# Synthesis, spectral and redox properties of a new series of aqua complexes of ruthenium(II)

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**Abstract**

A series of new aqua-ruthenium complexes containing the tridentate facial ligand tpm (tris(1-pyrazolyl)methane) and the 2,2′-bipyridine (bpy) ligand disubstituted in the 4,4′ positions with electron-donating and electron-withdrawing groups of general formula $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (X = H, $CH_3$, $NO_2$, $NH_2$, $COOC_2H_5$) have been prepared and characterised. Their spectroscopical and electrochemical properties have been investigated by means of UV–Vis, cyclic voltammetry and coulometry. The Ru(III/II) redox potential, measured versus the SSCE reference electrode, ranges from 0.56 V for the aqua ruthenium complex containing $4,4'\text{-}(NO_2)_2$-bpy to 0.21 V for the one that contains $4,4'\text{-}(NH_2)_2$-bpy. Similarly, the values for the Ru(IV/II) redox couples for the same complexes are 0.65 and 0.40 V, respectively. Thus a family of related oxidants, Ru(IV)=O, with tuneable redox potentials have been generated upon oxidation of the corresponding aqua complex.

*Key words:* Ruthenium complexes; Aqua complexes; Bidentate amine complexes; Chelate complexes; Redox properties

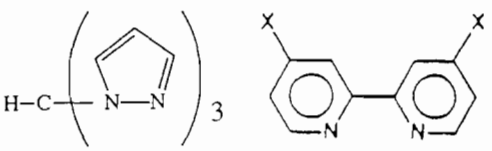
## Introduction

In recent years, many new ruthenium complexes have been prepared and characterised because of their interest in photophysics [1], catalysis [2] and bioinorganic chemistry [3].

Of special interest are aqua complexes of Ru(II) since they can be easily oxidised to higher oxidation states that have an extensive stoichiometric and catalytic chemistry as oxidants [4–13]. Those higher oxidation states can be reached by sequential oxidation and proton loss from the corresponding aqua complexes, e.g. eqn. (1) [4a, b].

$$Ru^{II}(H_2O)^{2+} \underset{+1e^-,\,+1H^+}{\overset{-1e^-,\,-1H^+}{\rightleftharpoons}} Ru^{III}(OH)^{2+} \underset{+1e^-,\,+1H^+}{\overset{-1e^-,\,-1H^+}{\rightleftharpoons}} Ru^{IV}(O)^{2+} \quad (1)$$

We were interested in creating a family of related oxidants, containing the same $Ru^{IV}$=O active species, but with controlled redox potentials. Therefore, we decided to prepare Ru–aqua complexes with systematic variations on a surrounding ligand but maintaining a constant metal environment. Here we report the synthesis, spectral and redox properties of a series of ruthenium–aqua complexes containing the tridentate facial ligand tpm (tris(1-pyrazolyl)methane) and 4,4′-disubstituted bpy of general formula $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (X = H, $CH_3$, $NO_2$, $NH_2$, $COOC_2H_5$).




tpm $4,4'\text{-}(X)_2\text{-bpy}$

## Experimental

### *Materials*

All reagents were ACS grade and were used without further purification. The water used was purified by a Millipure system. All reactions were carried out under argon unless explicitly specified. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

### *Preparations*

bpy and 4,4′-dimethyl-bpy ($4,4'\text{-}(CH_3)_2$-bpy) were supplied by Aldrich. 4,4′-diamino-bpy ($4,4'\text{-}(NH_2)_2$-bpy),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4,4'-dinitro-bpy (4,4'-$(NO_2)_2$-bpy) and 4,4'-diethylester-bpy (4,4'-$(COOC_2H_5)_2$-bpy) were prepared according to literature procedures [13]. $[(tpm)Ru^{II}(H_2O)_3](p\text{-}CH_3C_6H_4SO_3)_2 \cdot 1.5H_2O$ (**1**) was synthesised as previously described [14d].

*[(tpm)(b)Ru$^{II}$(H$_2$O)](X)$_2$ (2: X=PF$_6$, b=bpy; 3: X=ClO$_4$, b=bpy; 4: X=PF$_6$, b=4,4'-(CH$_3$)$_2$-bpy; 5: X=ClO$_4$, b=4,4'-(CH$_3$)$_2$-bpy; 6: X=PF$_6$, b=4,4'-(COOC$_2$H$_5$)$_2$-bpy)*

A 100 mg sample of $[(tpm)Ru^{II}(H_2O)_3](p\text{-}CH_3C_6H_4SO_3)_2 \cdot 1.5H_2O$ (**1**) was dissolved in 20 ml of a previously degassed solution of 0.1 M *p*-toluenesulfonic acid in water and 96% ethanol (1:1). Afterwards 100% excess of the stoichiometric amount of the 'b' ligand was added and the resulting yellow solution refluxed for 5 h (only 2 h for complex **6** since longer time yielded decomposition products). Then the volume of the solution was reduced till dryness at low pressure on a rotary evaporator. 40 ml or water were added and the insoluble 'b' ligand filtered off. Upon addition of 2 ml of a saturated solution of $X^-$ ($NH_4PF_6$ or $NaClO_4$) to the filtered solution, an orange solid appeared which was filtered on a Büchner funnel, washed with a minimum amount of cold water and dried under vacuum. **2**: yield 85.1 mg, 80.9%. *Anal.* Calc. for $C_{20}H_{20}F_{12}N_8OP_2Ru$: C, 30.81; H, 2.57; N, 14.38. Found: C, 30.97; H, 2.52; N, 14.69%. **3**: yield 66.2 mg, 71.28%. **4**: yield 91.4 mg, 83.9%. *Anal.* Calc. for $C_{22}H_{24}F_{12}N_8OP_2Ru$: C, 32.71; H, 2.97; N, 13.88. Found: C, 32.50; H, 2.75; N, 14.05%. **5**: yield 78.3 mg, 81.0%. **6**: yield 61.6 mg, 48.5%. $^1$H NMR ($d_6$-acetone): $\delta$ 1.43 (t, 6, $J_{CH_3CH_2}$=8.5 Hz, $CH_3$), 4.54 (q, 4, $CH_2$), 6.42 (dd, 1, $J_{\alpha'\beta'}$=2.7 Hz, $J_{\beta'\gamma'}$=1.9 Hz, $H_{\beta'}$), 6.95 (dd, 2, $J_{\alpha\beta}$=2.7 Hz, $J_{\beta\gamma}$=1.9 Hz, $H_\beta$), 7.00 (d, 1, $H_{\gamma'}$), 8.12 (dd, 2, $J_{ba}$=6.1 Hz, $J_{bd}$=1.4 Hz, $H_b$), 8.41 (d, 2, $H_\gamma$), 8.62 (d, 1, $H_{\alpha'}$), 8.86 (d, 2, $H_\alpha$), 9.22 (d, 2, $H_a$), 9.49 (d, 2, $H_d$), 9.98 (s, 1, $H_8$). *Anal.* Calc. for $C_{26}H_{30}F_{12}N_8O_6P_2Ru$: C, 33.15; N, 11.90; H, 3.19. Found: C, 32.84; N, 12.06; H, 3.31%.

Complexes **3** and **5** have been previously described and characterised, using an alternative synthesis [14a].

*[(tpm)(4,4'-(NH$_2$)$_2$-bpy)Ru$^{II}$(H$_2$O)](p-CH$_3$C$_6$H$_4$SO$_3$)$_2$·1H$_2$O (7)*

A 100 mg sample of **1** was dissolved in 20 ml of a previously degassed solution of 0.1 M *p*-toluenesulfonic acid in water and 96% ethanol (1:1). Then 50 mg of 4,4'-$(NH_2)_2$-bpy were added and the resulting yellow solution refluxed for 18 h. On cooling, orange crystals appeared which were filtered on a Büchner funnel, washed with a small amount of cold ethanol and dried under vacuum. Yield 60.2 mg, 50.7%. $^1$H NMR ($d_6$-acetone: $D_2O$, 3:1): $\delta$ 2.30 (s, 6, $CH_3$), 6.37 (dd, 1, $J_{\alpha'\beta'}$=2.7 Hz, $J_{\beta'\gamma'}$=1.9 Hz, $H_{\beta'}$), 6.7–6.8 (m, 5, $H_{\beta'+\gamma'+b}$), 7.18 (d, 4, $J_{AB}$=7.8 Hz, $H_A$), 7.63 (d, 4, $H_B$), 7.68 (d, 2, $J_{bd}$=2.1 Hz, $H_d$), 8.10 (d, 2, $J_{ab}$=6.6 Hz, $H_a$), 8.37 (d, 2, $J_{\gamma\beta}$=1.9 Hz, $H_\gamma$), 8.48 (d, 1, $H_{\alpha'}$), 8.61 (d, 2, $J_{\alpha\beta}$=2.7 Hz, $H_\alpha$). *Anal.* Calc. for $C_{34}H_{38}N_{10}O_8S_2Ru$: C, 46.42; H, 4.32; N, 15.93. Found: C, 46.51; H, 4.48; N, 15.69%.

*[(tpm)(4,4'-(NO$_2$)$_2$-bpy)Ru$^{II}$(H$_2$O)](ClO$_4$)$_2$ (8)*

A 100 mg sample of **1** was dissolved in 20 ml of a previously degassed solution of 0.1 M *p*-toluenesulfonic acid in water and 96% ethanol (1:1). Then 67 mg of 4,4'-$(NO_2)_2$-bpy were added and the resulting yellow solution refluxed for 5 h. On cooling a white solid of unreacted bpy ligand precipitated which was filtered off. Then the volume was reduced to approximately 5 ml, on a rotary evaporator, and upon addition of 1 ml of saturated $NaClO_4$ a brownish red solid appeared which was filtered on a Büchner funnel, washed with a small amount of cold water and dried under vacuum. Yield 75.7 mg, 72.1%. $^1$H NMR ($d_4$-methanol:$D_2O$, 1:1): $\delta$ 6.39 (dd, 1, $J_{\alpha'\beta'}$=2.7 Hz, $J_{\beta'\gamma'}$=1.9 Hz, $H_{\beta'}$), 6.72 (d, 1, $H_{\gamma'}$), 6.92 (dd, 2, $J_{\alpha\beta}$=2.7 Hz, $J_{\beta\gamma}$=1.9 Hz, $H_\beta$), 8.37 (d, 2, $H_\gamma$), 8.41 (dd, 2, $J_{ba}$=6.8 Hz, $J_{bd}$=2.8 Hz, $H_b$), 8.48 (d, 1, $H_{\alpha'}$), 8.66 (d, 2, $H_\alpha$), 9.10 (d, 2, $H_a$), 9.62 (d, 2, $H_d$). *Anal.* Calc. for $C_{20}H_{18}N_{10}O_{13}Cl_2Ru$: C, 30.85; H, 2.31; N, 17.99. Found: C, 30.66; H, 2.31; N, 17.94%.

The $^1$H NMR labels for the tpm and substituted bpys are keyed to Fig. 1. For the *p*-toluenesulfonate anion, the aromatic ring hydrogen atoms have been labelled $H_A$ and $H_B$. $H_A$ stands for the two equivalent hydrogen atoms proximate to the methyl group whereas $H_B$ represents the two hydrogen atoms nearest to the sulfur atom.

*Measurements*

All measurements were performed at 25±0.1 °C. Cyclic voltammetry measurements were carried out by using a PAR model 173 potentiostat/galvanostat or a PAR 264A polarographic analyser. Coulometric measurements were made using a PAR 179 digital coulometer. The cyclic voltammetric measurements utilised a teflon-sheathed glassy-carbon disk (1.5 mm radius) as a working electrode; a platinum wire as the auxiliary electrode and a saturated sodium chloride calomel electrode (SSCE) in a one compartment cell. The concentrations of the complexes were approximately 0.5 mM, and unless explicitly specified the scan rate was 100 mV/s. The pH measurements were made with a Radiometer pHM62 pH-meter. In aqueous solutions the pH was adjusted from 0 to 2 with either perchloric acid or *para*-toluenesulfonic acid. Sodium perchlorate or sodium *para*-toluenesulfonate, respectively, were

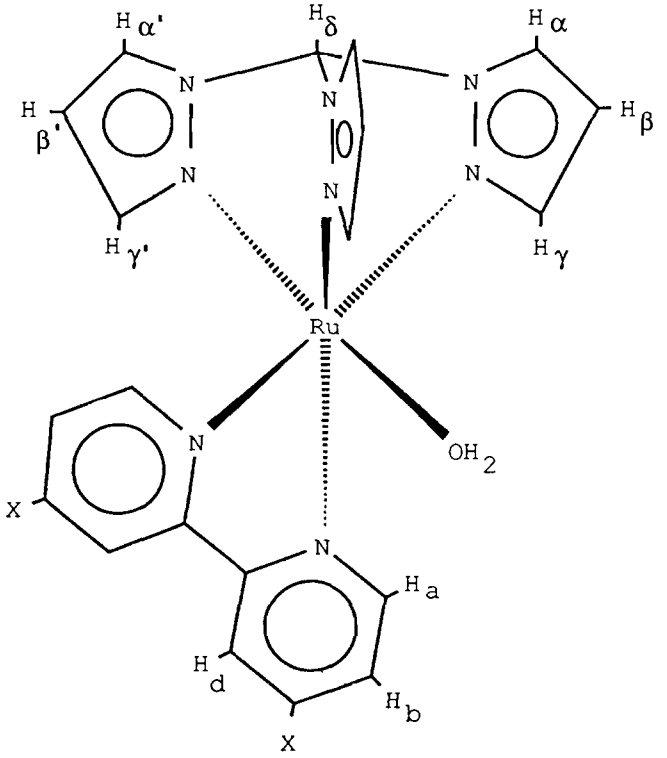


Fig. 1. Drawn structure of $[(tpm)(4,4'\text{-}X_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ illustrating the coordination geometry. The tpm and 4,4-$X_2$-bpy protons are labelled according to their assignment in 'Experimental'.

added to keep a minimum ionic strength $\mu = 0.1$ M, from pH = 2–9 with $\mu = 0.1$ M phosphate buffers and from pH 9 to 12 with $\mu = 0.1$ M borate buffers. Dilute NaOH, $CO_2$ free solutions were used to reach pH 12–13 with sodium perchlorate added as the electrolyte. All $E_{1/2}$ values reported in this work were estimated from cyclic voltammetry as the average of the oxidative and reductive peak potentials $(E_{p,a} + E_{p,c})/2$. UV–Vis spectra were recorded using a Hewlett-Packard model 8451A UV–Vis diode-array spectrophotometer with 1 cm quartz cells. The $^1H$ NMR spectra were recorded on an IBM AC-200 spectrometer.

## Results and discussion

The synthetic strategy used here to prepare the different Ru–aqua complexes consists of the substitution of two aqua groups of the $[(tpm)Ru^{II}(H_2O)_3]^{2+}$ complex by a bipyridine ligand

$$[(tpm)Ru^{II}(H_2O)_3]^{2+} + 4,4'\text{-}(X)_2\text{-}bpy \longrightarrow [(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+} + 2H_2O$$

leading to mono-aqua complexes of general formula $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (X = H, $CH_3$, $NO_2$, $NH_2$, $COOC_2H_5$). This synthetic method runs under very mild conditions and forms the mono-aqua complexes in high yields.

*Spectral properties*

The $^1H$ NMR spectra of the mono-aqua ruthenium complexes **6**, **7** and **8** were recorded in $d_6$-acetone, $d_6$-acetone/$D_2O$ (3:1) and $d_4$-methanol/$D_2O$ (1:1), respectively. The assignments are listed in 'Experimental' and were made by taking advantage of the symmetry of the complexes and the different magnitude of the coupling constants of the pyrazolyl and pyridyl rings [15]. Because of the molecular symmetry there is an equivalence of two pyrazolyl rings of the tpm ligand and the two pyridyl rings of the bpy ligand which greatly simplifies the spectra and their assignments. The methylenic proton of the tpm ligand is only observed in the spectrum of **6** since in **7** and **8** there is a fast exchange process with $D_2O$. A similar phenomenon prevents the observation of the $NH_2$ protons in the $^1H$ NMR spectrum of the $[(tpm)(4,4'\text{-}(NH_2)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ complex.

The UV–Vis spectra of the $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (X = $NH_2$, H, $NO_2$) complexes recorded in a $\mu = 0.1$ M phosphate buffer solution at pH = 7 are depicted in Fig. 2. UV–Vis spectral features of these complexes and their $Ru^{III}$ oxidised analogs at pH = 7 are summarised in Table 1. For the $Ru^{II}H_2O$ complexes, the low energy absorption bands are $d\pi \rightarrow \pi^*$ (bpy) in character [16] whereas the bands between 320 and 330 nm are mainly $d\pi \rightarrow \pi^*$ (tpm) [14b]. This assignment has been made bearing in mind that for the $[(tpm)Ru^{II}(H_2O)_3]^{2+}$ complex the $d\pi \rightarrow \pi^*$ transition occurs at 326 nm [14d]. While the tpm based transitions remain more or less unchanged as expected, systematic trends do exist in the pattern of the bpy based transitions. The absorptions, observed in the UV–Vis spectra for the $Ru^{III}OH$ analogs, can be tentatively assigned to MLCT type of transitions based on their high extinction coefficients.

The energy gaps between the $(d\pi)^6$ ground state and the $(d\pi)^5(\pi^*)^1$ excited states increases for electron-donating substituents. This happens because the donating substituents increase the energy of the $\pi^*(4,4'\text{-}(X)_2\text{-}bpy)$ acceptor orbitals to a greater degree than they do the $d\pi(Ru)$ donor orbitals [14b]. The greater sensitivity of the $\pi^*$ (bpy) orbitals to substituent changes is expected since the substituents are directly bonded to bpy. The influence on the $d\pi(Ru)$ orbital is lower but still notable given the approximately 6 Å distance separating the substituents from the metal. The opposite effect is observed for electron-withdrawing substituents thus decreasing the gap between the $(d\pi)^6$ ground state and the $(d\pi)^5(\pi^*)^1$ excited states.

Chemical oxidations to higher oxidation states were monitored spectrophotometrically. The $Ru^{III}OH$ species

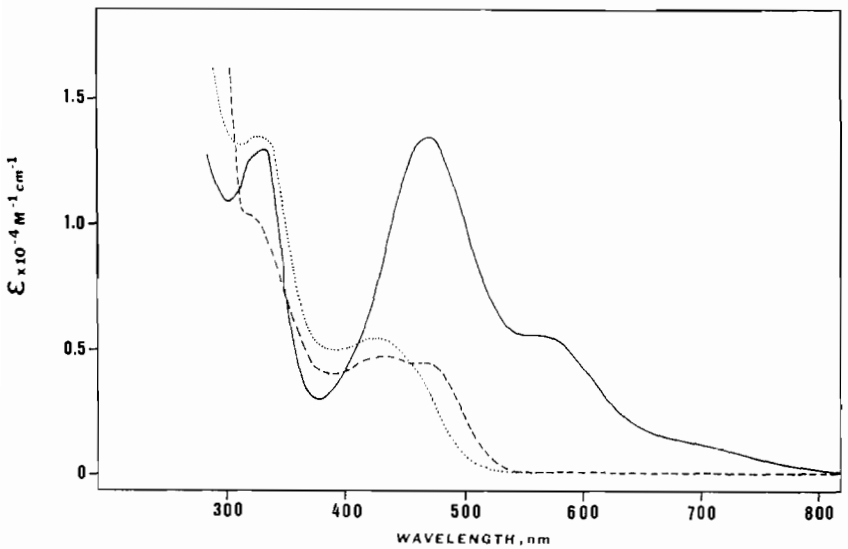


Fig. 2. UV–Vis spectra at pH 7 of complex $[(tpm)(bpy)Ru^{II}(H_2O)]^{2+}$ (3) (– – –), $[(tpm)(4,4'\text{-}(NH_2)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (7) (· · · · ·) and $[(tpm)(4,4'\text{-}(NO_2)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (8) (——).

TABLE 1. UV–Vis absorption maxima and extinction coefficients for $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (X = H, $NO_2$, $NH_2$) complexes in a $\mu = 0.1$ M phosphate buffer solution at pH = 7 and for their corresponding oxidised species $Ru^{III}OH$ at the same pH

| X | λ (nm) (log ε) | |
|---|---|---|
| | $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)\text{-}Ru^{II}(H_2O)]^{2+}$ | $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)\text{-}Ru^{III}(OH)]^{2+}$ |
| H | 470 (3.63) $d\pi \rightarrow \pi^*$ (bpy) | 380 (3.77) |
| | 426 (3.66) $d\pi \rightarrow \pi^*$ (bpy) | |
| | 328 (3.97) $d\pi \rightarrow \pi^*$ (tpm) | |
| $NH_2$ | 420 (3.76) $d\pi \rightarrow \pi^*$ (bpy) | 520 (4.00) |
| | 330 (4.15) $d\pi \rightarrow \pi^*$ (tpm) | 350 (3.32) |
| $NO_2$ | 570 (3.76) $d\pi \rightarrow \pi^*$ (bpy) | 470 (3.83) |
| | 470 (4.13) $d\pi \rightarrow \pi^*$ (bpy) | 380 (3.81) |
| | 330 (4.11) $d\pi \rightarrow \pi^*$ (tpm) | 320 (4.11) |

are stable and can be reached by adding an equivalent of $ClO^-$ to the $Ru^{II}H_2O$ complexes in a pH = 7 buffered solution. When two equivalents of the oxidising agent $ClO^-$ are added to the initial $Ru^{II}H_2O$ solution, the $Ru^{IV}O$ species are generated. In all cases, the UV–Vis spectra of the $Ru^{IV}O$ species from 300 to 820 nm are featureless. For the 4,4′-disubstituted complexes, spectral changes were observed to appear within minutes after the addition of the oxidising agent indicating that decomposition processes were occurring. A possible explanation for the instability of the $Ru^{IV}O$ species is that upon reaching oxidation state IV one of the Ru–N bonds of a pyrazolyl ring might be broken with subsequent coordination of a solvent molecule in the free position. A similar phenomenon had been observed for the $[(tpm)Ru^{II}(H_2O)_3]^{2+}$ complex upon reaching higher oxidation states [14d]. For the $[(tpm)(4,4'\text{-}(NH_2)_2\text{-}bpy)Ru^{IV}(O)]^{2+}$ (7) complex, the oxo group might be capable of oxidising the amino group of another molecule of 7 giving rise to an additional intermolecular decomposition pathway.

*Redox chemistry*

$pK_a$ and electrochemical data at pH = 7 in a $\mu = 0.1$ M phosphate buffer solution for the aqua complexes prepared in this work are given in Table 2. The Pourbaix diagrams for complexes $[(tpm)(4,4'\text{-}(NH_2)_2\text{-}bpy)\text{-}Ru^{II}(H_2O)]^{2+}$ (7) and $[(tpm)(4,4'\text{-}(NO_2)_2\text{-}bpy)Ru^{II}\text{-}(H_2O)]^{2+}$ (8) are depicted in Figs. 3 and 4, respectively, including the experimental points and with labelling of predominant zones for each species. The redox potentials in all cases were measured from cyclic voltammogram experiments which were run at a scan rate of

TABLE 2. $pK_a$ and electrochemical data at pH = 7 in a $\mu = 0.1$ M phosphate buffer solution for the aqua complexes $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (X = H, $CH_3$, $NH_2$ $NO_2$)

| X | $pK_{a,II}$ | $pK_{a,III}$ | $E_{1/2}$ (V) | | | $\Delta E^a$ |
|---|---|---|---|---|---|---|
| | | | IV/III | III/II | IV/II | |
| H[b] | 10.8 | 1.9 | 0.71 | 0.40 | 0.55 | 0.31 |
| $CH_3$[c] | 11.0 | 2.05 | 0.67 | 0.35 | 0.51 | 0.32 |
| $NH_2$[c] | 11.4 | 3.5 | 0.59 | 0.21 | 0.40 | 0.38 |
| $NO_2$[c] | 8.7 | 1.0 | 0.75 | 0.56 | 0.65 | 0.19 |

[a]$\Delta E$ represents, $E_{1/2}$ Ru(IV/III) − $E_{1/2}$ Ru(III/II) in volts. [b]Ref. 14a. [c]This work.

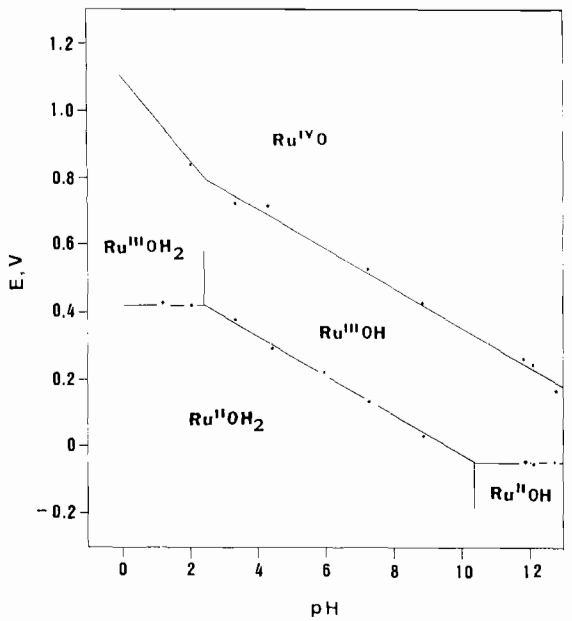


Fig. 3. $E_{1/2}$ vs. pH or Pourbaix diagram of $[(tpm)(4,4'\text{-}(NH_2)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (**7**). The pH–potential regions of stability for the various oxidation states and their dominant proton composition are indicated by using abbreviations such as $Ru^{II}OH_2$, for example for $[(tpm)(4,4'\text{-}(NH_2)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$. The $pK_a$ values are shown by the vertical solid lines in the various $E$–pH regions.

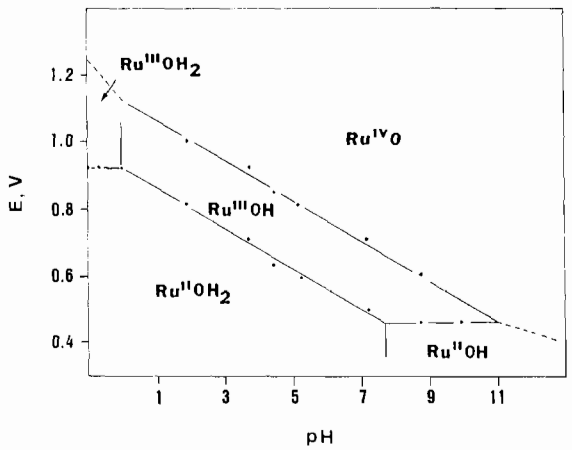


Fig. 4. $E_{1/2}$ vs. pH or Pourbaix diagram of $[(tpm)(4,4'\text{-}(NO_2)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (**8**).

100 mV/s in 0.1 M ionic strength solutions versus the SSCE reference electrode. Even though the free ligand 4,4'-$(NH_2)_2$-bpy can be easily protonated, when coordinated to a metal centre it becomes a very weak base [17, 18] which remains unprotonated within the pH range 1–13. As a consequence, the Pourbaix diagram of complex **7** does not show any pH interaction due to the acid–base properties of the amino group.

The electrochemistry of the mono-aqua complexes in aqueous solutions provides evidence for the presence of two pH dependent oxidative redox waves. The first oxidative wave is a one-electron reversible process ($E_{p,a} - E_{p,c} = 60$ mV) which is assigned to the Ru(III/II) redox couple. Coulometric experiments further corroborate the one-electron nature of this first wave. This III/II wave is electrochemically reversible over the pH range 0–13 in the conditions described above. The second redox wave is assigned to the Ru(IV/III) redox couple and is also reversible at basic pH. In contrast, at acidic pH the wave becomes electrochemically irreversible and for $pH < 2$ the wave is not observed for any of complexes reported here.

For the amino complex **7**, a third chemically irreversible ligand-based wave is observed at $E_{p,a} = 1.20$ V (pH = 2). This process is assigned to the irreversible oxidation of the amino group attached at the bpy ligand. Comparable processes at similar potentials have been previously described for the $[(bpy)_2Ru^{II}(5\text{-}NH_2\text{-}phen)]^{2+}$ (5-$NH_2$-phen is 5-amino-1,10-phenanthroline) and $[(bpy)_2Ru^{II}(4\text{-}NH_2\text{-}py)_2]^{2+}$ (4-$NH_2$-py is 4-aminopyridine) complexes [18].

As a general trend $E_{1/2}$ redox potentials decrease with electron donor groups in the 4,4' position of the bpy ligand whereas with electron-withdrawing groups the $E_{1/2}$ potentials increase as expected. The III/II couple is more sensible than the IV/III couple to changes in the electron-donating or -withdrawing nature of the 4,4' substituent. As a consequence, the $\Delta E_{1/2}$ potential (IV/III − III/II), and therefore the zone of stability of the $Ru^{III}OH$ species, increases with electron-donating groups and decreases with electron-withdrawing groups when compared to the unsubstituted bpy complex $[(tpm)(bpy)Ru^{II}(H_2O)]^{2+}$ (**3**) (see Table 2). Thus at pH = 7, a bpy ligand that contained a sufficiently strong electron-withdrawing group would have an Ru(III/II) redox couple with a higher redox potential than the corresponding Ru(IV/III) redox couple.

In an electronic sense the substituent effects are transmitted to the metal by a combination Ru–N(bpy) $\sigma$ and $\pi$ bonding. Thus a plausible justification for the higher sensitivity of the Ru(III/II) couple, with respect to the Ru(IV/III) couple, to the electronic nature of the substituent might be an enhanced stabilisation of $d\pi \rightarrow \pi^*$ backbonding for the Ru(II) oxidation state.

$pK_a$ values are also influenced by the nature of the 4,4' substituents; with electron-donating groups the $pK_a$ increases while the opposite happens with electron-withdrawing groups as could have been predicted.

It is interesting to note that at $pH < 1$ all the Ru–aqua complexes described in the present work have the same Ru(IV/III) redox potential, regardless of the electronic nature of the bpy substituent. This observation reveals the existence of a linear correlation between $pK_{a,III}$ ($Ru^{III}H_2O^{3+} \rightarrow Ru^{III}OH^{2+} + H^+$) and the Ru(IV/III) redox potential as a fonction of the electronic nature of the bpy substituent which is plotted in Fig. 5. For the complexes studied in the present work the redox

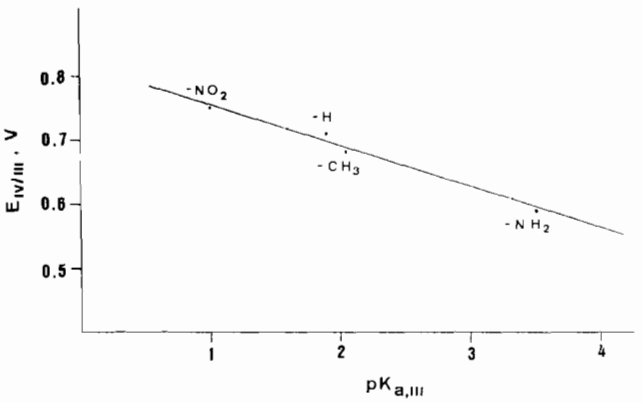


Fig. 5. Plot of $E_{1/2}$ Ru(IV/III) at pH = 7 vs. $pK_{a,III}$ for the complexes $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ (X = H, $CH_3$, $NH_2$, $NO_2$). The substituents at 4,4' positions of the bpy ligands are indicated on the graph (data taken from Table 2).

potential at pH lower than one can be calculated knowing for instance the Ru(IV/III) redox potential at pH = 7 and $pK_{a,III}$. Thus, the linear correlation comes about because as described above the electronic nature of the bpy substituent affects both the Ru(IV/III) redox potential and the $pK_{a,III}$ but in opposite directions.

## Conclusions

A series of tpm–monoaqua–ruthenium complexes with substituted bpy ligands has been prepared and characterised. Their spectral and electrochemical properties display the effects imposed by the electronic nature of the bpy substituent. Thus a series of $Ru^{IV}=O$ active species has been generated with tuneable redox potentials. Even though the $Ru^{IV}=O$ species alone are not very stable they are highly reactive. Thus, in the presence of an adequate substrate the Ru(IV) complex is reduced to lower oxidation states before it decomposes. Further work is underway in my laboratory in order to relate the kinetics of oxidation of a particular substrate with the different thermodynamic potentials of the $Ru^{IV}=O$ species described in this paper.

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