Hypodentate Ligands: Systematic Approaches to Complexes containing Didentate 2,2′:6′,2″-Terpyridine (terpy) and the Crystal and Molecular Structures of [Ru(bipy-*N,N′*)$_2$(terpy-*N,N′*)][PF$_6$]$_2$ and [Ru(bipy-*N,N′*)$_2$(bterpy-*N,N′*)][PF$_6$]$_2$ (bipy = 2,2′-bipyridine, bterpy = 6-bromo-2,2′:6′,2″-terpyridine)†

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A series of complexes containing hypodentate didentate 2,2′:6′,2″-terpyridine (terpy) ligands of general formula [Ru(L-*N,N′*)$_2$(terpy-*N,N′*)]$^{2+}$ [L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline] have been prepared. The complexes [Ru(bipy-*N,N′*)$_2$(terpy-*N,N′*)][PF$_6$]$_2$ and [Ru(bipy-*N,N′*)$_2$(bterpy-*N,N′*)][PF$_6$]$_2$ (bterpy = 6-bromo-2,2′:6′,2″-terpyridine) have been structurally characterised and shown to contain the didentate terpy ligand in the solid state.

Oligopyridines and ligands incorporating multiple oligopyridine metal-binding domains have proved to be ideal touchstones for probing metal-directed helicate assembly processes in metallosupramolecular chemistry.[1,2] The key feature in the understanding of such self-assembly processes lies in the coding of the various metal-binding domains within the 'molecular thread'.[1] When the ligand consists of oligopyridine domains [2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2′:6′,2″-terpyridine (terpy), *etc.*] separated by spacer groups (phenylene,[3] biphenylene,[4] polymethylene,[5] polyoxymethylene,[6] *etc.*) the partitioning into individual metal-binding regions is defined unambiguously by the ligand structure. A judicious choice of the spacer groups between the metal-binding domains allows a subtle control over the selective assembly of double or triple helicates.[7,8]

In the case of the oligopyridines themselves, helication is a consequence of twisting about the interannular C–C bonds.[1,2] This twisting is a direct consequence of the splitting of the compound into a number of separate metal-binding domains. However, the way in which the metal might control the partitioning into individual metal-binding domains is less obvious. For example, the six nitrogen donor atoms of 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2‴″-sexipyridine (spy) might give rise to three didentate, two tridentate or a single hexadentate domain.[9–11] In the course of our studies upon helicate self-assembly we have systematically investigated the ways in which metal ions may address individual domains within oligopyridine ligands. We[12,13] and others[11,14] have reported that 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) can form monohelical or double-helical complexes upon treatment with appropriate metal ions. Futhermore, we have shown that a consideration of the favoured co-ordination numbers and geometries of metal ions allows the specific formation of heterodimetallic double helicates [M^{1}M^2(qpy)$_2$]$^{n+}$ in a controlled and predictable manner.[15]

Most of the approaches discussed hitherto have utilised labile metal ions, implicit in this choice is the assumption that the desired structural features represent a local thermodynamic minimum in the system. The basis of this assumption and its implication for self-assembly has been discussed elsewhere.[8] In this paper we discuss an alternative approach to the partitioning of oligopyridine ligands into discrete domains, and describe the use of kinetically inert ruthenium(II) centres in specifically addressing some, but not all, of the donor sites of a potentially multidentate ligand. Elsewhere, we have described an approach to complexes containing didentate terpy ligands based upon the mechanism of chelate complex formation.[16] We have termed a ligand co-ordinated in this way 'hypodentate'.[2] Complexes containing hypodentate ligands are the key to helicate self-assembly and kinetically inert species may be used as preformed (preorganised?) components for the assembly of novel helicate structures and we describe here approaches to complexes containing didentate terpy ligands. Some of this work has been reported previously in communication form.[17]

Experimental

The complexes [Ru(bipy-*N,N′*)$_2$Cl$_2$],[18] [Ru(phen-*N,N′*)$_2$Cl$_2$],[18] [Ru(terpy-*N,N′,N″*)Cl$_3$][19,20] and the compounds terpy[21] and 6-phenyl-2,2′-bipyridine (Hpbipy)[22–24] were prepared by the literature methods, as were the ligand precursors [3-(6-bromo-2-pyridyl)-3-oxopropyl]dimethylammonium chloride[25] and *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide.[26]

Preparations.—[Ru(bipy-*N,N′*)$_2$(terpy-*N,N′*)][PF$_6$]$_2$. A mixture of [Ru(bipy-*N,N′*)$_2$Cl$_2$] (0.100 g, 0.192 mmol) and terpy (0.045 g, 0.193 mmol) in methanol (20 cm^3) was heated to reflux for 10 h to give a red solution. After filtration, the red solution was treated with an excess of methanolic ammonium hexafluorophosphate solution to give a bright orange precipitate. This was filtered off, washed with diethyl ether (20 cm^3) and recrystallised from methanol to give red crystals of [Ru(bipy-*N,N′*)$_2$(terpy-*N,N′*)][PF$_6$]$_2$ (0.130 g, 46%) (Found: C, 44.5; H, 2.9; N, 10.4. Calc. for $C_{35}H_{27}F_{12}N_7RuP_2 \cdot 0.5H_2O$: C, 44.4; H, 3.0; N, 10.4%). Mass spectrum (positive FAB): *m/z*

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

792 [Ru(bipy)$_2$(terpy)(PF$_6$)], 647 [Ru(bipy)$_2$(terpy)], 490 [Ru(bipy)(terpy)], 414 [Ru(bipy)$_2$] and 334 [Ru(terpy)]. UV/VIS (MeCN): 450 (ε = 12 200), 287 (ε = 57 900), 241 (ε = 27 100) and 196 nm (ε = 57 800 dm^3 mol^{-1} cm^{-1}).

[Ru(bipy-*N*,*N*′)$_2$(Hpbipy)][PF$_6$]$_2$. The complex [Ru(bipy-*N*,*N*′)$_2$Cl$_2$]·2H$_2$O (0.40 g, 0.077 mmol) and Hpbipy (0.018 g, 0.078 mmol) were heated to reflux in ethane-1,2-diol (10 cm^3) for 1 h to give a red solution which was then cooled, diluted with water (30 cm^3) and treated with an excess of methanolic ammonium hexafluorophosphate solution to give an orange precipitate. This was filtered off, washed with diethyl ether (20 cm^3) and dried *in vacuo* to give [Ru(bipy-*N*,*N*′)$_2$(Hpbipy)][PF$_6$]$_2$ (0.036 g, 50%). Mass spectrum (positive FAB): *m*/*z* 791 [Ru(bipy)$_2$(Hpbipy)(PF$_6$)], 646 [Ru(bipy)$_2$(Hpbipy)], 489 [Ru(bipy)(Hpbipy)] and 414 [Ru(bipy)$_2$]. UV/VIS (MeCN): 447 (ε = 10 000), 290 (ε = 53 800), and 242 nm (ε = 26 400 dm^3 mol^{-1} cm^{-1}).

[Ru(phen-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$. The complex [Ru(phen-*N*,*N*′)$_2$Cl$_2$] (0.040 g, 0.071 mmol) and terpy (0.018 g, 0.077 mmol) were heated to reflux in methanol (20 cm^3) for 14 h to give a red solution. This was filtered through cotton-wool and the filtrate treated with an excess of methanolic ammonium hexafluorophosphate solution to give an orange precipitate which was filtered off, washed with diethyl ether (20 cm^3) and dried *in vacuo* to give [Ru(phen-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ (0.045 g, 83%). Mass spectrum (positive FAB): *m*/*z* 840 [Ru(phen)$_2$(terpy)(PF$_6$)], 694 [Ru(phen)$_2$(terpy)], 514 [Ru(phen)(terpy)], 462 [Ru(phen)$_2$] and 349 [Ru(terpy)]. UV/VIS (MeCN): 444 (ε = 8400 d), 280 (sh), 262 (ε = 51 000) and 226 nm (ε = 41 200 dm^3 mol^{-1} cm^{-1}).

[Ru(phen-*N*,*N*′)$_2$(bipy-*N*,*N*′][PF$_6$]$_2$. A mixture of [Ru(phen-*N*,*N*′)$_2$Cl$_2$] (0.034 g, 0.064 mmol) and bipy (0.010 g, 0.064 mmol) was heated to reflux in methanol (10 cm^3) for 4 h to give a red solution. This was then treated with an excess of methanolic ammonium hexafluorophosphate solution to give an orange precipitate which was filtered off, washed with diethyl ether (20 cm^3) and dried *in vacuo* to give [Ru(phen-*N*,*N*′)$_2$(bipy-*N*,*N*′)][PF$_6$]$_2$ (0.044 g, 76%). Mass spectrum (positive FAB): *m*/*z* 763 [Ru(phen)$_2$(bipy)(PF$_6$)], 618 [Ru(phen)$_2$(bipy)], 462 [Ru(phen)$_2$] and 437 [Ru(phen)(bipy)]. UV/VIS (MeCN): 445 (ε = 16 400), 283 (ε = 49 400), 260 (ε = 68 700) and 224 nm (ε = 60 600 dm^3 mol^{-1} cm^{-1}).

6-*Bromo*-2,2′:6′,2″-*terpyridine* (*bterpy*). [3-(6-Bromo-2-pyridyl)-3-oxopropyl]dimethylammonium chloride (1.01 g, 3.44 mmol), *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (1.12 g, 3.40 mmol) and ammonium acetate (4.0 g) were heated to reflux in methanol (30 cm^3) for 4 h after which time a white flaky solid had precipitated. The reaction mixture was cooled and the off-white precipitate filtered off and washed with cold ethanol to give bterpy (0.690 g, 64%) (Found: C, 57.5; H, 3.1; N, 13.1. Calc. for C$_{15}$H$_{10}$BrN$_3$: C, 57.7; H, 3.2; N, 13.4%). Mass spectrum (electron impact, EI): *m*/*z* 311/313 (M^+) and 232 (M^+ − Br). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.36 (1 H, tdd, H$^{5''}$), 7.54 (1 H, dd, H^5), 7.75 (1 H, t, H^4), 7.88 (1 H, tdd, H$^{4''}$), 7.98 (1 H, t, H$^{4'}$), 8.40 (1 H, dd, H$^{3'}$), 8.49 (1 H, dd, H$^{5'}$), 8.59 (1 H, dd, H$^{3'}$), 8.61 (1 H, dd, H^3) and 8.69 (1 H, ddd, H$^{6''}$).

[Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$. A mixture of [Ru(bipy-*N*,*N*′)$_2$Cl$_2$] (0.034 g, 0.064 mmol) and bterpy (0.020 g, 0.064 mmol) in methanol (10 cm^3) was heated to reflux for 16 h to give a deep red solution which was treated with an excess of methanolic ammonium hexafluorophosphate solution and allowed to cool slowly to give deep red crystals of [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ (0.035 g, 54%) (Found: C, 41.2; H, 2.7; N, 9.6. Calc. for C$_{35}$H$_{26}$BrF$_{12}$N$_7$RuP$_2$: C, 41.4; H, 2.6; N, 9.9%). Mass spectrum (positive FAB): *m*/*z* 1017 [Ru(bipy)$_2$(bterpy)(PF$_6$)$_2$], 872 [Ru(bipy)$_2$(bterpy)(PF$_6$)] and 727 [Ru(bipy)$_2$(bterpy)].

Crystal Structure Determinations of [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ *and* [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$.—Red single crystals of [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ and [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ were obtained by the slow diffusion of diethyl ether vapour into acetonitrile solutions of the complexes.

Crystal data. [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$. C$_{35}$H$_{27}$F$_{12}$N$_7$P$_2$Ru, red blocks, crystal size 0.50 × 0.45 × 0.45 mm, *M* = 936.65, triclinic, space group $P\bar{1}$, *a* = 8.367(2), *b* = 11.821(4), *c* = 19.398(5) Å, α = 93.83(2), β = 95.25(2), γ = 89.62(2)°, *U* = 1906 Å^3, *F*(000) = 936, *Z* = 2, D_c = 1.63 g cm^{-3}, μ(Mo-Kα) = 5.78 cm^{-1}.

[Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$. C$_{35}$H$_{26}$BrF$_{12}$N$_7$P$_2$Ru, red plates, crystal size 0.75 × 0.15 × 0.05 mm, *M* = 1015.55, triclinic, space group $P\bar{1}$, *a* = 8.572(4), *b* = 11.689(7), *c* = 19.417(11) Å, α = 84.63(4), β = 82.74(4), γ = 88.53(4)°, *U* = 1921 Å^3, *F*(000) = 1004, *Z* = 2, D_c = 1.76 g cm^{-3}, μ(Mo-Kα) = 16.1 cm^{-1}.

Data collection and refinement. Red single crystals were mounted on glass fibres, and all geometric and intensity data were taken from these crystals using an automated four-circle Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-Kα radiation. The ω–2θ technique was used to measure 6886 reflections [6401 unique, *R*(merge) = 0.036] for [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ and 7164 reflections [6679 unique, *R*(merge) = 0.058] for [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ in the range $5 \leqslant 2\theta \leqslant 50°$. Three standard reflections (remeasured every 97 scans) showed a regular drop of 10% in intensity during data collection for [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ whilst there was no significant loss in intensity during data collection for [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$. For [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ the data were corrected for Lorentz and polarisation effects and for crystal decay whilst for [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ the data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied. The 5084 unique data with $I \geqslant 1.5\sigma(I)$ for [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ and the 4682 unique data with $I \geqslant 2.5\sigma(I)$ for [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ were used to solve and refine the structures in the triclinic space group $P\bar{1}$.

Structural analyses and refinement. The structures were solved by Patterson methods and developed using alternating cycles of least-squares refinement and Fourier-difference syntheses. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common anisotropic thermal parameter (*U* = 0.08 Å^2). In each case one of the hexafluorophosphate anions is well defined whilst the second such anion in the asymmetric unit is characterised by anomalously high thermal parameters. As these anions make no short intermolecular contacts with the cations of interest this imperfect anisotropic model was accepted. The final cycle of least-squares refinement for [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ included 514 parameters for 5084 variables and did not shift any parameter by more than 0.003 times its standard deviation, whilst that for [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ included 523 parameters for 4682 variables and did not shift any parameter by more than 0.004 times its standard deviation. For [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ the final *R* values were 0.0745 and 0.0771 and the final Fourier-difference map was featureless, with the largest peak of 1.03 e Å^{-3} close to the poorly defined hexafluorophosphate anion. For [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ the final *R* values were 0.0734 and 0.0758 and the final Fourier-difference map was featureless, with the largest peaks of 1.20 e Å^{-3} close to the metal and 1.05 e Å^{-3} close to the poorly defined hexafluorophosphate anion. Structure solution used SHELXTL PLUS[27] on a Micro Vax II computer. Atomic coordinates for [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ and [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ are presented in Tables 4 and 5 and selected bond lengths and angles in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Selected bond lengths (Å) and angles (°)

	[Ru(bipy-*N*,*N'*)$_2$(terpy-*N*,*N'*)][PF$_6$]$_2$	[Ru(bipy-*N*,*N'*)$_2$-(bterpy-*N*,*N'*)][PF$_6$]$_2$
Ru-N(1)	2.064(6)	2.041(7)
Ru-N(2)	2.056(6)	2.065(7)
Ru-N(3)	2.088(5)	2.086(6)
Ru-N(4)	2.106(6)	2.080(7)
Ru-N(5)	2.052(6)	2.059(7)
Ru-N(6)	2.133(6)	2.136(7)
N(1)-Ru-N(3)	84.4(2)	82.9(3)
N(1)-Ru-N(5)	97.3(2)	96.6(3)
N(1)-Ru-N(4)	98.4(2)	97.3(3)
N(2)-Ru-N(3)	97.6(2)	96.9(3)
N(2)-Ru-N(5)	88.2(2)	87.7(3)
N(3)-Ru-N(6)	99.8(2)	101.4(3)
N(2)-Ru-N(6)	101.9(2)	101.6(3)
N(4)-Ru-N(5)	95.3(2)	96.7(3)
N(4)-Ru-N(6)	81.3(2)	82.3(3)
N(1)-Ru-N(6)	175.6(2)	175.4(3)
N(1)-Ru-N(2)	78.7(2)	79.1(3)
N(2)-Ru-N(4)	175.7(2)	174.6(3)
N(3)-Ru-N(5)	174.1(2)	175.2(3)
N(3)-Ru-N(4)	78.9(2)	78.6(3)
N(5)-Ru-N(6)	78.4(2)	79.0(3)

Results and Discussion

We began by considering the features that would lead to the formation of complexes containing didentate terpy ligands. Although complexes containing such ligands have been postulated for many years[2] it is only recently that unambiguous spectroscopic and structural[16,17,28-41] data have been presented. Double-helical dinuclear complexes assembled from terpy ligands have very recently been reported.[42] Many of these systems are dynamic in solution, and we considered that a static didentate bonding mode could be forced on a terpy ligand when a kinetically inert metal centre is involved. Specifically, we thought that a d^6 metal centre bearing two chelating didentate ligands would provide a suitable challenge to the terpy ligand. We anticipated two possible consequences: the first would be the formation of a ligand-field-destabilised seven-co-ordinate complex containing two chelating didentate ligands and one chelating tridentate ligand, whilst the second would be the formation of a six-co-ordinate complex containing three chelating didentate ligands.

The reaction of *cis*-[Ru(bipy-*N*,*N'*)$_2$Cl$_2$] with terpy in methanol gave an orange-red solution from which [Ru(bipy)$_2$(terpy)][PF$_6$]$_2$ was precipitated as an orange solid upon the addition of methanolic ammonium hexafluorophosphate. Similarly, the reaction of the black complex *cis*-[Ru(phen-*N*,*N'*)$_2$Cl$_2$] with terpy in methanol gave a red solution, from which [Ru(phen)$_2$(terpy)][PF$_6$]$_2$ was isolated as an orange complex upon the addition of methanolic ammonium hexafluorophosphate.

An X-ray crystallographic study of a single crystal of the complex [Ru(bipy)$_2$(terpy)][PF$_6$]$_2$ has been undertaken to determine whether a six- or a seven-co-ordinate structure is present in the solid state. The structure of the cation (showing the numbering scheme used) is shown in Fig. 1. The most obvious feature is that the terpy ligand is didentate, and the compound should be formulated as [Ru(bipy-*N*,*N'*)$_2$(terpy-*N*,*N'*)][PF$_6$]$_2$ in the solid state. The ruthenium–nitrogen bond lengths range from 2.052(6) to 2.133(6) Å. The bonds to the bipy ligands Ru-N(1), Ru-N(2) and Ru-N(5) [2.064(6), 2.056(6) and 2.052(6) Å respectively] are similar to those observed in the [Ru(bipy)$_3$]$^{2+}$ salts[43] [2.056(6) Å] while the others [Ru-N(3), Ru-N(4) and Ru-N(6)] are significantly lengthened [2.088(5), 2.106(6) and 2.133(6) Å respectively]. This increase in bond length {with respect to the [Ru(bipy)$_3$]$^{2+}$ cation} is a result of the steric interactions between rings 3 and 7 (rings numbered according to the nitrogen atom they contain). The bipy ligand containing rings 1 and 2 is approximately planar (interplanar angle 3.7°), but the second bipy exhibits a twisting of 15.4° about the interannular C–C bond as a result of the interaction with the non-co-ordinated ring. Within the terpy ligand the major twisting of 52.3° occurs between the co-ordinated ring 6 and the non-co-ordinated ring 7. This large inter-ring angle is typical of compounds containing non-co-ordinated aromatic rings. A graphic representation is presented in Fig. 2, which shows inter-ring dihedral angles for all complexes of terpy found in the Cambridge Crystallographic Data Centre files.†[44] The two dihedral angles between pyridine rings within a terpy ligand are denoted θ and φ. The dihedral angle θ was defined as being between two co-ordinated pyridine rings. The other dihedral angle, φ, was left with undefined connectivity to the metal centre. Fig. 2 shows a plot of θ against φ for all of the data found. The most noticeable feature is that there are three distinct types of correlation. By far the largest number of data lie in zone 1, where complexes are found in which θ ≈ φ, and both angles lie within the range 0–20°. This corresponds to the 'normal' complexes, in which the terpy behaves as a near-coplanar chelating tridentate ligand.[45] Zone 2 is characterised by complexes in which the angle θ is 'normal', corresponding to the expected near-planar co-ordination of the bipy unit, but in which the dihedral angle between the central co-ordinated ring and the other ring is found to lie between 50 and 80°. This represents the known structurally characterised species containing didentate terpy ligands.[28-41] Finally, there is a most interesting region in which both θ and φ are approximately equal and in the range 25–40°. This region corresponds to dinuclear double-helical complexes in which the terpy ligand bridges two metal centres.[42] We note that similar dihedral angles to those in zone 2 are observed in non-cyclometallated complexes of 6-phenyl-2,2'-bipyridine, in which the phenyl group cannot co-ordinate to the metal centre.[22,24]

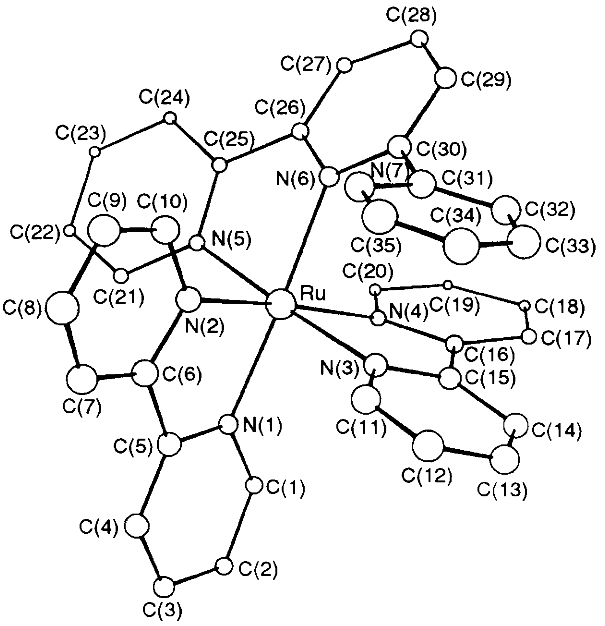

Fig. 1 Crystal and molecular structure of one of the enantiomers of the cation [Ru(bipy-*N*,*N'*)(terpy-*N*,*N'*)]$^{2+}$ present in the lattice of [Ru(bipy-*N*,*N'*)(terpy-*N*,*N'*)][PF$_6$]$_2$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity

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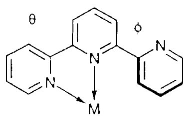
† Compounds were retrieved using QUEST and geometry analyses were made with GSTAT. Compounds in which the terpy domain was incorporated into a macrocyclic ring were excluded from the analysis. From the 171 hits, a total of 338 data for inter-ring angles between directly connected pyridine rings were obtained.

One consequence of the steric interactions is an offset stacking interaction between rings 7 and 3, which are approximately coplanar [Fig. 3(*a*)] with short graphitic-type contacts (centroid–centroid 3.46 Å), although this distance may simply represent the minimum van der Waals approach of the two rings. There is also a significant twisting (17.6°) between rings 5 and 6. The assignment of C(32) and N(7) is unambiguous and only the conformation indicated, which places N(7) closest to the metal, is present in the crystal lattice. There is a short interaction between N(7) and C(10) (3.15 Å) indicative of an N(7) ··· H(10) distance of about 2.7 Å. This interaction is shown in Fig. 3(*b*) and may explain the observed orientation. This orientation may also be dictated by the directing of the negative dipole of the pyridine *towards* the metal centre, in other words the complex is trapped at the beginning of the reaction coordinate leading to a (non-observed) seven-co-ordinate species.

In order to probe the effect of sterically demanding substituents in these reactions we have also investigated the reactions of bterpy. This compound is expected on steric and electronic grounds to favour the formation of complexes with a non-co-ordinated 2-bromopyridyl ring. The free compound was prepared in 64% yield as a white solid from the Krohnke-type reaction of [3-(6-bromo-2-pyridyl)-3-oxopropyl]dimethylammonium chloride, *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide and ammonium acetate in methanol (30 cm^3) for 4 h. The reaction of *cis*-[Ru(bipy-*N*,*N'*)$_2$Cl$_2$] with bterpy proceeded smoothly in methanol to give a deep red solution, from which a red compound was precipitated upon the addition of ammonium hexafluorophosphate. Red crystals obtained from methanol gave analytical data consistent with a formulation [Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$.

The crystal structural analysis of this compound reveals that it contains a didentate bterpy ligand in which the bromopyridyl ring is non-co-ordinated, and confirms the formulation [Ru(bipy-*N*,*N'*)$_2$(bterpy-*N*,*N'*)][PF$_6$]$_2$. The structure of the cation (showing the numbering scheme used) is shown in Fig. 4. It generally resembles that discussed above, with very similar patterns of bond lengths and angles. Within the bterpy ligand the major twisting of 56° again occurs between rings 6 and 7. Similar stacking and N(7) ··· H(10) interactions are present in this complex. An overlay representation of the two structures is presented in Fig. 5.



We have also addressed the question of the solution structures of these complexes. Acetonitrile solutions of the complexes exhibit in their cyclic voltammograms fully reversible ruthenium(II)–ruthenium(III) processes typical of species with N$_6$ donor sets {[Ru(bipy)$_2$(terpy)]$^{2+}$, +0.91 V; [Ru(bipy)$_2$(bterpy)]$^{2+}$, +0.89 V; [Ru(bipy-*N*,*N'*)$_3$]$^{2+}$, +0.85 V; [Ru(bipy-*N*,*N'*)(Hpbipy-*N*,*N'*)]$^{2+}$, +0.85 V; [Ru(phen)$_2$-(terpy)]$^{2+}$, +0.91 V; [Ru(phen-*N*,*N'*)$_2$(bipy-*N*,*N'*)]$^{2+}$, +0.91 V; [Ru(phen-*N*,*N'*)$_3$]$^{2+}$, +0.93 V, all potentials *vs.* ferrocene–ferrocenium}. The electronic spectra of aceteontrile solutions of the complexes show similar broad metal-to-ligand charge transfer (m.l.c.t.) absorption bands {[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$, 450 nm, ε = 12 000; [Ru(bipy)$_3$][PF$_6$]$_2$, 452 nm, ε = 13 000; [Ru(bipy)(terpy)(py)][PF$_6$]$_2$ (py = pyridine), 467 nm, ε = 10 000; [Ru(phen)$_2$(terpy)][PF$_6$]$_2$, 444 nm, ε = 8400; [Ru(phen)$_2$(bipy)][PF$_6$]$_2$, 445 nm, ε = 16 400; [Ru(phen)$_3$]-[PF$_6$]$_2$, 444 nm, ε = 18 500 dm^3 mol^{-1} cm^{-1}}. Combination of the electrochemical and spectroscopic data suggests that the [Ru(bipy)$_2$(terpy)]$^{2+}$ and [Ru(bipy)$_2$(bterpy)]$^{2+}$ complexes each possess a six-co-ordinate structure with three didentate ligands, as observed in the solid state. In particular, the differences in λ_{max} from the complex [Ru(bipy)(terpy)-(py)][PF$_6$]$_2$ with one tri-, one di- and one mono-dentate ligand, which acts as a model for isomeric species such as [Ru(terpy-*N*,*N'*,*N''*)(bipy-*N*,*N'*)(bipy-*N*)][PF$_6$]$_2$ supports this conclusion.[46] Accordingly, each of the new complexes also contains a didentate terpy ligand in solution.

The final question relates to the dynamic behaviour of these complexes in solution, and we now describe detailed ^{1}H NMR spectroscopic studies of the complex [Ru(bipy-*N*,*N'*)$_2$(terpy-*N*,*N'*)][PF$_6$]$_2$. The 400 MHz spectrum in CD$_3$CN solution is presented in Fig. 6; the full assignment was made with the aid of 250 MHz correlation spectroscopy (COSY) (Fig. 7) and 400 MHz nuclear Overhauser enhancement spectroscopy (NOESY)

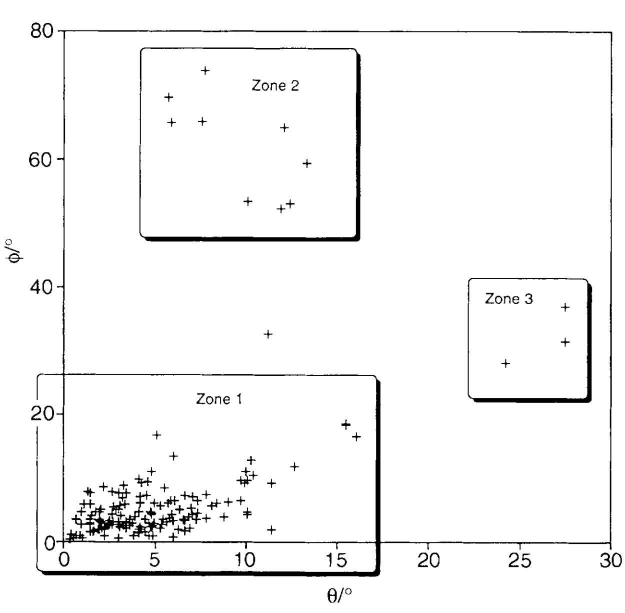


Fig. 2 Correlation of inter-ring dihedral angles for all metal 2,2′:6′,2″-terpyridine complexes found in the Cambridge Crystallographic Data Centre files

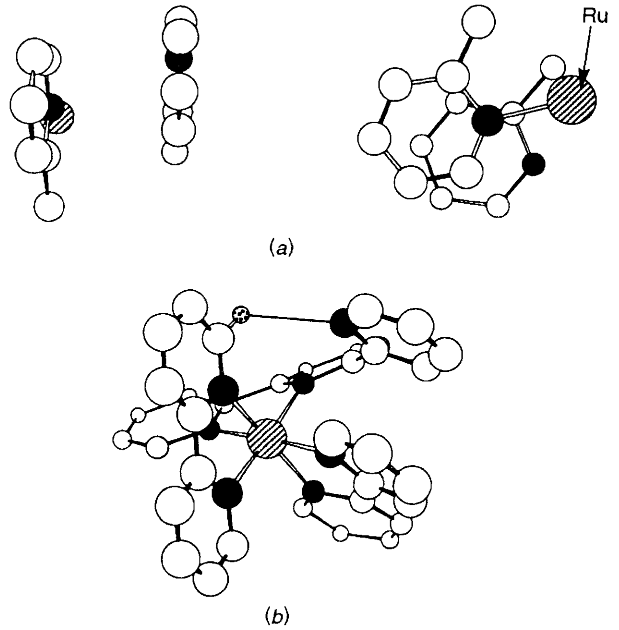


Fig. 3 (*a*) The stacking interactions observed between rings C and D in the cation [Ru(bipy-*N*,*N'*)(terpy-*N*,*N'*)]$^{2+}$ and (*b*) the interaction between the non-co-ordinated nitrogen and H^{6G}

(Fig. 8) experiments. The COSY experiments established the connectivity within each ring, whilst the NOESY spectra allowed the two rings of each 2,2′-bipyridine ligand to be unambiguously matched. In the NOESY experiment, with a mixing time of 1.5 s, the only cross-peaks observed were between H^3 and $H^{3'}$ of each 2,2′-bipyridine ring. The expected cross-peak between H^{3A} and H^{3B} is not observed as these two protons are coincident. It is also noticeable that two of the resonances are broadened at room temperature and that these do not show cross-peaks in the COSY spectrum. These resonances were assigned by separate decoupling experiments at 323 K in the course of variable-temperature studies (Fig. 9). Full assignments are presented in Table 2 together with details of the spectra of model compounds which were prepared to aid the assignment.

Some characteristic and diagnostic features are present. In octahedral ruthenium(II) complexes of oligopyridine ligands the protons of the co-ordinated pyridine rings show characteristic chemical shifts with $\delta(H^3) < \delta(H^4) < \delta(H^6) \approx \delta(H^5)$. In contrast, in non-co-ordinated pyridine rings the typical pattern is $\delta(H^6) < \delta(H^4) < \delta(H^5) \approx \delta(H^3)$. The coupling constant $^3J(H^5H^6)$ is typically between 5 and 6 Hz, and is consistently smaller than the other three-bond couplings $^3J(H^3H^4)$ and $^3J(H^4H^5)$ which are over 7 Hz, and this allows an unambiguous assignment of the spectra after the connectivity has been established from COSY experiments. As seen in Fig. 7, the chemical shifts of the resonances on ring C are quite different to those of the corresponding resonances of all the other rings and of the cations $[Ru(bipy)_3]^{2+}$ and $[Ru(terpy)_2]^{2+}$. The resonance 6C is shifted downfield with respect to the other H^6 resonances while the resonances 3C, 4C and 5C all experience an upfield shift, consistent with increased shielding as the protons lie above the π cloud of ring D.[47] Fig. 3(*b*) emphasises that 6C does not lie directly over the π cloud. The resonances of ring D are also shifted upfield with respect to the corresponding protons in $[Ru(bipy)_3]^{2+}$. Resonance 6G experiences a downfield shift as a consequence of the interaction with the nitrogen of ring C, which was noted in the solid-state structure. All of these data are consistent with ring C being non-co-ordinated in solution, and also with the absence of any fluxional processes of the windscreen-wiper type.

The two broadened resonances in the spectrum correspond to the protons 6G and 3C, and sharpen as the temperature is increased to 323 K and broaden more upon decreasing the temperature to 254 K. This variable-temperature experiment also provides no evidence for the exchange of the terminal co-ordinated and non-co-ordinated rings of the terpy ligand, in contrast to other systems containing a didentate terpy ligand.[28–33] We believe that the observed broadening and fluxional behaviour merely represents a 'ring-wobbling' process involving rings C and D. We have commented previously upon the broadening of spectra of non-co-ordinated aryl rings; most

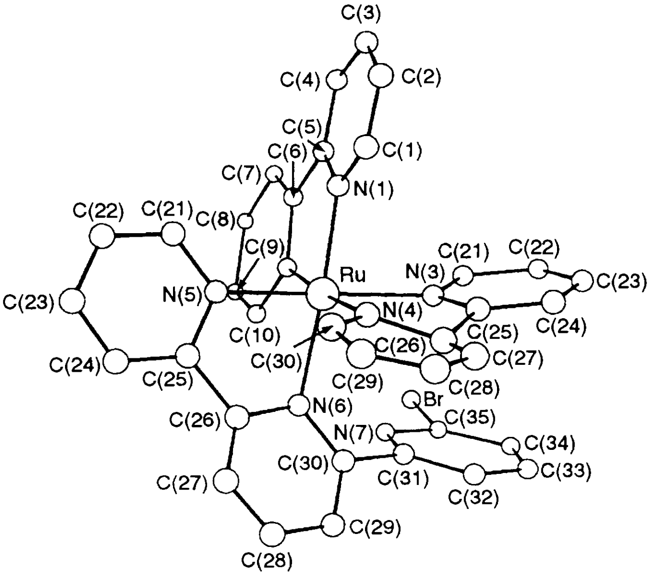


Fig. 4 Crystal and molecular structure of one of the enantiomers of the cation [Ru(bipy-*N*,*N*′)(bterpy-*N*,*N*′)]$^{2+}$ present in the lattice of [Ru(bipy-*N*,*N*′)(bterpy-*N*,*N*′)][PF$_6$]$_2$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity

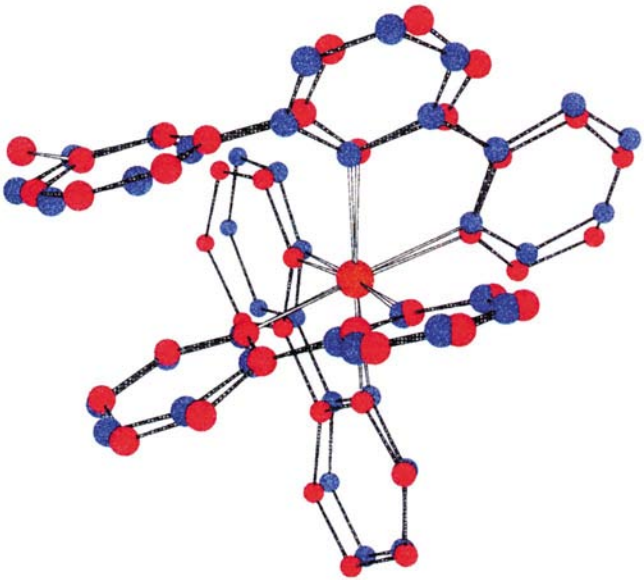


Fig. 5 Overlay of the structures of the [Ru(bipy-*N*,*N*′)(terpy-*N*,*N*′)]$^{2+}$ (blue) and [Ru(bipy-*N*,*N*′)(bterpy-*N*,*N*′)]$^{2+}$ (red) cations emphasising their similarity

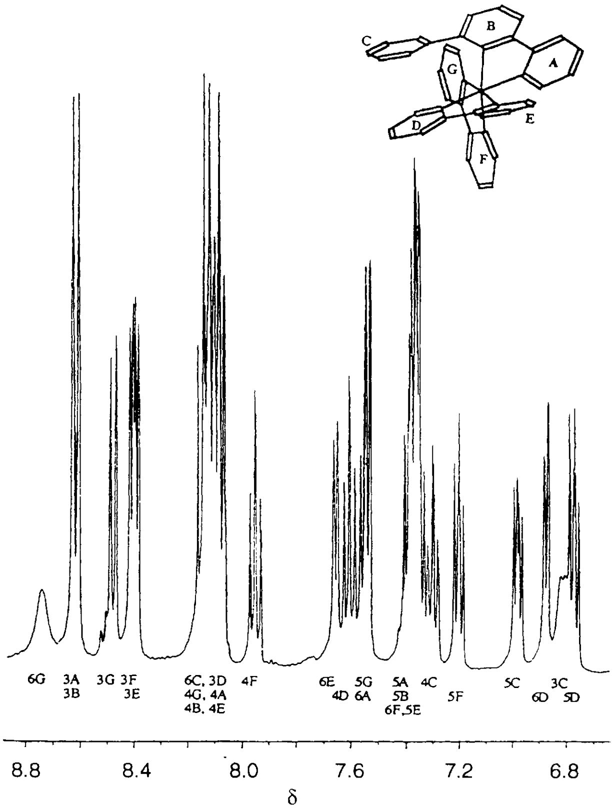


Fig. 6 The 400 MHz ^1H NMR spectrum of a CD_3CN solution of [Ru(bipy-*N*,*N*′)(terpy-*N*,*N*′)][PF$_6$]$_2$ showing the assignments resulting from detailed two-dimensional studies

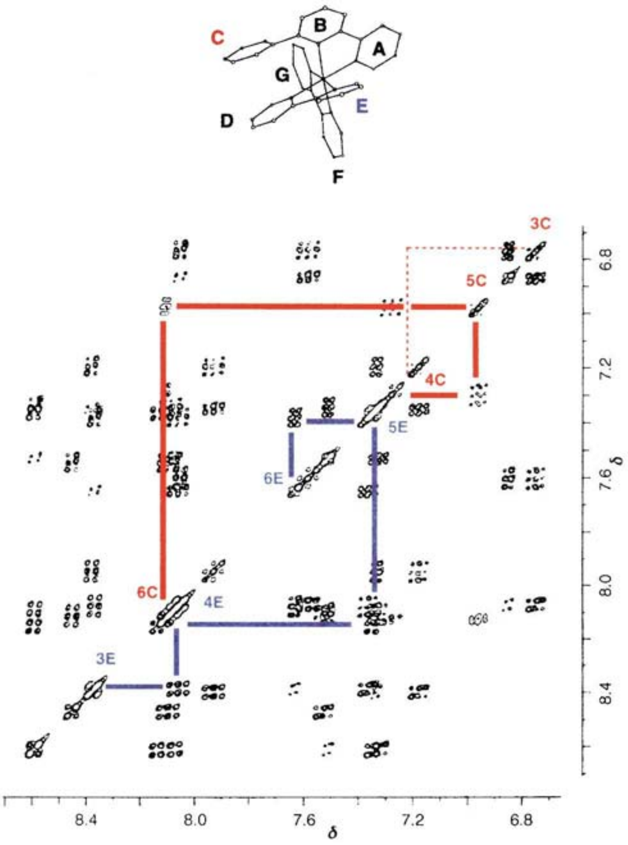


Fig. 7 The 250 MHz ^1H NMR COSY spectrum of a CD_3CN solution of [Ru(bipy-*N*,*N*′)(terpy-*N*,*N*′][PF_6]$_2$ showing the characteristic sequences for co-ordinated and non-co-ordinated rings. The non-co-ordinated ring has the red connectivity and a typical co-ordinated ring is denoted in blue

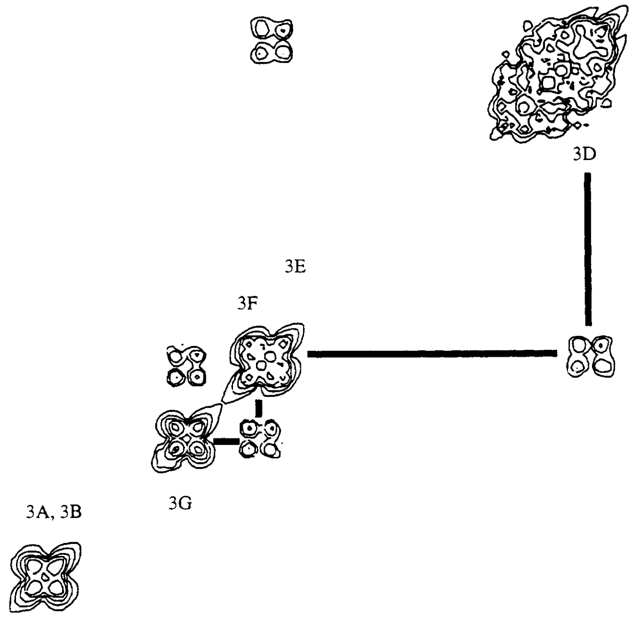


Fig. 8 The 400 MHz ^1H NMR NOESY spectrum of part of the aromatic region of a CD_3CN solution of [Ru(bipy-*N*,*N*′)(terpy-*N*,*N*′)][PF_6]$_2$ showing the NOESY cross-peaks which allow the assignment of the individual rings of the bipy ligands

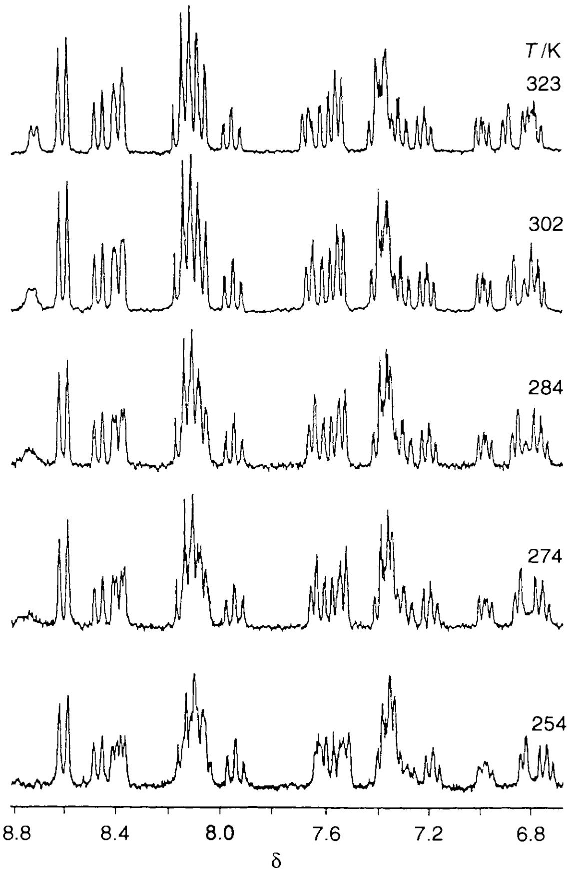


Fig. 9 Variable-temperature 250 MHz ^1H NMR spectra of CD_3CN solutions of [Ru(bipy-*N*,*N*′)(terpy-*N*,*N*′)][PF_6]$_2$

significantly, similar broadening is observed in the analogous complexes of Hpbipy, in which a windscreen-wiper motion is not possible.[47,48] The observed spectra are subjectively quite different in CD_3COCD_3 solution, and all of the resonances of [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF_6]$_2$ are shifted downfield with respect to CD_3CN solution, as are those for the related complexes [Ru(terpy)$_2$]$^{2+}$ and [Ru(bipy)$_3$]$^{2+}$. Furthermore, in contrast to the behaviour in CD_3CN solution, at room temperature the spectrum shows no broadened peaks, suggesting that the ring-wobbling motion is fast in this solvent.

As can be seen from Table 2, one of the important compounds involved in the understanding of the spectra of [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF_6]$_2$ was [Ru(bipy-*N*,*N*′)$_2$-(Hpbipy-*N*,*N*′)][PF_6]$_2$. The Hpbipy ligands in this complex act as a model for the hypodentate terpy; the only difference arises from the replacement of a nitrogen atom by a CH group. The electronic and steric factors are expected to be very similar in the two complexes. The complex was prepared by heating Hpbipy with *cis*-[Ru(bipy-*N*,*N*′)$_2$Cl$_2$] in ethane-1,2-diol; dilution with water and addition of methanolic [NH_4][PF_6] led to the precipitation of orange [Ru(bipy-*N*,*N*′)$_2$(Hpbipy-*N*,*N*′)][PF_6]$_2$. The FAB mass spectrum shows peaks with the correct isotopic distribution corresponding to Ru(bipy)$_2$-(Hpbipy)(PF_6), Ru(bipy)$_2$(Hpbipy), Ru(bipy)(Hpbipy) and Ru(bipy)$_2$; the cyclic voltammogram of an acetonitrile solution of Hpbipy shows a reversible oxidation at +0.85 V and two reversible reductions at −1.76 and −1.91 V (*vs.* ferrocene–ferrocenium). The absorption spectrum of the complex in acetonitrile solution shows a broad band in the visible region with a maximum at 447 nm (ε = 10 000 dm^3 mol^{-1} cm^{-1}).

The 400 MHz ^1H NMR spectrum of the complex in CD_3CN solution was assigned with the help of COSY experiments; the chemical shifts are generally similar to those of [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF_6]$_2$. The resonances corresponding to the protons on the non-co-ordinated pyridine ring, C, in [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF_6]$_2$ are absent in the spectrum of [Ru(bipy-*N*,*N*′)$_2$(Hpbipy-*N*,*N*′)][PF_6]$_2$, providing further support for the assignment of this ring. These

Table 2 Proton NMR spectroscopic data for [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ and [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$ together with reference data for a number of related compounds

		δ			
	Solvent	H^6	H^5	H^4	H^3
Ring A					
[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$	CD_3CN	7.50	7.35	8.10	8.59
	CD_3COCD_3	7.90	7.55	8.30	8.95
[Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$	CD_3CN	7.50	7.35	8.10	8.60
[Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$	CD_3CN	7.55	7.30	8.10	8.60
[Ru(bipy)$_3$][PF$_6$]$_2$	CD_3CN	7.75	7.41	8.06	8.53
	CD_3COCD_3	8.07	7.59	8.23	8.83
[Ru(terpy)$_2$][PF$_6$]$_2$	CD_3CN	7.35	7.15	7.90	8.50
	CD_3COCD_3	7.70	7.30	8.10	8.80
Ring B					
[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$	CD_3CN		7.25	8.10	8.59
	CD_3COCD_3		7.60	8.35	8.90
[Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$	CD_3CN		7.35	8.10	8.35
[Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$	CD_3CN		7.35	8.15	8.65
[Ru(terpy)$_2$][PF$_6$]$_2$	CD_3CN		8.75	8.4	8.75
	CD_3COCD_3		9.10	8.60	9.10
Ring C					
[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$	CD_3CN	8.10	6.95	7.28	6.80 (br)
	CD_3COCD_3	8.30	7.10	7.50	7.10
[Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$	CD_3CN		6.72 (br)	7.18	6.80 (br)
[Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$	CD_3CN	*	*	*	*
Ring D					
[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$	CD_3CN	6.85	6.74	7.58	8.10
	CD_3COCD_3	7.20	7.00	7.80	8.40
[Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$	CD_3CN	7.03	6.91	7.64	8.05
[Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$	CD_3CN	6.95	6.80	7.55	8.00
Ring E					
[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$	CD_3CN	7.63	7.35	8.10	8.37
	CD_3COCD_3	8.00	7.55	8.25	8.70
[Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$	CD_3CN	7.55	7.35	8.10	8.60
[Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$	CD_3CN	7.80	7.45	8.10	8.37
Ring F					
[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$	CD_3CN	7.35	7.18	7.92	8.38
	CD_3COCD_3	7.70	7.40	8.15	8.70
[Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$	CD_3CN	7.35	7.18	7.96	8.45
[Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$	CD_3CN	7.30	7.25	7.90	8.30
Ring G					
[Ru(bipy)$_2$(terpy)][PF$_6$]$_2$	CD_3CN	8.70 (br)	7.50	8.20	8.80
	CD_3COCD_3	9.05	7.70	8.30	8.95
[Ru(bipy)$_2$(bterpy)][PF$_6$]$_2$	CD_3CN	8.9 (br)	7.55	8.10	8.50
[Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$	CD_3CN	8.05	7.50	8.10	8.40

* The signals for the unco-ordinated phenyl ring in the complex [Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$ are broadened. Four broad resonances are observed at δ 6.0, 6.7, 7.0 and 7.2. A further broad resonance is hidden within one of the multiplets.

resonances are replaced by a series of broad resonances corresponding to the phenyl ring. The resonance assigned to H^{6G} is shifted upfield by δ 0.65 with respect to [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$. This provides support for the interaction of this proton with the nitrogen of the non-co-ordinated ring in the complex [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$; this interaction is absent in [Ru(bipy)$_2$(Hpbipy)][PF$_6$]$_2$.

Finally, we prepared an analogue of [Ru(bipy-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ containing 1,10-phenanthroline. The reaction of *cis*-[Ru(phen-*N*,*N*′)$_2$Cl$_2$] with terpy in methanol gave a red solution, from which the orange complex [Ru(phen-*N*,*N*′)$_2$(terpy-*N*,*N*′)][PF$_6$]$_2$ was isolated on the addition of methanolic ammonium hexafluorophosphate. The electronic spectrum shows a broad absorption with a maximum at 444 nm (ε = 8400 dm^3 mol^{-1} cm^{-1}). This compares favourably with the data for the related complexes [Ru(phen-*N*,*N*′)$_2$(bipy-*N*,*N*′)][PF$_6$]$_2$ (λ_{max} = 445 nm, ε = 16 400 dm^3 mol^{-1} cm^{-1}) and [Ru(phen-*N*,*N*′)$_3$][PF$_6$]$_2$ (λ_{max} = 444 nm, ε = 18 500 dm^3 mol^{-1} cm^{-1}). The complex shows a reversible oxidative wave at +0.91 V (*vs.* ferrocene–ferrocenium) corresponding to the ruthenium(II)–ruthenium(III) couple {*cf.* [Ru(phen-*N*,*N*′)$_2$(bipy-*N*,*N*′)][PF$_6$]$_2$, +0.91 V and [Ru(phen-*N*,*N*′)$_3$][PF$_6$]$_2$, +0.93 V}.

The 250 MHz ^{1}H NMR spectrum of a CD_3CN solution of the complex is sharp and well resolved, with the exception of two broad resonances, one at low and the other at high field (Fig. 10). These broadened resonances sharpen as the temperature of the solution is raised, and coupling constants reveal that they are to be assigned to a terpy H^3 (δ 6.25) and a phen H^2 proton (δ 9.00). It seems likely that the fluxional process is analogous to the 'ring-wobbling' process observed in the complex $[Ru(bipy)_2(terpy)][PF_6]_2$. The spectrum has been analysed by COSY and NOESY spectroscopy and assignments are presented in Table 3. The connectivities of the broad resonances at δ 9.00 and 7.95 were determined by separate decoupling experiments at 320 K. In contrast to the spectrum of $[Ru(bipy\text{-}N,N')_2(terpy\text{-}N,N')][PF_6]_2$ all of the resonances assigned to protons on the non-co-ordinated ring are broadened at room temperature, implying that the barrier to the ring-wobbling process is lower in $[Ru(phen\text{-}N,N')_2(terpy\text{-}N,N')][PF_6]_2$. The stacking interaction between the non-co-ordinated ring and the phen ligand may also be weaker than that between two pyridine rings as may the interaction between the non-co-ordinated nitrogen and the nearby proton. The chemical shifts of the terpy resonances are similar to those of the terpy resonances in the complex $[Ru(bipy\text{-}N,N')_2(terpy\text{-}N,N')][PF_6]_2$.

In conclusion, we have demonstrated that kinetically inert metal centres may be used for the systematic preparation of complexes containing hypodentate oligopyridine ligands. In a forthcoming paper we will describe the extension of this methodology to the preparation of complexes containing hypodentate 2,2′:6′,2″:6″,2‴-quaterpyridine, 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine and 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridine ligands, together with studies of the reactivity of the non-co-ordinated metal-binding domains.

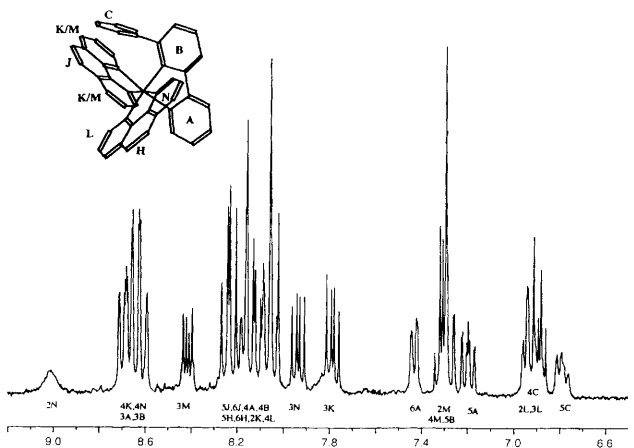


Fig. 10 The 400 MHz ^1H NMR spectrum of a CD_3CN solution of $[Ru(phen\text{-}N,N')(terpy\text{-}N,N')][PF_6]_2$ showing the assignments resulting from detailed two-dimensional studies

Table 3 Proton NMR spectroscopic data (δ) for $[Ru(phen\text{-}N,N')_2(terpy\text{-}N,N')][PF_6]_2$ in CD_3CN solution

terpy resonances

6A	5A	4A	3A	3B	4B	5B	3C	4C	5C	6C
7.35	7.20	8.10	8.65	8.65	8.65	8.10	6.25	6.90	6.80	*

phen resonances

5H	6H	5J	6J	2K	3K	4K	2L	3L	4L	2M	3M	4M	2N	3N	4N
8.05	8.25	8.15	8.25	8.20	7.80	8.70	6.95	6.9	8.1	7.3	8.4	7.3	9.0	7.95	8.7

* Not unambiguously assigned.

Table 4 Atomic coordinates (× 10^4) for all non-hydrogen atoms in $[Ru(bipy\text{-}N,N')_2(terpy\text{-}N,N')][PF_6]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	694(1)	2 329(1)	2 243(1)	C(22)	−2 476(11)	1 443(8)	389(4)
N(1)	2 046(7)	978(5)	1 893(3)	C(23)	−3 439(11)	2 384(10)	340(5)
N(2)	−422(7)	992(4)	2 626(3)	C(24)	−3 239(11)	3 250(8)	858(5)
N(3)	2 560(7)	2 545(5)	3 032(3)	C(25)	−2 027(9)	3 171(7)	1 382(4)
N(4)	2 002(7)	3 647(5)	1 880(3)	C(26)	−1 755(9)	4 058(6)	1 971(4)
N(5)	−1 055(7)	2 263(5)	1 427(3)	C(27)	−2 325(10)	5 146(7)	1 921(5)
N(6)	−805(7)	3 718(5)	2 528(3)	C(28)	−2 011(12)	5 918(8)	2 493(5)
N(7)	−505(9)	3 115(6)	3 980(3)	C(29)	−1 175(12)	5 576(7)	3 075(5)
C(1)	3 324(10)	1 063(7)	1 519(4)	C(30)	−594(9)	4 458(6)	3 101(4)
C(2)	4 294(11)	154(7)	1 384(5)	C(31)	150(9)	4 034(6)	3 765(4)
C(3)	3 951(11)	−891(7)	1 617(5)	C(32)	1 413(11)	4 632(8)	4 154(5)
C(4)	2 646(10)	−990(7)	1 992(4)	C(33)	2 023(13)	4 229(11)	4 768(6)
C(5)	1 692(8)	−46(6)	2 128(3)	C(34)	1 389(14)	3 285(12)	4 999(5)
C(6)	269(9)	−48(6)	2 530(3)	C(35)	103(13)	2 756(10)	4 592(5)
C(7)	−338(11)	−1 016(7)	2 779(4)	P(1)	5 946(3)	2 281(2)	6 158(1)
C(8)	−1 702(12)	−929(7)	3 129(5)	P(2)	1 762(4)	2 323(3)	9 369(2)
C(9)	−2 472(11)	117(7)	3 210(5)	F(1)	6 527(10)	1 075(5)	6 381(4)
C(10)	−1 789(10)	1 048(6)	2 962(4)	F(2)	7 463(8)	2 856(6)	6 589(3)
C(11)	2 928(10)	1 841(7)	3 542(4)	F(3)	5 017(9)	2 415(7)	6 839(4)
C(12)	4 267(11)	1 972(9)	4 000(4)	F(4)	4 397(8)	1 714(6)	5 734(3)
C(13)	5 308(11)	2 852(9)	3 938(5)	F(5)	6 855(10)	2 172(10)	5 501(4)
C(14)	4 967(10)	3 582(8)	3 403(4)	F(6)	5 359(11)	3 493(7)	5 957(6)
C(15)	3 574(9)	3 410(7)	2 950(4)	F(7)	834(14)	2 707(9)	8 699(5)
C(16)	3 158(9)	4 098(6)	2 358(4)	F(8)	3 156(12)	3 032(10)	9 243(8)
C(17)	3 847(11)	5 131(7)	2 261(5)	F(9)	511(14)	1 331(8)	9 313(7)
C(18)	3 410(13)	5 685(7)	1 660(6)	F(10)	2 295(19)	2 187(13)	10 107(5)
C(19)	2 325(12)	5 195(8)	1 172(6)	F(11)	684(23)	3 203(15)	9 671(7)
C(20)	1 601(10)	4 179(7)	1 303(4)	F(12)	2 826(19)	1 357(10)	9 209(14)
C(21)	−1 293(10)	1 399(7)	918(4)				

Table 5 Atomic coordinates (× 10^4) for all non-hydrogen atoms in [Ru(bipy-*N*,*N*′)$_2$(bterpy-*N*,*N*′)][PF$_6$]$_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	818(1)	2436(1)	2755(1)	C(21)	−1165(11)	1406(8)	4071(5)
Br	−212(2)	1887(1)	29(1)	C(22)	−2359(12)	1367(10)	4606(5)
N(1)	2146(8)	1076(6)	3097(3)	C(23)	−3411(13)	2279(11)	4651(6)
N(2)	−222(8)	1098(6)	2368(3)	C(24)	−3201(12)	3218(10)	4157(6)
N(3)	2701(8)	2647(6)	1963(4)	C(25)	−1961(10)	3210(8)	3623(5)
N(4)	2069(8)	3722(6)	3105(4)	C(26)	−1672(10)	4146(8)	3058(5)
N(5)	−936(8)	2304(6)	3585(4)	C(27)	−2283(12)	5230(8)	3095(6)
N(6)	−673(8)	3852(6)	2478(4)	C(28)	−1986(14)	6059(9)	2576(7)
N(7)	−133(8)	3422(6)	1006(4)	C(29)	−1061(12)	5764(8)	1966(6)
C(1)	3385(10)	1124(8)	3466(5)	C(30)	−452(10)	4659(7)	1933(5)
C(2)	4319(12)	184(9)	3633(5)	C(31)	405(10)	4338(8)	1265(5)
C(3)	3979(13)	−864(9)	3409(6)	C(32)	1640(12)	5023(9)	917(6)
C(4)	2702(12)	−956(8)	3033(5)	C(33)	2350(12)	4691(11)	285(7)
C(5)	1817(9)	27(7)	2887(4)	C(34)	1847(12)	3765(11)	13(6)
C(6)	444(9)	39(7)	2481(4)	C(35)	572(12)	3175(9)	396(6)
C(7)	−94(12)	−902(3)	2231(6)	P(1)	5541(3)	2139(3)	8765(2)
C(8)	−1393(12)	−798(8)	1868(6)	F(1)	7078(7)	2677(6)	8314(4)
C(9)	−2135(12)	262(9)	1783(6)	F(2)	3967(9)	1629(8)	9206(4)
C(10)	−1529(10)	1195(8)	2033(5)	F(3)	4932(13)	3421(8)	8840(7)
C(11)	3058(11)	1960(8)	1448(5)	F(4)	4734(10)	2294(10)	8077(5)
C(12)	4457(12)	2063(10)	997(5)	F(5)	6054(14)	949(7)	8590(6)
C(13)	5518(12)	2862(10)	1090(6)	F(6)	6247(13)	2191(16)	9423(5)
C(14)	5180(11)	3588(9)	1609(6)	P(2)	1782(5)	2344(4)	5590(2)
C(15)	3759(9)	3470(7)	2047(5)	F(7)	3196(13)	2916(14)	5793(10)
C(16)	3305(10)	4149(8)	2644(5)	F(8)	747(14)	2705(12)	6248(7)
C(17)	4040(12)	5153(8)	2740(6)	F(9)	559(15)	1344(11)	5639(9)
C(18)	3555(15)	5691(9)	3321(8)	F(10)	2483(22)	2324(19)	4856(7)
C(19)	2352(13)	5263(9)	3821(7)	F(11)	2803(22)	1359(12)	5745(15)
C(20)	1667(11)	4267(8)	3668(5)	F(12)	784(27)	3258(18)	5323(9)

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