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Preparation of Iron and Cobalt Phthalocyanine-1,2 : 3,4 : 8,9 : 10,11 : 15,16 : 17,18 : 22,23 : 24,25-octakis(*N*-decyldicarboximide) and Their Catalytic Behavior for Electroreduction of Oxygen

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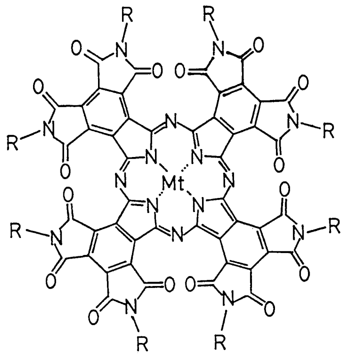
The iron and cobalt phthalocyanines included in the title have been synthesized. Their absorption spectra are unusual compared to other metallophthalocyanines, showing intense hypochromism in the Q band region. The cobalt and iron derivatives show 4-electron reduction capability in the electroreduction of oxygen over the entire range of pH values and in neutral and alkaline pH, respectively, although the potentials are not necessarily positive enough.

In the electroreduction of oxygen using monomeric iron and cobalt macrocyclic complexes as catalysts, there is a general agreement that cobalt complexes promote the O_2 reduction process via two electrons to give H_2O_2 whereas iron complexes can catalyze the more desired 4-electron reduction to water.[1] Phthalocyanines (Pcs) are not exceptions from this category. In the presence of CoPcs, oxygen is reduced to H_2O_2 over the entire range of pH values, and FePcs are active in alkaline media for the 4-electron reduction.[2] In this study, we have attempted to prepare Co- and FePcs which are active for the 4-electron reduction over a wide range of pH values. If such Pcs exist, they must be different from common Pcs in some respect, and we have selected the shape of absorption spectra as a measure of departure from the behavior of the common Pcs. Absorption spectra reflect the electronic structure of molecules, and the catalytic activity of catalysts has often been discussed in terms of their electronic structures.[3] Hence, if we use Co- and FePcs having common electronic spectra, there is a strong possibility that their behavior will not differ from the general results described above. Conversely, the use of Pcs with unusual spectroscopic shape may provide an opportunity to obtain better catalytic activity. From these considerations, we have synthesized the Co- and FePc included in the title (Scheme 1). Their absorption spectra have been found to be unusual compared to those of common Pcs as a result of strong perturbation by the 8 imide groups, and they do show a desired 4-electron reduction over a wide range of pH values.



R=H, Mt=Co; CoOIPc
R=H, Mt=Fe; FeOIPc
R=$C_{10}H_{21}$, Mt=Co; CoODIPc
R=$C_{10}H_{21}$, Mt=Fe; FeODIPc

Experimental

Measurements. Absorption spectra were obtained on a Shimadzu UV-360 spectrophotometer and magnetic circular dichroism (MCD) on a JASCO J-400X spectrodichrometer equipped with an electromagnet which produced magnetic fields up to 1.17 Tesla (T). Cyclic potential sweeps were generated by an NF circuit design FG-100 AD function generator in conjunction with a potentiostat which was built according to the literature,[4] while differential pulse voltammetric responses were obtained on a Yanaco Model P-1000 voltammetric analyzer. For rotating ring-disk experiments, an electrode rotator (Nikko-RRD-1) was used and voltammograms were recorded with a Princeton Applied Research Model 173 instrument.

Materials. For cyclic voltammetric measurements, a highly oriented pyrolytic graphite (HOPG, Union Carbide) of area 0.22 cm^2 was used. The rotating ring-disk electrode (RRDE) consisted of a glassy carbon (GC, Tokai Carbon) disk (area=0.26 cm^2) surrounded by a platinum (Pt) ring mounted in a Teflon rod (Nikko Keisoku Co.). The collection efficiency was determined to be 0.33 at 100 rpm with the ferrocyanide-ferricyanide redox couple. The Pt ring and the GC surface of the RRDE were first polished with no. 2000 emery paper and then with alumina slurry (particle sizes 1 and 0.05 μm) and well rinsed with 2 and 0.05 M (1 M=1 mol dm^{-3}) H_2SO_4 and distilled water before each run. In order to obtain a fresh surface of HOPG, a piece of Scotch tape was briefly pressed onto the surface and then gently lifted off. Usually at least two layers were removed between each adsorption study. Immobilization of the catalysts to electrodes was effected by pipetting aliquots of the catalyst solutions in chloroform onto a fresh electrode and allowing the solvent to evaporate slowly.

o-Dichlorobenzene for spectroscopy was stored for several days over molecular sieves (4Å) and distilled under nitrogen and reduced pressure. 0.05 M H_2SO_4, 0.1 M potassium phosphate buffer (pH 7.0), and 1 M NaOH were used for aqueous experiments.

Most of the chemicals used for synthesis were commercially available guaranteed reagents and used as received.

Cobalt- and Iron Phthalocyanine-1,2:3,4:8,9:10,11:15,16:17,18:22,23:24,15-octakis(dicarboximide) (CoOIPc and FeOIPc). Benzene hexacarboxylic acid (mellitic acid) prepared from the corresponding hexamethyl ester (Tokyo Kasei) by acid hydrolysis[5] was changed to its trianhydride by refluxing it in acetic anhydride for 3 h.[6] 0.15 mol of the trianhydride, 3.75×10^{-3} mol of $CoCl_2$, 0.1 mol of urea, 2.12×10^{-4} mol of ammonium molybdate were mixed in a mortar and then charged in a 50 ml round bottomed flask containing 10 ml of nitrobenzene. The mixture was heated to ca. 200 °C for 2 h, after which a further 0.1 mol of urea was added. After heating for a further 2 h, the green-black solid was washed with 6 M HCl, boiling water, and methanol. This procedure was repeated three times until the washings remained colorless. The product was added to 3 ml of concentrated sulfuric acid, shaken for 5 h at room temperature and then filtered. The filtrate was then added to crushed ice. After standing for several hours, the mixture was centrifuged, the supernatant liquid decanted, and the precipitate was collected on a glass filter, washed with water until the washings were nearly neutral, and then with ethanol. The solid was dried at reduced pressure over diphosphorus pentaoxide for 24 h. Yield 83.5%. Found: C, 49.68; H, 0.66; N, 20.31%. Calcd for $C_{48}H_8N_{16}O_{16}Co$: C, 51.31; H, 0.72; N, 19.94%. FeOIPc was similarly obtained in 37.1% yield using $FeCl_2$ instead of $CoCl_2$ in the above procedure. Found: C, 49.77; H, 0.64; N, 20.52%. Calcd for $C_{48}H_8N_{16}O_{16}Fe$: C, 51.45; H, 0.72; N, 20.00%. The compounds have IR bands at 3000—3200, 1770—1780, 1700—1720, 1460, 1400, 1050, and 760—800 cm^{-1}. The former 3 bands are ascribed to cyclic imides,[7] and the others are the common vibrations of phthalocyanine compounds.[8]

Cobalt and Iron Phthalocyanine-1,2:3,4:8,9:10,11:15,16:17,18:22,23:24,25-octakis(*N*-decyldicarboximide) (CoODIPc and FeODIPc). To 2×10^{-3} mol of CoOIPc in DMF (30 ml) was added 9×10^{-3} mol of sodium hydride and stirred for 1 h, after which the whole solution was cooled in an ice-water bath and 9×10^{-3} mol of decyl bromide was added dropwise with stirring. After 12 h, a small amount of saturated NH_4Cl was added and the solvent was removed under reduced pressure. The residue was dissolved in 1,2-dichloroethane and filtered through a G4 glass filter. The filtrate was washed with water and the organic layer dried over anhydrous $MgSO_4$. After removal of the $MgSO_4$ by filtration the solvent in the filtrate was removed by using an evaporator, and the residue was imposed on a silica-gel column using chloroform-ethanol as eluent. A black-colored portion was collected, and after evaporation of the solvent, the residue was recrystallized from chloroform-ether. The precipitate was then imposed on a Bio-beads SX-2 column using dichloromethane as eluent. The first colored eluate was collected and dried. Yield 4.9%. Found: C, 68.43; H, 7.45; N, 9.71%. Calcd for $C_{128}H_{168}N_{16}O_{16}Co$: C; 68.46; H, 7.54; N, 9.98%. FeODIPc was obtained similarly in 3.4% yield. Found: C, 68.44; H, 7.45; N, 10.24%. Calcd for $C_{128}H_{168}N_{16}O_{16}Fe$: C, 68.56; H, 7.55; N, 9.99%.

Results and Discussion

Absorption and MCD Spectra. Absorption and MCD spectra of Co- and FeODIPc are shown in Fig. 1. The shape of the absorption spectra are markedly different from those of common Pcs with first row transition metals.[9] A very intense reduction of the absorption coefficients (hypochromism) is observed, particularly in the Q band region, and the Soret band is more intense than the Q band. Also, as has been observed for phthalocyanine-2,3:9,10:16,17:23,24-tetrakis(*N*-alkyldicarboximide),[10] the Q band extends into the near-IR region (ca. 1000 nm). Thus, the attachment of a 5-membered imide ring greatly affects the electronic structure of Pcs. Since Pcs with a 5-membered anhydride ring show the normal type absorption spectra,[10] the cause of these unusual spectra is attributed to the nitrogen in the imide ring. On the other hand, the MCD spectra obtained are those expected from metallophthalocyanines with D_{4h} symmetry.[11] Faraday *A* terms appeared corresponding to the main Q bands and the region of the Soret bands. From the shape of the MCD spectra, the Soret bands of Co- and FeODIPc appear to lie at around 350 and 380—90 nm, respectively. These Q and Soret bands are shifted to longer wavelength by ca. 20—40 nm compared with those of common Pcs, reflecting the polysubstitution in the Pc periphery.[12]

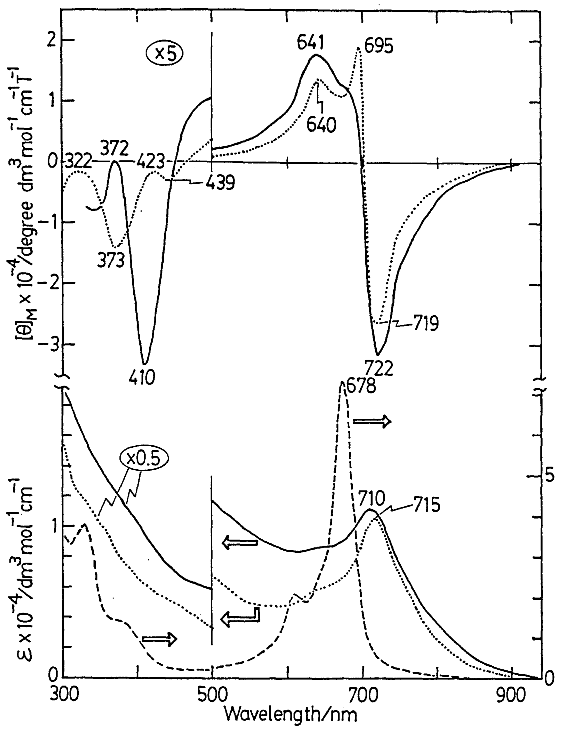


Fig. 1. UV-visible absorption (bottom) and MCD (top) spectra of FeODIPc (solid lines) and CoODIPc (dotted lines) in *o*-dichlorobenzene. [FeODIPc]/M=1.09×10^{-4} and [CoODIPc]/M=1.00×10^{-4}. Cell pathlength was 5 and 10 mm. The absorption spectrum of tetraneopentoxyphthalocyaninatocobalt(II) in *o*-dichlorobenzene (broken line) is reproduced from Ref. 20 as a typical spectrum of common phthalocyanines.

Catalytic Electroreduction of Oxygen. Figure 2 shows cyclic voltammetric (CV) diagrams and differential pulse (DP) voltammograms on Fe- and CoODIPc-adsorbed electrodes, recorded in oxygen-

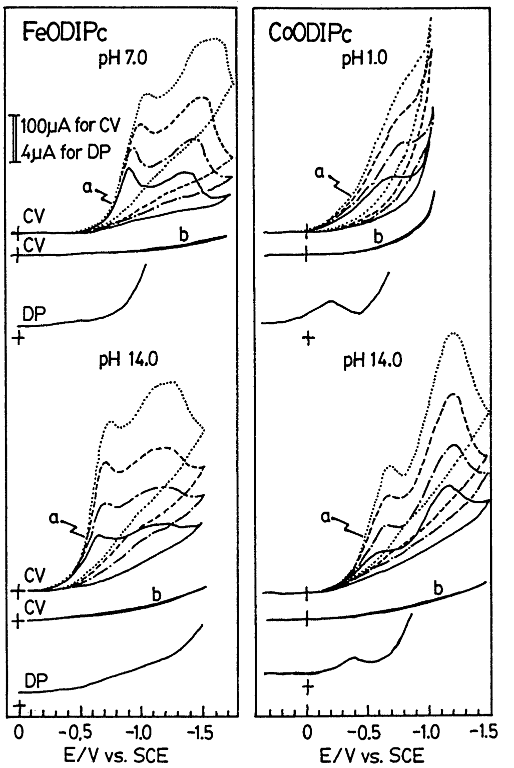


Fig. 2. CV diagrams at FeODIPc- (left) and CoODIPc (right)-adsorbed electrodes (curves **a**) and at a bare HOPG electrode (curves **b**) in the presence of oxygen, and DP voltammograms at FeODIPc- (left) and CoODIPc (right)-adsorbed electrodes in the absence of oxygen. CV curves **a** were recorded at sweep rates of 20, 50, 100, and 200 mV s^{-1} and curves **b** at 50 mV s^{-1}, while DP responses were obtained at sweep rate of 2 mV s^{-1}.

saturated or nitrogen-saturated solution at several pHs. Redox couples of FeODIPc cannot be seen even by the DP method. However, O_2 reduction proceeds in two steps at pH's 7 and 14 (CV diagram). The currents at these two peaks are proportional to the O_2 concentration and the square root of the scan rate, indicating that the current is controlled by diffusion of O_2. In the case of the CoODIPc-adsorbed electrode, a cobalt redox couple (plausibly the $Co^{II/I}$ couple) is discerned in the DP diagram. When oxygen is admitted into the solution, the onset of O_2 reduction commences at approximately the same potential as the $Co^{II/I}$ couple. One O_2 reduction wave is observed at pH 1, and two at 14. Responses at the CoODIPc-adsorbed electrode at pH 7 are close to those observed at pH 14.

O_2 reduction was further studied by using a rotating ring-disk electrode (Fig. 3). In the case of previously reported FePc catalysts, oxygen is reduced to water only in alkaline solution.[2] At the FeODIPc-adsorbed electrode, however, oxygen is reduced to water at both pH 7 and 14, although its potential is fairly negative (ca. −1.2—−1.3 V).[13] Using Eq. 1, which is applicable to a rotating disk electrode,[14] the calculated n values

$$i = 0.62\, n\mathbf{F}AD^{2/3}\nu^{-1/6}\omega^{1/2}c \qquad (1)$$

are 3.7 and 3.2 at pH 7 and 14, respectively. In Eq. 1, i, $\mathbf{F}$, A, D, c, ω, and ν are the limiting disk current, Faraday's constant, the electrode area, the diffusion coefficient of O_2, the O_2 bulk concentration, the rotation speed, and the kinematic viscosity of water, respectively, and the following values are used: $D=1.7\times10^{-5}$ $cm^2\ s^{-1}$,[15] $c=1$, 1, and 1.2 mM[16] at pH 1, 7, and 14, respectively, $\omega=13.3\ \pi$ rad s^{-1}, and $\nu=0.01$ $cm^2\ s^{-1}$.[2d,15] Judging from the responses at the ring, the production of H_2O_2 is larger at pH 7 than 14. In addition, the difference between the onset potential of O_2 reduction and the potential required for 4-electron reduction of O_2 is about twice as large as for previously reported FePc catalyst systems.[2]

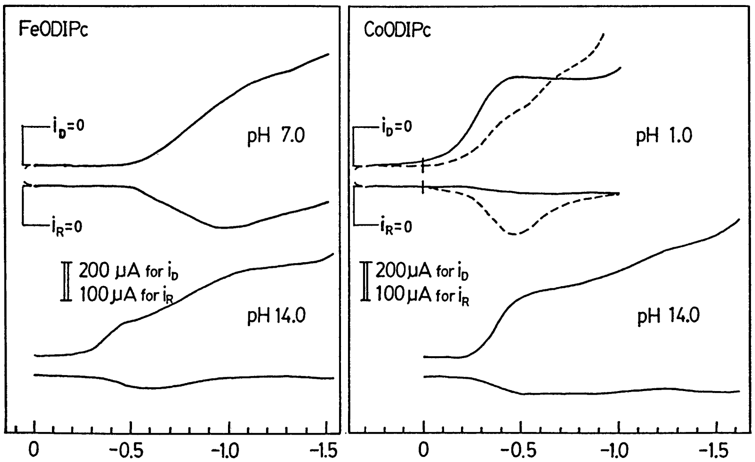


Fig. 3. Ring-disk i-E curves for the reduction of O_2 at FeODIPc- (left) or CoODIPc (right)-adsorbed electrodes. Ring potentials were set at 1.04, 0.90, and 0.72 V vs. SCE at pH 1, 7, and 14, respectively. Rotation rate/rpm=400. Broken curves are responses after several sweeps.

The behavior at the CoODIPc-adsorbed electrode is also different from that reported previously for CoPcs, in that a 4-electron reduction is obtained. The limiting disk currents at −0.5 V in pH 1 and at around −1.2— −1.3 V in pH 14 solutions correspond to ca. 3.5 electrons. Recently, Ikeda et al.[17)] reported that a polymeric catena-cyano-$Co^{III}Pc$-adsorbed electrode shows 4-electron reduction capability only in the onset of O_2 reduction. In our system, oxygen appears to be reduced to water in one step at pH 1 at a freshly prepared electrode (solid lines). However, the responses after several scans (broken lines) indicate that O_2 is reduced in two steps to water via H_2O_2,[18)] as interpreted for similar *i-E* curves of iron porphyrins.[1f,16)] Although not yet proven in any similar system by spectroscopy, such a decrease of catalytic activity after several scans has been attributed to either degradation of the catalysts or to partial removal of the catalysts from the electrode surface. In the present system, at least the latter possibility is conceivable, since a steep increase in disk current (probably hydrogen production) was recognized at a fairly negative potential (broken line, ca. −1.0 V). At pH 14, O_2 reduction proceeds in two steps even at a freshly prepared electrode, and the H_2O_2 to H_2O process occurs at a significantly more negative potential than the O_2 to H_2O_2 process.

The mechanism of O_2 reduction at the FeODIPc-adsorbed electrode is difficult to deduce because no redox couple of FeODIPc could be detected under a nitrogen atmosphere. However, from results in Figs. 2 and 3, the following mechanisms may be appropriate for the reduction at CoODIPc-adsorbed electrodes.

$$2Co^{II}ODIPc + 2e^- \rightarrow 2Co^{I}ODIPc \quad E_1 \qquad (2)$$

$$2Co^{I}ODIPc + 1/2O_2 + 2H^+ \rightarrow 2Co^{II}ODIPc + H_2O \qquad (3)$$

and

$$2Co^{II}ODIPc + 2e^- \rightarrow 2Co^{I}ODIPc \quad E_1 \qquad (4)$$

$$Co^{I}ODIPc + 1/2O_2 + H^+ \rightarrow Co^{II}ODIPc + 1/2H_2O_2 \qquad (5)$$

$$Co^{I}ODIPc + 1/2H_2O_2 + H^+ \rightarrow Co^{II}ODIPc + H_2O \qquad (6)$$

Equations 2 and 3 are for fresh electrodes at pH 1 and Eqs. 4—6 are for electrodes after several scans at pH 1 or fresh electrodes at pH 14.

The effect of substituents on the electroreduction of oxygen has been discussed previously for iron porphyrin catalysts.[1f,9)] The rate constants for O_2 reduction and the amount of catalyst required to achieve 4-electron reduction were greatly affected by the nature and number of substituents.[1f,g)] In the case of Pcs however, no such report has appeared to date. Irrespective of the kind of Pc, 4-electron reduction has been achieved by the use of FePcs in alkaline solution, and 2-electron reduction has been observed with CoPc catalysts.[2)] Our present results indiate, however, that substituent groups do affect the catalytic activity of phthalocyanines if they are able to cause a strong perturbation of the Pc electronic structure. Oxygen was reduced to water in both neutral and alkaline solution by an FePc and the whole range of pH by a CoPc. With porphyrins, the monocobalt complex of a cofacial diporphyrin is known to catalyze the 4-electron reduction of oxygen,[19)] although general cobalt porphyrin monomers show only a 2-electron reduction capability. No reason has been given for this phenomenon. However, this fact and our results in the present study strongly indicate that the catalytic activity can be controlled by changing the surroundings of the catalytic center (i.e. metal) in metalloporphyrins and phthalocyanines.

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