

NMR Studies of π -Cation Radical Complexes of Iron(III) and Oxoiron(IV) Chlorins. Models for Reaction Intermediates of Chlorin-Containing Heme Enzymes

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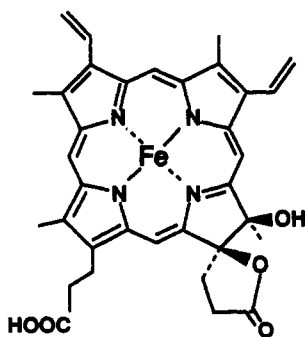
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Abstract: We have prepared π -cation radical complexes of iron(III) and oxoiron(IV) chlorins and examined their electronic structures and magnetic properties by NMR spectroscopy. The high- and low-spin iron(III) π -cation radicals of tetramesitylchlorin (TMC) exhibit well-resolved hyperfine-shifted NMR resonances, which demonstrates that radical orbitals of these π -cation radicals are of a_2 type. The hyperfine shifts of the pyrroline ring protons revealed the magnetic interaction between the iron spin and π -radical spin in the iron(III) TMC π -cation radicals. The large *upfield* shift (~ 174 ppm) of the pyrroline proton resonance for the high-spin iron(III) TMC π -cation radical implies antiferromagnetic coupling between the iron spin ($S = 5/2$) and π -radical spin ($S = 1/2$). On the other hand, large *downfield* shift (~ 460 ppm) for the low-spin iron(III) TMC π -cation radical is rationalized by very weak antiferromagnetic coupling of the iron ($S = 1/2$) and π -radical spin ($S = 1/2$). The antiferromagnetic coupling of the high-spin complex has been verified by the simulation of the temperature dependence of the pyrroline NMR resonance ($J = -60$ cm $^{-1}$). While deuterium NMR spectra of the oxoiron(IV) TMC π -cation radical are consistent with a_2 radical state, the detailed electronic structure is unclear because of failure in detection of the pyrroline deuterium signal. We have also examined the reactivities of the oxoiron(IV) chlorin π -cation radicals for norbornene by using two types of chlorin complexes, TMC and tetrakis(2,6-dichlorophenyl)chlorin (TDCPC). The oxoiron(IV) π -cation radicals of both chlorins are less reactive than those of the corresponding tetramesitylporphyrin (TMP) complex. Since the ring oxidation potential of (TDCPC)-Fe^{III}Cl (1.08 V) is nearly identical with that of (TMP)Fe^{III}Cl (1.09 V), the lowered reactivity of the chlorin complexes could not be attributed to the oxidation potentials of the chlorin macrocycles.

Introduction

Many proteins and enzymes containing iron chlorin complexes as a prosthetic group play important roles in biological systems.¹ Examples of the iron chlorin containing enzymes include catalases isolated from *Escherichia coli*² and *Neurospora crassa*,³ and cytochrome *d*.⁴ HP II in *E. coli* is a monofunctional catalase having one chlorin prosthetic group per subunit.² The structure of the chlorin prosthetic group has been proposed as illustrated.^{2c}



Further, the prosthetic group of *N. crassa* catalase has been shown

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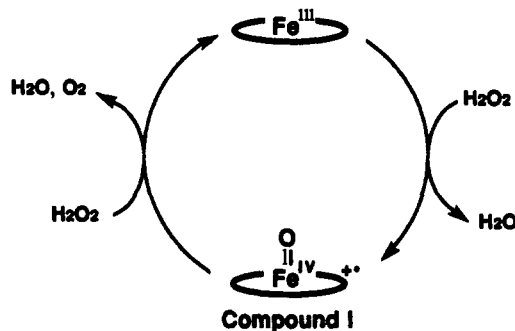
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to be an iron chlorin complex,³ while the detailed structure remains undetermined. These enzymes catalyze dismutation of hydrogen peroxide to water and dioxygen. In the catalytic cycle of the catalase reaction, oxoiron(IV) chlorin π -cation radicals (chlorin compound I) are considered to serve as the crucial reaction intermediate.



Theoretical and experimental studies of metallochlorin π -cation radicals⁵⁻⁹ show that metallochlorin complexes are easily oxidized

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relative to metalloporphyrin complexes to yield the corresponding π -cation radicals and that the chlorin π -cation radicals have predominantly the a_2 radical state. While iron porphyrin π -cation radical complexes have been extensively studied as models for reaction intermediates in the catalytic cycle of catalases, peroxidases, and monooxygenases, investigation of iron chlorin π -cation radicals is still sparse.^{6d,7,10} We have previously characterized the electronic structures and magnetic properties of nitrosyliron(II) π -cation radical complexes of chlorin and isobacteriochlorin as models for reaction intermediates of nitrite reductases by NMR spectroscopy.⁷ Further, we have reported successful formation of a model complex for chlorin compound I (oxoiron(IV) chlorin π -cation radical) and its deuterium NMR spectra.¹⁰ However, the electronic structures and magnetic properties of high-valent iron chlorin π -cation radicals have not been examined yet and remain to be studied. Theoretical studies on compound I of *N. crassa* catalase suggested that chlorin compound I could occupy the a_2 ground state with a spin distribution and optical spectra analogous to zinc(II) and cobalt(III) chlorin π -cation radicals.⁹ Along with this line, preparation and characterization of suitable model complexes for the putative high-valent iron chlorin intermediates have been required to understand the details of compound I of chlorin-containing heme enzymes.

In this paper, we describe the electronic structures and magnetic properties of high- and low-spin iron(III) and oxoiron(IV) π -cation radicals of tetramesitylchlorin (TMC) examined by NMR spectroscopy. It has been shown here that the iron(III) chlorin π -cation radicals afford well-resolved hyperfine-shifted NMR resonances, indicative of the a_2 radical state. Further, the oxoiron(IV) π -cation radicals of two types of chlorins show lower reactivities toward olefins than those of the corresponding porphyrin π -cation radicals. The lowered reactivity of the chlorin complexes could not be ascribed to the oxidation potentials of the chlorin macrocycles.

Experimental Section

Spectral Measurements. Electronic absorption spectral measurements were made on a Hitachi 330 spectrometer and a Shimadzu UV-2200 spectrometer. Low-temperature absorption spectra were obtained by using a DN1704 variable-temperature liquid nitrogen cryostat equipped with digital temperature controller DTC2 (Oxford Instruments). ESR spectra were recorded on a JEOL PE-2X spectrometer operating at X-band frequencies. Proton NMR spectra at 300 MHz and deuterium NMR spectra at 46.1 MHz were measured on a Nicolet NT-300 spectrometer. Proton chemical shifts were referenced to a Me₄Si internal standard, and downfield shifts are given a positive sign. Cyclic voltammetric measurements were performed on a Yanagimoto POLAROGRAPHIC ANALYZER P-1100 with a conventional three-electrode configuration. Working and counter electrodes were platinum wires. A saturated calomel electrode (SCE) was used as the reference electrode. The sample concentration for cyclic voltammetric studies was 1.0 mM in dichloromethane containing 0.1 M tetra-*n*-butylammonium perchlorate as a supporting electrolyte.

Materials. Dichloromethane and *n*-hexane were refluxed over CaH₂ and distilled under an argon atmosphere just before use. Pyridine was distilled from K₂CO₃ and stored over 4-Å molecular sieves. Tetra-*n*-butylammonium iodide (TBAI, Nacalai Tesque) and norbornene (Tokyo Chemical Industry) were used as received. Imidazole was purchased from Sigma and used without further purification. A deuterated imidazole derivative (2-position) was prepared as described,¹¹ and imidazole-1,2,4,5-*d*₄ was obtained from MSD Isotopes. *m*-Chloroperoxybenzoic acid (mCPBA, Tokyo Chemical Industry) was purified by washing with phosphate buffer (pH 7.4).¹² Phenoxathiin hexachloroantimonate (Phenox⁺SbCl₆⁻) was synthesized by the published procedure.¹³

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Tetramesitylchlorin (H₂TMC).¹⁴ A mixture of 260 mg (0.332 mmol) of tetramesitylporphyrin (H₂TMP), 98 mg of *p*-toluenesulfonylhydrazide, 345 mg of anhydrous potassium bicarbonate, and 25 mL of dry pyridine was heated at 120 °C under an argon atmosphere. After 1 and 2 h, pyridine solutions of 100 mg of *p*-toluenesulfonylhydrazide were added. After heating for 3 h (total), the reaction mixture was cooled and poured into 200 mL of water. The precipitated product was filtered off, washed with water followed by methanol, and dried in vacuo. The residue was dissolved in dichloromethane (150 mL). To the dichloromethane solution was added 63 mg of tetrachloro-1,2-benzoquinone, and the mixture was stirred at room temperature for 1 h. Methanol (50 mL) was then added to the resultant solution. The solution was concentrated by evaporation and filtered to afford crude H₂TMC. The crude product was purified by silica gel column chromatography (3:1 *n*-hexane/CH₂Cl₂) to give 177 mg (0.225 mmol, 68%) of H₂TMC. FAB MS (relative intensity): *m/z* 784 (M⁺, 100), 785 (M⁺ + H, 100). Synthesis of tetrakis(2,6-dichlorophenyl)chlorin (H₂TDCPC) was accomplished by a similar procedure (43 mg, 58%).

The pyrroline-*d*₂-pyrrole-*d*₆ TMC derivative was prepared from pyrrole-*d*₈ TMP. The *meta-d*₈ TMC complex was synthesized from *meta-d*₈ TMP complex, which was obtained by the condensation of *meta-d*₈ mesitaldehyde and pyrrole.

Iron Chlorin Complexes. Chloroiron(III) complexes of TMC (**1a-Cl**) and TDCPC (**1b-Cl**) were prepared as described.¹⁵ Iron(III) chlorin complexes bearing hydroxo ligands (**1a-OH** and **1b-OH**) were obtained by passing **1a-Cl** and **1b-Cl** through a basic Al₂O₃ column (eluent EtOAc) before use. **1a-** and **1b-**(*m*-chlorobenzoate, mCB) were generated by adding an excess amount of *m*-chlorobenzoic acid into dichloromethane solutions of **1a-** and **1b-OH**, *in situ*. UV-vis (CH₂Cl₂) [λ_{\max} , nm (ϵ , mM)]: **1a-Cl**, 746 (3.1), 671 (2.2), 601 (17.0), 562 (6.7), 487 (6.4), 415 (54.0), 387 (59.8); **1a-OH**, 662 (10.0), 548 (7.4), 414 (78.9), 334 (21.5), 309 (21.4); **1a-mCB**, 735 (3.5), 661 (2.9), 596 (13.4), 482 (6.6), 412 (69.7); **1b-Cl**, 751 (3.7), 670 (2.6), 606 (23.0), 564 (6.7), 490 (8.0), 413 (63.7), 384 (65.4); **1b-OH**, 663 (15.7), 549 (8.3), 410 (79.4), 310 (25.1); **1b-mCB**, 740 (4.2), 600 (18.0), 486 (8.2), 411 (80.0). ¹H-NMR (CDCl₃, 23 °C): **1a-Cl**, δ -9.1 (4 H, pyrroline), 3.9, 4.0 (12 H, *p*-CH₃), 13.6, 15.2, 16.0, 17.5 (8 H, phenyl meta), 67.9, 78.1, 86.2 (6H, pyrrole); **1b-Cl**, δ -2.4, -1.3 (4 H, pyrroline), 7.9, 8.2 (4 H, phenyl para), 12.1, 13.4, 13.8, 14.8 (8 H, phenyl meta), 68.1, 79.4, 86.8 (6 H, pyrrole). FAB MS (relative intensity) for **1a-Cl**: *m/z* 838 (M⁺ - Cl, 100), 839 (M⁺ + H - Cl, 76).

(TMC)Fe^{III} π -Cation Radical (2a). To a dry dichloromethane (20 mL) solution of 15.1 mg (0.0173 mmol) of (TMC)Fe^{III}Cl (**1a-Cl**) was added 8.8 mg (0.0164 mmol) of Phenox⁺SbCl₆⁻. The suspension was stirred at 0 °C for 15 min. After filtration, *n*-hexane was added to the filtrate followed by concentration of the solution to 5 mL. A fine black precipitate of (TMC)Fe^{III}Cl(SbCl₆) (**2a**) was obtained by filtration (15.5 mg, 0.0128 mmol (74 %)).

Imidazole Adduct of (TMC)Fe^{III}Cl(SbCl₆) (3a). A dichloromethane solution (0.020 mM) of (TMC)Fe^{III}Cl(SbCl₆) (**2a**) in UV cuvette was cooled to -80 °C. To the solution was added a dichloromethane solution of 2 mol equiv of imidazole in one portion. NMR samples (~3 mM) were also prepared under similar conditions.

(TMC)Fe^{IV}=O π -Cation Radical (4a). In a typical run, to a dichloromethane solution (0.018 mM) of (TMC)Fe^{III}(*m*-chlorobenzoate) (**1a-mCB**) was added 1 mol equiv of *m*-chloroperoxybenzoic acid (mCPBA) as a dichloromethane solution in one portion at -80 °C. (TDCPC)Fe^{IV}=O π -cation radical (**4b**) was generated in the same manner.

Reaction of Norbornene. In a typical reaction, to a dichloromethane solution (0.02 mM) of (TMC)Fe^{IV}=O π -cation radical (**4a**) was added a dichloromethane solution of norbornene (1000 equiv per **4a**) in one portion at -80 °C. The reaction was monitored by electronic absorption spectroscopy. The reaction of norbornene with (TDCPC)Fe^{IV}=O π -cation radical (**4b**) was carried out under similar conditions.

Results

Oxidation Potentials of Chlorin Complexes. The first oxidation potentials for H₂TMC and H₂TDCPC and their iron(III)

(14) Abbreviations: TMC, 7,8-dihydro-tetrakis(2,4,6-trimethylphenyl)porphyrin (tetramesitylchlorin); TDCPC, 7,8-dihydro-tetrakis(2,6-dichlorophenyl)porphyrin; TMP, tetrakis(2,4,6-trimethylphenyl)porphyrin (tetramesitylporphyrin).

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Table 1. First Oxidation Potentials of Both Free Bases and Iron(III) Complexes of Porphyrin and Chlorin in Dichloromethane Solutions^a

compd	$E_{1/2}^b$, V (vs SCE)	compd	$E_{1/2}^b$, V (vs SCE)
H ₂ TMC	0.80	(TDCPC)Fe ^{III} Cl (1b-Cl)	1.08
(TMC)Fe ^{III} Cl (1a-Cl)	0.89	H ₂ TMP	0.98
H ₂ TDCPC	0.98	(TMP)Fe ^{III} Cl ^c	1.09

^a Abbreviations are used according to ref 14. ^b $E_{1/2} = (E_{p,c} + E_{p,a})/2$, 50 mV/s scan rates, 0.1 M *n*-Bu₄NClO₄ supporting electrolyte, $i_{p,c} \approx i_{p,a}$. ^c 20 mV/s scan rate.

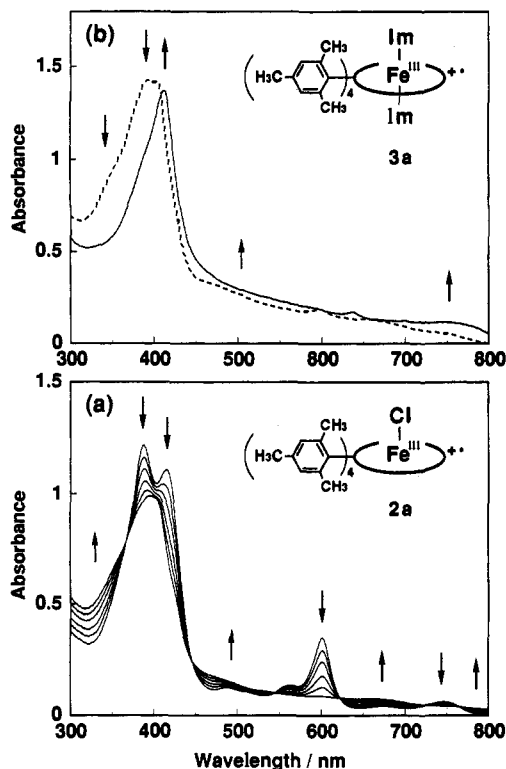
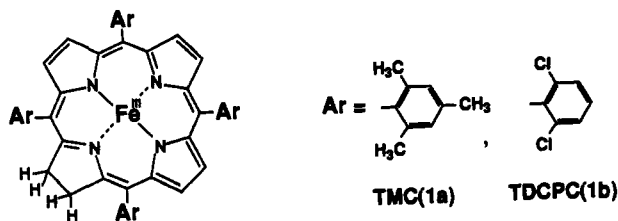


Figure 1. Electronic absorption spectral changes of (a) (TMC)Fe^{III}Cl (1a-Cl) (0.020 mM) with aliquot additions (0.2 equiv each) of phenoxathiin hexachloroantimonate in dichloromethane at room temperature and (b) (TMC)Fe^{III}Cl(SbCl₆) (2a) (0.020 mM) titrated with 2 mol equiv of imidazole in dichloromethane at -80 °C.

complexes (1a,b) have been examined by cyclic voltammetry.



The oxidation potentials of tetramesitylporphyrin (TMP) derivatives were also measured, and the results are summarized in Table 1. The oxidation potentials of the chlorin and porphyrin complexes are as follows: TMC(1a) < TDCPC (1b) \approx TMP. The facile ring oxidation of 1a in comparison with TMP is consistent with the previous experimental and theoretical studies.^{5-10,16-18} However, introduction of strongly electron-withdrawing Cl to the

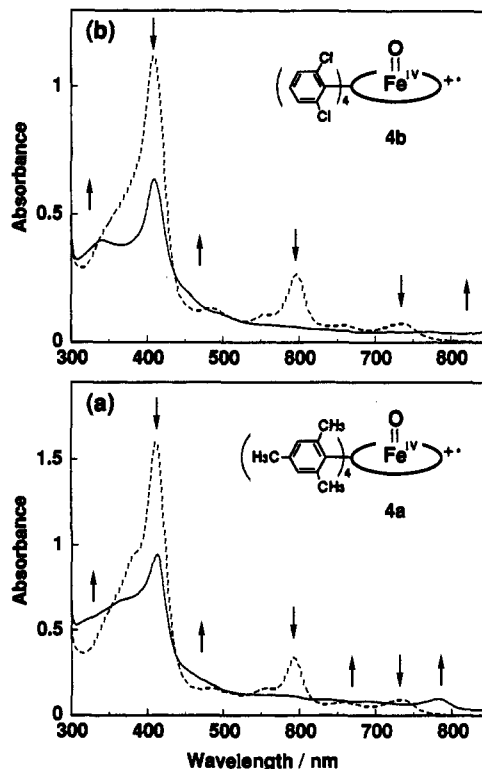


Figure 2. Electronic absorption spectra of (a) 0.018 mM (TMC)Fe^{III}-(mCB) (1a-mCB) (dashed line) and the oxidation product with 1 mol equiv of mCPBA (4a) (solid line) and (b) 0.013 mM (TDCPC)Fe^{III}-(mCB) (1b-mCB) and the oxidation product with 2 equiv of mCPBA (4b) (solid line) in dichloromethane at -80 °C.

substituted phenyl groups makes the basicity of the chlorin macrocycle (1b) nearly identical to that of (TMP)Fe^{III}.

Formation of Chlorin π -Cation Radical Complexes. Oxidation of (TMC)Fe^{III}Cl (1a-Cl) has been performed with phenoxathiin hexachloroantimonate (Phenox⁺SbCl₆⁻) in dichloromethane at room temperature. The oxidation of 1a-Cl accompanies decreased intensity of the Soret band, loss of the characteristic band for chlorin complexes (601 nm), and appearance of a broad band stretching into the near infrared region to yield a new complex, 2a (Figure 1a). Reduction of 2a with tetra-*n*-butylammonium iodide (TBAI) reproduces the absorption spectrum of 1a. The absorption spectral features of 2a are characteristic of chlorin π -cation radicals,⁵⁻¹⁰ indicating the formulation of the (TMC)-Fe^{III}Cl π -cation radical for 2a.

Introduction of 2 mol equiv of imidazole into the dichloromethane solution of 2a at -80 °C affords a new species, 3a (Figure 1b). The absorption spectrum of 3a is still characteristic of chlorin π -cation radicals. Addition of TBAI to the solution of 3a at -80 °C brought about immediate reduction to give (TMC)Fe^{III}(Im)₂⁺. These results demonstrate that 3a is an imidazole adduct of the iron(III) chlorin π -cation radical. ESR spectra of both π -cation radicals (2a and 3a) were found to be silent in dichloromethane even at 77 K, as observed for iron(III) porphyrin π -cation radicals.¹³

Formation of the (TMC)Fe^{IV}=O π -cation radical (4a) in the reaction of 1a-(*m*-chlorobenzoate, mCB) with *m*-chloroperoxybenzoic acid (mCPBA) at -80 °C was evidenced by an absorption spectral change¹⁰ similar to those of iron(III) chlorin π -cation radicals (Figure 2a). When the temperature was raised to -60 °C, 4a was completely transformed to the iron(III) TMP complex in 2 h. The oxidation of (TDCPC)Fe^{III}(mCB) (1b-mCB) with 2 mol equiv of mCPBA in dichloromethane at -80 °C also afforded the characteristic spectrum for chlorin π -cation radicals to form the (TDCPC)Fe^{IV}=O π -cation radical, 4b (Figure 2b). 4a,b did not show any ESR signals in dichloromethane at 77 K.

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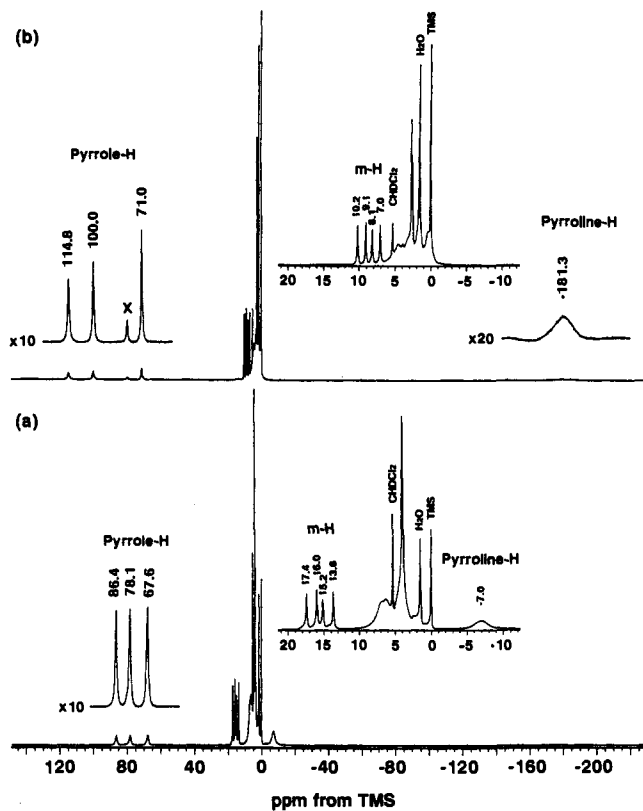


Figure 3. Proton NMR spectra of (a) (TMC)Fe^{III}Cl (**1a-Cl**) and (b) (TMC)Fe^{III}Cl(SbCl₆) (**2a**) in dichloromethane-*d*₂ at 23 °C. Sample concentrations are 3 mM. The signals labeled X are due to the (TMP)-Fe^{III} complex.

NMR Spectra of Iron(III) Chlorin π -Cation Radicals (2a** and **3a**).** Proton NMR spectra of (TMC)Fe^{III}Cl (**1a-Cl**) exhibited well-resolved hyperfine-shifted proton NMR resonances as shown in Figure 3a. Signal assignment was accomplished by selective deuteration and by their relative intensities. For example, the pyrrole proton signals of **1a-Cl** are observed at 86.4, 78.1, and 67.6 ppm and the pyrroline proton resonances exhibit a small upfield shift (-7.0 ppm). These spectral features are very similar to those of (TPC)Fe^{III}Cl.¹⁹ Upon oxidation of **1a-Cl** by Phenox⁺SbCl₆, the pyrroline proton signal shows a large upfield shift and the pyrrole proton resonances exhibit small downfield shifts (Figure 3b). Phenyl meta protons experience small upfield shifts. Splitting of the meta proton signals of **2a** into four lines indicates that the chloride ion binds to the iron of **2a** as well as **1a** to make the two protons above and beneath the macrocycle plane nonequivalent. The large upfield shift (~180 ppm) of the pyrroline proton resonance of **2a** is hardly due to the metal oxidation but rather results from the chlorin π -cation radical formation in which a substantial amount of π -spin density on the α -carbons of the pyrroline ring is delocalized onto C _{β} H via hyperconjugation.^{7,20} According to MO calculations,^{8,9} two nearly degenerated ground states (²A₂ and ²B₂) can be possible for chlorin π -cation radicals. The a₂ radical orbital bears large spin density at the α -carbons of the pyrroline ring, whereas the b₂ radical has spin density at the meso carbons and the pyrrole nitrogens (Figure 4). The large upfield shift (~180 ppm) for the pyrroline protons of **2a** is translated into large π -spin density on the pyrroline α -carbons and is reasonably attributed to the a₂ radical state. Variable-temperature NMR measurements for **2a** were also performed in the temperature range (from -80 to 23 °C). While

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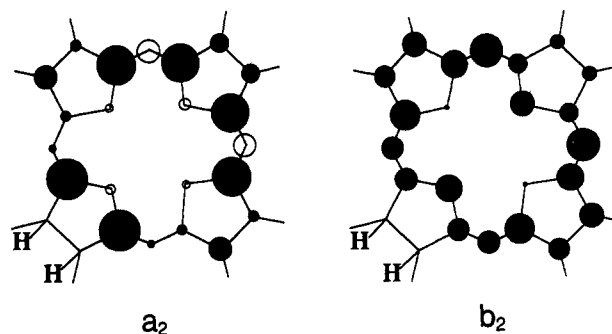


Figure 4. Electron spin distribution of chlorin π -cation radicals (a₂ and b₂) by SCF Pariser-Parr-Pople MO calculations from ref 8. Filled and open circles correspond to positive and negative spin densities, respectively.

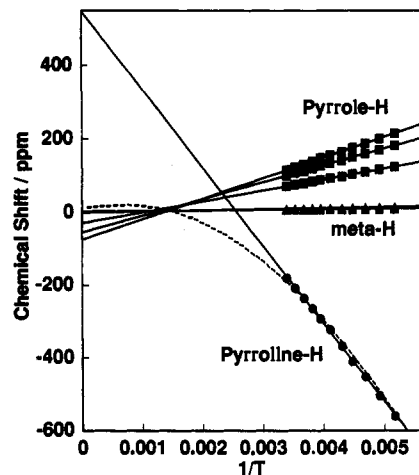


Figure 5. Temperature dependence of the proton NMR resonances of (TMC)Fe^{III}Cl(SbCl₆) (**2a**). The chemical shifts are plotted against 1/*T* (Curie law plot). The dashed line represents the simulation results (see text).

all resonances are linear, the pyrroline proton resonance exhibits a far upfield intercept at the infinite temperature (1/*T* = 0) as depicted in Figure 5, possibly due to thermal admixture of two or more different states (see the Discussion).

When 2 mol equiv of imidazole was added to the solution of **2a** at -80 °C, the proton NMR resonances of **2a** were replaced with those of **3a** as demonstrated in Figure 6. Identification of NMR signals of **3a** was established by using selectively deuterated derivatives. The pyrrole proton resonances experience large upfield shifts (-82.0, -102.2, and -128.4 ppm), and the signals for phenyl protons are observed in a diamagnetic region (Figure 6b). Three signals at 31.7, 24.2, and 19.1 ppm are assigned to coordinated imidazole protons of **3a** by utilizing selectively deuterated imidazole derivatives,²¹ which implies the coordination of imidazole to the iron in **3a**. The pyrroline proton resonances exhibit far downfield shifts (~500 ppm), indicative of chlorin π -cation radical formulation for **3a**. Furthermore, the large downfield shift of the pyrroline proton resonances of **3a** is rationalized by the a₂ radical state. The pyrrole and pyrroline proton resonances of **3a** exhibit Curie law behavior (Figure 7) in the temperature range from -90 to 65 °C except for the large downfield intercepts of the pyrroline resonances. When the temperature was raised to -60 °C, the resonances of **3a** were changed into those of (TMC)Fe^{III}(Im)₂Cl and (TMP)Fe^{III}(Im)₂Cl. The proton NMR shift values of **2a** and **3a** are summarized in Table 2.

Deuterium NMR Spectra of the Oxoiron(IV) Chlorin π -Cation Radical (4a**).** Upon oxidation of **1a-mCB** by 1 mol equiv of mCPBA at -80 °C, the pyrrole deuterium signals of **1a-mCB** at

(21) Imidazole-*d*₃ (2,4,5-positions) and -*d*₁ (2-position) derivatives were used for the signal assignment.

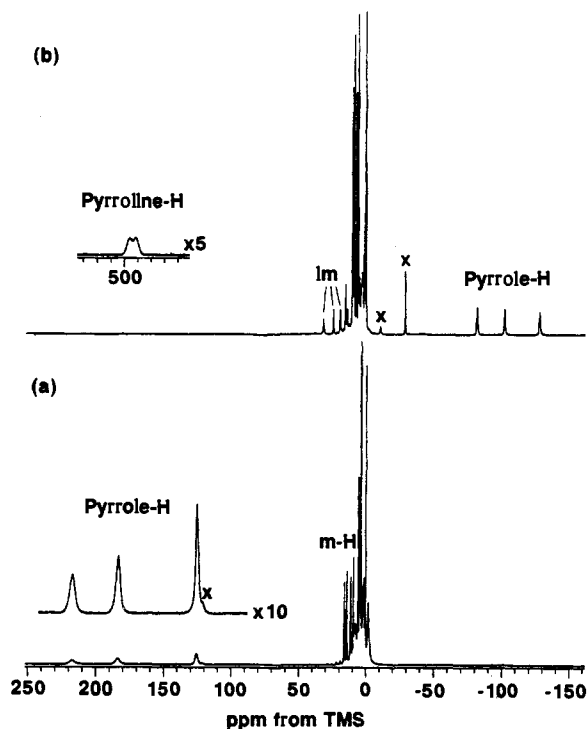


Figure 6. Proton NMR spectral changes of (TMC)Fe^{III}Cl(SbCl₆) (**2a**) (a) before and (b) after addition of 2 mol equiv of imidazole in dichloromethane-*d*₂ at -80 °C. Sample concentrations are 3.4 mM. The signal labeled X is due to the (TMP)Fe^{III} complex.

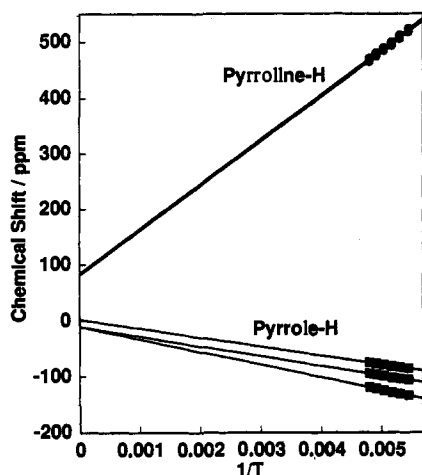


Figure 7. Temperature dependence of the proton NMR resonances of (TMC)Fe^{III}(Im)₂Cl(SbCl₆) (**3a**). The chemical shifts are plotted against 1/*T* (Curie law plot).

135, 119, and 96 ppm were replaced by new resonances (23, -48, and -77 ppm) of **4a** as shown in Figure 8. The unusual features of the three pyrrole signals of **4a** (Figure 8b) could be attributed to the chlorin π -cation radical in which substantially different π -spin densities are distributed on the β -carbons of the pyrrole rings,^{8,9} rather than to the iron-centered paramagnetic effect. Further, small downfield shifts (36 and 23 ppm) of the meta deuterium resonances are observed (not shown).¹⁰ Upon reduction of **4a** with TBAI, the complete recovery of **1a**-mCB was observed by the deuterium NMR spectra. As shown in Figure 8b, the pyrrole deuterium resonance of the (TMP)Fe^{III} complex is observed at 120 ppm due to the decomposition of **4a**. This signal gradually grew up with concomitant decrease of the pyrrole deuterium resonances of **4a** even when the temperature of the NMR sample (\sim 3 mM) was kept at -80 °C. Unfortunately, attempts to detect the pyrroline ring deuterium resonances, which are expected to be sizably hyperfine-shifted,⁷ were unsuccessful

Table 2. Proton NMR Shift Values of Iron(III) Chlorin Complexes in Dichloromethane-*d*₂^a

	(TMC)Fe ^{III} Cl (1a -Cl) ^b	(TMC)Fe ^{III} Cl- (SbCl ₆) (2a) ^b	δ_{radical}
pyrrole	86.4, 78.1, 67.6	114.8, 100.0, 71.0	28.4, 21.9, 3.4
pyrroline	-7.0	-181.3	-174.3
phenyl meta	17.4, 16.0, 15.2, 13.6	10.2, 9.1, 8.1, 7.0	-7.2, -6.9, -7.1, -6.6
	(TMC)Fe ^{III} - (Im) ₂ Cl ^c	(TMC)Fe ^{III} (Im) ₂ - Cl(SbCl ₆) (3a) ^c	δ_{radical}
pyrrole	-2.4, -12.3, -47.1	-82.0, -102.2, -128.4	-79.6, -89.9, -81.3
pyrroline	38.3	499, 494	460.7, 455.7
Im (1H)		24.2	
(2H)	-24 ^{d,e}	10.4 ^d	(34.4)
(4H)	1.9 ^{d,e}	31.7	(29.8)
(5H)	1.9 ^{d,e}	19.1	(17.2)

^a At \sim 3 mM. ^b At 23 °C. ^c At -80 °C. ^d Values obtained from deuterium signals. ^e In CHCl₃ at -70 °C.

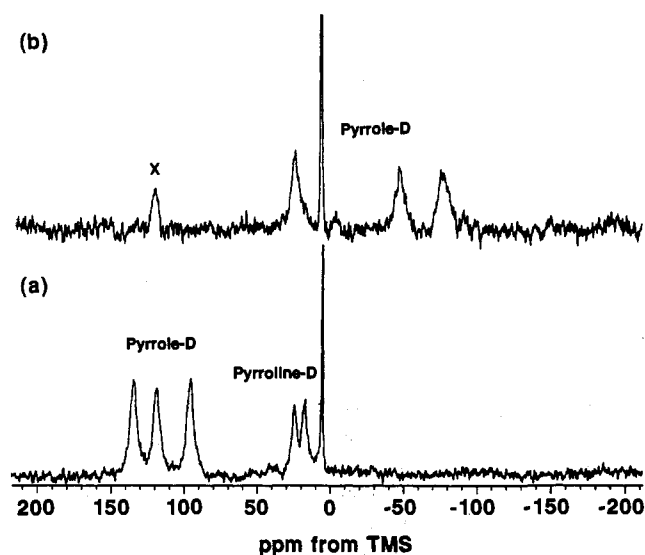


Figure 8. Deuterium NMR spectra of (a) pyrroline-*d*₂-pyrrole-*d*₆ (TMC)-Fe^{III}(mCB) (**1a**-mCB) and (b) its oxidation product with 1 mol equiv of mCPBA (**4a**) in dichloromethane at -80 °C. Sample concentrations are 3.1 mM. The signal labeled X is due to the (TMP)Fe^{III} complex.

at this time. Temperature dependences of the pyrrole signals are visualized as Curie law plots in Figure 9. These signals exhibit downfield intercepts at infinite temperature.

Reaction of Norbornene with Oxoiron(IV) Chlorin π -Cation Radicals (4a,b**).** In order to examine the reactivities of oxoiron(IV) chlorin π -cation radical complexes, the reaction of norbornene with **4a,b** have been carried out at -80 °C. Upon addition of 1000 equiv of norbornene to the solution of **4a**, the absorption spectrum of **4a** showed no changes for 3 h. The parent complex **1a**, was reproduced at this time by the reduction with TBAI. On the contrary, the corresponding porphyrin (TMP) π -cation radical reacted with norbornene even at -80 °C to give norbornene oxide in 3 h.²² The TDCPC complex (**4b**), which shows a ring oxidation potential (1.08 V) nearly identical to that of the TMP derivative (1.09 V), also exhibited no reactivity toward norbornene at -80 °C. Further, when the solution temperature was raised from -80 to -40 °C in the presence of 1000 equiv of norbornene, the absorption spectrum of **4b** was changed into that of the corresponding iron(III) porphyrin complex rather than that of the chlorin complex (**1b**) by the reduction. These results demonstrate that the oxoiron(IV) chlorin π -cation radical

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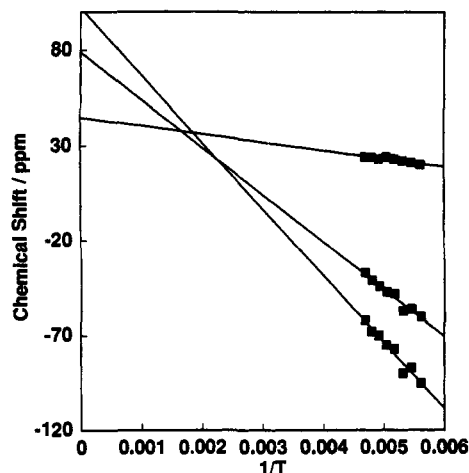


Figure 9. Temperature dependence of the deuterium NMR resonances of (TMC)Fe^{IV}=O(mCB) (4a). The chemical shifts are plotted against 1/T (Curie law plot).

complexes (4a,b) have lower reactivities toward olefins than the porphyrin π -cation radicals.

Discussion

Electronic Structures of Iron Chlorin π -Cation Radicals. It has been demonstrated here that high- and low-spin iron(III) and oxoiron(IV) tetramesitylchlorin (TMC) π -cation radical complexes are successfully prepared by chemical oxidation and these π -cation radicals exhibit well-defined NMR spectra (Figures 3, 6, and 8). The isotropic NMR hyperfine shift for the π -radical system is related to the π -electron spin density at the pyrrole β -carbons (ρ_C , eq 2) and the pyrroline α -carbons (ρ_{C-CH} , eq 3) through eqs 1–3. Here, eq 1 relates the observed isotropic

$$\left(\frac{\Delta H}{H}\right)_{\text{iso}} = A^H \frac{\gamma}{\hbar} \frac{g\beta S(S+1)}{3kT} \quad (1)$$

$$A^H = Q\rho_C \quad (2)$$

$$A^H = (B_0 + B_2 \cos^2 \theta) \rho_{C-CH} \quad (3)$$

shift $(\Delta H/H)_{\text{iso}}$ with the proton hyperfine coupling constant (A^H).²⁰ Equations 2 and 3 are the McConnell relations which connect A^H with the π -spin density on the pyrrole β -carbons and the pyrroline α -carbons, respectively. B_0 and B_2 are constants, and θ is the dihedral angle between the $2p_z$ orbital of the pyrroline α -carbon and the plane defined by the α - and β -carbons and the proton of the pyrroline ring.⁸ By using these equations, the observed hyperfine shifts of the pyrrole and pyrroline ring protons are readily translated into the π -spin density at the pyrrole β -carbons and the pyrroline α -carbons, respectively.

The unusually large downfield shifts ($\delta_{\text{radical}} = 460.7$ and 455.7 ppm at -80 °C) for the pyrroline protons of 3a (Table 2) are translated into a large π -spin density of $\rho = 0.050$ – 0.070 (θ ranges between 30° and 45° in chlorins⁸) on the α -carbons of the pyrroline ring and are in good agreement with the a_2 radical state. Further, the upfield shifts ($\delta_{\text{radical}} = -79.6$, -89.9 , and -81.3 ppm at -80 °C) for the pyrrole ring protons of 3a (Table 2) correspond to a π -spin density of $\rho = 0.031$ – 0.035 on the pyrrole β -carbons. While the large upfield shift ($\delta_{\text{radical}} = -174.3$ ppm at 23 °C) for the pyrroline protons of 2a (Table 2) is also attributed to large π -spin density on the α -carbons of the pyrroline ring (a_2 radical state), we could not estimate the π -spin density on the α -carbons owing to thermal admixture of two states (*vide infra*).²³

The deuterium NMR spectrum of 4a exhibits distinctive features as compared with those of the iron(III) chlorin π -cation

radicals (2a and 3a). Large splitting (~ 100 ppm) of the pyrrole deuterium resonances of 4a (Figure 8b) implies substantially different π -spin densities on the β -carbons of the pyrrole ring. Further, the small downfield shifts (36 and 23 ppm at -80 °C)¹⁰ of the meta deuterium resonances are consistent with the a_2 radical state rather than the a_{2a} radical of TMP (70.6 ppm at -80 °C).²⁴ However, failure in detection of the pyrroline deuterium resonances of 4a²⁵ prevents unambiguous determination of the radical type.

Magnetic Properties of Iron Chlorin π -Cation Radicals. The large contact shifts for the pyrroline protons of the high- and low-spin iron(III) chlorin π -cation radical complexes (2a and 3a) are consistent with the a_2 radical state, while the radical-induced contact shifts exhibit an opposite direction between 2a (*upfield*) and 3a (*downfield*). Since the π -radical spin on the α -carbons of the pyrroline ring is directly transferred to the pyrroline protons by hyperconjugation through a pseudo π -orbital (eq 3), the spin densities on the α -carbons and the protons of the pyrroline ring have the same sign.^{7,26} Thus, the hyperfine shift of the pyrroline protons could reflect the amount as well as the sign of the spin density on the pyrroline α -carbons. When an iron chlorin π -cation radical exhibits intramolecular antiferromagnetic coupling of the iron and π -radical spin, the large *upfield* shifts are expected for the pyrroline protons due to flipped π -radical spin (negative spin) on the pyrroline α -carbons. On the other hand, very weak antiferromagnetic coupling of an iron chlorin π -cation radical could induce the large *downfield* shifts for the pyrroline ring protons. Therefore, the large upfield (2a) and downfield (3a) shifts are indications of the antiferromagnetic and very weak antiferromagnetic couplings between the iron and π -radical spins in 2a and 3a, respectively.²⁷

The pyrroline proton resonance of 2a exhibits unusual temperature dependence as illustrated in Figure 5, in which the large downfield intercept is observed (~ 550 ppm). We attempted simulation of this variable-temperature behavior of 2a as described below. The high-spin iron ($S = 5/2$) and the π -radical spin ($S = 1/2$) of 2a could be antiferromagnetically coupled. Suppose that the ferromagnetically coupled state ($S = 3$) possesses slightly higher energy than the antiferromagnetically coupled state ($S = 2$) due to a moderate spin coupling (J). The $S = 3$ state can be thermally admixed to the $S = 2$ state at room temperature. Further, we assume that the radical state of 2a is in thermal mixing of a_2 and b_2 with an energy separation gap of E . It is thus likely that the observed NMR shift (δ_{obs}) is represented as follows.²⁸

$$\delta_{\text{obs}} = \alpha(J) \beta(E) + \frac{\delta_{\text{iron}}}{T} + \delta_{\text{dia}} \quad (4)$$

$$\alpha(J) = \frac{-5 + 7 \exp\left(\frac{-3J}{kT}\right)}{5 + 7 \exp\left(\frac{-3J}{kT}\right)} \quad (5)$$

$$\beta(E) = \frac{\frac{\delta_{a_2}}{T} + \frac{\delta_{b_2}}{T} \exp\left(\frac{-E}{kT}\right)}{1 + \exp\left(\frac{-E}{kT}\right)} \quad (6)$$

δ_{iron}/T is the shift for the unoxidized iron(III) TMC complex, and δ_{dia} is the diamagnetic correction (H_2 TMC). δ_{a_2}/T and δ_{b_2}/T are the limiting shifts for the a_2 and b_2 radicals obtained from the spin densities (0.138 and 0.042 for a_2 and b_2 radicals, respectively)⁸ on the pyrroline α -carbons through eqs 1 and 3.

(23) If eqs 1 and 3 are simply applied to the case of 2a, the observed hyperfine shift ($\delta_{\text{radical}} = -174.3$ ppm at 23 °C) will correspond to the *negative* π -spin densities of $\rho = -0.029$ to -0.041 on the pyrroline α -carbons.

(24) Fujii, H. *J. Am. Chem. Soc.* 1993, 115, 4641–4648.

(25) While the reason for this is unclear, the signal would be much broadened possibly due to an unusually large contact shift and/or thermal mixing of other states.

Then, we have simulated the Curie law plot of the pyrroline proton NMR resonance of **2a** by using eqs 4–6. As shown in Figure 5 (dashed line), the values of $J = -60 \text{ cm}^{-1}$ and $E \approx 400 \text{ cm}^{-1}$ fit well with experimental NMR shifts. It is therefore concluded that the high-spin Iron(III) chlorin π -cation radical (**2a**) prefers the a_2 ground state and that the iron spin and π -radical spin of **2a** are antiferromagnetically coupled.³⁰ The value of $J = -60 \text{ cm}^{-1}$ for **2a** is compatible with that of $J = -85 \text{ cm}^{-1}$ for (TPC)Fe^{III}-Cl(SbCl₆) in the solid state.³¹

Reactivities of Oxoiron(IV) Chlorin π -Cation Radicals. Although the oxoiron(IV) chlorin π -cation radicals (**4a,b**) do not react with norbornene under the given conditions, the corresponding porphyrin (TMP) π -cation radical readily reacts with norbornene to give norbornene oxide.²² These results led us to conclude that the oxoiron(IV) chlorin π -cation radical complexes (**4a,b**) have lower reactivity toward olefins than the porphyrin (TMP) π -cation radicals. The lowered reactivity of the chlorin complexes could not be rationalized by the oxidation potentials of the chlorin macrocycles, since **4b** exhibits ring oxidation at a potential (1.08 V) nearly identical to that of the TMP complex (1.09 V) while the ring oxidation potential of **4a** (0.89 V) is lower than that of TMP.

Although the (TMP)Fe^{IV}=O complex does not react with various olefins, the (TMP)Fe^{IV}=O π -cation radical readily oxidizes them.^{22,32} The greater reactivity of the (TMP)Fe^{IV}=O π -cation radical as compared with (TMP)Fe^{IV}=O would be ascribed to the increased positive charge on the oxo ligand as well as the a_{2u} radical orbital which interacts with the p_z orbital of the central metal by utilizing a large spin density on the pyrrole nitrogens.³³ On the other hand, the a_{1u} radical, having nodes at the pyrrole nitrogens, is expected to exhibit lower reactivity than

the a_{2u} radical owing to less effective interaction of the porphyrin radical with the central metal.³³ In fact, the reactivities of the π -cation radicals of (TMP)Ru^{VI}(O)₂ and (OEP)Ru^{VI}(O)₂, which are of a_{1u} type, relative to the corresponding Ru^{VI}(O)₂ complexes were enhanced less than expected for the complexes bearing a_{2u} radical orbitals.³³ On the basis of these considerations, the lowered reactivities of the oxoiron(IV) chlorin π -cation radicals (**4a,b**) presented here would be attributed to their $a_2(a_{1u})$ type radical orbitals.

Previously, Fujii has studied the effects of oxidation potentials and radical types on the reactivities of oxoiron(IV) porphyrin π -cation radical complexes by using several meso- and β -pyrrole-substituted porphyrins.²⁴ The oxoiron(IV) porphyrin π -cation radical complexes bearing higher ring oxidation potentials were more reactive toward cyclohexene than those having lower oxidation potentials. Further, the oxoiron(IV) porphyrin π -cation radicals with the a_{1u} states were almost as reactive as those with the a_{2u} states. Thus, he concluded that the reactivity of the oxygen atom of oxoiron(IV) porphyrin π -cation radicals depends on their ring oxidation potentials and is not affected by the a_{1u}/a_{2u} orbital occupancy.²⁴ If this conclusion were applicable to the iron chlorin systems, the oxoiron(IV) π -cation radical of the TDCPC complex (**14b**) would be as reactive as that of the TMP complex. This is not the case for the oxoiron(IV) chlorin π -cation radicals. The apparent inconsistency in these two interpretations^{24,33} concerning the reactivities of π -cation radicals should be the subject of further studies. While we could not offer sufficient explanation for the lowered reactivities of the chlorin complexes relative to the corresponding porphyrin complexes at this time, the reactivities of the oxoiron(IV) chlorin π -cation radicals may be controlled by several factors including oxidation potential and radical orbital type.

In summary, we have prepared iron(III) and oxoiron(IV) chlorin π -cation radical complexes and examined their electronic structures and magnetic properties by NMR spectroscopy. The high- and low-spin iron(III) chlorin π -cation radicals exhibit well-resolved hyperfine-shifted NMR spectra, indicative of the a_2 radical state. Further, the hyperfine shifts of the pyrroline proton resonances of these complexes revealed their magnetic coupling between the iron spin and π -radical spin. The oxoiron(IV) chlorin π -cation radicals are shown to be less reactive than the corresponding porphyrin complexes, which could not be rationalized by the oxidation potentials of the chlorin macrocycles.

Acknowledgment. We thank Dr. M. Sasaki of Tokyo University for FAB mass spectral measurements.

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(27) While ferromagnetic coupling between the iron and π -radical spins could also induce a large *downfield* shift for the pyrroline protons, this magnetic interaction is expected to exhibit a sizable large *upfield* intercept for the pyrroline proton resonance in the Curie law plot. However, the pyrroline proton signals of **3a** show large *downfield* intercepts (Figure 7), consistent with the very weak antiferromagnetic coupling for **3a**.

(28) A reviewer suggested that this π -radical system could be interpreted by an antiferromagnetic coupling observed for 2Fe–2S ferredoxins²⁹ instead of our description (eqs 4–6). In the case of the 2Fe–2S system, the unpaired electron is almost localized on each iron atom, whereas in our system, the π -radical spin (one of the two paramagnetic centers) is very much delocalized on the chlorin macrocycle. Thus, the situation of chlorin π -cation radicals is considered to be different from that of the 2Fe–2S system. However, the analysis used for the 2Fe–2S system could be a possible method for considering the hyperfine shifts of chlorin π -cation radicals.

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(30) The magnetic properties of **2a** and **3a** could be established more firmly by solution magnetic susceptibility measurements. Owing to the contamination of the iron(III) TMP complex, we did not perform these measurements at this time.

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