to 16.2 for An). When the macrocyclic ligand is L_2, the activation enthalpy increases over that for L_1, as discussed earlier, but is still substantially less than those observed for TAAB. Apparently, then, L_1, and to a lesser extent L_2, exerts a stronger labilizing influence on N-donor axial ligands than does TAAB.

The differences among the three macrocyclic ligands may be discussed primarily in terms of ring size and inherent donor abilities of the imine nitrogens, since the degree of unsaturation in the inner ring is the same for all three ligands. For constant ring size, as we have seen above, changing the imine substituents from CH_3 to C_6H_5 has a marked effect, in the expected direction, on the iron(II)–axial ligand bond strength. This reflects a reduction in the inherent donor ability of the macrocyclic ligand. Similarly, when the size of the inner ring is increased by two, as in the TAAB ligand, the metal ion is not "squeezed" as tightly by the macrocycle; consequently, electron donation by the ring is lessened. This is manifested in an enhanced iron(II)–axial ligand interaction and hence an increased activation barrier for dissociation.

It is also notable that the ordering of ΔH^{*} values for L_1 and TAAB is consistent with the relative magnitudes of the in-plane ligand fields produced by these macrocycles. (Dq_{xy}(TAAB) = 1465 cm^{-1} and $Dq_{xy}(L_1)$ = 1767 cm^{-1}, measured from the electronic spectra of (dithiocyanato)nickel complexes of the macrocycles.[33]) Although Dq_{xy} for L_2 has not been determined, we predict on the basis of the data in Table I that it should lie between those for L_1 and TAAB.

In conclusion, we have shown that in complexes of the type $FeL(Y)_2^{2+}$, where L = L_1 and L_2 and Y = acetonitrile and *N*-methylimidazole, structural changes on the periphery of the macrocyclic ligand have a substantial effect on the ability of L to labilize the axial sites. We are in the process of extending our investigation to include several additional ligands of the type L = $[X_4(14)tetraeneN_4]$, where X represents a variety of groups, to examine more fully the effects of peripheral substituents on the axial labilizing ability of the macrocycle.

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Note Added in Proof. Since this paper was accepted for publication, a report describing the synthesis of $FeL_2(An)_2(PF_6)_2$ has appeared.[34] Electronic spectral data are in reasonable agreement with ours.

Registry No. $FeL_1(An)_2^{2+}$, 49861-52-1; $FeL_2(An)_2(PF_6)_2$, 70369-09-4; MeIm, 616-47-7; Im, 288-32-4; 1,3-diaminopropane, 109-76-2; benzil, 134-81-6.

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Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Monomeric and Dimeric Pyrazole and Pyrazolyl Complexes of Ruthenium

B. PATRICK SULLIVAN, DENNIS J. SALMON, THOMAS J. MEYER,* and JUDY PEEDIN

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The first examples of well-characterized, monomeric ruthenium–pyrazole complexes have been obtained. The complexes include $[(bpy)_2Ru(pzH)_2]^{2+}$, $[(bpy)_2Ru(pz)(pzH)]^{+}$, and $(bpy)_2Ru(pz)_2{\cdot}H_2O$ (bpy = 2,2′-bipyridine, pzH = pyrazole, pz = pyrazolyl anion). From the results of cyclic voltammetry and electronic spectral measurements it is concluded that, in the complexes, the pzH ligand is a poorer π acceptor than pyridine while in its deprotonated form (pz), it is a better π donor than Cl^- ion. The pyrazole complexes can be deprotonated in solution giving the complex $(bpy)_2Ru(pz)_2$ which is itself capable of reacting as a chelating ligand. It undergoes a reaction with the labile solvent complex $[(bpy)_2Ru((CH_3)_2CO)_2]^{2+}$ giving the doubly bridged dimer $[(bpy)_2Ru^{II}(pz)_2Ru^{II}(bpy)_2]^{2+}$. The reactivity of the mixed-valence form of this ion, $[(bpy)_2Ru^{II}(pz)_2Ru^{III}(bpy)_2]^{3+}$, is similar to that reported for the previously characterized chloro-bridged dimers $[(bpy)_2RuCl_2Ru(bpy)_2]^{3+}$, in that it undergoes an asymmetrical cleavage reaction in CH_3CN solution.

Trofimenko has described syntheses and physical properties for the ions $HB(pz)_3^-$ and $B(pz)_4^-$ which can function as either η^2 or η^3 ligands when bound to metal ions.[1] Dimeric complexes such as $(CO)_2Rh(pz)_2Rh(CO)_2$[2] and $[(\eta^5\text{-}C_5H_5)Ti(pz)_2Ti(\eta^5\text{-}C_5H_5)]$[3] have also been prepared by using the pyrazolyl group (pz) as a bridging ligand. The preparations involve the direct

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reaction of the pyrazolyl anion with appropriate precursor metal complexes.

From the work of Dwyer and co-workers[4] and our more recent work, systematic procedures exist for the preparation of a series of complexes of the type *cis*-$[(bpy)_2RuXY]^{n+}$ (bpy is 2,2′-bipyridine).[5] The Ru–bpy complexes are of interest as chemical systems because of their high chemical stabilities, their reversible redox chemistry, and the versatility associated with their synthetic chemistry. They have provided important examples for the study of excited-state redox reactions,[6] have led to well-defined mixed-valence compounds,[7] and have provided a basis for the design of complexes which have promise as oxidation catalysts.[8]

We describe here the preparation, properties, and acid–base chemistry of the complex $[(bpy)_2Ru(pzH)_2]^{2+}$ (pzH is 1*H*-pyrazole). Our interests in the system included the determination of the differences in electronic effects exerted at the metal between the protonated (pyrazole) and deprotonated (pyrazolyl) forms of the ligand, the possible introduction of a potential proton-acceptor site at a bound ligand which could be of value in the design of future oxidation catalysts, and, by analogy with the polypyrazolylborates, the use of the fully deprotonated complex $(bpy)_2Ru(pz)_2$ as a chelating ligand.

Experimental Section

Measurements. Ultraviolet, visible, and near-infrared spectra were recorded with either Cary Model 14 or Bausch and Lomb Model 210 spectrophotometers. Molar extinction coefficients were obtained from absorbance measurements by using at least two different concentrations of complex. Luminescence spectral data for the complexes were recorded on a Hitachi Perkin-Elmer Model MPF-2A spectrofluorometer at room temperature (22 ± 2 °C). Excited-state lifetime data were obtained by laser flash photolysis as previously described.[9] Proton NMR spectra were determined by using a 100-MHz Varian Fourier transform spectrometer with Me_4Si as an internal standard. Electrochemical measurements were made vs. the saturated sodium chloride–calomel electrode (SSCE) at 25 ± 2 °C and are uncorrected for junction potential effects. The $E_{1/2}$ values for reversible couples were calculated from half the difference between E_p values for the anodic and cathodic waves from cyclic voltammetry. $E_{1/2}$ values are used as formal reduction potentials with the assumption that differences in diffusion coefficients for the oxidized and reduced species are negligible. The measurements were made by using a PAR Model 173 potentiostat for potential control with a PAR Model 175 Universal Programmer as a sweep generator for voltammetry measurements. Values for n, where n is the number of electrons transferred per complex in an exhaustive electrolysis experiment at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. The reactions were considered complete after the current had fallen to 1% of the initial value. All coulometry measurements were performed at platinum screen electrodes with use of MCB Spectrograde acetonitrile as the solvent and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the electrolyte. Elemental analyses were performed by Integral Microlabs.

Materials. TBAH was prepared in accordance with previously published techniques,[10] recrystallized from hot ethanol–water three times, and vacuum-dried at 70 °C for 10 h. Acetonitrile (MCB Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical experiments and used without drying for spectral measurements. Deuterioacetonitrile (99.9%) was purchased from Stohler Isotope Chemicals. Water was deionized and then distilled from alkaline permanganate. All solvents used in preparations were reagent grade and were used without further purification. Ligands were purchased from Aldrich Chemical Co. and were used as received.

Preparations. Preparation of $[(bpy)_2Ru(pzH)_2][PF_6]_2$. To 100 mL of deaerated water were added 520 mg (1 mmol) of *cis*-$(bpy)_2RuCl_2$[11] and 150 mg of pyrazole (2.2 mmol). The mixture was heated at reflux under nitrogen for 1.5 h and then cooled to room temperature and filtered. An excess of NH_4PF_6 was added to the filtrate as the solution was magnetically stirred. After the precipitation of the bright orange solid appeared to be complete, the solid was collected by filtration. The solid was air-dried and dissolved in a minimum of acetonitrile. The solution was filtered and the solid was precipitated slowly by adding a minimum amount of diethyl ether slowly. The precipitation procedure was repeated twice more and the final solid was dried at the pump overnight. The yield was 800 mg (95%). Anal. Calcd for $[(bpy)_2Ru(pzH)_2][PF_6]_2$: C, 37.18; N, 13.34; H, 2.86. Found: C, 37.14; N, 13.08; H, 2.98.

Preparation of $(bpy)_2Ru(pz)_2\cdot H_2O$. The same proportions of reactants were used as in the preparation of $[(bpy)_2Ru(pzH)_2][PF_6]_2$ and 400 mg of KOH was also added. After a reflux time of 1 h, the reaction mixture was cooled to ice temperature and filtered. A purple, microcrystalline solid was isolated. The solid was washed with 10 mL of ice-cold H_2O, washed copiously with Et_2O, and then air-dried to give 391 mg (69%) of product. Addition of ClO_4^- or PF_6^- to the combined filtrates from above gave $[(bpy)_2Ru(pz)(pzH)]X$ (X = PF_6^- or ClO_4^-). Anal. Calcd for $(bpy)_2Ru(pz)_2\cdot H_2O$: C, 55.12; N, 19.72; H, 4.07. Found: C, 54.96; N, 19.39; H, 4.07.

Preparation of $[(bpy)_2Ru(pz)(pzH)][PF_6]$. To 50 mL of warm $MeOH-H_2O$ (1:1 by volume) was added 150 mg of $(bpy)_2Ru(pz)_2\cdot H_2O$. The resulting solution was stirred for 20 min and then an excess of NH_4PF_6 was added; stirring was continued with gentle heating for 30 min. After this period the solution was reduced in volume on a rotary evaporator to ca. 10 mL and filtered. The crude, red-violet precipitate which was collected was washed first with H_2O and then copiously with Et_2O. It was carefully reprecipitated from a concentrated CH_3CN solution by dropping the solution into a flask containing Et_2O with constant stirring. Anal. Calcd for $[(bpy)_2Ru(pz)(pzH)][PF_6]$: C, 48.17; N, 17.30; H, 3.55. Found: C, 47.85; H, 17.03; H, 3.38.

Preparation of $[(bpy)_2Ru(pz)_2Ru(bpy)_2][ClO_4]_2$. An acetone solution of $[(bpy)_2Ru(acetone)_2]^{2+}$[11] was prepared by stirring 260 mg of *cis*-$(bpy)_2RuCl_2$ with 208 mg of $AgClO_4$ in 30 mL of deaerated, *dry* acetone. The solution containing suspended AgCl was stirred for 3 h at ambient temperature after which time AgCl was filtered by gravity. The filtrate was combined with 30 mL of EtOH and 280 mg of $(bpy)_2Ru(pz)_2\cdot H_2O$; the resulting mixture was deaerated with a N_2 stream and heated at reflux for 12 h. After this period the solution was evaporated to dryness on a rotary evaporator and the solid was dissolved in a minimum of acetone. Careful addition of Et_2O to this solution until the point of turbidity, followed by prolonged cooling at −20 °C, resulted in dark violet crystals of the salt. The precipitation was repeated on the mother liquor two more times. The total yield was 272 mg (47%). The same reaction using $AgPF_6$ gave the PF_6^- salt. Anal. Calcd for $[(bpy)_2Ru(pz)_2Ru(bpy)_2][PF_6]_2\cdot 3(CH_3)_2CO$: C, 45.50; N, 11.49; H, 3.86. Found: C, 44.88; N, 11.26; H, 3.31.

Results and Discussion

Bis(pyrazole) Complexes. The synthesis of the bis(pyrazole) complex $[(bpy)_2Ru(pzH)_2]^{2+}$ involved heating solutions containing *cis*-$Ru(bpy)_2Cl_2$ and pyrazole (pzH) in excess (eq 1).

$$2pzH + cis\text{-}(bpy)_2RuCl_2 \xrightarrow[H_2O]{\Delta} [(bpy)_2Ru(pzH)_2]^{2+} + 2Cl^- \quad (1)$$

The formulation of the complex as the cis isomer is based on its chemical and physical properties, as discussed below. The complex is conveniently isolated at its PF_6^- salt, which was characterized by elemental analysis and by its 100-MHz ^1H NMR spectrum in CD_3CN with Me_4Si as an internal standard. The NMR spectrum included resonances assignable to both bpy and pyrazole carbon protons which appear in the region between τ 0.91 and 3.04. A first-order coupling scheme predicts six doublets and five triplets (in C_2 symmetry), each of relative area two. The actual spectrum is complicated because of extensive overlap but is consistent with the presence of two pyrazole and two bpy groups. When an isolated low-field doublet in the aromatic region was assigned as a reference of area two, the total number of aromatic protons was found to be 22, as expected. A broad, low-field resonance at τ −3.97 is assignable to the pyrazole nitrogen protons.

Chemical studies show that the protons on the pyrazole nitrogens can be removed, but the resulting acid–base chemistry is somewhat complicated. If the preparation in eq 1 is

Table I. Electronic Spectral Data for the Pyrazole, Pyrazolyl, and Related Complexes

complex	λ_{max}, nm (ϵ)					foot-note
$[(bpy)_2Ru(pzH)_2][PF_6]_2$	470 (5.18×10^3)	~323 (~5×10^3)	289 (4.58×10^4)	252 (~1.7×10^4)	243 (1.93×10^4)	*a*
$[(bpy)_2Ru(py)_2][PF_6]_2$	455 (8.2×10^3)	338 (1.59×10^4)	289 (5.00×10^4)	254	243 (2.40×10^4)	*b*
$[(bpy)_2Ru(pz)(pzH)][PF_6]$	510 (4.89×10^3)	363 (4.45×10^3)	292 (3.99×10^4)	250 (~1.5×10^4)	242	*a*
$[(bpy)_2Ru(py)Cl][PF_6]$	496 (8.10×10^3)	350 (1.04×10^4)	293 (4.22×10^4)	255	242 (1.84×10^4)	*b*
$(bpy)_2Ru(pz)_2 \cdot H_2O$	581 (4.62×10^3)	434 (4.10×10^3)				*c*
$(bpy)_2RuCl_2$	553 (9.1×10^3)	380 (8.85×10^3)	297 (5.0×10^4)		243 (2.1×10^4)	*b*
$[(bpy)_2Ru(pz)]_2[PF_6]_2$	507 (1.38×10^4)	357 (1.28×10^4)	294 (7.13×10^4)	288 (~7.0×10^4)	244 (4.2×10^4)	*a*

[a] In CH_3CN solution. [b] J. Walsh, unpublished data (CH_3CN solution). [c] $(bpy)_2Ru(pz)_2 \cdot H_2O$ data recorded in dry DMF solution.

carried out in the presence of excess KOH, a dark purple crystalline solid can be isolated (eq 2). Elemental analyses

$$(bpy)_2RuCl_2 + 2OH^- + 2pzH \xrightarrow[\Delta]{EtOH/H_2O} (bpy)_2Ru(pz)_2 \cdot H_2O + 2Cl^- + H_2O \quad (2)$$

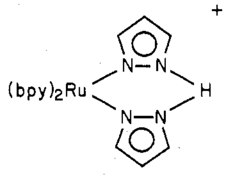
for the solid were consistent with the hydrate formulation $(bpy)_2Ru(pz)_2 \cdot H_2O$. The purple solid, which is soluble in MeOH, DMF, Me_2SO, and hot water, slightly soluble in acetone, and insoluble in CH_3CN, CH_2Cl_2, and benzene, can also be prepared by the treatment of $[(bpy)_2Ru(pzH)_2]Cl_2$ with KOH in aqueous solution at room temperature. The addition of a few drops of HPF_6 (85% in H_2O) to a MeOH solution of $(bpy)_2Ru(pz)_2 \cdot H_2O$ gave back $[(bpy)_2Ru(pzH)_2]^{2+}$ quantitatively as determined by cyclic voltammetry and visible spectroscopy.

The actual state of $(bpy)_2Ru(pz)_2 \cdot H_2O$ in solution depends on the solvent conditions used. Solutions of the compound in aqueous methanol are red, and, if $LiClO_4$ is added, a salt can be isolated whose elemental analysis is consistent with the formulation $[(bpy)_2Ru(pz)(pzH)][ClO_4]$. Solutions of $(bpy)_2Ru(pz)_2 \cdot H_2O$ in dry DMF are purple, but the addition of water gives $[(bpy)_2Ru(pz)(pzH)]^+$ rapidly as shown by spectral and cyclic voltammetry studies. When $(bpy)_2Ru(pz)_2 \cdot H_2O$ is dissolved in wet acetonitrile, spectral and electrochemical studies show that the dominant form of the complex is $[(bpy)_2Ru(pz)(pzH)]^+$. These experiments indicate that $(bpy)_2Ru(pz)_2$ is the dominant form in dry solvents but that the complex is a relatively strong base which can remove protons even from trace amounts of water in the solvent.

Detailed pK_a studies in water were not possible because of the insolubility of $(bpy)_2Ru(pz)_2 \cdot H_2O$, but it seems apparent that the neutral bis(pyrazolyl) complex is a strong base (eq 3) and that the pK_a of the conjugate acid $[(bpy)_2Ru(pz)(pzH)]^+$

$$(bpy)_2Ru(pz)_2 + H_2O \rightarrow [(bpy)_2Ru(pz)(pzH)]^+ + OH^- \quad (3)$$

is probably >13. Models show that the remaining proton in $[(bpy)_2Ru(pz)(pzH)]^+$ could interact with both pyrazole groups by H bonding (structure 1) and that the water



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of hydration in $(bpy)_2Ru(pz)_2 \cdot H_2O$, which is tenaciously held in the solid, could also act as a bridge between the two ligands by H bonding. Unfortunately, the proton NMR spectrum of the salt $[(bpy)_2Ru(pz)(pzH)][ClO_4]$ in acetone-d_6 gave no useful structural information because of the complexity of the spectrum which consisted of a series of overlapping resonances between τ 1.28 and τ 3.83.

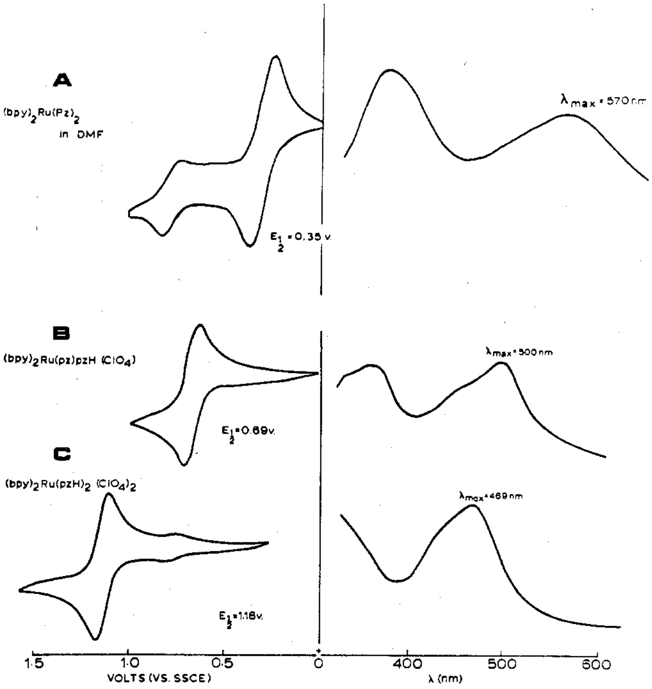


Figure 1. Electronic spectra (right) and cyclic voltammetry (left) of the pyrazole monomers: (A) $(bpy)_2Ru(pz)_2$ in DMF solution; (B) $[(bpy)_2Ru(pz)(pzH)][ClO_4]$ in CH_3CN solution; (C) $[(bpy)_2Ru(pzH)_2][ClO_4]_2$ in CH_3CN solution. The solution in A clearly contains some of the monoprotonated complex.

The pK_a of $[(bpy)_2Ru(pzH)_2]^{2+}$ is considerably lower. Even with weak pyridine bases like collidine, the complex is deprotonated to give $[(bpy)_2Ru(pz)(pzH)]^+$. One interesting observation is that the superoxide ion can function as a clean, mild base for the deprotonation of the pyrazole complexes. In nondeoxygenated acetonitrile containing $[(bpy)_2Ru(pz)(pzH)]^+$, an anodic potential sweep after an initial cathodic sweep through the $O_2 \rightarrow O_2^-$ reduction wave at $E_{p,c} \approx 0.7$ V resulted in the appearance of a reversible wave for the $[(bpy)_2Ru(pz)_2]^{+/0}$ couple ($E_{1/2} = 0.30$ V; see below) and a greatly diminished wave for the $[(bpy)_2Ru(pz)(pzH)]^{2+/+}$ couple ($E_{1/2} = 0.60$ V). In solutions containing $[(bpy)_2Ru(pzH)_2]^{2+}$, sweeps past the O_2/O_2^- wave resulted in the appearance of waves for both the $[(bpy)_2Ru(pz)(pzH)]^{2+/+}$ and $[(bpy)_2Ru(pz)_2]^{+/0}$ couples in the following anodic sweep. The same effect could be reproduced in dry, deoxygenated acetonitrile by adding an excess of solid KO_2. The chemistry presumably involves electrochemical generation of O_2^- ($O_2 \xrightarrow{+e^-} O_2^-$), deprotonation of the pyrazole complexes ($[(bpy)_2Ru(pz)(pzH)]^+ + O_2^- \rightarrow (bpy)_2Ru(pz)_2 + HO_2$), and subsequent disproportionation of HO_2 ($O_2^- + HO_2 \rightarrow O_2 + HO_2^-$). The same type of reactivity has been observed for protic aromatic hydrocarbons in nonaqueous media.[12]

Deprotonation of the bound pyrazole groups has a profound effect on both the redox and spectral properties of the complexes. In all three of the complexes there are four well-defined

Table II. $E_{1/2}$ Values (V) for the Pyrazole, Pyrazolyl, and Related Complexes[a]

		couples		
complex	Ru^{IV}/Ru^{III}	Ru^{III}/Ru^{II}	ligand-localized reductions	
$[(bpy)_2Ru(pzH)_2][PF_6]_2$		+1.18 (80)	−1.52 (100)[e]	−1.76 (110)
$[(bpy)_2Ru(py)_2][PF_6]_2$[b]		+1.30 (65)	−1.32 (70)	−1.56 (75)
$[(bpy)_2Ru(pz)(pzH)][PF_6]$	+1.75[c]	+0.69 (80)	−1.50 (80)	−1.72 (120)
$[(bpy)_2Ru(py)Cl][PF_6]$[b]		+0.77 (70)	−1.50 (75)	−1.83 (85)
$(bpy)_2Ru(pz)_2\cdot H_2O$[d]		+0.30 (75)		
$(bpy)_2RuCl_2$	+1.95[b]	+0.32 (70)	−1.67[c]	−1.78[c]
$[(bpy)_2Ru(pz)]_2[PF_6]_2$		+1.21 (90), +0.83 (80)	−1.55[e]	−1.92[c]

[a] In CH_3CN solution with 0.1 M TBAH as supporting electrolyte (Pt-bead electrode; scan rate 200 mV/s). $E_{1/2}$ values were calculated as the average of the anodic and cathodic peak potentials. The values in parentheses are differences in anodic and cathodic peak potentials ($E_{p,a} - E_{p,c}$). [b] D. J. Salmon, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1976. [c] The waves are chemically irreversible. The data given are peak potentials only. [d] In DMF solution with 0.1 M TBAH as supporting electrolyte (Pt-bead electrode; scan rate 200 mV/s). Ligand-localized reductions and the expected Ru(IV)/Ru(III) wave were not observable because of the limited cathodic and anodic scan ranges imposed by the medium. [e] The wave is reversible but complicated by an adsorption prewave.

regions of absorption in the visible and ultraviolet spectra (Figure 1 and Table I). The same pattern of absorption bands has been observed for other $(bpy)_2Ru^{II}L_2$ complexes where the two lowest energy transitions have been assigned to the MLCT processes $\pi_1^*(bpy) \leftarrow d\pi(Ru)$ and $\pi_2^*(bpy) \leftarrow d\pi(Ru)$ and two higher energy transitions, which occur at ~290 and ~240 nm, to bpy-localized transitions, $\pi_1^*(bpy) \leftarrow \pi_b(bpy)$ and $\pi_2^*(bpy) \leftarrow \pi_b(bpy)$.[13] For $[(bpy)_2Ru(pzH)_2]^{2+}$, the MLCT bands are at 470 and 323 nm in acetonitrile. They appear at 510 and 363 nm for $[(bpy)_2Ru(pz)(pzH)]^+$ in CH_3CN and at 581 and 434 nm for $(bpy)_2Ru(pz)_2$ in DMF.

Earlier work has shown that the $\pi^*(bpy) \leftarrow d\pi(Ru)$ CT band energies in the complexes *cis*-$(bpy)_2Ru^{II}L_2$ respond in a consistent and systematic way to changes in the remaining two ligands, L.[14] If L is a good π-acceptor ligand, back-bonding from Ru(II) to L results in stabilization of the $d\pi$ levels relative to $\pi^*(bpy)$ and an increase in the MLCT band energy. A decrease in MLCT band energy is observed when L is a relatively good π-donor ligand. On the basis of λ_{max} values for the first MLCT band in complexes like $[(bpy)_2Ru(py)_2]^{2+}$ (λ_{max} 455 nm; py is pyridine) compared with those in $[(bpy)_2Ru(en)]^{2+}$ (λ_{max} 485 nm; en is ethylenediamine), where π-bonding effects are not important, it can be concluded that the pyrazole ligand is a relatively weak π-acceptor ligand in $[(bpy)_2Ru(pzH)_2]^{2+}$.

On the other hand, the low energies for the MLCT bands for $(bpy)_2Ru(pz)_2$ compared, for example, with those for $(bpy)_2RuCl_2$ (λ_{max} 553 and 375 nm in DMF) argue that the bound pyrazolyl group has the capacity to act as a π-donating ligand. Single deprotonation of the bis(pyrazole) complex leads to $[(bpy)_2Ru(pz)(pzH)]^+$, which is a case intermediate between the other two.

The stepwise effect of deprotonation of the pyrazole ligands also shows up clearly in Ru(III)/Ru(II) reduction potential values measured by cyclic voltammetry (Figure 1 and Table II). Potentials for the couples $[(bpy)_2Ru(pzH)_2]^{3+/2+}$, $[(bpy)_2Ru(pz)(pzH)]^{2+/+}$, and $[(bpy)_2Ru(pz)_2]^{+/0}$ (1.18, 0.69, 0.30 V) decrease with deprotonation of the ligand. The decrease in potentials also shows, at least in part, the effects of changes in π-acceptor or π-donor ability of the ligands on the energy of the $d\pi(Ru)$ levels relative to the SSCE reference electrode. Potential values for related chloro and pyridine complexes are included in Table II for purposes of comparison.

A cyclic voltammogram of $[(bpy)_2Ru(pzH)_2]^{2+}$ in acetonitrile in the potential range +2.0 to −2.0 V includes two reversible waves in the cathodic region at −1.52 and −1.75 V which have the same peak currents as the Ru(II)/Ru(III) wave. The Ru(II)/Ru(III) wave was shown to be a one-electron oxidation by coulometry. The reduction waves which correspond to stepwise, one-electron reductions at the bpy ligands are seen in related complexes of the type $[(bpy)_2RuL_2]^{2+}$.

In addition to the Ru(III)/Ru(II) and bpy reduction waves, an irreversible oxidation occurs at $E_p = +1.75$ V for the complex $[(bpy)_2Ru(pz)(pzH)]^+$. The wave presumably corresponds to a Ru(III) → Ru(IV) wave analogous to the $[(bpy)_2RuCl_2]^{2+/+}$ couple at 1.95 V, again suggesting the existence of pyrazolyl → Ru donation in stabilizing the higher oxidation states of Ru. Presumably, there is also a Ru(III)–Ru(IV) oxidation in $[(bpy)_2Ru(pz)_2]^+$ at an even lower potential, but if so, the wave is past the oxidation limit (~1.3 V) in the solvent used (DMF).

Given our interest in the chemical and physical properties of MLCT excited states like $[Ru(bpy)_3{}^{2+*}]$, we have investigated the luminescence properties of the series of pyrazole and pyrazolyl complexes. The emission spectrum of $[(bpy)_2Ru(pzH)_2]^{2+}$ in CH_3CN at room temperature (22 ± 2 °C) includes a relatively weak luminescence at λ_{max} 627 ± 4 nm with a well-defined shoulder at 661 ± 4 nm. The excitation spectrum for the luminescence closely matches the absorption spectrum of the complex. As for $[Ru(bpy)_3]^{2+}$ and related complexes of the type $(bpy)_2Ru^{II}L_2$,[15] the origin of the emission is probably from a $\pi^*(bpy) \leftarrow d\pi(Ru)$ MLCT excited state. In degassed acetonitrile solutions the quantum yield for emission of $[(bpy)_2Ru(pzH)_2]^{2+}$ (~4×10^{-5} M) is ~10^{-4} compared with 0.04 for $Ru(bpy)_3{}^{2+}$,[9] and the excited-state lifetime, determined by laser flash photolysis, was found to be 350 ns compared to 850 ns for $[Ru(bpy)_3{}^{2+*}]$.[9]

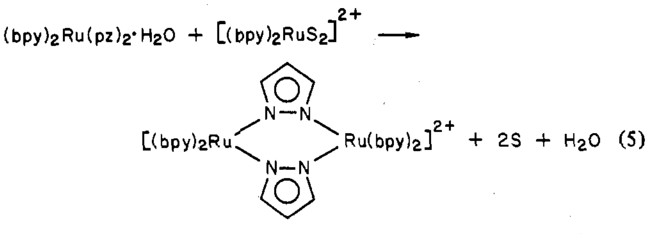
A very weak emission was found to occur for $[(bpy)_2Ru(pz)(pzH)]^+$ at λ_{max} 722 ± 4 nm in CH_3CN solution (~5×10^{-5} M). The emission appears to be at the lowest energy yet reported for complexes of the type $[(bpy)_2RuL_2]^{n+}$ and shows that the luminescence energy can be changed dramatically by varying L. The quantum yield for emission was estimated to be 10^{-5}; the lifetime was not measured. Both $(bpy)_2Ru(pz)_2$ and the dimer $[(bpy)_2Ru(pz)]_2{}^{2+}$ to be discussed later had no detectable emissions in the region 500–800 nm in either DMF or CH_3CN solutions.

The λ_{max} (emission) values for the pyrazole complexes are noticeably red shifted compared to that for $[Ru(bpy)_3]^{2+}$. The red shifts in the emission spectra follow the lower energies of the $\pi^*(bpy) \leftarrow d\pi$ absorption bands. The origins of the red shifts are somewhat related in both cases and reflect, once again, the effects of stabilization of the $d\pi(Ru)$ levels caused by changes in the electron-donor or -acceptor properties of the ligands L in complexes of the type $(bpy)_2Ru^{II}L_2$.

The Pyrazolyl-Bridged Dimer $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{2+}$. The preparation of the pyrazolyl dimer $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{2+}$ described here follows straightforwardly from known Ru–bpy chemistry. The labile, disolvento complex $[(bpy)_2Ru((CH_3)_2CO)_2]^{2+}$ was generated in solution by treatment of $(bpy)_2RuCl_2$ with Ag^+ (eq 4). The dimer was prepared by heating equimolar amounts of $(bpy)_2Ru(pz)_2\cdot H_2O$ and the diacetone complex at reflux in acetone–ethanol (eq 5). The

$$(bpy)_2RuCl_2 + 2Ag^+ + 2S \rightarrow [(bpy)_2RuS_2]^{2+} + 2AgCl \qquad (4)$$

S is acetone



$$(bpy)_2Ru(pz)_2{\cdot}H_2O + [(bpy)_2RuS_2]^{2+} \rightarrow [(bpy)_2Ru(pz)_2Ru(bpy)_2]^{2+} + 2S + H_2O \qquad (5)$$

S is acetone

dark red-purple dimer which resulted was isolated conveniently as either the ClO_4^- or the PF_6^- salt and purified by column chromatography on alumina with an CH_3CN/CH_2Cl_2 mixture as eluant. It is clear from initial studies not reported here that the bis(pyrazolyl) complex is capable of acting in a general way as a bidentate ligand and that a series of multimetallic complexes can be prepared from it.

The proton NMR spectrum of the dimer in CD_3CN solution was complex with the aromatic proton region extending from τ 1.15 to τ 3.63, but an isolated low-field doublet of area two was used as a reference to show the total number of bpy and pyrazole protons was 38 by integration.

The dimer (as the PF_6^- salt) is readily soluble in polar organic solvents such as CH_2Cl_2, acetone, CH_3CN, and DMF. The absorption spectrum of the complex in acetone is shown in Figure 2. Treatment of the dimer with aqueous HPF_6 in acetonitrile solution resulted in an unsymmetrical bridge cleavage reaction (eq 6) as shown both by cyclic voltammetry

$$[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{2+} + 2H^+ + 2S \rightarrow [(bpy)_2Ru(pzH)_2]^{2+} + [(bpy)_2RuS_2]^{2+} \qquad (6)$$

S is CH_3CN

and by the position of the low-energy MLCT absorption bands for the products of eq 6: for $[(bpy)_2Ru(pzH)_2]^{2+}$, $E_{1/2} = 1.18$ V, λ_{max} 470 nm; for $[(bpy)_2Ru(CH_3CN)_2]^{2+}$, $E_{1/2} = 1.44$ V, λ_{max} 425 nm.

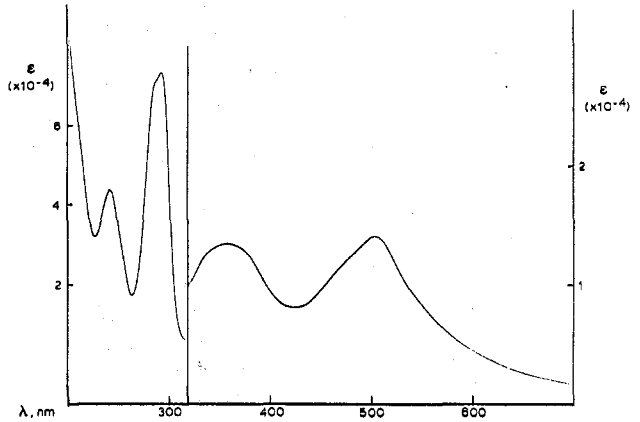


Figure 2. Electronic absorption spectrum of $[(bpy)_2Ru(pz)]_2[ClO_4]_2$ in acetone solution.

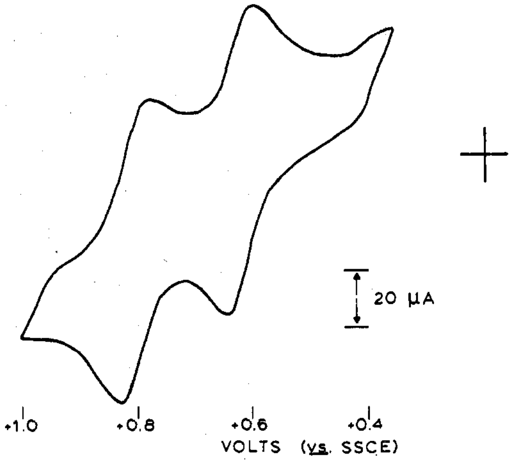


Figure 3. Cyclic voltammogram of $[(bpy)_2Ru(pz)]_2^{2+}$ in CH_3CN (0.1 M $[N(n\text{-}C_4H_9)_4][PF_6]$) solution taken at a scan rate of 200 mV/s with a Pt-bead electrode.

A cyclic voltammogram of $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{2+}$ in CH_3CN solution (Figure 3, Table II) includes four apparently reversible waves, two of which are reductions and two of which are oxidations. All of the waves had approximately equal peak currents. Controlled-potential coulometry at 0.98 V in CH_3CN showed that the first anodic wave (+0.83 V) was a one-electron oxidation. However, cyclic voltammetry of the oxidized solution showed the presence of the couples $[(bpy)_2Ru(CH_3CN)_2]^{3+/2+}$, $[(bpy)_2Ru(pz)(pzH)]^{2+/+}$, $[(bpy)_2Ru(pzH)_2]^{3+/2+}$ and, to a lesser extent, $[(bpy)_2Ru(pz)_2]^{+/0}$. Electrolysis past the second oxidation wave gave $n > 1$ and as products mainly a mixture of $[(bpy)_2Ru(CH_3CN)_2]^{2+}$ and $[(bpy)_2Ru(pzH)_2]^{3+}$. The results of the cyclic voltammetry and electrolysis experiments suggest that the mixed-valence $[(bpy)_2Ru^{II}(pz)_2Ru^{III}(bpy)_2]^{3+}$ and Ru(III)–Ru(III) $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{4+}$ dimers are stable on the cyclic voltammetry time scale (eq 7) (seconds) but on the longer time

$$[B_2Ru(pz)_2RuB_2]^{2+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [B_2Ru(pz)_2RuB_2]^{3+} \qquad (7)$$

$$[B_2Ru(pz)_2RuB_2]^{3+} + 2CH_3CN \rightarrow [B_2Ru(CH_3CN)_2]^{2+} + [B_2Ru(pz)_2]^+ \qquad (8)$$

B is 2,2′-bipyridine

scale for electrolysis (minutes) are unstable with respect to an unsymmetrical bridge-splitting reaction (eq 8). The appearance of the protonated monomeric complexes is consistent with the basicity of the bound pyrazolyl ligand. Just as $(bpy)_2Ru(pz)_2{\cdot}H_2O$ when dissolved in CH_3CN gives $[(bpy)_2Ru(pz)(pzH)]^+$, the appearance of the pyrazole complexes as products following oxidation can be accounted for by removal of protons from trace amounts of water in the solvent.[16]

The instability of the mixed-valence ion is extremely disappointing since we were unable to search for a low-energy intervalence-transfer absorption band. Such bands appear to be a characteristic feature of mixed-valence Ru–bpy complexes, and from their properties, insight can be gained into the nature and extent of the electronic interaction between the Ru sites. The situation is entirely analogous to the di-μ-chloro-bridged dimer $[(bpy)_2RuCl_2Ru(bpy)_2]^{2+}$ where, upon oxidation in acetonitrile, the products are the monomeric complexes $[(bpy)_2RuCl_2]^+$ and $[(bpy)_2Ru(CH_3CN)_2]^{2+}$.

For the chloro-bridged dimer, it has been concluded that the large difference between the $[(bpy)_2RuCl_2Ru(bpy)_2]^{3+/2+}$ and the $[(bpy)_2RuCl_2Ru(bpy)_2]^{4+/3+}$ waves (0.55 V)[17] compared to 0.38 V for the difference between the $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{3+/2+}$ and the $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{4+/3+}$ waves arises because of electrostatic effects and not because of extensive delocalization in the mixed-valence ion. Further, it has been concluded that because of back-bonding to the bpy groups, the Ru sites are relatively electron deficient and that, as a consequence, orbital overlap and therefore electronic delocalization between sites are small. Because of the slight electronic delocalization, the excess electron is vibrationally trapped at one site, at least on a rapid time scale, and the system is a localized-valence case. The same conclusions can presumably be drawn concerning the mixed-valence pyrazolyl dimer $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{3+}$. The unsymmetrical bridge-splitting reaction (eq 8) then follows because of the greater strength of the Ru(III)–pz bonds in an unsymmetrical dimer.

Our hope in preparing the pyrazolyl dimer was that the π-donor properties of the pyrazolyl ligand could be exploited to gain a strong Ru–Ru electronic interaction. In complexes like $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$ (pyr is pyrazine), the orbital mechanism for Ru–Ru interaction appears to be $d\pi$(Ru(II))–π^*(pyr) mixing which carries the Ru(II) wave functions to the Ru(III) site and leads to electron delocalization from Ru(II) to Ru(III).[18] Given the extremely high π–π^* separation in pyrazole compared to that in pyrazine, the importance of Ru–Ru interactions by $d\pi(\mathrm{Ru(II)}) \rightarrow \pi^*(\mathrm{pz})$ mixing is probably small, but, in principle, π(pz)–$d\pi$(Ru(III)) mixing could lead to Ru–Ru interactions by electron-hole donation from Ru(III) to Ru(II). If such an effect is important, the electronic resonance energy involved is apparently insufficiently strong to overcome the vibrational trapping energy and the result is a localized mixed-valence case.

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Registry No. $[(bpy)_2Ru(pzH)_2][PF_6]_2$, 71230-43-8; $(bpy)_2Ru(pz)_2$, 71230-42-7; $[(bpy)_2Ru(pz)(pzH)][PF_6]$, 71230-41-6; $[(bpy)_2Ru(pz)_2Ru(bpy)_2][ClO_4]_2$, 71230-40-5; $[(bpy)_2Ru(pz)(pzH)][ClO_4]$, 71230-39-2; $[(bpy)_2Ru(pzH)_2][ClO_4]_2$, 71230-37-0; $[(bpy)_2Ru(py)_2][PF_6]_2$, 71230-35-8; $[(bpy)_2Ru(py)Cl][PF_6]$, 36413-31-7; *cis*-$(bpy)_2RuCl_2$, 19542-80-4; $[(bpy)_2Ru(pz)]_2[PF_6]_2$, 71230-34-7; $[(bpy)_2Ru(pzH)_2]^{3+}$, 71230-32-5; $[(bpy)_2Ru(pz)(pzH)]^{2+}$, 71230-31-4; $[(bpy)_2Ru(pz)(pzH)]^{3+}$, 71230-30-3; $[(bpy)_2Ru(pz)_2]^{+}$, 71230-29-0; $[(bpy)_2RuCl_2]^{+}$, 47514-47-6; $[(bpy)_2RuCl_2]^{2+}$, 71230-28-9; $[(bpy)_2Ru(pz)]_2^{3+}$, 71249-99-5; $[(bpy)_2Ru(pz)]_2^{4+}$, 71230-27-8.

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Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Electron-Transfer Reactions of Some Derivatives of Pentaammine(pyridine)ruthenium(II) and -ruthenium(III)

GILBERT M. BROWN, HEINZ J. KRENTZIEN, MOTOKO ABE, and HENRY TAUBE*

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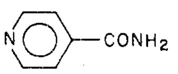
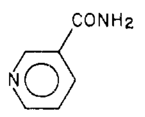
The pseudo exchange rate for the pentaammine(pyridine)ruthenium(II)–(III) couple has been determined by studying the rates of the reaction of $Ru(NH_3)_5isn^{3+}$ with $Ru(NH_3)_5nic^{2+}$ and the reverse. The rate constant is 4.7×10^5 M^{-1} s^{-1} at 25 °C in 1.0 M CF_3SO_3H, and the equilibrium quotient is 2.1, the latter to be compared with 2.5 ± 0.5 as determined from electrochemical measurements. The enthalpy and entropy of activation are 2.9 kcal mol^{-1} and −23 cal deg^{-1} mol^{-1}, respectively. Examination of the data on the rates of cross reactions in light of the Marcus correlation reveals no anomalies for reactions among the (pyridine)pentaammineruthenium reactions or for the reactions of the ruthenium complexes with V(II), but, as noted earlier by others, for the $Fe^{3+/2+}$ couple, the observed rate constants tend to be lower than those calculated. The discrepancy appears to be largely an entropic effect, suggesting the operation of a significant nonadiabatic factor in the $Fe^{3+/2+}$ couple.

The reactions of ammine complexes of ruthenium(III) have played an important role in demonstrating the effects of electronic structure of the participating metal ions on the mechanism of inner-sphere electron-transfer reactions.[1] The discovery of intervalence transfer transitions in ligand-bridged mixed-valence ruthenium ammine complexes[2,3] has stimulated a great deal of interest in this area.[4-8] The reactions of ligand-bridged precursor complexes of ruthenium(II) and cobalt(III) are being systematically investigated in a search for evidence of nonadiabatic effects.[9-11] The systems which have been mentioned so far involve intramolecular electron transfer. Evidence for nonadiabatic effects may also be found in bimolecular electron-transfer reactions.

We have determined the rate constants and activation parameters for the bimolecular electron-exchange reaction of the pentaammine(pyridine)ruthenium(II)–(III) couple. This exchange reaction was studied by making use of the spectral differences in the ruthenium complexes of two pyridine derivatives, namely, isonicotinamide and nicotinamide. A comparison of the free energy of activation for this electron-ex-



isonicotinamide (isn)



nicotinamide (nic)

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