Examination of Cobalt "Picket Fence" Porphyrin and Its Complex with 1-Methylimidazole as Catalysts for the Electroreduction of Dioxygen

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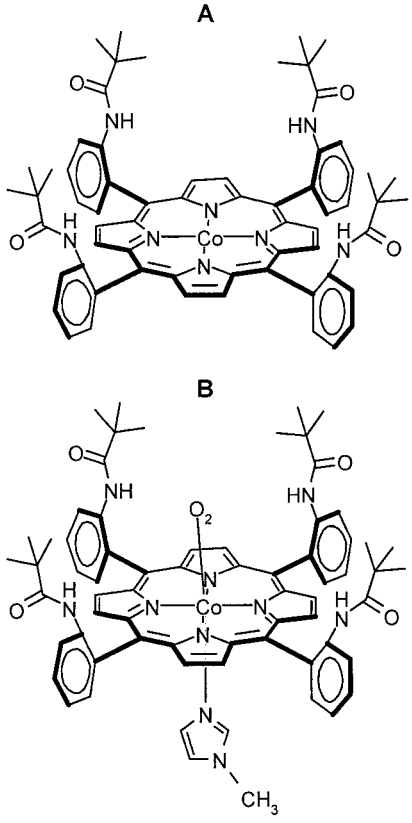
The electrochemical behavior of cobalt 5,10,15,20-tetrakis(α,α,α,α-2-pivalamidophenyl)porphyrin (Co^{II}TpivPP) was examined in benzonitrile solutions. The electrochemical responses were changed significantly by the addition of 1-methylimidazole which coordinates once to the Co(II) and twice to the Co(III) porphyrin. The corresponding equilibrium binding constants were estimated as 2.9×10^3 M^{-1} and 1.7×10^{20} M^{-2}. The cyclic voltammetric responses were affected by the rates of the ligand association/dissociation reactions. Formation of the O_2 adduct of the Co(II) porphyrin resulted in only small changes in the cyclic voltammetric pattern. Comparison between Co^{II}TpivPP and cobalt tetraphenylporphyrin (Co^{II}TPP) as catalysts for the electroreduction of O_2 showed the latter to be the superior catalyst both when adsorbed on graphite electrodes and when dissolved in thin layers of acidified benzonitrile where Co^{II}TpivPP exhibited unimpressive catalytic activity compared with Co^{II}TPP, which appeared to catalyze the reduction of O_2 by significantly more than 2 electrons per molecule.

Introduction

Cobalt porphyrins have been extensively investigated as catalysts for the electroreduction of dioxygen in aqueous solution.[1] The catalysis can be homogeneous when water-soluble porphyrins are employed, or heterogeneous when insoluble porphyrins are adsorbed (or otherwise immobilized) on the surfaces of electrodes. The mechanism that leads to the catalytic reduction is believed to commence with the coordination of O_2 to the cobalt(II) center of the metalloporphyrin.[1−3] However, the evidence supporting this mechanism is largely circumstantial because the quantity of Co(II)−O_2 adduct formed in aqueous solution is typically too small to be observed. That enhanced rates of reduction of O_2 are nevertheless observed is usually attributed to the high electrochemical reactivity of the Co(II)−O_2 adduct and its ready reformation during the catalytic cycle.

With the objective of observing the catalytically important Co(II)−O_2 adduct directly, we were drawn to the cobalt "picket fence" porphyrin, 5,10,15,20-tetrakis(α,α,α,α-2-pivalamidophenyl)porphyrin (Co^{II}TpivPP), of Collman et al.[4] (Chart 1) because of its unique ability to form substantial concentrations of a Co(II)−O_2 adduct at room temperature in hydrocarbon solvents.[4] The electrochemical behavior of Co^{II}TpivPP and its O_2 adduct have not been previously explored in detail. We found that, in addition to its formation in hydrocarbons, the adduct could also be formed in common electrochemical solvents. Using benzonitrile (BN) as solvent and 1-methylimidazole (1-MeIm) as axial base, it was possible to discern some of the electrochemical properties of the (1-MeIm)$Co^{II}(O_2)$ adduct. A small response attributed to the reduction of the coordinated O_2 was observed.

Chart 1. Structures of Cobalt "Picket Fence" Porphyrin (Co^{II}TpivPP) (A) and the Adduct of Co^{II}TpivPP with O_2 with 1-Methylimidazole as the Axial Base (B)



This report summarizes the results obtained including equilibrium constants for the binding of 1-MeIm and O_2 to Co^{II}-

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TpivPP in benzonitrile and a comparison of Co^{II}TpivPP with cobalt tetraphenylporphyrin (Co^{II}TPP) as catalysts for the electroreduction of O_2. The four molecular "pickets" that are appended to one side of the porphyrin ring in Co^{II}TpivPP, and that are responsible for the unusually high affinity for O_2 of the 1-MeIm complex of the porphyrin, appear to hinder (rather than to enhance) its catalytic activity toward the electroreduction of O_2.

Experimental Section

Materials. The synthesis of the "picket fence" porphyrin, 5,10,15,-20-tetrakis(α,α,α,α-2-pivalamidophenyl)porphyrin, and its metalation with Co(II) were accomplished by procedures similar to those of Collman et al.[4] as described in a recent report.[5] Cobalt 5,10,15,20-tetraphenylporphyrin (Co^{II}TPP) was prepared according to procedures in the literature.[6−8] Other high-purity reagents were obtained from commercial sources and used as received except for benzonitrile (BN), which was purified by passage through a column of activated Linde 3A molecular sieves followed by distillation under reduced pressure.

Apparatus and Procedures. Conventional electrochemical cells and instrumentation were employed. Glassy carbon (GC) working electrodes from Bioanalytical Systems were polished with 0.05 mm alumina before use. Edge plane pyrolytic graphite (EPG) electrodes from Advanced Ceramics Corp. were polished on 600 grit SiC paper followed by sonication in water. The coordination of 1-MeIm by Co^{II}TpivPP in BN saturated with argon was monitored spectrophotometrically following conventional procedure.[9,10] An equilibrium association constant of 2.6×10^3 M^{-1} was estimated from the spectral data.

The coordination of O_2 by (1-MeIm)Co^{II}TpivPP was followed spectrophotometrically[4] in solutions containing sufficient 1-MeIm to convert essentially all of the Co^{II}TpivPP into (1-MeIm)Co^{II}TpivPP. The equilibrium constant for the coordination of O_2 by (1-MeIm)Co^{II}TpivPP obtained from the spectrophotometric data was ~3.9 $(atm)^{-1}$ at 25 °C and ~9.4 $(atm)^{-1}$ at 5 °C.

Except where otherwise noted, electrochemical experiments were conducted at the ambient laboratory temperature (22 ± 2 °C). Reference electrodes employed were a saturated calomel electrode (SCE), an aqueous Ag/AgCl/3 M NaCl reference electrode (−40 mV vs SCE) or a sodium chloride saturated calomel electrode, SSCE (5 mV vs SCE).

Thin layers of BN separating polished EPG electrodes from aqueous electrolyte solutions were prepared and utilized according to procedures that have been described.[11] Supporting electrolyte ($HClO_4$) partitioned into the thin layers from the aqueous supporting electrolyte solutions. The quantities of $HClO_4$ that partitioned into BN from aqueous solutions of the acid were determined by titration of aliquots of the BN phase with standard solutions of NaOH.

Results

Cyclic Voltammetry of Co^{II}TpivPP. Co^{II}TpivPP exhibited the same pattern of voltammetric responses in a variety of organic solvents. The data in this report were obtained using BN because of the good solubility of the porphyrin in this solvent (even below room temperature). In addition, the low volatility of BN facilitated the formation of stable thin layers of the solvent on the surface of graphite electrodes.

Shown in Figure 1A is a cyclic voltammogram for a solution of Co^{II}TpivPP in BN. Two reversible responses were obtained

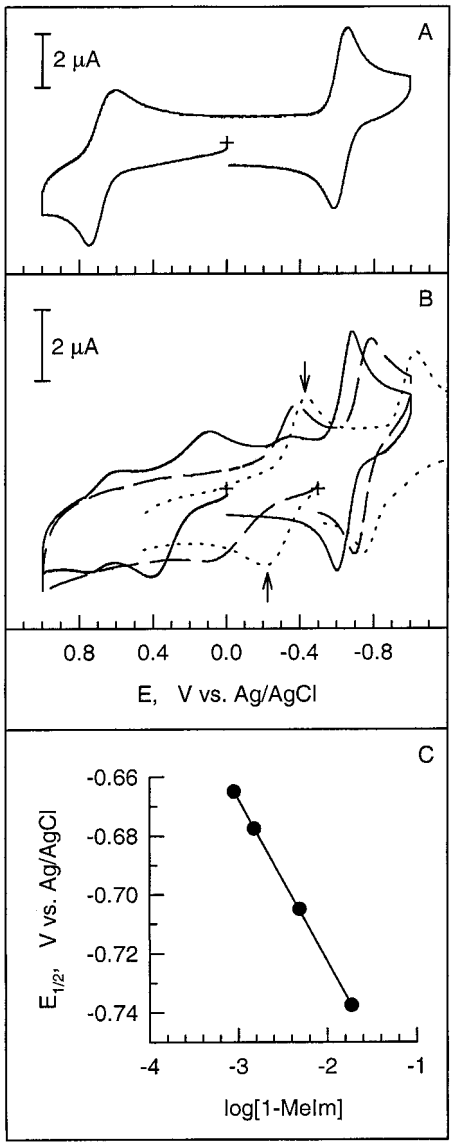

Figure 1. (A) Cyclic voltammetry of 0.5 mM Co^{II}TpivPP in benzonitrile (BN). The initial electrode potential was 0 V. Scan rate: 50 mV s^{-1}. Supporting electrolyte: 0.1 M tetrabutylammonium perchlorate (TBAP). Glassy carbon electrode (0.07 cm^2). (B) Repeat of A in the presence of 1-MeIm. The concentrations of 1-MeIm and the initial electrode potentials were (solid curve) 0.2 mM, 0 V; (dashed curve) 19 mM, −0.6 V; and (dotted curve) 1.4 M, −0.6 V. (C) Dependence of the average of the cathodic and anodic peak potentials ($E_{1/2}$) of the Co(II/I) response on the concentration of 1-MeIm.

at 0.68 and −0.62 V that can be assigned to the Co(III/II) and the Co(II/I) couples, respectively. These assignments are based on the similarity of the responses to those obtained with other cobalt porphyrins.[12]

Effect of 1-Methylimidazole on the Voltammetry. The affinity of Co^{II}TpivPP for O_2 is enhanced substantially by coordination of a suitable base in the axial coordination site on the unencumbered side of the porphyrin ring.[4] 1-MeIm is particularly effective for this purpose, so it was important to examine the effect of 1-MeIm on the electrochemistry of Co^{II}-TpivPP (at first, in the absence of O_2). Upon coordination to the cobalt center, 1-MeIm causes the voltammetric responses for both the Co(III/II) and the Co(II/I) couples to shift to more negative potentials. Shown in Figure 1B are cyclic voltammo-

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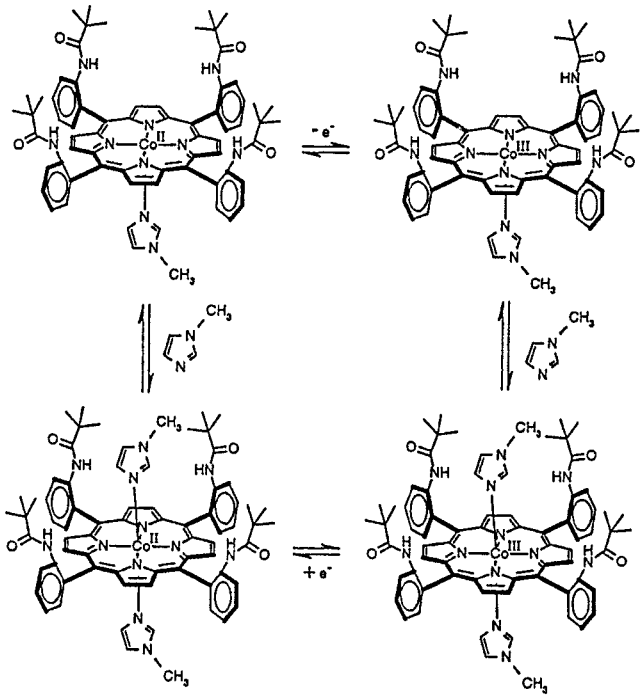
Scheme 1



grams for Co^{II}TpivPP in the presence of 1-MeIm. The responses obtained differ in three important respects from that shown in Figure 1A: (i) The oxidation of the Co(II) porphyrin occurs over a broad potential range (−0.4 to +0.6 V), and the position of the anodic response is very sensitive to the concentration of 1-MeIm. The anodic peaks are less sharp than the single anodic peak in Figure 1A, and they appear to involve more than a single electrode reaction. (ii) The Co(III) products of the oxidation give rise to several cathodic peaks with positions and magnitudes that depend upon the concentration of 1-MeIm. (iii) The response from the Co(II/I) couple lies in the range between −0.7 and −1.1 V and is not split into multiple peaks. The average of the cathodic and anodic peak potentials for the Co(II/I) couple shifts to more negative values as the concentration of 1-MeIm increases. The shift amounts to about 55 mV per decadic change in the concentration of 1-MeIm (Figure 1C), indicating that one more 1-MeIm ligand is coordinated to Co^{II}TpivPP than to $[Co^{I}TpivPP]^{-}$. With toluene as solvent, it is known that Co^{II}TpivPP coordinates only one 1-MeIm.[4] It is therefore highly likely that no 1-MeIm is coordinated to $[Co^{I}TpivPP]^{-}$ in BN. An equilibrium constant of 2.9×10^3 M^{-1} (at 25 °C) for reaction 1 in BN (containing 0.1 M tetrabutylammonium perchlorate (TBAP)) was calculated from the shift of −0.12 V in the formal potential of the Co(II/I) couple caused by the presence of 37.5 mM 1-MeIm. Analogous experiments at 5 °C and 2.5 mM

$$Co^{II}TpivPP + 1\text{-MeIm} = (1\text{-MeIm})Co^{II}TpivPP \quad (1)$$

1-MeIm yielded an equilibrium constant of 6.4×10^3 M^{-1}. The value at 25 °C is comparable to that evaluated spectrophotometrically ($K = 2.6 \times 10^3$ M^{-1}), but it is smaller than the value reported[4] with toluene as the solvent and in the absence of supporting electrolyte ($K = 1.7 \times 10^4$ M^{-1} (at 20 °C)).

To evaluate the corresponding equilibrium constant for the coordination of 1-MeIm to $[Co^{III}TpivPP]^{+}$ it was necessary to obtain the formal potential of the Co(III/II) couple in the presence of 1-MeIm. The pattern of the voltammetric responses in Figure 1B suggests a mechanistic "square scheme" such as the one depicted in Scheme 1. If the rates of the coordination−dissociation steps shown in Scheme 1 were sufficiently large, the response from the Co(III/II) couple would resemble that of the Co(II/I) couple. That is, the addition of 1-MeIm would cause the response near 0.68 V in Figure 1A to shift to more negative potentials but only one anodic and one cathodic peak would be present. The different pattern observed experimentally (Figure 1B) indicates that the coordination reactions in Scheme 1 proceed too slowly for equilibrium to be maintained during the recording of the cyclic voltammograms. However, with a sufficiently high concentration of the ligand, the Co(III/II) response more nearly resembles that of the Co(II/I) couple (Figure 1B) and the average of the resulting anodic and cathodic peak potentials (marked by arrows in Figure 1B) provides a reasonable approximation to the formal potential of the couple. A value of −0.32 V was obtained in the presence of 1.4 M 1-MeIm. The significant negative shifts in the formal potential of the Co(III/II) couple caused by the addition of 1-MeIm show that the number of these ligands coordinated to $[Co^{III}TpivPP]^{+}$ must exceed the number (one) coordinated to Co^{II}TpivPP. Since only two open coordination sites are available on CoTpivPP (Chart 1), $[Co^{III}TpivPP]^{+}$ must coordinate two 1-MeIm ligands with one located inside the "picket fence" attached to the porphyrin ring. Using the shift in the formal potentials of the Co(III/II) couple caused by the presence of 1.4 M 1-MeIm, an equilibrium constant of 1.7×10^{20} M^{-2} was calculated for reaction 2. The affinity of $[Co^{III}TpivPP]^{+}$ for 1-MeIm molecules as axial ligands is clearly much greater than that of Co^{II}TpivPP ($K = 2.9 \times 10^3$ M^{-1}).

$$[Co^{III}TpivPP]^{+} + 2\ 1\text{-MeIm} \rightarrow [(1\text{-MeIm})_2Co^{III}TpivPP]^{+} \quad (2)$$

Voltammetry of (1-MeIm)CoTpivPP(O_2). The addition of O_2 to solutions of Co^{II}TpivPP in BN containing 1-MeIm causes the formation of the (1-MeIm)CoTpivPP(O_2) complex. The assignment of oxidation states to Co and O_2 in the complex is arbitrary (Co(II) and O_2 or Co(III) and $O_2^{\bullet-}$), but spectral evidence favors the Co(III)−$O_2^{\bullet-}$ combination. In what follows we will not assign individual oxidation states in depicting the complex.

The changes in the cyclic voltammetry of (1-MeIm)Co^{II}-TpivPP that occur in the presence of O_2 are shown in Figure 2. The experiments were carried out at 5 °C where the coordination of O_2 is more extensive than at room temperature. In Figure 2A are voltammograms obtained when the electrode potential was scanned to more positive values from an initial potential of −0.6 V. Before O_2 was introduced into the solution, the response resembled that in Figure 1B with the oxidation of (1-MeIm)Co^{II}TpivPP proceeding as depicted in Scheme 1. The equilibration of the solution with first 0.2 and then 1.0 atm of O_2 converted first 66% and then 93% of the complex to the O_2 adduct and produced notable effects in the voltammetry: The broad response near 0.05 V was depressed as a new peak developed near 0.5 V. The pattern observed is consistent with a competition between O_2 and 1-MeIm for coordination to the cobalt center. The anodic response near 0.05 V corresponds to the generation of $[(1\text{-MeIm})_2Co^{III}TpivPP]^{+}$ by oxidation of (1-MeIm)Co^{II}TpivPP according to Scheme 1. In the presence of O_2 the site where the second 1-MeIm ligand coordinates is occupied by an O_2 molecule that must dissociate before the incoming 1-MeIm ligand can be accommodated. The diminished current near 0.05 V in the presence of O_2 indicates that this ligand substitution process is less facile than when the sixth coordination site on the Co(II) center is unoccupied (except,

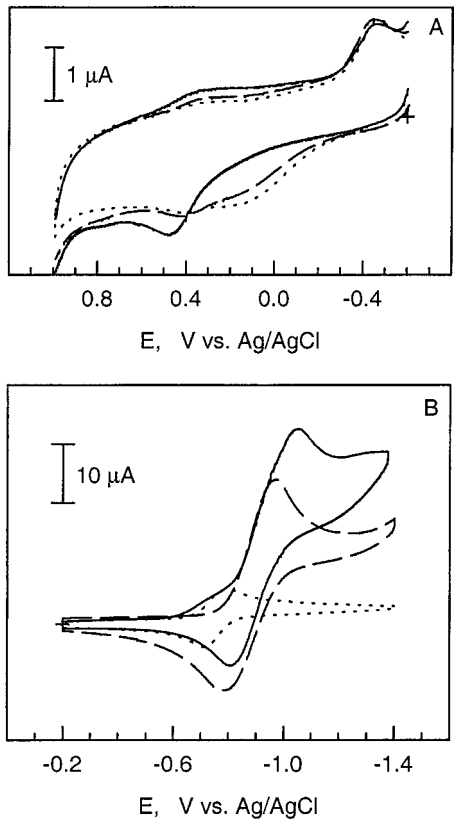


Figure 2. Effect of O_2 on the cyclic voltammetry of (1-MeIm)Co^{II}-TpivPP. (A) Electrode potential scanned from −0.6 V toward more positive potentials in a BN solution containing 0.5 mM Co^{II}TpivPP, 19 mM 1-MeIm, and 0.1 M tetrabutylammonium hexafluorophosphate. The solution was equilibrated with O_2 at partial pressures of (dotted curve) 0, (dashed curve) 0.2, and (solid curve) 1.0 atm. Scan rate: 50 mV s^{-1}. Glassy carbon electrode (0.07 cm^2). Solution temperature: 5 °C. (B) Electrode potential scanned from −0.2 V toward more negative potentials in a BN solution containing (dotted curve) 1.0 mM Co^{II}-TpivPP + 3 mM 1-MeIm, (dashed curve) 3 mM 1-MeIm and equilibrated with 0.2 atm of O_2, and (solid curve) 1.0 mM Co^{II}-TpivPP + 3 mM 1-MeIm and equilibrated with 0.2 atm of O_2. Other conditions as in panel A.

possibly, by a weakly bound solvent molecule). The new anodic peak near 0.5 V is believed to arise from the oxidation of the (1-MeIm)CoTpivPP(O_2) complex. The initial oxidation product is eventually converted to $[(1\text{-MeIm})_2Co^{III}TpivPP]^+$ (the species responsible for the cathodic peak near −0.4 V), but comparison with Figure 1B (dashed curve) shows that this ligand substitution at cobalt(III) is delayed as compared with the situation in the absence of O_2.

The cathodic voltammetry of (1-MeIm)Co^{II}TpivPP in the presence of O_2 is complicated by the fact that the reversible reduction of O_2 to $O_2^{\bullet-}$ falls in the same potential range as the reduction of the porphyrin complex. Shown in Figure 2B are cyclic voltammograms for O_2 alone, for (1-MeIm)Co^{II}TpivPP alone, and for a mixture of the two in a BN solution also containing 1-MeIm. Careful comparison of the solid and dotted curves near −0.75 V shows that the reduction of (1-MeIm)-CoTpivPP(O_2) commences slightly before the reduction of (1-MeIm)Co^{II}TpivPP. This reduction can occur at a potential less negative than that needed to reduce uncoordinated O_2 because of the stabilization of the reduction products, $O_2^{\bullet-}$ and Co(II), provided by their coordination to each other. The subsequent reduction of uncoordinated O_2 appears not to be influenced by the presence of $[Co^{I}TpivPP]^-$ at the electrode surface (compare the dashed and solid curves in Figure 2B), suggesting that the anionic $[Co^{I}TpivPP]^-$ complex has little affinity for $O_2^{\bullet-}$. The only feature in the cathodic voltammetry for the mixture in Figure 2B that differs from the sum of the responses of the two components of the mixture is the small wave at the foot of the solid curve.

Comparison of the Electroreduction of O_2 as Catalyzed by Co^{II}TpivPP or Co^{II}TPP in the Presence of Protons. The ability of a variety of cobalt porphyrins to serve as electrocatalyst for the reduction of O_2 in the presence of acid is well established.[2] Frequently, the catalyst is irreversibly adsorbed on the surface of graphite disk electrodes which are rotated in acidified solutions of O_2. As the electrode potential is scanned to more negative values, the reduction of O_2 produces steady-state plateau currents with magnitudes that increase with the rate of rotation of the electrode. Shown in Figure 3A is a set of such current−potential curves for the reduction of O_2 at a rotating graphite disk electrode coated with Co^{II}TPP. The presence of the Co^{II}TPP on the electrode surface causes the reduction of O_2 to occur at significantly more positive potentials than is the case when an uncoated electrode is used (dashed curve in Figure 3A). The catalysis is reasonably efficient because there is no indication that unreduced O_2 remains at the electrode surface where it would be reduced at the more negative potentials observed with uncoated electrodes (dashed curve).

The behavior observed when the experiments of Figure 3A were repeated with Co^{II}TpivPP adsorbed on the electrode is shown in Figure 3B. The reduction of O_2 occurs at about the same potential as with Co^{II}TPP, but the increase of the plateau currents with the electrode rotation rate is significantly smaller. Levich plots[13] of the plateau currents vs (rotation rate)$^{1/2}$ with Co^{II}TPP or Co^{II}TpivPP as the adsorbed catalyst are shown in Figure 3C, where the insensitivity of the plateau currents to the rotation rate at the Co^{II}TpivPP-coated electrode is evident. The pattern of behavior exhibited in Figure 3B,C is indicative of a mechanism in which a chemical step preceding the electrode reaction limits the magnitude of the plateau currents at the higher rotation rates. This step is most likely the coordination of O_2 to the Co(II) center of the adsorbed porphyrins. The rate of this coordination is evidently slower for Co^{II}TpivPP than for Co^{II}-TPP.

Catalytic Reduction of O_2 within Thin Layers of BN at the Electrode Surface. Further insight into the catalyzed reduction of O_2 was obtained by dissolving the porphyrin catalysts in a thin layer of BN next to the electrode instead of adsorbing them directly on the electrode surface. The utility of such adherent thin layers of organic solvents on electrode surfaces has been recently described.[11] In the present instance the thin layer methodology allowed readily measurable responses to be obtained for the reduction of O_2 in BN that was equilibrated with an aqueous solution of $HClO_4$ which partitioned into the BN layer to serve as the supporting electrolyte. Shown in Figure 4A are cyclic voltammograms obtained with an EPG electrode on which was placed a 30 μm layer of BN containing Co^{II}TPP. The electrode was immersed in 2 M (aqueous) $HClO_4$. The dashed curve is the response from the reversible Co(III/II) couple in the absence of O_2. After the aqueous solution was saturated with air, the solid curve was obtained. The large peak results from the catalyzed reduction of the O_2 present in the air-saturated BN layer. (The concentration of O_2 in air-saturated BN is ca. 1.3 mM.) The initial reduction current decays to a pseudo-steady-state value that is controlled by the rate at which O_2 can be supplied to the BN

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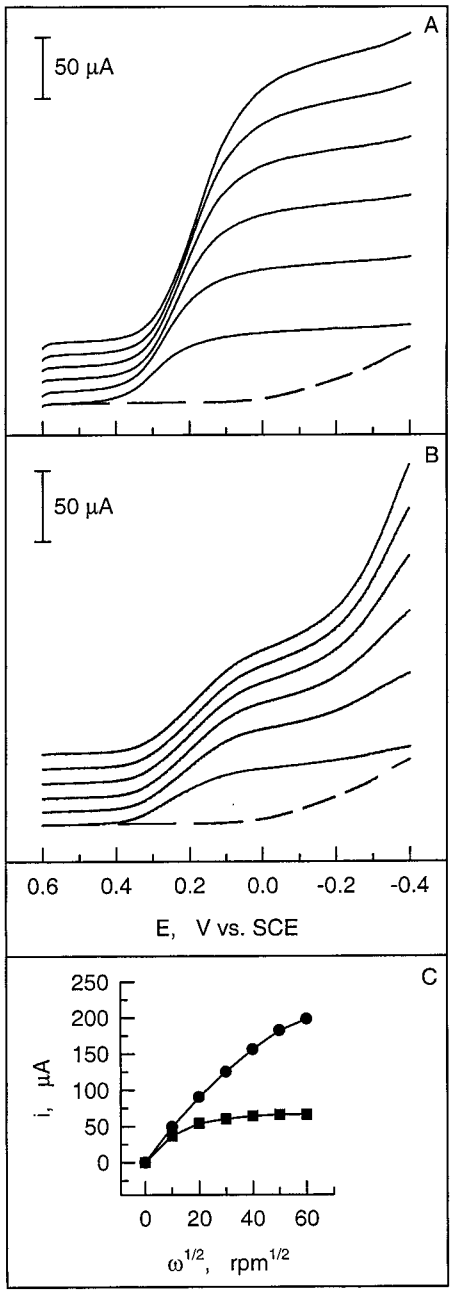

Figure 3. Current−potential curves for the electroreduction of O_2 at a rotating graphite disk electrode coated with 2×10^{-9} mol cm^{-2} of (A) Co^{II}TPP or (B) Co^{II}TpivPP. Supporting electrolyte: 0.5 M $HClO_4$ + 0.5 M NH_4PF_6 (previously shown to help stabilize porphyrin coatings on electrodes) saturated with air. Electrode rotation rates (bottom to top): 100, 400, 900, 1600, 2500, 3600 rpm. Potential scan rate: 5 mV s^{-1}. The dashed curves were obtained with the uncoated electrode at a rotation rate of 100 rpm. (C) Levich plots of the plateau currents of A (●) and B (■) vs (rotation rate)$^{1/2}$.

layer by diffusion and partitioning from the aqueous solution where the concentration of O_2 is only 0.28 mM. The catalytic efficiency of the Co^{II}TPP dissolved in the BN layer is evidently reasonably high as judged by the absence of a second cathodic peak at the potential where the uncatalyzed reduction of O_2 proceeds (dotted curve in Figure 4A).

The catalyzed reduction of O_2 begins at the same potential where the [Co^{III}TPP]$^+$ is reduced to Co^{II}TPP. This correspondence indicates that the CoTPP(O_2) adduct (presumed to be the reactive intermediate in the catalytic cycle) is reduced at potentials no less positive than 0.25 V. In the absence of

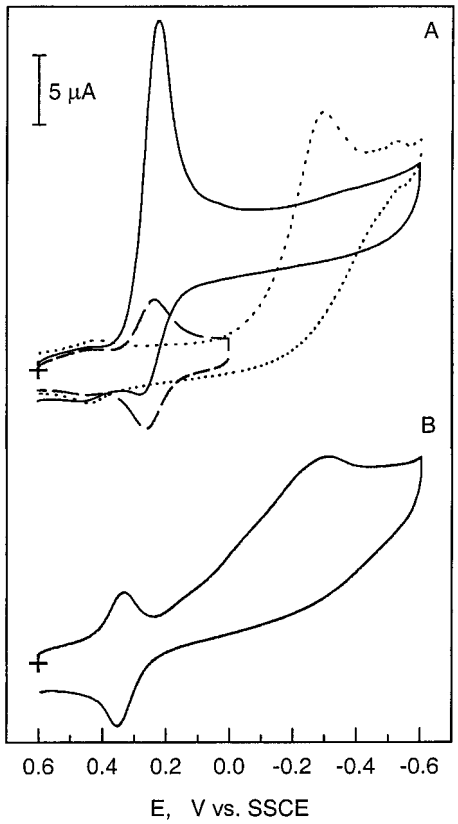

Figure 4. Cyclic voltammetry of Co^{II}TPP and Co^{II}TpivPP dissolved in thin layers of acidified BN in the presence of O_2. (A) 1.8 mM Co^{II}-TPP in a 30 μm thin layer of BN placed on an EPG electrode (0.32 cm^2) that was immersed in 2 M aqueous $HClO_4$. Dashed curve: in the absence of O_2. Solid curve: after the aqueous phase (and the equilibrated thin layer of BN) was saturated with air. Scan rate: 5 mV s^{-1}. The concentration of $HClO_4$ in the equilibrated thin layer of BN was ca. 25 mM. The dotted curve is the response obtained for the reduction of O_2 when the BN layer contained no porphyrin. (B) As for the solid curve in panel A except that 1.9 mM Co^{II}TpivPP was used in place of Co^{II}TPP.

Co^{II}TPP the reduction of O_2 occurs near −0.3 V (dotted curve in Figure 4A). The positive shift of 0.55 V in the potential where O_2 is reduced reflects the catalytic potency of Co^{II}TPP in acidified BN.

The charge represented by the flow of the pseudo-steady-state current of ca. 10 μA in Figure 4A for 140 s amounts to ca. 1400 μC. The maximum quantity of O_2 that could diffuse to the BN/H_2O interface during this time period from the 0.28 mM solution can be calculated as 4.9×10^{-9} mol. The reduction of this quantity of O_2 would consume 480 μC per electron involved in the reduction. Comparison of this value with the experimentally observed value of 1400 μC indicates that the O_2 is reduced by significantly more than 2 electrons per molecule. When adsorbed on the surface of EPG electrodes, Co^{II}TPP catalyzes the reduction of O_2 only to H_2O_2.[14] Its apparent ability to carry the reduction beyond H_2O_2 in acidified BN is noteworthy. Additional tests are called for to determine how general this novel behavior may be.

The measurements of Figure 4A were repeated with Co^{II}-TpivPP dissolved in the BN layer, and the response obtained is shown in Figure 4B. Co^{II}TpivPP is a considerably weaker catalyst than Co^{II}TPP: The catalyzed reduction begins only at more negative potentials than that where [Co^{III}TpivPP]$^+$ is

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reduced to Co^{II}TpivPP, and the wave for the reduction of O_2 is more drawn out and overlaps the wave for the uncatalyzed reduction of O_2 (dotted curve in Figure 4A). The implication is that the CoTpivPP(O_2) complex is less reactive or is formed more slowly than CoTPP(O_2), or both. Thus, Co^{II}TPP exhibits greater catalytic activity than does Co^{II}TpivPP toward the reduction of O_2 in the presence of acid both when the two porphyrins are adsorbed on graphite electrodes (Figure 3) and when they are dissolved in acidified BN (Figure 4).

Discussion

Electrochemistry of Co^{II}TpivPP. The attachment of the pivalamido "pickets" to the four phenyl rings of Co^{II}TPP does not result in significant changes in the voltammetric responses from the Co(III/II) or Co(II/I) couples of the porphyrin in BN. Except for a positive shift in formal potentials, nothing in the response shown in Figure 1A for Co^{II}TpivPP distinguishes it from that exhibited by Co^{II}TPP in the same solvent. However, Saveánt et al.[15] have shown that in solvents such as 1,2-dichloroethane a 2-electron oxidation of the TpivPP ligand occurs to produce an internal isoporphyrin. The oxidation of the cobalt(II) center of Co^{II}TpivPP occurs near the same potential so that a net 3-electron anodic peak is observed in 1,2-dichloroethane solutions of Co^{II}TpivPP.[16] That this pattern of reactivity is not seen in BN solutions reflects the greater coordinating ability of BN which shifts the potential of the Co(III/II) couple to less positive values (Figure 1A) where no oxidation of the TpivPP ligand accompanies the oxidation of the cobalt center.

Coordination of 1-MeIm by Co^{II}TpivPP in BN. The coordination of one and only one molecule of 1-MeIm by Co^{II}TpivPP in BN, as indicated by the data in Figure 1C, conforms with its behavior in toluene solutions.[4] The ~6-fold smaller equilibrium constant for the coordination in BN presumably reflects the greater nucleophilicity of BN which can compete with 1-MeIm to occupy the coordination site. The fact that a 1-MeIm ligand does not enter the cavity defined by the four "pickets" on one side of the porphyrin ring of Co^{II}TpivPP is probably a reflection of a steric barrier imposed by the pickets. However, the ligand is strongly bound to both axial coordination sites in $[Co^{III}TpivPP]^+$ (reaction 2) so the steric barrier is not insurmountable. The significantly lower intrinsic affinity of Co(II) for the 1-MeIm ligand must account for the lack of formation of $(1\text{-MeIm})_2Co^{II}$TpivPP, at least at ligand concentrations below ~1 M. The low affinity of (1-MeIm)Co^{II}TpivPP for a second 1-MeIm ligand facilitates the formation of the O_2 complex, (1-MeIm)CoTpivPP(O_2), in which the electron in the d_{z^2} orbital of the Co(II) center can participate in the bonding to the coordinating O_2 molecule.

The multiple anodic and subsequent cathodic peaks that result when 1-MeIm is added to solutions of Co^{II}TpivPP before it is anodically oxidized (Figure 1B) suggest a "square scheme" such as the one shown in Scheme 1. The anodic oxidation of (1-MeIm)Co^{II}TpivPP induces the coordination of a second ligand to produce the ultimate product, $[(1\text{-MeIm})_2Co^{III}TpivPP]^+$, but the electron-transfer and ligand association steps are evidently not concerted. The delay in the coordination step is not attributable to the presence of the molecular "pickets" because a voltammetric pattern like the one shown in Figure 1B is also obtained when Co^{II}TPP is oxidized in the presence of 1-MeIm.[16] The behavior exhibited by both cobalt porphyrins suggests that the displacement of BN on the Co(III) center by 1-MeIm may be the slow step.

Once the concentration of 1-MeIm exceeds a few millimolar, the position of the cathodic peak for the reduction of $[(1\text{-MeIm})_2Co^{III}TpivPP]^+$ (marked by the upper arrow in Figure 1B) is affected only slightly by further increases in the concentration of the ligand. This behavior indicates that the decomposition of the product of the reduction, $(1\text{-MeIm})_2Co^{II}$-TpivPP, into its stable form, (1-MeIm)Co^{II}TpivPP, is not rapid.

The absence of evidence of slow coordination steps during the reduction of (1-MeIm)Co^{II}TpivPP (and the subsequent oxidation of $[Co^{I}TpivPP]^-$ indicates that the dissociation of the single 1-MeIm ligand from Co(I) is more rapid than from Co(II); and during the oxidation of the four-coordinate Co(I) complex there is no impediment to the rapid re-entry of the ligand to the unoccupied coordination site. As pointed out by a reviewer, the observed pattern of 2, 1, 0 axial ligands for the Co(III,II,I) porphyrins echoes the coordination behavior of the cobalt center in vitamin B-12.[17]

The shifts in the formal potentials of the Co(III/II) and Co(II/I) couples of CoTPP in the presence of 1-MeIm correspond to equilibrium constants of ca. 6×10^2 M^{-1} and 1×10^{19} M^{-2} for the coordination reactions analogous to reactions 1 and 2, respectively.[16] The somewhat stronger association of 1-MeIm with $[Co^{III}TpivPP]^+$ than with $[Co^{III}TPP]^+$ may indicate a higher electron affinity of the former complex as reflected in its more positive formal potential. There is no corresponding difference in formal potentials for the two Co(II/I) couples, and the equilibrium constants for the binding of 1-MeIm to the Co(II) porphyrins do not differ greatly.

Electrochemistry of (1-MeIm)CoTpivPP(O_2). The coordination of O_2 by (1-MeIm)Co^{II}TpivPP produces only small changes in its electrochemical response (Figure 2). The coordinated O_2 apparently adds to the delay in the rate of addition of a second 1-MeIm ligand to the oxidized (Co(III)) porphyrin (Figure 2A), and the small wave at the foot of the solid curve in Figure 2B was proposed to arise from the reduction of the (1-MeIm)CoTpivPP(O_2) complex. The reduction of O_2 to $O_2^{\bullet-}$ is diffusion-controlled in BN and, therefore, not subject to catalysis. In the presence of protons or metal ions that react with $O_2^{\bullet-}$, catalysis of the reduction of O_2 *does* occur to produce different reduction products: H_2O_2 or metal$-O_2^{\bullet-}$ complexes.[18] The results shown in Figure 2B indicate that, however one may choose to assign oxidation states within (1-MeIm)CoTpivPP(O_2), its reduction takes place at a potential more positive than that where the reversible reduction of O_2 to $O_2^{\bullet-}$ occurs.

Co^{II}TpivPP exhibits some activity as a catalyst for the reduction of O_2 in the presence of acid. However, both when adsorbed on graphite electrodes (Figure 3) and when dissolved in a thin layer of acidified BN (Figure 4), it is a less effective catalyst than Co^{II}TPP. Thus, under conditions (necessarily nonacidic) where substantial quantities of the (1-MeIm)-CoTpivPP(O_2) complex are formed, there is only a small positive shift in the potential where the reduction of O_2 proceeds. In acidified media, where 1-MeIm H^+ is not coordinated by Co^{II}TpivPP, the formation (of much smaller quantities) of a reductively reactive CoTpivPP(O_2) complex is indicated by the catalytic reduction of O_2 (Figure 4B) but the catalytic turnover rate is unimpressive. Thus, the enhanced affinity for O_2 that is

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realized by the addition of pivalamido "pickets" to $Co^{II}TPP$ is not accompanied by an improvement in catalytic activity toward the reduction of O_2 in aqueous or nonaqueous solution. However, it should be noted that creation of a superior O_2 reduction catalyst was not the goal of the synthesis of cobalt picket fence porphyrin. The objective of preparing a cobalt porphyrin with an unusually high affinity for O_2 in a variety of solvents was certainly fully realized.[4]

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