Metal-metal interactions in dinuclear ruthenium complexes containing bridging 4,5-di(2-pyridyl)imidazolates and related ligands

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The dinuclear bis(2,2’-bipyridine)ruthenium complex of 4,5-di(2-pyridyl)imidazolates has been prepared and separated into its (meso and rac) diastereoisomers. The 2-phenyl substituted analogue forms the meso isomer selectively. All three complexes have been characterised by 1H NMR and X-ray crystallography. Electrochemical measurements and spectroelectrochemistry of the mixed-valence states reveal strong metal-metal interactions and IVCT bands that are highly dependent on the electrolyte.

Introduction

For several decades, ligand-mediated metal-metal interactions have been the subject of extensive study in a variety of contexts, ranging from pure inorganic to applied biological chemistry. Much of this effort has been centred on bridging nitrogen-containing heterocyclic ligands, which are well known to facilitate interactions between metal atoms through the π-system of the ligand.1,3 Within this context ruthenium complexes of doubly-chelating bridging ligands have been particularly well studied.2 For example, 2,2’-bipyrimidine (1) and 2,2’-azobis(pyridine) (2) (Figure 1) both chelate to two metal centres and have been shown to demonstrate strong inter-metal interactions, which are particularly strong for complexes of (2).5 Numerous other bridging ligands have been reported and various explanations have been forwarded to explain the magnitude of the communication between the metal centres. Factors such as the metal-metal distance, the degree of conjugation between the metal centres and the electronic properties of the ligand and metals are generally accepted as being important.1,2 Nevertheless, there still remains much uncertainty as to what really mediates these effects.

As part of a programme involving the study of new bridging ligands,6 we described the preparations and complexes of two ligands, (3) and (4), incorporating 1,2,5-oxadiazole and 1,2,5-thiadiazole bridging subunits.7 Electrochemical studies of dinuclear ruthenium complexes of these ligands revealed remarkably strong metal-metal interactions, greater than those found in the corresponding complexes of (1), despite the greater inter-metal separation, and greater than those previously reported in complexes of 2,3-di(2-pyridyl)pyrazine (5) and 4,6-di(2-pyridyl)pyrimidine (6) despite the obvious similarities in geometry. Furthermore, we observed an intriguing difference between the magnitude of the metal-metal interactions for the two diastereoisomeric (meso and rac) forms of the dinuclear complexes containing the Ru(bpy)2 terminal moieties (bpy = 2,2’-bipyridine).7 Table 1 summarises these previous reports.

Table 1 Kc values for dinuclear Ru(bpy)2 complexes of (1) - (6)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kc (V)</th>
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<tbody>
<tr>
<td>1racb</td>
<td>1,510</td>
</tr>
<tr>
<td>1meso</td>
<td>1,760</td>
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<tr>
<td>2rac</td>
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<td>5</td>
<td>747</td>
</tr>
<tr>
<td>6</td>
<td>506</td>
</tr>
</tbody>
</table>

*a Comproportionation constant, Kc = exp(ΔEoxF/RT), where F/RT takes the value 38.92 V⁻¹, in [[(C5H5)Ni][PF6]/CH3CN at 298 K. Values from ref. 4c. ref. 5d. ref. 8. ref. 9.

In search of an explanation for the origin of this amplified communication between the metals and to ascertain whether the presence of a heteroatom in the ligand facilitates this increased interaction, we have synthesised a number of structurally-related bridging ligands for investigation. Here we report the synthesis and electrochemical properties of dinuclear ruthenium complexes of two 4,5-di(2-pyridyl)imidazolates, (7) and (8), which contain carbon atoms in place of the oxygen/sulfur atoms of the central ring, along with spectroelectrochemical studies of these and related complexes.

Results and discussion

Ligand syntheses

4,5-Diaryl-1H-imidazoles are readily prepared by reaction of a 1,2-diketone with the appropriate aldehyde in the presence of a large excess of ammonium acetate in acetic acid. The preparations of the protonated forms of (7)10 and (8)11 have previously been described using this method, albeit in low yields. During the course of our work a more efficient synthetic route to 1H-imidazoles was reported12 that utilises microwave

![Fig.1 Bridging doubly-chelating ligands.](image-url)
irradiation. We found that this method eliminated the problem of side products being formed and resulted in improved yields. In this way the parent imidazole (7) was prepared from the reaction of 2,2'-pyridil and hexamethylenetetramine as a source of formaldehyde. The 2-phenyl derivative (8) was prepared similarly from reaction between 2,2'-pyridil and benzaldehyde. In both cases using a solely thermal method resulted in the formation of significant amounts of a second major product possessing a fused imidazo[1,5-a]pyridine ring system.14

The ligands were unambiguously characterised by NMR and mass spectrometry. An interesting feature of the NMR spectra of both compounds was the broad nature of the peaks corresponding to the four pyridyl protons. Although prototropic tautomerism of 1H-imidazoles is normally fast on the NMR time-scale,15 this process is substantially slowed in the present compounds due to intramolecular hydrogen bonding between the NH hydrogen and the adjacent pyryld nitrogen, thereby explaining the broadening of the pyridyl signals. In contrast, sharp signals are observed for the proton in the 2-position in (7) and the three peaks corresponding to the five phenyl protons in (8), which are not subject to symmetrisation by the tautomerism process.

Ruthenium complexes of (7) and (8)

Dinuclear ruthenium complexes of both the bridging ligands were conveniently synthesised from the reaction of two equivalents of [Ru(bpy)2Cl2]·2H2O and the appropriate ligand. We have found a microwave-assisted method to give the shortest reaction times and the cleanest reaction products. Using this technique, reactions were carried out in ethylene glycol, with the addition of a small amount of sodium hydroxide to deprotonate the ligand, to afford the desired dinuclear products in high yields. The three peaks corresponding to the five phenyl protons in the latter isomer. Figure 2 shows the NMR spectra of (9rac) and (9meso) along with that of the crude mixture for comparison. For each isomer the 1H NMR signals were readily grouped (Table 2) into the five separate pyridine rings [Py(a) – (d)] by means of 1D-TOCSY and/or 2D-COSY spectra but the specific rings within the structure could not be unambiguously distinguished.

The structures of the two isomers were further confirmed by X-ray crystallography. In both cases it was possible to grow crystals suitable for X-ray diffraction by slow evaporation of a acetonitrile:toluene solution of the complex. The rac isomer (9rac) crystallises as thin red plates in the chiral trigonal space group P3_121, with a full dinuclear cation in the asymmetric unit along with two full and two half PF6^- anions. The latter lying on

![Fig. 2 NMR spectra of (9) showing the mixture and the two isomers after separation.](image)
The selective formation of a single diastereoisomer is unusual. The curvature of the bridging ligand which is substantially nonplanar. This shows that the central phenyl ring is neatly sandwiched about a center of inversion. Figure 3 shows two perspective views of each isomer (rac) and (meso), which serves to show the very different shapes of these two stereoisomers.

When we attempted to synthesise dinuclear complexes of (8) we observed the formation of the meso isomer (10meso) only. The X-ray crystal structure of this compound was also determined. It crystallises in the orthorhombic space group Cmca with the dinuclear cation lying on a crystallographic mirror plane passing through C2 of the imidazole ring and the attached phenyl ring. The asymmetric unit also contains two half PF₆⁻ anions (one on a two-fold rotation axis and the other on a mirror plane), two quarter PF₆⁻ anions (one on a site of 2/m symmetry) and a highly disordered toluene solvate molecule. A space-filling diagram of the dinuclear cation (10meso) is shown in Figure 4. This shows that the central phenyl ring is neatly sandwiched between two pyridine rings of bpy ligands that are significantly bowed towards one another. This deformation results from a curvature of the bridging ligand which is substantially nonplanar. The selective formation of a single diastereoisomer is unusual for such complexes and probably occurs in this case to maximise the observed π−π stacking of the aryl rings and minimise unfavourable steric interactions that would exist in the corresponding rac isomer.

![Fig. 3 Perspective views of (9rac), top, and (9meso), bottom.](image)

![Fig. 4 Space-filling diagram of (10meso).](image)

### Table 3. Redox potentials and Kc values for the stereoisomers of compounds (5), (6), (9) and (10) compared to Ru(bpy)₃²⁺

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electrolyte</th>
<th>ΔEoxᶜ</th>
<th>Eox²</th>
<th>Eox¹</th>
<th>Ered²</th>
<th>Ered¹</th>
<th>Ered³</th>
<th>Kc</th>
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<tr>
<td>5rac</td>
<td>PF₆⁻</td>
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<td>1244</td>
<td>1032</td>
<td>-1048</td>
<td>-1560</td>
<td>-1888</td>
<td>3830</td>
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<tr>
<td>5meso</td>
<td>PF₆⁻</td>
<td>212</td>
<td>1256</td>
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<td>-1540</td>
<td>-1900</td>
<td>690</td>
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<td>-1920</td>
<td>690</td>
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<tr>
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<td>PF₆⁻</td>
<td>506</td>
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<td>1060</td>
<td>-876</td>
<td>-1500</td>
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<td>506</td>
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<td>9rac</td>
<td>PF₆⁻</td>
<td>344</td>
<td>884</td>
<td>540</td>
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<td>-2064</td>
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<tr>
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<td>(C₅F₅)₂⁺</td>
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<td>931</td>
<td>584</td>
<td>-1832</td>
<td>-2310</td>
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<tr>
<td>9meso</td>
<td>(C₅F₅)₂⁺</td>
<td>341</td>
<td>941</td>
<td>592</td>
<td>-1840</td>
<td>-2104</td>
<td>****</td>
<td>793,000</td>
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<tr>
<td>[Ru(bpy)₃]²⁺</td>
<td>-</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>-1640</td>
<td>-1820</td>
<td>-2080</td>
<td>-</td>
</tr>
</tbody>
</table>

* ΔEox = Eox² - Eox¹. Comproportionation constant, Kc = exp(ΔEox/FRT), where F/RT takes the value 38.92 V⁻¹ at 298 K.

### Electrochemistry

In order to probe the metal-metal communication between the ruthenium centres in complexes (9) and (10) electrochemical studies were carried out. As noted above, the two diastereoisomers of complexes of ligands (3) and (4) were found to display unusually different Kc values. The corresponding complexes of ligands (5) and (6) have only been previously measured as mixtures of isomers and various values of Kc have been reported for the complexes of (5).³ We therefore decided to separate these compounds into the rac and meso isomers and measure the Kc values of the individual isomers. The redox potentials for the complexes (5rac), (5meso), (6rac) and (6meso) are listed in Table 3. The Kc values for the two stereoisomers of the complexes of (5) are identical and at the high end of the range of values previously reported for the mixture of diastereoisomers.³ The Kc values for (6rac) and (6meso) are significantly lower and do show a measurable difference between the two isomers. Table 3 also shows the results for the three complexes which are the focus of this study, along with data for [Ru(bpy)₃]²⁺ as a comparison. Redox potentials of complexes (9) and (10) are cathodically shifted relative to [Ru(bpy)₃]²⁺ due to the anionic nature of the bridging ligand.

![Fig. 5 Cyclic voltammogram of (10meso) 0.1M [(n-C₄H₉)₄N]PF₆/CH₃CN media. Pt working electrode; vs. FeCp₂/FeCp₂⁺](image)
and (9meso) were now very similar. The greater separation of the potentials associated with the oxidation processes, and the resultant higher $K_c$ values, obtained in $B(C_6F_5)_{3}I$ compared with PF$_6$ media is not unexpected and reflects a higher association of the latter anion with the cations, which in turn lowers the potential of the oxidation processes.$^5d$ This lowering of the potential is more pronounced for the second oxidation process as the charges are greater, thus lowering $\Delta E_{ox}$. In $B(C_6F_5)_{3}I$ media, the association is very much less, and apparently does not differ significantly between the two diastereoisomers (9rac) and (9meso). The fact that a difference in $\Delta E_{ox}$ is observed between the diastereoisomers in PF$_6$ media reflects the fact that where association is present, its extent is different between the diastereoisomers giving rise to different values of $\Delta E_{ox}$.

It is interesting to note (Table 3) that the $\Delta E_{ox}$ values for the rac diastereoisomer (9rac) are virtually the same in both media, whereas they differ significantly for the meso form (9meso). This is consistent with the proposal that there is considerable ion association between the PF$_6$ anion and the meso diastereoisomer in particular. This is the isomer with a substantially larger cavity, above and below the plane of the bridging ligand, that can accommodate the anion (Fig. 3).

A recent publication$^{17}$ has warned about the use of electrochemically-derived $K_c$ values as a means of measuring metal-metal communication, due to the effect of ion pairing. In the present case, the differences in $\Delta E_{ox}$ (and therefore $K_c$) determined in the two media reflect differences in ion association rather than inter-metal communication. For even more strongly associating anions, such as 4-toluene sulphonate, the differential association can be quite profound, a fact that we actually use to our advantage when separating the two isomers by cation exchange chromatography.

For complexes (9) and (10) we see two $2e^-$ reversible reduction processes that correspond to reduction of two different bpy rings. With dinuclear ruthenium complexes containing π-deficient diazine bridging ligands, such as (1), (5) and (6), the first reduction usually involves electron transfer into the bridging ligand.$^{12}$ However, the imidazolate ring is a π-excessive system with a much higher energy LUMO orbital. Thus the bpy ligands are the first to be reduced. In compounds (9rac) and (9meso) a subsequent $1e^-$ reduction was observed that corresponds to reduction of the bridging ligand. When using the $B(C_6F_5)_{3}I$ counterion, this reduction was beyond the limits of the solvent system.

**Spectroelectrochemistry**

The UV/Vis spectral properties of the 4+ forms of the complexes of (3) and (4) have been described previously,$^7$ but no spectroelectrochemical studies were carried out. As part of the present study, we have now recorded the UV/Vis/NIR spectra for the diastereoisomers of (3)$^{4+}$ and (4)$^{4+}$ ($n = 4, 5$) over the range 3050-20000 cm$^{-1}$ (Electronic Supplementary Information, Table S1). The spectral progression accompanying the oxidation of (3meso)$^{4+}$ to (3meso)$^{5+}$ in 0.1 M $[(n-C_6H_{14})_2N]PF_6/CH_3CN$ at -35°C is shown in Figure 6(a). The lowest energy absorption bands in the spectra of the 4+ species are assigned as $\pi$(BL) MLCT transitions. These bands decreased in energy and intensity following one-electron oxidation to the mixed-valence (5+) species, and collapsed completely on further oxidation to the 6+ state. The new bands in the regions 3050-9000 cm$^{-1}$ and 14000-16000 cm$^{-1}$ in the mixed-valence species are assigned as IVCT and LMCT transitions, respectively. The former are absent in the spectra of the 6+ species, while the latter increase in intensity, and are consistent with the $\pi$(bpy)$^*$ to $\pi^*(BL)$ MLCT transitions at 14815 and 17160 cm$^{-1}$ in $[Ru^{3+}$(bpy)$_3]^3+$.$^{18}$ Comparable behaviour was observed for (3rac)$^{4+}$, and for the two diastereoisomers of (4)$^{4+}$.

The UV/Vis/NIR spectral properties for the diastereoisomers of (9)$^{n+}$ ($n = 3, 4, 5$) in 0.1 M $[(n-C_6H_{14})_2N]PF_6/CH_3CN$ and 0.02 M $[(n-C_6H_{14})_2N]B(C_6F_5)_{3}I/CH_3CN$ at -35°C are reported in Table S2, and the spectra of (9rac)$^{n+}$ in PF$_6$ media are shown in Figure S1 (Electronic Supplementary Information). The MLCT transitions exhibited similar behaviour on oxidation to that described for (3)$^{n+}$ and (4)$^{n+}$. The mixed-valence (4+) state is characterised by two new bands in the regions 3050-8000 cm$^{-1}$ and 8000-15000 cm$^{-1}$ which are assigned as IVCT and LMCT transitions, respectively. Further oxidation to the 5+ species causes a disappearance of the IVCT band, and a blue-shift in the LMCT band. While the latter contradicts the expected red-shift in LMCT bands with oxidation, similar behaviour has been observed for other dinuclear ruthenium complexes incorporating anionic bridging ligands such as 3,5-bis(pyrazin-2-yl)-1,2,4-triazolato.$^{19}$ In contrast to (3)$^{n+}$ and (4)$^{n+}$ in which electron transfer involves a superexchange-assisted electron transfer mechanism via the $\pi,\pi^*$ bridging ligand orbitals, the lowest energy orbitals (LUMOs) of (9)$^{n+}$ lie relatively high in energy. As a result, hole transfer via the highest occupied molecular orbitals (HOMOs) of the bridging ligand is the dominant electron transfer pathway. These observations are corroborated by the electrochemical data which show that the first reduction is
bpy-based in \((9)^+\), rather than bridging ligand-based as is the case for \((3)^+\) and \((4)^+\).

Figure 6(b) shows the NIR bands for the diastereoisomers of \((3)^+\) and \((4)^+\) (in \(PF_6^-\) media), and Figure 7 shows the NIR bands for the diastereoisomers of \((9)^+\) (in \(PF_6^-\) and \(B(C_6F_5)_4^-\) media). The energy \((\nu_{\text{max}})\), intensity \((|\epsilon/\nu|_{\text{max}})\), bandwidth \((\Delta \nu_{\text{v/2}})\) and the band area (zeroth-moment, \(M_0\)) for the IVCT bands are reported in Table 4. The parameters for the bands obtained from Gaussian deconvolution of the manifolds are reported in Tables S2 (for \((3)^+\) and \((4)^+\)) and S3 (for \((9)^+\), Electronic Supplementary Information. In each case, the IVCT bands were fitted by three Gaussian-shaped components, denoted IVCT(1), (2) and (3) in order of increasing energy; however IVCT(1) was obscured at the detector limit for \((9)^+\). The LMCT bands for \((9)^+\) were also fitted by three Gaussian components. For all complexes, IVCT(2) exhibited the highest intensity and dominated the IVCT manifold.

![Fig. 7. NIR spectra for \((9)^+\) in 0.1 M \([\text{n-C}_6\text{H}_{14} \text{H}_2 \text{N}]\text{PF}_6/\text{CH}_3\text{CN} \text{ meso} \) (--), \( \text{rac} \) (-----) \text{ and } 0.02 M \([\text{n-C}_6\text{H}_{14} \text{H}_2 \text{N}]\text{Br(C}_6\text{F}_5)_4/\text{CH}_3\text{CN} \text{ meso} \) (--), \( \text{rac} \) (-----)) at -35°C. The inset shows the best Gaussian deconvolution of the \(7\text{rac}^+\) in 0.1 M \([\text{n-C}_6\text{H}_{14} \text{H}_2 \text{N}]\text{PF}_6/\text{CH}_3\text{CN} \text{ at } 35\text{°C} \).](image)

The three IVCT components arise due to separate electronic excitations from one of the three \(d_{z^2}\) (\(n = 1-3\)) orbitals at Ru\(^{10}\) to the hole in the corresponding \(d_{x^2-y^2}\) orbital which is present in any of the three spin-orbit states at Ru\(^{11}\)\(^{22}\). The magnitude of the separation between the components (ca. 1000 cm\(^{-1}\)) is consistent with the energy splittings between the three \(d_{z^2}\) orbitals which arise due to the combined effects of spin-orbit coupling \((\xi \approx 1100 \text{ cm}^{-1} \text{ for Ru}\(^{11}\))\(^3\) and ligand-field asymmetry. If the \(xy\) plane defines the plane of the bridging ligands and \(z\) lies perpendicular to the plane, the three \(d_{z^2}\) orbitals may be more closely represented by \(d_{x^2}, d_{y^2}, d_{z^2}\). The enhanced stabilisation of the former due to the relatively greater overlap with the \(\pi,\pi^*\) orbitals of the bridging ligands, accounts for the higher intensity of IVCT(2) relative to IVCT(3).

For all complexes, the bandwidths are narrow compared with the theoretical predictions for \(\Delta \nu_{\text{v/2}}\), which together with the significant intensity of the NIR manifolds suggest that the systems are delocalised (Class III). The IVCT components are more accurately assigned as transitions between bonding and non-bonding orbitals within the molecular orbital manifolds of the dinuclear complexes, as described within the three-state model of Ondrechen, and illustrated schematically in Figure S2.\(^{24}\) For \((3)^+\) and \((4)^+\), the salient feature of the model is the \(d_{z^2} \rightarrow \pi^*(BL)\) energy gap, which is larger for the former due to its enhanced \(\pi\)-acceptor nature.\(^3\) The relatively greater separation between the bonding and non-bonding orbitals is manifested as a blue-shift in the NIR band for \((3)^+\) relative to \((4)^+\). For delocalised mixed-valence complexes, the energy of the NIR transition provides a direct measure of the electronic coupling parameter, \(H_{\text{ab}}\) \((H_{\text{ab}} = \gamma \nu_{\text{max}}\), Table 4).\(^{22}\)

As shown in Table 4, the parameters of the NIR bands differ for the same diastereoisomer of \((3)^+\) and \((4)^+\), and between the two diastereoisomer forms of the same complex. For both complexes, the integrated intensity of the manifold is greater for the \(\text{meso}\) relative to the \(\text{rac}\) forms. X-ray structural studies\(^7\) revealed comparable inter-metal distances for the diastereoisomers of \((3)^+\)\(^{6.016 \text{ Å for } \text{meso}, \text{ } 6.014 \text{ Å for } \text{rac}}\) which would be similar for \((4)^+\). The differences in the IVCT parameters between the diastereoisomers of the same complex are ascribed to differential ion-pairing interactions and specific solvent effects. The \(H_{\text{ab}}\) values suggest that for a given diastereoisomer, \((3)^+\) exhibits greater electronic coupling relative to \((4)^+\). The degree of aromaticity of the bridge has been postulated to facilitate electronic coupling between metal centres. The 1,2,5-oxadiazole system has a low degree of aromaticity and high "diene" character, with the electronnegative oxygen atom contributing little of its electron density into the ring.\(^{25}\) Since sulfur is less electronegative than oxygen and does not reduce the electron density of the ruthenium centres to the same extent, \((4)^+\) would be expected to be a more delocalised system because of the greater polarisability of the larger sulfur atom. However, the relatively low aromatic character of the bridge in \((3)^+\)\(^7\) has not restricted the electronic communication between the metals. In fact, the low aromatic character has served to enhance the electronic coupling, as exemplified by the higher \(H_{\text{ab}}\) values in \((3)^+\).\(^7\)

While the diastereoisomers of \((9)^+\) exhibit comparable band parameters to one another in each electrolyte system, the characteristics of the IVCT and LMCT bands are markedly

| Table 4 | NIR spectral data of the reduced absorption spectra (\(\epsilon/\nu\) vs. \(\nu\)) for \((3)^{\text{meso}}\), \((4)^{\text{meso}}\) and \((9)^{\text{meso}}\) in 0.1 M \([\text{n-C}_6\text{H}_{14} \text{H}_2 \text{N}]\text{PF}_6/\text{CH}_3\text{CN} \text{ and } \text{meso}\) in 0.02 M \([\text{n-C}_6\text{H}_{14} \text{H}_2 \text{N}]\text{Br(C}_6\text{F}_5)_4/\text{CH}_3\text{CN} \text{ at } -35^\circ\text{C} \). |
|---|---|---|---|---|---|
| Electrolyte | Complex | \(\nu_{\text{max}}\) \(\pm 10\) \(\text{cm}^{-1}\) | \(\epsilon/\nu_{\text{max}}\) \(\pm 0.0001\) | \(\Delta \nu_{\text{v/2}}\) \(\text{cm}^{-1}\) | \(\Delta \nu_{\text{v/2}}\) \(\text{cm}^{-1}\) | \(M_0\) \(\text{M}^{-1}\text{cm}^{-1}\) | \(H_{\text{ab}}\) \(\text{cm}^{-1}\) |
| PF\(_6^-\) | \(3\text{meso}\)\(^{+}\) | 6590 | 1.5218 | 1470 | 3480 | 3211 | 3295 |
| | \(3\text{rac}\)\(^{+}\) | 6460 | 1.2737 | 1492 | 3440 | 2650 | 3230 |
| | \(4\text{meso}\)\(^{+}\) | 5625 | 1.4908 | 1346 | 3210 | 2538 | 2813 |
| | \(4\text{rac}\)\(^{+}\) | 5628 | 0.8995 | 1516 | 3215 | 1656 | 2814 |
| | \(9\text{rac}\)\(^{+}\) | 4475 | 1.4816 | 1112 | 2866 | c | 2238 |
| | \(9\text{meso}\)\(^{+}\) | 4560 | 1.2061 | 1029 | 2893 | c | 2280 |
| B(C\(_6\)F\(_5\))\(_4^-\) | \(9\text{rac}\)\(^{+}\) | 4120 | 0.9668 | 1148 | 2750 | c | 2060 |
| | \(9\text{meso}\)\(^{+}\) | 4105 | 0.9119 | 1160 | 2745 | c | 2053 |

\(^{a}\text{\(\Delta \nu_{\text{v/2}}\) }\) \((= [1836(\nu_{\text{max}})])^2\) at 238 K.\(^{20}\) \(^{b}\) Bandwidth for the high-energy side of the IVCT manifold. The lower energy side was obscured at the detector limit. \(^{c}\) The \(M_0\) for the full band manifold could not be measured reliably. \(^{d}\) \(H_{\text{ab}}\) determined as \(\gamma \nu_{\text{max}}\), assuming that the complexes are delocalised (Class III).\(^7\)
dependent on the identity of the electrolyte counter-ion. In 
B(C6F5)3Cl media, the IVCT bands are red-shifted and narrower 
and the parameters (ϕν)max, δM and δH are decreased compared 
with their values in PF6 electrolyte. Ion-pairing effects have 
been shown to influence the IVCT characteristics in a number 
of dinuclear ruthenium26 and iron27 systems. Qualitatively, the 
experimental observations in the present study are similar to 
these previous literature reports which have shown that IVCT 
bands are blue-shifted in the presence of relatively strongly ion-
pairing electrolytes (PF6− in the present case). The effect is 
attributed to ion-pair formation which induces an additional 
energy contribution to ωmax. The results show that in (9) the 
significant electronic communication between the metal centres 
is most likely to occur via the highest occupied molecular orbital 
HOMO of the bridging ligand, rather than the LUMO in the case 
of (3)2 and (4)2. In addition, the electronic coupling is 
enhanced in the presence of a stronger ion-pairing electrolyte 
(PF6−).

Conclusions

The results reported here show that it is not the inclusion of a 
derivative in the aromatic ring system that is inherently 
responsible for the improvement in metal-metal communication 
we observe in such systems. There is no obvious trend in the 
degree of communication as we move from imidazole- to 
oxadiazole-to thiadiazole-bridge. It should perhaps be noted that 
this pattern is most evident in the case when making direct comparisons. Nevertheless, it would 
appear that the inclusion of a five-membered ring in the bridge is 
the most important factor for such strong inter-metal 
communication. Furthermore, beyond a broad consideration of 
intermetallic distances, it would not appear to be possible to 
accurately predict the extent of communication in any particular 
bridging ligand system.

Experimental

General

1H NMR experiments were performed on a Varian INOVA 
500 MHz NMR spectrometer at room temperature. 1H NMR 
assignments were made with the assistance of 1D-TOCSY 
experiments to identify each pyridine ring spin system, while 
individual protons within a ring were assigned on the basis of 
their chemical shifts and the following typical 1J coupling 
patterns for pyridine protons: H3 (d, J = 8 Hz), H4 (t, J = 8 Hz), 
H5 (dd, J = 8, 5 Hz), H6 (d, J = 5 Hz). Mass spectra were 
recorded using a Kratos MS80RFA mass spectrometer with a 
Mach 3 data system. Electron Impact (EI) spectra were obtained 
at 70 eV with a source temperature of 250 °C. Electrochemical 
measurements were performed under argon using a Bioanalytical 
Systems BAS 100A Electrochemical Analyser. Cyclic and 
differential pulse voltammograms were recorded under Ar in 
0.02 M [([σ-C6H4]3N)2RuCl2]Cl/CH3CN at +25 °C using a glassy 
carbon working electrode, a platinum wire auxiliary electrode 
and an Ag/AgCl (0.02 M [([σ-C6H4]3N)2RuCl2]Cl/CH3CN) 
reference electrode; or in 0.1 M [([σ-C6H4]3N)2RuCl2]Cl/CH3CN 
using an Ag/AgCl (0.1 M ([([σ-C6H4]3N)2RuCl2]Cl/CH3CN 
reference electrode. Ferrrocene was added as an internal standard 
on completion of each experiment [the ferrocene / ferrocenium 
couple (FeCp2+/FeCp2) occurred at +550 mV vs. Ag/AgCl]: all 
potentials are quoted in mV versus FeCp2+/FeCp2. Cyclic 
voltammetry was performed with a sweep rate of 100 mV s−1; 
differential pulse voltammetry was conducted with a sweep rate 
of 4 mV s−1 and a pulse amplitude, width and period of 50 mV, 
60 ms and 1 s, respectively. In order to obtain reasonable 
electrochemical response, measurements in the 0.02 mol dm−3 
([σ-C6H4]3N)2RuCl2/CH3CN electrolyte required a concentration of complex which was approximately double that in 
0.1 mol dm−3 ([σ-C6H4]3N)2PF6/CH3CN.

Electronic spectra were recorded using a CARY 5E 
UV/Vis/NIR spectrophotometer interfaced to Varian WinUV 
software. The absorption spectra of the electrogenerated mixed-
valence complexes (3)2, (4)2 and (9)2 were obtained in situ 
by the use of an Optically Semi-Transparent Thin-Layer 
Electrolytic (OSTLE) cell mounted in the path of the 
spectrophotometer.28 Solutions for the spectroelectrochemical 
experiments contained 0.1 M [([σ-C6H4]3N)2RuCl2], or 0.02 M [([σ-
C6H4]3N)2RuCl2]Cl/CH3CN. The mixture was diluted with water (25 mL) 
and neutralised with ammonium hydroxide solution and was then filtered through 
Celite to yield a green solution. The green solution was extracted 
with CH2Cl2 (3 x 25 mL), the combined organic fractions were 
dried over sodium sulfate and the solvent removed to yield a 
dark tarry residue containing both the desired product and a 
second product containing an imidazol[1,5-a]pyridine ring 
system. The mixture was purified by column chromatography on 
silica eluting with 10% MeOH in CHCl3 to yield a pale brown 
solid. Yield 0.15 g (13%). EI mass spectrum: calc. m/z for 
C13H10N4: 222; found 221. 1H NMR (CDCl3) δ: 8.58 (2H, d, H6); 8.34 (2H, bs, H3); 7.73 (3H, m, H4, 
H5); 7.18 (2H, t, H5). Preparation of 4,5-di(2-pyridyl)-imidazole.

Hexamethylenetetramine (0.13 g, 0.27 x 10−4 mol) was added to 
a solution of 2,2'-pyridil (1.10 g, 5.18 x 10−3 mol) and a 
enfold excess of ammonium acetate (4g, 5.18 x 10−2 mol) in 
acetic acid (25 mL). The mixture was refluxed for 1 hour and 
subsequently allowed to cool to room temperature. The dark 
mixture was diluted with water (25 mL) and neutralised with 
ammonium hydroxide solution and was then filtered through 
Celite to yield a green solution. The green solution was extracted 
with CH2Cl2 (3 x 25 mL), the combined organic fractions were 
dried over sodium sulfate and the solvent removed to yield a 
dark tarry residue containing both the desired product and a 
second product containing an imidazol[1,5-a]pyridine ring 
system. The mixture was purified by column chromatography on 
silica eluting with 10% MeOH in CHCl3 to yield a pale brown 
solid which solidified on standing. Yield 0.15g, (13%). EI mass 
spectrum: calc. m/z for C13H10N4: 222; found 221. 1H NMR 
(CDCl3) δ: 8.58 (2H, d, H6); 8.34 (2H, bs, H3); 7.73 (3H, m, H4, 
H5); 7.18 (2H, t, H5). Preparation of 4,5-di(2-pyridyl)-2-phenylimidazole.

Benzaldehyde (0.375 g, 3.53 x 10−3 mol) was added to a solution of 
2,2'-pyridil (0.75 g, 3.53 x 10−3 mol) in acetic acid (10 mL). The 
mixture was heated in a microwave for 5 minutes (5 x 1 minute 
with swirling of the flask between periods of heating). The 
reaction mixture was allowed to cool to room temperature and 
normalised with conc. ammonium solution. The pale yellow 
precipitate that formed was collected and washed with water and 
a small amount of cold ethanol, to afford the desired product in 
46 % yield (0.48 g). EI mass spectrum: calc. m/z for C9H8N2: 
297; found 297. 1H NMR (CDCl3) δ: 8.60 (2H, d, H6); 8.33 (2H, 
br s, H3); 8.02 (2H, d, H ortho); 7.83 (2H, t, H4); 7.45 (2H, t, 
Hmeta); 7.38 (1H, t, Hpara); 7.20 (2H, t, H5).
Preparation and separation of rac and meso
[(bpy)2Ru(μ-7)Ru(bpy)2](PF6)3, (9rac) and (9meso)

[(bpy)2Ru(bpy)2Cl2]·2H2O (66.0 mg, 1.28 x 10^-4 mol) was added to a suspension of 4,5-di(2-pyridyl)imidazole (13.5 mg, 0.06 x 10^-4 mol) in ethylene glycol (2.5 mL) and 2 drops of conc. NaOH. The mixture was heated in a microwave for 2 minutes in 20 – 30 second intervals swirling the flask between each period of heating. The dark red-brown mixture was cooled to room temperature and water (5 mL) was added. The desired complex was isolated as the hexafluorophosphate salt by addition of an excess of ammonium hexafluorophosphate in acetone. Water was added and partial removal of the solvent under reduced pressure. The residue was then dissolved in acetone and adsorbed onto a short silica column, washed with water and acetone, and then removed from the silica gel with a 5% solution of ammonium hexafluorophosphate solution, and collected by filtration.

The rac and meso isomers were readily separated by cation exchange chromatography. The hexafluorophosphate salt was converted to the chloride salt by stirring in water with excess Amberlite resin IRA – 400(Cl) for 20 mins and any mononuclear compound removed by gradient elution on SP Sephadex C-25 with NaCl solution (0.125 M – 0.50 M). The product was precipitated by addition of saturated ammonium hexafluorophosphate solution, and collected by filtration.

Preparation of (bpy)2Ru(μ-8)Ru(bpy)2](PF6)3, (10meso)

[(bpy)2Ru(bpy)2Cl2]·2H2O (55.0 mg, 1.07 x 10^-4 mol) was added to a suspension of 4,5-di(2-pyridyl)-2-phenylimidazole (13.5 mg, 4.53 x 10^-5 mol) in ethylene glycol (2.5 mL) and 2 drops of conc. NaOH added. The mixture was heated in a microwave for 2 minutes in 20 – 30 second intervals swirling the flask between each heating. The dark red brown mixture was cooled to room temperature and water (5 mL) added. The desired complex was isolated as the hexafluorophosphate salt by addition of an excess of an aqueous saturated ammonium hexafluorophosphate solution. The dark precipitate that formed was collected by filtration and dried in vacuo. Yield, 72.8 mg (3.31 x 10^-5 mol, 77%). For NMR data see Figure 2 and Table 2.

X-ray crystallography

The crystal data, data collection and refinement parameters for compounds (9rac), (9meso) and (10meso) are given in Table 5. Measurements were made with a Siemens CCD area detector using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The intensities were corrected for Lorentz and polarisation effects and for absorption.33 The structures were solved by direct methods using SHELXS,34 and refined on F^2 using all data by full-matrix least-squares procedures using SHELXL-97.35 Due to the weakness of the data from these small crystals many of the atoms in each structure were restrained to approximate to isotropic behaviour. Hydrogen atoms were included in calculated positions with isotopic displacement parameters 1.2 times the isotropic equivalent of their carrier carbon atoms. The functions minimised were \[ \Sigma_w(F_o^2 - F_c^2), \] with \[ w = (\sigma^2(F_o^2) + aP^2 + bP^3)^{-1}, \] where \[ P = (\max(F_o^2) + 2F_c^2)^{1/2}. \]

Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos 271748-271750). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

Table 5 X-ray crystal data.

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a \[ R = \Sigma|F_o| - |F_c|)/\Sigma |F_o|; \] \[ b \] \[ wR = (\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)])^{1/2}. \]
Acknowledgements

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References


