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PREPARATION AND ELECTROCHEMICAL BEHAVIORS OF IRON(III) OCTAETHYLPORPHYRINS COORDINATED BY CATECHOL MONO ANIONS

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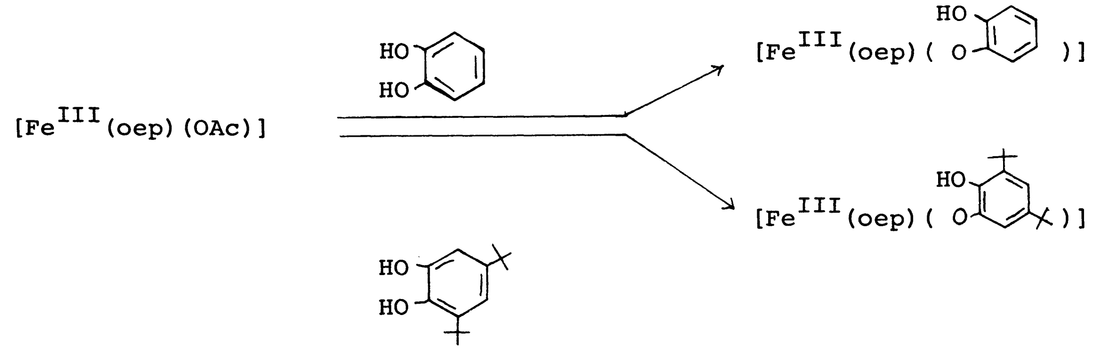
Iron(III) octaethylporphyrin complexes coordinated by mono anions of catechol and 3,5-di-*tert*-butylcatechol were prepared. These Fe(III) high-spin complexes showed an irreversible one-electron redox couple for the coordinated catechol anion, in addition to two one-electron quasi-reversible Fe^{II}/Fe^{III}, and Fe^{III}/Fe^{IV} redox couples.

It is well known that various types of phenols and catechols are oxidized to the corresponding phenoxy or semiquinone radicals as substrates of oxidized peroxidases.[1,2] Moreover, even in non-heme enzymes such as pyrochatechase and protocatechuate 3,4-dioxygenase, catechols are said to coordinate to the iron atom in the active site of the enzymes as substrates.[3,4] Consequently, it seems to be interesting to know the basic physicochemical properties, especially electrochemical behaviors of iron(III) porphyrins having catechol anions as an axial ligand. Although there have been many electrochemical investigations about iron(III) porphyrins,[5,6] These iron(III) complexes previously studied generally had electrochemically inert counter anions such as halide ions or other inorganic anions, where only redox couples of porphyrin ligand itself could be observed except metal oxidoreductions. In this study, we prepared iron(III) porphyrins having catechol mono anions as an axial ligand, and investigated electrochemical behaviors of the complexes.

To a dichloromethane solution of octaethylporphyrinatoiron(III) acetate, $[Fe^{III}(oep)(OAc)]$ was added a slightly excess amount of catechols, and the reaction



(1)

(2)

mixture was stirred for 3 4 h. After removal of solvent, the residual solid was recrystallized from dichloromethane-methanol to give fine purple crystals in about 50 70% yields. All new complexes gave satisfactory elemental analyses.7) Infrared spectra of these complexes showed a sharp band at about 3460 cm^{-1} clearly indicating existence of a hydroxyl group. Moreover, electronic absorption spectra were typical ones to five-coordinated Fe(III) high-spin complexes such as halides, although the absorption maxima were considerably different.8) Compared with the acetato complex,8) the Soret band was shifted toward longer wavelength region and visible bands to shorter wavelength, respectively. The values of the absorption maxima were similar to those of the fluoro complex, [Fe^{III}(oep)F].8) Resonance Raman spectra in dichloromethane9) and magnetic moments in solid state10) indicated also that these complexes are of the usual high-spin type. From these results, it can be concluded that complexes 1 and 2 are five-coordinated high-spin complexes.

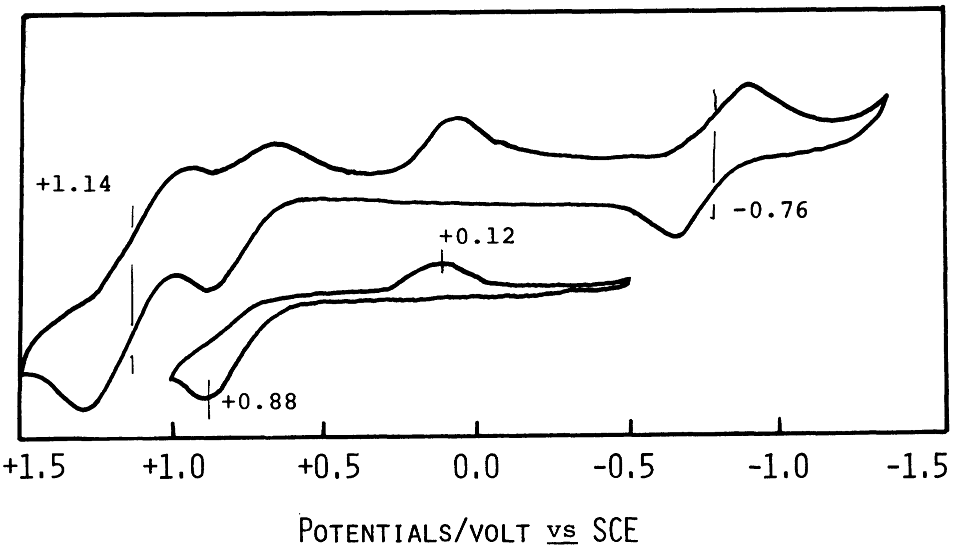
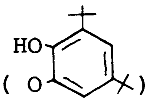
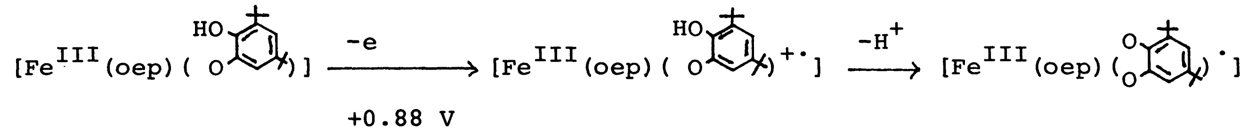


FIGURE 1. Cyclic voltammograms of [Fe^{III}(oep)()] in CH_2Cl_2.

The cyclic voltammogram of 2 in dichloromethane is illustrated in Fig 1. From the controlled potential coulometry and the spectroelectrochemistry,11) the quasi-reversible redox couples at $E_{1/2}$=-0.76 and +1.14 V could be assigned to the Fe^{II}/Fe^{III} and Fe^{III}/Fe^{IV}, respectively.5) In addition to these redox couples, there is a one-electron oxidation peaks13) at +0.88 V and the corresponding reduction peak at +0.12 V. Therefore, the oxidized species at +0.88 V can be assigned to the iron(III) porphyrin coordinated by semiquinone radical.14) As shown in Fig 2, spectroelectrochemistry of 2 at +0.88 V revealed that the oxidation of 2 gave only one oxidized species. This was fairly stable in the solution, although an attempt of isolation was unsuccessful. Shifts of absorption maxima of Soret and



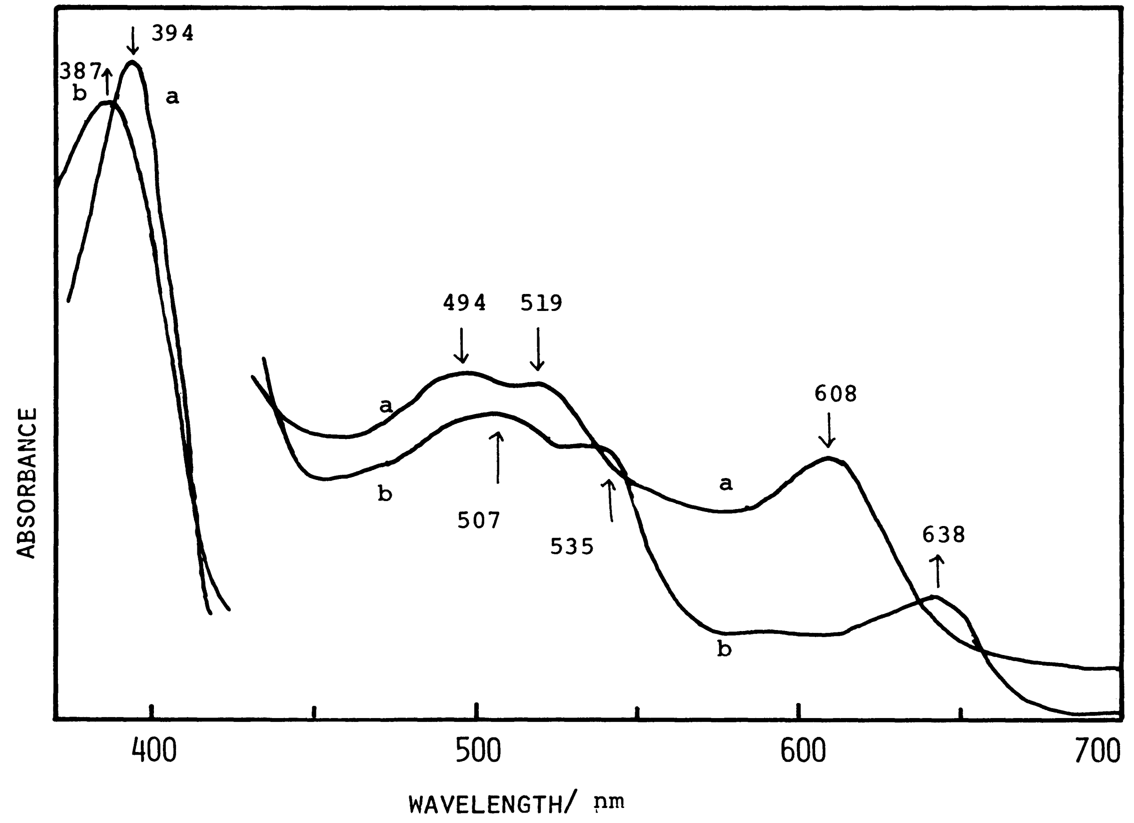
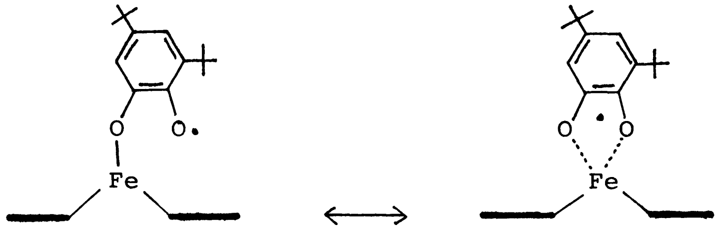


FIGURE 2. UV-VIS spectral changes by the oxidation at +0.88 V, in CH_2Cl_2 (a) before oxidation, (b) after complete oxidation.

visible bands suggested the decrease of the electron-donation from axial anion to iron(III). The electronic spectrum of the oxidized species, however, was similar not to that of ferric perchlorato complex, but to that of chloro complex.8) The high stability of the o-semiquinone complex suggests the ligation of the o-semiquinone as bidentate ligand to the iron(III), such as stable o-semiquinone complexes of iron(III) or other metals.15,16,17)

Further physicochemical investigations of the new oxidized species including ESR and resonance Raman spectra are now in progress.



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7) Elemental analyses. (1) Found: C,71.38; H, 7.13; N, 7.93%.
Calcd for $C_{42}H_{49}N_4O_2Fe\cdot(H_2O)_{1/2}$:C,71.68; H, 7.05; N, 8.23%.
(2) Found: C, 73.33; H, 8.12; N, 6.84%.
Calcd for $C_{50}H_{65}N_4O_2Fe\cdot(H_2O)_{1/2}$: C, 73.65; H, 7.96; N, 7.03%.
8) Electronic absorption maxima of (1) and (2) and other ferric complexes in CH_2Cl_2; $\lambda_{max}(\log\varepsilon)$.

(1)	392(4.96),		495(3.69),	520(3.67),		611(3.52)
(2)	394(4.87),		494(3.89),	519(3.87),		608(3.79)
[Fe(oep)(OAc)]	381(5.01),	460(3.88),	508(3.97),	537(3.99),	584(3.46),	640(3.65)
[Fe(oep)F]	395(4.96)		481(3,95),	514(3.86)		599(3.80)
[Fe(oep)Cl]	381(4.93),	461(3.76),	508(3.87),	536(3.89),	584(3.33),	640(3.58)
[Fe(oep)ClO_4]	391(5.06)		498(3.97)	535(3.84)		629(3.37)

9) Some characteristic Raman bands of (1) and (2) in CH_2Cl_2.

(1)	1630, 1583, 1565, 1406, 1376
(2)	1629, 1583, 1566, 1408, 1375
[Fe(oep)Cl]	1629, 1582, 1568, 1406, 1374 cm^{-1}

10) Both complexes (1) and (2) showed 5.9 BM at 10°C.
11) The cell was similar to that reported previously by Lexa et. al.[12)] with a platinum grid working electrode and platinum wire counter electrode.
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13) The number of electron was determined by the controlled potential coulometry at +0.88 V.
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