Multinucleating 2,2′:6′,2″-Terpyridine Ligands as Building Blocks for the Assembly of Co-ordination Polymers and Oligomers

Edwin C. Constable* and Alexander M. W. Cargill Thompson
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

The co-ordination properties of the tridentate ligand 2,2′:6′,2″-terpyridine (terpy) make it an ideal structural unit from which to assemble co-ordination oligomers and polymers with a linear connectivity about the metal centre. The dinucleating 'back-to-back' 2,2′:6′2″-terpyridine ligands 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine L^1 and 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene L^2 give rise to a linear connectivity at the ligand, whereas 1,3,5-tris(2,2′:6′,2″-terpyridin-4′-yl)benzene L^3 is a trinucleating species which can give rise to arrays with a connectivity of three at the ligand. The co-ordination oligomers $[(X\text{-terpy})RuLRu(X\text{-terpy})]^{4+}$ (L = L^1 or L^2) and $[\{(X\text{-terpy})Ru\}_3L^3]^{6+}$ (X-terpy = 4′-substituted 2,2′:6′,2″-terpyridine) have been prepared and characterised for a variety of electron-donating and -withdrawing substituent groups X.

Co-ordination oligomers and polymers can be prepared by the interaction of suitable metal ions with multidentate ligands designed for multinuclear binding.[1] The simplest structural requirement for such a ligand is two polydentate functionalities linked by a spacer group. Such a ligand will give rise to an oligomer with a connectivity of two at the ligand; this will be denoted [2]. Three or more polydentate functionalities may be linked by a spacer group to give oligomers with connectivities of [3] or higher at the ligand. The oligopyridines are ideal functionalities to incorporate into ligands for this application, as they spontaneously undergo self-assembly with a wide variety of metal ions to give stable, relatively non-labile complexes.[2] 2,2′-Bipyridine (bipy) functionalities bind metals favourably, but give rise to stereoisomerism at six-co-ordinate centres due to their didentate nature. A complex cation $[M(bipy)_3]^{n+}$ exists in two enantiomeric forms. If the bipy ligand bears a single substituent, two geometrical forms with *facial* or *meridional* arrangements are found; each of these isomers can exist as one of two enantiomers (Fig. 1). A further drawback is that the co-ordination of three bipyridyl units to a six-co-ordinate metal centre would give rise to complex spatial properties in any oligomers or polymers formed. The assembly of two or more $[M(bipy)_3]^{n+}$ units into an oligomer will result in the possibility of many different diastereomers. Although the mononuclear enantiomeric pairs possess identical *chemical* properties, the diastereomers possess different relative spatial arrangements of the metal centres, and hence differing electronic, electrochemical and photophysical properties. Even if oligomers assembled with the specific formation of *meridional* or *facial* isomers, it is unlikely that single diastereomeric species would be formed (for example, equal mixtures of all Δ and all Λ oligomers). The formation of an oligomer from a ligand which presents a single monosubstituted 2,2′-bipyridyl group to each six-co-ordinate metal may be said to possess a connectivity of [3] at the metal. It is possible to control the spatial properties of co-ordination oligomers at both the *metal* and the *ligand* centres (Fig. 2). In contrast to the behaviour with bipy, a six-co-ordinate metal forms a single isomer of the achiral $[M(terpy)_2]^{n+}$ complex cation upon reaction with 2,2′:6′,2″-terpyridine (terpy). The introduction of a single substituent onto terpy ligands presents no additional problems; there is a single geometric isomer of the $[M(terpy)_2]^{n+}$ cation (Fig. 1). We have, therefore, investigated the use of 4′-substituted 2,2′:6′,2″-terpyridyl (X-terpy) functionalities in the assembly of co-ordination oligomers and polymers. Furthermore, the connectivity of tridentate terpyridine ligands at a six-co-ordinate metal centre is [2], hence the spatial properties of the oligomers and polymers produced are simply controlled by the arrangement of the terpyridinyl units in the multinucleating ligand.[1,3] For this reason, we have concentrated on the use of multinucleating ligands containing the 2,2′:6′,2″-terpyridinyl functionality to assemble co-ordination oligomers.

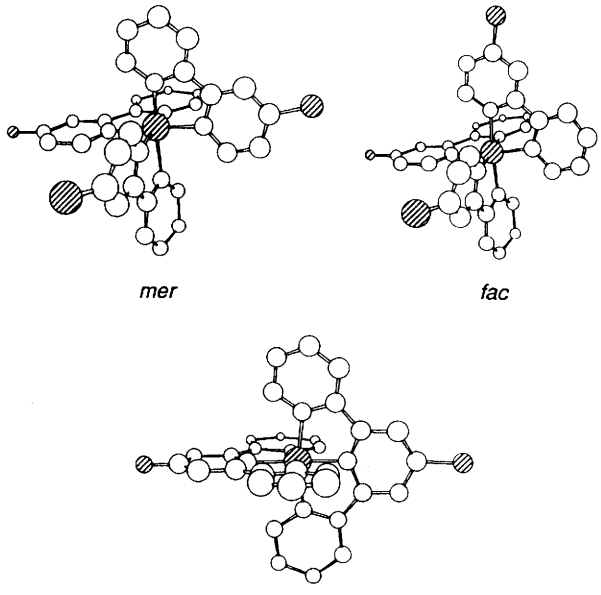


Fig. 1 Stereochemical consequences associated with the formation of six-co-ordinate tris(2,2′-bipyridine) and bis(2,2′:6′,2″-terpyridine) complexes

The binucleating 'back-to-back' 2,2′:6′,2″-terpyridine ligands 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine L^1 (ref. 4) and 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene L^2 (ref. 5) (Fig. 3) can be used to assemble infinite linear co-ordination polymers, or discrete oligomers if mononucleating terpyridine ligands are used to terminate the chains (Fig. 4). In order to investigate the interactions of the metal centres in such polymers, we have prepared the sixteen binuclear species [(X-

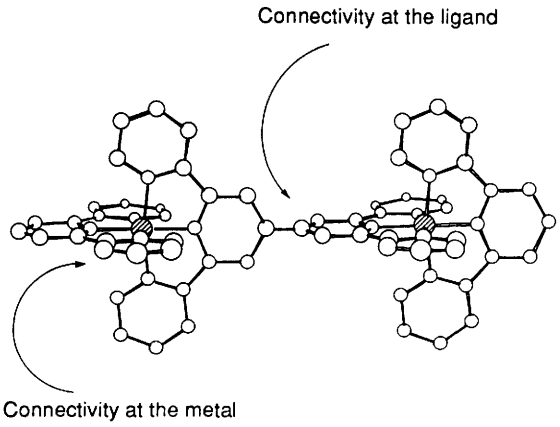


Fig. 2 General scheme indicating the ways in which the connectivity in co-ordination polymers may be controlled. The generic structure assumes a sterically favoured orthogonal arrangement of the terpy functionalities at the interannular connection

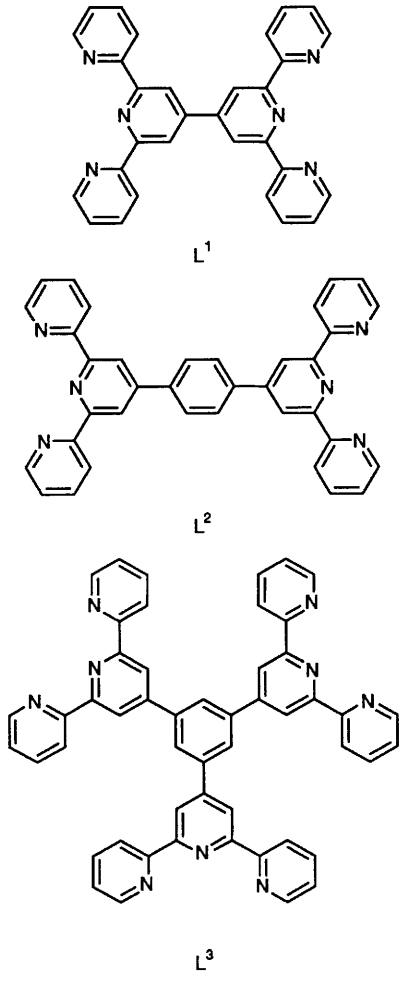


Fig. 3 The multinucleating ligands 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine L^1, 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene L^2 and 1,3,5-tris(2,2′:6′,2″-terpyridin-4′-yl)benzene L^3

terpy)RuLRu(X-terpy)]$^{4+}$ (L = L^1 or L^2; X = H, OH, OEt, Cl, Ph, NMe_2, SMe or SO_2Me). We have also designed and prepared the novel trinucleating tris-terpyridine ligand 1,3,5-tris(2,2′:6′,2″-terpyridin-4′-yl)benzene L^3 (ref. 6) which acts as a branch point with a connectivity of [3], and report the synthesis and characterisation of the eight trinuclear species [{(X-terpy)Ru}$_3L^3$]$^{6+}$ (X = H, OH, OEt, Cl, Ph, NMe_2, SMe or SO_2Me).

Experimental

Proton NMR spectra were recorded on a Bruker WM-250 spectrometer. Infrared spectra were recorded on a Philips PU9624 Fourier-transform spectrophotometer in compressed KBr discs; electronic spectra were recorded on a PU8730 scanning spectrophotometer. Fast atom bombardment (FAB), fast ion bombardment (FIB) and electron impact (EI) mass spectra were recorded on Kratos MS-890, Kratos MS-50 or Kratos MS-902 spectrometers; for FAB and FIB spectra, the sample was loaded using acetonitrile as solvent, and 3-nitrobenzyl alcohol as supporting matrix. Cyclic voltammetry experiments were performed using an Amel model 553 potentiostat, connected to an Amel model 567 function generator, and an Amel model 560-A recorder interface, using platinum bead working and auxiliary electrodes, with Ag–AgCl or $Ag-Ag^+$ electrodes as references. The experiments were conducted using purified acetonitrile as solvent and 0.1 mol dm^{-3} [NBu^n_4][BF_4] as supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference.

2-Acetylpyridine, benzene-1,4-dicarbaldehyde and benzene-1,3,5-tricarbonyl trichloride, were used as supplied by Aldrich. Benzene-1,3,5-tricarbaldehyde,[7] *N*-[2-oxo-2-(2′-pyridyl)-ethyl]pyridinium iodide,[5] 4′-methylthio-2,2′:6′,2″-terpyridine (MeS-terpy)[8] and 4′-(methylsulfonyl)-2,2′:6′,2″-terpyridine (MeO_2S-terpy)[8] were prepared by the literature methods. The complexes [Ru(X-terpy)Cl_3] (X = H, OH, OEt, Cl, Ph, MeS, MeO_2S or NMe_2) were prepared as previously reported.[9,10]

Preparations.—*6′,6″-Bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine* L^1. The complex [$Ni(PPh_3)_2Cl_2$] (3.93 g, 6.0 mmol) and PPh_3 (3.14 g, 12.0 mmol) were added to degassed dimethylformamide (50 cm^3) and stirred for 10 min to give a blue solution. Zinc dust (0.40 g, 6.0 mmol) was added, and over the next 0.5 h the colour of the resulting suspension changed to green, brown and finally red. 4′-Chloro-2,2′:6′,2″-terpyridine (Cl-terpy) (0.80 g, 3.0 mmol) was added, resulting in an immediate colour change to green-brown. The suspension was stirred at room temperature under nitrogen for 8 h. The solvent was then removed *in vacuo*, and the black residue was thoroughly extracted twice with chloroform (150 cm^3), to remove any unreacted PPh_3. The chloroform extracts contained neither unreacted Cl-terpy, or L^1. The resulting brown residue was dried thoroughly, added to aqueous ammonia (0.88 specific gravity, 300 cm^3) and stirred for 20 h. After this time, the solid residue was collected by filtration, dried thoroughly, and extracted with chloroform (200 cm^3). The brown extract was reduced in volume to 20 cm^3, and methanol (20 cm^3) was added. The precipitated solid was collected by filtration, washed well with methanol, and air-dried, to give an off-white crystalline solid (58–65%), m.p. 318–321 °C. FAB MS: *m/z* 464 (Found: C, 77.5; H, 4.3; N, 18.3. Calc. for $C_{30}H_{20}N_6$: C, 77.6; H, 4.3; N, 18.1%). ^{1}H NMR ($CDCl_3$): δ 8.96 (s, $H^{3'}$), 8.76 (d, H^6), 8.70 (d, H^3), 7.91 (dd, H^4) and 7.38 (dd, H^5); $J(H^5H^6)$ = 4.2, $J(H^3H^4)$ = 8.0 Hz. IR (KBr): 1581s, 1566s, 1543m, 1471s, 1379s, 793s, 745s and 631s cm^{-1}.

1,4-Bis[1,5-dioxo-1,5-bis(2-pyridyl)pentan-3-yl]benzene. 2-Acetylpyridine (10.0 cm^3, 90 mmol) was added to a stirred solution of benzene-1,4-dicarbaldehyde (2.68 g, 20 mmol) in warm ethanol (200 cm^3). After 2 min, aqueous sodium hydroxide (10 cm^3, 1.0 mol dm^{-3}) was added. The solution immediately darkened in colour and a white precipitate formed. After stirring for 8 h at room temperature, the precipitate was collected by filtration, washed well with ethanol and dried *in vacuo* to give the tetraketone as a white solid (7.4 g, 64%). IR (KBr): 1702s, 1584m, 1438m, 1398m, 1368m, 1310m and 1000s cm^{-1}. FAB MS: *m/z* 582.

1,4-Bis(2,2′:6′,2″-terpyridin-4′-yl)benzene L^2. A suspension of 1,4-bis[1,5-dioxo-1,5-bis(2-pyridyl)pentan-3-yl]benzene (1.0 g, 1.72 mmol) and ammonium acetate (5.0 g) in ethanol (50 cm^3) was heated to reflux for 5 d. After this time, the reaction mixture was cooled, and the solid product collected by

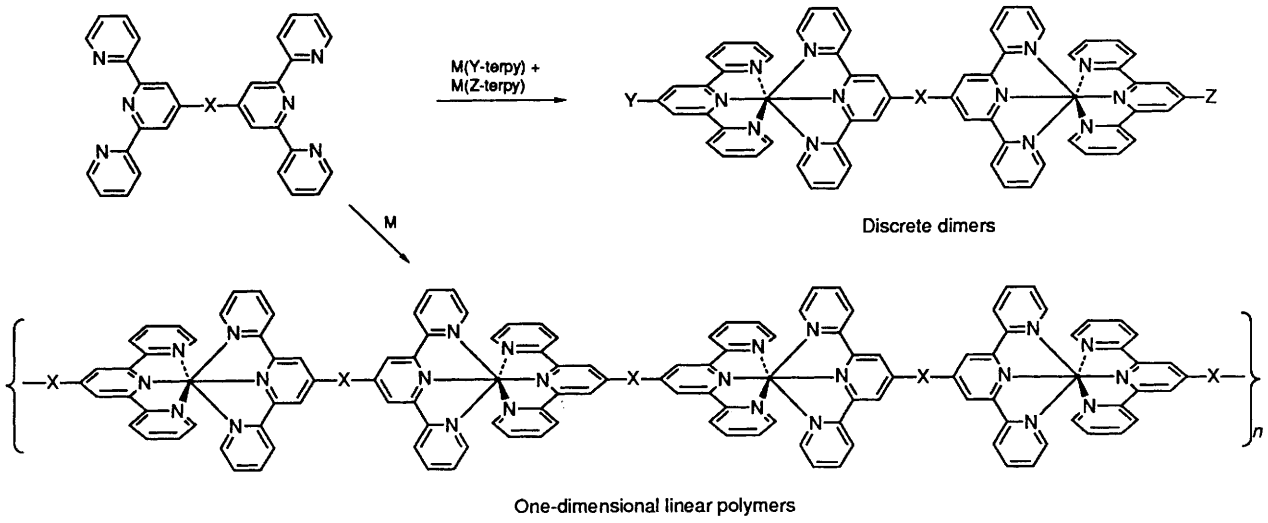


Fig. 4 The use of 'back-to-back' 2,2′:6′,2″-terpyridine ligands to assemble co-ordination polymers or oligomers bearing specific terminator groups; X = spacer unit

filtration, washed well with ethanol, and dried *in vacuo* to yield 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene as an off-white solid (0.34 g, 39%) (Found: C, 79.8; H, 4.5; N, 15.3. Calc. for $C_{36}H_{24}N_6$: C, 80.0; H, 4.4; N, 15.6%). EI MS: *m/z* 540. ^{1}H NMR ($CDCl_3$): δ 8.85 (s, $H^{3'}$), 8.78 (d, H^6), 8.72 (d, H^3), 8.10 (s, H_{arom}), 7.93 (dd, H^4) and 7.40 (dd, H^5); $J(H^5H^6)$ = 4.2, $J(H^3H^4)$ = 8.0 Hz. IR (KBr): 1603m, 1588s, 1568m, 1472m, 1390m, 788s and 731m cm^{-1}.

1,3,5-*Tris*[3-*oxo*-3-(2-*pyridyl*)*propen*-1-*yl*]*benzene*. Benzene-1,3,5-tricarbaldehyde (0.30 g, 1.9 mmol) was dissolved in warm ethanol (50 cm^3) and 2-acetylpyridine (0.78 cm^3, 6.5 mmol) was added and the mixture stirred. After 2 min, aqueous sodium hydroxide (2 cm^3, 1.0 mol dm^{-3}) was added. The solution immediately darkened in colour and a white solid separated. Stirring was continued for 2 h at ambient temperature, after which time the precipitate was collected by filtration, washed well with ethanol and dried *in vacuo* to give 1,3,5-tris[3-oxo-3-(2-pyridyl)propen-1-yl]benzene as a white solid (0.30 g, 34%). IR (KBr): 1678s, 1605s, 1583s, 1441m, 1323m, 1034m, 995m and 790s cm^{-1}. FAB MS: *m/z* 471 (M^+) and 393 ($M^+ - C_5H_4N$). ^{1}H NMR ($CDCl_3$): δ 8.79 (d, H^6), 8.42 (d, *J* = 16, COC*H*=CH), 8.22 (d, H^3), 8.07 (s, H_{arom}), 7.99 (d, *J* = 16 Hz, COCH=C*H*), 7.90 (dd, H^4) and 7.53 (dd, H^5).

1,3,5-*Tris*(2,2′:6′,2″-*terpyridin*-4′-*yl*)*benzene* L^3. 1,3,5-*Tris*[3-oxo-3-(2-pyridyl)propen-1-yl]benzene (0.200 g, 0.42 mmol), *N*-[2-oxo-2-(2′-pyridyl)ethyl]pyridinium iodide (0.414 g, 1.26 mmol) and ammonium acetate (4.0 g) were added to absolute ethanol (25 cm^3) and the suspension heated to reflux for 4 h under an atmosphere of dinitrogen. After this time, the reaction mixture was cooled, the product was collected by filtration, washed well with ethanol, and dried *in vacuo* to yield 1,3,5-tris(2,2′:6′,2″-terpyridin-4′-yl)benzene as a yellow-green solid (0.106 g, 33%). IR (KBr): 1584s, 1569m, 1384m and 793s cm^{-1}. FAB MS: *m/z* 771. ^{1}H NMR ($CDCl_3$): δ 8.87 (s, $H^{3'}$), 8.73 (d, H^6), 8.71 (d, H^3), 8.38 (s, H_{arom}), 7.90 (dd, H^4) and 7.35 (dd, H^5).

General method for [{(X-terpy)Ru}$_2$L][PF_6]$_4$ (L = L^1 or L^2; X = H, OH, OEt, Cl, Ph, NMe_2, SMe *or* SO_2Me). A suspension of the binucleating ligand (0.10 mmol) and [Ru(X-terpy)Cl_3] (0.20 mmol) in methanol (10 cm^3) was treated with *N*-ethylmorpholine (2 drops) and then heated to reflux for 24 h to yield a deep red solution. Column chromatography [silica, MeCN–saturated aqueous KNO_3–water (7:1:0.5 v/v) as eluent] was used to separate the desired major product band from smaller amounts of impurities. The product fraction was evaporated to dryness, and then dissolved in the minimum volume of methanol. Excess of methanolic [NH_4][PF_6] (or HPF_6 in the case of X = OH) was then added to precipitate the complex as the hexafluorophosphate salt. Recrystallisation from acetone–methanol or acetonitrile–water gave the complexes as analytically pure (Table 1) red-brown powders in 12–25% yields.

General method for [{(X-terpy)Ru}$_3$$L^3$][$PF_6$]$_6$ (X = H, OH, OEt, Cl, Ph, NMe_2, SMe *or* SO_2Me). A suspension of L^3 (0.05 mmol) and [Ru(X-terpy)Cl_3] (0.15 mmol) in methanol (10 cm^3) was treated with *N*-ethylmorpholine (2 drops) and the mixture heated to reflux for 24 h, to give a deep red solution. The trinuclear species was separated from impurities by column chromatography, as for the binuclear cases above, to give analytically pure (Table 1) brown powders in 12–25% yields.

Results and Discussion

We have previously reported[4] the preparation of the binucleating ligand 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine L^1 by the dimerisation of 4′-chloroterpyridine with stoichiometric quantities of [Ni(PPh_3)$_n$] (*n* = 3 or 4) generated by the *in situ* reduction of [Ni(PPh_3)$_2$$Cl_2$] with zinc dust in the presence of excess of PPh_3. We have now optimised this preparation, and by a variation in work-up, yields of L^1 in excess of 60% may be achieved routinely. The principal change involves an ammoniacal work-up replacing the cyanide demetallation. The ^{1}H NMR spectrum of a $CDCl_3$ solution of L^1 is shown in Fig. 5(*a*) for comparison with the other ligands described.

The literature preparation[5] of the binucleating ligand L^2 involves the reaction of benzene-1,4-dicarbaldehyde with 2 equivalents of 2-acetylpyridine in basic ethanolic solution to yield a bis-chalcone. This bis-chalcone is then condensed with 2 equivalents of the ylide precursor *N*-[2-oxo-2-(2′-pyridyl)-ethyl]pyridinium iodide and excess of monium acetate to yield L^2. In our hands, the compound produced in this way tended to be of variable composition and colour. Accordingly, we have modified the preparation. The reaction of benzene-1,4-dicarbaldehyde with 4.5 equivalents of 2-acetylpyridine results in the formation of a tetraketone in 64% yield, rather than the chalcone (Scheme 1). The tetraketone is related to the chalcone by the addition of the enolate of 2-acetylpyridine. The carbonyl stretching mode in the IR spectrum, $\nu_{C=O}$ 1701 cm^{-1}, is characteristic of the non-conjugated carbonyl group. The ^{1}H NMR spectrum of a $CDCl_3$ solution of this tetraketone is very poorly resolved, presumably due to the occurrence of keto–enol tautomerism on the NMR time-scale. We have previously noted this phenomenon in other 1,5-dicarbonyl compounds used for

Table 1 Partial microanalytical data (%) for the ruthenium complexes

Complex			Found			Calc.		
		M	C	H	N	C	H	N
1a $[\{(terpy)Ru\}_2L^1][PF_6]_4$	$C_{60}H_{42}F_{24}N_{12}P_4Ru_2$	1712	40.85	2.45	9.35	42.05	2.45	9.80
1b $[\{(Cl\text{-}terpy)Ru\}_2L^1][PF_6]_4$	$C_{60}H_{40}Cl_2F_{24}N_{12}P_4Ru_2$	1781	40.95	2.40	8.75	40.45	2.25	9.45
1c $[\{(HO\text{-}terpy)Ru\}_2L^1][PF_6]_4$	$C_{60}H_{42}F_{24}N_{12}O_2P_4Ru_2$	1744	41.55	2.70	9.35	41.30	2.40	9.65
1d $[\{(EtO\text{-}terpy)Ru\}_2L^1][PF_6]_4$	$C_{64}H_{50}F_{24}N_{12}O_2P_4Ru_2$	1800	40.70	2.70	8.85	42.65	2.80	9.35
1e $[\{(Me_2N\text{-}terpy)Ru\}_2L^1][PF_6]_4$	$C_{64}H_{52}F_{24}N_{14}P_4Ru_2$	1798	42.00	3.05	10.15	42.70	2.90	10.90
1f $[\{(Ph\text{-}terpy)Ru\}_2L^1][PF_6]_4$	$C_{72}H_{50}F_{24}N_{12}P_4Ru_2$	1864	45.35	3.00	8.10	46.35	2.70	9.00
1g $[\{(MeS\text{-}terpy)Ru\}_2L^1][PF_6]_4$	$C_{62}H_{46}F_{24}N_{12}P_4Ru_2S_2$	1804	41.50	2.70	9.05	41.25	2.55	9.30
1h $[\{(MeO_2S\text{-}terpy)Ru\}_2L^1][PF_6]_4$	$C_{62}H_{46}F_{24}N_{12}O_4P_4Ru_2S_2$	1868	39.35	2.55	8.90	39.85	2.45	9.00
2a $[\{(terpy)Ru\}_2L^2][PF_6]_4$	$C_{66}H_{46}F_{24}N_{12}P_4Ru_2$	1788	45.05	2.80	8.95	44.30	2.55	9.40
2b $[\{(Cl\text{-}terpy)Ru\}_2L^2][PF_6]_4$	$C_{66}H_{44}Cl_2F_{24}N_{12}P_4Ru_2$	1857	42.70	2.45	8.90	42.65	2.35	9.05
2c $[\{(HO\text{-}terpy)Ru\}_2L^2][PF_6]_4$	$C_{66}H_{46}F_{24}N_{12}O_2P_4Ru_2$	1820	41.50	2.70	8.60	43.50	2.55	9.25
2d $[\{(EtO\text{-}terpy)Ru\}_2L^2][PF_6]_4$	$C_{70}H_{54}F_{24}N_{12}O_2P_4Ru_2$	1876	43.25	2.90	8.65	44.80	2.90	8.95
2e $[\{(Me_2N\text{-}terpy)Ru\}_2L^2][PF_6]_4$	$C_{70}H_{56}F_{24}N_{14}P_4Ru_2$	1874	44.00	3.15	9.80	44.80	3.00	10.45
2f $[\{(Ph\text{-}terpy)Ru\}_2L^2][PF_6]_4$	$C_{78}H_{54}F_{24}N_{12}P_4Ru_2$	1940	48.70	2.85	8.25	48.25	2.80	8.65
2g $[\{(MeS\text{-}terpy)Ru\}_2L^2][PF_6]_4$	$C_{68}H_{50}F_{24}N_{12}P_4Ru_2S_2$	1880	42.25	2.60	8.70	43.40	2.65	8.95
2h $[\{(MeO_2S\text{-}terpy)Ru\}_2L^2][PF_6]_4$	$C_{68}H_{50}F_{24}N_{12}O_4P_4Ru_2S_2$	1944	40.50	3.00	8.40	42.00	2.55	8.65
3a $[\{(terpy)Ru\}_3L^3][PF_6]_6$	$C_{96}H_{66}F_{36}N_{18}P_6Ru_3$	2643	43.35	2.55	9.65	43.60	2.50	9.55
3b $[\{(Cl\text{-}terpy)Ru\}_3L^3][PF_6]_6$	$C_{96}H_{63}Cl_3F_{36}N_{18}P_6Ru_3$	2746.5	40.85	2.55	8.70	41.95	2.30	9.20
3c $[\{(HO\text{-}terpy)Ru\}_3L^3][PF_6]_6$	$C_{96}H_{66}F_{36}N_{18}O_3P_6Ru_3$	2691	41.90	2.45	8.85	42.80	2.45	9.35
3d $[\{(EtO\text{-}terpy)Ru\}_3L^3][PF_6]_6$	$C_{102}H_{78}F_{36}N_{18}O_3P_6Ru_3$	2775	44.20	2.75	9.10	44.10	2.80	9.10
3e $[\{(Me_2N\text{-}terpy)Ru\}_3L^3][PF_6]_6$	$C_{102}H_{81}F_{36}N_{21}P_6Ru_3$	2772	44.30	3.10	9.80	44.15	2.90	10.60
3f $[\{(Ph\text{-}terpy)Ru\}_3L^3][PF_6]_6$	$C_{114}H_{78}F_{36}N_{18}P_6Ru_3$	2871	47.85	3.00	8.60	47.65	2.70	8.80
3g $[\{(MeS\text{-}terpy)Ru\}_3L^3][PF_6]_6$	$C_{99}H_{72}F_{36}N_{18}P_6Ru_3S_3$	2781	42.60	2.70	8.65	42.70	2.60	9.05
3h $[\{(MeO_2S\text{-}terpy)Ru\}_3L^3][PF_6]_6$	$C_{99}H_{72}F_{36}N_{18}O_6P_6Ru_3S_3$	2877	41.80	2.65	8.70	41.30	2.50	8.75

Table 2 Mass spectroscopic data for the 24 oligomeric complexes (data given for ^{102}Ru and ^{35}Cl isotopomers)

Complex	*M*	$M^+ - PF_6$	$M^+ - 2PF_6$	$M^+ - 3PF_6$	$M^+ - 4PF_6$	$[Ru(X\text{-}terpy)L]^+$
1a[a]	1714	1569	1424	1279	—	799
1b[b]	1782	1637	1492	1347	—	—
1c[b]	1746	1601	1456	1311	1166	815
1d[b]	1802	1657	1512	—	—	—
1e[b]	1800	1655	1510	1365	—	842
1f[b]	1866	1721	1576	1431	—	—
1g[a]	1806	1661	1516	1371	—	—
1h[c]	—	—	—	—	—	—
2a[b]	1790	1645	1500	1355	1210	875
2b[b]	1858	1713	—	—	—	—
2c[b]	1822	—	—	1387	1242	891
2d[b]	1878	1733	1588	1443	1298	919
2e[b]	1876	1731	1586	1441	—	918
2f[b]	1942	1797	1652	1507	—	951
2g[b]	1882	1737	1592	1447	1302	—
2h[a]	1946	1801	1656	1511	—	—
3a[a]	2646	—	2356	2211	2066	—
3b[a]	2748	2603	2458	2313	—	—
3c[a]	2694	—	2404	2259	2114	—
3d[a]	2778	2633	2488	2343	—	—
3e[a]	2775	—	2485	2340	—	—
3f[a]	2874	2729	2584	2439	2294	—
3g[a]	2784	2639	2494	2349	—	—
3h[a]	2880	2735	2590	2445	—	—

[a] Positive-ion FIB. [b] Positive-ion FAB. [c] Sample did not show parent or fragmentation peaks by any technique.

the preparation of pyridines.[4] The tetraketone reacts with an excess of ammonium acetate at reflux in absolute ethanol to give L^2 as an analytically pure off-white solid in 39% yield. The ^1H NMR spectrum of a $CDCl_3$ solution of L^2 [Fig. 5(*b*)] indicates that the molecule is symmetrical on the NMR time-scale, with the two terpyridine moieties and each terminal 2-pyridyl ring equivalent. The 1,4-phenylene spacer group exhibits a singlet at δ 8.10.

The novel trinucleating ligand L^3 was also prepared by a Krohnke-type[5] strategy. Benzene-1,3,5-tricarbaldehyde was prepared by the literature method involving the reduction of benzene-1,3,5-tricarbonyl trichloride with lithium tris(*tert*-butoxy)hydridoaluminate.[7] The reaction of this trialdehyde with 3 equivalents of 2-acetylpyridine in ethanol made basic with aqueous NaOH gave the tris-chalcone as a white powder in 34% yield (Scheme 2). The IR spectrum exhibits a strong carbonyl absorption, $\nu_{C=O}$ at 1678 cm^{-1} characteristic of a chalcone. The tris-chalcone is the sole product from the reaction even if 6 or more equivalents of 2-acetylpyridine are used, suggesting that this species may be too hindered for the formation of a hexaketone.

The ^1H NMR spectrum of a $CDCl_3$ solution of the tris-chalcone is sharp and well resolved and includes a pair of doublets J = 16 Hz, characteristic of the *trans*-alkene present. The remainder of the spectrum consists of a singlet (δ 8.07) assigned to the three equivalent protons of the benzene ring,

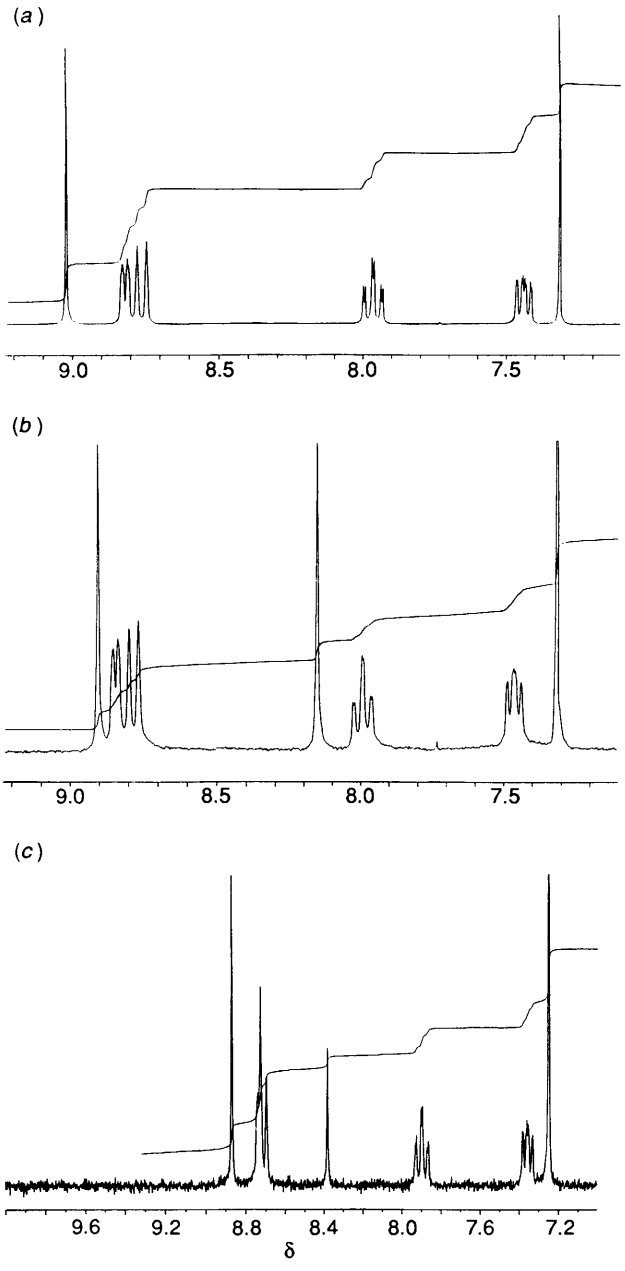
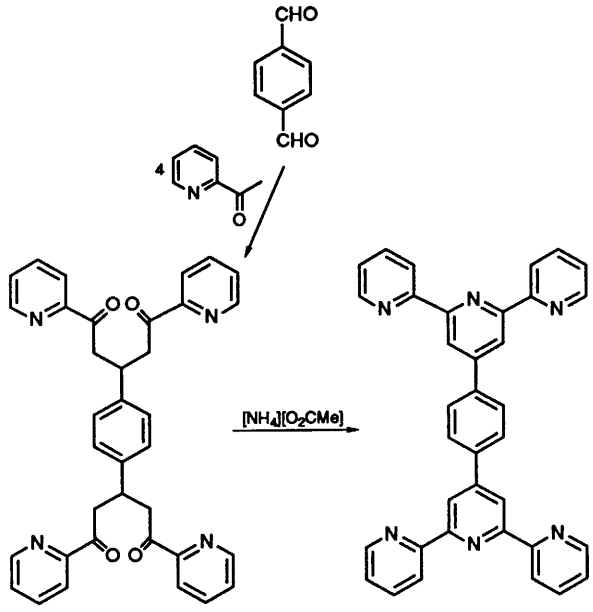


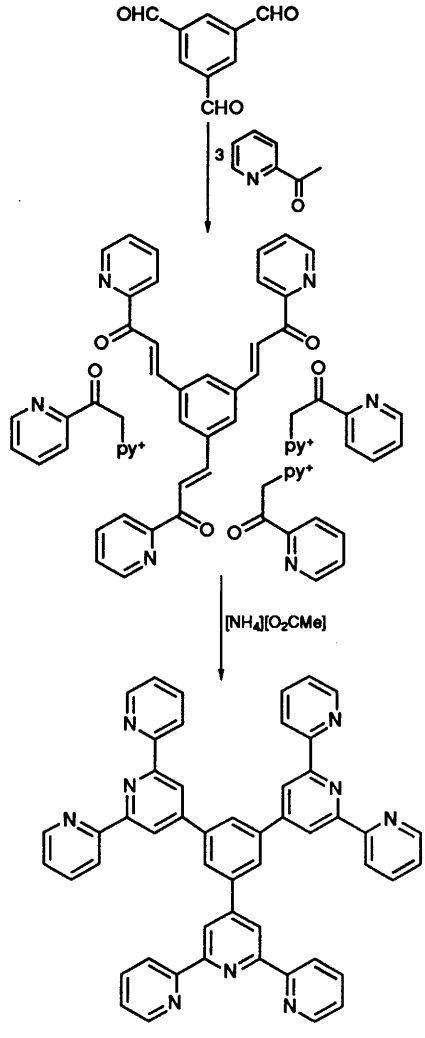
Fig. 5 Proton NMR spectra of $CDCl_3$ solutions of (*a*) L^1, (*b*) L^2 and (*c*) L^3

and a characteristic set of four resonances for the 2-pyridyl ring. The small number of observed resonances confirms that the tris-chalcone possesses three-fold symmetry on the NMR time-scale. The final step in the synthesis is the condensation of the tris-chalcone with 3 equivalents of *N*-[2-oxo-2-(2′-pyridyl)ethyl]-pyridinium iodide and excess of $[NH_4][O_2CMe]$ at reflux in absolute ethanol under an atmosphere of dinitrogen. The ligand L^3 is obtained as a yellow-green solid in 30–35% yield. The compound exhibits a parent ion at *m*/*z* 771 in its FAB mass spectrum. The ^1H NMR spectrum of a $CDCl_3$ solution of L^3 is shown in Fig. 5(*c*), and only exhibits six environments, demonstrating the high molecular symmetry on the NMR time-scale.

Having prepared the bridging ligands, we now prepared specific dinuclear and trinuclear complexes with the relatively non-labile ruthenium(II) six-co-ordinate centre as a connectivity [2] metal site. The 'external' co-ordination sites remaining on the ruthenium centres were occupied by terminator ligands with specific electron releasing or electron withdrawing properties.



Scheme 1



Scheme 2 $py^+ = C_5H_5N^+$

In this paper we will only report the complexes in which all the terminator ligands are the same. We will also limit the descriptions in this paper to those compounds containing a single connectivity [2] or connectivity [3] ligand. This may be

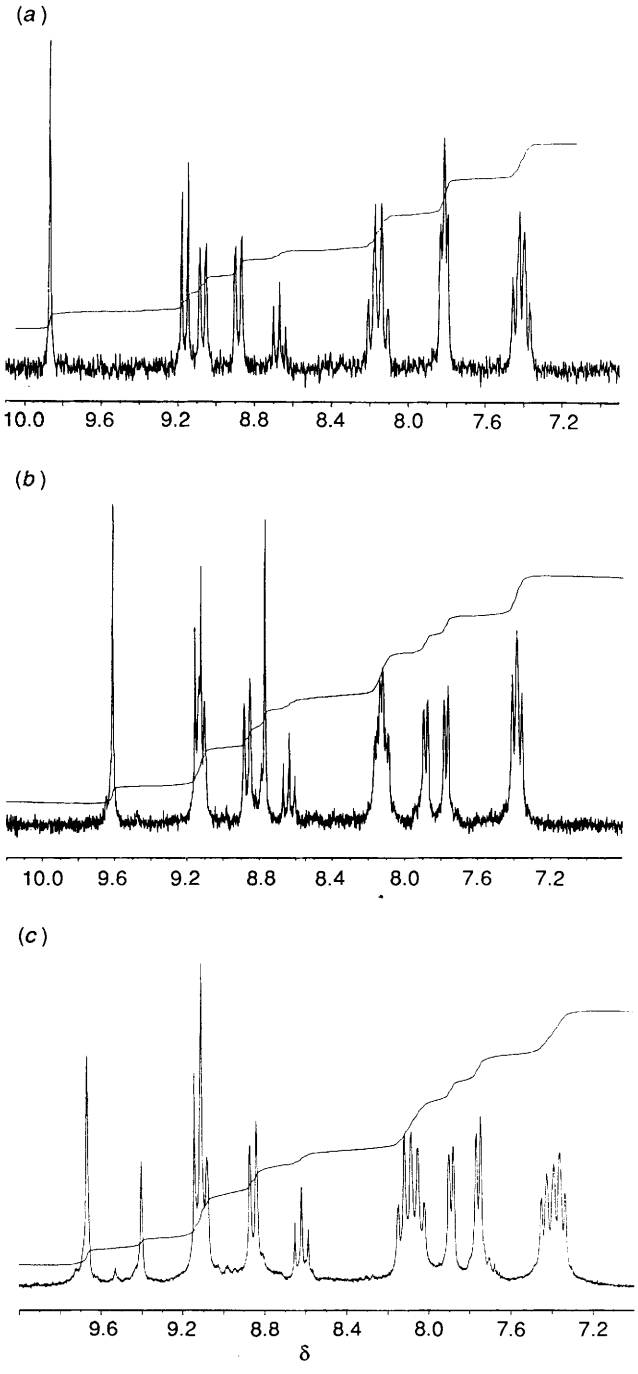


Fig. 6 Proton NMR spectra of $(CD_3)_2CO$ solutions of (*a*) $[\{(terpy)Ru\}_2L^1][PF_6]_4$ **1a**, (*b*) $[\{(terpy)Ru\}_2L^2][PF_6]_4$ **2a** and (*c*) $[\{(terpy)Ru\}_3L^3][PF_6]_6$ **3a**

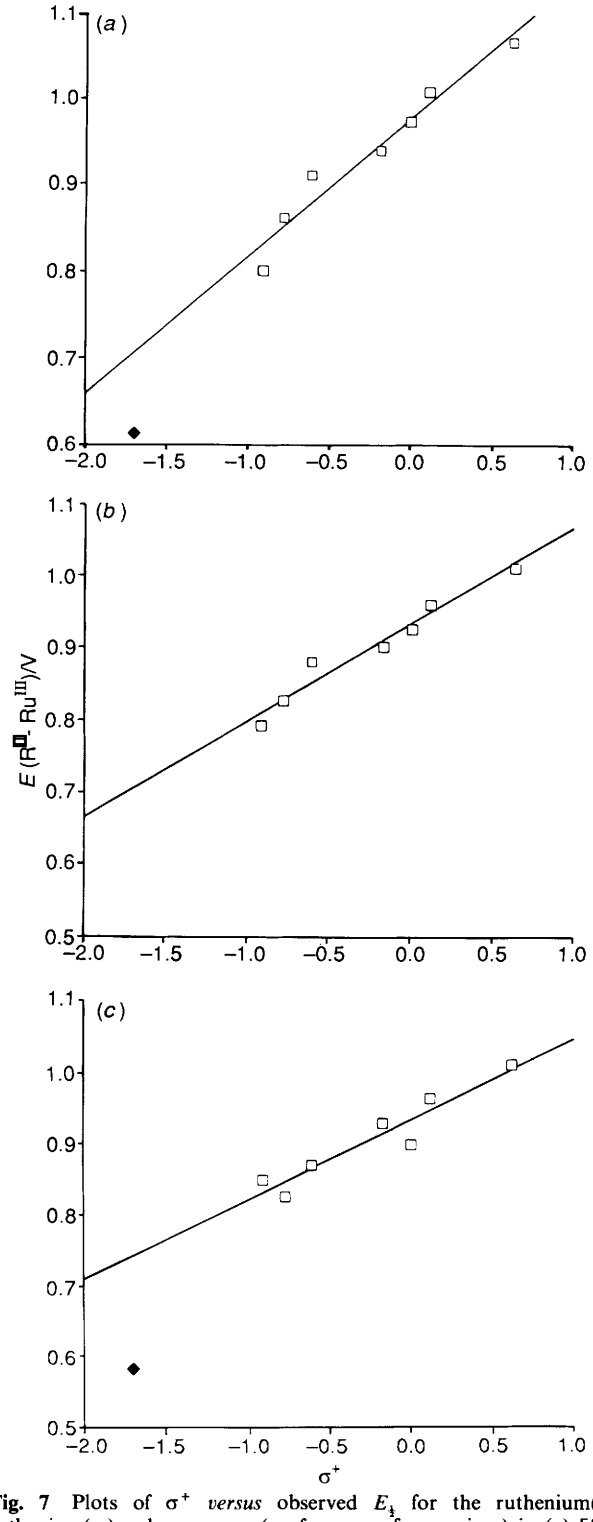


Fig. 7 Plots of σ^+ *versus* observed $E_{\frac{1}{2}}$ for the ruthenium(II)–ruthenium(III) redox process (*vs.* ferrocene–ferrocenium) in (*a*) $[\{(X\text{-}terpy)Ru\}_2L^1][PF_6]_4$ **1** (*b*) $[\{(X\text{-}terpy)Ru\}_2L^2][PF_6]_4$ **2** and (*c*) $[\{(X\text{-}terpy)Ru\}_3L^3][PF_6]_6$ **3**; (◆) corresponds to Me_2N-terpy derivatives **1e**, **2e** and **3e**

viewed as the construction of the first tier of a cascade polymer.[10,11] The reaction of 2 equivalents of $[Ru(X\text{-}terpy)Cl_3]$ (X = H, OH, OEt, Cl, Ph, NMe_2, SMe or SO_2Me) with 1 equivalent of binucleating ligand (L^1 or L^2) in methanol in the presence of the reducing agent *N*-ethylmorpholine resulted in the formation of deep red solutions. Thin layer chromatography (TLC) showed this to be a mixture containing a major crimson product, and various minor orange and pink impurities, one of which is invariably the mononuclear species $[Ru(X\text{-}terpy)_2]^{2+}$.[10] A solvent system consisting of 7 parts acetonitrile: 1 part saturated aqueous potassium nitrate: 0.5 parts water was found to optimise separation using silica TLC plates. The use of less water in the mixture increased the separation of peaks, but slowed the rate of travel of the species. The deep red reaction mixture was reduced to minimum volume, placed on a silica column (40 cm long, 3 cm diameter), and eluted with this solvent system. The main, deep red fraction was collected, and the $[NO_3]^-$ counter ions exchanged for $[PF_6]^-$ by precipitation to give the binuclear complexes $[\{(X\text{-}terpy)Ru\}_2L][PF_6]_4$ (L = L^1 **1** or L^2 **2**). In most cases the complexes were precipitated as hexafluorophosphate salts by the addition of methanolic $[NH_4][PF_6]$; the sole exception was with the 4′-hydroxy-2,2′:6′,2″-terpyridine ligand when HPF_6 is

Table 3 Proton NMR data (δ) for the ruthenium(II) complexes in CD_3COCD_3 solution (except where otherwise stated)

	Multinucleating ligand L						X-terpy					
Complex	H^3	H^4	H^5	H^6	$H^{3'}$	H_{arom}	H^3	H^4	H^5	H^6	$H^{3'}$	Other
1a	9.05	8.17	7.43	7.81	9.84		8.88	8.13	7.40	7.81	9.16	8.67 (H^4)
1a*	8.90	8.10	7.29	7.48	9.48		8.57	8.00	7.21	7.47	8.82	8.50 (H^4)
1b*	8.85	8.08	7.28	7.50	9.44		8.55	8.00	7.26	7.50	8.92	—
1c	9.03	8.18	7.48	7.94	9.82		8.76	8.10	7.35	7.74	8.59	11.25 (br, OH)
1d	9.08	8.17	7.45	7.90	9.87		8.90	8.11	7.35	7.75	8.78	4.73 (q, 2 H, CH_2CH_3), 1.69 (t, 3 H, CH_2CH_3)
1e	9.04	8.17	7.50	7.94	9.82		8.88	8.05	7.28	7.66	8.43	3.62 (s, 6 H, Me)
1f	9.09	8.18	7.45	7.93	9.98		9.14	8.18	7.42	7.83	9.52	8.37 (d, 2 H, Ph), 7.77 (m, 3 H, Ph)
1g	9.03	8.17	7.44	7.91	9.83		8.95	8.11	7.37	7.77	8.99	3.06 (s, 3 H, Me)
1h*	8.85	8.08	7.32	7.58	9.46		8.74	8.04	7.26	7.46	9.20	3.55 (s, 3 H, Me)
2a	9.12	8.13	7.38	7.88	9.62	8.77	8.87	8.13	7.38	7.78	9.14	8.64 (H^4)
2b	9.12	8.15	7.38	7.87	9.60	8.77	8.95	8.15	7.42	7.93	9.26	—
2c	9.08	8.13	7.42	7.88	9.56	8.74	8.74	8.07	7.33	7.81	8.55	—
2d	9.09	8.13	7.41	7.86	9.57	8.74	8.76	8.09	7.34	7.82	8.75	4.72 (q, 2 H, CH_2CH_3), 1.67 (t, 3 H, CH_2CH_3)
2e	9.09	8.13	7.46	7.89	9.55	8.73	8.86	8.04	7.27	7.73	8.41	3.61 (s, 6 H, Me)
2f	9.12	8.16	7.40	7.89	9.62	8.80	9.12	8.16	7.40	7.89	9.49	8.37 (d, 2 H, Ph), 7.77 (m, 3 H, Ph)
2g	9.10	8.12	7.40	7.87	9.58	8.74	8.93	8.09	7.36	7.87	8.96	3.05 (s, 3 H, Me)
2h*	8.73	8.01	7.20	7.38	9.17	8.59	8.73	8.01	7.30	7.56	9.19	3.53 (s, 3 H, Me)
3a	9.09	8.05	7.43	7.89	9.66	9.40	8.86	8.12	7.36	7.76	9.12	8.62 (H^4)
3b	9.08	8.06	7.47	7.94	9.65	9.39	8.94	8.15	7.36	7.85	9.25	—
3c	9.16	8.07	7.41	7.88	9.73	9.41	8.75	8.07	7.38	7.85	8.58	11.25 (br, OH)
3d	9.08	8.06	7.39	7.87	9.64	9.37	8.89	8.10	7.39	7.83	8.76	4.72 (q, 2 H, CH_2CH_3), 1.67 (t, 3 H, CH_2CH_3)
3e	9.08	8.08	7.45	7.89	9.63	9.36	8.87	8.03	7.31	7.74	8.41	3.61 (s, 6 H, Me)
3f	9.15	8.08	7.45	7.92	9.73	9.43	9.11	8.16	7.38	7.87	9.49	8.37 (d, 2 H, Ph), 7.77 (m, 3 H, Ph)
3g	9.08	8.06	7.41	7.85	9.64	9.38	8.93	8.10	7.38	7.85	8.96	3.05 (s, 3 H, Me)
3h	9.16	8.06	7.53	8.00	9.71	9.44	9.12	8.20	7.32	7.77	9.44	3.60 (s, 3 H, Me)

* Recorded in CD_3CN solution.

Table 4 Electrochemical data for polynuclear ruthenium(II) complexes reported (MeCN solvent, $[NBu^n_4][BF_4]$ supporting electrolyte, *versus* internal ferrocene–ferrocenium)

		$E^{o\,b}$/V	
Complex	Hammett $\sigma^{+\,a}$	Ru^{II}–Ru^{III}	1st redn.
1a	0	0.96	−1.36[c]
1b	+0.114	1.00	*d*
1c	−0.92	0.80	*d*
1d	−0.778	0.86	−1.39[c]
1e	−1.7	0.61	−1.42[c]
1f	−0.179	0.94	−1.34[c]
1g	−0.60	0.91	−1.36[c]
1h	+0.63	1.07	*d*
2a	0	0.93	*d*
2b	+0.114	0.96	−1.57[c]
2c	−0.92	0.79	*d*
2d	−0.778	0.83	*c*
2e	−1.7	0.58	*c*
2f	−0.179	0.90	−1.62[c]
2g	−0.60	0.88	−1.62[c]
2h	+0.63	1.01	*d*
3a	0	0.90	−1.63[c]
3b	+0.114	0.97	−1.55[c]
3c	−0.92	0.85	−1.72[e]
3d	−0.778	0.83	−1.65[c]
3e	−1.7	0.58	−1.69[c]
3f	−0.179	0.93	−1.64[c]
3g	−0.60	0.87	−1.63[c]
3h	+0.63	1.01	−1.38[c]

[a] Hammett σ^+ value for substituent group X on X-terpy. [b] Potentials estimated to be accurate to ±30 mV, all potentials quoted *versus* internal ferrocene–ferrocenium. [c] Absorption spike obscures other reductive processes. [d] Reductive processes are poorly resolved. [e] Only one reductive process observed.

used to ensure that the hydroxy group of the ligand is not deprotonated.

The trinuclear complexes $[\{(X\text{-terpy})Ru\}_3L^3][PF_6]_6$ **3** were prepared analogously by treating 3 or more equivalents of $[Ru(X\text{-terpy})Cl_3]$ with 1 equivalent of the trinucleating ligand L^3. Once again the complexes were isolated as red-brown hexafluorophosphate salts after chromatographic purification over silica.

All 24 homoleptic complexes prepared gave good elemental analyses (Table 1), although in some cases the analysis for carbon was observed to be low, probably due to the formation of metal carbides in the combustion process. This is a feature which we have consistently observed for ruthenium(II) oligopyridine complexes. FAB or FIB mass spectrometry with 3-nitrobenzyl alcohol as matrix was also used to characterise the complexes. The binuclear species typically exhibit peaks corresponding to $\{Ru_2(X\text{-terpy})_2L(PF_6)_n\}^+$ (n = 3, 2, or 1) and in some cases $\{Ru_2(X\text{-terpy})_2L\}^+$ and $\{Ru(X\text{-terpy})L\}^+$ (Table 2). As an example, $[\{(terpy)Ru\}_2L^2][PF_6]_4$ **2a** exhibits ions at m/z 1645, 1500, 1355, 1210 and 875 (based on ^{102}Ru) corresponding to $[\{(terpy)Ru\}_2L^2(PF_6)_3]^+$, $[\{(terpy)Ru\}_2L^2(PF_6)_2]^+$, $[\{(terpy)Ru\}_2L^2(PF_6)]^+$, $[\{(terpy)Ru\}_2L^2]^+$ and $[Ru(terpy)L^2]^+$ fragments respectively. For no apparent reason, samples of $[\{(MeO_2S\text{-terpy})Ru\}_2L^1][PF_6]_4$ **1h** consistently gave no peaks above m/z 1050, although the elemental analysis and ^1H NMR spectrum both agree with this binuclear formulation. The trinuclear species derived from the L^3 ligand typically exhibited peaks corresponding to $[\{(X\text{-terpy})Ru\}_3L^3(PF_6)_n]^+$ (n = 5, 4, or 3) in their FIB mass spectra. As an example, $[\{(terpy)Ru\}_3L^3][PF_6]_6$ **3a** exhibited peaks at m/z 2356, 2211 and 2066 corresponding to $[\{(terpy)Ru\}_3L^3(PF_6)_4]^+$, $[\{(terpy)Ru\}_3L^3(PF_6)_3]^+$ and $[\{(terpy)Ru\}_3L^3(PF_6)_2]^+$ fragment ions respectively. In all cases the correct isotopomer distribution patterns were observed.

The ^1H NMR spectra of CD_3COCD_3 solutions of the complexes all show two sets each of five or six resonances in the aromatic region, one set due to the multinucleating ligand and one set due to the terpyridine ligand X-terpy (Table 3). Typical examples of the spectra of the terpy terminated complexes $[\{(terpy)Ru\}_2L^1][PF_6]_4$ **1a**, $[\{(terpy)Ru\}_2L^2][PF_6]_4$ **2a** and $[\{(terpy)Ru\}_3L^3][PF_6]_6$ **3a** are shown in Fig. 6(*a*)–(*c*). The resonances can be unambiguously assigned by comparison with the previously reported spectra of CD_3COCD_3 solutions of the

Table 5 Electronic spectroscopic data λ/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}) for polynuclear ruthenium(II) complexes reported (MeCN solvent)

	X							
Complex	H	Cl	MeO_2S	Ph	EtO	MeS	HO	NMe_2
1 $[\{(X\text{-terpy})Ru\}_2L^1][PF_6]_4$	514 (49.6)	492 (51.0)	509 (59.9)	519 (53.2)	522 (51.4)	523 (42.8)	524 (45.2)	537 (62.3)
2 $[\{(X\text{-terpy})Ru\}_2L^2][PF_6]_4$	492 (44.3)	494 (57.9)	496 (55.4)	498 (66.2)	501 (58.6)	502 (65.0)	503 (49.6)	512 (54.9)
3 $[\{(X\text{-terpy})Ru\}_3L^3][PF_6]_6$	487 (65.9)	489 (69.1)	499 (81.5)	493 (79.5)	494 (72.0)	496 (83.1)	495 (64.3)	507 (76.0)

mononuclear species $[Ru(X\text{-terpy})_2][PF_6]_2$ and $[Ru(X\text{-terpy})(Y\text{-terpy})][PF_6]_2$, where we have shown that the chemical shifts of the X-terpy ligand resonances in $[Ru(X\text{-terpy})(Y\text{-terpy})][PF_6]_2$ are not significantly affected by the nature of the other 4′-substituted terpyridine ligand present (Y-terpy).[10] We now see that this behaviour is repeated in these complexes with bridging ligands. The ^{1}H NMR resonances of the terminator ligands X-terpy are almost invariant of the nature of the bridging ligand, and almost unshifted with respect to $[Ru(X\text{-terpy})_2][PF_6]_2$.[10] It is also relevant that the resonances assigned to the bridging ligands are equally invariant of the nature of the terminator X-terpy group. It is noteworthy that some of the complexes containing electron-withdrawing ligands, $[\{(MeO_2S\text{-terpy})Ru\}_2L^2][PF_6]_4$ **2h**, $[\{(MeO_2S\text{-terpy})Ru\}_2L^1][PF_6]_4$ **1h** and $[\{(Cl\text{-terpy})Ru\}_2L^1][PF_6]_4$ **1b** are not significantly soluble in CD_3COCD_3 and the NMR spectra of these were obtained in CD_3CN solutions. There is no obvious explanation for these observed solubility differences. These spectra were assigned by comparison with spectra of CD_3CN solutions of $[Ru(Cl\text{-terpy})_2][PF_6]_2$, $[Ru(MeO_2S\text{-terpy})_2][PF_6]_2$ and $[\{(terpy)Ru\}_2L^1][PF_6]_4$.

All 24 complexes are electrochemically active in MeCN solution with $[NBu^n_4][BF_4]$ as the supporting electrolyte. A single quasi-reversible oxidative process is observed in all cases corresponding to the ruthenium(II)–ruthenium(III) process. For each multinucleating ligand these oxidation couples are found to vary between 0.5 and 1.1 V (*versus* ferrocene–ferrocenium) according to the electronic nature of the X-terpy ligand (Table 4), as expected by analogy with the mononuclear species $[Ru(X\text{-terpy})_2][PF_6]_2$ and $[Ru(X\text{-terpy})(Y\text{-terpy})][PF_6]_2$.[10] The presence of a single oxidative process within the solvent window at all scan rates leads us to conclude that all of the metal centres in each complex are identical, and more importantly, non-interacting. If there were significant interactions between the metal centres, then the oxidation of the *first* ruthenium centre will affect the potential at which the other centres in the complex are oxidised. We have previously shown that the average of the Hammett σ^+ parameters for the X and Y substituents upon the ligands in the complexes $[Ru(X\text{-terpy})(Y\text{-terpy})][PF_6]_2$ provides a good parameter for correlation with the Ru^{II}–Ru^{III} oxidation potential, and we have defined the parameter σ', where $\sigma' = 0.5[\sigma^+(X) + \sigma^+(Y)]$ as being useful in such systems.[10] Such correlations also exist for each of the multinucleating ligands. When the oxidation potentials of the complexes are plotted against the Hammett σ^+ parameters for the substituents X on the X-terpy ligands straight lines can be fitted to data with correlation coefficients, R^2 of 0.90 or higher [Fig. 7(*a*)–(*c*)]. The data for the 4′-dimethylamino-2,2′:6′,2″-terpyridine (Me_2N-terpy) ligand are anomalous, as we have previously demonstrated for mononuclear complexes.[10] We are confident that the oxidation processes observed for the complexes with the Me_2N-terpy ligand are *metal* rather than *ligand* centred.[10] The linear relationships allow us to use the observed electrode potentials to extract effective σ^+ parameters for the new ligands L^1–L^3. In each case the σ^+ parameter that is extracted is identical within experimental error with that of a phenyl substituent. In other words, in electronic terms the bridging ligands effectively behave as a simple 4′-phenyl substituted terpyridine, and there is no effective electronic interaction between the various 2,2′:6′,2″-terpyridyl substituents or the metals co-ordinated to them. Several reversible or pseudo-reversible reductive processes are also observed for each species, although these are often masked by sharp absorption processes. Where observed, the potentials of the first reduction process are also indicated in Table 4.

The complexes all dissolve in MeCN to give red-brown solutions, the electronic spectra of which exhibit a single, broad, asymmetric metal-to-ligand charge-transfer (m.l.c.t.) band. Attempts to deconvolute this band have been unsuccessful. The position of this absorption varies with λ_{max} in the range 492–537 nm for L^1, 492–512 for L^2 and 487–507 nm for L^3. These data are presented in Table 5. There is a shift to lower energy in these multinuclear systems compared to mononuclear $[Ru(terpy)_2]^{2+}$ with λ_{max} 475 nm (ε 11.6 × 10^3 dm^3 mol^{-1} cm^{-1}) and the more conjugated $[Ru(Ph\text{-terpy})_2]^{2+}$ with λ_{max} 488 nm (ε 26.6 × 10^3 dm^3 mol^{-1} cm^{-1}).[10] The observed shift is least for the trinucleating ligand L^3, in which the crowding of three 4′-linked 2,2′:6′,2″-terpyridyl units around the central 1,3,5-benzene spacer means that conjugation will be minimal. Increased conjugation in the less sterically hindered L^2 complexes results in the m.l.c.t. process being slightly lower in energy than in the L^3 complexes. The decrease in transition energy for complexes of the binucleating ligand L^1 could indicate some interaction between the two metal centres in the complexes, although this is not in accord with the electrochemical behaviour. The ruthenium(II) centre will be relatively electron rich due to its N_6 donor set, and will tend to π-donate charge into the π* orbitals of both terpyridine functionalities co-ordinated to it. Thus, each ruthenium centre in $[\{(terpy)Ru\}_2L^1]^{4+}$ acts as a donor, pushing electron density towards the other, increasing λ_{max}. The presence of the strongly electron-donating substituent NMe_2 on a terpyridine ligand co-ordinated to a ruthenium(II) centre is also observed to shift λ_{max} to higher wavelength.[10] For the binuclear species, the absorption coefficients (ε = 43 × 10^3–66 × 10^3 dm^3 mol^{-1} cm^{-1}) are approximately double those observed for mononuclear species, as expected given the presence of two identical, independent, ruthenium(II) centres per molecule. Similarly the absorption coefficients (ε = 64 × 10^3–83 × 10^3 dm^3 mol^{-1} cm^{-1}) for the trinuclear complexes are of the order of three times those of the mononuclear species.

To conclude, we have shown that 2,2′:6′,2″-terpyridine moieties linked by suitable spacer groups provide a powerful route into designed co-ordination polymers and oligomers. To all intents and purposes the ground-state interaction between metal centres in these oligomers is negligible, and the metal centres are independent and similar to those in related mononuclear model compounds. It is possible that the metal centres may mutually influence each other to a very slight extent in the complexes of L^1, but this is only evident in the energies of the m.l.c.t. transitions in the electronic spectra. We are currently preparing photoactive derivatives in which

photoactive centres are located in the second or third tier of cascade polymers.

Acknowledgements

We should like to thank the SERC for support, Johnson Matthey for the loan of precious metals and the Royal Society and Isaac Newton Trust for grants towards the cost of spectrometers.

References

1 E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, in *Supramolecular Chemistry*, eds. V. Balzani and L. De Cola, NATO ASI Series, Reidel, Dordrecht, 1992, p. 219.

2 G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc.*, 1992, **114**, 2944; L. De Cola, F. Barigelletti, V. Balzani, P. Belser, A. Von Zelewsky, C. Seel, M. Frank and F. Vogtle, *Coord. Chem. Rev.*, 1991, **111**, 255; C. A. Bignozzi, R. Argazzi, C. Chiorboli, S. Roffia and F. Scandola, *Coord. Chem. Rev.*, 1991, **111**, 261; S. Campagna, G. Denti, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, 1991, **30**, 3728; S. Serroni, G. Denti, S. Campagna, M. Ciano and V. Balzani, *J. Chem. Soc., Chem. Commun.*, 1991, 944; G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chim. Acta*, 1990, **176**, 175; G. Denti, S. Serroni, S. Campagna, V. Ricevuto and V. Balzani, *Coord. Chem. Rev.*, 1991, **111**, 227; L. De Cola, P. Belser, F. Ebmeyer, F. Barigelletti, F. Vogtle, A. Von Zelewsky and V. Balzani, *Inorg. Chem.*, 1990, **29**, 495; C. A. Bignozzi, S. Roffia and F. Scandola, *J. Am. Chem. Soc.*, 1985, **107**, 1644; S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *J. Chem. Soc., Chem. Commun.*, 1989, 1500; C. A. Bignozzi, S. Roffia, C. Chiorboli, J. Davila, M. T. Indelli and F. Scandola, *Inorg. Chem.*, 1989, **28**, 4350.

3 J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1991, **30**, 4230; J. R. Kirchhoff, D. R. Mcmillin, P. A. Marnot and J. P. Sauvage, *J. Am. Chem. Soc.*, 1985, **107**, 1138; J. P. Collin, S. Guillerez and J. P. Sauvage, *Inorg. Chem.*, 1990, **29**, 5009; *J. Chem. Soc., Chem. Commun.*, 1989, 776; J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Flamigni, L. De Cola and V. Balzani, *Coord. Chem. Rev.*, 1991, **111**, 291; M. Beley, J. P. Collin, J. P. Sauvage, H. Sugihara, F. Heisel and A. Miehe, *J. Chem. Soc., Dalton Trans.*, 1991, 3157; J. C. Chambron, C. Coudret and J. P. Sauvage, *New J. Chem.*, 1992, **16**, 361.

4 E. C. Constable and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1990, 1405.

5 F. Krohnke, *Synthesis*, 1976, 1.

6 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, 1992, 617.

7 H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 1958, **80**, 5377; W. P. Cochrane, P. L. Pauson and T. S. Stevens, *J. Chem. Soc. C*, 1968, 630.

8 K. T. Potts, *Org. Synth.*, 1985, **64**, 189; K. T. Potts, M. J. Cipullo, P. Ralli and G. Theodoridis, *J. Org. Chem.*, 1982, **47**, 3027; K. T. Potts and D. Konwar, *J. Org. Chem.*, 1982, **56**, 4815; K. T. Potts, *Bull. Soc. Chim. Belg.*, 1990, **99**, 741; K. T. Potts, D. A. Usifer, A. Gudalupe and H. D. Abruna, *J. Am. Chem. Soc.*, 1987, **109**, 3961.

9 N. Armaroli, V. Balzani, E. C. Constable, M. Maestri and A. M. W. Cargill Thompson, *Polyhedron*, in the press.

10 E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher and M. A. M. Daniels, *New J. Chem.*, in the press.

11 G. R. Newkome, Z. Q. Yao, G. R. Baker and V. K. Gupta, *J. Org. Chem.*, 1985, **50**, 2003; G. R. Newkome, G. R. Baker, M. J. Saunders, P. S. Russo, V. K. Gupta, Z. Q. Yao, J. E. Miller and K. Bouillion, *J. Chem. Soc., Chem. Commun.*, 1986, 752; G. R. Newkome, Z. Q. Yao, G. R. Baker, V. K. Gupta, P. S. Russo and M. J. Saunders, *J. Am. Chem. Soc.*, 1986, **108**, 849; G. R. Newkome, C. N. Moorefield and K. J. Theriot, *J. Org. Chem.*, 1988, **53**, 5552; G. R. Newkome, G. R. Baker, S. Arai, M. J. Saunders, P. S. Russo, K. J. Theriot, C. N. Moorefield, L. E. Rogers, J. E. Miller, T. R. Lieux, M. E. Murray, B. Phillips and J. Pascal, *J. Am. Chem. Soc.*, 1990, **112**, 8458; G. R. Newkome, C. N. Moorefield, G. R. Baker, A. L. Johnson and R. K. Behera, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1176; G. R. Newkome, X. F. Lin and C. D. Weis, *Tetrahedron Asymm.*, 1991, **2**, 957; G. R. Newkome, G. R. Baker, R. K. Behera, A. L. Johnson, C. N. Moorefield, C. D. Weis, W. J. Cao and J. K. Young, *Synthesis*, 1991, 839; C. D. Weis and G. R. Newkome, *J. Org. Chem.*, 1990, **55**, 5801; G. R. Newkome, R. K. Behera, C. N. Moorefield and G. R. Baker, *J. Org. Chem.*, 1991, **56**, 7162; D. Tomalia, *New Scientist*, 1991, **132**, 30; *Science*, 1991, **252**, 1231; G. R. Newkome and C. D. Weis, *J. Org. Chem.*, 1991, **56**, 4798.

Received 23*rd June* 1992; *Paper* 2/03315A