Our preliminary work does, however, clearly demonstrate that the matrix emission and excitation spectra exhibit sharp vibronic structure, and together with photoselection studies can provide extensive information about porphyrin-type molecules.

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Polymeric Ligands as Anchoring Groups for the Attachment of Metal Complexes to Graphite Electrode Surfaces

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Abstract: Coatings of poly(4-vinylpyridine) (PVP) and polyacrylonitrile (PAN) have been applied to pyrolytic graphite electrodes by simple exposure of the electrodes to solutions of the polymers. The resulting coatings are very durable and extract metal complexes from solutions as dilute as 5×10^{-8} M. With higher concentrations, very large quantities of metal complexes can be bound to the polymer coatings and their electrochemical responses observed. The behavior of attached Ru(edta), Ru(NH$_3$)$_5$, and Cu(II) complexes is described. Ru^{II}(edta) undergoes ligand substitution reactions while bound to the PVP coating to form cross-links between pyridine sites in the polymer. Examples are given of polymeric coatings to which two different metal complexes are bound as well as electrodes on which both PVP and PAN coatings are present.

Polymeric molecules have been advanced as potent modification agents in experiments with chemically modified electrodes.[1-4] Some of the first reports involved the coating of electrodes with electroinactive polymers,[1] but more recently electrodes coated with polymeric molecules containing electroactive groups have been described.[2-5] One of the most attractive aspects of polymeric coatings is the relative ease with which they can be applied—simple dip coating by immersion of the electrode in a solution of the polymer[1-5] often suffices to produce quantities of anchored ligand sites as great as or greater than result from more elaborate coating procedures.[3,6,7]

By attaching molecules such as polyvinylpyridine (PVP) or polyacrylonitrile (PAN) that contain many sites for metal coordination, electrode surfaces that accept a variety of metal ions can be prepared. In a recent communication[5] we described experiments in which large quantities of Ru(edta) and Ru(NH$_3$)$_5$ complexes were coordinatively attached to pyrolytic graphite electrodes coated with PVP or PAN. In the present report these studies have been expanded to include mixed coatings of two different polymeric ligands as well as electrode surfaces to which two different metal complexes are attached simultaneously. Among the special properties of the PVP coatings are an ability to extract metal ions from solutions as dilute as 5×10^{-8} M. When Ru(edta) complexes are attached to the PVP coating a rich surface coordination chemistry ensues that can be modified by control of the electrode potential.

Experimental Section

Materials. Pyrolytic graphite disks were cut from cylindrical stock (Union Carbide Corp., Parma, Ohio) with the basal planes of the graphite perpendicular to the axis of the cylinder. The disks were sealed to the ends of glass tubing by means of heat-shrinkable polyolefin tubing (Alpha Wire Co.). Electrical contact was made to the rear face of the disks using a few drops of mercury. The mounted disks were freshly cleaved before each set of experiments by cutting a thin section through the polyolefin sheath and the graphite disk with a scalpel. The exposed area of each disk was 0.17 cm^2.

Poly(4-vinylpyridine) (Borden Inc., Philadelphia, Pa.) was recrystallized twice from methanol-diethyl ether. The average molecular weight of the sample, determined viscometrically,[8] was 7.4×10^5 corresponding to about 7000 pyridine groups per molecule of polymer. Polyacrylonitrile was provided by Dr. S. Margel. Its molecular weight was not measured.

Aquoethylenediaminetetraacetatoruthenium(III) prepared from RuCl$_3$ as described by Mukaida et al.[9] was found to contain chloride. A chloride-free product was obtained by dissolving the initial yellow-green solid in water, reducing the volume to ca. 10 mL/g, and allowing the solution to stand overnight at room temperature. The resulting yellow precipitate was washed with water and methanol and dried under vacuum. Anal. Calcd for RuC$_{10}$H$_{15}$N$_2$O$_{10}$: C, 29.0; H, 3.72; N, 6.81. Found: C, 29.4; H, 3.70; N, 6.86.

Solutions of aquoethylenediaminetetraacetatoruthenium(II) were prepared by reducing solutions of the Ru(III) complex with amalgamated zinc or by controlled-potential electrolysis at a mercury pool electrode.

Solutions of aquopentaammineruthenium(II) were prepared by electrolytic reduction of chloropentaammineruthenium(II) at a mercury pool electrode.

Reagent grade chemicals were used without futher purification. Aqueous solutions were prepared from triply distilled water. The supporting electrolyte for most electrochemical measurements was 0.2 M CF$_3$COONa adjusted to the desired pH with CF$_3$COOH.

Apparatus and Procedures. Voltammograms were obtained with a PAR (Princeton Applied Research) Model 174 instrument and an *x-y* recorder (Houston Instruments). Conventional two-compartment
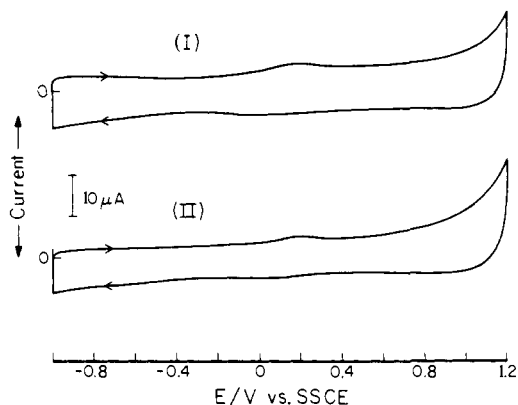
Figure 1. Steady-state cyclic voltammograms for a pyrolytic graphite electrode before (I) and after (II) coating with PVP. Supporting electrolyte: 0.2 M CF_3COONa adjusted to pH 4.2 with CF_3COOH. Scan rate: 200 mV s^{-1}.

Figure 2. (A) Cyclic voltammograms for 0.5 mM $Ru^{III}(edta)OH_2$ at a pyrolytic graphite electrode (uncoated): I, supporting electrolyte 0.2 M CH_3COONa adjusted to pH 2.7 with CF_3COOH; II, supporting electrolyte 0.2 M CH_3COONa + 5 mM pyridine (pH 2.7). Scan rate 50 mV s^{-1}. (B) Cyclic voltammograms recorded at various times after an electrode coated with PVP was immersed in a 2×10^{-6} M solution of Ru^{III}-(edta). The immersion time is indicated for each curve. Supporting electrolyte: 0.2 M CF_3COOH (pH 3.3). Scan rate: 200 mV s^{-1}. The electrode was at open circuit between scans.

cells were employed. Controlled-potential reductions of $Ru^{III}(edta)$ were carried out at a stirred mercury pool electrode in a conventional compartmentalized cell with a PAR Model 173 potentiostat and Model 179 digital coulometer. A sodium chloride-saturated calomel reference electrode was used. Its potential was 4 mV more negative than that of a standard SCE in the supporting electrolytes employed. Experiments were conducted at room temperature, 22 ± 2 °C.

Electrode Coating Procedures. Adherent coatings of poly(4-vinylpyridine) or polyacrylonitrile were obtained by immersing mounted and freshly cleaved electrodes for 15 min in a 0.5% solution of the polymer in methanol (PVP) or dimethyl sulfoxide (PAN). After coating, the electrodes were washed repeatedly with solvent and then soaked for 15 min in pure solvent. Any adhering solvent was removed with a soft tissue and the electrodes were immersed in aqueous solutions of the metal complexes to produce coordination of the complexes to the coating. The time of exposure of the coated electrodes to the solutions of metal complexes varied depending on the concentration of the complex and the objective of the experiment.
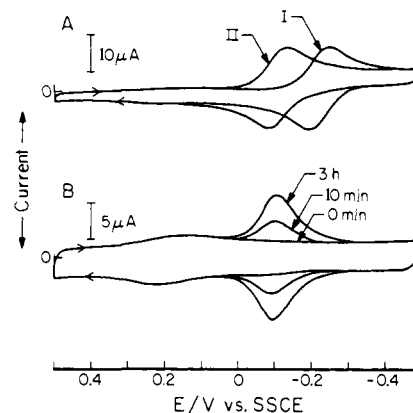
Results and Discussion

Attachment of Poly(4-vinylpyridine) to Graphite Electrodes. With the relatively high molecular weight samples of PVP employed in this study extensive attachment to graphite electrodes was readily achieved by soaking the electrodes for a few minutes in a 0.5% solution of the polymer in methanol. The binding interaction between the polymer and the graphite surface is evidently extremely strong because prolonged soaking of coated electrodes in pure methanol, in which PVP is quite soluble, does not produce a polymer-free surface. The attachment is insensitive to the detailed structure of the graphite: both the basal and edge planes of pyrolytic graphite electrodes readily accepted the PVP coatings and significant differences were not observed among oxidized, reduced, and plasma etched[10,11] surfaces.

Cyclic voltammetric background currents for coated and uncoated electrodes typically showed small differences, Figure 1, but these were not major nor reproducible enough to serve as indicators of the extent of the coating. We relied primarily upon the capacity of electrodes bearing PVP coatings to bind Ru(edta) complexes to their surfaces (vide infra) to confirm the presence of the coatings.

Electrodes exposed to high concentrations of 4-ethylpyridine or 1,2-di(4-pyridyl)ethane exhibited no affinity for $Ru^{III}(edta)$, which indicates, not surprisingly, that the attachment of PVP to graphite requires a minimum degree of polymerization. (We are presently examining the effect of molecular weight on the extent of attachment of PVP to graphite.) This suggests that the attachment arises from bonding interactions between a number of the pyridine rings in each attached molecule and the graphite surface, probably via overlap of pyridine π electrons with unoccupied orbitals in the graphite. Such an inter-

action would resemble that proposed previously to account for the strong, spontaneous, but shorter lived adsorption on graphite of low molecular weight molecules containing several aromatic centers.[12,13] However, the fact that adherent polyacrylonitrile coatings are also readily prepared indicates that aromatic centers are not essential to the spontaneous binding of polymeric molecules.

Coordination of $Ru^{III}(edta)$ to PVP-Coated Electrodes. As has been previously pointed out,[14] the $Ru^{III/II}$ redox couple has special virtues as an attachable, electroactive probe in studies of electrode surfaces on which ligand sites have been introduced synthetically. Both the aquopentaamine and aquoethylenediaminetetraacetato complexes serve the purpose and the attachment of both will be described. However, we have concentrated on the edta complexes in this study because, in contrast with the pentaammine complexes, coordination to pyridine centers proceeds facilely in both the 3+ and 2+ oxidation states.[15]

Figure 2A shows cyclic voltammograms for a 0.5 mM solution of $Ru^{III}(edta)OH_2$ both in the absence and in the presence of excess pyridine. The shift in peak potential that signals the rapid coordination of a pyridine ligand to the Ru(III) center[15] makes the aquo and pyridine forms of the Ru(edta) complex easy to distinguish.[16] The addition of pyridine to solutions of $Ru^{III}(edta)OH_2$ converts the original voltammogram (I) to the one labeled II in Figure 2A by the time it can be recorded. This rapid coordination of pyridine by $Ru^{III}(edta)OH_2$ is expected on the basis of the kinetic results of Matsubara and Creutz[15] for the analogous ligand, isonicotinamide. There was no evidence of further reaction to produce a $Ru^{III}(edta)$ complex containing more than one coordinated pyridine ligand under the conditions employed in Figure 2A or even if the pH was increased to 6-7.

Fortunately, the binding of both $Ru^{III}(edta)$ (and Ru^{II}-(edta)) to PVP-coated electrodes is sufficiently strong and extensive that it is possible to observe the attachment as it is occurring by recording cyclic voltammograms with coated electrodes in solutions of the complex that are too dilute to yield measurable currents with uncoated electrodes. Figure 2B shows cyclic voltammograms obtained with a PVP-coated electrode in a 2×10^{-6} M solution of $Ru^{III}(edta)OH_2$ as a function of the time the coated electrode spent in the solution. The voltammogram recorded immediately after the electrode was immersed in the solution exhibits a curve indistinguishable
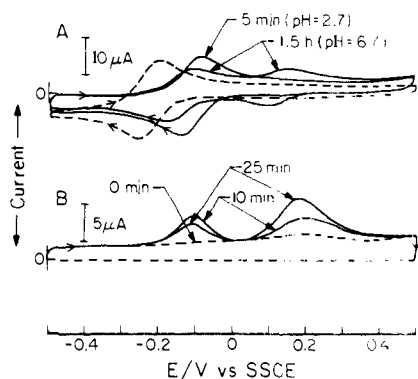
Figure 3. (A) Cyclic voltammograms for 0.5 mM Ru^{II}(edta): (- - - -) supporting electrolyte 0.2 M CF$_3$COONa; (——) supporting electrolyte 0.2 M CF$_3$COONa + 5 mM pyridine adjusted to pH values where the pyridine is protonated (2.7) or unprotonated (6.7). The time since the pyridine was added to the supporting electrolyte and its pH are indicated on each curve. Scan rate 50 mV s^{-1}. (B) Voltammograms recorded at various times after a PVP-coated electrode was immersed in a 2 × 10^{-6} M solution of Ru^{II}(edta). The immersion time is indicated for each curve. Supporting electrolyte: 0.2 M CF$_3$COONa (pH 3.3). Scan rate: 200 mV s^{-1}. The electrode was at open circuit between scans.
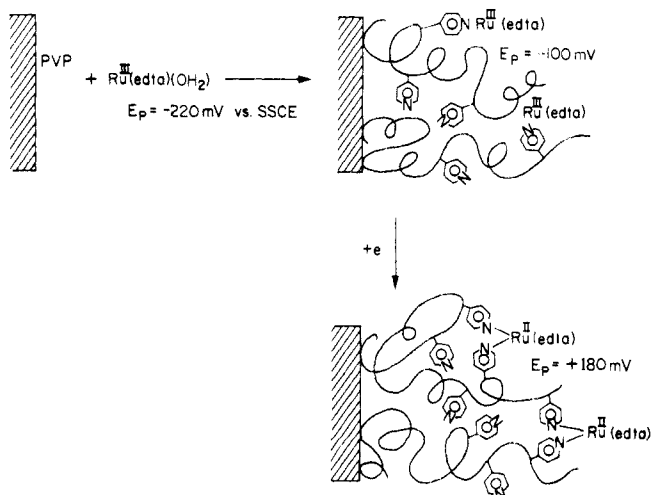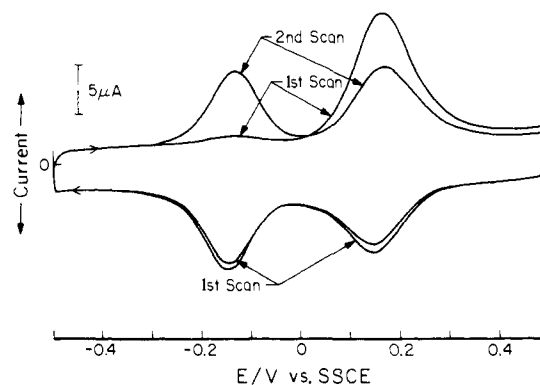

Figure 4. Schematic picture of ligand substitution chemistry proceeding within a coating of PVP to which Ru(edta) is coordinatively bound. The second coordinated pyridine group probably displaces a coordinated carboxyl group from the Ru(II) center.

Figure 5. Cyclic voltammograms for a PVP-coated electrode after it had been immersed for 4.5 h in a 2 × 10^{-6} M solution of Ru^{II}(edta). Supporting electrolyte: 0.2 M CF$_3$COONa (pH 4.2).

from that for a solution containing no Ru^{III}(edta). However, voltammetric waves begin to appear as the polymer coating extracts complex from the solution. The waves increase in magnitude until a constant response is obtained after 3–4 h. The symmetrical shape of the voltammograms, their 90 ± 5 mV width at half-peak current, the linear dependence of their peak currents on scan rate, and the near identity of the anodic and cathodic peak potentials all confirm that the voltammograms arise from an attached reactant undergoing a rapid charge transfer.[17] The area of the final voltammogram corresponds to the presence of 6.5 × 10^{-10} mol cm^{-2} of complex bound to the surface. Larger quantities of the complex are bound from more concentrated solutions (vide infra) but no new waves appear; the wave at −0.10 V merely increases in area.

The average of the anodic and cathodic peak potentials for voltammograms of the bound complex in Figure 2B, −0.10 V, matches the corresponding average for the Ru(edta)–pyridine complex in Figure 2A.

The small, time-independent wave centered near +0.20 V in Figure 2 appears on both coated and uncoated graphite electrodes in the presence and absence of dissolved reactants.

Its position is pH dependent and it is believed to arise from the reduction and oxidation of functionalities on the graphite surface that resemble the hydroquinone/quinone couple.[10] Its persistence on PVP-coated electrodes implies that the coating does not insulate the graphite electrode from the solution thoroughly enough to inhibit this oxidation and reduction of its surface.

Coordination of Ru^{II}(edta) to PVP-Coated Electrodes. Soaking the PVP-coated electrode in a 2 × 10^{-6} solution of Ru^{II}(edta) under argon produced the voltammograms shown in Figure 3B. The wave at −0.10 V obtained with Ru^{III}(edta) appears initially but with increasing times of exposures its magnitude diminishes and a second wave appears near +0.18 V. The magnitudes of the two waves continue to shift for several hours until the second wave eventually dominates the voltammogram and only a vestige of the wave at −0.10 V remains. The wave at +0.18 V matches a wave that develops in homogeneous solutions of Ru^{II}(edta) in the presence of small excesses of pyridine at higher pH values where pyridine is largely unprotonated (Figure 3A). It is most reasonably attributed to a complex containing two pyridine ligands coordinated to Ru(II).[18] The gradual development of this wave with coated electrodes thus represents the coordination of two pyridine groups in the polymer coating to the bound Ru^{II}(edta) so that the complex becomes a cross-linking bridge in the polymer layer. The schematic representation in Figure 4 indicates the coordination chemistry that we envision proceeding within the polymer coating on the electrode surface.

The failure of Ru^{III}(edta) to accept more than one pyridine ligand either in solution or from the polymer coating (Figure 2A,B) is in accord with the much weaker π basicity of Ru(III).[19] This is emphatically demonstrated by the cyclic voltammogram in Figure 5 which includes a cathodic scan and a second anodic scan. The pair of waves in the cathodic half of the voltammogram have very different magnitudes than their anodic counterparts in the first scan. The wave at the more positive potential arising from the reduction of the complex in which two pyridine ligands are coordinated to the ruthenium center is smaller than the corresponding oxidation wave and the wave at −0.14 V, corresponding to the reduction of the monopyridine complex, is much larger than the corresponding oxidation wave in the first scan. These features seem clearly to show that one of the two pyridine ligands in the cross-linking Ru(II) complex is displaced at an appreciable rate once the complex is oxidized to Ru(III). The resulting monopyridine complex of Ru^{III}(edta) is reduced at −0.14 V to produce the monopyridine complex of Ru^{II}(edta) that gives rise to the large oxidation peak near this potential on the second anodic scan. The original first-scan voltammogram can be restored by maintaining the electrode at a potential, e.g., −0.50 V, where the attached complex is present at Ru(II) for 10–15
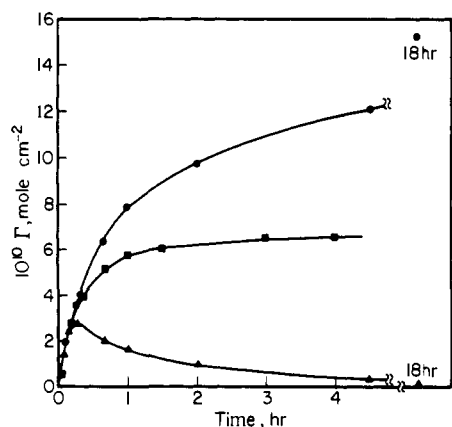
Figure 6. Time dependence of the attachment of $Ru^{III}(edta)$ and Ru^{II}-(edta) to PVP-coated electrodes from 2×10^{-6} M solutions of the complex. Supporting electrolyte: 0.2 M CF_3COONa (pH 3.3). (■), Ru^{III}-(edta); (▲), $Ru^{II}(edta)$ bound to a single pyridine group in the coating; (●), $Ru^{II}(edta)$ bound to two pyridine groups in the coating.
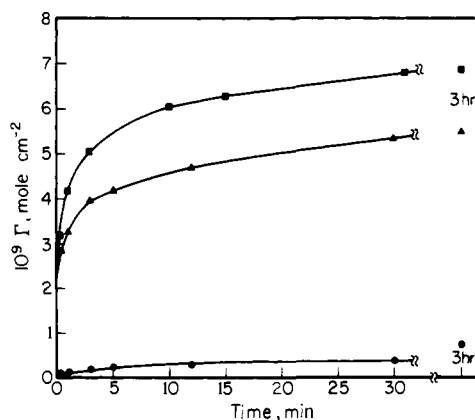

Figure 7. Time dependence of the attachment of $Ru^{III}(edta)$ and Ru^{II}-(edta) to PVP-coated electrodes from 5 mM solutions of the complex. (■), $Ru^{III}(edta)$; (▲), $Ru^{II}(edta)$ bound to a single pyridine group in the coating; (●), $Ru^{II}(edta)$ bound to two pyridine groups in the coating.

min—the time required for the reattachment of a second pyridine molecule to be complete. On the other hand, if the electrode is maintained at +0.50 V for 10 min, a voltammogram resembling those in Figure 2B results, along with some loss of the complex from the surface (vide infra).

The rate of development of the wave at +0.12 V in homogeneous solutions of $Ru^{II}(edta)$ and excess pyridine (Figure 3A) can be used to estimate the rate at which a second pyridine ligand coordinates to the rapidly formed $Ru^{II}(edta)$ py complex. The pseudo-first-order rate constant resulting from measurements with a 4 mM pyridine solution was ca. 1×10^{-4} s^{-1}.

To obtain an estimate of the corresponding rate constant for the addition of a second pyridine to $Ru^{II}(edta)$ on the surface of a PVP-coated electrode, an electrode to which $Ru^{III}(edta)$ had been attached was transferred to a solution of pure supporting electrolyte and maintained at -0.5 V where the attached complex was present as $Ru^{II}(edta)py$. The magnitude of the new wave at +0.18 V was then monitored periodically to evaluate a first-order rate constant of $6 \times 10^{-4} s^{-1}$ for formation of $Ru^{II}(edta)(py)_2$. The difference between the two constants may reflect a high effective concentration of pyridine ligands within the PVP layer on the electrode surface or greater reactivity of the polymerized ligand or both.

Figure 6 summarizes the behavior of the PVP-coated electrodes in binding the Ru(edta) complexes from 2×10^{-6} M solutions. Larger quantities of $Ru^{II}(edta)$ are attached upon long exposure times as would be expected if the relative affinities of Ru(II) and Ru(III) for pyridine governed the attachment equilibria. Note that, at the point where the PVP-coated electrode reaches apparent equilibrium with respect to the attachment of $Ru^{III}(edta)$, only about 20% of the available pyridine ligands can be bound to Ru(III) because almost 2.5 times more $Ru^{II}(edta)$ is attached after 18 h and two pyridines are coordinated to almost every Ru(II) center on the surface at this point.

Attachment from More Concentrated Solutions. If more concentrated solutions of Ru(edta) are employed to bind the complexes to PVP-coated electrodes, revealing differences appear in the time dependence of the attachment (Figure 7). The quantities of the complexes that are bound after extensive soaking are much larger and more nearly equal for both oxidation states than was true when more dilute solutions were used for the attachments. This is the behavior that would be expected if the available pyridine sites were approaching saturation so that the intrinsic difference in the affinity of Ru(II) and Ru(III) for pyridine is not expressed.
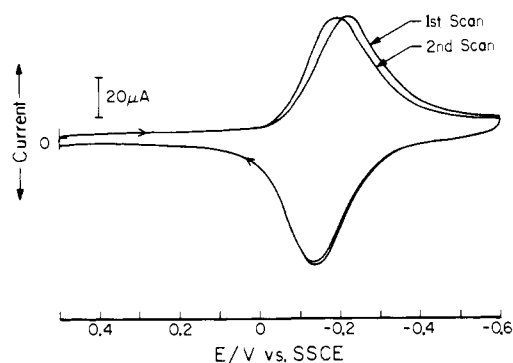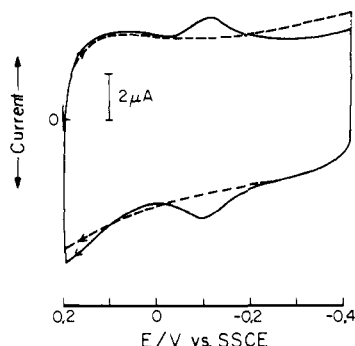

Figure 8. Cyclic voltammogram for a PVP-coated electrode that had been soaked in 5 mM $Ru^{III}(edta)$ for 3 h, washed, and transferred to a supporting electrolyte of 0.2 M CF_3COONa (pH 3.4). Scan rate: 200 mV s^{-1}.

Note also that much less of the bound $Ru^{II}(edta)$ is converted to the bispyridine complex than was the case when the coated electrode was exposed to a more dilute solution of $Ru^{II}(edta)$ (Figure 6). With the larger concentration of complex the more rapid formation of the monopyridine complex probably consumes most of the available pyridine groups within the polymer coating before the competitive but slower reaction to produce the bispyridine complex can proceed. The total quantity of $Ru^{II}(edta)$ that is bound to a PVP-coated electrode is the same from both 5 and 20 mM solutions of the complex. After 24 h of soaking, the coverage reaches ca. 10^{-8} mol cm^{-2}. If this value is regarded as a measure of the total number of pyridine groups present on the coated electrode, it corresponds to ca. 1.4×10^{-12} mol/cm^2 of PVP (mol wt 7.4 $\times 10^5$) in the coating on the electode surface.

The Ru(edta) bound to electrodes coated with PVP remains on the surface for extended periods. Washed and dried electrodes that have been stored for several weeks retain their electroactive coatings. If the electrodes are placed in electrolyte solutions containing no Ru(edta), the complex is slowly removed from the coating at a rate determined by the rate of rupture of the ruthenium-pyridine bond.[20] This rate is greater for the Ru(III) than for the Ru(II) complex as is true for related homogeneous complexes.[15]

Voltammograms recorded with electrodes having coatings that are nearly saturated with $Ru^{III}(edta)$ retain their symmetrical shapes (Figure 8) but the cathodic peak potential is shifted about 50 mV in the negative direction and there is a small but reproducible difference in the response obtained from the first and all subsequent cathodic scans. Both of these fea-

Figure 9. Steady-state cyclic voltammogram for a PVP-coated electrode 2 h after immersion in a 5×10^{-8} M solution of Ru^{II}(edta). Supporting electrolyte: 0.2 M CF_3COONa (pH 3.4). Scan rate: 200 mV s^{-1}. The dashed curve is the background current obtained in the absence of Ru^{II}-(edta).

Figure 10. Effect on ionic strength on the steady-state cyclic voltammograms for Ru^{III}(edta) attached to a PVP-coated electrode by soaking in a 5 mM solution for 15 min. Supporting electrolyte: I, 0.2 M CF_3COONa; II, 0.002 M CF_3COONa. Scan rate: 200 mV s^{-1}.

tures may reflect the presence of stronger Coulombic interactions among the attached complexes as the coverages approach saturation.

Attachment from Highly Dilute Solutions. PVP-coated electrodes extract Ru(edta) from very dilute solutions. Figure 9 shows the voltammogram obtained after a coated electrode was soaked for 2 h in a 5×10^{-8} M solution of Ru^{II}(edta). The area under the clearly discernible wave for the monopyridine complex corresponds to ca. 6×10^{-11} mol cm^{-2} of extracted complex. With such small quantities present on the surface the wave near +0.2 V due to the oxidation and reduction of the graphite surface (Figure 1) interferes with the wave for the bispyridine form of attached Ru^{II}(edta) so that steady-state voltammograms were recorded to convert the attached complex to its monopyridine form (cf. Figure 5 and associated text). Using the previously obtained estimate of 10^{-8} mol/cm^2 as the total quantity of pyridine in the PVP coating the 6×10^{-11} mol/cm^2 of complex extracted from a 5×10^{-8} M solution represents a ratio of free to coordinated pyridine groups in the coating of 6×10^3. This implies an equilibrium constant of ca. 10^5 M^{-1} for the heterogeneous reaction

$$PVP_{(s)} + Ru^{II}(edta) \rightleftharpoons PVPRu^{II}(edta)_{(s)} \qquad (1)$$
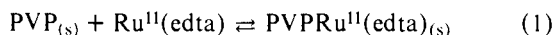
where the subscript (s) represents species attached to the electrode surface. The equilibrium constant for the corresponding homogeneous reaction has not been measured for pyridine as the ligand but with isonicotinamide a value of 7×10^6 M^{-1} has been reported.[15] Thus, the affinity of the pyridine groups in the PVP coating for Ru^{II}(edta) probably does not differ greatly from the affinity of monomeric pyridine in homogeneous solutions. However, the observation that electrodes coated with a polymeric ligand can extract easily measurable quantities of a metal complex from highly dilute solutions suggests an analytically useful potential that merits further exploration.

Influence of Supporting Electrolyte Concentration. When 10^{-8} mol cm^{-2} of Ru^{III}(edta), an uncharged species at pH values below ca. 2,[21] is reduced to Ru^{II}(edta) almost 10^3 μC cm^{-2} of immobile anionic charge is generated within the polymer coating. The creation of such large charge densities would be expected to be sensitive to changes in the nature and concentration of the supporting electrolyte that supplies the counterions needed to balance the electrogenerated charge in the polymer layer. Figure 10 compares the voltammograms obtained with the same coated electrode in 0.2 and 0.002 M supporting electrolyte solutions. Decreasing the concentration of supporting electrolyte produces a large increase in the difference between cathodic and anodic peak potentials and appears to diminish the area under the voltammogram. A portion of the increased separation between peak potentials arises from
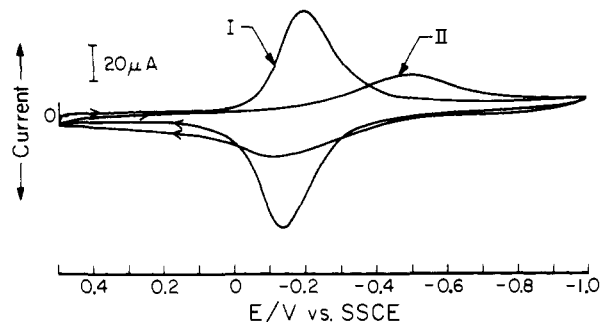
ohmic drops in the more dilute electrolyte but this contribution was determined from the peak separation obtained in voltammograms recorded with an uncoated electrode in a 0.8 mM solution of Ru^{III}(edta) which yielded the same peak current as resulted with the attached complex. The observed peak separation was 360 mV so that only ca. 300 mV (360 less the 60 mV separation always present in cyclic voltammograms for diffusing reactants) of the 420-mV separation obtained in Figure 10 is attributed to ohmic factors. The remaining separation between the peaks must reflect the additional potential drop generated within the polymer layer by the high density of anchored anionic charge. The apparent decrease in the area of the voltammogram at low ionic strength was shown to result primarily from a broadening of the range of potentials where the faradaic charge is consumed. Electronic integration of the voltammograms between potentials well in advance and well beyond the peak current produced surface concentrations measured at low ionic strength that were within 10-15% of the values measured at higher ionic strengths and independent of scan rate between 50 and 500 mV s^{-1}.

Effects on the shapes of voltammograms for attached reactants resulting from changes in the size of the supporting electrolyte ions have been reported previously for electrodes coated with multiple layers of a silyl ferrocene.[22] Steric factors were invoked in that case to account for the observations. The present case makes it clear that changes in the ionic strength of supporting electrolytes composed of small, sterically unhindered ions can have equally profound effects on voltammograms for reactants anchored to electrode surfaces. The general subject of "double layer effects" on charge-transfer kinetics with attached reactants clearly stands in need of a more thorough elaboration if kinetic studies with such systems[23] are to be pursued.

Simultaneous Attachment of Two Transition-Metal Complexes to Polymer-Coated Electrodes. The pentaammine complex of Ru(II) is also readily bound to PVP-coated electrodes by soaking them in a solution of $Ru(NH_3)_5OH_2^{2+}$.[5] Figure 11A shows a typical voltammogram for the attached pentaammine complex. If the same electrode is subsequently exposed to a solution of Ru^{III}(edta), this complex is also bound as shown by the double-peaked voltammogram in Figure 11B. The larger quantities of the Ru^{III}(edta) complex that are bound despite the lower concentration and smaller soaking time employed must reflect a difference in the kinetics of the two coordination reactions because the affinity of $Ru^{II}(NH_3)_5OH_2$ for pyridine ($K = 2.4 \times 10^{7}$ [19]) is almost certainly greater than that of Ru^{III}(edta) ($K = 7 \times 10^6$ for isonicotinamide[15]).

Figure 12A shows the voltammogram that results when Cu(II) is attached to a PVP-coated electrode by soaking in a solution of $CuCl_2$. The current response can be identified with a Cu(II)-Cu(I) pyridine complex on the basis of comparison with the homogeneous electrochemistry of Cu(II)-pyridine
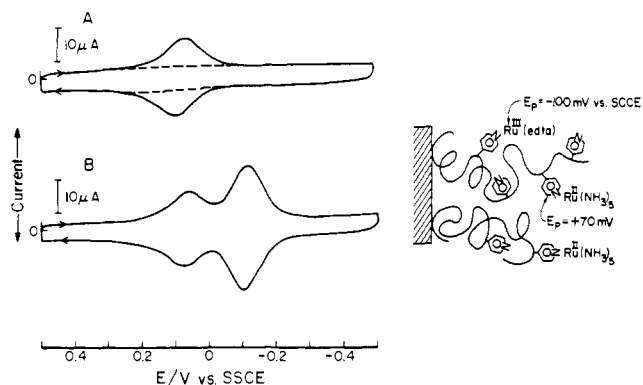
Figure 11. (A) Steady-state cyclic voltammogram for a PVP-coated electrode that was soaked for 15 min in 10 mM $Ru(NH_3)_5OH_2^{2+}$, washed, and transferred to a supporting electrolyte of 0.2 M CF_3COONa (pH 4.2). Scan rate: 200 mV s^{-1}. The dashed line is the curve obtained before soaking. (B) Voltammogram resulting when the electrode from A was soaked for 2.5 min in 0.1 mM Ru^{III}(edta), washed, and transferred to the same supporting electrolyte. Scan rate: 200 mV s^{-1}.

Figure 12. (A) Steady-state cyclic voltammogram for a PVP-coated electrode that was soaked for 15 min in 50 mM $CuCl_2$, washed, and transferred to a supporting electrolyte of 0.2 M CF_3COONa (pH 4.2). Scan rate: 200 mV s^{-1}. (B) Voltammogram resulting when the electrode from A was soaked for 2.5 min in 0.1 mM Ru^{III}(edta), washed, and transferred to the same supporting electrolyte. Scan rate: 200 mV s^{-1}.

solutions.[24] ($Cu(II)$ is also bound by PAN-coated electrodes, although it is held much less strongly.) The waves are broader and the peak potentials more separated than those for the complexes of ruthenium, which may reflect less facile electron-transfer rates. The bound $Cu(II)$ is removed from the electrode surface more rapidly than are the ruthenium complexes. For example, 75% is lost if the electrode is soaked for 45 min in pure supporting electrolyte.

When the electrode used to record Figure 12A was exposed to a solution of Ru^{III}(edta) the voltammogram shown in Figure 12B resulted. Clearly, a surface containing both attached $Cu(II)$ and Ru^{III}(edta) has been produced. The possibilities for extending this procedure to create surfaces bearing even greater varieties of attached complexes are apparent. The exploitation of such surfaces in catalytic cycles depending upon two or more metal catalysts as well as in studies of intermolecular charge-transfer rates between attached complexes seems well worth pursuing.

Electrode Surfaces Coated with Two Polymeric Ligands. In a previous report[5] the successful attachment of $Ru^{II}(NH_3)_5$ to an electrode surface coated with polyacrylonitrile (PAN) was described. The voltammogram for the attached complex appears at +0.30 V, well removed from the wave for the same complex bound to a PVP coating. We therefore examined the possibility of preparing surfaces containing both PVP and PAN coatings to which $Ru^{II}(NH_3)_5$ could be bound at two different ligand sites. Figure 13 shows the result. The double waves appear at the potentials expected for pyridine- and nitrile-bound complexes. The surface nitrile-ruthenium bond is much shorter lived than the corresponding pyridine bond, which made it difficult to explore the competition between the two polymeric ligands for the attached complex within the surface layer. However, this topic would be well worth developing in future studies to provide a basis for comparing the relative binding capacity and kinetics of mixed polymer coatings.

Conclusions

The purpose of this study was to explore the range of surface coordination chemistry that may be exploited to attach metal complexes to electrode surfaces prepared by coating with appropriate polymeric ligands. The results have been very encouraging. Extremely durable coatings of PVP are easily introduced onto the surfaces of pyrolytic graphite electrodes where they can serve as potent binding sites for a variety of metal complexes. Such large quantities of electroactive species can be attached to electrode surfaces by means of polymeric anchors that the problems of sensitivity inherent in studies of
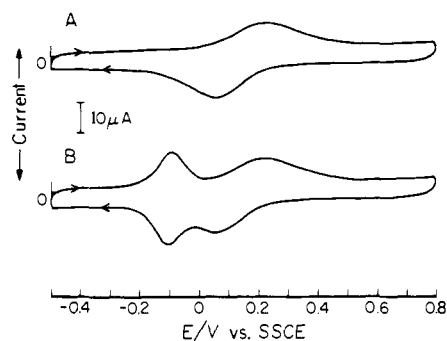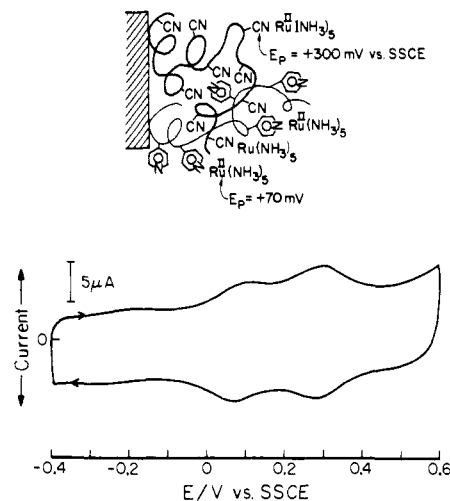
Figure 13. Steady-state cyclic voltammogram for a PAN-coated electrode that was soaked for 15 min in 10 mM $Ru(NH_3)_5OH_2^{2+}$, washed, soaked for 5 min in 0.5% PVP in methanol, washed with methanol, soaked again for 15 min in 10 mM $Ru(NH_3)_5OH_2^{2+}$, washed, and transferred to a supporting electrolyte of 0.2 M CF_3COONa (pH 4.2). Scan rate: 200 mV s^{-1}.

monolayers or less of attached reactants are essentially eliminated. Nevertheless, it is certainly too soon to abandon studies of monolayer quantities of attached reactants. The greater electrochemical responses obtained with multilayers of attached reactants is paid for by lesser knowledge of the chemical environment and structure of the attached molecules. It seems quite likely that interpreting the behavior of multilayers of attached reactants will require considerable additional information on the behavior of monolayers.

It has been argued that the larger quantities of attached catalysts realizable via polymeric coatings offer the most promise in attempts to employ attached reactants electrocatalytically.[25] This conclusion is very dependent on the model that was used in comparing catalysts distributed as monolayers, polylayers or homogeneously in the solution. Experimental tests are certainly called for in order to verify this prediction.

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M₃L₉(ligand) Complexes

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Abstract: The frontier orbitals of an $M_3(CO)_9$ unit are constructed from three $M(CO)_3$ pieces or by removing three ligands from a D_{3h} $M_3(CO)_{12}$. They consist of a relatively low-lying Walsh-like set $1a_1 + 1e$ and a higher cyclopropenium-like $2a_1 + 2e$. The latter are empty for a d^8 M. These orbitals are used to analyze the electronic and geometrical structure of M_3L_9(ligand) complexes where the ligand is CO, S, $(CO)_2$, S_2, CR, CCH_2^+, ethylene, acetylene, or acyclic and cyclic polyenes. In the case of $(CO)_3Co_3CCH_2^+$ the symmetrically topped structure is not a local energy minimum, but instead there are three equivalent unsymmetrical structures of a complexed ethylidene type.

The rich and beautiful chemistry of metal clusters is unfolding only now.[1,2] Perhaps its most highly developed aspect is the reactivity of trinuclear compounds. Both structural data and reactivity studies cover a wide range of such complexes including systems with both bridging and terminal carbonyls or hydrides or highly complicated molecules where the ligand no longer can be separated from the cluster unit.

Following earlier work on binuclear complexes,[3] we are interested in building a detailed understanding of the electronic determinants of structure and reactivity in these molecules. In this study we concentrate on complexes of the symmetric M_3L_9 unit. The ligands which bond to this fragment, commonly organic systems, can be divided into several groups. An example of a ligand bonded through a single atom is shown in **1**.[4] Unsaturated π-bonded ligands are found, such as the iron acetylene compound **2**,[5] or cyclic systems of the type **3**.[6]

1　　　**2**　　　**3**
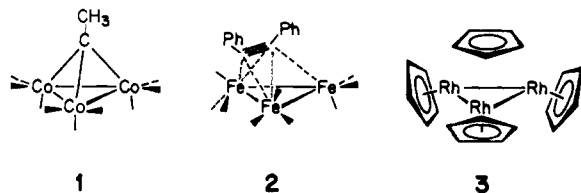
The basic unit is $M_3(CO)_9$ or variations thereof, such as M_3Cp_3. We will construct the frontier orbitals of this fragment and then interact it with a range of organic and inorganic caps. Symmetry based arguments will be supported by extended Hückel calculations for M = Fe, with details given in the Appendix.

Orbitals of the Fe₃(CO)₉ Fragment

The orbitals of a C_{3v} $M_3(CO)_9$ fragment may be constructed by interacting three $M(CO)_3$ groups or by stripping three carbonyls from a D_{3h} $M_3(CO)_{12}$. The former procedure gives more detail, while the latter provides a pedagogically simple entry into the problem. We will proceed with both approaches, starting with $M_3(CO)_{12}$ first.

It is well-known that only $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have a D_{3h} structure,[7] while $Fe_3(CO)_{12}$ has two bridging carbonyls in a C_{2v} geometry.[8] Also these molecules are fluxional in character.[9] Nevertheless, for the sake of simplicity we aim for the orbitals of the C_{3v} $M_3(CO)_9$ and so begin with a D_{3h} $M_3(CO)_{12}$.

4

A D_{3h} $M_3(CO)_{12}$ is a "saturated" electron precise molecule, the inorganic analogue of a cyclopropane. It may be assembled from three octahedral fragment $M(CO)_4$ units. The orbitals of such a fragment[10] are shown below. Above the remnants of the octahedral t_{2g} set there are two hybrids pointing toward the missing octahedral sites, a_1 and b_2. These are analogous to the σ and p orbitals, respectively, of a methylene.[11] The $Fe(CO)_4$ and CH_2 fragments are isolobal,[12] each with two electrons in these upper frontier orbitals. Thus the formation of a symmetric trimer $Fe_3(CO)_{12}$, Figure 1, is analogous to the formation of cyclopropane from three methylenes.[13] While the three t_{2g} levels interact little, to generate a low-lying cluster of nine orbitals, all filled, the upper $b_2 + a_1$ set interacts greatly to generate a Walsh-like set[13] of orbitals—$1e'$ and $1a_2'$ from b_2, $1a_1'$ and $2e'$ from a_1. This picture has been constructed earlier.[14] The main difference from cyclopropane is that in the latter the e' set derived from the peripheral orbitals is at higher