

A Single Stranded Diruthenium(II) Helical Complex

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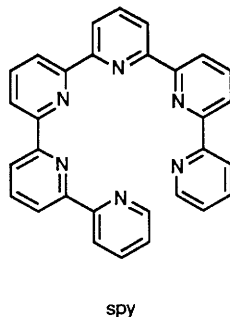
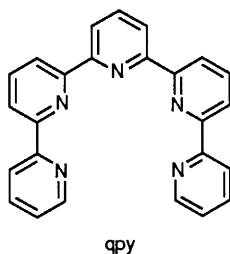
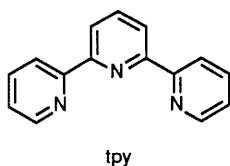
2,2':6',2'':6'',2''':6''',2''':6''''-Quinquepyridine (qpy) forms a binuclear complex $[(\text{tpy})\text{Ru}(\text{qpy})\text{Ru}(\text{tpy})\text{Cl}][\text{PF}_6]_3$ (tpy = 2,2':6',2'':6''-terpyridine) which has been structurally characterised and shown to possess a helical structure with two six-co-ordinate ruthenium centres bridged by the qpy ligand; the complex is electrochemically active, but there are no significant interactions between the two metal centres.

We have recently shown that the ligand 2,2':6',2'':6'',2''':6''',2''':6''''-quinquepyridine (qpy) may form complexes exhibiting a range of bonding modes including planar pentadentate mononuclear¹ and double helical binuclear.^{2,3} To date, the only characterised double helical complex with second or third row transition metals is $[\text{Pd}_2(\text{qpy})_2][\text{PF}_6]_4$ which contains two five-co-ordinate palladium centres.⁴ The related ligand 2,2':6',2'':6'',2''':6''',2''':6''''-sexipyridine (spy) forms double helical complexes containing two octahedral second and third row transition metals, and we have structurally characterised the compound $[\text{Cd}_2(\text{spy})_2][\text{PF}_6]_4$.⁵ The double helical topology occurs commonly in biological molecules such as the nucleic acids, proteins, and carbohydrates, but is relatively unusual in inorganic systems. The formation of double helical co-ordination compounds is favoured by the use of oligopyridine ligands which provide a flexible ligand environment in which π -stacking interactions dictate the overall ligand conformation. Such double helical co-ordina-

tion compounds may exhibit novel and useful interactions with helical biological molecules. In this communication we wish to report the formation of a single helical binuclear complex of qpy with a second row transition metal.

The direct reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ or $[\text{Ru}(\text{dmsO})_4\text{Cl}_2]$ (dmsO = dimethyl sulphoxide) with qpy resulted in the formation of complexes with a 1:1 Ru:qpy ratio, but for which FAB MS suggested the presence of an $\text{Ru}_2(\text{qpy})_2$ core. However, these compounds contained varying amounts of labile co-ordinated chloride and solvent and have not been fully characterised. In order to obtain more readily characterised products we investigated the reaction of $[\text{Ru}(\text{tpy})\text{Cl}_3]$ (tpy = 2,2':6',2'':6''-terpyridine) with qpy in the presence of *N*-ethylmorpholine. A red complex was obtained with analytical and mass spectral data consistent with the formulation $[\text{Ru}_2\text{Cl}(\text{qpy})(\text{tpy})_2][\text{PF}_6]_3$ [FAB MS (3-NBA matrix); m/z 867 $\{\text{Ru}(\text{qpy})(\text{tpy})(\text{PF}_6)\}$ based on ^{102}Ru]. The ^1H NMR spectrum of the compound is complex and contains numerous overlapping (but well-resolved) signals in the aromatic region; even using 2D techniques we have been unable to make a complete assignment of the 400 MHz ^1H NMR spectrum. However, a doublet at δ 10.18 is very characteristic of H_6 of a polypyridine ligand *cis* to a co-ordinated chloride.⁶

The crystal and molecular structure of the $[\text{Ru}_2(\text{qpy})(\text{tpy})_2\text{Cl}]^{3+}$ cation is shown in Figure 1.† The qpy ligand acts as a bridge between the two ruthenium(II) centres and serves as a bidentate donor to one and a terdentate to the other. Each ruthenium is six-co-ordinate; Ru(1) is co-ordinated to a tpy and a 'tpy' fragment of the qpy to give an N_6 environment reminiscent of the $[\text{M}(\text{bpy})_3]^{2+}$ cation ($\text{M} = \text{Ru}$ or Os).⁷ The other metal is co-ordinated to a chloride, a tpy, and a 'bpy' fragment of the qpy ligand. The co-ordination to the two tpy ligands closely resembles that observed in other ruthenium(II) tpy complexes with short bonds to the central pyridine ring (1.982, 1.983 Å) and longer bonds to the terminal rings (2.040, 2.094, 2.087, 2.077 Å).^{8,9} The qpy ligand is non-planar and shows a greatest twist of 105.1° about the interannular bond between the 'bpy' and 'tpy' fragments, although smaller interannular angles of 23.9° (rings 7 and 8, described according to the nitrogen numbering), 19.7° (rings 5 and 6), and 2.3° (rings 4 and 5) are observed between the other



† Crystal data: $\text{C}_{55}\text{H}_{39}\text{N}_{11}\text{ClF}_{18}\text{P}_3\text{Ru}_2$, red blocks, $M = 1526.55$, triclinic, space group $P1$, $a = 13.108(5)$, $b = 14.376(3)$, $c = 18.582(6)$ Å, $\alpha = 86.75(2)$, $\beta = 69.88(2)$, $\gamma = 79.05(2)^\circ$, $U = 3228$ Å³, $Z = 2$, $D_c = 1.57$ g cm⁻³, Mo- K_α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-}K_\alpha) = 6.7$ cm⁻¹. 8768 Reflections collected on a four circle diffractometer with $2\theta(\text{max.})$ 45°. The data were averaged and 4713 unique reflections with $I \geq 3 \sigma(I)$ were used in structure determination and refinement. The structure was solved by direct methods followed by iterative least-squares refinement and difference Fourier synthesis and refined (Ru, P, Cl anisotropic) to $R = 0.0889$, $R_w = 0.0956$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

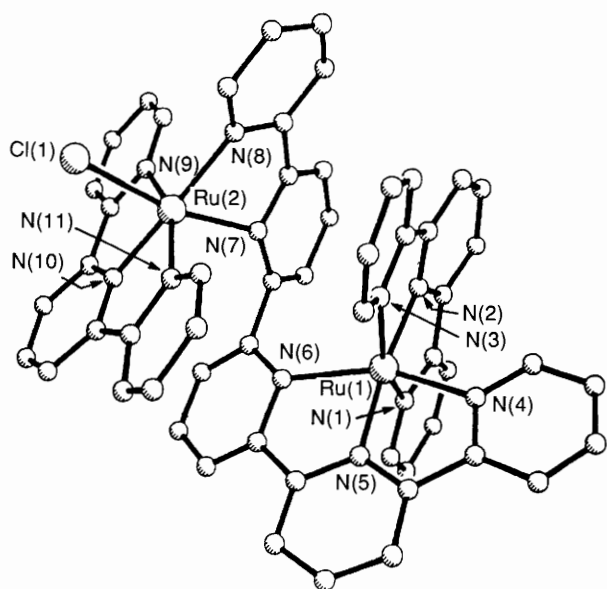


Figure 1. A view of the $[\text{Ru}_2(\text{qpy})(\text{tpy})_2\text{Cl}]^{3+}$ cation in $[\text{Ru}_2(\text{qpy})(\text{tpy})_2\text{Cl}][\text{PF}_6]_3$ showing the numbering scheme adopted. Selected bond lengths (Å): Ru(1)–N(1) 2.040(11), Ru(2)–Cl(1) 2.390(4), Ru(1)–N(2) 1.982(13), Ru(2)–N(7) 2.109(11), Ru(1)–N(3) 2.087(12), Ru(2)–N(8) 2.072(13), Ru(1)–N(4) 2.055(18), Ru(2)–N(9) 2.094(14), Ru(1)–N(5) 2.003(14), Ru(2)–N(10) 1.983(14), Ru(1)–N(6) 2.190(16), Ru(2)–N(11) 2.077(15).

rings. The large twist between the 'bpy' and 'tpy' fragments is similar to, but larger than, that observed between the 'bpy' and the unco-ordinated pyridyl ring in the complex $[\text{Ru}(\text{tpy})(\text{CO})_2\text{Br}_2]$ which contains a bidentate tpy.⁹ The structure may thus be regarded as a single helical qpy ligand linking two ruthenium centres. The twist between the 'bpy' and 'tpy' fragments is considerably greater than that observed in double helical binuclear complexes with first row transition metals,^{1–4} and it is clear that this is a result of the greater rotational freedom which the ligand has in the single helical array. The Ru(1)–Ru(2) distance is 5.38 Å which is considerably greater than the intermetallic distances observed previously in double helical binuclear complexes with first row transition metals,^{1–3} and also greater than that observed in $[\text{Cd}_2(\text{spy})_2][\text{PF}_6]_4$.⁵ Once again, π -stacking plays an important role in the formation of the helical structure and ring 7 is co-planar with ring 2 of the tpy attached to Ru(1), with an interplanar distance of 3.419 Å which is comparable to the interlamellar distance of 3.354 Å in graphite.¹⁰

The complex is electrochemically active, and exhibits two reversible oxidations (0.46 and 0.97 V, $E_a - E_p$ 70–80 mV, scan rate independent, Figure 1), an apparently reversible reduction (–1.79 V, $E_a - E_p$ 60 mV), and a quasi-reversible reduction (–2.10 V, $E_a - E_p$ 120 mV) in its cyclic voltammogram (MeCN, vs. internal Fc/Fc⁺, $E_a - E_p$ 64 mV). The two oxidations are probably associated with the sequential oxidation of Ru(2) {c.f. $[\text{Ru}(\text{bpy})(\text{tpy})\text{Cl}]^+$, 0.50 V vs. Fc/Fc⁺} and Ru(1) {c.f. $[\text{Ru}(\text{tpy})_2]^{2+}$, 0.97 V vs. Fc/Fc⁺}. The –1.79 V process is due to near coincident reductions of Ru(1) {reversible, c.f. $[\text{Ru}(\text{tpy})_2]^{2+}$, –1.74 V vs. Fc/Fc⁺} and Ru(2) {irreversible, $[\text{Ru}(\text{bpy})(\text{tpy})\text{Cl}]^+$, –1.66 V vs. Fc/Fc⁺}. The asymmetry of the +0.46 V process is associated with the return wave from the –1.79 V process. The difference in potential between the two oxidations of 0.51 V is comparable

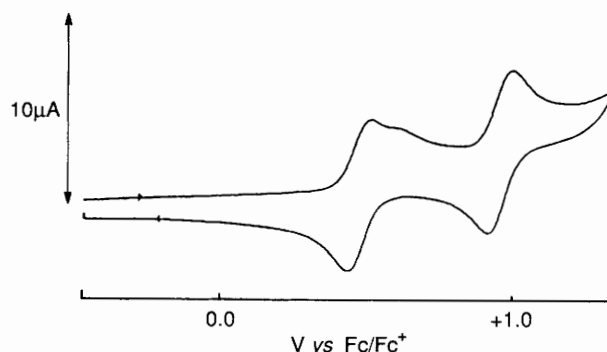


Figure 2. Oxidative cyclic voltammogram of $[(\text{tpy})\text{Ru}(\text{qpy})-\text{Ru}(\text{tpy})\text{Cl}][\text{PF}_6]_3(\text{MeCN})$, $[\text{Bu}_4\text{N}][\text{BF}_4]$ supporting electrolyte, reference internal ferrocene, 23°C, 100 mV s^{–1}.

to that of 0.47 V between $[\text{Ru}(\text{tpy})_2]^{2+}$ and $[\text{Ru}(\text{bpy})(\text{tpy})\text{Cl}]^+$ which are in similar environments to Ru(1) and Ru(2) respectively. The oxidations at +0.46 and +0.97 V are approximately one-electron processes (1.3 and 0.9 electron mol^{–1} respectively) and the reduction at –1.79 V approximately a two-electron process (2.3 electron mol^{–1}) as determined by the integration of the polarogram for a solution of known concentration to which a known amount of ferrocene was added as a one-electron reference.

The development of single stranded helical binuclear complexes offers a new approach to the design of photo- and electro-active molecules with controlled metal–metal interactions and configurations. The helical arrangement of ligands may be considered as a flexible ligand set which may accommodate metal ions in a range of geometries and oxidation states.

We thank the SERC for the award of a studentship (M. D. W.) and for funds towards the purchase of a diffractometer, and Johnson Matthey for the loan of ruthenium.

Received, 29th January 1990; Com. 0/004351

References

- E. C. Constable, M. G. B. Drew, G. Forsyth, and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1988, 1450.
- M. D. Ward, Ph.D Thesis, University of Cambridge, 1989.
- E. C. Constable, M. G. B. Drew, and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1987, 1600; M. G. B. Drew, R. C. S. McQueen, J. C. Nutkins, and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1988, 2655; E. C. Constable, M. G. B. Drew, G. Forsyth, and M. D. Ward, *Polyhedron*, 1989, **8**, 2551; E. C. Constable, J. Lewis, and M. Schröder, *Polyhedron*, 1982, **1**, 311.
- E. C. Constable, S. M. Elder, J. A. Healy, M. D. Ward, and D. A. Tocher, *J. Am. Chem. Soc.*, accepted.
- E. C. Constable, M. D. Ward, and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 1256.
- J. D. Birchall, T. D. O'Donoghue, and J. R. Wood, *Inorg. Chim. Acta*, 1979, **37**, L461.
- D. P. Lillema, D. S. Jones, and H. A. Levy, *J. Chem. Soc., Chem. Commun.*, 1979, 849; E. C. Constable, P. R. Raithby, and D. N. Smit, *Polyhedron*, 1989, **8**, 367.
- P. A. Adcock, F. R. Keene, R. S. Smythe, and M. R. Snow, *Inorg. Chem.*, 1984, **23**, 2336.
- G. B. Deacon, J. M. Patrick, B. W. Skelton, N. C. Thomas, and A. H. White, *Aust. J. Chem.*, 1984, **37**, 929.
- N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements,' Pergamon Press, Oxford, 1984.
- A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser, and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.