to our knowledge detailed molecular orbital calculations on *closo*-MC_2B_4 cage systems are not yet available (although the hypothetical borane analogue $Fe(\eta^5\text{-}B_6H_6)_2{}^{6-}$ has been examined[14]). In any event, the close similarity observed for the species examined in this study points to a common shielding mechanism in which the metal plays a major role.

Experimental Section

The carboranes and metallaboron cluster compounds examined were obtained via procedures described in the references cited, and all solutions were prepared from dried solvents. Concentrations of each compound in different solvents were held constant by employing the same solid sample and dissolving in an identical volume of each solvent. Corrections for bulk diamagnetic susceptibilities were not made.[15] Boron-11 FT NMR spectra at 115.8 MHz were recorded at 25 ± 1 °C on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and data manipulation utilized standard Nicolet software with a 1280/293B data system. Spectra were recorded unlocked in a stable (measured drift rate <2 × 10^{-3} Hz/h) magnetic field (8.5 T). Referencing was to an external solution of $BF_3 \cdot O(C_2H_5)_2$. Uninterrupted, incoherent ^1H decoupling at low levels (~2 W) was employed.

Acknowledgment. This work was supported in part by the National Science Foundation, Grant No. 81-19936.

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[15] Corrections for bulk susceptibility are seldom, if ever applied in ^{11}B NMR spectroscopy owing to the small effects (less than normal line widths) and the relatively large uncertainty in the calculated corrections (cf: Bothner-By, R. E.; Glick, A. K. *J. Chem. Phys.* **1957**, *26*, 1647).

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Relation between the Reduction Potentials of Adsorbed and Unadsorbed Cobalt(III) Tetrakis(*N*-methylpyridinium-4-yl)porphyrin and Those Where It Catalyzes the Electroreduction of Dioxygen

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Most commonly, monomeric cobalt porphyrins, CoP, are irreversibly adsorbed on graphite or carbon electrodes and catalyze the electroreduction of O_2 to H_2O_2 at potentials significantly more negative than the formal potential of the $Co^{III/II}$ couple for the adsorbed porphyrin.[1,2] This observation is most simply explained by a catalytic mechanism in which the reduction of the cobalt center of the porphyrin from Co(III) to Co(II) is not coupled to the catalytic cycle. The latter involves coordination of O_2 to the reduced cobalt center followed by the reduction of the adduct at potentials determined by its electrochemical properties rather than those of the original cobalt porphyrin.[2] This mechanistic scheme has accommodated the results we have obtained with a series of monomeric cobalt porphyrins.[1,2] However, the Co(III/II) formal potential for cobalt tetrakis(*N*-methylpyridinium-4-yl)porphyrin, CoTMPyP, evaluated recently by Rohrbach et al.[3] (0.175 V vs. SCE) is more negative, instead of more positive, than the potential where this porphyrin catalyzes the reduction of O_2, (~0.25 V).

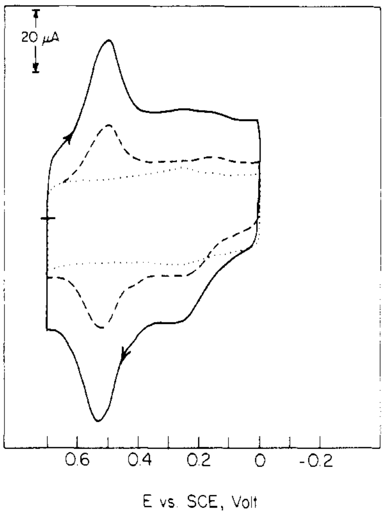

Figure 1. Steady-state cyclic voltammetry of 0.2 mM CoTMPyP in 0.5 M CF_3COOH saturated with argon (dotted curve no CoTMPyP present). Scan rates: dashed curve and dotted curve, 100 mV s^{-1}; solid curve, 200 mV s^{-1}.

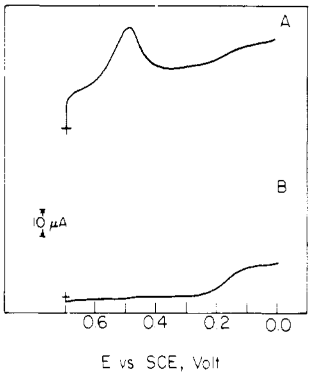

Figure 2. (A) Non-steady-state current-potential response obtained with a rotating disk electrode in the solution used to record Figure 1 (rotation rate 400 rpm; potential scanned at 100 mV s^{-1}). (B) Repeat of part A under steady-state conditions. Potential scan rate = 0 mV s^{-1}.

The origin of this apparently dissimilar behavior was traced to an unusually large change in the formal potential of the $Co^{III/II}$ couple upon the adsorption of the porphyrin on the graphite-electrode surface. The purpose of this note is to draw attention to the magnitude of the shifts in cobalt porphyrin formal potentials that their adsorption on electrode surfaces can produce and to assess its significance on the mechanism of the catalyzed reduction of O_2.

Experimental Section

$[Co^{II}TMPyP](PF_6)_4$ was prepared as previously described[4] and purified according to the procedure of Kobayashi et al.[5] $Co^{III}TMPyP$ was generated by controlled-potential oxidation at 0.6 V at a graphite-plate electrode.

The electrochemical apparatus, instrumentation, and procedures were similar to those previously described.[6,7] The working electrodes were cylindrical pyrolytic graphite rods mounted to expose the edges of the graphite planes (Union Carbide Co., Chicago). They were polished with No. 600 SiC paper (3M Co., Minneapolis, MN) and mounted as described previously.[2] Measurements were conducted at 22 ± 2 °C with solutions prepared from distilled water that had been passed through a purification train (Barnsted Nanopure + Organopure). Potentials are given with respect to a saturated calomel electrode, SCE.

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Table I. Formal Potentials ($Co^{III/II}$) and O_2 Reduction Potentials for Substituted Cobalt Porphyrins[a]

entry no.	porphyrin	E^f V vs. SCE adsorbed	E^f V vs. SCE dissolved	E_{O_2}, V vs. SCE $E_{1/2}{}^{b,d}$	E_{O_2}, V vs. SCE $E_p{}^{c,d}$	ref
1	tetraphenyl	0.75		0.18		1
2	octaethyl	0.60		0.18		1
3	tetrakis(*p*-methoxyphenyl)	0.64		0.15		1
4	tetrakis(*p*-sulfonatophenyl)	0.50		0.20		1
5	monomeric porphyrin I in ref 2	0.52		0.20		2
6	tetrapyridyl	0.55		0.20		1
7	tetrakis(*N*-methylpyridinium-4-yl)	0.52	0.18; 0.175[e]		0.23	this work
8	tetrapyridyl	0.175	−0.095		0.105	13
9	tetrakis(*o*-aminophenyl)	0.27[f]			0.05	12
10	tetrakis(*N*,*N*′,*N*″-trimethylanilinium-4-yl)	0.12–0.16	0.14		0.08	14
11	5,10,15,20-tetrakis[1-(2-hydroxyethyl)pyridinium-4-yl]		−0.035		−0.07	5

[a] Porphyrins 1–7: edge plane graphite electrode; 0.5 M CF_3COOH supporting electrolyte. Porphyrins 8–11: glassy carbon electrode; 0.05 M H_2SO_4 supporting electrolyte. [b] Half-wave potential for reduction of O_2 at a rotating disk electrode. [c] Voltammetric peak potential for the reduction of O_2 at a stationary electrode. [d] The precise values of $E_{1/2}$ and E_p show weak dependences on electrode rotation rate, potential scan rate, and catalyst concentration. [e] Reported in ref 3. [f] The origin of the single wave is unclear from the data presented.

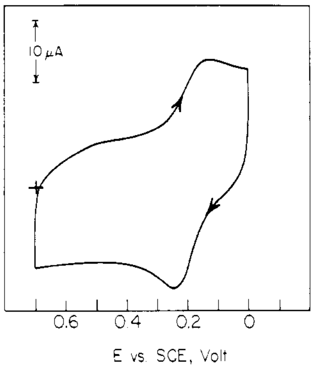

Figure 3. Steady-state cyclic voltammogram for CoTMPyP at a stationary gold electrode (0.458 cm²) (scan rate 100 mV s⁻¹). Other conditions as in Figure 1.

Results and Discussion

Cyclic voltammograms recorded with an edge-plane pyrolytic graphite electrode in a 0.2 mM solution of $Co^{III}TMPyP$ are shown in Figure 1. There is a prominent response near 0.5 V but little evidence of electroactivity in the vicinity of the reported formal potential for the $Co^{III/II}TMPy$ couple, 0.175 V.[3] The couple near 0.5 V evidently arises from adsorbed reactant because (i) the response persists when the electrode is transferred to a pure supporting electrolyte solution (cf. the first wave in Figure 4B), (ii) the peak currents are linear functions of scan rate, and (iii) the response is present when the potential of a rotating disk electrode is scanned at 100 mV s⁻¹ (Figure 2A) but absent when the voltammogram is recorded at steady state (Figure 2B). The peaked response at 0.5 V in Figure 2A matches that obtained at the stationary electrode in Figure 1, as expected if both responses arise from adsorbed reactant. The stable wave obtained in Figure 2B has a half-wave potential of 0.18 V, very close to the solution formal potential of the $Co^{III/II}TMPyP$ couple measured by Rohrbach et al.[2] This wave is therefore assignable to the reduction of $Co^{III}TMPyP$ in solution. The steady-state limiting current measured on the plateau of the wave, 25 μA cm⁻², is smaller than the value calculated from the Levich equation,[8] 36 μA cm⁻², using the reported diffusion coefficient for $Co^{III}TMPyP$ of 2.3×10^{-6} cm² s⁻¹.[9] This may result from the adsorbed porphyrin's acting as a barrier to the diffusion of the dissolved porphyrin to the electrode surface. Penetration of the adsorbed layer by the dissolved porphyrin is probably required because the rate of electron self-exchange between the +3 and +2 oxidation states of CoTMPyP would not be expected to be high enough to provide an efficient pathway for transport of electrons from the electrode surface across the adsorbed layer to the dissolved reactant. The same effect is presumably responsible for the lack of a clear second peak in the voltammograms of Figure 1. Only by combining cyclic and rotating disk voltammetry were the two, well-separated responses for the adsorbed and unadsorbed porphyrin revealed clearly.

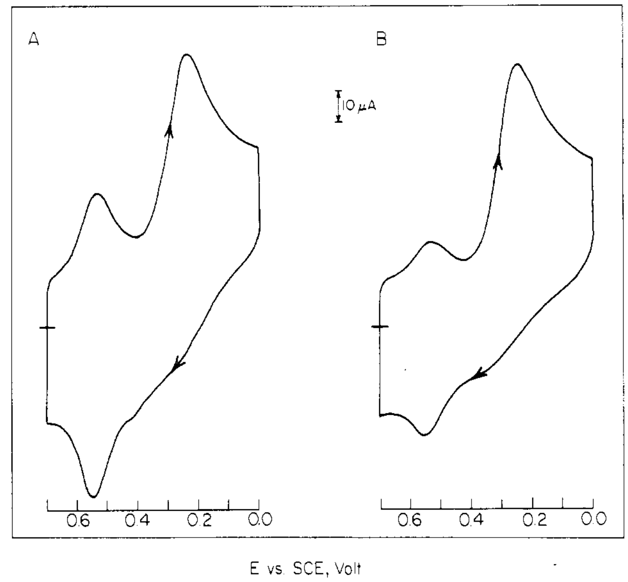

Figure 4. Reduction of O_2 as catalyzed by CoTMPyP at a stationary edge-plane pyrolytic graphite electrode (scan rate 100 mV s⁻¹): (A) for 0.5 M CF_3COOH electrolyte + 0.2 mM CoTMPyP saturated with air; (B) after the electrode from A was transferred to 0.5 M CF_3COOH saturated with air.

The adsorption of CoTMPyP is much weaker on gold than on graphite electrodes, and the voltammetric response is correspondingly more normal. Figure 3 contains a cyclic voltammogram recorded at a gold electrode. The single wave obtained with E^f = 0.18 V has a peak current close to that calculated for a diffusion-controlled reduction, and no response remains if the electrode is transferred to pure supporting electrolyte.

The result of repeating the 100 mV s⁻¹ scan of Figure 1 at a graphite electrode in the presence of air is shown in Figure 4A.

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(8) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; p 522.

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(10) Bettelheim, A.; Chan, R. J. H.; Kuwana, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *110*, 93.

(11) The possibility that the "EC catalytic" mechanism might not apply to the cobalt tetrakis(*o*-aminophenyl)porphyrin catalyzed reduction of O_2 has been mentioned in a previous preliminary report,[12] but the consequences of this possibility were not elaborated.

(12) Kobayashi, N.; Matsue, T.; Fujihira, M.; Osa, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *103*, 427.

The large wave corresponding to the catalyzed reduction of O_2 is well-separated from the surface wave for the reduction of adsorbed $Co^{III}TMPyP$. Although the O_2 reduction wave appears in the same vicinity as the *solution* formal potential of the $Co^{III/II}$ couple, the dissolved porphyrin contributes little or nothing to the catalysis because the catalytic current is not diminished when the electrode is transferred to a solution containing no dissolved $Co^{III}TMPyP$ (Figure 4B). Thus, adsorbed CoTMPyP, with a formal potential near 0.5 V catalyzes the reduction of O_2 at potentials near 0.23 V.

The greater visibility of the wave for the reduction of dissolved CoTMPyP in steady-state rotating disk current-potential curves (Figure 2B) than in cyclic voltammograms (Figure 1) is attributable, in part, to the relatively high background current that flows at edge-plane graphite electrodes when their potentials are scanned at the 100-200 mV s^{-1} rates that are typical of cyclic voltammetry.

The rate of oxidation of $Co^{II}TMPyP$ by O_2 was examined spectrophotometrically by mixing the two reactants and monitoring the spectra of the resulting solution in the region between 400 and 500 nm. In 0.1 M H_2SO_4 saturated with air, an electrolyte similar to that employed in some previous studies,[5,13,14] the spectrum observed matched that reported for $Co^{II}TMPyP$[3] for at least 60 s after mixing; even after 1 h the oxidation was less than 50% complete. Addition of a slight excess of Fe^{3+} produced an immediate conversion to the spectrum of $Co^{III}TMPyP$.[3] The oxidation of $Co^{II}TMPyP$ (5 μM) by O_2 in 0.5 M trifluoroacetic acid, the electrolyte employed in this study, proceeds somewhat more rapidly, but the half-life of $Co^{II}TMPyP$ is still over 5 min. Thus, $Co^{II}TMPyP$ and O_2 can coexist in solution for periods that are long compared to the time required for reactants to cross the diffusion layer in typical cyclic or rotating disk voltammetric experiments (0.1-1 s).

The large difference in the Co(III/II) formal potentials between adsorbed and unadsorbed CoTMPyP as measured with graphite electrodes indicates unusually favorable interactions between the cobalt center and the electrode surface when the cobalt is in the reduced state. It has been suggested in previous studies[10] that organic functional groups known to be present on the graphite surface may serve as ligands that stabilize Co(II) more than Co(III). Whatever the origin of the shift in formal potential, it is responsible for the separation between the potentials where the cobalt center exhibits its redox activity and the potentials where the porphyrin catalyzes the reduction of O_2. Because of the magnitude and direction of this separation, the mechanism of the catalysis is best regarded as "CE catalytic". That is, the O_2 substrate undergoes a chemical reaction (C) with the (reduced) catalyst that precedes its electrochemical reduction (E). Since the reduced catalyst and substrate can coexist in solution for periods that are long compared with the effective measurement times in electrochemical experiments, the "EC catalytic" mechanism (in which catalyst reduction triggers substrate reduction) that has been proposed for some porphyrin-catalyzed electroreductions of O_2[5,13,14] is clearly inapplicable to the present case.[11] The fact that the catalyzed reduction of O_2 proceeds not far from the formal potential of the $Co^{III/II}$ couple for the unadsorbed porphyrin is coincidental and does *not* imply that outer-sphere electron transfer between O_2 and the reduced catalyst is the rate-limiting step.

The literature now contains reports on the catalysis of the electroreduction of O_2 by a variety of cobalt porphyrins that includes both water-soluble and water-insoluble examples. Table I is a summary of the reported formal redox potentials of the cobalt porphyrins and of the potentials where they exhibit catalytic activity toward the reduction of O_2. The pattern that emerges from the potentials listed in Table I is of catalysts that exhibit redox activity in the adsorbed state at potentials more positive than those where they catalyze O_2 reduction and those where the dissolved porphyrin is electroactive. The redox activity of the dissolved cobalt porphyrin catalysts appears at potentials on both sides of those where O_2 reduction proceeds as would be expected if the dominant catalytic pathway involved the (inevitably present) adsorbed catalyst.

Acknowledgment. This work was supported by the National Science Foundation. We appreciated discussions with Professor T. Kuwana and access to a preprint of unpublished work from his laboratory.

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Gas-Phase Structure of Perfluoronitrosocyclobutane

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While a rather large number of acyclic nitrosofluoroalkanes have been synthesized, only a few nitrosofluoro aromatic compounds and only two fluoronitrosocycloalkanes are known.[2] In the present case, perfluoronitrosocyclobutane, it is of interest to examine the effect of the substituent on the geometry of the ring relative to perfluorocyclobutane and to compare the orientation of the NO group and structural data of the cyclic compound with that of acyclic perfluoronitrosoalkanes.

Perfluoronitrosocyclobutane was prepared from nitrosyl chloride and perfluorocyclobutane in the presence of anhydrous potassium fluoride and acetonitrile.[2] The sample was purified on a Hewlett-Packard 5710 A gas chromatograph equipped with Valco gas sample injection valves. The separation was done on a 11 ft × $^1/_4$ in. column containing 25% w/w Kel-F oil No. 3 on Chromosorb P maintained at room temperature. The injection and detector temperature was 100 °C. The sample was transferred from Idaho to Germany under liquid nitrogen.

The electron diffraction intensities were recorded on 13 × 18 cm Kodak Electron Image plates with a Balzers KD-G2 gas diffractograph[3] at two camera distances (25 and 50 cm). The accelerating voltage was about 60 kV. The sample was kept at about -50 °C during the experiment, and the inlet system and nozzle (0.25 mm diameter) were at room temperature. The background pressure in the diffraction chamber never exceeded 2×10^{-5} torr. Exposure times were 5-10 and 25-35 s for the long and short camera distances respectively. The electron wavelength was determined from ZnO diffraction patterns. Two plates for each camera distance were analyzed by the usual procedure[4] and the averaged molecular intensities for the s ranges 1.4-17 and 8-35 $Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ are presented in Figure 1.

Six possible conformations have to be considered for perfluoronitrosocyclobutane, depending on the position (axial or equatorial) and orientation (endo, exo, or gauche) of the nitroso group. A preliminary analysis of the radial distribution function (Figure 2) indicates that both exo conformers (ax-exo and eq-exo) are compatible with the experiment. A clear distinction between axial or equatorial position of the NO group is not possible. In the least-squares analysis a diagonal weight matrix was applied to the molecular intensities and scattering amplitudes and phases of ref 5 were used. The following constraints were introduced: (1) C-C and C-F bond lengths were made equal; (2) the N-O

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