

SYNTHESES AND MAGNETIC PROPERTIES OF ARYLIRON(III) COMPLEXES OF OCTAETHYLPORPHYRINS

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Summary

Aryliron(III) octaethylporphyrins, OEP-Fe^{III}(4-XC₆H₄) [X = H(1), OCH₃(2), and CH₃(3)] were obtained from octaethylporphyrinatoiron(III) perchlorate, OEP-Fe^{III}(ClO₄) and arylmagnesium bromides. In order to confirm the ESR parameters, the isotope-labelled, meso-deuterated and ¹⁵N-enriched iron(III) complex, (OEP-*d*₄-¹⁵N)Fe^{III}(4-OCH₃C₆H₄) was prepared. The spin state of the complexes was determined to be of low-spin state (*s* = 1/2) from the magnetic moments in the temperature range from 4.2 to 273 K. Mössbauer parameters of the complex **2** are closely similar to those of the ferric low-spin complex. The anisotropic *g*-values of the labelled complex in the ESR spectrum are *g*₁ = 2.023, *g*₂ = 2.001 and *g*₃ = 1.982 in toluene glass at 77 K. Aryliron(III) complexes are sensitive to molecular oxygen or light, to give biphenyl derivatives and ferrous porphyrin complexes due to the homolytic cleavage of the carbon—iron(III) bond.

Introduction

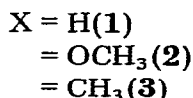
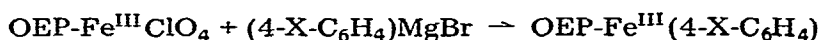
It has been reported that the iron(II) porphyrins and the reduced hemo-proteins are susceptible to oxidation by alkyl halides and that the reaction products are closely similar to those of dehalogenation in biological systems [1,2]. Organometallic porphyrins have never been reported in biological systems. Although a first attempt to synthesize the organoiron(III) porphyrins has been reported by Johnson and his coworkers, the magnetic and spectroscopic properties have not been established yet [3]. In recent reports, Mansuy and his coworkers have prepared the carbene complex of the iron(II) porphyrin

[4]. Both X-ray crystallographic [5] and ^1H NMR studies [6] indicated that one-electron oxidation of the carbene complex resulted in insertion of carbene into an iron—nitrogen bond. These new organoiron complexes are related to an enzymatic intermediate for HRP-compound I and cytochrome P-450. Very recently, two groups have reported the formation of σ -bonded alkyliron(III) porphyrins. The reactions of methyl radical with ferric and ferrous porphyrins generate methyliron(III) porphyrins [7]. Spectroscopic evidence from the steady state radiolysis of a methyl chloride-saturated neutral solution of the hemin was given to characterize the methyliron(III) porphyrin. Lexa and her coworkers have reported the formation of alkyliron(III) porphyrins obtained from the reaction of electrogenerated iron(I) porphyrin with alkyl halides [8]. Similar spectroscopic studies of the iron(III) porphyrins generated in situ indicate formation of a low-spin complex, which coincides with our preliminary results for the chemically isolated aryliron(III) porphyrins [9].

We have found a facile pathway to synthesize rather stable aryliron(III) porphyrins. These aryliron(III) porphyrins have anomalous features compared with the usual ferric porphyrin complexes: 1) Their magnetic susceptibilities, Mössbauer parameters, and ESR spectra show that these complexes are of the penta-coordinate low-spin state. 2) Reductive and photochemical cleavage of the iron—carbon bond takes place to give a ferrous porphyrin and biphenyl derivatives.

Results and discussion

The aryliron(III) octaethylporphyrins were prepared in good yield by treatment of the perchlorate salt of ferric octaethylporphyrin, $\text{OEP-Fe}^{\text{III}}\text{ClO}_4$ with arylmagnesium bromides. Although a chloro or bromo complex of ferric porphyrin is also available, as reported by Johnson et al. [3], the reaction of the perchlorate complex and Grignard reagents gives much improved yields of the organoiron(III) porphyrins. Figure 1 shows the absorption spectra of **2** in benzene and pyridine. The positions of absorption maxima are largely different from those of the 4-methylphenyliron(III) complex of aetioporphyrin-I in CHCl_3 [3]. Johnson has reported its absorption maxima as 357, 395 and 584 nm



with an inflection at 469 nm. The electronic structure of the complexes **1–3** should be similar to that of the aryliron(III) complex of aetioporphyrin-I, because of the structural resemblance of the porphyrin ligands. It was noted that the aryliron(III) porphyrin decomposed slowly in chloroform solution. As is noted by Johnson et al., organoiron(III) complexes are very sensitive to molecular oxygen and light. Electronic spectra in their report may include those of decomposed products. The spectral pattern of the aryliron(III) complexes is similar to those of the organocobalt(III) porphyrins, which show absorption maxima at 395, 520, and 550 nm [10]. The spectral features of these aryliron(III) complexes are similar to those of methyliron(III) deuterio-

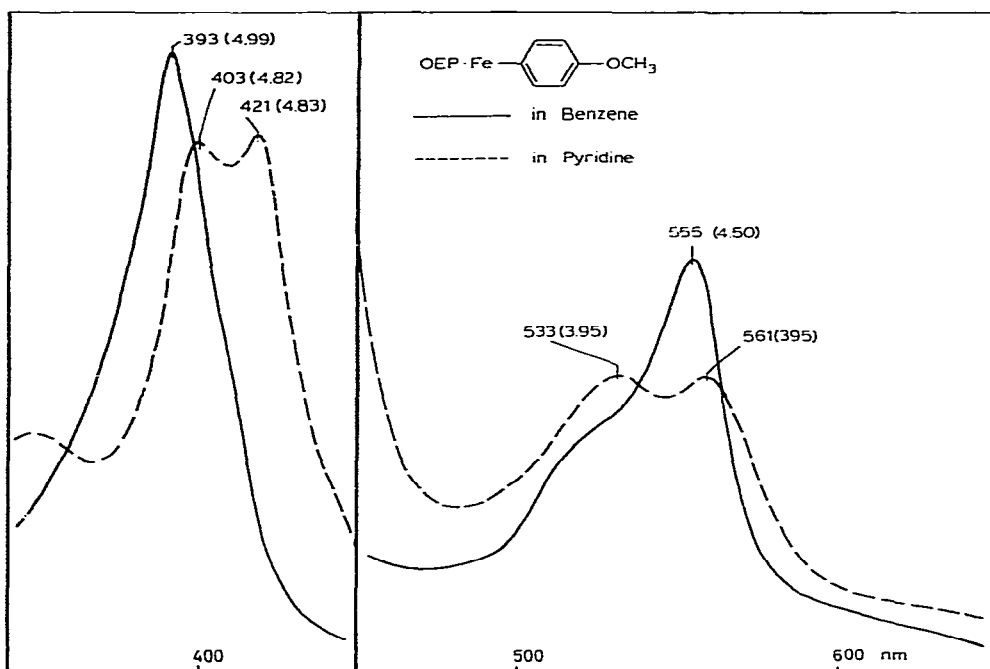


Fig. 1. Absorption spectra of $\text{OEP-Fe}^{\text{III}}(4\text{-OCH}_3\text{C}_6\text{H}_4)$ in benzene (solid trace) and pyridine (dashed trace) at room temperature. The values in parentheses denote absorption strength in the corresponding logarithmic molar extinction coefficients ($\log \epsilon_{\text{max}}$).

porphyrin-IX, generated from a radical reaction [7], rather than those of alkyliron(III) porphyrin, generated electrochemically [8]. For the latter complex, the absorption strength of the 540 nm band is weaker than that of the absorption at 520 nm. Addition of pyridine causes splitting of the Soret band and the decrease in the relative intensity of the α -band compared to the β -band, as shown in Fig. 1. The spectral features of the aryliron(III) complexes are quite different from that of the pentacoordinated ferric porphyrins.

The magnetic susceptibilities of complex 2 were measured from 4.2 to 273 K. Figure 2 shows the variation of the effective magnetic moment and the reciprocal molar susceptibility with temperature. The effective magnetic moment of 2.25–2.65 B.M. provides evidence for the low-spin ferric ($s = 1/2$) complex. Although the pentacoordinated ferric porphyrins are usually of high-spin state ($s = 5/2$), recent paramagnetic NMR studies suggest that the monocyano complex of hemin is of the low-spin state in DMSO solution [11].

Mössbauer spectra of the 4-methoxyphenyliron(III) porphyrin complex 2 were measured in the range 40–300 K. Table 1 summarizes the Mössbauer parameters, isomer shifts (δ , mm/sec) and quadrupole splitting (ΔE_Q , mm/sec). As shown in Fig. 3, a narrow symmetric doublet is observed at 300 K. The high-velocity line markedly broadened and the shape of the spectrum became asymmetric at 40 K. The Mössbauer parameters and temperature dependence of the spectra are different from those of the high-spin, pentacoordinate ferric porphyrin complexes. The δ and ΔE_Q values of high-spin iron(III) porphyrins

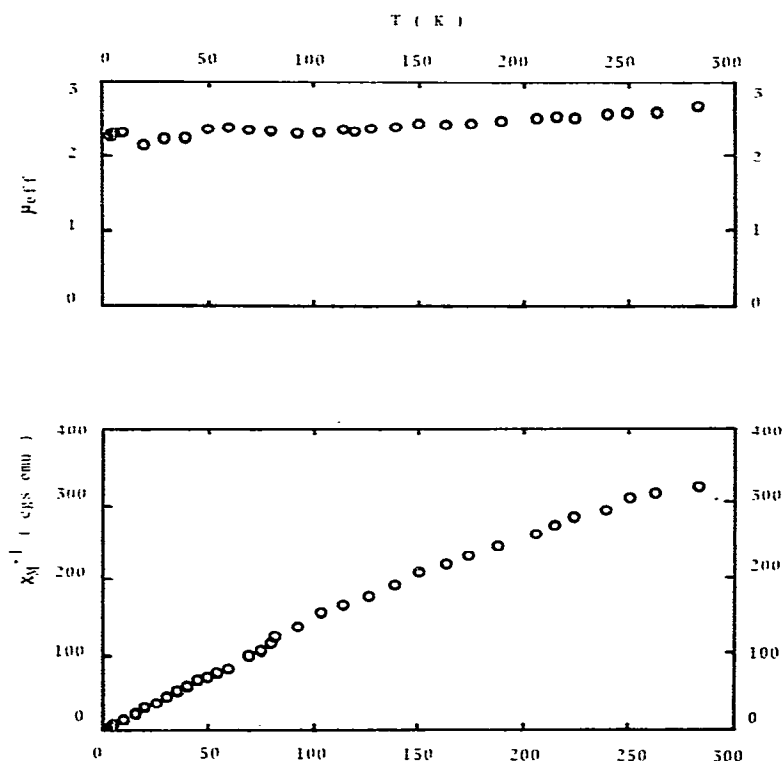


Fig. 2. The effective molar susceptibilities of OEP-Fe^{III}(4-OCH₃C₆H₄) vs. temperatures.

are 0.38 ± 0.06 and 0.88 ± 0.15 mm/sec, respectively [12]. Hexacoordinate and low-spin iron(III) porphyrins show δ values at $0.23(289\text{ K})$ and $0.01\text{--}0.16(77\text{ K})$. The quadrupole splitting generally falls into the range 2.0 ± 0.3 mm/sec [13]. The δ -values of **2** are larger than those of low-spin bisamine iron(III) porphyrin by ca. 0.1 mm/sec. Comparison of Mössbauer parameters leads us to conclude that the aryliron(III) porphyrins are of the low-spin state.

TABLE I

MÖSSBAUER PARAMETERS OF ARYLIRON(III) PORPHYRIN ^a

	<i>T</i> (K)	δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)
OEP-Fe ^{III} (4-CH ₃ OC ₆ H ₄)	300	0.23	2.18
	212	0.25	2.24
	162	0.31	2.30
	77	0.31	2.32
	60	0.29	2.34
	40	0.30	2.36
Hemin(imd) ₂ Cl	289	0.14	2.17 [12]
	77	0.24	2.30
Hemin(py) ₂ Cl	77	0.23	1.88 [12]

^a Isomer shifts are relative to metallic iron.

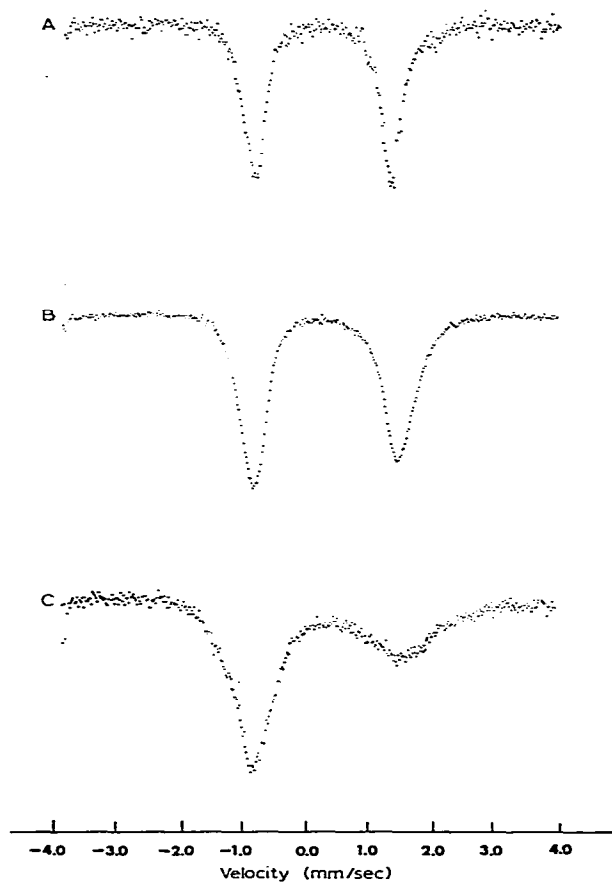


Fig. 3. Mössbauer spectra of OEP-Fe^{III}(4-OCH₃C₆H₄) at 300 (A), 77 (B), and 40 K (C).

Figure 4 shows the ESR spectra of complex **2** and of the complex labelled with ²H and ¹⁵N at 77 K in toluene glass. Assignment of the complicated spectrum of **2** has not yet been completed. Isotope substitution with ²H and ¹⁵N of the meso protons and the pyrrolic nitrogen gave a simple spectrum characteristic of the low-spin complex. Three *g*-values are clearly determined as *g*₁ =

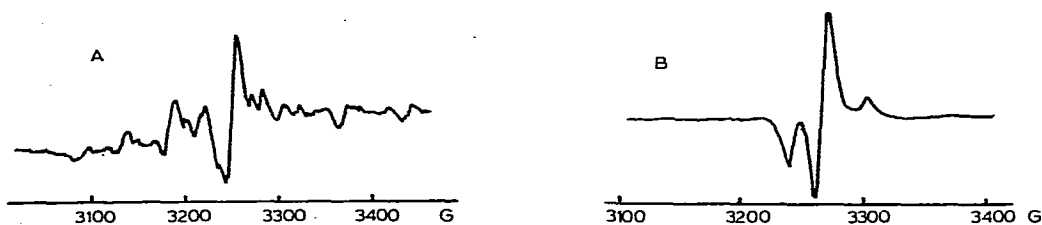
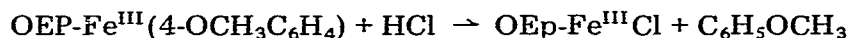


Fig. 4. The ESR spectra of OEP-Fe^{III}(4-OCH₃C₆H₄) (A) and (OEP-d₄-¹⁵N)Fe^{III}(4-OCH₃C₆H₄) (B) in toluene glass at 77 K.

2.023, $g_2 = 2.001$ and $g_3 = 1.982$. These values are less anisotropic than those of the low-spin hexacoordinate ferric complexes [14]. The ESR spectrum of OEP-Fe^{III}(imd)₂Cl shows three g -values at $g_1 = 2.955$, $g_2 = 2.248$ and $g_3 = 1.53$. The ESR spectrum of *n*-butyliron(III) tetraphenylporphine generated electrochemically shows g -values at 2.69, 2.25 and 1.84 at 77 K [8]. Addition of nitric oxide to ferric peroxidase gives a paramagnetic product due to formation of the low-spin species. The nitrosyl adduct of the enzyme shows three g -values at 2.008, 2.004 and 1.95 [15]. Anomalous ESR parameters are explained by marked charge transfer from the NO group to the ferric enzyme. An unpaired electron is located in the d_{z^2} orbital [16]. The complicated ESR spectrum of **2** seems to result from strong coupling between the pyrrolic nitrogen and the methene protons of the porphyrin core. Therefore, a strong d_π - p_π interaction between the iron atom and the porphyrin may be responsible for the anomalous feature of the spectrum. Further theoretical treatment on the organoiron(III) porphyrin is required to elucidate the electronic structure. Formation of the strong σ -bond between the iron and carbanion raises the energy level of the d_{z^2} orbital, which leads to a favorable low-spin complex.

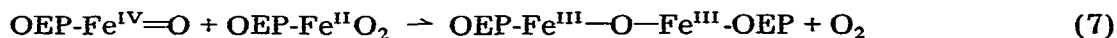
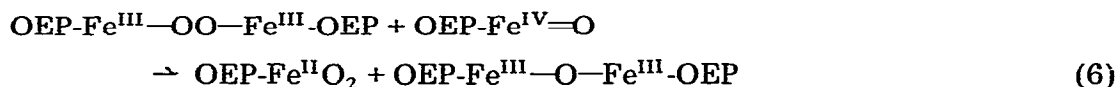
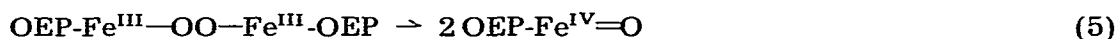
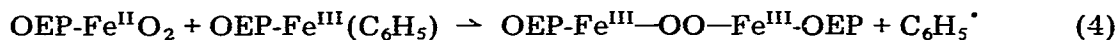
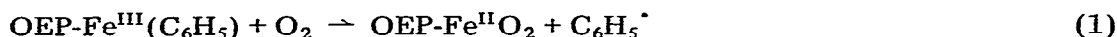
Reactivity of aryliron(III) porphyrins

When a tetrahydrofuran solution of 4-methoxyphenyliron(III) complex **3** was treated with aqueous hydrochloric acid, chlorohemin and anisole were obtained in quantitative yield. Wade and Castro reported that treatment of heme with an alkyl halide in acidic medium afforded an alkane and chlorohemin [1,2]. Hydrogenolysis of an alkyl halide to an alkane in biological systems is



thought to be initiated by oxidation of heme with alkyl halide and successive attack of proton. Nucleophilic attack of chloride releases a carbanion which is quenched by a proton.

Aryliron(III) complexes are fairly stable under anaerobic conditions. Monitoring the absorption spectrum of the complex in refluxing benzene did not show a significant change. On the other hand, refluxing a benzene solution of **1** under aerobic conditions afforded immediately the μ -oxo-dimer complex, [OEP-Fe^{III}]₂O and biphenyl in quantitative yields. Formation of the products can be explained by the following mechanism.

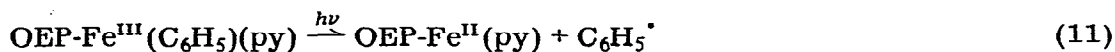
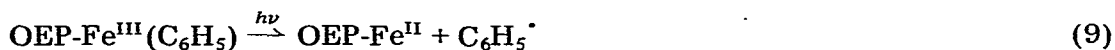




In aprotic solvents, the ferryl complex $\text{OEP-Fe}^{\text{IV}}=\text{O}$, derived from decomposition of the peroxo ferric complex, seems to be a reasonable reaction intermediate to give the μ -oxoferric complex according to reactions 4–7 [17]. Homolytic cleavage of the carbon–iron bond gives a phenyl radical and the dioxygen complex. The dioxygen complex, $\text{OEP-Fe}^{\text{II}}\text{O}_2$, reacts with the aryliron complex to yield the μ -peroxo-bridged complex, $\text{OEP-Fe}^{\text{III}}-\text{OO}-\text{Fe}^{\text{III}}-\text{OEP}$ and phenyl radical. The existence of the μ -peroxo complex at 193 K was confirmed by NMR spectroscopy [17]. The O–O bond cleavage of the dioxygen-bridged complex generates the highly reactive ferryl complex. Reactions 6 and 7 have been proposed to explain the formation of the μ -oxo complex initiated by the ferryl complex. Under the present reaction conditions, it is most likely that the reaction of $\text{OEP-Fe}^{\text{IV}}=\text{O}$ with **1** affords the μ -oxo complex and phenyl radical as shown in eq. 8. Biphenyl may be formed from the dimerization reaction of phenyl radicals. In case of the organocobalt(III) complexes such as benzyl- and allyl-cobaloximes reaction with molecular oxygen affords an organoperoxo complex [18].

Reaction of the aryliron(III) complex in pyridine solution gave no μ -oxo complex or biphenyl. As is shown in Fig. 1, a marked change of the absorption spectrum in pyridine indicates strong coordination of pyridine to the iron(III) as the sixth ligand. Strong ligation of pyridine to the iron atom may inhibit homolytic fission of the iron–carbon bond. This suggests that the axially coordinated pyridine protects the complex against attack of molecular oxygen at the *trans* position relative to the aryl group. No phenolic compound has been detected by gas chromatography. The reactivity of the aryliron(III) complex to molecular oxygen is different from that of the organocobalt(III) complexes hitherto reported.

When a benzene solution of the phenyliron(III) complex was irradiated with a high pressure mercury lamp for several minutes under anaerobic conditions, the absorption spectrum of the reaction mixture showed complete formation of ferrous porphyrin, $\text{OEP-Fe}^{\text{II}}$. The absorption spectrum is identical to that of the ferrous complex of mesoporphyrin-IX dimethyl ester [19,20]. The present reaction provides an alternative method to prepare $\text{OEP-Fe}^{\text{II}}$. Homolytic cleavage of the Fe–C bond takes place in a process similar to that in the photolysis of alkylcobalamine [21]. Photochemical reaction of **1** in pyridine afforded the bispyridine iron(II) porphyrin, $\text{OEP-Fe}^{\text{II}}(\text{py})_2$, and biphenyl in high yields. Photochemical reduction of both penta- and hexa-coordinate ferric complexes to the ferrous complex results in elimination of the axial aryl group as a radical species.



Treatment of the ferrous porphyrin with allyl bromide under anearobic conditions gave biallyl and cyclohexene in 26% and 35% yields, respectively [1]. Castro and Wade proposed the formation of a relatively stable allyliron(III) porphyrin complex as an intermediate to account for the formation of the unusual product cyclohexene. We have attempted to isolate the allyliron(III) porphyrin, but it decomposed slowly during separation due to its high reactivity towards molecular oxygen and its low thermal stability. However, generation of the allyliron(III) porphyrin was evidenced by the absorption maxima at 393, 515, and 555 nm in benzene. Addition of allyl bromide to a benzene solution of allyliron(III) complex generated in situ yielded only biallyl in 59% yield. Product analysis did not show the formation of cyclohexene. It is, therefore, concluded that the mechanism of the reaction giving cyclohexene in the oxidation of heme with allyl bromide cannot involve the usual coupling scheme [22].

Experimental

(A) Syntheses of aryliron(III) octaethylporphyrins

General procedure

Octaethylporphyrinatoiron(III) perchlorate [23] (100 mg) was stirred magnetically in 50 ml of benzene dried over sodium sulfate and freshly distilled. To the solution was added 10 ml of an ethereal solution of arylmagnesium bromide prepared from 200 mg of magnesium and 1.5 ml of an aryl bromide. The reaction mixture was stirred for 1 h at room temperature and condensed to a small portion under reduced pressure. The residue was chromatographed on a column of silica gel (Waka C200) with benzene as eluent. Solvent was removed under reduced pressure. Crystallization of the residual solid from benzene-petroleum ether afforded dark red prisms.

Phenyliron(III) octaethylporphyrin, OEP-Fe^{III}(C₆H₅) (1)

Recrystallization from benzene-petroleum ether gave purple red crystals (89 mg) in 94% yield. The visible absorption maxima were: $\lambda_{\max}$ (benzene) 393 nm (ϵ 9.83×10^4 dm³ mol⁻¹ cm⁻¹), 514 (8.3×10^3), 555 (1.65×10^4). (Found: C, 75.86; H, 7.94; N, 8.31. C₄₂H₄₉N₄Fe calcd.: C, 75.78; H, 7.42; N, 8.42%).

4-Methoxyphenyliron(III) octaethylporphyrin, OEP-Fe^{III}(4-OCH₃C₆H₄) (2)

Recrystallization from benzene afforded purple red crystals (81 mg) in 95% yield. The visible absorption maxima were as follows: $\lambda_{\max}$ (benzene) 393 (ϵ 9.79×10^4 dm³ mol⁻¹ cm⁻¹), 514 (8.10×10^3), 555 (1.77×10^3). (Found: C, 74.92; H, 7.42; N, 7.72. C₄₃H₅₁N₄OFe calcd.: C, 74.23; H, 7.39; N, 8.05%).

4-Methylphenyliron(III) octaethylporphyrin, OEP-Fe^{III}(4-CH₃C₆H₄) (3)

Recrystallization from benzene afforded purple red crystals (85 mg) in 94% yield. The absorption maxima were as follows: $\lambda_{\max}$ (benzene) 393 (ϵ 9.98×10^4 dm³ mol⁻¹ cm⁻¹), 514 (8.00×10^3), 555 (1.64×10^3). (Found: C, 75.83; H, 7.76; N, 8.02. C₄₃H₅₁N₄Fe calcd.: C, 75.98; H, 7.56; N, 8.24%).

Meso-deuterated and ¹⁵N-enriched 4-methoxyphenyliron(III) octaethylporphyrin, (OEP-d₄-¹⁵N)Fe^{III}(4-OCH₃C₆H₄) (4)

The meso protons of octaethylporphyrin were deuterated with D₂SO₄-D₂O

[24]. Deuteration of the meso protons was confirmed by both NMR and IR spectroscopic measurements. The ^{15}N atoms were incorporated in porphyrin through the Knorr synthesis of ethyl 3-acetyl-4-ethyl-2-methylpyrrole-5-carboxylate by using $\text{Na}^{15}\text{NO}_2$ (Merck Co Ltd. 97.3%) [24]. Meso-deuterated and ^{15}N -enriched complex **4** was prepared from treatment of $(\text{OEP-}d_4\text{-}^{15}\text{N})\text{Fe}^{\text{III}}\text{-ClO}_4$ with the arylmagnesium bromide.

Spectral measurements

A Faraday magnetic balance was employed for the measurement of magnetic susceptibilities from 4.2 to 273 K. The magnetic susceptibility of anhydrous hexaammine chromium(III) chloride powder was used as a "thermometer", and was calibrated for each run to an atmospheric liquid helium temperature with correction for the Hg-barometer and gravitational constant following the procedure of Linder [25]. The accuracy for the measurement was not less 10%. The diamagnetic susceptibilities of the porphyrin ligand and axial ligands were corrected by measurement for octaethylporphyrin and calibration from Pascal's rule, respectively [26]. Mössbauer spectra were obtained with a scanned velocity spectrometer operating in time mode. The velocity scale was calibrated absolutely from an independent Mössbauer run using a thin metallic iron absorber. The center of symmetry of the spectra was taken as zero velocity. The ESR spectra were recorded at 77 K in toluene glass by means of an X-band JOEL Model JES-FE-3X ESR spectrometer.

Reaction of 3 with hydrochloric acid

To a tetrahydrofuran solution of complex **3** (100 mg, 0.04 mmol) was added 10% hydrochloric acid (1 ml). The color of the reaction mixture immediately turned from red to dark brown. The dark red precipitates were collected and purified by crystallization from CH_2Cl_2 -petroleum ether. Spectroscopic measurements and microanalysis of the crystals show the formation of chlorohemin $\text{OEP-Fe}^{\text{III}}\text{Cl}$ and anisol in quantitative yield [27].

Reaction of 1 with molecular oxygen

Phenyliron(III) complex **1** (100 mg, 0.15 mmol) was dissolved in deaerated benzene (10 ml). Dry oxygen was introduced into the solution for 5 min. The color of the solution turned from red to dark green. Addition of n-pentane to the reaction mixture afforded a red-brown solid. Crystallization of the solid material from CH_2Cl_2 - CH_3OH gave dark red crystals of the μ -oxo dimer $[\text{OEP-Fe}^{\text{III}}]_2\text{O}$ in 95% yield [28]. The filtrate was evaporated to small portion under reduced pressure. Crystallization of the residual solid from CH_3OH gave biphenyl (10.6 mg) in 92% yield.

Reaction of 3 with molecular oxygen in pyridine

Dry oxygen was introduced into a pyridine solution of complex **3** during 30 min. Monitoring the absorption spectrum of the reaction mixture showed no change. Complex **3** was quantitatively recovered after evaporation of pyridine under reduced pressure.

Photochemical reaction of 1

The phenyliron(III) complex **1** (100 mg, 0.145 mmol) in benzene was irradi-

ated with a 100 W high pressure lamp for 5 min. The visible spectrum of the solution showed evidence for formation of OEP-Fe^{II} [20]. Pyridine was added to the solution. The reaction mixture was stirred for 5 min and condensed to dryness. Crystallization of the residual material from CH₂Cl₂-petroleum ether gave red crystals of the bis-pyridine adduct, OEP-Fe^{II}(py)₂ (105 mg) in 95% yield. Then biphenyl (10.5 mg) was isolated from the filtrate in 94% yield. Similar photochemical reaction of 1 in pyridine afforded OEP-Fe^{II}(py)₂ in 97% and biphenyl in 96% yield.

Reaction of allyliron(III) complex with allyl bromide

Octaethylporphyriniron(III) perchlorate, OEP-Fe^{III}ClO₄ (690 mg, 1.0 mmol) in benzene (100 ml) was treated with an equimolar amount of allyl magnesium bromide. Reaction mixture was stirred for 5 min. Oxygen-free water was added to the benzene solution. The benzene layer was separated and dried over anhydrous sodium sulfate in an argon atmosphere. This benzene solution of the allyliron(III) complex was added dropwise to a benzene solution (10 ml) of an equimolar amount of allyl bromide (121 mg, 1.0 mmol). After stirring for 1 h, allylallyl was isolated in 59% yield and no other products were detected by gas chromatography.

Acknowledgement

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