Energy Transfer Pathways in Dinuclear Heteroleptic Polypyridyl Complexes: Through-Space vs Through-Bond Interaction Mechanisms

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A series of homo- and heteronuclear ruthenium and osmium polypyridyl complexes with the bridging ligands 1,3-bis(5-(2-pyridyl)-1H,1,2,4-triazol-3-yl)benzene (H₂ML) and 1,4-bis(5-(2-pyridyl)-1H,1,2,4-triazol-3-yl)benzene (H₂LP) are reported. The photophysical properties of these compounds are investigated, and particular attention is paid to the heteronuclear (RuOs) compounds, which exhibit dual emission. This is in contrast to phenyl-bridged polypyridine Ru–Os complexes with a similar metal–metal distance, in which the Ru emission is strongly quenched because the nature of the bridging ligand allows for an efficient through-bond coupling. The results obtained for the compounds reported here suggest that energy transfer is predominantly taking place via a dipole–dipole, Förster type, mechanism, that may dominate when through-bond coupling is weak. This is in stark contrast to ground state interaction, which is found to be critically dependent on the nature of the bridging unit employed.

Introduction

The design and synthesis of multicomponent systems such as polynuclear metal complexes containing electroactive and photoactive units are topics of great current interest, not only in terms of fundamental studies of energy and electron transfer processes but also due to the potential of multicomponent systems as building blocks for supramolecular assemblies, molecular devices, and electroluminescent displays. Central to the development of multicomponent devices is the role of the bridging units employed in connecting active units and an understanding of the true role played by these bridges in mediating energy/electron transfer processes. In the case of multinuclear transition metal complexes, the crucial role played by the bridging ligand in determining the ground state metal–metal interaction is already well recognized, with multinuclear systems employing imidazole, pyrazine, and ortho-metalated phenyl containing bridging units attracting significant attention.


considerable attention. In contrast, however, the role of bridging ligands in mediating excited state interaction has received less attention, especially as regards the relative importance of the Förster and Dexter mechanisms of energy transfer.

In recent years, the role of bridging ligands based on the 1,2,4-triazolato anion (e.g., 3,5-bis(2-pyridyl)-1H-1,2,4-triaz-olato, bpt−) in mediating ground state interaction (i.e., the degree of delocalization of the singly occupied molecular orbital of the mixed valence complex (MII/MIII) over the metal centers) has been examined extensively. 1,2,4-Triazolato anion based ligands hold significant advantages over other bridging systems, due to the possibility of both the formation of coordination isomers and an accessible acid/base chemistry, which enable both synthetic and environmental manipulation of the photochemical and photophysical properties of Ru(II) and Os(II) homo- and heterometallic complexes incorporating these ligands.10–13 Indeed it is clear from these studies that ground state interaction between metal centers in the dinuclear complexes is mediated by the bridge through a hole transfer HOMO assisted superexchange mechanism.

A further important attribute of these systems is the ability to modify excited state properties independently of the ground state metal–metal interaction, a feature that is essential to the development of multicomponent systems exhibiting rationally designed properties. As with other systems (vide supra) the nature of the mechanisms responsible for excited state energy transfer in these systems has received much less attention.

In this contribution the synthesis, characterization, and physical properties of a series of mononuclear and dinuclear Ru(II) and Os(II) complexes containing the ligands H2ML and H2LPL (Figure 1) are described. Earlier electrochemical and spectroelectrochemical studies have demonstrated that in the ground state metal–metal interaction takes place via a hole transfer mechanism and this interaction can be tuned by changing structural features of the bridging ligand, such as meta vs para substitution.14 Importantly the ground state interaction in these systems is critically dependent on the protonation state of the ligand. The aim of this study is to investigate the role these same structural parameters and the protonation state play in excited state interaction.

**Experimental Section**

**Materials.** All solvents employed were of HPLC grade or better and used as received unless otherwise stated. All reagents employed

![Figure 1. Structures of the ligands H2ML and H2LPL.](Image)

1,3-bis(5-(2-pyridyl)-1H-1,2,4-triazol-3-yl)benzene (H2ML)

1,4-bis(5-(2-pyridyl)-1H-1,2,4-triazol-3-yl)benzene (H2LPL)
in synthetic procedures were of reagent grade or better. cis-[Ru(bpy)Cl2]2H2O14 and cis-[Os(bpy)Cl2]2H2O15 were prepared by literature procedures. The ligands 1,3-bis(5-(2-pyridyl)-1H-1,2,4-triazol-3-yl)benzene (H2mL) and 1,4-bis(5-(2-pyridyl)-1H-1,2,4-triazol-3-yl)benzene (H2pL) were prepared using standard methods normally used for the synthesis of pyridyltriazole ligands.14 Detailed synthetic procedures are available as Supporting Information.

**H2mL** Characterization: mp 310–322 °C 1H NMR [(CD3)2SO]: δ (ppm) 8.88 (1H, s, phenyl H2), 8.16 (2H, phenyl H3), J = 7.9 Hz), 7.65 (1H, t, phenyl H4, J = 7.9 Hz), 8.23 (1H, d, pyridyl H5, J = 7.9 Hz), 8.02 (1H, dd, pyridyl H6, J = 7.9 Hz), 7.55 ppm (1H, dd, pyridyl H7, J = 6 Hz), 8.72 (1H, d, pyridyl H8, J = 5 Hz), 14.90 (1H, s (broad), HNH). 13C NMR [(CD3)2SO]: δ (ppm) 121.53, 123.38, 123.62, 125.06, 126.58, 129.41, 131.40, 137.80, 146.31, 149.52, 149.72. Elemental anal. Calcd for C20H14N8: C, 65.56; H, 3.85; N, 30.59. Found: C, 65.39; H, 3.76; N, 30.57.

**H2pL** Characterization: mp > 300 °C 1H NMR [(CD3)2SO]: δ (ppm) 8.23 (2H, s, phenyl H), 8.19 (1H, d, pyridyl H, J = 7.9 Hz), 8.02 (1H, dd, pyridyl H, J = 7.9 Hz), 7.54 (1H, dd, pyridyl H, J = 6 Hz), 8.72 (1H, d, pyridyl H, J = 5 Hz), 14.90 (1H, s (broad), HNH). 13C NMR [(CD3)2SO]: δ (ppm) 121.52, 123.21, 125.11, 126.40, 126.81, 127.45, 137.88, 149.69, 150.41. Elemental anal. Calcd for C20H14N8: C, 65.56; H, 3.85; N, 30.59. Found: C, 65.39; H, 3.76; N, 30.57.

 cis-[Ru(bpy)2Cl2]2H2O (mRu). H2mL (0.732 g, 2 mmol) dissolved in DMF/H2O (2:1 v/v), cis-[Os(bpy)Cl2]2H2O (0.39 g, 0.75 mmol) was added to the solution, which was heated at reflux for 8 h. Upon cooling, the solution was filtered to remove unreacted ligand. A few drops of a saturated aqueous NH4PF6 solution were added, and the DMF/H2O was removed by evaporation under reduced pressure. The resulting solid was recrystallized by slow evaporation from acetone/water (2:1 v/v).

All complexes reported in this Communication were purified by column chromatography on neutral alumina unless otherwise stated. The mononuclear compounds contained dinuclear complex as the main impurity and vice versa. Purification by chromatography on neutral Al2O3 gave an excellent separation of bands associated with the mononuclear and dinuclear species, respectively. The dinuclear complexes were eluted using acetonitrile, while the mononuclear complexes, which remained at the top of the column, were eluted by the addition of methanol (50–100%) to the mobile phase.

mRu was isolated as the hexafluorophosphate salt and recrystallized from acetone/water (2:1 v/v) to which a few drops of aqueous NH4OH were added. Yield = 0.32 g (45%). Elemental anal. Calcd for Ru2CoH3N15OPF6: C, 50.98; H, 3.26; N, 17.84. Found: C, 50.62; H, 3.60; N, 17.54.

cis-[Ru(bpy)2Cl2]2H2O (mRu). H2mL (0.732 g, 2 mmol) dissolved in DMF/H2O (2:1 v/v), and the mixture was heated at reflux for 4 h. Following the addition of a few drops of a saturated aqueous solution of NH4PF6, the reaction mixture was evaporated to dryness under reduced pressure. The resulting solid was purified as described for mRu. Yield = 0.515 g (87%). Elemental anal. Calcd for Ru2CoH3N15OPF6: C, 50.82; H, 3.46; N, 14.25. Found: C, 46.09; H, 3.43; N, 14.08. Mass spectrometry, EI-MS: [(Ru(bpy)2)2(mL)]PF6+, found 595.5, theoretical 595.5; [(Ru(bpy)2)2((mL))2]PF6+, found 1336, theoretical 1336.


[(Os(bpy))$_2$(pL)]PF$_6$·4H$_2$O (pOsOs). This complex was prepared as described for mOsOs. The resulting solid was purified as described for mRu. Yield = 0.16 g (44%). Elemental anal. Calcld for Os$_5$C$_{40}$H$_{52}$N$_{16}$O$_4$P$_2$F$_{12}$: C, 41.62; H, 3.06; N, 12.62. Found: C, 41.62; H, 3.10; N, 12.69. Mass spectrometry, EI-MS: [(Os(bpy))$_2$-
(pL)]$^+$, found 648.5, theoretical 648.5.

[Ru(bpy)$_2$Os(bpy)$_2$(pL)]PF$_6$·3H$_2$O (pRuOs). This complex was prepared as described for mRuOs from [Ru(bpy)$_2$(H$_2$P)$_2$]PF$_6$ (0.10 g, 0.13 mmol) and cis-[Os(bpy)$_2$Cl$_2$]$_2$H$_2$O (0.08 g, 0.13 mmol). The resulting solid was purified as described for mRu. Yield = 0.1 g (50%). Elemental anal. Calcld for Ru$_3$Os$_6$C$_{40}$H$_{52}$N$_{16}$O$_4$P$_2$F$_{12}$: C, 44.35; H, 3.10; N, 13.79. Found: C, 44.51; H, 3.03; N, 13.70. Mass spectrometry, EI-MS: [Ru(bpy)$_2$]([Os(bpy)$_2$-
(pL)]$^+$), found 640, theoretical 640.

**Nuclear Magnetic Resonance.** $^1$H NMR spectra were recorded on a Bruker AC400 (400 MHz) instrument. The solvents used were $d_6$-DMSO for ligands and $d_6$-acetonitrile or $d_6$-acetonitrile for complexes. The chemical shifts were recorded relative to TMS. The spectra were converted from their free induction decay (FID) profiles using a Bruker WINNMR software package.

**Absorption and Emission Measurements.** UV/visible spectra were obtained using a Shimadzu UV3100 UV–vis–NIR spectrophotometer interfaced to an Elonex PC433 personal computer. Extinction coefficients are ±5%. Emission spectra in the range 500–850 nm were obtained on a Perkin-Elmer LS50-B luminescence spectrometer equipped with a red sensitive Hamamatsu R928 detector, interfaced with an Elonex PC466 personal computer employing Perkin-Elmer FL WinLab custom built software. At room temperature, excitation and emission slit widths of 10 nm were employed. At 77 K measurements were carried out in ethanol/methanol (4:1 v/v) using excitation and emission slit widths of 5 nm. The spectra were not corrected for the photomultiplier response. To ensure protonation/deprotonation, a few drops of perchloric acid or NH$_4$H$_2$O/diethylammonium solution were added to the sample.

**Luminescent Lifetime Measurements.** Three different methods were used to obtain the emission lifetimes. Below 20 ns fluorescence lifetimes were measured with a time-correlated single-photon counting setup described elsewhere.$^{16}$ Briefly, the samples were excited with 150 fs laser pulses at 400 nm with a repetition frequency of 200 kHz. The emission was detected using several alternative filters. For the Ru-based emission, a 600 nm interference filter was used for the acid forms of the complexes and a 695 nm cutoff for the base forms. For the Os-based emission, cutoff filters at 715 and 780 nm were used for the acid and base forms, respectively. The instrumental response function (fwhm) was ca. 120 ps, as determined with a scattering sample and a 400 nm interference filter. The samples were prepared in spectroscopic grade acetonitrile (Merck), with an optical density of ca. 0.3 at 400 nm, and were purged with N$_2$ before and during measurements. Room temperature lifetimes >20 ns were also measured using the third harmonic (355 nm) of a Spectron Q-switched Nd:YAG spectrum laser system. Emission was detected in a right angled configuration to the laser using an Oriel model IS520 gated intensified CCD coupled to an Oriel model MS125 spectrograph. Room temperature lifetimes were carried out in acetonitrile, unless otherwise stated. The samples used were all of low concentration (10$^{-1}$–10$^{-3}$ M), and degassing was carried out by bubbling nitrogen through the sample for at least 20 min. Luminescent lifetimes at 77 K were measured using an Edinburgh Analytical Instruments nF900 TCSPC described elsewhere.$^{10}$ The lifetime is estimated to be ±10%. Good agreement between the three methods was obtained.

** Förster Energy Transfer Calculations.** The Förster energy transfer rate constants were calculated from eq 1$^{17}$ The following

$$k_{	ext{ET}} = \left(8.79 \times 10^{-25}\right) \left(\Phi_{	ext{r}}/r^6\right) \left(\pi/\varepsilon^4\right) J/s$$

values were used in these calculations: $r = 1.3 \times 10^{-2} \text{ cm} (13 \AA)$; $\Phi = 6.1 \times 10^{-6} \text{ s}^{-1}$ and $1.7 \times 10^{-6} \text{ s}^{-1}$ for the protonated and unprotonated forms, respectively; and $n = 1.344$. The spectral overlap integrals were calculated as $J = 4 \times 10^{-14} \text{ M}^{-1} \text{ cm}^3$ and $J = 4 \times 10^{-14} \text{ M}^{-1} \text{ cm}^3$ for the protonated and unprotonated forms, respectively. $x^2 = x_0^2$ for a sample of randomly oriented dipoles. In the present case the geometry of the complexes will exclude orientations where the dipoles are oriented along the interdipole axes, so that $x^2$ is not likely to be higher than $x_0^2$. A detailed calculation of $x^2$ would require information of the rotational force fields in the molecules. After inspection of rotational geometries possible, however, we estimate that $x^2$ is not likely to lie outside the range 0.25–0.75, which gives an accuracy sufficient for the present discussion.

**Electrochemistry.** Cyclic voltammetry was carried out using a CH instruments model 660 electrochemical workstation interfaced to an Elonex 486 PC. A scan rate of 100 mV s$^{-1}$ was used for electrochemical measurements. HPLC grade solvents dried over molecular sieves were used. The electrolyte was 0.1 M tetrabutylammonium perchlorate (TEAP). The electrochemical cell used was a conventional three-compartment cell with glass frits. The reference electrode used was a saturated calomel electrode (SCE). Ferrocene was used as an internal reference. Its potential was taken to be +0.38 V vs SCE.$^{18,19}$ The working electrode was a 3 mm diameter Teflon shrouded glassy carbon electrode, and a platinum wire was used as the counter electrode. Prior to cathodic measurements the solutions were degassed for 15 min with nitrogen. Protonation and deprotonation of the complexes was achieved by addition of perchloric acid or NH$_4$OH, respectively.

**High Performance Liquid Chromatography.** Analytical HPLC experiments were carried out using a Waters HPLC system, consisting of a model 501 pump, a 20 $\mu$L injector loop, a Partisil SCX radial PAK cartridge mounted in a radial compression Z module, and a 990 photodiode array detector. The detection wavelength used was 280 nm, and the mobile phase was 80:20 CH$_3$CN:H$_2$O containing KNO$_3$ (0.12 M), with an acquisition time of between 300 and 900 $\mu$s. The pK$_a$ values were determined in Britton–Robinson buffer (0.04 M boric acid, 0.04 M acetic acid, 0.04 M phosphoric acid). The pH was adjusted by adding concentrated NaOH or concentrated H$_2$SO$_4$ and was measured using a Corning 240 digital pH meter. The pK$_a$ values were determined from the point of inflection of the absorbance versus pH plot.

Mass spectra were obtained using a Bruker-Esquire LC 005000 electrospray ionization mass spectrometer at positive polarity with cap-exit voltage of 167 V. Spectra were recorded in the scan range 50–2200 m/z with an acquisition time of between 300 and 900 $\mu$s and a potential of between 30 and 70 V. Each spectrum was recorded by summation of 20 scans.

Elemental analyses were carried out by the Microanalytical laboratories at University College Dublin.

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are more complicated due to the presence of resonances for both the free and bound pyridyltriazole arms. A full assignment of the triazole-based ligands is available as Supporting Information (See Tables S1 and S2). In the compounds obtained the metal centers may be bound to the triazole moiety via N1 or N4 of the triazole ring (see Figure 1). Analysis of the $^1$H NMR data obtained for both mononuclear and dinuclear complexes and comparison of the chemical shifts observed for N1-bound complexes of other similar pyridyltriazole-based systems indicate that coordination takes place via N1.12,25 Crystal structures of analogous pyridyltriazole complexes containing the ligands 3-methyl-5-(2-pyridyl)-4H-1,2,4-triazole26 and 3-(2-hydroxyphenyl)-5-(2-pyridyl)-4H-1,2,4-triazole27 also indicate that the Ru(bpy)$_2^+$ unit is coordinated via N1. Considering steric considerations this finding is not surprising.10

**Electrochemical Properties.** The electrochemical and spectroelectrochemical properties of the homonuclear ruthenium based complexes are reported in depth in an earlier contribution and will be discussed only briefly here.12 The oxidation and reduction potentials of all complexes are given in Table 1. The waves in the anodic region of the cyclic voltammograms are assigned to metal-centered oxidation processes.28 The protonated complexes, obtained by addition of a few drops of HClO$_4$ to the solution, show an anodic shift of between 250 and 300 mV compared to their deprotonated analogues. The oxidation potentials of the osmium compounds are approximately 400 mV less positive than observed for the analogous ruthenium complexes, due to the lower binding energy of the Os(II) 5d orbitals compared with the Ru(II) 4d orbitals.29 The reduction waves observed for all the complexes have been assigned as bpy-based by comparison with related compounds,28 the 1,2,4-triazole ligands being weaker π-acceptors than bpy. The homonuclear RuRu complexes show a single two electron redox wave at 0.84 V vs SCE without any evidence of splitting (<20 mV).12 This is indicative of an, at best, weak interaction between the two metal centers in the ground state. The fact that the oxidation potentials of the Os(II) and Ru(II) centers in their respective mononuclear and dinuclear complexes are identical, within experimental uncertainty, is in agreement with this observation. Spectroelectrochemical investigations on the compounds were also carried out. The spectroscopic features of the Ru(III) and Os(III) species are as expected and are listed in Table S3.

The spectro-electrochemical features of the intervalence compounds pRu(II)Ru(III) and mRu(II)Ru(II) were reported in an earlier contribution.12 For pRu(II)Ru(III) an intervalence band was observed at approximately 8000 cm$^{-1}$.

but no such feature was observed in the mRu(II)Ru(III) analogue. No intervalence features were observed for the protonated species pRu(II)Ru(III)H and mRu(II)Ru(III)-H. These observations further confirm that the interaction between the two metal centers in these dinuclear compounds is very weak. The fact that, for the protonated compounds, no intervalence features are observed suggests for the present system a superexchange hole transfer interaction (vide infra).

The absence of an intervalence band in the absorption spectrum of mRu(II)Ru(III) is in agreement with the expected reduced electronic coupling for meta- vs para-based systems. Similarly, during the oxidation of pOsOs, a weak band at 9400 cm⁻¹ appears and subsequently disappears during the course of the oxidation but no such bands are observed for the mOsOs or their protonated forms.

In contrast to the homolecptic complexes, where the absence of a separation between the first and second metal oxidation processes renders generation of the mixed valence species difficult, for the heteroleptic complexes the large separation (∆E < 350 mV) between the Os(II)- and Ru(II)-based oxidations results in a very high comproportionation constant (Kc) for the mixed valent Ru(II)Os(III) species, and hence generation of the Ru(II)Os(III) oxidation state is rendered more straightforward. No evidence of an intervalence transition was observed for mRuOs, mRuOsH, or pRuOsH. Surprisingly for pRuOs no intervalence transitions were observed. Due to the redox asymmetry of the mixed-metal system, it is expected that the energy of an IVCT band for pRuOs would be higher than vmax for the analogous pRuRu complex. The intervalence band, if present, would therefore be masked by the Os(III) LMCT bands.

### Electronic Properties

Electronic absorption and emission data for the complexes in their protonated and deprotonated forms are presented in Table 2. The electronic absorption spectra of all the complexes are dominated in the visible region by dπ–π* metal-to-ligand charge transfer (MLCT) transitions typical of complexes of this type and in the UV region (250–350 nm) by intense ligand-based π–π* transitions associated with the 2,2'-bipyridyl and bridging ligands.

### Table 1. Redox Properties

<table>
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<tr>
<th>complex</th>
<th>E_{1/2} M(II)/(III)</th>
<th>E_{1/2} ligand</th>
<th>E_{1/2} M(II)/(III)</th>
<th>E_{1/2} ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>mRu ≡ Ru(II)Ru(III)</td>
<td>0.47, −1.60</td>
<td>mRuH</td>
<td>1.18, −1.47</td>
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<tr>
<td>mOs ≡ Os(II)Os(III)</td>
<td>0.48, −1.71</td>
<td>mOsH</td>
<td>0.76, −1.46</td>
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<tr>
<td>mRuRu ≡ Ru(II)Ru(II)</td>
<td>0.84, −1.69</td>
<td>mRuRuH</td>
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</tr>
<tr>
<td>mOsOs ≡ Os(II)Os(II)</td>
<td>0.48, −1.71</td>
<td>mOsOsH</td>
<td>0.72, −1.43</td>
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<tr>
<td>pRu ≡ Ru(III)Ru(III)</td>
<td>0.48, −1.61</td>
<td>pRuH</td>
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<tr>
<td>pOs ≡ Os(III)Os(III)</td>
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<td>pOsH</td>
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<tr>
<td>pRuRu ≡ Ru(III)Ru(III)</td>
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<td>pRuRuH</td>
<td>1.14, −1.52</td>
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<td>pOsOs ≡ Os(III)Os(III)</td>
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<td>pRuOs</td>
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<td>pRuOsH</td>
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### Table 2. Absorption and Emission Data

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<th>absorbance λ_{max.} (nm (10^4 cm⁻¹))</th>
<th>emission λ_{max.} (nm 300 K)</th>
<th>lifetime, ns at 300 K</th>
<th>emission λ_{max.} (nm 77 K)</th>
<th>lifetime (ns) at 77 K</th>
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<tbody>
<tr>
<td>mRu</td>
<td>482 (0.85)</td>
<td>688</td>
<td>117</td>
<td>612</td>
<td>3150</td>
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<tr>
<td>mRuH</td>
<td>440</td>
<td>613</td>
<td>2.5 (60); 10 (40)</td>
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<td>5200</td>
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<tr>
<td>mRuRu</td>
<td>482 (2.00)</td>
<td>687</td>
<td>115</td>
<td>618</td>
<td>2600</td>
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<tr>
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<td>611</td>
<td>2.5 (50); 10 (50)</td>
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<td>4800</td>
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<tr>
<td>mOs</td>
<td>503 (1.13), 652 (0.23)</td>
<td>813</td>
<td>23</td>
<td>759</td>
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<td>mOsH</td>
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<td>814</td>
<td>&lt;20</td>
<td>761</td>
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<tr>
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<td>4950</td>
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<td>4700</td>
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<td>pOs</td>
<td>501 (1.05), 644 (0.22)</td>
<td>814</td>
<td>&lt;20</td>
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<td>720</td>
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<tr>
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<tr>
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<td>684, 795</td>
<td>5.7⁴</td>
<td>615 (w), 750</td>
<td>10, 325⁵, 740⁶</td>
</tr>
<tr>
<td>pRuOsH</td>
<td>568, 424</td>
<td>725</td>
<td>0.6, 37⁴</td>
<td>585, 710</td>
<td>5.6, 740⁶</td>
</tr>
</tbody>
</table>

⁴ Absorbance and emission λ_{max.} unless otherwise stated, were measured in acetonitrile. Protonation of the complexes was achieved by the addition of perchloric acid.
⁵ Measured in 4/1 ethanol/methanol. ⁶ Samples deoxygenated using N₂. For biexponential decays the contribution of each component is given in parentheses.

† Ru(II). ‡ Os(II)-based emission.
Energy Transfer Mechanisms in Dinuclear Complexes

Upon protonation of the triazole ring, the ligand (H$_2$mL/H$_2$-pL) becomes a weaker $\sigma$-donor and a stronger $\pi$-acceptor, lowering the energy of the metal-based orbitals, which results in the observed blue shift in the absorption spectrum.$^{26,32}$ For the Os(II) complexes, additional absorption bands are observed at 600–660 nm, which can be assigned to formally forbidden triplet $dz^2-\pi^*_{bpy}$ MLCT transitions.$^{33}$ The absorption spectra of equimolar solutions of the heterodinuclear complexes mRuOs and pRuOs and 1:1 mixtures of the corresponding homodinuclear species, pRuRu/pOsOs and mRuRu/mOsOs, were found to be identical. This indicates that the electronic structure of each metal center in the dinuclear complexes is largely independent of the other metal center and hence suggests that, as for ground state interaction (vide supra), excited state intercomponent interaction is, at best, very weak.

As is typical of pyridyltriazole-based Ru(II) and Os(II) complexes, a well-defined acid–base chemistry is observed. The $pK_a$ values obtained are in the range 3.3 ± 0.3. The values obtained for the individual compounds are given in the Supporting Information (Table S4).$^{26,34}$ It is notable that for the dinuclear species only one $pK_a$ value is obtained.$^{13}$ The absence of a ground state interaction between the two 1,2,4-triazole moieties demonstrates the weakness of the bridging phenyl group in mediating intercomponent interactions. The $pK_a$ values observed for the Os(II)-based homoleptic complexes are only marginally lower than that of the analogous Ru(II)-based complexes (by at most 0.3 pH unit), and hence in the case of the mRuOs and pRuOs, each of the protonation steps is too close to be distinguished.$^{35}$

As for the absorption spectra, protonation of the complexes results in a blue shift of the emission maxima (Table 2). The emission maxima obtained at room temperature as well as at 77 K are as expected for this class of compounds.$^{11}$ No difference is observed between the emission maxima of mononuclear and homodinuclear compounds, again indicating at best a weak interaction between the two metal centers in the dinuclear species.

One initially surprising observation is the different effect that protonation of Ru(II) and Os(II) complexes has on the emission lifetime (Table 2). While the emission energy in all complexes increase upon protonation, the effect of protonation on their emission lifetime is quite different. There is a dramatic decrease in the excited state lifetime of the Ru(II) emission, while the Os(II) emission lifetimes are significantly increased. The observation can be rationalized by considering the two main factors that control the excited state lifetime for this type of complex: the energy gap law$^{36}$ (governed by the energy gap between the ground and emitting states) and the gap between the emitting $1\text{MLCT}$ state and the deactivating $3\text{MC}$ state. For the Ru(II) complexes the latter factor controls most of the excited state decay in the compounds. Protonation of the triazole decreases the $\sigma$-donor capacity of the ligand. Consequently the ligand field splitting is decreased, which favors thermal population of the strongly deactivating $\epsilon^*_1$ ($3\text{MC}$) state and faster radiationless decay, resulting in shorter lifetimes.$^{37}$ However, for the Os(II) complexes the strength of the ligand field is large and the $3\text{MC}$ level cannot be populated. As a result the emission lifetime is primarily governed by the energy gap law and, due to the higher $1\text{MLCT}$ energy, the emission lifetime is increased.

The time-resolved emission decays for all the protonated mononuclear and homodinuclear Ru(II) complexes are biexponential. The presence of the exponents with approximately equal amplitudes implies that this behavior cannot be due to an impurity (this is apparent from the NMR data and the fact that the same samples in a basic solution gave single exponential decays).

Earlier studies have found that coordination isomers, bound via either the N1 or N4 nitrogen of the 1,2,4-triazole ring (see Figure 7), yield compounds with very different electronic properties.$^{38}$ Similarly, methylation at either the N2 or N4 position of [Ru(bpy)$_3$(pytr)]$^+$ also results in complexes exhibiting different electronic properties, in particular differing emission lifetimes.$^{16}$ These studies demonstrate the inequivalence of the N1/N2 and N4 positions toward modification; and because only one site may be protonated and neither site is particular favored above the other, it is probable that in solution an equilibrium mixture of two species {protonated at either the N2 or N4 position} is

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*Figure 3.* Room temperature emission spectrum for mRuOs (solid line) and mRuOsH (dashed line) (~10$^{-5}$ M, excitation at the isosbestic point). The ruthenium and osmium contributions to the emission envelope are indicated as Ru and Os, respectively.

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(35) For the mononuclear complexes it would be expected that a second deprotonation step (due to the unbound 1,2,4-triazole ring) would be observed at higher pH. However, the effect on the absorption spectrum of the complex of deprotonation of such a peripheral group would be expected to be negligible, considering the limited influence that substituents in the C3 position of the 1,2,4-triazole have on the electronic properties of this class of complexes.$^{24}$


present, i.e., RuH₄ and RuH₃N₂. Hence two limiting situations are possible: (1) the rate of exchange between N₂ and N₄ protonation is much faster than the emission decay rate of either species and an averaged lifetime is observed and (2) the rate of exchange is much slower than the emission decay rate of each center and biexponential behavior is observed. The assumption that RuH₄ and RuH₃N₂ will have different emission lifetimes is not unreasonable since such differences in emission lifetime have been observed for N₂ and N₄ methylated complexes.¹⁶

In dry acetonitrile, the rate of proton exchange is quite slow and equilibrium may not be established within the emission lifetime. Hence, the biexponential behavior observed for the homonuclear Ru(II) complexes is likely to be due to protonation of inequivalent sites.³⁹ For the Os(II) containing complexes only a monoexponential decay is observed. The absence of a biexponential emission decay may possibly be explained by the much longer emission lifetime for these complexes that allows proton equilibration during the excited state lifetime. Alternatively, the difference between the protonation isomers may be less important for the Os(II) complexes that decay predominantly by internal conversion to the ground state, instead of by activated decay via metal-centered states as for the Ru(II) complexes.

Figure 4. Emission spectrum of dinuclear complexes at 77 K in basic (left) and acidic (right) 5/1 v/v ethanol/methanol (spectral intensity is adjusted for clarity).

Figure 5. Room temperature emission spectra of pRuOsH, pRuRuH, and pOsOsH and of an equimolar mixture of pRuRuH and pOsOsH in CH₃CN (~10⁻⁵ M) (excitation at the isosorptive point).

Figure 6. Time-resolved decay of the Ru emission observed at 600 nm for mRuRuH (upper curve) and mRuOsH (lower curve) in CH₃CN (~10⁻⁵ M). The dashed line is the instrumental response function. Inset: Decay of the Os-based emission at λ > 715 nm for mRuOsH.

Figure 7. Coordination isomers of mononuclear complexes discussed in text.

In protic media the rate of proton exchange is expected to be much faster than the lifetime of the excited state and hence an averaged lifetime is observed (i.e., single exponential) and hence addition of protic solvents to the acetonitrile solutions would be expected to result in a monoexponential lifetime being observed. The reduction in emission intensity in the presence of protic solvents, however, makes such experiments ambiguous.

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Energy Transfer Mechanisms in Dinuclear Complexes

Table 3. Emission Lifetimes and Calculated Energy Transfer Parameters

<table>
<thead>
<tr>
<th></th>
<th>$\tau_{\text{Ru}}$/ns</th>
<th>$k_{\text{ET}}$/s$^{-1}$ $k_{\text{Ru/hs}}$/s$^{-1}$</th>
<th>$k_{\text{Os/hs}}$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-based</td>
<td>5.7</td>
<td>$&lt;6$</td>
<td>1.6 $\times 10^7$</td>
</tr>
<tr>
<td>Os-based</td>
<td>6.3</td>
<td>$&lt;6$</td>
<td>1.5 $\times 10^7$</td>
</tr>
<tr>
<td>$p_{\text{RuOs}}$</td>
<td>0.6</td>
<td>$&lt;6$</td>
<td>1.4 $\times 10^7$</td>
</tr>
<tr>
<td>$m_{\text{RuOs}}$</td>
<td>6.3</td>
<td>$&lt;6$</td>
<td>1.5 $\times 10^7$</td>
</tr>
<tr>
<td>$m_{\text{RuOs}^+}$</td>
<td>$\approx 1$ ($&lt;50%$)</td>
<td>3.8</td>
<td>2.6 $\times 10^7$</td>
</tr>
<tr>
<td>$m_{\text{OsOs}^+}$</td>
<td>$\approx 1$ ($&lt;50%$)</td>
<td>3.8</td>
<td>2.6 $\times 10^7$</td>
</tr>
</tbody>
</table>

* Measured by time-correlated single-photon counting. * Calculated from the time-resolved data (see text). * Calculated using the parameters given in the Experimental Section.

Intercomponent Interaction in RuOs Compounds. At room temperature both $m_{\text{RuOs}}$ and $p_{\text{RuOs}}$ exhibit a weak dual emission with maxima at around 680 and 800 nm. The spectrum observed for $m_{\text{RuOs}}$ is shown as an example in Figure 3. By comparison with homodinuclear complexes these two emissions may be assigned to the Ru-bound and Os-bound sites, respectively. For both complexes, the emission from the Ru-bound component is slightly stronger than that from the Os-bound unit. Examination of the emission spectra of the protonated $m_{\text{RuOs}^+}$ (See Figure 3) and $p_{\text{RuOs}^+}$ complexes reveals that in both cases emission from the Os-bound site is now the predominant spectral feature. The Ru-based emission appears as a very weak band preceding the tail of the Os(II) luminescence.

At 77 K emission from both sites can be seen. From the luminescence maxima at 77 K, it can be seen that the Ru→Os energy transfer step in $m_{\text{RuOs}}$ and $p_{\text{RuOs}}$ is energetically allowed by approximately 0.36 eV. These observations suggest quenching of the Ru(II)-based luminescence via an energy transfer mechanism. Such dual luminescence is unusual, although some well-documented examples have been reported by Barigelletti(40,41) and co-workers. The relative intensities of the Ru(II) and Os(II) emission for $m_{\text{RuOs}}$ and $p_{\text{RuOs}}$ and their protonated forms are, however, more complicated than at 298 K. For $m_{\text{RuOs}}$, the Os-based luminescence is found to be twice as intense as the Ru-based luminescence, while for $p_{\text{RuOs}}$, the Ru-based emission is more intense than the Os-based luminescence. The emission lifetime data at 77 K (Table 3) show that the Ru-emission is quenched by 99%. A detailed analysis of the difference in the intensity of the ruthenium-based emission in the two types of compounds is precluded because of the sensitivity of the emission intensities to small amounts of unquenched Ru(II) impurities (Figure 4).

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To further investigate the dual emission properties, the emission properties of equimolar solutions of $p_{\text{RuRuH}}$, $p_{\text{OsOsH}}$, and $p_{\text{RuOsH}}$ at the isosbestic point (457 nm) is shown in Figure 5. The emission spectrum obtained for $p_{\text{RuOsH}}$ indicates that the Ru-based emission is almost completely quenched, giving only 2% of the intensity in $p_{\text{RuRuH}}$. Furthermore, it was found that the Os-based luminescence in $p_{\text{RuOsH}}$ is as intense as that of an equimolar $p_{\text{OsOsH}}$ solution, a finding consistent with energy transfer.

The steady state results are reflected in the excited state lifetimes. Figure 6 shows examples of emission traces for $m_{\text{RuRuH}}$ and $m_{\text{RuOsH}}$. In $m_{\text{RuOs}}$ and $p_{\text{RuOs}}$ the lifetime of the Ru-based emission at 300 K is much shorter than in the corresponding homodinuclear complexes (Table 2). We attribute the reduction in lifetime to energy transfer to the Os(II) center, consistent with the emission spectral results above. As for the homometallic complexes, the Ru-based emission decay was not single-exponential for $m_{\text{RuOsH}}$, presumably due to the presence of two protonation isomers (vide supra). The more short-lived emission in $p_{\text{RuOsH}}$ ($\tau = 0.6$ ns) appeared single-exponential, possibly because the energy transfer is rapid enough compared to the excited state decay to make the observed lifetime difference between the two emitting centers (i.e., Ru and Os) indistinguishable.

In the protonated complexes $p_{\text{RuOsH}}$ and $m_{\text{RuOsH}}$ a more long-lived and single-exponential (ca. 37 ns) Os-based emission is observed. The lifetime of this Os emission is very similar to the emission lifetime of $p_{\text{OsOsH}}$ and $m_{\text{OsOsH}}$. No rise of the Os-based emission due to energy transfer could be observed in the heterodinuclear complexes because the Ru emission was more intense—in terms of number of photons per time unit—even at longer wavelengths. Instead, evidence for sensitization of the Os emission by energy transfer was provided by the steady state emission data above.

In the deprotonated complexes, $p_{\text{RuOs}}$ and $m_{\text{RuOs}}$, a single-exponential ca. 6 ns lifetime was observed at all wavelengths examined (600–800 nm), also with an interference filter at 600 nm where any Os-based emission is negligible. Thus, we attribute the ca. 6 ns component to Ru-based emission. This is ca. 5% of the lifetime for the corresponding RuRu complexes, in good agreement with the relative emission yields from the emission spectra above. No Os-based emission could be resolved, however. The emission lifetime of the complex $p_{\text{OsOs}}$ is $\sim 6$ ns, and hence the Os-based emission in $p_{\text{RuOs}}$ is likely to have a lifetime that is accidentally very similar to that for the Ru emission.

Energy Transfer Mechanism. The experimental rate constant for energy transfer from the Ru(II) to the Os(II) center, $k_{\text{ET}}$, can be calculated from the difference in Ru emission decay rate in the Ru−Os and the corresponding

RuRu complex using the equation $k_{\text{EnT}} = 1/\tau_{\text{RuOs}} - 1/\tau_{\text{RuRu}}$. The values obtained in this manner for the different compounds are given in Table 3. In the case of the protonated complexes at room temperature, which exhibit biexponential emission decay, approximate values were calculated by assuming that the more long-lived Ru protonation state also gave the slower energy transfer in the Ru–Os complex. The energy transfer rate constants are very similar at 293 and 77 K, except for $\text{pRuOsH}$, where it is an order of magnitude faster at 293 K (see discussion below). Energy transfer is relatively slow in the present complexes compared to other Ru–Os complexes that were linked by phenyl groups but where all ligands were polypyridines, and the lowest MLCT states of the complexes involved the bridging ligands. This difference is likely to be due to the localization of the lowest $^3$MLCT states of both the Ru and the Os centers on the peripheral (bpy) ligands (the $^3$MLCT states involving the bridging ligand are much higher in energy also in the protonated complexes). This serves to increase the effective energy transfer distance and decreases through-bond coupling. The energy transfer rates in the complexes presented here are instead similar to those reported for a series of phenyl-bridged complexes where the bridging ligands are cyclo-metallating dipyridinebenzene fragments. Also in these complexes one may expect that the lowest MLCT states were localized on the peripheral ligands, and that the MLCT states of the bridging ligands are much higher in energy.

The energy transfer in the present complexes can occur either through a direct dipolar coupling (Förster) or by an exchange mechanism (Dexter). In the latter case, the coupling is mediated through bonds and would occur by an interligand hopping of the excited MLCT state. Hopping would give a transient population of the MLCT state of the bridging ligand followed by energy transfer to the Os center:

\[
(bpy)(bpy^{\ast})\text{Ru}^{\text{III}}(\text{ptzH})^-\text{Os}^{\text{II}}(\text{bpy}) \leftrightarrow (bpy)\text{Ru}^{\text{III}}(\text{ptzH}^{\ast})^-\text{Os}^{\text{II}}(bpy) \rightarrow \text{EnT}
\]

and Table 3) are smaller than those obtained experimentally. The somewhat larger experimental rate constant for $\text{pRuOsH}$ than for $\text{mRuOsH}$ at 293 K may, however, indicate an additional contribution from an exchange mechanism in the former complex. This assignment is supported by the temperature-dependent data: at 77 K the rate constants for $\text{pRuOsH}$ and $\text{mRuOsH}$ are equal. This is expected for an essentially temperature-independent Förster mechanism. The activated Dexter energy transfer is instead negligible at 77 K but significant at 293 K for $\text{pRuOsH}$. This complex is both protonated and para-substituted, which favors the through-bond energy transfer.

In conclusion, the excited state energy transfer interaction seems to be dominated by through-space Förster contributions. A through-bond Dexter mechanism seems to be significant only in $\text{pRuOsH}$. This is in contrast to the ground state interactions, as revealed by electrochemical data and intervalence absorption spectra. These show large differences between the complexes with para- and meta-substituted states on the peripheral and the bridging ligands. This is in contrast to the ground state interactions, as revealed by electrochemical data and intervalence absorption spectra. These show large differences between the complexes with para- and meta-substituted ligands.
bridging ligands and between protonated and unprotonated complexes, suggesting a through-bond hole transfer interaction.

Conclusions

The study of the ground and excited state intercomponent interaction in multinuclear complexes incorporating the 1,2,4-triazolato anion has enabled the development of a detailed picture of the mechanisms that mediate such interactions. For compounds based on the different bridging ligands shown in Figure 8, it was observed that ground state interaction via hole transfer is strong for bpt$^{-}$ type systems (compound 1 in Figure 8), but decreases going from bpt$^{-}$ to bispytr$^{2-}$ (compound 2) to the compounds reported here and the dimethoxy analogue (compound 3) but increases for compound 4. Significantly, the effect of protonation on the ground state internuclear interaction in all cases is to reduce its strength. Given that protonation results in a lowering of the bridging-ligand HOMO energy and together with the effect of synthetic variation of the HOMO energy by variation of the “spacer” group (i.e., phenyl, dimethoxypyphenyl, and thiényl), the nature of ground state interaction can be identified as occurring through a hole transfer mechanism through the bridging ligand HOMO orbitals. The effect of meta vs para coupling on the interaction strength supports the conclusion that a through-bond mechanism is in operation since if a through space mechanism were to be important then the meta substitution would serve to reduce internuclear separation and hence increase rather than decrease coupling.

From the similarities in absorption, emission, and acid/base properties, it is clear that the electronic structure of each unit in the binuclear complexes is largely unperturbed by the bridging ligand, and hence each unit can be viewed as being a distinct molecular unit rather than a part of a larger “delocalized” molecule. In contrast to ground state interaction, the contribution of a superexchange (through-bond) mechanism for the excited state energy transfer in these systems is much less significant and a through-space mechanism is dominant. For the bpt$^{-}$ system energy transfer from the Ru(II) to the Os(II) center was found to be efficient with no emission from the ruthenium site being observed. In the compounds reported here (based on the ligands H$_2$mL and H$_2$pL), it is evident that the interaction between the metal centers is reduced considerably, resulting in dual emission being observed. The increasing distance between the metal centers can explain this reduced efficiency of energy transfer, and the behavior observed is indicative of a predominantly dipole−dipole (Förster type) mechanism for energy transfer, which may dominate when through-bond coupling is very weak.

Acknowledgment. The authors thank Enterprise Ireland for financial support.

Supporting Information Available: Synthetic procedures for ligands H$_2$mL and H$_2$pL. Table S1 containing $^1$H NMR data for the complexes with H$_2$mL. Table S2 containing $^1$H NMR data for the complexes with H$_2$pL. Table S3 containing UV/vis/NIR absorption data for the fully oxidized complexes of H$_2$mL and H$_2$pL in their protonated and deprotonated forms. Table S4 containing pK$_a$ values for the coordinated triazole rings in the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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