A Binuclear Ruthenium(II) Complex of 2,2′:3′,2″:6″,2‴-Quaterpyridine containing RuN$_5$Cl and Cyclometallated RuN$_5$C Fragments linked by a Bridging (N,C-donor) Pyridyl Residue

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Reaction of the binucleating compound 2,2′:3′,2″:6″,2‴-quaterpyridine (HL), which normally acts as a bis(bipyridyl) ligand with two N,N-bidentate binding sites, with 2 equivalents of $[Ru(terpy)Cl_3]$ (terpy = 2,2′:6′,2″-terpyridine) in the presence of *N*-methylmorpholine afforded the unusual binuclear complex $[Cl(terpy)Ru(\mu\text{-}L)Ru(terpy)][PF_6]_2$ **1** in which L is acting as an N,N-bidentate donor to one metal and an N,N,C-cyclometallating terdentate donor to the other. One of the pyridyl residues is therefore acting as an N-donor to one ruthenium(II) centre and a C-donor to the other *via* the C^4 position. Complex **1** was fully characterised by elemental analysis, ^{1}H NMR (including correlation) and fast-atom bombardment mass spectrometry. Cyclic and square-wave voltammetry shows two reversible one-electron metal-centred oxidations at potentials consistent with the metal co-ordination environments, and the electronic spectrum is also consistent with the complex formulation.

Co-ordination complexes containing cyclometallated ligands[1] have recently been the focus of interest due to their unusual photophysical and electrochemical properties.[2–6] Some of the commonest recent examples are based on oligopyridine analogues such as 2-phenylpyridine [an N,C-chelating analogue of 2,2′-bipyridine (bipy)][2] and 6-phenyl-2,2′-bipyridine [an N,N,C-chelating analogue of 2,2′:6′,2″-terpyridine (terpy)].[3–5] A characteristic feature of these compounds compared to their oligopyridyl counterparts is that, by virtue of being stronger σ donors, they increase the ligand field and the electron density at the metal centre. This results, for example, in enhanced luminescence lifetimes of ruthenium(II) complexes by increasing the energy gap between ligand(π^*) and Ru(d_σ^*) levels (thereby inhibiting one of the non-radiative decay pathways),[4] and in strong electrochemical interactions between electron-rich metal centres in binuclear ruthenium(II) complexes.[6]

Much rarer, in contrast, are polydentate chelating ligands in which a terminal pyridyl moiety cyclometallates by binding in a 'turned around' manner *via* the C^3 atom, with the N atom pointing outwards. The first well characterised example was an iridium(III) complex in which one bipy ligand was observed to bind as an N,C-chelate with the external pyridyl site protonated.[7] Similarly, in complexes of the type $[Pt(bipy)R_2]$ (R = σ-bonded aryl) elimination of RH is accompanied by a change in co-ordination of the bipy ligand to a deprotonated 'turn around' mode, and a binuclear platinum(II) complex has been crystallographically characterised in which a doubly depronated bipy ligand acts as a turn-around N,C-chelate to *both* metal centres in a co-ordination mode reminiscent of 2,2′-bipyrimidine.[8] The 'turned around' cyclometallated binding mode can be enforced on bipy by N-methylation of one of the pyridyl rings,[9] and 2,4′-bipyridine in which the 4-pyridyl ring has been quaternised also binds as an N,C-chelate.[10]

A recent paper on the co-ordination chemistry of the asymmetric quaterpyridine ligand HL described the preparation of various binuclear complexes in which the two bipyridyl fragments co-ordinated to identical or different metal fragments [Fig. 1(*a*)];[11] this binding mode requires a substantial dihedral twist between the two independent bipyridyl fragments to minimise steric interactions. In principle it is also possible for cyclometallation to occur at an 'inner' binding pocket by loss of the H^4 proton from ring B of the ligand [Fig. 1(*b*)], affording bridged binuclear complexes in which L acts as a conventional bipyridyl donor to one metal ion and a cyclometallating N,N,C-donor to another with ring B as a pyrazine-like bridge. This paper describes the preparation, characterisation and properties of $[Cl(terpy)Ru(\mu\text{-}L)Ru(terpy)][PF_6]_2$ **1**, a unique example of such a complex.

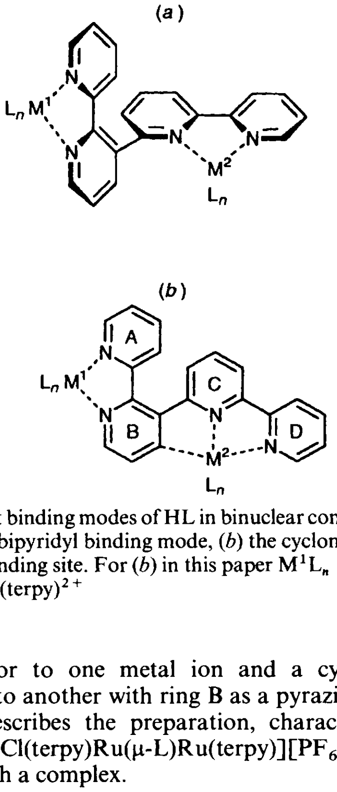


Fig. 1 Different binding modes of HL in binuclear complexes: (*a*) is the conventional bisbipyridyl binding mode, (*b*) the cyclometallating mode at the internal binding site. For (*b*) in this paper M^1L_n = Ru(terpy)Cl$^+$ and M^2L_n = Ru(terpy)$^{2+}$

Experimental

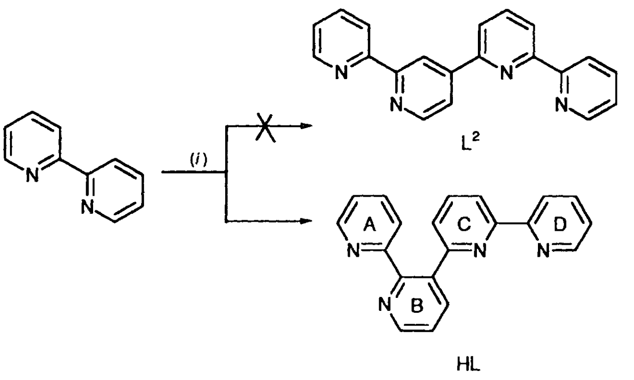
Details of the electrochemical and spectroscopic instrumentation used have been described previously,[11] with the exceptions that fast-atom bombardment (FAB) mass spectra (3-nitrobenzyl alcohol matrix) were recorded on a VG Autospec instrument at the University of Bristol, and that a glassy-carbon working electrode was used for the electrochemical experiments. The compounds HL (ref. 8) and $[Ru(terpy)Cl_3]$[12] were prepared according to the published methods. Molecular-mechanics calculations were performed using the CAChe suite of programs.[13]

Preparation of Complex **1**.—A mixture of HL (101 mg, 0.33 mmol), [Ru(terpy)Cl$_3$] (303 mg, 0.69 mmol, 2.1 equivalents) and *N*-methylmorpholine (1 cm^3) in ethylene glycol (20 cm^3) was heated to reflux in air for 2 h to afford a deep violet solution. After cooling and addition of aqueous KPF$_6$ a purple precipitate appeared which was filtered off, washed with water and dried. The crude material was purified by preparative-scale thin-layer chromatography on 2 mm-thick silica plates (Merck, article 5717) using MeCN–water–saturated aqueous KPF$_6$ (100:5:5) as eluent. The product appeared as a thick purple band bracketed by traces of [Ru(terpy)Cl(HL)][PF$_6$] and [{Ru(terpy)Cl}$_2$(μ-HL)][PF$_6$]$_2$ (both red-brown). The purple band was carefully scraped off, and **1** separated from it with the elution solvent. The purple solution was concentrated *in vacuo* until **1** precipitated from the (largely aqueous) solution. This material was examined by TLC and, if necessary, was rechromatographed until all traces of the by-products had disappeared. After filtration and drying complex **1** was finally recrystallised from CH$_2$Cl$_2$–hexane or MeCN–diethyl ether. Yield: 20–50%. FAB mass spectrum: *m/z* (relative intensity, assignment): 1305 (5, **1**), 1160 (50, **1** − PF$_6$), 1014 (17, **1** − 2PF$_6$) and 645 {100%, [Ru(terpy)(HL)]} (Found: C, 46.4; H, 3.0; N, 10.4. Calc. for C$_{50}$H$_{35}$ClF$_{12}$N$_{10}$P$_2$Ru$_2$: C, 46.1; H, 2.7; N, 10.7%).

Results and Discussion

Structure of the Bridging ligand.—The initial paper describing the synthesis of HL by coupling of the radical anion of bipy assumed the structure to be 2,2′:4′,2″:6″:2‴-quaterpyridine (L^2).[11] This was based on the assumption that an asymmetric coupling of the bipy radical anions had occurred *via* C^2 and C^4. Coupling of the radical anion of pyridine is known to afford a mixture of 4,4′-, 2,2′- and 2,4′-bipyridine in varying amounts.[14] Likewise coupling of the radical anion of 3,3′-bipyridine occurs at the 4 position,[15] and coupling of the radical anion of 4,4′-bipyridine (where the 4 position is blocked) occurs at the 2 position.[16] All of these results indicated that the radical anions of pyridyl rings could only undergo dimerisation *via* C^2 or C^4. The dimerisation of bipy following formation of the radical anion afforded a quaterpyridine the ^{1}H NMR spectrum of which showed 14 inequivalent aromatic protons. Since the product could clearly not be the 'linear' quaterpyridine arising from C^2–C^2 coupling or the 'back-to-back' quaterpyridine arising from C^4–C^4 coupling, both of which would have seven ^{1}H NMR signals, the only plausible explanation (both to the author and the referees of the paper!) seemed to be that an asymmetric C^2–C^4 coupling had occurred to give L^2. Full assignment of the ^{1}H NMR spectrum was not possible since some signals were not clearly resolved but occurred as parts of multiplets of several overlapping signals.

We have recently obtained a crystal structure of a complex containing this ligand,[17] which shows clearly that the structure is not as we thought but is actually 2,2′:3′,2″:6″:2‴-quaterpyridine (HL), arising from the asymmetric C^2–C^3 coupling of bipy radical anions (Scheme 1). This is a hitherto unprecedented mode of coupling of pyridyl radical anions. Why this should occur is not clear, especially as HL is the only significant product from the reaction. Loss of a C^3 proton may be related to the occasional tendency of bipy to cyclometallate in this position with the ligand in the 'turned around' binding mode.[7,8] Unfortunately the protons of ring B of the ligand are amongst those that are obscured as part of multiplets in the ^{1}H NMR spectrum. It should be emphasised that the main part of ref. 11, describing the syntheses, electrochemical, spectroscopic and luminescence properties of complexes of HL, is still entirely valid.



Scheme 1 (*i*) (*a*) Li[NPr$^i_2$], diethyl ether, −78 °C; (*b*) water; (*c*) KMnO$_4$, acetone

Synthesis and Structure of the Cyclometallated Complex.—Reaction of HL with 2 equivalents of [Ru(terpy)Cl$_3$] gave a mixture of products in varying proportions depending on the conditions. In ethylene glycol at reflux the main product is the expected binuclear complex [{Ru(terpy)Cl}$_2$(μ-HL)]$^{2+}$, with a small amount of mononuclear [Ru(terpy)Cl(HL)]$^+$ also formed in which it is presumed that the Ru(terpy)Cl moiety is attached to the 'outer', more accessible, bipyridyl site.[11] However in the presence of *N*-methylmorpholine, a mild basic reducing agent which was added to assist in the reduction of the ruthenium(III) starting material to Ru^{II} in the product, the principal product was instead found to be the deep purple complex **1** with the 'expected' mono- and bi-nuclear species only formed in trace amounts. The yields of the components were somewhat variable, with the best yield of **1** being 50%. A recent study of the reaction of 6-phenyl-2,2′-bipyridine (Hpbipy) with [Ru(terpy)Cl$_3$] found that cyclometallation to give [Ru(terpy)(pbipy)]$^+$ occurred to varying extents in aqueous or alcoholic solvents, but not in acidic media where Hpbipy acts only as a N,N-bidentate donor.[5] The present results indicate that cyclometallation is promoted by the presence of *N*-methylmorpholine. Initially it seemed possible that this compound might be promoting cyclometallation by acting as a weak base, which is reasonable given that cyclometallation ultimately requires elimination of H$^+$ and Cl$^-$ (not necessarily at the same time) from the initially formed RuN$_5$Cl fragment; however no cyclometallation occurred when *N*-methylmorpholine was replaced by triethylamine or KOH. An alternative possibility is that *N*-methylmorpholine displaces the coordinated chloride ion of the RuN$_5$Cl fragment. There is still much uncertainty about the mechanism(s) by which cyclometallation occurs and further speculation is inappropriate. No cyclometallated products were obtained from reaction of [Ru(bipy)$_2$(HL)]$^{2+}$ with [Ru(terpy)Cl$_3$], with or without *N*-methylmorpholine in the reaction mixture: the only product in all cases was the previously described[11] [(bipy)$_2$Ru(μ-HL)-Ru(terpy)Cl]$^{3+}$, with 'external' RuN$_6$ and 'internal' RuN$_5$Cl metal fragments.

The formulation of complex **1** was established by fast-atom bombardment mass spectrometry, elemental analysis and ^{1}H NMR spectrometry. The main peaks in the FAB mass spectrum at *m/z* 1014, 1160 and 1305 correspond to the mass of the complex cation with zero, one or two associated [PF$_6$]$^-$ ions and have the appropriate isotopic pattern. The ^{1}H NMR spectrum shows the presence of 35 inequivalent aromatic protons, and may be partially assigned with the aid of a ^{1}H–^{1}H correlation (COSY) spectrum (Fig. 2). Coupled sets of four and three protons may be identified for some of the pyridyl rings, but in some areas of the spectrum many signals overlap and complete assignments are not possible and have not been attempted. Fortunately, however, the most important feature of the spectrum is quite clear: there are two doublets at the extremes of the spectrum (δ 6.48 and 8.77) which are coupled to each other (J = 5.5 Hz), and neither proton is coupled to anything else. This can only be explained by formation of a cyclometallated structure involving the metal at the inner site;

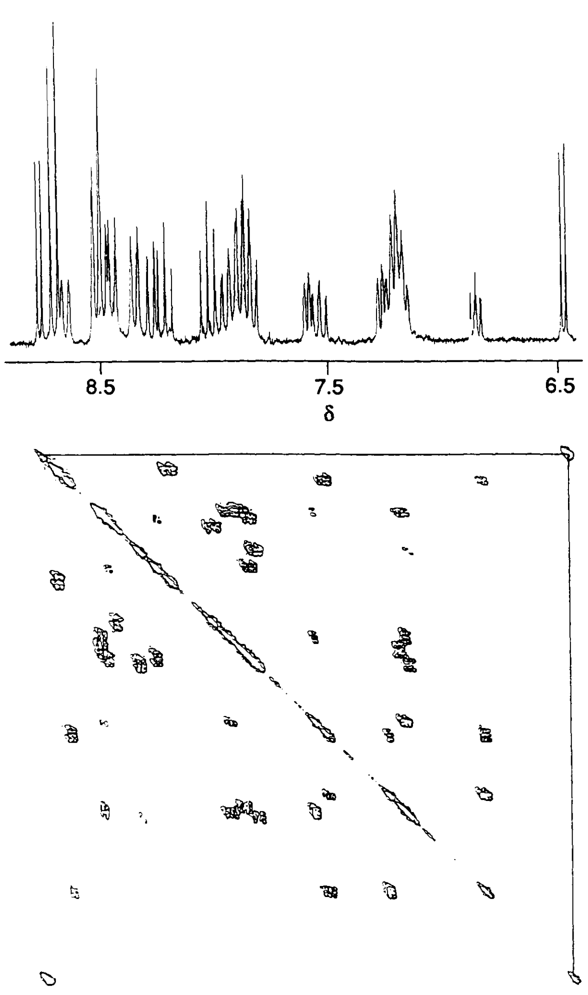


Fig. 2 Proton NMR spectrum (270 MHz, CD_3CN) and COSY spectrum of complex **1**

loss of the H^4 proton of ring B leaves only H^5 and H^6. The magnitude of the coupling constant (5.5 Hz) is only consistent with this *ortho* coupling [$J(H^5–H^6)$ for a pyridyl ring is typically 4.5–6 Hz]. The COSY spectrum is sensitive enough to detect weak *meta* and *para* couplings where they occur, but none is present for this pair. The mode of co-ordination of L is therefore as depicted in Fig. 1(*b*), with ring B acting as an N-donor to the 'outer' metal and a C^4-donor to the 'inner' metal, a cyclometallating analogue of pyrazine-based bridging ligands.

In the absence of X-ray quality crystals (despite several attempts) a molecular mechanics energy minimisation of the proposed structure was carried out using CAChe software.[13] The global minimum is depicted in Fig. 3; MM2 parameters were used and adjusted for the oxidation states of the atoms (Ru, +2; Cl, −1; C bonded to Ru, −1). There are no very unfavourable steric interactions; the pyridyl rings A and C of L, on either side of the bridging pyridyl ring B, are not coplanar with B but twisted slightly to relieve the steric interaction between their H^3 protons which would otherwise be directed at one another. Complex **1** may be considered to arise from the initially formed binuclear complex $[\{Ru(terpy)Cl\}_2(\mu\text{-}HL)]^{2+}$,[11] and its formation involves the loss, at some stage, of H^+ and Cl^-. The structure of this precursor, as predicted by MM2 energy minimisation,[13] is in Fig. 4. Rotation about the central C–C bond of the complex, to allow the inner Ru atom to form a Ru–C bond, is facile so there is no apparent steric barrier to formation of **1**.

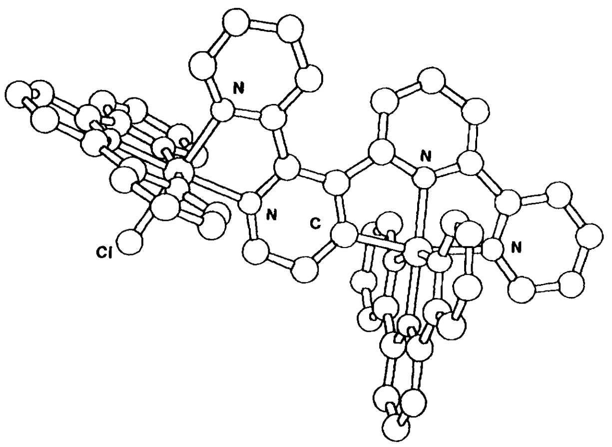


Fig. 3 Energy-minimised structure of complex **1** predicted by MM2 calculations.

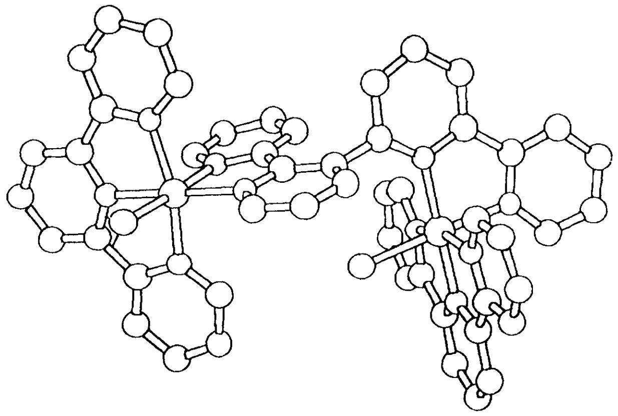


Fig. 4 Energy-minimised structure of $[\{Ru(terpy)Cl\}_2(\mu\text{-}HL)]^{2+}$, the precursor to complex **1**

Spectroscopic and Electrochemical Properties.—Oxidative cyclic and square-wave voltammograms of complex **1** are depicted in Fig. 5. At a glassy carbon working electrode the complex undergoes two reversible one-electron oxidations at $E_{\frac{1}{2}}$ = +0.32 and +0.50 V *vs.* the ferrocene–ferrocenium couple (ΔE_p = 80 mV in each case, at a scan rate of 0.2 V s^{-1}). The mononuclear complexes $[Ru(terpy)(bipy)Cl]^+$ (N_5Cl donor set) and $[Ru(terpy)(pbipy)]^+$ (N_5C donor set) have $Ru^{II}–Ru^{III}$ couples at +0.12 and +0.42 V respectively *vs.* ferrocene–ferrocenium,[5] so the oxidations of **1** probably correspond to such couples of the 'external' RuN_5Cl and 'internal' RuN_5C fragments respectively. The +0.2 V shift in the oxidation of the RuN_5Cl fragment compared to that of the mononuclear analogue is too large to be ascribed solely to the increased charge on the binuclear complex (+2 instead of +1) and must therefore result in part from an interaction with the second metal *via* the bridging pyridyl ligand. The RuN_5Cl fragment would appear to be rendered more electron deficient by this interaction, making it harder to oxidise. The oxidation potential of the cyclometallated RuN_5C fragment is not directly comparable to that of $[Ru(terpy)(pbipy)]^+$ since in the latter case the cyclometallating ligand is a phenyl rather than a pyridyl ring, so it is not possible to determine the extent to which this redox potential is perturbed by the presence of the RuN_5Cl fragment. Use of a conventional platinum-wire working electrode was less successful since the oxidised complex undergoes adsorption onto the electrode surface, resulting in a strong stripping peak which obscured the return waves. Coulometric measurements, which require bulk electrolysis at a platinum-grid electrode, were therefore not possible.

Reductive voltammetry shows one reversible reduction at −1.69 V *vs.* ferrocene–ferrocenium (ΔE_p = 80 mV, scan rate 0.2 V s^{-1}). The half-wave potentials of subsequent reductions could not be determined from cyclic voltammetry as the return

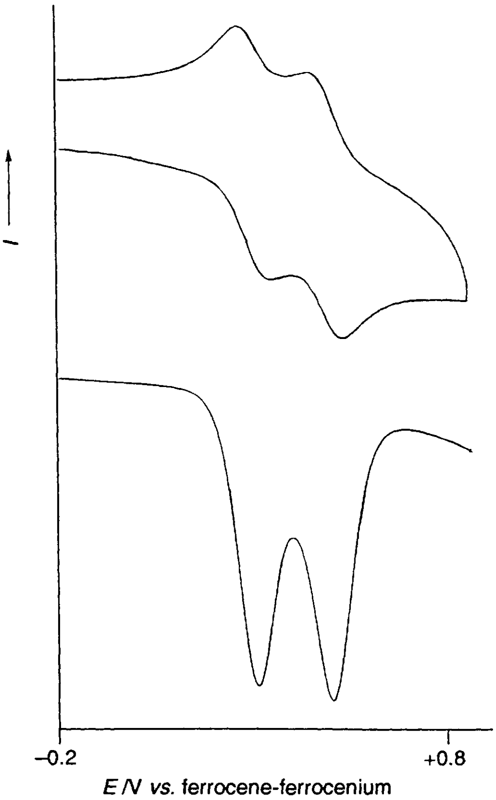


Fig. 5 Cyclic and Osteryoung square-wave voltammograms of complex **1** in CH_2Cl_2 at a glassy carbon working electrode

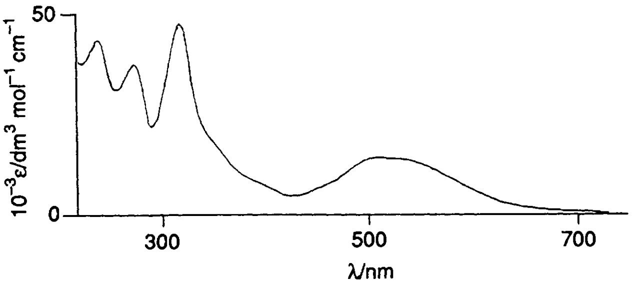


Fig. 6 Electronic spectrum of complex **1** in CH_2Cl_2

waves are partly obscured by the presence of a strong stripping peak, but the peak potentials could be determined from square-wave voltammetry and occur at –2.00 and –2.37 V. In both cases the peaks are broad and rather flat, possibly indicating the presence of two pairs of closely spaced reductions.

The electronic spectrum of complex **1** is shown in Fig. 6. Unfortunately the characteristic maxima of the metal-to-ligand charge-transfer (m.l.c.t.) processes for the component chromophores are expected to be virtually coincident: the λ_{max} values for $[Ru(terpy)(bipy)Cl]^+$ and $[Ru(terpy)(pbipy)]^+$ are 502 (ε = 11 100) and 512 nm (ε = 13 800 $dm^3\ mol^{-1}\ cm^{-1}$) in acetonitrile.[5] Complex **1** has a broad transition at λ_{max} = 508 nm (ε = 13 600 $dm^3\ mol^{-1}\ cm^{-1}$) which doubtless comprises the m.l.c.t. processes of both metal fragments: attempts to deconvolute the expected two maxima by taking the second-derivative spectrum were not conclusive. The expected peaks in the UV region, corresponding to ligand-based π–π^* transitions and high-energy m.l.c.t. processes, are also present (λ_{max} = 318, 276 and 239 nm; ε = 48 000, 38 000 and 44 000 $dm^3\ mol^{-1}\ cm^{-1}$ respectively). The most striking result of the electronic spectral properties of **1**, which is not obvious from the spectrum but obvious to the naked eye, is the beautiful deep purple colour which is characteristic of cyclometallated RuN_5C complexes.[4,5]

In conclusion, an unusual binuclear complex, containing a bridging pyridyl residue which acts simultaneously as an N-donor to one metal and a cyclometallating C-donor to the other, has been prepared.

Acknowledgements

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References

1 E. C. Constable, *Polyhedron*, 1984, **3**, 1037.
2 E. C. Constable and J. M. Holmes, *J. Organomet. Chem.*, 1986, **301**, 203; K. A. King and R. J. Watts, *J. Am. Chem. Soc.*, 1987, **109**, 1589; F. Barigelletti, D. Sandrini, M. Maestri, V. Balzani, A. von Zelewsky, L. Chassot, P. Jolliet and U. Maeder, *Inorg. Chem.*, 1988, **27**, 3644; E. C. Constable, T. A. Leese and D. A. Tocher, *Polyhedron*, 1990, **9**, 1613; E. C. Constable and C. E. Housecroft, *Polyhedron*, 1990, **9**, 1939; K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson and R. J. Watts, *Inorg. Chem.*, 1991, **30**, 1685; J. H. van Diemen, J. G. Haasnoot, R. Hage, J. Reedijk, J. G. Vos and R. Wang, *Inorg. Chem.*, 1991, **30**, 4038; J. H. van Diemen, J. G. Haasnoot, R. Hage, E. Müller and J. Reedijk, *Inorg. Chim. Acta*, 1991, **181**, 245; E. C. Constable, A. M. W. Cargill Thompson, T. A. Leese, D. G. F. Reese and D. A. Tocher, *Inorg. Chim. Acta*, 1991, **182**, 93; G. Frei, A. Zilian, A. Raselli, H. U. Güdel and H.-B. Bürgi, *Inorg. Chem.*, 1992, **31**, 4766; A. Zilian and H. U. Güdel, *Inorg. Chem.*, 1992, **31**, 830; U. Maeder, A. von Zelewsky and H. Stoeckli-Evans, *Helv. Chim. Acta*, 1992, **75**, 1320; M. G. Colombo, T. C. Brunold, T. Riedner, H. U. Güdel, M. Förtsch and H.-B. Bürgi, *Inorg. Chem.*, 1994, **33**, 545.
3 E. C. Constable, R. P. G. Henney, T. A. Leese and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1990, 513; *J. Chem. Soc., Dalton Trans.*, 1990, 443; T. Karlen, A. Ludi, H. U. Güdel and H. Riesen, *Inorg. Chem.*, 1991, **30**, 2249.
4 J.-P. Collin, M. Beley, J.-P. Sauvage and F. Barigelletti, *Inorg. Chim. Acta*, 1991, **186**, 91.
5 E. C. Constable and M. J. Hannon, *Inorg. Chim. Acta*, 1993, **211**, 101.
6 E. C. Constable, A. M. W. Cargill Thompson and S. Greulich, *J. Chem. Soc., Chem. Commun.*, 1993, 1444; M. Beley, J.-P. Collin, R. Louis, B. Metz and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1991, **113**, 8521.
7 J. L. Kahl, K. W. Hanck and K. De Armond, *J. Inorg. Nucl. Chem.*, 1979, **41**, 495; W. A. Wickramasinghe, P. H. Bird and N. Serpone, *J. Chem. Soc., Chem. Commun.*, 1981, 1284; G. Nord, A. C. Hazell, R. G. Hazell and O. Farver, *Inorg. Chem.*, 1983, **22**, 3429; A. C. Hazell and R. G. Hazell, *Acta Crystallogr., Sect. C*, 1984, **C40**, 806; N. Serpone and M. A. Jamieson, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1986, vol. 4, p. 1097.
8 A. J. Skapski, V. F. Sutcliffe and G. B. Young, *J. Chem. Soc., Chem. Commun.*, 1985, 609.
9 S. Dholakia, F. L. Wimmer and R. D. Gillard, *Inorg. Chim. Acta*, 1983, **69**, 179; F. L. Wimmer and S. Wimmer, *Polyhedron*, 1985, **4**, 1665; P. Castan, J. Jaud, S. Wimmer and F. L. Wimmer, *J. Chem. Soc., Dalton Trans.*, 1991, 1155; P. S. Braterman, J.-I. Song, F. M. Wimmer, S. Wimmer, W. Kaim, A. Klein and R. D. Peacock, *Inorg. Chem.*, 1992, **31**, 5084.
10 P. Castan, F. Dahan, S. Wimmer and F. L. Wimmer, *J. Chem. Soc., Dalton Trans.*, 1990, 2971; S. Wimmer and F. L. Wimmer, *J. Chem. Soc., Dalton Trans.*, 1994, 879.
11 M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1993, 1321.
12 B. P. Sullivan, J. M. Calvert and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 1404.
13 CAChe work system, CAChe Scientific, Beaverton, OR, 1994.
14 G. R. Newkome and D. C. Hager, *J. Org. Chem.*, 1982, **47**, 599 and refs. therein; S. Hunig and I. Wehner, *Synthesis*, 1989, 552.
15 T. Kaufmann and R. Otter, *Chem. Ber.*, 1983, **116**, 479.
16 M. A. Hayes, C. Meckel, E. Schatz and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 703.
17 J. C. Jeffery and M. D. Ward, unpublished work.

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