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Electronic Structures of Five-Coordinate Iron(III) Porphyrin Complexes with Highly Ruffled Porphyrin Ring

Takanori Sakai,[†] Yoshiki Ohgo,[‡] Akito Hoshino,[†] Takahisa Ikeue,[‡] Takashi Saitoh,[‡]
Masashi Takahashi,[§] and Mikio Nakamura*,[†,‡]

Department of Chemistry, School of Medicine, Toho University, Tokyo 143-8540, Japan,
Division of Biomolecular Science, Graduate School of Science, Toho University,
Funabashi 274-8510, Japan, and Department of Chemistry, Faculty of Science,
Toho University, Funabashi 274-8510, Japan

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The spin states of the iron(III) complexes with a highly ruffled porphyrin ring, [Fe(TEtPrP)X] where X = F^-, Cl^-, Br^-, I^-, and ClO_4^-, have been examined by ^{1}H NMR, ^{13}C NMR, EPR, and Mössbauer spectroscopy. While the F^-, Cl^-, and Br^- complexes adopt a high-spin ($S = {}^{5}/_{2}$) state, the I^- complex exhibits an admixed intermediate-spin ($S = {}^{5}/_{2}, {}^{3}/_{2}$) state in CD_2Cl_2 solution. The I^- complex shows, however, a quite pure high-spin state in toluene solution as well as in the solid. The results contrast those of highly saddled [Fe(OETPP)X] where the I^- complex exhibits an essentially pure intermediate-spin state both in solution and in the solid. In contrast to the halide-ligated complexes, the ClO_4^- complex shows a quite pure intermediate-spin state. The ^{13}C NMR spectra of [Fe(TEtPrP)ClO_4] are characterized by the downfield and upfield shifts of the *meso* and pyrrole-α carbon signals, respectively: $\delta(meso) = +342$ and $\delta(\alpha\text{-py}) = -287$ ppm at 298 K. The data indicate that the *meso* carbon atoms of [Fe(TEtPrP)ClO_4] have considerable amounts of positive spin, which in turn indicate that the iron has an unpaired electron in the d_{xy} orbital; the unpaired electron in the d_{xy} orbital is delocalized to the *meso* positions due to the iron(d_{xy})–porphyrin(a_{2u}) interaction. Similar results have been obtained in analogous [Fe(T^{i}PrP)X] though the intermediate-spin character of [Fe(T^{i}PrP)X] is much larger than that of the corresponding [Fe(TEtPrP)X]. On the basis of these results, we have concluded that the highly ruffled intermediate-spin complexes such as [Fe(TEtPrP)ClO_4] and [Fe(T^{i}PrP)ClO_4] adopt a novel $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1$ electron configuration; the electron configuration of the intermediate-spin complexes reported previously is believed to be $(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^1$.

Introduction

Iron(III) porphyrin complexes with an anionic axial ligand usually show the high-spin ($S = {}^{5}/_{2}$) or admixed intermediate-spin ($S = {}^{3}/_{2}, {}^{5}/_{2}$) states depending on the field strength of the axial ligands.[1−6] For example, the complexes carrying halides as axial ligands always show the high-spin ($S = {}^{5}/_{2}$) state while those with perchlorate exhibit the admixed intermediate-spin ($S = {}^{3}/_{2}, {}^{5}/_{2}$) state. The situation is quite different, however, if porphyrin is replaced by porphyrin analogues such as porphycene; not only the perchlorate but also the iodide complexes showed a quite pure intermediate-spin state.[7−9] The results are ascribed to (i) the short $Fe-N_P$ bond lengths, (ii) the narrow cavity area surrounded by the four nitrogen atoms, and (iii) the small deviation of the iron atom from the mean porphyrin plane.[8] We have expected

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[*] To whom correspondence should be addressed. E-mail: mnakamu@med.toho-u.ac.jp.

[†] Division of Biomolecular Science, Graduate School of Science.

[‡] Deparment of Chemistry, School of Medicine.

[§] Department of Chemistry, Faculty of Science.

(1) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543−555.
(2) Scheidt, W. R.; Gouterman, M. In *Iron Porphyrin, Part I*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; pp 89−139.
(3) Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 3, Chapter 16, pp 49−112.
(4) Walker, F. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 5, Chapter 36, pp 81−183.
(5) Walker, F. A. *Inorg. Chem.* **2003**, *42*, 4526−4544.
(6) Walker, F. A. *Chem. Rev.* **2004**, *104*, 589−616.
(7) Rachlewicz, K.; Latso-Grazynski, L.; Vogel, E.; Ciunik, Z.; Jerzykiewicz, L. B. *Inorg. Chem.* **2002**, *41*, 1979−1988.
(8) Ohgo, Y.; Neya, S.; Ikeue, T.; Takahashi, M.; Takeda, M.; Funasaki, N.; Nakamura, M. *Inorg Chem.* **2002**, *41*, 4627−4629.
(9) Ikeue, T.; Ohgo, Y.; Takahashi, M.; Takeda, M.; Neya, S.; Funasaki, N.; Nakamura, M. *Inorg. Chem.* **2001**, *40*, 3650−3652.

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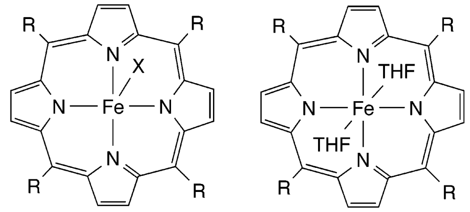
that the conditions to stabilize the intermediate-spin state could be satisfied even in the porphyrin complexes if they have a deformed porphyrin ring. In fact, highly deformed six-coordinate complexes such as saddled [Fe(OETPP)(THF)$_2$]ClO$_4$ and ruffled [Fe(TMCP)(EtOH)(H$_2$O)]ClO$_4$ and [Fe(T^{i}PrP)(THF)$_2$]ClO$_4$ have shown an essentially pure intermediate-spin state in a wide range of temperatures as is revealed by ^{1}H NMR, ^{13}C NMR, EPR, Mössbauer, and SQUID measurements (the following is a list of abbreviations used in this paper: T^{i}PrP, TEtPrP, T^{n}PrP, OETPP, TMCP, EtioP, and TPP = dianions of *meso*-tetraisopropylporphyrin, *meso*-tetrakis(1-ethylpropyl)porphyrin, *meso*-tetrapropylporphyrin, 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, *meso*-tetramethylchiroporphyrin, etioporphyrin, and 5,10,15,20-tetraphenylporphyrin; PyNO = pyridine *N*-oxide; 4-CNPy = 4-cyanopyridine).[10,11] As expected, the X-ray crystallographic analyses have revealed that [Fe(TMCP)(EtOH)(H$_2$O)]ClO$_4$ and [Fe(T^{i}PrP)(THF)$_2$]ClO$_4$ have short Fe−N$_P$ bonds, 1.950(5) and 1.967(12) Å on average, respectively.[11,12] Thus, the bond distances are significantly shorter than those of the analogous complexes with admixed intermediate-spin state such as [Fe(TEtP)(THF)$_2$]ClO$_4$, [Fe(TPP)(THF)$_2$]ClO$_4$, and [Fe(OEP)(THF)$_2$]ClO$_4$; the average Fe−N$_P$ bond distances of these complexes are reported to be 2.006, 2.016, and 1.999 Å, respectively.[13−15] It would be quite natural to expect that the five-coordinate complexes with a weak anionic ligand could be in a quite pure intermediate-spin state if they have a deformed porphyrin ring. In fact, the highly saddled [Fe(OETPP)ClO$_4$] and [Fe(OETPP)I] have shown an essentially pure intermediate-spin state in a wide range of temperatures.[16,17] In this paper, we will report on the spin states of five-coordinate complexes with another type of the deformed porphyrin ring, i.e., highly ruffled [Fe(TRP)X] where R's are 1-ethylpropyl (1-EtPr) and isopropyl (^{i}Pr), and X's are F$^-$, Cl$^-$, Br$^-$, I$^-$, and ClO$_4^-$. We will also report that the highly ruffled intermediate-spin complexes such as five-coordinate [Fe(TRP)ClO$_4$] and six-coordinate [Fe(TRP)(THF)$_2$]ClO$_4$ adopt an electron configuration that should be represented by $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1$.[18] The complexes examined in this study are shown in Scheme 1.

Scheme 1. Complexes Examined in this Study



[Fe(TRP)X]
(R = 1-EtPr, ^{i}Pr)
(X = F, Cl, Br, I, ClO$_4$)

[Fe(TRP)(THF)$_2$]ClO$_4$
(R = 1-EtPr, ^{i}Pr)

Experimental Section

General Procedure. UV−vis spectra were measured on a SHIMADZU MultiSpec-1500 spectrophotometer at ambient temperature. FAB-MS spectra were measured on JEOL JMS-600H. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL LA300 spectrometer operating at 300.4 MHz for ^{1}H. Chemical shifts were referenced to the residual peak of dichloromethane (δ = 5.32 ppm for ^{1}H and 53.8 ppm for ^{13}C). EPR spectra were measured at 4.2 K with a Bruker E500 spectrometer operating at X-band and equipped with an Oxford helium cryostat. The concentrations of EPR samples were 5−8 mM. The *g* values were estimated by the simulation of the observed spectra. Iron-57 Mössbauer spectra were measured on a Wissel Mössbauer spectrometer system consisting of an MDU-1200 function generator, a DFG-1200 driving unit, and an MVT-100 velocity transducer, incorporating with a model 7800 multichannel analyzer form Seiko EG&G Co. Ltd. The samples were kept in a Heli-Tran LT-3 gas-flow cryostat from Advanced Research System Inc. equipped with a 9620 digital temperature controller from Scientific Instruments Inc., and the ^{57}Co(Rh) source was kept at room temperature. The data were analyzed by the usual least-squares method. The isomer shift (δ) is given relative to α-iron foil at room temperature. The solid-state magnetic susceptibilities were measured over the temperature range 2−300 K under a magnetic field of 0.5 T with a SQUID magnetometer (Quantum Design MPMS-7). The measured data were corrected for diamagnetic contributions.

Synthesis. (a) [Fe(TEtPrP)Cl]. (TEtPrP)H$_2$ was prepared according to the literature method.[19] Insertion of iron was carried out using FeCl$_2$·4H$_2$O (2.0 g, 10.0 mmol) in refluxing CHCl$_3$−CH$_3$OH (3:1) solution under argon atmosphere. The reaction mixture was treated with diluted HCl solution. The organic layer was separated and dried over sodium sulfate. Evaporation of the solvents yielded dark brown solid, which was purified by chromatography on silica gel using CH$_2$Cl$_2$−CH$_3$OH as eluent. The fractions containing iron(III) porphyrin complexes were treated with 1.0 M aqueous HCl. The organic layer was separated and dried over sodium sulfate. After the evaporation of the solvent, the purple solid was obtained, which was recrystallized from CH$_2$Cl$_2$−heptane. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 93.1 (8H, pyrrole-H); 20.5 (4H, α-H); 12.0 (8H, β-H); 2.08 (24H, γ-H). Other β-CH$_2$(8H) signals are hidden by the γ-CH$_3$ signals. ^{13}C NMR (CD$_2$Cl$_2$, 25 °C): 1122 (pyrrole-α); 1399 (pyrrole-β); 655 (*meso*); −178.0 (meso-C$_\alpha$); 329.2, 345.6 (meso-C$_\beta$); 35.0 (meso-C$_\gamma$). FAB-MS: *m*/*e* = 644 (M$^+$ − 35).

(b) 2-Ethylbutanal(1-^{13}C). 1-Ethylpropylmagnesium bromide was prepared from 3-bromopentane (2.21 g, 14.6 mmol) and magnesium (0.356 g, 14.6 mmol) in 40 mL of dry diethyl ether.

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(10) Ikeue, T.; Saitoh, T.; Yamaguchi, T.; Ohgo, Y.; Nakamura, M.; Takahashi, M.; Takeda, M. *Chem. Commun.* **2000**, 1989−1990.

(11) Simonato, J.-P.; Pécaut, J.; Pape, L. Le; Oddou, J.-L.; Jeandey, C.; Shang, M.; Scheidt, W. R.; Wojacynski, J.; Wolowiec, S.; Latos-Grazynski, L.; Marchon, J.-C. *Inorg. Chem.* **2000**, *39*, 3978−3987.

(12) Ohgo, Y.; Saitoh, T.; Nakamura, M. *Acta Crystallogr.* **2001**, *C57*, 233−234.

(13) Ohgo, Y.; Saitoh, T.; Nakamura, M. *Acta Crystallogr.* **1999**, *C55*, 1284−1286.

(14) Chen, L.; Yi, G.-B.; Wang, L.-S.; Dharmawardana, U. R.; Dart, A. C.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1998**, *37*, 4677−4688.

(15) Cheng, B.; Safo, M. K.; Orosz, R. D.; Reed, C. A.; Debrunner, P. G.; Scheidt, W. R. *Inorg. Chem.* **1994**, *33*, 1319−1324.

(16) Barkigia, K. M.; Renner, M. W.; Fajer, J. *J. Porphyrins Phthalocyanines* **2001**, *5*, 415−418.

(17) Nakamura, M.; Ikeue, T.; Ohgo, Y.; Takahashi, M.; Takeda, M. *Chem. Commun.* **2002**, 1198−1199.

(18) A preliminary report on this subject has already been published: Sakai, T.; Ohgo, Y.; Ikeue, T.; Takahashi, M.; Takeda, M.; Nakamura, M. *J. Am. Chem. Soc.* **2003,** *125*, 13028−13029.

(19) Senge, M. O.; Bischoff, I.; Nelson, N. Y.; Smith, K. M. *J. Porphyrins Phthalocyanines* **1999**, 3, 99−116.

Table 1. ^1H and ^{13}C NMR Chemical Shifts and Int(%) Values of [Fe(TRP)X] Taken in CD_2Cl_2 at 298 K with Data at 213 K Given in Parentheses

X	^1H NMR Py-H	^1H NMR CH(α)	^{13}C NMR *meso*	Int(%)[a]
		[Fe(TEtPrP)X]		
F	97.0	15.8	509	0
	(140)[b]		(644, 681, 711)	(0)
Cl	93.1	20.5	655	3
	(128.7)		(808,851, 889)	(6)
Br	85.2	22.2	643	9
	(106.5)		(749, 786, 821)	(17)
I	60.4	22.7	551	28
	(32−37)[c]		(543, 568, 593)	(53)
I[d]	85.1	23.5	575	9
	(119.3)[b]		(700, 737, 774)	(10)
ClO_4	−32.8	10.8	342	100
	(−57.8)		(208)[e]	(100)
$(THF)_2$	−32.3	6.9	104	
	(−54.3)		(85, 91, 98)	
		[Fe(T^{i}PrP)XI]		
F	97.1	22.3	*f*	0
	(137.9)			(0)
Cl	90.4	28.3	*f*	5
	(120.6)			(9)
Br	73.9	28.8	*f*	18
	(64.2)			(38)
I	20.7	22.8	*f*	60
	(−15.5)			(79)
ClO_4	−31.2	13.8	327	100
	(−56.0)[e]			(100)
$(THF)_2$	−35.5	5.7	115	
	(−58.6)			

[a] Contribution of the intermediate-spin state. [b] Very broad. [c] Several signals. [d] In toluene-d_8 solution. [e] Extrapolated from high temperature. [f] Not measured.

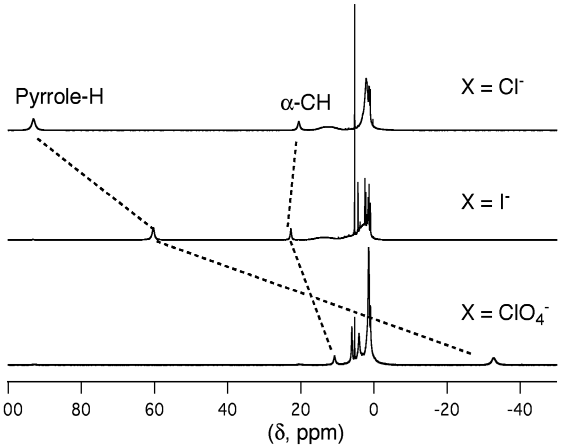

Figure 1. ^1H NMR spectra of [Fe(TEtPrP)X] in CD_2Cl_2 at 298 K where X = Cl^-, I^-, and ClO_4.

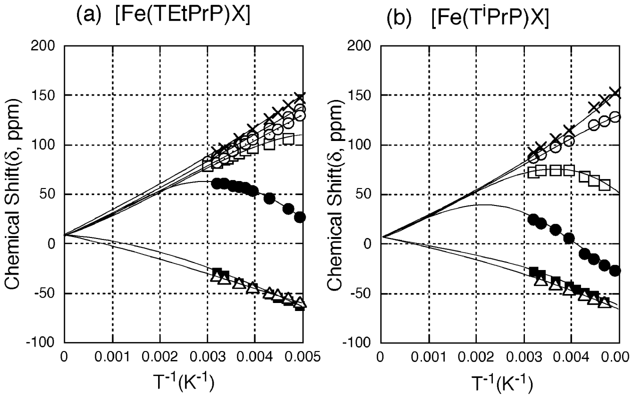

Figure 2. Curie plots of the pyrrole-H signals taken in CD_2Cl_2 solution: X = F (×), Cl (○), Br (□), I (●), ClO_4 (■), and $(THF)_2$ (△). Curie plots of [Fe(TEtPrP)I] determined in toluene-d_8 solution are given by (⊙).

The ether solution of 1-ethylpropylmagnesium bromide was added slowly to the diethyl ether solution (30 mL) containing ethylformate-(1-^{13}C) (1.00 g, 13.3 mmol) at −78 °C. After the solution stirred for 1 h, 30 mL of 2-propanol was added slowly to the reaction mixture at −78 °C. The reaction mixture was gradually heated to room temperature. The white suspension, after the addition of 50 mL of chloroform, was treated with diluted HCl to neutralize the solution. The solution was left for 2 h, and then, the organic layer was separated, which was dried over sodium sulfate. Evaporation of the solvent yielded 2-ethylbutanal(1-^{13}C). ^1H NMR($CDCl_3$, δ): 9.56 (CHO, $^1J_{^{13}C-^1H} = 167.4$ Hz; $^2J_{^{13}C-^1H} = 2.9$ Hz).

(c) *meso*-^{13}C Enriched [Fe(TEtPrP)Cl]. *meso*-^{13}C enriched [Fe(TEtPrP)Cl] was similarly prepared using 2-ethylbutanal(1-^{13}C) and pyrrole. ^{13}C NMR(δ, CD_2Cl_2, 25 °C): 657 ppm (*meso*). FAB-MS: *m*/*e* = 648($M^+ - 35$).

(d) [Fe(TRP)X] (X = F, Cl, Br, I, ClO_4; R = 1-EtPr, ^{i}Pr). Synthetic details of these complexes are given in Supporting Information.

Results and Discussion

Spin States of Five-Coordinate Complexes. Table 1 lists the ^1H NMR chemical shifts of a series of [Fe(TEtPrP)X] and [Fe(T^{i}PrP)X] (X = F^-, Cl^-, Br^-, I^-, and ClO_4^-) determined in CD_2Cl_2 solutions at 298 K. The chemical shifts of the bis(THF) complexes, [Fe(TEtPrP)$(THF)_2$]ClO_4 and [Fe(T^{i}PrP)$(THF)_2$]ClO_4, are also listed for comparison.[10,18] The ^1H NMR spectra of [Fe(TEtPrP)X] where X = Cl^-, I^-, and ClO_4^- are shown in Figure 1 as typical examples. The Curie plots of the pyrrole signals of [Fe(TEtPrP)X] and [Fe(T^{i}PrP)X] are shown in Figure 2a,b, respectively; the chemical shifts instead of the isotropic shifts were plotted against 1/*T*. The Curie lines are drawn so that they intercept the axis of ordinate at the chemical shifts of the corresponding diamagnetic complexes, ca. 9.5 ppm. In both [Fe(TEtPrP)X] and [Fe(T^{i}PrP)X], the pyrrole signals of the F^- complexes appeared in the most downfield position, ca. δ = 97 ppm at 298 K, and moved further downfield linearly against 1/*T*. The pyrrole signals of the Cl^- complexes showed similar temperature dependence. The results suggest that both the F^- and Cl^- complexes are in a pure high-spin state. By contrast, the pyrrole signals of the ClO_4^- complexes were observed in the most upfield positions, −31 to −33 ppm, and moved further upfield almost linearly against 1/*T*. Thus, the complex is considered to be in an essentially pure intermediate-spin state. The pyrrole signals of the Br^- and I^- complexes appeared between those of the corresponding F^- and ClO_4^- complexes, suggesting that they are in the admixed intermediate-spin ($S = {}^3/_2, {}^5/_2$) with a sizable contribution of the $S = {}^5/_2$.

Some differences were observed, however, between [Fe(TEtPrP)X] and [Fe(T^{i}PrP)X] as shown in Figure 2a,b. For example, while the Curie line of the pyrrole protons in [Fe-

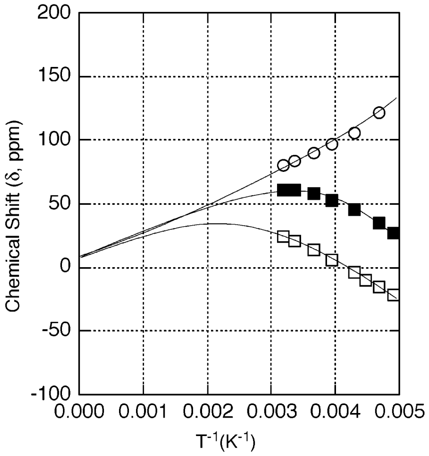

Figure 3. Curie plots of the pyrrole proton signals of [Fe(T^{n}PrP)I] (○), [Fe(TEtPrP)I] (■), and [Fe(TiPrP)I] (□).

(TEtPrP)Br] showed only a small deviation from linearity, that in [Fe(T^{i}PrP)Br] exhibited considerable curvature and showed a negative slope at lower temperature. Figure 2 also indicates that the pyrrole signals of the Br^{-} and I^{-} complexes in [Fe(TEtPrP)X] appeared considerably more downfield than those in the corresponding [Fe(T^{i}PrP)X]; the pyrrole chemical shifts of [Fe(TEtPrP)Br] and [Fe(TEtPrP)I] are 106.5 ppm and ca. 35 ppm at 213 K, while those in [Fe(T^{i}PrP)Br] and [Fe(T^{i}PrP)I] are 64.2 and −15.5 ppm at the same temperature, respectively. Since the upfield shift of the pyrrole signal is a direct measure for the contribution of the $S = {}^{3}/_{2}$ spin state in the spin-admixed system,[20,21] the results clearly indicate that the $S = {}^{3}/_{2}$ character in [Fe(T^{i}PrP)X] is much larger than that in [Fe(TEtPrP)X] for the same X. These results should be ascribed to the difference in ruffling of the porphyrin cores caused by the steric effects of the *meso*-alkyl groups. This is because the ruffling of the porphyrin core always shortens the Fe−N$_{P}$ bonds,[3,22,23] destabilizes the $d_{x^2-y^2}$ orbital, and consequently increases the contribution of the $S = {}^{3}/_{2}$ spin state. Figure 3 shows the Curie plots of the pyrrole-H signals in [Fe(T^{n}PrP)I], [Fe(TEtPrP)I], and [Fe(T^{i}PrP)I]. Among these complexes, [Fe(T^{n}PrP)I] exhibits the pyrrole-H signal much more downfield than [Fe(T^{i}PrP)I] and [Fe(TEtPrP)I], because [Fe(T^{n}PrP)I] is supposed to have a less ruffled porphyrin core than the other two complexes. The ruffling dihedral angles in analogous [Fe(T^{i}PrP)Cl] are 42.8° and 33.5° while those in [Fe(T^{n}PrP)Cl] are 22.3° and 21.2°.[24,25] Thus, the ^{1}H NMR results suggest that the porphyrin core in [Fe(T^{i}PrP)X] is more ruffled than that in [Fe(TEtPrP)X]. The result is quite unusual because the complex with the much bulkier 1-EtPr group at the *meso* positions is less ruffled. Although the direct structural comparison is unable to be made between [Fe(T^{i}PrP)X] and [Fe(TEtPrP)X] at present, the X-ray molecular structures of analogous [Cu(T^{i}PrP)] and [Cu(TEtPrP)] support the idea mentioned above; the ruffling of [Cu(T^{i}PrP)] is much larger than that of [Cu(TEtPrP)].[19] It should be noted, however, that the ruffling varies depending on the central metal ions. In the case of the nickel complexes, [Ni(T^{i}PrP)] and [Ni(TEtPrP)], the ruffling of the porphyrin cores is reported to be quite similar; the average deviation of the *meso* carbon atoms from the N4-plane is 0.74 and 0.81 Å, respectively.[19]

As mentioned, [Fe(TEtPrP)I] and [Fe(T^{i}PrP)I] are not the pure intermediate-spin but the admixed intermediate-spin ($S = {}^{3}/_{2}, {}^{5}/_{2}$) complexes with a sizable contribution of the $S = {}^{5}/_{2}$. The result is different from the case of highly saddled [Fe(OETPP)X] where not only the I^{-} but also the Br^{-} complex exhibited a quite pure intermediate-spin state.[17] The reasons for the difference in spin states between ruffled and saddled complexes will be discussed later in this paper. If we assume that the F^{-} and ClO$_4^{-}$ complexes are in a pure high-spin and an intermediate-spin state, respectively, then the contribution of the intermediate-spin state, Int(%), can be estimated on the basis of the pyrrole-H chemical shifts by eq 1, where δ_{F}, $\delta_{\mathrm{ClO_4}}$, and δ_{X} are the pyrrole-H chemical shifts of the F^{-}, ClO$_4^{-}$, and X^{-} complexes, respectively:

$$\mathrm{Int}(\%) = [(\delta_{\mathrm{F}} - \delta_{\mathrm{X}})/(\delta_{\mathrm{F}} - \delta_{\mathrm{ClO_4}})] \times 100 \qquad (1)$$

It should be noted here that the Int(%) value determined by eq 1 is an approximate value because the chemical shifts of the pyrrole protons in the pure high-spin or pure intermediate-spin complexes could change depending on the kind of axial ligands. The Int(%) values of [Fe(TRP)X] calculated at 298 and 213 K by eq 1 are listed in Table 1. The data in Table 1 indicate that the Int(%) value is very much dependent on the solvent used. While the Int(%) of [Fe(TEtPrP)I] is 53% at 213 K in CD$_2$Cl$_2$ solution, it is only 10% in toluene-d_8 solution at the same temperature.

Figure 4 shows the temperature dependence of the *meso*-carbon signal in *meso*-^{13}C enriched [Fe(TEtPrP)Cl]. The *meso*-carbon gave a broad signal at 630 ppm at 313 K, which split into three signals below 298 K. The phenomenon should be ascribed to the hindered rotation of the *meso* alkyl groups around the C$_{meso}$−C$_{\alpha}$ bond as was observed in analogous [Fe(TCHP)Cl] and [Fe(T^{i}PrP)Cl] rather than to the ring inversion of the ruffled porphyrin ring; the *meso* signal should split into two signals with equal intensities in the latter case.[24,26,27] Since the stable conformation of the alkyl groups should be the one where the pyrrole ring bisects the 1-ethylpropyl groups as shown in Scheme 2a,[19] four stereoisomers such as αααα (1 signal for the *meso*-^{13}C), αααβ (4 signals), αα$\beta\beta$ (2 signals), and αβαβ (1 signal) should exist; the symbols α and β represent the directions of the CH proton of the 1-EtPr group. Scheme 2b shows the αααα isomer as

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[20] Reed, C. A.; Guiset, F. *J. Am. Chem. Soc.* **1996**, *118*, 3281−3282.

[21] Evans, D. R.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 4660−4667.

[22] Jentzen, W.; Simpson, M. C.; Hobbs, J. D.; Song, X.; Ema, T.; Nelson, N. Y.; Medforth, C. J.; Smith, K. M.; Veyrat, M.; Mazzanti, M.; Ramasseul, R.; Marchon, J.-C.; Takeuchi, T.; Goddard, W. A., III; Shelnutt, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11085−11097.

[23] Ohgo, Y.; Ikeue, T.; Saitoh, T.; Nakamura, M. *Chem. Lett.* **2002**, 42−43.

[24] Ikeue, T.; Ohgo, Y.; Uchida, A.; Nakamura, M.; Fujii, H.; Yokoyama, M. *Inorg. Chem.* **1999**, *38*, 1276−1281.

[25] Ohgo, Y.; Ikeue, T.; Nakamura, M. *Acta Crystallogr.* **1999**, *C55*, 1817−1818.

[26] Veyrat, M.; Ramasseul, R.; Marchon, J.-C.; Turowska-Tyrk, I.; Scheidt, W. R. *New J. Chem.* **1995**, *19*, 1199−1202.

[27] Wolowiec, S.; Latos-Grazynski, L.; Toronto, D.; Marchon, J.-C. *Inorg. Chem.* **1998**, *37*, 724−732.

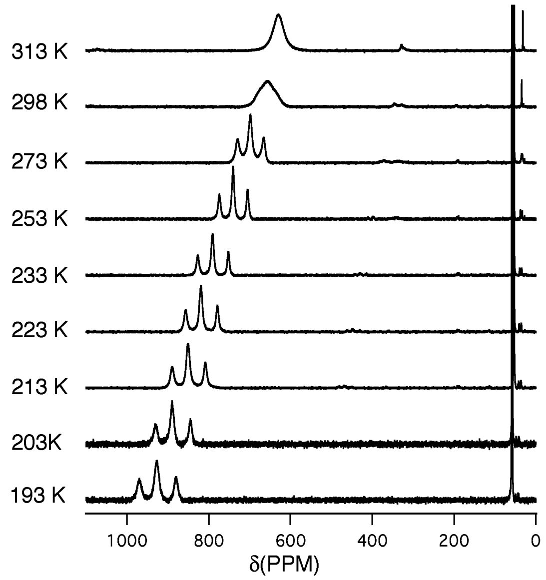
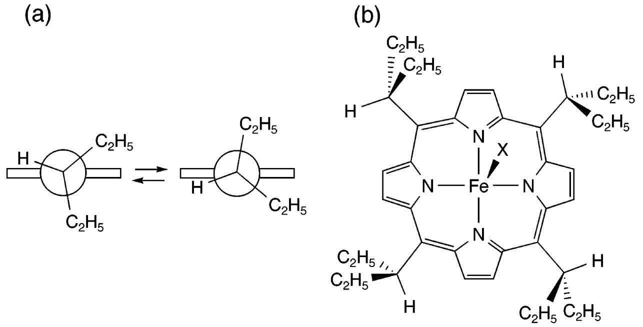


Figure 4. Temperature dependent *meso*-^{13}C signals in *meso*-^{13}C enriched [Fe(TEtPrP)Cl.

Scheme 2. Stable Conformations of the (a) *meso*-1-EtPr groups and (b) the αααα Isomer[a]



[a] Note that the single signal is expected for the *meso*-carbon atoms in this conformer.

a typical example. Thus, in total eight *meso*-^{13}C signals are expected. The ^{13}C NMR spectra shown in Figure 4 suggest that some of the *meso*-^{13}C signals overlap due to the small difference in chemical shifts. Other five-coordinated [Fe(TEtPrP)X] species examined in this study exhibited similar temperature dependence. The chemical shifts of the *meso*-^{13}C signals at 298 and 213 K are added to Table 1. The large difference in chemical shifts, which reaches as much as 81 ppm at 213 K in the case of [Fe(TEtPrP)Cl], could be ascribed to the difference in porphyrin deformation among the rotational isomers. Namely, the difference in the degree of ruffling affects the interaction between iron d_{xy} and porphyrin a_{2u} orbitals, which in turn affects the chemical shift of the *meso* carbons.

Figure 5 shows the Curie plots of the *meso*-carbon signals of [Fe(TEtPrP)X] taken in CD_2Cl_2 solutions; the chemical shifts instead of the isotropic shifts were plotted against 1/*T*. To remove any ambiguity in the assignment of the *meso*-carbon signal, the *meso*-^{13}C enriched (99% ^{13}C) [Fe(TEtPrP)X] was used for the measurements. As mentioned, the *meso*-carbon gave three signals at lower temperature. In the Curie plots, the average value of the three *meso*-carbon signals was taken as the chemical shift. The Curie lines were drawn so that they intercept the axis of ordinate at the chemical shifts of the corresponding diamagnetic complexes, ca. 117 ppm. Although the high-spin F^- and Cl^- complexes showed good linear lines, the deviation from the linearity increased on going from the Br^- to the I^- complex. In the case of the ClO_4^- complex, clear anti-Curie behavior was observed. Therefore, the Curie line of the *meso*-carbon signal in [Fe(TEtPrP)ClO$_4$] is in sharp contrast to that of the pyrrole-H signal; the latter showed a relatively good linear line intercepting the diamagnetic position. The difference in Curie behavior between the *meso*-^{13}C and pyrrole-H will be discussed later.

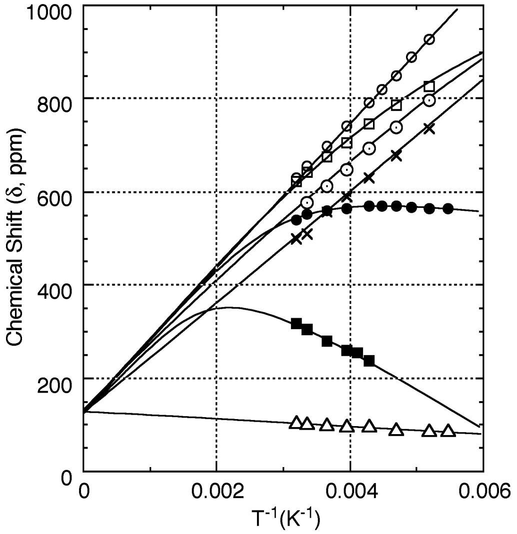


Figure 5. Curie plots of the meso-^{13}C signals of [Fe(TEtPrP)X] taken in CD_2Cl_2 solution: X = F (×); Cl (○); Br (□); I (●); ClO_4 (■); $(THF)_2$ (△). Curie plots of the *meso*-^{13}C signal of [Fe(TEtPrP)I] in toluene-d_8 solution are given by ⊙.

The data in Table 1 indicate that the *meso*-carbon signal of the ClO_4^- complex appeared at the most upfield position among the five-coordinate complexes examined in this study. The order of the upfield shift is, however, not simple as is given by eq 2:

$$Cl^- \leq Br^- < I^- < F^- \ll ClO_4^- \qquad (2)$$

Although the F^- complex is considered to be the purest high-spin complex on the basis of the pyrrole-H chemical shifts, it showed the *meso*-^{13}C signal more upfield than the other halide-ligated complexes. Goff and co-workers reported similar results for [Fe(TPP)X];[28] the *meso*-^{13}C chemical shifts were 353, 500, 505, and 478 ppm at 303 K for X = F^-, Cl^-, Br^-, and I^-, respectively. Quite recently, the importance of the bonding interaction between iron (d_{z^2}) and porphyrin (a_{2u}) orbitals has been pointed out in five-coordinate high-spin iron(III) complexes on the basis of the density functional theory.[29,30] Since the a_{2u} orbital has large coefficients at the

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(28) Goff, H, M.; Shimomura, E. T.; Phillippi, M. A. *Inorg. Chem.* **1983**, *22*, 66−71.

(29) Ghosh, A.; Vangberg, T.; Gonzalez, E.; Taylor, P. J. *J. Porphyrins Phthalocyanines* **2001**, *5*, 345−356.

(30) Cheng, R.-J.; Chen, P.-Y.; Lovell, T.; Liu, T.; Noodleman, L.; Case, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 6774−6783.

meso positions, this interaction increases the spin densities at the *meso* carbons and induces their downfield shift. In the six-coordinate high-spin complexes, however, the d_{z^2}–a_{2u} interaction should be negligibly small since the iron is located in the center of the N4 plane. Thus, the *meso* carbons are expected to show a large upfield shift.[30] In fact, the *meso*-^{13}C chemical shifts of six-coordinate high-spin $[\mathrm{Fe(TPP)(DMSO)_2}]^+$ and $[\mathrm{Fe(TPP)(PyNO)_2}]^+$ are reported to be 13 ppm (303 K) and 28 ppm (298 K), respectively.[28,31,32] Note that the pyrrole-H chemical shifts of five- and six-coordinate high-spin complexes are not much different; they are 80.3 and 69.0 ppm at 298 K for [Fe(TPP)Cl] and $[\mathrm{Fe(TPP)(PyNO)_2}]^+$, respectively.[31] The relatively upfield shifted *meso*-^{13}C signal in high-spin [Fe(TEtPrP)F] could then be explained if we assume the smaller displacement of the iron atom from the least-squares plane of the four nitrogen atoms. Although the structural data of [Fe(TEtPrP)X] are not available, our recent study on the molecular structures of analogous [Fe(EtioP)X] supports the assumption mentioned above.[8] The deviation of the iron(III) atom from the N4 plane increases on going from F^-, to Cl^- and Br^-, and then to I^-; the values are 0.409(1), 0.444(2), 0.440(3), and 0.454(4) Å, respectively. On the basis of these results, we have ascribed the upfield shift of the *meso*-^{13}C signal in [Fe(TEtPrP)F] to the smaller deviation of the iron(III) atom from the N4 plane rather than to the larger contribution of the $S = {}^3/_2$ spin state.

As mentioned, the Curie plots of the *meso*-^{13}C signal of $[\mathrm{Fe(TEtPrP)ClO_4}]$ showed an anti-Curie behavior though the complex is considered to be a quite pure intermediate-spin as revealed by the Curie plots of the pyrrole-H. At present, it is difficult to explain the discrepancies on the temperature dependence between ^{1}H NMR and ^{13}C NMR chemical shifts. One possible reason is the change in the out-of-plane deviation of the iron atom depending on the temperature. If we assume that the iron atom moves toward the N4 plane as the temperature is lowered, the Curie line is expected to show curvature. This is because the chemical shif of the *meso* carbon is sensitively affected by the out-of-plane deviation of the iron atom as mentioned in the previous paragraph. The fact that the six-coordinate intermediate-spin complex $[\mathrm{Fe(TEtPrP)(THF)_2}]\mathrm{ClO_4}$ shows a good linear line supports the hypothesis given above.

Figure 6 shows the EPR spectra of [Fe(TEtPrP)X] taken in frozen CH_2Cl_2 solutions at 4.2 K. The halide coordination was unambiguously verified from the hyperfine coupling in the $g_{\|}$ signals in the F^- and Br^- complexes; the values were 39 and 20 G, respectively. In the case of the I^- complex, the $g_{\|}$ signal was too broad to detect the hyperfine coupling. Furthermore, the EPR spectra of the I^- complexes showed a contamination of a small amount of the Cl^- complexes despite the repeated purification. In Table 2 are listed the g values of [Fe(TEtPrP)X] and $[\mathrm{Fe(T^iPrP)X}]$. The Int(%) values are estimated by eq 3, and they are also listed in Table 2.[33]

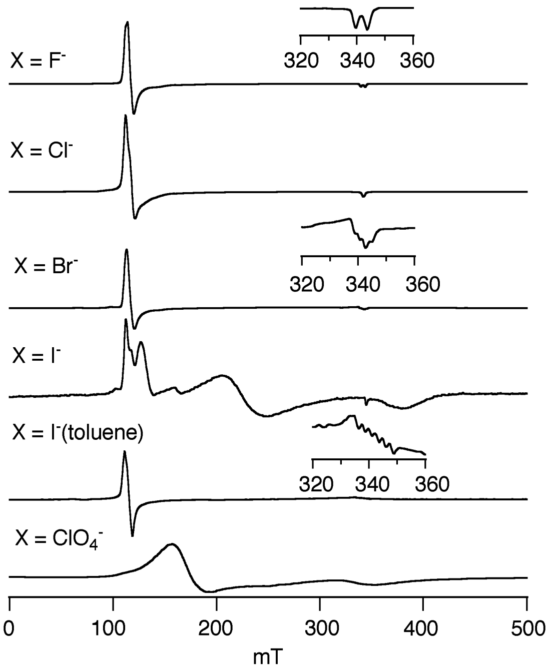

Figure 6. EPR spectra of [Fe(TEtPrP)X] taken in frozen CH_2Cl_2 solution at 4.2 K.

Table 2. EPR g Values and Int(%) Values Obtained in Frozen CH_2Cl_2 Solution at 4.2 K

porphyrin	X	g_1	g_2	g_3	hfs	Int(%)
TEtPrP	F	5.92	5.92	1.99	39	4
	Cl	6.11	5.90	2.00		0
	Br	5.95	5.93	1.99	20	3
	I	5.50	3.02	1.80	*a*	87
	I^b	5.94	5.94	2.01	24	3
	I^c	5.98	5.98	2.05	*a*	1
	$ClO_4{}^c$	4.09	4.09	1.98		96
	$(THF)_2$	4.15	4.15	2.00		93
$\mathrm{T^iPrP}$	F	5.95	5.95	2.00	39	3
	Cl	6.16	5.71	2.00		3
	Br	5.92	5.92	1.99	*a*	4
	I	5.34	3.02	1.85	*a*	91
	I^b	5.27	3.32	1.90	*a*	85
	I^d	5.80	2.70	1.75	*a*	88
	ClO_4	4.90	3.50	1.90		90
	$(THF)_2$	3.99	3.99	1.97		100

[a] Too broad to determine. [b] In toluene. [c] Taken in the solid. [d] 1.0 equiv of Bu_4NI was added into the CH_2Cl_2 solution of $[\mathrm{Fe(T^iPrP)(THF)_2}]^+$.

$$\mathrm{Int}(\%) = [(6.0 - g_{\perp})/2] \times 100 \qquad (3)$$

The data in Table 2 suggest that while the F^-, Cl^-, and Br^- complexes are essentially in the high spin state, the I^- complexes [Fe(TEtPrP)I] and $[\mathrm{Fe(T^iPrP)I}]$ adopt the admixed intermediate-spin state with the Int(%) of 87% and 91%, respectively. Since the Int(%) values of [Fe(TEtPrP)I] and $[\mathrm{Fe(T^iPrP)I}]$ are estimated by the ^{1}H NMR method to be 53% and 79% at 213 K, respectively, they have increased as the temperature is lowered from 213 to 4.2 K. In contrast, the Int(%) values of [Fe(TEtPrP)Br] and $[\mathrm{Fe(T^iPrP)Br}]$ have

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(31) Nakamura, M.; Hoshino, A.; Ikezaki, A.; Ikeue, T. *Chem. Commun.* **2003**, 1862–1863.

(32) In the previous paper, we reported the *meso*-^{13}C chemical shifts of several six-coordinate high-spin complexes such as $[\mathrm{Fe(TPP)(PyNO)_2}]\mathrm{ClO_4}$ and $[\mathrm{Fe(TPP)F_2}]\mathrm{ClO_4}$ as the first examples.[31] However, we noticed later that Goff and co-workers reported the *meso*-^{13}C chemical shift of high-spin six-coordinate $[\mathrm{Fe(TPP)(DMSO)_2}]\mathrm{NO_3}$.[28]

(33) Palmer, G. In *Iron Porphyrin, Part II*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; pp 43–88.

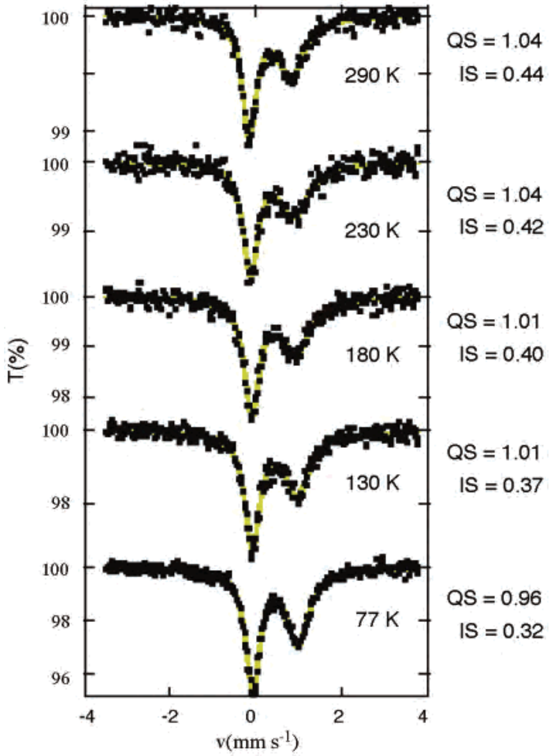

Figure 7. Mössbauer spectra of [Fe(TEtPrP)I] taken for a microcrystalline sample. QS and IS values (mm/s) are also listed.

shown an appreciable decrease as the temperature is lowered from 213 to 4.2 K. The data in Table 2 also indicate that the Int(%) of [Fe(TEtPrP)I] varies depending on the conditions. Although the complex exhibited a spin admixture in CH_2Cl_2 solution, it showed a quite pure high-spin state both in toluene solution and in the solid; the $g_\perp$ and $g_\|$ values are 5.94 and 2.01 in toluene solution and 5.98 and 2.05 in the solid, respectively. On the basis of the ^{1}H NMR, ^{13}C NMR, and EPR results, the following conclusions can be extracted about the spin states of highly ruffled [Fe(TEtPrP)X] and [Fe(T^{i}PrP)X]: (i) both the F^- and Cl^- complexes exhibit a quite pure high-spin state; (ii) the intermediate-spin character increases as the axial ligand changes from Br^- to I^- in the NMR temperature range; (iii) the I^- complex [Fe(TEtPrP)I] exhibits the admixed intermediate-spin ($S = {}^3/_2, {}^5/_2$) state with a major contribution of the $S = {}^3/_2$ in CH_2Cl_2 solution while it shows a quite pure high-spin state in toluene solution as well as in the solid; (iv) the ClO_4^- complexes have shown an essentially pure intermediate-spin state in all the temperature range examined.

Figure 7 shows the Mössbauer spectra of [Fe(TEtPrP)I] taken for a microcrystalline sample at 290−77 K. The quadrupole splitting (QS) and the isomer shift (IS) values are also listed. The QS and IS values are in the ranges 1.04−0.96 and 0.44−0.32 mm s^{-1}, respectively. Mössbauer parameters are one of the powerful probes to determine the spin states of the iron(III) porphyrin complexes.[34−36] While the IS values of the high-spin and intermediate-spin complexes are quite similar, 0.5−0.3 mm s^{-1}, the QS values are very much different between these two spin systems; they are ≤1.0 and ≥3.0 mm s^{-1} for the high-spin and intermediate-spin complexes, respectively. The fact that the QS values of [Fe(TEtPrP)I] are in the range 1.04−0.96 mm s^{-1} at 290−77 K strongly suggests that the complex maintains the high-spin state in this temperature range. Therefore, the Mössbauer results obtained for the solid sample are quite different from the NMR results obtained for the solution sample although both spectra were taken in the same temperature range; [Fe(TEtPrP)I] has shown 30−50% of the $S = {}^3/_2$ character at 300−200 K as is revealed by the ^{1}H NMR experiments. The Mössbauer results are, however, consistent with the EPR results since both methods have revealed the high-spin state for this complex in the solid.

The difference in spin states of the complex between solid and solution may not be a very unusual phenomenon. In fact, we have recently observed that while iodo(ethiohemiporphycenato)iron(III) exhibits the $S = {}^3/_2$ spin state with minor contribution of the $S = {}^5/_2$ in solution, the same complex shows a quite pure $S = {}^5/_2$ spin state in the solid.[37] The difference has been ascribed to the extraordinarily labile nature of the iodide ligand in iodo(ethiohemiporphycenato)-iron(III). Thus, the iron is dragged toward the N4 cavity in solution, and consequently, the complex adopts the intermediate-spin state; one of the structural differences between the high-spin and intermediate-spin iron(III) porphyrin complexes is the larger deviation of the iron atom from the average N4 plane of the porphyrin ring in the former complexes.[1−3] In the crystal lattice, however, the packing force could contract the labile Fe−I bond. Therefore, the iron is lifted from the N4 cavity toward the iodide, resulting in the formation of a typical high-spin five-coordinate structure. The difference in spin state of [Fe(TEtPrP)I] between solution and solid can be explained similarly. In addition, the spin state of this complex differs even in the same CH_2Cl_2 solution depending on the temperature; the Int(%) values are 28% and 87% at 298 and 4.2 K, respectively. The Int(%) value decreased, however, when the solvent was changed from CD_2Cl_2 to toluene-d_8 as shown in Figures 2, 5, and 6. These results could again be ascribed to the structural flexibility of the five-coordinated iron(III) porphyrin complexes. That is, the structural parameters such as the out-of-plane displacement of the iron(III) atom from the N4 plane, the Fe−I bond length, and the tilting of the Fe−I bond from the heme normal could be easily perturbed not only by the packing force in the crystal but by the temperature and solvents. Changing the solvent from CD_2Cl_2 to the less polar toluene-d_8 can strengthen the ligand field of the iodide. As a result, the iron(III) ion is dragged toward the axial ligand, resulting in the change in spin state toward the $S = {}^5/_2$ direction.[38]

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(34) Sams, J. R.; Tsin, T. B. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. 4, Chapter 9, pp 425−478.

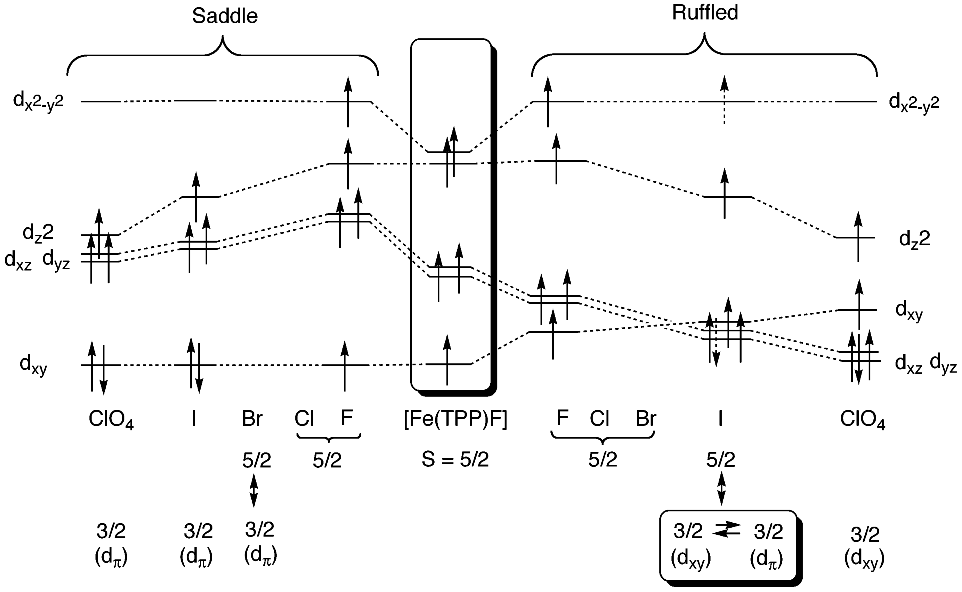
(35) Debrunner, P. G. In *Iron Porphyrin Part III*; Lever, A. B. P., Gray, H. B., Eds.; VCH: New York, 1989; pp 139−234.

(36) Gütlich, P.; Ensling, J. In *Inorganic Electronic Structure and Spectroscopy*, *Vol. 1*; Solomon, E. I., Lever A. B. P., Eds.; John Wiley & Sons: New York, 1999; pp 161−211.

(37) Ohgo, Y.; Neya, S.; Takahashi, M.; Takeda, M.; Funasaki, N.; Nakamura, M. *Chem. Lett.* **2003**, *32*, 526−527.

(38) Ikezaki, A.; Nakamura, M. *Inorg. Chem.* **2002**, *41*, 6225−6236.

Scheme 3. Schematic Representation of the Change in Energy Levels of the Iron d Orbitals in Ruffled [Fe(TRP)X] and Saddled [Fe(OETPP)X] When the Axial Ligand (X) Changes from F^-, to Cl^-, to Br^-, to I^-, and then to ClO_4^-



The labile nature of the spin state mentioned above should be one of the characteristic features of the five-coordinate iron(III) porphyrin complexes, because similar ambiguity in the spin state has been observed in the five-coordinated iron(III) porphyrin complexes in the biological system such as cytochromes c′. The heme iron in cytochromes c′ is five-coordinate with a solvent-exposed histidine residue. The oxidized cytochromes c′ have been studied by various methods such as NMR,[39−41] EPR,[42,43] resonance Raman,[44,45] Mössbauer,[46] and EXAFS spectroscopy.[47] The contribution of the $S = {}^{3}/_{2}$ state differs not only by the bacterial source of the proteins but by the spectroscopic methods applied for the measurement as we have experienced in this study. For example, the EPR method has revealed that the $S = {}^{3}/_{2}$ contributions of the cytochromes c′ isolated from photosynthetic bacteria such as *Rb. capsulatus* and *R. palustri* are ca. 40% at pH 7.2 while they are only 13% in the cytochromes c′ isolated from *R. molischianum* and *R. rubrum*.[43] Furthermore, NMR study has revealed that the iron(III) ions in the latter proteins are essentially in a pure high-spin state.[39] In the previous paper, we have prepared a series of mono-imidazole ligated iron(III) porphyrin complexes as models for cytochomes c′. These complexes have actually shown the change in spin states by the steric and electronic effects of imidazoles as well as by the solvent effects.[38]

Comparison of the Spin State with Saddle Shaped Complexes. As mentioned, the spin states of the iodide complexes are quite different between ruffled [Fe(TEtPrP)I] and saddled [Fe(OETPP)I]. While the saddled [Fe(OETPP)I] has exhibited an essentially pure intermediate-spin state not only in solution but in the solid,[17] the ruffled [Fe(TEtPrP)I] has shown the admixed intermediate-spin state with a sizable contribution of the $S = {}^{5}/_{2}$ state in CH_2Cl_2 solution. Furthermore, [Fe(TEtPrP)I] has shown a high-spin state both in toluene solution and in the solid. We have proposed in the previous papers that the saddled deformation tends to stabilize the intermediate-spin state because of the following two reasons.[48−50] (i) The saddled deformation destabilizes the iron $d_{x^2-y^2}$ orbital due to the contraction of the $Fe-N_P$ bonds commonly observed in the deformed complexes. The interaction between the iron $d_{x^2-y^2}$ and porphyrin a_{2u} orbital, which is possible when the porphyrin ring is saddled, also contributes to the destabilization of the $d_{x^2-y^2}$ orbital.[51] (ii) The saddled deformation also destabilizes the iron d_π (d_{xz} and d_{yz}) orbitals due to the stronger iron d_π and porphyrin $3e_g$ interactions caused by the effective orbital overlaps in the saddle shaped porphyrin ring. The replacement of the axial F^- ligand by much weaker Cl^- and then by Br^- ligand in [Fe(OETPP)X] continuously lowers the energy level of the d_{z^2} orbital. When the axial ligand is I^-, the destabilized d_π orbitals and the stabilized d_{z^2} orbital are supposed to be quite close each other in the energy diagram as shown in Scheme 3, leading to the formation of an essentially pure intermediate-spin state.

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(39) La Mar, G. N.; Jackson, J. T.; Dugad, L. B.; Cusanovich, M. A.; Bartsch, R. G. *J. Biol. Chem.* **1990**, *265*, 16173−16180.

(40) Clark, K.; Dugad, L. B.; Bartsch, R. G.; Cusanovich, M. A.; La Mar, G. N. *J. Am. Chem. Soc.* **1996**, *118*, 4654−4664.

(41) Tsan, P.; Caffrey, M.; Daku, M. L.; Cusanovich, M.; Marion, D.; Gans, P. *J. Am. Chem. Soc.* **2001**, *123*, 2231−2242.

(42) Maltempo, M. M. *J. Chem. Phys.* **1974**, *61*, 2540−2547.

(43) Fujii, S.; Yoshimura, T.; Kamada, H.; Yamaguchi, K.; Suzuki, S.; Shidara, S.; Takakuwa, S. *Biochim. Biophys. Acta*. **1995**, *1251*, 161−169.

(44) Kitagawa, T.; Ozaki, Y.; Kyogoku, Y.; Horio, T. *Biochim. Biophys. Acta* **1977**, *495*, 1−11.

(45) Othman, S.; Richaud, P.; Verméglio, A.; Desbois, A. *Biochemistry* **1996**, *35*, 9224−9234.

(46) Maltempo, M. M.; Moss, T. H.; Spartalian, K. *J. Chem. Phys.* **1980**, *73*, 2100−2106.

(47) Korszun, Z. R.; Bunker, G.; Khalid, S.; Scheidt, W. R.; Cusanovich, M. A.; Meyer, T. E. *Biochemistry* **1989**, *28*, 1513−1517.

(48) Ikeue, T.; Ohgo, Y.; Yamaguchi, T.; Takahashi, M.; Takeda, M.; Nakamura, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2617−2620.

(49) Ikeue, T.; Ohgo, Y.; Ongayi, O.; Vicente, M. Graça, H.; Nakamura, M. *Inorg. Chem.* **2003**, *42*, 5560−5571.

(50) Ikeue, T.; Ohgo, Y.; Saitoh, T.; Yamaguchi, T.; Nakamura, M. *Inorg. Chem.* **2001**, *40*, 3423−3434.

(51) Ghosh, A.; Halvorsen, I.; Nilsen, H. J.; Steene, E.; Wondimagegn, T.; Lie, R.; van Caemelbecke, E.; Guo, N.; Ou, Z.; Kadish, K. M. *J. Phys. Chem. B* **2001**, *105*, 8120−8124.

Table 3. Spin States, Electron Configurations, and ^{13}C NMR Chemical Shifts of Some Iron(III) Complexes with Highly Ruffled Porphyrin Rings

		electron configuration					δ(*meso*-^{13}C)			δ(Py-^{13}C)		
complexes	spin states	d_{xy}	d_{yz}	d_{zx}	d_{z^2}	$d_{x^2-y^2}$	C	C_α	C_β	α	β	ref
[Fe(TEtPrP)ClO_4]	$S = {}^3/_2$	1	2	1	1	0	342	−22	134	−287	69	*a*, 18
[Fe(TEtPrP)$(THF)_2]^+$	$S = {}^3/_2$	1	2	1	1	0	104	68	21	−89	56	*a*, 18
[Fe(T^{i}PrP)ClO_4]	$S = {}^3/_2$	1	2	1	1	0	327	−31	123	−277	60	*a*
[Fe(T^{i}PrP)$(THF)_2]^+$	$S = {}^3/_2$	1	2	1	1	0	115	51	14	−122	22	*a*, 10
[Fe(T^{i}PrP)(4-CNPy)$_2]^+$	$S = {}^1/_2$	1	2	2	0	0	707	−166	315	−176	93	57

[a] This work.

The situation is different in the ruffled complexes. When the porphyrin is ruffled, the energy levels of the d orbitals are affected differently. As mentioned, the $d_{x^2-y^2}$ orbital is destabilized due to the short Fe$-N_P$ bonds expected for the highly ruffled porphyrin ring.[3,12,23] The d_{xy} orbital is also destabilized due to the $d_{xy}-a_{2u}$ interaction caused by the ruffling of the porphryin ring.[50,52−57] As a result, the energy gap between the highest $d_{x^2-y^2}$ and the lowest d_{xy} orbitals does not increase as in the case of the saddled complexes; the d_π orbitals should be stabilized due to the less effective overlaps with the $3e_g$ orbitals in ruffled complexes. Since one of the factors to stabilize the $S = {}^3/_2$ ground state in the iron(III) porphyrin complexes is the large energy gap between the highest and the lowest orbitals, it is understandable that the $S = {}^3/_2$ ground state is difficult to attain in five-coordinate iron(III) complexes with highly ruffled porphyrin ring. When the axial F^- is replaced by the ligands with much weaker field strength such as Cl^-, Br^-, and I^-, both the d_{z^2} and d_π orbitals should be stabilized. Thus, the energy level of the d_π orbitals approaches that of the d_{xy} orbital. Consequently, the $d_{xy}-a_{2u}$ interaction is strengthened to raise the energy level of the d_{xy} orbital. Thus, the d_π orbitals could be the lowest if the axial ligand is a fairly weak ClO_4^-. Under this situation, the unpaired electron in the $d_{x^2-y^2}$ orbital drops to one of the d_π orbitals to form an essentially pure intermediate-spin state as shown in Scheme 3.

Electron Configuration of the Intermediate-Spin Complexes with Ruffled Porphyrin Ring. We have then examined the electron configuration of the intermediate-spin complexes such as [Fe(TRP)ClO_4] and [Fe(TRP)$(THF)_2$]ClO_4 (R = 1-EtPr, ^{i}Pr). Table 3 lists the ^{13}C NMR chemical shifts of these complexes. The most characteristic feature of the ^{13}C NMR spectra in five-coordinate intermediate-spin [Fe(TRP)ClO_4] is the downfield shift of the *meso* and the upfield shift of the pyrrole-α signals; these signals appeared at 342 and −287 ppm, respectively, in the case of [Fe(TEtPrP)ClO_4]. The results indicate that the ruffled complexes have an unpaired electron in the d_{xy} orbital, which is transferred to the *meso* positions by the iron (d_{xy}) and porphyrin (a_{2u}) interaction to induce a downfield shift of the *meso* carbon signal. The iron (d_{z^2}) and porhyrin (a_{2u}) interaction should also contribute to the downfield shift of the *meso* carbon signal.[30] The spin density at the *meso* carbon is transferred to the neighboring carbons such as pyrrole-α and *meso*-C_α by the spin polarization mechanism and shifts them upfield. The situation is similar to the low-spin complexes with the $(d_{xz}, d_{yz})^4(d_{xy})^1$ electron configuration such as [Fe(T^{i}PrP)(4-CNPy)$_2]^+$, which also exhibit the *meso* and pyrrole-α signals at fairly downfield and upfield positions, respectively, due to the strong $d_{xy}-a_{2u}$ interactions; they were 707 and −176 ppm, respectively, in [Fe(T^{i}PrP)(4-CNPy)$_2]^+$ as listed in Table 3. Since the influence of both the $d_{xy}-a_{2u}$ and the $d_{z^2}-a_{2u}$ interactions on the chemical shifts of the pyrrole-H is considered to be negligibly small, the large upfield shift of the pyrrole-H signals, ca. −33 ppm, should be ascribed to the unpaired electron in one of the d_π orbitals.

In the case of the six-coordinate intermediate-spin complexes [Fe(TEtPrP)$(THF)_2]^+$ and [Fe(T^{i}PrP)$(THF)_2]^+$, the unpaired electron in the d_{z^2} orbital is transferred to the axial ligand through σ bonds and should induce the downfield shift of the ^{13}C and ^{1}H signals of the axial ligand. The direct observation of the coordinated THF signals in [Fe(TRP)$(THF)_2]^+$ was hampered because of the weak coordination of the THF ligands; the complete formation of these complexes was attained only in the presence of a large excess of THF. However, we observed the THF signals at 84 and 169 ppm in the sample consisting of [Fe(TEtPrP)ClO_4] and 6 equiv of THF. These signals moved upfield by the further addition of THF. Thus, the complex has an unpaired electron in the d_{z^2} orbital. The large differences in the *meso*-^{13}C chemical shifts between five- and six-coordinate complexes, which reached as much as 238 and 212 ppm in [Fe(TEtPrP)$(THF)_2]^+$ and [Fe(T^{i}PrP)$(THF)_2]^+$, respectively, also support the existence of the unpaired electron in the d_{z^2} orbital; the $d_{z^2}-a_{2u}$ interaction is possible only in the five-coordinate complex.[29,30]

In previous communications, we reported that the highly saddled complexes such as [Fe(OETPP)(4-CNPy)$_2]^+$ and [Fe(OETPP)$(THF)_2]^+$ are in an essentially pure intermediate-spin state on the basis of ^{1}H NMR, ^{13}C NMR, EPR, and Mössbauer spectroscopy as well as SQUID magnetometry.[18,48] These complexes exhibit completely different ^{13}C NMR spectra; the *meso* and pyrrole-α carbon signals in [Fe(OETPP)(4-CNPy)$_2]^+$ appeared at −451 and 591 ppm, respectively, at 223 K. We have ascribed these isotropically shifted signals to the strong iron (d_π)−porphyrin ($3e_g$)

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(52) Safo, M. K.; Gupta, G. P.; Watson, C. T.; Simonis, U.; Walker, F. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 7066−7075.

(53) Safo, M. K.; Walker, F. A.; Raitsimring, A. M.; Walters, W. P.; Dolata, D. P.; Debrunner, P. G.; Scheidt, W. R. *J. Am. Chem. Soc.* **1994**, *116*, 7760−7770.

(54) Nakamura, M.; Ikeue, T.; Fujii, H.; Yoshimura, T. *J. Am. Chem. Soc.* **1997**, *119*, 3274−3283.

(55) Wolowiec, S.; Latos-Grazynski, L.; Mazzanti, M.; Marchon, J.-C. *Inorg. Chem.* **1997**, *36*, 5761−5771.

(56) Pilard, M.-A.; Guillemot, M.; Toupet, L.; Jordanov, J.; Simonneaux, G. *Inorg. Chem.* **1997**, *36*, 6307−6314.

(57) Ikeue, T.; Ohgo, Y.; Saitoh, T.; Nakamura, M.; Fujii, H.; Yokoyama, M. *J. Am. Chem. Soc.* **2000**, *122*, 4068−4076.

interactions in the saddle shaped intermediate-spin complexes with the $(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^1$ electron configuration;[18] the previously reported intermediate-spin complexes are believed to adopt the $(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^1$ electron configuration though the systematic ^{13}C NMR study has not been carried out.[5,58,59] The strong $d_\pi-3e_g$ interactions in saddle shaped complexes induce large spin densities on the pyrrole ring and shift the pyrrole-α and -β signals to the downfield region. Since the $3e_g$ orbital has a node at the *meso* positions, the *meso* carbon signal shifts upfield due to the spin polarization effect from the neighboring pyrrole-α carbon.[21,60] Therefore, we have concluded that the ruffled intermediate-spin complexes, which exhibit the ^{13}C NMR spectra that are completely different from those of the saddled intermediate-spin complexes, should have an electron configuration represented as $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1$.

Conclusion

The spin states of a series of five-coordinated iron(III) porphyrin complexes with a ruffled porphyrin ring, [Fe(TEtPrP)X] and [Fe(T^{i}PrP)X] ($X = F^-$, Cl^-, Br^-, I^-, and ClO_4^-), have been examined by ^{13}C NMR, ^{1}H NMR, EPR, and Mössbauer spectroscopy. The ^{1}H and ^{13}C NMR results have revealed that while the F^- and Cl^- complexes are in the high-spin state, the Br^- and I^- complexes are in the admixed intermediate-spin state in CD_2Cl_2 solutions at 200−300 K. EPR spectra taken in frozen CH_2Cl_2 solution at 4.2 K have revealed, however, that not only the F^- and Cl^- but also the Br^- complex is in the quite pure high-spin state. In contrast, the I^- complex has maintained the admixed intermediate-spin state with minor contribution of the high-spin state. The spin state of [Fe(TEtPrP)I] has changed, however, from mainly $S = {}^3/_2$ in CH_2Cl_2 to a pure $S = {}^5/_2$ in toluene solution and in the solid. The versatile nature of the spin state in five-coordinate [Fe(TEtPrP)I], which is also seen in naturally occurring five-coordinate heme proteins such as cytochromes c′, is ascribed to the change in the out-of-plane deviation of iron depending on the solvents, temperatures, and phases. In contrast to the case of halide ligated complexes, the ClO_4^- complexes have exhibited a quite pure intermediate-spin state in a wide range of temperatures. The ^{13}C NMR spectra of the ClO_4^- complexes have exhibited the downfield shifted *meso* and the upfield shifted pyrrole-α signals. The results indicate the occupation of the unpaired electron in the d_{xy} orbital. On the basis of these results, we have concluded that the ruffled intermediate-spin complexes such as [Fe(TRP)ClO$_4$] and [Fe(TRP)(THF)$_2$]ClO$_4$ (R = ^{i}Pr and 1-EtPr) adopt a novel $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1$ electron configuration.

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Supporting Information Available: Synthesis of [Fe(TRP)X]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(58) Tony, G. E.; terHaar, L. W.; Savrin, J. E.; Gold, A.; Hatlfield, W. E.; Sangaiah, R. *Inorg. Chem.* **1984**, *23*, 2561−2563.

(59) Tony, G. E.; Gold, A.; Savrin, J. E.; terHaar, L. W.; Sangaiah, R. *Inorg. Chem.* **1984**, *23*, 4350−4352.

(60) After we finished writing this manuscript, a paper appeared describing that the intermediate-spin [Fe(OETPP)(4-CNPy)$_2$]$^+$ has a significant population of the $S = 2$ Fe(II), $S = {}^1/_2$ porphyrin π-cation radical state, with antiferromagnetic coupling between the metal and the porphyrin unpaired electron.[61] It is true that the *meso* carbon has a considerable amount of negative spin as is revealed by the upfield shifted *meso* and downfield shifted *ipso* carbon signals, −295 and 369 ppm at 298 K, respectively. We are currently doing research to reveal the reason for the negative spin at the *meso* carbon atoms in [Fe(OETPP)(4-CNPy)$_2$]$^+$ with the $(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^1$ ground state.

(61) Yatsunyk, L. A.; Walker, F. A. *Inorg. Chem.* **2004**, *43*, 757−777.