Contribution from the Departments of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514, and The University of North Carolina at Charlotte, Charlotte, North Carolina 28223

Redox Properties of Ruthenium(II) Tris Chelate Complexes Containing the Ligands 2,2'-Bipyrazine, 2,2'-Bipyridine, and 2,2'-Bipyrimidine[1]

D. PAUL RILLEMA,*[2a] G. ALLEN,[2b] T. J. MEYER,*[2b] and D. CONRAD[2a]

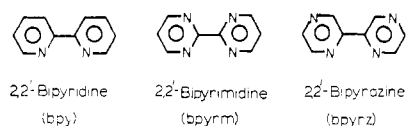The synthesis and properties of $Ru(bpy)_n(bpyrz)_{3-n}^{2+}$ and $Ru(bpy)_n(bpyrm)_{3-n}^{2+}$, where $n = 0-2$ and bpy is 2,2'-bipyridine, bpyrz is 2,2'-bipyrazine, and bpyrm is 2,2'-bipyrimidine, are described. Absorption spectra contained bands (250-290 nm) in the ultraviolet region that are assignable to ligand $\pi \rightarrow \pi^*$ transitions and visible bands (360-470 nm) that are assignable to $d\pi \rightarrow \pi^*$ MLCT transitions. The $d\pi \rightarrow \pi^*$ absorptions shift to the red as the number of bipyridine ligands is increased in mixed-ligand complexes. Emission spectra maxima were observed from 600 to 700 nm and also were found to shift to the red with substitution for bipyridine. Redox potentials were found to vary in a systematic way. The potentials for $Ru^{3+/2+}$ couples varied from ~ 1.30 to ~ 2.00 V vs. SSCE. Reductions were sequential one-electron-transfer steps equal in number to the number of bidentate ligands. The accumulated evidence indicates that each reduction step is associated with one of the ligands and that the steps occur in the following order: first bipyrazine, then bipyrimidine, and finally bipyridine. Trends were found between $E_{1/2}$ values and the number of ligands, n, given in the above formulations. Reduction potentials for the $Ru^{3+/2+}$ couples and for the first ligand-based reductions ($Ru^{2+/+}$ couples) within the $Ru(bpy)_n(bpyrz)_{3-n}^{2+}$ or $Ru(bpy)_n(bpyrm)_{3-n}^{2+}$ series were found to correlate in a linear manner. However, variations in the potential for the $Ru^{III/II}$ couple with changes in ligands were 2-3 times greater than variations in potential for the first ligand reduction step. A one to one correspondence was found between the energy of the emission maxima and the difference between the potential for the $Ru^{III/II}$ couple and the potential for the first ligand reduction. Excited-state reduction potentials were determined from the difference between emission energy maxima and ground-state redox potentials. Excited-state $Ru^{2+*/+}$ couples ranged from 0.8 to 1.4 V; those of $Ru^{3+/2+*}$ ranged from -0.1 to -0.8 V. The influence of the heterocyclic ligands on the $d\pi$ orbitals of ruthenium(II) complexes can be attributed to a combination of σ and π effects.

Introduction

The photophysical properties of $Ru(bpy)_3^{2+*}$, where bpy is 2,2'-bipyridine, has led to two general divisions of study. Electron-transfer reactions to and from the triplet excited state have been and continue to be extensively investigated primarily because of their potential application to energy storage and conversion.[3] More recently, photochemical substitution reactions have been noted in dichloromethane[4] and photodecomposition has been observed in DMF[5,6] and water.[7,8] In related studies, photochemical cis $\rightleftarrows$ trans isomerization has been observed for $Ru(bpy)_2(OH_2)_2^{2+}$ [9] and photochemical substitution in cis-$Ru(bpy)_2(py)_2^{2+}$, where py is pyridine, has been shown to be of synthetic value.[10]

More recently the photochemistry of tris(2,2'-bipyridine)-ruthenium(II) has been extended to include the tris complex of 2,2'-bipyrazine.[11,12] The photophysics of tris(2,2'-bipyrazine)ruthenium(II) appears to parallel that of the bipyridine analogue. Both electron transfer and photochemistry from the excited states were noted.

Due to a continued interest in electron transfer and the photochemistry of charge-transfer excited states, we have prepared a series of symmetrical and mixed-ligand, tris chelate complexes of 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpyrm) and 2,2'-bipyrazine (bpyrz) with Ru(II). The two primary

2,2'-Bipyridine (bpy)   2,2'-Bipyrimidine (bpyrm)   2,2'-Bipyrazine (bpyrz)

goals of our study were to demonstrate that excited-state redox potentials could be varied systematically over a wide range for luminescing compounds of ruthenium(II) by the appropriate combination of ligands and to develop a better understanding of the photophysical properties of ruthenium(II) heterocyclic compounds. This paper addresses the former goal; the latter will be the topic of the second paper in the sequence.

Our desire to vary excited-state redox potentials is related to practical applications of photocatalysis. Examples of the methods that we have used to exploit the triplet charge-transfer state of $Ru(bpy)_3^{2+*}$ include the design and operation of photoelectrochemical cells[13-15] based on electron-transfer quenching and the production of hydrogen by direct photolysis in the presence of a suitable quencher and finely divided

(1) A preliminary account of this work was given at the Biennial Inorganic Symposium held in Bloomington, IN, May 16-19, 1982.
(2) (a) The Univerisity of North Carolina at Charlotte. (b) The University of North Carolina at Chapel Hill.
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Table I. Visible-UV Spectra of Ruthenium(II) Parent and Mixed-Ligand Complexes in Acetonitrile[a]

compd	$d\pi \rightarrow \pi_1{}^*$	$d\pi \rightarrow \pi_2{}^*$	$\pi \rightarrow \pi^*$
[Ru(bpyrz)$_3$]$^{2+}$ [b]	440 (1.3 ×10^4), 415 (sh)	338 (sh)	291 (5.1 ×10^4), 240 (2.0 ×10^4)
[Ru(bpyrz)$_2$(bpy)]$^{2+}$	463 (1.2 ×10^4), 415 (9.2 ×10^3)	375 (5.6 ×10^3), 338 (sh)	294 (4.9 ×10^4), 240 (2.2 ×10^4)
[Ru(bpy)$_2$(bpyrz)]$^{2+}$	473 (9.9 ×10^3), 414 (1.0 ×10^4)	386 (sh), 343 (sh)	283 (6.3 ×10^4), 242 (2.4 ×10^4)
[Ru(bpyrm)$_3$]$^{2+}$	454 (8.6 ×10^3), 418 (8.2 ×10^3)	362 (sh), 332 (1.7 ×10^4)	252 (4.9 ×10^4)
[Ru(bpyrm)$_2$(bpy)]$^{2+}$	460 (sh), 420 (9.4 ×10^3)	368 (9.8 ×10^3), 326 (1.2 ×10^4)	283 (2.8 ×10^4), 255 (3.9 ×10^4)
[Ru(bpy)$_2$(bpyrm)]$^{2+}$ [c]	480 (sh), 422 (9.7 ×10^3)	360 (6.4 ×10^3), 322 (sh)	294 (4.8 ×10^4), 236 (4.0 ×10^4)
[Ru(bpy)$_3$]$^{2+}$ [d]	451 (1.4 ×10^4)	345 (6.5 ×10^3), 323 (6.5 ×10^3)	285 (8.7 ×10^4), 250 (2.5 ×10^4), 238 (3.0 ×10^4)

[a] λ_{max} in nm, error ±1 nm. ϵ values follow in parentheses, in M^{-1} cm^{-1}; $T = 20 \pm 1$ °C. [b] Values similar to those of ref 11. [c] From ref 19. [d] From ref 12.

platinum.[16] The value of having an extended range of excited-state redox potentials is obvious in that it extends the possible range of excited-state photocatalytic applications.

The purpose of this paper is to demonstrate that excited-state redox potentials can be varied systematically for heterocyclic ligand complexes of ruthenium(II) by appropriate combinations of the above ligands. In addition to redox potentials, the photophysical and photochemical properties of the excited states including lifetimes, emission quantum yields, and protonation of the remote nitrogens on the ligands are addressed.

Experimental Section

Materials. RuCl$_3$·3H$_2$O and ligands 2,2′-bipyridine and 2,2′-bipyrimidine were purchased commercially and used without further purification. Tetraethylammonium perchlorate, TEAP, was recrystallized three times from water and a final time from a 1:1 methanol-acetone mixture before drying under vacuum. Acetonitrile was chromatographic or pesticide grade and dried over 4-Å molecular sieves before use in electrochemistry. All other reagents, including propylene carbonate (Burdick and Jackson distilled in glass), were purchased commercially as reagent grade chemicals and were used without further purifiation. Nitrogen was scrubbed by passing it through a 2.4 M HCl solution containing ~0.4 M chromous chloride generated from chromic chloride over zinc amalgam. Elemental analyses were carried out by Integral Laboratories Inc., Raleigh, NC. These accompany the manuscript as supplementary material.

Preparation of Compounds. Ru(bpy)$_2$Cl$_2$·2H$_2$O,[17] Ru(bpy)Cl$_4$,[18] and [Ru(bpy)$_2$(bpyrm)](PF$_6$)$_2$[19,20] were prepared by literature methods. [Ru(bpyrm)$_3$](PF$_6$)$_2$ was prepared by a modification of the method given by Ludi.[21]

2,2′-Bipyrazine. The ligand was prepared by modifying the method of Lafferty and Case.[22] In a typical preparation 12.5 g of 2-pyrazinecarboxylic acid was dissolved in 15 M NH$_3$ and the solution was heated to dryness with a rotary evaporator. The resulting solid was added to 500 mL of a solution containing saturated Cu(C$_2$H$_3$-O$_2$)$_2$·H$_2$O. A blue solid formed as the mixture was stirred for 1 h at room temperature. The solid was removed by filtration, washed with ethanol followed by ether, and then dried by suction under vacuum.

The solid was then pyrolyzed at about 270 °C in three portions. Each portion was added to a 50-mL round bottom flask containing a 19/22 ground-glass joint that was interconnected to a condenser via a short three-way adapter. The flask was immersed in an oil (silicon) bath up to the neck. Pyrazine was sublimed into the upper portion of the condenser, and the crude ligand was sublimed into the lower portion of the adapter. The crude ligand was collected and recrystallized from ether; mp 186 °C (lit.[22] mp 185 °C).

[Ru(bpyrz)$_3$](PF$_6$)$_2$·2H$_2$O, [Ru(bpyrz)$_2$(bpy)](PF$_6$)$_2$, [Ru-(bpyrm)$_2$(bpy)](PF$_6$)$_2$, and [Ru(bpy)$_2$(bpyrz)](PF$_6$)$_2$. Approximately 1 mmol of Ru(bpy)$_2$Cl$_2$·2H$_2$O, Ru(bpy)Cl$_4$, or RuCl$_3$·3H$_2$O was added

to a 2- or 3-fold excess of 2,2′-bipyrazine or 2,2′-bipyrimidine needed to prepare the appropriate complex. The solids were suspended in 20 mL of ethylene glycol, and the resulting suspension was heated at reflux for 30 min. The solution was cooled to room temperature to remove unreacted ligand. About 3 mL of an aqueous, saturated KPF$_6$ solution was then added to precipitate the complex as the hexafluorophosphate salt. After 20 mL of water was added, the precipitate was filtered, redissolved in acetonitrile, and then precipitated by addition of the acetonitrile solution to ether. The compound was air-dried by suction and then purified by chromatography.

The compound was redissolved in a minimum quantity of acetonitrile and added to a 40 mm diameter column containing neutral alumina to a depth of ~4 in. The column had previously been developed with acetonitrile. It was necessary to use a very slow flow rate to separate the desired material from a brown band at the top of the column. The eluent was then concentrated to ~10 mL, and then the compound was precipitated upon addition of the concentrated eluent to ether. The product was then filtered and air-dried.

Physical Measurements. Visible-UV spectra were recorded with the Cary 14 or 17 spectrophotometer. Solution spectra were obtained in matched cells for the compounds reported here.

Polarograms and/or cyclic voltammograms were obtained in acetonitrile at a Pt-button working electrode with 0.1 M TEAP as the supporting electrolyte. The measurements were made vs. the saturated sodium chloride calomel electrode (SSCE). Electrochemistry was carried out with a PAR 174 polarographic analyzer or the PAR 173 potentiostat in conjunction with a PAR 175 programmer. Polarograms were recorded with a Houston Omnigraphic X-Y recorder.

Lifetime measurements were obtained from room-temperature solutions in Pyrex tubes with use of a Molectron UV-400 nitrogen laser as a pulsed light source. The emitted radiation was monitored at right angles to the incident beam by an EM 19785B photomultiplier tube, which was preceded by a BL 33-66-79 monochromator, a Corning 3-70 filter, and a 2-cm cell of nitromethane to absorb scattered light from the laser. The output of the photomultiplier was fed to a Tektronix Model R 7912 transient digitizer and then into a Digital PDP 11/34 minicomputer. The lifetimes were determined by a weighted least-squares fit to a simple exponential decay.

Uncorrected emission spectra and proton-quenching measurements were determined with the Hitachi Perkin-Elmer MPF-A or 650-40 spectrofluorimeter. Corrected emission spectra were obtained with the SLM Instruments, Inc., fluorescence instrument.

Proton-quenching measurements were made in aqueous solutions that were mixtures of 1.0 M HCl and 1.0 M NaOH. The pH of the solution was determined with the Radiometer Model pHM-62 pH meter calibrated with the appropriate buffer solution at room temperature.

Results

Electronic Spectra. The visible spectra of the bipyrazine series shown in Figure 1 are illustrative of the observations for both bipyrazine and bipyrimidine complexes. Starting with the parent complexes, as the number of bipyridine ligands increases, the low-energy transition shifts to the red. The red shift is also observed for Ru(bpy)$_2$L′$^{2+}$, where L′ is biimidazole[20] or bibenzimidazole,[23] Ru(bpy)$_2$L″$_2${}$^{2+}$, where L″ is pyrazole,[24] and Ru(bpy)$_2$LX$^+$,[25] where L is pyrazine and

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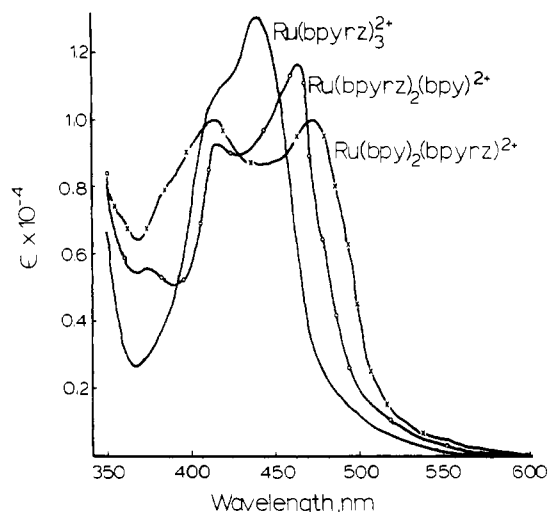(20) Dose, E. V.; Wilson, L. *Inorg. Chem.* **1978**, *17*, 2660.
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Figure 1. Absorption spectra of $[Ru(bpyrz)_3]^{2+}$ (—), $[Ru(bpyrz)_2$-$(bpy)]^{2+}$ (-O-O), and $[Ru(bpy)_2(bpyrz)]^{2+}$ (-X-X) in acetonitrile.

Table II. Polarographic Half-Wave Potentials for Ruthenium(II) Parent and Mixed-Ligand Complexes[a,b]

|	oxidn	redns		
compd	$E_{1/2}$	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$
$[Ru(bpyrz)_3]^{2+\,c}$	1.98	−0.68	−0.87	−1.14
$[Ru(bpyrz)_2(bpy)]^{2+}$	1.72	−0.79	−1.02	−1.58
$[Ru(bpy)_2(bpyz)]^{2+}$	1.49	−0.91	−1.45	−1.68
$[Ru(bpyrm)_3]^{2+}$	1.69	−0.91	−1.08	−1.28
$[Ru(bpyrm)_2(bpy)]^{2+}$	1.55	−0.95	−1.13	e
$[Ru(bpy)_2(bpyrm)]^{2+\,d}$	1.40	−1.02	−1.45	e
$[Ru(bpy)_3]^{2+}$	1.27	−1.31	−1.50	−1.77

[a] Potentials are in V vs. SSCE. [b] Solutions were 0.1 M in TEAP or TBAH; the solvent was acetonitrile; $T = 25 \pm 1\,°C$. [c] Our data are ∼0.1 V more positive than those of ref 11. [d] From ref 19. [e] Adsorption waves interfered with determination of these potentials.

X is chloride, and can be rationalized on the basis of reduction in symmetry and σ donor or π withdrawal properties of the L, L', L'', and X ligands. A summary of the important visible–ultraviolet features is given in Table I. The probable assignments for the absorptions based on the spectrum of $Ru(bpy)_3^{2+\,26}$ will be given in the discussion section below.

Electrochemistry. $E_{1/2}$ values were determined from the peak currents of differential pulse polarograms. As the number of bipyrazine ligands increases, the potential of the $Ru^{III/II}$ couple also increases. Bipyrimidine complexes follow a similar pattern. These data along with reductions of bipyrimidine and bipyrazine complexes are recorded in Table II.

$E_{1/2}$ values were also determined from cyclic voltammograms and gave results complementary to the differential pulse measurements. Peak positions ΔE_p, $\Delta E_p = E_{ox} - E_{red}$, varied from 60 to 70 mV and were nearly scan-rate independent, indicating that the processes were reversible one-electron transfers.[27] Cyclic voltammograms for reductions of bipyrazine complexes are illustrated in Figure 2. The sequence of steps is best interpreted as the stepwise reduction of each ligand π^* system. This explanation certainly seems plausible given that the reductions occur in the regions ascribed to parent complexes and parallel the number and type of ligand bound
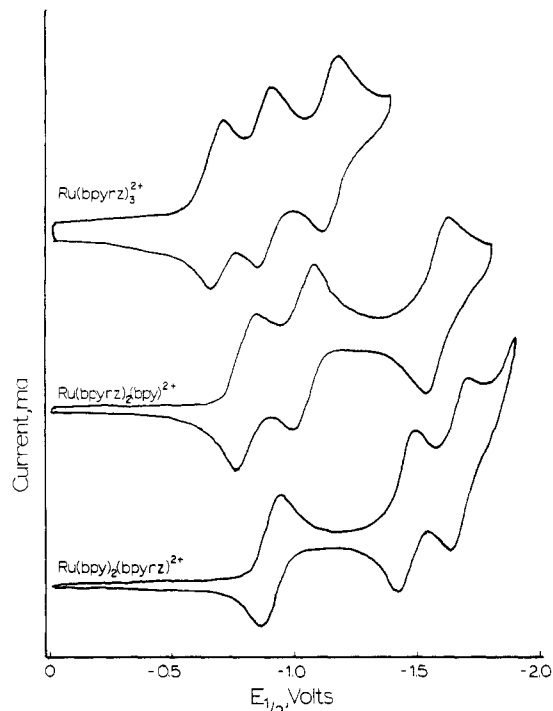
Figure 2. Cyclic voltammograms for successive one-step reductions of each bidentate ligand bound to ruthenium(II). See text for a description of the stepwise reduction processes.
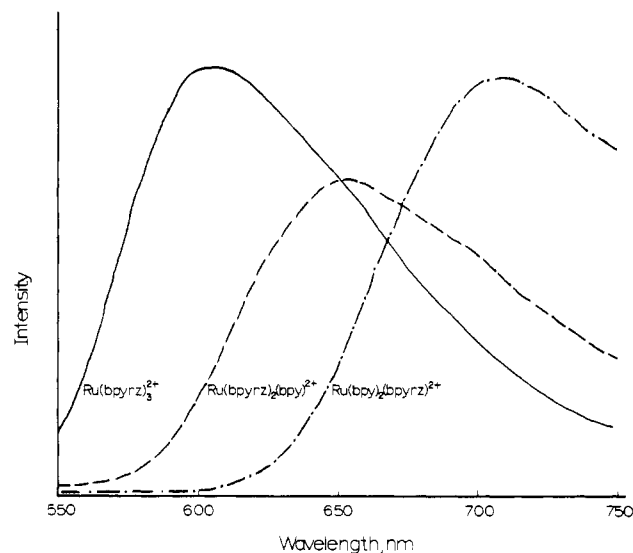

Figure 3. Corrected luminescence spectra of $[Ru(bpyrz)_3]^{2+}$ (—), $[Ru(bpyrz)_2(bpy)]^{2+}$ (- - -), and $[Ru(bpy)_2(bpyrz)]^{2+}$ (· · · ·) in acetonitrile. The intensity axis is in arbitrary units. See Table III for quantum yields; $\lambda_{ex} = 436$ nm.

Table III. Emission Maxima, Quantum Yields, and Excited-State Lifetimes for Ruthenium(II) Parent and Mixed-Ligand Complexes in Propylene Carbonate

compd[a]	$\lambda_{em}(max)$, nm[b,c]	$\Phi_{em}^{c,d}$	τ_0, ns[c,e]
$[Ru(bpyrz)_3]^{2+}$	610	7.4×10^{-2}	795
$[Ru(bpyrz)_2(bpy)]^{2+}$	654	7.9×10^{-2}	1099
$[Ru(bpy)_2(bpyrz)]^{2+}$	710	1.9×10^{-2}	376
$[Ru(bpyrm)_3]^{2+}$	639	1.1×10^{-2}	131
$[Ru(bpyrm)_2(bpy)]^{2+}$	670	1.1×10^{-2}	182
$[Ru(bpy)_2(bpyrm)]^{2+}$	710	3.6×10^{-3}	76
$[Ru(bpy)_3]^{2+\,f}$	620	4.0×10^{-2}	850

[a] PF_6^- salts. [b] Corrected. [c] $25 \pm 1\,°C$. [d] $\lambda_{ex} = 436$ nm. [e] N_2 degassed. [f] Reference 46, p 151.

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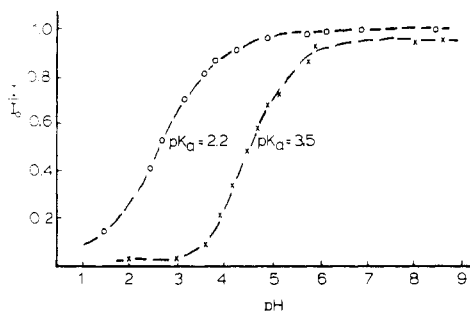
Figure 4. Dependence of luminescence intensity for [Ru(bpyrz)$_2$-(bpy)]$^{2+*}$ (-X-X) and [Ru(bpyrm)$_2$(bpy)]$^{2+*}$ (-O-O) on the pH of the solution. Excited-state pK_a values are 3.5 and 2.2, respectively.

to ruthenium. Thus, bound bipyrazine ligands are reduced commencing at –0.7 V, bipyrimidine at –0.9 V, and bipyridine at –1.3 V. This explanation is also consistent with DeArmond's[28] evidence of an electron localized in the π^* levels of one ligand rather than delocalized over the whole ligand π system in Ru(bpy)$_3$$^+$.

Luminescence Spectra—Lifetimes—Quantum Yields. Luminescence spectra were obtained for all the complexes in propylene carbonate and were corrected for phototube response. Emission maxima are recorded in Table III, and spectra are illustrated in Figure 3. Concomitant with the red shift in the visible spectrum is a red shift in the emission spectrum of approximately the same energy.

Excited-state lifetimes are also recorded in Table III. The lifetimes of bipyrazine complexes are 6–7 times longer than those of the corresponding bipyrimidine analogues. The second member of each series, Ru(bpyrz)$_2$(bpy)$^{2+}$ and Ru-(bpyrm)$_2$(bpy)$^{2+}$, have longer lifetimes than either the parent or the member containing two bipyridine ligands. The excited states are quenched by molecular oxygen, electron-transfer quenchers, and protons.

The remote nitrogen atoms of the bipyrazine or bipyrimidine ring become better bases upon optical excitation of the complex as shown in Figure 4. The three bipyrimidine complexes behave similarly and give an apparent excited-state pK_a value of 2.2; the bipyrazine systems give a value of 3.5. The apparent pK_a values were obtained from the midpoint of the break in the titration curve of luminescence intensity vs. pH shown in Figure 4. Lever reports that the remote nitrogen atoms can be protonated sequentially and the luminescence spectra can be studied in very strongly acidic solution, although the luminescence is very weak.[29] An interesting point arises from the apparent pK_a values for the excited states of the differing ligands in that the values are inverted from the ground-state values of 1.3 for pyrimidine[30] and 0.80 for pyrazine.[31] The inversion indicates that the remote nitrogen para to the coordinated nitrogen is more strongly affected by localization of the electron on the ring than is the meta nitrogen.

Quantum yields for luminescence were determined in propylene carbonate. The method of Guilbault was used for their determination.[32] These were deduced by comparison to Ru(bpy)$_3$$^{2+}$ having a known quantum yield of 0.04 at λ_{ex} = 436 nm.[24] Quantum yields are given in Table III. A rough correlation between quantum yields and excited-state lifetimes in noted rather than any direct correlation with λ_{em}. The
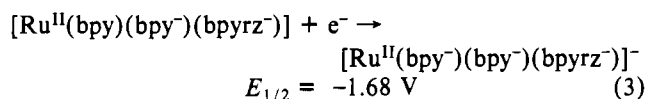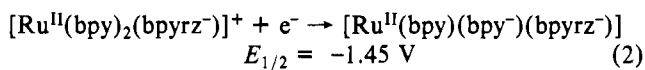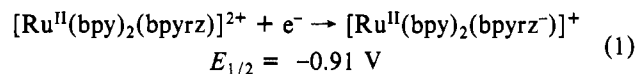
reasons for these observations are related to the detailed photophysical behavior of these complexes and will be the focus of a second paper as mentioned above.

Discussion

Spectra. The visible–ultraviolet spectra contain absorption bands characteristic of ruthenium(II) heterocyclic ligand complexes. The high-energy absorptions in the 240–290-nm region are generally assigned as $\pi \rightarrow \pi^*$ transitions.[26,33] The π^* levels of bipyridine, bipyrimidine, and bipyrazine are at different energies (reductions of free ligands occur at –2.21,[34] –1.99,[35] and –1.76 V[12] vs. SSCE, respectively). Thus, mixed-ligand complexes are expected to give rise to different d$\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions characteristic of ligands coordinated to the metal center. For Ru(bpy)$_3$$^{2+}$ itself, there are a series of d$\pi \rightarrow \pi^*$ transitions.[26] The first of these are assigned as d$\pi \rightarrow \pi_1^*$ transitions, and a second series approximately 6000 cm^{-1} in energy are assigned as d$\pi \rightarrow \pi_2^*$. In mixed-ligand complexes, the detailed spectra are expected to be more complex. The low-energy d$\pi \rightarrow \pi_1^*$ MLCT transition clearly shifts to the red as the number of bipyridine ligands increases in mixed-chelate bpy–bpyrz or bpy–bpyrm complexes. The red shift correlates with the Ru$^{III/II}$ redox potentials in a given sequence and is in agreement with the greater ease of oxidation of rutheniumII). The lowest energy transition can be assigned to the ligand containing the lowest π^* level.[19] In the case for the mixed-ligand systems studied here, it is consistent with the lowest energy transition assignable to d$\pi \rightarrow \pi^*$(bpyrz) the intermediate one assignable to d$\pi \rightarrow \pi^*$(bpyrm), and the highest one assignable to d$\pi \rightarrow \pi^*$(bpy).

Optical excitation by visible or UV light gives rise to luminescence decay similar to that found in Ru(bpy)$_3$$^{2+*}$. Theoretical studies indicate that absorption is dominated by excitation to charge-transfer states largely singlet in character and emission by states largely triplet in character.[26,36] The reader interested in the theoretical bases for these assignments is asked to consult the recent paper by Kober and Meyer and references therein for details.[26b]

Electrochemistry. Reductions of ruthenium(II) complexes studied here are ligand centered. The order of decreasing ease of reduction in the complexes is bpyrz > bpyrm > bpy, and the potential differences roughly parallel the reduction potential differences of the free ligands. The effect of the metal is to lower the energy of the ligand π^* level approximately 1 V. With, as a typical example, [Ru(bpy)$_2$(bpyrz)]$^{2+}$, the potentials can be assigned as

$$[Ru^{II}(bpy)_2(bpyrz)]^{2+} + e^- \rightarrow [Ru^{II}(bpy)_2(bpyrz^-)]^+$$
$$E_{1/2} = -0.91 \text{ V} \tag{1}$$

$$[Ru^{II}(bpy)_2(bpyrz^-)]^+ + e^- \rightarrow [Ru^{II}(bpy)(bpy^-)(bpyrz^-)]$$
$$E_{1/2} = -1.45 \text{ V} \tag{2}$$

$$[Ru^{II}(bpy)(bpy^-)(bpyrz^-)] + e^- \rightarrow$$
$$[Ru^{II}(bpy^-)(bpy^-)(bpyrz^-)]^-$$
$$E_{1/2} = -1.68 \text{ V} \tag{3}$$

Within a sequence, a plot of the number of a given type of ligand (e.g. bpyrz) vs. the $E_{1/2}$ value for the first reduction is linear. Slopes are 8.7 and 17.7 decades/V for the bipyrazine and bipyrimidine systems, respectively, and correlation coefficients are 0.99 in both cases.

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(36) (a) Klaasen, A. M.; Crosby, G. A. *J. Chem. Phys.* **1968**, *48*, 1853. (b) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.
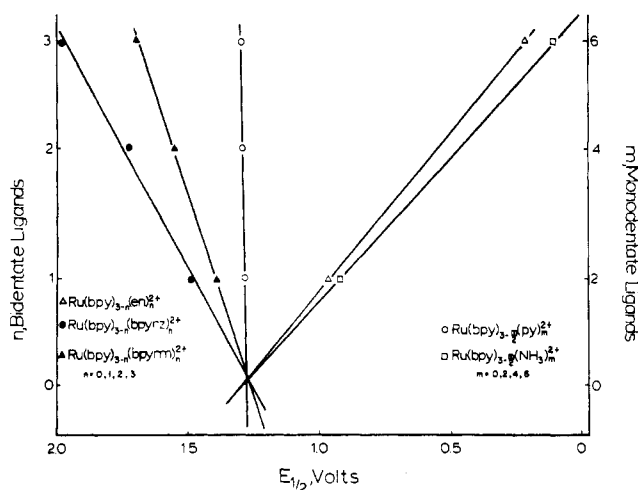
Figure 5. Correlation of the number of bidentate ligands, n, and the number of monodentate ligands, m, as a function of the ruthenium-(III/II) potentials ($E_{1/2}$ in volts vs. SSCE) for a series of parent complexes and mixed-ligand complexes of ruthenium(II) containing 2,2'-bipyridine. Correlation coefficients are 0.99 for lines consisting of at least three points.
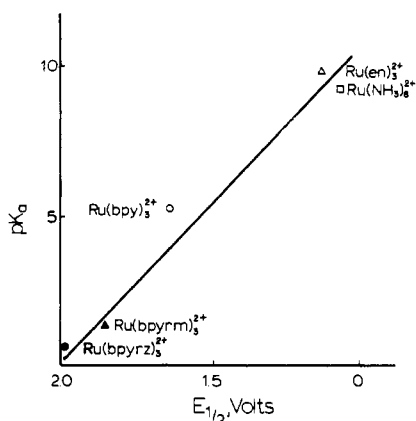
Figure 6. Dependence of the ($\bullet$) $[Ru(bpyrz)_3]^{3+/2+}$, ($\blacktriangle$) $[Ru(bpyrm)_3]^{3+/2+}$, ($\bigcirc$) $[Ru(bpy)_3]^{3+/2+}$, ($\triangle$) $[Ru(en)_3]^{3+/2+}$, and ($\square$) $[Ru(NH_3)_6]^{3+/2+}$ potentials ($E_{1/2}$ in volts vs. SSCE) on the pK_a values of pyrazine (0.8), pyrimidine (1.3), pyridine (5.25), ethylenediamine (9.93), and ammonia (9.25). The correlation coefficient is 0.98; the slope is −4.96 decades/V.

Similarly, plots of the number of ligands vs. $E_{1/2}$ values for the $Ru^{III/II}$ couples of the bipyrazine and bipyrimidine series are linear. These are illustrated in Figure 5. Also included are literature data for ruthenium(II) mixed-ligand bipyridine complexes containing pyridine (py), ethylenediamine (en), and ammonia (NH_3),[37] along with their symmetrical analogues (i.e. $Ru(NH_3)_6^{3+/2+}$).[38,39] The observation of linear correlations for each sequence and the fact that the lines for each sequence intersect near the potential for the $Ru(bpy)^{3+/2+}$ couple are both of some interest.

Potential variations of $Ru^{3+/2+}$ couples with ligands in Figure 5 may be related to the σ donor strength and π-bonding properties of the ligands. Figure 6 shows a linear correlation between the potential of the $Ru^{3+/2+}$ couple and the pK_a of the bound ligand, which is a measure of the σ donor ability of the coordinated ligand. A similar correlation was found by Cloninger and Callahan[40] for a series of tris(phenanthro-
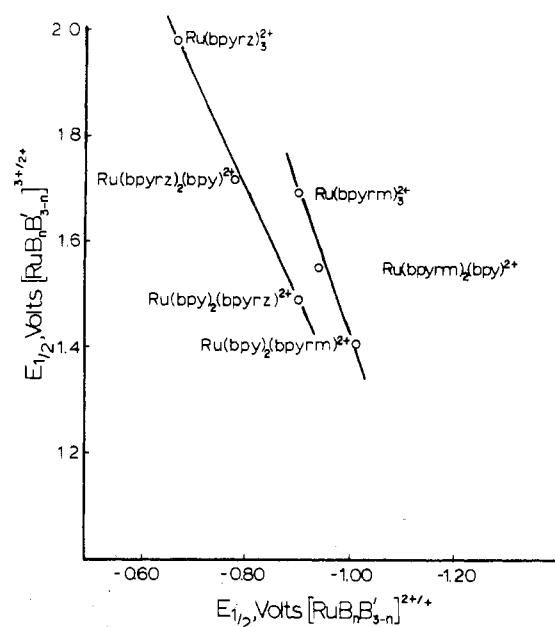
Figure 7. Free energy correlation for the first oxidation ($E_{1/2}$ for $[RuB_nB'_{3-n}]^{3+/2+}$ in volts vs. SSCE) and the first reduction ($E_{1/2}$ for $[RuB_nB'_{3-n}]^{2+/+}$ in volts vs. SSCE) for the ruthenium bipyrazine and bipyrimidine series studied here. Correlation coefficients of the lines were 0.99. Slopes were 2.1 for the bipyrazine series and 2.6 for the bipyrimidine series.

line)ruthenium(II) complexes. From the potential data of the $Ru^{3+/2+}$ couple, the most obvious effect of weaker σ donation is stabilization of Ru(II).

According to Lever,[12] the weaker σ donor capacity of the ligand gives rise to a greater effective nuclear charge on the ruthenium and this results in stabilization of the metal d orbitals. It can be argued that the greater effective nuclear charge on the ruthenium would have the synergistic effect of lowering the energy of the ligand π^* level through charge interaction.[41,42] Further stabilization of Ru(II) could then occur by back-bonding of the dπ orbitals with the π^* level of the coordinating ligands. This interpretation would suggest that the lower π^* levels in a ligand like bipyrazine would result in more effective mixing with the metal dπ energy levels and result in stabilization of the $(d\pi)^6$ configuration for Ru(II).

The importance of π-bonding effects in related complexes has been rationalized on the basis of ligand types that withdraw[33,41] or donate[24] electrons through dπ—π^* interaction. The Ru–N bond distance in $Ru(bpy)_3^{2+}$ is reported to be 2.050 Å and justified on the basis of π bonding.[43] Other evidence for the importance of π back-bonding has been reported by Krause and Krause[44] for $Ru(Azpy)_2Cl_2$, where Azpy is 2-(phenylazo)pyridine. The $\nu(N=N)$ vibration for the compound was shifted ~ 100 cm^{-1} below the free ligand value, and this large shift was interpreted to result from the π-bonding influence of the Azpy ligand.

In subsequent work, Krause and Krause[45] concluded that it was necessary to consider both σ- and π-bonding effects in order to account for bonding of heterocyclic ligands to ruthenium for complexes of the type $Ru(Azpy)_2AB,^{n+}$ where AB

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(42) The reductions of the coordinated ligands compared to those of free ligands shift positively by 1.08 V for bipyrazine and bipyrimidine and 0.95 V for bipyridine. However, care must be exercised in these comparisons due to the fact that at least one of the couples (bipyrimidine) is an irreversible couple.[36]

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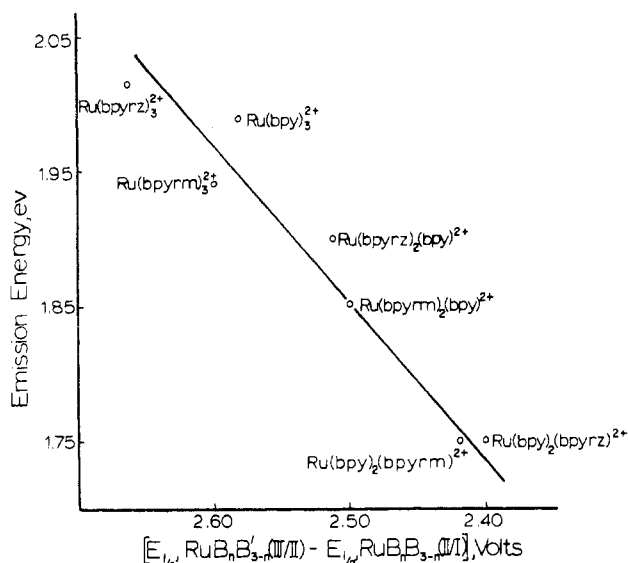
Figure 8. Correlation of the ground-state energy gap, determined by the difference in $E_{1/2}$ values between the $[RuB_nB'_{3-n}]^{3+/2+}$ couple and the $[RuB_nB'_{3-n}]^{2+/+}$ couple in volts vs. SSCE, with the emission energy in eV. The slope is 1, the correlation coefficient is 0.97, and the intercept is −0.95 eV.

represents π-accepting coligands. The importance of both σ and π effects in systems reported here can be qualitatively understood from Figure 7.

Figure 7 is a comparison of $E_{1/2}$ for the $Ru^{3+/2+}$ couple and $E_{1/2}$ for the first ligand reduction. As the bipyridine is replaced by bipyrimidine or bipyrazine, the first reduction shifts positively. This is in accord with the arguments presented before, namely, the decrease in σ donor strength of the ligands results in a greater effective nuclear charge on ruthenium, which then lowers the energy of the ligand π* orbitals. The subsequent effect of dπ−π* back-bonding would stabilize the metal dπ orbitals but destabilizes the ligand π* level. Thus, if both σ and π effects are important, one would expect the plots in Figure to exhibit this. Indeed, the changes in $E_{1/2}$ values for the bipyrazine series are greater than for the bipyrimidine series. The slopes also differ and are 2.1 and 2.6 for the bipyrazine and bipyrimidine series, respectively. The slopes indicate that the metal dπ orbitals are stabilized 2−3 times more than the π* orbitals of the ligands. The fact that the slopes differ suggests again that σ- and π-bonding effects are important for ruthenium complexes containing heterocyclic ligands that accept π electrons as previously suggested by Krause and Krause.[45]

Excited-State Redox Properties. Figure 8 shows that there is a one to one correspondence (slope of 1) between the emission energy maximum (eV) and the difference in potential between the HOMO and LUMO of ruthenium(II). The behavior is expected due to the similarity of the complexes. The intercept of the plot in Figure 8 is −0.95 eV. The intercept is a function of a number of variables that will be analyzed in a future paper on the photophysical properties of a series of osmium complexes.[46]

The energy of emission for the compounds varies over a small range from 1.8 to 2.1 eV. Past results indicate that excellent estimates of excited-state redox potentials can be made for polypyridine or porphyrin ruthenium complexes[46–48]

(46) Dressick, W. J., Ph.D. Thesis, The University of North Carolina, 1981; Chapter 5.
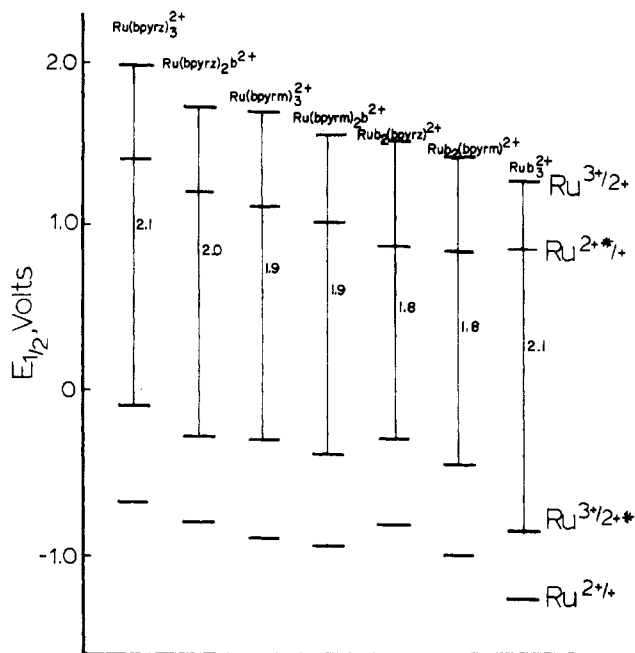
Figure 9. Redox potential diagram containing excited-state potential estimates based on the difference in energy of the emission maxima (eV) and the ground-state redox processes.

by calculating the difference between the ground-state potential and the excited-state emission energy in eV: i.e., $E_{1/2}^{3+/2+*} \simeq E_{1/2}^{3+/2+} - E_{em}$; $E_{1/2}^{2+*/+} = E_{1/2}^{2+/+} + E_{em}$. The values are lower limits since the luminescence energy contains a contribution from vibrational distortion between ground and excited states. These calculations lead to the results given in Figure 9. The $Ru^{3+/2+*}$ potentials vary from −0.1 to −0.86 V; the $Ru^{2+*/+}$ potentials vary from +1.4 to +0.8 V.

The results obtained are of interest from a number of points of view. It is clear that emission energies remain fairly constant through the series even though ground-state and excited-state redox potentials vary widely. Thus, it is possible to adjust excited-state potentials by changing the ligand or ligands coordinated to the appropriate metal center and yet retain a relatively constant chromophoric character. However, the most impressive point is the wide range in redox potentials illustrated in Figure 9. The redox potential data show the availability of an extended series of excited states having a broad range of redox potentials for possible applications in excited-state redox chemistry.

Registry No. [Ry(bpyrz)₃](PF₆)₂, 80907-56-8; [Ru(bpyrz)₂(bpy)](PF₆)₂, 85335-52-0; [Ru(bpy)₂(bpyrz)](PF₆)₂, 85335-54-2; [Ru(bpyrm)₃](PF₆)₂, 85335-55-3; [Ru(bpyrm)₂(bpy)](PF₆)₂, 85335-57-5; [Ru(bpy)₂(bpyrm)](PF₆)₂, 65013-23-2; Ru(bpy)₂Cl₂, 15746-57-3; Ru(bpy)Cl₄, 63338-26-1; bpyrz, 10199-00-5.

Supplementary Material Available: A listing of elemental analyses (1 page). Ordering information is given on any current masthead page.

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