Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Multinucleating 2,2':6',2''-terpyridine ligands as supramolecular building blocks; heterotrinuclear complexes and the crystal and molecular structure of 6',6''-bis(2-pyridyl)-2,2':4',4'':2'',2'''-quaterpyridine (btpy)

Edwin C. Constable[a]; Alexander M. W. Cargill Thompson[a]; Derek A. Tocher[b]
[a] Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge, UK [b] Department of Chemistry, University College London, London, UK

To cite this Article Constable, Edwin C. , Thompson, Alexander M. W. Cargill and Tocher, Derek A.(1993) 'Multinucleating 2,2':6',2''-terpyridine ligands as supramolecular building blocks; heterotrinuclear complexes and the crystal and molecular structure of 6',6''-bis(2-pyridyl)-2,2':4',4'':2'',2'''-quaterpyridine (btpy)', Supramolecular Chemistry, 3: 1, 9 — 14

To link to this Article: DOI: 10.1080/10610279308029831

URL: http://dx.doi.org/10.1080/10610279308029831

SUPRAMOLECULAR CHEMISTRY, Vol. 3, pp. 9–14
Reprints available directly from the publisher
Photocopying permitted by license only

COMMUNICATION

Multinucleating 2,2′:6′,2″-terpyridine ligands as supramolecular building blocks; heterotrinuclear complexes and the crystal and molecular structure of 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine (btpy)

EDWIN C. CONSTABLE*[1], ALEXANDER M. W. CARGILL THOMPSON[1] and
DEREK A. TOCHER[2]

[1] *Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK and* [2] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

(Received January 13, 1993)

The crystal structure of the dinucleating 2,2′:6′,2″-terpyridine ligand 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine (btpy) has been determined and the two metal-binding tpy domains shown to be essentially planar and co-planar ($P\bar{1}$, $a = 6.304(2)$, $b = 8.208(2)$, $c = 11.535(3)$ Å, $\alpha = 97.42(2)$, $\beta = 104.25(2)$, $\gamma = 96.23(2)°$, $Z = 1$, $d_c = 1.36$ g cm^{-3}, 2214 unique observed reflections with $I > 1.5\sigma(I)$, $R = 0.0583$); a methodology involving sequential reaction with non-labile and labile metal centres allows the specific assembly of heterometallic supramolecular oligomers such as [(Xtpy)Ru(btpy)M-(btpy)Ru(Ytpy)]$^{n+}$ (M = cobalt(II), cobalt(III) or iron).

Supramolecular coordination oligomers and polymers are of considerable interest and can be prepared by the interaction of suitable metal ions with multidentate ligands containing two or more metal-binding domains.[1–4] 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.[5] Three 2,2′-bipyridine (bpy) ligands can be arranged around an octahedral metal centre.[6] Such a centre is chiral and if multinucleating ligand bpy domains are used to assemble multinuclear complexes, diastereomers are produced. In contrast, when two 2,2′:6′,2″-terpyridine (tpy) functionalities are coordinated to a six-coordinate centre the resulting complex is achiral. We are currently using multinucleating ligands containing tpy domains for the assembly of coordination oligomers and polymers and describe in this paper the structure of a multinucleating ligand and the systematic synthesis of heteronuclear oligomers.[7]

The dinucleating ligand btpy is prepared in good yield by the nickel(0) coupling of 4′-chloro-2,2′:6′,2″-terpyridine,[4,8] and slow evaporation of a chloroform solution yields pale yellow needles. The crystal and molecular structure of btpy is presented in Fig 1.[9] Each of the tpy domains of the ligand adopts a *trans, trans* conformation about the interannular C-C bonds as has been observed in all previous examples of free oligopyridine ligands.[3,10,11] There are no significant interactions between the pairs of atoms N(1) and N(3a). The individual tpy units are only approximately planar with angles of 23.9 and 22.0° between the planes of rings 1 and 2 and rings 2 and 3 respectively (rings defined by the nitrogen atom they contain). This is somewhat greater than observed in other 2,2′:6′,2″-terpyridine derivatives,[10] but is less than is observed in the related ligand 2,3,5,6-tetra(2-pyridyl)pyrazine.[12] There is a crystallographic inversion centre between C(8) and C(8a) relating the two tpy domains. The molecules are stacked up along the crystallographic *a* axis (6.304 angstroms) with no significant short contacts between molecules.

---

* To whom correspondence should be addressed.

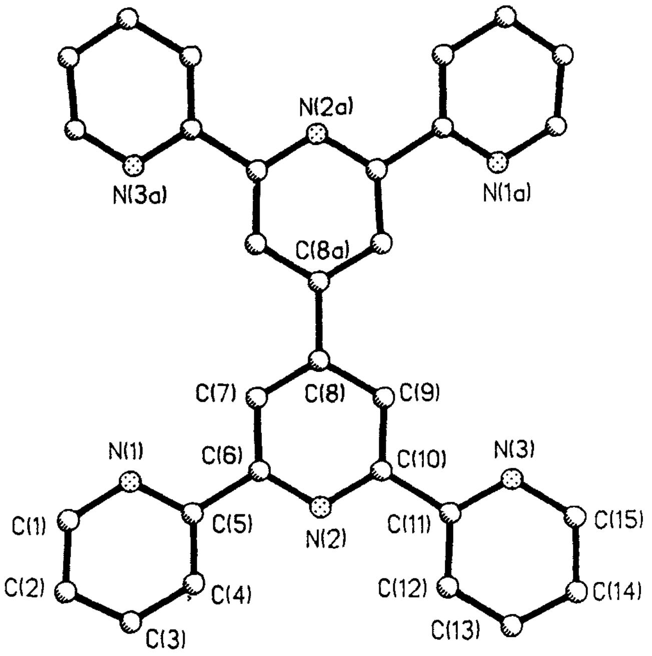
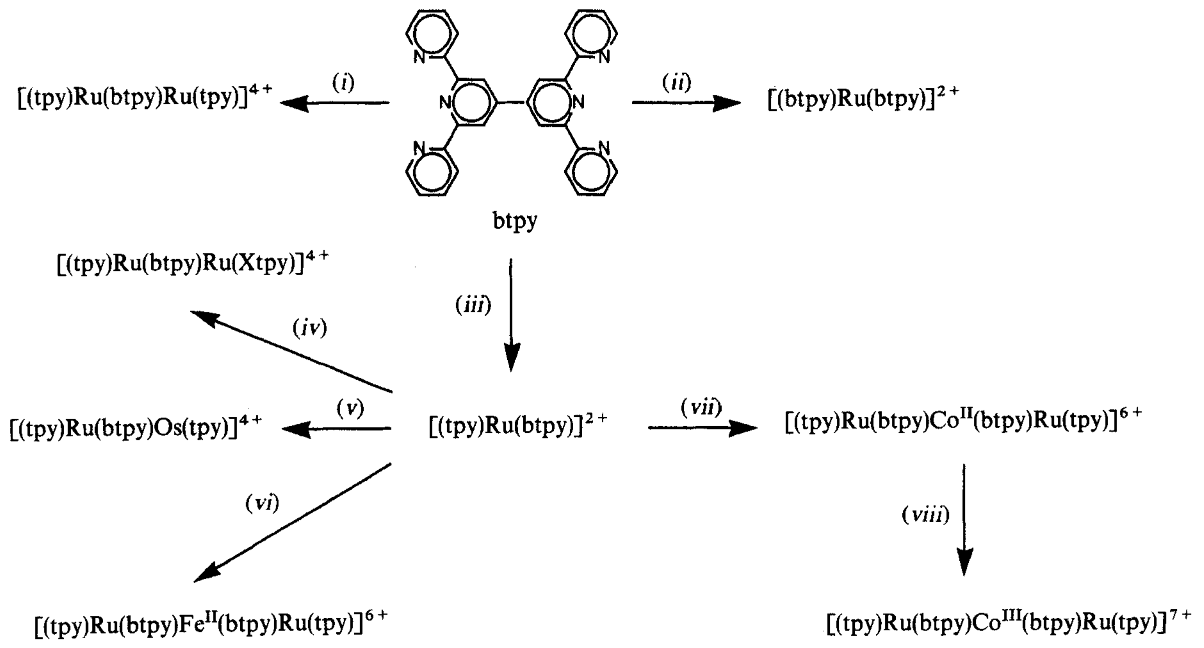
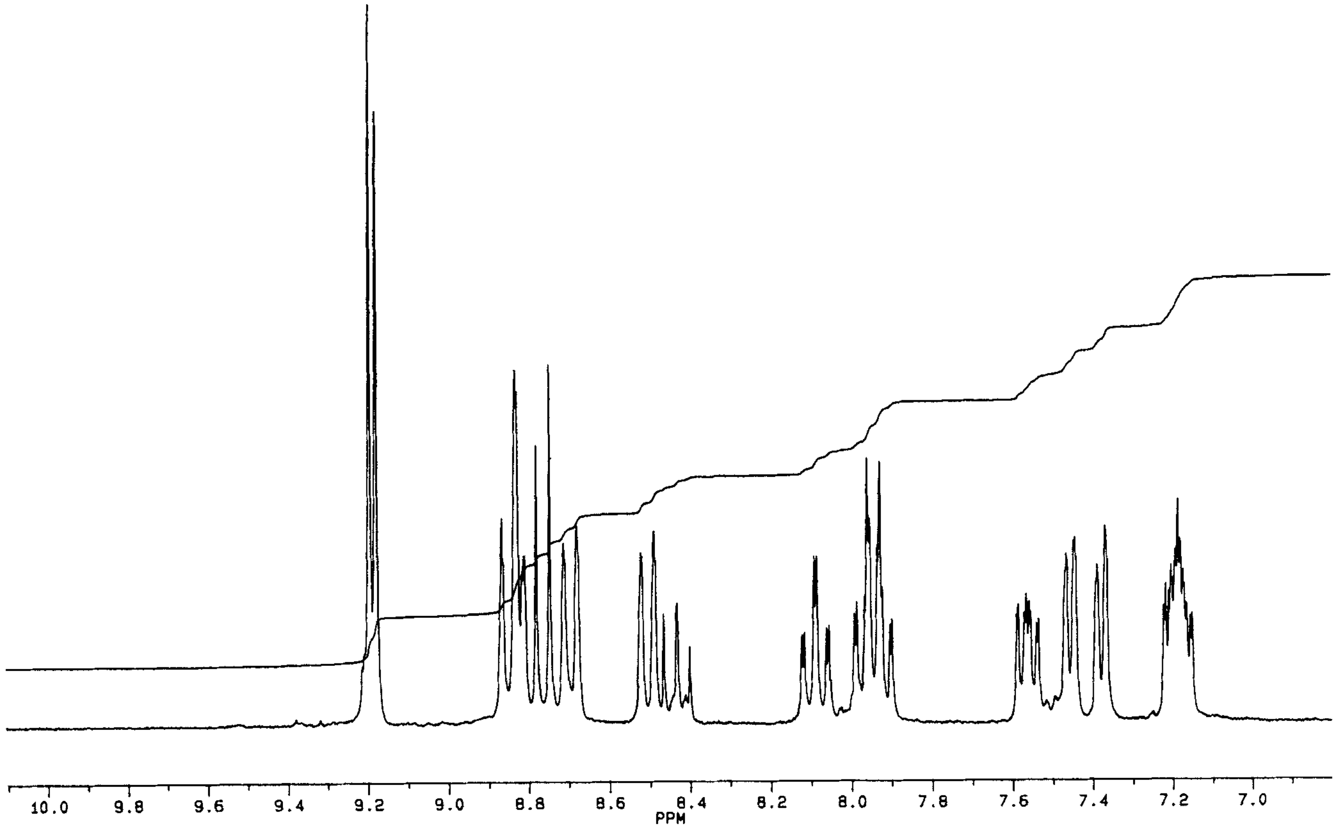


Figure 1 The crystal and molecular structure of btpy, plan view, showing numbering scheme adopted.

We have previously shown that the homoleptic dinuclear complexes $[(Xtpy)M(btpy)M(Xtpy)]^{n+}$ (Xtpy = 4'-substituted-tpy) are readily prepared.[4] The reaction of btpy with 1 equivalent of $Ru(tpy)Cl_3$ in hot $HOCH_2CH_2OH$ for 20 minutes gives a deep red solution from which the salt $[(tpy)Ru(btpy)][PF_6]_2$ containing an un-coordinated tpy domain, was isolated in 41% yield. The FAB mass spectrum (3-nitrobenzyl alcohol matrix) exhibits peaks at *m/z* 944 $[(tpy)Ru(btpy)][PF_6]$ and 799 [(tpy)Ru(btpy)], with no significant peaks at higher mass. The ^1H NMR spectrum (Fig 2(a)) contains 16 resonances, 6 due to the tpy, and 5 each due to the coordinated and free tpy fragments of the btpy ligand. This new cations, $[(tpy)Ru(btpy)]^{2+}$, with a coordinatively unsaturated btpy ligand is synthetically extremely versatile. Reaction with $[Ru(Xtpy)Cl_3]$ in the presence of a reducing agent yields the heteroleptic species $[(tpy)Ru(btpy)Ru(Xtpy)]^{4+}$ in which the two ruthenium centres are non-equivalent. The FAB mass spectrum of the complex $[(tpy)Ru(btpy)Ru(tpy)][PF_6]_4$ exhibits peaks clustered about *m/z* 1570 $[(tpy)Ru(btpy)Ru(tpy)][PF_6]_3$, 1424 $[(tpy)Ru(btpy)Ru(tpy)][PF_6]_2$ and 1280 $[(tpy)Ru(btpy)Ru(tpy)][PF_6]$, whilst that of $[(tpy)Ru(btpy)Ru(MeO_2Stpy)][PF_6]_4$ exhibits peaks clustered about *m/z* 1647 $[(tpy)Ru(btpy)Ru(MeO_2Stpy)][PF_6]_3$, 1502 $[(tpy)Ru(btpy)Ru(MeO_2Stpy)][PF_6]_2$ and 1356 $[(tpy)Ru(btpy)Ru(MeO_2Stpy)][PF_6]$. Similarly, $[(tpy)Ru(btpy)Os(Xtpy)]^{4+}$ species which are expected to exhibit interesting photochemical properties can be obtained by reaction of $[(tpy)Ru(btpy)][PF_6]_2$ with $[Os(tpy)Cl_3]$. The FAB mass spectrum of the complex $[(tpy)Ru(btpy)Os(tpy)][PF_6]_4$ exhibits peaks clustered about *m/z* 1656 $[(tpy)Ru(btpy)Os(tpy)][PF_6]_3$, 1512 $[(tpy)Ru(btpy)Os(tpy)][PF_6]_2$ and 1367 $[(tpy)Ru(btpy)Os(tpy)][PF_6]$. Heterotrinuclear species of the form $[(tpy)Ru(btpy)M(btpy)Ru(tpy)]^{6+}$ (M = Fe, Co) can be simply prepared by adding a solution of excess of $[(tpy)Ru(btpy)]^{2+}$ to a solution of a labile cobalt(II) or iron(II) salt in 1:1 H_2O: MeCN. These complexes do not exhibit parent ions in either their FAB or laser desorption time-of-flight mass spectra, but show fragmentations peaks at *m/z* 943 $[(tpy)Ru(btpy)][PF_6]$ and 798 [(tpy)Ru(btpy)]. The paramagnetic diruthenium(II)cobalt(II) complex can readily be oxidized chemically or electrochemically to the diagmagnetic species $[(tpy)Ru^{II}(btpy)Co^{III}(btpy)Ru^{II}(tpy)]^{7+}$. The diruthenium(II)iron(II) and diruthenium(II)cobalt(II) complex cations both contain only low-spin d^6 metal centres and are diamagnetic, exhibiting 16 aromatic resonances in their ^1H NMR spectra, assigned to the three non-equivalent coordinated tpy fragments. Assignments have been made by 2D COSY experiments and the ^1H NMR spectrum of a CD_3CN solution of the diruthenium(II)iron(II) complex $[(tpy)Ru^{II}(btpy)Fe^{II}(btpy)Ru^{II}(tpy)][PF_6]_6$ is shown in Fig 2(b). In the diruthenium(II)cobalt(II) complex, the five resonances of the tpy domains coordinated to the cobalt(II) centre



(*i*) $[Ru(tpy)Cl_3]$ (0.8–2.5 equivalents), N-ethylmorpholine, MeOH; (*ii*) $RuCl_3.nH_2O$ (0.5 equivs.), dimethylformamide; (*iii*) $[Ru(tpy)Cl_3]$ (1 equiv.), $HOCH_2CH_2OH$; (*iv*) $[Ru(Xtpy)Cl_3]$ (1 equiv.), N-ethylmorpholine, MeOH; (*v*) $[Os(tpy)Cl_3]$ (1 equiv.), $HOCH_2CH_2OH$; (*vi*) $[Fe(H_2O)_6][BF_4]_2$ (0.5 equivs.), $MeCN/H_2O$; (*vii*) $[Co(CH_3COO)_2(H_2O)_4]$ (0.5 equivs.), $MeCN/H_2O$; (*viii*) Cl_2, $MeCN/H_2O$.



(a)

Figure 2 250 MHz ^1H NMR spectrum of CD_3CN solutions of (a) $[(tpy)Ru(btpy)][PF_6]_2$ (b) $[(tpy)Ru(btpy)Fe(btpy)Ru(tpy)][PF_6]_6$ and (c) paramagnetically shifted $[(tpy)Ru(btpy)Co^{II}(btpy)Ru(tpy)][PF_6]_6$. In spectrum c) a broad peak is also observed at ~90 g.

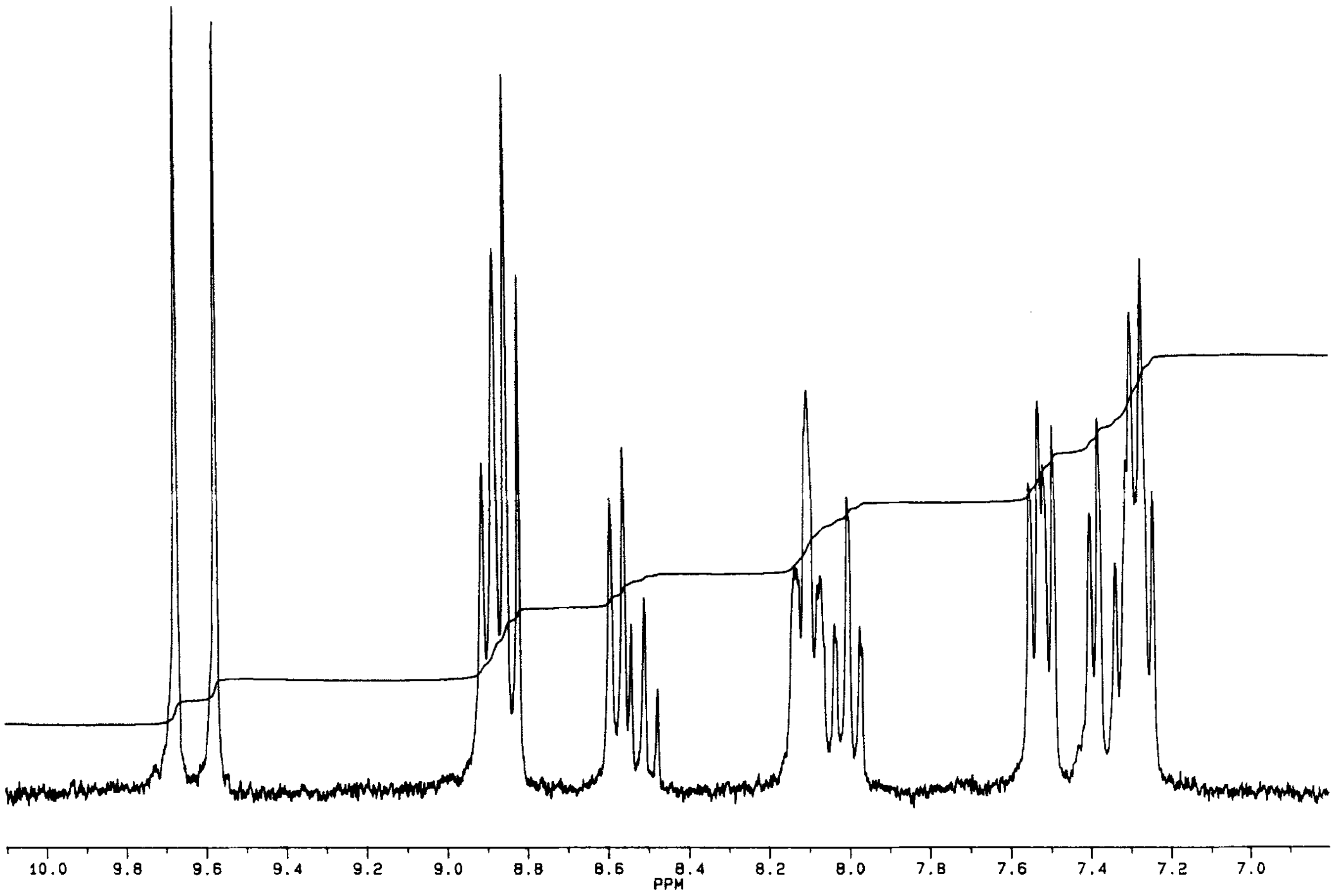


Figure 2b

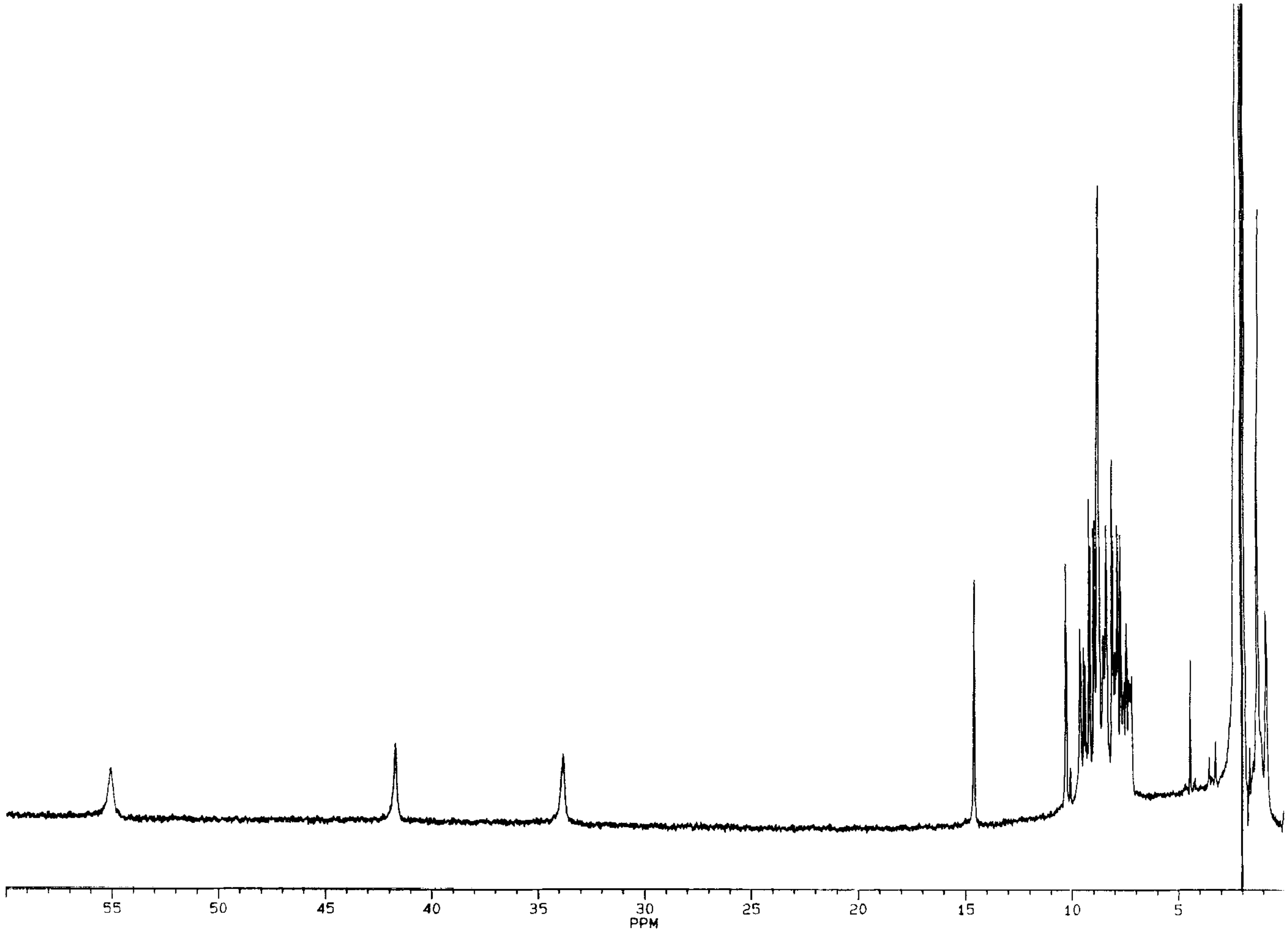


Figure 2c

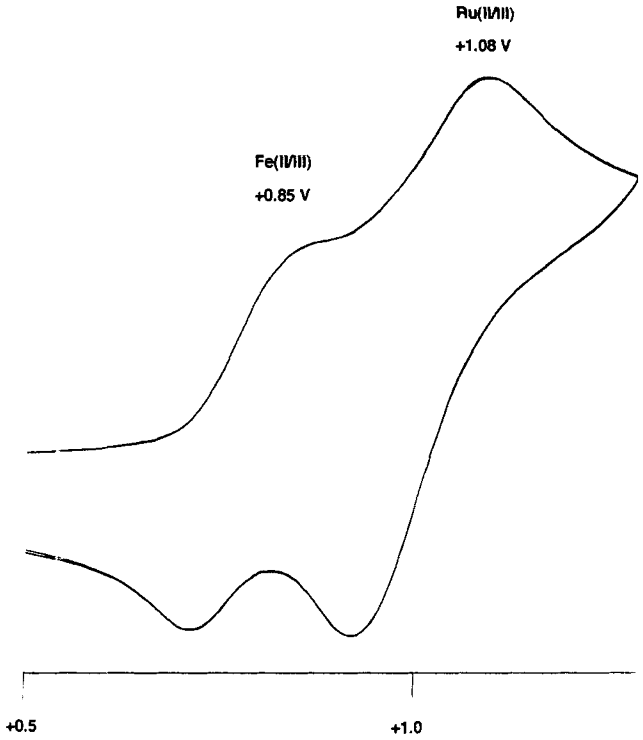


Figure 3 Cyclic voltammogram of an acetonitrile solution of $[(\mathrm{MeO_2Stpy})\mathrm{Ru(btpy)Fe(btpy)Ru}(\mathrm{MeO_2Stpy})][\mathrm{PF_6}]_6$ ($[\mathrm{Bu}^n_4\mathrm{N}][\mathrm{BF_4}]$ supporting electrolyte), showing separate iron(II/III) and ruthenium(II/III) oxidation waves.

are paramagnetically shifted downfield and significantly broadened, whilst the proton resonances of the two tpy domains coordinated to the ruthenium(II) centres are unshifted and only slightly broadened (Fig 2(c)).

The cyclic voltammogram of $[(\mathrm{tpy})\mathrm{Ru(btpy)}][\mathrm{PF_6}]_2$ shows a single quasi-reversible oxidation (0.977 V) and two reversible reductions (−1.56 V, −1.89 V), as expected for a ruthenium(II) centre in a bis-tpy environment[3] (acetonitrile solution, $[\mathrm{Bu}^n_4\mathrm{N}][\mathrm{BF_4}]$ supporting electrolyte, all potentials quoted *versus* internal $\mathrm{Fc/Fc^+}$). In contrast, the trinuclear species $[(\mathrm{tpy})\mathrm{Ru^{II}(btpy)Fe^{II}(btpy)Ru^{II}(tpy)}][\mathrm{PF_6}]_6$ exhibits a reversible one electron oxidation of the iron(II) centre at approximately 0.80 V which is partially obscured by a similar two electron process at 0.968 V corresponding to the simultaneous oxidation of the ruthenium(II) centres. Various ligand based reductions are also observed. In the related complex $[(\mathrm{MeO_2Stpy})\ \mathrm{Ru^{II}}\ (\mathrm{btpy})\ \mathrm{Fe^{II}}\ (\mathrm{btpy})\ \mathrm{Ru^{II}}\ (\mathrm{MeO_2Stpy})]$ $[\mathrm{PF_6}]_6$ ($\mathrm{MeO_2Stpy}$ = 4′-methylsulphonyl-tpy) the strongly electron withdrawing methylsulphonyl substituent destabilises the ruthenium(III) state and shifts the two electron ruthenium(II/III) couple to 1.075 V revealing the unaffected iron(II/III) couple as a one electron process at 0.850 V (Fig 3).

We are currently investigating mixed ligand ($[(\mathrm{Xtpy})\mathrm{Ru(btpy)Ru(Ytpy)}]^{4+}$) and mixed metal/ligand ($[(\mathrm{Xtpy})\mathrm{Ru(btpy)Os(Ypty)}]^{4+}$) dinuclear systems and extending these approaches by a "complexes as ligands/complexes as metals" strategy[13] to longer chain oligomers.

ACKNOWLEDGMENT

We thank the SERC for grants towards the purchase of a diffractometer (D.A.T.), molecular graphics facilities (E.C.C.) and a studentship (A.M.W.C.T.), and the Royal Society and the Isaac Newton Trust for grants enabling the purchase of spectrometers (E.C.C.).

REFERENCES

1 Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V.; *J. Am. Chem. Soc.* **1992**, *114*, 2944; Denti, G.; Serroni, S.; Sabatino, L.; Ciano, M.; Ricevuto, V.; Campagna, S.; *Gazz. Chim. Ital.* **1991**, *121*, 37; Denti, G.; Serroni, S.; Campagna, S.; Ricevuto, V.; Balzani, V.; *Inorg. Chim. Acta* **1991**, *182*, 127; Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V.; *ibid.* **1990**, *176*, 175; Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V.; *Inorg. Chem.* **1990**, *29*, 4750; Denti, G.; Sabatino, L.; Derosa, G.; Bartolotta, A.; Dimarco, G.; Ricevuto, V.; Campagna, S.; *ibid.* **1989**, *28*, 3309; Campagna, S.; Denti, G.; Serroni, S.; Ciano, M.; Juris, A.; Balzani, V.; *ibid.* **1992**, *31*, 2982; Denti, G.; Serroni, S.; Campagna, S.; Ricevuto, V.; Balzani, V.; *Coord. Chem. Rev.* **1991**, *111*, 227; De Cola, L.; Barigelletti, F.; Balzani, V.; Belser, P.; Von Zelewsky, A.; Seel, C.; Frank, M.; Vögtle, F.; *ibid.* **1991**, *111*, 255; Crane, J.D.; Sauvage, J.-P.; *New J. Chem.* **1992**, *16*, 649; Chambron, J.C.; Coudret, C.; Sauvage, J.-P.; *ibid.* **1992**, *16*, 361; Beley, M.; Collin, J.-P.; Sauvage, J.-P.; Sugihara, H.; Heisel, F.; Miehe, A.; *J. Chem. Soc., Dalton Trans.* **1991**, 3157; Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; *J. Chem. Soc., Chem. Commun.* **1989**, 776; *Inorg Chem.* **1990**, *29*, 5009; Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Decola, L.; Flamigni, L.; Balzani, V; *ibid.* **1991**, *30*, 4230; Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Flamigni, L.; De Cola, L.; Balzani, V.; *Coord. Chem. Revs.* **1991**, *111*, 291; Kirchhoff, J.R.; Mcmillin, D.R.; Marnot, P.A.; Sauvage, J.-P.; *J. Am. Chem. Soc.* **1985**, *107*, 1138.

2 Constable, E.C.; Hannon, M.J.; Lenman, M.M.; Cargill Thompson, A.M.W.; Tocher, D.A.; Walker, J.V.; *Supramol. Chem.*, in the press; Constable, E.C.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Dalton Trans.* **1992**, 3467; Constable, E.C.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Chem. Commun.* **1992**, 617; Constable, E.C.; Cargill Thompson, A.M.W.; Tocher, D.A.; in *Supramolecular Chemistry* (Balzani, V. and De Cola, L., eds), Klewer, **1992**, p. 219; Constable, E.C.; *Tetrahedron* **1992**, *48*, 10013.

3 Constable, E.C.; Cargill Thompson, A.M.W.; Tocher, D.A.; Daniels, M.A.M.; *New J. Chem.* **1992**, *16*, 855.

4 Constable, E.C.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Dalton Trans.* **1992**, 2947.

5 Constable, E.C.; *Adv. Inorg. Chem. Radiochem.* **1987**, *30*, 69.

6 Constable, E.C.; *Adv. Inorg. Chem.* **1989**, *34*, 1.

7 Constable, E.C., Cargill Thompson, A.M.W.; Tocher, D.A.; *Polym. Preprints* **1993**, *34*, 110; *Makromol. Chem.*, in the press.

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

9 Crystal Data: $\mathrm{C_{30}H_{20}N_6}$, triclinic, $P\bar{1}$, $a = 6.304(2)$, $b = 8.208(2)$, $c = 11.535(3)$ Å, $\alpha = 97.42(2)$, $\beta = 104.25(2)$, $\gamma = 96.23(2)°$, $U = 567$ Å^3, M = 464.53, $Z = 1$, $d_c = 1.36\ \mathrm{g\,cm^{-3}}$, $F(000)$ 242, $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å, $\mu(\mathrm{Mo_{K\alpha}}) = 5.78\ \mathrm{cm^{-1}}$. The structure was solved by direct methods followed by iterative least-squares refinement and difference Fourier synthesis; C, H, N anisotropic,

H atoms riding on appropriate carbon atom with fixed isotropic *U*. 2832 Reflections measured ($5 < 2\theta < 55°$), corrected for absorption, 2214 unique observed reflections, $R = 0.0583$, $wR = 0.0812$.

10 Merritt, L.L.; Schroeder, E.D.; *Acta Crystallogr.* **1956**, *9*, 801; Nakatsu, K.; Yoshioka, H.; Matsui, M.; Koda, S.; Ooi, S.; *Acta Crystallogr., Sect. A* **1972**, *28*, S24; Chisholm, M.H.; Huffman, J.C.; Rothwell, I.P.; Bradley, P.G.; Kress, N.; Woodruff, W.H.; *J. Am. Chem. Soc.* **1981**, *103*, 4945.

11 Constable, E.C.; Lewis, J.; Liptrot, M.C.; Raithby, P.R.; *Inorg. Chim. Acta* **1990**, *178*, 47; Constable, E.C.; Khan, F.K.; Raithby, P.R.; Marquez, V.E.; *Acta Crystallogr., Sect. C.* **1992**, *48*, 932; Bessel, C.A.; See, R.F.; Churchill, M.R.; Takeuchi, K.J.; *J. Chem. Soc. Dalton Trans.* **1992**, 3223.

12 Bock, H.; Vaupel, T.; Näther, C.; Ruppert, K.; Havlas, Z.; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 299.

13 Denti, G.; Serroni, S.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V.; in *Perspectives in Coordination Chemistry* (Williams, A.F., Floriani, C. and Merbach, A.E., eds), **1992**, p. 153 VCH Weinheim **1992**.