Synthesis and Co-ordination Behaviour of 6',6"-Bis(2-pyridyl)-2,2':4,4":2",2'''-quaterpyridine; 'Back-to-back' 2,2':6',2"- Terpyridine

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The oligopyridine 6',6"-bis(2-pyridyl)2,2':4,4":2",2'''-quaterpyridine (L) has been prepared. It may be regarded as a 'back-to-back' analogue of the well known 2,2':6'2"-terpyridine (terpy). Complexes with ruthenium(II) and palladium(II) have been characterised. The diruthenium(II) complex cation [(terpy)RuLRu(terpy)]$^{4+}$ has been shown to exhibit no Ru–Ru interactions, and behaves as two non-interacting Ru(terpy)$_2$ units.

Transition-metal complexes of the di-imine ligands 2,2'-bipyridine (L^1)[1] and 2,2':6',2"-terpyridine (terpy, L^2)[1,2] have been widely investigated, and it has been shown that a wide range of high and low oxidation states may be stabilised. These ligands have frequently been used to modify metal-centred properties (redox potentials, absorption maxima and absorption coefficient, emission spectra) through relatively well understood ligand-field effects. The ability to stabilise a range of oxidation states has led to studies of intra- and inter-molecular electron-transfer reactions in homo- and hetero-metallic systems, particularly with a view to elucidating mechanisms of biological electron-transfer reactions and facilitating electron transfer in photochemical and photoelectrochemical cells. Theoretical understanding of electron-transfer reactions is based upon systems with known equilibrium intermetallic distances. We and others have been particularly interested in the synthesis of polynuclear complexes which exhibit intramolecular interactions between metal ions.[3] Binuclear complexes incorporating bridging atoms and molecules are well known, and there has been considerable ingenuity in designing bridging ligands which mimic the behaviour of known mononucleating ligands. Ligands such as L^1 or L^2 have been modelled by pyrazine[4,5] and 4,4'-bipyridine.[5,6] An early report suggested that 2,3,5,6-tetrapyridylpyrazine (L^3) could not form binuclear complexes,[7] although more recently binuclear ruthenium complexes with this ligand have been described.[8] In this paper we describe the synthesis and some of the co-ordination properties of the novel potentially binucleating ligand 6',6"-bis(2-pyridyl)-2,2':4,4":2",2'''-quaterpyridine (L); this ligand may be regarded as a 'back-to-back' analogue of L^2 which does not have the steric restrictions associated with L^3.

Experimental

Proton and ^{13}C n.m.r. spectra were recorded on Brüker WM250 or AM400 spectrometers in CD$_2$Cl$_2$, CDCl$_3$, or CD$_3$SOCD$_3$ solution. Infra-red spectra were recorded on Perkin-Elmer 1710FT or 983 spectrophotometers in compressed KBr discs; fast-atom bombardment mass spectra were measured using a Kratos MS-50 spectrometer, and were loaded using acetonitrile as solvent with 3-nitrobenzyl alcohol as supporting matrix. Electrochemical experiments were performed with an Amel model 553 potentiostat connected to an Amel model 567 function generator and an Amel model 560-A recorder interface; all experiments were conducted using purified acetonitrile as solvent with 0.1 mol dm^{-3} [NBu$^n_4$][BF$_4$] as supporting electrolyte. For the cyclic voltammetry experiments, platinum beads were used as working and auxiliary electrodes with an Ag–AgCl electrode as reference; in all cases, ferrocene was added at the end of the experiment as an internal


L^3
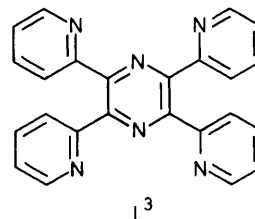
reference. All solvents and acetone were dried and distilled before use; [Ni(PPh$_3$)$_2$Cl$_2$][9] and [Ru(terpy)Cl$_3$][10] were prepared by the literature methods. 'Ruthenium trichloride trihydrate' and palladium acetate were used as supplied (Johnson Matthey).

Preparations.—1,5-*Bis*(2'-*pyridyl*)*pentane*-1,3,5-*trione* (L^4). A solution of acetone (1.84 cm^3, 25 mmol) and ethyl 2-pyridinecarboxylate (10.12 cm^3, 75 mmol) in 1,2-dimethoxyethane (50 cm^3) was added to a suspension of sodium hydride (50% dispersion in mineral oil, 5.0 g, 0.125 mmol NaH) in 1,2-dimethoxyethane (50 cm^3) maintained under an atmosphere of dry dinitrogen. The mixture was stirred at room temperature until a very vigorous reaction occurred and a bright orange suspension was obtained. This was then heated to reflux for 6 h, the solvent removed *in vacuo*, and the orange paste **CAUTIOUSLY** treated with water (100 cm^3). The orange solution was filtered through Celite, and the filtrate adjusted to pH 7 by dropwise addition of dilute hydrochloric acid. The yellow solid so obtained was collected by filtration and washed with water. The solid retains water tenaciously, and is best dried by dissolution in diethyl ether and drying the solution so obtained over anhydrous magnesium sulphate. Evaporation of the diethyl ether solution to dryness yields 1,5-bis(2'-pyridyl)pentane-1,3,5-trione (L^4) as a yellow solid (5.36 g, 80%), m.p. 103—105 °C, m/z 268 [electron-impact (e.i.) mass spectrum] (Found: C, 66.6; H, 4.7; N, 10.1. Calc. for C$_{15}$H$_{12}$N$_2$O$_3$: C, 67.2; H, 4.5; N, 10.5%).

2,6-*Bis*(2'-*pyridyl*)-4-*pyridone* (L^5). A solution of 1,5-bis-(2'-pyridyl)pentane-1,3,5-trione (2.0 g, 7.46 mmol) and ammonium acetate (4.0 g, excess) in ethanol (50 cm^3) was heated to reflux for 6 h, after which the dark brown solution was concentrated to half volume. The solution was cooled, and the white precipitate so formed was collected by filtration and washed well with diethyl ether. Recrystallisation from ethanol yielded white needles of compound L^5 (1.46 g, 80%), m.p. 166—168 °C, m/z 249 (e.i. mass spectrum) (Found: C, 71.9; H, 4.5; N, 16.6. Calc. for C$_{15}$H$_{11}$N$_3$O: C, 72.3; H, 4.4; N, 16.9%).

4'-*Chloro*-2,2':6',2"-*terpyridine* (L^6). A mixture of compound L^5 (1.0 g, 4.00 mmol) and PCl$_5$ (2.0 g, excess) in POCl$_3$ (50 cm^3) was heated to reflux for 12 h, after which the solvent was
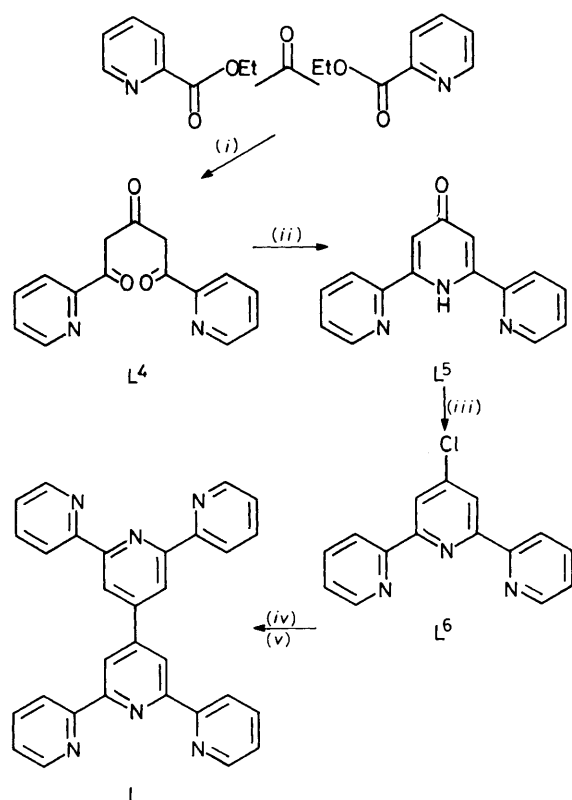
Scheme. (i)NaH, MeOCH$_2$CH$_2$OMe; (ii) [NH$_4$][O$_2$CMe], EtOH; (iii) PCl$_5$, POCl$_3$; (iv) [Ni(PPh$_3$)$_2$Cl$_2$], Zn, PPh$_3$, dmf; (v) NaCN

removed *in vacuo*. The residue was treated cautiously with water (50 cm^3) and the strongly acidic solution made basic with aqueous KOH solution. The white suspension so formed was extracted with CHCl$_3$ (3 × 30 cm^3), the extract dried (MgSO$_4$) and evaporated to dryness. The pale brown solid so obtained was recrystallised from methanol (charcoal decolorisation) to yield off-white needles which were collected by filtration and washed well with diethyl ether. Recrystallisation from ethanol yielded white needles of 4'-chloro-2,2':6',2''-terpyridine (L^6) (0.58 g, 62%), m.p. 149—152 °C, *m/z* 267/269 (e.i. mass spectrum) (Found: C, 67.0; H, 3.8; N, 15.8. Calc. for C$_{15}$H$_{10}$ClN$_3$: C, 67.3; H, 3.7; N, 15.7%).

6',6''-Bis(2-pyridyl)-2,2':4',4'':2'',2'''-quaterpyridine (L). A solution of [Ni(PPh$_3$)$_2$Cl$_2$] (5.89 g, 9.0 mmol) and PPh$_3$ (4.71 g, 18 mmol) in dimethylformamide (dmf) (25 cm^3) was treated with zinc dust (0.59 g, 9 mmol) and the mixture stirred for 30 min to give a deep red suspension. This suspension was treated with 4'-chloro-2,2':6',2''-terpyridine (1.2 g, 9 mmol) which resulted in an immediate colour change to dark green. After stirring at room temperature for 8 h the solvent was removed *in vacuo* and the residue boiled with water (100 cm^3) for 10 min. The suspension was filtered and the green-brown filtrate treated with ammonium hexafluorophosphate (3.0 g, 18 mmol) and the precipitate so formed was collected by filtration. The solid was dissolved in aqueous acetonitrile (1:4, 100 cm^3) and heated to reflux with sodium cyanide (3.0 g) for 1 h. The yellow solid which separated was collected by filtration, washed well with methanol and dried to yield 6',6''-bis(2-pyridyl)-2,2':4',4'':2'',2'''-quater-pyridine (L) (20—70%), (m.p. 318—321 °C, *m/z* 464 and 232 (e.i. mass spectrum) (Found: C, 77.1; H, 4.0; N, 17.8. Calc. for C$_{30}$H$_{20}$N$_6$: C, 77.6; H, 4.3; N, 17.8%).

[(terpy)RuLRu(terpy)][PF$_6$]$_4$. A mixture of L (0.05 g, 0.11 mmol) and [Ru(terpy)Cl$_3$] (0.095 g, 0.22 mmol) in methanol (25 cm^3) was heated to reflux for 24 h to yield a deep red

solution. This was filtered, and the filtrate treated with ammonium hexafluorophosphate. The dark red crystalline product was collected by filtration and recrystallised twice by the diffusion of diethyl ether vapour into an acetonitrile solution to yield [(terpy)RuLRu(terpy)][PF$_6$]$_4$ (Found: C, 40.5; H, 2.4; N, 10.0. Calc. for C$_{60}$H$_{42}$F$_{24}$N$_{12}$P$_4$Ru$_2$: C, 42.0; H, 2.5; N, 9.8%).

[(MeCO$_2$)PdLPd(O$_2$CMe)][PF$_6$]$_2$. A mixture of L (0.05 g, 0.11 mmol) and palladium(II) acetate (0.05 g, 0.22 mmol) in methanol (25 cm^3) was heated to reflux for 5 min, whereupon a clear solution had been obtained. This was treated with ammonium hexafluorophosphate to yield a yellow-brown precipitate which was collected by filtration and recrystallised by diffusion of diethyl ether vapour into a dmf solution to yield yellow microcrystals (Found: C, 37.3; H, 2.7; N, 8.0. Calc. for C$_{34}$H$_{26}$F$_{12}$N$_6$O$_4$P$_2$Pd$_2$: C, 42.0; H, 2.5; N, 7.7%).

Results and Discussion

The novel potentially binucleating ligand L was prepared as shown in the Scheme. The strategy adopted involved the preparation of a 4'-substituted 2,2':6',2''-terpyridine by ring synthesis of the central pyridine ring, followed by C–C bond formation through the 4' positions of two 2,2':6',2''-terpyridine units. The key intermediate for the synthesis of the 4-substituted 2,2':6',2''-terpyridine is the 1,3,5-trione L^4 which is prepared by analogy with the known 3-pyridyl analogue.[11] The compound is obtained in 80% yield by the reaction of 2 equivalents of ethyl pyridine-2-carboxylate with (effectively) the dianion of acetone as a bright orange solid. The compound is insoluble in water, but very readily soluble in acid or base and all common organic solvents. The e.i. mass spectrum exhibits the expected parent ion at *m/z* 268. The ^{1}H n.m.r. spectrum is complex, and it is clear that three of the possible keto-enol tautomers are present in solution, as has been reported for other 1,3,5-triketones.[12] The reaction of the triketone with [NH$_4$][O$_2$CMe] in ethanol results in the formation of compound L^5 in 80% yield. This exhibited the expected parent ion in the e.i. mass spectrum (*m/z* 249) and a simple ^{1}H n.m.r. spectrum (Table). In CD$_3$SOCD$_3$ solution the NH resonance is observed at δ 11.0. Prolonged reaction of L^5 with PCl$_5$ in boiling POCl$_3$ yields 4'-chloro-2,2':6',2''-terpyridine (L^6) in 62% yield. The e.i. mass (*m/z* 267/269) and ^{1}H n.m.r. spectra (Table) were fully in accord with the proposed structure. The corresponding 4'-bromo compound could be prepared by the reaction of L^6 with HBr in acetic acid.[13]

We investigated a wide range of methods for the conversion of L^6 into the desired 6',6''-bis(2-pyridyl)-2,2':4',4'':2'',2'''-quaterpyridine (L). Conventional Ullman couplings using metallic copper or copper alloys were unsuccessful, but nickel(0) reagents proved to be satisfactory.[14] The best yields were obtained using stoicheiometric amounts of [Ni(PPh$_3$)$_2$Cl$_2$] reduced *in situ* by metallic zinc in the presence of an excess of PPh$_3$. Lower yields were obtained when the nickel(0) reagent was generated from [Ni(H$_2$O)$_6$]Cl$_2$ or when catalytic amounts of the nickel complexes were used. This latter problem is associated with the formation of nickel(II) complexes of L^6 and L. Indeed, the desired compound L is obtained from the coupling reaction as its nickel(II) complex, and is only obtained free after demetallation with cyanide. Yields in these reactions vary between 20 and 70%. The new ligand L is a pale yellow solid, moderately soluble in toluene, which exhibits peaks at *m/z* 464 and 232 in the e.i. mass spectrum. The ^{1}H n.m.r. spectrum (Table and Figure 1) shows five resonances. The most noticeable features are the large downfield shift of the singlet assigned to H$^{3',5'}$ and the shift of H^3 to lower field than that of H^6. This latter feature is particularly surprising as the terminal rings are not expected to be *directly* affected by the 4' substitution, and with 2,2':6',2''-terpyridine itself H^6 is to lower field. Although no crystallographic study of 2,2':6',2''-terpyridine has been

Table.

	L					terpy					
	6	5	4	3	3'[a]	6	5	4	3	3'	4'
L[5b]	8.70	7.48	7.98	8.59	7.87						
L[6c]	8.71	7.37	7.88	8.60	8.49						
L[d]	8.53	6.81	7.37	8.72	9.33						
terpy[e]						8.70	7.33	7.86	8.62	8.46	7.96
[Ru(terpy)$_2$]$^{2+}$ [e]						7.34	7.17	7.92	8.50	8.76	8.42
[Ru$_2$(terpy)$_2$L]$^{3+}$	7.48	7.29	8.10	8.90	9.48	7.47	7.21	8.00	8.57	8.82	8.50

[a] 3' = 5'. [b] In CD$_2$Cl$_2$. [c] In CDCl$_3$. [d] In C$_6$D$_5$CD$_3$. [e] In CD$_3$CN.
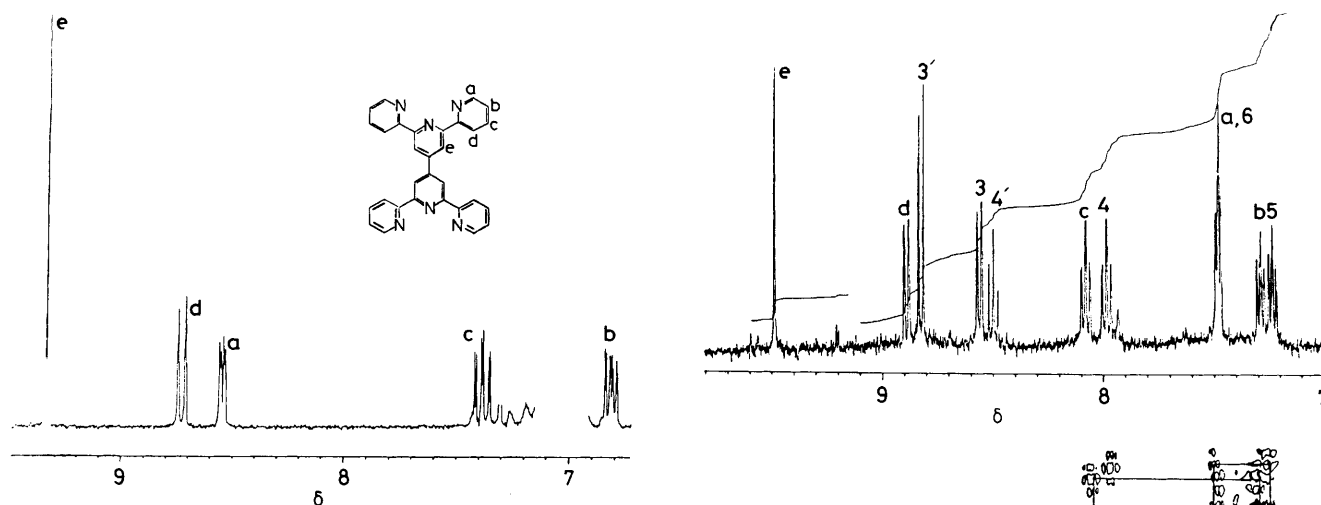
Figure 1. 250-MHz Proton n.m.r. spectrum of a C$_6$D$_5$CD$_3$ solution of L. peaks due to partially protonated solvent have been removed

Figure 2. 400-MHz Proton n.m.r. and double-quantum-filtered COSY spectrum of a CD$_3$CN solution of [(terpy)RuLRu(terpy)][PF$_6$]$_4$

reported, we have determined the structure of 4'-phenyl-2,2':6',2"-terpyridine and demonstrated that the terminal rings adopt a transoid configuration with respect to the central ring.[2,15] In solution a similar configuration is expected, although a greater degree of twisting about the interannular bond is anticipated. It is significant that both H^3 and H$^{3'}$ are shifted downfield; we believe this to be indicative of the adoption of the cisoid configuration, with the downfield shifts due to deshielding van der Waals interactions of the type well characterised in the tris complexes of 2,2'-bipyridine, for which the lowest-field resonances are those due to H^3.[5,16]

The reaction of 1 equivalent of L with 2 equivalents of [Ru(terpy)Cl$_3$] in methanol in the presence of the reducing agent N-ethylmorpholine resulted in the formation of an intensely coloured deep red solution. Treatment of this solution with ammonium hexafluorophosphate resulted in the precipitation of a purple complex for which microanalysis suggested a formulation [(terpy)RuLRu(terpy)][PF$_6$]$_4$. The fast-atom bombardment mass spectrum of the compound in a 3-nitrobenzyl alcohol matrix exhibited peaks at m/z 1 569, 1 424, 1 279, 944, 799, 713, and 568 (based on [102]Ru) corresponding to [Ru$_2$(terpy)$_2$L(PF$_6$)$_3$]$^+$, [Ru$_2$(terpy)$_2$L(PF$_6$)$_2$]$^+$, [Ru$_2$(terpy)$_2$-L(PF$_6$)]$^+$, [Ru$_2$(terpy)L(PF$_6$)]$^+$, [Ru$_2$(terpy)L]$^+$, [Ru(terpy)$_2$(PF$_6$)]$^+$, and [Ru(terpy)$_2$]$^+$ respectively. All peaks exhibited the correct isotopic distribution patterns for the formulations. The ^{1}H n.m.r. spectrum of the complex in CD$_3$CN solution is shown in Figure 2. As expected, the spectrum exhibits eleven resonances, six from the two equivalent 2,2':6',2"-terpyridine ligands and five from the bridging ligand L. The observation of the eleven resonances confirms that a Ru(terpy) fragment is co-ordinated to each end of the ligand L, and also
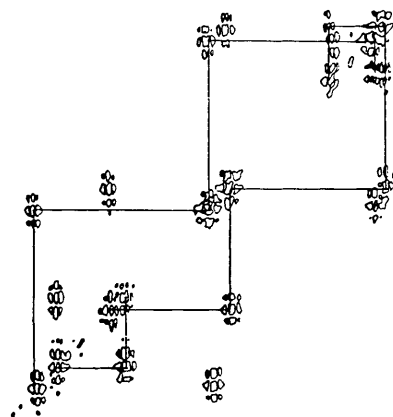
confirms the symmetrical structure of the complex on the n.m.r. time-scale. The singlet at δ 9.48 is unambiguously assigned to the equivalent H$^{3',5',3'',5''}$ protons of L. The remaining resonances were assigned upon the double-quantum-filtered correlation spectroscopy (COSY) experiment (Figure 2). The two types of terminal pyridyl rings from the ligand L and the 2,2':6',2"- terpyridine are clearly seen as two sets of four coupled resonances, with the resonances at δ 7.47, 7.21, 8.00, and 8.57 comprising one ring, whilst those at δ 7.48, 7.29, 8.10, and 8.90 comprise the second [both given in the sequence H^6,H^5,H^4,H^3, made on the basis of the differing coupling constants J(H^{5}H^6) and J(H^{3}H^4)]. The remaining two resonances at δ 8.82 and 8.50 are assigned to H^{3,5} and H^4 of the central pyridine ring of the 2,2':6',2"-terpyridine respectively. The assignment of the resonances δ 7.47, 7.21, 8.00, and 8.57 to the 2,2':6',2"-terpyridine ligand is on the basis of a nuclear Overhauser enhancement (n.O.e.) from the resonance at δ 8.82 to that at δ 8.57, and by analogy with the chemical shifts of [Ru(terpy)$_2$]$^{2+}$
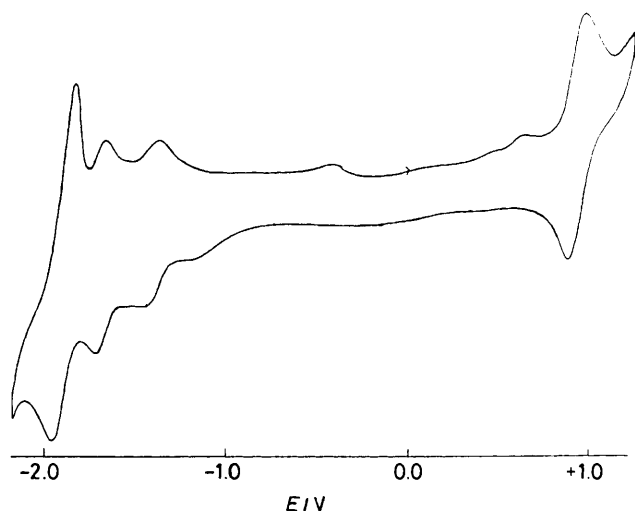
Figure 3. Cyclic voltammogram of [(terpy)RuLRu(terpy)][PF$_6$]$_4$ (MeCN, [NBu$^n_4$][BF$_4$] supporting electrolyte, 200 mV s^{-1}, potentials quoted vs. internal ferrocene added at the end of the experiment)

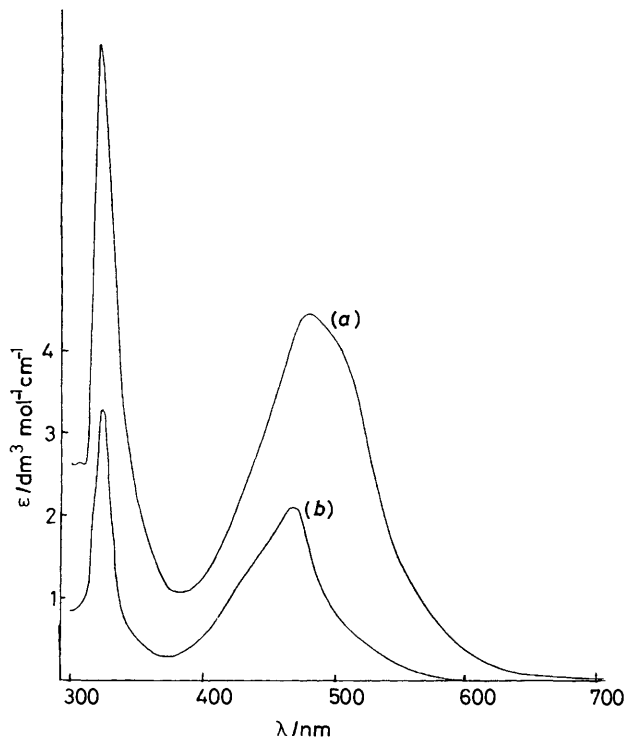Figure 4. Electronic spectra of 0.01 mol dm^{-3} ethanolic solutions of (a) [Ru$_2$(terpy)$_2$L]$^{4+}$ and (b) [Ru(terpy)$_2$]$^{2+}$

and [(terpy)RuL^{3}Ru(terpy)].[8] Assignments are presented in the Table.

The complex [(terpy)RuLRu(terpy)][PF$_6$]$_4$ is electrochemically active, and the cyclic voltammogram of a solution in MeCN is shown in Figure 3. A single quasi-reversible (ΔE_p = 80—90 mV at scan rate 200 mV s^{-1}) oxidation to ruthenium(III) is observed at +0.92 V vs. ferrocene–ferrocenium (+1.47 V vs. n.h.e.). This oxidation wave of the binuclear complex is at a near-identical potential to the oxidation wave of the mononuclear analogue [Ru(terpy)$_2$][PF$_6$]$_2$, which is oxidised at a potential of +0.90 V vs. ferrocene–ferrocenium in acetonitrile. No further oxidation waves could be observed within the solvent window, in direct contrast to the observation of two oxidation processes
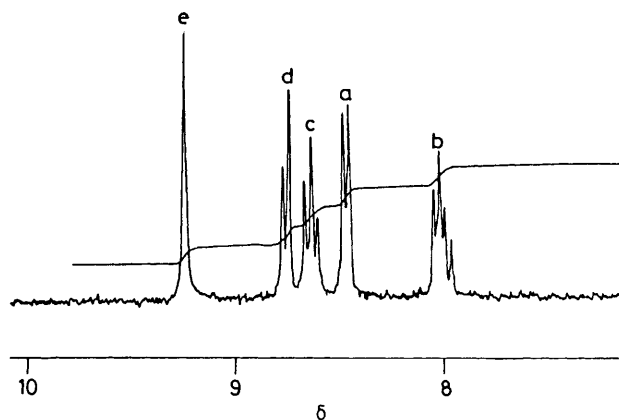

Figure 5. 250-MHz Proton n.m.r. spectrum of [(MeCO$_2$)PdLPd-(O$_2$CMe)][PF$_6$]$_2$ in CD$_3$SOCD$_3$

for [(terpy)RuL^{3}Ru(terpy)]$^{4+}$ (0.743 and 1.123 V) and [(NH$_3$)$_3$RuL^{3}Ru(NH$_3$)$_3$]$^{4+}$ (0.503 and 1.00 V vs. ferrocene–ferrocenium).[8] The presence of a single oxidation potential within the solvent window at all scan rates suggests that the two ruthenium centres in the binuclear complex are oxidising at the same potential, as is expected for non-interacting centres in similar (or identical) environments. A controlled-potential electrolysis of the solution at +1.02 V resulted in the loss of the deep red colour characteristic of the bis ruthenium(II) complex, and the formation of a pale green solution. Coulometry indicated the passage of two electrons per mol of complex in this process. This green solution is paramagnetic and e.s.r. active; a frozen acetonitrile glass exhibits a weak, featureless absorption at g = 2.07. From these data it is evident that the new ligand L is not as efficient as the substituted pyrazine in effecting metal–metal interactions. We ascribe this to the binuclear complex adopting a conformation in which the two 'terpyridine' fragments of the ligand L are mutually perpendicular. This relieves any steric interactions between the 3 protons at the expense of conjugation and π overlap between the two 'terpyridine' moieties.

The complex also exhibits two clean reductive waves in its cyclic voltammogram at −1.41 (ΔE_p = 70) and −1.70 V (ΔE_p = 50 mV) and a third process centred at −1.90 V which is partially obscured by an absorption spike (all potentials quoted vs. ferrocene–ferrocenium). These values closely parallel those observed for [Ru(terpy)$_2$]$^{2+}$ (−1.58 and −1.82 V), and differ markedly from those reported for [(terpy)RuL^{3}Ru(terpy)]$^{4+}$ and [(NH$_3$)$_3$RuL^{3}Ru(NH$_3$)$_3$]$^{4+}$.[8] Once again, this suggests that the complex of L is best regarded as two non-interacting Ru(terpy)$_2$ fragments.

The electronic spectrum of a methanol solution of [(terpy)-RuLRu(terpy)]$^{4+}$ is shown in Figure 4, together with that of [Ru(terpy)$_2$]$^{2+}$; the spectra very closely resemble one another with λ_{max} for [(terpy)RuLRu(terpy)]$^{4+}$ at 470 nm and for [Ru(terpy)$_2$]$^{2+}$ at 482 nm, the major difference being that the absorption coefficient of [(terpy)RuLRu(terpy)]$^{4+}$ is approximately twice that of [Ru(terpy)$_2$]$^{2+}$. This also supports the formulation of the complex in terms of two non-interacting Ru(terpy)$_2$ fragments.

We have also prepared the complex [(MeCO$_2$)PdLPd-(O$_2$CMe)][PF$_6$]$_2$ by the reaction of L with palladium(II) acetate followed by treatment with ammonium hexafluorophosphate. The compound is obtained as a pale yellow microcrystalline solid after recrystallisation from dmf by the diffusion of diethyl ether vapour. The ^{1}H n.m.r. spectrum is shown in Figure 5, and clearly demonstrates the presence of the ligand L in a single environment. The spectrum exhibits a

dramatic downfield shift of the resonance assigned to H_c, as is observed for H^4 in palladium 2,2'-bipyridine and 2,2':6',2"-terpyridine complexes. The co-ordinated acetate ligands are assumed to be monodentate on the basis of the observation of two modes in the i.r. spectrum (1 562 and 1 367 cm^{-1}, $\Delta v = 195$ cm^{-1}).[17] The fast atom bombardment mass spectrum of the complex exhibits peaks assigned to $[PdL]^+$, $[Pd_2L]^+$, $[Pd_2L + 166]^+$, $[Pd_2L + 166 + 166]^+$, and $[Pd_2L(PF_6) + 166 + 166]^+$. The observation of peaks at $+166$ mass units is a common feature we have observed in the mass spectra of complexes containing free or co-ordinated acetate groups. We believe that these peaks arise from a reaction of the acetate with the 3-nitrobenzyl alcohol, with replacement of the nitro group by an acetato group.

In conclusion, we have prepared a novel bridging ligand which behaves as a 'back-to-back' analogue of 2,2':6',2"-terpyridine. The cyclic voltammogram of the binuclear di-ruthenium(II) complex cation $[(terpy)RuLRu(terpy)]^{4+}$ indicates no interactions between the metal centres. We are currently investigating the co-ordination chemistry of other binucleating ligands which do not possess the steric restraints which we believe to be responsible for forcing two 'terpyridine' fragments to adopt a perpendicular arrangement in the complexes.

Acknowledgements

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