

Poly(pyridine) Complexes of Ruthenium(II) Bound to Poly(4-vinylpyridine). Synthesis, Characterization, and Thin-Film Electrochemistry of a Series of Bis(bipyridine) Metallopolymers

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The preparation of a series of bis(2,2'-bipyridine) complexes of ruthenium(II) bound to poly(4-vinylpyridine), $\text{Ru}(\text{bpy})_2(\text{PVP})\text{X}^{n+}$ ($\text{X} = \text{PVP}, \text{CN}^-, \text{CH}_3\text{CN}, \text{NO}_2^-, \text{NO}_3^-, \text{NO}^+, \text{N}_3^-, \text{OH}_2, \text{OH}^-; n = 1, 2, \text{ or } 3$), is described. The physical and chemical properties of the polymer-bound metal complex sites have been investigated both in homogeneous solution and as films applied to electrode surfaces, and their properties are compared to those of the monomeric analogues $\text{Ru}(\text{bpy})_2(\text{py})\text{X}^{n+}$.

Introduction

By now a number of polymeric materials have been reported having bound redox couples based on organic, organometallic or inorganic sites. The methods of synthesis include covalent or electrostatic binding to a preformed polymer or polymerization of vinyl monomers. The polymeric materials are of interest for their potential applications in such areas as catalysis, photoredox systems, and studies of the fundamental properties of film-coated electrodes.^{1,2}

We have a continuing interest in metallopolymers based on ruthenium complexes covalently bound to poly(4-vinylpyridine) (PVP). There is a background chemistry in this area based on the attachment and redox properties of ruthenium pentammine, ethylenediaminetetraacetate, and bipyridine complexes.^{3,4} Our own work has included the synthesis, characterization, and properties of complexes of PVP containing the $-\text{Ru}(\text{trpy})(\text{bpy})^{2+}$ group (trpy is 2,2',2''-terpyridine and bpy is 2,2'-bipyridine)² and the use of an attached $\text{Ru}-\text{OH}_2^{2+}/\text{Ru}=\text{O}^{2+}$ couple as the basis for an electrode-supported oxidation catalyst.⁵

Poly(pyridyl) complexes of ruthenium are notable because of their chemical diversity. The chemical diversity includes well-established photochemical and electron-transfer properties and a series of interesting reactions at coordinated ligands, which when taken together can provide the basis for useful catalytic properties. The point of the work described here was an attempt to extend the diversity that is inherent in monomeric complexes to related polymeric materials, both in homogeneous solution and as thin films on electrode surfaces.

Experimental Section

Materials. Water was doubly distilled from alkaline KMnO_4 . Acetonitrile (J. T. Baker Photrex) was distilled in an all-glass apparatus from fresh P_2O_5 and then redistilled from CaH_2 . 4-Vinylpyridine (vpy) (Aldrich) was distilled at reduced pressure (77 °C (31 torr)). All other solvents, acids, bases, and synthetic materials were of reagent quality and were used without further purification. Azide, chloride, cyanide, and nitrite anions were used as their sodium salts. NH_4PF_6 was used as a filtered, saturated aqueous solution.

Measurements. UV-vis absorption measurements were made with Bausch & Lomb 210UV and Varian 634 spectrophotometers. Emission spectra, uncorrected for phototube response, were recorded on a Perkin-Elmer MPF-2A spectrofluorimeter. A Beckman 4250 spectrometer was used for infrared measurements. Samples for IR analysis were prepared as KBr disks or as thick films, which were produced by evaporation of concentrated metallopolymer solutions onto NaCl plates. Polymeric solids do not seem to produce uniform, clear pellets so these materials are best examined as films. A PHM62 Radiometer Copenhagen pH meter was used for pH measurements.

Monomer Syntheses

The complexes $[\text{Ru}(\text{bpy})_2(\text{py})(\text{NO}_2)](\text{PF}_6)$,^{6,7} $[\text{Ru}(\text{bpy})_2(\text{py})(\text{NO})](\text{PF}_6)$,⁶ $[\text{Ru}(\text{bpy})_2(\text{py})(\text{NO}_3)](\text{PF}_6)$,^{6,7} $[\text{Ru}(\text{bpy})_2(\text{py})(\text{CH}_3\text{CN})](\text{PF}_6)$,⁷⁻⁹ $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}](\text{PF}_6)$,^{7,10} $[\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)](\text{PF}_6)$,^{7,10} $\text{Ru}(\text{bpy})_2(\text{CO}_3)\cdot 2\text{H}_2\text{O}$,¹¹ and *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ ¹² were prepared according to previously published procedures. $\text{Ru}(\text{bpy})_2(\text{py})(\text{OH})^+$ was prepared in situ by addition of NaOH to aqueous solutions of $[\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)](\text{PF}_6)$.¹⁰ $[\text{Ru}(\text{bpy})_2(\text{py})(\text{N}_3)](\text{PF}_6)$ ⁸ and *cis*- $[\text{Ru}(\text{bpy})_2(\text{py})_2](\text{PF}_6)$ ¹³ were also synthesized as described in the literature but were purified by chromatography on a column of adsorption alumina using acetonitrile/toluene mixtures as eluants.

$[\text{Ru}(\text{bpy})_2(\text{vpy})(\text{N}_3)](\text{PF}_6)$. A solution containing 35 mL of absolute ethanol, 35 mL of water, and 0.13 mL of 4-vinylpyridine (1.20 mmol) was thoroughly bubble deaerated with N_2 . *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ (520 mg, 1.00 mmol) was added, and the mixture was heated at reflux for 2.5 h under an N_2 atmosphere. NaN_3 (78 mg, 1.20 mmol) was then added, and the reflux was continued for another 3.5 h. The solution was reduced to approximately one-third of its original volume, and a small amount of solid was removed by filtration. A saturated aqueous solution of NH_4PF_6 (1.5 mL) was added to the filtrate, and the resulting red-brown precipitate was cooled to 0 °C and then collected by filtration. The product was washed three times with 15-mL portions of cold water and then dried. Purification was achieved by column chromatography on alumina using a 1:1 (v/v) acetonitrile/toluene mixture as eluant, followed by reprecipitation from acetonitrile into diethyl ether; yield 85%, on the basis of starting Ru. The complex was stored in a desiccator.

$[\text{Ru}(\text{bpy})_2(\text{py})(\text{CN})](\text{PF}_6)$. A flask containing either $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}](\text{PF}_6)$ or $[\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)](\text{PF}_6)$ and excess NaCN in a solution of 20% ethanol/water was heated at reflux for 1.5 h. The solvent was removed by rotary evaporation to approximately half its original volume, and after the mixture was cooled, the resulting orange

- (1) For a fairly complete listing of electrochemical investigations of polymer-modified electrodes, see ref 1-16 in: Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W., submitted for publication in *Inorg. Chem.*
- (2) Detailed references for applications of metallopolymeric materials have been detailed in the first paper of this series. See ref 1-3 in: Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 27-33.
- (3) (a) Scott, N. S.; Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *110*, 303-10. (b) Oyama, N.; Anson, F. C. *Ibid.* **1980**, *127*, 640-7. (c) Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1979**, *101*, 3450-6.
- (4) (a) Haas, O.; Kriens, M.; Vos, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 1318-9. (b) Haas, O.; Vos, J. G. *J. Electroanal. Chem.* **1980**, *113*, 139-49.
- (5) Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 307-12.

- (6) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruña, H. D.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1896-1903.
- (7) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860-5.
- (8) Moyer, B. A.; Sipe, B. K.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1475-80.
- (9) Brown, G. M.; Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1915-21.
- (10) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436-44.
- (11) Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211-4.
- (12) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334-41.
- (13) Dwyer, F. P.; Goodwin, H. A.; Gyarfás, E. C. *Aust. J. Chem.* **1963**, *17*, 544-8.

precipitate was filtered and dried. Repeated attempts to purify the complex by chromatography (as described above) were not successful in eliminating the *cis*-Ru(bpy)₂(CN)₂ complex, which is also a product of the reaction.

Polymer Synthesis

The preparation and characterization of the PVP used in these experiments have been described previously.² The average degree of polymerization was found to be 36, yielding a number-average molecular weight of approximately 3800. The dispersity of the sample was not determined. The polymer sample used in this work is the same as that employed in the earlier report.

Metallopolymer Syntheses

***cis*-Ru(bpy)₂(PVP)₂²⁺.** Preparation of the bis[poly(vinylpyridine)] complex was accomplished by a variation of known synthetic routes.^{4b,5} The procedure given below is for a metallopolymer in which PVP and ruthenium are combined in a 5:1 ratio to produce a complex with two out of every five pyridyl sites along the polymer chain bound to the metal complex. It should be noted that the extent of metal loading is a useful variable, as shown by our earlier paper on terpyridine complexes of PVP. However, in this work only metallopolymers with a stoichiometric PVP:Ru ratio of 5:1 are employed.

PVP (106 mg, 1.01 mmol) was dissolved with stirring in a 100-mL round-bottomed flask containing 15 mL of methanol. In a separate container under subdued lighting, Ru(bpy)₂(CO₃)·2H₂O (95 mg, 0.20 mmol) was added to 10 mL of warm water. To the resulting solution/suspension was added 0.5 mL of neat CF₃COOH. The blood red solution was adjusted to pH 9.0 with a stock solution of NaOH. At this point, the solution contained *cis*-Ru(bpy)₂(OH)₂²⁺. Methanol was then added to bring the reaction volume to 50 mL. The mixture was protected from light and heated at reflux until the reaction was judged to be complete by spectrophotometric measurements (growth of an absorption band at 460 nm). A typical reflux time for the preparation of a polymer complex of this degree of metalation was 75 h. After being cooled to room temperature, the solution containing the Ru(bpy)₂(PVP)₂²⁺ complex was stored in the dark. Numerous attempts to isolate the material as a soluble ClO₄⁻ or PF₆⁻ salt were unsuccessful.

Protection of the ruthenium complexes from light is an important caveat since the *cis*-diaquo complex is subject to *cis*-*trans* photoisomerization¹⁴ and the ruthenium-pyridine bond in both *cis*-Ru(bpy)₂(py)₂²⁺ and *cis*-Ru(bpy)₂(PVP)₂²⁺ complexes is known to undergo photolabilization upon irradiation with visible light.⁷

Syntheses to produce polymer complexes of higher metalation than the 5:1 ratio just outlined resulted in a mixture of mono- and disubstituted polymer-bound products even after 2 weeks of heating at reflux. The product distribution observed was probably due to a combination of effects such as electrostatic repulsions between the dipositively charged metal centers and steric crowding arising from the bulkiness of the metal complex sites.

Metallopolymers with much lower ruthenium content, for example, PVP:Ru = 20:1, were completely formed after only 2.5 h of heating at reflux, which is comparable to the time required for the reaction of *cis*-Ru(bpy)₂(OH)₂²⁺ with two monomeric pyridine ligands.¹³ The comparison here between the reaction times for the monomeric and polymeric pyridine ligands is only meant to be a qualitative indication of the similarity in the intrinsic reactivity between the two types of ligand for the particular ruthenium complex used. The reaction times can only be compared in an absolute sense under conditions where identical concentrations of PVP and pyridine are allowed to react with the diaquo complex.

Ru(bpy)₂(PVP)(OH)₂²⁺. A portion of the stock solution of the (PVP)₂ complex was diluted with 80% methanol/water to yield a solution approximately 10⁻⁴ M in ruthenium. The solution was then transferred to a round-bottomed flask and photolyzed with a GE 275 W sunlamp held at a distance of 10 in. from the flask. The mixture was stirred magnetically, and a water-jacketed condenser was employed to prevent loss of solvent. The photolysis proceeded cleanly. The reaction was monitored spectrophotometrically and judged to be complete when the absorption band with λ_{max} = 474 nm reached a maximum, which occurred after ~60 min. Continued photolysis led to a decrease in absorbance at the MLCT maximum, followed by

oxidation of the resulting diaquo product.

Solutions containing the aquo complex were stored in the dark and were stable at room temperature for long periods of time. Storage at reduced temperature was necessary to prevent the slow but apparently thermodynamically favored conversion of the aquo complex to the (PVP)₂ complex. We have found that for a polymer with the extent of metal binding used in these experiments (two out of every five pyridyl groups coordinated to ruthenium), displacement of an aquo ligand by a second pyridyl site on the polymer is difficult to achieve and requires heating a solution containing the Ru(bpy)₂(PVP)(OH)₂²⁺ site for several days at reflux. This observation is essential with regard to our ability to create a variety of functionalized metallopolymers.

Reactions

Reactions of Ru(bpy)₂(PVP)(OH)₂²⁺ with N₃⁻, NO₂⁻, and Cl⁻. A known volume of the stock solution 10⁻⁴ M in the aquo polymer was transferred to a round-bottomed reaction vessel. The approximate number of moles of ruthenium complex present was calculated from the absorbance of the solution (vs. an 80% methanol/water reference solution) by using the extinction coefficient for the related monomer Ru(bpy)₂(py)(OH)₂²⁺ (8.40 × 10³ M⁻¹ cm⁻¹ at 470 nm in 1 M HClO₄)¹⁰. In the preparations a five- to tenfold excess of anion was used. The reaction mixture was heated at reflux with stirring for 3–4 h. The volumes of the solutions were reduced to a minimum by rotary evaporation and diluted with ethanol. The evaporation/dilution procedure was repeated several times to ensure removal of the majority of methanol/water from the solutions. The products are stable in the ethanolic medium and were stored tightly capped at room temperature in the dark.

Reaction of Ru(bpy)₂(PVP)(OH)₂²⁺ with CH₃CN. A portion of the aquo polymer stock solution was reduced to one-fourth its original volume by rotary evaporation, leaving a mostly aqueous solution of the complex. The evaporated solution was diluted by adding enough acetonitrile to again produce a 10⁻⁴ M solution. The resulting mixture was heated at reflux for 3 h to form the bright yellow product complex. Water was removed from the solution by repeated rotary evaporation followed by dilution with CH₃CN. The metallopolymer solution was stored as above.

Reaction of Ru(bpy)₂(PVP)(OH)₂²⁺ with OH⁻. The acid-base behavior of the polymeric complex is very similar to that of the monomer Ru(bpy)₂(py)(OH)₂²⁺. The yellow-brown aquo polymer is rapidly converted to the red-brown Ru(bpy)₂(PVP)(OH)⁺ complex in strongly basic solutions, and the measured pK_a for the monomer (pK_a = 10.8)¹⁰ is probably a reasonable approximation for the polymeric complex as well.

Reaction of Ru(bpy)₂(PVP)(NO₂)⁺ with H⁺. Addition of a small volume of concentrated acid to solutions of the polymer nitro complex induces the well-known nitrite-nitrosyl conversion.¹⁵ Reaction of yellow solutions of Ru(bpy)₂(PVP)(NO₂)⁺ in both aqueous and nonaqueous media with a variety of acids resulted in decoloration of the solution due to formation of Ru(bpy)₂(PVP)(NO)³⁺. The solid nitrosyl polymer was isolated for infrared analysis by the following method. Concentrated HClO₄ was added dropwise to an ethanolic solution of the nitro complex, which was stirred until decoloration was complete. Solvent was removed by rotary evaporation, and the insoluble [Ru(bpy)₂(PVP)(NO)](ClO₄)₃ that coated the walls of the flask was dried with ether and removed by scraping. The hygroscopic solid was stored in a desiccator.

Reaction of Ru(bpy)₂(PVP)(OH)₂²⁺ with CN⁻. As in the case of the monomeric complex, reaction of the polymeric aquo complex with cyanide in aqueous, alcoholic solution led to formation of both Ru(bpy)₂(PVP)(CN)⁺ and Ru(bpy)₂(CN)₂. We have thus far been unable to develop a synthetic route for preparation of the metallopolymer free of the dicyano complex. It is important to note that displacement of the pyridyl group by attack of a second CN⁻ results in the "stripping" of Ru sites from the polymer backbone and, consequently, renders uncertain the previously well-known stoichiometry of Ru:PVP in the metallopolymer.

Electrochemical Instrumentation, Materials, and Procedures

Electrochemical instrumentation involved a locally designed waveform generator,¹⁶ a Princeton Applied Research Model 174A

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polarographic analyzer, and a Hewlett-Packard 7015B X-Y recorder. Disposable 20-mL scintillation vials were found to be extremely convenient when a one-compartment cell was acceptable under the conditions of an experiment. Otherwise, three-compartment cells ("H-cells") of conventional design were used. The reference electrode was a saturated sodium chloride calomel electrode (SSCE), and a Pt wire served as the counterelectrode. Working electrodes consisted of Teflon-shrouded platinum or glassy carbon disks (3- and 4-mm diameter, respectively). Electrodes were cleaned by mechanical polishing with 1- μ m diamond paste (Buehler).

Acetonitrile for electrochemical experiments was distilled as described earlier in this section and stored over Davison 3- \AA molecular sieves. Tetra-*n*-ethylammonium perchlorate (TEAP) was prepared from the corresponding bromide salt (Eastman) with the use of a previously published procedure.¹⁷ Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by dissolving the iodide salt (Eastman) in a hot, equimolar water/ethanol/acetone mixture followed by addition of 65% HPF₆. The solution was reduced to approximately half the original volume and then cooled to room temperature. The resulting white solid was filtered off and recrystallized three times from boiling ethanol. Following preparation, both TEAP and TBAH were dried in a vacuum oven at 70 °C for 12 h and then stored in a desiccator.

Measurements on monomeric complexes were performed in homogeneous solution, while the metallopolymers were examined as thin films deposited onto electrodes. Electrodes were coated by applying a drop of polymer solution to a vertically mounted electrode and allowing the solvent to evaporate. Deposition solutions were all 10⁻⁴ M in complex sites, on the basis of the absorbance of each complex at its λ_{max} . Specific deposition solutions and rinsing procedures (where necessary) used with the various metallopolymer systems are as follows.

Ru(bpy)₂(PVP)₂²⁺: deposited from 50% methanol/water
 Ru(bpy)₂(PVP)(OH)₂²⁺: deposited from 80% methanol/water
 Ru(bpy)₂(PVP)(CH₃CN)²⁺: deposited from acetonitrile/HClO₄
 Ru(bpy)₂(PVP)(X)⁺ (X = Cl⁻, CN⁻): deposited from ethanol
 Ru(bpy)₂(PVP)(N₃)⁺: deposited from ethanol; rinsed in 0.1 M NaClO₄(aq), followed by rinse in 0.1 M TEAP/CH₃CN for nonaqueous electrochemistry
 Ru(bpy)₂(PVP)(NO₂)⁺: deposited from ethanol; for aqueous electrochemistry—rinsed in 0.1 M NaClO₄(aq); for nonaqueous electrochemistry—aqueous NaClO₄ rinse followed by 0.1 M TEAP/CH₃CN
 Ru(bpy)₂(PVP)(OH)⁺: deposited from methanol/water with added NaOH

The electrode material used for spectroelectrochemical experiments consisted of rectangular pieces of heavily doped, vapor-deposited SnO₂ on glass (PPG Industries), cut so as to fit into the cell holder compartment of the spectrophotometer (45 mm long \times 10 mm wide \times 3 mm thick). Electrodes were coated by evaporating a concentrated solution of Ru(bpy)₂(PVP)(N₃)⁺ onto the SnO₂ surface. Electrical contact was achieved by folding a piece of Cu foil over the edge of the electrode and connecting it to an alligator clip. Spectra of the coated surface were taken by inserting two electrodes in a back-to-back fashion into the cell compartment. This technique served to increase the amount of chromophore observed by the spectrophotometer and to minimize contributions in the spectrum from interference fringes that arise due to the SnO₂ coating.

It has been reported by Anson^{3a} that, in a metallopolymer film, oxidation or reduction of some of the redox sites can be inhibited apparently by electron-transfer or mass-transport limitations. In order to investigate the point, several film-covered electrodes with reversible couples were subjected to the following procedure. In a cyclic voltammetric (CV) experiment the potential was swept through the redox couple several times, after which the potential was held at 200 mV anodic of the oxidative peak maximum ($E_{p,a}$). The oxidative current was allowed to decay completely. When zero current was reached, the potential was held for varying periods of time and the electrodes scanned reductively. It was observed that the reductive trace always encompassed a greater area (~10%) than the original cyclic voltammogram, but the increase in area was largely attributable

to an increase in background current. We conclude that, if oxidation or reduction of some of the sites in the film is inhibited, the number of such sites must be relatively small. The same behavior was observed regardless of whether the electrode gave a cyclic voltammogram with symmetric surface wave characteristics or exhibited waves with tailing edges and diffusional-like behavior.¹⁸

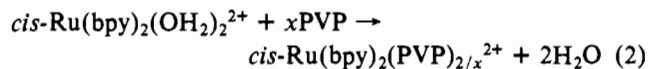
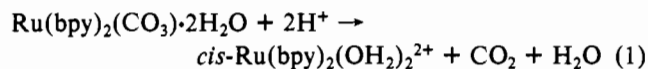
The effective surface coverages, Γ , of the polymers on the coated electrodes were determined by measuring the areas under cyclic voltammetric traces to establish total charge passed. It should be noted that the coverages reported accurately reflect only the effective surface concentration of redox sites and cannot be translated into units of monolayers without making assumptions concerning the molecular volume of the polymer complexes.

Reductively initiated electropolymerization of vinyl-containing transition metal complexes has recently been reported as a means of producing metal-containing polymers on electrode surfaces.¹⁹ This technique was used to produce a coating containing a ruthenium(II) azide complex. A platinum disk electrode was immersed in a TBAH/CH₃CN solution, which was deaerated by nitrogen bubbling and which was 4 mM in Ru(bpy)₂(vpy)(N₃)(PF₆). The potential was then cycled for 60 min between -0.71 and -1.65 V to accomplish the polymerization. The electrode was removed from the cell, rinsed with CH₃CN, and air-dried.

Results and Discussion

The aim of this work was to explore our ability to transfer the chemical properties inherent in monomeric ruthenium/bipyridyl complexes to polymers and to examine the polymeric materials both in solution and as thin films. There was the additional thought that in the polymeric materials new properties should appear that have their origin in the chemical and physical properties of the matrix.

In the course of the work it was necessary to develop a general preparative procedure for the metallopolymers. All of the syntheses rely initially on the binding of *cis*-Ru(bpy)₂(OH)₂²⁺ to PVP by ligand displacement using the series of reactions in eq 1 and 2. The value of x in eq 2 gives the



ratio of polymer pyridyl groups to ruthenium. As previously mentioned, only PVP:Ru ratios of 5:1 were used in the metallopolymers described in this work.

Binding of the pyridyl polymer to ruthenium appears to be a stepwise, rather than concerted, process. The evidence for this lies in the smooth, continuous shift of the spectral maximum of the reaction mixture from the diaquo starting material to the (PVP)₂ product. A spectrum of the same reaction via a concerted process would simply exhibit a decrease at the diaquo wavelength and a corresponding increase at the (PVP)₂²⁺ wavelength. The sequential nature of the process

- (18) For theoretical descriptions of the expected voltammetric wave shapes for reactants (polymeric and otherwise) confined to an electrode surface, see: (a) Brown, A. P.; Anson, F. C. *Anal. Chem.* **1977**, *49*, 1589-95. (b) Laviron, E. *J. Electroanal. Chem.* **1979**, *100*, 263-70. (c) Laviron, E. *Ibid.* **1980**, *112*, 1-9. (d) Laviron, E.; Roullier, L.; Degrand, C. *Ibid.* **1980**, *112*, 11-23. (e) Laviron, E. *Ibid.* **1981**, *122*, 37-44. (f) Smith, D. F.; Willman, K.; Kuo, K.; Murray, R. W. *Ibid.* **1979**, *95*, 217-27. (g) Pearce, P. J.; Bard, A. J. *Ibid.* **1980**, *114*, 89-115. (19) (a) Abruña, H. D.; Calvert, J. M.; Ellis, C. D.; Meyer, T. J.; Murray, R. W.; Murphy, W. R.; Walsh, J. L. *ACS Symp. Ser.*, in press. (b) Calvert, J. M.; Sullivan, B. P.; Meyer, T. J. *Ibid.*, in press. (c) Ellis, C. D.; Murphy, W. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 7480-3. (d) Abruña, H. D.; Denisevich, P.; Umaña, M.; Meyer, T. J.; Murray, R. W. *Ibid.* **1981**, *103*, 1-5. (e) Ikeda, T.; Schmehl, R.; Denisevich, P.; Willman, K.; Murray, R. W. *Ibid.*, in press. (f) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.*, in press. (g) Ikeda, T.; Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.*, in press. (h) Denisevich, P.; Willman, K. W.; Murray, R. W. *Ibid.* **1981**, *103*, 4727-37.

(16) Woodward, W. S.; Rocklin, R. D.; Murray, R. W. *Chem. Biomed. Environ. Instrum.* **1979**, *9*, 95-105.

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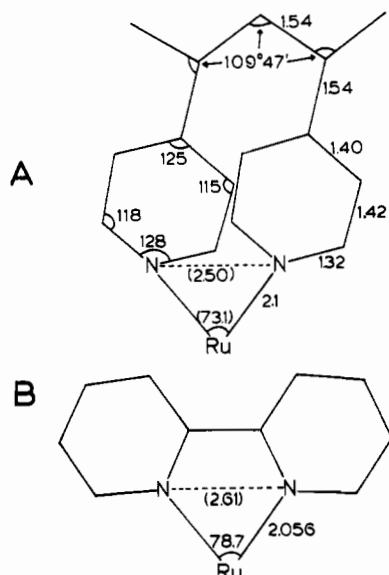


Figure 1. Comparison of structural properties of Ru(II) bound to (A) adjacent pyridyl groups of PVP and (B) 2,2'-bipyridine. Bond lengths are in angstroms; angles are in degrees. Calculated values are in parentheses. See ref 21 for original data. The aromatic nature of the pyridyl rings is not indicated in the figure for clarity.

is further supported by the existence of the relatively stable $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$ complex and the subsequent difficulty with which the $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$ polymer is formed in samples of high metalation (see Metallopolymer Syntheses).

Some general comments should also be made concerning probable polymer structure. As in protein biochemistry, problems related to structure arise at several different levels: (1) What is the ligand composition and stereochemistry at the bound metal sites? (2) For metal complex sites where more than one of the ligands is donated by the polymer, is the binding to the polymer intra- or interchain? If intrachain, are the ligating sites involved at adjacent or separated positions along the polymer backbone? (3) Is the shape of a continuous metallopolymer strand rodlike, spherical, random coil, etc.? (4) Do interstrand interactions exist that have their origins in van der Waals forces, hydrogen bonding, covalent links, or electron donor/acceptor interactions?

On the basis of the available spectral and electrochemical evidence, the primary structure at the $(\text{PVP})_2$ metallopolymer, that is, the nature of the coordination geometry at the bound metal site, can be confidently assigned as the cis isomer of the complex.

From solubility considerations—the polymeric complex is appreciably soluble in the original reaction medium (≤ 4 mM, based on Ru^{2+})—we conclude that a highly cross-linked network involving interchain linkages is unlikely. The conclusion is supported by Agnew's observation that reaction of PVP with various divalent, first-row transition-metal halides to form metallopolymers with a trans, i.e., interchain cross-linked, configuration yields insoluble materials.²⁰ The solubility of the metallopolymer also argues against separated pyridyl sites being involved since a material of this type would be expected to form a dense, insoluble structure, which might be likened to a ball of yarn. The remaining possibility of adjacent pyridyl site binding is the most appealing. A material of this configuration would be anticipated to have greater solubility than the previous two possibilities. Molecular models also show that the "bite" size and angle of adjacent pyridines of PVP are calculated to be 2.50 Å and 73°, respectively (Figure 1A).^{21a} An X-ray crystal structure of $\text{Ru}(\text{bpy})_3^{2+}$

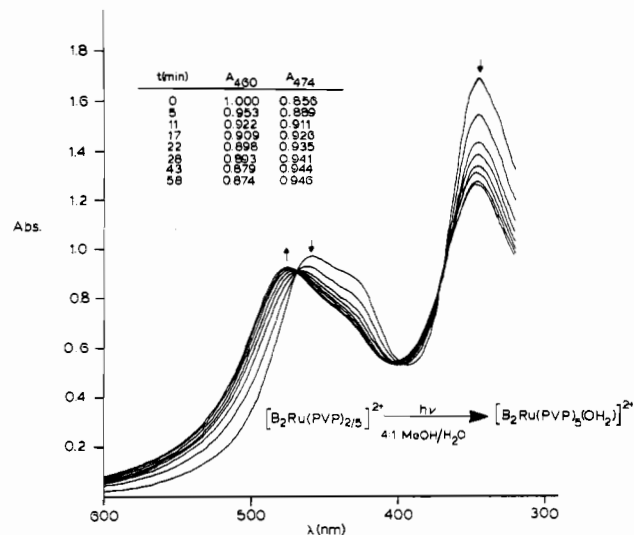


Figure 2. Photochemical conversion of $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$ to $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$ in 80% MeOH/ H_2O (photolysis time 75 min).

was found to give values of 2.6 Å and 78.7° for the bite size and angle of 2,2'-bipyridine (Figure 1B) upon coordination to ruthenium.^{21b} The similarities in values suggest that, as in the case of bpy, reaction of Ru with neighboring pyridyl groups of PVP could be accomplished with facility, requiring minimal torsional strain of the polymer-bound pyridine rings to accommodate the metal complex. Hence, we conclude that the most reasonable possibility for the secondary structure of $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$ involves intrachain, adjacent-site coordination.

A metallopolymer strand containing metal sites in the configuration just described would exhibit a rodlike shape, especially at high metalation, because of the stereochemical and electrostatic demands of the poly(pyridyl)ruthenium units. However, molecular models show that an isotactic or "same side" arrangement of the metal sites is not possible due to overlap of the van der Waals radii of adjacent metal complex units. The driving force to achieve a conformation of minimum potential arising from steric repulsion must be achieved by staggering the metal sites in the space about the polymer backbone axis. A conceivable tertiary structure that satisfies these considerations is a helical arrangement of bis(bipyridyl)ruthenium units around the polymer strand.

$\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$. As first noted by Vos,^{4b} visible photolysis of solutions containing $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$ results in the quantitative conversion of the $(\text{PVP})_2$ complex into the aquo polymer (eq 3), as shown by the sequential spectra in

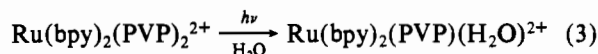


Figure 2. Detailed photochemical and photophysical information is available for the related monomer $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$,⁷ and similar studies have been carried out on the polymeric complex.

There are several alternate approaches to the preparation of the polymer-bound aquo complex. One method involves the reaction in basic solution (pH 10–11) between $\text{Ru}(\text{bpy})_2(\text{OH})(\text{OH}_2)^+$ and PVP, which produces initially and cleanly the mono(pyridyl) product, $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH})^+$.⁵ In solutions of pH ≤ 10 , the hydroxy group is protonated, giving the aquo polymer. The synthesis in basic solution is complicated by the need for strict control of pH since solutions

(20) Agnew, N. H. *J. Polym. Sci., Polym. Chem. Ed.* 1976, 14, 2819–30.

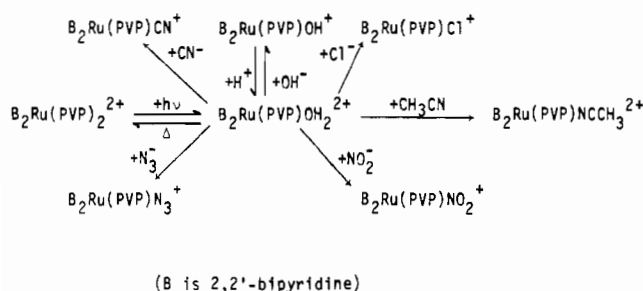
(21) (a) Structural parameters for PVP are taken from: Ghesquière, D.; Ban, B.; Chachaty, C. *Macromolecules* 1977, 10, 743–52. (b) Rillema, D. P.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* 1979, 849–51.

Table I. Spectral and Redox Potential Data

complex	polymeric analogue	λ_{\max}^a , nm	λ_{em}^a , nm	ν_x^b , cm^{-1}	$E_{1/2}, E^{\circ}, E^{\circ\prime}, E^{\circ\prime\prime}$, V
Ru(bpy) ₂ (py) ₂ ²⁺		455	606		1.24
Ru(bpy) ₂ (py)(CN) ⁺	Ru(bpy) ₂ (PVP) ₂ ²⁺	460	611		1.24
Ru(bpy) ₂ (py)Cl ⁺	Ru(bpy) ₂ (PVP)(CN) ⁺	469	620 ⁱ	2080 ^j	1.04
Ru(bpy) ₂ (py)(CH ₃ CN) ²⁺	Ru(bpy) ₂ (PVP)Cl ⁺	498 ^e	610 ⁱ	2080 ^j	0.99 ^m
Ru(bpy) ₂ (py)(NO ₂) ⁺	Ru(bpy) ₂ (PVP)(CH ₃ CN) ²⁺	438			0.80
Ru(bpy) ₂ (py)(NO ₂) ³⁺	Ru(bpy) ₂ (PVP)(NO ₂) ⁺	434			0.76
Ru(bpy) ₂ (py)(NO ₃) ⁺	Ru(bpy) ₂ (PVP)(NO ₂) ³⁺	450 ^e		1300, 1340 ^k	1.28
Ru(bpy) ₂ (py)(N ₃) ⁺	Ru(bpy) ₂ (PVP)(NO ₃) ⁺	446 ^e		1290, 1350 ⁱ	1.24 ⁿ
Ru(bpy) ₂ (py)(OH ₂) ²⁺	Ru(bpy) ₂ (PVP)(N ₃) ⁺	325, 290		1953 ^k	1.06
Ru(bpy) ₂ (py)(OH) ⁺	Ru(bpy) ₂ (PVP)(OH ₂) ²⁺	330, 289		1940 ^k	1.05
	Ru(bpy) ₂ (PVP)(OH) ⁺	488 ^f		1460, 1288, 1000 ^k	0.53
		498			0.91
		497		2030 ^k	0.90
		474 ^g		2075 ⁱ	0.58
		474 ^g			0.57
		506 ^h			0.71, 0.82 ^o
		506 ^h			0.73, 0.84 ^o
					0.23 ^h
					0.24 ^h

^a All data in acetonitrile solution unless otherwise noted. Emission maxima are uncorrected for phototube response. ^b ν_x is an infrared band, characteristic of the unique functional group in the complex; e.g., for Ru(bpy)₂(py)(N₃)⁺, ν_{N_3} is the symmetric azide stretching frequency at 2030 cm^{-1} . ^c $E_{1/2}$ is the cyclic voltammic half-wave potential for homogeneous solutions of the monomer complexes; E° is the formal potential determined by cyclic voltammetry of films of the polymer complexes deposited on glassy-carbon or Pt electrodes. ^d The electrolyte was 0.1 M TEAP/CH₃CN unless otherwise noted. All potentials are reported in volts vs. SSCE. ^e Ethanol solution. ^f CH₂Cl₂ solution. ^g 4:1 methanol/water solution. ^h 0.1 M NaOH. ⁱ H₂O solution. ^j Nujol mull. ^k KBr pellet. ^l Polymer film on NaCl plate. ^m 0.2 M TBAH/CH₂Cl₂. ⁿ 0.1 M Na₂SO₄, pH 2. ^o Protonated film.

Scheme I



that are too basic lead to the rapid formation of Ru(III) oxo-bridged species and, in less basic solutions, significant concentrations of Ru(bpy)₂(OH₂)₂²⁺ are left at the end of the reaction.

Other routes to the aquo polymer are available, utilizing the chemical reactivity of various functional groups bound to ruthenium, e.g., oxidative decomposition of an azido polymer in aqueous solution or aquation of a chloro polymer, which will be described in later sections.

Syntheses of Polymers Containing Substituted Ruthenium Sites. The polymer-bound aquo site Ru(bpy)₂(PVP)(OH₂)²⁺ is a convenient precursor for a series of polymer complexes based on thermal substitution of the aquo group. The background chemistry involved is summarized in Scheme I. The substitution reactions all proceed in a straightforward manner, and preparative details are given in the sections on syntheses. Further reactions and properties of the individual polymeric complexes are discussed in later sections.

A summary of the important spectral properties of the metal complex sites on the polymer as well as redox potentials of the sites in the polymers as films on electrodes are listed in Table I. Data for relevant monomers are included for comparison.

Chemical and Physical Properties of the Complexes [Ru(bpy)₂(PVP)(L)]ⁿ⁺. L = PVP. The properties of the (PVP)₂²⁺ complex are basically those expected for a coordination environment of six pyridyl-type ligands. There are close similarities in spectral and redox potential values between Ru(bpy)₃²⁺,⁷ Ru(bpy)₂(py)₂²⁺,⁷ Ru(bpy)₂(PVP)₂²⁺, Ru(trpy)(bpy)(py)₂²⁺,² and Ru(trpy)(bpy)(PVP)₂²⁺.² A particularly interesting feature is the easily observable luminescence of the (PVP)₂ polymer in solution at room temperature. Emission

is also observed from solid samples and films. The photochemical and photochemical properties of the (PVP)₂ polymers will be discussed in a forthcoming paper.

L = CN⁻. Although it has not been possible to prepare either the monomeric or polymeric cyanopyridine complexes free of Ru(bpy)₂(CN)₂, the mono- and dicyano species are sufficiently different to allow characterization of spectral and redox properties when both are present. The data in Table I show that the inherent properties of the complex Ru(bpy)₂(py)(CN)⁺ are maintained in the metallopolymer. As in the case of the (PVP)₂ complex, a notable characteristic of this material is its luminescence in solution at room temperature. Unfortunately, further investigation of the excited-state behavior was not feasible because of the competing emission from the dicyano complex present as an impurity.²²

L = OH₂ and OH⁻. As suggested by the presentation of data so far, clear similarities are maintained among monomers, polymers in solution, and polymers as thin films on electrodes. The substitution and acid/base reactions of the Ru(II) aquo and hydroxy complexes were alluded to in the reaction sections. There are several aspects of the thin-film electrochemistry that merit special attention.

The electrochemistry of the monomeric aquo system has been described in detail by Moyer.¹⁰ Briefly, it was found that in the pH range 2 ≤ pH ≤ 9, a cyclic voltammogram of Ru(bpy)₂(py)(OH₂)₂²⁺ exhibits two pH-dependent, essentially reversible waves involving Ru(IV/III) and Ru(III/II) couples. The peak heights for the Ru(IV/III) couple are strongly sweep-rate dependent and distinctly resolvable only at scan rates (v) $v \leq 20$ mV/s. Because of the change in proton content on oxidation, Ru(bpy)₂(py)OH₂²⁺ → Ru(bpy)₂(py)O²⁺ + H⁺ + e⁻ and Ru(bpy)₂(py)H₂O²⁺ → Ru(bpy)₂(py)OH²⁺ + H⁺ + e⁻, both couples are pH dependent. The potential of the Ru(III/II) couple as a function of pH is given by

$$E_{1/2} = (840 - 56.5(\text{pH}_{\text{measd}})) \text{ mV} \quad (4)$$

It has been suggested¹⁰ that the scan rate/peak height de-

(22) For descriptions of the excited-state chemistry of Ru(bpy)₂(CN)₂ see: (a) Nagle, J. K. Ph.D. Dissertation, The University of North Carolina at Chapel Hill, 1979. (b) Nagle, J. K.; Dressick, W. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3993-5. (c) Demas, J. N.; Peterson, S. H. *Ibid.* **1979**, *101*, 6571-7.

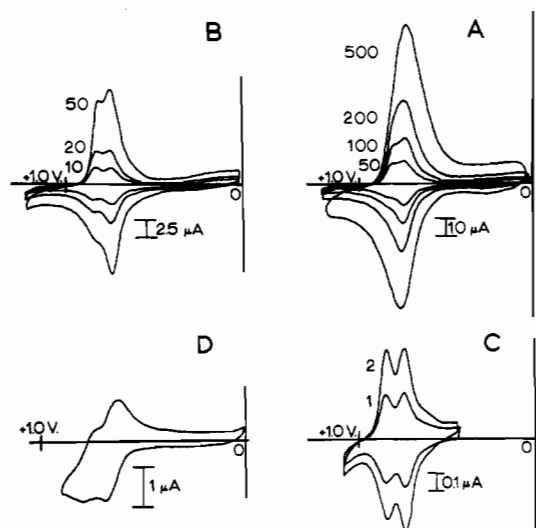
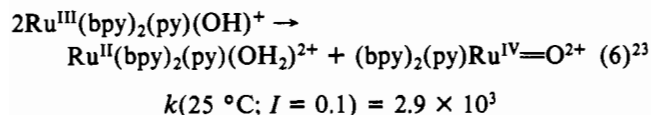
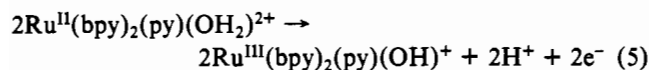


Figure 3. (A–C) Sweep rate dependence of a $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$ film on glassy carbon in aqueous electrolyte (0.1 M Na_2SO_4 , pH 2). Sweep rates in mV/s are listed to the left of each trace. (D) Cyclic voltammogram of $\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)^{2+}$ in homogeneous solution (Au wire, 0.1 M LiClO_4 , pH 3, $v = 20$ mV/s; taken from ref 10).

pendence of the Ru(IV/III) couple can be explained mechanistically as an “EC” electrochemical process—an electrochemical step with a subsequent chemical reaction. Specifically, it was suggested that oxidation of Ru(III) to Ru(IV) occurs via initial oxidation of Ru(II) to Ru(III) (eq 5) at the first wave, followed by disproportionation of Ru(III) into Ru(II) and Ru(IV) (eq 6) and diffusion-controlled oxidation of Ru(II).



An important consequence of this work was the subsequent application of the related Ru(IV) oxo complex $\text{Ru}(\text{trpy})(\text{bpy})\text{O}^{2+}$ as a catalyst for the electrooxidation of a large variety of organic substrates.

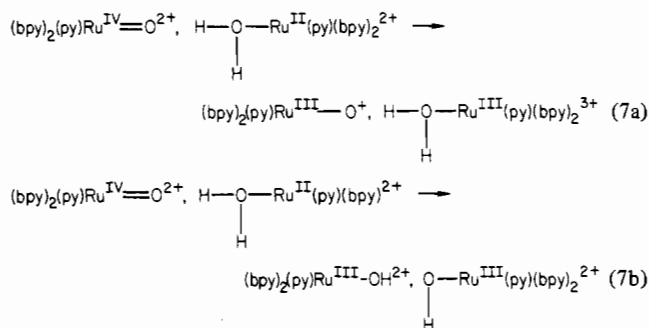
Samuels later demonstrated the ability to transfer these features to the polymer-bound system.⁵ He also noted an additional effect, which was termed a “pH encapsulation effect”. Experimentally, what was observed was that the redox potentials of the Ru(IV/III) and Ru(III/II) couples are no longer pH dependent as the basicity of the external solution is increased above the pK of the unbound pyridyl groups of PVP. Past the pK of these sites (but below the pK of the aquo group), the observed potential of the aquo couple reflects only the pH environment within the film.

We have investigated these films in more detail. Cyclic voltammetry reveals the presence of two stable, well-defined redox couples with formal potentials of 0.71 and 0.82 V in a pH 2 sulfate medium. It is notable that the Ru(III/II) potential is within 20 mV of that predicted by eq 4 for the analogous homogeneous couple. At pH 2 the polymer film is fully protonated and, as a highly charged polyelectrolyte, should have an open, solvent-swollen structure and be subject to minimal, if any, kinetic limitations to charge transport through the membrane.

Figure 3 shows cyclic voltammograms of $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$ at sweep rates ranging from 500 to 1 mV/s. At 200 mV/s a shoulder is discernible on the anodic side of the reverse wave. As the scan rate decreases, the size of the

second couple increases and its definition improves. For the solution experiments based on the monomeric aquo complex, the second wave is generally only 50% as large as the first at the lowest practical sweep rates. However, with the polymeric complex, sweep rates as low as necessary can be used since the electroactive site is immobilized at the surface. Upon reaching 1 mV/s, the voltammogram exhibits two essentially ideal surface waves (symmetrically shaped, $\Delta E_p = 0$ mV) of almost identical areas ($\Gamma_{\text{Ru}^{\text{III/II}}} = 7.4 \times 10^{-10}$ mol/cm²; $\Gamma_{\text{Ru}^{\text{IV/III}}} = 6.2 \times 10^{-10}$ mol/cm²). The sweep rate dependence is qualitatively consistent with the contention that the electron-transfer process interrelating $\text{Ru}^{\text{IV}}=\text{O}$ and $\text{Ru}^{\text{III}}-\text{OH}$ at the electrode occurs via the disproportionation pathway. At fast scan rates, disproportionation is relatively slow. At sufficiently slow scan rates, disproportionation provides a facile pathway for the net oxidation of $\text{Ru}^{\text{III}}-\text{OH}$ to $\text{Ru}^{\text{IV}}=\text{O}$.

The problem with direct oxidation at the electrode is apparently in the proton demand associated with the Ru(IV/III) couple. Oxidation of $\text{Ru}^{\text{III}}-\text{OH}$ involves a net proton loss, and reduction of $\text{Ru}^{\text{IV}}=\text{O}$, a net proton gain. The importance of such effects is evidenced by the dramatic solvent isotope effect observed in stopped-flow experiments for the reverse of eq 7, the comproportionation reaction involving Ru(IV) and



Ru(II), where $k_H/k_D = 16$.²³ From these results it was concluded that the electron-transfer mechanism under these conditions was not simple one-electron oxidation of $\text{Ru}^{\text{III}}-\text{OH}$ to $\text{Ru}^{\text{IV}}-\text{OH}$ (eq 7a), which is a thermodynamically unfavorable process by ~ 12.7 kcal/mol because of the resulting proton distribution in the products.²³ Rather, it was proposed that electron transfer occurs by a proton-coupled electron-transfer pathway involving nuclear tunneling (eq 7b). At an electrode, direct electron transfer would also be disfavored. In addition, the proton-coupled electron-transfer pathway may not be accessible at an electrode because of the rather specific demands imposed by the pathway.

Equation 7b suggests the importance of having in close proximity both a proton donor site at the reductant and a proton acceptor site at the oxidant. Given the demands of the pathway and the evidence cited later for the isolation of sites and the suppression of bimolecular, intrafilm reactions, it is surprising that the disproportionation pathway appears to exist within the polymer films. One factor that may contribute is the fact that in acid solution the unbound pyridyl sites are protonated and may play a role in the proton demands associated with electron transfer.

We attempted to investigate further the proposed disproportionation mechanism and the associated isotope effect by examining the electrochemical responses of the monomeric and polymeric aquo complexes in water and D_2O . The solutions consisted of a series of $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures, saturated in Na_2SO_4 , where the mole fraction of D_2O ($X(\text{D}_2\text{O})$) ranged from 0 to 1 in intervals of 0.25. The acid concentration of the

(23) Binstead, R. A.; Moyer, B. A.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897–9.

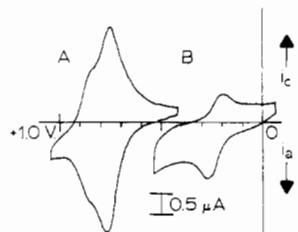


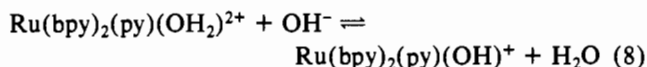
Figure 4. Acid/base interconversion of aquo and hydroxo polymers (glassy carbon disk, 20 mV/s): (A) $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)]^{2+}$ surface in pH 2 sulfate; $\Gamma = 4.4 \times 10^{-9}$ mol/cm². (B) Same electrode in 0.1 M NaOH, initial scan; $\Gamma = 1.04 \times 10^{-9}$ mol/cm².

electrolyte was adjusted to 0.01 M with concentrated H₂SO₄.

In the solution cyclic voltammogram of $\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)^{2+}$, the peak height of the second wave relative to the first wave is successively diminished at increasing $X(\text{D}_2\text{O})$. Unfortunately, the voltammetric waves were not separated sufficiently well to allow accurate measurement of peak heights for the determination of $k_{\text{H}}/k_{\text{D}}$. However, the observed behavior lends additional credence to the idea that the disproportionation step in eq 6 is involved in the observed electrode character of the $\text{Ru}^{\text{IV}}=\text{O}/\text{Ru}^{\text{III}}-\text{OH}$ couple.

The electrochemistry of the polymeric aquo complex was also examined in the various H₂O/D₂O electrolytes. It was hoped that in this case, given the excellent definition of the Ru(IV/III) couple at slow sweep rates (see Figure 3C), it would be possible to obtain a fairly accurate determination of $k_{\text{H}}/k_{\text{D}}$. Unlike the solution behavior of the monomeric analogue, electrodes coated with thin films of $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$ did not readily respond to similar sequential changes in $X(\text{D}_2\text{O})$ of the external solution—the two-wave pattern illustrated in Figure 3 is maintained in all mixtures, including pure D₂O. Surprisingly, the apparent absence of a D₂O effect has a kinetic origin. The effect of D₂O in the external solution is seen as a decrease in size of the second wave, as expected, but only after the film had been soaked for a period of several hours in an electrolyte containing D₂O. The observation of an exceedingly slow rate of H/D exchange at the aquo group is especially striking, given the response of the films to changes in pH in the external solution under conditions where the unbound pyridyl groups of the PVP backbone are protonated (pH ≤ 4).⁵ A possibly related observation involving a greatly diminished reactivity toward aquation for Ru-chloro sites under similar conditions will be discussed in a later section.

$\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)^{2+}$ is a weak acid ($\text{p}K_{\text{a}} = 10.8$), which is converted into the hydroxo complex $\text{Ru}(\text{bpy})_2(\text{py})(\text{OH})^+$ in basic solutions (eq 8).¹⁰ The aquo polymer behaves sim-



ilarly in solution (see Reactions), and the acid/base interconversion can also be observed in thin films. A cyclic voltammogram of a surface produced by exposure of a $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$ surface to 0.1 M NaOH yields a poorly defined, diffusional shaped wave ($E^{\circ'} = 0.24$ V) on the initial sweep. In subsequent sweeps the wave decays after several scans to background level (Figure 4). (Note: when the electrochemistry of film-covered electrodes is performed in highly basic solution, care must be taken to avoid potential excursions to the anodic solvent limit. Scanning into the O₂-evolution wave results in rapid removal of the film from the electrode surface.) The integrated area of the voltammetric wave for the hydroxo couple is a factor of 4 less than that of an aquo couple derived from the same electrode by cycling in the pH 2 sulfate medium used above. This effect is likely due to the decrease in charge in the deprotonated film, causing

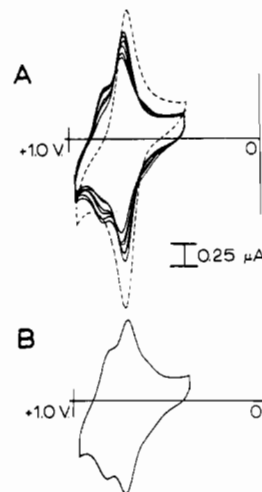


Figure 5. Cyclic voltammograms of a $\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}^+$ film on glassy-carbon disk in aqueous electrolyte (0.1 M Na₂SO₄, pH 2 H₂SO₄; sweep rate 20 mV/s): (A) trace taken immediately after immersion (---) and after soaking for 0.5, 1.0, 1.5, 2.5, 5.5, and 8.5 h; (B) final voltammogram at 8.5 h.

deswelling of the membrane and resulting in a decreased charge-transport rate. The interconversion between acid and base forms is nearly reversible, with only a few percent (<5%) of the electroactivity being lost in an acid/base/acid cycle.

The Ru(III/II) couple is an excellent indicator of the pH of an aqueous solution because of the well-defined relationship between $E_{1/2}$ and pH, given by eq 4. When the pH encapsulation effect, which was described above, occurs, the surface wave appears at 0.63 V, which, from eq 4, indicates that the pH of the environment sensed by the redox couple, i.e., the external film environment, is 3.7. This is in good agreement with the estimated $\text{p}K_{\text{a}}$ value for PVP of 3.5.²⁴ Above this pH, the pH properties of the external solution are excluded. However, at a sufficiently high pH value, protons can be transferred from the $\text{Ru}^{\text{II}}-\text{OH}_2$ sites in the film to the external solution and the redox properties of the film are controlled by the $\text{Ru}-\text{OH}^{2+/+}$ couple, which is pH independent. The diminished response from the hydroxo couple is nevertheless clear evidence that there are most likely charge-transport restrictions present in the deprotonated film. It is interesting to note that, even in the "pH encapsulation" region before deprotonation, the response of the $\text{Ru}^{\text{III}}(\text{bpy})_2(\text{PVP})\text{OH}_2^{2+}/\text{Ru}^{\text{II}}(\text{bpy})_2(\text{PVP})\text{OH}_2^{2+}$ couple shows no evidence for significant charge-transfer restrictions.

L = Cl⁻. Films of $\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}^+$ deposited from ethanolic solutions show good electrochemical behavior in TEAP/CH₃CN, exhibiting a stable, reversible, symmetrically shaped surface wave for the Ru(III/II) couple at a potential consistent with that observed for the analogous chloropyridine monomer complex in solution (see Table I).

A characteristic feature of Ru(II) chloro complexes is the lability of the Ru-Cl bond in aqueous solution. In particular, $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}](\text{ClO}_4)$ undergoes aquation within time of mixing when added to water either as a solid or when dissolved in acetone. The observed rate of aquation, k_{aq} , for a similar complex, $\text{Ru}(\text{bpy})_2(\text{py})(\text{ONO}_2)^+$, has been measured as $5.1 \times 10^{-1} \text{ s}^{-1}$ ($t_{1/2} = 1.3$ s) at 25 °C.²⁵ The rate for the chloro complex is at least as rapid, thus allowing the estimate $k_{\text{aq}} = 1 \text{ s}^{-1}$. We have observed that the aquation reaction also occurs in the chloro polymer films, although the reaction occurs on a much slower time scale. In Figure 5 is shown the cyclic voltammetric behavior of a $\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}^+$ film in aqueous

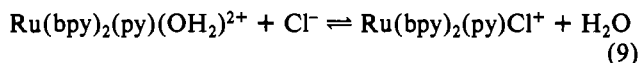
(24) Kirsh, Y. E.; Komarova, O. P. *Polym. Sci., USSR* 1976, 18, 223-8.
(25) DeGiovanni, W.; Meyer, T. J., submitted for publication.

sulfate solution at pH 2. Immediately after immersion of the coated electrode in aqueous electrolyte, the chloro complex is still intact as demonstrated by the single wave for the chloro couple at 0.70 V (Figure 5A, dotted trace). The film was allowed to soak in the electrolyte solution with Ru in the 2+ oxidation state and was monitored periodically over a span of 8.5 h. The relatively slow aquation of the chloro polymer is evidenced by the continued growth of the second wave ($E^{\circ'} = 0.84$ V) due to the PVP/aquo complex. Using 1 h as an estimate for the half-life of the aquation of the polymer-bound chloro sites yields a value of $\sim 2 \times 10^{-4} \text{ s}^{-1}$ for k_{aq} . Compared to k_{aq} for the chloropyridine complex in homogeneous solution (see above), the reaction rate within the film has been slowed down by a factor of at least 5000.

It has been previously reported by Vos et al. that films of $\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}^+$ do not undergo aquation,^{4b} but in the presence of 4 M Cl^- , several factors may have contributed to their seemingly contradictory conclusion:

(i) Cl^- ion loss is not rapid and sufficient time may not have been allowed for the process to occur.

(ii) The already slow loss of Cl^- within the film is likely to be further retarded by the addition of 4 M Cl^- ion to the electrolyte since under these conditions a significant amount of the chloropyridine complex is in equilibrium with the aquo monomer. From a spectral experiment, K_{eq} for the reaction



was found to be ~ 0.03 .

(iii) The diagnostic second wave for the aquo couple cannot be observed¹⁰ under the reported conditions of pH and sweep rate (pH 1, 200 mV/s) used by Vos et al.

Solutions of $\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}^+$ exhibit carryover in their photochemical properties as well. Visible irradiation of both the monomeric and polymeric chloropyridine complexes in acetonitrile solution leads to formation of only $\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}^+$ ($\lambda_{\text{max}} = 480$), indicating photochemical loss of the pyridyl ligand. The photochemical result in acetonitrile and the observation of thermal aquation lend uncertainty to the contention in an earlier report^{4a} that photolysis of $(\text{PVP})\text{Cl}^+$ films induces loss of Cl^- rather than py. The earlier result might well have involved thermal substitution rather than photochemical substitution.

$\text{L} = \text{CH}_3\text{CN}$. The spectral properties of acetonitrile-containing polymeric sites show a good correspondence between monomer and polymer. However, thin films prepared by evaporation of acetonitrile solutions of $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{CH}_3\text{CN})^{2+}$ gave poor electrochemical response in CH_3CN with TEAP as supporting electrolyte. Greatly improved voltammograms were obtained when the solution containing the polymer was treated with a trace amount of HClO_4 prior to deposition onto the electrode. This served to protonate the unbound pyridyl groups, which apparently imparts a somewhat more permeable, solvent-swollen structure to the film.

$\text{L} = \text{N}_3^-$. The spectral and electrochemical properties of the polymer-bound azido complex are comparable to those of the monomer, $\text{Ru}(\text{bpy})_2(\text{py})(\text{N}_3)^+$. The characteristic azide stretch in the infrared region was found to be somewhat medium sensitive, occurring at slightly higher energies when the metallopolymer was examined as a film (2075 cm^{-1}) as opposed to a KBr pellet containing the monomer (2030 cm^{-1}).

One of the reasons for our interest in preparing the polymeric azido complex was the known redox chemistry of the monomer. It has been shown that chemical or electrochemical oxidation of Ru(II) azido complexes by one electron to give Ru(III) leads to net oxidation of the bound azide ion to N_2 .⁹ Loss of N_3^- from the coordination sphere by the metal as N_2 leaves a vacant coordination site, which is replaced by a solvent

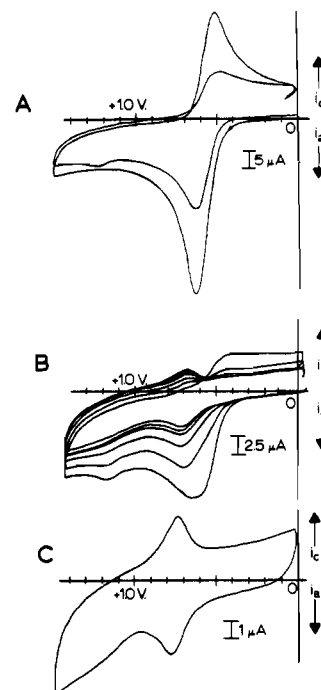
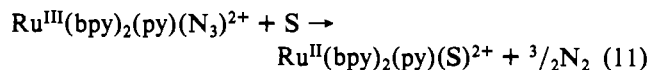
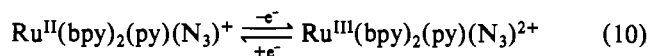


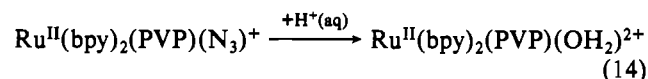
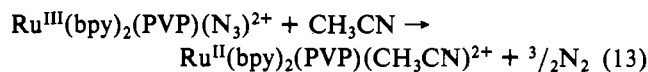
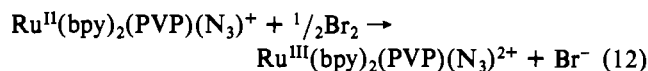
Figure 6. Cyclic voltammograms of a $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)^+$ -coated Pt-disk electrode in 0.1 M TEAP/ CH_3CN (sweep rate 200 mV/s, $\Gamma = 3.4 \times 10^{-9} \text{ mol/cm}^2$): (A) scans 1 and 2; (B) scans 3-8; (C) final trace after repeated cycling, $\Gamma = 9.24 \times 10^{-11} \text{ mol/cm}^2$. Note the differences in vertical scale from A to C.

molecule, S. We felt that the sequence of reactions for the monomer in eq 10 and 11 could provide a means of generating



synthetically useful solvent complex intermediates preattached to the polymer backbone based on $\text{Ru}(\text{bpy})_2(\text{PVP})\text{N}_3^+$.

To demonstrate the carryover in chemical reactivity between the monomer and polymer, we studied the oxidation of $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)^+$ in acetonitrile solution by Br_2 (eq 12) and the acid-catalyzed decomposition reaction in aqueous solution (eq 14).^{26a} From the observation that both reactions occur



for the polymer, it appears that the polymer-bound azido group has maintained the same intrinsic chemical reactivity as the monomer.

Given the similarities between the reactions in solution of the monomer and polymer, the results obtained in an electrochemical study on thin films of $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)^+$ were unexpected. A series of cyclic voltammograms is shown in Figure 6, which summarizes the oxidative electrochemistry of films containing the azido sites. An important feature to notice with regard to these cyclics is the change in the current sensitivity between scans 1 and 9 by a factor of 5. Following

(26) (a) Thompson, M. S., Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1981. (b) Thompson, M. S., unpublished results.

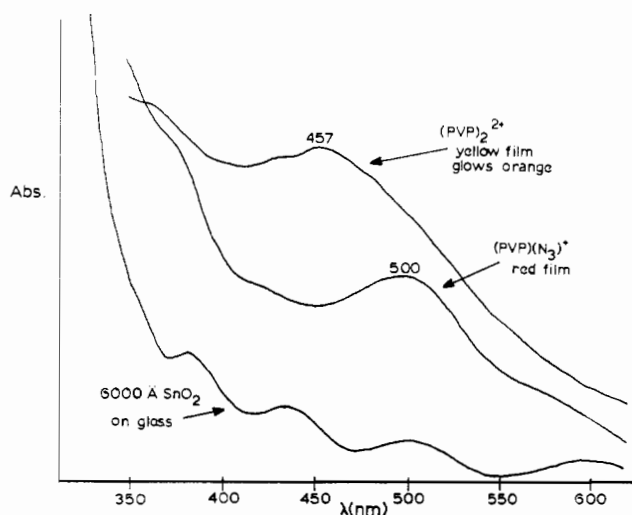


Figure 7. Spectra of film-covered SnO_2 electrodes: (A) spectrum of original $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)]^+$ coating; (B) spectrum after electrochemical oxidation.

initial oxidation of Ru(II) to Ru(III) the complex undergoes decomposition, as evidenced by the smaller return wave, and the film seems to lose most of its electrochemical activity by the final scan. A transient wave appears at $E_{\text{p,a}} = 1.2$ V, but it is only present during scans 2–6. The final voltammogram shows only a single, symmetrically shaped couple at $E^{\circ'} = 0.76$ V. This general behavior is also observed in dichloromethane with $[\text{N}(n\text{-C}_4\text{H}_9)_4](\text{PF}_6)$ as electrolyte, although the potentials are somewhat shifted and wave shapes less well-defined. The potential shifts and wave distortions may have their origin in an increase in film resistance caused by the poorer film-swelling properties of CH_2Cl_2 as compared to those of CH_3CN .

At first glance, the observations made here are unexpected since the predicted result was that, following oxidation of the film, the acetonitrile-containing polymer site would appear and its voltammetric properties were described in an earlier section. However, the only wave observed in the final product is at ~ 0.8 V, which is in the potential range expected for a complex such as $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{Cl})^+$ and could arise from the presence of chloride ion in the electrolyte due to leakage from the SSCE reference electrode. An even more puzzling feature is that the final product wave represents less than 3% of the original electroactive material (calculated from the areas of the Ru(II/III) oxidative waves). Visual inspection of the electrode surface showed that the initially reddish $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)]^+$ film had changed color after oxidation, taking on a yellowish cast, thus indicating that the coating remains on the surface.

Insight into the chemical nature of the now largely electroinactive film was gained in a spectroelectrochemical experiment. Optically transparent SnO_2 electrodes were coated with the azido polymer as described in the electrochemical section. The λ_{max} for the coated electrode was found to be ~ 500 nm as compared to 497 nm for the $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)]^+$ complex in acetonitrile solution. The film was oxidized by potentiostating at 200 mV past the Ru(III/II) couple. As the oxidation proceeded, the polymer film visually changed color from red to yellow. A spectrum of the yellow electrode gave a broad but distinct maximum at 455 nm, close to the value of 460 nm observed for $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ in solution (Figure 7). The film also displays an orange luminescence, which is consistent with the value of 611 nm reported in Table I for the $(\text{PVP})_2$ complex in solution.

The process that occurs within the film gives a material with the same basic coordination environment as $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$, as shown by the essentially identical absorption and emission characteristics, but the materials have drastically different

redox properties. In the film environment, the spatially most accessible pyridine group will bind to ruthenium, and we are forced to conclude that in contrast to the solution-prepared $(\text{PVP})_2$ material, where *intrastrand* chelation appears to occur, in the electrochemically generated material extensive *interstrand* cross-linking must occur to give a dense, rigid metallopolymer network. The electrochemical response of such a rigid film could well be significantly diminished due to the inhibition of charge transport between redox sites. The origin of the inhibition could be in the loss of facile counterion movement through the cross-linked membrane or in restricted segmental motions of the polymer, which could decrease the electron-hopping rate through the film by affecting the extent of electronic coupling between sites.

The observation of the small, but reasonably well-defined surface wave (approximate symmetric shape; $\Delta E_p = 50$ mV at 200 mV/s, 20 mV at 20 mV/s) for the chloro complex (see above and Figure 6C) argues in favor of the latter explanation, i.e., that electron-transfer restrictions are the source of the charge-transport problems. This conclusion follows because the chloro sites are by definition part of the same polymer network as the $(\text{PVP})_2$ sites and as such are subject to the same mass-transport limitations. If mass-transport considerations were the limiting factor in the charge-transport kinetics, the electrochemistry of such a film would exhibit responses from either both or neither of the redox sites, but not from one or the other.

In an attempt to capture a substantial fraction of the vacated azido sites with chloride, the electrochemical oxidation of a $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)]^+$ -coated electrode was done in the presence of added Cl^- (as $(n\text{-C}_4\text{H}_9)_4\text{NCl}$). A cyclic voltammogram of the resulting film exhibited not only an enhanced wave due to the chloro polymer ($E^{\circ'} = 0.76$ V) but, for the first time, a response from the $(\text{PVP})_2$ complex ($E^{\circ'} = 1.23$ V) as well. The experiment indicates that the transient wave observed at 1.2 V in the original experiment likely arises from the incipient formation of the $(\text{PVP})_2$ complex, which is only detectable during the early stages of the decomposition process before interstrand linking restricts charge transfer on the time scale of the potential sweep. The experiment also supports the previous assignment of the 0.76-V couple as being due to the presence of $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$ sites in the polymer. It also reinforces the conclusions reached about the effects of interstrand coupling on charge transfer through the polymer films. In the presence of excess Cl^- , fewer points for interstrand cross-linking exist because of competitive capture by Cl^- . The resulting film matrix should be less rigid and the film more open to charge transport.

With the above evidence in hand, we can now make a tentative conclusion about the fate of the approximately 97% electroinactive sites in the film. Oxidation of Ru(II) to Ru(III) is followed by decomposition of the azido complex and subsequent capture of the open coordination site by an unbound pyridyl ligand from the PVP backbone. Note that initial capture by solvent could not have occurred since the resulting acetonitrile complex would have been stable. This is a surprising result and it suggests that the effective concentration of acetonitrile in the films near the redox sites may be relatively low.

To provide a graphic demonstration of the effect of the pendant pyridyl groups from PVP on the observed electrochemical behavior of the films, we examined azide-containing films produced by electroreductive polymerization of $[\text{Ru}(\text{bpy})_2(\text{vpy})(\text{N}_3)]^+$ (see electrochemical section). In these films there is by definition a 1:1 relationship between pyridyl units of the polymer and the attached ruthenium complexes; therefore, there are no unbound ligands to trap open coordination sites vacated by azide loss.

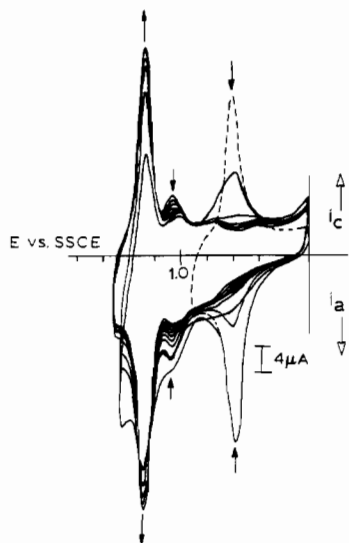


Figure 8. Cyclic voltammograms of the electropolymerized Ru(bpy)₂(vpy)(N₃)⁺-based, surface-bound polymer (Pt disk, 200 mV/s, 0.1 M TBAH/CH₃CN; $\Gamma = 7.8 \times 10^{-9}$ mol/cm²). Dotted line indicates trace observed if potential sweep is reversed at 0.9 V. Arrows indicate growth or decay of the different redox couples. The couples at 1.30, 1.10, and 0.58 V are Ru(bpy)₂(py)(CH₃CN)^{3+/2+}, Ru(bpy)₂(py)(OCIO₃)^{2+/+}, and Ru(bpy)₂(py)(N₃)^{2+/+}, respectively.

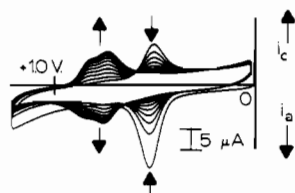


Figure 9. Cyclic voltammograms of a Ru(bpy)₂(PVP)(N₃)⁺ film on a glassy-carbon disk in aqueous electrolyte (0.1 M SO₄²⁻, pH 2; 200 mV/s). Arrows indicate growth and decay of aquo and azido couples, respectively.

In TEAP/CH₃CN solution, electrochemical oxidation of the azido polymer formed by reductive electropolymerization shows clear evidence for the production of both the acetonitrile ($E^{\circ} = 1.30$ V) and perchlorato ($E^{\circ} = 1.10$ V)⁷ complexes (Figure 8), showing that a competition exists between the solvent and counterion for capture of the site vacated by N₃⁻. Subsequent potential scans show that ClO₄⁻ is slowly displaced by CH₃CN, as would be expected. The couple assigned to the perchlorato complex is absent if the electrochemistry is performed when the counterion is PF₆⁻, a noncoordinating anion for Ru(II).

The behavior of Ru(bpy)₂(PVP)(N₃)⁺ films has also been investigated in acidic aqueous solution in an attempt to acquire additional information about the reactivity of the azide ligand that was unobtainable from previous solution experiments on the monomeric complex. A cyclic voltammogram of a (PVP)(N₃)⁺ film in pH 2 sulfate solution (Figure 9) shows the oxidative decomposition of the azido polymer followed by direct conversion to Ru(bpy)₂(PVP)(OH₂)²⁺ as shown by the presence of the characteristic waves for the aquo complex.

$L = \text{NO}_2^-, \text{NO}_3^-, \text{NO}^+$. There is an extensive chemistry of the nitro and nitrosyl groups in poly(pyridyl) complexes of ruthenium. Early work in homogeneous solution revealed that nitro complexes of Ru(III) are unstable, yielding a mixture of nitrosyl and nitrate products.^{30a} Recently, a series of

Scheme II

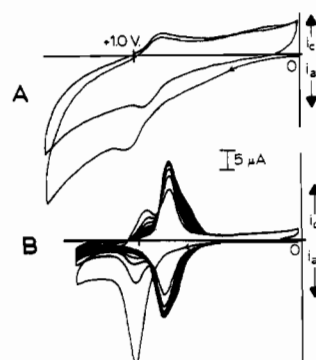
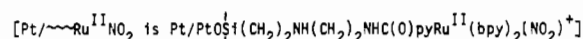
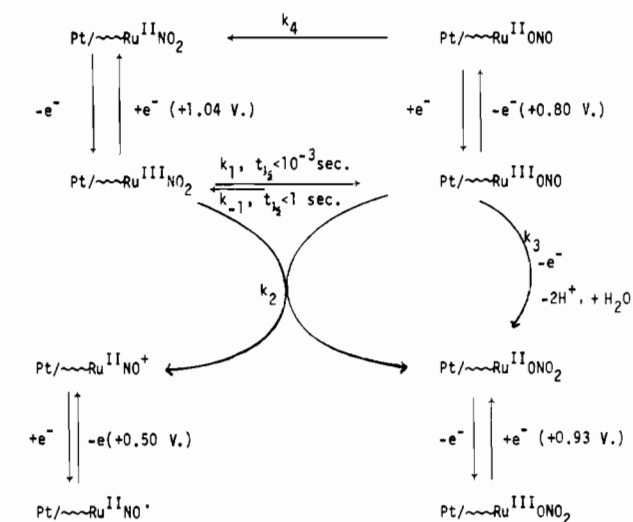


Figure 10. Cyclic voltammograms of surface-bound Ru(bpy)₂(PVP)(NO₂)⁺ films (200 mV/s): (A) Pt disk, 0.1 M TEAP/CH₃CN; showing the conversion of RuNO₂ sites ($E_{p,a} = 1.05$ V) to RuONO₂ sites ($E_{p,a} = 0.90$ V). (B) glassy-carbon disk, aqueous electrolyte (0.1 M Na₂SO₄, pH 2); showing the conversions RuNO₂ → RuONO₂ → Ru-OH₂.

experiments performed on nitro complexes bound to Pt electrodes by using an alkylsilane link were used to elucidate the mechanistic details of the overall reaction.^{30b,c} The results are illustrated in Scheme II, and the main conclusions are summarized below:

(i) Oxidation of Ru^{II}-NO₂ to Ru^{III}-NO₂ is a chemically irreversible process in the net sense.

(ii) A rapid linkage isomerization pathway exists (k_1, k_{-1}), which interconverts Ru^{III} nitro (N-bound) and Ru^{III} nitrito (O-bound) forms. The O-bound isomer is observable only at low temperatures or at fast sweep rates (>3 V/s).

(iii) Nitro and nitrito isomers react via a bimolecular disproportionation (k_2) to yield nitrosyl and nitrate products.

(iv) The nitrate complex (Ru-ONO₂) can also be formed by one-electron oxidation of Ru^{III}-ONO (k_3). The source of the additional oxygen atom is uncertain.

(v) In the electrochemical oxidation of a homogeneous solution of Ru(bpy)₂(py)(NO₂)⁺ the bimolecular step (k_2) dominates the reactivity, producing an equimolar mixture of nitrosyl and nitrate products. However, for the silane-attached species it appears that the k_2 and k_3 paths are initially com-

(27) Calculated with an assumed density for the metallopolymer of 0.5 g/cm³.²⁸

(28) Shigehara, K.; Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1981**, *103*, 2552-8.

(29) Facci, J. S.; Murray, R. W., manuscript in preparation.

(30) (a) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2384-7. (b) Abruña, H. D.; Walsh, J. L.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1981**, *20*, 1481-6. (c) Abruña, H. D.; Walsh, J. L.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 3272-4.

petitive but the k_3 step dominates as the nitro sites are depleted.

In Figure 10A is shown a cyclic voltammogram of a Ru-(bpy)₂(PVP)(NO₂)⁺-coated electrode using CH₃CN/TEAP as electrolyte. Despite the diffusional appearance of the waves, it can be clearly seen that irreversible oxidation ($E_{p,a} = 1.05$ V) of the Ru^{II} nitro complex is followed by quantitative conversion to the nitrate complex ($E^{o'} = 0.90$ V). An important feature to note is the absence of the nitrosyl wave at ~ 0.5 V.

Examination of the nitro polymer coated electrode in aqueous acidic solution (pH 2 sulfate) gives much improvement in the definition of the electrochemistry (Figure 10B). The existence of isopotential points³¹ at 0.88 and 0.90 V clearly demonstrates the appearance of Ru(bpy)₂(PVP)(NO₃)⁺ as product. The nitrate complex is unstable with respect to aquation, and subsequent slow-scan voltammograms exhibit the characteristic two-wave pattern of the surface-bound aquo polymer. Once again, the aquation rate within the film is *far* slower than for the monomer, Ru(bpy)₂(py)(NO₃)⁺, in water.

The striking result here is that the appearance of the nitrate complex as the sole product dictates that the only reaction pathway that operates under these conditions in the film is the k_3 pathway. Apparently, the ligand-based disproportionation reaction has been completely quenched—most likely as a consequence of the spatial separation of the electroactive sites, which are located (on the average) at five pyridyl unit intervals along the polymer backbone. It can also be inferred that the metal complexes are, perhaps somewhat surprisingly, evenly distributed along the polymer chain since a totally random distribution could, in some cases, lead to adjacent metal sites and give rise to nitrosyl formation via the k_2 pathway. The reactivity of thin films containing Ru(bpy)₂(PVP)(NO₂)⁺ is yet another example of a modification in chemical properties induced by the inherent structural characteristics of the polymer.

Structure-Reactivity Relationships. In homogeneous solution the Ru(II) nitro complexes have total freedom with respect to mobility. The electrochemistry under these conditions shows that both the disproportionation (k_2) pathway and the nitrito \rightarrow nitrate (k_3) conversion are operational, although k_2 dominates. With silane-attached nitro species in monolayer coverages, there must be some restriction in the motion of the nitro group in comparison to the solution species. However, the relatively long organosilane chain is flexible, and electron transfer is believed to occur when reorientations (or "flopping motions") bring the immobilized redox site close to the electrode surface.³² In this system the k_2 path has become of less importance than k_3 under normal conditions (ambient temperature, sweep rates < 1 V/s). Under appropriate conditions such as low temperatures (-78 °C) or fast sweep rates (> 3 V/s), the bimolecular reaction is completely eliminated. In films prepared by the electroreductive polymerization of Ru-(bpy)₂(vpy)(NO₂)⁺ the RuNO₂ groups are held in adjacent sites and the k_2 path is still in evidence, particularly at low coverages.

In the 5:1 polymer nitro complex, the equilibrium spatial separation of the ruthenium centers is calculated (assuming a rodlike structure) to be 13.5 Å (see Figure 11). With use of this model, the most favorable orientation of nitro groups on neighboring sites gives a *minimum* nitrogen-oxygen separation of 7 Å between the N and O atoms of nitro groups. Apparently, this distance is adequately long and/or site mobility is sufficiently low to block completely the disproportionation reaction.

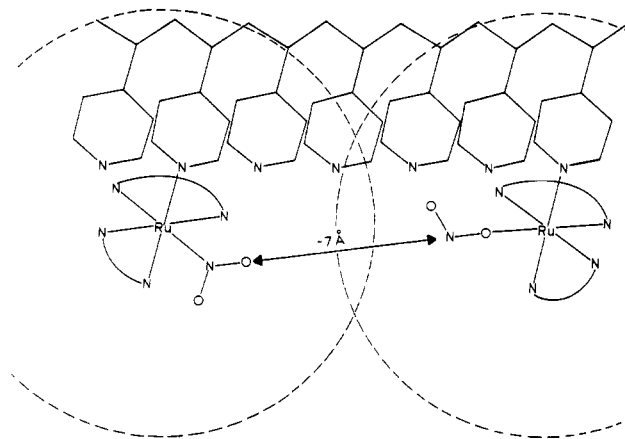
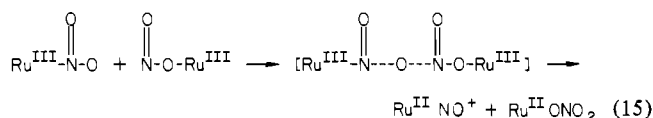


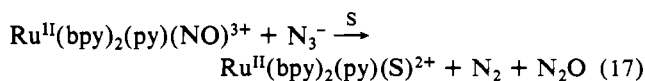
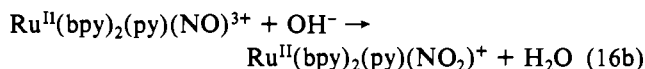
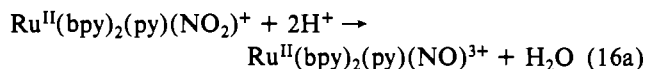
Figure 11. Structural representation of Ru(bpy)₂(PVP)(NO₂)⁺ in a configuration of closest approach for bimolecular reaction. Data for the PVP polymer framework were taken from ref 21a (see also Figure 1). Parameters for the metal complex are from ref 33. The dashed circles represent the van der Waals radii of the complexes, 7.4 Å.

A reasonable explanation for the observed differences between film and solution reactivity lies in the differing structural demands of the k_2 and k_3 reactions. The bimolecular path involves O atom transfer and, of necessity, strong electronic coupling along the reaction coordinate:



By contrast, the k_3 route involves only simple electron transfer in the initial step. Consequently, spatial demands are minimal because only slight electronic orbital overlap is required between donor and acceptor sites to make the reaction adiabatic. The fact that electron transfer is rapid in the system (relative to the time scale of the experiment) is evidenced by the electrochemical wave shapes, which show nearly ideal surface behavior.¹⁸

Two other well-documented examples of the chemical reactivity of nitroruthenium(II) complexes are the acid/base induced nitro/nitrosyl interconversion¹⁵ (eq 16) and the synthetically useful reaction between azide ion and the bound nitrosyl group³⁴ (eq 17). In homogeneous solution, the



S = solvent

polymeric analogues display similar behavior in both cases. Attempts to observe similar reactions for the metal complex sites within the polymer film have been fraught with difficulty. The major difficulty arises from the hygroscopic nature of Ru(bpy)₂(PVP)(NO)³⁺ (see electrochemical section) which has prevented us from preparing films of reasonable quality. In addition, the nitro/nitrosyl interconversion within the film

(31) Untereker, D. F.; Bruckenstein, S. *Anal. Chem.* **1972**, *44*, 1009–20. See also ref 30b.

(32) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135–41.

(33) Phelps, D. W.; Kahn, E. M.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 2486–90.

(34) Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994–9.

appears to be quite slow. The only conclusion that can safely be drawn at this stage is that, while the chemical and redox reactivities of the nitro and nitrosyl metallopolymers are maintained in solution, the film environment must play a major role in either altering or eliminating the usual reactivity of the sites.

Conclusions

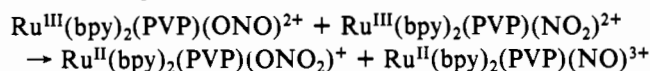
We have prepared a series of metallopolymers and investigated their chemical and physical properties. The work has led to a number of important conclusions which are summarized below:

(1) Preparation of the metallopolymers can be accomplished by using synthetic procedures that are based on the known chemistry of monomeric analogues.

(2) The polymer-bound metal complex sites retain the chemical and physical properties inherent in related monomers, as shown by spectral measurements and the observation of net reactions of the various materials in homogeneous solutions.

(3) Interestingly, modifications in the chemical and redox reactivities of the polymer-bound sites do occur in certain cases when the metallopolymers are examined as films evaporatively deposited onto electrode surfaces. The origin of the differences is believed to be due to two major factors:

(A) *Spatial separation* of the chemical sites along the polymer chain can change the net chemistry by slowing or eliminating bimolecular reactions with strict orientational demands, e.g.



(B) Changes in the *local environment* at the chemical sites due to the presence of protonated or unprotonated pyridyl groups from the main chain of the polymer can also change the net chemistry, e.g.: (i) the loss of pH dependence for the Ru(III/II) couple of $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$ at $\text{pH} > 4$; (ii) the change in the course of the decomposition chemistry of $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)^{2+}$, where a labile intermediate appears to be captured by an unbound pyridyl group rather than by solvent; (iii) the decrease in rates of chemical reactions within the film environment, e.g., the slowness of the aquation of $\text{Ru}^{\text{II}}\text{-chloro}$ and $\text{Ru}^{\text{II}}\text{-ONO}_2$ sites, of nitro/nitrosyl interconversion and of H/D exchange at $\text{Ru}^{\text{II}}\text{-aquo}$ sites.

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Registry No. $[\text{Ru}(\text{bpy})_2(\text{vpy})(\text{N}_3)](\text{PF}_6)$, 82731-41-7; $[\text{Ru}(\text{bpy})_2(\text{py})(\text{CN})](\text{PF}_6)$, 82740-43-0; *cis*- $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$, 82769-08-2; $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)^{2+}$, 75931-35-0; $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{CN})^+$, 82731-42-8; $\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}^+$, 75675-25-1; $\text{Ru}(\text{bpy})_2(\text{PVP})\text{-}(\text{CH}_3\text{CN})^{2+}$, 80864-62-6; $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{NO}_2)^+$, 80864-61-5; $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{NO})^{3+}$, 82731-43-9; $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{NO}_3)^+$, 82731-44-0; $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{N}_3)^+$, 82731-40-6; $\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH})^+$, 82731-45-1; $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$, 63338-38-5; $\text{Ru}(\text{bpy})_2(\text{py})(\text{CN})^+$, 82731-46-2; $\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}^+$, 33519-09-4; $\text{Ru}(\text{bpy})_2(\text{py})(\text{CH}_3\text{CN})^{2+}$, 82769-09-3; $\text{Ru}(\text{bpy})_2(\text{py})(\text{NO}_2)^+$, 34398-55-5; $\text{Ru}(\text{bpy})_2(\text{py})(\text{NO})^{3+}$, 82769-10-6; $\text{Ru}(\text{bpy})_2(\text{py})(\text{NO}_3)^+$, 82769-11-7; $\text{Ru}(\text{bpy})_2(\text{py})(\text{N}_3)^+$, 82769-12-8; $\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)^{2+}$, 67202-42-0; $\text{Ru}(\text{bpy})_2(\text{py})(\text{OH})^+$, 75495-06-6; *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$, 19542-80-4; $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]\text{PF}_6$, 62387-78-4; $[\text{Ru}(\text{bpy})_2(\text{py})(\text{OH}_2)](\text{PF}_6)_2$, 75495-09-9; $\text{Ru}(\text{bpy})_2(\text{CO}_3)$, 59460-48-9.

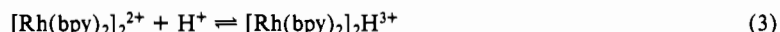
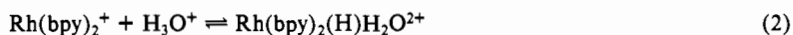
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Nature of Bis(2,2'-bipyridine)rhodium(I) in Aqueous Solutions

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Spectrophotometric studies of aqueous solutions of bis(2,2'-bipyridine)rhodium(I) ($\text{Rh}(\text{bpy})_2^+$) as a function of pH and rhodium(I) concentration provide evidence for four species as shown in eq 1-3. At room temperature $\log K_1 = 4.0 \pm$



0.2, $\log K_2 = 7.3 \pm 0.1$, and $\log K_3 = 9.3 \pm 0.3$. Both monomer and dimer in eq 1 are purple; $\lambda_{\text{max}}(\text{monomer}) = 505 \text{ nm}$ ($\epsilon \approx 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and $\lambda_{\text{max}}(\text{dimer}) \approx 530 \text{ nm}$ ($\epsilon/\text{rhodium} \approx 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The rhodium(III) hydride (eq 2) does not absorb in the visible region but the "protonated dimer" (eq 3) is brown: $\lambda_{\text{max}}(\epsilon/\text{rhodium}) = 960 \text{ nm}$ ($2.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), $\sim 500 \text{ nm}$ ($4.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, sh), 420 nm ($4.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The properties elucidated for these species are compared with those of other d^8 systems.

The preparation of purple salts and solutions containing bis(2,2'-bipyridine)rhodium(I) species was first reported by Waing and Martin in 1958;^{1,2} the results of more extensive magnetic measurements and the spectral properties of dilute ethanolic solutions were reported subsequently.³ Interest in the reactivity and the nature of these species in aqueous solution has recently been stimulated by the results of photochemical experiments in which water is reduced to hydrogen.⁴⁻⁷

Bis(2,2'-bipyridine)rhodium(I) ($\text{Rh}(\text{bpy})_2^+$) was found to be a product in some of the experiments and has been postulated to be a reactive intermediate in hydrogen formation under some conditions.⁸⁻¹⁰ Preliminary results⁶ indicated the nature

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(8) The original postulate that $\text{Rh}(\text{bpy})_2^+$ reduces water to hydrogen over platinum^{4,5} at pH 7-8 has been shown to be incorrect. There is, however, evidence^{6,7,9,10} that $\text{Rh}(\text{bpy})_2(\text{H})(\text{H}_2\text{O})^{2+}$ may provide a catalyst for reduction of water by $\text{Rh}(\text{bpy})_3^{2+}$ in more acidic solutions.