

# Electrocatalysis of the Reduction of Dioxygen by Adsorbed Cobalt 5,10,15,20-Tetraarylporphyrins to Which One, Two, or Three Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> Centers Are Coordinated

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The reactions of Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> with the pyridine sites in (5-(4-pyridyl)-10,15,20-triphenylporphyrinato)cobalt(II), (5,10-bis(4-pyridyl)-15,20-diphenylporphyrinato)cobalt(II), (5,10-bis(4-pyridyl)-15,20-bis(4-(trifluoromethyl)phenyl)porphyrinato)cobalt(II), (5,15-bis(4-pyridyl)-10,20-diphenylporphyrinato)cobalt(II), and (5,10,15-tris(4-pyridyl)-20-phenylporphyrinato)cobalt(II) adsorbed on pyrolytic graphite electrodes produce the mono-, di-, and triruthenated complexes. The adsorbed complexes act as catalysts for the reduction of dioxygen. The mono- and diruthenated complexes catalyze the two-electron reduction of dioxygen to hydrogen peroxide, whereas the triruthenated complex catalyzes the four-electron reduction to water. The preparation and electrocatalytic behavior of the catalysts are described. A comparison of the catalysts has provided additional insight into the mechanisms by which they operate in catalyzing the electroreduction of dioxygen.

## Introduction

In recent studies, a method for the coordination of four Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> groups to (5,10,15,20-tetrakis(4-pyridyl)porphyrinato)cobalt(II) (CoP(py)<sub>4</sub>) incorporated in Nafion coatings on electrode surfaces<sup>1</sup> or adsorbed directly on the surface of pyrolytic graphite electrodes<sup>2</sup> was described. The resulting tetraruthenated complex is an effective catalyst for the four electron reduction of dioxygen to water while its nonruthenated precursor catalyzes only the two-electron reduction. Evidence was presented that the four-electron reduction of O<sub>2</sub> occurred only when the reducing electrons were passed to the O<sub>2</sub> via the coordinated Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> centers.<sup>1</sup> However, it was not established if four coordinated Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> centers were required to achieve the four-electron reduction or if, for example, one or two rapidly cycling centers might suffice. To address this question experimentally, we decided to compare the behavior of the set of cobalt porphyrins with all possible combinations of 4-pyridyl or phenyl groups as substituents. The structures of the set of porphyrins examined in this study are shown in Figure 1.

In addition to providing possible electron donors, the introduction of substituents onto the porphyrin ring also affects the formal potential of the Co(III)/Co(II) couple of the porphyrin which would be expected to alter the interaction of the Co(II) center with O<sub>2</sub>.<sup>3</sup> An attempt was made to explore the effect of this factor on the catalytic activity of the cobalt porphyrins by comparing the behavior of an additional porphyrin derivative in which a strongly electron-withdrawing functionality was present in the phenyl groups. The preparation of electrode surfaces coated with the cobalt porphyrins of Figure 1, the coordination of Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> and Ru(edta)<sup>2-</sup> to them, and the electrocatalytic behavior of the resulting complexes toward the reduction of O<sub>2</sub> are described in this report. The results provide additional insight into the mechanisms by which the catalysts function.

## Experimental Section

**Materials.** All chemicals were reagent grade unless otherwise specified. The preparation of solutions of Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> was previously de-

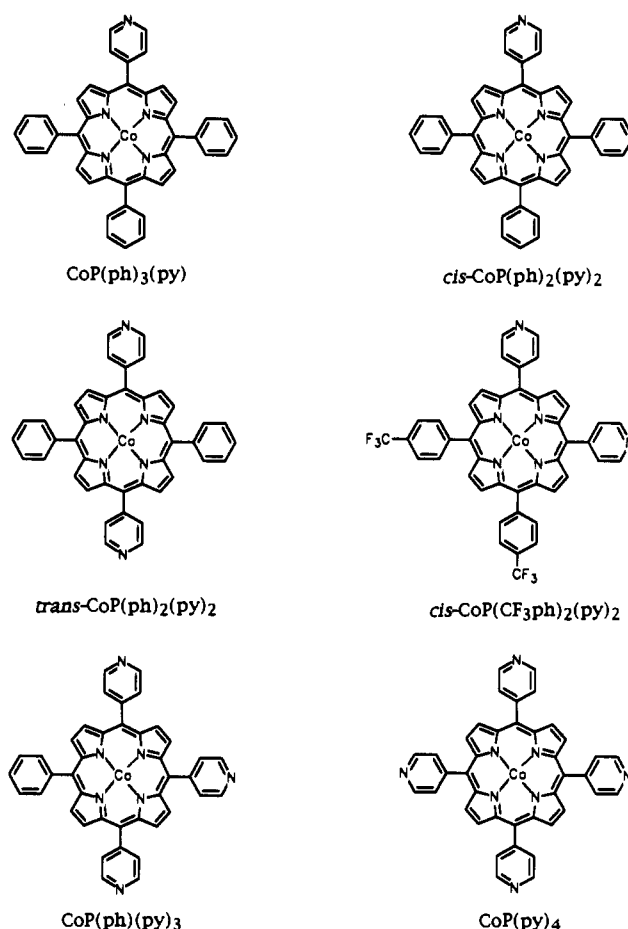


Figure 1. Structures of the cobalt(II) porphyrins examined in this study.

scribed.<sup>2</sup> The following mixed pyridine- and phenyl-substituted porphyrins are known compounds which were synthesized and purified according to a published procedure<sup>4</sup> (in some cases, the mole ratios of benzaldehyde to 4-pyridinecarboxaldehyde were altered to improve yields): 5,10,15,20-tetraphenylporphyrin (PPh<sub>4</sub>), 5-(4-pyridyl)-10,15,20-triphenylporphyrin (PPh<sub>3</sub>py), 5,10-bis(4-pyridyl)-15,20-diphenylporphyrin (*cis*-PPh<sub>2</sub>(py)<sub>2</sub>), 5,15-bis(4-pyridyl)-10,20-diphenylporphyrin (*trans*-PPh<sub>2</sub>(py)<sub>2</sub>),

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<sup>†</sup> Contribution No. 8769.

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5,10,15-tris(4-pyridyl)-20-phenylporphyrin (PPh(py)<sub>3</sub>), and 5,10,15,20-tetrakis(4-pyridyl)porphyrin (P(py)<sub>4</sub>)<sup>5</sup>.

5,10-Bis(4-pyridyl)-15,20-bis(4-(trifluoromethyl)phenyl)porphyrin (*cis*-P(CF<sub>3</sub>Ph)<sub>2</sub>(py)<sub>2</sub>) was prepared by a procedure analogous to that employed for the other porphyrins but with some modifications: Freshly distilled pyrrole (7.0 mL, 100 mmol), freshly distilled 4-pyridinecarboxaldehyde (7.1 mL, 75 mmol), and 98% 4-(trifluoromethyl)benzaldehyde (3.4 mL, 25 mmol) were added to 250 mL of 99% propionic acid, and the mixture was refluxed open to the air for 1 h. The reaction mixture was cooled in an ice-water bath for 15 min. Then 50 mL of the reaction mixture was added to a cooled (ice-water bath) solution consisting of 50 mL of 29% aqueous ammonia in 200 mL of methanol. The resulting precipitate was collected by suction filtration on a Buchner funnel (4–5.5- $\mu$  fritted glass disk) and washed with methanol. The procedure was repeated with additional 50-mL portions of the reaction mixture until it was all consumed. After air-drying of the crude product, 1.84 g of a violet powder was obtained. The product was inspected by silica gel thin-layer chromatography and found to be a mixture of six components, as would be expected if all possible pyridyl- and (trifluoromethyl)phenyl-substituted porphyrins were present. The *R<sub>f</sub>* values of the components in 97% chloroform/3% ethanol were 0.74, 0.57, 0.42, 0.24, 0.16, and 0.10. By comparison with the *R<sub>f</sub>* values for the known pyridyl-phenyl porphyrins<sup>4</sup> it was possible to assign the *R<sub>f</sub>* values respectively to 5,10,15,20-tetrakis(4-(trifluoromethyl)phenyl)porphyrin, 5-(4-pyridyl)-10,15,20-tris(4-(trifluoromethyl)phenyl)porphyrin, 5,15-bis(4-pyridyl)-10,20-bis(4-(trifluoromethyl)phenyl)porphyrin, 5,10-bis(4-pyridyl)-15,20-bis(4-(trifluoromethyl)phenyl)porphyrin, 5,10,15-tris(4-pyridyl)-20-(4-(trifluoromethyl)phenyl)porphyrin, and 5,10,15,20-tetrakis(4-pyridyl)porphyrin.

The porphyrins were separated by column chromatography with silica gel (Baker for flash chromatography) and a chloroform/ethanol solvent system consisting initially of reagent grade chloroform and gradually changing to a final mixture of 90% chloroform/10% ethanol. The mixture of separated products in the order of decreasing *R<sub>f</sub>* values given above consisted of a trace, 0.5%, 2%, 12.5%, 48%, and 37%. Only *cis*-P(CF<sub>3</sub>Ph)<sub>2</sub>(py)<sub>2</sub> was further purified by sublimation (5  $\times$  10<sup>-3</sup> Torr, 330 °C) and characterized. Its identity was confirmed by elemental analysis, visible spectroscopy, NMR spectroscopy, and comparison with spectroscopic data of the known *cis*-PPh<sub>2</sub>(py)<sub>2</sub><sup>4</sup> and P(CF<sub>3</sub>Ph)<sub>4</sub>.<sup>6</sup>

Anal. Calcd for *cis*-P(CF<sub>3</sub>Ph)<sub>2</sub>(py)<sub>2</sub>, C<sub>44</sub>H<sub>26</sub>N<sub>6</sub>: C, 70.21; N, 11.16; H, 3.48. Found: C, 69.90; N, 11.10; H, 3.56. Visible spectrum [ $\lambda$ , nm, in CHCl<sub>3</sub> ( $\epsilon \times 10^{-4}$  cm<sup>-1</sup> M<sup>-1</sup>): 416 (35), 512 (1.8), 546 (0.6), 588 (0.6), 644 (0.3)]. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.03 (4H, d, pyridyl 2,6), 8.81 (8H, t, pyrrole  $\beta$ ), 8.31 (4H, d, *o*-(trifluoromethyl)phenyl), 8.13 (4H, d, pyridyl 3,5), 8.02 (4H, d, *m*-(trifluoromethyl)phenyl), -2.87 (2H, s, internal pyrrole).

Cobalt(II) was inserted into the porphyrins by reacting a small excess of cobalt acetate tetrahydrate (1.2 mol equiv) and 100 mg of the porphyrin in 15 mL of refluxing *N,N*-dimethylformamide under argon for 30 min.<sup>7</sup> A sample of the reaction mixture in chloroform was analyzed by visible spectroscopy. The spectrum indicated that the cobalt insertion was complete, with the four Q bands of the free base ( $\lambda = 514, 548, 588, \text{ and } 644$  nm) collapsing to one band ( $\lambda = 528$  nm) and the Soret band shifting from 416 to 408 nm. At that point, the reaction mixture was cooled in an ice-water bath for 15 min, 20 mL of chilled distilled water was added, and the resulting precipitate was collected by suction filtration, washed with water and methanol, and dried to give a violet microcrystalline powder.

**Spectroscopic Measurements.** UV-visible spectra were recorded on a Hewlett-Packard 8450A diode-array spectrophotometer and plotted by a Hewlett-Packard 7470A plotter. <sup>1</sup>H NMR spectra were obtained on a 500-MHz Bruker AM 500 spectrometer. <sup>1</sup>H chemical shifts are reported in parts per million downfield of tetramethylsilane at ambient temperature.

**Electrochemical Measurements.** The pyridine used as a solvent was spectral grade (Baker). Tetrabutylammonium perchlorate (Southwestern Analytic, Inc., polarographic grade) was recrystallized from methanol and dried under reduced pressure.

Cyclic, rotating disk, and rotating ring-disk voltammetry were carried out either with previously described instrumentation<sup>1</sup> or with a Bioanalytical Systems, Inc., Model BAS 100B instrument using an MSR rotator (Pine Instruments). Commercial reference electrodes were employed.

Potentials are quoted vs a saturated calomel electrode (SCE) except for the experiments carried out with pyridine as solvent, in which a Ag/AgCl (3 M NaCl) electrode was utilized.

Porphyrins were adsorbed on the surface of pyrolytic graphite electrodes by transferring 15- $\mu$ L aliquots of 0.4 mM solutions of the porphyrins in chloroform (sonication and warming were required to dissolve some of the porphyrins) to the surface of the electrode and allowing the solvent to evaporate at room temperature. Much of the porphyrin in the resulting deposits was lost when the electrodes were subsequently transferred to aqueous solutions, but the quantity of residual, strongly bound porphyrin was reasonably reproducible. The quantities of porphyrin retained on the graphite surface were smaller with chloroform as the solvent than when aqueous solutions of the water-soluble porphyrins were transferred to the electrode surfaces as in ref 2. This difference appears to result from the less rapid evaporation of the aqueous solvent, which leads to more uniform deposits.

To calculate the Levich limiting currents at rotating disk electrodes, the following parameters were used: kinematic viscosity of water, 0.01 cm<sup>2</sup> s<sup>-1</sup>; diffusion coefficient for dioxygen, 1.7  $\times$  10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>; solubility of O<sub>2</sub> in air-saturated solutions, 0.28 mM at 22 °C. Cyclic voltammograms of metalloporphyrins dissolved in pyridine were recorded with a glassy carbon electrode which was polished with 0.05- $\mu$ m alumina to a mirrorlike surface. Experiments were conducted at 22  $\pm$  1 °C.

## Results and Discussion

**Catalyst Preparation.** As in our previous study,<sup>2</sup> the cobalt porphyrin derivatives were adsorbed on the surface of pyrolytic graphite electrodes where they were reacted with Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> to obtain the ruthenated complexes. Like CoPPh<sub>4</sub><sup>8</sup> and CoP(py)<sub>4</sub>,<sup>9</sup> all of the cobalt porphyrins shown in Figure 1 are strongly and irreversibly adsorbed on graphite electrode surfaces. To prepare porphyrin-coated electrodes, aliquots of dilute solutions of the cobalt porphyrins in chloroform were deposited on the surfaces of pyrolytic graphite electrodes and the solvent was allowed to evaporate. The coated electrodes were transferred to an aqueous solution for reaction with Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup>. Unfortunately, the electrochemical responses from the Co(III)/Co(II) couple of the adsorbed porphyrins were too ill-defined to be useful for coulometric estimates of the quantities of the adsorbed porphyrins that remained on the electrode surfaces after they were transferred to aqueous electrolytes. The adsorbed CoP(py)<sub>4</sub> molecule yielded well-defined cyclic voltammograms in pure supporting electrolyte solutions in dimethylformamide,<sup>2</sup> but this property was not exhibited by the other cobalt porphyrins in Figure 1. The quantities of the cobalt porphyrins present on the electrode surfaces were therefore evaluated by means of the cyclic voltammetric responses of the Ru(NH<sub>3</sub>)<sub>5</sub>py<sup>3+/2+</sup> couple produced by reaction of the adsorbed porphyrins with solutions of Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup>.

To coordinate Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> groups to the pyridine sites of the adsorbed porphyrins, the coated electrodes were immersed in an argon-saturated 0.025 M solution of Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> for several hours at room temperature. The reaction solution also contained 0.05 M NH<sub>4</sub>PF<sub>6</sub>. The low solubility of the PF<sub>6</sub><sup>-</sup> salts of the ruthenated porphyrins helped to prevent losses of the adsorbed porphyrins from the electrode surface as the ruthenation reaction proceeded.<sup>2</sup> Although the attachment of Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> groups to the adsorbed porphyrins became evident within 1 h, the reaction was allowed to proceed for 48 h to obtain as much attachment as possible. The extent to which the ruthenation reaction had proceeded was monitored by transferring the electrode from the reaction solution to a supporting electrolyte consisting of 0.5 M NH<sub>4</sub>PF<sub>6</sub> + 0.5 M HClO<sub>4</sub> under argon where cyclic voltammograms were recorded. In Figure 2 are shown the voltammograms obtained for the six cobalt porphyrins both before and after the electrodes on which they were adsorbed had been exposed to the solution of Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> for 48 h. The lack of a response

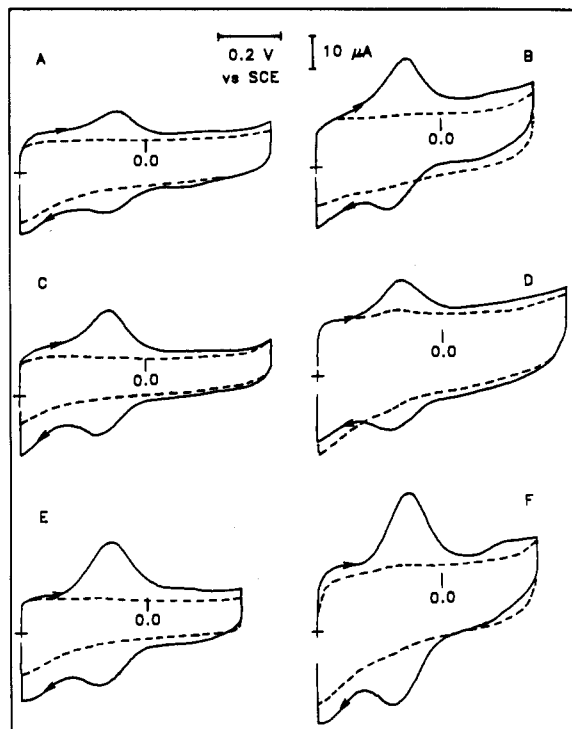
(5) For the nomenclature of porphyrins, see: Nomenclature of Tetrapyrroles (IUPAC Recommendations, 1986). *Pure Appl. Chem.* **1987**, *59*, 779.

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**Figure 2.** Cyclic voltammetry of six cobalt porphyrins adsorbed on pyrolytic graphite electrodes before (---) and after (—) exposure to a 0.025 M solution of  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$  for 48 h: (A)  $\text{CoPPh}_3(\text{py})$ ; (B) *trans*- $\text{CoPPh}_2(\text{py})_2$ ; (C) *cis*- $\text{CoPPh}_2(\text{py})_2$ ; (D) *cis*- $\text{CoP}(\text{CF}_3\text{Ph})_2(\text{py})_2$ ; (E)  $\text{CoPPh}(\text{py})_3$ ; (F)  $\text{CoP}(\text{py})_4$ . In each case 15  $\mu\text{L}$  of a 0.4 mM solution of the porphyrin in chloroform were spread on the graphite surface and the solvent allowed to evaporate. Supporting electrolyte: 0.5 M  $\text{NH}_4\text{PF}_6$ -0.5 M  $\text{HClO}_4$  saturated with argon. Initial potential was 0.4 V. Scan rate = 50  $\text{mV s}^{-1}$ .

**Table I.** Quantities of  $\text{Ru}(\text{NH}_3)_5^{2+}$  Coordinated to the Pyridine Sites of Cobalt Porphyrins Adsorbed on Graphite Electrodes

adsorbed porphyrin	$10^9 \Gamma_{\text{Ru}}^a$ mol $\text{cm}^{-2}$	ratio <sup>b</sup>
$\text{CoPPh}_3\text{py}$	0.55	1
<i>cis</i> - $\text{CoPPh}_2(\text{py})_2$	1.15	2.1
<i>trans</i> - $\text{CoPPh}_2(\text{py})_2$	1.2	2.2
<i>cis</i> - $\text{CoP}(\text{CF}_3\text{Ph})_2(\text{py})_2$	1.1	2.0
$\text{CoPPh}(\text{py})_3$	1.6	2.9
$\text{CoP}(\text{py})_4$	2.1	3.8

<sup>a</sup> Quantity of  $\text{Ru}(\text{NH}_3)_5^{3+/2+}$  groups coordinated to the adsorbed porphyrins as estimated from the areas of cyclic voltammograms such as those in Figure 2. <sup>b</sup> The ratio of  $\Gamma_{\text{Ru}}$  for each porphyrin to  $\Gamma_{\text{Ru}}$  measured for  $\text{CoPPh}_3\text{py}$ .

from the  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  couple in the range of potentials surveyed is evident. Even when the potential range was extended to 0.8 V, no response from the  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  couple was observed. The reversible voltammetric response obtained after the exposure to the  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$  solution appeared near the potential expected for the  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$  couple<sup>10</sup> in each case.

The total quantities of  $\text{Ru}(\text{NH}_3)_5^{2+}$  centers present on the electrode surface were estimated from the areas under the cathodic peaks and are summarized in Table I. The quantities of  $\text{Ru}(\text{NH}_3)_5^{2+}$  groups attached to each porphyrin increased with the number of pyridine groups it contained, as expected if the quantity of porphyrin retained by the electrode surface was about the same for each derivative and the ruthenation was complete in each case (Table I). As was observed with the tetra-ruthenated complex,<sup>2</sup> the quantities of the mono-, di-, and triruthenated complexes stably adsorbed on the electrodes corresponded to multilayers of the complexes. The responses shown in Figure 2 were stable for many hours in electrolytes containing  $\text{PF}_6^-$  anions. In the presence of other anions ( $\text{CF}_3\text{COO}^-$ ,  $\text{ClO}_4^-$ ,  $\text{HSO}_4^-$ ), the porphyrins gradually desorbed from the surface.

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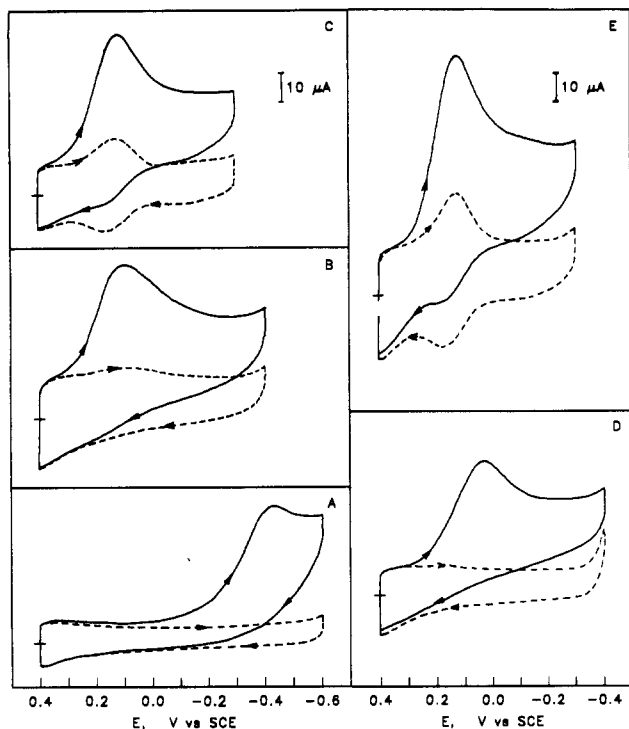
**Table II.** Formal Potentials of the  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$  Couple Coordinated to Cobalt Porphyrins Adsorbed on Graphite Electrodes and Half-Wave Potentials for the Reduction of  $\text{O}_2$  at the Same Electrodes

adsorbed porphyrin	$E^{\circ}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})^a$ V vs SCE	$E_{1/2}(\text{O}_2)^b$ V vs SCE
$\text{CoPPh}_3\text{pyRu}(\text{NH}_3)_5^{2+}$	0.12	$0.17 \pm 0.01$
<i>cis</i> - and <i>trans</i> - $\text{CoPPh}_2(\text{pyRu}(\text{NH}_3)_5)_2^{4+}$	0.14	$0.195 \pm 0.02$
<i>cis</i> - $\text{CoP}(\text{CF}_3\text{Ph})_2(\text{pyRu}(\text{NH}_3)_5)_2^{4+}$	0.15	$0.18 \pm 0.01$
$\text{CoPh}(\text{pyRu}(\text{NH}_3)_5)_3^{6+}$	0.14	$0.22 \pm 0.02$
$\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4^{8+}$	0.14	$0.23 \pm 0.015$

<sup>a</sup> From cyclic voltammograms recorded at 50  $\text{mV s}^{-1}$  in argon-saturated 0.5 M  $\text{NH}_4\text{PF}_6$ -0.5 M  $\text{HClO}_4$ . The values were reproducible to ca.  $\pm 10$  mV. <sup>b</sup> Half-wave potential for the reduction of  $\text{O}_2$  at a rotating pyrolytic graphite disk electrode coated with the porphyrin; rotation rate 100 rpm; supporting electrolyte 0.5 M  $\text{NH}_4\text{PF}_6$ -0.5 M  $\text{HClO}_4$  saturated with air. The values given are the arithmetic mean of several measurements with standard deviations shown.

**Electrochemical Responses of the Adsorbed Complexes.** The average of the cathodic and anodic peak potentials of the cyclic voltammograms in Figure 2 produced essentially the same formal potential of 0.14 V for the  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$  centers in all six of the ruthenated porphyrins in Figure 1 (Table II). This potential is ca. 60 mV more positive than the formal potential of the  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$  couple in solution.<sup>10</sup> The difference in formal potentials probably reflects the presence of the porphyrin molecule in the para position of the pyridine ring, but differences in the strength of the adsorption of the oxidized and reduced complexes and in the supporting electrolyte could also contribute. As was true of the tetra-ruthenated complex examined previously,<sup>2</sup> the porphyrins containing two or three pyridine sites exhibited only single cathodic and anodic voltammetric peaks in the range of potentials near the formal potential of the  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$  couple (Figure 2). The  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$  centers in all of the adsorbed complexes interact with each other too weakly to produce separated voltammetric peaks. The voltammetric responses in Figure 2 have peak widths at half-height of 130, 140, and 150 mV, respectively, for the doubly, triply, and quadruply ruthenated porphyrins, rather than the 90.6 mV expected for an adsorbed, ideally Nernstian couple. In addition, anodic and cathodic peak potentials are separated by ca. 40 mV for all of the complexes instead of the 0 mV expected for Nernstian couples. The response from the singly ruthenated porphyrin was not substantially different; the peak width at half-height was 120 mV. This behavior is indicative of nonideality which may arise from interactions among the closely packed  $\text{Ru}(\text{NH}_3)_5\text{py}$  centers on the electrode surface which, however, are not sufficiently strong to produce multiple peaks in the voltammograms.

**Electrocatalysis of the Reduction of  $\text{O}_2$  by the Adsorbed Cobalt Porphyrins.** The cyclic voltammetric responses for the reduction of  $\text{O}_2$  at graphite electrodes coated with the ruthenated porphyrins from Figure 1 fell into two classes depending on the number of  $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$  groups present in the catalyst. The  $\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4^{8+}$  and  $\text{CoPPh}(\text{pyRu}(\text{NH}_3)_5)_3^{6+}$  catalysts comprised the first class which produced the highest currents. All of the other catalysts belonged to the second class, which yielded smaller reduction currents. A comparison of representative cyclic voltammetric responses obtained with a catalyst from each class is shown in Figure 3. A voltammogram for the reduction of  $\text{O}_2$  at the uncoated electrode is shown in Figure 3A. That in Figure 3B was obtained after *trans*- $\text{CoPPh}_2(\text{py})_2$  was adsorbed on the electrode (the responses from other members of this class were essentially similar). The shift of the reduction to more positive potentials at the coated electrode is typical of cobalt porphyrins, and the magnitude of the peak current is consistent with a two-electron reduction. The response obtained after the adsorbed porphyrin was reacted with  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$  to form  $\text{CoPPh}_2(\text{pyRu}(\text{NH}_3)_5)_2^{4+}$  is shown in Figure 3C. After the contribution from the catalyst itself (dashed line in Figure 3C) was subtracted,



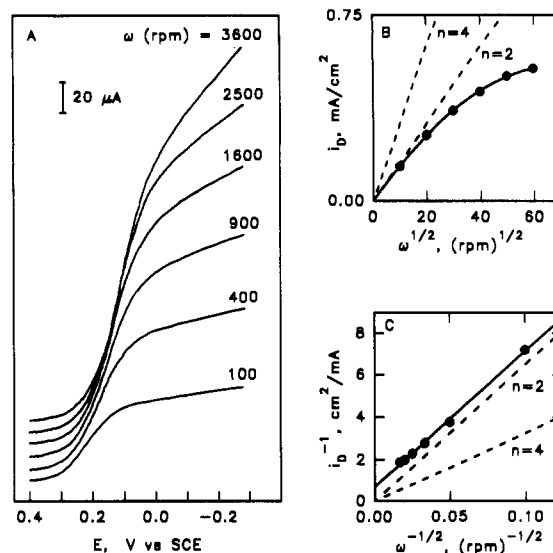
**Figure 3.** Cyclic voltammograms from the reduction of  $O_2$  at electrodes coated with two representative porphyrins: (A) before the pyrolytic graphite electrode was coated; (B) after the electrode was coated with  $trans\text{-CoPPH}_2(\text{py})_2$ ; (C) after the adsorbed porphyrin from (B) was ruthenated by reaction with  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$ ; (D) after the electrode from (A) was coated with  $\text{CoPPH}(\text{py})_3$ ; (E) after the adsorbed porphyrin from (D) was ruthenated by reaction with  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$ . The supporting electrolyte,  $0.5\text{ M NH}_4\text{PF}_6\text{-}0.5\text{ M HClO}_4$ , was saturated with air. The dashed curves are the responses obtained in argon-saturated solutions. Other conditions are as in Figure 2.

the peak current was not changed significantly. The somewhat narrower peak shape suggests that the  $\text{pyRu}(\text{NH}_3)_5^{2+}$  centers may participate in the reduction but the magnitude of the peak current remained consistent with the reduction of  $O_2$  by two electrons.

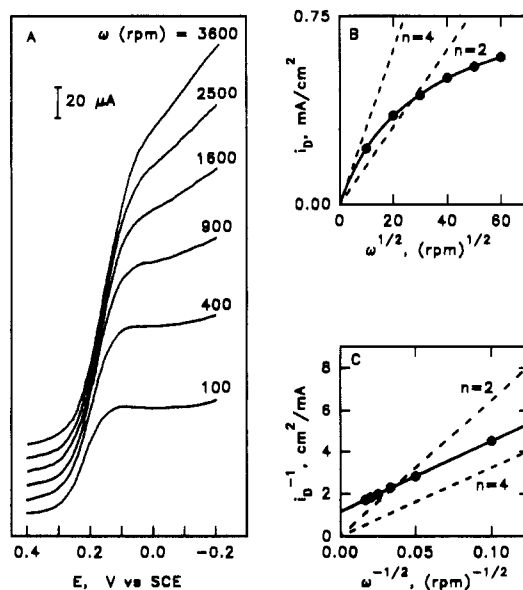
The reduction of  $O_2$  at an electrode coated with  $\text{CoPPH}(\text{py})_3$  is shown in Figure 3D. The current is about the same as that in Figure 3B. However, after three  $\text{Ru}(\text{NH}_3)_5^{2+}$  groups were coordinated to the pyridine sites, the reduction of  $O_2$  produced a larger peak current (Figure 3E), as expected if the reduction involved more than two electrons. The persistence of a small anodic response from the  $\text{pyRu}(\text{NH}_3)_5^{2+}$  groups in the presence of  $O_2$  in Figures 3C and 3E is probably attributable to the portion of the  $\text{pyRu}(\text{NH}_3)_5^{2+}$  centers in the multiple layers of adsorbed catalyst which are not fully accessible to the  $O_2$ . The anodic response was not present when the quantity of catalyst adsorbed was restricted to a single monolayer or less.

**Voltammetry at Rotating Disk and Ring-Disk Electrodes.** More quantitative kinetic data on the behavior of the various catalysts were obtained by means of rotating disk voltammetry. A typical set of results for the same pair of catalysts employed in Figure 3 is shown in Figures 4 and 5. Larger plateau currents resulted when three rather than two  $\text{pyRu}(\text{NH}_3)_5^{2+}$  groups were present in the adsorbed catalyst (compare Figures 4A and 5A); however, both catalysts produced curved Levich plots (Figures 4B and 5B) and the slopes of the Koutecky-Levich plots<sup>11</sup> of (plateau current)<sup>-1</sup> vs (rotation rate)<sup>-1/2</sup> (Figures 4C and 5C) show that with the triply ruthenated catalyst the reduction of  $O_2$  consumes close to four electrons while with the doubly ruthenated catalyst it does not.

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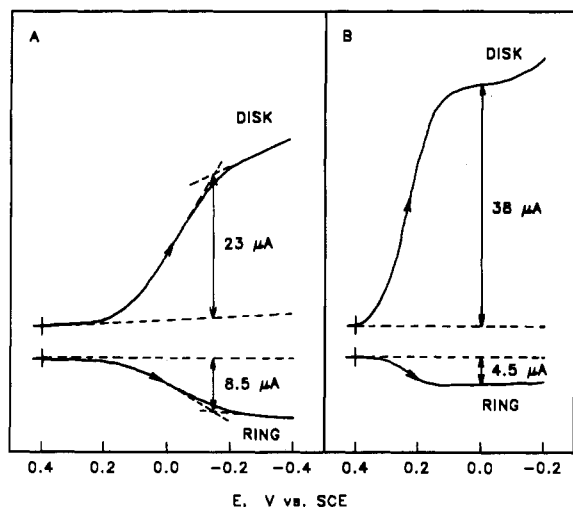
**Figure 4.** Reduction of  $O_2$  at a rotating graphite disk electrode coated with  $4.0 \times 10^{-10}\text{ mol cm}^{-2}$  of  $trans\text{-CoPPH}_2(\text{pyRu}(\text{NH}_3)_5)_2^{4+}$ : (A) current-potential curves for the electrode rotation rates shown (for clarity, the base of each successive curve was adjusted upward; scan rate =  $2\text{ mV s}^{-1}$ ); (B) Levich plot of the plateau currents from (A); (C) Koutecky-Levich plot of the data from (B). The dashed lines are the calculated responses for the diffusion-convection-limited reduction of  $O_2$  by two or four electrons. Supporting electrolyte is as in Figure 3.



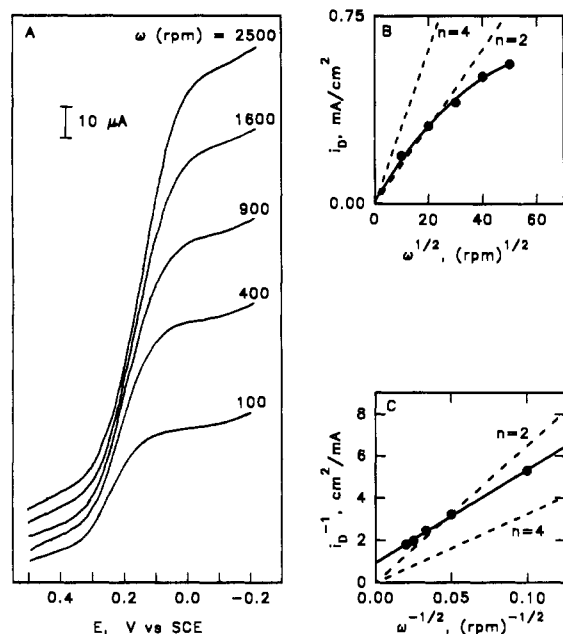
**Figure 5.** Reduction of  $O_2$  at a rotating graphite disk electrode coated with  $9.3 \times 10^{-10}\text{ mol cm}^{-2}$  of  $\text{CoPPH}(\text{pyRu}(\text{NH}_3)_5)_3^{6+}$ . The plots and conditions are as in Figure 4.

None of the complexes in Figure 1 are catalysts for the reduction of  $H_2O_2$ . Thus, the four-electron reductions of  $O_2$  obtained with  $\text{CoPPH}(\text{pyRu}(\text{NH}_3)_5)_3^{6+}$  and  $\text{Co}(\text{pyRu}(\text{NH}_3)_5)_4^{8+}$  do not involve a mechanism in which  $H_2O_2$  is an intermediate. Along the four-electron reduction pathway, the  $O_2$  (presumed to be) activated by coordination to the  $\text{Co}(\text{II})$  center of the catalyst accepts four electrons before  $H_2O_2$  is eliminated from the catalyst-substrate complex.

A rotating graphite disk-platinum ring electrode was employed to determine the quantity of  $H_2O_2$  that results from the reduction of  $O_2$  at electrodes coated with  $\text{CoPPH}(\text{py})_3$  or  $\text{CoPPH}(\text{pyRu}(\text{NH}_3)_5)_3^{6+}$ . The graphite disk was coated with the catalyst and the platinum ring was maintained at  $1.0\text{ V}$  to oxidize the  $H_2O_2$  generated by the reduction of  $O_2$  at the disk. The results are shown in Figure 6. When the graphite disk was coated with  $\text{CoPPH}(\text{py})_3$ , the reduction of  $O_2$  proceeded essentially exclusively to  $H_2O_2$ ; the observed ratio of ring to disk currents was 0.37

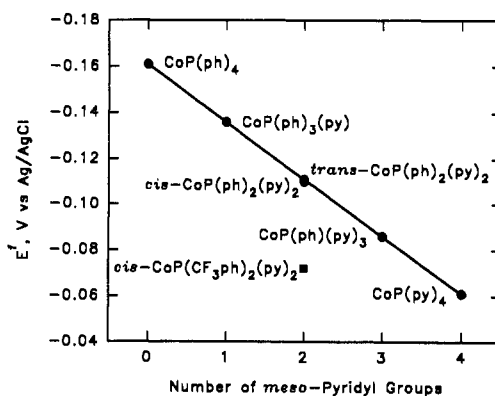


**Figure 6.** Reduction of  $O_2$  at a rotating platinum ring-graphite disk electrode with  $1.2 \times 10^{-9}$  mol  $cm^{-2}$  of (A)  $CoPPh(py)_3$  or (B)  $CoPPh(pyRu(NH_3)_5)_6^{6+}$  adsorbed on the disk. Ring potential = 1.0 V. Collection efficiency of the electrode = 0.39. Rotation rate = 100 rpm. Scan rate =  $2 \text{ mV s}^{-1}$ . Supporting electrolyte is as in Figure 3.



**Figure 7.** Reduction of  $O_2$  at the rotating graphite disk electrode of the commercial rotating ring-disk electrode used in Figure 6: (A) current-potential curves for the electrode rotation rates shown; (B) Levich plot of the plateau currents from (A); (C) Koutecky-Levich plot of the data from (B). Dashed lines and other conditions are as in Figure 4.

compared with a collection efficiency of 0.39 measured with the  $Fe(CN)_6^{3-/4-}$  couple. By contrast, when the graphite disk was coated with  $CoPPh(pyRu(NH_3)_5)_6^{6+}$  the ring current became smaller and the disk current larger. Their ratio corresponded to 70% of the disk current's resulting in the four-electron reduction of  $O_2$  to  $H_2O$ ; i.e., 54% of the  $O_2$  molecules were reduced to  $H_2O$  and 46% to  $H_2O_2$ . This amount of  $H_2O_2$  production is greater than would be expected on the basis of the slope of the Koutecky-Levich plot in Figure 5C for the same catalyst which corresponds to less than 10% of the  $O_2$  molecule's being reduced to  $H_2O_2$ . This apparent discrepancy was traced to differences in the behavior of the homemade and commercial rotating graphite disk electrodes. A set of disk current-potential curves for the commercial electrode is shown in Figure 7 along with the corresponding Levich and Koutecky-Levich plots. The slope of the Koutecky-Levich plot, shown in Figure 7C, is larger than that of the plot in Figure 5C and matches the value which can be calculated from the ratio of ring to disk currents in Figure 6B; the observed slope corresponds



**Figure 8.** Formal potentials of the  $Co^{III}/Co^{II}$  couple as measured by cyclic voltammetry at a glassy carbon electrode for ca. 1 mM solutions of the porphyrins in Figure 1 with pyridine as solvent. Supporting electrolyte: 0.1 M tetrabutylammonium perchlorate. Scan rate =  $10 \text{ mV s}^{-1}$ .

to an apparent  $n$  value of 3.0 compared with a calculated value of 3.1. Thus, the course of the reduction of  $O_2$  as catalyzed by the ruthenated cobalt porphyrins is somewhat dependent on the nature and preparation of the graphite electrode employed. Typically, the homemade, edge-plane pyrolytic graphite rotating disk electrode, which was aggressively polished with 600-grit SiC paper between runs, yielded larger plateau current densities than did the commercial platinum ring-edge-plane graphite disk electrode, which was polished less vigorously to avoid contamination of the disk with Pt from the ring. Both the quantity of catalyst adsorbed on disk electrodes and the surface textures of the polished electrodes were different for the homemade and the commercial electrodes. The underlying reasons for the sensitivity of the results to the electrode surface preparation are not apparent, but surface-dependent changes in the potentials where the two-electron reduction of  $O_2$  proceeds without participation of the  $Ru(NH_3)_5py_2^{2+}$  centers could account for the observed behavior.

**Observations on the Formal Potentials of the  $Co^{III}/Co^{II}$  Couple of the Porphyrins.** The systematic substitution of phenyl by pyridine in the series of cobalt porphyrins in Figure 1 would be expected to alter the formal potentials of the  $Co^{III}/Co^{II}$  couple of the porphyrins.<sup>3</sup> Since the voltammetry exhibited by most of the adsorbed cobalt porphyrins in aqueous media is essentially featureless in the range of potentials where the  $Co^{III}/Co^{II}$  couple is expected, it is not possible to obtain estimates of the formal potentials of all of the porphyrins adsorbed on graphite. We therefore examined the cyclic voltammetry of the porphyrins dissolved in pyridine. Well-formed, reversible responses were obtained from which the formal potentials shown in Figure 8 were obtained. The substitution of each phenyl by a pyridyl group produces a 25-mV positive shift in the formal potential of the  $Co^{III}/Co^{II}$  couple. This sensitivity of the  $Co^{III}/Co^{II}$  potential to the nature of the substituent in the porphyrin ring encouraged us to synthesize a phenyl-substituted derivative of  $cis-CoPPh_2(py)_2$  in order to compare the effect of changes in the  $Co^{III}/Co^{II}$  formal potential on the catalytic behavior of two catalysts having the same number of  $pyRu(NH_3)_5^{2+}$  groups. We therefore prepared a derivative in which the two phenyl groups were replaced by two *p*-(trifluoromethyl)phenyl groups. The formal potential of the  $Co^{III}/Co^{II}$  couple in the resulting porphyrin,  $cis-CoP(CF_3Ph)_2(py)_2$ , was 37 mV more positive than that of  $cis-$  and  $trans-CoPPh_2(py)_2$ . This formal potential is about halfway between those of the  $CoPPh(py)_3$  and  $CoP(py)_4$  derivatives (Figure 8), which, after ruthenation, achieve the four-electron reduction of  $O_2$ . When  $cis-CoP(CF_3Ph)_2(py)_2$  was adsorbed on a graphite rotating disk electrode, ruthenated, and tested as an electrocatalyst for the reduction of  $O_2$ , it performed essentially identically to the  $cis-CoPPh_2(pyRu(NH_3)_5)_2^{4+}$  complex. That is, it catalyzed the

two-electron reduction of  $O_2$  near the formal potential of the  $pyRu(NH_3)_5^{3+/2+}$  couple, which is insensitive to the nature of the other substituents in the series of porphyrins examined in this study. This result supports the idea that the formal potential of the  $Co^{III}/Co^{II}$  center does not strongly influence the potential where the catalyzed reduction of  $O_2$  proceeds. It is the potential where the adduct of  $O_2$  with the cobalt center of the porphyrin accepts electrons, either from the electrode or from the coordinated  $Ru(NH_3)_5py^{2+}$  centers, that controls the potential where the cobalt porphyrin molecules become catalysts for the reduction of  $O_2$ .<sup>12,13</sup> It should be noted that both the  $Ru(NH_3)_5py^{2+}$  complex unattached to the cobalt porphyrin and  $Ru(NH_3)_5py^{2+}$  centers attached to a cobalt-free porphyrin ring show negligible reactivity toward the reduction of  $O_2$  or  $H_2O_2$ .

The adsorbed cobalt porphyrin was also allowed to react with  $H_2OFe(CN)_5^{3-}$  anions to introduce  $pyFe(CN)_5^{3-}$  centers on the periphery of the porphyrin. A reversible response from the adsorbed  $pyFe(CN)_5^{2-/3-}$  couple was observed at 0.33 V, i.e., at potentials more positive than those where the catalyzed reduction of  $O_2$  occurred. The reduction of  $O_2$  appeared to be unaffected by the presence of the  $pyFe(CN)_5^{3-}$  centers, as expected if the reduction of the cobalt- $O_2$  adduct required a potential more negative than 0.33 V.

**Mechanistic Considerations.** Half-wave potentials for the reduction of  $O_2$  at rotating graphite disk electrodes coated with the various ruthenated porphyrins of Figure 1 are summarized in Table II along with the formal potentials of the  $pyRu(NH_3)_5^{3+/2+}$  couple for all of the adsorbed complexes. There is a trend for the potential where  $O_2$  is reduced to become more positive as the number of  $Ru(NH_3)_5^{2+}$  groups coordinated to the porphyrin is increased. This trend indicates that the rate with which  $O_2$  oxidizes the reduced catalysts is relatively high and apparently increases with the number of coordinated  $pyRu(NH_3)_5^{2+}$  groups. If it is assumed that the  $pyRu(NH_3)_5^{3+/2+}$  couple adheres to the Nernst equation, that intramolecular electron transfer between the  $pyRu(NH_3)_5^{2+}$  sites and the  $O_2$  molecule coordinated to the cobalt center proceeds much more rapidly than the coordination of  $O_2$  to the adsorbed, reduced catalyst, and that no  $O_2$  can be reduced without oxidation of  $pyRu(NH_3)_5^{2+}$  sites, the rate constant of the coordination reaction can be estimated from the difference between the formal potential of the  $pyRu(NH_3)_5^{3+/2+}$  couple and the half-wave potential where the catalyzed reduction of  $O_2$  proceeds.<sup>14</sup> For the  $CoP(pyRu(NH_3)_5)_3^{6+}$  catalyst, a value of  $5 \times 10^4 M^{-1} s^{-1}$  was calculated from a potential difference of 75 mV at an electrode rotation rate of 100 rpm and a catalyst coverage of  $9.3 \times 10^{-10} mol cm^{-2}$ . Similar values were obtained at higher rotating rates. Evaluation of the rate constant from the intercept of the Koutecky-Levich plot in Figure 5C produced a value of  $0.9 \times 10^4 M^{-1} s^{-1}$ . That the agreement between the two values is only modest is not surprising in view of the untested assumptions inherent in both calculations.<sup>14</sup> For example, if a portion of the  $O_2$  were reduced directly, without oxidation and rereduction of the  $pyRu(NH_3)_5$  sites, one would expect larger apparent rate constants to result from the calculation based on the difference in potentials.

It was not possible to carry out a comparison like that in Table II for the unruthenated porphyrins. The half-wave potentials for the reduction of  $O_2$  at electrodes coated with these porphyrins were much more erratic and spanned a range of  $\sim 300$  mV. Electrode surface preparation, catalyst application procedures, and the quantities of catalysts retained on the electrode surface all affected the  $O_2$  reduction potentials, and it proved difficult to obtain potentials which were reproducible to better than  $\pm 150$  mV.

The reason that the rate with which  $O_2$  reacts with the reduced catalyst apparently increases with the number of  $Ru(NH_3)_5py^{2+}$

groups present on the periphery of the porphyrin ring may be associated with the electron-donating character of the back-bonding  $Ru(NH_3)_5^{2+}$  centers. Although the pyridine rings are not expected to be coplanar with the porphyrin ring, neither are the two rings likely to be perpendicular to each other<sup>3b</sup> so that each back-bonding  $Ru(NH_3)_5py^{2+}$  center could enhance the electron density on the porphyrin ring. The result would be a stronger cobalt-dioxygen bond,<sup>3b,15</sup> which is consistent with the bond's forming more rapidly when more  $Ru(NH_3)_5py^{2+}$  groups are present.

To examine the dependence of the catalytic activity of the  $CoP(pyRu^{II}L_5)$  complex on the reducing strength of the electron-donating  $Ru^{II}L_5$  centers, the adsorbed  $CoP(py)_4$  porphyrin was allowed to react with  $Ru^{III}(edta)OH_2^-$  ( $edta$  = ethylenediaminetetraacetate) instead of  $Ru^{II}(NH_3)_5OH_2^{2+}$ . The greater lability of the water molecule of the  $Ru^{III}(edta)OH_2^-$  complex<sup>16</sup> facilitated the formation of the tetraruthenated complex,  $CoP(pyRu(edta))_4^{4-}$ , on the electrode surface. (Araki and Toma have prepared the same complex in solution and tested it as a catalyst for the electroreduction of  $O_2$ .<sup>17</sup>) The dashed curve in Figure 9A is a cyclic voltammogram for the adsorbed complex in the absence of  $O_2$ . The formal potential of the  $pyRu(edta)^{-/2-}$  couple responsible for the reversible response obtained is about 0.2 V more negative than that of the  $pyRu(NH_3)_5^{3+/2+}$  couple (Figure 2), as expected.<sup>18</sup> When  $O_2$  was introduced into the solution, a prominent new peak arising from the catalyzed reduction of  $O_2$  appeared in the cyclic voltammogram (solid curve in Figure 9A). The peak current and peak potential for the reduction of  $O_2$  matched those obtained when the unruthenated  $CoP(py)_4$  catalyst was employed to catalyze the reduction of  $O_2$  to  $H_2O_2$ . The response from the  $pyRu(edta)^{-/2-}$  centers of the adsorbed  $CoP(pyRu(edta))_4^{4-}$  catalyst remained virtually unchanged in the presence of  $O_2$  (Figure 9A). The voltammetry provided no evidence that the ruthenation of the porphyrin affected its catalytic activity toward the reduction of  $O_2$ . To investigate this somewhat surprising result in more detail, the experiment was repeated at a catalyst-coated rotating disk electrode. The resulting current-potential responses are shown in Figure 9B,C. The  $O_2$  reduction currents at an electrode coated with  $CoP(py)_4$  (Figure 9B) were similar to those obtained when  $CoP(pyRu(edta))_4^{4-}$  was prepared on the electrode (Figure 9C). Except for current plateaus at higher rotation rates which are somewhat less inclined with the ruthenated catalyst, the two catalysts behaved similarly. Particularly noteworthy is the absence of any increase in disk current as the disk potential was scanned to values where the coordinated  $pyRu(edta)^-$  centers were reduced (Figure 9C). Despite its greater reducing strength,  $pyRu^{II}(edta)^{2-}$  is ineffective in providing the electrons to produce the four-electron reduction of  $O_2$  under conditions where  $pyRu(NH_3)_5^{2+}$  accomplishes just that. Experiments with a rotating platinum ring-graphite disk electrode confirmed this observation (Figure 9D,E). The anodic ring current resulting from the oxidation of  $H_2O_2$  generated at the catalyst-coated disk exhibited no decrease in magnitude at disk potentials where the  $pyRu(edta)^-$  centers were reduced (Figure 9E). Note that this result cannot be explained by assuming that all (or most) of the  $O_2$  is reduced to  $H_2O_2$  at potentials positive of those where  $pyRu(edta)^-$  is reduced and presuming that the  $CoP(pyRu(edta))_4^{8-}$  complex lacks catalytic activity toward  $H_2O_2$ . The  $O_2$  molecules arriving at the electrode surface at potentials where the  $pyRu(edta)^-$  centers are reduced, must coordinate with the  $Co(II)$  center to undergo catalytic reduction and, while coordinated, would be available to accept electrons from the four coordinated  $pyRu(edta)^{2-}$  groups. However, the results in Figure 9C,E show that the  $pyRu(edta)^{2-}$  groups are unable to deliver

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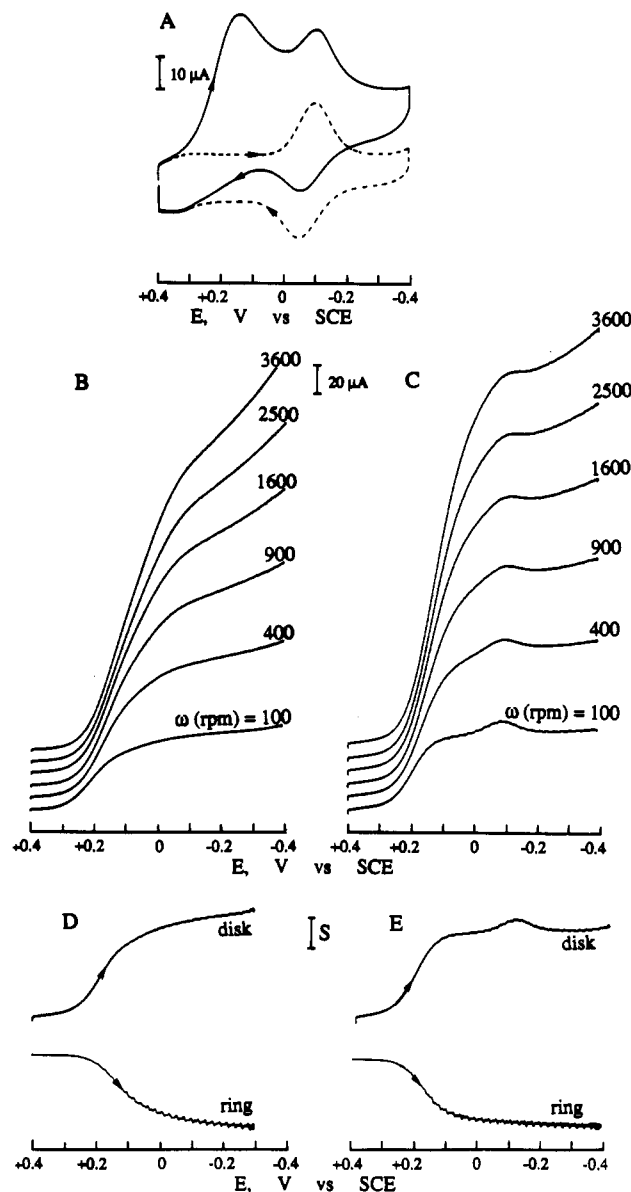
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**Figure 9.** Electrochemical responses obtained at electrodes coated with  $3.3 \times 10^{-10} \text{ mol cm}^{-2}$  of  $\text{CoP}(\text{py})_4$  or  $\text{CoP}(\text{pyRu}(\text{edta}))_4^{4+}$ . (A) Electrode coated with  $\text{CoP}(\text{pyRu}(\text{edta}))_4^{4+}$ : cyclic voltammety in the absence (---) and presence (—) of  $0.28 \text{ mM O}_2$ . (B) Electrode coated with  $\text{CoP}(\text{py})_4$ : rotating disk voltammety for  $0.28 \text{ mM O}_2$ . (C) Repeat of (B) with the electrode coated with  $\text{CoP}(\text{pyRu}(\text{edta}))_4^{4+}$ . (D) Reduction of  $0.28 \text{ mM O}_2$  at a rotating platinum ring-graphite disk electrode. The disk electrode was coated with  $\text{CoP}(\text{py})_4$ . Ring potential =  $1.0 \text{ V}$ . Rotation rate =  $100 \text{ rpm}$ .  $S = 10$  and  $5 \mu\text{A}$  for disk and ring currents, respectively. (E) Repeat of (D) with the electrode coated with  $\text{CoP}(\text{pyRu}(\text{edta}))_4^{4+}$ . Supporting electrolyte:  $0.1 \text{ M HClO}_4$ .

electrons rapidly enough to produce a reduction of  $\text{O}_2$  involving more than two electrons.

## Conclusions

By the coordination of  $\text{Ru}(\text{NH}_3)_5^{2+}$  groups to the pyridine sites of the set of cobalt porphyrins shown in Figure 1, it was established that the porphyrins containing two or fewer coordinated  $\text{Ru}(\text{NH}_3)_5^{2+}$  centers catalyze the reduction of  $\text{O}_2$  by only two electrons while the molecules containing three or four  $\text{Ru}(\text{NH}_3)_5^{2+}$  centers are able to catalyze the four-electron reduction. The transition in behavior is abrupt, not gradual: The singly and doubly ruthenated porphyrins produce only  $\text{H}_2\text{O}_2$  while the more highly ruthenated derivatives produce  $\text{H}_2\text{O}$  with very little  $\text{H}_2\text{O}_2$ . The observed stoichiometry of the reduction of  $\text{O}_2$  also depends

on the nature and preparation of the graphite electrode surfaces on which the catalysts are adsorbed. With aggressively polished, homemade, edge-plane pyrolytic graphite disk electrodes it was possible to obtain over 90% reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$  with both  $\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_3^{6+}$  and  $\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4^{8+}$  as catalysts. Changes in the formal potentials of the  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  couple of the unruthenated porphyrins (as measured with the porphyrins dissolved in pyridine) appeared not to influence the potentials where the corresponding ruthenated porphyrins acted as electrocatalysts in aqueous acid. Several mechanistic aspects of the catalytic processes remain to be resolved: It seems reasonable to suppose that both catalytic pathways start with the coordination of the  $\text{O}_2$  molecule to the cobalt(II) center of the adsorbed porphyrin. If the partitioning between the two- and four-electron reduction pathways depends on whether the electrons are supplied to the coordinated  $\text{O}_2$  molecules directly from the electrode (as with unruthenated porphyrins) or via the  $\text{Ru}(\text{NH}_3)_5^{2+}$  centers, it is unclear why a single such center does not suffice to produce a four-electron reduction because the reversible  $\text{pyRu}(\text{NH}_3)_5^{3+/2+}$  couple can be rapidly cycled between oxidation states. It may be that the rate of intramolecular electron transfer from  $\text{pyRu}(\text{NH}_3)_5^{2+}$  to the  $\text{Co}-\text{O}_2$  adduct controls the extent of the four-electron pathway and that this rate increases with the number of  $\text{pyRu}(\text{NH}_3)_5^{2+}$  centers present. Another possibility is that interactions between the  $\text{O}_2$  molecule and the d electrons of the cobalt(II) center to which it is coordinated, interactions which are presumably responsible for the activation of the  $\text{O}_2$  molecule toward reduction, may be enhanced by the presence of the back-bonding  $\text{Ru}(\text{NH}_3)_5^{2+}$  complexes around the periphery of the porphyrin ring. With three or four  $\text{Ru}(\text{NH}_3)_5^{2+}$  groups, the activation may be great enough to produce the four-electron reduction while, with fewer groups, only the two-electron pathway is accessible. This interpretation invokes the back-bonding of the  $\text{Ru}(\text{NH}_3)_5^{2+}$  groups rather than their oxidizability as the key factor. One measure of the relative back-bonding abilities of the two types of complexes of  $\text{Ru}(\text{II})$  is the magnitude of the shift in the formal potentials of the  $\text{Ru}(\text{III})/\text{Ru}(\text{II})$  couple when the sixth coordination position is changed from  $\text{H}_2\text{O}$  to pyridine (or pyrazine). The formal potentials are shifted in the positive direction for both complexes as expected when  $\pi$ -back-bonding dominates the coordination equilibria<sup>19</sup>. The shift in the formal potential amounts to  $0.24 \text{ V}$  in the case of  $\text{Ru}(\text{NH}_3)_5^{3+/2+}$  but  $0.11 \text{ V}$  for the  $\text{Ru}(\text{edta})^{-2-}$  case.<sup>10</sup> (With pyrazine as the  $\pi$ -acid ligand, the corresponding shifts are  $0.42$  and  $0.25 \text{ V}$ , respectively.) Estimates of the back-bonding abilities of the two types of complexes have also been made on the basis of spectroscopic measurements.<sup>20</sup> The same relative ordering was observed although the differences between the two types of complexes were much smaller. However, different  $\pi$ -acid ligands were involved in the spectral studies and the relevance to the behavior of the tetrapyrrolylporphyrin ligand is less clear. In any case, the negligible catalytic activity of coordinated  $\text{Ru}^{\text{II}}(\text{edta})^{2-}$  centers is compatible with their being better reductants but poorer back-bonders to pyridine ligands than is  $\text{Ru}(\text{NH}_3)_5^{2+}$ , and this ordering is supported by the relative magnitudes of the shifts in formal potentials just described.

Additional experiments with cobalt porphyrins containing different types of ligand sites around the ring are underway in an effort to establish the basis of the effectiveness of  $\text{Ru}(\text{NH}_3)_5^{2+}$  centers in converting a two-electron into a four-electron electrocatalyst for the reduction of  $\text{O}_2$ .

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