

Therefore, it is not likely to result in a difference between the reactivities at either sides of $[\text{Pt}(1,3\text{-dach})(\text{OH}_2)_2]$. The decrease in the rate for 1,3-dach, compared with the rate obtained in the case of Pt(dap), suggests that the cyclohexane ring of Pt(1,3-dach) somewhat retards the approach of 5'-GMP.

(4) In the second-step reaction, the rates for binding of the second 5'-GMP to the side cis to the NH_2 group (i.e. k_{2a}) are almost equal within experimental error, except for the case of Pt(1,3-dach), just as seen for the first binding step (i.e. k_{1b}). Thus, binding of the second 5'-GMP to the side cis to the N-substituted group is greatly hampered by the $\text{N}(\text{CH}_3)_2$ and $\text{N}(\text{CH}_2\text{CH}_3)$ groups. The decrease in k_{2a} and k_{2b} in the case of Pt(1,3-dach) arises from the steric hindrance due to the cyclohexane ring.

(5) In the second step of the reaction, the methyl group on Pt(mdap) hardly seems to impede an approach of 5'-GMP. In fact, the NMR spectrum showed that each H8 resonance due to the 1:1 compounds decreases with time by almost the same velocity to yield the corresponding 2:1 compound.

(6) In comparisons of the first- and second-step reactions for the binding of 5'-GMP to the side cis to the NH_2 group, the rate constant for the second 5'-GMP is almost 6 times smaller than that for the first 5'-GMP. This is likely to result from the steric effect of the bound 5'-GMP in the 1:1 compounds, making the approach of the second slower. It should be noted that changes in the amine ligands might have some small influence on the pK values of the hydrolysis and that some contribution to the different K values may originate from such a statistical contribution.

Concluding Remarks. In this paper the rotation of 5'-GMP about the Pt-N7 bond—an important process in the intrastrand reaction with DNA—in $[\text{Pt}(1,3\text{-diamine})(5'\text{-GMP-N7})(\text{OH}_2)_2]$ and $[\text{Pt}(1,3\text{-diamine})(5'\text{-GMP-N7})_2]$ has been described. The presence of the $\text{N}(\text{CH}_3)_2$ group significantly slows down the rotation of 5'-GMP, whereas the presence of the $\text{NH}(\text{CH}_3)$ group in Pt(mdap) and the cyclohexane ring in Pt(1,3-dach) still allows fast rotation of 5'-GMP. Our conclusions agree with those reported earlier by Marcellis et al.²¹ and Cramer and Dahlstrom²⁶ on two related ligands.

Our kinetic data appear to agree also with our results of the rotation study. The kinetics would not necessarily have to yield the same effects because steric hindrance in the kinetics would involve a five-coordinated intermediate, whereas the rotation of 5'-GMP is influenced by the structure in a square-planar complex.

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Registry No. Pt(dap)(OH_2)₂²⁺, 73946-66-4; Pt(1,3-dach)(OH_2)₂²⁺, 111348-91-5; Pt(tmdap)(OH_2)₂²⁺, 89172-79-2; Pt(mdap)(OH_2)₂²⁺, 111348-92-6; Pt(edap)(OH_2)₂²⁺, 111348-93-7; 5'-GMP, 85-32-5.

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“Multilayer” Activity and Implications of Hydrogen Peroxide in the Catalytic Reduction of Dioxigen by a Dicobalt Cofacial Bis(porphyrin) ($\text{Co}_2\text{FTF4}$)

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Highly purified samples of the dicobalt face-to-face porphyrin dimer $\text{Co}_2\text{FTF4}$ spontaneously adsorb onto graphite electrodes as “multilayer” assemblies. Coverages corresponding to 30 or more monolayers on the geometric electrode area are electroactive. These modified electrodes electrocatalytically reduce dioxigen to water at moderately high potentials in acidic solutions; however, not all of the electroactive film participates in the catalytic reaction. A quantitative assessment of the potential dependence of the product distribution (H_2O vs H_2O_2) is presented; $\text{Co}_2\text{FTF4}$ reduces O_2 exclusively to H_2O at high potentials but also produces H_2O_2 at potentials negative of the $\text{Co}^{\text{III}}\text{Co}^{\text{II}}/\text{Co}^{\text{II}}\text{Co}^{\text{II}}$ formal potential. The catalyst-coated electrode also reduces H_2O_2 to H_2O in acidic media; this finding is discussed in the context of the mechanism of O_2 reduction and the efficiency of the system as an oxygen cathode. Strategies are presented for increasing the efficiency of the system.

Introduction

One promising application of chemically modified electrodes is electrocatalysis.^{1,2} Many metal complexes of porphyrins,³⁻⁵ phthalocyanines,^{6,7} and other macrocycles^{8,9} have been irreversibly adsorbed onto graphite electrodes to yield electrochemically and electrocatalytically active assemblies. Some of these modified electrodes are capable of the electrocatalytic reduction of O_2 to H_2O without the intermediate production of H_2O_2 ; such catalysts may be useful for fuel cell applications. This four-electron pathway has been demonstrated, with varying degrees of success, for a few metal-containing macrocycles.^{10,11}

In a series of publications, Collman et al. have detailed the synthesis, characterization, and electrochemical properties in both aqueous and nonaqueous solutions of $\text{Co}_2\text{FTF4}$ (Figure 1); many

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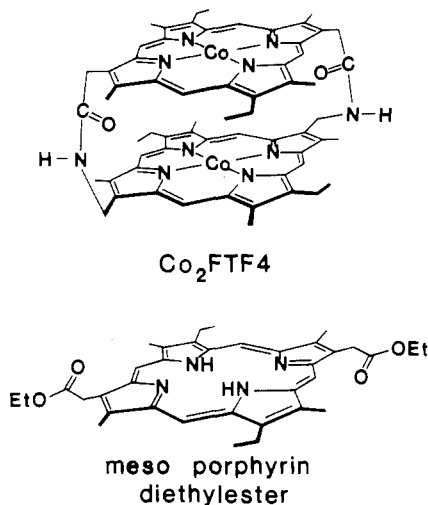


Figure 1. Porphyrins employed in this study.

other cofacial dimeric porphyrins have also been studied.^{3,12-22} Adsorbed $\text{Co}_2\text{FTF4}$ is an active catalyst for the four-electron reduction of O_2 at moderately high potentials in an acidic aqueous solution; in this respect $\text{Co}_2\text{FTF4}$ remains unsurpassed by any molecular catalyst. More recently, Chang et al. have prepared analogous dicobalt cofacial porphyrins and demonstrated that these dimers exhibit catalytic behavior similar to that of $\text{Co}_2\text{FTF4}$.^{28,29}

Recently, samples of $\text{Co}_2\text{FTF4}$ have been prepared and rigorously purified by chromatographic methods more powerful than

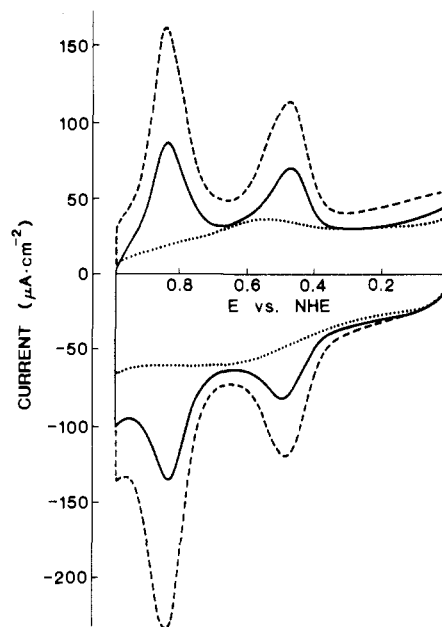


Figure 2. Cyclic voltammograms for surface-adsorbed $\text{Co}_2\text{FTF4}$ in 0.5 M $\text{CF}_3\text{CO}_2\text{H}$, N_2 -saturated solution (sweep rate = $100 \text{ mV}\cdot\text{s}^{-1}$): (—) $\Gamma_{\text{tot}} = 8 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$; (---) $\Gamma_{\text{tot}} = 2.8 \times 10^{-9} \text{ mol}\cdot\text{cm}^{-2}$; (···) response at the uncoated electrode. Potentials are referenced to NHE.

those employed in previous studies. Electrochemical experiments, in both the presence and absence of dioxygen, illustrate some notable differences when compared to early studies. In particular, greater quantities of electroactive $\text{Co}_2\text{FTF4}$ (corresponding to 30 or more monomolecular layers on the geometric electrode area) are irreversibly adsorbed onto edge-plane graphite electrodes. The relationship between the rate of catalytic O_2 reduction and the quantity of $\text{Co}_2\text{FTF4}$ applied to the electrode surface has been investigated. The results of these and related experiments are reported herein. The important issues in the present study are the following: (a) formation of a model that describes the kinetics of electrocatalysis; (b) the relationship between the electrode potential and the product distribution during O_2 reduction (e.g., H_2O vs H_2O_2).

Experimental Section

Apparatus and Procedures. Cyclic voltammetry and rotating-disk voltammetry were conducted with commercially available instrumentation and electrodes (Pine Instruments Co., Grove City, PA). A Teflon-shrouded, edge-plane pyrolytic graphite electrode (area = 0.45 cm^2) was coated with $\text{Co}_2\text{FTF4}$ by either (a) syringing from chloroform solutions of known concentration or (b) dip-coating from $\sim 10^{-4} \text{ M}$ solutions of methylene chloride. Before coating the electrode, it was polished with silicon carbide paper (3M Co. no. 600), sonicated for 1 min, and thoroughly washed with deionized water. Insofar as we can determine, there is no difference between the pretreatment described here and the method used in an earlier study of $\text{Co}_2\text{FTF4}$.¹⁶ In the present study, it was found that if the bare electrode is further polished with alumina (0.05 μm , Buehler, Ltd.) before application of $\text{Co}_2\text{FTF4}$, the resulting cyclic voltammetric waves under nitrogen are broad and ill-defined.

Potentiostatic determination of currents as a function of electrode rotation rate was conducted in a three-compartment cell, wherein the counter electrode was a platinum disk. All potentials were referenced to Ag/AgCl (saturated KCl) and are reported vs the normal hydrogen electrode (NHE).

In all $\text{Co}_2\text{FTF4}$ /dioxygen reduction experiments, catalyst-coated electrodes were, prior to data acquisition, "conditioned" in the following way: in the O_2 -saturated electrolyte, the electrode potential was turned on at +0.4 V vs NHE for 30 s. We established that electrodes treated in this way display more stable currents in potentiostatic $i_{\text{lim}}(\omega)$ determinations. For example, about 80% of the initial dioxygen reduction current remains after 1 h of catalysis at 0.4 V, when the electrode rotation rate is held constant at 4000 rpm. Without this conditioning, currents are much less reproducible from experiment to experiment.

For $\text{Co}_2\text{FTF4}$ -catalyzed dioxygen reduction, the slopes of Koutecky-Levich plots were determined by linear regression from data points acquired at 400, 1600, 2500, and 3600 rpm.

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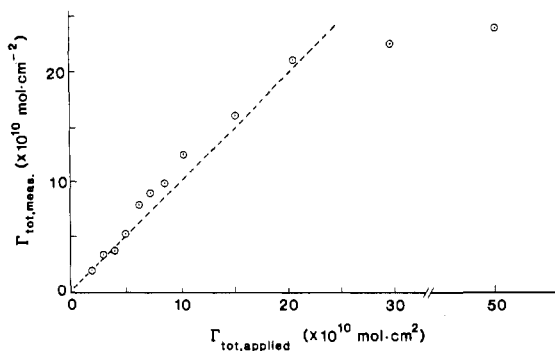


Figure 3. Comparison of the quantity of catalyst applied (Γ_{tot}) to the quantity measured by coulometry (Γ_{meas}). Γ_{meas} values were acquired from cyclic voltammetry in 1 M $\text{CF}_3\text{CO}_2\text{H}$ under a nitrogen atmosphere; sweep rate = $100 \text{ mV}\cdot\text{s}^{-1}$.

Materials. Mesoporphyrin diethyl ester and the free-base porphyrin dimer $\text{H}_4\text{FTF4}$ were synthesized as previously described.¹² In early studies, $\text{H}_4\text{FTF4}$ was purified on a gravity silica column. In the present study, $\text{H}_4\text{FTF4}$ was chromatographed twice on $3.5 \text{ cm} \times 14 \text{ cm}$ columns employing TLC grade silica gel (EM Science, 240–400 mesh) at elevated pressure ($\leq 14 \text{ psi}$). ^1H NMR spectroscopy (Nicolet, NMC 300) and UV-visible spectroscopy (Varian, Cary 219) were as previously reported for $\text{H}_4\text{FTF4}$.

Cobalt was inserted as before,¹² and mass spectral analysis (m/e 1096) was as previously reported.

Reagent grade trifluoroacetic acid (Aldrich), (\pm)-10-camphorsulfonic acid (Aldrich), hydrogen peroxide (3%, Baker), and dioxygen (Matheson) were used without further purification.

Results

Electrochemical and Electrocatalytic Activity. The cyclic voltammetric response of an edge-plane pyrolytic graphite electrode coated with highly purified $\text{Co}_2\text{FTF4}$ under nitrogen is shown in Figure 2. The solid and dashed curves correspond to relatively thin and thick coatings, respectively. Two reversible, surface-confined couples are observed near 0.8 and 0.5 V vs NHE. These voltammetric waves were originally assigned¹⁶ to the two cobalt(III/II) couples, which were thought to occur at different potentials because of repulsive interactions between the closely confined metal centers. Recent investigations of the voltammetry of the $\text{Co}_2\text{FTF4}$ surface waves show that the more positive wave is not a cobalt redox process but involves oxidation of one porphyrin ring. The couples are still considered to be one-electron processes.²² Coulometric assay of the voltammetric waves in Figure 2 affords an estimate of the amount of electroactive $\text{Co}_2\text{FTF4}$ confined to the electrode surface. Each wave gives equivalent values, although a background current at potentials above $\sim 0.9 \text{ V}$ slightly interferes with the more positive wave. The less positive wave was used for the present studies. The coverage of the thick coat is $28 \times 10^{-10} \text{ mol/cm}^2$ of geometric electrode area, while that of the thinner coat is $8 \times 10^{-10} \text{ mol/cm}^2$. In estimating the number of monolayers that would correspond to these coverages, we assume that the porphyrin lies flat on the electrode surface and occupies 250 \AA^2 of electrode area; on this basis, a tightly packed monolayer would be $\sim 0.65 \times 10^{-10} \text{ mol/cm}^2$ of geometric electrode area. By this analysis, the coverages cited above are equivalent to about 45 and 12 monolayers for the thick and thin coats, respectively. We stress that the surface morphology of the electrodes and the orientation of the adsorbed catalyst are presently unknown; therefore, our assumptions represent an idealized coverage/monolayer correlation. Electron microscope studies to address this problem are in progress.²³

In order to determine what portion of $\text{Co}_2\text{FTF4}$ applied to the graphite electrode is electroactive, the amount of surface-attached complex measured coulometrically was compared to that applied to an electrode by evaporating solutions of known concentrations on the electrode. The results, summarized in Figure 3, demonstrate that $\text{Co}_2\text{FTF4}$ is electroactive up to a coverage of $(\sim 25\text{--}30) \times 10^{-10} \text{ mol/cm}^2$ of geometric electrode area. No significant increase in electroactivity is observed beyond this value when electrodes are coated with additional quantities of complex. The limiting

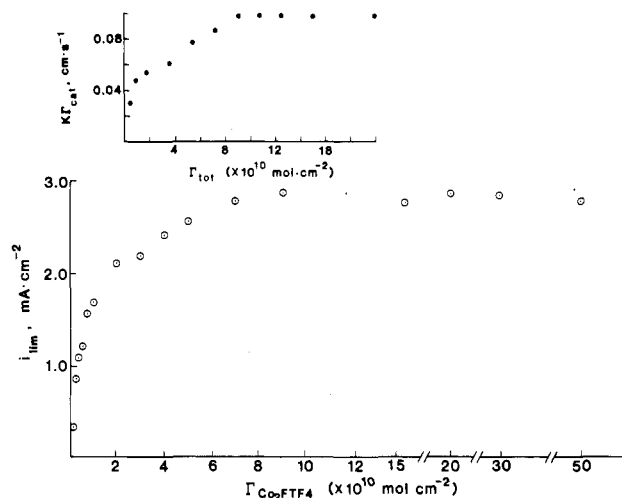


Figure 4. Variation in limiting currents for O₂ reduction at an electrode coated with increasing quantities of $\text{Co}_2\text{FTF4}$. Conditions: O₂-saturated solution, 1.0 M $\text{CF}_3\text{CO}_2\text{H}$, $\omega = 400 \text{ rpm}$, $E_{\text{app}} = +0.40 \text{ V}$ vs NHE.

electroactive coverage obtainable on the graphite surface varies between experiments; however, these values fall in the range cited above.

In an independent experiment, $\text{Co}_2\text{FTF4}$ was adsorbed onto graphite by dipping the electrode into a 10^{-4} M solution of the catalyst in CH_2Cl_2 . The amount of the complex adsorbed onto the graphite surface, estimated by spectrophotometric measurements of the decrease of the $\text{Co}_2\text{FTF4}$ concentration during adsorption, corresponds to coverages of $(20\text{--}30) \times 10^{-10} \text{ mol/cm}^2$. Washing these thick coatings with CH_2Cl_2 does not reduce the amount of electroactive material by more than 20% and generally much less. These results, obtained in a different manner, support the above observation that $\text{Co}_2\text{FTF4}$ is strongly adsorbed onto the graphite surface as a thick coating. Syringing more catalyst onto these coatings does not significantly increase the amount of electroactive $\text{Co}_2\text{FTF4}$.

The relationship between the limiting currents observed for O₂ reduction and the quantity of $\text{Co}_2\text{FTF4}$ applied to the surface is shown in Figure 4. The rate of catalytic O₂ reduction does not increase at coverages above $\sim 9 \times 10^{-10} \text{ mol/cm}^2$, despite the presence of larger quantities of electroactive catalyst (cf. Figure 3). This result might have arisen from the loss of material from the electrode surface upon exposure to O₂-saturated solutions until only $\sim 9 \times 10^{-10} \text{ mol/cm}^2$ remains or from incomplete utilization of catalytic sites within the thick film. It was verified that the former does not occur by assaying the electroactivity (under N₂) that remains after a thickly coated electrode is used briefly in catalytic O₂ reduction. The surface waves under nitrogen for such an electrode are broad and ill-defined; however, the amount of electroactivity as judged by the area under the voltammetric wave (under N₂) is not significantly reduced when compared to the freshly coated electrode. This demonstrates that more than the $9 \times 10^{-10} \text{ mol/cm}^2$ required to yield the maximum catalytic reaction rate remains electroactive on an electrode during dioxygen reduction.

A plot of $k\Gamma_{\text{cat}}$ vs Γ_{tot} , where Γ_{cat} and Γ_{tot} are the catalytically active and total surface coverages, respectively, is shown in the inset to Figure 4. The values of $k\Gamma_{\text{cat}}$ were extracted from the intercepts of Koutecky–Levich plots (with $n = 4$) determined at the coverages indicated on the horizontal axis of the inset. The slopes of these plots are independent of coverages. Considerable scatter is evident for the data at low coverages, possible due to nonuniform coatings. The data at high coverages ($> 10 \times 10^{-10} \text{ mol/cm}^2$) confirm that only a portion of these thicker coatings participates in dioxygen reduction catalysis.

The results described above suggest that dioxygen must diffuse through relatively thick coatings (multilayers or clusters) of porphyrin. To investigate this phenomenon we employed a platinumized graphite electrode at which the reduction of dioxygen is known to proceed exclusively to water and is nearly diffusion-

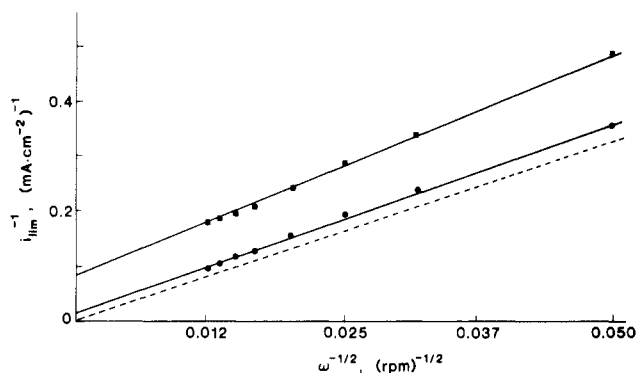


Figure 5. Koutecky-Levich plots for O_2 reduction in O_2 -saturated 0.5 M CF_3CO_2H ($E_{app} = +0.2$ V vs NHE): (●) platinized graphite electrode; (■) platinized graphite electrode with $\sim 7 \times 10^{-9}$ mol- cm^{-2} of mesoporphyrin diethyl ester (cf. Figure 1) adsorbed as outer coating; (---) calculated response for the diffusion-controlled four-electron O_2 reduction.

controlled at moderate electrode rotation rates.²⁴ The middle line in Figure 5 illustrates the i_{lim}^{-1} vs $\omega^{-1/2}$ data for catalytic dioxygen reduction at this electrode. The slope of this line indicates exclusive four-electron reduction and yields $D_{O_2}^{2/3}$ for O_2 that corresponds to literature values for the diffusion coefficient.²⁵ The top line depicts the results of an analogous experiment using a platinized electrode coated with 7×10^{-9} mol/ cm^2 of the unmetallated monomeric porphyrin shown in Figure 1. This free-base porphyrin was chosen because it does not reduce dioxygen and is not electroactive in the more positive potential region in which O_2 reduction occurs via Pt catalysis. From the data associated with the top line, two conclusions may be drawn: (a) the parallel slopes of the top and middle lines indicate that O_2 is still being reduced to H_2O and not H_2O_2 when the porphyrin coating is present, and (b) the higher intercept for the top line indicates diminished diffusion of O_2 through the multilayer coating of the monomeric porphyrin.

Theory^{36,38} and experimental techniques³⁸ for quantifying the diffusion of an electroactive substrate through a film to an underlying electrode surface have been discussed. The limiting current i_{lim} for electrochemical reaction of a solute is described by

$$\frac{1}{i_{lim}} = \frac{d}{nFAD_{s,pol}PC_s} + \frac{1}{0.62nFAD_s^{2/3}\nu^{-1/6}\omega^{1/2}C_s} \quad (1)$$

The linearity of the inverse Levich plots, together with the observed intercepts, signifies that diffusion of the substrate through the film is slow compared to its diffusion through the Levich layer. Assuming that the porphyrin is adsorbed uniformly, the quantity $PD_{s,pol}/d$ can be evaluated from the intercept, where P is the partition coefficient, $D_{s,pol}$ is the diffusion coefficient for substrate transport through the film, and d is the film thickness. Throughout this study we used a value of 1.6×10^{-5} $cm^2 s^{-1}$ for D_s , diffusion through water.

In order to estimate roughly the quantity $PD_{s,pol}$ for dioxygen diffusion through the electroinactive porphyrin film, we assign a value for d of 700 Å for the 7×10^{-9} mol/ cm^2 coat. We estimate that a layer of porphyrin, considering repulsive interactions, solvent swelling, etc., occupies 7 Å normal to the electrode surface. Our estimate of the relationship between the surface quantity of adsorbed porphyrin (mol/ cm^2 of geometric electrode area) and the number of monolayers has been discussed (vide supra). The calculated value for $PD_{s,pol}$ is 3.7×10^{-7} cm^2/s . A similar value (3.8×10^{-7} cm^2/s) was calculated for a porphyrin coverage of 14×10^{-9} mol/ cm^2 , which suggests that eq 1 is obeyed and that

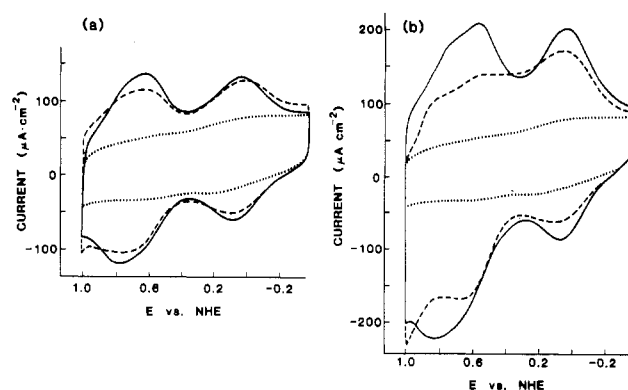


Figure 6. Effect of electrolyte on the cyclic voltammograms of surface-adsorbed Co_2FTF_4 (sweep rate = 100 $mV \cdot s^{-1}$): (—) 0.2 M trifluoroacetic acid; (---) 0.2 M (\pm)-10-camphorsulfonic acid; (···) background response in supporting electrolyte; (a) $\Gamma_{tot} = 1.2 \times 10^{-9}$ mol- cm^{-2} ; (b) $\Gamma_{tot} = 1.0 \times 10^{-8}$ mol- cm^{-2} .

diffusion of dioxygen through the film does not occur through large channels and pinholes.³⁸ Our calculated value for $PD_{s,pol}$ implies that dioxygen diffuses through the idealized film 40 times more slowly than it diffuses through aqueous solutions. Considering the assumptions we have made, this estimate appears reliable within a factor of 2–4.

That the “film” of free-base porphyrin is stable under conditions of catalytic O_2 reduction at the underlying Pt electrode was demonstrated by observing the time dependence of the O_2 reduction current. Had the catalyst been sloughing off the surface, the rate of platinum-catalyzed O_2 reduction would be expected to increase. No increase in current was observed over 5 min at a rotation rate of 6500 rpm, verifying that the free-base porphyrin coating is stable under these conditions. Additional studies have shown similar effects using the free-base cofacial dimer, H_4FTF_4 , as the electroinactive porphyrin coating.

The use of “multilayers” of Co_2FTF_4 instead of a monolayer in the electrocatalytic reduction of O_2 requires the additional consideration of ion transport through the Co_2FTF_4 film. Conductivity through this film undoubtedly occurs by electron transfer between porphyrins with metal ions in different valence states accompanied by migration of counteranions. To investigate this phenomenon, an electrolyte having a counterion bulkier than trifluoroacetate was employed. Figure 6a compares the cyclic voltammograms obtained under nitrogen in CF_3CO_2H and another acidic electrolyte, (\pm)-10-camphorsulfonic acid, for a 1.2×10^{-9} mol/ cm^2 coating of Co_2FTF_4 . The responses observed in each electrolyte were reproduced upon removing the coated electrode from one electrolyte and subsequently examining its response in the other electrolyte. The effects depicted in Figure 6 are not permanent; thus, decomposition does not occur in solutions of the camphorsulfonic acid. It is clear from the data in Figure 6b that the contrast between the two electrolytes is more dramatic at thicker Co_2FTF_4 coverages of 1.0×10^{-8} mol/ cm^2 . In this case, the more positive of the surface waves is completely broadened in the presence of the bulkier electrolyte. On the time scale associated with the cyclic voltammograms, fewer Co_2FTF_4 sites are electroactive in camphorsulfonic acid than in trifluoroacetic acid; this is true with both thin and thick coatings (cf. Figure 6a,b) and is to be expected if some of the porphyrins in the multilayer or cluster assemblies are less accessible to the camphorsulfonate ion.

Experiments were conducted to see if the effect of the bulkier electrolyte is manifested during the O_2 reduction. Limiting currents as a function of rotation rate were acquired potentiostatically in O_2 -saturated 0.2 M electrolyte solutions, first in one electrolyte and then in the other. Over coverages ranging (2 – 30) $\times 10^{-10}$ mol/ cm^2 of Co_2FTF_4 , no significant differences in the O_2 reduction rates are observed (Table I). However, at very thick coverages ($\sim 10^{-7}$ mol/ cm^2) the limiting currents in camphorsulfonic acid are somewhat lower (20%) than those observed in CF_3CO_2H .

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Table I. Comparison of Limiting Currents for O₂ Reduction in Trifluoroacetic Acid (HTFA) and (±)-10-Camphorsulfonic Acid (CSA)^a

Γ_{tot} , 10 ⁻¹⁰ mol·cm ⁻²	i_{lim} , ^b mA·cm ⁻²	
	0.2 M HTFA	0.2 M CSA
2	0.94 (1.28)	0.90 (1.23)
4	0.99 (1.49)	1.10 (1.68)
6	1.37 (2.04)	1.29 (1.85)
8	1.42 (2.12)	1.27 (1.86)
10	1.40 (2.10)	1.31 (1.95)
15	1.50 (2.36)	1.56 (2.34)
20	1.30 (2.13)	1.65 (2.40)

^a O₂-saturated solutions; $E_{\text{cell}} = +0.5$ V vs NHE. ^b $\omega = 300$ rpm for values without parentheses; $\omega = 900$ rpm for values within parentheses.

Dependence of the Product Distribution on Electrode Potential.

Dioxygen may be reduced by a two-electron pathway to H₂O₂ or a four-electron pathway to H₂O, depending on the nature and efficiency of the particular electrocatalyst.^{10,11} It is clear from rotating-ring-disk voltammetry (RRDV), in which the ring is employed as a detector of H₂O₂ produced at the catalyst-coated disk, that Co₂FTF4 produces increasing amounts of H₂O₂ as the disk potential is swept below 0.6 V vs NHE.^{30,39,40} We hoped to gain insight into the mechanisms of the four-electron O₂ reduction by quantifying this effect. RRDV has been used to quantify product distributions, but unfortunately the platinum electrode is subject to rapid poisoning in some electrolytes and such quantification is unreliable. Often only about 60% of the H₂O₂ anticipated on the basis of inverse Levich plots is detected at the ring.²⁶⁻²⁸

The current response for a Co₂FTF4-coated electrode in rotating-ring-disk voltammetry is complicated; the currents are only diffusion-controlled at low (<75 rpm) rotational frequencies, and the shapes of the voltammograms vary with rotational frequency, since the two- and four-electron O₂ reduction paths each have a distinct dependence upon potential.

We have noticed that the catalyst loses its activity if held in regions of relatively high potential (>0.55 V) in the presence of dioxygen, as evidenced by the fact that the $E_{1/2}$ of the rotating-disk voltammograms becomes increasingly more negative and the limiting currents become lower with successive scans. This is consistent with our finding²² that the porphyrin macrocycle is electroactive at potentials above ~0.6 V (cf. Figure 2); since the electrochemical response under nitrogen is not changed when the electrode potential is held as high as 0.8 V, it appears that a porphyrin radical cation is irreversibly attacked by dioxygen, with subsequent loss of the four-electron reduction activity. On the other hand, the electrocatalytic response is stable on the order of minutes if the potential is maintained below 0.55 V. For this reason, and to circumvent the difficulty with ring poisoning in RRDV quantification, we determined the product distribution for O₂ reduction by analysis of the slopes of Koutecky-Levich plots. The data were obtained potentiostatically, maintaining the electrode at potentials below 0.55 V. The four-electron reduction of O₂ at a platinized graphite electrode was employed as a standard against which the Koutecky-Levich slopes for Co₂FTF4 experiments were compared.

In Figure 7 the n values measured at various potentials are plotted on the same potential scale as that of the cyclic voltammogram for a Co₂FTF4-coated electrode obtained under N₂. From these data it can be seen that O₂ is reduced exclusively to water at potentials greater than +0.55 V. However, between +0.30 and -0.20 V, the calculated n value is nearly constant and suggests that the product distribution over this potential range slightly favors H₂O production.

Reduction of H₂O₂ by Co₂FTF4. During the reinvestigation of the electrocatalytic properties of highly purified Co₂FTF4 samples, an additional important difference in behavior was

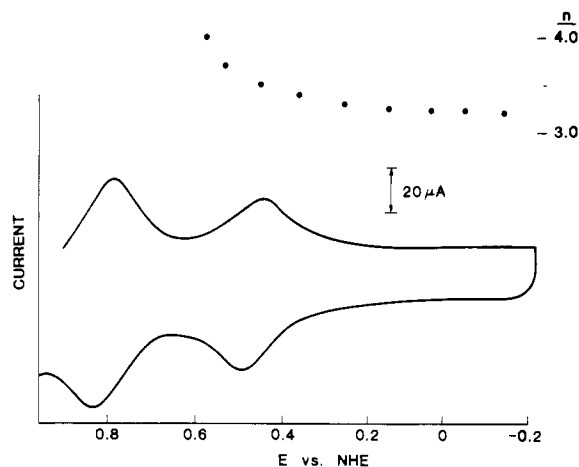


Figure 7. Dependence of the n value for O₂ reduction on the electrode potential. The values reported were obtained from i_{lim} vs $\omega^{-1/2}$ data in O₂-saturated 0.5 M trifluoroacetic acid. $\Gamma_{\text{tot}} = 1 \times 10^{-9}$ mol·cm⁻².

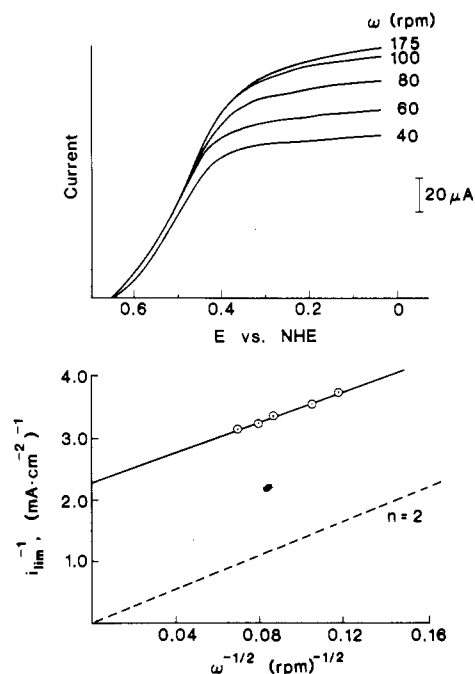


Figure 8. Top: Rotating-disk voltammetry for the reduction of H₂O₂ by surface-adsorbed Co₂FTF4. The electrolyte is 0.5 M CF₃CO₂H, N₂-saturated; [H₂O₂] = 1.0 mM. Bottom: Koutecky-Levich plot for H₂O₂ reduction catalyzed by Co₂FTF4 using currents obtained at +0.25 V. The dashed line is the calculated response for the mass-transfer-limited two-electron H₂O₂ reduction and was determined from data presented in ref 28.

discovered. In a previous investigation, it was reported that samples of Co₂FTF4 do not react with H₂O₂ in acidic media;¹² however, Figure 8 (top) depicts a rotating-disk voltammogram acquired at an electrode coated with pure Co₂FTF4 in an N₂-saturated aqueous acid solution containing 1 mM H₂O₂. The catalytic current present in Figure 8 (top) is due to the two-electron reduction of H₂O₂ to H₂O. The Koutecky-Levich plot for the Co₂FTF₄/H₂O₂ system is shown in Figure 8 (bottom); the slope of this plot is close to the calculated value for a two-electron reduction. The currents shown in Figure 8 (top) are not highly reproducible. From experiment to experiment, the maximum current occurs at electrode rotation rates varying from 150 to 200 rpm. This may be due to degradation of the catalyst by the powerful oxidant H₂O₂.

It has been observed that monomeric cobalt porphyrins do not catalyze H₂O₂ reduction at appreciable rates in acidic media;²⁹ however, such catalysis was reported by Anson and Chang et al.²⁹

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Table II. Surface Coverages (Γ_{tot}) for a Variety of Metal-Containing Macrocycles^a

entry	compd	Γ_{tot} , 10 ⁻¹⁰ mol·cm ⁻²	ref
1	iron(III) tetraphenylporphyrin	0.1	32
2	iron(III) protoporphyrin IX	25–30 ^b	33
3	cobalt(II) tetraphenylporphyrin	~1	34
4	cobalt(II) mesoporphyrin diethyl ester	4	26
5	rhodium(III) octaethylporphyrin	3–5	34
6	iron(III) tetrasulfonatophthalocyanine	~0.3	35
7	cobalt(II) tetrasulfonatophthalocyanine	~0.3	6
8	cobalt(II) tetrakis(<i>N,N,N</i> -trimethylanilinium-4-yl)porphyrin	3–4	41
9	Co ₂ FTF4	25–30	this work

^a Values were obtained on various types of graphite electrodes.

^b Although a value of 600 was reported by the authors, our calculations based on the data presented (cf. Figure 1c in ref 33) indicate that 25–30 is the true value.

for a dimeric cofacial porphyrin that is structurally similar to Co₂FTF4.³⁰ These authors observed that for this catalyst the rate of electrocatalytic reduction of H₂O₂ is very slow compared to the rate of O₂ reduction; from the results shown in Figure 8 (bottom) it is clear that this is also true for Co₂FTF4.

Discussion

"Multilayers". An inspection of the literature (cf. Table II) suggests that clearly defined surface waves are rarely observed for large quantities of metal macrocyclic complexes adsorbed onto graphite electrodes. We were quite surprised by the observation that dense coatings of Co₂FTF4 are stable on an electrode surface in the presence of an organic solvent, even though crystals of the complex readily dissolve in the same solvent. At present we are unable to distinguish between structural or electronic factors as the cause of this "multilayer" stability. Early studies of Co₂FTF4 suggested, on the basis of an ill-defined cyclic voltammetric response, that at most a few layers of electroactive material could be irreversibly adsorbed onto an electrode surface.^{12,16} If we assume, as have others,^{5,6,31} that a monolayer of adsorbed porphyrin is equal to (0.3–0.6) × 10⁻¹⁰ mol/cm², the thickly coated electrode in Figure 1 would correspond to 45–90 monolayers. We do not know the electrode roughness factor; the roughened edge-plane graphite which is *required* to support these coatings has an ill-defined morphology and chemical surface composition. However, the slow diffusion of O₂ and of bulky electrolytes implies thick regions of adsorbed catalyst. If the roughness factor is 2 or 3, as has been suggested for edge-plane pyrolytic graphite,²⁶ our thick coatings are equivalent to approximately 20–40 monolayers.²³ We have also considered the possibility that these large quantities of catalyst are somehow intercalated into the graphite electrode or are present as surface aggregates or "clusters", but in the absence of more information, the morphology of the catalyst on the electrode surface is unknown. A more detailed understanding of the structure of these thick coatings will require the application of surface analytical techniques such as electron microscopy. It is important to note that all of the Co₂FTF4 applied to the electrode surface is electroactive for coverages below about 25 × 10⁻¹⁰ mol/cm². Why greater quantities of the catalyst are not electroactive is not clear; however, the porphyrin catalyst adheres to the electrode (very thick coatings of the highly colored porphyrin are visible on the roughened, black surface, even after O₂ reduction catalysis). It may be that outer layers of Co₂FTF4 are situated in regions that have poor solvent penetration, insufficient counterion mobility, or poor physical/electrical contact.

We have no direct information about the morphology of the coated electrode and, as we have discussed, no precise measure

of the number of layers. However configured, the present results clearly demonstrate that large quantities of electroactive Co₂FTF4 are present on the electrode surface.

The compilation of reported surface coverages for porphyrins and phthalocyanines adsorbed onto graphite presented in Table II indicates that typically 0.1 × 10⁻¹⁰ to about 4 × 10⁻¹⁰ mol/cm² of electroactive material is observed, although one exception has been reported.³³ In the present studies, the Co₂FTF4 samples, subjected to repeated flash chromatography, are extremely pure and evidently yield unusually thick electroactive coatings. It is also possible that the unique structural features of the cofacial porphyrin dimer, or perhaps electronic characteristics associated with the mixed-valence complex Co^ICo^{III}, give rise to enhanced adsorption of electroactive metalloporphyrin.

"Multilayer" O₂ Reduction Catalysis. The most compelling evidence for the catalytic reduction of O₂ by clusters of Co₂FTF4 comes from an examination of Figures 3 and 4. There is considerably more electroactive material (Figure 3) than is required to yield the optimum O₂ reduction rate (Figure 4). Therefore, we can estimate that for a Co₂FTF4 coating of 25 × 10⁻¹⁰ mol/cm² approximately 30% of the adsorbed porphyrin is electrocatalytically active.

The results presented in Figure 5 indicating that O₂ can diffuse through thick coatings of surface-adsorbed porphyrin appear to be the first direct evidence for this phenomenon. While it is not surprising that such diffusion can occur, most studies on surface-adsorbed, nonpolymeric porphyrins have viewed the surface as an approximate monolayer coat.^{3,5,26} However, Anson et al. found that thick coats of certain iron porphyrins were electroactive and concluded that only the outermost portions of the catalyst coatings participate in catalytic O₂ reduction; either the reaction rate for O₂ reduction was too high, or the diffusion of O₂ too slow for catalysis to occur throughout the coating. In those studies, charge transport from the electrode to the solution film interface was sufficiently fast as not to impede the kinetics of catalysis.³³ The Co₂FTF4 system appears to be similar; however, it may be that O₂ diffuses further into the Co₂FTF4 "film", perhaps due to a slower reaction between O₂ and Co₂FTF4.

Although a rigorous theoretical treatment of the observed multilayer activity is not possible since the charge transport and permeability characteristics of the Co₂FTF4 coatings have not been measured quantitatively, a qualitative treatment is warranted. The constant catalytic efficiency at coverages of about (10–50) × 10⁻¹⁰ mol/cm² argues against charge-transport control. The participation of more than a single monolayer but less than the entire electroactive film in the catalytic reaction indicates that both the rate of chemical reaction and the rate of substrate (O₂) permeation are important.

Saveant et al. have described a kinetic model for the catalytic activity of redox polymer-coated electrodes. Schemes are discussed for the case when the primary reaction between the catalyst and the substrate is rate-determining.³⁶ The concentration–distance profiles of active catalyst and substrate in the film can take many forms, depending on the relative rates of charge and substrate transport through a film and the rate of the catalyst/substrate reaction. In the "R + S" case, diffusion of charge through the film is fast and the concentration of active catalyst sites is virtually constant through the film during catalysis. Here the current is limited by the transport of substrate through the solution and the film and the rate of the catalyst/substrate reaction.

The "SR" case differs from the "R + S" case only in the concentration–distance profile of substrate in the film. In the "R + S" case the entire film participates in reaction with the substrate, and the substrate concentration is nonzero at the electrode/film interface. In the "SR" case the substrate concentration falls to zero in the film, and the innermost region of film does not participate in catalysis except through the transport of charge to the outer-film region. It appears that the kinetics of catalytic dioxygen reduction by thick coats of Co₂FTF4 can be described by the "R + S" model at low coverages (<10 × 10⁻¹⁰ mol/cm²) and the "SR" model at higher coverages (up to about 30 × 10⁻¹⁰ mol/cm²). We have considered the possibility that electron transport from the

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electrode outward through the film limits the rate of dioxygen reduction. The high linearity in the slopes of the Koutecky–Levich plots is not, however, consistent with this analysis.³⁵ The limiting currents in O₂ reduction continue to increase with electrode rotation rate over the range studied ($\omega \leq 6500$ rpm), suggesting that increasing amounts of porphyrin participate in O₂ reduction as the rate of O₂ transport to the film is increased. For even thicker coats, dioxygen (and ions) must first diffuse through the electroinactive outer layers of Co₂FTF4 before reaching the electroactive portion of the film. We emphasize that these assignments are based on observation and plausible application of Saveant's theory. A more rigorous treatment would require quantitative assessment of the individual physical processes.

Dependence of Product Distribution on Electrode Potential. The dependence of the product distribution on electrode potential is plotted in Figure 7; included is a cyclic voltammogram for Co₂FTF4 obtained under N₂. The change in product distribution between 0.5 and 0.3 V coincides with the reduction of the mixed-valence Co^{III}Co^{II} form. This coincidence may be fortuitous; however, a plausible explanation is suggested by the observation that in nonaqueous solvents the mixed-valence Co^{III}Co^{II} complex has an extremely high affinity for dioxygen—much higher than does the Co^{II}Co^{II} form.²⁰ Electrocatalytic studies demonstrate that the four-electron O₂ reduction is exquisitely dependent on the precise structural nature of the cofacial catalyst. From EPR studies we know that the O₂ binding occurs inside the cavity.¹⁶ By analogy to the results observed in nonaqueous media, the adsorbed mixed-valence complex may have a higher intercavity binding affinity for O₂ than does the fully reduced catalyst. If the relative rates of O₂ binding are reflected in the equilibrium binding constants, then we expect that in the catalytic system O₂ binds to the mixed-valence compound faster than it binds to the fully reduced catalyst. Koutecky–Levich analysis indicates that the electrocatalytic reduction is preceded by a bimolecular chemical reaction that is suggested to be the binding of dioxygen to the catalyst. As the electrode potential is lowered to regions where Co^{III}Co^{II} is formed, the rate at which the catalyst reduces O₂ by two electrons via an extracavity mechanism (like cobalt monomeric porphyrins) would become competitive with the four-electron reduction pathway. In this case, the rate of intracavity binding of O₂ would decrease relative to that of extracavity binding.

We expect this two-electron reduction to become more favorable at these lower potentials, since the potential where the onset of H₂O₂ production with Co₂FTF4 occurs coincides with that at which many cobalt monomeric porphyrins reduce O₂ to H₂O₂. It is also possible that H₂O₂ "leaks" out of the cavity at an intermediate stage in O₂ reduction at the lower potentials. This could occur when one or both cobalt atoms are in the substitu-

tion-labile Co(II) state while the reduced O₂ species is present in the cavity.

H₂O₂ Reductions. In early reports, samples of Co₂FTF4 were found to be inactive for the reduction or disproportionation of H₂O₂.^{12,16} On the basis of this result and the failure to detect H₂O₂ in rotating-ring-disk O₂ reduction experiments, it was concluded that Co₂FTF4 reduces O₂ to H₂O by a direct path that does not involve the intermediacy of free H₂O₂. This conclusion is consistent with our results, which show that the reduction of H₂O₂ is too slow to account for the participation of free H₂O₂ as an intermediate in the four-electron reduction of O₂. From the intercepts of Koutecky–Levich plots, we calculate the heterogeneous rate constants $k\Gamma_{\text{cat}}$ for O₂ and H₂O₂ reductions to be 0.98 and 0.003 cm/s, respectively. The fact that only cofacial cobalt porphyrins, among cobalt macrocycles, catalyze H₂O₂ reduction in aqueous acid suggests that, as for O₂ reductions, the H₂O₂ reduction also occurs in the cavity of the cofacial catalyst. The observation that the heterogeneous rate constant for O₂ reduction is approximately 30 times larger than the value for H₂O₂ reduction may be attributed to the difference in the rates at which O₂ and H₂O₂ bind to Co₂FTF4.

Conclusions

Our discovery that thick films or clusters of Co₂FTF4 are both electroactive and electrocatalytically active toward dioxygen suggests strategies for the development of improved efficiency at the Co₂FTF4–oxygen cathode. When monomeric iron porphyrins are adsorbed on a graphite surface as electroactive multilayer assemblies, only a few outer layers are electrocatalytically active toward dioxygen reduction.³³ However, when iron porphyrins are incorporated into a polymeric matrix that possesses hydrophilic sites, many electroactive layers are also electrocatalytically active.²⁴ By incorporating large quantities of Co₂FTF4 into a suitable matrix, the number of electrocatalytically active sites (mol/cm³) remains high, and the charge-, ion-, and dioxygen-transport characteristics are favorable; this approach could therefore result in increased catalytic efficiency. We use the term catalytic efficiency here in the sense discussed by Anson et al.,³⁷ as the ratio of the observed limiting current to the mass-transfer-limited current.

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Registry No. Co₂FTF4, 71253-24-2; Co₂FTF₄⁺, 89906-36-5; O₂, 7782-44-7; HTFA, 76-05-1; H₂O₂, 7722-84-1; H₂O, 7732-18-5; Pt, 7440-06-4; mesoporphyrin diethyl ester, 74577-24-5; (±)-camphor-sulfonic acid, 5872-08-2.