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# Ruthenium(II) and osmium(II) polypyridyl complexes of an asymmetric pyrazinyl- and pyridinyl-containing 1,2,4-triazole based ligand. Connectivity and physical properties of mononuclear complexes †

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The synthesis, purification and characterisation of two coordination isomers of ruthenium(II) and osmium (II) complexes containing the ligand 3-(pyrazin-2′-yl)-5-(pyridin-2″-yl)-1,2,4-triazole (Hppt) are described. The X-ray and molecular structure of the complex $[Ru(bipy)_2(ppt)]PF_6 \cdot CH_3OH$ (**1a**) is reported, where the $Ru(bipy)_2$-centre is bound to the $ppt^-$ ligand *via* the pyridine nitrogen and the N1 atom of the triazole ring. $^1H$ NMR spectroscopic measurements confirm that in the second isomer (**1b**) the $Ru(bipy)_2$-moiety is bound *via* the N2 atom of the triazole ring and the pyrazine ring. Partially deuteriated metal complexes are utilised to facilitate interpretation of $^1H$ NMR spectra. The redox and electronic properties indicate that there are significant differences in the electronic properties of the two coordination isomers obtained. The acid–base properties of the compounds are also reported and show that the $pK_a$ of the 1,2,4-triazole ring varies systematically depending on the nature of the non-coordinating substituent. Analysis of these data indicates a significant electronic interaction between the pyridyl/pyrazyl rings and the 1,2,4-triazole ring in the coordinated $ppt^-$ ligand.

## Introduction

For many years, ruthenium(II) and osmium(II) polypyridyl complexes have attracted attention due to their well-defined spectroscopic, photophysical, photochemical, and electrochemical properties.[1] These properties are of particular use in the construction of supramolecular systems[2] and in the development of photochemically driven molecular devices.[3] Ruthenium(II) polypyridyl complexes have also received extensive attention as functional models for water-oxidation catalysis in photo-system II[4] and in the catalytic photochemical cleavage of water.[5] Of particular interest is their incorporation into the design of multinuclear structures capable of directing and modulating electron and energy transfer processes.[3] The ability to tune the excited state properties of these complexes is central to their potential for practical applications.

For these reasons there has been a detailed investigation of the synthesis and characterisation of multinuclear ruthenium(II) and osmium(II) polypyridyl complexes using negatively charged triazole based bridging ligands.[6,7] It was shown that with these ligands relatively strong interaction can be obtained between metal centres, so that both electron transfer and energy transfer processes can occur efficiently.[8] The immobilisation of such dinuclear complexes on nanocrystalline $TiO_2$ has also been reported.[9] In these studies the importance of the 1,2,4-triazole bridge in mediating electron transfer was demonstrated. By systematically changing the nature of the bridge, the effect on the nature of the lowest excited states of these multinuclear compounds and on metal–metal interaction has been examined in detail. It was found that by using ligands such as 3,5-bis(pyridin-2′-yl)-1,2,4-triazole (Hbpt, Fig. 1) the lowest energy

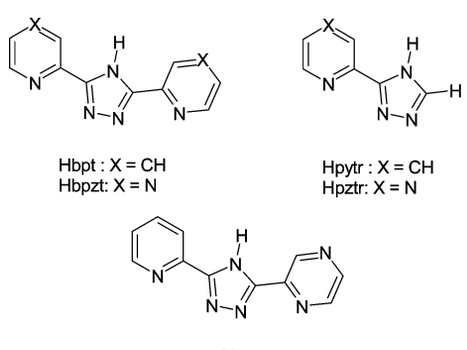


**Fig. 1** Ligands described in text.

excited state is located on the polypyridyl ligands (*i.e.* bipy) whilst with the ligand 3,5-bis(pyrazin-2′-yl)-1,2,4-triazole (Hbpzt, Fig. 1) the emitting state is located on the pyrazine bridging ligand.[6,7] This has important consequences for the photochemical properties of these compounds and indeed dinuclear $bpt^-$ and $bpzt^-$ complexes show different products when photolysed under the same conditions.[10] In addition, resonance Raman evidence suggested that in the dinuclear $bpzt^-$ complexes the excited state is located on *one* of the

† Electronic supplementary information (ESI) available: $^1H$ NMR spectra of **1a** and **1b**. See http://www.rsc.org/suppdata/dt/b2/b206667j/

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pyrazine rings of the bridge.[11] These results show clearly that the photophysical properties of these dinuclear structures can be manipulated by a careful choice of the bridging ligand.

To further investigate these systems we have extended our study to include the ligand 3-(pyrazin-2′-yl)-5-(pyridin-2″-yl)-1,2,4-triazole (Hppt) (see Fig. 1). The synthesis of these dinuclear complexes presents a major synthetic challenge. The asymmetry of the ligand may result in the formation of up to four different mononuclear coordination isomers as shown in Fig. 2 and as expected the reaction of one equivalent of the

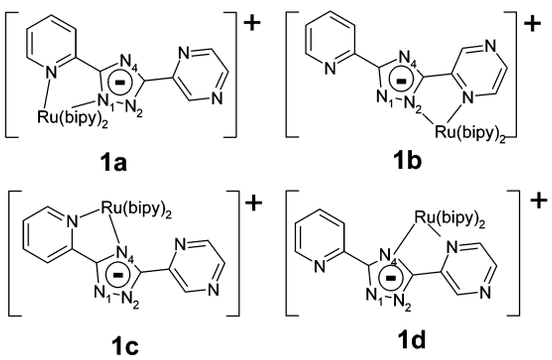


**Fig. 2** Possible coordination isomers of $[Ru(bipy)_2(ppt)]^+$.

bridging ligand with two equivalents of a $[M(bipy)_2]$ precursor leads to the formation of a mixture of different coordination isomers. Therefore in order to obtain well-defined dinuclear complexes an indirect route *via* the formation of mononuclear precursors has to be developed.

In this contribution the synthesis, purification and characterisation of two mononuclear coordination isomers of $Ru(bipy)_2$ and $Os(bipy)_2$ complexes with Hppt are reported. The compounds obtained have been separated using chromatographic techniques and were characterised using $^1$H NMR, electronic spectroscopy and electrochemistry. The X-ray crystal structure of one of the coordination isomers is reported. The acid-base properties of the coordination isomers are also investigated and are discussed, together with data obtained for related complexes. In particular the effect of substitution in the C5 position of the 1,2,4-triazole on the acid base properties is rationalised on the basis of the electron withdrawing/donating properties of the substituent.

## Results and discussion

### Synthesis and purification

The synthesis of the ligand Hppt[26] and of the mononuclear complexes[6,7] were carried out by previously reported procedures. Hppt is inherently asymmetric and as a result the synthesis of its mononuclear complexes is complicated by the possibility of the formation of four coordination isomers (Fig. 2). The metal centre may be bound *via* N1 of the triazole ring and the pyridine ring (**1a**), *via* N2 of the triazole ring and the pyrazine ring (**1b**), *via* N4 of the triazole ring and the pyridine ring (**1c**) and finally *via* N4 of the triazole ring and the pyrazine ring (**1d**). It has been shown for several 1,2,4-triazoles that the presence of bulky substituents in the 5- position of the 1,2,4-triazole ring results in preferential formation of the N2 isomer. The amount of N4 bound isomers varies from 50% (5 position occupied by H)[12] to less than 5% (5 position occupied by Br).[13] HPLC analysis of reaction products before purification shows that, in agreement with this observation, the amount of N4 bound isomers present is estimated at less than 5% and these are removed by recrystallisation. The remaining two coordination isomers **1a** and **1b** were subsequently separated by column chromatography as detailed in the experimental section.

### X-Ray crystallography

The molecular structure of **1a** is shown in Fig. 3. Complex **1a** co-crystallised with a molecule of methanol and a hexafluorophosphate counter anion (not shown). From the crystal structure it is clear that the ligand is bound through the pyridine-N and N1 of the triazole ring (*via* N(1) and N(2) in Fig. 3). The bite angle of the N(1)–Ru(1)–N(2) is 77.98 (6)°, which corresponds well with the bite angle obtained by Hage et al. of 78(1)° for $[Ru(bipy)_2(bpt)]PF_6\cdot\frac{1}{2}H_2O$,[6] and of 77.9(1)° for $[Ru(bipy)_2(3\text{-}(2\text{-hydroxy-phenyl})\text{-}5\text{-}(pyridin\text{-}2\text{-}yl)\text{-}1,2,4\text{-}triazole)]PF_6\cdot CH_3COCH_3$.[14] Bite angles of 78.87(7)° and 78.72(7)° for bipyridyl ligands are also typical for this class of complex. Ruthenium–nitrogen distances of 2.0398(16)–2.1033(17) Å are also comparable to those found in other complexes.[15] The ruthenium–pyridine distance Ru(1)–N(1) at 2.1033(17) Å is the longest Ru–N bond in the complex and the ruthenium–triazole distance Ru(1)–N(2) at 2.0398(16) Å is the shortest, in agreement with previously reported structures (*e.g.* 2.03(2) Å $[Ru(bipy)_2(bpt)]PF_6\cdot\frac{1}{2}H_2O$).[6] The isomer obtained is therefore identified as **1a**, where the metal centre is bound to N1 of the triazole ring and the pyridine moiety (Fig. 2).

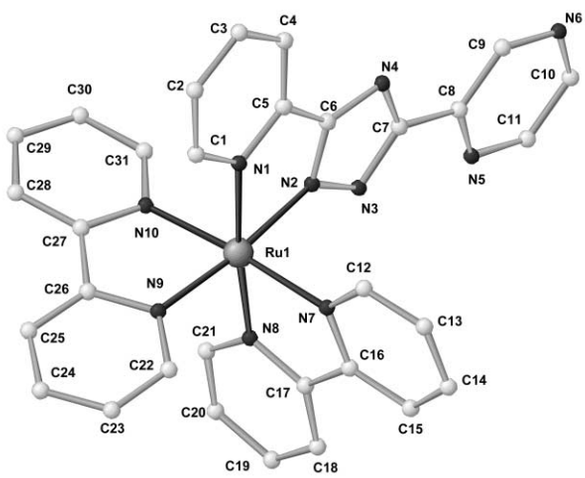


**Fig. 3** Molecular structure of the cation in **1a**.

### $^1$H NMR spectroscopy

It has been shown previously that $^1$H NMR spectroscopy can be used effectively to determine the coordination mode of triazole based ligands.[16] To this end, $^1$H and $^1$H COSY NMR spectroscopy together with specific deuteriation have been employed. In Table 1, the chemical shifts ($\delta$) of the ppt$^-$ proton resonances are presented together with those of the free ligand and of the analogous bpt$^-$ and bpzt$^-$ $Ru(bipy)_2$ complexes. The bipy resonances are as expected and are not listed (see supplementary material for spectra of **1a**/**1b**).[16]

Results obtained for the analogous bpt$^-$ and bpzt$^-$ mononuclear compounds show that coordination of a pyridyl/pyrazyl moiety results in a significant change in the chemical shift of its H6 proton while only minor changes to the H6 proton of the free ring are observed.[6,12] This is illustrated in the $^1$H NMR spectra of the partially deuteriated analogues **2a** and **2b** (Fig. 4). Partial deuteriation simplifies the analysis of the spectra, since ppt$^-$ based signals can be identified with ease. For **2a**, the H6 resonance of the coordinated pyridyl ring at 7.56 ppm is significantly different from the free ligand value of 8.72 ppm, in agreement with coordination being *via* the N1 of the 1,2,4-triazole ring and the pyridine moiety. Similarly for **2b** the change in the H6 resonance of the pyrazyl ring from 8.73 ppm in the free ligand to 7.63 ppm shows that coordination in this case, and for **1b**, is *via* the triazole N2 atom and the pyrazine ring.

**Table 1** $^1$H NMR resonances observed for the mononuclear ppt$^-$ complexes in $CD_3CN$, together with bpt$^-$ and bpzt$^-$ analogues

| Compound | | $H^3$ | $H^4$ | $H^5$ | $H^6$ |
|---|---|---|---|---|---|
| Hppt | pz | 9.42 s | – | 8.68 d | 8.73 d |
| | py | 8.26 d | 8.00 m | 7.52 m | 8.72 d |
| **2a** $[Ru(d_8\text{-bipy})_2(ppt)]^+$ | pz | 9.20 (−0.22) s | – | 8.52 (−0.16) d | 8.46 (−0.27) d |
| | py | 8.22 (0.04) d | 7.94 (−0.06) m | 7.20 (−0.32) m | 7.56 (−1.16) d |
| **2b** $[Ru(d_8\text{-bipy})_2(ppt)]^+$ | pz | 9.33 (−0.09) s | – | 8.28 (−0.40) d | 7.63 (−1.10) d |
| | py | 8.02 (−0.14) d | 7.78 (−0.22) m | 7.27 (−0.25) m | 8.54 (−0.18) d |
| **3a** $[Os(bipy)_2(ppt)]^+$ | pz | 9.19 (−0.16) s | – | 8.50 (−0.22) d | 8.43 (−0.29) d |
| | py | 8.13 (−0.07) d | 7.75 (−0.28) m | 7.07 (−0.49) m | 7.42 (−1.37) d |
| **3b** $[Os(bipy)_2(ppt)]^+$ | pz | 9.25 (−0.10) s | – | 7.64 (−1.08) d | 8.13 (−0.59) d |
| | py | 8.46 (+0.26) d | 7.31 (−0.72) m | 7.75 (+0.19) m | 8.53 (−0.26) d |
| $[Ru(bipy)_2(bpt)]^+$ | Ring A[a] | 8.23 (+0.08) d | 8.01 (+0.01) m | 7.26 (−0.26) m | 7.74 (−0.98) d |
| | Ring B[b] | 8.06 (−0.09) d | 7.74 (−0.26) m | 7.20 (−0.32) m | 8.45 (−0.22) d |
| $[Ru(bipy)_2(bpzt)]^+$ | Ring A[a] | 9.30 (−0.04) s | – | 8.36 (−0.42) d | 7.61 (−1.17) d |
| | Ring B[b] | 9.23 (−0.09) s | – | 8.46 (−0.32) d | 8.46 (−0.32) d |
| $[Os(bipy)_2(bpt)]^+$[c] | Ring A[a] | 8.32 (+0.17) d | 7.94 (−0.06) m | 7.30 (−0.26) m | 7.74 (−0.97) d |
| | Ring B[b] | 8.23 (+0.08) d | 8.14 (+0.07) m | 7.59 (−0.07) m | 8.65 (−0.02) d |
| $[Os(bipy)_2(bpzt)]^+$ | Ring A[a] | 9.23 (−0.11) s | – | 8.06 (−0.72) d | 7.57 (−1.21) d |
| | Ring B[b] | 9.20 (−0.14) s | – | 8.46 (−0.32) d | 8.46 (−0.32) d |

Values in parantheses are change with respect to free ligand {*i.e.* Hppt (in $CD_3CN$), Hbpt (in $(CD_3)_2SO$), Hbpzt (in $(CD_3)_2SO$)}. pz = pyrazine ring, py is pyridine ring {s = singlet, d = doublet, dd = doublet of doublets and m = multiplet}. [a] Coordinated ring. [b] Free ring. [c] From ref. 28 measured in $(CD_3)_2CO$.

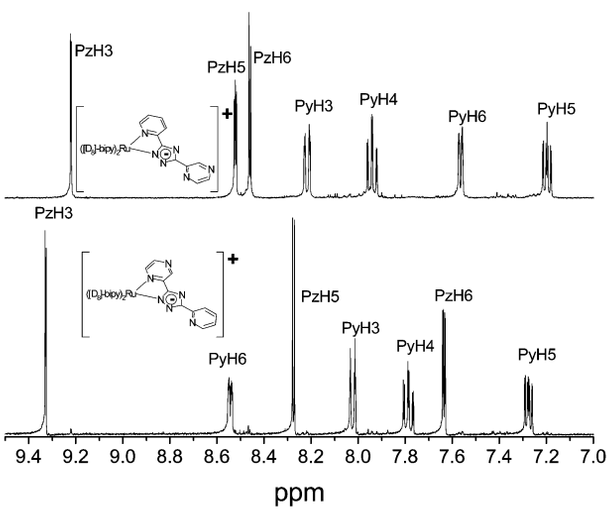


**Fig. 4** $^1$H NMR (400 MHz) spectra of **2a** (upper spectrum) and **2b** (lower spectrum) in $CD_3CN$.

For the osmium(II) complexes **3a**/**3b** the upfield shift of the H6 proton of the coordinated ring is greater than for the ruthenium complexes. This has been observed previously, and has been attributed to increased π-backbonding to the ligands by osmium(II) compared with ruthenium(II), which increases the ring current of the aromatic rings and hence the shielding effect felt by the H6 proton.[17]

In conclusion, with the X-ray structure of **1a** as reference, the coordination mode of mononuclear ppt$^-$ complexes in general can be determined conveniently by $^1$H NMR spectroscopy.

## Electronic properties

The visible absorption and emission data for the compounds obtained are listed in Table 2. The lowest energy absorption feature for the ruthenium complexes is assigned to several overlapping singlet metal-to-ligand-charge-transfer ($^1$MLCT) transitions (log ε ~ 4.2), involving both bpy and Hppt ligands, by comparison with other ruthenium polypyridyl complexes.[2] All compounds show strong absorptions (log ε ~ 5) at about 280 nm which are π–π* in nature. For the osmium(II) complexes **3a**/**3b** formally forbidden $^3$MLCT transitions are present at longer wavelengths (550 nm to 750 nm) similar to those observed for $[Os(bipy)_3]^{2+}$.[18] Overall the electronic properties are typical for pyridyl and pyrazine triazole complexes,[6,7] however, there are some significant differences in the electronic properties of the two isomers as the comparison below shows.

For the pyridine bound complexes **1a** and bpt$^-$, the absorption spectra of the protonated and deprotonated species are very different, with a substantial blue shift in the $\lambda_{max}$ occurring upon protonation (~ 40 nm) (see Fig. 5). However, for the pyrazine bound complexes (**1b** and bpzt$^-$) only a small blue shift in the $\lambda_{max}$ of the $^1$MLCT absorption bands occurs upon protonation (~ 10 nm) (Fig. 6). The effect of protonation on the pyridine and pyrazine bound isomers are similar to those of related mononuclear complexes (see Table 2). For the osmium analogues a similar behaviour is observed, however, the presence of formally spin forbidden transitions ($^3$MLCT) results in more complex spectra.

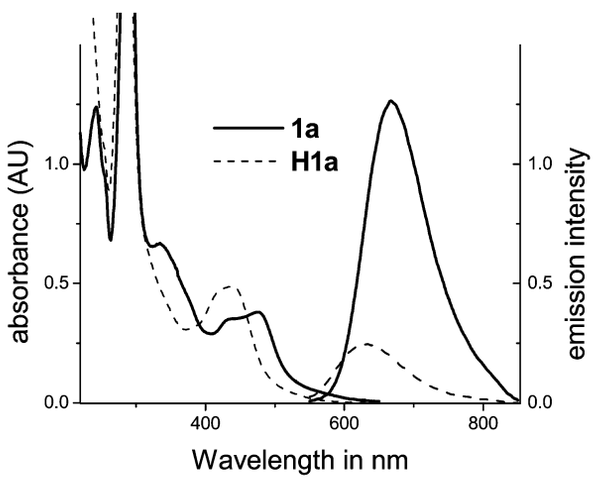


**Fig. 5** UV/vis absorption and emission spectra of **1a**, **H1a** in acetonitrile.

All complexes examined are luminescent in acetonitrile at room temperature and at 77 K. The ruthenium complexes examined all emit in the 650 to 700 nm region and a large blue shift is observed going from 300 to 77 K, typical for $^3$MLCT emission.[2] As for the absorption spectra, the emission maximum of **1a** (676 nm) is close to that of the analogous bpt$^-$ complex (678 nm). Upon protonation of **1a**, a blue shift in the spectrum and a reduction in the emission lifetime is observed

**Table 2** Redox and electronic data for non-deuteriated complexes

| Compound | Oxidation potential/V | Reduction potential/V | Absorption/nm (log $\varepsilon$) | [a]Emission/ nm ($\tau$/ns) |
|---|---|---|---|---|
| $[Ru(bipy)_2(ppt)]^+$ (**1a**) | 0.95 | −1.45, −1.70 | 475 (4.04) | 676 (72) |
| $[Ru(bipy)_2(Hppt)]^{2+}$ (**H1a**) | 1.25 | – | 438 | 640 (5) |
| $[Ru(bipy)_2(ppt)]^+$ (**1b**) | 1.05 | −1.50, −1.75 | 457 (4.35) | 657 (82) |
| $[Ru(bipy)_2(Hppt)]^{2+}$ (**H1b**) | 1.20 | – | 432 | 647 (29) |
| $[Ru(bipy)_2(bpt)]^{+\,b}$ | 0.85 | −1.47, −1.72 | 475 (4.05) | 678 (72) |
| $[Ru(bipy)_2(Hbpt)]^{2+\,b}$ | 1.06 | – | 429 (4.19) | 645 (45) |
| $[Ru(bipy)_2(bpzt)]^{+\,c}$ | 0.99 | −1.42, −1.62 | 453 (4.15) | 654 (88) |
| $[Ru(bipy)_2(Hbpzt)]^{2+\,c}$ | 1.24 | – | 446 (4.07) | 675 (28) |
| $[Os(bipy)_2(ppt)]^+$ (**3a**) | 0.52 | −1.42, −1.69 | 385 (3.95) 446 (3.74) 498 (3.82) 620 | 750 (45) |
| $[Os(bipy)_2(Hppt)]^{2+}$ (**H3a**) | 0.80 | – | 392 432 470 600 | 730 (39) |
| $[Os(bipy)_2(ppt)]^+$ (**3b**) | 0.63 | −1.44, −1.72 | 408 (4.04) 432 (4.07) 474 (4.11) 610 | 760 (16) |
| $[Os(bipy)_2(Hppt)]^{2+}$ (**H3b**) | 0.77 | – | 408 450 600 | 743 (5) |
| $[Os(bipy)_2(bpt)]^{+\,b}$ | 0.49 | −1.41, −1.69 | 392 (1.34) 438 (1.06) 486 (1.08) 610 (0.28) | 762 (55) |
| $[Os(bipy)_2(Hbpt)]^{2+\,b}$ | 0.89 | – | 394 (1.45) 438 (1.38) 476 (1.42) 570 (sh) | n/a (n/a) |
| $[Os(bipy)_2(bpzt)]^+$ | 0.64 | −1.41, −1.69 | 404, 436 (3.66), 483 (3.70), 600 | 783 (14) |
| $[Os(bipy)_2(Hbpzt)]^{2+}$ | 1.08 | – | 416, 452 | 791 (n/a) |

Redox potentials (*vs.* SCE) were obtained using CV and DPP in 0.1 M TEAP–acetonitrile (scan rate:10 mV $s^{-1}$). Protonation by addition of concentrated $HClO_4$.[a] Measured in aerated acetonitrile at 298 K. [b] Values obtained from ref. 6. [c] Values obtained from ref. 7.

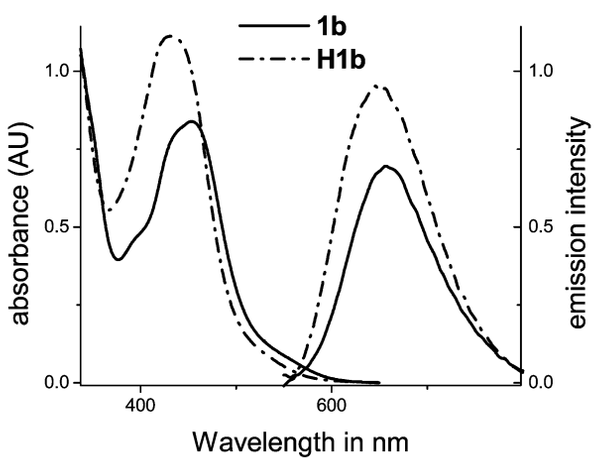


**Fig. 6** UV/vis absorption and emission spectra of **1b**, **H1b** in acetonitrile.

for the pyridine bound isomer. This reduction in emission lifetime, in contravention of the energy gap law, is due to the reduction in the σ-donor strength of the 1,2,4-triazole ligand and hence a lowering of the $^3$MC excited state, which is thermally accessible and provides a route for rapid non-radiative excited state deactivation.[6] For **1b** a 10 nm blue shift in the $\lambda_{max}$ occurs upon protonation, however, the reduction in emission lifetime is somewhat less dramatic than for **1a**. For the osmium complexes emission is observed at much lower energy (> 700 nm) as expected.[18] Both **3a** and **3b** undergo a blue shift in both absorption and emission spectra upon protonation.

### Acid–base properties

The acid–base properties of all compounds have been investigated by studying the pH dependence of their absorption spectra. The p$K_a$ values obtained from these studies and of some related complexes are presented in Table 3. The behaviour observed can be explained by protonation/deprotonation of the triazole moiety as indicated in eqn. (1).

$$[Ru(bipy)_2(ppt)]^+ + H^+ \leftrightarrow [Ru(bipy)_2(Hppt)]^{2+} \quad (1)$$

Although protonation of the coordinated pyrazine ring is possible, this occurs at only at negative pH (p$K_a \sim -1.5$).[8]

Given the structural similarities between the pyridine bound complex **1a** and the $bpt^-$ based mononuclear complex (and likewise the pyrazine bound isomer **1b** and the $bpzt^-$ based complex) it would be expected that the p$K_a$ values for the related complexes would be quite similar. Unusually the acid–base properties of **1a/1b** are found to display behaviour quite different to this expectation.

Table 3 shows that the acidity of the coordinated triazole ring is strongly dependent on the nature of the non-coordinated substituent in the C5 position. This dependence is reflected in the $\Delta$p$K_a$ values, with respect to the unsubstituted C–H analogues, given in Table 3. The effect of the introduction of a pyridine or pyrazine ring is particularly relevant. A comparison of the p$K_a$ values of the $pztr^-$ and $bpzt^-$ complexes shows that the triazole ring becomes more acidic by 1.7 pH units in the presence of an additional, free, pyrazine ring. A comparison of the values observed for the $pytr^-$ and $bpt^-$ complexes shows that the effect of the introduction of a pyridine ring is far less dramatic and does not result in a significant change in the p$K_a$ (+ 0.1 pH unit). This indicates that the free pyrazine group acts as a strong electron-withdrawing group. Within this framework the p$K_a$ values are as expected and indicate that there is substantial interaction between the different components of the Hppt ligand. Similar trends are observed for the analogous osmium(II) complexes. It is interesting to note the comparison of the substituent effect on the acid–base properties of the complexes and "Hammett" effects observed for organic systems such as substituted benzoic acids.

### Electrochemical properties

Electrochemical potentials for pyridine bound and pyrazine bound complexes are presented together with those of their analogous $bpt^-$ and $bpzt^-$ complexes in Table 2. As expected the pyrazine bound isomer (**1b**) has a more positive metal-based oxidation potential than the pyridine bound isomer (**1a**). This is due mainly to the weaker σ-donor/stronger π-acceptor properties of the pyrazine over the pyridine ligand.[19] The first two reduction potentials of the deprotonated complexes are reversible and are similar to those of $[Ru(bipy)_3]^{2+}$, suggesting they are bipy based reductions.[20] Due to hydrogen formation reduction potentials could not be obtained for the protonated complexes. The oxidation potentials of the osmium complexes, **3a** and **3b**, are approximately 400 mV lower than those of the corresponding ruthenium complexes. This is normal behaviour for these types of systems and is attributed to the higher energy of the 5d orbitals compared to the 4d orbitals.[17]

Overall the redox properties of all complexes are as expected. However the influence of the free pyrazine ring

**Table 3** Ground state p$K_a$ values of 1,2,4-triazole based mononuclear complexes

| Pyrazine bound complexes | p$K_a$ | $\Delta$p$K_a$ | Pyridine bound complexes | p$K_a$ | $\Delta$p$K_a$ |
|---|---|---|---|---|---|
| $[Ru(bipy)_2(pztr)]^{+a}$ | 3.7 | 0 | $[Ru(bipy)_2(pytr)]^{+a}$ | 4.1 | 0 |
| $[Ru(bipy)_2(bpzt)]^{+a}$ | 2.0 | −1.7 | **1a** | 2.7 | −1.4 |
| **1b** | 3.8 | +0.1 | $[Ru(bipy)_2(bpt)]^{+a}$ | 4.2 | +0.1 |
| $[Ru(bipy)_2(Mepztr)]^{+a}$ | 4.2 | +0.5 | $[Ru(bipy)_2(Mepytr)]^{+a}$ | 4.9 | +0.8 |
| $[Ru(bipy)_2(Brpztr)]^{+b}$ | 1.4 | −2.3 | $[Ru(bipy)_2(Brpytr)]^{+b}$ | 1.3 | −2.8 |
| $[Os(bipy)_2(bpzt)]^{+}$ | 1.2 | −2.5 | **3a** | 2.1 | −2.0 |
| **3b** | 3.5 | −0.2 | $[Os(bipy)_2(bpt)]^{+a}$ | 4.0 | −0.1 |

All measurements are carried out in Britton–Robinson buffer, values ± 0.1.[a] From ref. 28. [b] From ref. 29.

of **1a** and the $bpzt^-$ based complexes is of note with the redox potentials of these complexes being in every case significantly higher than for their –H substituted analogues. This is in agreement with the acid–base properties of these complexes, with the electron withdrawing influence of the pyrazine ring resulting in a reduction in the σ-donor strength of the 1,2,4-triazole ring (resulting in a lowering of the p$K_a$) and consequently a stabilisation of the metal centre towards oxidation.

## Conclusions

In this contribution the synthesis, structural, electrochemical and electronic characterisation of a series of ruthenium(II) and osmium(II) $(bipy)_2$ complexes based on the ligand Hppt are reported. The acid–base properties of the two major coordination isomers, taken together with a series of related complexes, provide for a much improved understanding of the effect of "spectator" or non-coordinated substituents on the 1,2,4-triazole ring. It is shown that these substituents are of major importance in determining the ground state properties of both the ruthenium(II) and osmium(II) based complexes. Overall the effect of protonation on the electronic and electrochemical properties of the complexes examined are as expected and confirm the assignments of coordination mode of the $ppt^-$ ligand made on the basis of $^1$H NMR spectroscopy and X-ray crystallography.

The isolation and identification of the major coordination isomers formed has been achieved and allows for the preparation of both homo- (RuRu, OsOs) and hetero- (RuOs) binuclear complexes of the ligand Hppt in a systematic and controlled manner. The inherent asymmetry of the Hppt ligand results in important differences in the ground state properties of the mononuclear coordination isomers. In further studies the effects of these differences on the excited state properties of the two parts of the $ppt^-$ ligand will be investigated in greater detail. Of particular interest is the location of the excited state and, for binuclear complexes, the degree of interaction between the metal centres mediated by the bridging $ppt^-$ ligand. In these studies selective deuteriation will be invaluable in understanding the excited state properties of mono- and bi-nuclear complexes, in particular in the interpretation of their resonance Raman spectra.[21]

## Experimental

### Materials

All solvents employed were of HPLC grade or better and used as received unless otherwise stated. For all spectroscopic measurements Uvasol (Merck) grade solvents were employed. All reagents employed in synthetic procedures were of reagent grade or better. $[D_8]$-2,2′-bipyridine,[22] *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$,[23] *cis*-$[Ru([D_8]\text{-bipy})_2Cl_2]\cdot 2H_2O$,[23] *cis*-$[Os(bipy)_2Cl_2]\cdot 2H_2O$,[24] and tetraethylammonium perchlorate (TEAP)[25] were prepared by previously reported methods.

### Syntheses

3-(Pyrazin-2′-yl)-5-(pyridin-2″-yl)-1*H*-1,2,4-triazole (**Hppt**) was prepared by standard procedures.[26]

**2-Pyrazylhydrazide.** 15 g of 2-pyrazylcarboxylic acid (0.12 mol) were heated at reflux for 3 h in 90 cm$^3$ ethanol and 15 cm$^3$ concentrated $H_2SO_4$. The solution was neutralised with saturated $Na_2CO_3$ solution and filtered. The volume was reduced *in vacuo* and extracted with four 30 cm$^3$ aliquots of dichloromethane. The combined fractions were washed with 10 cm$^3$ of water and dried over $MgSO_4$. The dichloromethane was removed *in vacuo* to yield the ethyl 2-pyrazylcarboxylate, which crystallised on cooling. The ester was dissolved in 20 cm$^3$ of ethanol and an equimolar amount of hydrazine monohydrate was added drop-wise. The solution was then kept a −4 °C for 12 h and crystalline 2-pyrazylhydrazide formed. The solid 2-pyrazylhydrazide was filtered off and air-dried. Yield 12 g, 74 %. $^1$H NMR in $(CD_3)_2SO$: $\delta$ 10.15 (1H, s, NH), 9.11 (1H, s), 8.81 (1H, d), 8.67 (1H, d), 4.65 (2H, s).

**1-(Pyrazin-2′-yl)-4-(pyridin-2″-yl)acylamidrazone.** Equimolar amounts of 2-cyanopyridine (as to the 2-pyrazylhydrazide, 12g) were dissolved in 30 cm$^3$ of methanol with 0.7 g of sodium and heated under reflux for 3 h. The 2-pyrazylhydrazide was added to the solution and heated for 15 min. The solution was cooled to room temperature and the precipitate formed (yellow) was filtered off and air-dried for 2 h. Yield 12.4 g, 67%. $^1$H NMR in $(CD_3)_2SO$: $\delta$ 9.19 (1H, d, H3″), 8.73 (1H, d, H6″), 8.60 (1H, dd, H5″), 8.19 (1H, d, H3′), 7.90 (1H, t, H4′), 7.51 (1H, t, H5′), 8.84 (1H, d, H6′).

**3-(Pyrazin-2′-yl)-5-(pyridin-2″-yl)-1*H*-1,2,4-triazole (Hppt).** 12.4 g (0.05 mol) of 1-(pyrazin-2′-yl)-4-(pyridin-2″-yl)-acylamidrazone was heated under reflux for 1 h in 10 cm$^3$ of ethylene glycol to yield the Hppt ligand. The ligand (white) was recrystalised from hot ethanol. Yield: 8 g (52%). $^1$H NMR in $(CD_3)_2SO$ $\delta$ 9.33 (1H, d, H3″), 8.72 (2H, m, H5″, H6″), 8.17 (1H, d, H3′), 8.01 (1H, t, H4′), 7.54 (1H, t, H5′), 8.77 (1H, d, H6′).

**$[Ru(bipy)_2(ppt)]PF_6\cdot 3H_2O$ 1a/$[Ru(bipy)_2(ppt)]PF_6\cdot H_2O.CH_3OH$ 1b.** 520 mg (1 mmol) of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ was added to 0.45 g (2.1 mmol) **Hppt** dissolved in 50 cm$^3$ of hot ethanol–water (1:1).The solution was heated at reflux for 4 h and evaporated to dryness. The residue was dissolved in 10 cm$^3$ of water and three drops of conc. aqueous ammonia and 5 cm$^3$ of saturated aqueous ammonium hexafluorophosphate were added to precipitate **1a/1b**. The isomers were separated by column chromatography using neutral alumina and acetonitrile as eluent. The pyridine bound isomer (**1a**) eluted first followed by the pyrazine bound isomer (**1b**). Only very small amounts of the N4 bound isomers were obtained subsequently by elution with methanol and were not further investigated. Further purification took place by recrystallisation from acetone–water (1:1 v/v). Yield of combined fractions: 420 mg (51 %). Mass spec: *m/z* **1a** 637 ($M^+$), **1b** 637 ($M^+$). Elemental analysis: Found (calc. for $C_{31}H_{23}F_6N_{10}PRu\cdot 3H_2O$ (**1a**)): C 44.6 (44.55); H 3.2

**Table 4** X-Ray parameters for $[Ru(bipy)_2(ppt)]PF_6 \cdot CH_3OH$

| | |
|---|---|
| Empirical formula | $C_{32}H_{27}F_6N_{10}OPRu$ |
| Formula weight/g mol$^{-1}$ | 813.67 |
| Temperature/K | 200(2) |
| Wavelength/Å | 0.71073 |
| Space group | $P\bar{1}$ (No. 2) |
| Crystal system | Triclinic |
| $a$/Å, $\alpha$/° | 9.9097(7), 93.8570(10) |
| $b$/Å, $\beta$/° | 12.5731(9), 93.4100(10) |
| $c$/Å, $\gamma$/° | 14.1156(10), 111.4390(10) |
| Volume/Å$^3$, $Z$ | 1626.6(2), 2 |
| Density (calc.)/Mg m$^{-3}$ | 1.661 |
| Crystal dimensions/mm | 0.6 × 0.5 × 0.4 |
| Absorption coeff./mm$^{-1}$ | 0.612 |
| $F$(000) | 820 |
| $\theta$ range for data collection/° | 1.45–28.30 |
| Limiting indices | $-12 \le h \le 12$; $-15 \le k \le 16$; $-18 \le l \le 18$ |
| No. eflections collected | 17142 |
| Independent reflec. ($R_{int}$) | 734 (0.0185) |
| Data/restraints/parameters | 7634/0/469 |
| GOF $F^2$ | 1.048 |
| Final $R$ indices [$I > 2\sigma(I)$] $R1$ ($wR2$) | 0.0293 (0.0726) |
| $R$ indices all data $R1$ ($wR2$) | 0.0342 (0.0749) |
| Largest difference peak and hole/e Å$^{-3}$ | 0.702 and −0.524 |

(3.11); N 16.2 (16.77) %. Found (calc. for $C_{31}H_{23}F_6N_{10}PRu.H_2O \cdot CH_3OH$ (**1b**)): C 45.0 (46.10); H 3.3 (3.36); N 17.2 (16.81) %. Crystals of **1a** suitable for X-ray analysis were grown from a methanol solution of **1a**.

**$[Ru([D_8]\text{-bipy})_2(ppt)]PF_6 \cdot CH_3OH \cdot 2H_2O$ 2a/$[Ru([D_8]\text{-bipy})_2(ppt)]PF_6 \cdot 2H_2O$ 2b.** As for **1a/1b**. Yield of combined fractions: 712 mg (93%). Mass spec: $m/z$ **2a** 653 ($M^+$), **2b** 653 ($M^+$). Elemental analysis: Found (calc. for $C_{31}H_7D_{16}F_6N_{10}PRu.CH_3OH.2H_2O$ (**2a**)): C 44.60 (44.29); H 2.85 (3.34); N 15.84 (16.15) %. Found (calc. for $C_{31}H_7D_{16}F_6N_{10}PRu.2H_2O$ (**2b**)): C 44.46 (44.66); H 2.77 (3.00); N 16.32 (16.81) %.

**$[Os(bipy)_2(ppt)]PF_6 \cdot 2H_2O$ 3a/$[Os(bipy)_2(Hppt)](PF_6)_2 \cdot 2H_2O$ H3b.** As for **1a/1b** except 575 mg (1 mmol) of *cis*-$[Os(bipy)_2Cl_2]$ was heated at reflux with 223 mg (1 mmol) of Hppt for 4 d with 50 mg of zinc powder. Yield of combined fractions: 0.82 g (78 %). Mass spec: $m/z$ **3a** 725 ($M^+$), Elemental analysis: Found (calc. for $C_{31}H_{23}F_6N_{10}POs \cdot 2H_2O$ (**3a**)): C 41.1 (41.05); H 2.80 (2.76); N 15.28 (15.45) %. Found (calc. for $C_{31}H_{24}F_{12}N_{10}P_2Os \cdot 2H_2O$ (**3b**)): C 35.6 (35.35); H 2.6 (2.47); N 13.5 (13.31) %.

**$[Os(bipy)_2(Hbpzt)](PF_6)_2 \cdot H_2O$.** As for **3a/3b** except 440 mg (2 mmol) of Hbpzt was heated at reflux with 575 mg (1 mmol) of *cis*-$[Os(bipy)_2Cl_2] \cdot 2H_2O$. Yield: 470 mg (0.42 mmol, 42%). Elemental analysis: Found (calc. for $C_{30}H_{23}F_{12}N_{11}P_2Os \cdot H_2O$): C 35.6 (34.78); H 2.34 (2.32); N 14.93 (14.83) %.

### X-Ray crystallography

Data for **1a** were collected on a Siemens SMART 1000 CCD-diffractometer fitted with a molybdenum tube ($K_\alpha$, $\lambda = 0.71073$ Å) and a graphite monochromator. Relevant experimental data are presented in Table 4. A full sphere of data was collected with the irradiation time of 4 s per frame. The structures were solved with direct methods and all non hydrogen atoms refined anisotropically with the SHELX program[27] (refinement by least-squares against $F^2$).

CCDC reference number 187996.

See http://www.rsc.org/suppdata/dt/b2/b206667j/ for crystallographic data in CIF or other electronic format.

### Instrumental methods

Elemental analysis on C, H and N was carried out at the Microanalytical Laboratory at University College Dublin using an Exador analytical CE440. $^1$H and $^1$H COSY spectra were recorded on a Bruker Avance (400 MHz) NMR spectrometer. Peak positions are relative to residual solvent peaks. Electrochemical measurements were carried out on a Model 660 electrochemical workstation (CH Instruments). Typical complex concentrations were 0.5 to 1 mM in anhydrous acetonitrile (Aldrich 99.8%) containing 0.1 M TEAP. A Teflon shrouded glassy carbon or platinum working electrode, a Pt wire auxiliary electrode and SCE reference electrode were employed. Solutions for reduction measurements were deoxygenated by purging with $N_2$ or Ar gas for 15 min prior to the measurement. Measurements were made in the range of −2.0 to 2.0 V (w.r.t SCE electrode). Protonation of complexes was achieved by addition of 0.1 M $HClO_4$ to the electrolyte solution. The scan rates used were typically 100 or 200 mV s$^{-1}$. UV/Vis absorption spectra were recorded on a Shimadzu UV/Vis-NIR 3100 spectrophotometer interfaced with an Elonex PC466 using UV/Vis data manager. Absorption maxima, ±2 nm. Molar absorption coefficients are ± 10%. Emission spectra (accuracy ±5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with an Elonex PC466 employing Perkin-Elmer FL WinLab custom-built software. Emission and excitation slit widths were 10 nm at 298 K and spectra are uncorrected for photomultiplier response; 10 mm pathlength quartz cells were used for recording spectra. pH titrations were carried out in Britton-Robinson buffer (0.04 M $H_3BO_3$, 0.04 M $H_3PO_4$, 0.04 M $CH_3CO_2H$). The pH was adjusted using concentrated sulfuric acid or sodium hydroxide solution.

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