Synthesis and Characterization of μ-Oxodiiron(III) Complexes of Porphycenes with Electron-withdrawing Substituents

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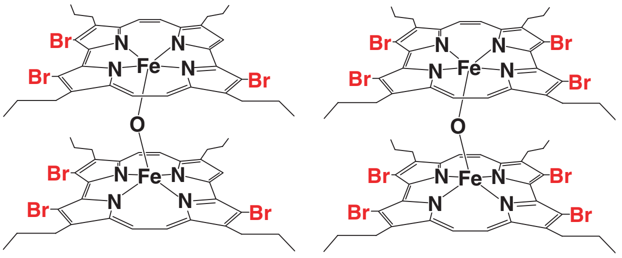
μ-Oxodiiron(III) complexes of porphycenes with electron-withdrawing Br-substituents have been synthesized. The crystal structure of a tetrabrominated complex was elucidated by X-ray analysis. The Br-substituted effects for the electronic spectra and electrochemical properties have been reported.

Porphycene is a unique isomer of porphyrin first synthesized by Vogel et al. in 1986.[1] This isomer exhibits geometries of the N4 coordination site which deviate noticeably from the ideal square shape of the porphyrin core, and its unique structural properties result in interesting catalysis of the complexes as it forms with metals.[2] In contrast, a number of Br-substituted porphyrins and their metal complexes have been synthesized and their high catalytic efficiency superior to those for non-halogenated porphyrin complexes have been reported.[3] These results prompted us to undertake of a β-pyrrol brominated porphycenato iron complex. We report here the first example of the synthesis of μ-oxodiiron(III) complexes with β-pyrrole brominated porphycenes as shown in Chart 1.



[Fe(Br$_3$TPrPc)]$_2$O **[Fe(Br$_4$TPrPc)]$_2$O**

Chart 1.

The μ-oxodiiron(III) porphycenato complexes were synthesized following the well-established procedure.[4] 3,6,13,16-Tetrabromo-2,7,12,17-tetra-*n*-propylporphycene (H_2Br_4TPrPc)[5] and 3,6,13-tribromo-2,7,12,17-tetra-*n*-propylporphycene (H_2Br_3TPrPc)[6] were heated under reflux with tris(acetylacetonato)iron(III) in phenol for 20 min and phenol was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and stirred with an aqueous NaOH solution over 1 h. The solution was washed with water, and the organic layer was dried over Na_2SO_4. After filtration, the filtrate was concentrated and dried in vacuo and recrystalized from $CHCl_3$/MeOH. The complexes were characterized by UV–vis, ^{1}H NMR, and ESI mass spectroscopy as well as elemental analysis.[7,8] The electronic spectra of the complexes show a characteristic μ-oxodiiron(III) porphycenato complex with a shoulder at near 430 nm.[4] The Q-bands are red-shifted with increase in the number of Br groups on TPrPc. A similar Br-substitution effect in the electronic spectrum was observed in the porphyrin, and this has been interpreted in terms of configurational interactions.[9] The formation of [Fe(Br$_4$TPrPc)]$_2$O and [Fe(Br$_3$TPrPc)]$_2$O has also been confirmed by ESI-MS. Each spectrum showed prominent peak clusters at m/z 1712 and 1554 for [Fe(Br$_4$TPrPc)]$_2$O and [Fe(Br$_3$TPrPc)]$_2$O, respectively. These mass values and isotope patterns are consistent with those of the corresponding ions $[M]^+$. The single crystals of [Fe(Br$_4$TPrPc)]$_2$O suitable for X-ray analysis were grown from CH_2Cl_2/MeOH/Et_2O, and the ORTEP drawing is shown in Figure 1.[10]

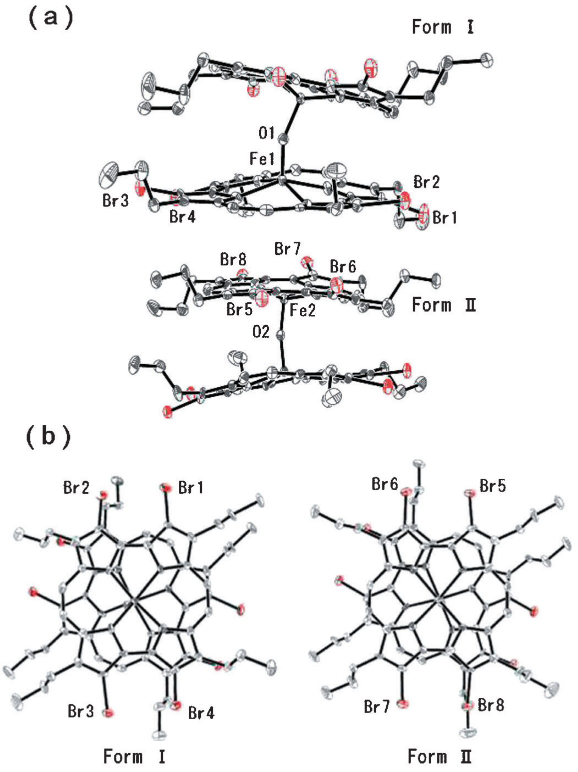


Figure 1. ORTEP diagram of [Fe(Br$_4$TPrPc)]$_2$O with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. (a) side view (b) top view.

Two discrete molecular structures (Form I and Form II) were observed in the unit cell. The Fe–O–Fe angles of each μ-oxodimer unit are 153.3° and 162.5° for Form I and Form II, respectively. These angles are somewhat larger than that of [Fe(TPrPc)]$_2$O with 145.3°[4] because of the steric bulky Br substituents between the two porphycene rings. Br groups attached to adjacent pyrrole units are warped to each other and cause distortion to porphycene core in both forms. The Fe–O lengths are 1.763 and 1.752 Å for Form I and Form II, respectively. In this way, the

X-ray structural study clearly demonstrates the diiron(III) μ-oxo structure.

Redox behavior of the complexes was investigated by cyclic voltammetry as shown in Figure 2.

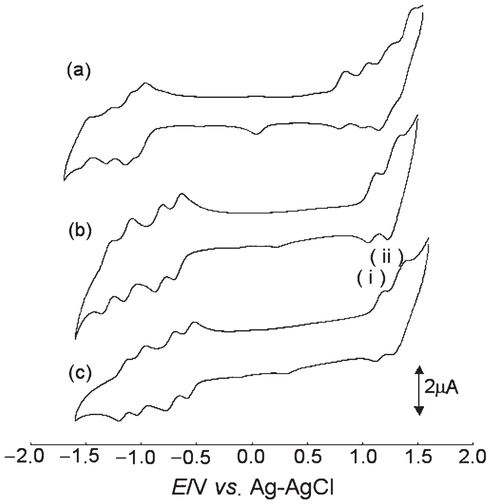


Figure 2. Cyclic voltammograms in PhCN containing 0.1 M n-Bu_4NClO_4 of (a) $[Fe(TPrPc)]_2O$ (b) $[Fe(Br_3TPrPc)]_2O$ (c) $[Fe(Br_4TPrPc)]_2O$. Scan rate = 0.1 V/s.

Both of the complexes undergo two reversible one-electron oxidations and four reversible one-electron reductions in PhCN containing 0.1 M n-Bu_4NClO_4. It is observed that both oxidation and reduction peaks of the complexes occur at a more positive potential relative to those found for the $[Fe(TPrPc)]_2O$.[11] The oxidations occurred at the central metal position, which was confirmed by UV–vis spectra on controlled potential electrolyses.[12] The good reversibility of the oxidation waves clearly shows that the electron-withdrawing ability of the Br substituent at the β-pyrrolic positions of porphycene would decrease the oxidative degradation reaction of a porphycene macrocycle as well as activate a high-valent metal intermediate.

$$[Fe^{III}Fe^{III}] \overset{(i)}{\rightleftharpoons} [Fe^{IV}Fe^{III}] \overset{(ii)}{\rightleftharpoons} [Fe^{IV}Fe^{IV}]$$

In summary, μ-oxodiiron(III) porphycenato complexes having Br substituents at the β-pyrrolic positions of a macrocycle have been synthesized. Further work on the reactivities of the complexes as oxygenation catalyst is now in progress in our laboratory.

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6 β-Pyrrole tribrominated porphycene (H_2Br_3TPrPc) was synthesized by the similar method for H_2Br_4TPrPc. Anal. Calcd for $C_{32}H_{35}N_4Br_3$: C 53.73, H 4.93, N 7.87%; Found, C 53.54, H 4.92, N 7.75%; MALDI-TOF-MS (m/z): $[M]^+$, 715.7.

7 $[Fe(Br_3TPrPc)]_2O$: Yield 91%; mp: 422–424 °C (dec); ^{1}H NMR ($Cl_2CDCDCl_2$, 500 MHz): δ 1.23 (s, $C\underline{H}_3$), 1.43 (s, $C\underline{H}_3$), 1.96 (s, β-$C\underline{H}_2$), 2.07 (s, β-$C\underline{H}_2$), 2.40 (s, β-$C\underline{H}_2$), 2.52 (s, β-$C\underline{H}_2$), 4.90 (s, α-$C\underline{H}_2$), 5.11 (s, α-$C\underline{H}_2$), 5.42 (s, α-$C\underline{H}_2$), 6.75 (s, α-$C\underline{H}_2$), 7.20 (s, methin), 14.85 (s, pyrrole); ESIMS (m/z): $[M]^+$, 1554; UV–vis (CH_2Cl_2) λ_{max}, nm (ε/dm^3 mol^{-1} cm^{-1}); 347 (89900), 432$_{sh}$ (242000), 649 (55700); Anal. Found: C, 49.45; H, 4.28; N, 7.21%; Calcd for $C_{64}H_{66}N_8Br_6Fe_2O$: C, 49.32; H, 4.30; N, 7.01%. Two structural isomers, which are racemi- and meso-forms, were detected by HPLC analysis, but these two isomers could not be isolated.

8 $[Fe(Br_4TPrPc)]_2O$: Yield 90%; mp: 440–442 °C (dec); ^{1}H NMR ($Cl_2CDCDCl_2$, 500 MHz): δ 1.25 (24H, s, $C\underline{H}_3$), 1.96 (16H, s, β-$C\underline{H}_2$), 4.87 (8H, s, α-$C\underline{H}_2$), 7.02 (8H, t, methin), 7.37 (8H, s, α-$C\underline{H}_2$); ESIMS (m/z): $[M]^+$, 1712; UV–vis (CH_2Cl_2) λ_{max}, nm (ε/dm^3 mol^{-1} cm^{-1}); 349 (95500), 437$_{sh}$ (27000), 656 (54200); Anal. Found: C, 44.90; H, 3.77; N, 6.54%; Calcd for $C_{64}H_{64}N_8Br_8Fe_2O$: C, 45.09; H, 4.08; N, 6.23%.

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10 Crystal data; $C_{64}H_{64}N_8Br_8Fe_2O$, $M_r = 1712.21$, orthorhombic, $a = 18.6374(11)$ Å, $b = 21.2087(13)$ Å, $c = 33.0005(19)$ Å, $V = 13044.3(13)$ Å^3, $T = 100$ K, space group $C222(1)$, $Z = 8$, μ(Mo Kα) = 5.394 mm^{-1}, 42988 reflections measured, 13376 unique ($R_{int} = 0.0728$). Final $R_1 = 0.0397$, $wR_2 = 0.0858$ for 13376 observed reflections data [$I > 2\sigma(I)$]. GOF = 0.944. Data were collected on a Bruker SMART APEX CCD area-detector diffractometer with monochromated Mo Kα radiation. The details of the crystal data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-235960.

11 Redox potentials for $Fe^{III}Fe^{III}/Fe^{IV}Fe^{III}$ are observed at 0.81, 1.09, and 1.15 V vs Ag–AgCl for $[Fe(TPrPc)]_2O$, $[Fe(Br_3TPrPc)]_2O$, and $[Fe(Br_4TPrPc)]_2O$, respectively.

12 UV–vis analysis of 0.5 mM $[Fe(Br_4TPrPc)]_2O$ was carried out at controlled potential electrolysis at (i) +1.1 V vs Ag–AgCl and (ii) +1.3 V vs Ag–AgCl in PhCN containing 0.1 M n-Bu_4NClO_4. $[Fe^{IV}Fe^{III}]$: λ_{max}, nm 370, 448, 596$_{sh}$, 649; $[Fe^{IV}Fe^{IV}]$: λ_{max}, nm 376, 445, 589$_{sh}$, 646. The similar spectral changes were observed for $[Fe(TPrPc)]_2O$[13]

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