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Novel Multinuclear Catalysts for the Electroreduction of Dioxygen Directly to Water

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The electroreduction of O₂ to H₂O in aqueous acid at potentials close to the thermodynamically permitted value remains a daunting challenge for designers of superior fuel cells and batteries that utilize dioxygen as the reducible reactant. The four-electron reduction of O₂, which involves the rupture of the O–O bond and the formation of four O–H bonds, requires the use of catalysts to obtain useful rates at cathode potentials of interest in practical applications. The standard potential of the O₂/H₂O couple

in solutions containing 1 M H⁺ and saturated with O₂ at 1 atm is ca. 1.0 V (vs the saturated calomel electrode, SCE), but the highest cathode potentials achievable with currently available catalysts are closer to 0.55 V. (Molecules, functional groups, or metallic deposits that accelerate the rates of electrode reactions when they are confined to the surfaces of electrodes are often called electrocatalysts, a terminology that will be adopted in this Account.) Finely divided platinum supported on high area carbon is the electrocatalyst employed most frequently to achieve the electroreduction of O₂ to H₂O in presently available fuel cells. However, this type of electrocatalyst suffers from the disadvantages of high cost and gradual loss in catalytic activity as the surface area of the active platinum particles decreases because of sintering, dissolution, physical dislodgment, and/or adsorption of impurities. Searches for superior electrocatalysts for the reduction of O₂ have often focused on cobalt porphyrins which are well-known to exhibit electrocatalytic activity toward the reduction of O₂,^{1–3} although H₂O₂ instead of H₂O is the usual product. However, it was discovered in recent years that a variety of molecular catalysts consisting of dimeric cofacial cobalt porphyrins adsorbed on the surface of graphite electrodes are able to catalyze the direct four-electron electroreduction of O₂ without passing through H₂O₂ as an intermediate.^{4–15} Both dimeric and monomeric iridium por-

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phyrins have also been found to accomplish the electroreduction of O_2 to H_2O at unusually positive potentials.^{16–18} The mechanisms through which dimeric electrocatalysts are believed to operate involve the simultaneous interaction of both metal centers with the two oxygen atoms of the O_2 molecule as the O–O bond is severed. The ideas and strategies that underlay the development of these electrocatalysts have been described.¹⁹

Recently, our group has explored a somewhat different approach in which cobalt porphyrin molecules with ligand sites attached to the periphery of the porphyrin ring are featured. The plan was to utilize the ligand sites to coordinate metal complexes chosen because of their propensity to serve as electron donors. The idea was that, upon reduction, each metal complex could supply an electron so that four electrons could be transmitted intramolecularly to O_2 molecules that were activated by coordination to the cobalt(II) center of the cobalt porphyrin catalyst to achieve the four-electron reduction of O_2 to H_2O .^{20,21} The oxidized metal complexes that would result could then be re-reduced electrochemically and the catalytic cycle repeated.

The idea that molecules containing multiple redox-active sites might be catalysts for multiple electron-transfers is not new. However, previous attempts in this direction have been only partially successful.^{22–24} The catalysts prepared in our studies did prove effective in achieving the reduction of O_2 by four electrons, but as related in this Account, the catalytic mechanism actually employed by the multinuclear cobalt porphyrin molecules that were synthesized turned out to involve π -back-bonding rather than rapid, intramolecular electron-transfer from the pendant electron donors to the O_2 substrate. The lessons learned in the course of the research to be described provide insights that may prove helpful in the design of even better electrocatalysts for the reduction of O_2 to H_2O .

Preparation of Multinuclear Electrocatalysts. The first series of catalysts that we prepared and tested was based on cobalt porphyrins in which the 5, 10, 15, and 20 positions of the porphyrin ring contained a pyridine ligand covalently linked to the porphyrin ring at the 4 position

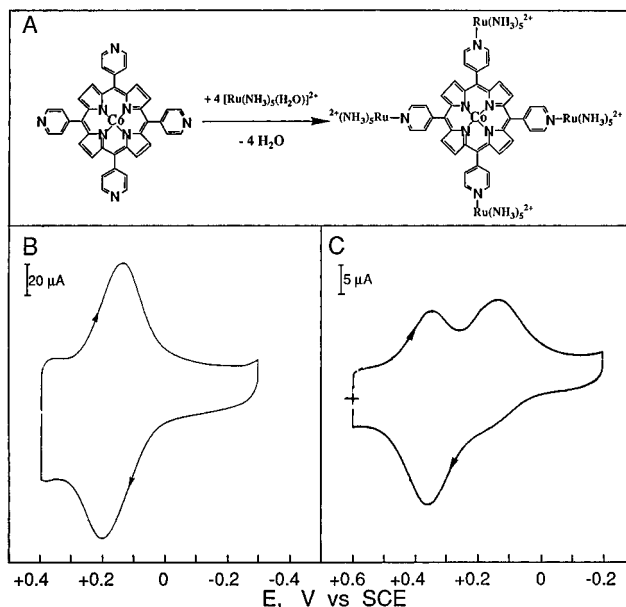


FIGURE 1. (A) Ruthenation of (5,10,15,20-tetrakis(4-pyridyl)porphyrinato)cobalt(II) (CoP(py)₄). (B) Cyclic voltammogram for a porphyrin-coated electrode after it was exposed to a 25 mM solution of $[Ru(NH_3)_5(OH_2)]^{2+}$ for 48 h. (C) Cyclic voltammetric response of CoP(py)₄ adsorbed on a graphite electrode after it was exposed to a 15 mM solution of *fac*- $[Ru(NH_3)_3(OH_2)_3]^{2+}$ for 48 h. Both peaks result from Ru(III/II) couples. Scan rate: 50 mV s^{-1} .

of the pyridine ring (Figure 1A). $Ru(NH_3)_5^{2+}$ was selected as the potential electron-donating group which was coordinated to the 4-pyridine ligands by exposing graphite electrodes on which the cobalt porphyrins were adsorbed to aqueous solutions of $[Ru(NH_3)_5(OH_2)]^{2+}$ for extended periods.^{20,21} The extent of the ruthenation of the adsorbed porphyrin was monitored by recording the cyclic voltammetric response from the $[Ru(NH_3)_5py]^{3+/2+}$ couple that grew in magnitude during the lengthy reaction period (Figure 1B). With the tetrapyridyl cobalt porphyrin the area under the final voltammetric peak corresponded to four $[Ru(NH_3)_5py]^{2+}$ groups for each molecule of adsorbed porphyrin, showing that all four of the pyridine sites were ruthenated. That a single, four-electron voltammetric peak was obtained instead of four, separated one-electron peaks showed that intramolecular interactions among the four $[Ru(NH_3)_5py]^{2+}$ groups in each porphyrin molecule were too weak to cause peak splitting. The appearance of a single, four-electron peak was fortunate because our objective was to deliver four electrons at essentially the same potential during the catalytic reduction of O_2 to H_2O .

With the intention of exploring the possibility of using more than one coordination site on the Ru(II) complex in preparing catalysts, the ruthenation of the cobalt porphyrin adsorbed on graphite electrodes was also carried out using *fac*- $[Ru(NH_3)_3(OH_2)_3]^{2+}$ as the ruthenating complex.²⁵ The catalyst coatings obtained in this way exhibited a doubly peaked cyclic voltammogram under argon which signaled the presence of two different types of ruthenium–pyridine complexes in the adsorbed coating (Figure 1C). The potentials of the peaks corresponded to those expected for the complexes in which one or two pyridines were coordinated to the Ru and the total area

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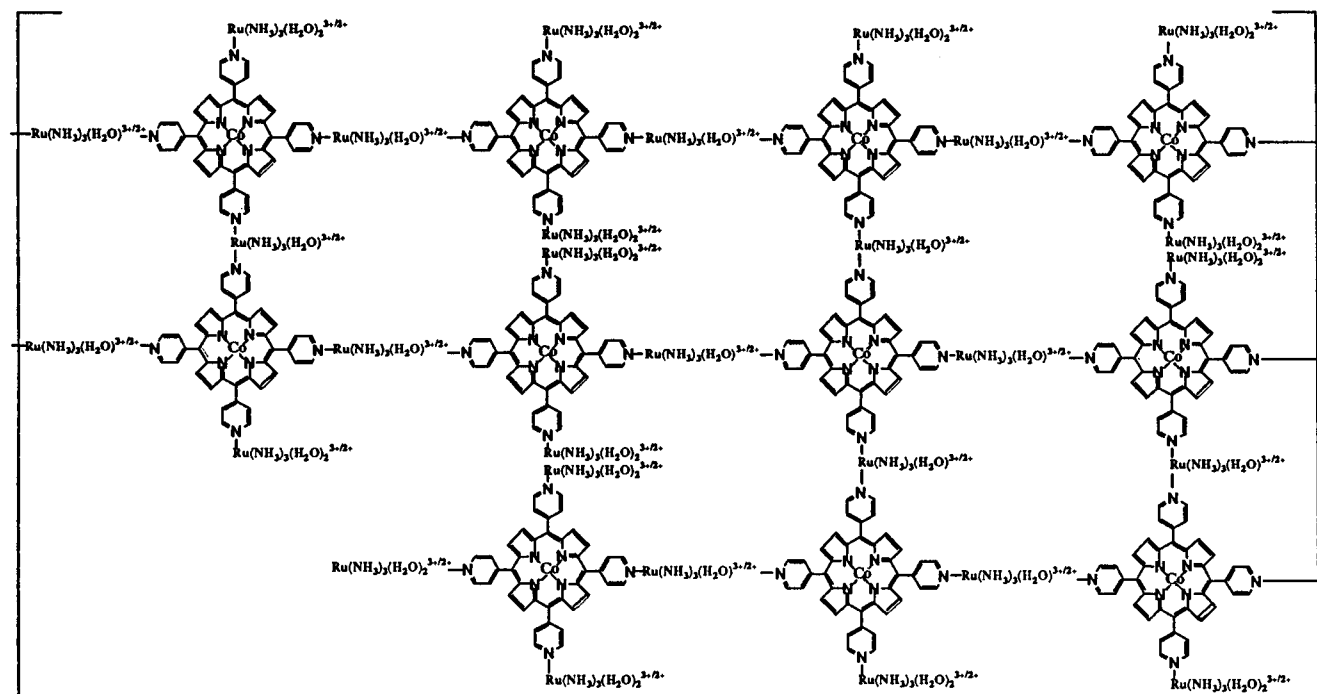


FIGURE 2. Possible structure for the product formed from the reaction between $[\text{Ru}(\text{NH}_3)_3(\text{OH}_2)_2]^{2+}$ and $\text{CoP}(\text{py})_4$ on a graphite electrode. The Ru(II) complexes that occupy bridging and terminal coordination positions correspond to the peaks in Figure 1C at the more and less positive potential, respectively.

under the peaks corresponded to about three Ru complexes per cobalt porphyrin instead of the four Ru complexes obtained when $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ was the ruthenating complex.²⁵ The results suggested that the ruthenation reaction had produced a cross-linked network on the electrode surface with a structure like the one shown in Figure 2. The coatings prepared with $[\text{Ru}(\text{NH}_3)_3(\text{OH}_2)_2]^{2+}$ were also notably more stable than those obtained from $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$, which was consistent with the decreased solubility to be anticipated from a polymeric structure such as the one depicted in Figure 2.

Monitoring the Products of the Electroreduction of O_2 . To compare the behavior of various electrocatalysts for the reduction of O_2 it is convenient to use the rotating ring-disk electrode.^{26,27} The catalysts of interest are irreversibly adsorbed on the central, circular graphite disk electrode which is closely circumscribed by a concentric platinum ring electrode. Rotation of the electrode about an axis perpendicular to the disk causes the products of the electroreduction of O_2 at the disk electrode to be swept across the narrow, insulating gap to the ring electrode which is adjusted to a potential (1.0–1.2 V vs SCE) where any H_2O_2 reaching it is rapidly oxidized to O_2 to produce an anodic ring current. H_2O is not oxidized at this ring potential so that the ring discriminates between H_2O_2 and H_2O as the products of the electroreduction of O_2 at the catalyst-coated disk electrode. The relative magnitude of the ring and disk currents provides a quantitative assessment of the fractions of the O_2 molecules that are reduced to H_2O_2 or to H_2O .

The effect of the coordination of $\text{Ru}(\text{NH}_3)_5^{2+}$ groups to the four pyridine groups of (5,10,15,20-tetrakis(4-pyridyl)-

porphyrinato)cobalt(II) (Figure 1A) on its catalytic activity toward the electroreduction of O_2 is shown in the rotating ring-disk current potential curves in Figure 3A,B. Before ruthenation, the adsorbed porphyrin catalyzes only the two-electron reduction of O_2 to H_2O_2 as demonstrated by the large anodic current at the platinum ring electrode (Figure 3A). The ratio of the currents at the disk and ring electrodes in Figure 3A showed that essentially all of the O_2 was reduced to H_2O_2 . After ruthenation, the disk current increased and the ring current decreased (Figure 3B). The ratio of the ring to the disk current in Figure 3B showed that about 72% of the O_2 was reduced to H_2O and only 28% to H_2O_2 .²¹

A rotating ring-disk experiment in which the disk electrode coating was of the polymeric type depicted in Figure 2 is shown in Figure 3C. The ratio of the ring to disk currents for this case corresponds to the reduction of ca. 90% of the O_2 by four electrons. (The disk current in Figure 3C is smaller than that in Figure 3B despite the higher proportion of four-electron reduction in Figure 3C. The reason is that the disk currents are controlled by the rate of association of the O_2 molecules with the porphyrins on the electrode surface.²⁵ This rate is somewhat smaller with the porphyrin coating in Figure 3C than with the coating in Figure 3B.)

The results shown in Figure 3B,C were consistent with the notion that rapid intramolecular electron-transfer within tetra-ruthenated cobalt porphyrin- O_2 complexes converted the reduction of O_2 from a two- to a (largely) four-electron process. Since the $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ centers bound to the adsorbed cobalt porphyrin could be rapidly converted to their reduced forms electrochemically (Figures 1B and 1C), it seemed possible that fewer than four coordinated $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ groups might suffice to produce the reduction of O_2 by four electrons. To explore

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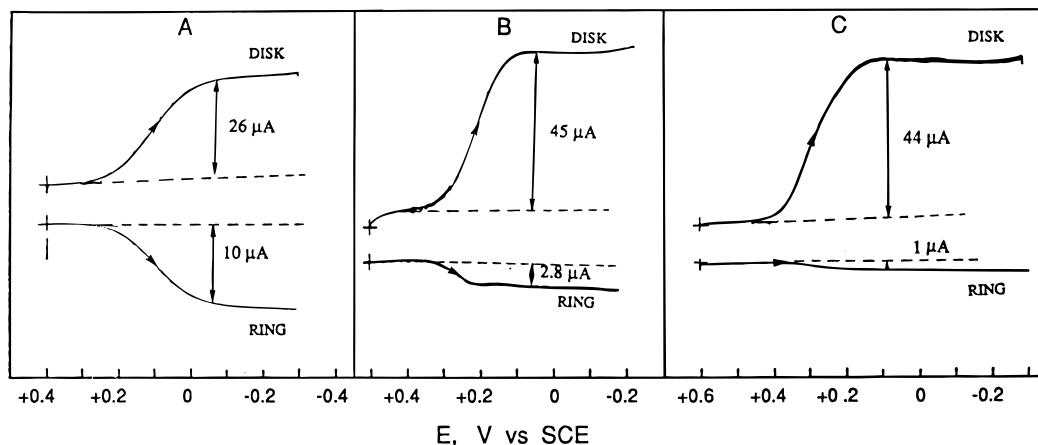


FIGURE 3. (A) Rotating ring–disk voltammetry during the reduction of O_2 at a graphite disk electrode coated with $CoP(py)_4$. The platinum ring electrode was held at 1.0 V to oxidize any H_2O_2 that was generated at the disk electrode and swept to the concentric ring by the rotation of the electrode. The electrode was rotated at 100 rpm. The supporting electrolyte was 0.5 M $NH_4PF_6/0.5$ M $HClO_4$ saturated with air. (B) Repeat of A but with the disk coated with $[Co^{III}P(pyRu^{III}(NH_3)_5)_4]^{13+}$. (C) Repeat of A but with a disk coating similar to that of Figure 2.

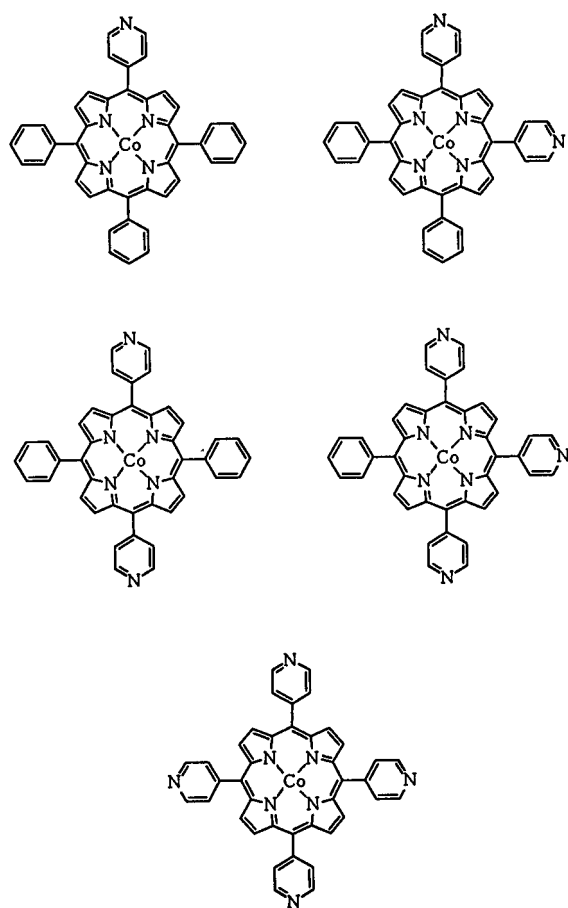


FIGURE 4. Set of cobalt porphyrins with various combinations of phenyl and 4-pyridyl groups in the 5, 10, 15, and 20 positions of the ring.

this possibility the set of porphyrins shown in Figure 4 was synthesized, adsorbed on the graphite electrode, fully ruthenated, and tested as electrocatalysts for the reduction of O_2 . The experiments showed that all of the porphyrins that contained fewer than three $[Ru(NH_3)_5py]^{2+}$ groups gave only two-electron reductions, while those with three or four $[Ru(NH_3)_5py]^{2+}$ groups accomplished the four-electron reduction.²⁸ The rapid electrochemical cycling between the oxidized and reduced forms of the Ru complexes coordinated to the adsorbed porphyrin mol-

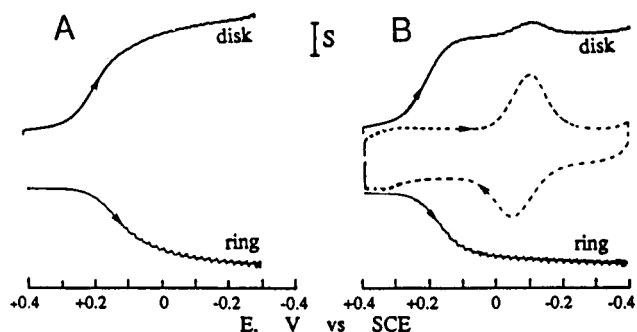


FIGURE 5. Reduction of O_2 at the rotating platinum ring–graphite disk electrode with the disk coated with (A) $Co^{II}P(py)_4$ or (B) $[Co^{II}P(pyRu^{III}(edta))_4]^{4-}$. $S = 10$ and $5 \mu A$ for the disk and ring currents, respectively. The electrode was rotated at 100 rpm. The scan rate was 5 mV s^{-1} . The dashed curve in B is the cyclic voltammetric response obtained from the $[Co^{II}P(pyRu^{III}(edta))_4]^{4-}$ couple in the absence of O_2 . The scan rate was 50 mV s^{-1} . $S = 10 \mu A$.

ecule, as seen in Figure 1B,C, indicated that a single $[Ru(NH_3)_5py]^{3+/2+}$ group ought to be able to serve as the source for all of the electrons needed to achieve the four-electron reduction of O_2 . As a result, we began to have some doubts about intramolecular electron-transfer as the catalytic mechanism that was followed by the ruthenated porphyrins. These doubts became even stronger when $[Ru^{III}(edta)(OH_2)]^-$ ($edta = \text{ethylenediaminetetraacetate}$) was used instead of $[Ru(NH_3)_5(OH_2)]^{2+}$ to prepare the tetra-ruthenated cobalt porphyrin catalyst. Both complexes exhibit high rates of electron-transfer at electrodes, but $[Ru^{II}(edta)py]^{2-}$ is a significantly stronger reductant than $[Ru(NH_3)_5py]^{2+}$ (the formal potentials of the two Ru(III/II) couples are -0.10 and $+0.14$ V vs SCE, respectively), so that one would expect the $[Ru(edta)py]^{2-}$ complex to engage in intramolecular electron-transfer even more readily than the $[Ru(NH_3)_5py]^{2+}$ complex. However, as shown in Figure 5, coordination of Ru(edta) groups to the four pyridine sites in the tetrapyridyl porphyrin, $CoP(py)_4$, failed to convert it from a two- to a four-electron catalyst. The adsorbed porphyrin catalyzed only the two-electron reduction of O_2 to H_2O_2 both before (Figure 5A) and after (Figure 5B) ruthenation.²⁸ This result required us to consider other possibilities for the catalytic mechanism.

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Before examining alternatives to intramolecular electron-transfer as the catalytic role of $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ groups, it may be helpful to describe the behavior of the four-electron electrocatalyst, $[\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4]^{12+}$, as a homogeneous catalyst for the reduction of O_2 .

Catalysis of the Homogeneous Reduction of O_2 by $\text{Ru}(\text{NH}_3)_6^{2+}$. The reaction between O_2 and $\text{Ru}(\text{NH}_3)_6^{2+}$ in aqueous acid is relatively slow ($k = 75 \text{ M}^{-1} \text{ s}^{-1}$) and yields H_2O_2 as the exclusive reduction product.²⁹ After devising a procedure for the generation of $[\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4]^{8+}$ in solution instead of only on the surface of graphite electrodes,³⁰ we added the tetra-ruthenated porphyrin to mixtures of O_2 and $\text{Ru}(\text{NH}_3)_6^{2+}$ to determine if the ruthenated catalyst might also provide access to a four-electron pathway for the homogeneous reduction of O_2 . It did not. Although the rate of the reduction of O_2 was higher in the presence of $[\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4]^{8+}$, the rate was also enhanced in the presence of the unruthenated porphyrin, solubilized by protonation of the pyridine groups, and in neither case did the reduction proceed beyond H_2O_2 .³⁰ When the $[\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4]^{8+}$ porphyrin was used as both catalyst and reductant, i.e., when no $\text{Ru}(\text{NH}_3)_6^{2+}$ was present, the rate of the reduction of O_2 became too slow to measure. Thus, at least in homogeneous solution, the rate of intramolecular electron-transfer from the $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ sites of the tetra-ruthenated porphyrin to O_2 coordinated to the Co(II) site in the center of the porphyrin is quite slow. This result added to our growing doubts that the four-electron reduction of O_2 at electrodes coated with $[\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4]^{8+}$ involves intramolecular electron-transfer from Ru(II).

The failure of the $[\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4]^{8+}$ complex to catalyze more than the two-electron reduction of O_2 by $\text{Ru}(\text{NH}_3)_6^{2+}$ is believed to reflect the requirement for multiple collisions between the catalyst- O_2 adduct and the one-electron reductant, $\text{Ru}(\text{NH}_3)_6^{2+}$. When the same adduct is formed on the surface of an electrode, multiple electrons can be supplied to the adduct from the electrode before the partially reduced O_2 dissociates from the activating Co(II) center. When the reduction is carried out in homogeneous solution, a competition is set up between the rates of the delivery of multiple electrons and the rate of dissociation of, say, H_2O_2 from the coordination sphere of the Co(II). The latter process wins the competition in homogeneous solution because of the extra time required for the delivery of four electrons by one-electron reductants. As a result, the reduction stops after two electrons are transferred. None of the cobalt porphyrins studied here, either in solution or adsorbed on electrodes, show significant catalytic activity toward the reduction of H_2O_2 .

Back-Bonding Instead of Electron-Transfer. The results just recounted and the behavior shown in Figure 5 led us to consider sources other than intramolecular electron-transfer to account for the enhanced catalytic activity produced when $\text{Ru}(\text{NH}_3)_5^{2+}$ groups are coordinated to the pyridine sites of $\text{CoP}(\text{py})_4$. Back-bonding by the Ru(II) centers seemed a possibility because $\text{Ru}(\text{NH}_3)_5^{2+}$ is a stronger back-bonder than $\text{Ru}(\text{edta})^{2-}$ as reflected, for

example, in the much larger positive shift in the formal potential of the Ru(III/II) couple when $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ is converted to $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ than when $[\text{Ru}(\text{edta})(\text{OH}_2)]^{2-}$ is converted to $[\text{Ru}(\text{edta})\text{py}]^{2-}$.³¹

To explore the possibility that back-bonding was the origin of the electrocatalytic activity, we prepared cobalt porphyrins with more strongly π -accepting 4-cyanophenyl ligands³² instead of pyridines in the 5, 10, and 15 positions of the porphyrin ring (Figure 6A). (The tetrakis(4-cyanophenyl) derivative was also synthesized, but its very weak solvation prevented the complete ruthenation that was possible when a charged, 4-*N*-methylpyridinium group was placed in the 20 position of the porphyrin ring.) The porphyrin was adsorbed on the electrode and reacted with $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ to produce the ruthenated derivative shown in Figure 6B. Before ruthenation, the porphyrin of Figure 6A catalyzed the reduction of O_2 to H_2O_2 (Figure 6C), but after three $\text{Ru}(\text{NH}_3)_5^{2+}$ groups were coordinated to the 4-cyanophenyl ligands, the cobalt porphyrin was converted into a potent catalyst for the reduction of O_2 to H_2O (Figure 6D). This result was in accord with our hypothesis that π -back-bonding is the key to the creation of the four-electron O_2 reduction catalysts.

The extent of transmission of π -back-bonding electron density into specific sites of aromatic nitrile ligands depends upon the point of attachment of the cyano group to the ring. For example, Clarke and Ford showed that the positive shift in the $\text{p}K_a$ of protonated cyanopyridines that results from coordination of $\text{Ru}(\text{NH}_3)_5^{2+}$ to the cyano group of the ligand was significantly greater for the 4-cyanopyridinium than for the 3-cyanopyridinium isomer.³³ The difference in the change in $\text{p}K_a$ values reflects the larger increase in electron density on the pyridinium nitrogen atom when the back-bonding $\text{Ru}(\text{NH}_3)_5^{2+}$ complex is coordinated to the 4-cyano than to the 3-cyano derivative. Reasoning that the same difference in the extent of π -back-bonding might be found with the cyanophenyl derivatives of cobalt porphyrins, we prepared the porphyrins shown in Figure 7A,B and tested them as electrocatalysts. Before ruthenation, the 3-cyanophenyl derivative (Figure 7A) behaved identically to the 4-cyanophenyl isomer to catalyze the electroreduction of O_2 to H_2O_2 .³⁴ After ruthenation, the 3-cyanophenyl derivative exhibited no change in its electrocatalytic behavior while the ruthenated 4-cyanophenyl derivative became a catalyst for the reduction of O_2 to H_2O . Thus, the transfer of the back-bonding electron density to the position of the phenyl ring where it is joined to the porphyrin ring and, presumably, into the porphyrin ring and the cobalt ion sitting in its center is so much less extensive with the 3- than with the 4-cyanophenyl derivative that the former remains a catalyst only for the reduction of O_2 to H_2O_2 even after ruthenation.³⁴

The extent to which π -back-bonding electron density is transmitted to the cobalt porphyrin ring was also modulated by introducing methyl groups in the 2 and 6 positions of the 4-cyanophenyl ligand. The phenyl ring is expected to be positioned more nearly orthogonal to

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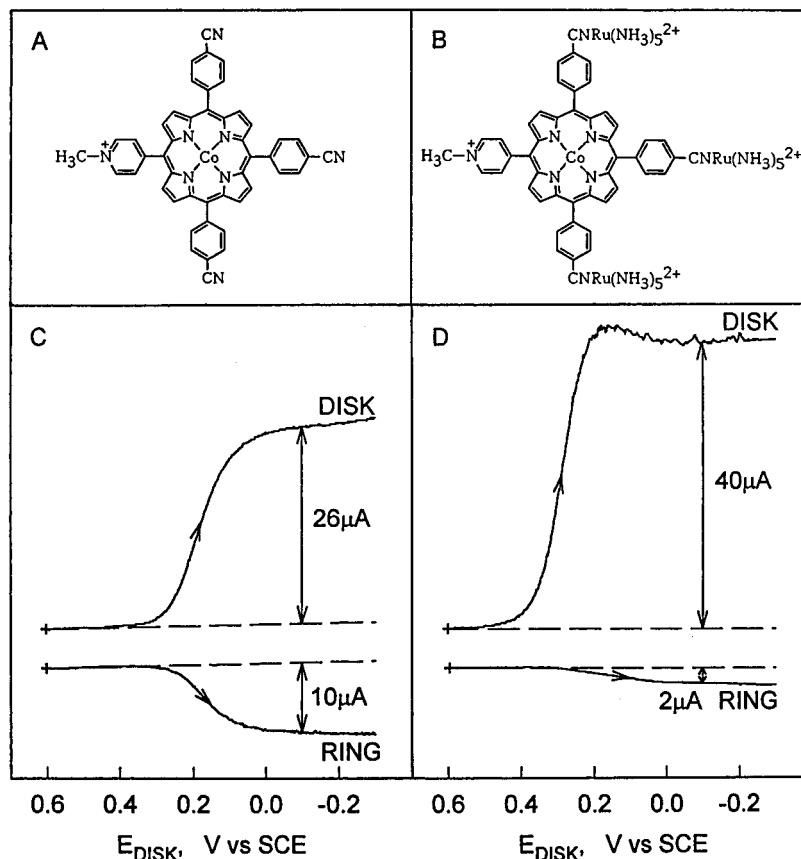


FIGURE 6. (A) Cobalt porphyrin with π -accepting 4-cyanophenyl ligands in the 5, 10, and 15 positions of the porphyrin ring. (B) Triply ruthenated product produced by the reaction of the porphyrin in A with $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$. (C) Reduction of O_2 at the rotating (100 rpm) platinum ring-graphite disk with the disk coated with the porphyrin from A. (D) Repeat of C with the disk electrode coated with the ruthenated porphyrin from B.

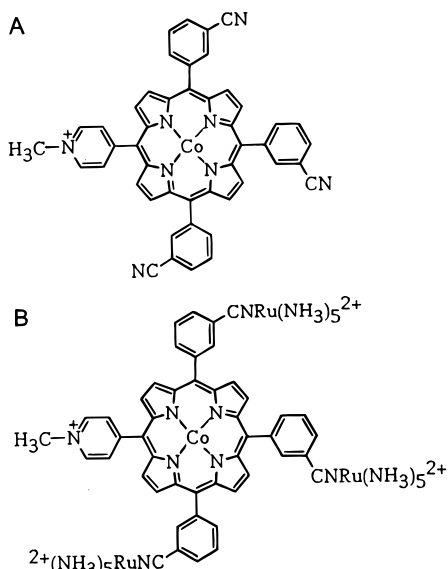


FIGURE 7. (A) Cobalt porphyrin containing 3-cyanophenyl ligands in the 5, 10, and 15 positions of the porphyrin ring. (B) After ruthenation of the porphyrin in A by reaction with $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$.

the porphyrin ring with methyl groups instead of hydrogen atoms in the 2 and 6 positions³⁵ with the result that less of the back-bonding electron density can be transmitted from the cyanophenyl ligand into the porphyrin ring. A comparison of the electrocatalytic behavior of the original with the dimethylated 4-cyanophenyl cobalt porphyrins showed that the largely four-electron reduction of O_2

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obtained with the unmethylated porphyrin was almost entirely eliminated with the dimethylated derivative.³⁵ Thus, a significant increase in the angle between the planes of the porphyrin ring and the 4-cyanophenyl rings attached to it eliminates the catalytic pathway that leads to the four-electron reduction of O_2 . This result provided additional evidence that it is the transfer of π -electron density into the cobalt porphyrin ring from sources covalently linked to it that is crucial in determining the electrocatalytic potency of these cobalt porphyrin derivatives.

Back-Bonding from $\text{Os}(\text{NH}_3)_5^{3+/2+}$. Unlike $\text{Ru}(\text{NH}_3)_5^{3+}$, $\text{Os}(\text{NH}_3)_5^{3+}$ exhibits sufficient π -donating capability to engage in back-bonding with π -acidic ligands.^{36–38} The formal potentials of the $\text{Os}(\text{III}/\text{II})$ couple of $\text{Os}(\text{NH}_3)_5\text{L}$ complexes (L = any sixth ligand) are also much more negative than the formal potentials of the $\text{Ru}(\text{III}/\text{II})$ couples of the corresponding $\text{Ru}(\text{NH}_3)_5\text{L}$ complexes. We therefore sought to coordinate $\text{Os}(\text{NH}_3)_5^{3+}$ groups to a suitable cobalt porphyrin to determine if an electrocatalyst for the four-electron reduction of O_2 could be prepared that operated at potentials where the Os remained as $\text{Os}(\text{III})$ so that catalytic mechanisms in which the coordinated $\text{Os}(\text{NH}_3)_5$ complex cycled between its oxidized and reduced states could be ruled out a priori. The propensity

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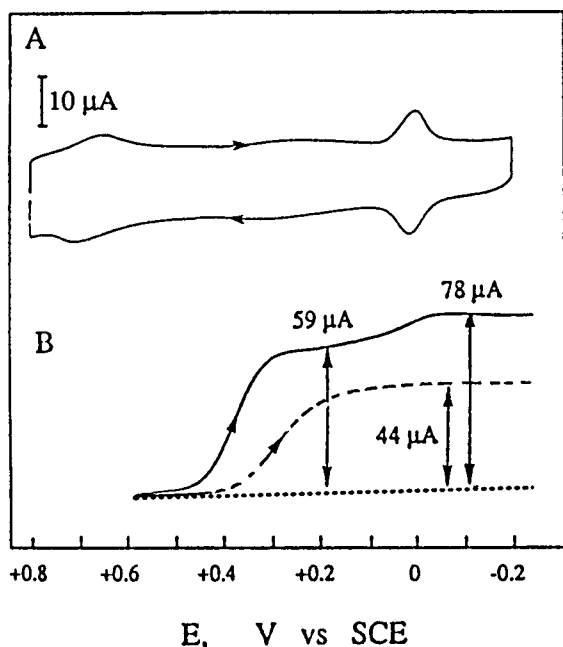


FIGURE 8. (A) Cyclic voltammetry of $[\text{CoP}(\text{py-CH}_3)_4]^{4+}[\text{Os}(\text{NH}_3)_5]^{2+}$ adsorbed on a graphite electrode. The reversible response near 0.0 V corresponds to the Os(III/II) couple. (B) Solid curve: Reduction of O_2 at a rotating (100 rpm) graphite disk electrode coated with the porphyrin from A. Dashed curve: Obtained when the disk was coated with $[\text{CoP}(\text{py-CH}_3)_4]^{4+}$ that had not been exposed to $[\text{Os}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$. Scan rates: (A) 50 mV s^{-1} ; (B) 5 mV s^{-1} .

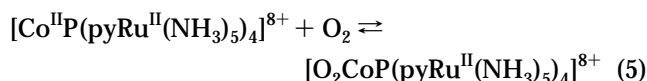
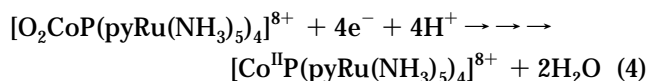
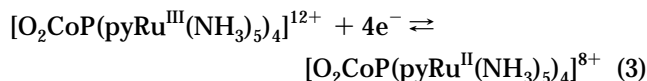
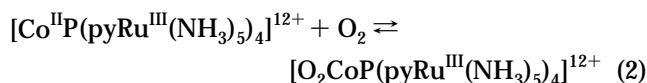
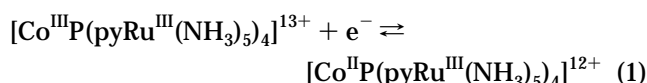
of Os(II) to coordinate to olefinic sites³⁸ led us to choose a cobalt porphyrin that contained no pendant ligand sites as the target for coordination of $\text{Os}(\text{NH}_3)_5^{3+}$ groups, namely, cobalt *meso*-tetrakis(*N*-methyl-4-pyridiniumyl)-porphyrin, $[\text{CoP}(\text{py-CH}_3)_4]^{4+}$. It proved possible to coordinate $\text{Os}(\text{NH}_3)_5^{2+}$ groups to the $[\text{CoP}(\text{py-CH}_3)_4]^{4+}$ in solution and to adsorb the resulting complex on the surface of graphite electrodes where a voltammetric response from the $\text{Os}(\text{NH}_3)_5^{3+/2+}$ couple coordinated to the porphyrin could be observed (Figure 8A).³⁹ Comparison with previous reports on the reactions of $[\text{Os}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ with pyrroles⁴⁰ indicated that the $\text{Os}(\text{NH}_3)_5^{2+}$ was probably coordinated in an η -2 form to a double bond in one of the pyrrole groups of the porphyrin. The Os(II)-porphyrin complex that is formed has not yet been isolated, but the magnitude of the response shown in Figure 8A corresponds to the coordination of about two $\text{Os}(\text{NH}_3)_5^{2+}$ complexes to each porphyrin ring. The resulting adsorbed complex catalyzed the reduction of about 30% of the O_2 molecules reaching the electrode to H_2O at potentials more positive than that where the coordinated $\text{Os}(\text{NH}_3)_5^{3+}$ was reduced to $\text{Os}(\text{NH}_3)_5^{2+}$. At more negative potentials, where the Os complex was present as $\text{Os}(\text{NH}_3)_5^{2+}$, almost 90% of the O_2 molecules reaching the electrode were reduced to H_2O (Figure 8B). That the coordination of $\text{Os}(\text{NH}_3)_5^{3+}$ converts $[\text{CoP}(\text{py-CH}_3)_4]^{4+}$ into a four-electron O_2 reduction catalyst at potentials where the Os complex cannot cycle between its oxidation states provides additional strong evidence in favor of back-bonding and against intramolecular electron-transfer as the operative electrocatalytic mechanism.

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Conclusions

The combination of data summarized in this Account leads to a mechanistic scheme for the electroreduction of O_2 in which the cobalt porphyrin is the site of the electrocatalysis and the Ru or Os complexes appended to the porphyrin ring serve as co-catalysts which affect the relative rates of the two competing electrocatalytic pathways for the reduction of O_2 . The co-catalysts engage in back-bonding to the cobalt porphyrins but do not cycle between oxidation states during the catalytic cycle. All of the electrons that reduce the O_2 substrate are supplied by the electrodes on which the cobalt porphyrin co-catalyst molecules are adsorbed. An outline of the mechanism that these new electrocatalysts are believed to follow in achieving the reduction of O_2 by four electrons is given in the scheme below. The tetraruthenated $[\text{CoP}(\text{pyRu}(\text{NH}_3)_5)_4]^{8+}$ complex is the catalyst shown in the scheme, but the general mechanism is believed to operate with the other ruthenated or osmiumated porphyrins as well.



Except for O_2 and H_2O , all of the reactants in the scheme are adsorbed on (or otherwise attached to) the graphite electrode surface. Reaction 1 generates the Co(II) porphyrin that coordinates the O_2 substrate. This reaction typically occurs at potentials more positive than those where the Ru(III) and coordinated O_2 are reduced. Reaction 2 generates the Co(II)- O_2 adduct that is more readily reduced than is the uncoordinated O_2 molecule. The equilibrium constant of reaction 2 is small, but the rate of the reaction in the forward direction is sufficient to sustain significant overall reduction rates. Reaction 3 generates the back-bonding Ru(II) cocatalyst that is responsible for facilitating the reduction of the coordinated O_2 by four electrons, as depicted in reaction 4. The Co(II)- O_2 adduct is regenerated by reaction 5, and the catalytic cycle is then carried by reactions 4 and 5. In most cases, reactions 3 and 4 proceed at the same electrode potential which implies that the potential where the back-bonding Ru(II) is produced is near to, or more negative than, that required for the reduction of the Co(II)- O_2 adduct when it experiences the electronic effects resulting from the back-bonding interactions.

The reasons that these back-bonding interactions promote the reduction of O₂ to H₂O remain to be fully elucidated. However, the electrocatalytic activity of all cobalt porphyrins depends upon the coordination of O₂ to Co(II) in a reaction that involves substantial transfer of d-electron density from the metal to the coordinated O₂.⁴²⁻⁴⁴ The attachment of electron donating groups (e.g., back-bonding metals) at the *meso* positions of the porphyrin ring might be expected to increase the extent of charge-transfer from Co(II) to O₂.⁴⁵ One result would be an enhancement in the rate and extent of formation of the Co(II)-O₂ adduct. Probably even more important is the weakening of the O-O bond that results from the transfer of electron density into antibonding orbitals. At least in the case of iron porphyrins, there is persuasive evidence showing that the rate of breakage of the O-O bond is accelerated by the presence of electron-donating groups in the *meso* positions of the porphyrin ring.⁴⁶ It seems likely that the enhancements in the rate of the electrocatalytic breakage of the O-O bond that proceeds as O₂ is reduced to H₂O have a similar origin.

The electronic effects on the Co(II)-O₂ adduct that are produced by the back-bonding of Ru(II), Os(II), or Os(III) complexes attached to the porphyrin ring might also be provided by suitable, electron-donating, nonmetallic functional groups that were attached to the porphyrin ring. Very recent experiments have shown that substantial four-electron reduction of O₂ molecules occurs at graphite electrodes on which is adsorbed a cobalt porphyrin with 4-hydroxyphenyl groups attached to the 5, 10, 15, and 20 positions of the porphyrin ring.⁴¹ No four-electron reduc-

Table 1. Metalloporphyrins Exhibiting Unusually High Activities as Electrocatalysts for the Direct Reduction of O₂ to H₂O

electrocatalyst ^a	E _{1/2} , V vs SCE ^b	ref
Co ₂ FTF4	0.48	6
Co ₂ DPB	0.46	10
Ir(OEP)H	0.48	16, 17
[Ir(OEP)] ₂ /DDAB	0.56	18
[CoP(pyRu(NH ₃) ₅) ₄]	0.23	21
[CoP(PhCNRu(NH ₃) ₅) ₄]	0.34	35
[CoP(py-CH ₃) ₄ (Os(NH ₃) ₅) ₂]	0.35	39

^a Structures of the electrocatalysts are given in the cited references. ^b Half-wave potentials for the reduction of O₂ at graphite disk electrodes coated with the electrocatalyst and rotated at 100 rpm in air- or O₂-saturated acidic electrolytes at pH 0-1. At higher pH values, the reduction of O₂ is shifted to less positive potentials and the fraction of O₂ that is reduced by four electrons diminishes.

tion results with phenyl, cyanophenyl, pyridyl, or *N*-methylpyridiniumyl groups in these positions. Thus, the 4-hydroxyphenyl groups apparently donate sufficient electron density to the porphyrin ring to affect the course of the catalytic pathway for the electroreduction of O₂. In contrast with the ruthenated and osmiumated derivatives, the reduction catalyzed by the 4-hydroxyphenyl porphyrins appears to proceed in two closely spaced steps with H₂O₂ as an intermediate.⁴¹ Nevertheless, the result obtained is encouraging because it suggests that a variety of cobalt porphyrins derivatized only with organic functional groups, and therefore more readily synthesized than cofacial or multinuclear catalysts, may also prove to be electrocatalysts for the four-electron reduction of O₂.

Table 1 contains a compilation of metalloporphyrin electrocatalysts that exhibit significant activity for the four-electron reduction of O₂ at notably positive potentials.

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