Synthesis and Co-ordination Chemistry of 2,2′:4′,2″:6″,2‴-Quaterpyridine, an Asymmetric Bridging Ligand with Inequivalent Bipyridyl Binding Sites

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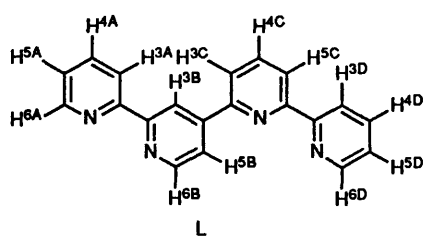
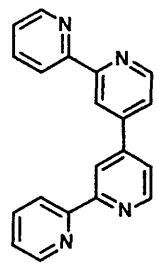
Reductive coupling of the radical anion of 2,2′-bipyridine (bipy) with lithium diisopropylamide as reducing agent resulted in the unexpected product 2,2′:4′,2″:6″,2‴-quaterpyridine (L) *via* a 2,4-coupling; its structure was confirmed unambiguously by ^{1}H NMR spectroscopy. The new asymmetric ligand L has two chelating bipyridyl binding sites which are inequivalent, one being much more sterically hindered than the other. By reaction with 1 equivalent of $[Ru(bipy)_2Cl_2]$ or $[Ru(terpy)Cl_3]$ (terpy = 2,2′:6′,2″-terpyridine) the mononuclear complexes $[Ru(bipy)_2L][PF_6]_2$ **1** and $[Ru(terpy)Cl(L)][PF_6]$ **3** could be prepared, in which the unhindered binding site only is occupied; their cyclic voltammograms show one-electron oxidations at +0.90 and +0.42 V respectively *vs.* the ferrocene–ferrocenium couple, consistent with the presence of $\{Ru(bipy)_3\}^{2+}$ and $\{Ru(terpy)(bipy)Cl\}^+$ groups. With 2 equivalents of the same reagents under more forcing conditions the binuclear analogues $[\{Ru(bipy)_2\}_2(\mu\text{-}L)][PF_6]_4$ **2** and $[\{Ru(terpy)Cl\}_2(\mu\text{-}L)][PF_6]_2$ **4** could be prepared; cyclic voltammetry shows two closely spaced oxidations indicative of a weak electrostatic interaction between the two metal centres. By reaction of **1** (which has a vacant bipyridyl binding site) with $[Ru(terpy)Cl_3]$, the 'mixed' binuclear complex $[\{Ru(bipy)_2\}(\mu\text{-}L)\{Ru(terpy)Cl\}][PF_6]_3$ **5** was prepared, and undergoes two well separated one-electron oxidations ($E_{\frac{1}{2}}$ = +0.89 and +0.40 V *vs.* ferrocene–ferrocenium) consistent with the presence of the different separate metal centres. Whereas **1** and **2** are luminescent at room temperature in MeCN solution (λ_{em} = 594 and 615 nm respectively), luminescence of the $\{Ru(bipy)_3\}^{2+}$ group in **5** is completely quenched by the $\{Ru(terpy)(bipy)Cl\}^+$ group.

The study of ways in which the excited-state energy of the chromophore $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) may be harnessed for use in photocatalytic processes continues to be of intense interest. Many recent developments have occurred in the area of 'supramolecular' photochemistry in which large, complex molecules, consisting of an assembly of covalently bound subunits each of which has a well defined property or function, may be prepared either by 'spontaneous self-assembly' of several components in one step or by a more deliberate stepwise assembly of component parts.[1] I have been interested in the latter 'stepwise' method, preparing derivatives of $[Ru(bipy)_3]^{2+}$ of $[Ru(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) which contain pendant metal-ion binding sites at the periphery, and then attaching these to separate metal centres using a 'complexes as ligands' approach.[2] The results are binuclear (or larger) species in which, in principle, the excited-state energy of the polypyridyl-ruthenium(II) 'antenna' group may be transferred in an intramolecular energy- or electron-transfer process to the adjacent reaction centre.

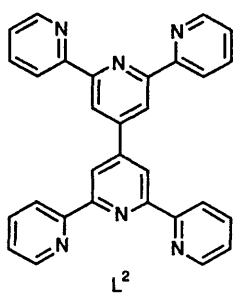
Recently two groups[3,4] have reported syntheses of the 'back-to-back' binucleating ligands L^1 and L^2; this permitted preparation of the binuclear complexes $[\{Ru(bipy)_2\}_2(\mu\text{-}L^1)]^{4+}$ and $[\{Ru(terpy)\}_2(\mu\text{-}L^2)]^{4+}$, which contain two chemically linked polypyridyl-ruthenium(II) chromophores. In an attempt to develop a one-step synthesis of L^1 by reductive coupling of 2,2′-bipyridine, it was found that the major reaction product was the unexpected ligand 2,2′:4′,2″:6″,2‴-quaterpyridine (L), which contains two inequivalent chelating binding sites. In this paper are described the synthesis of L and some of its mono- and bi-nuclear complexes with ruthenium, and it is shown how the differential reactivity of the two binding sites allows selective formation of a binuclear complex, containing two different metal centres, in which a $[Ru(bipy)_3]^{2+}$ core is quenched by the adjacent metal centre.



L



L^1



L^2

Experimental

Proton NMR spectra were recorded on JEOL GX270 or GX400 spectrometers. Electron-impact (EI) mass spectra were measured on a Kratos MS9 instrument, and fast-atom bombardment (FAB) mass spectra on a VG-Autospec at the SERC Mass Spectrometry Service Centre, Swansea, with 3-nitrobenzyl alcohol as matrix. Electronic spectra were recorded in MeCN or CH_2Cl_2 solution on a Perkin Elmer Lambda 2 spectro-

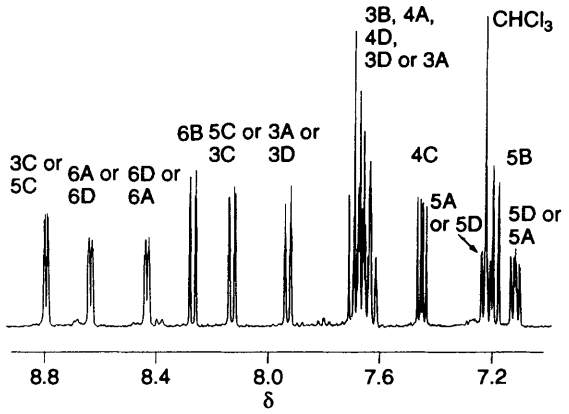


Fig. 1 ^{1}H NMR spectrum of L (400 MHz, $CDCl_3$)

photometer, and emission spectra on a Perkin Elmer LS-50 spectrophotometer using HPLC-grade acetonitrile as solvent. Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat. A standard three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and a saturated calomel electrode (SCE) reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted *vs.* the ferrocene–ferrocenium couple. The solvent was acetonitrile, purified by distillation from CaH_2, containing 0.1 mol dm^{-3} $[NBu_4][PF_6]$. 2,2′-Bipyridine (bipy) and 2,2′:6′,2″-terpyridine (terpy) were obtained from Aldrich and used as received. Lithium diisopropylamide was prepared immediately before use from equivalent amounts of *n*-butyllithium and distilled diisopropylamine in ether. The complexes $[Ru(bipy)_2Cl_2]\cdot 2H_2O$[5] and $[Ru(terpy)Cl_3]$[6] were prepared according to published methods.

Preparations.—*2,2′:4′,2″:6″,2‴-Quaterpyridine* (L). To a solution of 2,2′-bipyridine (5.0 g, 32 mmol) in dry diethyl ether (100 cm^3) under N_2 at −78 °C was added dropwise a solution of lithium diisopropylamide (40 mmol) in ether (50 cm^3). The mixture was allowed to warm up slowly to room temperature, during which time an intense purple colour developed, and stirred for 3 h. The reaction was quenched by addition of water (50 cm^3) with vigorous stirring, and the yellow-brown organic layer separated, dried ($MgSO_4$), and the solvent removed *in vacuo* to give a brown oil. This was redissolved in acetone (50 cm^3) and rearomatised by addition of an acetonic solution of $KMnO_4$ until the purple colour persisted. The MnO_2 was removed by filtration through Celite, the solvent removed *in vacuo* and the residue purified by chromatography on Al_2O_3 (Brockmann activity III), initially with CH_2Cl_2 as eluent to remove unreacted 2,2′-bipyridine, followed by CH_2Cl_2–MeOH (98:2 v/v). The product was isolated as a pale yellow oil which slowly crystallised on prolonged drying. Yield: 1.55 g (30%). EI mass spectrum: *m/z* 310 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (1 H, ddd, *J* 7.3, 4.9, 1.5), 7.23 (1 H, dd, *J* 7.8, 1.0), 7.27 (1 H, ddd, *J* 7.3, 4.9, 1.2), 7.49 (1 H, dd, *J* 7.8, 4.6), 7.64–7.74 (4 H, m), 7.96 (1 H, dt, *J* 8.1, 1.0), 8.15 (1 H, dd, *J* 7.8, 1.5), 8.28 (1 H, dd, *J* 7.8, 1.0), 8.44 (1 H, ddd, *J* 4.7, 1.6, 1.0), 8.64 (1 H, ddd, *J* 4.9, 1.7, 1.0), 8.80 (1 H, dd, *J* 4.6, 1.7 Hz). For assignments see Fig. 1 (Found: C, 77.4; H, 4.5; N, 18.0. Calc. for $C_{20}H_{14}N_4$: C, 77.4; H, 4.5; N, 18.1%).

$[Ru(bipy)_2L][PF_6]_2$ **1**. A mixture of L (0.11 g, 0.36 mmol) and $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.16 g, 0.31 mmol) was heated to reflux in ethanol (30 cm^3) for 4 h to yield a clear orange solution. The complex was precipitated by addition of aqueous KPF_6 and filtered. Chromatography on a preparative-scale alumina TLC plate (Merck, article 5726) with MeCN–toluene (3:2, v/v) as eluent gave pure **1** in 90% yield.

$[\{Ru(bipy)_2\}_2(\mu\text{-}L)][PF_6]_4$ **2**. A mixture of L (0.16 g, 0.52 mmol) and $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.61 g, 1.17 mmol) was heated to reflux in ethylene glycol (30 cm^3) for 1 h to yield a clear orange solution. After precipitation of the complex with aqueous KPF_6 and filtration, the crude mixture was purified by chromatography on alumina (Brockmann activity III). Initial elution with MeCN–toluene (1:1, v/v) removed traces of **1** and $[Ru(bipy)_3][PF_6]_2$; the major orange band was then eluted with neat MeCN to give **2** in 60% yield.

$[Ru(terpy)Cl(L)][PF_6]$ **3**. A mixture of L (0.093 g, 0.3 mmol) and $[Ru(terpy)Cl_3]$ (0.122 g, 0.28 mmol) was heated to 140 °C in ethylene glycol for 1.5 h to yield a purple solution. After precipitation with aqueous KPF_6 and filtration, the crude mixture was purified by chromatography on alumina (Brockmann activity III) with MeCN–toluene (1:1, v/v) as eluent. The desired product eluted first as a purple band ahead of various orange and brown by-products; the yield of pure **3** was 20%.

$[\{Ru(terpy)Cl\}_2(\mu\text{-}L)][PF_6]_2$ **4**. A mixture of L (0.072 g, 0.23 mmol) and $[Ru(terpy)Cl_3]$ (0.207 g, 0.47 mmol) was heated to reflux in ethylene glycol (30 cm^3) for 2 h. After precipitation with aqueous KPF_6 and filtration, the crude mixture was purified by chromatography on alumina (Brockmann activity III). Initial elution with MeCN–toluene (3:2, v/v) removed a small amount of mononuclear complex **3** followed by an orange band; the major red-purple fraction was then eluted with MeCN containing MeOH (2%, v/v) to give **4** in 30% yield.

$[\{Ru(bipy)_2\}(\mu\text{-}L)\{Ru(terpy)Cl\}][PF_6]_3$ **5**. A mixture of complex **1** (0.111 g, 0.11 mmol) and $[Ru(terpy)Cl_3]$ (0.07 g, 0.16 mmol) were heated to reflux in ethylene glycol for 2 h. After precipitation with aqueous KPF_6 and filtration, the crude mixture was purified by chromatography on a preparative-scale silica TLC plate (Merck, article 5717) using a mixture of MeCN (100 cm^3), saturated aqueous KPF_6 (6 cm^3) and water (6 cm^3) as eluent. The major dark brown band was scraped off and the complex **5** recovered from it in 70% yield.

Analytical and mass spectroscopic data for the complexes are given in Table 1.

Results and Discussion

Synthesis of the Ligand.—The new ligand 2,2′:4′,2″:6″,2‴-quaterpyridine (L) was prepared in 30% yield by reaction of 2,2′-bipyridine with $Li[NPr^i_2]$, which effects an asymmetric 2,4-coupling of the bipy radical anions. This was an entirely unexpected result. It is known that reaction of pyridine with $Li[NPr^i_2]$ affords predominantly 4,4′-bipyridine,[7] and use of sodium metal as the reducing agent likewise causes 4,4′-coupling of a variety of substituted pyridines.[8] Furthermore, reductive coupling of 3,3′-bipyridine with $Li[NPr^i_2]$ results in 3,3′:4′,4″:3″,3‴-quaterpyridine *via* coupling of 2 equivalents of the radical anion at the 4 position.[9] It seemed likely that reaction of 2,2′-bipyridine with $Li[NPr^i_2]$ would allow a simple, one-step synthesis of the 'back-to-back' bis-bipyridine L[1] which has been recently reported;[3] clearly an interesting ligand in many respects, its synthesis is a multi-step procedure requiring the initial preparation of 4-chloro-2,2′-bipyridine, and a single step preparation of L[1] directly from bipy would be of considerable value.

Although the EI mass spectrum and elemental analysis of the product confirmed formation of a quaterpyridine, the ^{1}H NMR spectrum (Fig. 1) clearly showed the presence of fourteen inequivalent aromatic protons rather than the expected seven. The assignments, given in Fig. 1, are based on a ^{1}H–^{1}H correlation (COSY) spectrum. There are two sets of four protons which correspond to the two terminal pyridyl rings (A and D); it is not clear which set of signals corresponds to which pyridyl ring, but this is not important in deducing the structure. The presence of a 4′,2″-linkage between the two central rings (B and C) is clear from examination of the signals corresponding to these two rings in the spectrum. Whereas the terminal H^{6A} and H^{6D} protons both give ddd patterns, with coupling constants of

Table 1 Analytical, mass spectroscopic and electrochemical data for the new complexes

Complex	Elemental analysis (%)[a] C	H	N	FAB mass spectra[b] *m/z* (% intensity) and assignment	Electrochemical properties $E_{\frac{1}{2}}$[c]/V (ΔE_p/mV)
1	47.4	3.2	11.0	869 (100) $[Ru(bipy)_2L(PF_6)]$ (869)	+0.90 (70), −1.66 (60),
	(47.3)	(3.0)	(11.0)	724 (80) $[Ru(bipy)_2L]$ (724)	−1.89 (80), −2.12 (70)
2·2Me_2CO[d]	42.5	3.5	8.9	1574 (100) $[\{Ru(bipy)_2\}_2(\mu\text{-}L)(PF_6)_3]$ (1573)	+1.06,[e] +0.99,[e] −1.46 (60),
	(43.2)	(3.2)	(9.2)	1429 (23) $[\{Ru(bipy)_2\}_2(\mu\text{-}L)(PF_6)_2]$ (1428)	−1.73 (60), −1.86 (70)
				869 (30) $[Ru(bipy)_2L][PF_6]$ (869)	
3·CH_2Cl_2[f]	47.5	3.0	11.4	680 (100) [Ru(terpy)Cl(L)] (680)	+0.42 (70)[g]
	(47.5)	(3.0)	(10.8)		
4	44.0	2.9	10.6	1341 (3) $[\{Ru(terpy)Cl\}_2(\mu\text{-}L)][PF_6]_2$ (1340)	+0.58,[e] +0.52[e,g]
	(44.8)	(2.7)	(10.5)	1200 (65) $[\{Ru(terpy)Cl\}_2(\mu\text{-}L)][PF_6]$ (1195)	
				1052 (13) $[\{Ru(terpy)Cl\}_2(\mu\text{-}L)]$ (1050)	
				682 (100) [Ru(terpy)Cl(L)] (680)	
5	43.2	2.7	10.1	1345 (20) $[\{Ru(terpy)\}(\mu\text{-}L)\{Ru(bipy)_2\}][PF_6]_2$ (1349)	+0.89 (80), +0.40 (70),
	(43.7)	(3.1)	(10.0)	644 (100) [Ru(terpy)L] (645)	−1.60 (70), −1.88 (70)

[a] Calculated values in parentheses. [b] Calculated values based on most abundant isotopes given in parentheses. [c] Referenced to ferrocene–ferrocenium. [d] Recrystallised from acetone–diethyl ether. [e] Potential determined by square-wave voltammetry, so no value for (ΔE_p) available. [f] Recrystallised from CH_2Cl_2–hexane. [g] Numerous overlapping, unresolved reductions.

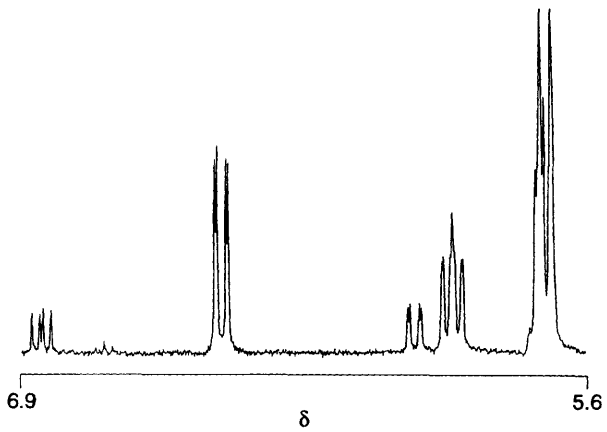


Fig. 2 Part of the ^1H NMR spectrum of complex **2** (400 MHz, CD_3CN)

approximately 4.8, 1.7 and 1.0 Hz to their neighbours in the 5-, 4- and 3-positions respectively on the same pyridyl ring, the signal for H^{6B} is just a dd with a large 8.1 Hz coupling to H^{5B} and a small *para* coupling of 1.0 Hz to H^{3B}. An intermediate coupling to H^{4B}, which would render the signal a ddd, is absent. Likewise H^{5A} and H^{5D} both give ddd patterns, whereas H^{5B} is just a dd, with one large (7.8 Hz) coupling to H^{6B} and one small (1.0 Hz) coupling to H^{3B}. The signal for H^{3B} is unfortunately obscured in the multiplet centred at δ 7.5, but it is clear from the H^{5B} and H^{6B} signals that the ring is substituted at the 4 position. Likewise inspection of the H^{3C}, H^{4C} and H^{5C} signals clearly shows that the remaining pyridyl ring is 2,6-disubstituted; H^{4C} has a dd pattern, with large couplings to H^{3C} and H^{5C}, and no smaller *meta* couplings. The structure of L, with two inequivalent bipyridyl binding sites, could therefore be determined unambiguously.

Syntheses of the Complexes.—Reaction of L with 1 equivalent of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ followed by treatment with KPF_6 afforded the mononuclear complex $[Ru(bipy)_2L][PF_6]_2$ **1** in 90% yield. In principle, the $\{Ru(bipy)_2\}^{2+}$ fragment could bind at either of the two binding sites to give one of two isomeric products, or a mixture of both. However TLC of **1** with a variety of solvent mixtures always gave a single spot, and the ^1H NMR spectrum in CD_3CN, although complex, showed signals in the region δ 7.1–8.8 consistent with the presence of thirty inequivalent protons of equal abundance. Complex **1** is therefore a single positional isomer, and although there is no direct evidence it seems very likely that the $\{Ru(bipy)_2\}^{2+}$ fragment is attached at the 'terminal' bipyridyl binding site (rings A and B), rather than the much more sterically hindered 'internal' binding site (rings C and D). Complex **1** therefore contains a $\{Ru(bipy)_3\}^{2+}$ chromophore with a pendant 2,2′-bipyridyl binding site to which other metals may be attached in a separate reaction (see below).

Under more vigorous reaction conditions (ethylene glycol at reflux) in the presence of 2.2 equivalents of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$, the binuclear complex $[\{Ru(bipy)_2\}_2(\mu\text{-}L)][PF_6]_4$ **2** was obtained in 60% yield. Since this contains two inequivalent chiral centres in close association, up to *eight* stereoisomers are possible (*RR′*,*R′R*,*SS′*,*S′S*,*RS′*,*R′S*,*SR′*,*S′R*); the ^1H NMR spectrum of **2** in CD_3CN is, not surprisingly, unhlepful as the majority of the signals (46 inequivalent protons per stereoisomer) occur in an overlapping mass in the range δ 6.7–8.9; no useful information could be gleaned from this even at 500 MHz. However the presence of a few clearly resolved signals at chemical shifts as low as δ 5.7 (Fig. 2) indicates that, due to the proximity of the two metal centres, some protons at one metal centre are affected by the ring current of nearby aromatic rings at the other. Examination of Corey–Pauling–Koltun molecular models confirms that the 'internal' binding site of L is very hindered. Metal binding at this site must involve a large dihedral twist between rings B and C, and whichever diastereoisomer of **2** is constructed it is clear that some of the protons of the bipyridyl ligands at the internal binding site must lie directly above the centres of aromatic rings of ligands associated with the external binding site.

Reaction of L with 1 equivalent of $[Ru(terpy)Cl_3]$ in ethylene glycol at 140 °C followed by treatment with KPF_6 gave, after chromatographic separation, the purple mononuclear complex $[Ru(terpy)Cl(L)][PF_6]$ **3** in 20% yield. The ^1H NMR spectrum in CD_3CN shows only an unresolved set of rather broad overlapping signals in the region δ 7–9; their broadness may be due to stereochemical non-rigidity. As with **1**, there is the possibility of formation of two positional isomers since the two binding sites of L are inequivalent; although there is no direct evidence, it again seems most likely that the unhindered terminal binding site is bound to the $\{Ru(terpy)Cl\}^+$ fragment. The binuclear analogue $[\{Ru(terpy)Cl\}_2(\mu\text{-}L)][PF_6]_2$ **4** was prepared in 30% yield by reaction of L with 2 equivalents of $[Ru(terpy)Cl_3]$ in ethylene glycol at reflux. Although most of the (rather broad) peaks in the ^1H NMR spectrum occur in the region δ 7–9, a few isolated signals occur in the region δ 5.5–6.6 due to ring-current effects.

Reaction of **1**, which has a free external bipyridyl binding site, with $[Ru(terpy)Cl_3]$ gave the 'mixed' complex $[\{Ru(bipy)_2\}(\mu\text{-}L)\{Ru(terpy)Cl\}][PF_6]_3$ **5** in 70% yield. The ^1H NMR spectrum (Fig. 3) clearly contains a mixture of the sharp

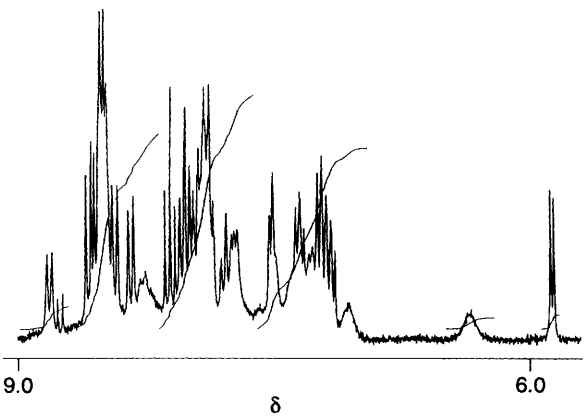


Fig. 3 ^{1}H NMR spectrum of complex **5** (270 MHz, CD_3CN)

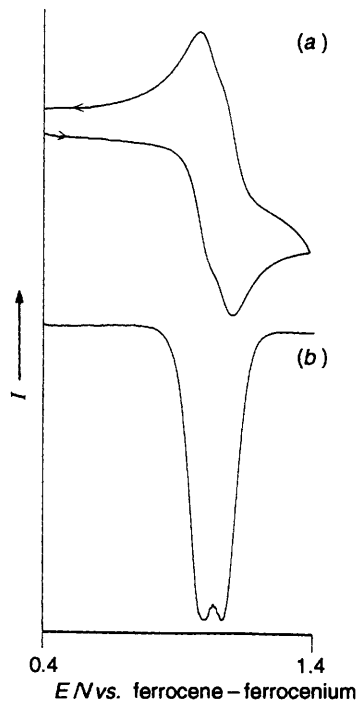


Fig. 4 (*a*) Cyclic voltammogram at 0.2 V s^{-1}, and (*b*) square-wave voltammogram of complex **2** in MeCN with 0.1 mol dm^{-3} $[NBu_4][PF_6]$ at a platinum-bead electrode

resonances expected for the stereochemically rigid $\{Ru(bipy)_3\}^{2+}$ group and the broader resonances from the $\{Ru(terpy)(bipy)Cl\}^+$ group. Most of the signals occur in the region δ 7–9, but the presence of a sharp doublet at δ 5.87 and a broad singlet at δ 6.36 confirms, as with the other binuclear complexes, the proximity of some of the protons at one metal centre to the aromatic rings of the other. This reaction demonstrates how the differential reactivity of the two binding sites in L may be exploited by permitting the stepwise synthesis of binuclear complexes in which an $[Ru(bipy)_3]^{2+}$ group may be covalently attached to another metal centre. Such complexes are of intense current interest for the study of supramolecular photocatalysts.[1,2]

Electrochemistry.—The cyclic voltammogram of **1** is very similar to that of $[Ru(bipy)_3]^{2+}$,[10] showing the expected reversible Ru^{II}–Ru^{III} couple at +0.90 V *vs.* the ferrocene–ferrocenium couple and three well resolved, reversible, ligand-based reductions at −1.66, −1.89 and −2.12 V. By 'reversible' is meant that the cathodic and anodic peak currents are equal, and the separation of the cathodic and anodic peaks is in the range 60–80 mV and independent of scan rate; under identical

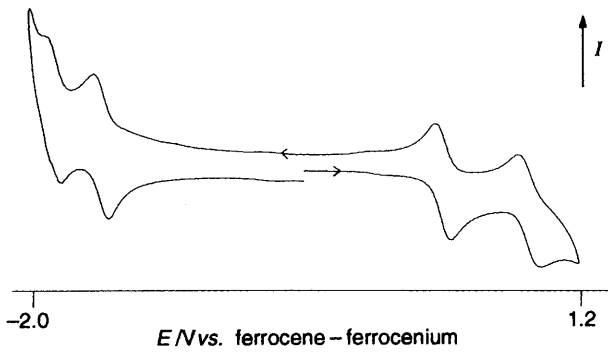


Fig. 5 Cyclic voltammogram of complex **5** at 0.2 V s^{-1}, in MeCN with 0.1 mol dm^{-3} $[NBu_4][PF_6]$ at a platinum-bead electrode

conditions the peak-peak separation of the ferrocene–ferrocenium couple was 70 mV. The oxidative cyclic voltammogram of **2** shows two closely overlapping waves in the region expected for the Ru^{II}–Ru^{III} couples; they can be just resolved by square-wave voltammetry (Fig. 4). The first oxidation, at +0.99 V is 90 mV more positive than that of **1** due to the presence of a higher overall charge on the complex (+4 instead of +2). The second oxidation is at +1.06 V *vs.* ferrocene–ferrocenium. The splitting of 70 mV between the two oxidations in **2** is very similar to that observed in the symmetrical binuclear complex $[\{Ru(bipy)_2\}_2(\mu\text{-}L^1)]^{4+}$,[3] so it is probably associated with a weak electrostatic interaction between the metal centres rather than any inequivalence in the metal sites. Although peak-peak separations for the oxidations cannot be measured from the cyclic voltammogram, there is no reason to suppose that they are not reversible. Complex **2** also shows reversible reductions characteristic of ligand-based processes, at −1.46, −1.73 and −1.86 V *vs.* ferrocene–ferrocenium; further reductions at more negative potentials were obscured by absorption/desorption processes. Of the three resolved reductions the latter two are in the region consistent with reduction of the bipy ligands, so the reduction at −1.46 V is probably based on the more highly conjugated ligand L.

Complex **3** shows a single reversible oxidation at +0.42 V *vs.* ferrocene–ferrocenium, consistent with the presence of a $\{Ru(bipy)(terpy)Cl\}^+$ fragment.[10] For **4**, as for **2**, the two metal-centred oxidations are not resolved by cyclic voltammetry but may be just resolved by square-wave voltammetry; they occur at +0.52 and +0.58 V. The first oxidation of **4** is at a potential 100 mV more positive than that of **3**, again as a result of the increased positive charge on the binuclear complex. Both **3** and **4** display a series of poorly defined, overlapping processes in the region characteristic of ligand-based reductions.

Complex **5** contains one $\{Ru(bipy)_3\}^{2+}$-type centre and one $\{Ru(bipy)(terpy)Cl\}^+$-type centre, and this is reflected in the cyclic voltammogram (Fig. 5) which shows two reversible oxidations, at +0.40 and +0.89 V *vs.* ferrocene–ferrocenium. The first two reductions are also clearly resolved, occurring at −1.60 and −1.88 V. This complex offers an interesting comparison with $[\{Ru(terpy)\}(\mu\text{-qpy})\{Ru(terpy)Cl\}][PF_6]_3$ (qpy = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine), a helical complex which contains $\{Ru(terpy)_2\}^{2+}$ and $\{Ru(terpy)(bipy)Cl\}^+$ fragments and therefore has similar electrochemical and spectroscopic properties.[11]

UV/VIS and Fluorescence Properties.—The UV/VIS spectra of **1** and **2** at the same concentration are shown in Fig. 6(*a*); they are qualitatively similar, with the spectrum for **2** being approximately double the intensity of the spectrum for **1**. The characteristic $d_\pi(Ru) \longrightarrow \pi^*(bipy)$ metal-to-ligand and charge-transfer (^{1}m.l.c.t.) band appears at 450 nm in both spectra; the peaks at 286 nm in each spectrum are ligand-based π–π* transitions, and those just below 250 nm are also m.l.c.t. processes.[10] The spectra of **3** and **4** at the same concentration

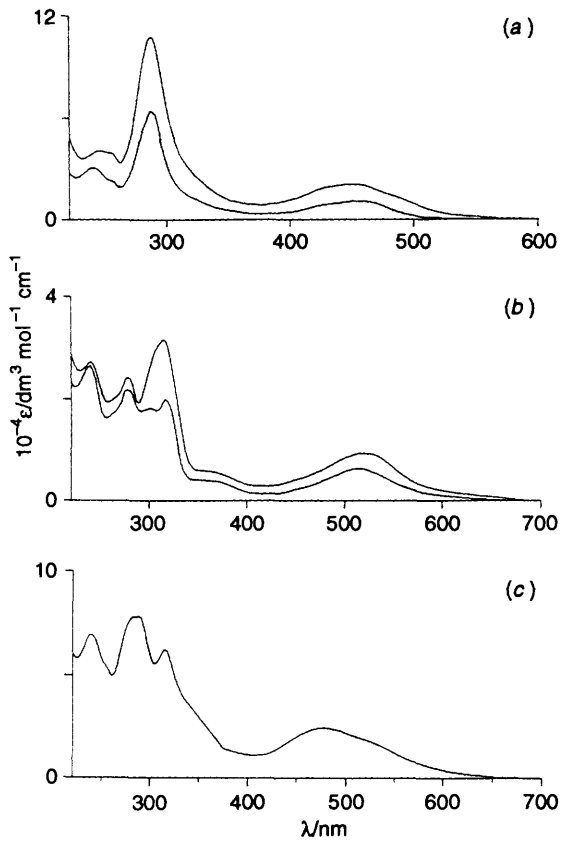


Fig. 6 UV/VIS spectra of (*a*) **1** (lower trace) and **2** (upper trace) in MeCN at the same concentration; (*b*) **3** (lower trace) and **4** (upper trace) in CH_2Cl_2 at the same concentration; (*c*) **5** in MeCN

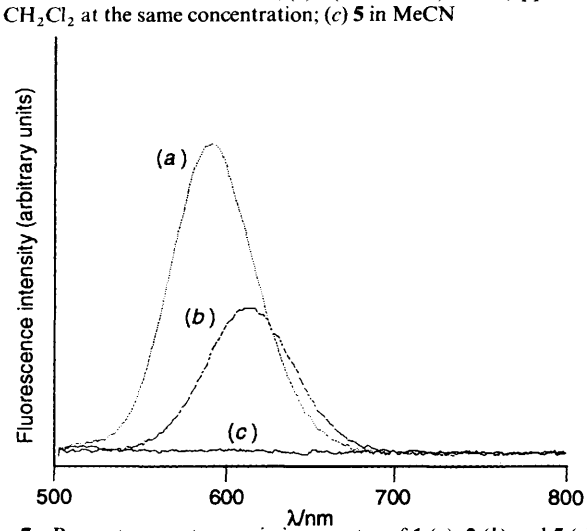


Fig. 7 Room-temperature emission spectra of **1** (*a*), **2** (*b*) and **5** (*c*) in MeCN at the same concentration

[Fig. 6(*b*)] show the ^{1}m.l.c.t. transition at 514 nm, at a longer wavelength than the analogous transition in **1** and **2** due to the lower overall ligand-field strength resulting from the presence of chloride in the co-ordination sphere {the ^{1}m.l.c.t. absorption in $[Ru(terpy)(bipy)Cl]^+$ occurs at 506 nm}.[10] The spectrum of **5** [Fig. 6(*c*)] is, with minor perturbations, a composite of the spectra of the component parts. The ^{1}m.l.c.t. band for the $\{Ru(bipy)_3\}^{2+}$ component of **5** occurs at 478 nm, with the weaker transition for the $\{Ru(terpy)(bipy)Cl\}^+$ component appearing as a shoulder at approximately 525 nm. Likewise the π–π^* transitions of the component parts (at 286 and 314 nm for **1** and **3** respectively) are both visible in the spectrum of **5** (at 288 and 315 nm).

Both **1** and **2**, as expected, are luminescent at room temperature in acetonitrile solution, with emission maxima of 594 and 615 nm respectively (Fig. 7) using an excitation wavelength of 450 nm. However the fluorescence intensity of **2**, which contains two light-absorbing ruthenium centres, is approximately *half* that of **1** at the same concentration. The reason for this is not yet known.

Complex **5** is completely quenched in acetonitrile at room temperature (Fig. 7). Quenching of the $\{Ru(bipy)_3\}^{2+}$ fragment by the $\{Ru(terpy)(bipy)Cl\}^+$ fragment could occur in principle either by electron transfer or energy transfer. Excited-state $[Ru(bipy)_3]^{2+}$ is reduced to $[Ru(bipy)_3]^+$ at +0.84 V *vs.* SCE (+0.47 V *vs.* ferrocene–ferrocenium), and it has already been shown that the $\{Ru(terpy)(bipy)Cl\}^+$ centre of **5** oxidises at +0.40 V *vs.* ferrocene–ferrocenium, and is therefore capable of effecting reductive quenching of the excited $[Ru(bipy)_3]^{2+}$ chromophore. Alternatively an energy-transfer mechanism, resulting in collapse of the m.l.c.t. excited state of the $\{Ru(bipy)_3\}^{2+}$ fragment with concomitant promotion of the $\{Ru(terpy)(bipy)Cl\}^+$ centre to its (lower-energy) m.l.c.t. excited state, is also a possibility.

Conclusion

Asymmetric reductive coupling of 2,2′-bipyridine with lithium diisopropylamide results unexpectedly in formation of L, with two inequivalent binding sites. By varying the reaction conditions the two binding sites may be occupied sequentially, allowing preparation of a binuclear complex in which a $\{Ru(bipy)_3\}^{2+}$ centre is quenched by an adjacent $\{Ru(terpy)(bipy)Cl\}^+$ centre. These results are of relevance to the synthesis of potential photocatalysts in which light-harvesting polypyridyl-ruthenium(II) chromophores are directly linked to potential reaction centres.

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