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A principle for the assembly of novel mononuclear building blocks for supramolecular chemistry

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The controlled assembly of supramolecular coordination oligomers may be achieved by the use of multinucleating ligands which contain two or more metal-binding domains. Examples of such ligands commonly consist of discrete metal-binding sites linked by appropriate spacers. We now show that a consideration of the donor properties of a ligand and the acceptor properties of a metal ion may be used to induce multinucleating behaviour in oligopyridine ligands which conventionally chelate to single metal centres. Such species are key building blocks for the assembly of a variety of supramolecular species in which the non-coordinated donor atoms may later interact with other metal centres. The crystal structure of the complex [Ru(bpy-*N,N'*)$_2$(tpy-*N,N'*)][PF$_6$]$_2$ ($P\bar{1}$, $a = 8.367(2)$, $b = 11.821(4)$, $c = 19.398(5)$ Å, $\alpha = 93.83(2)$, $\beta = 92.25(2)$, $\gamma = 89.62(2)°$, $Z = 2$, $d_c = 1.63$ g cm^{-3}, 5084 unique observed reflections with $I > 1.5\sigma(I)$, $R = 0.0745$) which contains a bidentate tpy ligand is presented.

INTRODUCTION

The oligopyridines are widely used in coordination chemistry as polydentate ligands.[1] In the vast majority of cases, the oligopyridines act as mononucleating ligands exhibiting their maximum denticity, as dictated by the chelate effect. We have recently been developing systematic approaches to the synthesis of supramolecular coordination polymers in which the extended three-dimensional structure is defined by the matching of ligand donor properties to metal-acceptor requirements.[2] The basic building blocks for such materials are compounds in which one metal-binding domain is coordinated to one metal-centre, whilst one or more other such domains are available for binding additional metal ions.[2,3] Ligands intended for the formation of helicate complexes have similar structural requirements, and we have demonstrated the versatility of oligopyridines in such applications.[4] In this paper we wish to describe the deliberate design of complexes in which some, but not all, of the donor atoms of an oligopyridine are coordinated to a single metal centre.

Although the assembly of dinuclear helicates incorporating bridging oligopyridine ligands presumably involves the intermediacy of such species, there are remarkably few characterized examples of oligopyridines coordinating to a single metal centre with less than their maximum denticity. Bidentate 2,2':6',2"-terpyridine (tpy) ligands have been proposed in a number of complexes,[5] but only two structurally characterized examples are known,[6] although a fluxional process which involves bidentate tpy ligands has been reported.[7] Our approach to such systems relies upon the use of a non-labile ruthenium(II) centre in which some of the coordination sites are occupied by non-labile chelated ligands. If *n* coordination sites remain available, then reaction with an oligopyridine possessing more than *n* donor atoms will give a complex containing a ligand which exhibits less than its maximum denticity.

The reaction of [Ru(bpy-*N,N'*)$_2$Cl$_2$] (bpy = 2,2'-bipyridine) with tpy in methanol results in the formation of the orange-red solutions containing the complex cation [Ru(bpy-*N,N'*)$_2$(tpy-*N,N'*)]$^{2+}$ from which the solid hexafluorophosphate salt [Ru(bpy-*N,N'*)$_2$(tpy-*N,N'*)][PF$_6$]$_2$ is readily precipitated in 80% yield. The fast atom bombardment (FAB) mass spectrum of this salt exhibits ions corresponding to [Ru(bpy)$_2$(tpy)][PF$_6$], [Ru(bpy)$_2$(tpy)] and [Ru(bpy)(tpy)]. The complex exhibits a single reversible ruthenium(II)/(III) oxidation process at +0.91 V (versus Fc/Fc$^+$) in its cyclic voltammogram, which compares favourably with a value of +0.85 V

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for $[\text{Ru(bpy)}_3]^{3+}$.[8] An exactly comparable complex cation $[\text{Ru(phen-}N,N')_2(\text{tpy-}N,N')]^{2+}$ is obtained from the reaction of tpy with $[\text{Ru(phen-}N,N')_2\text{Cl}_2]$. These two complexes each contain a bidentate tpy ligand.

In a similar manner, the reaction of $[\text{Ru(tpy)Cl}_3]$ with 2,2′:6′,2″:6″,2″-quaterpyridine (qtpy) in methanol in the presence of the reducing agent *N*-ethylmorpholine followed by precipitation with $[\text{NH}_4][\text{PF}_6]$ results in the formation of the complex $[\text{Ru(tpy-}N,N',N'')(\text{qtpy-}N,N',N'')][\text{PF}_6]_2$ which contains a tridentate tpy ligand and a tridentate qtpy ligand. The FAB mass spectrum of this complex exhibits ions corresponding to $[\text{Ru(tpy)(qtpy)}][\text{PF}_6]$, $[\text{Ru(tpy)(qtpy)}]$ and $[\text{Ru(qtpy)}]$. This complex is also redox active and exhibits a single reversible oxidation process at +0.98V versus Fc/Fc^+. This approach to the formation of complexes containing such ligands is not limited to those with a monodentate noncoordinated group. For example, the reaction of $[\text{Ru(tpy)Cl}_3]$ with one equivalent of 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) in the presence of reducing agents yields $[\text{Ru(tpy-}N,N',N'')(\text{qpy-}N,N',N'')]^{2+}$ in which there is a tridentate qpy ligand with a non-coordinated bidentate 2,2′-bipyridyl moiety. Significantly, the reaction of qpy with two equivalents of $[\text{Ru(tpy)Cl}_3]$, or of $[\text{Ru(tpy-}N,N',N'')(\text{qpy-}N,N',N'')]^{2+}$ with an additional equivalent of $[\text{Ru(tpy)Cl}_3]$ yields the previously known mono-helical binuclear complex cation $[(\text{tpy-}N,N',N'')\text{Ru(qpy-}\kappa^3N,N',N'':\kappa^2N'''N'''')\text{-Ru(tpy-}N,N',N'')\text{Cl}]^+$.[9]

Our primary characterisation of these complexes came from a study of their ^{1}H-NMR spectra, and the 250 MHz ^{1}H-NMR spectra of a CD_3COCD_3 solution of $[\text{Ru(tpy-}N,N',N'')(\text{qtpy-}N,N',N'')][\text{PF}_6]_2$ is shown in Fig. 1. The assignments (rings denoted as in the reaction schemes) have been made on the basis of 2D-COSY studies on this and a series of related complexes in a variety of solvents and at different fields. The assignment of the D ring is unambiguous as it is the only one with H_6 to lowest field. One feature which is immediately noticed in the ^{1}H-NMR spectrum of **2** is that the two terminal rings of the tpy ligand (E) are equivalent, but all four rings of the qtpy

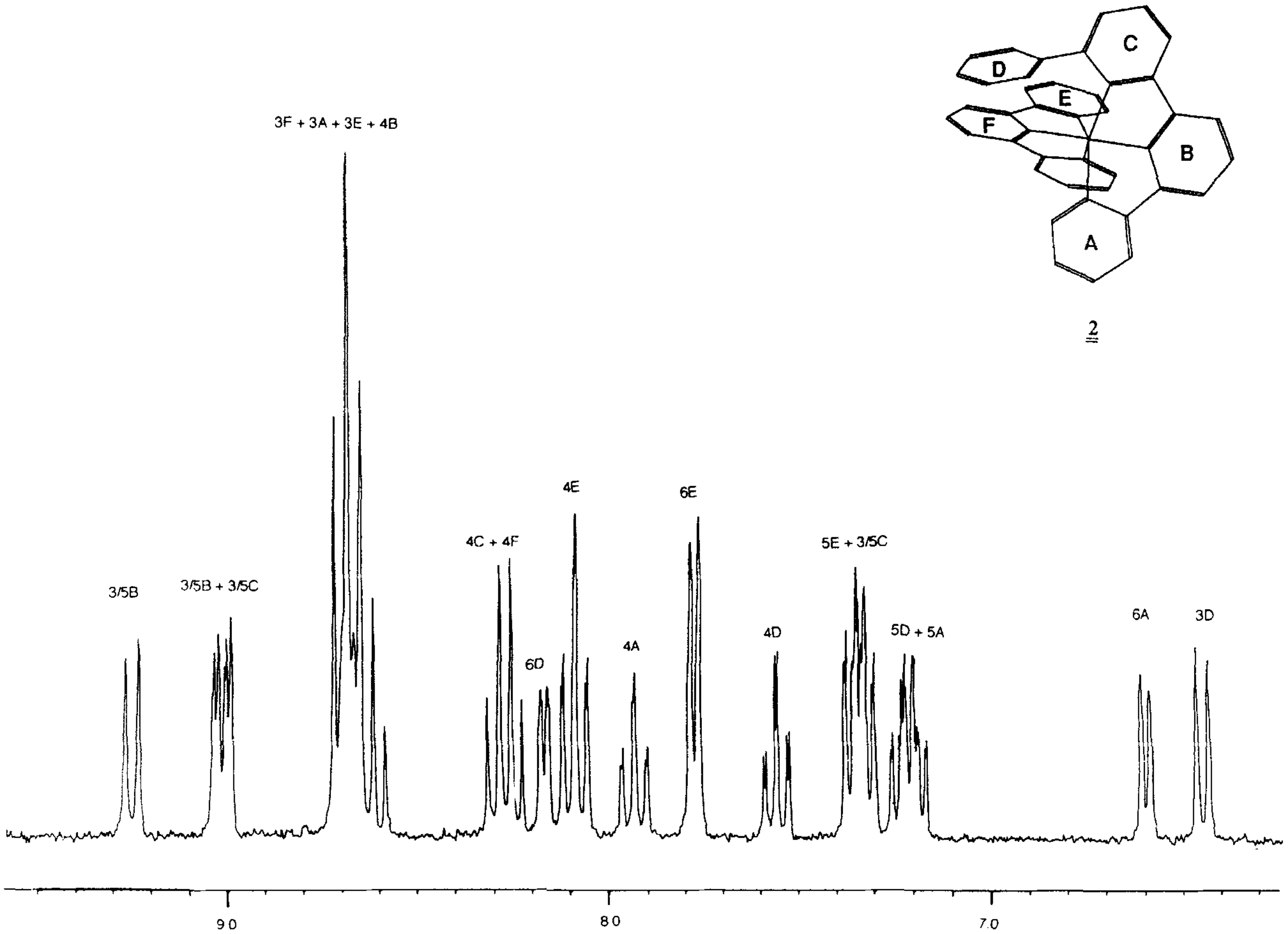
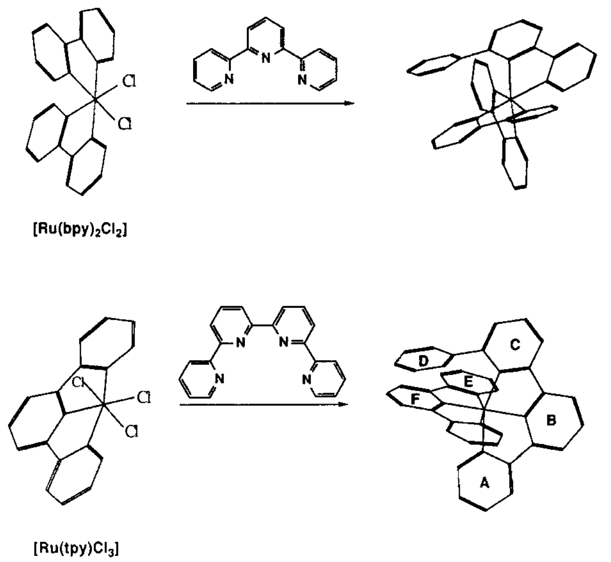


Figure 1 250 MHz ^{1}H-NMR spectrum of $[\text{Ru(tpy-}N,N',N'')(\text{qtpy-}N,N',N'')][\text{PF}_6]_2$ in CD_3COCD_3 solution; assignments according to the notation in the scheme.



Scheme 1 The labelling of the rings corresponds to the assignment of the ^{1}H-NMR spectrum in Figure 1.

are nonequivalent. This indicates that the non-coordinated pyridine ring of the qtpy ligand (D) is undergoing free rotation about the interannular bond connecting it to the adjacent bonded ring on the NMR time-scale. We have noted that this feature of rotational mobility about an interannular C-C bond is associated with non-coordinated aryl rings.[10] It is significant to note that the ^{1}H-NMR spectrum of [Ru(tpy-*N*,*N*′,*N*″)(qtpy-*N*,*N*′,*N*″)][PF$_6$]$_2$ shows no evidence for a fluxional behaviour of the bidentate ligand similar to that described by Abel.[7] Note that the equivalence of the E rings is not compatible with fluxionality of the tpy ligand nor is the spectrum compatible with any Ru-N bond-breaking process involving the qtpy ligand. The upfield shift of resonance 3D is attributed to this proton lying in a strongly shielding region adjacent to rings E and F. The ^{1}H-NMR spectra of [Ru(tpy-*N*,*N*′,*N*″)(qtpy-*N*,*N*′,*N*″)][PF$_6$]$_2$ or [Ru(tpy-*N*,*N*′)(bpy-*N*,*N*′)$_2$][PF$_6$]$_2$ show significant changes upon the addition of acid, consistent with the protonation of the non-coordinated pyridine ring.

Definite confirmation of the bidentate tpy ligand in the [Ru(bpy-*N*,*N*′)$_2$(tpy-*N*,*N*′)]$^{2+}$ cation has come from a single crystal structure determination of [Ru(bpy-*N*,*N*′)$_2$(tpy-*N*,*N*′)][PF$_6$]$_2$.[11] The structure of the [Ru(bpy-*N*,*N*′)$_2$(tpy-*N*,*N*′)]$^{2+}$ cation is shown in Fig. 2. The ruthenium centre is six-coordinate with two bidentate bpy ligands and a bidentate tpy ligand bonded. The Ru-N(1) and Ru-N(2) distances are typical,[12] but the longer contacts to N(3), (2.088(5)Å) and N(4) (2.106(6)Å) are a result of steric effects associated with the presence of the noncoordinated aryl ring of the tpy ligand. The interaction between the ruthenium and the bonded terminal ring of the tpy (2.052(6)Å) is also typical, but the steric effects of the non-coordinated ring result in a lengthening of the Ru-N(6) bond to 2.133(6)Å. The bpy ligand containing rings 1 and 2 (rings numbered according to the nitrogen atom they contain) is approximately planar (interplanar angle, 3.7°), but the second bpy exhibits a twisting of 15.4° about the interannular C—C bond as a result of the interaction with the non-coordinated ring. Within the tpy ligand, there is significant twisting between rings 5 and 6 (17.6°), but the major twisting of 52.3° occurs between the coordinated ring 6 and the non-coordinated ring 7. This is exactly as predicted[4] and is in accord with the two other examples of bidentate tpy ligands which have been characterized.[6] Rings 3 and 7 are approximately coplanar (169.1°) and exhibit short graphitic-type contacts in the range 3.10–3.45Å. There is no doubt about the assignment of atoms C(32) and N(7), and only the conformation indicated is present in the crystal lattice. There are no short intermolecular or interionic contacts.

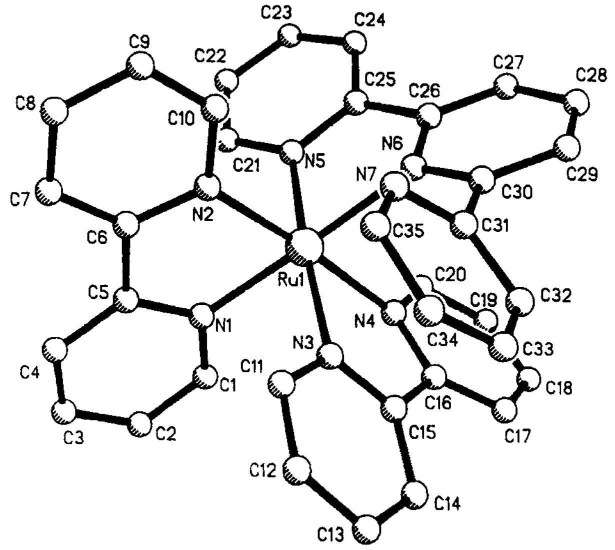


Figure 2 Molecular structure of the cation [Ru(bpy-*N*,*N*′)$_2$(tpy-*N*,*N*′)]$^{2+}$ showing the numbering scheme adopted. Important bond lengths [Å] and angles [°]: Ru(1)-N(1) 2.064(6), Ru(1)-N(2) 2.056(6), Ru(1)-N(3) 2.088(5), Ru(1)-N(4) 2.106(6), Ru(1)-N(5) 2.052(6), Ru(1)-N(6) 2.133(6), N(1)-Ru(1)-N(2) 78.7(2), N(3)-Ru(1)-N(4) 78.9(2), N(5)-Ru(1)-Ru(6) 78.4(2).

We have demonstrated a designed and facile strategy for the preparation of complexes containing oligopyridine ligands exhibiting less than their maximum denticity based upon the principle of a mismatch between the donor properties of a ligand and the number of coordination sites available at a non-labile metal centre. We are currently incorporating these principles in the preparation of coordination oligomers and helicates.

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11 Crystal data: $C_{35}H_{27}F_{12}N_7P_2Ru$, triclinic, $P\bar{1}$, $a = 8.367(2)$, $b = 11.821(4)$, $c = 19.398(5)$Å, $\alpha = 93.83(2)$, $\beta = 95.25(2)$, $\gamma = 89.62(2)°$, $V = 1906$ Å^3, $M = 998.6$, $Z = 2$, $d_c = 1.63$ g cm^{-3}, $F(000) = 936$, $\mathrm{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu(\mathrm{Mo}_{K\alpha}) = 5.78$ cm^{-1}. The structure was solved by Patterson methods and refined by alternating cycles of least-squares refinement and difference-Fourier synthesis; Ru, C, N, P, F anisotropic; H atoms riding on appropriate carbon atom with fixed isotropic *U*. One of the PF_6 anions is well-defined, but the second is characterized by anomalously high thermal parameters. As this anion makes no short intramolecular contacts this imperfect anisotropic model was accepted. 6886 reflections measured ($5 < 2\theta < 50°$), corrected for absorption, 5084 unique observed reflections with $I > 1.5\sigma(I)$, $R = 0.0745$, $wR = 0.0771$.

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