Electrocatalysts for the four-electron reduction of dioxygen based on adsorbed cobalt tetrapyridylporphyrin molecules linked by aquaammine complexes of ruthenium(II)

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Abstract

Prolonged exposure of graphite electrodes coated with cobalt tetrapyridylporphyrin to solutions of *fac*-$Ru(NH_3)_5(OH_2)_3{}^{2+}$ results in the formation of stable, apparently polymeric complexes on the surface in which the porphyrins are linked by bridging Ru centers. Electrochemical evidence in support of this assertion is presented. The coatings obtained endow the coated electrodes with the ability of catalyze the four-electron reduction of O_2 at unusually positive potentials.

Keywords: Electrocatalysis; Dioxygen reduction; Cobalt complexes; Porphyrin complexes; Ruthenium complexes; Ammine complexes

1. Introduction

Recent reports from this laboratory have described the preparation of coatings on the surfaces of graphite electrodes consisting of adsorbed cobalt *meso*-tetrakis(4-pyridyl)porphyrins, $CoP(py)_4$, in which an $Ru(NH_3)_5$ group was coordinated to each of the four pyridine groups [1,2]. These tetra-ruthenated cobalt porphyrins accomplish the direct reduction of dioxygen to water under conditions where their non-ruthenated counterparts yield only hydrogen peroxide as the reduction product. Related studies have indicated that the co-ordinated ruthenium centers serve as more than mere electron donors in diverting the electroreduction of dioxygen from a two- to a four-electron pathway [3,4]. In an attempt to vary the character of the ruthenium complexes coordinated to the pyridine groups of the tetrapyridyl porphyrin, we sought ammine complexes of ruthenium that also contained more than one ligand which might be replaced with other ligands to alter both the formal potential of the Ru^{3+}/Ru^{2+} couple and the extent of backbonding interactions of the ruthenium centers with the pyridine ligands pendant to the porphyrin ring. Results obtained with the tri-aquatriammineruthenium(III) complex are the subject of the present report. The electrochemical behavior of the $Ru(NH_3)_3(OH_2)_3{}^{3+/2+}$ complexes in homogeneous solutions, both in the absence and in the presence of pyridine, is dealt with first. Next, the preparation of electrode coatings by reacting $Ru(NH_3)_3(OH_2)_3{}^{2+}$ with $CoP(py)_4$ adsorbed on graphite electrodes is described and some suggestions as to the likely composition of the unusually stable coatings are offered. Finally, the use of the coatings as electrocatalysts in the reduction of dioxygen is demonstrated.

2. Experimental

2.1. Materials

$[Ru_2Cl_3(NH_3)_6]Cl_2 \cdot 2H_2O$, was prepared by a modified version of the method of Bottomley and Tong [5]. 0.8 g of $Ru(NH_3)_6Cl_3$ was dissolved in 9 ml of water and reacted with Zn(Hg) under an argon atmosphere to reduce $Ru(NH_3)_6{}^{3+}$ to $Ru((NH_3)_6{}^{2+}$. After removal of the Zn(Hg), the yellow solution was heated to 80 °C and 6 ml of 12 M HCl were added. The resulting deep blue solution was filtered hot, the filtrate was cooled

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to 5 °C and allowed to stand overnight while a blue, crystalline precipitate formed. The solid was washed with ethanol and ether, and then recrystallized from water–ethanol. A solution prepared from the solid exhibited a UV–Vis spectrum which matched that in the literature [5]. The ruthenium content of the solid was determined spectrophotometrically [6]. *Anal.* Calc. for [$Ru_2Cl_3(NH_3)_6$]$Cl_2 \cdot 2H_2O$: Ru, 39.07. Found: Ru, 39.78%.

Solutions of *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ were prepared by reducing argon-saturated solutions containing 7.5 mM $Ru_2Cl_3(NH_3)_6^{2+}$ in 30 mM NH_4PF_6 (pH = 3.7) with Zn(Hg) until all traces of the original blue color were removed. The solutions were freshly prepared and utilized immediately. During the reduction, which typically required 2 to 3 h, the pH of the solution increased to between 5 and 5.5.

Fac-$Ru(NH_3)_3Cl_3$ was prepared by adapting the procedure described in Ref. [7]. [$Ru_2Cl_3(NH_3)_6$]$Cl_2 \cdot 2H_2O$ was dissolved in 1 M HCl and the solution was heated to boiling for ~10 min. The initially blue solution turned orange–red during the heating period. The solution was cooled overnight in the refrigerator. The resulting red crystals were collected and washed with H_2O. The solid does not dissolve readily but solutions were prepared by treating the solid with 1 M HCl on a steam bath with periodic sonication. The ruthenium content of the salt was determined spectrophotometrically [6]. *Anal.* Calc. for $Ru(NH_3)_3Cl_3$: Ru, 39.11. Found: Ru, 39.09%.

Cis-[$Ru(NH_3)_4Cl_2$]Cl was available in the laboratory from previous studies. Solutions of the salt were converted to *cis*-$Ru(NH_3)_4(OH_2)_2^{2+}$ by reduction with Zn(Hg).

Cobalt *meso*-tetrakis(4-pyridyl)porphyrin was prepared from the commercially available ligand as previously described [1]. Other chemicals were reagent grade and used as received. Solutions were prepared from laboratory deionized water which was further purified by passage through a purification train (Milli-Q Plus by Millipore).

2.2. Apparatus and procedures

Cyclic voltammetry was performed with conventional electrochemical cells and instrumentation using edge plane pyrolytic graphite working electrodes (0.32 cm^2). Electrodes were coated with $CoP(py)_4$ by transferring 20 μl aliquots of solutions of the porphyrin in 0.5 M CF_3COOH to the surface of freshly polished edge plane pyrolytic graphite electrodes and allowing the solvent to evaporate in air. To prepare ruthenated coatings the resulting electrodes were transferred to solutions containing 15 mM *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ in 30 mM NH_4PF_6 at pH 3.5 and allowed to react under argon until the desired extent of ruthenation of the coating

was achieved. Rotating disk and ring–disk voltammetry were carried out with an ASR2 rotator and RDE4 bipotentiostat (Pine Instrument Co.) and a Kipp and Zonen x-y-y' recorder. The platinum ring–graphite disk electrode employed (AFDTI 39, Pine Instrument Co.) had a 0.125 cm gap separating the ring and disk electrodes which was sufficiently wide to prevent coatings applied to the disk from contaminating the ring electrode. The collection efficiency of the electrode was 0.39 as measured in a solution of $Fe(CN)_6^{3-}$. Potentials were measured and are quoted with respect to a saturated calomel electrode (SCE). Experiments were conducted at the ambient laboratory temperature, 22 ± 2 °C.

3. Results and discussion

3.1. Electrochemistry of the $Ru_2Cl_3(NH_3)_6^{2+}$ complex in solution

The dispositions of the ligands about both of the ruthenium centers in the intensely blue, dimeric complex, [$Ru_2Cl_3(NH_3)_6$]$^{2+}$, were assigned as belonging to the facial geometrical isomers by Mercer and Gray [8] on the basis of a single Ru–Cl stretch in the IR spectrum and, most convincingly, by the demonstration that all three of the chloro ligands were coordinated to both ruthenium centers. Reduction of the dimer induces dissociation and aquation providing a convenient route to the desired $Ru(NH_3)_3(OH_2)_3^{2+}$ complex. We presume that this complex is obtained as the facial geometrical isomer because ligand rearrangement is not expected to accompany the reductive aquation. We will begin with an examination of the redox chemistry of the dimeric cation. Mercer and Gray [8] described some aspects of the voltammetric behavior of $Ru_2Cl_3(NH_3)_6^{2+}$ (hereafter Ru_2^{2+}) but no extensive study of its electrochemistry has been reported. In agreement with Mercer and Gray [8], we observed an anodic oxidation of Ru^{2+} at 0.33 V at a pyrolytic graphite electrode (Fig. 1(A) and (C)). The electrode reaction is reversible and the magnitude of the anodic plateau current of the rotating disk voltammogram corresponds to a one-electron process for a reactant with a diffusion coefficient of 5.0×10^{-6} cm^2 s^{-1}. The Ru_2^{2+} cation has been shown to be a mixed-valence complex [8] containing one Ru(II) and one Ru(III) center (or a pair of Ru(II$\frac{1}{2}$) centers) so the anodic half-reaction is

$$Ru_2^{2+} - e \rightleftharpoons Ru_2^{3+} \qquad (1)$$

The formal potential of 0.33 V of the Ru_2^{3+}/Ru_2^{2+} couple is much more positive than those for monomeric chloroammine complexes of Ru(III)/Ru(II). Some representative values for the latter class of complexes are [9]: $Ru(NH_3)_5Cl^{2+/+}$, $E^f = -0.28$ V, *cis*-

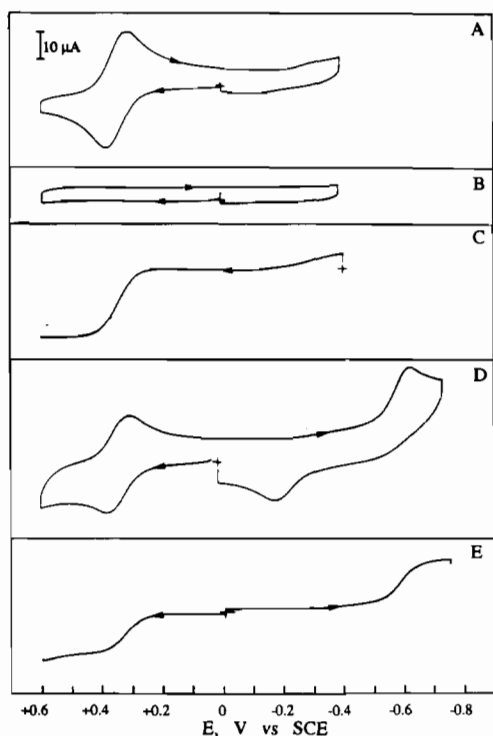Fig. 1. (A) Cyclic voltammetry of 0.6 mM *fac*-[Ru$_2$Cl$_3$(NH$_3$)$_6$]$^{2+}$ in 0.1 M CF$_3$COOH. Scan rate: 50 mV s^{-1}. (B) Voltammetric response recorded in the pure supporting electrolyte, 0.1 M CF$_3$COOH. (C) Rotating disk voltammetry of 0.6 mM *fac*-[Ru$_2$Cl$_3$(NH$_3$)$_6$]$^{2+}$. Rotation rate: 100 rpm; potential scan rate: 10 mV s^{-1}. (D, E) Repeat of (A) and (C) in 1.0 M KCl as supporting electrolyte.

Ru(NH$_3$)$_4$Cl$_2$$^{+/0}$, $E^f = -0.34$ V, *trans*-Ru(NH$_3$)$_4$Cl$_2$$^{+/0}$, $E^f \sim -0.32$ V. The much more positive value observed for the [(NH$_3$)$_3$RuCl$_3$Ru(NH$_3$)$_3$]$^{3+/2+}$ couple is presumably the result of the substantial electronic interaction between the two ruthenium centers via the three bridging chloro ligands.

Electroreduction of the Ru$_2$$^{2+}$ cation was more difficult to monitor because the reduction wave appeared at potentials only slightly positive of those where the reduction of H$_3$O$^+$ occurred. Proton reduction appears to be strongly catalyzed in the presence of the reduced ruthenium complex. Mercer and Gray [8] made the same observation. By working in less acidic supporting electrolytes it was possible to obtain a reasonably well-formed reduction wave for the Ru$_2$$^{2+}$ dimer as shown in Fig. 1(D) and (E). The cathodic plateau current of the rotating disk voltammogram in Fig. 1(E) is essentially equal to that for the anodic plateau current of the wave at 0.33 V, as expected if the cathodic wave corresponds to the one-electron reduction of the Ru$_2$$^{2+}$ complex.

$$Ru_2^{2+} + e \rightleftharpoons Ru_2^+ \tag{2}$$

Exhaustive reduction of the blue Ru$_2$$^{2+}$ cation by controlled potential electrolysis at -0.7 V at a vitreous carbon electrode or by reaction with Zn(Hg) produced a light yellow solution from which a new, reversible cyclic voltammetric response was obtained. The voltammogram recorded with a partially reduced solution is shown in Fig. 2(A). The residual response at 0.33 V is from the unreduced Ru$_2$$^{2+}$ and the prominent new couple that is present has a formal potential of -0.1 V. After more extensive reduction with Zn(Hg) only the second couple remains (Fig. 2(B)) and its peak currents are about twice as large as those of the original Ru$_2$$^{2+}$ complex (Fig. 1(A)). In Fig. 2(C) are shown anodic voltammograms recorded at a rotating disk electrode with a solution of Ru$_2$$^{2+}$ before (curve 1) and after (curve 2) the cation was reduced completely with Zn(Hg). The anodic plateau current of curve 2 is very close to twice as large as that of curve 1 in agreement with the cyclic voltammetric results (Figs. 1(A) and 2(B)).

The more negative formal potential of the new reversible couple in Fig. 2(A) and the tendency for chloroammine complexes of Ru(III) to undergo facile aquation when reduced to Ru(II) are consistent with
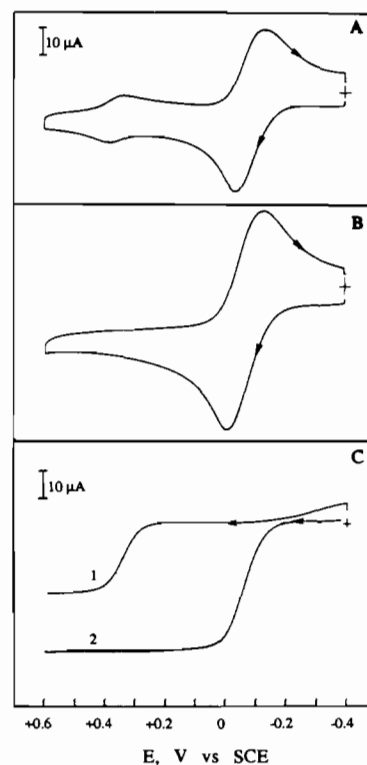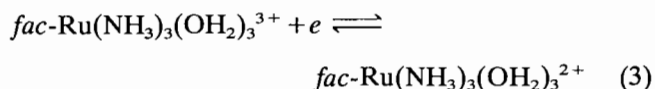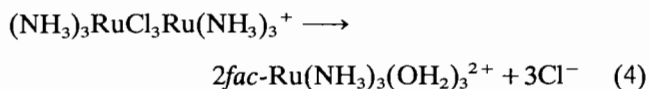

Fig. 2. (A) Cyclic voltammetry of a 0.6 mM solution of *fac*-[Ru$_2$Cl$_3$(NH$_3$)$_6$]$^{2+}$ after partial reduction with Zn(Hg). (B) Repeat of (A) after the reduction was complete; other conditions as in Fig. 1(A). (C) Rotating disk voltammetry of 0.6 mM [Ru$_2$Cl$_3$(NH$_3$)$_6$]$^{2+}$ before (curve 1) and after (curve 2) reduction with Zn(Hg); other conditions as in Fig. 1(C).

assignment of the couple at -0.1 V to half-reaction (3).

$$fac\text{-Ru(NH}_3)_3(\text{OH}_2)_3^{3+} + e \rightleftharpoons$$

$$fac\text{-Ru(NH}_3)_3(\text{OH}_2)_3^{2+} \quad (3)$$

The fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{3+}$ complex is believed to be formed by the dissociative decomposition and aquation of the reduced dimer, Ru$_2$$^+$, in which both ruthenium centers are in oxidation state $+2$ (reaction (4)).

$$(\text{NH}_3)_3\text{RuCl}_3\text{Ru(NH}_3)_3^+ \longrightarrow$$

$$2fac\text{-Ru(NH}_3)_3(\text{OH}_2)_3^{2+} + 3\text{Cl}^- \quad (4)$$

The doubling of the peak and plateau currents in Fig. 2(B) and (C) is thus attributable to the conversion of the dimeric complex, in which the average oxidation state of each ruthenium center is 2.5, to two fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ complexes each of which can be oxidized to fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{3+}$. These electrochemical results show that the chemical or electrochemical reduction of the readily prepared Ru$_2$Cl$_3$(NH$_3$)$_6$$^{2+}$ cation [5,8] is a convenient route to fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$.

In agreement with Mercer and Gray [8], we sometimes observed a small reduction wave at -0.28 V with solutions prepared from older samples of the Ru$_2$$^{2+}$ complex or with solutions of the freshly prepared complex which were exposed to dioxygen for extended periods (curve 1 in Fig. 2(C)). When present, the wave could be eliminated by cation exchange as described by Mercer and Gray [8]. The complex likely to be responsible for the wave is fac-Ru(NH$_3$)$_3$Cl$_3$ which is a known decomposition product of the Ru$_2$$^{2+}$ dimer [7]. To test this speculation, solid samples of fac-Ru(NH$_3$)$_3$Cl$_3$ were prepared and isolated as described in Section 2. Although the red solid is only sparingly soluble, saturated solutions prepared in 0.1 M HCl yielded a clear cyclic voltammetric response at -0.28 V (Fig. 3). Reduction of solutions of fac-Ru(NH$_3$)$_3$Cl$_3$ with Zn(Hg) produced a solution which exhibited a

voltammetry identical to that obtained by the reduction of the Ru$_2$$^{2+}$ complex by Zn(Hg) (Fig. 2(B)).

3.2. Reaction of fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ with pyridine

Our ultimate objective was to coordinate the fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ complex to the pyridine ligands of CoP(py)$_4$ molecules adsorbed on graphite electrode surfaces. To prepare for such experiments we examined the reaction between fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ and pyridine in homogeneous solutions. To facilitate the coordination reaction it was necessary to increase the pH of the reaction solution which produced a significant effect on the electrochemistry of the fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ complex even before pyridine was added to the solution. Voltammograms for the oxidation of fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ at several pH values are shown in Fig. 4. Increasing the pH causes the main oxidation wave to shift to less positive potentials, the peak current to decrease and additional smaller peaks to appear. The diminished currents produced by increasing the pH are only partially restored if the pH is readjusted to its initial value of 1 (Fig. 4(D)). We believe that increasing the pH leads to oligomerization of the complex which diminishes its diffusion coefficient

Fig. 4. Cyclic voltammetry of 1.0 mM fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ as a function of pH. (A) pH = 1; (B) pH = 4.5 (0.05 M phthalate buffer); (C) pH = 6.5 (0.05 M phthalate buffer); (D) repeat of (C) after the solution pH was adjusted to 1 by addition of concentrated CF$_3$COOH. Scan rate: 50 mV s^{-1}.
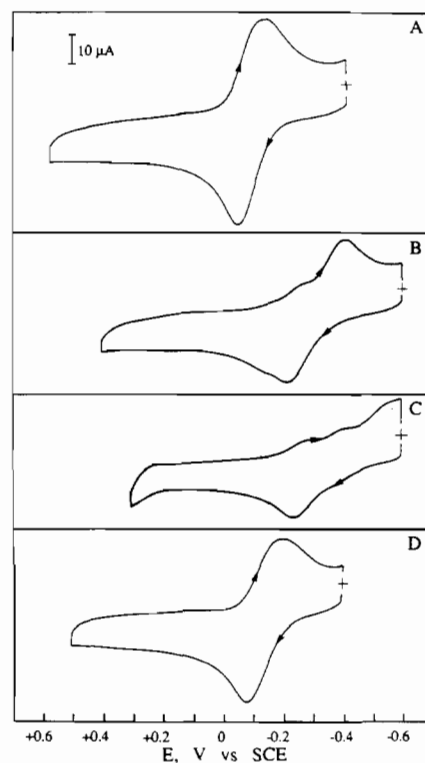

Fig. 3. Cyclic voltammetry of a saturated solution of fac-Ru(NH$_3$)$_3$Cl$_3$ in 0.1 M HCl. Scan rate: 5 mV s^{-1}.

and, thereby, the voltammetric currents. The same behavioral pattern is observed in the voltammetry of the $Ru(OH_2)_6^{3+/2+}$ couple [10] which would be even more likely to form hydroxo- or oxo-bridged oligomers as the pH is increased.

Whatever the origin of the diminished currents in solutions of *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ at pH values above 4, the Ru(II) complexes present in such solutions coordinated pyridine when this ligand was also present. The slow coordination reactions were readily monitored by cyclic voltammetry because the replacement of each aqua ligand by a pyridine produced a positive shift in the formal potential of the Ru(III)/Ru(II) couple. In Fig. 5 is shown a set of cyclic voltammetric responses as increasing quantities of pyridine are coordinated to the Ru(II) center of the *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ complex. The single anodic peak obtained before the pyridine was added (Fig. 5(A)) is gradually replaced by three additional peaks which are reasonably assignable to the $Ru(NH_3)_3(OH_2)_{3-n}(py)_n^{3+/2+}$ ($n=1,2,3$) couples. The peaks labeled I, II and III in Fig. 5 are assigned
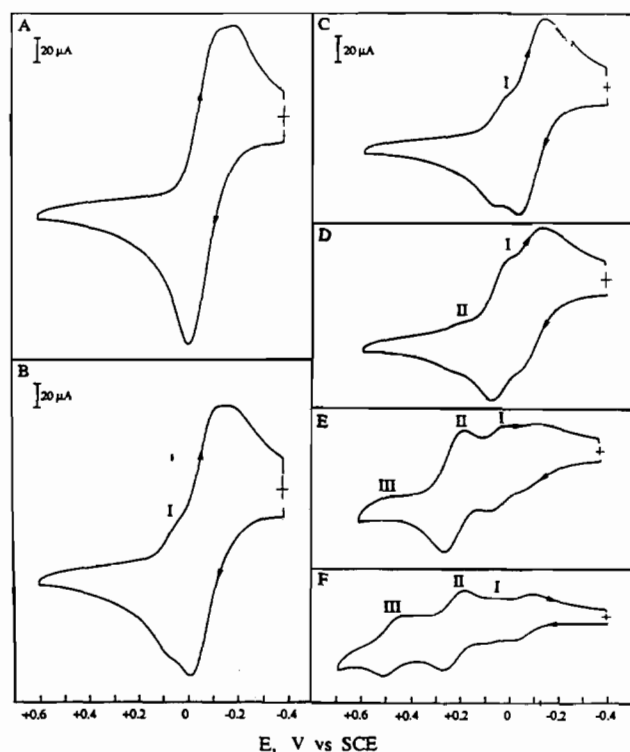

Fig. 6. Formal potentials of the three reversible couples of Fig. 5(E) and (F) as a function of pH.

Fig. 5. Cyclic voltammetry of *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ in the presence of pyridine. (A) 4 mM *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ in 0.1 M CH_3SO_3Na at pH 3.45; (B) after addition of 1.2 mM pyridine and 30 min of reaction; (C) repeat of (B) after 15 h of reaction; (D) after the pyridine concentration was increased to 2.5 mM and an additional reaction time of 2 h; (E) after increase in the pyridine concentration to 10 mM and an additional reaction time of 6 h; (F) after increase in the pyridine concentration to 20 mM and an additional reaction time of 24 h. Scan rate: 50 mV s^{-1}. In every case the pH was decreased to 3.45 just before the voltammogram was recorded.
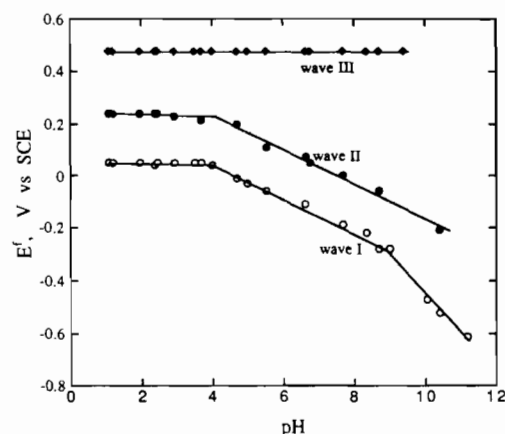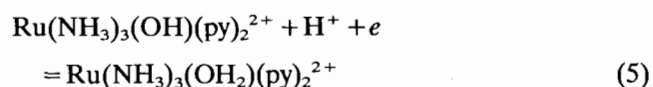
to $n=1,2$ and 3, respectively. The steady decrease in the peak currents as the pyridine concentration was increased is believed to be the result of the corresponding increases in the pH of the solution which leads to diminished diffusion coefficients as was shown in Fig. 4.
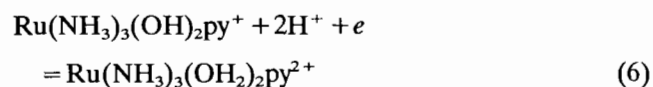
The pH dependences of the formal potentials of the couples labeled I, II and III in Fig. 5 are shown in Fig. 6. This behavior is in accord with the proposed assignments of the couples in Fig. 5: at pH values above the pK_a values of the remaining aqua ligands of the $Ru(NH_3)_3(OH_2)_2py^{3+}$ and $Ru(NH_3)_3(OH_2)(py)_2^{3+}$ complexes the electrode half-reaction involves one or two protons per electron, e.g.
Couple II

$$Ru(NH_3)_3(OH)(py)_2^{2+} + H^+ + e$$
$$= Ru(NH_3)_3(OH_2)(py)_2^{2+} \qquad (5)$$

and
Couple I

$$Ru(NH_3)_3(OH)_2py^+ + 2H^+ + e$$
$$= Ru(NH_3)_3(OH_2)_2py^{2+} \qquad (6)$$

The lack of pH dependence and more positive formal potential of wave III are in accord with its assignment to the *fac*-$Ru(NH_3)_3py_3^{3+/2+}$ couple.

The value to the present study of the cyclic voltammograms in Fig. 5 was the demonstration they provided that *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ can coordinate one, two or three pyridine ligands under suitable reaction conditions. This information was utilized to prepare the desired ruthenium derivatives of $CoP(py)_4$ adsorbed on electrode surfaces.

3.3. Coordination of $Ru(NH_3)_3(OH_2)_n^{2+}$ $(n=2,1)$ centers to $CoP(py)_4$ adsorbed on graphite electrodes

The procedures for coordinating $Ru(NH_3)_5^{2+}$ centers to $CoP(py)_4$ on the surface of pyrolytic graphite electrodes described in preceding reports [2,3] were adapted and applied to the case of fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ as described in Section 2. A pyrolytic graphite electrode on which a known quantity of $CoP(py)_4$ had been deposited was immersed in a solution of fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ through which argon was continuously bubbled. The extent of coordination of Ru centers to the pyridine ligands of the adsorbed porphyrin after various reaction times was determined by transferring the electrode to a supporting electrolyte solution containing 0.5 M $HClO_4$ + 0.5 M NH_4PF_6 (to diminish the solubility of the adsorbed complex [2,3]) and recording cyclic voltammograms. Examples of voltammograms obtained are shown in Fig. 7. The almost featureless voltammogram in Fig. 7(A) was obtained with an elec-

Fig. 7. Cyclic voltammetry of 3.7×10^{-9} mol cm^{-2} of $CoP(py)_4$ adsorbed on a graphite electrode before (A, B) and after (C, D) reaction with 15 mM fac-$Ru(NH_3)_3(OH_3)_3^{2+}$. (A) Voltammetry in 0.5 M $HClO_4$ + 0.5 M NH_4PF_6 as supporting electrolyte. Scan rate: 10 mV s^{-1}. (B) Voltammetry in DMF with 0.1 M NH_4PF_6 as supporting electrolyte. Scan rate: 50 mV s^{-1}. (C) Repeat of (A) after the electrode was exposed to the fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ solution for 3 h. (D) Repeat of (A) after a total reaction time of 48 h. The dashed curve was recorded at a scan rate of 200 mV s^{-1}. The current scale, S, is 5 and 50 μA for the solid and dashed curves, respectively.

trode coated with $CoP(py)_4$ before it was exposed to the fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ solution. The small couple near 0.38 V is also present in the voltammogram for an uncoated electrode. It corresponds to the oxidation and reduction of functional groups present on the graphite surface. No response corresponding to the oxidation or reduction of the cobalt center in the porphyrin is observed in aqueous media but a clear reversible response is obtained when the coated electrode is transferred to dimethylformamide solutions as shown in Fig. 7(B). This behavior has been previously described [2].

In Fig. 7(C) is shown the voltammogram obtained after the coated electrode had been exposed to 15 mM fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ for 3 h and then transferred to pure (aqueous) supporting electrolyte. The formal potentials of the two couples evident in the voltammogram show that they correspond to ruthenium centers coordinated to the pyridine ligands of the adsorbed porphyrin. In previous experiments, where $Ru(NH_3)_5OH_2^{2+}$ was reacted with the adsorbed porphyrin, only one prominent voltammetric couple from the ruthenated porphyrin was observed and it appeared at the potential expected for the $Ru(NH_3)_5py^{3+/2+}$ couple [2,3]. (A less prominent, second couple which sometimes develops when $Ru(NH_3)_5(OH_2)^{2+}$ is the ruthenating agent has been tentatively assigned to a doubly pyridine-substituted product [11].) The appearance of a pair of prominent cathodic peaks in the present experiments indicates that more than one type of complex results from the ruthenation of the adsorbed porphyrin by fac-$Ru(NH_3)_3(OH_2)_3^{2+}$. (The possibility that the double peaks are the result of splittings arising from intramolecular interactions between Ru centers coordinated to pyridine ligands on the same porphyrin molecule is unlikely because only a single prominent peak is obtained when $Ru(NH_3)_5^{2+}$ centers are coordinated to all four pyridine ligands of the adsorbed $CoP(py)_4$ molecule [2].) The peak labeled I in Fig. 7(C) has a formal potential somewhat more positive than peak I in Fig. 5(D) (0.10 versus 0.05 V) but we believe it can be assigned to the $[Ru(NH_3)_3(OH_2)_2pyP(py)_3Co]_{ads}^{3+/2+}$ couple because the formal potential could be affected by the possible oligomerization of fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ in the reaction solution at pH 4–5, the $CoP(py)_3py$ ligand differs from the simple pyridine ligand of Fig. 5, and the formal potential of the adsorbed complex could differ from the value measured in solution for $Ru(NH_3)_3(OH_2)_2py^{3+/2+}$. The peak labeled II in Fig. 7(C) is believed to arise from Ru centers in which two of the original aqua ligands have been replaced by pyridine ligands of the adsorbed $CoP(py)_4$. The difference between the potentials of peaks I and II in Fig. 7 is similar to the difference between the peaks in Fig. 5 which were identified as arising from
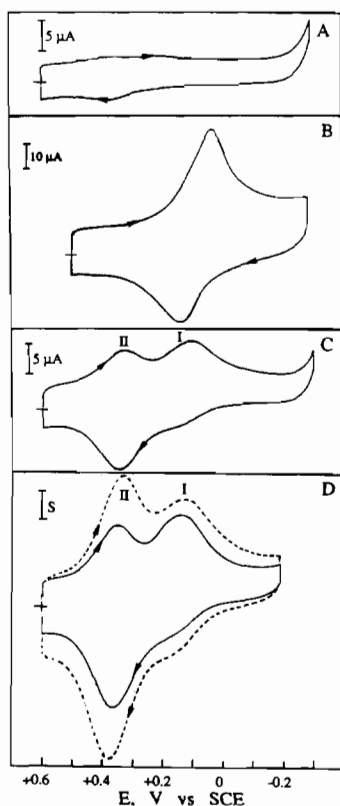
the $Ru(NH_3)_3(OH_2)_2py^{3+/2+}$ and $Ru(NH_3)_3(OH_2)$-$(py)_2^{3+/2+}$ couples, which supports the proposed assignment of the two peaks in Fig. 7. No evidence of the formation of $Ru(NH_3)_3(OH_2)(py)_2^{2+}$ was seen in the voltammograms recorded in homogeneous solutions of pyridine and fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ (Fig. 5) where the latter was present in a three-fold molar excess. Under these conditions only the $Ru(NH_3)_3(OH_2)_2py^{2+}$ complex is formed which is not surprising. The fact that the doubly substituted complex is apparently formed when adsorbed $CoP(py)_4$ is reacted with a very large excess of fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ is presumably because the relative molar excesses are reversed on the electrode surface where an abundance of pyridine ligands awaits the first $Ru(NH_3)_3(OH_2)_2^{2+}$ centers that coordinate to the adsorbed porphyrin.

Increasing the length of time that the adsorbed $CoP(py)_4$ was allowed to react with fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ increased the magnitudes of the two voltammetric waves but did not produce additional waves (Fig. 7(D)). Thus, no evidence of the formation of fac-$Ru(NH_3)_3(py)_3^{2+}$ centers was found. This result is not difficult to understand considering the steric difficulties that would be encountered in attempting to coordinate three pyridine ligands and the large porphyrin to which they are bonded onto a single triangular face of the coordination octahedron about the Ru(II) center.

If freshly polished graphite electrodes are exposed to solutions of fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ without first depositing $CoP(py)_4$ on their surfaces, the cyclic voltammetric response remains constant and featureless as in Fig. 7(A).

A voltammetric response with a pair of reduction peaks very similar to those shown in Fig. 7(C) and (D) was also obtained with cis-$Ru(NH_3)_4(OH_2)_2^{2+}$ as the ruthenation reagent. Thus, the presence of (at least) two possible coordination sites on the Ru(II) center appears to be sufficient to produce the double reduction peaks. The peaks shown in Fig. 7(D) were quite stable and did not undergo further changes if the reaction time was extended. The anodic peak of couple I is notably smaller than its cathodic counterpart while the converse is true of couple II. In addition, the relative magnitudes of the cathodic peaks change with the scan rate. Peak II increases at the expense of peak I as the scan rate is increased (dashed curve in Fig. 7(D)). The pattern is consistent with the presence of a 'square scheme' in which the coordination environment of the ruthenium centers changes when their oxidation state is altered. However, it seems very unlikely that pyridine–ruthenium bonds could be broken and reformed in the highly acidic supporting electrolyte employed. Thus, although the origin of the pair of voltammetric peaks seems reasonably clear (vide supra), the reason

for the inequality of the anodic and cathodic peak currents remains to be established.

The total area inscribed by both of the waves in Fig. 7(D) is essentially equal for the cathodic and anodic pairs. The averages of the cathodic and anodic charges obtained from the areas of voltammograms for several electrodes were used to determine the total quantity of ruthenium present on the electrode surface. The total quantity of cobalt porphyrin present was evaluated similarly from the area of voltammograms recorded in DMF (Fig. 7(B)). A summary of the results obtained is given in Table 1. About 2.9 ruthenium centers per porphyrin molecule are present on electrode surfaces which are coated with $CoP(py)_4$ and exposed to fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ for 48 h. This result contrasts with the ~4 ruthenium centers per porphyrin molecule that were obtained when $Ru(NH_3)_5OH_2^{2+}$ was the ruthenating reagent [2,3].

The voltammetric evidence in Fig. 7 that both singly and doubly pyridine-substituted Ru centers are generated by the reaction of fac-$Ru(NH_3)_3(OH_2)_3^{2+}$ and adsorbed $CoP(py)_4$ requires that the doubly substituted Ru centers are coordinated to two different cobalt porphyrins because the coordination of two pyridine ligands from one $CoP(py)_4$ molecule to the same Ru center is not sterically possible. The relatively large number of doubly pyridine-substituted Ru centers evident from the magnitude of peak II in Fig. 7(D) suggests that a polymeric network of ruthenium-bridged porphyrins may be formed. A structure such as the one shown in Fig. 8(A) would produce an average ratio of Ru centers to cobalt porphyrins of about 3 which is near the observed value of 2.9 (Table 1). However, the structure corresponds to about twice as many singly as doubly pyridine-substituted Ru centers while the areas of the cathodic waves in Fig. 7(D) indicates comparable quantities of each type of Ru center. It is

Table 1
Average number of Ru(II) centers coordinated to the pyridine sites in 3.7×10^{-9} mol cm^{-2} of $CoP(py)_4$[a] adsorbed on graphite electrodes

Electrode number	10^9 $(\Gamma_{Ru})_{cat}$[b] (mol cm^{-2})	10^9 $(\Gamma_{Ru})_{an}$[c] (mol cm^{-2})	10^9 Γ_{Ru}[d] (mol cm^{-2})	Γ_{Ru}/Γ_{Co}
1	10.2	10.7	10.5	2.8
2	10.6	10.8	10.7	2.9
3	11.0	10.2	10.6	2.9
4	12.1	11.1	11.6	3.1
5	10.7	9.4	10.0	2.7
				2.9 av.

[a]Evaluated from the area of voltammograms such as the one in Fig. 7(B).
[b]Quantity of Ru on the surface evaluated from the area inscribed by cathodic waves such as those in Fig. 7(D).
[c]Quantity of Ru on the surface evaluated from the area inscribed by anodic waves such as those in Fig. 7(D).
[d]The average of $(\Gamma_{Ru})_{cat}$ and $(\Gamma_{Ru})_{an}$.

not possible to specify a precise structure of the adsorbed catalyst coating on the basis of the available evidence, but a cross-linked polymeric structure like that in Fig. 8(B) which contains comparable quantities of the two types of Ru centers is one possibility among the many that could be envisaged. Additional evidence supporting the formation of a cross-linked network of the type shown in Fig. 8(B) during the ruthenation reaction is the unusual stability of the coatings that are obtained. Coatings prepared by ruthenation with *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ (and *cis*-$Ru(NH_3)_4(OH_2)_2^{2+}$) are retained on the electrode surface during many cyclic voltammetric sweeps in 0.5 M $HClO_4$ while coatings prepared from $Ru(NH_3)_5OH_2^{2+}$ are lost from the surface at a much higher rate under these conditions (Fig. 9). (The loss of the latter coatings from electrode surfaces can be observed from the gradual increase in the yellow color of the supporting electrolyte solution. No color develops with coatings prepared from *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$.) The higher stability of the coatings obtained with *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ and the relatively positive potential of the first Ru(III)/Ru(II) couple made them attractive as potential electrocatalysts for the reduction of O_2.

3.4. Catalysis of the electroreduction of O_2 by coatings believed to be of the type depicted in Fig. 8(B)

The cyclic voltammetric response obtained in the absence and presence of O_2 from a freshly polished graphite electrode which had been exposed to the ruthenating solution for several hours is shown in Fig. 10(A). A modest increase in the catalytic activity of the electrode surface results from its lengthy exposure to solutions of *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$, possibly as a result of insoluble condensation products which slowly accumulate on the electrode surface. The origin of the activity is uncertain but it did not interfere significantly in subsequent measurements because it occurs at potentials substantially more negative than those obtained with electrodes on which $CoP(py)_4$ is adsorbed. The cyclic voltammetry of a coating of unruthenated $CoP(py)_4$ in the presence and absence of O_2 is shown in Fig. 10(B). The corresponding responses obtained after the coating was ruthenated by reaction with *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ are shown in Fig. 10(C). With the ruthenated coating, the catalyzed reduction of O_2 begins at the potential where the doubly pyridine-substituted Ru(III) centers are reduced to Ru(II) and the reduction current is notably larger than that obtained at electrodes coated only with unruthenated $CoP(py)_4$ (Fig. 10(B)). There is no additional enhancement evident in the rate of reduction of O_2 near the potential (0.1 V) where the singly pyridine-substituted ruthenium centers are reduced, probably because most of the O_2 is consumed in the catalytic reduction which proceeds at the first
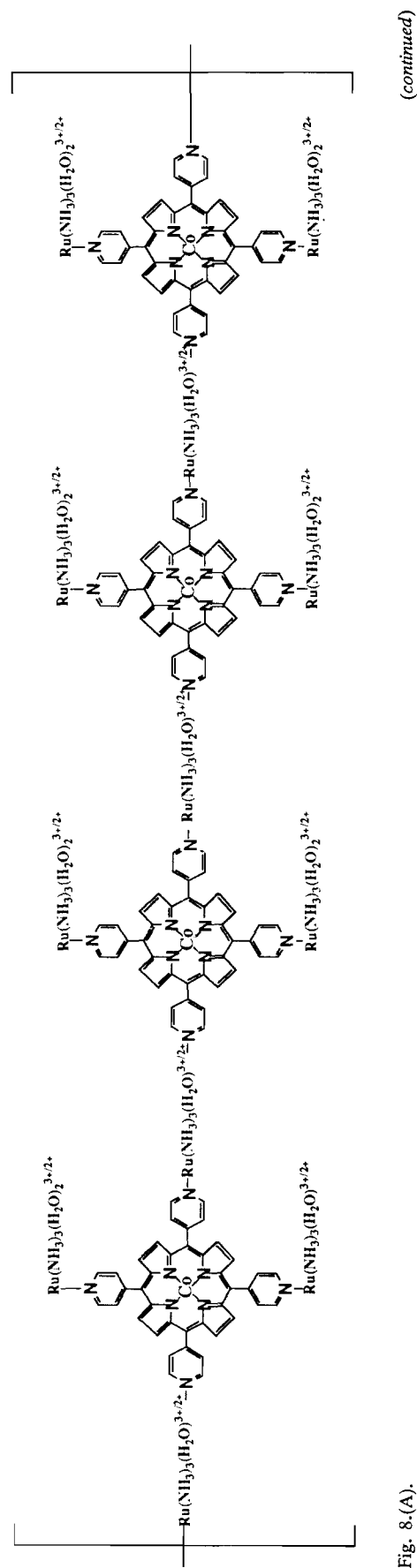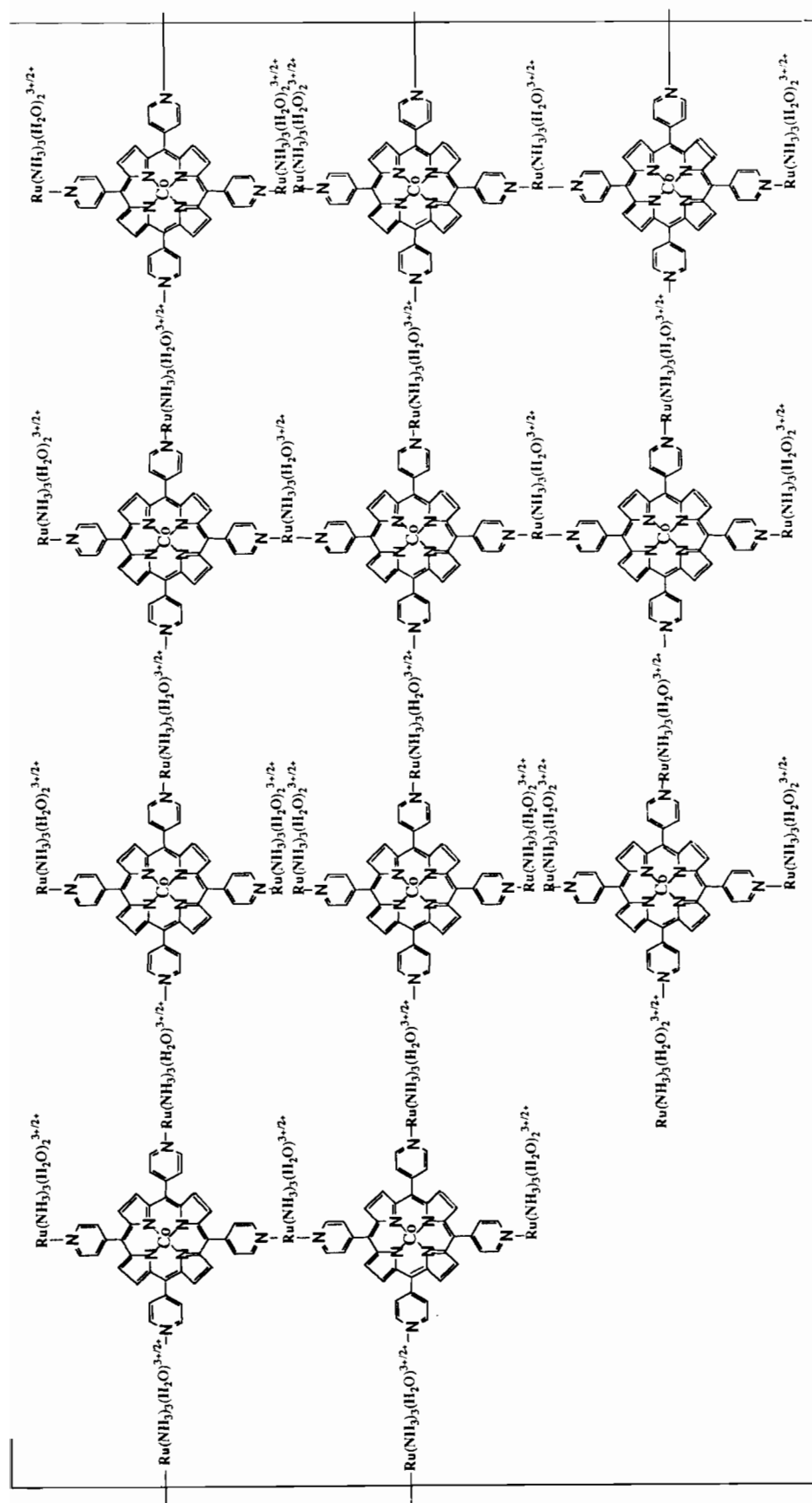

Fig. 8.(A).

(continued)

Fig. 8. (A) A ruthenium-bridged network of adsorbed CoP(py)$_4$ molecules containing about 3 Ru centers per CoP(py)$_4$ molecule. (B) Example of a coating structure containing comparable quantities of terminal and bridging Ru centers.

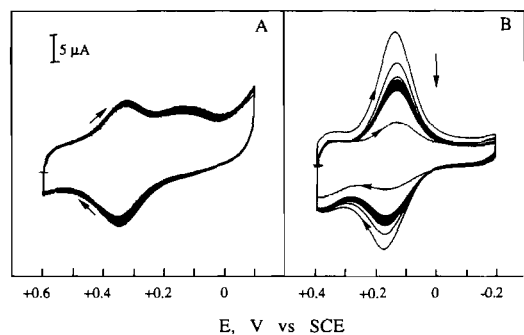Fig. 9. Repetitive cyclic voltammograms of coatings prepared by reaction of CoP(py)$_4$ adsorbed on graphite electrodes with (A) fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$ or (B) Ru(NH$_3$)$_5$(OH$_2$)$^{2+}$. After the ruthenation reaction was complete the electrodes were transferred to a 0.5 M HClO$_4$ supporting electrolyte and scanned continuously between 0.6 and −0.1 V at 10 mV s^{-1} for 90 min.
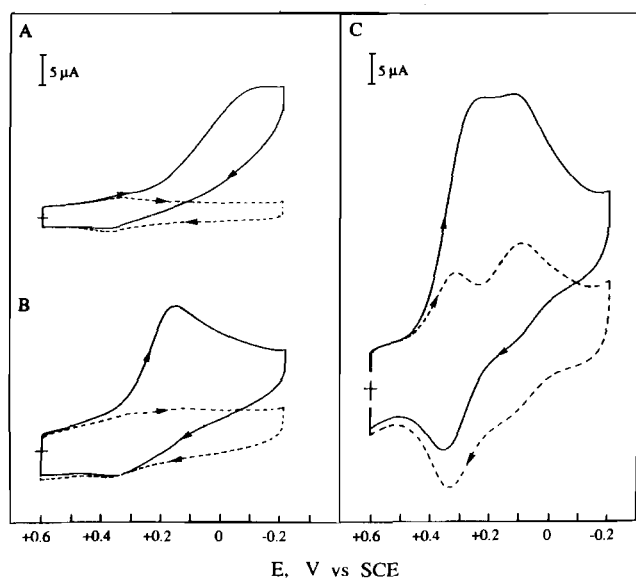

Fig. 10. Cyclic voltammetry with graphite electrodes in the absence (dashed lines) and in the presence (solid lines) of 0.28 mM O$_2$. (A) The freshly polished electrode was immersed in a 15 mM fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$ solution for 6 h and transferred to the pure supporting electrolyte to record the voltammograms. (B) Electrode coated with 3.7×10^{-9} mol cm^{-2} of CoP(py)$_4$. (C) After the coating in (B) had been ruthenated by reaction with fac-Ru(NH$_3$)$_3$(OH$_2$)$_3$$^{2+}$. Supporting electrolyte: 0.5 M HClO$_4$ + 0.5 M NH$_4$PF$_6$. Scan rate: 10 mV s^{-1}.

Ru(III) reduction wave. To obtain more quantitative data, rotating disk electrodes were employed.

Shown in Fig. 11(A) are current–potential curves for the reduction of O$_2$ at a rotating graphite disk electrode coated with the ruthenated catalyst. The response from the catalyst coating in the absence of O$_2$ is shown at the bottom of Fig. 11(A). The Levich and Koutecky–Levich plots [11] are shown in Fig. 11(B) and (C), respectively. The reduction of O$_2$ at the rotating disk electrode begins at potentials near the catalyst wave labeled II and the slope of the Koutecky–Levich plot (Fig. 11(C)) indicates that a four-electron reduction
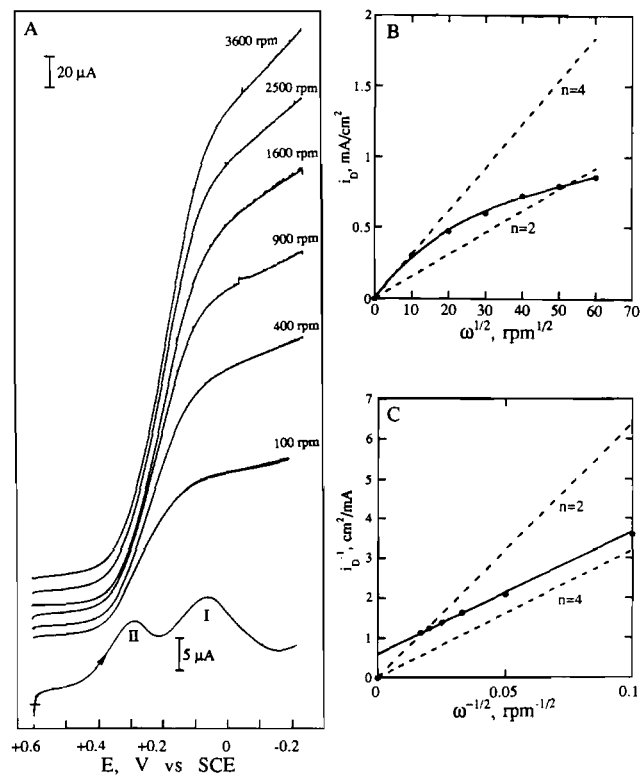

Fig. 11. (A) Current–potential curves for the reduction of 0.28 mM O$_2$ at a catalyst-coated rotating graphite disk electrode. The rotation rates are indicated and the electrode potential was scanned at 2 mV s^{-1}. The lowest curve shows the response obtained from the catalyst coating in the absence of O$_2$ at a scan rate of 10 mV s^{-1} and a higher current sensitivity. Supporting electrolyte: 0.5 M HClO$_4$ + 0.5 M NH$_4$PF$_6$. (B) Levich plot of plateau current vs. (rotation rate)$^{1/2}$ for the curves in (A). (C) Koutecky–Levich plot of the data in (B). The dashed lines are the calculated responses for the diffusion–convection controlled reduction of O$_2$ by 2 or 4 electrons.
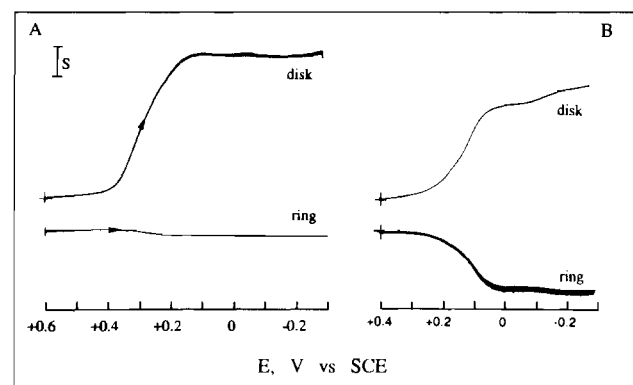
Fig. 12. Reduction of 0.28 mM O$_2$ at a rotating platinum ring–graphite disk electrode. (A) The graphite disk was coated with ruthenated catalyst as in Fig. 11. (B) The disk was coated with CoP(py)$_4$. The platinum ring was maintained at 1.0 V where H$_2$O$_2$ is oxidized to O$_2$. Rotation rate: 100 rpm. Scan rate: 2 mV s^{-1}. $S = 10$ μA for disk currents and 5 μA for ring currents.

is obtained. This point was confirmed in an experiment with a rotating platinum ring–graphite disk electrode, as shown in Fig. 12. The graphite disk was coated with

CoP(py)$_4$ and exposed to *fac*-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ to prepare the catalyst. The resulting electrode was then used to reduce O$_2$ at the disk and any H$_2$O$_2$ produced was detected with the platinum ring electrode. Before the CoP(py)$_4$ coating was exposed to *fac*-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ the current at the platinum ring electrode corresponded to essentially quantitative reduction of O$_2$ to H$_2$O$_2$ (Fig. 12(B)). However, after ruthenation of the adsorbed porphyrin the much smaller ring current corresponded to less than 10% reduction of O$_2$ to H$_2$O$_2$. The remaining O$_2$ is reduced to H$_2$O as was inferred from the slope of the Koutecky–Levich plot in Fig. 11(C). Thus, the ruthenation of the adsorbed cobalt porphyrin with *fac*-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ converts it from a two- to a four-electron electrocatalyst for the reduction of O$_2$. In separate experiments the ruthenated porphyrin was shown to be inactive toward the reduction of H$_2$O$_2$ so the four-electron reduction of O$_2$ does not proceed in sequential steps with H$_2$O$_2$ as an intermediate. Ruthenation with *fac*-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ of cobalt-free tetrapyridyl-porphyrin adsorbed on the electrode surface produced clear responses from the ruthenium centers coordinated to the pyridine sites but no corresponding catalytic activity for the reduction of O$_2$.

The voltammogram for the catalyst in the absence of O$_2$ is shown at the bottom of Fig. 11(A). It was recorded at a higher scan rate than was used to record the rotating disk voltammograms in order to obtain clear peaks from the adsorbed catalyst. As was true of the cyclic voltammogram in Fig. 10(C), the catalysis of the reduction of O$_2$ commences near the peak potential of wave II where the doubly pyridine-substituted, bridging Ru centers of the catalyst coating are reduced. A significant quantity of the Ru centers in structures such as that in Fig. 8(B) are singly pyridine-substituted and are therefore not reduced before the potential reaches wave I. (A structure in which *only* doubly pyridine-substituted rutheniums were present, would have only 2 Ru centers per cobalt porphyrin instead of the 2.9 observed.) Thus, complete reduction of all ruthenium centers coordinated to the cobalt porphyrin is evidently not required to initiate the four-electron catalyzed reduction of O$_2$ (Fig. 11(A)). When the potential of the rotating disk electrode reaches the vicinity of 0.1 V, where the remaining Ru centers are reduced, there is no marked increase in the O$_2$ reduction current (Fig. 11(A)). Since it is clear from the non-linearity of the Levich plot in Fig. 11(B) that substantial amounts of unreduced O$_2$ remain at the electrode surface at rotation rates above 400 rpm, the insensitivity of the current to the reduction of the singly pyridine-substituted Ru centers shows that these additional Ru centers provide no dramatic increase in the catalytic activity of the adsorbed coating. The enhancement in reactivity toward the four-electron reduction of O$_2$

provided by the Ru(II) sites becomes largely expressed near 0.3 V where only the bridging, doubly pyridine-substituted Ru centers are reduced. The tendency for the plateaux of the current–potential curves in Fig. 11(A) to become more inclined as the rotation rate increases (and more unreduced O$_2$ remains at the electrode surface) may reflect increasing participation in the catalytic reduction of O$_2$ by the less active electrocatalytic sites produced on the graphite electrode surface by its lengthy exposure to the solution of *fac*-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ (Fig. 10(A)).

Deviations from linearity of data such as those in Fig. 11(B) have been attributed in previous studies [2,3] to the limitation on the O$_2$ reduction currents imposed by the kinetics of the association reaction between O$_2$ and the cobalt center of the adsorbed porphyrin, reaction (7).

$$CoP + O_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} PCoO_2 \qquad (7)$$

The rate of reaction (7) in the forward direction can be estimated from the current derived from the intercept of Koutecky–Levich plots such as the one in Fig. 11(C) [12]. The reciprocal of the intercept defines a kinetic current, i_k, given by Eq. (8) [13]

$$i_k = nFAk_f\Gamma_{cat}C_{o2} \qquad (8)$$

where $n = 4$ for the four-electron reduction, F is Faraday's constant, A is the electrode area, Γ_{cat} is the quantity of catalyst on the electrode surface, C_{o2} is the concentration of O$_2$ in the solution and k_f is the rate constant governing the forward direction of reaction (7). Values of i_k were evaluated from the intercepts of Koutecky–Levich plots obtained with four concentrations of O$_2$ prepared from mixtures of O$_2$ and Ar of known compositions. The results are plotted in Fig. 13. The linearity of the plot shows that the current-limiting reaction is first-order in O$_2$ and the slope of
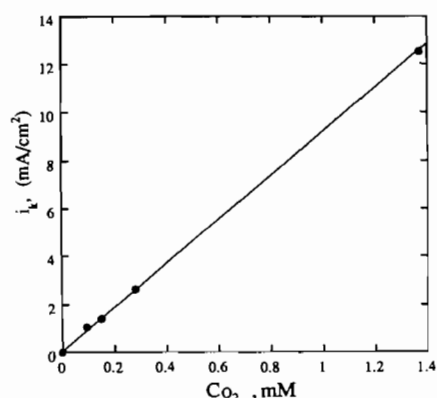

Fig. 13. Kinetic currents for the forward direction of reaction (7) evaluated from the intercepts of Koutecky–Levich plots such as the one in Fig. 11 (C). The concentration of O$_2$ which was varied by means of a calibrated mixing valve. Supporting electrolyte: 0.5 M HClO$_4$ + 0.5 M NH$_4$PF$_6$.

Table 2
Comparison of ruthenated cobalt porphyrins as electrocatalysts for the reduction of dioxygen

Catalyst	$E^f(Ru^{3+/2+})^a$ (V vs. SCE)	$E_{1/2}(O_2)^b$ (V vs. SCE)	n^c	$10^{-4}\,k_f^d$ $(M^{-1}\,s^{-1})$	Ref.
CoP(Py)$_4$		+0.16	2.0	0.75	[14]
[CoP(pyRu(NH$_3$)$_5$)$_4$]$^{8+}$	+0.14	0.23	3.97	0.44	[2,11]
[CoP(Ph)$_x$(pyRu(NH$_3$)$_5$)$_{4-x}$]$^{(8-2x)+\,e}$					
$x=1$	+0.14	0.22	3.84	5.3	[3]
$x=2$	+0.15	0.195	1.98	4.9	[3]
$x=3$	+0.12	0.17	1.97	1.5	[3]
See Fig. 8(B)	+0.33^f	0.29	4.0	2.3	this work

[a] Formal potential of the Ru(III)/Ru(II) couple coordinated to the pyridine ligands of the adsorbed cobalt porphyrins.
[b] Half-wave potential for the reduction of O_2 at catalyst-coated rotating disk electrodes in air-saturated solutions at 100 rpm.
[c] Apparent number of electrons involved in the reduction of O_2 as estimated from the slopes of Koutecky–Levich plots.
[d] Rate constant for the reaction between O_2 and the adsorbed catalyst as estimated from the intercepts of Koutecky–Levich plots.
[e] Ph = phenyl.
[f] Formal potential of the more positive, catalytically active couple.

the line corresponds to $k_f = 2.3 \times 10^4$ M^{-1} s^{-1}. This value of k_f is in the same range as values obtained in previous studies with adsorbed cobalt porphyrin catalysts (Table 2).

4. Comparison and concluding remarks

It may be of interest to compare the new electro-catalyst for the reduction of O_2 prepared from fac-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ and CoP(py)$_4$ with the analogs which have been described previously [2,3]. A comparative summary is given in Table 2. The replacement of Ru(NH$_3$)$_5$OH$_2^{2+}$ by fac-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ as the ruthenating agent leads to an adsorbed catalyst which operates at more positive potentials than the previous examples and yields comparable plateau currents, i.e. comparable values of k_f. In addition, the formation of what is believed to be a ruthenium-cross-linked polymeric coating results in a catalyst which is retained on the electrode surface for longer periods.

The initiation of the catalytic reduction at the potential where the first reduction of the bridging Ru centers proceeds is consistent with the proposal that electronic effects at the cobalt center, transmitted via backbonding by the reduced Ru centers, are responsible for the enhanced, four-electron catalytic activity exhibited by ruthenated CoP(py)$_4$ molecules [3]. The persistence of this phenomenon with the doubly pyridine-substituted Ru centers generated in this study allowed the catalysis of the reduction of O_2 to proceed at the more positive potential where these Ru centers are reduced. Attempts to shift the potential to even more positive values by coordinating a third pyridine or a pyrazine ligand to the Ru centers were not successful. No substitution of the last aqua ligand of the Ru(NH$_3$)$_3$(pyPpy$_3$Co)$_2$(OH$_2$)$^{2+}$ complex was observed, presumably because of the steric barrier presented by

the two porphyrin molecules bound to the same triangular face of the coordination octahedron of Ru(II).

It would be of interest to attempt to prepare similar catalyst coatings using mer-Ru(NH$_3$)$_3$(OH$_2$)$_3^{2+}$ as the ruthenating agent because bridging Ru centers with $trans$ configurations of two pyridine ligands (and the porphyrin molecules to which they are pendant) could be more susceptible to replacement of the remaining aqua group by a suitable unsaturated ligand to produce a catalyst which might function at potentials as positive as 0.35–0.40 V versus SCE.

Of course, attempts to shift the operating potential of electrocatalysts for the reduction of O_2 based on cobalt porphyrins to more positive values will ultimately be limited by the formal potential of the adsorbed Co^{III}P/Co^{II}P couple because only Co^{II}P is capable of binding and activating O_2 molecules. The formal potential of the Co^{III}P/Co^{II}P couple of CoP(py)$_4$ has been reported as 0.55 V [14]. To fashion electrocatalysts for the four-electron reduction of O_2 which would operate at potentials closer to the formal potential of the O_2/H$_2$O couple (1.0 V versus SCE in 1 M H$^+$) will require porphyrin derivatives with more positive formal potentials for the Co^{III}P/Co^{II}P couple or new molecules based on entirely different catalytic centers.

Acknowledgements

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