Effect of Co-ordination Mode on the Physical Properties of Pyrazinyltriazole Ligands bound to Bis(2,2′-bipyridyl)-ruthenium(II)

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The physical properties of the two co-ordination isomers of the bis(2,2′-bipyridyl)ruthenium(II) complex of 3-(pyrazin-2-yl)-1,2,4-triazole have been studied. In particular the acid–base properties have been analysed with respect to the nature of the ligand and the co-ordination mode of the triazole ring. The ground-state pK_a(acid) values of 3.1 and 5.3 obtained for the N^2 and N^4 isomers respectively indicate that the N^2 site of the triazole ring is a stronger σ donor than is the N^4 atom. The excited-state pK_a values obtained for deprotonation of the triazole ring are unusual and support earlier suggestions that in the compounds containing the neutral pyrazinyltriazole ligands the lowest π* level is based on the pyrazinyltriazole ligand, while for the deprotonated ligands this level is 2,2′-bipyridine based.

The properties of a great number of ruthenium(II) complexes have been studied extensively, because of their possible use as photocatalysts or redox catalysts.[1–6] Most attention has been focused on 2,2′-bipyridine (bipy) or 1,10-phenanthroline ligands, although a considerable amount of data for ruthenium systems with 2,2′-bipyrazine, 2,2′-bipyrimidine, bis(quinoline) and bis(imidazole) ligands has been published.[6–18] An important conclusion from this work is that the electrochemical and photophysical properties of the complexes can be tuned by a judicious choice of the ligand system.

Recently, we started a systematic study on the synthesis and properties of ruthenium(II) complexes with chelating pyridyltriazoles, pyridyltriazines and pyrazinyltriazoles.[19–29] In such asymmetric ligands two sites are in principle available for co-ordination to the Ru(bipy)$_2$ moiety, namely the N^2 and N^4 atoms of the triazole ring. By using high-performance liquid chromatography (HPLC) techniques, we have been able to separate the co-ordination isomers for the Ru(bipy)$_2$ complex of 3-(pyridin-2-yl)-1,2,4-triazole.[27,28] interestingly, there are substantial differences in the electrochemical and excited-state properties of the two isomers and also in their ground-state and in the excited-state acid–base properties.

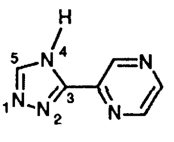
In this contribution, the separation of the two co-ordination isomers of the complex of Ru(bipy)$_2$ with 3-(pyrazin-2-yl)-1,2,4-triazole (HL^1) (compounds **1** and **2**) is reported and the effect of the co-ordination geometry on the spectroscopic and acid–base properties of the isomers will be discussed. Results on some related Ru(bipy)$_2$ compounds with the ligands 3-methyl-5-(pyrazin-2-yl)-1,2,4-triazole (HL^2), compound **3**, and with 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L^3), compound **4** are also presented. We denote the deprotonated analogues of compounds **1**–**3** **1a**, **2a** and **3a**. The acid–base properties of **1**–**3** are compared with those recently reported for the two isomers obtained for the Ru(bipy)$_2$ compound of 3-(pyridin-2-yl)-1,2,4-triazole (HL^4), compounds **5** and **6**, and with those of the Ru(bipy)$_2$ compound of 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole (HL^5), compound **7**.[27,29] The deprotonated analogues of these compounds are denoted as **5a**, **6a** and **7a**.

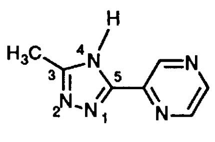
Such investigations are of interest as results obtained for Ru(bipy)$_2$ pyridyltriazole compounds suggest that when the pyrazinyltriazole ligand is protonated the lowest unoccupied molecular orbital (LUMO) is based on this ligand, while when the ligand is deprotonated the LUMO is bipy based.[24] These unusual properties are expected to affect the acid–base properties, especially in the excited state and it is therefore anticipated that the results obtained will differ substantially from those found for corresponding pyridyltriazole compounds, as in the latter the LUMO is always bipy based.[19,27,29]

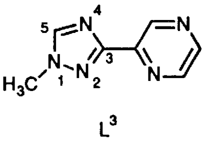
Results and Discussion

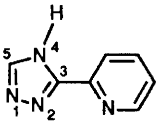
General.—In an earlier publication we reported the isolation of only one pure isomer for the HL^1 compound in an overall yield of about 30%.[24] In further experiments we have now obtained, in a 90% yield, a material containing both isomers and these isomers have subsequently been separated by semi-preparative HPLC. In the material obtained the ratio between the two isomers was approximately 1 : 1. In the present work the first isolated isomer, with a retention time of 20 min, is called compound **1**, the other **2** (retention time 25 min). The fact that only one isomer was obtained the first time can be explained by the fact that compound **2** is slightly less soluble.

Proton NMR Spectroscopy.—It has been shown before[19,20,24–33] that proton NMR spectroscopy is very useful for the characterisation of ruthenium(II) diimine compounds and also an invaluable tool in the determination of the co-ordination mode of triazole ligands. The NMR data for **3**, **3a** and **4** have been reported in a previous article[24] and will not be further discussed here. It was concluded that HL^2 is bound *via* N^2 of the triazole ring to the metal ion, while L^3 is co-ordinated *via* N^4. To determine the co-ordination mode of the pyrazinyltriazole ligand in compounds **1** and **2** an analysis of the spectra of these compounds is given below. The NMR spectrum of the protonated compound **1** is depicted in Fig. 1(*a*) (pH 0.80) and that of the second isomer in Fig. 1(*b*) (pH 1.13). The assignments of the pyrazinyltriazole signals are listed in Table 1 and are based on comparison with related compounds.[19–33] The bipy signals are as expected and not included. The H^5 proton is observed as a sharp singlet, thus making the assignment of this proton straightforward. The chemical shift of the H^5 proton of compound **1** is at much higher field than observed for the


HL^1


HL^2


L^3


HL^4

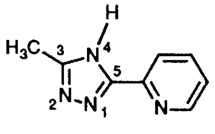

HL^5

Table 1 Proton NMR resonances obtained for co-ordinated HL^1 and L^{1-} in compounds **1**, **1a**, **2** and **2a**. Measurements in D_2O–$(CD_3)_2CO$ (9:1)

Compound	pH	$H^{3'}$	$H^{5'}$	H^6	H^5
1	0.80	9.33	7.82	8.34	8.41
1a	7.47	9.16	7.73	8.18	7.60
2	1.13	9.37	7.97	8.45	8.78
2a	6.34	9.26	7.88	8.33	8.09

Table 2 Electronic spectra and oxidation potentials of the $Ru(bipy)_2$ complexes with HL^1 and HL^2

Compound	Absorption,[a] λ_{max}/nm	Emission,[b] λ_{max}/nm 77 K	300 K	Oxidation potential[c]/V *vs.* SCE
1 (N^4)	439 (–)[d]	596 (4.1)	657 (0.13)	1.31
1a (N^4)	457 (–)[d]	603 (4.3)	659 (0.08)	1.00
2 (N^2)	440 (1.32)	612 (4.9)	662 (0.10)	1.20
2a (N^2)	456 (1.14)	618 (4.1)	668 (0.08)	0.95
3	441 (1.27)	620 (5.2)	665 (0.14)	1.29
3a	458 (1.21)	627 (3.8)	670 (0.07)	0.92
4	440 (1.45)	575 (7.8)	630 (0.07)	1.30

[a] Obtained in CH_3CN. [b] Values within brackets are emission lifetimes in μs; measurements carried out in propionitrile–butyronitrile (4:5 v/v). [c] Obtained in CH_3CN containing 0.1 mol dm^{-3} NBu_4ClO_4. [d] Not measured.

second isomer (see Fig. 1 and Table 1). Structural models reveal that when the triazole ring is bound *via* N^4 the H^5 proton will be directed to a neighbouring bipy ring, but for the N^2-bound isomer this proton will not interact with any part of the molecule. It seems, therefore, likely that in compound **1** the pyrazinyltriazole ligand is co-ordinated *via* the N^4 atom, while in **2** the N^2 atom is co-ordinated to the ruthenium centre.

Electrochemistry and Electronic Spectroscopy.—The reduction potentials of the complexes are -1.44 V *vs.* a saturated calomel electrode (SCE) for the deprotonated complexes and approximately -1.26 V *vs.* SCE for compounds containing the neutral ligands.[24] For HL^1 the oxidation potentials for the N^2-bound compound **2** (protonated and deprotonated) are somewhat lower than those of the N^4 compound (Table 2). Most likely the stronger σ-donor capacity of the N^2 site (see below) causes a higher electron density on the metal centre and, therefore, a lower oxidation potential. The absorption spectra of the complexes exhibit strong m.l.t.c. (metal-to-ligand charge-transfer) bands in the visible region, as observed for many other ruthenium(II) systems.[1–6] One remarkable aspect is the small effect that deprotonation has on the absorption and emission maxima of compounds **1**–**3**. This behaviour will be further discussed in the acid–base section.

Ground-state and Excited-state Acid–Base Properties.—The complexes **1a**, **2a** and **3a** can be protonated on the triazole ring, pK_a(acid), and on the pyrazine ring, pK_a(base), as shown in equation (1). The protonation of the pyrazine ring is independent of the co-ordination mode of the triazole ring. For compounds **1**–**4** the absorption spectrum originally observed at about 450 nm disappears upon protonation of the pyrazine ring and two new bands appear at 400 and 530 nm.[24] Resonance-Raman spectra have shown that the lowest-energy band can be described as a Ru ⟶ π*(H_2L) transition.[24] Using UV/VIS spectroscopy, a pK_a(base) of -1.8 has been obtained for all four pyrazinyltriazole complexes, typical for a pyrazine protonation.[34–37]

$$[Ru(bipy)_2L]^+ \underset{pK_a(\text{acid})}{\overset{H^+}{\rightleftharpoons}} [Ru(bipy)_2(HL)]^{2+} \underset{pK_a(\text{base})}{\overset{H^+}{\rightleftharpoons}} [Ru(bipy)_2(H_2L)]^{3+} \quad (1)$$

Also in the range pH 2–7 the absorption spectra of compounds **1**–**3** are pH dependent (see Fig. 2). This reversible variation of the absorption spectrum with pH has been attributed to the acid–base properties of the triazole ring. A remarkable feature of these experiments is the small effect that deprotonation of the triazole ring has on the absorption spectrum. For compound **4**, containing the ligand L^3, no variation of the absorption spectrum with pH was observed in this range, clearly indicating that the spectral changes are related to the acid–base properties of the triazole NH group. The pK_a(acid) values obtained are presented in Table 3.

Information about the acid–base behaviour can also be obtained from ^1H NMR spectroscopy. An example of the determination of the pK_a(acid) is given in Fig. 3, where the chemical shift of the H^5 proton of both compounds **1** and **2** has been plotted *vs.* pH. The pK_a(acid) values obtained in this manner are 5.0 ± 0.2 for compound **1** and 2.8 ± 0.2 for **2**.

The excited-state acidity has been investigated by a study of the pH dependence of the emitting properties of the compounds. An example of a plot of the emission intensity *vs.* pH is given in Fig. 4. These emission titrations were carried out by excitation into the appropriate isosbestic point. The wavelengths taken were 440 nm for compound **1**, 420 for **2** (see Fig. 2) and 427 for **3**. At very low pH values the emission intensity for compounds **1**–**4** is negligible. The luminescence becomes stronger when the pH is increased until a maximum intensity is reached at around pH 3. For the compounds **1**–**3** the emission intensities decrease between pH 3 and 6 (see Fig. 4). For compound **4** no decrease in the emission intensity is observed in this pH range. This is again consistent with the absence of a triazole NH group in this compound.

By investigating the acid–base behaviour of this type of ruthenium compounds important information about their electronic properties can be obtained.[19,25,26,34–41] The ground-state behaviour tends to be a measure of the amount of electron donation from the ligand to the metal, while the excited-state measurements can give information about the nature of the emitting state. Upon co-ordination to ruthenium, the acidity of the triazole proton in the ground state increases considerably, which is generally explained by σ donation from the ligand to the metal centre.[19,20,24–27] As the N^2 isomer is considerably more acidic than the N^4 isomer, the N^2 co-ordination site appears to be a better σ donor. This observation is in agreement with the oxidation potentials obtained for the two isomers. The ground-state pK_a(acid) values for the compounds reported here are similar to those found for the corresponding pyridyltriazole compounds (see Table 3) suggesting that electron donation

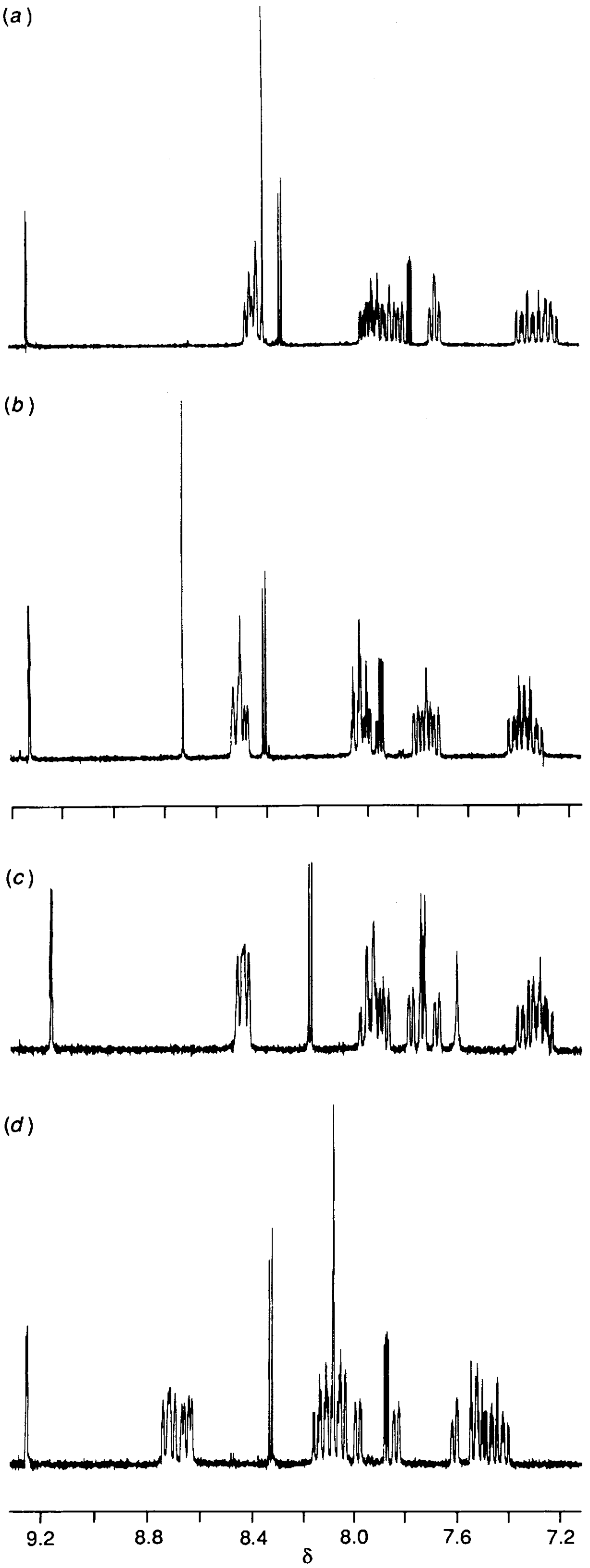


Fig. 1 Proton NMR spectra of compound **1** at pH 0.80 (*a*), **2** at pH 1.13 (*b*) **1a** at pH 7.47 (*c*) and **2a** at pH 6.34 (*d*)

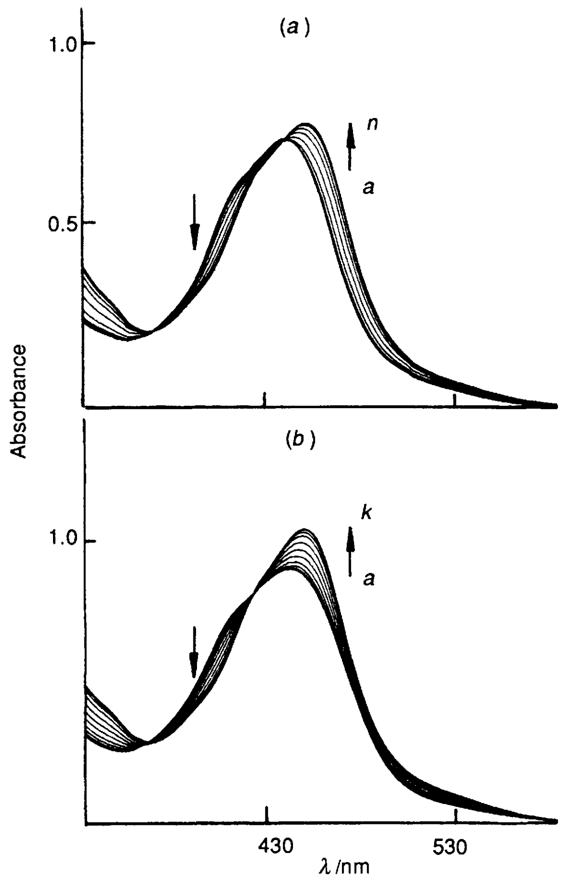


Fig. 2 pH Dependence of the absorption spectra of (*a*) compound **1**, concentration 0.6 × 10^{-4} mol dm^{-3} (curves *a*–*n*, pH 1.91, 2.39, 2.84, 3.05, 3.39, 3.86, 4.28, 4.73, 5.22, 5.64, 5.98, 6.38, 6.80, 7.30) and (*b*) **2**, concentration 9.4 × 10^{-5} mol dm^{-3} (curves *a*–*k*, pH 1.21, 2.89, 3.19, 3.50, 3.76, 4.08, 4.46, 4.91, 5.58, 6.20, 7.04)

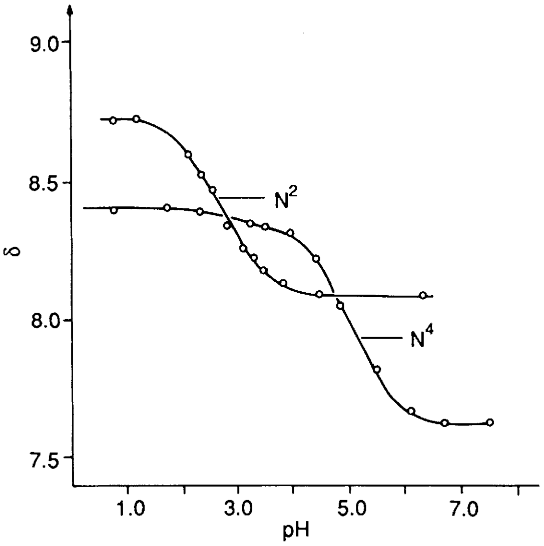


Fig. 3 The chemical shifts of the H^5 proton *versus* the pH for compounds **1** and **2**. Solvent D_2O–$(CD_3)_2CO$ (9:1)

from the triazole ring to the metal is similar in both types of compounds. The pK_a(acid) values obtained by the use of UV/VIS spectroscopy are very close to those obtained by using proton NMR spectroscopy, thus showing that also for this type of compound both methods are useful for pK_a determinations.

The absence of a detectable emission at low pH can be explained by the energy-gap law,[3] by proton-induced quenching or by irreversible proton binding.[37,38] Because of the absence of a clear emission signal for the doubly protonated species, the pH$_i$(base) inflection points can therefore only be taken as apparent pK_a* values. Similar quenching processes have recently been reported for ruthenium complexes containing tetraazaphenanthrene and tetraimines.[37,38] The decrease of the emission intensity for compounds **1**–**3** between pH 3 and 6 can

Table 3 Ground- and excited-state acid–base properties of compounds **1**–**7** obtained in Britton–Robinson buffer

Compound	pK_a(acid)[a]	pH$_i$(base)[b]	pH$_i$(acid)[b]	pK_a*(acid)[c]
1 (N^4)	5.3 (8.7)	2.5	5.5	5.5
2 (N^2)	3.7 (8.7)	2.0	3.9	3.8
3	4.2 (9.4)	2.4	4.4	4.5
4	—	3.2	—	—
5 (N^4)	5.95 (9.20)	—	5.1	4.2
6 (N^2)	4.07 (9.20)	—	2.8	2.2
7	4.87 (9.80)	—	4.2	4.4

[a] Values in parentheses are the pK_a(acid) constants of the free ligands. [b] pH$_i$ values are the inflection points of the emission titration curves. [c] Values obtained using equation (2); data for compounds **5**–**7** taken from ref. 29.

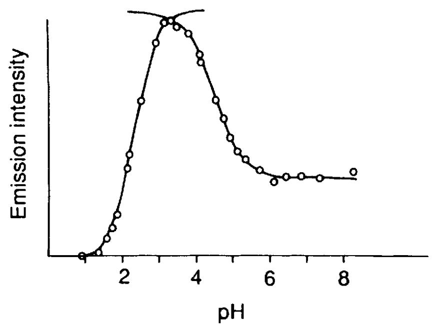


Fig. 4 Variation of the luminescence intensity of compound **3** between pH 1 and 8. Emission spectra were obtained in aqueous solution at room temperature

be explained by the deprotonation of the triazole ring.[19,24,29] The excited-state pK_a(acid), pK_a* (acid), values can be obtained from equation (2). The values in the last column of Table 3 are

$$\mathrm{p}K_a{}^* = \mathrm{pH_i} + \log(\tau_a/\tau_b) \qquad (2)$$

the pK_a*(acid) values as obtained using equation (2), with pH$_i$ as the inflection point from the luminescence intensity titration curve; τ_a and τ_b are the emission lifetimes of the protonated and deprotonated species, respectively. For these calculations the lifetimes given in Table 2 were used. Calculations using lifetimes obtained in Britton–Robinson buffers give the same results. Since the lifetimes obtained in aqueous solution are very short (15 ± 5 ns) and have a relatively large error, the MeCN values are preferred. Interestingly, the pK_a*(acid) values obtained for the complexes are very similar to the ground-state pK_a(acid) values and if anything they are slightly higher. The difference observed between the pK_a(acid) values of compounds **1** and **2** in the ground state is mirrored in the excited state. The ground- and excited-state pK_a(acid) values observed for compound **3** show that the effect of the introduction of a methyl group on the pyrazinyltriazole ligand is as observed for the corresponding pyridyltriazole compound **7**. In compound **3** the co-ordination mode of the triazole ring is *via* N_2 and pK_a(acid) values should be compared with those observed for compound **2**. It can be seen that the presence of the electron-donating methyl group does slightly increase the basicity of the co-ordinated ligand, both in the ground and the excited state.

Because of the absence of a detectable emission for compounds containing a protonated pyrazine ring, no emission maxima and lifetimes could be obtained for these species. It was, therefore, not possible to use equation (2) for an estimate of the pK_a* (base) values. Although it should be borne in mind that the inflection points obtained in the emission titrations are not real pK_a(base) values, they suggest nevertheless that the complexes containing neutral pyrazinetriazole ligands are up to four orders of magnitude more basic in the excited state than in the ground state [pK_a(base) = −1.8, pH$_i$(base) 2.0]. It is of interest that in the ground state no evidence for the presence of protonated pyrazine species was obtained above pH 1.

With regard to the excited-state acidity, two types of ruthenium complexes have so far been reported. In the first class of compounds the pK_a* value is lower than the ground-state pK_a. In these compounds upon excitation the electron becomes located on the auxiliary bipy ligands. The then formally $\mathrm{Ru^{III}}$ centre withdraws more electron density from the ligand which shows acid–base behaviour, with the result that the complex becomes more acidic in the excited state. Examples of this behaviour have been observed for compounds of the type $[\mathrm{Ru(bipy)_2(HL)}]^{2+}$, where HL is 4,7-dihydroxy-1,10-phenanthroline,[39] imidazoles,[17,40] triazoles,[24,25,29,40] and cyanide complexes.[41] On the other hand, if in the excited state the electron resides on the ligand showing acid–base properties then the ligand becomes more basic in the excited state. Such behaviour has been observed for $\mathrm{Ru(bipy)_2}$ complexes containing bipyrazine,[34,35] tetraazaphenanthrene[37] and 2,3-bis(pyridyl)pyrazine.[36,38] By comparison with these other pyrazine-based systems the increased basicity in the excited state obtained for the pyrazine-based protonation in the compounds reported here suggests that for the species involved in this protonation process the excited electron is located on the pyrazinetriazole ligand.

The trend observed for the pK_a*(acid) values of compounds **1**–**4** is quite different from that found for the corresponding pyridyltriazole compounds (see Table 2). The pK_a*(acid) values for the compounds reported here are slightly *higher* than in the ground state, while for the pyridyltriazole compounds a substantial *decrease* is observed compared to the ground-state values. Therefore the pyridyltriazole complexes clearly fall in the class of compounds where the excited electron is located on the bipy ligands, in contrast to the pyrazinetriazole-containing compounds. For the corresponding bipyrazine compound an increase of 4.2 pH units was observed for the first protonation step.[34] On the basis of resonance-Raman data a switch from a bipy-based LUMO for the deprotonated complexes to a pyrazinyltriazole-based LUMO for the protonated species has been suggested.[24] The similarities in ground- and excited-state pK_a(acid) values and also the small shift in absorption and emission maxima upon deprotonation further support this suggestion. Furthermore, the relatively small increase of the pK_a*(acid) value compared to the ground-state value suggests that while the excited electron is clearly located on the pyrazinyltriazole ligand when protonated, the major part of this electron density is present in the pyrazine ring.

Conclusion

The results obtained show that also for these pyrazinyltriazole ligands the co-ordination mode of the triazole ring strongly affects the physical properties of the ruthenium complexes. It is furthermore clear that the presence of the pyrazine ring, which lowers the LUMO in the complexes, leads to an increased basicity of the excited state. This is especially so for the protonation process involving the pyrazine ring. The small shifts observed for the absorption and emission maxima as a result of the acid–base behaviour of the triazole ring are unusual and in agreement with a shift from the pyrazinyltriazole-based LUMO for the protonated compound to a bipy-based one in the deprotonated species. Finally the slightly increased pK_a* value of the triazole ring suggests strongly that in the excited state there is an appreciable interaction between the triazole and the pyrazine ring.

Experimental

Materials.—$\mathrm{RuCl_3{\cdot}}x\mathrm{H_2O}$ was obtained from Johnson Matthey and used without further purification. Other chemicals were also used as received.

Syntheses of the Complexes.—An isomeric mixture of compounds **1** and **2**, and **3** and **4**, were synthesised as reported before.[24] Compounds **1** and **2** were separated by using a semi-preparative HPLC system consisting of a Gilson apparatus with a Linear UVIS 203 detector, a pre-column containing Whatman Pellicular cation exchange and a Magnum 9 Partisil cation-exchange column (10 mm × 25 cm). The mobile phase was acetonitrile–water (80:20) containing 0.08 mol dm^{-3} $LiClO_4$, with a flow rate of 2.0 cm^3 min^{-1}. Crystallisation as the PF_6^- salts from acetone–water yielded the pure isomers.

Physical Measurements.—Proton NMR spectra were obtained on a Bruker 300 MHz spectrometer. All peak positions are relative to tetramethylsilane. The NMR titration experiments were carried out by titrating a $(CD_3)_2CO$–D_2O (9:1) mixture with 1 mol dm^{-3} DCl–D_2O and 1 mol dm^{-3} NaOD–D_2O. The spectrophotometric pK_a determinations were carried out on a Shimadzu UV-240 spectrophotometer. The emission titrations were obtained on a Perkin-Elmer LS-5 luminescence spectrophotometer equipped with a red-sensitive Hamamatsu R928 photomultiplier tube. An emission slit width of 10 nm was used and the data were corrected for photomultiplier response. A Britton–Robinson buffer (a mixture of 0.04 mol dm^{-3} acetic acid, phosphoric acid and boric acid) was used as solvent for the spectrophotometric titrations. The compound was predissolved in the minimum amount of acetone or acetonitrile before addition to the buffer. The pH was adjusted by concentrated HCl or NaOH and measured by using a Corning 240 pH meter. HPLC-grade CH_3CN was used as solvent throughout the electrochemical measurements and was dried over 4 A molecular sieves and then filtered before use. Tetraethylammonium perchlorate was made by adding 70% $HClO_4$ to an aqueous tetraethylammonium bromide solution. The precipitate was collected by filtration, recrystallised three times from water and then dried at 50 °C in a vacuum oven overnight before use. Differential pulse polarographic measurements between -2.0 and $+2.0$ V were carried out in a 0.1 mol dm^{-3} solution of tetrabutylammonium perchlorate in CH_3CN, by using an EG & G Par C 303 instrument combined with an EG & G 384 B polarographic analyser. The scan rate was 4 mV s^{-1} with a pulse height of 20 mV; for the cyclic voltammograms a scan rate of 100 mV s^{-1} was used. The reference electrode was a saturated potassium chloride calomel electrode (SCE) in combination with a glassy carbon working electrode and a platinum wire as counter electrode. Before each measurement the CH_3CN solutions were purged with argon for 30 s. Lifetime experiments were performed on a modified Applied Photophysics single-photon counting instrument. At room temperature the measurements were carried out in acetonitrile and at 77 K in propionitrile–butyronitrile (4:5 v/v). Elemental analyses were carried out at University College Dublin.

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References

1 E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984.
2 T. J. Meyer, *Acc. Chem. Res.*, 1978, **11**, 94.
3 T. J. Meyer, *Pure Appl. Chem.*, 1986, **58**, 1193.
4 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
5 K. Kalyanasundaram, M. Grätzel and E. Pelizetti, *Coord. Chem. Rev.*, 1986, **69**, 57.
6 R. A. Krause, *Struct. Bonding (Berlin)*, 1987, **67**, 1.
7 S. D. Ernst and W. Kaim, *Inorg. Chem.*, 1989, **28**, 1520.
8 S. D. Ernst, Ph.D. Thesis, Frankfurt am Main, 1987.
9 F. Barigelletti, A. Juris, V. Balzani, P. Belser and A. von Zelewsky, *Inorg. Chem.*, 1987, **26**, 4115.
10 A. Juris, S. Campagna, V. Balzani, G. Gremaud and A. von Zelewsky, *Inorg. Chem.*, 1988, **27**, 3652.
11 E. S. Dodsworth and A. B. P. Lever, *Chem. Phys. Lett.*, 1985, **119**, 61.
12 L. De Cola and F. Barigelletti, *Inorg. Chim. Acta*, 1989, **159**, 169.
13 D. P. Rillema, G. Allen, T. J. Meyer and D. Conrad, *Inorg. Chem.*, 1983, **22**, 1617.
14 D. P. Rillema, D. G. Taghdiri, D. S. Jones, C. D. Keller, L. A. Worl, T. J. Meyer and H. A. Levy, *Inorg. Chem.*, 1987, **26**, 578.
15 G. H. Allan, R. P. White, D. P. Rillema and T. J. Meyer, *J. Am. Chem. Soc.*, 1984, **106**, 2613.
16 M. Haga, T. Mastumara-Inoue and S. Yamabe, *Inorg. Chem.*, 1987, **26**, 4148.
17 M. Haga, *Inorg. Chim. Acta*, 1983, **75**, 29.
18 A. M. Bond and M. Haga, *Inorg. Chem.*, 1986, **25**, 4507.
19 R. Hage, R. Prins, J. G. Haasnoot, J. Reedijk and J. G. Vos, *J. Chem. Soc., Dalton Trans.*, 1987, 1389.
20 R. Hage, A. H. J. Dijkhuis, J. G. Haasnoot, R. Prins, J. Reedijk, B. E. Buchanan and J. G. Vos, *Inorg. Chem.*, 1988, **27**, 2185.
21 F. Barigelletti, L. De Cola, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Inorg. Chem.*, 1989, **28**, 4344.
22 R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Inorg. Chim. Acta*, 1986, **118**, 73.
23 R. Hage, J. G. Haasnoot, D. J. Stufkens, T. L. Snoeck, J. G. Vos and J. Reedijk, *Inorg. Chem.*, 1989, **28**, 1413.
24 H. A. Nieuwenhuis, J. G. Haasnoot, R. Hage, J. Reedijk, T. L. Snoeck, D. J. Stufkens and J. G. Vos, *Inorg. Chem.*, 1991, **30**, 48.
25 B. D. J. R. Fennema, J. G. Haasnoot, R. Hage, J. Reedijk and J. G. Vos, *Inorg. Chim. Acta*, 1990, **171**, 223.
26 R. Hage, J. G. Haasnoot, J. Reedijk, R. Wang, E. Ryan, J. G. Vos, A. L. Spek and A. J. M. Duisenberg, *Inorg. Chim. Acta*, 1990, **174**, 77.
27 B. E. Buchanan, R. Wang, J. G. Vos, R. Hage, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1990, **29**, 3263.
28 B. E. Buchanan, E. McGovern, P. Harkin and J. G. Vos, *Inorg. Chim. Acta*, 1988, **154**, 1.
29 B. E. Buchanan, J. G. Vos, M. Kaneko, W. J. M. van der Putten, J. M. Kelly, R. Hage, R. A. G. de Graaff, R. Prins, J. G. Haasnoot and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1990, 2425.
30 P. J. Steel and E. C. Constable, *J. Chem. Soc., Dalton Trans.*, 1990, 1389.
31 E. C. Constable, R. P. G. Henney, T. A. Leese and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 443.
32 E. C. Constable, S. M. Elder, J. Healy and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 1669.
33 C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1990, 621.
34 R. J. Crutchley, N. Kress and A. B. P. Lever, *J. Am. Chem. Soc.*, 1983, **105**, 1170.
35 K. Shinozaki, Y. Kaiza, H. Hirai and H. Kobayashi, *Inorg. Chem.*, 1989, **28**, 3675.
36 W. Hosek, S. A. Tysoe, H. D. Gafney, A. D. Baker and T. C. Strekas, *Inorg. Chem.*, 1989, **28**, 1228.
37 A. Kirsch-de Mesmaeker, L. Jacquet and J. Nalsielski, *Inorg. Chem.*, 1988, **27**, 4451.
38 M. K. Nazeeruddin and K. Kalyanasundaram, *Inorg. Chem.*, 1989, **28**, 4251.
39 P. J. Giordano, C. R. Bock and M. S. Wrighton, *J. Am. Chem. Soc.*, 1978, **100**, 6960.
40 C. Long and J. G. Vos, *Inorg. Chim. Acta*, 1984, **89**, 125.
41 J. Davila, C. A. Bignozzi and F. Scandola, *J. Phys. Chem.*, 1989, **93**, 1373.

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