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Multiple Intramolecular Electron Transfer in the Catalysis of the Reduction of Dioxygen by Cobalt *meso*-Tetrakis(4-pyridyl)porphyrin to Which Four $Ru(NH_3)_5$ Groups Are Coordinated

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Abstract: The reaction of $Ru(NH_3)_5OH_2^{2+}$ with $CoP(py)_4$ (cobalt *meso*-tetrakis(4-pyridyl)porphyrin) within Nafion coatings on graphite electrodes produces $[CoP(pyRu(NH_3)_5)_4]^{8+}$. This complex, immobilized within the polyelectrolyte coating, achieves electronic contact with the electrode underlying the coating by means of electron hopping between adjacent pairs of $Ru(NH_3)_5^{3+/2+}$ groups coordinated to the pyridine sites. The four $Ru(NH_3)_5py^{3+/2+}$ groups in each molecule do not interact strongly and have essentially the same formal potential. The $CoP(pyRu(NH_3)_5)_4^{8+}$ complex acts as a catalyst for the four-electron reduction of O_2 under conditions where mixtures of the same porphyrin with uncoordinated $Ru(NH_3)_6^{2+}$ or $Ru(NH_3)_5py^{2+}$ do not. The results provide evidence for the intramolecular delivery of four electrons from the four-coordinated $Ru(NH_3)_5^{2+}$ groups to O_2 molecules associated with the Co(II) center of the porphyrin.

The direct, four-electron reduction of O_2 to H_2O is difficult to achieve at electrodes at potentials near the thermodynamically allowed values, and metalloporphyrins are frequently employed as catalysts to enhance the rate of the electroreduction of O_2.[1-26] Cobalt porphyrins, which catalyze the reduction at the most positive potentials, typically do not carry the reduction beyond the two-electron step to H_2O_2,[9-21] and iron porphyrins, which serve as catalysts for the reduction of O_2 to H_2O_2 and of H_2O_2 to H_2O,[9-21] operate only at much more negative potentials. The direct, four-electron electroreduction of O_2 at unusually positive potentials has been achieved by a few electrocatalysts including a dimeric, cofacial cobalt porphyrin,[23,24] some related derivatives,[25,26] and a dimeric iridium porphyrin.[27]

A strategy to achieve rapid, multiple-electron transfers (while avoiding undesired intermediates) that has been tested with a variety of substrates involves the synthesis of catalysts containing multiple centers which can serve as electron donors or acceptors. For example, Bruice and co-workers have prepared tetraferrocenyl derivatives of tetraphenylporphyrins and examined their catalytic properties,[28] and Meyer and co-workers have sought to achieve multiple-electron reductions of NO_2^- and NO by means of intramolecular electron transfer from the reducible methylpyridinium groups in iron *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin.[29] In very recent studies, Araki and Toma[30] reacted iron or cobalt *meso*-tetrakis(4-pyridyl)porphyrin ($CoP(py)_4$) with $Ru^{III}(edta)OH_2^-$ (py = pyridine; edta = ethylenediaminetetraacetate) to obtain the tetrametalated derivatives whose activities as catalysts for the reduction of O_2 were shown to be enhanced by the appended Ru(edta) centers.[30] The substitutional lability of the ligand, L, occupying the sixth coordination position in $Ru^{III}(edta)L$ complexes[31] required the presence of excess $Ru^{III}(edta)OH_2^-$ in the studies of Araki and Toma, which complicated the responses they obtained in electrochemical experiments.[30] To avoid this difficulty, we have been attempting to coordinate substitutionally inert $Ru^{III}(NH_3)_5$ centers to $CoP(py)_4$. However, our efforts were thwarted by the deposition of dark precipitates from aqueous solutions containing $CoP(py)_4$ and various $Ru(NH_3)_5L^{n+}$ complexes. Araki and Toma experienced similar difficulties.[32] Since the reactants in the desired coordination

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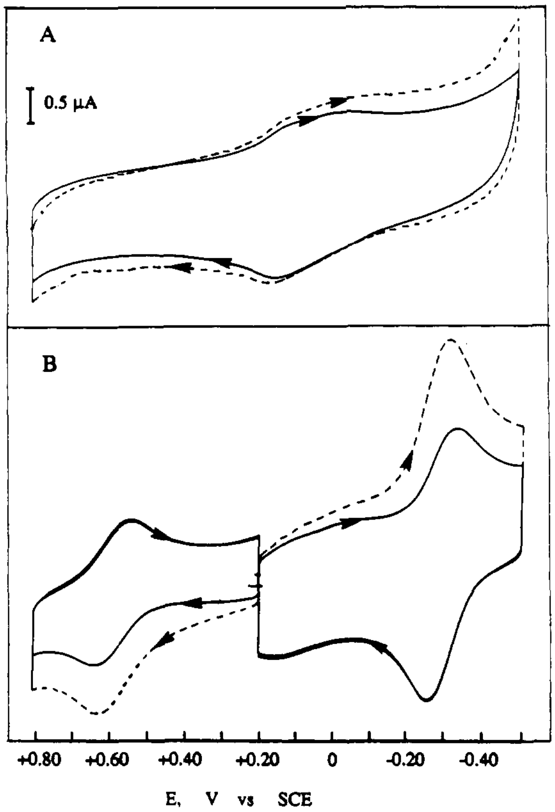

Figure 1. A: Cyclic voltammograms recorded with an edge plane pyrolytic graphite electrode coated with Nafion. The coating contained 1.1 × 10^{-7} mol cm^{-2} of sulfonate groups. The solid line was obtained with the Nafion coating alone; the dashed line resulted after incorporation of 2.2 × 10^{-10} mol cm^{-2} of $CoP(py)_4$ in the coating. Supporting electrolyte; 0.1 M acetate buffer (pH 4.5) saturated with argon; scan rate, 10 mV s^{-1}. B: Voltammograms recorded with the coating from A after 3.9 × 10^{-10} mol cm^{-2} of $Os(bpy)_3^{2+}$ and 1.0 × 10^{-9} mol cm^{-2} of $Ru(NH_3)_6^{3+}$ were incorporated. Supporting electrolyte as in A. Scan rate, 10 mV s^{-1}. The initial and final potentials were 0.2 V for every scan. The dashed curves were obtained during the first scan after the cobalt center in the incorporated $CoP(py)_4$ had been oxidized or reduced (see text).

process were all cationic, we subsequently attempted to carry out the reaction with the reactants confined to coatings of Nafion applied to graphite electrode surfaces. The polyelectrolyte Nafion[33] is known to yield very stable coatings in which charged cations can be incorporated and retained,[34,35] and we reasoned that the immobilization of the reactants within the Nafion might prevent the formation of the insoluble precipitates which result when they are mixed in homogeneous solution. This strategy proved successful, and the electrochemical behavior of the $[CoP(pyRu(NH_3)_5)_4]^{8+}$ complex formed within the Nafion coatings was characterized. Evidence that this tetrametalated complex acts as a catalyst for the intramolecular, four-electron reduction of O_2 is presented in this report.

Experimental Section

Materials. Cobalt *meso*-tetrakis(4-pyridyl)porphyrin was prepared by reaction of the metal-free ligand (Strem Chemicals) with cobalt acetate according to a published procedure.[36] The reaction product was purified by chromatography on neutral alumina (Fisher) using chloroform as the solvent and methanol-chloroform (5–95%) as the eluent. $[Ru(NH_3)_5Cl]Cl_2$ was prepared from $[Ru(NH_3)_6]Cl_3$ (Matthey-Bishop).[37] All other chemicals were high-purity materials and were used as received. Solutions were prepared from laboratory distilled water, which was further purified by passage through a purification train (Sybron-Barnsted Nanopure). Nafion (equivalent weight = 1100) was obtained as a 5 wt % solution (Aldrich), which was diluted 10-fold with 2-propanol to prepare the stock solution used to prepare electrode coatings. Pyrolytic graphite with the edge planes exposed was obtained in the form of cylindrical rods 6.35 mm in diameter (Union Carbide Co.). Short segments of the rods were mounted on stainless steel shafts with heat-shrinkable tubing to obtain rotating disk electrodes. The mounted electrodes were polished on a polishing wheel with 0.5-μm alumina followed by sonication in pure water.

Apparatus and Procedures. Conventional electrochemical cells and instrumentation were employed. Chronocoulometric experiments were carried out with a computer-controlled instrument similar to one described previously.[38] Rotating disk and ring–disk voltammetry was performed with an ASR2 rotator and RDE3 potentiostat (Pine Instrument Co.) and a Kipp and Zonen X-Y-Y' recorder. The rotating platinum ring–graphite disk electrode (Pine Instrument Co.) had a relatively wide gap to facilitate the application of Nafion to the disk without coating the ring and a thick ring electrode to provide good collection efficiency despite the wide gap. The collection efficiency of the electrode measured in a solution of $Fe(CN)_6^{3-}$ was 0.39. Potentials were measured with respect to a standard saturated calomel electrode (SCE).

Electrodes were coated with Nafion by transferring 10 μL of the 0.5% stock solution to the surface (0.32 cm^2) of the freshly polished electrodes and allowing the solvent to evaporate at room temperature. That the coverage of the electrode surfaces with Nafion was essentially complete was demonstrated by the absence of significant reduction current during the recording of current–potential curves in solutions containing 1 mM $Fe(CN)_6^{3-}$. A coating thickness of ca. 0.85 μm was calculated from the reported density of 1.35[39] for swollen Nafion films.

Results and Discussion

Incorporation of $CoP(py)_4$ in Nafion Coatings. Although the $CoP(py)_4$ molecule becomes a tetrapositive cation ($CoP(pyH)_4^{4+}$) when it is dissolved in aqueous acid, it is not incorporated rapidly by Nafion coatings. Under conditions where less highly charged cations such as $Ru(NH_3)_6^{3+}$ or $Os(bpy)_3^{2+}$ are rapidly and extensively incorporated by Nafion coatings, $CoP(pyH)_4^{4+}$ cations undergo cation exchange only slowly with the proton counterions in Nafion. This difference in behavior may be the result of the very strong binding of the hydrophobic, cationic metalloporphyrin with the Nafion. The narrow ionic channels present in Nafion coatings[40] are the primary sites of the ion-exchange reactions responsible for the incorporation of new counterions. If the incoming cations are large, like $CoP(pyH)_4^{4+}$, and are bound very tightly near the entrances to these channels, the initially exchanged counterions could block the channels and decrease the rate of entry of additional counterions. The relatively slow rate of ion exchange exhibited by the $CoP(pyH)_4^{4+}$ cations required that the Nafion coatings be soaked for several hours in 0.5 mM solutions of the porphyrin in 0.1 M H_2SO_4 in order to obtain moderate loadings of the coatings. The rate of incorporation was not increased significantly by increasing the concentration of $CoP(pyH)_4^{4+}$ as might be expected if the rate of diffusion of the cations within the Nafion coatings limited their rate of incorporation.

In aqueous acid, cyclic voltammograms of $CoP(pyH)_4^{4+}$ exhibit a single, reversible couple corresponding to the oxidation and reduction of the cobalt center.[41a] However, no corresponding

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Table I. Coulometric Assays of Quantities of $CoP(pyH)_4^{4+}$ Incorporated in Nafion Coatings[a]

electrode no.	$10^{10}\Gamma_{Co}$,[b] mol cm^{-2}	$10^{10}\Gamma_{Co}$,[c] mol cm^{-2}
1	4.7	4.3
2	2.2	2.2
3	2.3	2.2

[a] See Figure 1B and associated text. Each coating contained 1.1 × 10^{-7} mol cm^{-2} of sulfonate groups. [b] Measured from the difference in the areas under the cathodic peaks during the first and subsequent scans of the $Ru(NH_3)_6^{3+/2+}$ couple. [c] Measured from difference in the areas under the anodic peaks during the first and subsequent scans of the $Os(bpy)_3^{3+/2+}$ couple.

response is obtained from Nafion coatings containing $CoP(pyH)_4^{4+}$ counterions. In Figure 1A, cyclic voltammograms recorded with a Nafion-coated electrode are shown before and after the incorporation of $CoP(pyH)_4^{4+}$. The lack of a voltammetric response from the incorporated reactant can be attributed to its very small diffusion coefficient with Nafion. (The small, broad peak in Figure 1A originates in the graphite surface itself.) Similar behavior has been reported in earlier studies where cobalt tetraphenylporphyrin (42) or cobalt-*meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin (43) was incorporated in Nafion.

To provide electronic coupling between the incorporated $CoP(pyH)_4^{4+}$ counterions and the graphite electrode surface it was necessary to add to the coatings suitable redox mediators with much larger diffusion coefficients. Figure 1B shows the cyclic voltammetric response obtained from a Nafion coating which contained $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and $Ru(NH_3)_6^{3+}$ as well as $CoP(pyH)_4^{4+}$. The pair of current peaks near −0.25 V arises from the $Ru(NH_3)_6^{3+/2+}$ couple and the pair near 0.6 V from the $Os(bpy)_3^{3+/2+}$ couple. This pair of mediators was chosen because they both have reasonable diffusional rates in Nafion and their formal potentials lie on either side of the formal potential of the $CoP(pyH)_4^{5+/4+}$ couple (−0.1 V[41b]), so that the cobalt center of the porphyrin could be repetitively oxidized and reduced by the mediator counterions which were oxidized and reduced by the electrode (Scheme I).

Scheme I

Mediated Oxidation

$$Os(bpy)_3^{2+} - e \rightleftharpoons Os(bpy)_3^{3+}$$

$$Os(bpy)_3^{3+} + CoP(pyH)_4^{4+} \rightarrow Os(bpy)_3^{2+} + CoP(pyH)_4^{5+}$$

Mediated Reduction

$$Ru(NH_3)_6^{3+} + e \rightleftharpoons Ru(NH_3)_6^{2+}$$

$$Ru(NH_3)_6^{2+} + CoP(pyH)_4^{5+} \rightarrow CoP(pyH)_4^{4+} + Ru(NH_3)_6^{3+}$$

The two mediator couples were incorporated by ion exchange into Nafion coatings containing $CoP(pyH)_4^{4+}$. The incorporation of the mediators was slower in Nafion coatings which contained the cobalt porphyrin than in pure Nafion. The quantity of each complex incorporated was controlled by adjusting its concentration in the solution employed for the ion exchange. The mediators in Figure 1B were incorporated from a solution containing 0.05 mM $Os(bpy)_3^{2+}$ and 0.1 mM $Ru(NH_3)_6^{3+}$.

The dashed curves with the larger peak currents in Figure 1B were obtained during the first voltammetric scan from 0.2 V, with the cobalt center of the incorporated porphyrin in its oxidized state (enhanced cathodic peak for reduction of $Ru(NH_3)_6^{3+}$) or its reduced state (enhanced anodic peak for oxidation of $Os(bpy)_3^{2+}$). The solid curves show the steady responses obtained in the absence of incorporated porphyrin or when the voltammetric scans were restricted to the range between 0.2 and −0.5 V or between 0.2 and 0.8 V so that the cobalt center remained in its reduced or oxidized state, respectively. The areas between the dashed and solid curves in Figure 1B were used to measure the quantity of $CoP(pyH)_4^{4+}$ incorporated in Nafion coatings. The areas became independent of scan rate below 50 mV s^{-1}, and the values obtained from the reductive and oxidative voltammograms were equal. Table I summarizes a set of coulometric assays of the quantity of $CoP(pyH)_4^{4+}$ incorporated in a Nafion coating.

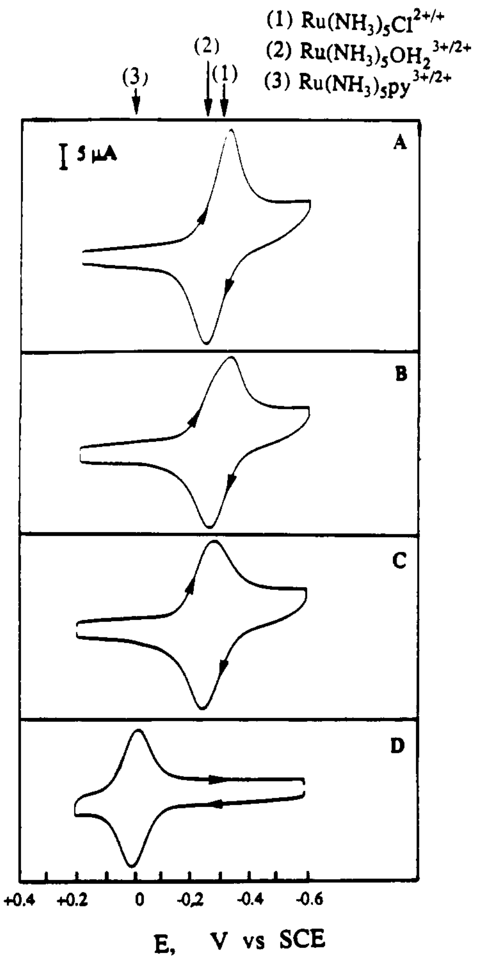

Figure 2. Conversion of $Ru(NH_3)_5Cl^{2+/+}$ to $Ru(NH_3)_5OH_2^{3+/2+}$ within a Nafion coating as monitored by cyclic voltammetry. A: First voltammogram recorded after incorporation of $Ru(NH_3)_5Cl^{2+}$. B: Voltammogram obtained after several cycles. C: Voltammogram obtained after the electrode potential was maintained at −0.6 V for several minutes. D: Voltammogram obtained when the electrode from C was transferred to a supporting electrolyte containing 0.12 M pyridine. Supporting electrolyte; 0.1 M Na_2SO_4; scan rate, 50 mV s^{-1}. The numbered arrows at the top mark the formal potentials of the indicated couples.

Coordination of $Ru(NH_3)_5$ Centers to $CoP(py)_4$ in Nafion Coatings. A primary objective of this study was to attempt to coordinate $Ru(NH_3)_5^{3+/2+}$ groups to the four pyridine sites present in the $CoP(py)_4$ molecule. To do so, the $Ru(NH_3)_5OH_2^{2+}$ complex, with a moderately labile aqua ligand, was introduced into Nafion coatings by incorporating $Ru(NH_3)_5Cl^{2+}$ as a precursor complex. Electrochemical reduction of this complex to $Ru(NH_3)_5Cl^{+}$ causes it to aquate at a modest rate, and the conversion to $Ru(NH_3)_5OH_2^{2+}$ was monitored electrochemically.[44]

The first cyclic voltammogram recorded after $Ru(NH_3)_5Cl^{2+}$ is incorporated in a Nafion coating exhibits the single wave corresponding to the reversible interconversion of the $Ru(NH_3)_5Cl^{2+/+}$ complexes (Figure 2A). However, with repetitive scanning, some of the $Ru(NH_3)_5Cl^{+}$ generated in the coating spontaneously aquates to yield $Ru(NH_3)_5OH_2^{2+}$. The formal potential of the $Ru(NH_3)_5OH_2^{3+/2+}$ couple is slightly positive of that for the chloro complexes, and the cyclic voltammogram is distorted slightly by the presence of the second couple (Figure 2B). The incorporated chloro complex can be completely con-

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verted to the aqua complex by maintaining the electrode potential for several minutes at a value (−0.6 V) where the complex is reduced to the Ru(II) oxidation state. Following such a treatment, the voltammetry again consists of a single wave at the potential corresponding to the $Ru(NH_3)_5OH_2^{3+/2+}$ couple (Figure 2C).

The conversion of the incorporated aqua complex into the pyridine complex was also examined to provide a basis for comparison with the target reaction involving the tetrapyridylporphyrin. Transfer of the coating containing the aqua complex to a solution containing pyridine produced the voltammogram in Figure 2D. The large positive shift in formal potential provides a clear indication of the substitution of pyridine for the labile aqua ligand in the incorporated complex.[45] This response is not altered if the coating is transferred back to a supporting electrolyte free of pyridine because the rate of aquation of the pyridine complex is much lower than that of the chloro complex.[46]

With the cyclic voltammograms in Figure 2 as guides, the voltammetric responses obtained in Nafion coatings in which both $CoP(pyH)_4^{4+}$ and $Ru(NH_3)_5Cl^{2+}$ are incorporated can be understood. The presence of $CoP(pyH)_4^{4+}$ in Nafion coatings impeded the entry of other cations such as $Ru(NH_3)_5Cl^{2+}$. Even when the pH of the bathing solution was raised to 7.5 to convert the incorporated porphyrin into its uncharged form, $CoP(py)_4$, the incorporation of $Ru(NH_3)_5Cl^{2+}$ by the Nafion coating remained slow. (The uncharged form of the porphyrin was not lost from the Nafion probably because of its strong hydrophobic interaction with the fluorocarbon portions of the coating.) To obtain the desired quantities of the $Ru(NH_3)_5Cl^{2+}$ complex in the coatings, they were soaked for 20–30 min in solutions containing 1.4 mM $Ru(NH_3)_5Cl^{2+}$. To prevent the slow loss of this complex when the loaded coatings were transferred to supporting electrolyte solutions free of the complex, ca. 5×10^{-6} mol L^{-1} of the complex was added to the solution. This tactic avoided the loss of $Ru(NH_3)_5Cl^{2+}$ from the coating without producing a significant voltammetric response from the complex in solution.

After both reactants were incorporated in the Nafion coating, the reaction between them was monitored by cyclic voltammetry. The quantities of $Ru(NH_3)_5Cl^{2+}$ incorporated were typically greater than four times the amount of $CoP(py)_4$ present in order to drive the ligand-exchange reaction to completion.

The series of cyclic voltammograms in Figure 3A shows the conversion of $Ru(NH_3)_5Cl^{2+/+}$ to $Ru(NH_3)_5OH_2^{3+/2+}$ (as in Figure 2B), followed by the gradual appearance of a reversible couple near 0.1 V corresponding to the substitution of the aqua ligand by pyridine (as in Figure 2D). Each successive voltammogram was recorded after the coated electrode had been held at −0.6 V for increasing times. The peaks near −0.25 V, corresponding to the overlapping $Ru(NH_3)_5Cl^{2+/+}$ and $Ru(NH_3)_5OH_2^{3+/2+}$ couples, were gradually replaced by the single set of peaks near 0.1 V, corresponding to the $Ru(NH_3)_5py^{3+/2+}$ couple.

The peak near 0.1 V increased to a maximum value within ca. 2 h, after which there were no further changes. Transfer of the electrode to pure 0.25 M Na_2SO_4 at this point left the prominent peak near 0.1 V unchanged as the small excess of $Ru(NH_3)_5OH_2^{2+}$ present in the coating was gradually lost by reverse ion exchange. The final voltammetric response obtained, shown in Figure 3B, was very stable. Coatings prepared in the way just described continued to exhibit responses such as that in Figure 3B after storage for several months.

The reaction between $CoP(py)_4$ and $Ru(NH_3)_5OH_2^{2+}$ inside Nafion coatings is strongly affected by changes in the pH of the solution in which the coating is immersed. In acidic solutions, e.g., 0.5 M CF_3COOH, the pyridine groups in the $CoP(py)_4$ complex are protonated, and the reaction of the complex with $Ru(NH_3)_5OH_2^{2+}$ is prevented. The cyclic voltammograms in Figure 3C were obtained when the experiments that produced the results in Figure 3A were repeated in 0.5 M CF_3COOH as the supporting electrolyte. The conversion of $Ru(NH_3)_5Cl^{2+/+}$ to $Ru(NH_3)_5OH_2^{3+/2+}$ proceeds, but there is no evidence of the further reaction that occurs in less acidic media (Figure 3A). The complex that is formed at higher pH and that is responsible for the voltammograms shown in Figure 3B is quite stable if the coating is transferred to acidic solutions. For example, the voltammogram remained unaltered for 2 months when the coating was transferred to 0.5 M CF_3COOH. This result is consistent with the substitutional inertness of the $Ru(NH_3)_5py^{3+}$ complex.[46]

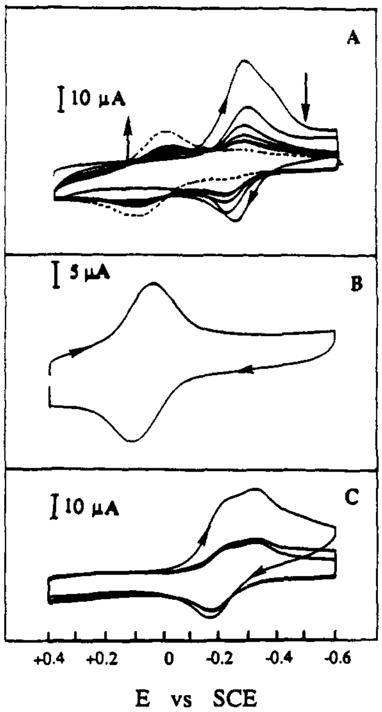

Figure 3. Cyclic voltammetry with Nafion coatings containing both 3.8×10^{-10} mol cm^{-2} of $CoP(py)_4$ and excess $Ru(NH_3)_5Cl^{2+}$. A: The first voltammogram (outermost curve) was recorded from an initial potential of 0.4 V, and the initial scan direction was to more negative potentials. Subsequent voltammograms were recorded from −0.6 V, and the initial scan direction was to more positive potentials. The electrode was maintained at −0.6 V for 10 min between the first and second and subsequent pairs of voltammograms. The dashed curve is the response obtained after all changes had ceased (2 h). B: Voltammetric response after 120 min at −0.6 V. Any unreacted $Ru(NH_3)_5OH_2^{2+}$ was lost from the coating by reverse ion exchange during the 2-h reaction period. Supporting electrolyte, 0.25 M Na_2SO_4 + 5×10^{-6} M $Ru(NH_3)_5Cl^{2+}$. C: Repeat of A in 0.5 M CF_3COOH as supporting electrolyte. The three curves correspond to 0, 10, and 20 min with the electrode at −0.6 V. Scan rate, 50 mV s^{-1}.

The stoichiometry of the reaction between $CoP(py)_4$ and $Ru(NH_3)_5OH_2^{2+}$ inside Nafion coatings was determined by combining two coulometric assays. A pair of identical Nafion-coated electrodes was loaded with $CoP(py)_4$ by immersion in a loading solution for the same length of time. The quantity of $CoP(py)_4$ incorporated in one coating was determined by coulometric assay according to the procedure described in connection with Figure 1B, after $Os(bpy)_3^{2+}$ and $Ru(NH_3)_6^{3+}$ were incorporated in the coating to serve as mediators. The second coating was loaded with $Ru(NH_3)_5Cl^{2+}$ and subjected to the treatment that produced the voltammogram in Figure 3B. The total quantity of $Ru(NH_3)_5py^{3+}$ groups present in the resulting coating was determined by measurement of the area under the voltammetric peak near 0.1 V recorded at a low scan rate (10 mV s^{-1}). The results of several experiments of this type are summarized in Table II. The data show that $Ru(NH_3)_5$ centers are coordinated to all four of the pyridine groups in the $CoP(py)_4$ molecules incorporated in the Nafion. Thus, the coordination reaction that proceeds within the Nafion coatings is

$$CoP(py)_4 + 4Ru(NH_3)_5OH_2^{2+} \rightarrow CoP(pyRu(NH_3)_5)_4^{8+} \quad (1)$$

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[45] Lieber, C. M.; Schmidt, M. H.; Lewis, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 6103.

[46] Ford, P.; Rudd, D. F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

Table II. Stoichiometric Ratio in the Reaction Between CoP(py)$_4$ and Excess Ru(NH$_3$)$_5$OH$_2^{2+}$ in Nafion Coatings[a]

coating no.	$10^{10}\Gamma_{Co}$,[b] mol cm^{-2}	$10^{10}\Gamma_{Co-Ru}$,[c,d] mol cm^{-2}	$\Gamma_{Co-Ru}/\Gamma_{Co}$
1	4.5	18.1	4.0
2	2.2	9.3	4.2
3	2.25	8.5	3.8

[a] Each coating contained 1.1 × 10^{-7} mol cm^{-2} of sulfonate groups. [b] Quantity of CoP(py)$_4$ present in the coating; taken as the average of the values obtained in Table I. [c] Quantity of Ru(NH$_3$)$_5$py^{3+} groups present in the coating as measured from the cathodic charge under voltammograms such as the one in Figure 3B, recorded at a scan rate of 10 mV s^{-1}. [d] To assure that there was no contribution to Γ_{Co-Ru} from any Co(III) centers present in the incorporated porphyrin, a coulometric assay of CoP(py)$_4$ in Nafion was attempted as in Table I but with Ru(NH$_3$)$_5$py^{2+} substituted for Ru(NH$_3$)$_6^{2+}$ as the reductive mediator. The cathodic assay failed because the Co(III) centers were not reduced by the Ru(NH$_3$)$_5$py^{2+} complex at a significant rate. Thus, even if some Co(III) centers were present, they would not contribute to the measured cathodic charges used to evaluate Γ_{Co-Ru}.

and the electrode process responsible for the voltammogram in Figure 3B is

$$\mathrm{CoP(pyRu(NH_3)_5)_4^{12+} + 4e \rightleftarrows CoP(pyRu(NH_3)_5)_4^{8+}} \quad (2)$$

The fact that only a single voltammetric wave is observed for the four-electron process involved in reaction 2 indicates that the four-coordinated Ru(NH$_3$)$_5$ centers accept and release electrons at essentially the same potential. The separation between cathodic and anodic peak potentials in voltammograms recorded at scan rates large enough to introduce diffusional control into the responses (e.g., 2 V s^{-1}) was 197 mV. The Ru(NH$_3$)$_6^{3+/2+}$ couple exhibited a peak separation of 180 mV under the same conditions. Probably because of the presence of uncompensated resistances in the coating, these separations are larger than the 59 mV expected for a diffusion-controlled response. However, their similarity indicates that the CoP(pyRu(NH$_3$)$_5$)$_4^{12+/8+}$ couple exhibits the voltammetric shape of a one-electron couple. Such behavior is expected when multiple electroactive centers behave independently and have essentially the same formal potential.[47] This property is desirable in applications where catalysts for the transfer of multiple electrons at the same potential are sought.

Electron Transport Within Nafion Coatings Containing CoP(pyRu(NH$_3$)$_5$)$_4^{12+/8+}$. Cyclic voltammograms such as the one in Figure 3B demonstrate that electronic contact between the electrode surface and the CoP(pyRu(NH$_3$)$_5$)$_4^{12+/8+}$ complexes prepared in the Nafion coatings is achieved in the absence of co-incorporated, mobile mediator couples such as the Os(bpy)$_3^{3+/2+}$ and Ru(NH$_3$)$_6^{3+/2+}$ couples that were required to shuttle electrons between the electrode surface and the immobile CoP(py)$_4$ centers in Figure 1B. The Ru(NH$_3$)$_5$ centers coordinated to the CoP(py)$_4$ porphyrin are likely to be even less mobile than the porphyrin itself because of the high positive charge that is present on the tetraruthenium complex, yet their electrooxidation or -reduction is readily achieved without the addition of mobile redox mediators (Figure 3B). This behavior is consistent with a much larger electron self-exchange rate between the coordinated Ru(NH$_3$)$_5$py groups than between the cobalt centers in CoP(py)$_4$,[48] so that electron hopping between adjacent Ru(NH$_3$)$_5$py groups (present at a concentration 4-fold greater than that of the cobalt centers) can provide a pathway for the propagation of electrons throughout the Nafion coating.[49]

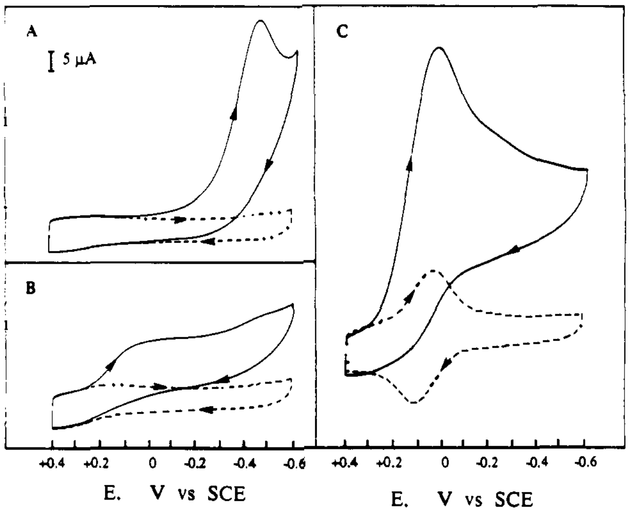

Figure 4. Voltammetric reduction of O$_2$ at Nafion-coated electrodes. A: Electrode coated with 1.1 × 10^{-7} mol cm^{-2} of sulfonate groups. B: Repeat of A after 3.76 × 10^{-10} mol cm^{-2} of CoP(py)$_4^{4+}$ was incorporated in the Nafion coating. C: Repeat of B after the incorporated porphyrin was converted to CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$. Supporting electrolyte, 0.5 M CF$_3$COOH saturated with air. The dashed curves were recorded in the absence of O$_2$. Scan rate, 50 mV s^{-1}.

However, the limiting electron propagation rates which can be obtained within Nafion coatings containing CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ are much smaller than those which can be realized in coatings containing the same quantity of simple redox mediators such as Ru(NH$_3$)$_6^{3+}$. The effective diffusion coefficient of the CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ complex in Nafion was lower than those of smaller redox couples, and this factor became important in the experiments to be described next where the tetraruthenium complex was utilized to catalyze the electroreduction of O$_2$.

Catalysis of the Electroreduction of O$_2$ by CoP(py)$_4$ and CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$. The uncatalyzed reduction of O$_2$ at a Nafion-coated graphite electrode is shown in Figure 4A. The incorporation of CoP(py)$_4$ in the Nafion coating caused the reduction of O$_2$ to commence at more positive potentials (Figure 4B), probably because a small amount of the CoP(py)$_4$ adsorbs directly on the electrode surface where it acts as a catalyst for the reduction of O$_2$ that diffuses through the Nafion to reach the underlying electrode. The smaller total reduction current in Figure 4B than in 4A is believed to be the result of an inhibition of the direct reduction of O$_2$ at the graphite surface by the adsorbed CoP(py)$_4$. The reduction of O$_2$ at uncoated graphite involves catalytic sites intrinsic to the graphite,[50] which may be eliminated or deactivated by the adsorbed porphyrin whose own catalytic activity is saturated at less negative potentials. The incorporated porphyrin was converted to CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ by the procedures described above, and a cyclic voltammogram for the converted catalyst in the absence of O$_2$ is shown in the dashed curve in Figure 4C. In the presence of O$_2$ the solid curve in Figure 4C was obtained. The evident catalysis of the reduction of O$_2$ proceeds at the potential where the ruthenium centers are reduced, which shows that the Ru(NH$_3$)$_5$ centers coordinated to the porphyrin ring serve both to shuttle electrons from the electrode to the immobilized catalyst molecules and to deliver the electrons to the Co–O$_2$ adduct that is presumed to be the species being reduced.

To establish the stoichiometry of the catalyzed reduction of O$_2$, the coated electrodes were employed in rotating disk experiments. Rotating disk current–potential curves are shown in Figure 5 along with the corresponding Levich and Koutecky–Levich plots.[51] The nonlinear Levich plot in Figure 5B indicates that a step preceding the electroreduction limits the current to values below those corresponding to the convection–diffusion-limited reduction of all

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(47) Flanagan, J.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(48) (a) Rate constants for electron self-exchange have been reported for the tetra N-methylated derivative of the tetrapyridylporphyrin, CoP(pyMe)$_4^{5+/4+}$, as 20 M^{-1} s^{-1} [48b] and for Ru(NH$_3$)$_5$py$^{3+/2+}$ as 4.7 × 10^5 M^{-1} s^{-1}.[48c] (b) Rohrbach, D. F.; Deutsch, E.; Heineman, W. R.; Pasternack, R. F. *Inorg. Chem.* **1977**, *16*, 2650. (c) Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374.

(49) For analyses of the relation between diffusion coefficients and self-exchange rates for redox couples in Nafion, see: Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685. Anson, F. C.; Blauch, D. N.; Savéant, J.-M.; Shu, C.-F. *J. Am. Chem. Soc.* **1991**, *113*, 1992 and references therein.

(50) Jiang, R.; Anson, F. C. *J. Electroanal. Chem.* **1991**, *305*, 171.

(51) Levich, V. G. *Physiochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1962. Koutecky, J.; Levich, V. G. *Zh. Fiz. Khim.* **1956**, *32*, 1565. Oyama, N.; Anson, F. C. *Anal. Chem.* **1980**, *52*, 1192.

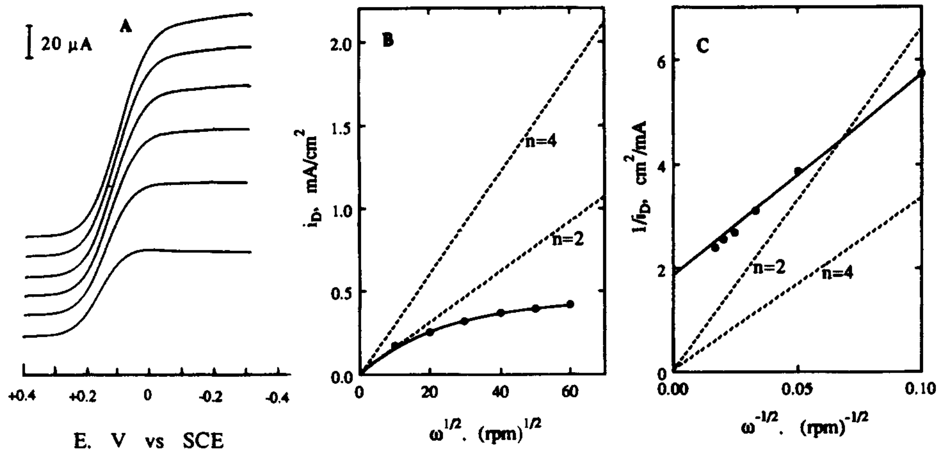

Figure 5. Catalyzed reduction of O_2 at a Nafion-coated rotating disk electrode coated with 1.1×10^{-7} mol cm^{-2} of sulfonate groups and 3.8×10^{-10} mol cm^{-2} of $CoP(pyRu(NH_3)_5)_4{}^{8+}$. A: Current-potential curves at electrode rotation rates (bottom to top) of 100, 400, 900, 1600, 2500, and 3600 rpm. For clarity, the base line for each successive curve was adjusted upward. B: Levich plot of the plateau currents vs (rotation rate)$^{1/2}$. C: Koutecky-Levich plot of the reciprocal plateau currents vs (rotation rate)$^{-1/2}$; the dashed lines are the calculated responses for the diffusion-convection-limited reduction of O_2 by two or four electrons. Supporting electrolyte, 0.5 M CF_3COOH saturated with air.

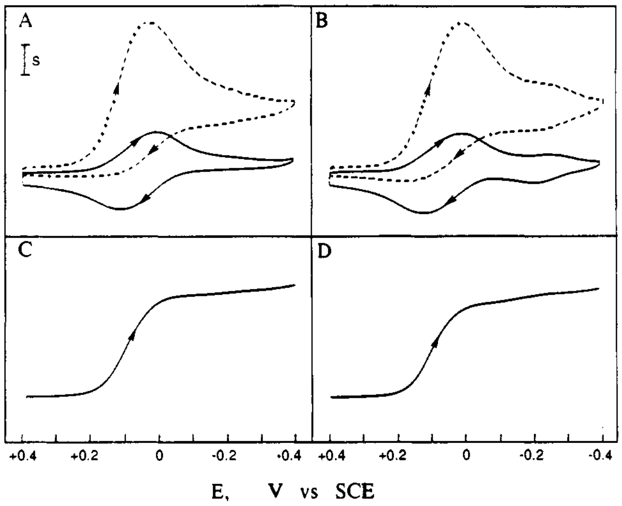

Figure 6. Lack of effect of added $Ru(NH_3)_6{}^{3+}$ on the rate of reduction of O_2 as catalyzed by $CoP(pyRu(NH_3)_5)_4{}^{8+}$. A: Cyclic voltammetry with a Nafion-coated electrode containing 1.1×10^{-7} mol cm^{-2} of sulfonate groups and 5.2×10^{-10} mol cm^{-2} of $CoP(pyRu(NH_3)_5)_4{}^{8+}$. Solid line, absence of O_2; dashed line, with an air-saturated solution. Supporting electrolyte, 0.5 M CF_3COOH; scan rate, 20 mV s^{-1}; current scale, $S = 5$ μA. B: Repeat of A after 2.8×10^{-10} mol cm^{-2} of $Ru(NH_3)_6{}^{3+}$ was incorporated in the coating. C: Repeat of A with the electrode rotated at 100 rpm. Scan rate, 2 mV s^{-1}; current scale, $S = 10$ μA. D: Repeat of C with 2.8×10^{-10} mol cm^{-2} of $Ru(NH_3)_6{}^{3+}$ added to the coating.

O_2 molecules that arrive at the coated electrode surface. The diffusion of O_2 through Nafion coatings is known to proceed at rates corresponding to much larger currents than those obtained in Figure 5B,[52,53] so that permeation of the coating by O_2 is not likely to be the current-limiting process. The rate of electron transfer between the $Ru^{II}(NH_3)_5$ centers and the $Co-O_2$ adduct was shown not to be current-limiting by adding $Ru(NH_3)_6{}^{3+}$ to the Nafion coating containing the $CoP(pyRu(NH_3)_5)_4{}^{8+}$ catalyst. No increase in the catalytic current for the reduction of O_2 resulted near −0.2 V where the added $Ru(NH_3)_6{}^{3+}$ was reduced to $Ru(NH_3)_6{}^{2+}$ (Figure 6). This behavior showed that the coordinated $Ru^{II}(NH_3)_5py$ groups were able to supply electrons to the reactive $Co-O_2$ adduct as rapidly as it formed so that this process could be eliminated as a current-limiting step. This leaves the formation of the $Co-O_2$ adduct as the probable process which limits the current. The rate of this reaction can, in many cases, be obtained from the intercept of the Koutecky-Levich plot in Figure 5C.[51] We did not attempt to estimate a rate constant for the present system because, with higher rotation rates or concentrations of O_2, the currents began to be limited by the rate of electron hopping between the immobile catalyst molecules, which severely complicated the kinetic analysis.[54] Of more interest in the present study was the slope of the plot in Figure 5C. The data fall on a line nearly parallel to that calculated for the four-electron reduction of O_2. This result indicates that the $CoP(pyRu(NH_3)_5)_4{}^{8+}$ complex, in contrast with other monomeric cobalt porphyrins, is able to catalyze the reduction of O_2 to H_2O.

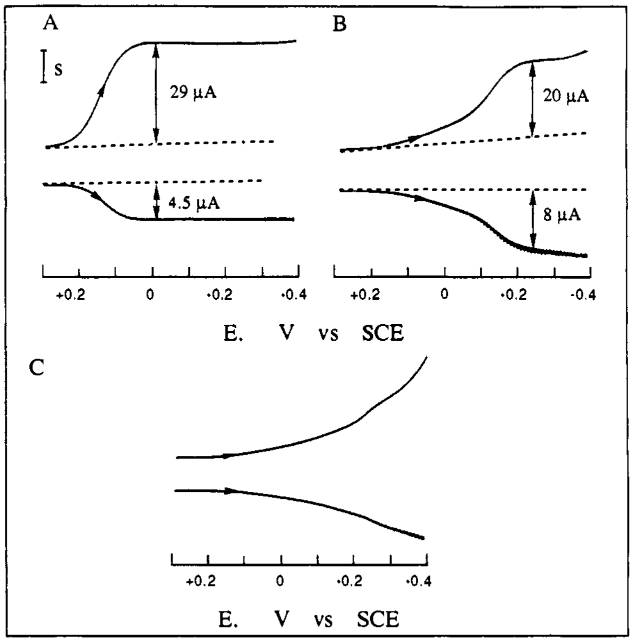

Figure 7. Reduction of O_2 at a rotating graphite disk-platinum ring electrode. The Nafion-coated disk contained 1.1×10^{-7} mol cm^{-2} of sulfonate groups. The Nafion coating contained (A) 7×10^{-10} mol cm^{-2} of $CoP(pyRu(NH_3)_5)_4{}^{8+}$; (B) 7×10^{-10} mol cm^{-2} of $CoP(pyH)_4{}^{4+}$ and 1.2×10^{-9} mol cm^{-2} of $Ru(NH_3)_6{}^{3+}$; and (C) 7×10^{-10} mol cm^{-2} of $CoP(pyH)_4{}^{4+}$. The ring potential was maintained at 1.0 V. Current scale, $S = 5$ μA for the ring and 10 μA for the disk; rotation rate, 100 rpm; scan rate, 2 mV s^{-1}; supporting electrolyte, 0.5 M CF_3COOH.

The stoichiometry of the catalyzed reduction of O_2 was also examined with a rotating platinum ring-graphite disk electrode.[55]

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[52] Gottesfeld, S.; Raistrick, I. D.; Srinivasan, S. *J. Electrochem. Soc.* **1987**, *134*, 1455.

[53] Lawson, D. R.; Whiteley, L. D.; Martin, C. R.; Szentirmay, M. N.; Song, J. I. *J. Electrochem. Soc.* **1988**, *135*, 2247.

[54] Andrieux, C.-P.; Dumas-Bouchiat, J.-M.; Savéant, J.-M. *J. Electroanal. Chem.* **1982**, *131*, 1.

The disk was coated with Nafion containing either the $CoP(pyRu(NH_3)_5)_4^{8+}$ catalyst or a mixture of $CoP(pyH)_4^{4+}$ and $Ru(NH_3)_6^{3+}$, and the ring electrode was used to detect the H_2O_2 generated at the disk as in previous experiments.[24] The results are shown in Figure 7. Some H_2O_2 is produced when the O_2 reduction is catalyzed by the $CoP(pyRu(NH_3)_5)_4^{8+}$ complex (Figure 7A), because, as mentioned earlier, the $CoP(pyH)_4^{4+}$ adsorbed on the underlying graphite electrode proved unreactive toward $Ru(NH_3)_5OH_2^{2+}$ and remained non-ruthenated under conditions where the unadsorbed complex was fully converted to $CoP(pyRu(NH_3)_5)_4^{8+}$. The non-ruthenated, adsorbed $CoP(pyH)_4^{4+}$ would be expected to continue to catalyze the reduction of O_2 to H_2O_2, which accounts for part of the H_2O_2 detected at the ring electrode in Figure 7A. The response obtained when the Nafion coating on the disk electrode contained $CoP(pyH)_4^{4+}$ is shown in Figure 7C. The reduction of O_2 is catalyzed only by the porphyrin that is adsorbed on the graphite surface. The current is smaller and the production of H_2O_2 is essentially quantitative, as judged from the ratio of the disk and ring currents obtained. If the ring current obtained in Figure 7C at 0 V is subtracted from that in 7A, the resulting ratio of (corrected) ring-to-disk current gives a collection efficiency of 12%, which corresponds to about 70% of the disk current arising from the four-electron reduction of O_2.

The ring–disk electrode response that resulted when the same quantity of $CoP(pyH)_4^{4+}$ along with $Ru(NH_3)_6^{3+}$ was incorporated in the Nafion coating on the disk is shown in Figure 7B. This mixture produced a smaller O_2 reduction current at the disk and a ring current corresponding to an essentially quantitative yield of H_2O_2.

The coordination of the $Ru(NH_3)_5$ groups to the meso pyridine ligands of the porphyrin ring is essential to access the four-electron reduction pathway. Nafion coatings in which both $CoP(pyH)_4^{4+}$ and $Ru(NH_3)_6^{3+}$ (as mediator) are incorporated yield only two-electron reductions of O_2 (Figure 7B). Similarly, Nafion coatings containing $CoP(pyH)_4^{4+}$ and $Ru(NH_3)_5py^{2+}$, a much weaker reducing agent than $Ru(NH)_3)_6^{2+}$, are much less active toward the electroreduction of O_2, and only the two-electron reduction is observed. These results support the supposition that intermolecular electron transfer is not important during the four-electron reduction of O_2. All four of the $Ru^{III}(NH_3)_5$ centers coordinated to the pyridine sites on the porphyrin ring are reduced at the same potential, so that four electrons become available essentially simultaneously for intramolecular transfer to O_2 molecules coordinated to the cobalt center. Uncoordinated $Ru(NH_3)_5py^{2+}$ complexes exhibit low reactivity toward transfer of electrons to O_2 molecules bound to $CoP(pyH)_4^{4+}$. For this reason, intermolecular electron transfer from $Ru(NH_3)_5py^{2+}$ groups of one porphyrin to an oxygen molecule coordinated to the cobalt center of a second porphyrin seems unlikely to be able to compete with intramolecular electron transfer from the four ready and waiting $Ru(NH_3)_5py^{2+}$ groups of the second porphyrin.

The cobalt ion in the porphyrin ring is also essential for the catalysis. Incorporation of the metal-free tetrapyridylporphyrin ligand in Nafion followed by reaction with $Ru(NH_3)_5OH_2^{2+}$ to obtain what is presumed to be the $H_2P(pyRu(NH_3)_5)_4^{8+}$ complex does not produce a catalyst for the reduction of O_2.

Thus, the coordination of four electron-donating $Ru(NH_3)_5^{2+}$ groups to the pyridine sites of $CoP(py)_4$ produces a catalyst which can transfer four electrons to O_2 molecules under conditions where mixtures of $CoP(py)_4$ with uncoordinated $Ru(NH_3)_5py^{2+}$ complexes with essentially the same formal potential (or with $Ru(NH_3)_6^{2+}$ complexes which have an even more negative formal potential) do not. The combination of experimental observations just described indicates that the four-electron transfer follows an intramolecular pathway. The full mechanistic implications of these results remain to be explored, but it seems reasonable to surmise that the coordinated $Ru(NH_3)_5^{2+}$ centers are in more intimate electronic contact with the cobalt(II) center in the porphyrin ring and with the O_2 molecules that may coordinate to it than are uncoordinated Ru(II) complexes also present in the coatings. The production of H_2O_2 instead of H_2O during the catalysis of the electroreduction of O_2 by most cobalt porphyrins presumably results from the escape of partially reduced intermediates from the coordination sphere of the cobalt center before they can be further reduced. By pre-attaching the four electron-donating centers to the porphyrin ring in $CoP(pyRu(NH_3)_5)_4^{8+}$, the rate of intramolecular electron delivery to the cobalt center, and substrates coordinated to it, is evidently sufficiently enhanced to accomplish the complete reduction to H_2O of a large portion of the O_2 molecules that coordinate to the Co(II) center before the intermediate reduction products escape into solution. (It was established in separate experiments that the $CoP(pyRu(NH_3)_5)_4^{8+}$ complex is not a catalyst for the electroreduction of H_2O_2.)

Limitation on Turnover Rate. The relatively positive potential at which the $CoP(pyRu(NH_3)_5)_4^{8+}$ complex reduces O_2 to H_2O makes it an attractive candidate as an electrocatalyst for the reduction of O_2. However, because of the relatively small effective diffusion coefficient of the $CoP(pyRu(NH_3)_5)_4^{8+}$ complex in Nafion, the turnover rates for the reduction of O_2 become limited by the rate of electron propagation within the Nafion when pure O_2 is substituted for air. The rates may be increased by the addition of a mediator redox couple to the Nafion coatings, as in previous studies,[42,43] but the formal potential of the mediator couple then controls the operating potential of the electrocatalyst. It would be of interest to adsorb the $CoP(pyRu(NH_3)_5)_4^{8+}$ catalyst directly on the surface of uncoated graphite electrodes to measure the turnover rates available when the rate of electron propagation imposes no limit. Unfortunately, we have not yet devised a method for preparing the catalyst directly on the electrode surface. The precursor complex, $CoP(py)_4$, is readily adsorbed on pyrolytic graphite electrodes, but the adsorbed complex appears not to react with $Ru(NH_3)_5OH_2^{2+}$ to generate the desired tetraruthenium product which, thus far, we have been able to prepare only within Nafion coatings.

Conclusions

The use of the polyelectrolyte Nafion as a medium in which to prepare the tetraruthenium derivative of $CoP(py)_4$ proved valuable in this study. Under conditions where only insoluble and uncharacterized products were obtained when the preparative reactions were attempted in solution, reasonable yields of the desired product were obtained within Nafion coatings. The reason for the significant difference in behavior is probably associated with the occurrence of aggregation reactions leading to high molecular weight products when the reactions are carried out in solution. The demonstrated lack of mobility of $CoP(pyH)_4^{4+}$ molecules incorporated in Nafion could prevent the aggregation that produces the insoluble material in solution.

The availability of the $CoP(pyRu(NH_3)_5)_4^{8+}$ complex in Nafion coatings allowed its potency as a four-electron catalyst for the reduction of O_2 to be demonstrated. This result is encouraging for the strategy of synthesizing potential catalyst molecules with the capacity to transfer multiple electrons at the same energy. Previous attempts to realize multiple-electron catalysis with derivatives of metalloporphyrin derivatives[28,29] have shown that the presence of multiple electron-donating groups is not sufficient to ensure multiple-electron catalysis. However, the present results show that the approach can be successful, and additional experiments to establish the range of substrates for which the $CoP(pyRu(NH_3)_5)_4^{8+}$ molecule and its analogues are effective multiple-electron catalysts seem worthy objectives for future work.

Acknowledgment. This work was supported by the National Science Foundation and DARPA/ONR. Discussions with Dr. Koiti Araki were very insightful and helpful.

Registry No. Py, 110-86-1; CoP(Py), 14244-55-4; $[CoP(PyRu(NH_3)_5)_4]^{8+}$, 136795-61-4; O_2, 7782-44-7; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_5Py$, 21360-09-8; $Os(bpy)_3^{2+}$, 23648-06-8; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_5Cl^{2+}$, 21560-19-0; $Ru(NH_3)_5Cl^{+}$, 29933-34-4; $Ru(NH_3)_5OH_2^{3+}$, 25590-52-7; $Ru(NH_3)_5OH_2^{2+}$, 21393-88-4; Na_2SO_4, 7757-82-6; CF_3COOH, 76-05-1; H_2O, 7732-18-5; graphite, 7782-42-5.

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