Synthesis, Spectroscopic, and Electrochemical Properties of Bis(2,2'-bipyridyl)-ruthenium Compounds of some Pyridyl-1,2,4-triazoles

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A series of bis(2,2'-bipyridyl)ruthenium compounds with pyridin-2-yl-1,2,4-triazoles has been prepared and characterised by their ^1H and ^{13}C n.m.r. spectra and their electronic and electrochemical properties. The ^1H n.m.r. spectra have been used to ascertain the co-ordination mode of the ligands. The ligands bind in a bidentate fashion and they have π-acceptor properties that are weaker than 2,2'-bipyridyl (bipy). The excited-state properties of the complexes are similar to those of $[Ru(bipy)_3]^{2+}$ but important variations in the energies of the absorption and the emission maxima are observed.

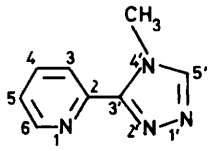
There is at present a great interest in the chemistry of polypyridyl complexes of ruthenium because of possible use of such complexes in the photochemical storage of energy [1–6] or as redox catalysts.[7–10] In particular the photochemical and photophysical properties of compounds such as $[Ru(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridyl) have been studied in great detail and these studies have led to a better general understanding of photochemical processes in inorganic compounds.[11–15] The properties of the excited state, such as the temperature dependence of the luminescence lifetime and the quantum yield of emission, have been investigated as a function of the electronic properties of the co-ordinated ligands.[16–28]

We have started a systematic investigation of the physical properties of ruthenium compounds with asymmetric ligands of the type L–L', where L–L' is a bidentate nitrogen-donor ligand with two chemically different co-ordinating sites. Although a series of complexes with pyridylazole bidentate ligands such as pyridylpyrazole,[26] pyridylimidazole,[25] and pyridylthiazole[23,24] has been reported, no systematic investigation of their physical properties has been carried out. Our work is concentrating on the synthesis and investigation of the physical properties of a series of complexes $[Ru(bipy)_{3-n}(pytrz)_n]^{2+}$, where pytrz represents a series of pyridyl-1,2,4-triazoles and n = 1—3. It is well known that five-membered rings such as 1,2,4-triazole, pyrazole, and imidazole have only weak π-acceptor properties, but strong σ-donor properties.[26,29–31] In pyridyltriazoles the two co-ordinating nitrogen atoms therefore will have quite different electronic properties. The effect of this asymmetry on the physical properties of the complexes will be investigated. Introduction of substituents and variation of the nature of the pyridyl–azole bond may result in detailed information about the photochemical and photophysical properties of complexes with asymmetric ligands. In the first paper of a series we report here the synthesis, characterisation, electronic and electrochemical properties of complexes of the type $[Ru^{II}(bipy)_2(L–L')]^{n+}$, where L–L' is a series of pyridyl-1,2,4-triazoles and n = 1 or 2.

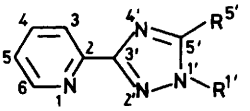
Results and Discussion

Preparation of Complexes.—A series of compounds of the type *cis*-$[Ru(bipy)_2(L–L')]^{n+}$ (**1**)—(**8**) has been prepared by treating *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ with equimolar amounts of L–L as in reaction (1). In this way the new compounds (**1**)—(**8**)

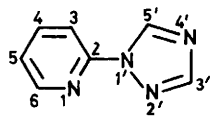
$$cis\text{-}[Ru(bipy)_2Cl_2]\cdot 2H_2O + L–L' \longrightarrow cis\text{-}[Ru(bipy)_2(L–L')]^{n+} \quad (1)$$



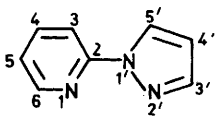
L^1



HL^2 $R^{1'}=R^{5'}=H$
HL^3 $R^{1'}=H, R^{5'}=CH_3$
L^4 $R^{1'}=CH_3, R^{5'}=H$



L^5



L^6

were obtained (see Table 1). Compounds with N-substituted pyridyltriazoles have been isolated as bivalent cations with PF_6^- counter ions. For the ligands HL^2 and HL^3, deprotonation occurs easily and under ambient conditions unipositive species of the type $[Ru(bipy)_2L]PF_6$ (L = L^2 or L^3) are obtained. The triazole N–H proton appears to be very labile on co-ordination of the ligand especially in protic solvents such as ethanol and water. The compounds (**1**) and (**3**) act as rather strong acids and a pK_a of 4.4 ± 0.2 for $[Ru(bipy)_2(HL^2)][PF_6]_2$ has been calculated (see Figure 1). Further experiments on the acid–base behaviour of these complexes, both in the ground state and in the excited state, are in progress. To obtain pure complexes with protonated HL^2 and HL^3, weakly acidic solutions were employed (see Experimental section). Recrystallisation of these compounds was carried out in acetone–water mixtures in the presence of small amounts of acid.

Spectroscopic Properties.—For certain of the ligands such as HL^2, HL^3, and L^4 different co-ordination modes are possible. Co-ordination to the triazole ring can occur either through the $N^{2'}$ or the $N^{4'}$ atom. It is anticipated that the co-ordination mode will have an effect on the electronic properties of the ligand, *e.g.* its π-acceptor properties, because of the localised nature of the double bond in 1,2,4-triazoles. It is therefore important to establish which triazole N atom is, in addition to the N atom of the pyridine ring, co-ordinated to the central

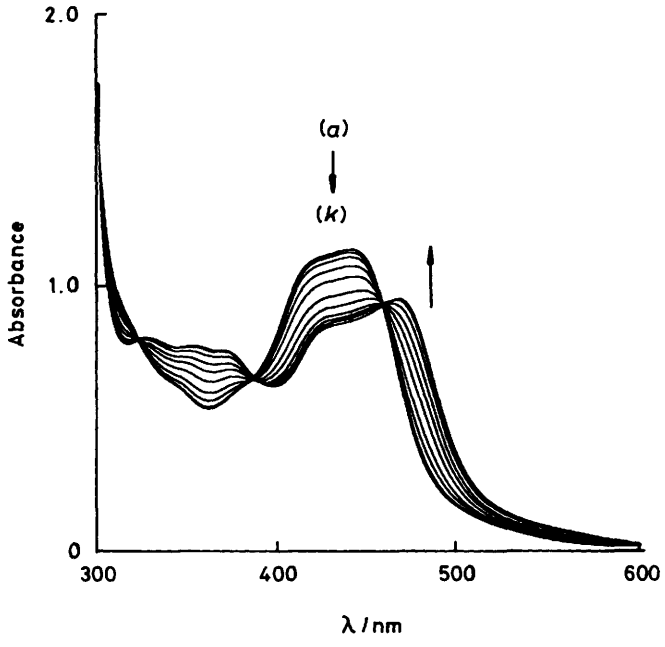


Figure 1. pH Dependence of the absorption spectrum of $[Ru(bipy)_2(HL^2)]^{2+}$ (1.05×10^{-4} mol dm^{-3}) in an aqueous Britton Robinson buffer (0.04 mol dm^{-3} in acetic acid, phosphoric acid, and boric acid). For curves (*a*)–(*k*): pH 1.98, 2.40, 3.06, 3.62, 4.00, 4.49, 4.99, 5.55, 6.03, 6.53, and 7.10; pK_a obtained 4.4 ± 0.2

metal ion. Because of the presence of two bipyridyl ligands neither u.v.–visible spectroscopy nor the electrochemical properties of the compounds can be used to identify unambiguously the way in which the ligand is bound to the ruthenium ion. It is expected that n.m.r. and in particular ^1H n.m.r. spectroscopy will yield more information.

Proton n.m.r. The proton resonance signals observed have been attributed to the different protons by comparison with literature data.[22,26,32–36] The pyridyltriazole protons in the ruthenium compounds have been identified by detailed analysis of the H–H coupling constants observed for the compounds and comparison with those found for the free ligand. The coupling constants of the free ligands are given in the Experimental section. An assignment of the proton spectra is given in Table 1. It proved difficult to differentiate between the 6-protons of the bipy ligands and the 6-proton of the pyridine ring of the pyridyltriazole ligand. This should be taken into account when interpreting the data in Table 1. The proton n.m.r. spectra clearly confirm a *cis* geometry for all our compounds.[22,33]

For the ligands HL^2, HL^3, and L^4, in particular, the resonance positions of $R^{1'}$ and $R^{5'}$ are expected to be influenced by the co-ordination mode of the ligand. If a neighbouring nitrogen atom is co-ordinated to ruthenium, these groups will be affected not only by a change in electron density in the five-membered ring but also by the presence of the shielding cone of a bipyridyl ring. Comparison with literature data suggests that for co-ordination through $N^{4'}$, $R^{5'}$ will be shielded, while in the case of $N^{2'}$ co-ordination, the resonance for $R^{1'}$ should be found at higher field than for the free ligand. This effect was very clearly shown by Steel *et al.*[26] for the complex $[Ru(bipy)_2L^7]^{2+}$ where L^7 = 3,5-dimethyl-1-(pyridin-2-yl)pyrazole. Relative to the free ligand a shift of −0.72 p.p.m. was observed for the methyl group on the 3′-position close to the co-ordinating $N^{2'}$, while the methyl group on the 5′-position was shifted downfield by +0.26 p.p.m. Taking these considerations into account it seems likely that the triazole ring in HL^3 is bound through the $N^{2'}$ atom, that in L^4 through the $N^{4'}$ atom, and, as expected, the triazole ring in L^1 through the $N^{2'}$ atom. For L^5 only one chelating co-ordination is possible, namely through the pyridine nitrogen and $N^{2'}$. It is more difficult to obtain information about the co-ordination mode from $H^{5'}$ or $H^{3'}$ proton resonances than from methyl groups in these positions. Analysis of the spectra of the complexes of HL^2, L^5, and L^6 shows that the $H^{5'}$ (for HL^2) and $H^{3'}$ (L^5 and L^6) protons are deshielded in all cases. In the last two compounds the proton is adjacent to the co-ordinating nitrogen atom. The shift to higher field can be explained by electron donation from the nitrogen atom to the metal ion. This would also in this case suggest that in HL^2 the $H^{5'}$ proton is adjacent to a co-ordinating nitrogen, $N^{4'}$. However, for the complex of L^4 where steric factors predict co-ordination at $N^{4'}$, only a small positive shift is observed. In addition it is expected that the position of the $H^{5'}$ proton in HL^2 will depend on the location of the N–H proton and this further complicates the analysis of the spectra. Therefore it is postulated that co-ordination of HL^2 occurs at $N^{4'}$ although on the basis of the proton n.m.r. spectra no unambiguous assignment can be made.

Deprotonation of co-ordinated HL^2 has a strong influence on the resonance frequency of the $H^{5'}$ triazole proton and appreciable shifts for the protons in the pyridyl ring are also observed. Shifts in the bipy resonances are small but nevertheless significant (see Table 1). For compound (**4**) similar shifts are observed. The shift in the resonance positions of the triazole protons can be explained by the increased electron density in the triazole ring,[30] which probably also affects the electron density in the pyridyl ring of the pyridyltriazole ligand. Also the change in the overall charge of the compound is likely to influence the resonance frequencies. From the position of the CH_3 resonance it has been assumed that co-ordination of the triazole ring in L^3 in compound (**4**) is at $N^{1'}$. For compound (**2**) the n.m.r. data are not conclusive.

^{13}C N.m.r. The ^{13}C chemical shifts are given in Table 2. The signals have been assigned by comparison with reported values for bipyridine.[26,37,38] Direct and long-distance C–H coupling constants were used to assign C^2 of pyridyl and $C^{3'}$ and $C^{5'}$ of the triazole moieties. The asymmetric ligand makes the four bipyridine rings non-equivalent and in most cases four peaks are observed. The shifts of the carbon atoms of pyridyltriazole upon co-ordination depend on the positions of the methyl groups attached to the triazole ring. Deprotonation of HL^2 and HL^3 has a large effect on the resonance position of the carbon atoms from the pyridyltriazole and bipyridine ligands. The $C^{3'}$ and $C^{5'}$ atoms of the triazole ring and C^2 of the pyridine ring show especially large shifts (see Table 2).

Earlier studies on a series of complexes of the type $[Ru(NH_3)_5(py)]^{2+}$ (py = various substituted pyridine rings) have suggested that the resonance position of the pyridine C^4 reflects the degree of π-backbonding in the ligand.[39] This has been contradicted on the basis of π-electron-density calculations.[40] Studies on $[Ru(bipy)_{3-n}(L^7)_n]^{2+}$ (n = 3—0) showed that the resonance positions of C^4 of both bipy and pyridinepyrazole ligands are quite similar and not very dependent on the mixture of the ligands in the compounds.[26] The resonance positions of the bipy C^4 atoms in the dications reported here do not vary greatly. The chemical shift of these atoms does however change by about 2 p.p.m. when HL^2 and HL^3 are deprotonated, more than for the other carbon atoms. It can be concluded that the π-acceptor properties of the pyridyltriazole ligands only have a small effect on the resonance position of the bipy C^4 atom, but that changes in the donor properties of these ligands (deprotonation), and/or a change in the overall charge of the ruthenium complex, do have a noticeable influence on the chemical shift of the carbon atom *'para'* to the co-ordinated nitrogen. The data also show that the carbon atoms in the pyridyl ring of the pyridyltriazole ligands

Table 1. Proton n.m.r. data (δ scale) for the complexes $[Ru(bipy)_2(L\text{–}L')]^{n+}$ in $(CD_3)_2SO$

		Pyridyltriazole ligands						Bipyridyl ligands			
	Compound	CH_3	$H^{5'}$	H^3	H^4	H^5	H^6	H^3	H^4	H^5	H^6
(1)	$[Ru(bipy)_2(HL^2)]^{2+}$	—	8.96 (+0.69)	8.37 (+0.28)	8.08 (+0.10)	7.42 (−0.09)	7.68 (−1.02)	8.71—8.82	8.11—8.17	7.46—7.53	7.78, 7.81
(2)	$[Ru(bipy)_2L^2]^+$	—	7.87 (−0.40)	8.02 (−0.07)	7.96 (−0.02)	7.23 (−0.28)	7.69 (−1.01)	8.68—8.81	8.06—8.10	7.38—7.50	7.55, 7.85
(3)	$[Ru(bipy)_2(HL^3)]^{2+}$	2.40 (+0.04)	—	8.24 (+0.22)	8.08 (+0.18)	7.41 (−0.02)	7.63 (−1.00)	8.53—8.62	7.95—8.03	7.31—7.38	7.57—7.73
(4)	$[Ru(bipy)_2L^3]^+$	2.20 (−0.16)	—	8.02 (+0.00)	7.99 (+0.09)	7.23 (−0.20)	7.67 (−0.96)	8.68—8.79	8.06—8.09	7.40—7.60	7.81—7.93
(5)	$[Ru(bipy)_2L^1]^{2+}$	4.19 (+0.21)	8.88 (+0.26)	8.43 (+0.32)	8.09 (+0.14)	7.44 (−0.03)	7.65 (−1.01)	8.72—8.85	8.12—8.20	7.51—7.58	7.76—7.83
(6)	$[Ru(bipy)_2L^4]^{2+}$	3.97 (+0.00)	8.73 (+0.12)	8.36 (+0.24)	8.10 (+0.19)	7.46 (+0.03)	7.58 (−1.00)	8.79—8.84	8.11—8.17	7.50—7.55	7.74, 7.87
(7)	$[Ru(bipy)_2L^5]^{2+}$	9.99[a] (+0.62)	8.39 (+0.09)	8.59 (+0.29)	8.19 (+0.13)	7.53 (+0.06)	7.97 (−0.56)	8.75—8.85	8.20—8.30	7.55—7.65	8.05, 8.20?
(8)	$[Ru(bipy)_2L^6]^{2+}$	6.94, 9.35[b] (+0.4, 1.01)	8.45 (+0.2)	8.45 (+0.65)	8.20 (+0.30)	7.40 (+0.10)	7.91 (−1.01)	8.75—8.85	8.13—8.25	7.50—7.62	7.70—7.86
	$[Ru(bipy)_3]^{2+}$							8.90	8.12	7.53	7.71

Figures in parentheses are shifts compared to the free ligand, those to higher field being positive. [a] $H^{3'}$. [b] $H^{4'}$, $H^{3'}$.

Table 2. ^{13}C N.m.r. data (p.p.m.) for $[Ru(bipy)_2(L\text{–}L')]^{n+}$ complexes in $(CD_3)_2SO$

	Pyridyltriazole ligands								Bipyridyl ligands				
Compound	CH_3	$C^{5'}$	$C^{3'}$	C^2	C^3	C^4	C^5	C^6	C^2	C^3	C^4	C^5	C^6
(1)	—	147.7 (−4.1)	156.8 (+2.0)	148.9 (+2.7)	123.7 (+1.8)	139.3 (+1.5)	127.8 (+2.8)	152.5 (+3.0)	158.0—158.6 (+2.7—3.3)	124.6—125.5 (+4.2—5.1)	138.4—138.7 (+1.5—1.8)	128.4—128.7 (+4.5—4.8)	152.6—153.1 (+3.5—4.0)
(2)	—	153.9 (+2.1)	160.0 (+5.2)	152.5 (+5.9)	120.2 (−1.7)	137.3 (+0.5)	127.3 (+2.3)	151.4 (+1.9)	156.9—157.4 (+1.6—2.1)	123.6—124.3 (+3.2—3.9)	136.4—136.9 (−0.5—+0.2)	127.3—127.6 (+3.4—3.7)	151.0—151.4 (+1.9—2.3)
(3)	12.3 (−0.7)	—	155.9 (−0.6)	147.9 (+0.4)	123.6 (+2.6)	138.9 (+1.6)	128.6 (+3.9)	152.0 (+1.8)	156.8—157.3 (+1.5—2.0)	124.5—125.0 (+4.1—4.6)	138.0—138.2 (+1.1—1.3)	127.5—127.7 (+3.6—3.8)	152.1—152.5 (+2.7—2.9)
(4)	14.4 (+1.4)	162.2 (+3.7)	160.2 (+3.7)	152.6 (+5.1)	119.9 (−1.7)	137.6 (+0.3)	126.8 (+2.5)	150.3 (+1.8)	156.8—157.4 (+1.5—2.1)	123.4—124.1 (+3.0—3.7)	136.2—136.8 (−0.7—−0.1)	127.3—127.5 (+3.4—3.6)	151.0—151.2 (+1.9—2.1)
(5)	34.1 (+0.7)	149.2 (+2.0)	152.9 (−1.8)	146.2 (−1.3)	124.4 (+1.6)	138.0 (+0.6)	127.0 (+2.8)	152.5 (+3.5)	156.6—157.1 (+1.3—1.8)	123.7—124.4 (+3.3—4.0)	137.4—137.6 (+0.5—0.7)	127.5—127.7 (+3.6—3.8)	151.4—152.4 (+2.3—3.1)
(6)	38.1 (+2.0)	147.4 (+1.6)	160.9 (−0.3)	148.7 (−1.0)	122.8 (+1.4)	137.5 (+0.6)	127.3 (+3.5)	151.4 (+1.9)	156.6—157.4 (+1.4—2.1)	124.0—124.4 (+3.6—4.0)	137.5—137.7 (+0.6—0.8)	127.6—127.9 (+3.6—4.0)	151.8—152.0 (+2.7—2.9)
(7)	—	147.0 (+5.0)	155.7 (+2.7)	149.6 —	115.1 (+2.2)	141.2 (+1.0)	126.7 (+3.1)	151.9 (+3.2)	158.2—158.5 (+2.9—3.4)	124.9—125.3 (+4.5—4.9)	138.9—139.1 (+2.0—2.2)	128.1—128.6 (+4.2—4.7)	153.0—153.3 (+3.9—4.2)
(8)	111.9* (+3.8)	132.5 (+5.6)	144.6 (+2.5)	151.1 (+0.3)	112.8 (+0.9)	140.1 (+0.8)	127.4? (+5.6)	150.2 (+2.0)	156.5—157.0 (+1.2—1.7)	124.1—124.4 (+3.7—4.0)	137.0 +1.0	127.4—127.8 (+3.5—3.9)	151.1—151.7 (+2.0—2.6)

Figures in parentheses are shifts compared to the free ligand, those to higher field being positive. * $C^{4'}$.

Table 3. Electronic and electrochemical data for complexes $[Ru(bipy)_2(L\text{–}L')]^{n+}$

	Compound	Absorption[a] $\lambda_{max.}$(log ε)	Emission (nm)[b] 300	77 K	Redox potentials[c] $Ru^{III/II}$	Ligand based		$\Delta E_{\frac{1}{2}}$(V)	$E^{3+/2+*}$(V)	$E^{2+*/+}$(V)
(1)	$[Ru(bipy)_2(HL^2)]^{2+}$	448 (4.03)	600	575	1.20	−1.51	−1.72	2.71	−0.96	0.65
(2)	$[Ru(bipy)_2L^2]^{+}$	474 (3.96)	660	602	0.86	−1.51	−1.77	2.37	−1.19	0.54
(3)	$[Ru(bipy)_2(HL^3)]^{2+}$	444 (4.03)	600	587	1.20	−1.55	−1.81	2.75	−0.91	0.56
(4)	$[Ru(bipy)_2L^3]^{+}$	476 (3.93)	660	610	0.79	−1.50	−1.72	2.29	−1.24	0.53
(5)	$[Ru(bipy)_2L^1]^{2+}$	440 (4.16)	600	584	1.21	−1.42	−1.64	2.63	−0.91	0.70
(6)	$[Ru(bipy)_2L^4]^{2+}$	452 (4.03)	600	585	1.20	−1.42	−1.64	2.62	−0.92	0.70
(7)	$[Ru(bipy)_2L^5]^{2+}$	420 (3.73)	—	562	1.36	−1.39	−1.66	2.75	−0.84	0.81
(8)	$[Ru(bipy)_2L^6]^{2+}$	450 (3.97)	609	572	1.26	−1.40	−1.59	2.66	−0.91	0.77
	$[Ru(bipy)_2L^8]^{2+}$[d]	452 (—)	598	—	1.26					
	$[Ru(bipy)_2(HL^9)]^{2+}$[e]	460 (4.02)	625	596	1.14	−1.52	−1.78	2.66	−0.96	0.56
	$[Ru(bipy)_2L^9]^{+}$[e]	500 (3.96)	690	—	0.76	−1.49	−1.73	2.25		
	$[Ru(bipy)_3]^{2+}$[f]	452 (4.11)	608	582	1.22	−1.36	−1.53	2.58	−0.90	0.76

[a] Measured in CH_3CN; λ in nm, ε in $dm^3\ mol^{-1}\ cm^{-1}$. [b] Spectra at room temperature in CH_3CN, at 77 K in ethanol; λ in nm. [c] Measured in CH_3CN with 0.1 mol dm^{-3} NEt_4ClO_4. Volts *vs.* s.c.e.; n.h.e. ≡ s.c.e. +0.2415 V. [d] Ref. 24. L^8 = pyridylthiazole. [e] Ref. 25. HL^9 = 1-(pyridin-2-yl)imidazole. [f] Ref. 19.

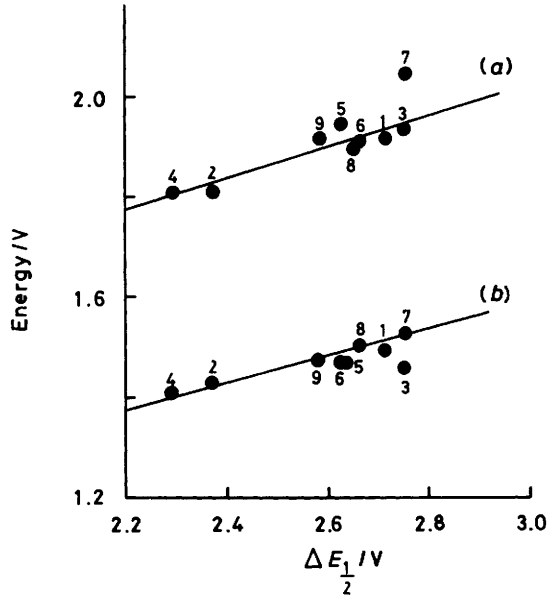


Figure 2. Plots of $\Delta E_{\frac{1}{2}}$ *vs.* absorption (*a*) and emission energies (*b*) for compounds (**1**)—(**8**) and $[Ru(bipy)_3]^{2+}$. Absorption spectra and values for $\Delta E_{\frac{1}{2}}$ were obtained at room temperature in acetonitrile. Emission maxima were obtained at 77 K in ethanol

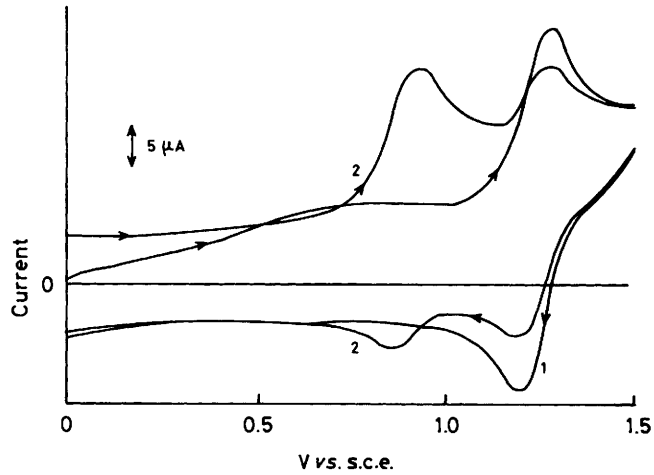


Figure 3. Cyclic voltammogram of $[Ru(bipy)_2(HL^2)]^{2+}$ in 0.1 mol dm^3 NEt_4ClO_4 in CH_3CN. (1) First cycle; (2) second cycle, after cycling down to −1.9 V *vs.* s.c.e.

affected most by deprotonation are C^2 and C^3 rather than C^4.

Electronic spectra and redox properties. The electronic and the electrochemical properties of the complexes are listed in Table 3 together with the excited-state redox potentials, $E^{3+/2+*}$ and $E^{2+*/+}$,[41] and $\Delta E_{\frac{1}{2}}$, the difference between the Ru^{II}–Ru^{III} oxidation potential and the Ru^{II}–Ru^{I} reduction potential. The spectral features are similar to those of $[Ru(bipy)_3]^{2+}$ but significant variations are observed.[18,19] As for other ruthenium bipyridyl complexes, the absorption bands of lowest energy can be assigned to $d_\pi \longrightarrow \pi^*$ metal-to-ligand charge-transfer (m.l.c.t.) bands. The position of these bands is determined by both σ and π effects.[19] For the dications the position of the m.l.c.t. band is found at slightly higher energy than for $[Ru(bipy)_3]^{2+}$. The electrochemical data suggest that all ligands with the possible exception of L^5 are weaker π acceptors than bipy. Deprotonation of HL^2 and HL^3 complexes leads to a shift to lower energy for the m.l.c.t. band. Similar behaviour has been observed for a series of bis(bipyridyl) ruthenium compounds of 1,2,4-triazole, imidazole, and pyrazole and has been explained by an increase in the π-donor properties of the deprotonated ligands.[31,32] Deprotonation also has a strong effect on the emission spectra. Interestingly the compounds with the deprotonated ligands do emit at room temperature. For most compounds a well defined vibrational progression is observed in the emission spectra measured at 77 K. The splitting between the components is of the order of 1 300 cm^{-1} and has been assigned in related compounds to ν(bipy) vibrations.[19] For compounds (**2**) and (**4**) shifts of 1 500 and 1 300 cm^{-1} respectively are observed for the $\lambda_{max.}$ emission on going from 303 to 77 K. This compares to a value of 700 cm^{-1} for $[Ru(bipy)_3]^{2+}$.[18,19] The larger shift for compounds (**2**) and (**4**) might suggest either a different arrangement of the emitting states of these compounds or a particularly strong rigidochromism.[42]

For many $[Ru(bipy)_2L_2]^{2+}$ compounds reported in the literature a linear relationship exists between the energy of the lowest m.l.c.t. band and $\Delta E_{\frac{1}{2}}$, and between $\Delta E_{\frac{1}{2}}$ and the emission energy.[19,43] These relationships also hold for the compounds reported here (see Figure 2) indicating emission from the same

^{3}m.l.c.t. level as is observed for other ruthenium polypyridyl complexes. This is further substantiated by the energy difference between the absorption and the emission (77 K) measured for these complexes (between 4 500 and 5 500 cm^{-1}). For $[Ru(bipy)_3]^{2+}$ a value of 5 000 cm^{-1} is obtained.[18] Compound (7) might be the only exception, for which the difference is 6 000 cm^{-1}. Figure 2(*a*) shows that this compound does not follow the m.l.c.t.–$\Delta E_{\frac{1}{2}}$ relationship normally observed for $Ru(bipy)_2$ compounds. This could suggest a direct involvement of the ligand L^5 in the excited-state processes. In this context it is important that we could not detect any emission from compound (7) at room temperature. It is well known that the intensity of emission depends, among other things, on the energy difference between the deactivating antibonding *d–d* orbital and the emitting ^{3}m.l.c.t. state.[11–15] In $[Ru(bipy)_3]^{2+}$ the energy of this *d–d* orbital is about 4 000 cm^{-1} higher than that of the emitting ^{3}m.l.c.t. band. Thermal population of this *d–d* level is therefore possible at room temperature.[2,18,19] Possible explanations for the absence of room-temperature emission for compound (7) are that the energy difference between the two levels is much smaller, which will result in a more efficient population of the *d–d* level, or that deactivating L^5 ligand states are involved in the emission process.

The electrochemical data indicate that all pyridyltriazole ligands are less efficient π-acceptor ligands than is bipyridyl. This is particularly evident from the Ru^{II}–Ru^{I} reduction potentials. In general these potentials become less negative with increasing π-acceptor abilities of the ligands. The position of the reduction potentials of the HL^2 and HL^3 complexes needs further discussion. In acetonitrile an extra Ru^{II}–Ru^{III} oxidation wave appears after cycling past the first reduction wave (see Figure 3). The area under this second wave is scan-rate dependent. Recently Sullivan *et al.*[44] reported the electrochemically induced anion substitution in organic solvents for a series of $[Ru(bipy)_2L(Cl)]^+$ compounds. This process was thought to be promoted by the formation of a neutral species, as this eliminates the need for ion pairing. The peak potential of the second wave suggests that for complexes (1) and (3) deprotonation of the reduced species occurs as in reactions (2) and (3).

$$[Ru(bipy)_2(HL^2)]^{2+} \xrightarrow{+e} [Ru(bipy)_2(HL^2)]^+ \quad (2)$$

$$[Ru(bipy)_2(HL^2)]^+ \longrightarrow [Ru(bipy)_2L^2] + H^+ \quad (3)$$

Included in Table 3 are the oxidation and reduction potentials of the excited state, $E^{3+/2+*}$ and $E^{2+*/+}$. These potentials were obtained from the ground-state redox properties and the emission spectra at low temperature as described in the literature.[41] The electrochemically induced deprotonation process makes it difficult to determine accurately the reduction potentials of complexes (1) and (3). This will be reflected in the values obtained for $\Delta E_{\frac{1}{2}}$ and $E^{2+*/+}$. Although little variation with the nature of the ligand is observed in the excited-state reduction potential, changes in $E^{3+/2+*}$ are substantial. This behaviour is in agreement with that reported for similar complexes.[18] The values obtained for the excited-state redox potentials suggest that from the thermodynamic point of view the compounds reported here have the ability to split water.[2]

Final Remarks.—The data presented above indicate that the pyridyl-1,2,4-triazoles, with the possible exception of L^5, are weaker π-acceptor ligands than bipy. The compounds described have similar excited-state properties to $[Ru(bipy)_3]^{2+}$ but there are some significant differences, *e.g.* for compounds (2), (4), and (7). The strong emission observed for the compounds with deprotonated ligands is surprising as in general the emission observed from ruthenium compounds of the type $[Ru(bipy)_2L(X)]^+$ is rather weak. For (7) no emission was detected at room temperature. As the corresponding pyridylpyrazole compound (8) does emit at that temperature, the presence of a N–N bond in the chelating ring cannot be the reason for this behaviour. The variation of the absorption and the emission properties with the nature of the ligand L–L′ is small and with the present data it is not possible to differentiate between the electronic properties of these ligands. A more detailed investigation of the photochemical and photophysical properties of these complexes is in progress. In particular the effect of deprotonation and the overall charge of the compound on the excited-state properties will be studied. It is anticipated that these experiments will yield more precise information about the role of the ligands L–L′ in the excited state. Another point of interest is the number of excited states involved in the emitting process. Recently Kober and Meyer[13] reported a detailed discussion of the excited-state properties of $[Ru(bipy)_3]^{2+}$ and came to the conclusion that there are four emitting ^{3}m.l.c.t. bands. It was pointed out in the same paper that for compounds of the type $[Ru(bipy)_2L(X)]^+$ more states might be involved. The present series of compounds is ideally suited to investigate this hypothesis.

Experimental

U.v.–visible spectra were recorded on a Perkin-Elmer 330 spectrophotometer or a Shimadzu UV-240 spectrophotometer using matched 1-cm^3 quartz cells. Absorption coefficients are accurate to 5%. Emission spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrometer using an emission slit width of 10 nm at room temperature and 2.5 nm at 77 K and are not corrected for photomultiplier response. Proton n.m.r. spectra were obtained on a JEOL JNM-FX 200-MHz spectrometer, ^{13}C n.m.r. spectra on a JEOL 50.1-MHz spectrometer; peak positions were measured relative to $SiMe_4$. Electrochemical measurements were carried out using an E.G. and G. Par model 174A polarographic analyser with an E.G. and G. Par 175 Universal Programmer. A saturated potassium calomel electrode (s.c.e.) was used as reference electrode. Measurements were carried out in AnalaR grade acetonitrile dried over molecular sieves, with 0.1 mol dm^{-3} NEt_4ClO_4 as a supporting electrolyte. Both platinum and glassy carbon working electrodes were used but for a number of complexes strong adsorption occurred at platinum. The values reported are therefore those obtained on glassy carbon. The scan rate used was 100 mV s^{-1}. Elemental analyses were carried out at University College Dublin.

Materials.—Hydrated ruthenium trichloride was obtained from Janssen Chimica and used without further purification. The complex $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ was prepared as described in the literature.[45] All other reactants were reagent-grade materials and used as received.

Procedures for Preparation of the Ligands.—All pyridylazole ligands except 5-methyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole were prepared as described in the literature.

3-(*Pyridin-2-yl*)-1H-1,2,4-*triazole* (HL^2). M.p. 158—160 °C (lit.,[46] 164—165 °C). N.m.r.: ^{1}H [$(CD_3)_2SO$], 14.62 (s, N–H), 8.70 (1 H, d, H^6), 8.27 (1 H, s, $H^{5'}$), 8.09 (1 H, d, H^3), 7.98 (1 H, t, H^4), and 7.51 (1 H, t, H^5), $J(H^5H^6)$ 4.9, $J(H^4H^6)$ 1.0, $J(H^4H^5)$ 7.3, $J(H^3H^5)$ 1.4, and $J(H^3H^4)$ 7.8 Hz; ^{13}C ($CDCl_3$), 154.8 ($C^{3'}$), 151.8 ($C^{5'}$), 146.6 (C^2), 137.8 (C^4), 125.0 (C^5), and 121.9 (C^3) p.p.m.

1-*Methyl*-3-(*pyridin-2-yl*)-1H-1,2,4-*triazole* (L^4). M.p. 51—54 °C (lit.,[47] 47—48 °C). N.m.r. [$(CD_3)_2SO$]: ^{1}H, 8.66 (1 H, d, H^6), 8.61 (1 H, s, $H^{5'}$), 8.16 (1 H, d, H^3), 7.91 (1 H, t, H^4), 7.43 (1 H, t, H^5), and 3.97 (3 H, s, Me), $J(H^5H^6)$ 4.8, $J(H^4H^6)$ 1.1,

$J(H^4H^5)$ 6.8, $J(H^3H^5)$ 1.1, and $J(H^3H^4)$ 8.0 Hz; ^{13}C, 36.1 (Me), 121.4 (C^3), 123.8 (C^5), 136.9 (C^4), 145.8 ($C^{5'}$), 149.5 (C^6), 149.7 (C^2), and 161.2 ($C^{3'}$) p.p.m.

4-Methyl-3-(pyridin-2-yl)-4H-1,2,4-triazole (L^1). M.p. 96—99 °C (lit.,[48] 104—105 °C). N.m.r.: ^1H [$(CD_3)_2SO$], 8.66 (1 H, d, H^6), 8.62 (1 H, s, $H^{5'}$), 8.11 (1 H, d, H^3), 7.95 (1 H, t, H^4), 7.47 (1 H, t, H^5), and 3.99 (1 H, s, Me), $J(H^5H^6)$ 4.8, $J(H^4H^6)$ 1.0, $J(H^4H^5)$ 7.3, $J(H^3H^5)$ 1.9, and $J(H^3H^4)$ 7.8 Hz; ^{13}C ($CDCl_3$), 33.4 (Me), 122.8 (C^3), 124.2 (C^5), 137.4 (C^4), 147.2 ($C^{5'}$), 147.5 (C^2), 149.0 (C^6), and 151.1 ($C^{3'}$) p.p.m.

5-Methyl-3-(pyridin-2-yl)-1H-1,2,4-triazole (HL^3). Equimolar amounts of 2-cyanopyridine and hydrazine monohydrate were mixed and a small amount of ethanol was added to obtain a clear solution. After standing overnight at room temperature, the almost colourless crystals of 2-pyridinecarboxamidrazone could be filtered off. The product was washed with diethyl ether and dried in the air. The solid obtained (130 g) was added to a mixture of acetic acid and acetic anhydride (1:1,600 cm^3) at 0 °C and the solution was stirred at room temperature for 2 h. The solution was then concentrated under vacuum and the resulting oil heated at 130 °C for 1 h. The solid obtained was purified by repeated crystallisation from di-isopropyl ether, yield 60%. The product proved to be identical with a sample prepared by a literature method.[47] M.p. 163—165 °C (lit.,[47] 165—166 °C). N.m.r.: ^1H [$(CD_3)_2SO$], 14.2 (s, N–H), 8.83 (1 H, d, H^6), 8.02 (1 H, d, H^3), 7.90 (1 H, t, H^4), 7.43 (1 H, t, H^5), and 2.36 (3 H, s, Me), $J(H^5H^6)$ 4.6, $J(H^4H^6)$ 1.0, $J(H^4H^5)$ 6.2, $J(H^3H^5)$ 1.5, and $J(H^3H^4)$ 8.0 Hz; ^{13}C ($CDCl_3$), 13.0 (Me), 121.6 (C^3), 124.3 (C^5), 137.3 (C^4), 147.5 (C^2), 149.2 (C^6), 156.5 ($C^{3'}$), and 158.5 ($C^{5'}$) p.p.m.

1-(Pyridin-2-yl)-1H-1,2,4-triazole (L^5). M.p. 90—93 °C, (lit.,[49] 92—94 °C). N.m.r. [$(CD_3)_2SO$]: ^1H, 9.37 (1 H, s, $H^{3'}$), 8.53 (1 H, d, H^6), 8.30 (1 H, s, $H^{5'}$), 8.06 (1 H, t, H^4), 7.86 (1 H, d, H^3), and 7.47 (1 H, q, H^5), $J(H^5H^6)$ 4.5, $J(H^4H^6)$ 1.8, $J(H^4H^5)$ 7.6, $J(H^3H^5)$ 1.2, and $J(H^3H^4)$ 8.1 Hz; ^{13}C, 112.9 (C^3), 123.6 (C^5), 140.2 (C^4), 142.0 ($C^{5'}$), 148.7 (C^6), 153.0 ($C^{3'}$) p.p.m.

1-(Pyridin-2-yl)pyrazole (L^6). M.p. 38—40 °C (lit.,[49] 38—40 °C). N.m.r. [$(CD_3)_2SO$]: ^1H, 8.60 (1 H, d, $H^{3'}$), 8.44 (1 H, d, H^6), 7.92—7.80 (3 H, m, H^4, H^3, $H^{5'}$), 7.30 (1 H, m, H^5), and 6.54 (1 H, s, $H^{4'}$); ^{13}C, 108.1 ($C^{4'}$), 111.9 (C^3), 121.8 (C^5), 126.9 (C^4), 139.3 ($C^{5'}$), 142.1 ($C^{3'}$), 148.2 (C^6), 150.8 (C^2) p.p.m.

Procedure for Preparation of Co-ordination Compounds.—$[Ru(bipy)_2(HL^2)][PF_6]_2$ (**1**). The complex *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (520 mg, 1 mmol) was heated at reflux for 3 h in ethanol–water (2:1, 50 cm^3) in the presence of HL^2 (1.2 mmol). In order to ensure complete protonation of the bound pyridyltriazole ligand, concentrated HCl (1 cm^3) was added at the end of the reaction. This solution was then added dropwise to a concentrated solution of NH_4PF_6 in water. The precipitate formed was filtered off and further purified by column chromatography, using neutral alumina and ethanol as eluant. The compound was recrystallised from slightly acidic (HCl or HPF_6) acetone–water mixtures, yield 500 mg (60%) (Found: C, 38.0: H, 2.9: F, 26.9; N, 13.1; P, 7.0. $C_{27}H_{22}F_{12}N_8P_2Ru$ requires C 38.2; H, 2.6; F, 26.8; N, 13.9; P, 7.3%).

$[Ru(bipy)_2L^2]PF_6\cdot 3H_2O$ (**2**). This compound was prepared as for (**1**) but no concentrated HCl was added, yield 450 mg (60%) (Found: C, 42.3; H, 3.1; N, 14.8; P, 3.9. $C_{27}H_{27}F_6N_8O_3PRu$ requires C, 42.8; H, 3.6; N, 14.8; P, 4.1%).

$[Ru(bipy)_2(HL^3)][PF_6]_2\cdot H_2O$ (**3**). This compound was prepared as for (**1**), yield 550 mg (60%) (Found: C, 38.5; H, 3.1; F, 26.5; N, 12.6; P, 6.9. $C_{28}H_{26}F_{12}N_8OP_2Ru$ requires C, 38.2; H, 3.1; F, 25.9; N, 12.7; P, 7.0%).

$[Ru(bipy)_2L^3]PF_6\cdot 4H_2O$ (**4**). This compound was prepared as for (**2**), yield 500 mg (60%) (Found: C, 42.7; H, 3.3; N, 14.4; P, 3.6. $C_{28}H_{31}F_6N_8O_4PRu$ requires C, 42.6; H, 3.9; N, 14.2; P, 3.9%).

$[Ru(bipy)_2L^1][PF_6]_2$ (**5**). This compound was prepared as for (**2**), yield 800 mg (90%) (Found: C, 38.7; H, 2.8; N, 12.5. $C_{28}H_{24}F_{12}N_8P_2Ru$ requires C, 39.0; H, 2.8; N, 13.0%).

$[Ru(bipy)_2L^4][PF_6]_2\cdot H_2O$ (**6**). This compound was prepared as for (**2**), yield 750 mg (85%) (Found: C, 38.4; H, 2.8; N, 12.7. $C_{28}H_{26}F_{12}N_8OP_2Ru$ requires C, 38.1; H, 3.0; N, 12.7%).

$[Ru(bipy)_2L^5][PF_6]_2$ (**7**). This compound was prepared as for (**2**), yield 750 mg (90%) (Found: C, 38.4; H, 2.7; N, 13.4. $C_{27}H_{22}F_{12}N_8P_2Ru$ requires C, 38.7; H, 2.6; N, 13.4%).

$[Ru(bipy)_2L^6][PF_6]_2$ (**8**). This compound was prepared as for (**2**), yield 800 mg (95%) (Found: C, 39.6; H, 2.7; N, 11.7. $C_{28}H_{23}F_{12}N_7P_2Ru$ requires C, 39.6; H, 2.7; N, 11.6%).

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