The effect of the nature of the polypyridyl ligand on the physical properties of ruthenium polypyridyl compounds containing pyridyltriazoles

Eleanor M. Ryan, Renyi Wang, Johannes G. Vos*
School of Chemical Sciences, Dublin City University, Dublin 9 (Ireland)

Ronald Hage
Unilever Research Laboratory, Olivier van Noortlaan 120, 3133 AT Vlaardingen (Netherlands)

and Jaap G. Haasnoot
Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (Netherlands)

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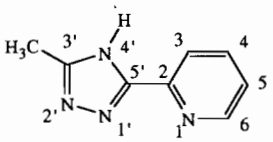
Abstract

The synthesis and characterisation of a series of compounds of the type $[Ru(L\text{-}L)_2(L\text{-}L')]^{2+}$, where L-L = 1,10-phenanthroline (phen) or 4,4′-dimethyl-2,2′-bipyridyl (dmbpy) and L-L′ a number of pyridyltriazole ligands, are reported. With phen and dmbpy a number of coordination isomers were obtained which were not found for the corresponding 2,2′-bipyridyl (bpy) compounds. The ratio of these isomers together with their spectroscopic properties confirm the earlier assignments made for the bpy complexes on the basis of proton NMR alone. The spectroscopic, electrochemical and acid–base properties both in the ground state and excited state of the phen and dmbpy complexes are similar to those reported for the bpy analogues. The data obtained suggest that the N^2 atom of the triazole ring is a stronger σ-donor than the N^4 atom.

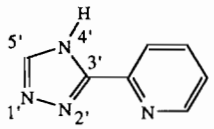
Introduction

Recently a series of mononuclear and dinuclear ruthenium bis(bpy) compounds (bpy = 2,2′-bipyridyl) containing the pyridyltriazole moiety have been reported [1, 2]. These complexes showed some very interesting properties as a result of the electronic properties of the triazole ring. In the triazole ring the N1′ (or N2′) atom and the N4′ atom are not equivalent and depending on the substitution pattern in the triazole ring different coordination modes can be obtained. The triazole ring can also be deprotonated and this leads to an extensive ground-state and excited-state acid–base chemistry. The negative charge that can be introduced on the triazole ring by deprotonation results in strong interaction between the two metal centres in dinuclear complexes [2]. In this contribution the synthesis and properties of ruthenium(II) complexes of the type $[Ru(L\text{-}L)_2(L\text{-}L')]^{2+}$ are described, where L-L = 1,10-phenanthroline (phen) or 4,4′-dimethyl-2,2′-bipyridyl (dmbpy) and L-L′ = 3-(pyridin-2-yl)-1,2,4-triazole (Hptr), 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole (H3Mptr), 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole (4Mptr) or 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole (1Mptr) (see Fig. 1 for structures). The properties of these compounds are compared to those of the earlier reported bpy complexes. The com-



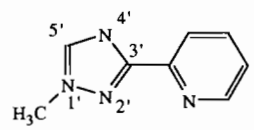
H3Mptr

3-methyl-5-(pyridin-2-yl)-1,2,4-triazole



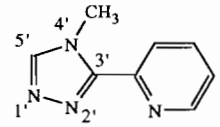
Hptr

3-(pyridin-2-yl)-1,2,4-triazole



1M3ptr

1-methyl-3-(pyridin-2-yl)-1,2,4-triazole



4Mptr

4-methyl-3-(pyridin-2yl)-1,2,4-triazole

Fig. 1. Structures, names, numbering schemes and abbreviations used for pyridyltriazole ligands.

*Author to whom correspondence should be addressed.

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plexes have been characterised using NMR, UV–Vis absorption spectroscopy, electrochemistry and emission spectroscopy. For some of the complexes, geometrical isomers were obtained which have been separated using semi-preparative HPLC techniques. The acid–base chemistry of the Hptr and H3Mptr complexes has been studied both in the ground state and excited state.

Experimental

Materials

The pyridyltriazole ligands were prepared as described before [1]. Hydrated ruthenium trichloride was obtained as a loan from Johnson Matthey and used without further purification. The complexes *cis*-$[Ru(dmbpy)_2Cl_2]\cdot 2H_2O$ and *cis*-$[Ru(phen)_2Cl_2]\cdot 2H_2O$ were prepared according to literature methods [3].

Synthesis of complexes

All complexes were made using methods reported for the analogous bpy compounds; an example for one typical preparation is given. All isomers were obtained in a pure form using semi-preparative chromatography.

$[Ru(dmbpy)_2(Hptr)](PF_6)_2\cdot H_2O$

The complex *cis*-$[Ru(dmbpy)_2Cl_2\cdot 2H_2O$ (1 mM) was heated at reflux in 100 ml water–ethanol (1:1) in the presence of excess pyridyltriazole ligand (1.2 mM) for 4 h. In order to ensure complete protonation of the bound ligand, 1–2 drops conc. HCl were added. The solvent was removed by rotary evaporation and the remaining residue was dissolved in 5 ml water and added dropwise to an aqueous solution of NH_4PF_6. The resulting precipitate was filtered and purified by recrystallisation from acidic (HCl) mixtures of acetone–water. Yield 730 mg (79%). *Anal.* Found: C, 40.28; H, 3.64; N, 11.76. Calc.: C, 40.30; H, 3.46; N, 12.13%.

$[Ru(dmbpy)_2(H3Mptr)](PF_6)_2\cdot 2H_2O$

Yield 633 mg (64%). *Anal.* Found: C, 39.41; H, 3.58; N, 11.55. Calc.: C, 40.21; H, 3.77; N, 11.73%.

$[Ru(dmbpy)_2(1Mptr)](PF_6)_2\cdot 2H_2O$

Yield 680 mg (69%). *Anal.* Found C, 40.35; H, 3.63; N, 11.37. Calc.: C, 40.21; H, 3.77; N, 11.73%.

$[Ru(dmbpy)_2(4Mptr)](PF_6)_2$

Yield 700 mg (76%). *Anal.* Found: C, 41.48; H, 3.57; N, 11.91. Calc.: C, 41.78; H, 3.48; N, 12.19%.

$[Ru(phen)_2(Hptr)](PF_6)_2$

Yield 694 mg (77%). *Anal.* Found C, 41.74; H, 2.80; N, 12.08. Calc.: C, 41.56; H, 2.46; N, 12.51%.

$[Ru(phen)_2(H3Mptr)](PF_6)_2\cdot 2H_2O$

Yield 760 mg (81%). *Anal.* Found C, 40.56; H, 3.01; N, 11.35. Calc.: C, 40.54; H, 2.96; N, 11.82%.

$[Ru(phen)_2(1Mptr)](PF_6)_2$

Yield 715 mg (78%). *Anal.* Found C, 42.14; H, 2.80; N, 11.99. Calc.: C, 42.15; H. 2.63; N, 12.29%.

$[Ru(phen)_2(4Mptr)](PF_6)_2$

Yield 698 mg (77%). Found: C, 42.19; H, 2.76; N, 12.09. Calc.: C, 42.15; H, 2.63; N, 12.29%.

Instrumentation and methods

Absorption spectra were obtained using either a Shimadzu UV 240 instrument or a Hewlett Packard 8452A diode array spectrometer in the region 350–800 nm. Extinction coefficients are accurate to 5%. Emission spectra were obtained on a Perkin-Elmer LS-5 luminescence spectrometer equipped with a red sensitive Hamamatsu R 928 photomultiplier tube. An emission slit width of 10 nm was used at room temperature and 5 nm at 77 K and the results were not corrected for photomultiplier response.

Acid–base titrations were carried out at room temperature in Britton-Robinson buffer (0.04 M boric acid, 0.04 M acetic acid and 0.04 M phosphoric acid). The pH of the solutions was adjusted using a 2 M NaOH solution. Luminescence titrations were carried out using an appropriate isosbestic point as the excitation wavelength. To facilitate dissolution of samples in aqueous solutions a minimal volume of acetone (<2 cm^3) was added.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with an EG&G Par 174A polarographic analyser and an EG&G Par 175 universal programmer. A saturated calomel electrode was used as the reference electrode. Measurements were carried out in spectroscopic HPLC grade CH_3CN dried over molecular sieves and with 0.01 M TEAP (tetraethylammoniumperchlorate) or TBAP (tetrabutylammoniumperchlorate) as supporting electrolyte. A glassy carbon electrode was used as the working electrode and a platinum electrode as the auxiliary electrode. The scan rate was 100 mV/s for the CV mode and 5 mV/s for the DPV mode. The pulse height in DPV measurements was 25 mV. Measurements were carried out at room temperature.

A Waters 990 photodiode array HPLC system was employed, in conjunction with a NEC APC111 computer, a Waters pump model 6000 or 501, a 20 μl injector loop and a μ Partisil SCX radial PAK cartidge. The mobile phases used were (a) CH_3CN:H_2O (80:20) containing 0.08 M $LiClO_4$ (about pH 6–7); (b) mobile phase (a) adjusted to pH 2–3 with $HClO_4$. The flow rate was 2.5 ml/min.

For semi-preparative HPLC an Applied Chromatography Services pump (model RR/066), detector (model 750/11 UV–Vis), a 1 ml injection loop and a Magnum 9μ Partisil cation exchange column (10 mm/25 cm) was used. The mobile phase was CH_3CN:H_2O (80:20) containing 0.08 M $LiClO_4$. The flow rate used ranged from 4.0 to 6.0 ml/min.

^1H NMR spectra were recorded on a Jeol JNM-FX 200 NMR spectrometer. The measurements were carried out in $(CD_3)_2CO$. The peak positions are relative to TMS. In order to ensure protonation/deprotonation of the complexes concentrated DCl or NaOD was added to the NMR solution when needed.

The lifetimes of the pyridyltriazole complexes were measured at Tulane University, New Orleans. The long lifetime components were measured using a Laser Photoionics LN 1000 MegaPlus nitrogen laser (excitation wavelength 337 nm, pulse width 600 picoseconds). The short lifetime components (<20 ns) were measured using the time correlated single photon counting system employing a mode locked, cavity dumped Ar^+ laser for excitation (doubled dye output at 295 nm).

The ruthenium pyridyltriazole complexes were measured at room temperature, in Britton–Robinson buffer and at 77 K in ethanol the pH was adjusted using either conc. NaOH or conc. H_2SO_4 and were degassed prior to measurement.

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

Results and discussion

Synthesis and purification

Preparation of complexes of the type $[Ru(L\text{-}L)_2(L\text{-}L')]^{2+}$ was carried out by the reaction of *cis*-$[Ru(L\text{-}L)_2Cl_2]\cdot 2H_2O$ where L-L = phen or dmbpy with equimolar amounts of ligand (L-L'). The compounds were isolated as the divalent cations with PF_6^- as the counter ion. For the ligands Hptr and H3Mptr, deprotonation occurs easily upon coordination, therefore to ensure protonation these complexes were recrystallised from acidified acetone/H_2O mixtures.

For three of the chelating ligands, Hptr, H3Mptr and 1Mptr, different coordination modes are possible, since chelation can take place through the pyridine nitrogen and the N1/N2 or the N4 nitrogen atom of the triazole ring. However, the preferred mode of coordination is anticipated to be affected by the position of the methyl substituent present on the triazole ring. The presence of a methyl substituent on the triazole ring will cause steric hindrance, therefore it is likely that coordination will be primarily through the N4 site for $[Ru(L\text{-}L)_2(1Mptr)]^{2+}$ and through the N1 site for $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ [4]. For all bpy complexes only the preferred coordination mode was observed, with for the Hptr complex a 1:1 mixture of the N2 and N4 isomers [1].

The purity of the complexes obtained and the presence of coordination isomers was checked using HPLC. Since the compounds $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ and $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ are easily deprotonated they were studied in both a neutral mobile phase and in an acidic mobile phase. Changes in retention time of the compounds of up to 1.2 min were observed for the Hptr and H3Mptr complexes upon changing the pH of the mobile phase. UV–Vis spectra of the compounds, obtained *in situ* with the photodiode array detector showed that the compounds remained protonated even in the neutral mobile phase where the pH is about 6–7. Considering the acid–base properties of these compounds (*vide infra*) this is somewhat surprising. This suggests that the changes in retention time observed in both mobile phases are caused by a medium effect and not by protonation/deprotonation of the complexes. For $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ two peaks, in a 1:1 ratio, were obtained in the HPLC trace, which were assigned as the two coordination isomers. As the isomers were better separated using the neutral mobile phase, they were separated on the semi-preparative HPLC system using this mobile phase.

Two isomers were also found for the compound $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ using HPLC analysis of the recrystallised products (see Fig. 2). Although this is not unexpected, only one isomer was observed for the bpy analogue of these compounds [4]. This may be due to solubility factors or to the manner in which the compounds were recrystallised. The ratios of the peaks were approximately 10–20% for isomer 1 (peak 1, retention times 2.28 and 3.00 min in neutral mobile phase for the dmbpy and phen complexes, respectively) and about 80–90% for isomer 2 (peak 2, retention times 2.96 and 4.94 min for dmbpy and phen, respectively). From these peak ratios, peak 1 is most likely the N4 isomer, since steric considerations will not favour the formation of this product.

The 1Mptr and 4Mptr compounds were investigated using the neutral mobile phase. Again, contrary to the results obtained for the analogous bpy compound, two peaks were obtained for the 1Mptr compounds. The ratios are reversed compared to the $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ isomers with ratios of about 90–95% for peak 1 (isomer 1, retention times 2.08 and 2.82 min for dmbpy and phen compounds, respectively) and 5–10% for peak 2 (isomer 2, retention times 2.62 and 4.00 min for dmbpy and phen compounds, respectively). This suggests that isomer 2 is the complex where coordination to the ruthenium is sterically hindered, i.e. through the N2 site on the triazole ring. It proved difficult to obtain isomer 2 in pure form, however about

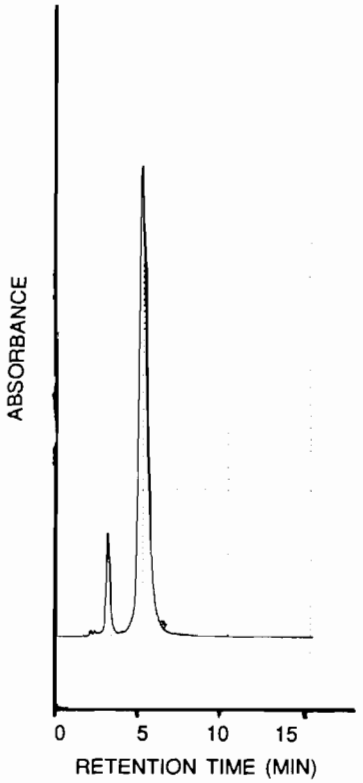

Fig. 2. Chromatogram of the isomers of $[Ru(phen)_2(H3Mptr)]^{2+}$ in acetonitrile:water (80:20) with 0.08 M $LiClO_4$. Flow rate = 2.5 ml/min.

80% purity was achieved. Only one peak was observed for $[Ru(L\text{-}L)_2(4Mptr)]^{2+}$ as expected.

It is interesting to note that even at this early stage in the characterisation of the various ruthenium compounds synthesised, it is possible to assign the coordination mode based on peak ratios alone. From the product ratios observed it can be seen that compounds with coordination through the N4 site on the triazole ring elute first (isomer 1) with N1/N2 coordinating compounds eluting second (isomer 2).

Proton NMR spectroscopy

^1H NMR techniques were used to unambiguously assign the mode of coordination for the pyridyltriazole ligands. The ^1H NMR data confirm *cis*-geometry for all the compounds [3, 5]. By using 2D COSY techniques and by comparison with assignments made for other similar compounds [1], a complete assignment of all the resonances was made. The proton resonances obtained for the coordinated pyridyl triazole ligands are given in Tables 1 and 2. The phen and dmbpy resonances are as expected and are not listed.

The two possible modes of coordination of ruthenium to the Hptr ligand are shown in Fig. 3. An analysis of the pyridyltriazole resonances is sufficient to establish the coordination mode of these ligands. For each pyridyltriazole ligand an upficld shift of the H6 proton of the pyridine ring ranging from 0.6 to 1.4 ppm, depending on the compound, resulted upon bidentate coordination to ruthenium. This shift can be explained by diamagnetic anisotropic interaction of this proton with the ring currents of dmbpy and phen ligands [1, 5–10]. The other protons have also been shifted somewhat because of the influence of the metal atom.

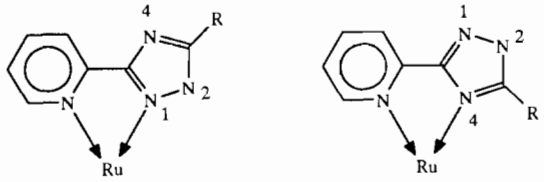

Fig. 3. Possible coordination modes for the pyridyltriazole ligands in the two isomers of $[Ru(L\text{-}L)_2(L\text{-}L')]^{2+}$.

For the ligands Hptr, H3Mptr and 1Mptr the resonance positions of the hydrogen/methyl substituent on the triazole ring are expected to be influenced by the coordination mode of the ligand. If a nitrogen atom is coordinated to ruthenium, the neighbouring group will be affected not only by a change in electron density in the five-membered ring but also by the shielding cone of a dmbpy or phen ring, as has been demonstrated for the bpy analogues, leading to upfield shifts of these resonances. These resonance positions are therefore indicative of the manner in which the pyridyltriazole ligand is coordinated to the ruthenium. This effect has also been shown by Steel *et al.* [10], for the complex $[Ru(bpy)_2(L\text{-}L')^{2+}$ where L-L′ = 3,5-dimethyl-1-(pyridin-2-yl)pyrazole.

For isomer 2 of $[Ru(L\text{-}L)_2(1Mptr)]^{2+}$, the methyl resonance has been shifted upfield by −0.53 and −0.72 ppm for (L-L) = dmbpy and phen, respectively, relative to the free ligand. This suggests that in this case coordination to the ruthenium atom is through the N2′ position of the pyridyltriazole ring. For isomer 1, the methyl resonance occurs at lower field for both the dmbpy and phen compounds relative to the free ligand. This shift is 0.11 and 0.06 ppm for the dmbpy and phen compounds, respectively. This suggests coordination via the N4′ on the pyridyltriazolc ligand. It is difficult to unambiguously assign the coordination mode based on the shifts of the H5′ proton as only small shifts were observed. Nonetheless, the H5′ resonances occurred at marginally higher field for the N4′ coordinated compounds. The effect is much smaller than for the methyl group because of the smaller radius of the protons compared to the radius of the methyl group.

The same effect on the methyl resonance is observed for the $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ compounds. For isomer 1 (protonated), the methyl resonance has been shifted upfield by −0.74 ppm for the dmbpy compound and

TABLE 1. ^{1}H NMR resonances for pyridyltriazole ligands in $[Ru(dmbpy)_2(L\text{-}L')^{n+}$ complexes

Compound	CH_3	H5′	H3	H4	H5	H6
$[Ru(dmbpy)_2(Hptr)]^{2+}$		8.38	8.26	7.94	7.30	7.62
Isomer 1 N4′ (a)		(+0.11)	(+0.17)	(−0.04)	(−0.21)	(−1.08)
$[Ru(dmbpy)_2(Hptr)]^{2+}$		8.66	8.22	7.98	7.32	7.69
Isomer 2 N2′ (a)		(+0.39)	(+0.13)	(+0.00)	(−0.19)	(−1.01)
$[Ru(dmbpy)_2(ptr)]^{+}$		7.47	8.20	7.91	7.19	7.53
Isomer 1 N4′ (b)		(−0.80)	(+0.11)	(−0.07)	(−0.32)	(−1.17)
$[Ru(dmbpy)_2(ptr)]^{+}$		7.97	7.98	7.82	7.12	7.53
Isomer 2 N2′ (b)		(−0.30)	(−0.11)	(−0.16)	(−0.39)	(−1.17)
$[Ru(dmbpy)_2(H3Mptr)]^{2+}$	1.62		8.16	7.89	7.23	7.83
Isomer 1 N4′ (a)	(−0.74)		(+0.14)	(−0.01)	(−0.20)	(−1.00)
$[Ru(dmbpy)_2(H3Mptr)]^{2+}$	2.44		8.14	7.97	7.31	7.55
Isomer 2 N1′ (a)	(+0.08)		(+0.12)	(+0.07)	(−0.12)	(−1.28)
$[Ru(dmbpy)_2(3Mptr)]^{+}$	1.37		8.00	7.78	7.07	7.43
Isomer 1 N4′ (b)	(−0.99)		(−0.02)	(−0.12)	(−0.36)	(−1.40)
$[Ru(dmbpy)_2(3Mptr)]^{+}$	2.35		8.20	8.00	7.24	7.68
Isomer 2 N1′ (b)	(−0.01)		(+0.18)	(+0.10)	(−0.19)	(−1.15)
$[Ru(dmbpy)_2(1Mptr)]^{2+}$	4.08	8.69	8.40	8.16	7.53	7.89
Isomer 1 N4′	(+0.11)	(+0.08)	(+0.24)	(+0.25)	(+0.10)	(−0.77)
$[Ru(dmbpy)_2(1Mptr)]^{2+}$	3.44	8.78	8.45	8.20	7.54	7.89
Isomer 2 N2	(−0.53)	(+0.17)	(+0.29)	(+0.29)	(+0.11)	(−0.77)
$[Ru(dmbpy)_2(4Mptr)]^{2+}$	4.39	8.75	8.60	8.20	7.57	8.09
	(+0.40)	(+0.13)	(+0.49)	(+0.25)	(+0.10)	(−0.57)

Complexes denoted (a) or (b) were measured in D_2O with a drop of conc. DCl or NaOD, respectively. The other compounds were measured in $(CD_3)_2CO$. Figures in parentheses are shifts compared to the free ligands measured in $(CD_3)_2SO$.

TABLE 2. ^{1}H NMR resonances for pyridyltriazole ligands in $[Ru(phen)_2(L\text{-}L')^{n+}$ complexes

Compound	CH_3	H5′	H3	H4	H5	H6
$[Ru(phen)_2(Hptr)]^{2+}$		8.37	8.34	8.10	7.24	7.61
Isomer 1 N4′ (a)		(+0.07)	(+0.25)	(+0.12)	(−0.27)	(−1.09)
$[Ru(phen)_2(Hptr)]^{2+}$		8.65	8.31	8.01	7.26	7.77
Isomer 2 N2′ (a)		(+0.38)	(+0.22)	(+0.03)	(−0.25)	(−0.93)
$[Ru(phen)_2(ptr)]^{+}$		7.43	8.18	7.87	7.06	7.51
Isomer 1 N4′ (b)		(−0.84)	(+0.09)	(−0.11)	(−0.45)	(−1.19)
$[Ru(phen)_2(ptr)]^{+}$		7.95	8.07	7.86	7.05	7.54
Isomer 2 N2′ (b)		(−0.32)	(−0.02)	(+0.12)	(−0.46)	(−1.16)
$[Ru(phen)_2(H3Mptr)]^{2+}$	1.37		8.25	7.93	7.18	7.53
Isomer 1 N4′ (a)	(−0.99)		(+0.23)	(+0.03)	(−0.25)	(−1.30)
$[Ru(phen)_2(H3Mptr)]^{2+}$	2.35		8.20	8.00	7.24	7.68
Isomer 2 N1′ (a)	(−0.01)		(+0.18)	(+0.10)	(−0.19)	(−1.15)
$[Ru(phen)_2(3Mptr)]^{+}$	1.10		8.10	7.82	7.01	7.42
Isomer 1 N4′ (b)	(−1.26)		(+0.08)	(−0.08)	(−0.42)	(−1.41)
$[Ru(phen)_2(3Mptr)]^{+}$	2.15		8.00	7.84	7.02	7.51
Isomer 2 N1′ (b)	(−0.21)		(−0.02)	(−0.06)	(−0.41)	(−1.32)
$[Ru(phen)_2(1Mptr)]^{2+}$	4.03	8.64	8.46	8.17	7.42	7.87
Isomer 1 N4′	(+0.06)	(+0.03)	(+0.30)	(+0.26)	(−0.01)	(−0.79)
$[Ru(phen)_2(1Mptr)]^{2+}$	3.25	8.77	8.58	8.20	7.43	7.86
Isomer 2 N2′	(−0.72)	(+0.16)	(+0.42)	(+0.29)	(+0.00)	(−0.80)
$[Ru(phen)_2(4Mptr)]^{2+}$	4.39	8.69	8.64	8.20	7.46	8.09
	(+0.40)	(+0.07)	(+0.53)	(+0.25)	(−0.01)	(−0.57)

Complexes denoted (a) or (b) were measured in D_2O with a drop of conc. DCl or NaOD, respectively. The other complexes were measured in $(CD_3)_2CO$. Figures in parentheses are shifts compared to the free ligands measured in $(CD_3)_2SO$.

by −0.99 ppm for the phen compound. This indicates that coordination is through the N4′ position on the triazole ring. For isomer 2 (protonated), the methyl resonances occur at about the same frequency as the free ligand. This is anticipated for coordination via the N1′ position on the pyridyltriazole ligand.

Deprotonation of $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ causes the triazole methyl resonances to shift upfield for both isomers. The shift in the resonance positions of the triazole protons can be explained by the increased electron density in the triazole ring of the pyridyltriazole ligand which probably also affects the electron density in the pyridine ring of the ligand [1, 11].

It is rather more difficult to assign the $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ isomers. The chemical shifts observed for the H5′ protons for the protonated isomers of the $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ compounds are similar, however, upon deprotonation there is a more substantial difference between the singlet (H5′) resonances of the two isomers; 0.50 ppm for $[Ru(dmbpy)_2(ptr)]^+$ isomers and 0.52 ppm for the $[Ru(phen)_2(ptr)]^+$ isomers (see Fig. 4). This difference in ppm greatly facilitates the assignment of the coordination mode. Figure 4 shows that for the two deprotonated isomers of $[Ru(dmbpy)_2(Hptr)]^{2+}$ the H5′ proton in isomer 1 is more shielded than isomer 2. This suggests that isomer 1 is that isomer where coordination is through the N4′ position of the pyridyltriazole ligand where the H5′ proton would be affected to a greater extent by the dmbpy/phen shielding cone [1].

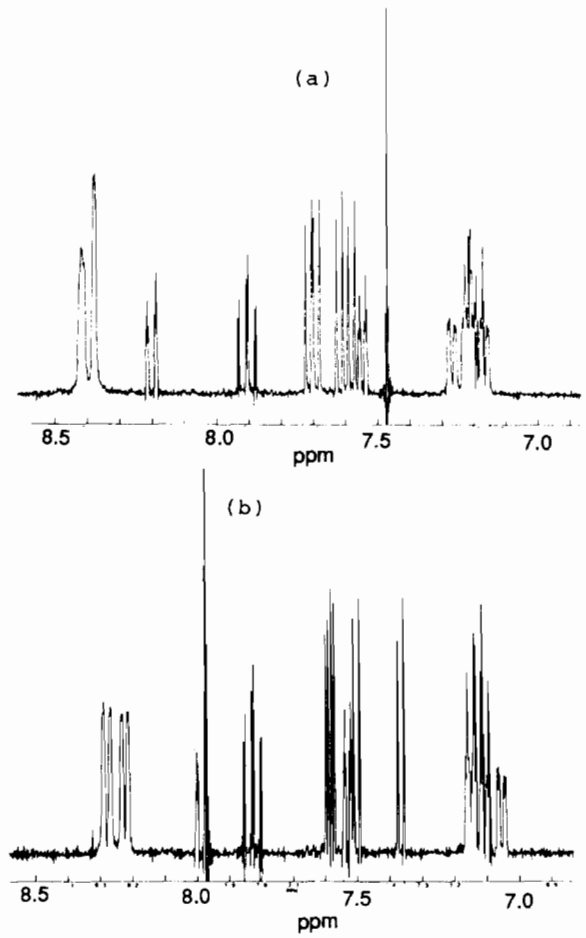

Fig. 4. ^1H NMR spectra of (a) isomer 1 and (b) isomer 2 of $[Ru(dmbpy)_2(ptr)]^+$. Spectra were obtained in D_2O with one drop of concentrated NaOD to ensure deprotonation.

Electronic spectra and redox properties

The electronic and the electrochemical properties of the complexes are listed in Tables 3 and 4. The absorption bands of lowest energy can be assigned to $d\pi$ to π^* MLCT transitions [12, 13]. The redox potentials presented have been determined by differential pulse polaragraphy. Cyclic voltammetry measurements indicate that all redox processes are quasi-reversible with the difference in peak positions for the oxidation waves in the range 60–90 mV. Protonation of the complexes was achieved by the addition of a few drops of conc. HCl. Under these conditions the values for the metal based oxidation potentials could be obtained but the ligand based reduction potentials could not be determined. Also for solutions where acid was not added, electrochemically induced deprotonation renders it difficult to determine the potentials of the polypyridyl based reduction processes accurately.

For the dications the position of the MLCT band occurs at about the same energy as their $[Ru(dmbpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ analogues and indeed $[Ru(bpy)_3]^{2+}$ (see Tables 3 and 4). The exception was isomer 2 of the $[Ru(L\text{-}L)_2(1Mptr)]^{2+}$ compounds where the ^{1}MLCT band is found at higher energy. The oxidation potential of isomer 2 for the 1Mptr coordinated compounds is higher than for the analogous $[Ru(phen)_3]^{2+}$ or $[Ru(dmbpy)_3]^{2+}$ compounds, while the first reduction potential is more negative than for the tris compounds but slightly less negative than for the other pyridyltriazole compounds. This indicates that in the N2 coordination mode of the ligand may act as a stronger π-acceptor or a weaker σ-donor.

Deprotonation of the $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ and $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ compounds causes profound changes in their absorption (see Fig. 5) and electrochemical properties. Deprotonation leads to a shift to lower energy for the MLCT band and a decrease in the oxidation potential. Deprotonation tends to destabilise the metal d orbitals causing the $d\pi$–π^* band to be shifted to lower energy. The reduction potentials also shift to a more negative value for the deprotonated compounds.

The first reduction potential of each complex is very similar to the first reduction potential of the appropriate $[Ru(phen)_3]^{2+}$ and $[Ru(dmbpy)_3]^{2+}$ analogues. This suggests that this reduction is dmbpy/phen based and also indicates that the π^* levels for the pyridyltriazole ligands are at higher energy than those of bpy, dmbpy and phen and therefore, the pyridyltriazole ligands are harder to reduce. This implies that phen and dmbpy act as the emitting ligand whilst the pyridyltriazole

TABLE 3. Electronic and electrochemical data for the $[Ru(dmbpy)_2(L\text{-}L')]^{n+}$ complexes

L-L'		Abs. max. (nm) (log ϵ)	Em. max. (nm)		Redox potentials[a] $Ru^{II/III}$ ligand based (V) vs. SCE
			303 K	77 K	
Hptr	isomer 1	450(4.00)	624	586	1.08, −1.59, −1.84
Hptr	isomer 2	443(4.02)	621	585	1.09
ptr	isomer 1	483(3.93)	667	609	0.72, −1.75, −1.85
ptr	isomer 2	482(3.96)	674	616	0.75, −1.63, −1.83
H3Mptr	isomer 1	452	624	590	1.06, −1.58, −1.81
H3Mptr	isomer 2	440(4.14)	629	583	1.09
3Mptr	isomer 1	484	673	623	0.71, −1.64, −1.88
3Mptr	isomer 2	480(4.02)	682	622	0.72, −1.60, −1.85
1Mptr	isomer 1	450(4.15)	620	582	1.08, −1.54, −1.75
1Mptr	isomer 2	432(4.09)	628	585	1.18, −1.49, −1.69
4Mptr		448(4.21)	622	600	1.09, −1.53, −1.72, −2.02
dmbpy		450	618		1.10, −1.45

For all measurements the solutions were protonated or deprotonated as appropriate with HCl or NaOH. [a]Measured in CH_3CN with 0.1 M NEt_4ClO_4 (TEAP), V vs. SCE. Peak to peak separation for all compounds was 60 mV for the metal based oxidations and 60–90 mV for the ligand based reductions.

TABLE 4. Electronic and electrochemical data for the $[Ru(phen)_2(L\text{-}L')]^{n+}$ complexes

L-L'		Abs. max (nm) (log ϵ)	Em. max. (nm)		Redox potentials[a] $Ru^{II/III}$ ligand based (V) vs. SCE
			303 K	77 K	
Hptr	isomer 1	445(4.22)	611	573	1.19, −1.51, −1.76, −2.03
Hptr	isomer 2	416(4.15) 435(sh)	607	568	1.18
ptr	isomer 1	478(4.08)	651	603	0.84, −1.64, −1.89
ptr	isomer 2	475(3.99) 420(sh)	663	600	0.86, −1.51, −1.75
H3Mptr	isomer 1	449	610	575	1.19
H3Mptr	isomer 2	426(4.21) 435(sh)	612	568	1.20
3Mptr	isomer 1	474	651	608	0.87, −1.57, −1.81
3Mptr	isomer 2	478(4.08)	673	608	0.71, −1.66, −1.90, −1.99
1Mptr	isomer 1	448(4.10)	594	568	1.19, −1.42, −1.65, −1.84
1Mptr	isomer 2	434	610	577	1.33, −1.40, −1.56, −1.75
4Mptr		440(4.23)	600	576	1.20, −1.46, −1.64
phen		442	604	568	1.27, −1.35

For all measurements the solutions were protonated or deprotonated as appropriate with HCl or NaOH. [a]Measured in CH_3CN with 0.1 M NEt_4ClO_4 (TEAP), V vs. SCE. Peak to peak separation for all compounds was 60 mV for the metal based oxidations and 60–90 mV for the ligand based reductions.

ligands act as spectator ligands as is also observed for the corresponding bpy complexes [1].

The absorption spectra of the isomers of the deprotonated compounds are very similar, so it would be difficult to differentiate between isomers on the basis of their deprotonated spectra. However, the spectra of the protonated isomers are quite dissimilar which allows the distinction between them.

The presence of a methyl substituent on either the N1' site of the triazole ring for isomer 2 of $[Ru(L\text{-}L)_2(1Mptr)]^{2+}$ or the N4' site of the triazole ring for $[Ru(L\text{-}L)_2(4Mptr)]^{2+}$ results in spectra which are comparable to the spectra for the protonated isomer 2 of the Hptr and H3Mptr coordinated compounds. The spectrum of $[Ru(L\text{-}L)_2(1Mptr)]^{2+}$ isomer 1 is similar to the protonated spectra of isomer 1 of $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ and $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$. This would be expected since the isomers 1 are all bound to ruthenium via the N4' position of the triazole ring and the isomer 2 compounds via the N1'/N2' position of the triazole ring.

All the compounds show emission at 77 K and at room temperature. The emission wavelengths are similar to those obtained for the bpy complexes. Substantial

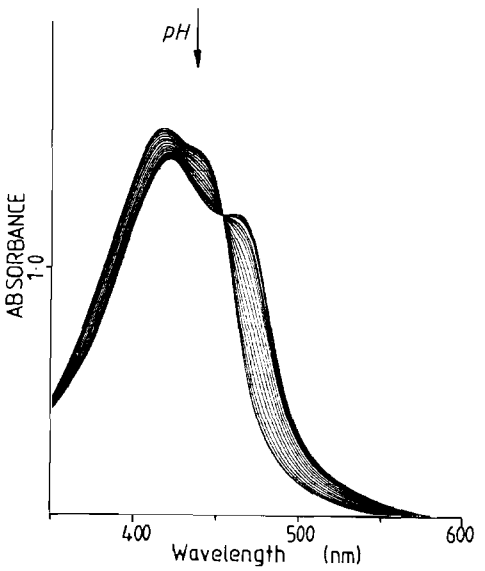

Fig. 5. pH dependence of the absorption spectrum of $[Ru(phen)_2(Hptr)]^{2+}$, isomer 2, (1)–(25): pH = 1.00, 1.50, 2.01, 2.53, 3.03, 3.55, 3.77, 3.92, 4.14, 4.28, 4.42, 4.60, 4.80, 4.92, 5.07, 5.24, 5.58, 5.73, 6.03, 6.40, 6.85, 7.01, 8.12, 10.06, 11.10.

differences are observed between the protonated and deprotonated Hptr and H3Mptr complexes, with the energy maximum shifting to lower energy upon deprotonation as is also observed for the absorption spectra.

For many $[Ru(bpy)_2(L_2)]^{2+}$ compounds reported in the literature, a linear relationship exists between the energy of the lowest energy ^{1}MLCT band and $\Delta E_{1/2}$, the difference between the oxidation and the first reduction potential, and between $\Delta E_{1/2}$ and the emission energy [12, 14]. This relationship also holds for the compounds investigated here and indeed for their bis(bpy) analogues (see Fig. 6), indicating that emission and the reduction processes involve the same polypyridyl based π^* orbitals.

Ground-state acid–base chemistry

In this section the pH dependence of the ground state and of the excited state of $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ (isomers 1 and 2) and $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ (isomer 2) has been studied using UV–Vis and luminescence spectrophotometry. Insufficient quantities of isomer 1 of $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ compounds were isolated to allow a pH titration to be carried out.

The effect of pH on the UV–Vis spectra of the ruthenium compounds was investigated by titrations in Britton–Robinson buffers. An example of such a titration is given in Fig. 5. All changes are fully reversible and independent of the direction of pH change. The pK_a values obtained are presented in Table 5. The observed behaviour can be explained by deprotonation of the pyridyltriazole ligands at higher pH yielding $[Ru(L\text{-}L)_2(ptr)]^+$ and $[Ru(L\text{-}L)_2(3Mptr)]^+$ as in eqn. (1)

$$[Ru(L\text{-}L)_2(Hptr)]^{2+} \xrightarrow[H^+]{pK_a(acid)} [Ru(L\text{-}L)_2(ptr)]^+ \qquad (1)$$

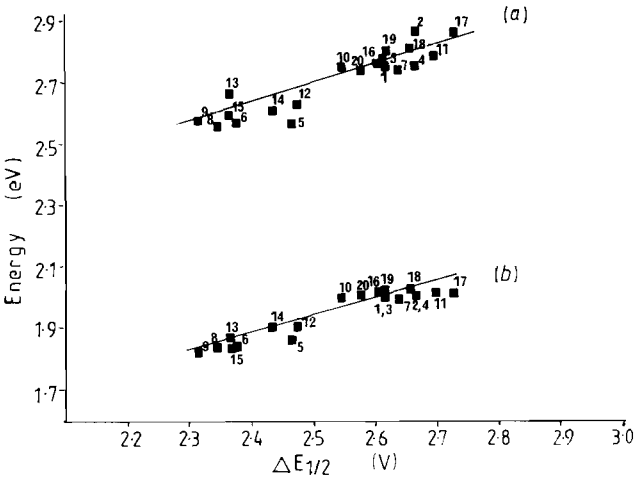

Fig. 6. Plots of $\Delta E_{1/2}$ vs. absorption (a) and emission (b) energies for compounds 1–20. (1) $[Ru(dmbpy)_2(1Mptr)^{2+}$, isomer 1; (2) $[Ru(dmbpy)_2(1Mptr)]^{2+}$, isomer 2; (3) $[Ru(dmbpy)_2(4Mptr)]^{2+}$; (4) $[Ru(dmbpy)_2(Hptr)]^{2+}$, isomer 1; (5) $[Ru(dmbpy)_2(ptr)]^+$, isomer 1; (6) $[Ru(dmbpy)_2(ptr)]^+$, isomer 2; (7) $[Ru(dmbpy)_2(H3Mptr)]^{2+}$, isomer 1; (8) $[Ru(dmbpy)_2(3Mptr)]^+$, isomer 1; (9) $[Ru(dmbpy)_2(3Mptr)]^+$, isomer 2; (10) $[Ru(dmbpy)_3]^{2+}$, Ref. 10; (11) $[Ru(phen)_2(Hptr)]^{2+}$, isomer 1; (12) $[Ru(phen)_2(ptr)]^+$, isomer 1; (13) $[Ru(phen)_2(ptr)]^+$, isomer 2; (14) $[Ru(phen)_2(3Mptr)]^+$, isomer 1; (15) $[Ru(phen)_2(3Mptr)]^+$, isomer 2; (16) $[Ru(phen)_2(1Mptr)]^{2+}$, isomer 1; (17) $[Ru(phen)_2(1Mptr)]^{2+}$, isomer 2; (18) $[Ru(phen)_2(4Mptr)]^{2+}$; (19) $[Ru(phen)_3]^{2+}$; (20) $[Ru(bpy)_3]^{2+}$.

The shift to lower energy upon deprotonation is consistent with a destabilisation of the metal d orbitals because of an increased σ-donor capacity of the triazole ring. As the π^* levels of dmbpy or phen are not altered significantly when the triazole ligand is deprotonated, this leads to a smaller energy difference between the filled d orbitals and the empty π^* orbitals of the polypyridyl ligand. The pK_a values are higher for the H3Mptr coordinated compounds which is expected from the electron donating properties of the methyl group. This has also been found for $[(NH_3)_5Ru(HM_2pz)^{3+}$ (HM_2pz) = 3,5-dimethyl-pyrazole) where the pK_a was found to be higher than the pK_a of $[(NH_3)_5Ru(Hpz)]^{3+}$ [15].

For most compounds the coordinated ligand is more acidic than the free ligand. This effect of increased acidity has been found for a number of compounds and may be attributed to electron donation from the ligand to the central metal atom. The only compound for which acidity has been decreased is $[Ru(NH_3)_5(Hpyz)]^{3+}$ (pyz = pyrazine), which may be attributed to backdonation of electron density from the filled metal based t_{2g} orbitals to the unoccupied π^* orbitals of the ligand [16].

TABLE 5. Acid–base data for the pyridyltriazole containing ruthenium polypyridyl complexes

Compound	Isomer no.	Emission lifetimes[a] (ns)		pK_a	pH_i	pK_a*[b] (1) (2)
		τ_a	τ_b			
$[Ru(phen)_2(Hptr)]^{2+}$	1	8	499	5.85	5.61	4.03 3.81
$[Ru(phen)_2(Hptr)]^{2+}$	2	6	428	4.28	3.84	2.31 1.99
$[Ru(dmbpy)_2(Hptr)]^{2+}$	1	11	95	6.13	5.93	4.78 4.99
$[Ru(dmbpy)_2(Hptr)]^{2+}$	2	7	80	4.40	3.40	2.16 2.34
$[Ru(phen)_2(H3Mptr)]^{2+}$	2			5.06	4.25	2.63
$[Ru(dmbpy)_2(H3Mptr)]^{2+}$	2			5.23	5.13	2.97
$[Ru(bpy)_2(Hptr)]^{2+}$	1	2	117	5.95	5.10	5.20 4.22[c]
$[Ru(bpy)_2(Hptr)]^{2+}$	2	9	90	4.07	2.70	3.40 2.12[c]
$[Ru(bpy)_2(H3Mptr)]^{2+}$				4.87	4.20	4.30 4.44[c]
Hptr				9.20[c]		
H3Mptr				9.80[c]		

[a]Lifetimes measured in Britton–Robinson buffer at room temperature. [b]pK_a* values were obtained from eqn. 3 (1) and eqn. 2 (2). [c]Data obtained from refs. 1 and 15. pK_a values ±0.1.

The pK_a values of the two isomers of the $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ compounds are quite different, the pK_a of isomer 2 is about two orders of magnitude lower than for isomer 1. This suggests that the N2 nitrogen is a better σ-donor than the N4 atom. The pK_a of isomer 2 of $[Ru(L\text{-}L)_2(H3Mptr)]^{2+}$ is comparable to the pK_a of isomer 2 of $[Ru(L\text{-}L)_2(Hptr)]^{2+}$ in agreement with coordination through the N1 position of the triazole ring. In agreement with the electron donor properties of the methyl ring the pK_a values for these compounds are higher than observed for the corresponding Hptr compounds. For the different polypyridyls the order for most complexes is dmbpy > phen > bpy.

Excited-state acid–base properties

The effect of pH on the emission properties of the complexes was also investigated. The emission spectrum as a function of pH of $[Ru(dmbpy)_2(Hptr)]^{2+}$, isomer 1, is presented in Fig. 7. The spectral changes observed are typical of these compounds, with the emission intensity increasing with pH and the λ_{max} of emission shifting to lower energy upon deprotonation.

Two methods exist to obtain the excited state pK_a value; pK_a*. The inflection point (pH_i) in an emission intensity versus pH plot gives an 'apparent pK_a*' value (given as pH_i in Table 5). This apparent pK_a value needs to be corrected for the different lifetimes of the protonated and deprotonated complexes, according to eqn. (2) [17].

$$pK_a^* = pH_i + \log(\tau_a/\tau_b) \quad (2)$$

where τ_a and τ_b are the excited-state lifetimes of the protonated and deprotonated compounds, respectively. The excited-state pK_a* values may also be determined using the Förster cycle as in eqn. (3) [17]

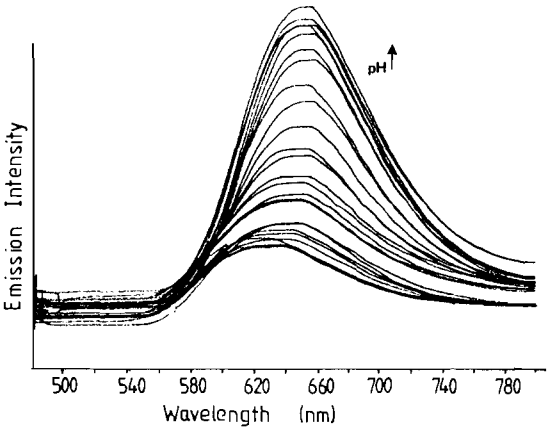

Fig. 7. pH dependence of the emission spectrum of $[Ru(dmbpy)_2(Hptr)]^{2+}$, isomer 1, (1)–(29): pH = 0.99, 1.21, 1.57, 1.74, 2.00, 2.24, 2.44, 2.62, 2.81, 3.02, 3.23, 3.43, 3.63, 3.83, 4.02, 4.27, 4.51, 4.73, 5.04, 5.27, 5.50, 5.73, 6.55, 7.01, 7.50, 8.06, 9.02, 9.97 and 11.07.

$$pK_a^* = pK_a + 0.625(\nu_b - \nu_a)/T \quad (3)$$

where ν_a and ν_b are the energies of the (0–0) transition involved in the deprotonation equilibrium, for the protonated and deprotonated forms, respectively, obtained using the λ_{max} emission values measured at 77 K, and pK_a is the ground state pK_a value. The pK_a* values obtained in this manner are given in Table 5. Population of the emitting triplet state in ruthenium polypyridyl complexes takes place in less than 10^{-12} s. This suggests that the proton equilibrium in the excited state is established in the triplet rather than in the singlet state. The pK_a* values obtained can therefore be considered as $pK_a(T_1)$ values.

From the results, it may be seen that the coordinated Hptr and H3Mptr ligands are more acidic in the excited

state than in the ground state, with quite good correlation between the two methods used for calculating pK_a^*. It should be pointed out that the short emission lifetimes observed at low pH indicate that at high acid concentrations no equilibrium is reached between protonated and deprotonated species in the excited state. Under these conditions eqn. (2) can formally not be used to obtain excited state pK_a values. The results suggest that the pyridyltriazoles act as spectator ligands and do not actively take part in the emission processes. The lifetime values indicate that the emission is strongly deactivated at low pH. This may be caused by population of the d–d level lying above the ^{3}MLCT state, which may become accessible upon protonation of the complexes and by proton quenching.

This increased acidity in the excited state has also been found for the bpy analogues and also other ruthenium compounds including ligands such as 4,7-dihydroxy-1,10-phenanthroline and 2,2'-benzimidazole [18–20]. The shift to lower energy of the emission energy upon deprotonation is consistent with the stronger σ-donation properties of the deprotonated pyridyltriazole ligand.

Conclusions

A series of pyridyltriazole compounds of the type $[Ru(L\text{-}L)_2\text{-}(L\text{-}L')]^{n+}$ have been synthesised and characterised, with (L-L) = dmbpy or phen and (L-L') = 1Mptr, 4Mptr, H3Mptr or Hptr.

The most interesting observation is that for all of the L-L' ligands, with the exception of 4Mptr, coordination through the N1'/N2' and N4' on the triazole ring is possible, irrespective of the location of the methyl groups. For the corresponding bpy complexes only the sterically preferred coordination modes were obtained. With the spectroscopic characterisation and the product ratio observed for these new isomers, the assignments made for the coordination modes in the bpy complexes are now positively confirmed. The spectroscopic properties of the phen and dmbpy complexes are similar to those observed for the analogous bpy complexes, in line with the expected similarity of the electronic properties of these polypyridyl complexes.

Also the acid–base properties of the coordinated pyridyltriazole ligands are not effected very much by the nature of the polypyridyl ligand. The pK_a values observed for the dmbpy compounds are somewhat higher. This can be explained by the stronger σ-donor properties of this polypyridyl ligand, which result in a reduced electron donation from the pyridyltriazole ligand to the metal centre. Finally as expected the emission lifetimes of the phen complexes containing deprotonated pyridyltriazole ligands are significantly longer than those observed for the bpy and dmbpy analogues.

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