5] In general, the redox-active centres in these metallosupramolecular systems are associated with metal atoms which can display one or two oxidation or reduction processes. Two or more redox-active metal centres can be linked to give di- or poly-nuclear redox aggregates, although the utility of these systems is often limited by the number of accessible charge states. Usually, the ligand is not redox-active. In order to access additional charge states we have been developing strategies for the synthesis of redox-functionalised ligands for metallosupramolecular chemistry. Although metallocenes have been used as redox-active sites in molecular[6] and supramolecular[3,7–9] systems and oligopyridine complexes are widely used as both redox- and photo-active sites in supramolecular arrays,[1,2,10] very few examples have been reported in which such centres are covalently coupled.[3,7] The development of such covalently coupled systems is of great interest, since electron-transfer processes are usually facilitated if through-bond pathways are available. Ligands incorporating oligopyridine domains have proved to be versatile systems for the development of metallosupramolecular chemistry and have opened new lines in the search for new topological molecular systems.[10] Among these systems 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine displays a particularly rich chemistry. As a part of our study of redox-active metallosupramolecular systems we have developed ligands in which redox-active ferrocenyl substituents, which are known to display reversible, single-electron processes at modest anodic potentials, are covalently attached to a metal-binding oligopyridine domain, and recently described the preparation and behaviour of 4′-ferrocenyl-2,2′:6′,2″-terpyridine.[3] In this paper we describe the preparation and co-ordination behaviour of a helicating ligand containing covalently attached ferrocene groups, 4′,4⁗-bis(ferrocenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (L), from commercially available ferrocenecarbaldehyde. This is the first time that such a redox-active substituent has been attached to a potentially helicating oligopyridine containing more than three pyridyl groups.

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 disks, ^1H NMR spectra on a Bruker WM-250 spectrometer, fast atom bombardment (FAB) mass spectra on a Kratos MS-50 spectrometer and electron paramagnetic resonance (EPR) spectra on a Varian E-109 spectrometer as frozen acetonitrile glasses at 90 K. Cyclic voltammetry experiments 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, whilst differential pulse voltammetry was performed on an Autolab PGSTAT20 instrument with a pulse amplitude of 25 mV, step rate of 10 mV s^{-1} and a drop time of 0.5 s. For cyclic voltammetry a conventional three-electrode configuration was used with platinum-bead working and auxiliary electrodes and $Ag-Ag^+$ electrode as reference. The solvent was purified acetonitrile or dichloromethane and the supporting electrolyte was 0.1 mol dm^{-3} $[NBu_4][BF_4]$ recrystallised twice from ethanol–water. Ferrocene was added at the end of each experiment as an internal standard.

N-[1-Oxo-2-(2-pyridyl)ethyl]pyridinium iodide,[11] 4′-ferrocenyl-2,2′:6′,2″-terpyridine,[3] and $[RuCl_3L']$ [L′ = 2,2′:6′,2″-terpyridine (terpy), 4′-dimethylamino- (dmterpy), 4′-methylsulfonyl- (msterpy) or 4′-ferrocenyl-2,2′:6′,2″-terpyridine (fterpy)][3,12,13] were prepared by literature methods; ferrocenecarbaldehyde and 2,6-diacetylpyridine were used as supplied by Aldrich.

2,6-*Bis*(3-*ferrocenyl*-1-*oxoprop*-2-*enyl*)*pyridine*.—Ferrocenecarbaldehyde (1.074 g, 5 mmol) and 2,6-diacetylpyridine (0.163 g, 1 mmol) were heated to reflux in a mixture of propanol (6 cm^3) and diethylamine (1 cm^3) for 3 h. Upon cooling, a brown precipitate was obtained, which was filtered off, washed with propanol and dried *in vacuo* to give the bis(enone) (0.471 mg, 85%) (Found: C, 66.9; H, 4.5; N, 3.0. Calc. for $C_{31}H_{25}Fe_2NO_2$: C, 67.1; H, 4.5; N, 2.5%). IR (KBr): 1664s, 1600s, 1569s, 1360m, 1317m, 1243m, 1105m, 1025m, 996m, 981m, 823m, 743m, 669m, 501m and 480m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.21 (C_5H_5, 10 H, s), 4.56 (C_5H_4, 4 H, t), 4.70 (C_5H_4, 4 H, t), 7.98 (CH, 2 H, s), 7.99 (CH, 2 H, s), 8.03 (C_5H_3N, 1 H, t) and 8.34 (C_5H_3N, 2 H, d). FAB mass spectrum: *m*/*z* 556.

4′,4⁗-*Bis*(*ferrocenyl*)-2,2′:6′,2″:6″,2‴:6‴,2⁗-*quinquepyridine* (L).—2,6-Bis(3-ferrocenyl-1-oxoprop-2-enyl)pyridine (0.555 g, 1 mmol), *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (0.652 g, 2 mmol) and ammonium acetate (4 g) were heated to reflux in ethanol (30 cm^3) for 6 h. After filtering, the filtrate deposited the orange-brown product upon cooling. This was washed with ethanol, methanol–hexane and water and then recrystallised from dichloromethane–hexane to give L (0.302 g, 40%) (Found: C, 71.6; H, 4.6; N, 9.5. Calc. for $C_{45}H_{33}Fe_2N_5$: C, 71.5; H, 4.4; N, 9.3%). IR (KBr): 1606s, 1582s, 1549s, 1474w, 1406m, 1385m, 1107w, 1022w, 1002w, 822m, 795m, 744w, 660w and 499m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.16 (C_5H_5, 10 H, s), 4.51 (C_5H_4, 4 H, t), 5.06 (C_5H_4, 4 H, t), 7.20 ($H^{5,5''''}$, 2 H, ddd), 7.90 ($H^{4,4''''}$ 2 H, dt), 8.06 ($H^{4''}$, 1 H, t), 8.55 ($H^{3',5'''}$, 2 H, d), 8.67 ($H^{3,3''''}$ and $H^{3'',5''}$, 4 H, d), 8.76 ($H^{6,6''''}$, 2 H, dm) and 8.84 ($H^{5',3'''}$, 2 H, d). FAB mass spectrum: *m*/*z* 756.

$[CoL(H_2O)_2][PF_6]_2$, $[FeL(H_2O)_2][PF_6]_2$, $[Ni_2L_2(H_2O)_2][PF_6]_4$ *and* $[Cu_2L_2][PF_6]_3$.—The appropriate metal acetate or $FeCl_2·4H_2O$ (0.5 mmol) and L (0.5 mmol) were added to methanol (30 cm^3) and the mixture subjected to ultrasound for 5 min and then heated to reflux for 1 h. After cooling, the reaction mixture was filtered and the filtrate treated with aqueous ammonium hexafluorophosphate; the mixture was then reduced to half its original volume and the solid so obtained filtered off, washed with water and dried *in vacuo*.

Complex $[FeL(H_2O)_2][PF_6]_2$: deep blue solid (0.397 g, 70%) (Found: C, 47.5; H, 3.2; N, 5.5. Calc. for $C_{45}H_{37}F_{12}Fe_3N_5O_2P_2$: C, 47.5; H, 3.3; N, 6.2%). IR (KBr): 1611s, 1574s, 1548m, 1486s, 1456m, 1412w, 1386w, 1356w, 1254w, 1168w, 1107w, 1061m, 844s, 559s and 500m cm^{-1}. FAB mass spectrum: *m*/*z* 956 and 812.

Complex $[CoL(H_2O)_2][PF_6]_2$: red solid (0.342 g, 60%) (Found: C, 47.5; H, 3.3; N, 5.6. Calc. for $C_{45}H_{37}CoF_{12}Fe_2N_5O_2P_2$: C, 47.4; H, 3.3; N, 6.1%). IR (KBr): 1610s, 1574m, 1550m, 1454m, 1412m, 1386w, 1355w, 1251w, 1166w, 1107w, 1033w, 1016w, 843s and 559m cm^{-1}. FAB mass spectrum: *m*/*z* 960 and 815.

Complex $[Cu_2L_2][PF_6]_3$: purple solid (0.414 g, 81%) (Found: C, 49.9; H, 3.2; N, 6.6. Calc. for $C_{90}H_{66}Cu_2F_{18}Fe_4N_{10}P_3·3H_2O$: C, 50.8; H, 3.4; N, 6.6%). IR (KBr): 1609s, 1569m, 1474m, 1402m, 1253w, 1107w, 1039m, 843s, 791m, 740w, 559s and 486w cm^{-1}. FAB mass spectrum: *m*/*z* 1928, 1783 and 817.

Complex $[Ni_2L_2(H_2O)_2][PF_6]_4$: blue solid (0.398 g, 75%) (Found: C, 47.4; H, 3.2; N, 5.8. Calc. for $C_{90}H_{70}F_{24}Fe_4N_{10}Ni_2O_2P_4·H_2O$: C, 47.7; H, 3.4; N, 6.2%). IR (KBr): 1610s, 1570m, 1545m, 1477m, 1455m, 1401m, 1252w, 1169w, 1108w, 1037w, 841s, 559m and 484w cm^{-1}. FAB mass spectrum: *m*/*z* 813.

$[RuL(L')][PF_6]_2$ (L′ = terpy, dmterpy, msterpy *or* fterpy).—The appropriate $[RuCl_3L']$ complex (0.5 mmol) and L (0.5 mmol) were heated to reflux in methanol–chloroform (1:1 w/w, 40 cm^3) in the presence of *N*-ethylmorpholine (0.2 cm^3). After 5 h at reflux the reaction mixture was allowed to cool and evaporated to dryness *in vacuo*. The crude red solid so obtained was then dissolved in acetonitrile and chromatographed over silica using MeCN–aqueous saturated KNO_3 solution–water (14:2:1) as the mobile phase. In all cases the desired compound was eluted as a red band. This fraction was treated with distilled water and an excess of $[NH_4][PF_6]$. The red precipitate obtained was filtered off, washed with water and dried *in vacuo*.

$[RuL(terpy)][PF_6]_2$: yield 0.130 g (10%) (Found: C, 51.3; H, 3.15; N, 7.9. Calc. for $C_{60}H_{44}F_{12}Fe_2N_8P_2Ru·H_2O$: C, 51.55; H, 3.3; N, 8.0%). IR (KBr): 1608s, 1584m, 1564m, 1546m, 1494w, 1448m, 1408m, 1385s, 1246w, 1106w, 1028w, 841s, 766m and 558s cm^{-1}. FAB mass spectrum: *m*/*z* 1234 and 1089.

$[RuL(dmterpy)][PF_6]_2$: yield 0.106 g (15%) (Found: C, 50.3; H, 3.6; N, 8.4. Calc. for $C_{62}H_{49}F_{12}Fe_2N_9P_2Ru·3H_2O$: C, 50.4; H, 3.7; N, 8.5%). IR (KBr): 1637m, 1618s, 1545m, 1522w, 1427m, 1408w, 1385w, 1162w, 1106m, 1038w, 753w, 620m, 558s and 487m cm^{-1}. FAB mass spectrum: *m*/*z* 1278 and 1133.

$[RuL(msterpy)][PF_6]_2$: yield 0.145 g (20%) (Found: C, 49.2; H, 3.1; N, 7.5. Calc. for $C_{61}H_{46}F_{12}Fe_2N_8O_2P_2RuS·H_2O$: C, 49.6; H, 3.3; N, 7.6%). IR (KBr): 1638m, 1615s, 1585m, 1477w, 1411m, 1385w, 1322m, 1152s, 1107m, 1027m, 964w, 844s, 787m, 755m, 619m, 558s and 482m cm^{-1}. FAB mass spectrum: *m*/*z* 1458, 1313 and 1168.

$[RuL(fterpy)][PF_6]_2$: yield 0.156 g (20%) (Found: C, 51.4; H, 3.2; N, 6.5. Calc. for $C_{70}H_{52}F_{12}Fe_3N_8P_2Ru·3H_2O$: C, 52.0; H, 3.6; N, 6.9%). IR (KBr): 1609s, 1567m, 1547w, 1494m, 1432w, 1408m, 1385m, 1249w, 1106m, 1060w, 843s, 787m, 753m, 558s and 486m cm^{-1}. FAB mass spectrum: *m*/*z* 1563, 1419 and 1274.

$[L'RuLRuCl(L')][PF_6]_3$ (L′ = terpy, dmterpy, msterpy *or* fterpy).—*Method* (*a*). A suspension of $[RuCl_3L']$ (0.3 mmol) and L (0.5 mmol) in $MeOH-CHCl_3$ (1:1 w/w, 40 cm^3) and *N*-ethylmorpholine (0.2 cm^3) was heated to reflux for 5 h, after which period an additional portion of $[RuCl_3L']$ (0.5 mmol) was added and the heating continued for 3 d. The solution was then evaporated to dryness *in vacuo*, and the crude solid product was dissolved in MeCN and chromatographed on silica using MeCN–aqueous saturated KNO_3 solution–water (14:2:1) as the mobile phase. The purple band which was eluted after the first red band of $[RuL(L')]^{2+}$ was collected and treated with distilled water and an excess of $[NH_4][PF_6]$. The purple precipitate so obtained was filtered off, washed with water and dried *in vacuo*.

Method (*b*). A mixture of $[RuL(L')][PF_6]_2$ (0.1 mmol), $[RuCl_3L']$ and *N*-ethylmorpholine (0.2 cm^3) in methanol (25 cm^3) was heated to reflux for 3 d. The dark red solution was then evaporated to dryness *in vacuo* and the purple compound purified by column chromatography as described above.

$[(terpy)RuLRuCl(terpy)][PF_6]_3$: yield 20–25% (Found: C, 45.9; H, 2.95; N, 7.9. Calc. for $C_{75}H_{55}ClF_{18}Fe_2N_{11}P_3Ru_2·2H_2O$: C, 46.7; H, 3.1; N, 8.0%). IR (KBr): 1608s, 1558w, 1494w, 1448m, 1410w, 1386m, 1285w, 1249w, 1164w, 1107w, 1002w, 840s, 771s, 559s and 491m cm^{-1}. FAB mass spectrum: *m*/*z* 1748, 1607 and 1460.

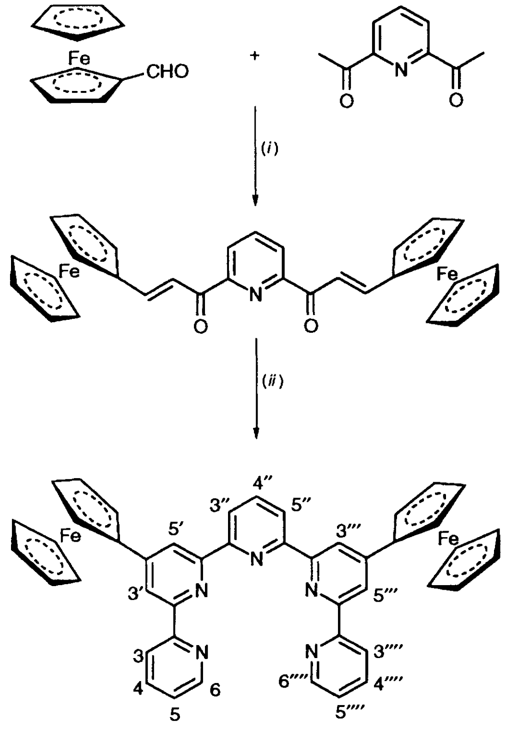
[(dmterpy)RuLRuCl(dmterpy)][PF$_6$]$_3$: yield 15–20% (Found: C, 46.5; H, 3.5; N, 8.8. Calc. for $C_{79}H_{65}ClF_{18}Fe_2N_{13}P_3Ru_2 \cdot 2H_2O$: C, 47.0; H, 3.4; N, 9.0%). IR (KBr): 1615s, 1524m, 1495w, 1428m, 1385s, 1255w, 1231w, 1164w, 1107w, 1062w, 844s, 784m, 754w, 559s and 495w cm^{-1}. FAB mass spectrum: *m*/*z* 1836 and 1690.

[(msterpy)RuLRuCl(msterpy)][PF$_6$]$_3$: yield 20–25% (Found: C, 41.95; H, 3.0; N, 6.9. Calc. for $C_{77}H_{59}ClF_{18}Fe_2N_{11}O_4P_3Ru_2S_2 \cdot 4H_2O$: C, 43.55; H, 3.2; N, 7.3%). IR (KBr): 1610m, 1486w, 1385s, 1320w, 1151m, 1108m, 1019w, 969w, 843s, 788m, 757w, 559s and 495w cm^{-1}. FAB mass spectrum: *m*/*z* 2052, 1908 and 1759.

[(fterpy)RuLRuCl(fterpy)][PF$_6$]$_3$: yield 25–30% (Found: C, 48.45; H, 2.95; N, 6.75. Calc. for $C_{95}H_{71}ClF_{18}Fe_4N_{11}P_3Ru_2 \cdot 3H_2O$: C, 49.2; H, 3.3; N, 6.65%). IR (KBr): 1608s, 1494m, 1430m, 1385s, 1353s, 1262w, 1107m, 1030w, 842s, 787m, 753w, 558s, 487m and 420m cm^{-1}. FAB mass spectrum: *m*/*z* 2262, 2117 and 1973.

Results and Discussion

The new ligand L has been prepared in two steps from 2,6-diacetylpyridine. In the first the bis(enone), 2,6-bis(3-ferrocenyl-1-oxoprop-2-enyl)pyridine, was obtained from the reaction of 2,6-diacetylpyridine and an excess of ferrocenecarbaldehyde in the presence of diethylamine. The IR spectrum of the bis(enone) shows a characteristic single ν(C=O) stretching mode at 1664 cm^{-1}. The absence of absorptions around 1700 cm^{-1} confirms that no significant amounts of the monoenone, 2-acetyl-6-(3-ferrocenyl-1-oxoprop-2-enyl)pyridine, are formed under the experimental conditions. The ^{1}H NMR spectrum exhibits a singlet δ 4.21 corresponding to the unsubstituted cyclopentadienyl ring, two apparent triplets at δ 4.56 and 4.70 assigned to the substituted cyclopentadienyl ring, and an AB multiplet centred at δ 7.99 for the olefinic protons, a triplet at 8.03 (H^4) and a doublet at δ 8.34 (H^{3,5}). The FAB mass spectrum (*m*/*z* = 556) and elemental analysis are also in agreement with the proposed formulation.



L

Scheme 1 (*i*) Propanol, diethylamine, 3 h, reflux; (*ii*) EtOH, *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide, [NH$_4$][O$_2$CMe], 6 h, reflux

In the second step the bis(enone) is treated with *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide in ethanol in the presence of an excess of ammonium acetate (see Scheme 1), giving the desired compound L as an orange solid. The formulation was supported by the observation of a parent ion at *m*/*z* = 756 in the FAB mass spectrum and by elemental analysis. The ^{1}H NMR spectrum of a CDCl$_3$ solution of L is characteristic (Fig. 1) and further confirms the structure. The ferrocenyl rings give rise to a singlet (δ 4.16) and two apparent triplets (δ 4.51 and 5.06); eight resonances are observed for the pyridine protons. The pyridine resonances were fully assigned by a correlation spectroscopy (COSY) experiment. The resonances of the terminal and the central pyridine rings are essentially unshifted with respect to all other quinquepyridines which we have studied;[14] the chemical shifts of the protons on the substituted pyridine rings closely resemble those for the related fterpy[3] whilst those of the ferrocenyl substituents are essentially identical to those of fterpy.

Both of these new compounds are electrochemically active. Cyclic voltammetric studies upon CH$_2$Cl$_2$ solutions reveal a single one-electron reversible iron(II)–iron(III) process at +0.08

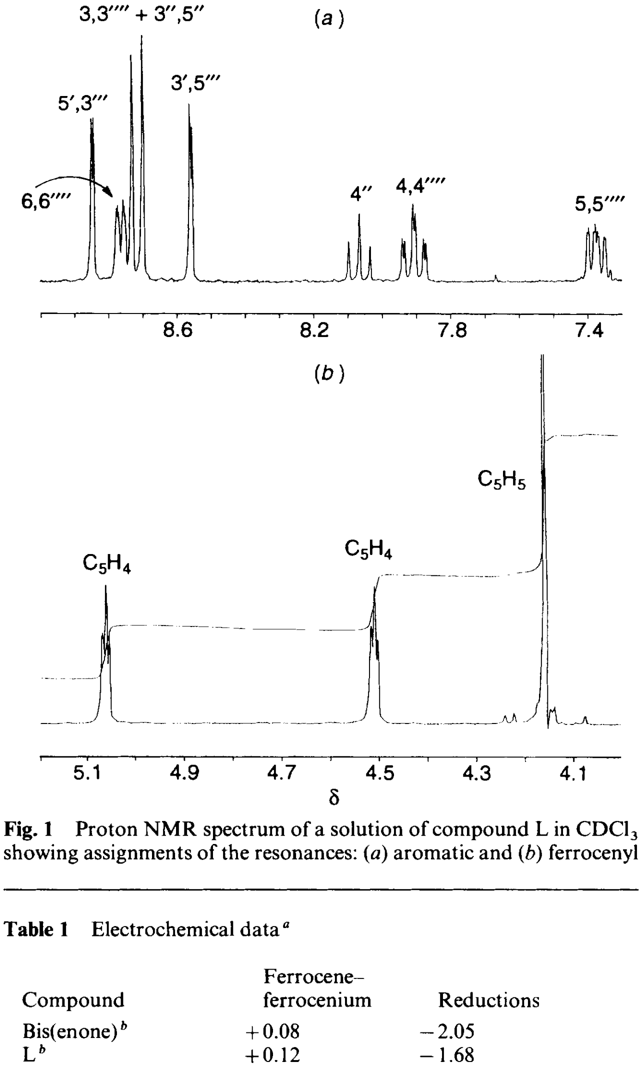


Fig. 1 Proton NMR spectrum of a solution of compound L in CDCl$_3$ showing assignments of the resonances: (*a*) aromatic and (*b*) ferrocenyl

Table 1 Electrochemical data[a]

Compound	Ferrocene–ferrocenium	Reductions
Bis(enone)[b]	+0.08	−2.05
L[b]	+0.12	−1.68
[CoL(MeCN)$_2$]$^{2+}$[c]	+0.21	−1.16, −1.52, −1.76, −2.07, −2.12
[FeL(MeCN)$_2$]$^{2+}$[c]	+0.24	−0.99, −1.49, −1.71
[Cu$_2$L$_2$]$^{3+}$[c,d]	+0.24	−1.26, −1.81, −2.03, −2.19
[Ni$_2$L$_2$(MeCN)$_2$]$^{4+}$[c]	+0.21	−1.13, −1.86, −2.00

[a] 0.1 mol dm^{-3} [NBu$_4$][BF$_4$] as supporting electrolyte. Potentials in V and *vs.* ferrocene. Scan rate 0.1 V s^{-1}. [b] In CH$_2$Cl$_2$ solution. [c] In MeCN solution. [d] Copper redox processes: 0.03 and −0.49 V.

and +0.12 V (*vs.* ferrocene as internal standard) for the bis(enone) and L respectively. In each case a number of reduction waves were observed at cathodic potentials. The data are presented in Table 1. The ferrocenyl moieties in L are connected by an aromatic system which might act as an electron-delocalising framework linking the redox-active centres. However, for both of these compounds, the ΔE_p values found from cyclic voltammetry (which were very close to that found for the internal reference ferrocene using the same electrode configuration) appear to indicate that no strong interaction exists between the two ferrocenyl centres. Differential pulse voltammetry of CH_2Cl_2 solutions of the two compounds were also carried out and similar results were found. In each case a single process was observed with the same half-height width as that found for the ferrocene internal standard. These data all indicate that the organic group linking the ferrocenyl groups does not allow communication between the two centres and so, electrochemically, the two compounds are best described as systems containing two non-interacting monoelectronic redox groups. These data indicate that the comproportionation constant for equilibrium (1) is not far from

$$[Fe^{II}Fe^{II}]^{4+} + [Fe^{III}Fe^{III}]^{6+} \rightleftharpoons 2[Fe^{III}Fe^{II}]^{5+} \quad (1)$$

the characteristic statistical equilibrium constant $K_c = 4$, and therefore that the mixed-valence species $[Fe^{III}Fe^{II}]^+$ are not appreciably stabilised.[15]

The reaction of cobalt(II) acetate tetrahydrate with L in hot methanol resulted in the formation of a red solution, from which ammonium hexafluorophosphate precipitated a red solid. The compound L is only slightly soluble in hot methanol and the reaction time can be minimised by ultrasound treatment of the reaction mixture before heating. The dominant feature in the IR spectrum is the strong band at 843 cm^{-1} due to the PF_6^- anions as well as characteristic ferrocenyl absorptions such as the band at 1107 cm^{-1} attributed to the asymmetric ring-breathing mode.[16] The FAB mass spectrum exhibits ions at *m/z* 960 and 815 corresponding to $CoL(PF_6)$ and CoL fragments respectively, but with no higher-mass peaks due to double-helical species. These results, along with the elemental analysis data, lead us to formulate the complex as the trinuclear species $[CoL(H_2O)_2][PF_6]_2$. The ^1H NMR spectrum of a solution of this complex in CD_3CN is also fully in agreement with the proposed formulation as a trinuclear complex, and exhibits a total of 11 broad and paramagnetically shifted peaks (Fig. 2). We stress here that recrystallisation of cobalt(II) complexes with quinquepyridine and derivatives from methanol or acetonitrile gives compounds with ^1H NMR spectra in CD_3CN solution which are *only* compatible with monocobalt solution species.[14,17] Recrystallisation from nitromethane appears to give different species, which might be double-helical dicobalt complexes.[18] Three of the peaks in the ^1H NMR spectrum of a CD_3CN solution of $[CoL(H_2O)_2][PF_6]_2$, at δ 10, 6 and 5, are clearly assigned to the ferrocenyl groups. The remaining eight resonances are assigned to the quinquepyridine fragment, and indicate that the ligand is symmetrical about the central pyridine ring. This is only compatible with the formation of a monocobalt solution species (see Scheme 2) with the quinquepyridine acting as a pentadentate N_5-donor ligand co-ordinating one cobalt(II) centre with two axial solvent ligands. The paramagnetically shifted resonances of the pyridyl protons in this complex are at near-identical chemical shifts to those observed for the cobalt(II) quinquepyridine complex (Table 2).[14,17]

A very similar behaviour was found when the iron(II) complex of L was prepared by the reaction with $FeCl_2{\cdot}4H_2O$ in methanol. This gave a deep blue solution from which $[FeL(H_2O)_2][PF_6]_2$ was isolated. The IR spectrum very closely resembled that of the cobalt(II) complex discussed above, and the elemental analysis was in agreement with a 1 : 1 iron : ligand stoichiometry. The iron complex exhibited peaks in its FAB mass spectrum corresponding to the fragments $FeL(PF_6)$ and FeL at *m/z* 956 and 812 respectively, but no peaks to higher mass which could be assigned to double-helical species. The ^1H NMR spectrum (see Table 2) is characteristic of a high-spin paramagnetic species with broadened and shifted resonances. As in the case of the cobalt(II) complex, the three least-shifted signals at δ 4, 5 and 6 correspond to the ferrocenyl groups, with the remaining resonances assigned to the quinquepyridine fragment. The number of signals again indicates that, in the solution species, the ligand is symmetric about the central pyridine ring, in agreement with a monomeric formulation. This result is completely in accord with detailed studies that we have performed with iron(II) complexes with a wide variety of other substituted quinquepyridine ligands; the only solution species we observed are mononuclear.[14,19] We propose a distorted pentagonal-bipyramidal structure similar to that of the cobalt(II) complexes.

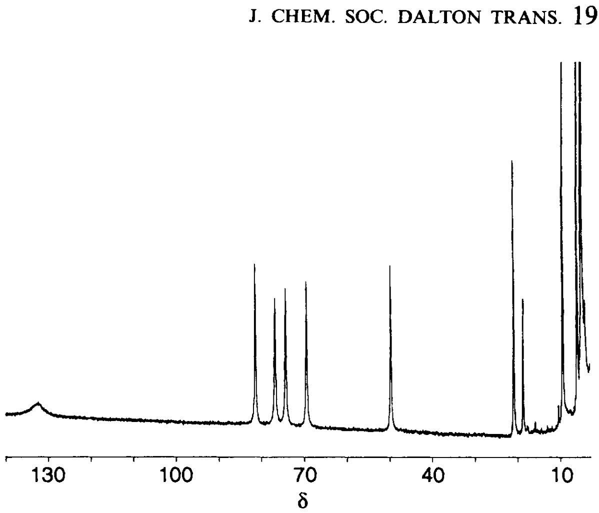
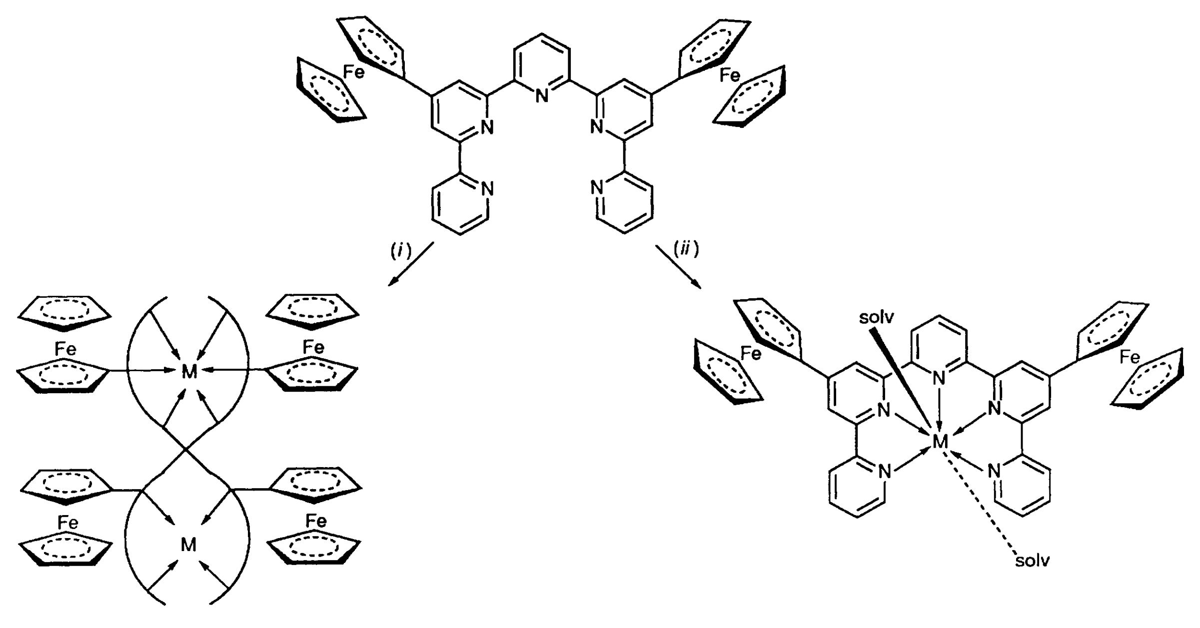


Fig. 2 Paramagnetically shifted ^1H NMR spectrum of a CD_3CN solution of the mononuclear cobalt complex of L

The electrochemical behaviour of $[CoL(H_2O)_2][PF_6]_2$ and $[FeL(H_2O)_2][PF_6]_2$ in acetonitrile solution has been investigated by cyclic voltammetry and differential pulse voltammetry (see Table 1). Both of the complexes exhibit a single, fully reversible iron(II)–iron(III) process upon sweeping at anodic potentials, corresponding to oxidation of the ferrocenyl moieties. This is observed at +0.21 and +0.24 V for the cobalt(II) and iron(II) complexes respectively. However, in each case, the additional processes involving the central metal core cobalt(II)–cobalt(III) or iron(II)–iron(III) transformations were not detected. This fact has been already commented upon as a consequence of the seven-co-ordinate pentagonal-bipyramidal geometry about the metal in mononuclear cobalt(II) and iron(II) complexes with substituted quinquepyridine ligands.[14,17] Both of the complexes also exhibit several ligand-centred reduction waves.

The ferrocene-functionalised ligand L reacts with $Cu(O_2CMe)_2{\cdot}H_2O$ in hot methanol to give a purple solution. Treatment of this solution with aqueous ammonium hexafluorophosphate results in the precipitation of a purple solid. The FAB mass spectrum of this solid shows high-intensity peaks at *m/z* 1928, 1783 and 817 corresponding to the fragments $Cu_2L_2(PF_6)_2$, $Cu_2L_2(PF_6)$ and CuL respectively. These results, the presence of strong PF_6^- absorption bands in the IR spectrum as well as the elemental analysis data lead us to formulate the solid as the $Cu^{II}Cu^{I}$ mixed-valence double-helical complex $[Cu_2L_2][PF_6]_3$. This is in accord with previous results which indicate that these double-helical mixed-valence species may be obtained with a variety of 4′,4‴-disubstituted quinquepyridine ligands.[14,18,20] In the complex $[Cu_2L_2][PF_6]_3$ the copper(I) centre is in a pseudo-tetrahedral environment created by two didentate bipyridine domains of the double-helical ligand array, and the copper(II) centre is in a six-co-



Scheme 2 (*i*) MeOH, 1 h, reflux; (*ii*) MeOH, 1 h, reflux

Table 2 Proton NMR data (δ) for the cobalt, iron and nickel complexes[a]

	Quinquepyridine (qpy) fragment									Ferrocenyl							
Complex	$H^{6/6''''}$						$H^{4'}$										
$[Co(qpy)X_2]^{2+}$[c]	134	82	76	75	69	51	22	20	19								
$[CoLX_2]^{2+}$	132	82	77	74	70	50		21	19	10	6	5					
	Quinquepyridine fragment									Ferrocenyl							
$[FeLX_2]^{2+}$	*d*	57	54	52	44	33	18	14		6	5	4					
	T										B						
$[Ni(terpy)_2]^{2+}$	135	75	71			44		19	14								
$[Ni_2(qpy)_2X_2]^{2+}$[c]	140	75	68	65	59	44	42	18	14	8	158	59	53	46	44	16	15
$[Ni_2L_2X_2]^{2+}$	*d*	75	67	63	59	45	40		14	8	*d*	59	52	46	45	15	
												7.8, 7.0, 6.1, 5.5, 4.5, 4.0[b]					

[a] Data obtained in CD_3CN solutions. [b] Ferrocenyl resonances. [c] Data from ref. 14. [d] Peak too broad to be observed.

ordinate site created by two tridentate domains (Scheme 2). The ^1H NMR spectrum of a solution of $[Cu_2L_2][PF_6]_3$ in CD_3CN shows very broad paramagnetically shifted peaks for which no assignment could be made. The EPR spectrum in a frozen acetonitrile glass shows a characteristic signal for copper(II), but without well resolved parallel and perpendicular features, and with an average *g* value of 2.18.

The double-helical complex $[Cu_2L_2][PF_6]_3$ is a hexanuclear complex containing two different metals in four different environments [copper(I), four-co-ordinate; copper(II), six-co-ordinate; ferrocene close to copper(I); ferrocene close to copper(II)]. Cyclic voltammetry experiments (MeCN solution, Ag–Ag^+ as reference electrode and ferrocene as internal standard reference, see Table 1) show two reversible oxidation peaks (the first being almost a shoulder of the second) at +0.03 and +0.24 V *vs.* ferrocene and attributed respectively to the oxidation of the copper(I) metal centre and of the pendant ferrocenyl moieties, respectively. Upon sweeping at cathodic potentials several reduction processes were found. The first one, at −0.49 V *vs.* ferrocene, is attributed to the reduction of the copper(II) centre, the remaining being assigned to ligand-based reduction processes. Differential pulse voltammetry gives similar results with three well differentiated peaks observed for the metal-based redox processes, the peak attributed to the oxidation of the ferrocenyl groups being four times more intense than the other two. This indicates that, at this potential, the four ferrocenyl groups are all being oxidised. The half peak widths from the differential pulse voltammetry experiments also indicate that the four ferrocenyl groups are electrochemically equivalent. We find no evidence in these systems for a nuclearity change to a trinuclear tricopper(I) species upon passing through the +0.03 V process, but have not made detailed spectroelectrochemical studies of these processes.[18]

The compound L also reacts with nickel(II) acetate in methanol solution. The addition of aqueous ammonium hexafluorophosphate to the very dark solution obtained yielded a blue solid. The ^1H NMR spectrum, the presence of absorptions corresponding to the PF_6^- groups in the IR spectrum and the microanalysis data all suggest that the nickel complex should be formulated as $[Ni_2L_2(H_2O)_2][PF_6]_4$, although the FAB mass spectrum only shows a peak corresponding to the NiL ion at *m*/*z* 813.

Nickel(II) acetate reacts with quinquepyridine[20,21] and its 4′,4‴-di(methylsulfonyl)[14,18] and -diaryl derivatives[14] (L″) to give double-helical complex cations of the type $[Ni_2L''_2(O_2CMe)]^{3+}$ or $[Ni_2L''_2X_2]^{4+}$ (X = solvent). The ^1H NMR spectrum of a solution of the new nickel(II) complex in acetonitrile shows resonances paramagnetically shifted downfield with all of the coupling information lost through broadening, although the broadening is not as marked as for the analogous copper complexes. Separate and well defined peaks were observed and these data are presented in Table 2. The number of peaks indicates that all of the pyridyl protons in an individual L ligand are non-equivalent, strongly suggesting that two L ligands are forming a double-helical ligand array with each ligand being partitioned into a tri- and a didentate domain (Scheme 2). The spectrum observed is directly comparable to that of the double-helical solution species obtained with quinquepyridine or its derivatives.[14] The protons corresponding to the terpyridine (T) and bipyridine fragments (B) have been assigned by comparing these ^1H NMR spectra with those of other nickel complexes of other quinquepyridine, terpy and 1,3-bis(bipyridinyl)benzene derivatives.[14,22] Additionally a total of six resonances were found for the ferrocenyl fragments. These signals, between δ 4.0 and 7.8, are less broadened than the remaining quinquepyridine protons and are also less shifted. The presence of six signals indicates the presence of two non-equivalent ferrocenyl groups and this is another piece of evidence to support the dinuclear double-helical formulation.

The nickel complex is redox active. Cyclic voltammetry studies of solutions in acetonitrile (Table 1) show a single reversible cathodic process at +0.21 V *vs.* ferrocene which is attributed to the concurrent oxidation of the four ferrocenyl groups. No other cathodic processes were observed up to the edge of the solvent window, indicating that the nickel(III) state is not accessible. A number of reduction waves are observed at negative potentials. Differential pulse voltammetry shows a unique peak in the oxidation process with a half peak width similar to that found for the ferrocene internal standard. Although the ^1H NMR data clearly show the presence of two non-equivalent ferrocenyl groups, from an electrochemical point of view the ΔE_p and half-peak width values indicate that the complex should be described as having four ferrocenyl one-electron reversible non-interacting groups.[15]

Ferrocene is a redox-active moiety but it is also a bulky group that in some instances can introduce steric effects.[23] The formation of the dinuclear double-helical complexes with nickel(II) and copper indicates that these steric effects are not sufficient to prevent helication.

We have further investigated the co-ordination behaviour of L by preparing mixed-ligand complexes utilising non-labile d^6 ruthenium(II) centres. We have previously demonstrated that quinquepyridine ligands can give rise to a variety of mono- or dinuclear helicates upon reaction with ruthenium complexes.[24,25] The new ligand L reacts with $[Ru(terpy)Cl_3]$ in chloroform–methanol (1:1) in the presence of the reducing agent *N*-ethylmorpholine to give a purple-red solution. Thin-layer chromatography of this solution showed one major red compound which can be isolated by column chromatography over silica using MeCN–aqueous saturated KNO_3 solution–water (14:2:1) eluent. By the addition of ammonium hexafluorophosphate to the eluate the compound $[RuL(terpy)][PF_6]_2$ is isolated as a red solid. The reaction involves the reduction of the ruthenium(III) starting material to Ru^{II} and the co-ordination of L to the metal centre. The FAB mass spectrum of $[RuL(terpy)][PF_6]_2$ shows ions at *m/z* 1234 and 1089 corresponding to $RuL(terpy)(PF_6)$ and RuL(terpy) fragments, respectively.

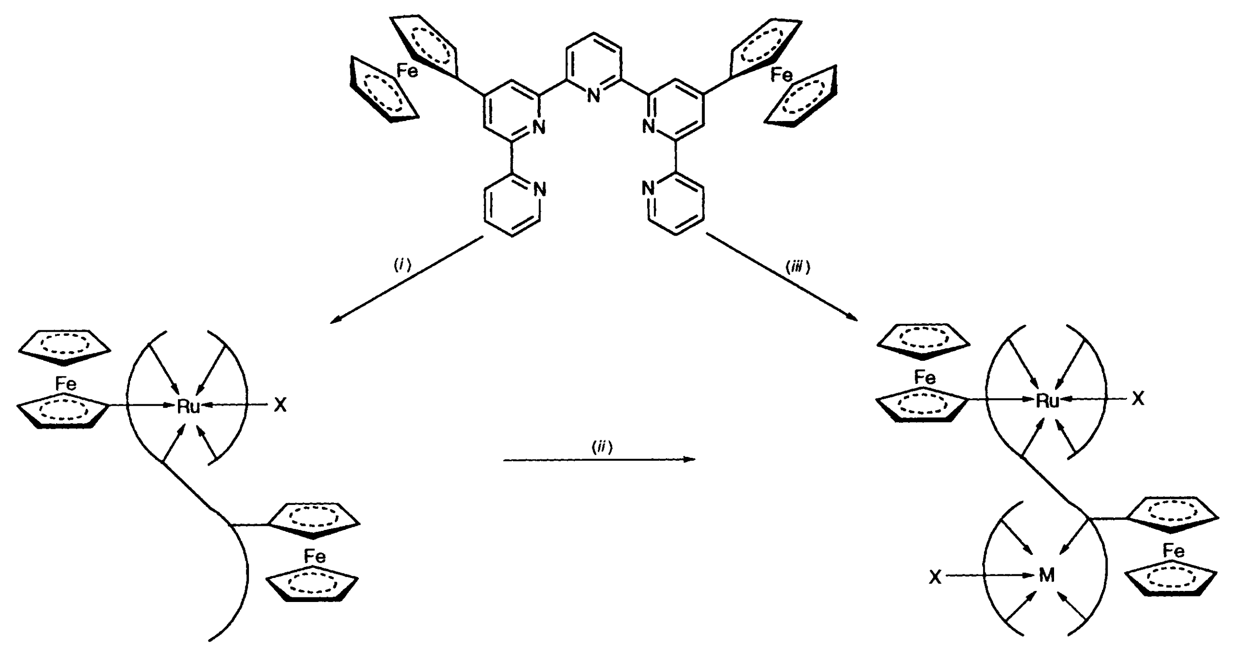
In $[RuL(terpy)][PF_6]_2$ the ruthenium(II) centre is co-ordinated by a terpy ligand and a hypodentate L ligand which is acting as a tridentate donor with two non-co-ordinated pyridine rings. Additional support for the presence of an N_6 co-ordination environment for the ruthenium can be obtained from an electrochemical study.[26] It is well known that ruthenium(II) metal centres in such an environment oxidise at about +1.0 V {*cf.* $[Ru(terpy)_2]^{2+}$ +0.97 V *vs.* ferrocene} whereas, for example, the oxidation process for a N_5Cl environment is found at about +0.5 V, *e.g.* $[Ru(bipy)(terpy)Cl]^{2+}$ (bipy = 2,2′-bipyridine), +0.50 V *vs.* ferrocene. Acetonitrile solutions of $[RuL(terpy)][PF_6]_2$ are electroactive. Two redox processes are clearly observed at +0.22 and +0.97 V *vs.* ferrocene upon sweeping at anodic potentials. These correspond to the iron(II)–iron(III) process of the ferrocenyl group and the ruthenium(II)–ruthenium(III) process respectively, supporting the suggestion of an N_6 environment for the ruthenium(II) atom. Similar results have been obtained with a variety of 4′,4‴-diarylquinquepyridines, as well as with quinquepyridine itself.[24,25] However, the ferrocene couple in $[RuL(terpy)][PF_6]_2$ is not totally reversible if observed after passage through the ruthenium process, although complete reversibility is observed if the sweep is reversed before the ruthenium-based process. Differential pulse voltammetry was also performed and gave comparable results. The value of ΔE_p from the cyclic voltammetry experiments and the half peak width from differential pulse voltammetry obtained for the ferrocenyl oxidation peaks are in agreement with the existence of two non-interacting ferrocenyl moieties. Additionally, two ligand-based reduction processes were found at −1.66 and −1.95 V *vs.* ferrocene.

The use of the non-substitution-labile ruthenium(II) ion has allowed us to isolate the hypodentate complex $[RuL(terpy)][PF_6]_2$. We have previously shown that it is simple to introduce substituents onto the terpy ligands that allow fine control of the redox potentials associated with the ruthenium(II)–ruthenium(III) processes.[3,12,13] We are now in a position to see whether the introduction of such substituents also allows control of the redox processes associated with the ferrocenyl units in the L ligand. Several 4′-substituted terpy derivatives with limiting electron-releasing and -withdrawing properties have been selected.

The reactions of L with $[RuCl_3L']$ (L′ = dmterpy, msterpy or fterpy) in chloroform–methanol (1:1 w/w) with *N*-ethylmorpholine as reducing agent gave purple-red solutions. In each case, using the same separation method as for $[RuL(terpy)][PF_6]_2$, the complexes $[RuL(L')][PF_6]_2$ were obtained as red or purple-red solids. The reaction mixtures have to be chromatographed to remove small amounts of the homoleptic complexes $[RuL'_2]^{2+}$ and a purple compound. The FAB mass spectra show, in all cases, ions corresponding to the fragments $RuL(L')(PF_6)$ and RuL(L′) at *m/z* 1278 and 1133 (dmterpy), 1313 and 1168 (msterpy) and 1419 and 1274 (fterpy). These synthetic routes are summarised in Scheme 3.

In all of these complexes the ruthenium(II) centre is co-ordinated by a terpy ligand and a tridentate hypodentate L ligand with two non-co-ordinated pyridyl rings. However L could bind in a tridentate manner in two different ways; by co-ordinating three terminal pyridyl groups, leaving a non-co-ordinated 2,2′-bipyridyl residue or by co-ordination of the central three pyridyl rings leaving two terminal non-co-ordinating pyridyl groups. The first possibility would lead to an asymmetrical L ligand whereas in the second a higher symmetry is expected.

Proton NMR spectra in acetonitrile of all of the complexes are similar and are characterised by the presence of ferrocenyl resonances in the range δ 3.95–5.81 and pyridyl resonances in the aromatic region between δ 6 and 9. In all cases the aromatic regions of the spectra are extremely complex, and contain numerous overlapping resonances. However, assignment can be made from two-dimensional COSY experiments and we have made detailed studies of related complexes with a wide variety of substituted quinquepyridine ligands as well as with related complexes such as $[Ru(terpy)_2][PF_6]_2$ and $[Ru(terpy)(qtpy)][PF_6]_2$ (qtpy = 2,2′:6′,2″:6″,2‴-quaterpyridine).[4,12,24,27] The general conclusion is that in all of these complexes containing hypodentate quinquepyridine ligands the less-symmetrical bonding mode with a non-co-ordinated 2,2′-bipyridyl residue is adopted. Table 3 shows the assignment of the obtained spectra



Scheme 3 (*i*) [RuCl$_3$L′], MeOH–CHCl$_3$ (1 : 1 w/w), *N*-ethylmorpholine, 5 h, reflux; (*ii*) [RuCl$_3$L′], MeOH, *N*-ethylmorpholine, 3 d, reflux; (*iii*) [RuCl$_3$L′], MeOH–CHCl$_3$ (1 : 1 w/w), *N*-ethylmorpholine, 3 d, reflux

Table 3 Proton NMR data (δ) for the [RuL(L′)][PF$_6$]$_2$ complexes in CD$_3$CN solution

Proton		terpy	dmterpy	msterpy	fterpy
Ferrocenyl	C_5H_5	4.81	4.11, 4.47	4.00, 4.40	3.95, 4.20, 4.37
Ferrocenyl	C_5H_4	5.18, 5.81	4.86, 5.48	4.84, 5.42	4.25, 4.39, 4.58, 4.64
			5.12	4.23, 4.62, 4.73, 5.09	4.69, 4.75, 4.97, 5.04
L	6	6.26	6.41	6.06	6.32
	5	6.99	7.03	6.96	7.06
	4	7.73	7.74	7.77	7.77
	3	8.37	8.42	8.46	8.49
	3′/5′	8.64	8.53	8.71	8.66
	5′/3′	8.78	8.86	8.95	8.98
	3″/5″	8.74	8.83	8.93	8.93
	4″	8.05	8.13	8.23	8.21
	5″/3″	7.05	6.98	7.33	7.35
	3‴	5.73	6.16	6.17	6.17
	5‴	8.05	8.12	8.07	8.03
	3⁗	7.33	7.42	7.43	7.44
	4⁗	7.73	7.74	7.83	7.81
	5⁗	7.47	7.50	7.58	7.54
	6⁗	8.78	8.80	8.90	8.79
L′	6	7.40	7.42	7.70	7.59
	5	7.17	7.17	7.36	7.25
	4	7.65	7.83	7.91	7.86
	3	7.45	8.02	8.07	7.92
	3′	8.35	8.41	8.48	8.66
	4′	8.06			
	5′	7.81	8.12	8.07	7.93
	3″	7.60	7.30	7.60	7.59
	4″	8.06	7.55	7.77	7.67
	5″	7.29	7.07	7.31	7.18
	6″	7.53	7.36	7.56	7.49
	CH_3		3.28	3.65	

for all of these compounds. The non-co-ordinated residues are the triply and quadruply primed rings. The asymmetrical bonding of the L ligand is also supported by the presence of non-equivalent ferrocenyl groups in the complexes [RuL(L′)]-[PF$_6$]$_2$. Thus, for example, [RuL(msterpy)][PF$_6$]$_2$ shows resonances corresponding to the presence of two different signals for the C_5H_5 groups at δ 4.00 and 4.40 and a total of six C_5H_4 resonances. In the free ligand L the α and α′ protons, and the β and β′ protons, of the C_5H_4 rings are equivalent, and the C_5H_4 groups usually appear as two characteristic triplets in the ^{1}H NMR spectrum. However, steric constraints in [RuL-(msterpy)][PF$_6$]$_2$ appear to be such that the four protons in one of the C_5H_4 groups become different. This conclusion is supported by the intensities of these six resonances. Molecular modelling suggests that the ferrocenyl group attached to the non-co-ordinated bipyridyl moiety has a greater restriction of rotation than the ferrocenyl attached to the co-ordinated fragment. We may thus assign the signals at δ 4.84 and 5.42

(integrating two protons each) to the ferrocenyl group attached to the co-ordinated tridentate domain of the L ligand, whereas those at δ 4.23, 4.62, 4.73 and 5.09 (integrating to one proton each) are associated with the ferrocenyl moiety attached to the non-co-ordinated didentate domain. Similarly, [RuL(fterpy)][PF$_6$]$_2$ contains three ferrocenyl groups which are non-equivalent on the ^{1}H NMR time-scale, with C_5H_5 signals appearing at δ 3.95, 4.20 and 4.37. However, a total of eight signals are found for the C_5H_4 protons in this complex. Two of them, each of intensity 2 H, are attributed to the ferrocenyl group attached to the co-ordinated tridentate domain of the L ligand; the remaining resonances correspond to the ferrocenyl moieties attached to the non-co-ordinated didentate domain (four resonances of 1 H intensity) and to the fterpy ligand (two resonances of 2 H intensity). For the complexes with terpy or dmterpy ligands the ferrocenyl groups are involved in one or more fluxional processes. With the dmterpy the signals are broadened, but resonances corresponding to two C_5H_5 and three C_5H_4 environments could be observed. However, for [RuL(terpy)][PF$_6$]$_2$ only very broad signals were found for the ferrocenyl rings. This fluxional process also causes some of the pyridyl signals of the terpyridine ligand to be broadened, but it is not sufficiently pronouned to prevent a complete assignment (Table 3) of the pyridyl protons. The fluxional processes appear to involve rotation about the C–C bond attaching the ferrocenyl group to the pyridine ring, but we have made no further detailed investigations.

The ^{1}H NMR spectra of the compounds [RuL(L′)][PF$_6$]$_2$ are complex but characteristic. A total of 15 resonances are observed corresponding to the pyridine CH protons of the L ligand. This is only consistent with an asymmetrical co-ordination mode of this ligand. Typical coupling constants were observed in all cases [$J(\mathrm{H^5H^6}) \approx 5$, $J(\mathrm{H^3H^4}) \approx J(\mathrm{H^4H^5}) \approx 7$, $J(\mathrm{H^3H^5}) \approx 1$ Hz].

The L′ ligands are also found to be asymmetric in the ^{1}H NMR spectrum. This is in contrast with the symmetrical terpy ligand found in the complex [Ru(terpy)(qtpy)]$^{2+}$ [4] which contains a hypodentate qtpy ligand. We have investigated the series of complexes [RuL′(L″)]$^{2+}$ and have shown that the two terminal rings of the terpy ligand are non-equivalent in each case.[24] In the case of the L ligand the asymmetry is particularly marked. Modelling studies suggest that the asymmetry of the terpy ligand is due to a restricted rotation of the non-co-ordinated 2,2′-bipyridyl fragment in the L ligand which results in a π-stacking interaction between the non-co-ordinated residue and the terpy ligand (Fig. 3). Support for this explanation comes from the π-stacking interactions which are observed in the complex [Ru(bipy)$_2$(terpy)]$^{2+}$ (bipy = 2,2′-bipyridine) which contains a hypodentate terpy ligand, and the fact that the ^{1}H NMR spectrum of this complex shows an upfield shift for the stacking rings.[4]

Cyclic voltammetry and differential pulse voltammetry experiments were carried out upon acetonitrile solutions of the compounds [RuL(L′)][PF$_6$]$_2$. In all cases two oxidation processes were observed along with a number of reduction waves. The presence of an electron-donating group on the terpy ligand in [RuL(dmterpy)][PF$_6$]$_2$ decreases the potential of the ruthenium(II)–ruthenium(III) process by 270 mV compared to that in [RuL(terpy)][PF$_6$]$_2$. This is comparable to the effects noted in [Ru(X-terpy)(Y-terpy)]$^{2+}$ complexes.[12,13,27] When the electron-withdrawing substituent MeO$_2$S is introduced in the terpy ligand the ruthenium(II)–ruthenium(III) oxidation process is less facile, and an increase of 110 mV in the potential with respect to [RuL(terpy)][PF$_6$]$_2$ is found. However, in none of the complexes [RuL(L′)][PF$_6$]$_2$ (L′ = terpy, dmterpy or msterpy) were appreciable variations detected in the potentials associated with the iron(II)–iron(III) processes of the ferrocenyl moieties (Fig. 4).

The use of the functionalised terpyridine ligand fterpy in the complex [RuL(fterpy)][PF$_6$]$_2$ introduces into the system a new ferrocenyl group. The cyclic voltammogram of an acetonitrile solution of this complex exhibits two reversible oxidation processes. The presence of the additional ferrocenyl group does not change the ruthenium(II)–ruthenium(III) potential appreciably (+0.98 V). A process at +0.22 V involves the oxidation of all three ferrocenyl groups at the same potential. The ΔE_p values obtained from cyclic voltammetry and the half peak widths found from differential pulse voltammetry indicate that the system contains three non-interacting ferrocenyl redox-active groups giving a {3 + 1} electron oxidation system in contrast with the {2 + 1} oxidation processes found in [RuL(L′)][PF$_6$]$_2$ (L′ = terpy, dmterpy or msterpy).

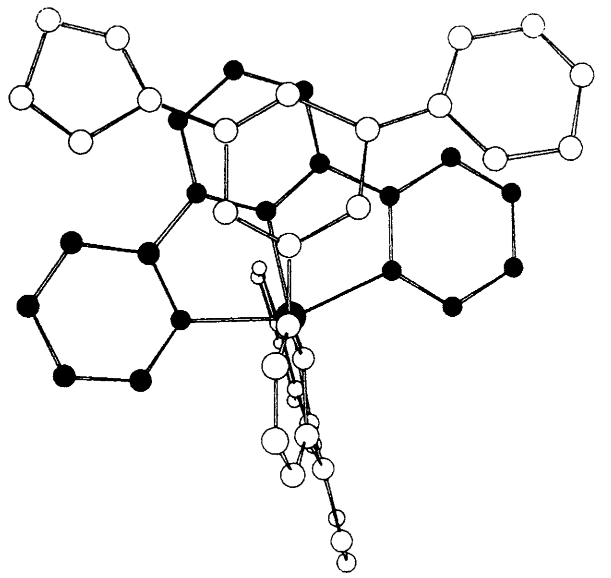


Fig. 3 The stacking process which renders the terminal rings of the L′ ligand non-equivalent in [RuL(L′)][PF$_6$]$_2$ complexes. The terpy ligand is shown in black and L in grey; one ferrocene group has been omitted for clarity, and only one cyclopentadienyl ring of the other is shown

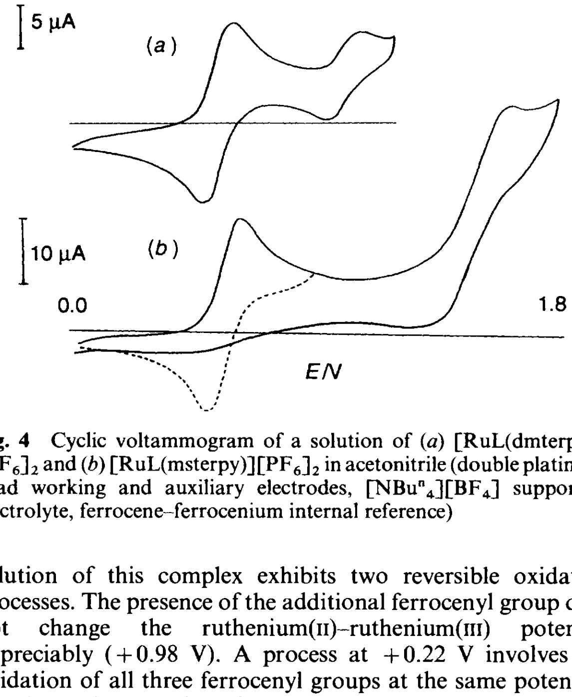


Fig. 4 Cyclic voltammogram of a solution of (a) [RuL(dmterpy)][PF$_6$]$_2$ and (b) [RuL(msterpy)][PF$_6$]$_2$ in acetonitrile (double platinum-bead working and auxiliary electrodes, [NBu$^n_4$][BF$_4$] supporting electrolyte, ferrocene–ferrocenium internal reference)

Each of the compounds [RuL(L′)][PF$_6$]$_2$ contains a hypodentate L ligand acting as a tridentate donor to a single ruthenium centre, leaving a didentate 2,2′-bipyridyl moiety which may co-ordinate to other metal centres. Accordingly, we have attempted to prepare dinuclear diruthenium complexes from these intermediates. The compound [RuL(terpy)][PF$_6$]$_2$ reacts with 1 equivalent of [RuCl$_3$(terpy)] in methanol in the presence of N-ethylmorpholine on heating at reflux for 3 d to give a mixture of three compounds; unreacted [RuL(terpy)][PF$_6$]$_2$, the homoleptic complex [Ru(terpy)$_2$]$^{2+}$ and a purple compound which can be separated from the mixture by column chromatography over silica using MeCN–aqueous saturated

KNO_3 solution–water (14:2:1). The addition of ammonium hexafluorophosphate allows us to isolate the purple complex $[(terpy)RuLRuCl(terpy)][PF_6]_3$. This new tetranuclear complex is strictly analogous to the structurally characterised species $[(terpy)RuL''RuCl(terpy)][PF_6]_3$ (L″ = quinquepyridine),[25] which is obtained from the reaction of quinquepyridine with an excess of $[RuCl_3(terpy)]$. In these complexes one ruthenium(II) centre is in a N_6 donor environment formed by the terpy ligand and a tridentate domain from the L ligand. The other ruthenium(II) centre is in a N_5Cl domain, being co-ordinated to a terpy ligand, a didentate domain from the L ligand and a chloride. The complexes are helical, with a major twisting about the interannular C–C bond between the tri- and di-dentate regions of the quinquepyridine ligands. A schematic representation of the $[(terpy)RuLRuCl(terpy)]^{3+}$ cation is given in Scheme 3. The FAB mass spectrum of $[(terpy)RuLRuCl(terpy)][PF_6]_3$ clearly shows peaks corresponding to $[(terpy)RuLRuCl(terpy)][PF_6]_2$, $[(terpy)RuLRuCl(terpy)]PF_6$ and $[(terpy)RuLRuCl(terpy)]$ at *m*/*z* 1748, 1607 and 1460 respectively. In a similar manner the complexes $[RuL(L')][PF_6]_2$ (L′ = dmterpy, msterpy or fterpy) react with $[RuCl_3L']$, to yield the diruthenium(II) monohelical complexes $[L'RuLRuCl(L')][PF_6]_3$. In each case the FAB mass spectrum exhibits peaks corresponding to $[L'RuLRuCl(L')][PF_6]_2$ and $[L'RuLRuCl(L')]PF_6$ at *m*/*z* 1836 and 1690 (L′ = dmterpy), 1908 and 1759 (msterpy) and 2117 and 1973 (fterpy). The IR spectra and the elemental analyses are in agreement with the proposed formulations. These complexes can also be obtained from the direct reaction of the L ligand with 2 equivalents of the appropriate $[RuCl_3L']$ complex in boiling chloroform–methanol (1 : 1 w/w) solution.

The ^1H NMR spectra in acetonitrile of the dinuclear complexes in CD_3CN solution are all similar with a large number of overlapping signals in the aromatic region. In all cases the number of resonances observed indicates that no pyridine ring is equivalent to any other. This corresponds to a total of 35 (L′) or 37 (terpy) different proton environments in the aromatic region. Most of the signals could be assigned to individual rings by COSY experiments, but a definitive assignment has not yet been achieved, although we have completed the assignments for a series of related complexes with a variety of other substituted quinquepyridine ligands.[24] However, there are sufficient common features in the spectra to indicate that all of the compounds have the same structure. The ^1H NMR spectra of all of the dinuclear complexes $[L'RuLRuCl(L')][PF_6]_3$ show two characteristic doublets at about δ 10.2 and 9.5. The former is assigned to the $H^{6''''}$ quinquepyridine proton which was observed to be close to the chloride atom in the structurally characterised analogous quinquepyridine complex.[25] This downfield shift is characteristic of a proton in such an environment. The ferrocenyl groups show similar sets of signals to those described above for the mononuclear hypodentate complexes.

Cyclic voltammetry and differential pulse voltammetry experiments have been performed to investigate the redox behaviour of acetonitrile solutions of the dinuclear complexes $[L'RuLRuCl(L')][PF_6]_3$ (Table 4). Upon sweeping at anodic potentials three processes were observed for $[(terpy)RuLRuCl(terpy)][PF_6]_3$ at +0.23, +0.64 and +1.02 V. The first wave is twice as intense as the other two, and is, therefore, attributed to oxidation of the ferrocenyl groups. The process at +0.64 V is attributed to the ruthenium(II)–ruthenium(III) couple of the metal in the N_5Cl environment and that at +1.02 V to the corresponding process for the ruthenium in the N_6 environment. As expected, the introduction of a suitable electron-withdrawing or -releasing substituent group in the 4′ position of the terpy ligand allows the redox processes of both ruthenium centres to be modified. Thus, in the complex $[(dmterpy)RuLRuCl(dmterpy)][PF_6]_3$ the use of the electron-releasing dmterpy ligand reduces the ruthenium(II)–ruthenium(III) potential for the metal in the N_5Cl environment by 250 mV from +0.64 to +0.39 V, whilst the use of the msterpy ligand increases the redox potential for this site by 20 mV. Similar and predictable effects are also observed for the ruthenium(II)–ruthenium(III) processes associated with the metal in the N_6 environment (Table 4).

The electrochemical data obtained for complexes $[RuL(L')][PF_6]_2$ and $[L'RuLRuCl(L')][PF_6]_3$ (L′ = terpy, dmterpy, msterpy or fterpy show that the different substituents on the terpy ligand change the oxidation potential of the central ruthenium(II) metal centre. The substituent effect may be quantified by using a Hammett-type relationship. Fig. 5 shows plots of the ruthenium(II) and ferrocenyl redox potentials against the σ^+ parameter for each substituent. The conventional σ^+ parameters have been used for the simple substituents: MeO_2S, 0.63; H, 0.00; NMe_2, −1.70.[27,28] The ruthenium(II)–ruthenium(III) process occurs after the ferrocenyl substituents have been oxidised to ferrocenium groups, and it is not appropriate to use the conventional σ^+ parameter for a ferrocenyl substituent of −0.65.[29] We have previously determined a value of σ^+ of −0.18 for the ferrocenium substituent.[3] From Fig. 5 it is seen that there are three distinct sets of data; these correspond to the processes associated with the ruthenium centre in the N_6 environment, the ruthenium in the N_5Cl environment and the ferrocenyl substituents. For the two different ruthenium environments a positive slope is found with a good correlation between the E° value and the σ^+ value for the X substituent in the L′ ligand. An almost zero slope was obtained for the plot of potential associated with the ferrocenyl oxidation against the substituent σ^+ value. This indicates that the iron(II)–iron(III) process for the ferrocenyl substituents is

Table 4 Electrochemical data * for ruthenium compounds

Complex	Ferrocene–ferrocenium	M^{II}–M^{III} N_5Cl	N_6	Reductions
$[RuL(L')][PF_6]_2$				
L′ = terpy	0.22		0.97	−1.66, −1.95
dmterpy	0.19		0.70	−1.70, −2.07
msterpy	0.22		1.08	−1.40, −1.84
fterpy	0.22		0.98	−1.38, −1.61
$[L'RuLRuCl(L')][PF_6]_3$				
L′ = terpy	0.23	0.64	1.02	−1.47, −1.70, −1.81, −2.11
dmterpy	0.21	0.39	0.77	−1.31, −1.58
msterpy	0.21	0.66	1.09	−1.48, −1.75
fterpy	0.18	0.69	0.98	−1.32, −1.88

* Obtained in MeCN–0.1 mol dm^{-3} $[NBu_4][BF_4]$ as supporting electrolyte. Potentials in V and *vs.* ferrocene. Scan rate 0.1 V s^{-1}.

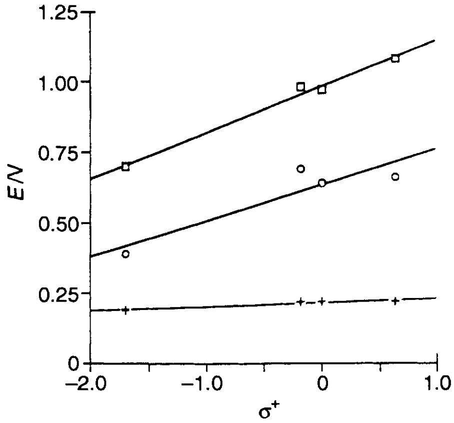


Fig. 5 Correlation of E° data with Hammett σ^+ parameters for ruthenium complexes of L: (□) Ru in N_6 environment; (○) Ru in N_5Cl environment; (+) ferrocenyl

essentially independent of the nature of the L′ ligand, corresponding to no appreciable change being found for the oxidation of the ferrocenyl moieties.

In conclusion, we have prepared a series of helical mono- and di-nuclear complexes with the ferrocenyl-functionalised ligand L. For the kinetically inert complexes $[RuL(L')][PF_6]_2$ and $[L'RuLRuCl(L')][PF_6]_3$ (L′ = terpy, dmterpy, msterpy or fterpy) the use of different substituents on the terpy ligand allows control of the oxidation potential of the ruthenium centres. The introduction of the redox-active derivative fterpy allows us to increase the number of electrons involved in the first oxidation process. All these data show that the use of suitable donor ligands along with the use of non-labile and electroactive metal ions such as ruthenium(II) will prove to be versatile in building different 'electron-reservoir' complexes.

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