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Structure, spectroscopic and electrochemical properties of novel binuclear ruthenium(II) copper(I) complexes with polypyridyl bridging ligands†

Sonya M. Scott,[a] **Keith C. Gordon** *[a] **and Anthony K. Burrell** *[b]

[a] *Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand.*
E-mail: kgordon@alkali.otago.ac.nz
[b] *Department of Chemistry, IFS, Massey University, Private Bag 11222, Palmerston North, New Zealand*

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Binuclear complexes of the type $[(bpy)_2Ru(BL)Cu(PPh_3)_2]^{3+}$, where bpy = 2,2′-bipyridine, BL = 2,3-di-2-pyridylpyrazine (dpp), 2,3-di-2-pyridylquinoxaline (dpq), or 6,7-dimethyl-2,3-di-2-pyridylquinoxaline ($dpqMe_2$), were readily formed by the reaction of $[Cu(PPh_3)_4]^+$ with mononuclear complexes $[Ru(bpy)_2(BL)]^{2+}$. The binuclear complexes are stable in CH_2Cl_2 solution at concentrations above 10^{-3} mol dm^{-3} having equilibrium constants for formation in the range 1000–2500 dm^3 mol^{-1}. Single crystal structures for $[(bpy)_2Ru(dpp)Cu(PPh_3)_2]^{3+}$ and $[(bpy)_2Ru(dpqMe_2)Cu(PPh_3)_2]^{3+}$ show distortions of the bridging ligand in the form of twisting and splaying of the ring systems. Electrochemical and UV/Visible data suggest the $\{Cu(PPh_3)_2\}^+$ moiety has little affect in stabilising the BL π* orbital. Resonance Raman spectra show the bichromophoric nature of the visible absorptions of the heteroleptic complexes; both bpy and BL ligand vibrations are enhanced depending on the excitation wavelength. Observation of a Ru–N vibration suggests that the dominant transition in the visible region is $Ru(d_\pi)\rightarrow BL(\pi^*)$ CT.

Introduction

There has been increased interest in recent years in the photochemical and electrochemical properties of supramolecular assemblies composed of mononuclear metal polypyridyl complexes.[1] Such systems have applications in solar energy harvesting[2] and in molecular device technology.[3] Of interest in the use of such assemblies is the possibility of programming them, through molecular design, so they may transduce energy in one particular direction. This is possible by using binuclear complexes with different metals, by having different terminal ligand substituents on each metal or by using asymmetric bridging ligands.[4]

A number of heterobimetallic systems have been studied using metals such as ruthenium(II)/osmium(II),[5] rhenium(I)/ruthenium(II)[6] or ruthenium(II) with chromium(III) and rhodium(III).[7] All of these heterobimetallics have metal sites with six-co-ordinate octahedral systems. d^6d^8 Heterobimetallic systems based on ruthenium(II) and platinum(II) have also been reported.[8] The ground and excited states of mononuclear complexes with these metals tend to have modest geometry changes upon photoexcitation into their metal-to-ligand charge-transfer (MLCT) excited states. Copper(I) polypyridyl complexes have significant co-ordination differences between the ground and ^{3}MLCT excited state,[9] as the formation of an excited state results in a copper(II) centre which prefers a five- or six-co-ordinate geometry. The synthesis of a binuclear system containing a ruthenium and copper site would produce a complex in which the excited state properties of the copper centre may be programmed by the steric substituents on the ligand.[10] The ruthenium site may be programmed using ligands which possess different electronic effects.[11]

Experimental

Complex synthesis

Mononuclear complexes, $[Ru(bpy)_2(dpp)][BF_4]_2$ **1**·$(BF_4)_2$ (dpp = 2,3-di-2-pyridylpyrazine), $[Ru(bpy)_2(dpq)][BF_4]_2$ **2**·$(BF_4)_2$ (dpq = 2,3-di-2-pyridylquinoxaline) and $[Ru(bpy)_2(dpqMe_2)][BF_4]_2$ **3**·$(BF_4)_2$ ($dpqMe_2$ = 6,7-dimethyl-2,3-di-2-pyridylquinoxaline), were prepared by literature procedures.[12]

$[(bpy)_2Ru(dpp)Cu(PPh_3)_2][BF_4]_3$ 4·$(BF_4)_3$. This was prepared by the addition of four equivalents (0.58 g (0.48 mmol)) of $[Cu(PPh_3)_4]BF_4$ to 0.1 g (0.12 mmol) of **1**·$(BF_4)_2$ in CH_2Cl_2 (10 mL). No change was observed from the original red-brown colour. The complex was recrystallised by diethyl ether diffusion and crystals collected. Yield 47% based upon ruthenium complex. Calc. for $[(bpy)_2Ru(dpp)Cu(PPh_3)_2][BF_4]_3\cdot 2CH_2Cl_2$: C, 51.91; H, 3.63; N, 6.72. Found: C, 52.43; H, 3.42; N, 6.40%. ^{1}H NMR ($CDCl_3$): δ 8.90 (m, 4 H); 8.12–8.38 (broad m, 8 H); 7.89–8.02 (broad m, 6 H); 7.45–7.72 (m, 8 H); 7.3–6.8 (m, 15 H, PPh_3) and 5.30 (s, CH_2Cl_2).

$[(bpy)_2Ru(dpq)Cu(PPh_3)_2][BF_4]_3$ 5·$(BF_4)_3$. This was prepared in an analogous fashion to complex **4** and recrystallised by ether diffusion. Yield 32% based upon ruthenium complex. Calc. for $[(bpy)_2Ru(dpq)Cu(PPh_3)_2][BF_4]_3$: C, 59.03; H, 3.90; N, 5.99. Found: C, 58.67; H, 3.71; N, 5.44%. ^{1}H NMR ($CDCl_3$): δ 8.70 (broad m, 4 H); 8.48 (broad m, 4 H); 8.15–8.05 (broad m, 8 H); 7.67 (td, 2 H); 7.64 (td, 2 H); 7.58 (d, 2 H); 7.48–7.35 (m, 6 H) and 7.3–6.8 (m, 15 H, PPh_3).

$[(bpy)_2Ru(dpqMe_2)Cu(PPh_3)_2][BF_4]_3$ 6·$(BF_4)_3$. This was prepared in an analogous fashion to complex **4** and recrystallised by ether diffusion. Yield 54% based upon ruthenium complex. Calc. for $[(bpy)_2Ru(dpqMe_2)Cu(PPh_3)_2][BF_4]_3\cdot CH_2Cl_2$: C, 55.73; H, 3.89; N, 6.75. Found: C, 55.84; H, 4.04; N, 7.08%. ^{1}H NMR ($CDCl_3$): δ 8.7 (broad m, 4 H); 8.5 (broad m, 4 H); 8.22

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† *Supplementary data available*: UV/Visible spectra for **1** and **2**. Available from BLDSC (No. SUP 57598, 1 pp.). See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

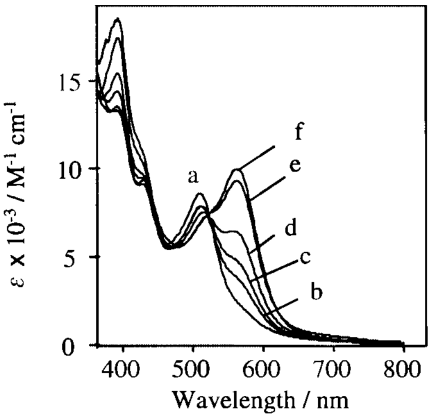

Fig. 1 Changes in the UV/Visible spectrum, in CH_2Cl_2, upon addition of $[Cu(PPh_3)_4]^+$ to **3**. Initial concentration of $\mathbf{3} = 1 \times 10^{-4}$ mol dm^{-3}; concentration of $[Cu(PPh_3)_4]^+$ is (a) 0, (b) 1×10^{-4}, (c) 2.5×10^{-4}, (d) 5×10^{-4}, (e) 1×10^{-2} and (f) 1×10^{-1} mol dm^{-3}.

(td, 2 H); 8.16 (td, 2 H); 8.06 (d, 2 H); 8.02 (s, 2 H); 7.99 (d, 2 H); 7.7 (broad m, 4 H); 7.5 (m, 4 H); 7.2–6.8 (m, 15 H, PPh_3) and 2.14 (s, 6 H, 2 CH_3).

Physical measurements

The instrumentation used in the measurement of UV/Visible, electrochemical and resonance Raman properties and the protocols used have been described elsewhere.[13]

Crystallography

Single crystals of complexes $\mathbf{4}\cdot(BF_4)_3\cdot2H_2O\cdot2CH_2Cl_2$ and $\mathbf{6}\cdot(BF_4)_3\cdot H_2O\cdot CH_2Cl_2$ were grown by slow diffusion of diethyl ether into a dichloromethane solution of $\mathbf{4}\cdot(BF_4)_3$ or $\mathbf{6}\cdot(BF_4)_3$, respectively. Red plate shaped crystals with approximate dimensions 0.26 × 0.18 × 0.15 and 0.26 × 0.25 × 0.24 mm were secured to the ends of glass fibres with cyanoacrylate glue and cooled to −100 °C in a nitrogen stream. Data collection, reduction, solution and refinement were performed as previously described.[13b,14,15]

Crystal data for $\mathbf{4}\cdot(BF_4)_3\cdot2H_2O\cdot2CH_2Cl_2$. $C_{72}H_{56}B_3Cl_4CuF_{12}N_8O_2Ru$, $M = 1694.03$, monoclinic, space group $P2_1/n$, $a = 12.905(3)$, $b = 13.264(3)$, $c = 45.357(4)$ Å, $\beta = 94.51(3)°$, $U = 7740(2)$ Å^3, $T = 173$ K, $Z = 4$, μ(Mo-Kα) = 0.727 mm^{-1}, 14852 reflections measured, 7242 unique ($R_{int} = 0.1652$) used in all calculations. The final $Rw(F_o^2) = 0.1826$ ($R(F_o) = 0.0745$).

Crystal data for $\mathbf{6}\cdot(BF_4)_3\cdot H_2O\cdot CH_2Cl_2$. $C_{77}H_{64}B_3Cl_2CuF_{12}N_8OP_2Ru$, $M = 1675.24$, triclinic, space group $P\bar{1}$, $a = 11.676(6)$, $b = 12.804(5)$, $c = 27.340(12)$ Å, $\alpha = 103.48(4)$, $\beta = 90.68(3)$, $\gamma = 112.34(3)°$, $U = 3671(3)$ Å^3, $T = 173$ K, $Z = 2$, μ(Mo-Kα) = 0.695 mm^{-1}, 7224 reflections measured, 6767 unique ($R_{int} = 0.0222$) used in all calculations. The final $Rw(F_o^2) = 0.1265$ ($R(F_o) = 0.0482$).

CCDC reference number 186/1541.

See http://www.rsc.org/suppdata/dt/1999/2669/ for crystallographic files in .cif format.

Results and discussion

It was found that the addition of $[Cu(PPh_3)_4]^+$ to solutions of complexes **1**, **2** and **3** resulted in a slight deepening in colour of the solutions. Fig. 1 shows the changes in the UV/Visible spectrum upon addition of $[Cu(PPh_3)_4]^+$ to **3**. Solutions of **1**, **2** and **3** containing an excess of $[Cu(PPh_3)_4]^+$ yielded crystalline samples of the binuclear complexes **4**, **5** and **6** respectively. Attempts to precipitate the binuclear complexes resulted in powdered samples containing mono- and bi-nuclear materials as a mixture. The paucity of the copper(I) to polypyridyl linkages also precluded the use of chromatography to purify the binuclear complexes. However the samples crystallised in a pure form and were used for microanalysis and physical measurements.

Table 1 Electronic absorption data for complexes in acetonitrile at 298 K

Complex	λ/nm (ε × 10^{-3}/dm^3 mol^{-1} cm^{-1})			
4		436 (12.7)	481 (12.8)	509sh (11)
5	387 (19.9)	421sh (12)		576 (14)
6	394 (25.9)	428sh (14)		563 (15.3)

sh = Shoulder.

The complexes were stable in the solid state, and in solution they remained stable, at sufficient concentration (see below), for a period of days. The changes in the UV/Visible spectra, in CH_2Cl_2 solution, as a function of concentration of $[Cu(PPh_3)_4]^+$ present provide a method of determining the equilibrium constant (K) for the formation of the binuclear complex: $K = [(bpy)_2Ru(BL)Cu(PPh_3)_2{}^{3+}]/[Ru(bpy)_2(BL)^{2+}]\cdot[Cu(PPh_3)_4{}^+]$. The series of spectra in Fig. 1 shows how the binuclear species, **6**, forms with increased concentrations of $[Cu(PPh_3)_4]^+$. If one assumes the binuclear complex is dominant at high concentrations of $[Cu(PPh_3)_4]^+$ then the intermediate spectrum, at which the band associated with the binuclear complex is half as intense as in the final spectrum, is measuring a system in which the concentration of $[Ru(bpy)_2(BL)]^{2+}$ (BL = bridging ligand) is equivalent to that of $[Ru(bpy)_2(BL)\cdot Cu(PPh_3)_2]^{3+}$. Assuming the concentration of $[Cu(PPh_3)_4]^+$ is much greater than those of the other species present then $K = 1/[Cu(PPh_3)_4]^+$. The values of K for the binuclear complexes based on the aforementioned assumptions are: $K(\mathbf{4}) = 1300$, $K(\mathbf{5}) = 2000$ and $K(\mathbf{6}) = 2500$ dm^3 mol^{-1}. The values are approximate, incorporating an error of 20%.

The dissociation of the binuclear complexes at low concentration meant that all physical measurements were made on solutions of 1×10^{-3} mol dm^{-3}. UV/Visible absorption data for 1×10^{-3} mol dm^{-3} solutions for samples **4**–**6** are shown in Table 1.

The structures of the complexes **4** and **6** are shown in Figs. 2 and 3, respectively. They are generally similar in that both contain the $\{Ru(bpy)_2\}^{2+}$ and $\{Cu(PPh_3)_2\}^+$ fragments co-ordinated at each of the binding sites on the ligands. While these binding sites are effectively equivalent, the extra aromatic ring and methyl groups on $dpqMe_2$ result in significant differences in the structures of complexes **4** and **6**. For example, the copper and ruthenium atoms are held at similar distances in each compound (6.82 Å distant in **4** and 6.88 Å distant in **6**). However little else is similar between the two complexes. This is most simply shown in Fig. 4 where the metals and bpy and PPh_3 ligands have been removed for clarity. The two related ligands appear to react to co-ordination in quite different fashions. The dpp ligand splays the two pyridyl groups apart, while $dpqMe_2$ both splays and twists the pyridyl groups. Surprisingly, the rest of the $dpqMe_2$ ligand appears unaffected by the distortions of the pyridyl groups. The consequence of these distortions is a major difference in the relative orientations of the $\{Cu(PPh_3)_2\}^+$ and $\{Ru(bpy)_2\}^{2+}$ fragments in **4** and **6**. In Figs. 2 and 3 the $\{Cu(PPh_3)_2\}^+$ portions are drawn from the same relative orientations to highlight the differences in orientation of the $\{Ru(bpy)_2\}^{2+}$ fragment. The reason for the differences in the distortions between **4** and **6** become apparent when CPK (Corey–Pauling–Koltun) models are examined. The space filling drawings shown in Fig. 5 indicate that the methyl groups on the $dpqMe_2$ are not causing the distortion because they are too distant from the co-ordination sites. However, the aromatic protons on the extra aromatic ring do cause significant steric

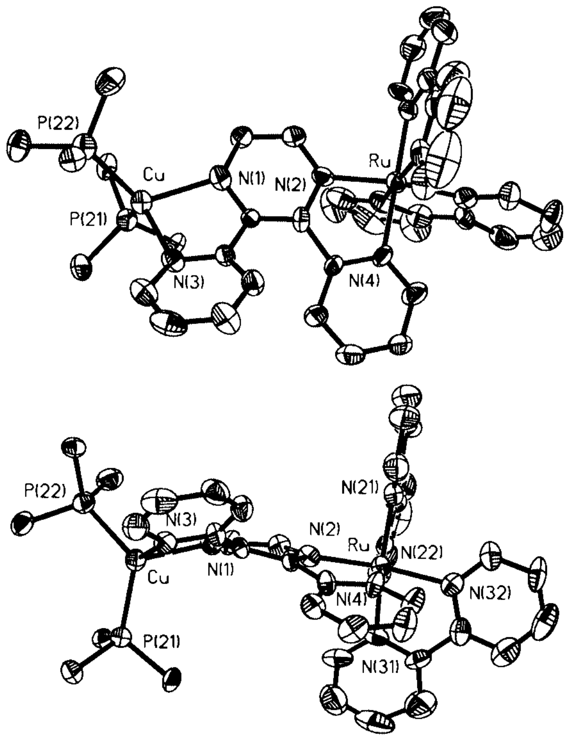

Fig. 2 An ORTEP[16] drawing of the cation of complex **4**. All but the *ipso*-carbons on the phenyl rings of the PPh_3 groups have been removed for clarity. Thermal ellipsoids are drawn at the 40% level.

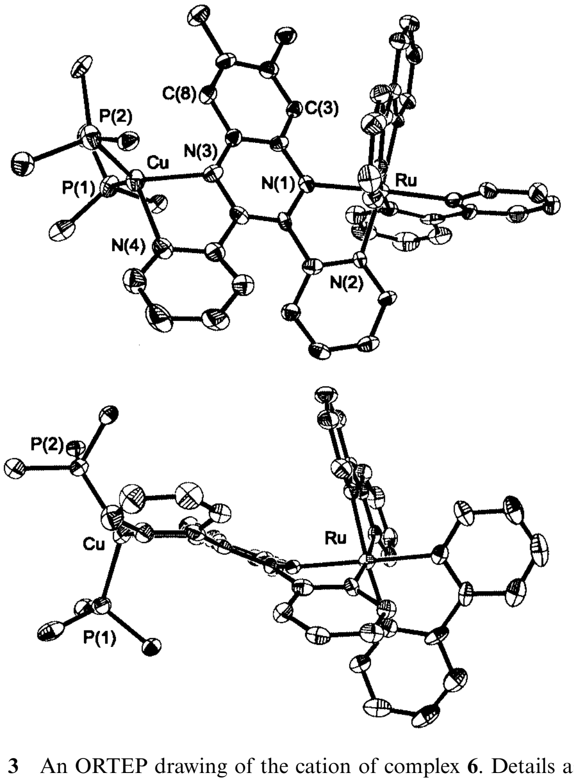

Fig. 3 An ORTEP drawing of the cation of complex **6**. Details as in Fig. 2.

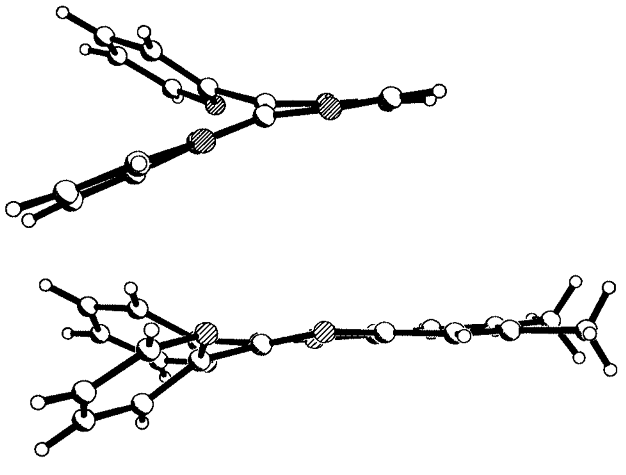

Fig. 4 Side on views of the dpp (top) and $dpqMe_2$ (bottom) ligands in complexes **4** and **6** respectively. The metal complexes have been removed for clarity.

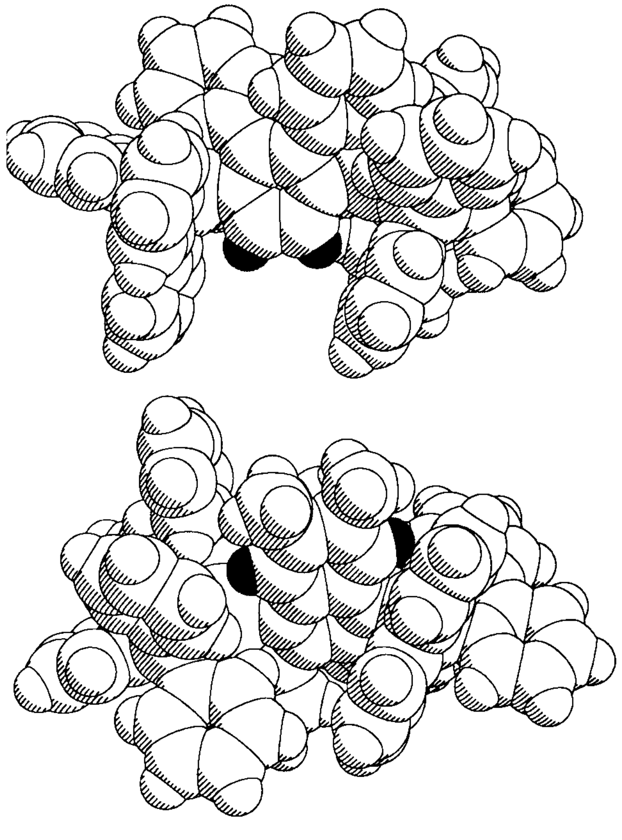

Fig. 5 Space filling drawings of complexes **4** (top) and **6** (bottom), with the aromatic protons of interest highlighted.

problems for the complexation on **6**. No such steric problems are apparent for **4**. The aromatic protons on **6** (dark) protrude directly in the positions that the $\{Ru(bpy)_2\}^{2+}$ occupies in **4**. To minimise unfavourable steric interactions the pyridyl groups on the $dpqMe_2$ ligand and both metal fragments on **6** distort from what could be considered the optimum geometry displayed by **4**. However, it is apparent that as the distortions in the $dpqMe_2$ ligand are restricted to the pyridyl groups changes in functionality on the body of the ligand should not affect the structure significantly, *i.e.* replacing methyl groups by hydrogens for example. This is relevant as there are no reported structures of bimetallic complexes involving $dpqMe_2$ although at least one structurally characterised complex is known.[17] In contrast a greater number of structurally characterised complexes of the dpq ligand[13,17–20] (where methyl groups are replaced by hydrogens) are known as well as the structure of the "free" ligand.[19] The only bimetallic complex involving dpq as a ligand is $[(Cu(PPh_3)_2)_2(dpq)]^{2+}$,[18] which shows none of the significant distortions observed in **6**. However, the structure of the $[Ru(dpq)(bpy)_2]^{2+}$ complex has been described[20] and although the distortions we note in **6** are not reported by the authors they are apparent in the structure. Clearly, the $\{Ru(bpy)_2\}^{2+}$ fragment is sterically demanding and its unique steric requirements are the dominant feature in the differences between the structures of **4** and **6**.

Table 2 Electrochemical data for complexes in acetonitrile at 298 K[a]

	$E^{\circ\prime}$/V			
Complex	Oxidation	Reduction		
1		1.38	−1.06	−1.48 (i)
2		1.40	−0.80	−1.48 (i)
3		1.37	−0.85	−1.49 (i)
4	1.0 (i)	1.47	−0.91	−1.46
5	0.9 (i)	1.49	−0.60	−1.38
6	0.8 (i)	1.45	−0.76	−1.40

[a] Potentials *versus* SCE ± 0.02 V. Supporting electrolyte 0.1 mol dm^{-3} NBu_4ClO_4. (i) = Irreversible process.

The electrochemical data for the ruthenium–copper complexes and their mononuclear counterparts are given in Table 2. The ruthenium(II) copper(I) binuclear complexes show an irreversible oxidation at 0.8 to 0.9 V *vs.* SCE. These are assigned as the oxidation $Cu^{I/II}$ couple. They lie at similar $E^{\circ\prime}$ values for other polypyridyl complexes with $\{Cu(PPh_3)_2\}^+$ moieties.[21] In the binuclear complexes, **4**–**6**, the first reduction is at less negative potentials than for the corresponding mononuclear ruthenium complexes. This reduction is assigned as $BL \longrightarrow BL^{\bullet -}$; consistent with this the ease of reduction follows the order dpq > $dpqMe_2$ > dpp. The reduction is made easier by *ca.* 0.1 V on binding of the $\{Cu(PPh_3)_2\}^+$ unit. This is considerably less than the stabilisation afforded on going from mono- to bi-nuclear complexes with $\{Re(CO)_3Cl\}$ or $\{Ru(bpy)_2\}^{2+}$ units. These stabilise by *ca.* 0.6 and 0.4 V respectively for the ligands used herein.[19,22] The $\{Cu(PPh_3)_2\}^+$ is less effective at stabilising the BL reduction because of its low charge and poor π-acid character.[23] The second reductions for **4**–**6** lie at *ca.* −1.4 V *vs.* SCE. These are at the $E^{\circ\prime}$ values associated with bpy reduction.[22,24]

The UV/Visible spectra of complexes **4**–**6** are consistent with the electrochemistry findings (Table 1). The strong visible absorptions observed for each of the complexes are assigned as MLCT Ru (d_π)→BL (π*). The energies of these transitions correlate with the ease of reduction of the bridging ligand. The shifts on going from mono- to bi-nuclear complexes for ruthenium(II) to ruthenium copper are less (*ca.* 2000 cm^{-1}) than those observed for ruthenium to a diruthenium complex (typically 3000 cm^{-1}).[24]

Resonance Raman spectra of complex **6** at a series of excitation wavelengths reveal something of the nature of the transitions in the region 450 to 632 nm (Fig. 6, Table 3). The resonance Raman spectrum at 457.9 nm is dominated by modes of 2,2′-bipyridine (bpy). These lie at 1599, 1564, 1490 and 1316 cm^{-1}.[25] They indicate that the dominant transition at this wavelength is Ru(d_π)→bpy(π*) charge transfer (CT) in nature. At 488 nm the intensity of the bpy modes is reduced with $dpqMe_2$ modes at 1468 and 1558 cm^{-1} increased in intensity. This trend continues at 514.5 and 632.8 nm. At 632.8 nm no bpy modes are observed; the spectrum shows features that are $dpqMe_2$ based. The Ru(d_π)→$dpqMe_2$(π*) and Cu(d_π)→$dpqMe_2$(π*) CT transitions can give rise to the enhancement of $dpqMe_2$ modes. The low wavenumber region of the resonance Raman spectrum shows very weak features. The most prominent of these is at 338 cm^{-1} and is assigned as a Ru–N stretch.[26] No bands are observed that may be assigned to the Cu–P stretch. Metal–phosphorus stretches for first row transition metals bonded to PPh_3 typically lie at less than 200 cm^{-1}.[27] The fact that the Ru–N band is enhanced suggests that the dominant transition in the visible region is Ru(d_π)→$dpqMe_2$(π*) CT. The complex appears stable in solution as there is no observable change in its electronic spectra over a period of hours. The resonance Raman spectrum of **6** in solution shows no features that could be assigned to the decomposition product **3**. The band positions for **4** and **5** are also presented in Table 3. These complexes behave in a very similar manner to that of **6**, with bpy modes enhanced at shorter wavelengths while the BL modes become enhanced to lower energy. No features of the monomers can be observed suggesting no detectable decomposition has occurred at the 1 mmol dm^{-3} concentrations used in these studies.

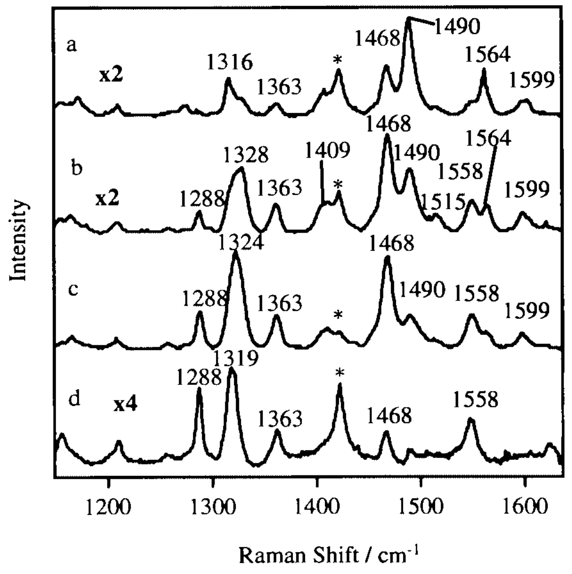

Fig. 6 Resonance Raman spectra of complex **6** in dichloromethane (1 × 10^{-3} mol dm^{-3}): (a) excitation wavelength = 457.9 nm, 30 mW; (b) excitation wavelength = 488 nm, 30 mW; (c) excitation wavelength = 514.5 nm, 30 mW; (d) excitation wavelength = 632.8 nm, 10 mW. * denotes solvent bands.

Electronic spectroelectrochemistry reveals that upon oxidation and reduction the binuclear complexes decompose to the mononuclear ruthenium(II) complexes within the timescale of the electrochemical experiment. This is unsurprising given the electrochemical data with the first oxidation being irreversible and the inherent instability of complexes with $\{Cu(PPh_3)_2\}^+$ to electrochemical oxidation and reduction processes.[21,23] We are currently investigating methods of increasing the electrochemical stability of such complexes.

The excited states of the complexes are weakly luminescent in CH_2Cl_2. Attempts to generate time-resolved resonance Raman spectra of the MLCT excited state of **4**–**6** by variable power single-colour experiments reveal that at low pulse energy a ground state spectrum is generated and as the power is increased several ground state features are reduced in intensity relative to solvent. However, no features are observed to grow in with increased photon flux at the excitation wavelength of 532 or 630.7 nm. The fact that only ground state features are observed, which appear barely affected by increased laser power, suggests that the excited state lifetime of **6** in CH_2Cl_2 is less than 5 ns.[28]

Conclusion

Crystal structures are presented for complexes **4** and **6**. Differences in orientations of the $\{Ru(bpy)_2\}^{2+}$ fragment are observed, caused by the presence of the aromatic protons on the extra aromatic ring as these protons on **6** protrude directly in the positions that the $\{Ru(bpy)_2\}^{2+}$ occupy in **4**.

The reduction of the BL occurs at a slightly more positive potential than is found in the monometallic ruthenium systems while a small red shift in the Ru→BL MLCT transition is found upon complexation of the $\{Cu(PPh_3)_2\}^+$ moiety. These small shifts are caused by the stabilisation of the ligand π* orbital by the substitution of the second metal centre. The changes observed are not as large as has been found for other bimetallic systems as the d^{10} copper system is not as efficient at stabilising the ligand π* orbital. Dilution of these complexes in CH_2Cl_2 below 5 × 10^{-4} mol dm^{-3} resulted in significant decomposition.

Table 3 Observed Raman bands (cm^{-1}) for complexes

	4		5		6		
λ_{exc}/nm	457.9	514.5	457.9	514.5	457.9	514.5	632.8
		1597w[a]		1598w[a]	1599w[a]	1599w[a]	
			1587w[b]	1587w[b]			
		1565w[a]	1563w[a]	1563w[a]	1564w[a]	1564w[a]	
	1554s[c]	1554s[c]			1558w[d]	1558w[d]	1558s[d]
	1508s[c]	1508s[c]			1515w[d]		
	1489s[a]	1489w[a]	1491s[a]	1491s[a]	1490s[a]	1490w[a]	
	1470w[c]	1470s[c]	1469s[b]	1469s[b]	1468s[d]	1468s[d]	1468w[d]
	1452w[c]	1452w[c]					
	1402w[c]	1402s[c]		1395w[b]	1409w[d]	1409w[d]	
				1362s[b]	1363w[d]	1363w[d]	1363w[d]
					1328w[d]	1324s[d]	
	1315w[a]	1315w[a]	1315w[a]	1314s[a]	1316w[a]		1319s[d]
		1301w					
				1281s[b]		1288w[d]	1288s[d]
	1267w[a]	1267s[a]					
	1246w[c]	1246s[c]					

s = Strong, w = weak. [a] bpy mode. [b] dpq mode. [c] dpp mode. [d] $dpqMe_2$ mode.

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