

Protonation Studies of Reduced Ruthenium(II) Complexes with Polypyridyl Ligands

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The pK_a values associated with protonation of the one-electron reduced forms of series of $[L'_2Ru^{II}L]^{2+}$ complexes $\{L' = \text{bidentate polypyridyl ligand}; L = \text{bidentate polypyridyl ligand with additional uncoordinated N atoms in the aromatic ring system: e.g., dpp} = 2,3\text{-bis(2-pyridyl)pyrazine, bpz} = 2,2'\text{-bipyrazine}\}$ were assessed using pulse radiolysis techniques by the measurement of spectral variations as a function of pH. A linear correlation was observed between pK_a and $E^\circ(RuL'_2L^{2+/+})$ for complexes in which the protonatable ligand was at the same time the site of reduction. In complexes where one or more of the nonprotonatable ligands (L') had very low π^* energy levels {e.g. $(CF_3)_4\text{bpy}$ }, reduction occurs on a nonprotonatable ligand and a dramatic decrease in the pK_a values was observed for the reduced species. In complexes where the energies of the protonatable and nonprotonatable ligands were comparable, the protonation behavior was consistent with some orbital mixing/delocalization of the electronic charge.

Introduction

Ruthenium(II) complexes containing polypyridyl ligands have been widely studied as potential photosensitizers in solar energy conversion schemes.^{4,5} Such polypyridyl ligands may contain noncoordinated nitrogen atoms in the ring system {e.g. bpm = 2,2'-bipyrimidine, bpz = 2,2'-bipyrazine and dpp = 2,3-bis(2-pyridyl)pyrazine}, which are therefore accessible to protonation reactions. The acid/base behavior of these moieties will differ between the ground state, excited state and one-electron reduced species, and accordingly these characteristics may provide information relevant to understanding physical properties of these types of complexes, such as distribution of electronic charge.^{6–10}

For this genre of complexes, in the ³MLCT excited state formed on irradiation, the excited electron is considered to ultimately reside on the ligand with the lowest π^* level, which is also the case for the one-electron reduced species.⁵ The two situations differ in that the metal centers are formally in the Ru(III) and Ru(II) oxidation states, respectively.

Hoffman et al^{6,9} have investigated the acid/base properties of the reduced and excited states of the series of complexes $[Ru(\text{bpy})_{3-m-z}(\text{bpm})_m(\text{bpz})_z]^{2+}$ (m and $z = 0, 1, 2, 3; m + z \leq 3; \text{bpy} = 2,2'\text{-bipyridine}$). In these particular complexes, the ligands capable of protonation have also been those with the lowest-lying π^* orbitals, so that protonation occurs on the uniquely reduced ligand in both reduced and excited states. Other studies of the basicity of peripheral N atoms in polypyridyl ligands coordinated to ruthenium centers have included the systems $[Ru(\text{bpy})_{3-p}(\text{pypm})_p]^{2+}$ ($\text{pypm} = 2\text{-}(2'\text{-pyridyl})\text{pyrimidine}$),⁸ and complexes containing bridging ligands such as 2,2'-bis(2-pyridyl)-6,6'-bibenzimidazole¹¹ and similar derivatives,^{12–14} 3,5-bis(2-pyridyl)-1,2,4-triazole^{15,16} and other pyridyltriazoles,¹⁷ and pyrazinyltriazoles.¹⁸

Tuning the properties of such complexes may be achieved through the incorporation of ligands with substantially different electronic natures.^{19,20} One of the particular aims of the current study was to investigate the influence of adjacent ligands on

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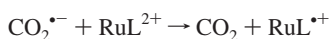
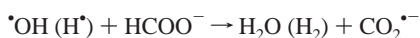
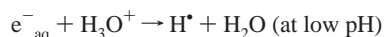
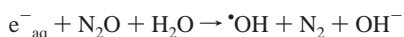
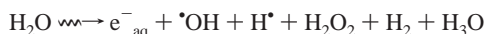
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the protonation processes, specifically Me₄bpy (4,4',5,5'-tetramethyl-2,2'-bipyridine) and (CF₃)_xbpy (*x* = 2 or 4; 4,4'-bis(trifluoromethyl)-2,2'-bipyridine and 4,4',5,5'-tetrakis(trifluoromethyl)-2,2'-bipyridine, respectively)²¹ to maximize electronic effects: (CF₃)₂bpy and (CF₃)₄bpy¹⁸ have strongly electron-withdrawing substituents on the bpy framework giving the ligand a low π* energy level, whereas Me₄bpy will have a high ligand π* energy as a consequence of the electron-donating methyl substituents. The case of (CF₃)₄bpy is particularly interesting, as the π* level of the ligand is substantially lower than those of the protonatable ligands (such as bpm, dpp, and bpz): accordingly, in complexes containing both (CF₃)₄bpy and such a protonatable ligand, the site of ligand reduction in the one-electron reduced species would be (CF₃)₄bpy rather than the protonatable ligand as has been the case in all previous studies. The consequences on the acidity of the latter ligand would provide a valuable insight into our understanding of the electronic nature of one-electron reduced (and ultimately, the excited state) species.

Experimental Section

Physical Measurements. Electronic spectra were recorded using a Cary 5E UV/Vis/NIR spectrophotometer, and NMR spectra using a Bruker AM300 or a Varian Mercury 300 MHz spectrometer. Electrochemical measurements were made in an argon-filled drybox using a Bioanalytical Systems (BAS) 100A electrochemical analyzer. Non-aqueous cyclic voltammetry was carried out using a platinum disk (1 mm diameter) working electrode, platinum wire counter electrode and Ag/Ag⁺ (0.01 M in acetonitrile) reference electrode. Potentials are quoted relative to a saturated sodium chloride calomel electrode (SCE); ferrocene was added as an internal standard {oxidation at +0.095 V vs Ag/Ag⁺ (+0.40 V vs SCE²²)}. Solutions contained 0.1 M [(*n*-C₄H₉)₄N]PF₆ as electrolyte. Typically, scan rates of 200 mV s⁻¹ were employed. For aqueous voltammetry, glassy carbon disk (1 mm diameter), gold disk (1 mm diameter) or hanging mercury drop electrodes (Metrohm) were used as working electrodes, with SCE as the reference electrode. Solutions contained 0.1 M Na₂SO₄ and were adjusted to pH 13 by the addition of NaOH to ensure that the complexes were nonprotonated upon reduction.

Rapid one-electron reduction of the complexes was achieved in aqueous solution using the pulse radiolysis facilities at the University of Auckland: details of the optical detection system and method of dosimetry have been published.²³ Pulsed electrons {3–4 Gy (J.kg⁻¹) in 200 ns from the 4 MeV Dynaray linear accelerator} were delivered to N₂O-saturated (25 mM) solutions containing sodium formate (0.1 M) and the respective complexes (50 μM). Extremes in pH were obtained using hydrochloric acid and sodium hydroxide solutions, otherwise phosphate buffers (10 mM) were used to prepare a range of solutions differing in pH. Under the above conditions, the radicals produced on the radiolysis of water were quantitatively converted into the reducing CO₂^{•-} species within the time scale of the electron pulse with a yield of 0.68 μmol J⁻¹,²⁴ which in turn reduced the complexes.



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Radical formation and transformations were followed by time-resolved UV/visible spectrophotometry. Spectra were measured immediately after the electron pulse (<5 μs): the lifetimes of the reduced species were dependent on the radiation dose (transient concentration), but under the conditions of the experiments half-lives of the second-order decay varied between ca. 100–300 μs. The radical spectra are presented as either (i) the change in absorbance per Gray relative to the absorbance of the unreduced parent complex or (ii) the extinction coefficient of the one-electron reduced forms of the complexes assuming complete reduction of the parent complex by the CO₂^{•-} radical species.

Microwave Techniques. Reactions were performed in a modified Sharp microwave oven (model R-2V55; 600 W, 2450 MHz) on medium-high power.^{25–27} Reactions were carried out in a round-bottom flask fitted with a reflux condenser.

Materials. Hydrated ruthenium trichloride ("RuCl₃·xH₂O"; Strem), 2,2'-bipyridine (bpy; Aldrich), 2,3-bis(2-pyridyl)pyrazine (dpp; Aldrich), ammonium hexafluorophosphate (NH₄PF₆; Aldrich), potassium hexafluorophosphate (KPF₆; Aldrich), AgNO₃ (Aldrich), Na₂SO₄ (Ajax), NaOH (Ajax), and sodium formate (NaHCO₂; Aldrich) were used as supplied. Tetra-*n*-butylammonium hexafluorophosphate [(*n*-C₄H₉)₄N]PF₆; Aldrich) was recrystallized twice from ethanol/water and dried at 60 °C under vacuum prior to use. Sephadex LH-20 and SP Sephadex C-25 (Pharmacia), silica gel (200–400 Mesh, 60 Å; Aldrich) and activated neutral alumina (standard grade 150 mesh; Aldrich) were used for chromatographic purification of ruthenium complexes. Reagent solvents were used without further purification. HPLC grade acetonitrile (Aldrich) was used for nonaqueous electrochemical and photophysical measurements. Distilled water, used for all aqueous physical measurements, was obtained using a Modulab PureOne water purification system. Aqueous buffers in various pH ranges used for pK_a measurements were as follows:²⁸ pH 0.5–2.1 HCl/KCl; pH 2.2–4.0 KHphthalate/HCl; pH 4.1–5.8 KHphthalate/NaOH; pH 5.8–8.0 NaH₂PO₄/NaOH; pH 8.1–9.0 Na₂B₄O₇/HCl. In all, ionic strength was maintained by the presence of sodium formate (0.1 M).

Column Chromatography. Routine purifications of complexes were performed using a column chromatography (dimensions 2 × 30 cm) with SP Sephadex C-25 cation exchanger. Details of eluents are given below for the respective complexes.

Syntheses. The complexes [RuCl₂(DMSO)₄]₂,²⁹ [Ru(bpy)₂Cl₂]·2H₂O,³⁰ [Ru(H₂O)₆](tosylate)₂,³¹ and [Ru(bpy)Cl₄]₂³² and the ligands 4,4',5,5'-tetramethyl-2,2'-bipyridine (Me₄bpy),³³ 4,4'-bis(trifluoromethyl)-2,2'-bipyridine {(CF₃)₂bpy},²¹ and 4,4',5,5'-tetrakis(trifluoromethyl)-2,2'-bipyridine {(CF₃)₄bpy}²¹ were prepared by the literature methods. The 2,2'-bipyrazine (bpz) was prepared by the published method³⁴ and recrystallized from boiling hexane. [Ru(bpy)(py)₄]²⁺ was formed as previously described³² and precipitated as its PF₆⁻ salt from the reaction mixture with aqueous KPF₆ solution. The complex [Ru(Me₄bpy)₃](PF₆)₂ was synthesized in a manner similar to the method of Togano et al.,^{30,35} and was isolated as the PF₆⁻ salt by the addition of KPF₆.

[Ru(Me₄bpy)₂Cl₂]. Method A (the method described by Togano et al. for analogous dichloro species):³⁰ "RuCl₃·xH₂O" (0.390 g; 1.68 mmol, based on 43.5% Ru) was dissolved in EtOH/H₂O (3:2; 15 cm³),

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and the mixture was heated at reflux until a shiny black ruthenium residue appeared on the surface of the flask (ca. 3 h). Me₄bpy (0.912 g, 4.30 mmol) in EtOH/concentrated HCl (14:1; 22.5 cm³) was added and the solution heated at reflux for a further 1 h. The volume of the reaction was reduced to ca. 10 cm³; the solids were collected by filtration and washed with acetone and diethyl ether. Reduction of the resultant [Ru(Me₄bpy)₂Cl₂Cl·xH₂O] intermediate was achieved by suspending it in dilute HCl (3 M; 250 cm³), adding SnCl₂ (70 mg) and boiling the mixture for 2.5 h. On cooling in ice the red-brown product precipitated, and was collected by filtration and washed with cold water. Yield: 0.88 g (88%).⁶⁰ ¹H NMR (CDCl₃), δ: 1.89 (s, 3H), 2.09 (s, 3H), 2.38 (s, 3H), 2.48 (s, 3H), 7.13 (s, 1H), 7.70 (s, 1H), 7.85 (s, 1H), 8.83 (s, 1H).

Method B: [RuCl₂(DMSO)₄] (30 mg, 0.062 mmol), (CH₃)₄bpy (28.4 mg, 0.13 mmol), and LiCl (100 mg, 2.3 mmol) were added to 1-methyl-2-pyrrolidinone (1 cm³). The mixture was heated at reflux for 15 min, cooled and poured into dichloromethane (12 cm³). Water (10 cm³) was added, the mixture rapidly shaken in a separating funnel, and the deep orange dichloromethane layer separated and dried over anhydrous Na₂SO₄. Following filtration, the dichloromethane was removed under vacuum. Diethyl ether (40 cm³) was added to the residue and the mixture was refrigerated. The resulting orange solid was collected and washed with diethyl ether. Yield: 31.4 mg (85%). The ¹H NMR spectrum was identical to that given above for the product from method A above.

[Ru{(CF₃)₂bpy}₂Cl₂] was synthesized using method A above using RuCl₃·xH₂O (235 mg, 1.13 mmol) dissolved in EtOH/H₂O (3:2; 5 cm³), and (CF₃)₂bpy (0.761 g, 2.6 mmol) in EtOH/concentrated HCl (6:1; 7 cm³). Yield: 0.311 g (35%). ¹H NMR (*d*₆-DMSO), δ: 10.12 (d, 2H, *J* = 6 Hz), 9.40 (s, 2H), 9.24 (s, 2H), 8.25 (dd, 2H, *J* = 6, <1 Hz), 7.93 (d, 2H, *J* = 6 Hz), 7.45 (dd, 2H, *J* = 6, <1 Hz). The complex could also be synthesized using a slight variation of method B (above): [RuCl₂(DMSO)₄] (82 mg, 0.17 mmol), (CF₃)₂bpy (99 mg, 0.34 mmol) and LiCl (73 mg, 1.7 mmol) were added to 1-methyl-2-pyrrolidinone (2 cm³). The mixture was heated at reflux for 15 min, cooled and poured into a mixture of water (5 cm³) and dichloromethane (12 cm³). The dark purple organic layer was separated and the aqueous layer extracted into dichloromethane (5 × 20 cm³). The combined organic layers were dried over anhydrous Na₂SO₄, and following filtration, the dichloromethane was removed under vacuum. Diethyl ether (50 cm³) was added to the residue and the mixture was refrigerated overnight. The resulting brown/purple solid was collected and washed with diethyl ether. Yield: 48 mg (37%). The ¹H NMR spectrum was identical to that given above for the alternative synthesis.

[Ru{(CF₃)₄bpy}₂Cl₂]. This precursor was prepared by method B (above), using [RuCl₂(DMSO)₄] (57 mg; 0.118 mmol), (CF₃)₄bpy (100.0 mg; 0.235 mmol), and LiCl (100 mg, 2.34 mmol). Yield: 42 mg (35%). ¹H NMR (*d*₆-DMSO), δ: 6.99 (s), 6.86 (s), 6.12 (s), 5.89 (s).

[Ru(bpz)₃](PF₆)₂. This complex was prepared by the method of Rillema et al.³⁶ and purified by chromatography on activated alumina, using acetonitrile as the eluent.

[Ru(Me₄bpy)₂(bpz)](PF₆)₂. A mixture of [Ru(Me₄bpy)₂Cl₂] (15 mg, 0.025 mmol) and bpz (8 mg, 0.05 mmol) in ethylene glycol (4 cm³) was heated in a modified microwave oven (7 min; Med-High setting). After cooling, water (15 cm³) was added and the solution applied to a cation exchange column (SP Sephadex C-25) and eluted with 0.19 M NaCl. Two bands were observed—the major orange-brown band was collected and extracted into dichloromethane as the PF₆⁻ salt after the addition of KPF₆. The extract was dried using Na₂SO₄, and after filtration the solvent removed. Yield: 21.4 mg (87%). Anal. Calcd for C₃₆H₃₈F₁₂N₈P₂Ru: C, 44.4; H, 3.93; N, 11.5. Found: C, 44.5; H, 3.83; N, 11.8. ¹H NMR (CD₃CN), δ: 9.67 (s, 2H, bpz), 8.47 (d, 2H, bpz), 8.25 (s, 2H, Me₄bpy), 8.22 (s, 2H, Me₄bpy), 7.80 (d, 2H, bpz), 7.24 (s, 2H, Me₄bpy), 7.22 (s, 2H, Me₄bpy), 2.44 (s, 3H, Me₄bpy), 2.42 (s, 3H, Me₄bpy).

[Ru{(CF₃)₂bpy}₂(bpz)](PF₆)₂. [Ru{(CF₃)₂bpy}₂Cl₂] (42 mg, 0.056 mmol) and 2,2'-bipyrazine (33 mg, 0.21 mmol) were added to ethylene glycol (2 cm³), and the mixture was heated in a microwave oven for 2

min, during which time the solution changed in color from purple to orange. After cooling, the solution was added to acetonitrile/water (2:3; 200 cm³), and chromatographically purified by absorption onto a column of SP Sephadex C-25 cation exchanger and elution with 3:2 v/v aqueous phosphate buffer/acetonitrile containing 0.2 M NaCl. The single orange band was collected and the acetonitrile removed by rotary evaporation. The product was precipitated by the addition of saturated KPF₆ solution, collected, and washed with water. Yield: 34 mg (54%). Anal. Calcd for C₃₂H₁₈F₂₄N₈P₂Ru: C, 33.9; H, 1.60; N, 9.9. Found: C, 33.9; H, 1.46; N, 9.7. ¹H NMR (CD₃CN), δ: 9.76 (s, 2H), 8.95 (s, 4H), 8.60 (d, 2H), 7.96 (d, 2H), 7.94 (d, 2H), 7.81 (d, 2H), 7.72 (d, 4H).

The conversion of the PF₆⁻ to the Br⁻ salt was achieved by metathesis in acetone solution using [(*n*-C₄H₉)₄N]Br.

[Ru{(CF₃)₄bpy}₂(bpz)](PF₆)₂ and [Ru{(CF₃)₄bpy]₂(PF₆)₂. [Ru{(CF₃)₄bpy]₂Cl₂] (30 mg; 0.029 mmol) and bpz (30 mg; 0.19 mmol) were suspended in ethylene glycol (10 cm³) with approximately 10 drops of water. The mixture was brought to reflux by microwave heating for 1 min. Silver nitrate (10 mg; 0.058 mmol) was added to the mixture, and heating continued for a further 4 min. The resultant dark brown solution was left to cool before the addition of water (15 cm³). The product was absorbed onto a cation exchange column directly from the reaction mixture and purified as previously described. Four separate bands were observed upon elution. The first three bands corresponded to the target compound {[Ru{(CF₃)₄bpy]₂(bpz)]²⁺ (band I)}, {[Ru{(CF₃)₄bpy]₂(bpz)]²⁺ (band II)} and {[Ru(bpz)₃]²⁺ (band III)}: the respective complexes were precipitated as their PF₆⁻ salts from the eluent solutions using aqueous KPF₆ solution. The fourth band consisted of unreacted material. [Ru{(CF₃)₄bpy]₂(bpz)](PF₆)₂: Yield: 10 mg (25%). ¹H NMR (CD₃CN), δ: 7.92 (dd, 2H, *J* = 3.0, 1.2 Hz); 8.04 (s, 2H); 8.13 (s, 2H); 8.74 (d, 2H, *J* = 3.3 Hz); 9.27 (m, 4H); 9.84 (d, 2H, *J* = 1.5 Hz). [Ru{(CF₃)₄bpy]₂(PF₆)₂·1.5H₂O·0.5 acetone: Yield: 15 mg (46%). Anal. Calcd for C_{31.5}H₂₂N₁₀F₂₄O₂P₂Ru: C, 31.7; H, 1.86; N, 11.7. Found: C, 31.4; H, 1.62; N, 11.6. ¹H NMR (CD₃CN), δ: 7.82 (dd, 2H, *J* = 3.3, 1.2 Hz); 7.85 (dd, 2H, *J* = 3.3, 1.2 Hz); 8.06 (s, 2H); 8.64–8.67 (m, 2H); 9.21 (s, 2H); 9.78 (s, 2H); 9.78 (s, 2H).

[Ru(dpp)₃](PF₆)₂. This complex has been previously reported,³⁷ but an improved synthesis was developed using [Ru(H₂O)₆](tosylate)₂³¹ as the ruthenium precursor. [Ru(H₂O)₆](tosylate)₂ (74 mg, 0.14 mmol) and dpp (200 mg, 0.85 mmol) were added to argon-purged methanol (8 cm³). After further deaeration (15 min) the mixture was heated at reflux for 1 h. The volume of the resulting deep red solution was reduced and the product precipitated as the PF₆⁻ salt by the addition of saturated aqueous NH₄PF₆ solution. The solid was collected by filtration and purified by chromatography on a Sephadex LH-20 column (MeOH eluent). The central portion of the major orange-red band was collected and evaporated to dryness. The complex was further purified by chromatography on an activated alumina column (acetonitrile eluent). Yield: 77 mg (50%). ¹H NMR chemical shifts corresponded to those reported in the literature.³⁸

[Ru(Me₄bpy)₂(dpp)](PF₆)₂. A mixture of [Ru(Me₄bpy)₂Cl₂] (81 mg, 0.128 mmol) and dpp (158 mg, 0.674 mmol) in 50% aqueous methanol (20 cm³) was purged with N₂ and heated at reflux for 3 h. The mixture was cooled, the methanol removed by rotary evaporation, and the product precipitated by the addition of solid NH₄PF₆. The precipitate was collected and washed with dilute NH₄PF₆ solution and water. Reprecipitation was achieved by dropwise addition of a saturated solution of the complex in acetone to stirring diethyl ether. The red-brown solid was collected and washed with diethyl ether. The crude product was further purified by passage through a SP Sephadex C-25 cation exchange column (0.15 M NaCl eluent), isolated as a PF₆⁻ salt by addition of solid NH₄PF₆, and finally recrystallized from acetone/diethyl ether. Yield: 87 mg (65%). Anal. Calcd for C₄₂H₄₂F₁₂N₈P₂Ru: C, 48.0; H, 4.03; N, 10.7. Found: C, 47.8; H, 3.91; N, 10.5.

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[Ru(bpy)₂(dpp)](PF₆)₂. An alternative synthesis was developed to that used previously.³⁹ The ligand dpp (150 mg; 0.62 mmol) was suspended in ethylene glycol (25 cm³) and dissolved by bringing the mixture to reflux in a microwave oven. [Ru(bpy)₂Cl₂]·2H₂O (90 mg; 0.173 mmol) was added and the mixture heated at reflux for a further 1 min, whereupon the solution underwent an immediate change from purple to dark orange. Upon cooling, water (20 cm³) was added and the solution applied directly onto a cation exchange column (SP Sephadex C-25) for chromatographic purification (eluent 0.2 M NaCl solution). The presence of a large proportion of a green dinuclear ruthenium species was noted. Purification of the mononuclear species was achieved through reprecipitation via the addition aqueous NH₄PF₆ to an acetone solution of the complex. After slow evaporation of the acetone under reduced pressure, the precipitate was collected and washed thoroughly with water and ether before drying under vacuum. Yield: 55 mg (34%).

[Ru(bpy)(dpp)₂](PF₆)₂·H₂O. The ligand dpp (250 mg; 1.06 mmol) was suspended in ethylene glycol (10 cm³) and dissolved by bringing the mixture to reflux in a microwave oven. [Ru(bpy)Cl₄] (40 mg 0.09 mmol) was added in small portions over 10 min and the mixture heated at reflux for a further 5 min. The solution underwent an immediate change from colorless to dark orange on addition of the [Ru(bpy)Cl₄]. Upon cooling, water (20 cm³) was added to the reaction mixture and then the compound was purified using cation exchange chromatography as described above. Following collection, purification of the mononuclear species was achieved through reprecipitation via the addition of aqueous NH₄PF₆ to an acetone solution of the complex. After slow evaporation of the acetone under reduced pressure, the precipitate was collected and washed thoroughly with water and ether before drying under vacuum. Yield: 65 mg (54%). Anal. Calcd for [Ru(bpy)(dpp)₂](PF₆)₂·H₂O, C₃₈H₃₀N₁₀F₁₂O₂P₂Ru: C 44.1; H 2.93; N 13.5. Found. C, 44.1; H, 2.92; N, 13.2. Because of the existence of geometric isomers in this complex, each with C₁ point group symmetry, characterization by NMR was extremely difficult.

[Ru{(CF₃)₂bpy}₂(dpp)](PF₆)₂. A solution of dpp (188 mg, 0.80 mmol) in 50% aqueous methanol (20 cm³) was purged with N₂. After addition of [Ru{(CF₃)₂bpy}₂Cl₂] (85 mg, 0.11 mmol) and further purging, the mixture was heated at reflux under N₂ for 3 h. The methanol was removed by rotary evaporation and the product precipitated by the addition of solid NH₄PF₆. The precipitate was washed with dilute NH₄PF₆ solution and water. The orange solid was further purified by chromatography on a SP Sephadex C-25 cation exchange column (0.2 M NaCl eluent). The central portion of the orange band was collected and the product precipitated by addition of saturated KPF₆ solution. The orange solid was collected and recrystallized from acetone/diethyl ether. Yield: 65 mg (56%). Anal. Calcd for C₃₈H₂₂F₁₂N₈P₂Ru: C, 37.7; H, 1.83; N, 9.3. Found: C, 37.8; H, 1.76; N, 9.6.

[Ru{(CF₃)₄bpy}(dpp)₂](PF₆)₂. The complex was obtained in an attempt to synthesize [Ru{(CF₃)₄bpy}₂(dpp)](PF₆)₂. The ligand dpp (30 mg; 0.097 mmol) was suspended in ethylene glycol (10 cm³) and dissolved by bringing the mixture to reflux in a microwave oven. [Ru{(CF₃)₄bpy}₂Cl₂] (20 mg; 0.019 mmol) was added and the mixture heated at reflux for a further 1 min. The solution underwent an immediate change from colorless to dark orange on addition of the [Ru{(CF₃)₄bpy}₂Cl₂]. Upon cooling, water (20 cm³) was added and the solution applied directly onto a cation exchange column (SP Sephadex C-25). Upon elution with 0.2 M NaCl solution, three overlapping orange-brown bands were observed. The central portion of the middle (major) band was collected and purification achieved through reprecipitation via the addition of aqueous NH₄PF₆ to an acetone solution of the complex. After slow evaporation of the acetone at reduced pressure, the precipitate was collected and washed thoroughly with water and ether before drying under vacuum. Yield: 15 mg (61%).⁶¹

X-ray Structure Analysis. Red-orange crystals of [Ru{(CF₃)₂bpy}₂(bpz)]Br₂·3H₂O were obtained by evaporation of an aqueous solution of the complex.

Structure Determination. A unique room-temperature diffractometer data set (*T* ~ 296 K; monochromatic Mo K α radiation, λ =

0.71073 Å; 2 θ / θ scan mode) was measured on an Enraf-Nonius CAD4 diffractometer, yielding *N*_o independent reflections, *N*_o with *I* > 3 σ (*I*) being considered "observed" and used in the large block least squares refinements.

Anisotropic thermal parameters were refined for all non-hydrogen atoms, except the oxygen atoms of the water molecules (due to high thermal motion). Hydrogen atoms were placed in calculated positions and were not refined. Conventional residuals *R*, *R*_w on |*F*| are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Neutral atom complex scattering factors were employed, and computation was by the XTAL 3.4 program system, implemented by S. R. Hall.⁴⁰ A summary of crystal data and refinement is compiled below and relevant structures are shown in the figures; material deposited in the Supporting Information comprises all atomic coordinates and thermal parameters, complete bond distances and angles tables, and full non-hydrogen atom geometries.

Crystal/refinement data: [Ru{(CF₃)₂bpy}₂(bpz)]Br₂·3H₂O. C₃₂H₂₄Br₂F₁₂N₈O₃Ru, *M* = 1057.46. Triclinic, space group *P*1̄ (No. 2), *a* = 10.084(1), *b* = 11.359(3), *c* = 18.751(3) Å, α = 92.35(1), β = 101.3(1), γ = 115.15(1)°, *V* = 1887.8(6) Å³. *D*_c (*Z* = 2) = 1.860 g cm⁻³. μ_{Mo} = 26.4 cm⁻¹. *N* = 7043, *N*_o = 3279; *R* = 0.073, *R*_w = 0.072.

Results

Syntheses. The [RuL'₂L]²⁺ complexes {L' = bidentate polypyridyl ligand; L = bidentate polypyridyl with additional uncoordinated N atoms in the aromatic ring system: e.g. dpp = 2,3-bis(2-pyridyl)pyrazine, bpz = 2,2'-bipyrazine} were generally prepared by heating the corresponding [RuL'₂Cl₂] precursor with an excess of bpz or dpp in MeOH/H₂O^{30,41} and purified by cation-exchange chromatography (SP Sephadex C-25). The poor basicity of the (CF₃)_xbpy (*x* = 2 or 4) and bpz ligands caused some synthetic difficulties using this method. However, the syntheses of complexes containing (CF₃)₄bpy, and of the complex [Ru{(CF₃)₂bpy}₂(bpz)]²⁺, were achieved by employing a microwave technique. In this method the [Ru{(CF₃)_xbpy}₂Cl₂] (*x* = 2 or 4) precursor was combined with excess bpz or dpp in ethylene glycol, and the mixture rapidly heated in a modified microwave oven. Some ligand scrambling was observed in the attempted synthesis of [Ru{(CF₃)₄bpy]₂(dpp)]²⁺, and [Ru{(CF₃)₄bpy}(dpp)₂]²⁺ was isolated as the major product. It is noted that in earlier studies involving the ligand (CF₃)₄bpy, difficulties were reported in obtaining bis(ligand) species.²¹

Crystal Structure of [Ru{(CF₃)₂bpy}₂(bpz)]Br₂·3H₂O. The X-ray crystal structure of [Ru{(CF₃)₂bpy]₂(bpz)]Br₂·3H₂O is reported, and the structure of the cation is shown in Figure 1. The complex crystallized in the triclinic space group *P*1̄ with one whole molecule comprising the asymmetric unit. Bond lengths (average Ru–N = 2.05 Å) and angles about the octahedral ruthenium(II) center were similar to those reported for analogous Ru(pp)₃ complexes (pp = bidentate polypyridyl ligand).^{35,42–45} An interesting feature is observed in the overall packing of the complex. The bromide anions occupy "voids" between the octahedral cations but appear to be involved in extended interactions with the arene rings of the heterocyclic ligands of the cations (the packing diagram is available in

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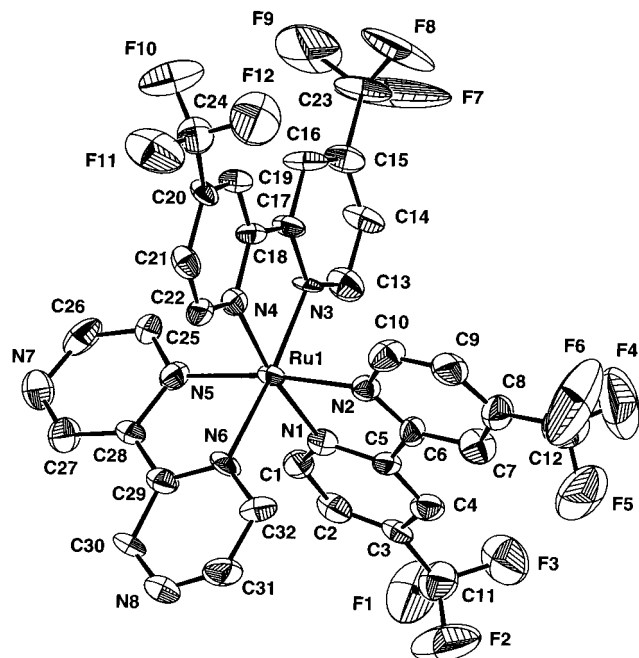


Figure 1. ORTEP diagram of the cation $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ (H atoms omitted for clarity).

Supplementary Information, Figure S1). Thus, Br(1) has contacts with five arene carbon atoms $\{\text{Br}(1)-\text{C}(4), 3.65, \text{Br}(1)-\text{C}(7), 3.67, \text{Br}(1)-\text{C}(13), 3.53, \text{Br}(1)-\text{C}(14), 3.61, \text{Br}(1)-\text{C}(32), 3.49 \text{ \AA}\}$, and Br(2) has two such contacts of 3.59 and 3.63 \AA with C(25) and C(30), respectively. These interactions are shorter than the sum (3.68 \AA) of the ionic radius of Br^- (1.95 \AA)⁴⁶ and the van der Waals radius of an aromatic ring (1.73 \AA).⁴⁷ Coupled with established $\text{F}\cdots\text{C}(\text{arene})$ $\{\text{F}\cdots\text{C}(\text{arene centroid}), 3.10\text{--}3.46 \text{ \AA}\}$ ⁴⁸ and $\text{I}\cdots\text{C}(\text{arene})$ $\{\text{I}\cdots\text{C}(\text{arene centroid}), 3.60\text{--}3.78 \text{ \AA}\}$, with the shortest $\text{I}\cdots\text{C}$ distance of 3.76(2) \AA ⁴⁹ distances in calixarene chemistry, these interactions are considered significant. Specific interactions of anions with complexes of this type have been noted recently,^{50,51} although from those studies Br^- would not have been expected to show substantial interaction, so that the present observation in the solid state is of interest. The Br^- anions are also involved in hydrogen bonding interactions with the water molecules of crystallization: Br(1) is hydrogen bonded to O(2) at 3.32(2) \AA and Br(1) is bound to O(1), O(3), and O(3') at 3.45(1), 3.06(2), and 3.65(3) \AA respectively.

Electrochemistry. Electrochemical characteristics of the complexes were studied in acetonitrile solution by cyclic voltammetry and differential pulse voltammetry. Table 1 lists the redox potentials of the $\text{Ru}^{\text{III/II}}$ couples and the sequential reduction couples for the various complexes.

Cyclic voltammograms in aqueous solution were generally determined at a glassy carbon working electrode, with the solutions at pH 13 (to ensure deprotonation) and containing 0.1 M Na_2SO_4 . Some complexes were unstable under these condi-

Table 1. Electrochemical Data for $[\text{RuL}_3]^{2+}$ Used in This Study

complexes	CH_3CN^a			H_2O^b	
	$\text{Ru}^{\text{III/II}}$	$E_{1/2}, \text{V vs SCE}^c$			
		ligand reductions		$E_{1/2}, \text{V}^c$	
				vs SCE ^d	
				$\text{Ru}^{2+/+}$	
$[\text{Ru}(\text{bpz})_3]^{2+}$	+1.97	-0.71	-0.89	-1.16	-0.74
$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{bpz})]^{2+}$	+1.35	-0.94	-1.62	-1.90	-1.02
$[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$	+1.80	-0.78	-0.98	-1.21	-0.91 ^e
$[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}_2(\text{bpz})]^{2+}$	$\sim 2.2^g$	-0.33	-0.46		-0.41 ^{e,f}
$[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}(\text{bpz})_2]^{2+}$	$> 2.0^g$	-0.31	-0.80	0.99	-0.41 ^{e,f}
$[\text{Ru}(\text{dpp})_3]^{2+}$	+1.62	-0.92	-1.11	-1.39	-0.98
$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dpp})]^{2+}$	+1.23	-1.10	-1.72	-1.97	-1.15 ^h
$[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$	+1.40	-1.04	-1.47	-1.70	-1.10
$[\text{Ru}(\text{bpy})(\text{dpp})_2]^{2+}$	+1.51	-0.98	-1.20	-1.66	-1.01
$[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$	+1.69	-0.85	-1.02	-1.29	-0.88 ^e
$[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}_2(\text{dpp})]^{2+}$	$\sim 2.2^g$	-0.38	-0.86	-1.06	-0.42 ⁱ
$[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_3]^{2+21}$	+1.75	-0.77	-0.93	-1.16	
$[\text{Ru}(\text{Me}_4\text{bpy})_3]^{2+}$	+1.04	-1.60	-1.80	-2.05	

^a Recorded at a Pt disk electrode; solutions contained 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6$. ^b Recorded at a glassy carbon electrode; solutions contained 0.1 M Na_2SO_4 and 0.1 M NaOH (pH 13 unless otherwise stated). ^c Uncertainty in $E_{1/2}$ values ca. ± 20 mV. ^d E° (SCE) = -0.24 V vs NHE. ^e Adsorbs to electrode; $E_{p,c}$ is listed. ^f pH 11. ^g Irreversible; $E_{p,a}$ is listed. ^h Irreversible; $E_{p,c}$ is listed. ⁱ pH 9.2.

tions and were instead measured at pH 9 or 11. The first ligand-based reduction was reversible except for complexes containing Me_4bpy , which exhibited irreversible or partially reversible reductions, and complexes with the ligand $(\text{CF}_3)_2\text{bpy}$, where the reduced species adsorbed to the electrode (indicated by a stripping peak during the reverse scan). Adsorption was also observed at gold disk and hanging mercury drop electrodes. For these complexes the cathodic peak potentials ($E_{p,c}$) are listed in Table 1.

The additive effects of the component ligands on the $\text{Ru}^{\text{III/II}}$ couple in acetonitrile, previously parametrized by Lever,⁵² were found to be predictable and consistent in the present series of complexes. For example, the oxidation of $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ (+1.80 V vs SCE) falls between that of $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_3]^{2+}$ (+1.75 V)²¹ and $[\text{Ru}(\text{bpz})_3]^{2+}$ (+1.97 V), and as expected it is closer to the former since it contains two $(\text{CF}_3)_2\text{bpy}$ ligands and one bpz ligand.

The assignment of the ligand-based reduction processes in the complexes $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ and $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$ is less clear. A parametrization procedure of Lever et al.⁵³ has been used successfully to differentiate between alternate possible ligand reduction sites in complexes where the choice has been ambiguous,¹⁹ using the relationship

$$E_{\text{red}} = S_L \sum E_L(L) + I_L$$

$\{E_{\text{red}}$ is the potential of the first ligand-based reduction, S_L and I_L are constants relating to a Ru center RuL where L is the ligand which is the site of the reduction, and E_L is the fundamental electrochemical parameter⁵² associated with the other (nonreduced) ligands}. From previous studies, the values for $\text{Ru}(\text{bpz})$ $\{S_L = 0.33, I_L = -0.95\}$ ⁵³ and $\text{Ru}(\text{dpp})$ $\{S_L = 0.38, I_L = -1.20\}$ ¹⁹ are known, and the values for $\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}$ may be calculated as $S_L = 0.34, I_L = -1.04$ using the electrochemical data for the series of complexes $[\text{Ru}(\text{bpy})_{3-n}\{(\text{CF}_3)_2\text{bpy}\}_n]^{2+}$ ($n = 1\text{--}3$).²¹ On this basis, the potential of the first reduction for $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ is predicted to be -0.74 V (vs SCE) if bpz is the site of reduction, and -0.76 V if $(\text{CF}_3)_2\text{bpy}$ is the site: the observed value is -0.78 V so that the technique

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Table 2. Lowest Energy MLCT Absorption λ_{max} , Emission λ_{em} , and Emission Lifetime, τ_{em} , for Complexes in CH_3CN Solution

complex	λ_{abs} (nm)	λ_{em} (nm)	τ_{em} (ns) ^a	$\Delta E_{1/2}$ ^b
$[\text{Ru}(\text{bpz})_3]^{2+}$	440	614	785	2.68
$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{bpz})]^{2+}$	492	720 ^c	210	2.29
$[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$	450	640	1630	2.58
$[\text{Ru}(\text{dpp})_3]^{2+}$	458	647	185	2.54
$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dpp})]^{2+}$	486	703 ^c	182	2.33
$[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$	457	632 ^c	1040	2.54

^a Estimated uncertainty $\pm 5\%$. ^b $\Delta E_{1/2} = E_{1/2}(\text{Ru}^{\text{III/II}}) - E_{1/2}(\text{first ligand reduction})$. ^c Uncorrected for detector response.

can clearly not be used to make the assignment for this complex system. Indeed, the potentials for the first reductions of the two homoleptic complexes based on the same ligands, viz. $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_3]^{2+}$, are extremely close so that the site of the reduction in the mixed-ligand complexes remains ambiguous. For $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$, the potential of the first reduction is predicted to be -0.92 V (vs SCE) if dpp is the site of reduction and -0.79 V if $(\text{CF}_3)_2\text{bpy}$ is the site, whereas the observed value is -0.85 V which is mid-way between the two calculated values. Again, the parametrization technique cannot provide a definitive assignment for the site of the reduction: however, since the first reductions of the two homoleptic complexes involving the same ligands, $[\text{Ru}(\text{dpp})_3]^{2+}$ and $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_3]^{2+}$, are -0.92 and -0.77 V (vs SCE) respectively, $(\text{CF}_3)_2\text{bpy}$ might be regarded as the more likely site of reduction in the mixed-ligand complexes.

Complexes containing the ligand $(\text{CF}_3)_4\text{bpy}$ exhibit ligand reduction potentials shifted anodically from their $(\text{CF}_3)_2\text{bpy}$ analogues by 0.5 V. In the mixed-ligand complexes $[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}_2(\text{bpz})]^{2+}$ and $[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}(\text{bpz})_2]^{2+}$, the first ligand reduction occurs at ca. -0.33 V vs SCE. The effect of the additional electron-withdrawing CF_3 substituents is not reflected in the $\text{Ru}^{\text{III/II}}$ potential, which shifts to more positive potentials by only 70 mV from $[\text{Ru}(\text{bpz})_3]^{2+}$ to $[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}_2(\text{bpz})]^{2+}$. In aqueous solution, the first reduction occurs at -0.41 V vs SCE for all three $(\text{CF}_3)_4\text{bpy}$ -containing complexes.

Electronic Absorption Spectra and Excited-State Properties. Absorption and emission spectra were recorded in both acetonitrile and aqueous solution. The lowest energy MLCT absorption maxima and the emission maxima are listed in Table 2, along with excited-state lifetimes and data for the relevant homoleptic species. In acetonitrile, there is a close correlation between the energies of the lowest MLCT absorption and the electrochemical quantity $\Delta E_{1/2}$, as generally expected for $\text{Ru}(\text{II})$ complexes involving polypyridyl ligands.⁵

The incorporation of ligands of different energies and electron-donating properties about the metal center demonstrate that the electronic effects of $(\text{CF}_3)_2\text{bpy}$ and dpp on the $\text{Ru}(\text{d}_\pi)$ level are not significantly dissimilar ($[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_3]^{2+}$: $E_{1/2}(\text{Ru}^{\text{III/II}}) = +1.75$ V; $[\text{Ru}(\text{dpp})_3]^{2+}$: $E_{1/2}(\text{Ru}^{\text{III/II}}) = +1.62$ V), whereas the presence of the electron-donating methyl substituents in the Me_4bpy ligand leads to a significant cathodic shift in the redox potential $\{[\text{Ru}(\text{Me}_4\text{bpy})_3]^{2+}$, $E_{1/2}(\text{Ru}^{\text{III/II}}) = +1.04$ V}.

Consequently the complexes $[\text{Ru}(\text{dpp})_3]^{2+}$ and $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$ possess a single nonsymmetric MLCT absorption band centered ca. 455 nm, while $[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dpp})]^{2+}$ has two distinct bands at 486 and 418 nm.^{19,20} The lowest energy MLCT transition for $[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dpp})]^{2+}$ $\{\text{Ru}(\text{d}_\pi) \rightarrow \pi^*(\text{dpp})\}$ is significantly red-shifted relative to that of $[\text{Ru}(\text{dpp})_3]^{2+}$ and $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$ due to the stabilization of the "hole" at $\text{Ru}(\text{III})$ by the presence of electron-donating methyl substituents in Me_4bpy .^{19,20} Similarly the $(\text{CF}_3)_2\text{bpy}$ and bpz ligands have

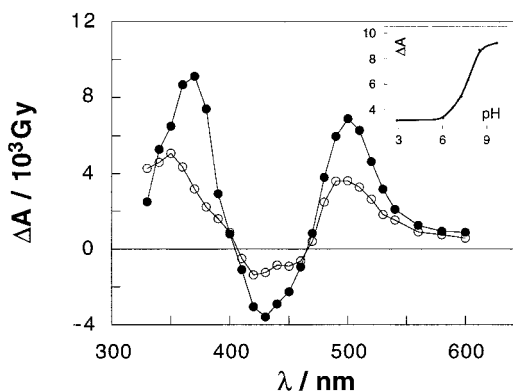


Figure 2. Transient absorbance difference spectra obtained from the pulse irradiation of N_2O -saturated aqueous solutions containing $50 \mu\text{M}$ $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ and 0.1 M HCO_2^- at pH 3 (O) and pH 12 (●). Inset: pH dependence of ΔA at 370 nm.

comparable electronic effects on the $\text{Ru}(\text{II})$ center, which are quite different to those of Me_4bpy . Hence the pattern of MLCT absorption for the bpz series is analogous to the dpp series.

The excited state properties of the complexes in acetonitrile appear to be entirely consistent with the ground-state electrochemical and spectral properties. The wavelength of the emission maximum, λ_{em} , is red-shifted relative to the corresponding absorption band, and the order of excited-state energies for the series of complexes matches that of the absorption energies and $\Delta E_{1/2}$. For example, the emission from $[\text{Ru}(\text{dpp})_3]^{2+}$ ($\lambda_{\text{em}} = 647$ nm, $\lambda_{\text{abs}} = 456$ nm, $\Delta E_{1/2} = 2.54$ V) occurs at lower energy than $[\text{Ru}(\text{bpz})_3]^{2+}$ ($\lambda_{\text{em}} = 614$ nm, $\lambda_{\text{abs}} = 444$ nm, $\Delta E_{1/2} = 2.68$ V). The significant difference in emission energy for the complexes of $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$ and $[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dpp})]^{2+}$ is a consequence of a difference in the $\text{Ru}(\text{d}_\pi)$ level due to the presence of electron-donating methyl substituents in the Me_4bpy ligand and the lowering of the π^* level due to the presence of the electron-withdrawing trifluoromethyl substituents in the $(\text{CF}_3)_2\text{bpy}$ ligand.^{19,20} Similarly $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ emits at higher energy than does $[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{bpz})]^{2+}$. It should be noted that some of the λ_{em} data are from spectra which have not been corrected for detector response. As the correction function is smooth and monotonically increasing the relative order of the emission energies would remain constant and thus the comparison remains valid. Corrected λ_{em} are red-shifted relative to the uncorrected λ_{em} .

The excited-state properties in aqueous buffer solution are analogous to those in CH_3CN . In general, the emission is slightly red-shifted in accordance with the stabilization of the excited state afforded by the more polar solvent.⁵⁴

Pulse Radiolysis. The concentrations of the compounds (50 – $100 \mu\text{M}$) were chosen to ensure their rapid reduction by the $\text{CO}_2^{\cdot -}$ species within a few μs following the electron pulse. The observed rapid reduction was consistent with the second-order rate constants being ca. $4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is near the upper limit reported for similar sized and charged complexes,⁵⁵ leading to spectral changes attributed to the loss of RuL^{2+} and the formation of $\text{Ru}^{\cdot +}$. Transient absorption spectra for $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ are presented in Figure 2.

The spectral changes are dependent on pH, with limiting values in acidic and basic solution. Measurement of these spectral changes at selected wavelengths as a function of pH leads to "titration curves", from which the pK_a of $\text{RuLH}^{\cdot 2+}$ can

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Table 3. Reduced-State pK_a Data

complex	$pK_a(\text{RuLH}^{2+})^a$
$[\text{Ru}(\text{bpz})_3]^{2+}$	7.1
$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{bpz})]^{2+}$	9.2
$[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$	7.6
$[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}_2(\text{bpz})]^{2+}$	2.3 ^b
$[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}(\text{bpz})_2]^{2+}$	2.9
$[\text{Ru}(\text{dpp})_3]^{2+}$	9.1
$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dpp})]^{2+}$	10.5
$[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$	10.5
$[\text{Ru}(\text{bpy})(\text{dpp})_2]^{2+}$	9.5
$[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$	8.6
$[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}(\text{dpp})_2]^{2+}$	1.6 ^b

^a Estimated uncertainty in pH values ± 0.1 unless otherwise shown.

^b An upper limit to the pK_a is quoted, as the lower (acid) limit of the pH curve could not be obtained (lower limit is less than pH 0.6).

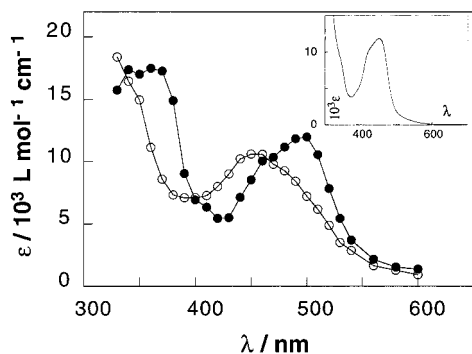


Figure 3. Absorption spectra of the one-electron reduced forms of $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ in aqueous solution corrected for the loss in absorption of the parent complex: $[\text{RuL}_3]^+$ (●); $[\text{RuL}_3\text{H}]^{2+}$ (○). Inset: Absorption spectrum of the parent compound, $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$.

be determined. The pK_a values of the one-electron-reduced species are listed in Table 3.

If it is assumed that all of the generated $\text{CO}_2^{\bullet-}$ reacts with RuL^{2+} , and $\Delta[\text{RuL}^{2+}] = -\Delta[\text{RuL}^{2+}] = 0.68 \mu\text{mol J}^{-1}$ of radiation energy absorbed,²¹ then $\Delta A = \Delta\epsilon l[\text{RuL}^{2+}]$, where $\Delta\epsilon = \epsilon(\text{RuL}^{2+}) - \epsilon(\text{RuL}^{2+})$. A knowledge of the dose per pulse, ΔA and $\epsilon(\text{RuL}^{2+})$ leads to the determination of $\epsilon(\text{RuL}^{2+})$ as a function of wavelength, as shown for $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]^{2+}$ in Figure 3. Table 3 lists pK_a values determined for the ground and reduced state (protonated and nonprotonated) species.

The UV/vis spectra of the reduced species show two band envelopes (ca. 350 and 500 nm) corresponding to the ligand-localized ($\pi \rightarrow \pi^*$) and MLCT ($d_\pi \rightarrow \pi^*$) transitions.^{6,53} Pulse radiolysis experiments on $\text{bpy}^{\bullet-}$ have shown that protonation causes the ligand-localized transitions to shift to higher energy.⁶ Similarly, protonation of RuL^{2+} results in a blue-shift of the visible spectral bands.

Relationships between Acid–Base Properties of Reduced States with Those of the Ground and Excited States. Hoffman et al. have investigated the acid/base properties of the complexes $[\text{Ru}(\text{bpy})_{3-m-z}(\text{bpm})_m(\text{bpz})_z]^{2+}$ (m and $z = 0, 1, 2$, and 3 and $m + z \leq 3$) and in particular determined the pK_a values of the one-electron reduced species, RuLH^{2+} .⁶ The monoprotonated one-electron reduced species of this series are much weaker acids than their monoprotonated nonreduced parent compounds.⁵⁷ In these reduced complexes, protonation occurs on the uniquely reduced ligand (bpz when present, or bpm) and the significantly higher pK_a values upon reduction are consequently due to the increased electron density on the reduced ligand.

Various workers have reported a correlation between the redox couples of the above complexes and the pK_a of the

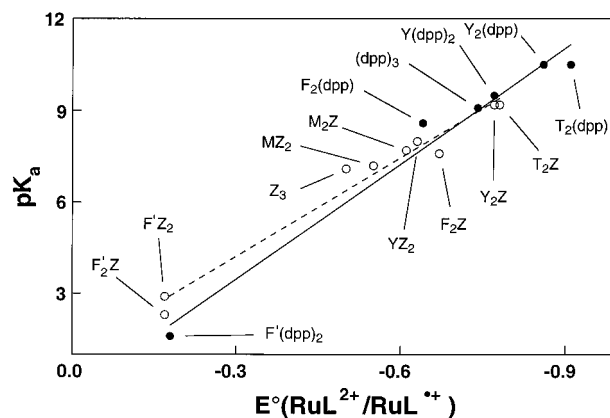


Figure 4. Relationship between pK_a and E° of the bpz (○) and the dpp (●) complexes investigated [$Y = \text{bpy}$; $M = \text{bpm}$; $T = \text{Me}_4\text{bpy}$; $Z = \text{bpz}$; $F = (\text{CF}_3)_2\text{bpy}$; $F' = (\text{CF}_3)_4\text{bpy}$]. The data for the complexes designated M_2Z , MZ_2 , YZ_2 and Y_2Z are taken from ref 6. The lines of best fit refer to dpp-containing (—) and bpz-containing (---) species.

conjugate acid of the free ligand.^{36,58,59} This has been interpreted as demonstrating that the σ -donor strength of the ligand modulates the d-orbital energy of the metal, altering the charge on the metal center and the resultant redox potential.^{6,36,58,59} Hoffman et al. extended this to show a correlation between the pK_a of RuLH^{2+} and the reduction potential of the complexes $[E^\circ(\text{RuL}^{2+}/\text{RuL}^{2+})]$.⁹ It was found that complexes in which 2,2'-bipyrazine was the site of both localized reduction and protonation could be clearly distinguished from those in which 2,2'-bipyrimidine was the uniquely reduced and protonated ligand. This was indicative of different σ -donor and σ -acceptor properties of the ligands and their π -back-bonding interactions with $\text{Ru}(\text{II})$.

This linear relationship between reduced-state pK_a and $E^\circ(\text{RuL}^{2+}/\text{RuL}^{2+})$ was also observed in the complexes presented here where the site of reduction was the protonatable ligand. However, in complexes containing one or more of the low energy $(\text{CF}_3)_4\text{bpy}$ ligands, the reduced-states exhibit a marked increase in acidity, with an upper limit to the pK_a for these complexes estimated at ca. 1.8. The pK_a values are shown in Figure 4 as a function of the E° values. These low pK_a values are rationalized in terms of the added electron upon reduction being located on a ligand adjacent to the protonated bpz or dpp. However, these species are less acidic than their ground-state parent analogues because of the reduced overall positive charge on the complex. Ground-state pK_a measurements on a series of

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(60) Some difficulties were experienced with obtaining a satisfactory microanalysis for this complex. It was apparent from the NMR studies that it was particularly susceptible to substitution of the chloro ligands. However, a characteristic of the Me_4bpy ligand is that all aliphatic and aromatic resonances will be singlets, and since the $[\text{Ru}(\text{Me}_4\text{bpy})_2\text{Cl}_2]$ product has C_{2v} point group symmetry, the ^1H NMR spectrum is quite definitive for characterization.

(61) Considerable difficulties were experienced with absolute characterization of this complex. By analogy with the corresponding bpz complexes (above), the major band corresponded to $[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}(\text{dpp})_2]^{2+}$; however, because of the unsymmetrical nature of the dpp ligand, the NMR spectrum of the resultant mixture of geometric isomers was not able to be interpreted. Furthermore, a satisfactory microanalysis could not be obtained. On the basis of the synthetic technique and the electrochemistry data obtained, it was felt that its identity was sufficiently established to include its protonation behavior in the present series of complexes.

related {bpm, bpz, pypm (= 2-(2'-pyridyl)pyrimidine)} complexes have been measured by Rügge et al.,⁵⁷ and found to be in the range -1.6 to -5.0 . Complexes of the type $[\text{Ru}(\text{bpy})_{3-m-z}(\text{bpm})_m(\text{bpz})_z]^{2+}$ (m and $z = 0, 1, 2,$ and 3 and $m + z \leq 3$), where bpz was the protonated ligand, had ground-state $\text{p}K_a$ values of -1.6 to -2.7 .

In the complex $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{2+}$, $(\text{CF}_3)_2\text{bpy}$ is possibly the site of reduction (see above). We might therefore expect a lower $\text{p}K_a$ for $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{*+}$ than is observed (8.6) and behavior similar to $[\text{Ru}\{(\text{CF}_3)_4\text{bpy}\}(\text{dpp})_2]^{*+}$, where the site of reduction is also adjacent to the dpp ligand. In fact it appears that the lowest energy π^* orbital in $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{*+}$ has a mixture of $(\text{CF}_3)_2\text{bpy}$ and dpp character, whereas the greater energy mismatch between $(\text{CF}_3)_4\text{bpy}$ and dpp ligands in $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{dpp})]^{*+}$ means that the site of reduction is essentially located on a $(\text{CF}_3)_4\text{bpy}$ π^* orbital.

On the basis that protonation occurs on the uniquely reduced ligand in both reduced and excited states, preliminary studies were undertaken of the pH dependence of the emission of the complexes reported in this study. Dramatic effects were observed in the resultant "titration curves" for complexes involving the $(\text{CF}_3)_4\text{bpy}$ ligand, in the same way as reported for the reduced species.

Conclusions/Summary

One-electron reductions of a series of $\text{L}'_2\text{Ru}^{\text{II}}\text{L}^{2+}$ complexes $\{\text{L}' = \text{bidentate polypyridyl ligand}; \text{L} = \text{bidentate polypyridyl with additional uncoordinated N atoms in the aromatic ring system: e.g. dpp} = 2,3\text{-bis}(2\text{-pyridyl})\text{pyrazine}, \text{bpz} = 2,2'\text{-bipyrazine}\}$ were achieved by pulse radiolysis. UV/vis spectra of the reduced species show two band envelopes corresponding to $\pi \rightarrow \pi^*(\text{L}^{\bullet-})$ (ca. 350 nm) and the $d\pi \rightarrow \pi^*_L$ (ca. 500 nm) transitions, and these bands undergo a blue shift upon proto-

nation. From the measurement of spectral variations as a function of pH, the $\text{p}K_a$ values of $\text{L}'_2\text{Ru}^{\text{II}}\text{LH}^{2+}$ were determined, and a linear correlation was observed between $\text{p}K_a$ and $E^\circ(\text{RuL}'_2\text{L}^{2+/+})$ for complexes in which the protonatable ligand L was also the site of reduction. In complexes where one or more of the ligands had very low π^* energy levels {e.g. $(\text{CF}_3)_4\text{-bpy}$ }, reduction occurred on the nonprotonatable ligand, L'. There was a dramatic decrease in the $\text{p}K_a$ values for these reduced species compared to complexes in which the same ligand was associated reduction and protonation. In complexes where the π^* levels of the ligands L and L' are comparable, the behavior of the complex is consistent with some orbital mixing/delocalization of the electronic charge.

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Supporting Information Available: Text listing of visible spectral data for complexes in the study (in acetonitrile solution), a figure of the packing diagram for the X-ray crystal structure of $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]\text{Br}_2 \cdot 3\text{H}_2\text{O}$, and X-ray crystallographic files in CIF format for $[\text{Ru}\{(\text{CF}_3)_2\text{bpy}\}_2(\text{bpz})]\text{Br}_2 \cdot 3\text{H}_2\text{O}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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