Evidence of the Importance of Back-Bonding in Determining the Behavior of Ruthenated Cyanophenyl Cobalt Porphyrins as Electrocatalysts for the Reduction of Dioxygen

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Cobalt porphyrins adsorbed on the surface of graphite electrodes are effective electrocatalysts for the reduction of O_2 to H_2O_2.[1] In a series of recent reports it was demonstrated that coordination of $Ru(NH_3)_5^{2+}$ centers to π-acid ligands pendant to the porphyrin ring can convert the resulting cobalt porphyrin into an electrocatalyst for the direct four-electron reduction of O_2 to H_2O.[1−5] The source of the enhanced catalytic activity exhibited by the ruthenated cobalt porphyrins has been speculated to result more from π-back-bonding interactions between the Ru(II) centers and the porphyrin ring than from intramolecular electron transfer from Ru(II) to O_2 molecules coordinated to the Co(II) center of the porphyrin.[3−5] In an attempt to examine this conjecture more extensively, we prepared (5,10,-15-tris(3-cyanophenyl)-20-(1-methylpyridinium-4-yl)porphyrinato)cobalt(II) and its triply-ruthenated derivative and compared its electrocatalytic behavior with that of the corresponding triply-ruthenated 4-cyanophenyl derivative that was described in a recent report.[5] Clarke and Ford[6] have demonstrated that back-bonding by $Ru(NH_3)_5^{2+}$ centers coordinated to the cyano sites in 3- or 4-cyanopyridine was substantially greater for the 4-cyano derivative. We anticipated that the same would be true of the corresponding cyanophenyl cobalt porphyrins so that the importance of back-bonding in determining electrocatalytic activities of ruthenated porphyrins might be discerned by comparing the behavior of the two isomers as catalysts for the electroreduction of O_2. The significantly different electrocatalytic behaviors observed for the two isomers, described in this report, support the proposal that back-bonding interactions are quite important in determining the electrocatalytic properties of ruthenated cobalt porphyrins.

Results

Synthesis. The (3-cyanophenyl)porphyrin (**I** in Figure 1) and the corresponding *N*-methylpyridinium cobalt porphyrin (**II** in Figure 1) were synthesized by procedures similar to those described recently for the 4-cyanophenyl isomers[5] (see the Experimental Section). As before,[5] stable coatings of porphyrin **II** were obtained by mixing it with a dilute alcoholic solution of Nafion, transferring aliquots of the mixture to the surface of the graphite electrode, and allowing the solvent to evaporate. The resulting coatings were exposed to a solution of $Ru(NH_3)_5OH_2^{2+}$ to obtain the triply-ruthenated porphyrin[5] (**III** in Figure 1).

Voltammetric Responses of the Adsorbed Porphyrins. The Co(III)/Co(II) couple of adsorbed **II** produced the broad but reproducible response shown by the solid line in Figure 2A. (The corresponding 4-cyanophenyl cobalt porphyrin behaved similarly.[5]) The area between the dashed (background current) and solid lines in Figure 2A corresponds to 2.0×10^{-9} mol cm^{-2} of porphyrin compared with the 2.1×10^{-9} mol cm^{-2} that was initially transferred to the electrode surface. This relatively good agreement allowed the use of the area between curves such as those in Figure 2A as a measure of the quantities of porphyrin present on electrode surfaces. After reaction of the adsorbed porphyrin with $Ru(NH_3)_5OH_2^{2+}$, the voltammetric response shown in Figure 2B was obtained. The prominent reversible response at 0.28 V corresponds to the $Ru(NH_3)_5(3\text{-}NCPh)^{3+/2+}$ couple of the ruthenated porphyrin. This formal potential matches that obtained previously with the $Ru(NH_3)_5(4\text{-}NCPh)^{3+/2+}$ couple confined on the surface of graphite electrodes.[5] The area between the dashed and solid curves in Figure 2A corresponds to 6.1×10^{-9} mol cm^{-2} of Ru which amounts to 2.9 Ru centers per cobalt porphyrin, indicating that the conversion of **II** to **III** (Figure 1) was essentially complete.

Catalysis of the Reduction of O_2. Cyclic voltammograms for the electroreduction of O_2 at graphite electrodes coated with porphyrin **II** or **III** (Figure 1) are shown in Figure 3A,B. The responses obtained with catalyst coatings prepared from the corresponding 4-cyanophenyl cobalt porphyrins[5] are shown in Figure 3C,D. Before ruthenation, the two cobalt porphyrins behave essentially identically in catalyzing the two-electron reduction of O_2 to H_2O_2.[1] After ruthenation the responses from the Ru centers are also essentially identical in the absence of O_2 (dashed curves in Figure 3B,D). However, much larger peak currents for the reduction of O_2 are obtained with the (4-cyanophenyl)- than the (3-cyanophenyl)porphyrin (solid curves in Figure 3B,D). Measurements with catalyst-coated rotating disk electrodes, using procedures previously described,[5] showed that the fully ruthenated (3-cyanophenyl)porphyrin catalyst accomplished only the two-electron reduction of O_2 while the 4-cyanophenyl isomer yielded largely a four-electron reduction. A summary of the behavior of the two porphyrins is given in Table 1.

Discussion

The results shown in Figure 3 and Table 1 clearly demonstrate the sensitivity of the two isomeric, ruthenated porphyrin catalysts to the nature of the linkage between the Ru(II) centers and the porphyrin ring. Clarke and Ford[6a] demonstrated that $(NH_3)_5RuNC(py)^{2+}$ (py = pyridine) is a significantly stronger base when the cyano group is in the 4- rather than the 3-position of the pyridine ring and concluded that the difference in basicity reflects a difference in the extent to which the electron density that enters the π^* orbitals of the coordinated cyano group because of back-bonding[6b] is transmitted to the nitrogen atom of the pyridine ring. Extension of this line of reasoning to the case of the (cyanophenyl)porphyrins provides a reasonable explanation for the differences in the behavior of the two catalysts recorded in Figure 3 and Table 1: The equivalence of the formal potentials of the Ru(III)/Ru(II) couples of the two isomeric complexes indicates comparable degrees of back-bonding from the Ru(II) centers to the π^* orbitals of the cyano group in each case. However, the extent of transmittal of the enhanced electron density in the cyanophenyl ligand to the porphyrin ring containing the cobalt−O_2 adduct that is the important intermediate in the catalytic cycle[5] is evidently greater when the Ru(II) is coordinated to the 4-cyanophenyl than to

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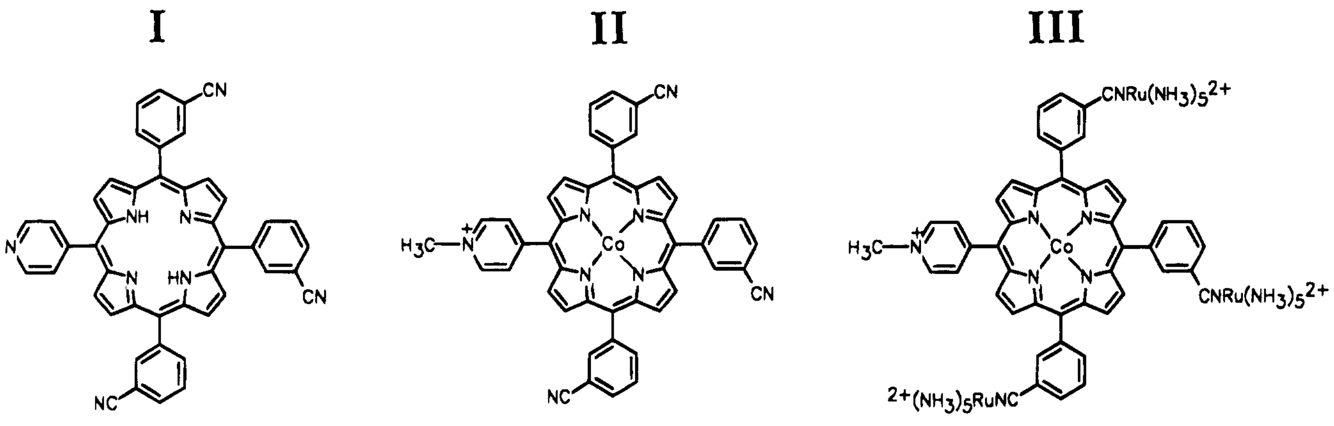

Figure 1. Structures of the porphyrins prepared as part of this study.

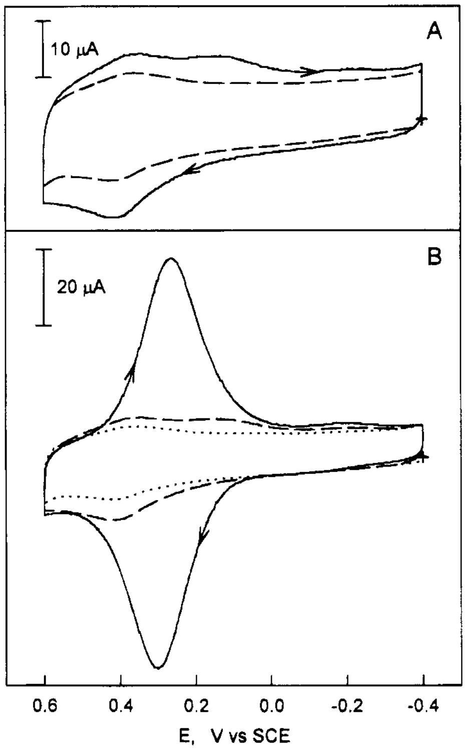

Figure 2. Cyclic voltammetry of cobalt(II) porphyrins confined on the surface of pyrolytic graphite electrodes. (A) 2.1 × 10^{-9} mol cm^{-2} of porphyrin **II** (Figure 1) plus Nafion (1.3 × 10^{-8} mol cm^{-2} of sulfonate groups). The dashed curve was recorded with the Nafion-coated electrode in the absence of porphyrin. (B) Response obtained after the porphyrin-coated electrode had been exposed to a 25 mM solution of $Ru(NH_3)_5OH_2^{2+}$ for 75 min. The dashed and dotted curves are the solid and dashed curves, respectively, from (A). Supporting electrolyte: 0.5 M NH_4PF_6–0.5 M $HClO_4$ saturated with Ar. Scan rate = 50 mV s^{-1}.

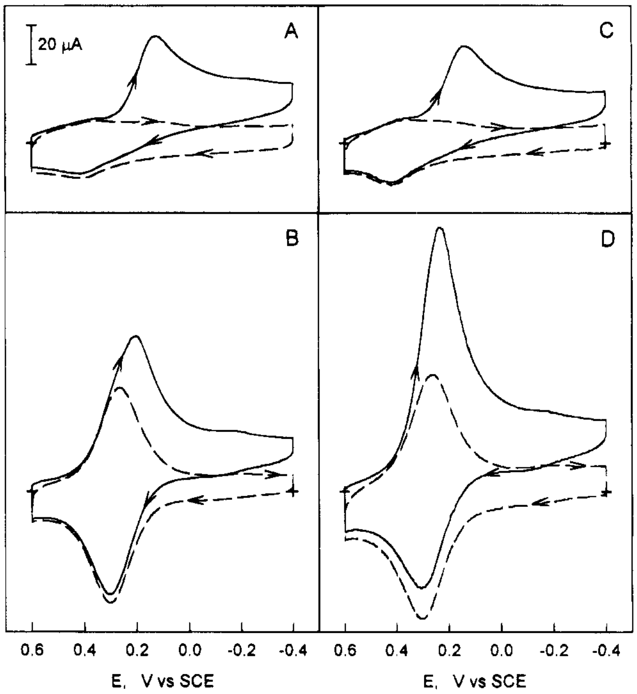

Figure 3. Comparison of the two isomeric cobalt (cyanophenyl)-porphyrins as electrocatalysts for the reduction of O_2: (A) voltammograms of graphite electrode coated with 2.1 × 10^{-9} mol cm^{-2} of porphyrin **II** (Figure 1) and 1.3 × 10^{-8} mol cm^{-2} of Nafion sulfonate groups; (B) voltammograms after the coating in (A) was ruthenated to produce porphyrin **III** (Figure 1); (C) repeat of (A) using the corresponding (4-cyanophenyl)porphyrin derivative; (D) repeat of (B) using the corresponding ruthenated (4-cyanophenyl)porphyrin. Supporting electrolyte: 0.5 M NH_4PF_6–0.5 M $HClO_4$ saturated with argon (dashed curves) or air (solid curves).

the 3-cyanophenyl ligand. The transmission of back-bonding electron density to the cobalt center in the porphyrin ring could be enhanced for both isomeric complexes from an increase in ligand π-acidity produced by formation of the Co–O_2 adduct. However, the ensuing catalytic reduction of the adduct prevents the observation of any difference in the formal potential of the Ru(III)/Ru(II) couple before and after formation of the Co–O_2 adduct. The underlying reason that the electronic interactions arising from the back-bonding divert the reduction of O_2 from a two- to a four-electron pathway remains to be elucidated. However, it seems likely that a change in the relative rates of the breaking of the cobalt–O_2 bond and the acceptance of electrons from the electrode by the bound, partially reduced O_2 is a key aspect of the back-bonding interactions.

It is relevant to draw attention to the work of Haim and co-workers,[7,8] who examined the effect of linkage isomerism on the rates of intramolecular electron transfer between $Fe^{II}(CN)_5$ and $Co^{III}(NH_3)_5$ centers bridged by pyridinecarboxylate[7] or cyanopyridine[8] ligands. With both ligands, the rate was significantly greater for the 4- than for the 3-pyridine derivative. No comparable study appears to have been conducted with $Ru(NH_3)_5^{2+}$ replacing the $Fe(CN)_5^{3-}$ groups, but it would not be surprising if a similar trend was observed. The results of Haim and co-workers could be used to argue that the difference in the behavior of the ruthenated 3- and 4-cyano porphyrins as electrocatalysts for the reduction of O_2 reflects the difference in rates of intramolecular electron transfer from the $Ru(NH_3)_5^{2+}$

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Table 1. Comparison of the Electrochemical and Electrocatalytic Properties of 3- and 4-Cyanophenyl Cobalt Porphyrins[a]

catalyst	$E^{f,e}$ V vs SCE	$E_{1/2}(O_2)$,[f] V vs SCE	n_{app}[g]
II[b]		0.19	2.2
III[b]	0.28	0.25	2.2
c		0.19	2.1
d	0.28	0.30	3.9

[a] Experimental conditions as in Figures 2 and 3. [b] See Figure 1. [c] The 4-cyanophenyl isomer of **II**.[5] [d] The 4-cyanophenyl isomer of **III**.[5] [e] Formal potenial of the Ru(III)/Ru(II) couple in the ruthenated porphyrin as estimated from cyclic voltammetric peak potentials recorded at 50 mV s^{-1} in the absence of O_2. [f] Half-wave potential for the reduction of O_2 in air-saturated solutions at a graphite disk electrode coated with catalyst and rotated at 100 rpm. [g] Number of electrons involved in the reduction of O_2 as estimated from the slopes of Koutecky–Levich plots.[5,11]

centers of the two linkage isomers to the partially reduced $Co^{II}-O_2$ adduct. However, arguing against this possibility is the observation that coordination of Ru^{II}(edta) (edta = ethylenediaminetetraacetate) centers to the four pyridine sites of cobalt tetrapyridyl porphyrin does not convert it into an electrocatalyst for the four-electron reduction of O_2 despite the fact that the Ru^{II}(edta) derivative is a stronger reducing agent than the corresponding $Ru^{II}(NH_3)_5$ derivative (which is a four-electron catalyst) by almost 0.25 V.[3] Araki and Toma[9] obtained a similar result using a solution of the $(Ru(edta))_4$ Co porphyrin derivative. The relative formal potentials of the Ru(III)/Ru(II) couples of the aqua, pyridine, and cyanophenyl complexes of $Ru(edta)^{2-}$ and $Ru(NH_3)_5{}^{2+}$ indicate that the Ru(II) center in $Ru(NH_3)_5{}^{2+}$ back-bonds more extensively to these ligands than does the former complex.[3] (We presume that this order remains the same when the ligand is porphyrin **II** or its 4-cyanophenyl isomer, although Shepherd and co-workers have pointed out that the relative extent of back-bonding by $Ru^{II}(NH_3)_5$ and Ru^{II}(edta) groups is sensitive to the nature of the unsaturated ligand.[12]) This comparison is one of the reasons for our speculation that back-bonding is more important than the rate of intramolecular electron transfer in determining the behavior of ruthenated cobalt porphyrins as electrocatalysts for the reduction of O_2.

Experimental Section

Materials. The reagents and reactants employed were the same as in ref 5 except for porphyrin **I** (Figure 1). The synthesis of this porphyrin by condensation with pyrrole of a three-to-one molar ratio of 3-cyanobenzaldehyde (Aldrich, 98%) and 4-pyridinecarboxaldehyde followed procedures very similar to that given in ref 5 with a few modifications: No precipitate was obtained when the reaction mixture was treated with aqueous ammonia and cooled to −20 °C overnight, so the aqueous and organic phases were separated and a residue was obtained by rotoevaporation of the latter. This material was shown by thin layer chromatography and comparison with the porphyrins prepared in ref 5 to consist chiefly of 5,10,15,20-tetrakis(3-cyanophenyl)porphyrin and 5,10,15-tris(3-cyanophenyl)-20-(4-pyridyl)porphyrin. The mixture was dissolved in 99% chloroform/1% ethanol, and the components were separated chromatographically on silica gel columns. (Two passes through the column were required.) The desired product, **I**, was recrystallized from dichloromethane/methanol and dried under vacuum at 100 °C for 6 h. Its identity was confirmed by elemental analysis, vis, IR, and ^1H NMR spectroscopies, and spectral comparison with the known 5,10,15,20-tetrakis(3-cyanophenyl)porphyrin.[10]

Porphyrin I (Figure 1). Anal. Calcd for $C_{46}H_{26}N_8$: C, 79.98; N, 16.22; H, 3.79. Found: C, 79.73; N, 16.15; H, 3.94. Visible spectrum [λ, nm, in $CHCl_3$ ($\epsilon \times 10^{-4}$ cm^{-1} M^{-1})]: 418 (43.10), 514 (2.06), 546 (0.63), 588 (0.63), 644 (0.27). Infrared spectrum [cm^{-1}]: 3319, 2230, 1593, 1473, 1350, 1231, 976, 908, 800, 726, 695, 661, 643. ^1H NMR [500 MHz, Me_2SO-d_6]: δ 9.05 (2H, d, 5.6 Hz, pyridyl 2,6), 8.90 (2H, s (broad), pyrrole 2,18), 8.87 (6H, s (broad), pyrrole 3,7,8,12,13,17), 8.74 (3H, s, H(2)-cyanophenyl), 8.56 (3H, d, 7.7 Hz) and 8.36 (3H, d, 7.9 Hz) (H(4)- and H(6)-cyanophenyl), 8.26 (2H, d, 5.9 Hz, pyridyl 3,5), 8.05 (3H, t, 7.8 Hz, H(5)-cyanophenyl), −3.02 (2H, s, internal pyrrole).

N-Methylation of Porphyrin I. The procedure given in ref 5 was followed except that an oil instead of a precipitate was obtained when the reaction mixture was added to 200 mL of ice cold ethyl ether. The oil was separated from the mixture by decantation, washed several times with ether, and subjected to the remainder of the procedure given in ref 5 to obtain the $PF_6{}^-$ salt. Anal. Calcd for $C_{47}H_{29}F_6N_8P{\cdot}H_2O$: C, 64.98; N, 12.90; H, 3.60. Found: C, 65.12; N, 12.83; H, 3.57. Visible spectrum [λ, nm, in acetone (relative intensity)]: 416 (1.0), 512 (0.065), 548 (0.025), 588 (0.023), 644 (0.012). Infrared spectrum [cm^{-1}]: 2230, 1640, 1472, 1412, 1402, 1350, 1232, 976, 908, 846, 801, 726, 695, 664, 640. ^1H NMR [500 MHz, Me_2SO-d_6]: δ 9.46 (2H, d, 6.3 Hz, pyridinium 2,6), 9.03 (2H, s (broad), pyrrole 2,18) superimposed by 9.01 (2H, d, 6.5 Hz, pyridinium 3,5), 8.99 (2H, s (broad), pyrrole 3,17), 8.90 (4H, s (broad), pyrrole 7,8,12,13), 8.74 (3H, s, H(2)-cyanophenyl), 8.56 (3H, d, 7.6 Hz) and 8.39 (2H, d, 7.9 Hz) superimposed by 8.38 (1H, d, 7.8 Hz) (H(4)- and (H(6)-cyanophenyl), 8.074 (2H, t, 7.8 Hz) superimposed by 8.067 (1H, t, 7.8 Hz) (H(5)-cyanophenyl), 4.71 (3H, s, *N*-methylpyridinium), −3.01 (2H, s, internal pyrrole).

Cobalt(II) was inserted into the N-methylated porphyrin by the procedure given in ref 5 to obtain porphyrin **II** (Figure 1). Stock solutions of porphyrin **II** (0.17 mM) were prepared by sonicating the solid in methanol at room temperature.

Preparation of Catalyst Coatings. Aliquots (5.2 μL) of mixtures of 100 μL of the porphyrin stock solution with 30 μL of 0.5 wt % Nafion in methanol were transferred to graphite electrode surfaces to obtain catalyst coatings which were dried and ruthenated as described.[5] Stable coatings of the porphyrins resulted with molar ratios of Nafion sulfonate groups to cobalt porphyrin of 6 or greater. However, careful control of this ratio was required to obtain complete ruthenation of the cyanophenyl groups in the coatings. Molar ratios of 8 or greater prevented complete ruthenation, and when the total quantity of porphyrin in the coatings exceeded ca. 2.1×10^{-9} mol cm^{-2} (e.g., 3×10^{-9} mol cm^{-2}), complete ruthenation was not obtained at any molar ratio of the two reactants.

Procedures. The spectroscopic and electrochemical measurements were carried out as described.[5]

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