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Acid–Base Chemistry of some 1,2,4-Triazole and Imidazole Complexes of Ruthenium(II)bis(2,2′-bipyridyl)

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The acid–base chemistry of $[Ru(2,2'\text{-bipyridyl})_2(\text{imidazole})_2]^{2+}$ *and* $[Ru(2,2'\text{-bipyridyl})_2(1,2,4\text{-triazole})_2]^{2+}$ *has been studied in both the ground and the excited state. From the pH dependence of emission and absorption spectra it was found that both complexes are stronger acids in the excited state compared to the ground state. In sulphuric acid media the 1,2,4-triazole complex is a stronger base in the excited state than in the ground state. pK values for the different proton-equilibria are reported.*

Introduction

Ruthenium complexes of 2,2′-bipyridyl (bpy) are of interest because they have possible applications as catalysts for the photochemical dissociation of water and as redox-catalysts on modified electrodes. They are also used as models for the study of electron-transfer and excited state processes [1, 2]. $Ru(bpy)_3^{2+}$ has been studied intensively and in a range of complexes of the type $[Ru(bpy)_2L_2]^{n+}$ the influence of the ligand L on the physical properties of the compounds has been examined [2, 3]. In most studies L is a N-donor ligand with π-acceptor properties. However less attention has been paid to N-donor ligands with weak π-acceptor properties. Although 5-membered rings such as pyrazole, imidazole and 1,2,4-triazole have an extensive coordination chemistry they have not been studied in detail when bound to Ru(bpy)-compounds. In an earlier paper, the synthesis and properties of some 1,2,4-triazole complexes of $Ru(bpy)_2$ and a preliminary study of the acid–base chemistry of the 1,2,4-triazole complex were reported [4]. The synthesis and properties of corresponding pyrazole complexes was reported by Meyer *et al.* [5]. It was proposed that the study of the acid–base chemistry in the excited state can provide information on the charge redistribution which occurs upon excitation [6, 7] and therefore the acid base chemistry of a number of Ru complexes has been studied [7–11]. An increased acidity in the excited state was reported for $Ru(bpy)_2[4,7\text{-dihydroxy-}1,10\text{-phenanthroline}]^{2+}$ [7], while $[Ru(bpy)_2(4,4'\text{-dicarboxylate-}2,2'\text{-bipyridine})]$ is a stronger base in the excited state than in the ground state [8]. The protonation of cyano-ligands when bound to $Ru(bpy)_2$ groups has been reported by Demas [9] and for the bisimidazole complex of $Ru(bpy)_2$ pK_a values for the ground state have been reported [10]. Protonation equilibria in both ground state and excited state of the related complex $Ru(\text{bipyrazine})_3^{2+}$ have been investigated by Crutchley *et al.* [11].

In this paper we report the acid–base chemistry of 1,2,4-triazole (Htrz) and imidazole (HIm) bound to a $Ru(bpy)_2$- moiety. It was hoped that the study of proton-transfer reactions in both the ground and in the excited state would provide information about bonding of these weakly π-accepting ligands. The protonation equilibria were studied by analysing the pH dependency of both the absorption and the emission spectra of these complexes. The data have been analysed using a graphical method which is based on that described by Coleman [12].

Experimental

Materials

Reagent grade solvents and starting materials were used without further purification. $[Ru(bpy)_2(4\text{-Allyl},1,2,4,\text{-triazole})_2](PF_6)_2$ and $Ru(bpy)_2(trz)_2\cdot H_2O$ were prepared according to literature procedures [4].

Preparation of $Ru(bpy)_2(HIm)_2Cl_2\cdot 4H_2O$

1 mmol of $Ru(bpy)_2Cl_2\cdot 2H_2O$ (520 mg) was refluxed in 100 ml water/methanol mixture (1:1) in the presence of 6 mmol of imidazole for 3 hours. The solvent was then removed by rotary evaporation. The resulting solid dissolved in a minimum volume of water (5–10 ml), precipitated in acetone, filtered and dried under vacuo at room temperature (Yield 550 mg, 90%).

Anal. $[Ru(bpy)_2(HIm)_2]Cl_2\cdot 4H_2O$. Found: C, 44.3; H, 4.3; N, 16.2; Cl, 10.7%. Calcd: C, 45.12; H, 4.62; N, 16.19; Cl, 10.26%.

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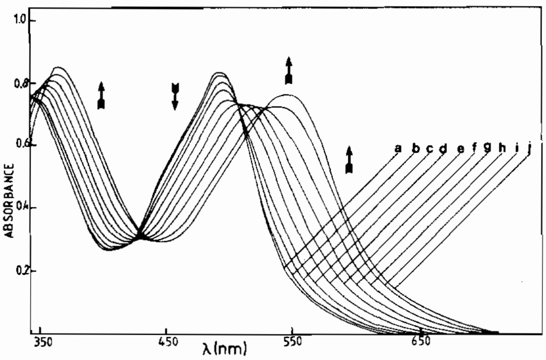

Fig. 1. pH Dependency of the absorption spectrum of $[Ru(bpy)_2(HIm)_2{}^{2+}]$ (1.1×10^{-4} *M*/l). Curves a–j are at pH 10.0; 10.6; 11.1; 11.4; 11.9; 12.3; 12.6; 13.0; 13.6; 14.0. The spectra were taken in a mixture of Britton-Robinson buffer and ethanol (1/1 v/v).

Preparation of $[Ru(bpy)_2(N\text{-}vinylimidazole)_2](PF_6)_2$

This compound was prepared by a method reported in the literature for corresponding 1,2,4-triazole complexes [4] (yield 60%). N-vinylimidazole = viz

Anal. $[Ru(bpy)_2(viz)_2](PF_6)_2$. Found: C, 40.1; H, 3.0; N, 12.6%. Calcd.: C, 40.39 H, 3.14; N, 12.57%.

A Britton-Robinson buffer containing acetic acid, phosphoric acid and boric acid (all 0.04 *M*) was used for experiments between pH 2 and 14. The pH of the buffer was changed by addition of a 10% NaOH solution in water.

Due to the insolubility in water of the deprotonated species $Ru(bpy)_2(trz)_2$ and $Ru(bpy)_2(Im)_2$ a mixture of 75% Britton-Robinson buffer and 25% ethanol was used as a solvent in the experiments described.

Equipment

Electronic spectra were recorded on a Pye-Unicam SP8-100 spectrophotometer. Peak positions are accurate to 1 nm. Emission spectra were obtained on a Perkin-Elmer LS5 – luminescence spectrometer. Spectra were recorded using an emission slitwidth of 10 nm and are not corrected for photomultiplier response. pH measurements were carried out using a PT1-6 pH meter.

Results

$[Ru(bpy)_2(HIm)_2]^{2+}$ *(1)*

The acid–base chemistry of this compound was studied using UV/VIS and emission spectroscopy. In Fig. 1 the absorption spectrum of compound 1 with varying pH is given. On increasing the pH a shift of the lowest metal to ligand charge transfer (MLCT) transition [4, 5] from 490 to 544 nm is observed. If the data are collected in a stepwise fashion, an initial isosbestic point at 506 nm degrades at pH = 12.3 with the eventual formation of a further isosbestic point at 527 nm. The changes are completely reversible and no decomposition of the Ruthenium complex is detected. The emission intensity (λ_{max} = 655 nm) decreases with increasing pH and no new emission is observed. In Fig. 2 the change in emission and absorption spectra is plotted as a function of the pH. For the corresponding N-substituted vinylimidazole complex; $[Ru(bpy)_2(viz)_2](PF_6)_2$ (*2*) no changes in absorption or emission spectra were obtained for pH values up to 14.

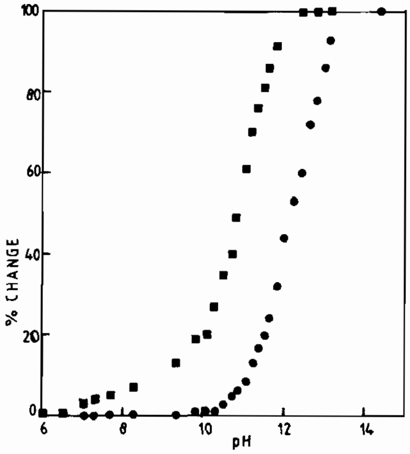

Fig. 2. Plots of percentage change in emission intensity at 655 nm (■) (excitation wavelength 490 nm) and percentage change in optical density at 490 nm (●) for $[Ru(bpy)_2(HIm)_2]^{2+}$ (0.9×10^{-4} *M*/l) in buffer/ethanol (3/1 v/v). The emission intensities have been corrected for change in optical density at 490 nm.

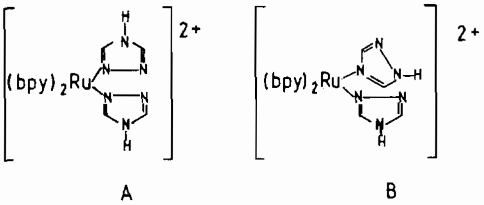

Fig. 3. Coordination isomers identified for $[Ru(bpy)_2(trz)_2]^{2+}$.

$[Ru(bpy)_2(Htrz)_2]^{2+}$ *(3)*

The $[Ru(bpy)_2(Htrz)_2]^{2+}$ complex obtained in the manner described in the literature [4] consists of a mixture of 2 coordination isomers. From infrared and ^1H NMR data it was concluded that about 70% has a type A structure while the remaining 30% has a structure of type B (see Fig. 3). Therefore both N-2 bound and N-4 bound Htrz is obtained. The deprotonated species $Ru(bpy)_2(trz)_2 \cdot H_2O$ (*4*)

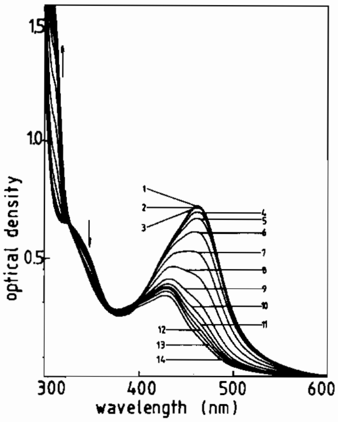

Fig. 4. pH Dependency of the absorption spectrum of [Ru$(bpy)_2(Htrz)_2]^{2+}$ (0.86×10^{-4} *M*/l) in sulphuric acid media. Curves 1–14 are at H_2SO_4 concentrations of 0; 1.5; 3.5; 6.8; 9.8; 14.0; 17.8; 22.3; 26.3; 29.9; 30.0; 35.9; 38.5; 40.9% (w/v).

could be isolated almost exclusively as the N-2 bound isomer. This isomer is probably preferred because of hydrogen bonding between the water molecules and the two free N-1 atoms. Infrared and NMR data suggest that when *4* is dissolved in acid and reprecipitated, isomer A is obtained, in yields better than 95%. This indicates that no isomerisation occurs in solution. It was decided to carry out the experiments exclusively with isomer A. $Ru(bpy)_2(trz)_2 \cdot H_2O$, was therefore used, this material is thought to be present for at least 95% in the N-2 bounded form. Protonation equilibria for the coordinated 1,2,4-triazole were studied using both UV/VIS and emission spectroscopy. Upon increasing pH a shift in the position of the lowest MLCT transition from 462 to 508 nm is observed. When the pH is changed in a stepwise fashion initially an isosbestic point at 476 nm is observed which at higher pH gives place to one at 492 nm. As for the corresponding imidazole complex a decrease of the emission intensity (λ_{max} 630 nm) with increasing pH is observed, no new emission was detected. For the corresponding 4-allyl,1,2,4-triazole complex [Ru$(bpy)_2(Altrz)_2](PF_6)_2$ no changes in absorption or emission spectra were observed for pH values up to 14.

[Ru(bpy)$_2$(Htrz)$_2$]$^{2+}$ in more Acidic Media

In slightly acidified water (pH = 4 approx.) the ultraviolet/visible spectrum of 3 has a λ_{max} at 460 nm with a shoulder at 425 nm. On lowering the pH, by the addition of concentrated H_2SO_4 (the concentration of ruthenium complex is maintained by appropriate addition of a concentrated solution of complex in water) the shoulder gains intensity, and the overall change is accompanied by the formation of an isosbestic point at approx. 410 nm. This isosbestic point is maintained to 14% H_2SO_4 (w/v) Further acidification degrades the isosbestic point with its eventual reformation at 390 nm. This isosbestic point in turn degrades at 38% H_2SO_4 (see Fig. 4). The emission intensity is found to decrease with increasing H_2SO_4 concentration (see Fig. 5). At high concentrations of H_2SO_4 a slow decomposition of the compound was observed. For *1*, the emission and absorption spectra are initially unaffected by increasing H_2SO_4 concentration, but at high H_2SO_4 concentrations, a rapid decomposition of the complex occurs.

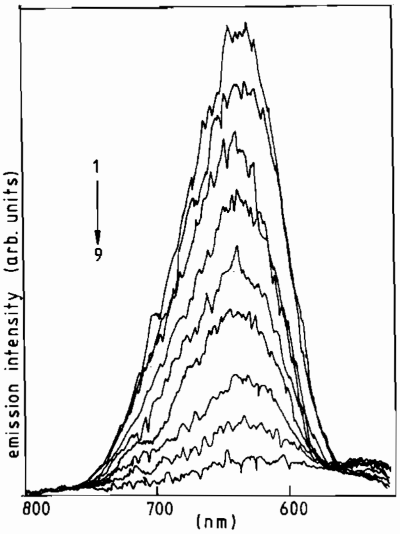

Fig. 5. pH Dependency of the emission spectrum of [Ru$(bpy)_2(Htrz)_2]^{2+}$ (0.86×10^{-4} *M*/l) in sulphuric acid media Curves 1–9 are at H_2SO_4 concentrations of 1.4; 3.5; 6.8; 9.8; 14.0; 17.8; 26.3; 30.0; 35.9% (w/v). Excitation wavelength 460 nm.

Discussion

[Ru(bpy)$_2$(HIm)$_2$]$^{2+}$ (1)

Absorption Spectra

The pH dependency of the absorption spectrum suggests a step-wise deprotonation of coordinated imidazole (eqn. (1))

$$\underset{\text{I}}{[Ru(bpy)_2(HIm)_2]^{2+}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{II}}{[Ru(bpy)_2(HIm)(Im)]^{+}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{III}}{Ru(bpy)_2(Im)_2} \qquad (1)$$

Further confirmation for this reaction scheme was provided by examining the UV/VIS spectrum of the corresponding N-substituted vinyl imidazole complex (*2*) which is pH independent. The changes observed in Fig. 1 and in particular the presence of

TABLE I. Spectra and pK_a Data for $[Ru(bpy)_2L_2]^{2+}$ Complexes and some Related Compounds.

Compound	Maxima for MLCT band of lowest energy[a]			pK_a	pK_a^*	Ref.
	Complex	Monodeprot. complex	Doubly deprot. complex			
$[Ru(bpy)_2(HIm)_2]^{2+}$	492	510	544	11.9 ± 0.2; 13.3 ± 0.3	10.8 ± 0.2	this work
imidazole				14.0		13
$[Ru(bpy)_2(Htrz)_2]^{2+}$	462	485	508	6.2 ± 0.2; 8.5 ± 0.2	5.2 ± 0.2	this work
1,2,4-triazole				10.26		14
$[Ru(bpy)_2(BiBzIH)]^{2+\,d}$	460	505	540^b	5.7 10.1		10
$(NH_3)Ru(HIm)Cl_3$				8.9		13
$[Ru(bpy)_2(4,7\text{-dihydroxyl}\cdot1,10\text{-phen}]^{2+}$	460		495^c	10.1	5.1	8

[a] Solvent Britton-Robinson buffer/ethanol (3:1 v/v). [b] 50% aqueous ethanol. [c] Aqueous solution. [d] BiBzIH; 2,2'-Bibenzimidazole.

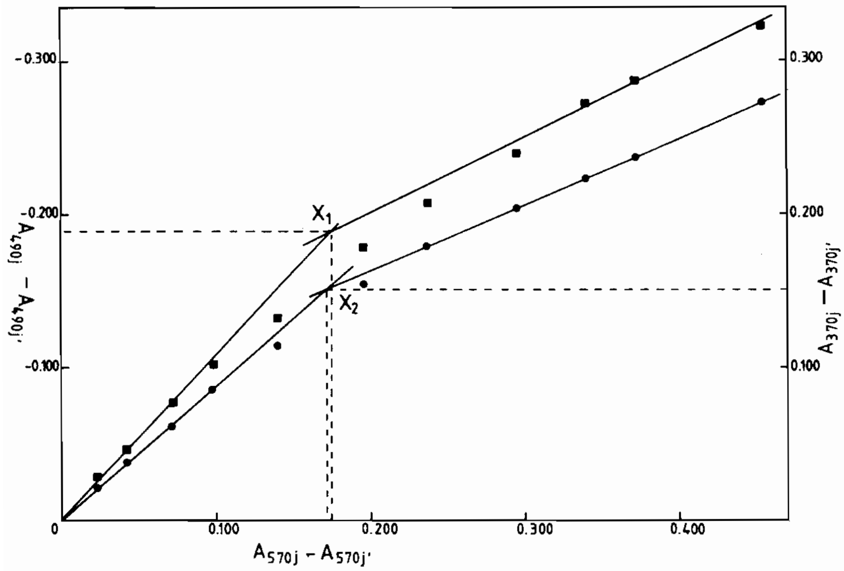

Fig. 6. Plot used for the estimation of the extinction coefficients at different wavelengths for the intermediate species $[Ru(bpy)_2(Htrz)(trz)]^+$. For details see text.

two successive isosbestic points suggest the existence of two closely spaced deprotonation steps. The number of species in solution can be determined by using a graphical method developed by Coleman *et al.* [12]. The absorbance of a complex mixture j at a wavelength i is denoted by A_{ij}. A plot of $A_{ij} - A_{ij'}$ *vs.* the corresponding difference at a different wavelength i' will give a straight line passing through the origin provided only two species are present. Such an analysis of our system shows that two species are present at both the low and the high end of the pH range, while more species are present at intermediate pH values. This tends to confirm the existence of two overlapping proton equilibria. It was found that this graphical method could also be used to estimate the pK_a values of the deprotonations steps observed in our systems. It was argued that at low pH values only species I and II are present and at high pH only II and III are present. The intercept of the two straight lines, obtained by plotting $A_{ij} - A_{ij'}$ against $A_{i'j} - A_{i'j'}$, should yield the optical density of the intermediate species II at wavelengths i and i'. If the optical density of the intermediate at a particular wavelength is obtained the pK_a values can be calculated using the formula

$$pH = pK_a + \log \frac{(acid)}{(base)} \qquad (2)$$

The concentrations of the acid and the base can now be calculated from the absorption spectra.

In Fig. 6, $A_{ij'}$ is the optical density at wavelength i at pH 9.94 and A_{ij} is the optical density at the same wavelength at pH values between 10.0 and 14. From the coordinates of X_1 and X_2 the optical density of the intermediate at 370, 490 and 570 nm can be calculated. Using this method, pK_a values with an accuracy of ±0.2 pH units were obtained. i and i′ were taken at different sides of an isosbestic point at wavelengths where the change in optical density with pH is large. The pK_a values obtained together with some values for related compounds have been given in Table I. The pK_a of the second deprotonation step was calculated assuming complete deprotonation in 25% ethanol, 75% (10% NaOH in water w/w) (v/v).

The two pK_a values found for *1* of 11.9 and 13.3 are lower than the value found for free imidazole (pK_a = 14). This indicates a reduction in electron density in the five-membered ring, in the ruthenium complex. This is most likely due to σ-donation from the imidazole ligand to the metal. The values for complex *1* fall in the range normally found for coordinated imidazoles [13]. Figure 1 shows that upon deprotonation a shift to lower energy is observed for the lowest energy MLCT band. This is possibly explained by increased π-donor properties of the imidazolyl ion [6].

Emission Spectra

The decrease of emission intensity with increasing pH has been attributed to the occurrence of the first deprotonation step. This is supported by the fact that the emission of the N-substituted vinyl-imidazole complex *2* is pH independent. No new emission for *1* was found at increasing pH but the presence of a very weak emission (<1% of original signal at pH = 2) can not be discounted. Emission titration curves have been used to calculate pK_a values in the excited state; pK_a^*. The most reliable values for pK_a^* are calculated from the luminescence lifetimes of the protonated and deprotonated species when both species are luminescent. As this method can not be used in our case, pK_a^* values were estimated from the luminescence titration curve. It is realised that the values obtained in this manner do not always represent the pK_a of the excited state [15]. However, we believe that in this case the pK_a^* can be estimated because the luminescence titration curve does not coincide with the ground state titration curve (see Fig. 2). The value of 10.8 calculated for pK_a^* from the titration curve, indicates an increased acidity of *1* in the excited state. This is in agreement with the observed shift to lower energy upon deprotonation of the lowest MLCT band. The position of the 0–0 transition in the absorption spectrum of the protonated and deprotonated species can be used to obtain an estimate of the pK_a^* [16].

$$pK_a^* = pK_a + \frac{2.86\Delta\nu}{2.3RT} \qquad (3)$$

The difference in position of the lowest MLCT band of the protonated and deprotonated species yields an approximate value for Δν. The value obtained for pK_a^* using this equation is 10.6 ± 0.3[‡]. This value agrees well with the one obtained from the luminescence titration curve. Discrepancies between values calculated from eqn. 1 and experimental values are most likely due to the absence of well defined 0–0 transitions.

$[Ru(bpy)_2(Htrz)_2]^{2+}$ (3)

Absorption Spectra

The pH dependency of the absorption spectrum of (*3*) and the absence of such a dependency for the corresponding 4-substituted allyl triazole complex $[Ru(bpy)_2(Altrz)_2](PF_6)_2$ (*4*) point to a deprotonation of the triazole ligand as in reaction 2.

$$[Ru(bpy)_2(Htrz)_3]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} [Ru(bpy)_2(Htrz)_3(trz)]^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} Ru(bpy)_2(trz)_2 \qquad (4)$$

The data suggest the presence of two different, but closely spaced protonation steps. Two pK_a values were calculated using the method outlined above (see Table I). The values obtained of 6.6 and 8.5 are well below the pK_a value of the free ligand 10.5. This is attributed to electron donation from triazole to the metal ion, which will reduce the electron density in the five-membered ring. The position of the lowest MLCT transition in the complexes *1* and *3* of respectively 492 and 462 nm for the protonated species and 508 and 544 nm for the deprotonated species seems to point to a somewhat better π-backbonding ability for Htrz while from these data the deprotonated imidazole complex is expected to have better electron donating properties. As expected the imidazole complex *1* is behaving more like the corresponding pyrazole complex [5]. The differences between the imidazole and pyrazole complexes and the triazole complex is explained by the presence of the extra nitrogen atom in triazole ring system.

Emission Spectra

A luminescence titration curve shows that in the excited state the coordinated triazole ligand has an increased acidity. The pK_a^* value of 5.2 obtained from this curve can be explained by an increase of electron donation from the triazole ligand in the excited state, in an effort to stabilise the Ru(III)

[‡] Δν was calculated using band maxima of 492 nm and 510 nm for $[Ru(bpy)_2(HIm)_2]^{2+}$ and $[Ru(bpy)_2(HIm)(Im)]^+$, respectively.

nucleus. From eqn. 3 a pK_a^* value of 5.0 ± 0.3 can be calculated[§], which agrees well with the experimental value. The difference between pK_a^* and pK_a, is relatively small, 1.4 and of the same order of magnitude as for *1* (1.1). The difference between the luminescence titration curve and the changes in optical density in the ground state are however large enough to assign the pH dependency of the emission spectra as an excited state and not as a ground state process. For *3* a decrease in emission intensity of 50% is measured where the change in optical density at 490 nm is only 5%. Figure 2 shows that for compound *1* a 15% change in optical density at the excitation wavelength (490 nm) corresponds to a drop of 50% in the emission intensity.

Behaviour of $[Ru(bpy)_2(Htrz)_2]^{2+}$ in Strongly Acidic Media

The changes observed in the emission and absorption spectra for *3* in strongly acidic media (pH < 1) have been attributed to a protonation of the free nitrogen atom. This is supported by the behaviour of compound *1*. At high acid concentration (>4 *M*) *3* appears to decompose slowly. This slow decomposition makes determination of the 'final' spectrum in the reaction sequence difficult, therefore no ground state pK_b values could be determined. The shift of the lowest MLCT band from 460 nm to 430 nm upon protonation indicates increased π-acceptor properties for H_2trz^+ (see Fig. 4). It could however not be established whether the species absorbing at 430 nm is the mono- or the diprotonated complex.

Emission Spectra

Irradiation of *3* into its lowest energy absorption band at 460 nm results in an emission at approximately 650 nm in slightly acidic water at room temperature. The intensity of this emission decreases with decreasing pH and in 14% H_2SO_4 (w/v) the intensity of the emission has been halved, while the optical density at the excitation frequency has diminished only by some 15%. Assuming that the emission is only due to the presence of $[Ru(bpy)_2(Htrz)_2]^{2+}$, a pK_b^* value for the first protonation step of this species can be estimated. A value of −0.5 for pK_b^* was obtained from a luminescence titration curve. The luminescence intensities were corrected for a decrease in optical density at the excitation wavelength. The pK_b^* value was calculated assuming complete dissociation for H_2SO_4. From the variation of UV/VIS spectra with pH, it would seem that the ground state pK_b s are significantly more negative than this.

Conclusions

The pH dependency of the absorption spectra of *1* and *3* show that both imidazole and 1,2,4-triazole are stronger acids when bound to the $Ru(bpy)_2$ moiety compared to the free ligands. Similar behaviour has been reported in the literature for other compounds. This has been explained by a reduced electron density in the five-membered ring caused by electron donation from the ligand to the metal [7, 13].

It was found from the emission data that both complexes are stronger acids in the excited state than in the ground state. The increased acidity is most likely due to the metal-to-bpy charge transfer process. This is thought to cause an increased electron drain from the five-membered ring. In the anionic form both ligands become strong π-donor ligands and are better able to stabilise the Ru(III) centre, which is formed by metal-to ligand charge-transfer.

In sulphuric acid media protonation of coordinated triazole occurs. However, a slow decomposition in strong acid prevents a detailed study. It is clear that in the protonated form the ligand (H_2trz^+) has stronger π-acceptor properties. This is evidenced by a shift to higher energy of the lowest MLCT band and by the increased basicity of the complex in the excited state.

It is rather unusual that the electronic behaviour of a ligand which can have a positive, neutral or a negative charge can be studied in all these three states in the same compound. The triazole complex $[Ru(bpy)_2(Htrz)_2]^{2+}$ is an example of such a compound. The change in charge has a dramatic effect on the electronic properties of triazole ligand. In fact the ligand changes from a π-donor ligand (trz^-) to a ligand with π-acceptor properties (H_2trz^+) as indicated by the change in the position of the lowest MLCT band.

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[§] $\Delta\nu$ was calculated using band maxima of 462 nm and 485 nm for $[Ru(bpy)_2(Htrz)_2]^{2+}$ and $Ru(bpy)_2[(Htrz)(trz)]^+$, respectively.

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