Electron Configuration of Ferric Ions in Low-Spin (Dicyano)(*meso*-tetraarylporphyrinato)iron(III) Complexes

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Received March 23, 1999

The electron configuration of a series of low-spin (dicyano){*meso*-tetrakis(2,4,6-trialkylphenyl)porphyrinato}-iron(III) complexes, $[Fe(R\text{-}TPP)(CN)_2]^-$ where R = Me, Et, or ^{i}Pr, together with the parent $[Fe(TPP)(CN)_2]^-$, has been examined in dichloromethane−methanol solution by ^{1}H NMR, ^{13}C NMR, and EPR spectroscopies. While the ferric ion of $[Fe(TPP)(CN)_2]^-$ has shown a common $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration, the ferric ions of the alkyl-substituted complexes $[Fe(R\text{-}TPP)(CN)_2]^-$ have exhibited the preference of a less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration. Spectroscopic characteristics of the complexes in which ferric ions take the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration are (i) axial type EPR spectra, (ii) downfield shifted pyrrole and meta signals in ^{1}H NMR spectra, and (iii) downfield shifted *meso*-carbon signals in ^{13}C NMR spectra. Occurrence of the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration in $[Fe(R\text{-}TPP)(CN)_2]^-$ has been ascribed to the electronic interaction between iron(d_π) and cyanide(p_π*) orbitals. The interaction stabilizes the d_π orbitals and induces $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration. Since the electron configuration of (dicyano){*meso*-tetrakis(2,6-dichlorophenyl)porphyrinato}iron(III), $[Fe(Cl\text{-}TPP)(CN)_2]^-$, which carries bulky electronegative chlorine atoms at the ortho positions, is presented as a common $(d_{xy})^2(d_{xz},d_{yz})^3$, the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration in $[Fe(R\text{-}TPP)(CN)_2]^-$ can be ascribed, at least partially, to the electron-donating ability of the *meso*-aryl groups.

Introduction

Studies on the electron configuration of ferric ions in porphyrin complexes are of great importance to understand the physicochemical properties of synthetic complexes as well as naturally occurring heme proteins.[1−4] In previous papers, we have reported that the spectroscopic properties of a series of low-spin six-coordinated (*meso*-tetraalkylporphyrinato)iron(III) complexes such as $[Fe(TRP)(CN)_2]^-$, [Fe(TRP)(CN)(L)], and $[Fe(TRP)(L)_2]^+$ (R = H, Me, Et, or ^{i}Pr, and L = 1-MeIm, 2-MeIm, or 2-^{i}PrIm)[5] significantly change as the bulkiness of the meso substituent increases.[6−8] For example, the pyrrole signal in $[Fe(T^iPrP)(CN)_2]^-$ was observed extremely downfield, δ 12.8 ppm at −35 °C, in the ^{1}H NMR spectrum as compared with that of the unsubstituted complex $[Fe(THP)(CN)_2]^-$, −21.7 ppm at the same temperature. The EPR spectrum of $[Fe(T^iPrP)(CN)_2]^-$ was also quite unusual; an axial type spectrum with $|g_x| = |g_y| = 2.35$ and $|g_z| = 1.82$ was observed in contrast to a large g_{max} type or a rhombic type spectrum in typical low-spin complexes.[9−12] The large spectral change was interpreted in terms of a change in electron configuration of the ferric ion from a common $(d_{xy})^2(d_{xz},d_{yz})^3$ to a less common $(d_{xz},d_{yz})^4(d_{xy})^1$ as the meso substituents become bulkier. We have ascribed the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration to the highly S_4 ruffled structure of the porphyrin ring especially in the ^{i}Pr complex; the $(d_{xz},d_{yz})^4(d_{xy})^1$ ground state is stabilized by the decrease in interaction

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(5) Abbreviations: R-TPP, dianion of *meso*-tetrakis(2,4,6-trialkylphenyl)porphyrin where R is methyl (Me), ethyl (Et), or isopropyl (^{i}Pr); Me-TPP, dianion of *meso*-tetramesitylporphyrin, usually abbreviated as TMP; $[Fe(R\text{-}TPP)(CN)_2]^-$, (dicyano){*meso*-tetrakis(2,4,6-trialkylphenyl)porphyrinato}iron(III); Cl-TPP, dianion of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin; OMTPP, dianion of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrin; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; 2-MeBzIm, 2-methylbenzimidazole; 4-CNPy, 4-cyanopyridine; ^{t}BuNC, *tert*-butyl isocyanide.

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10.1021/ic990328x CCC: $18.00

between iron $d_\pi(d_{xz},d_{yz})$ and porphyrin $3e_g$ orbitals,[7,8] as well as the increase in interaction between iron d_{xy} and porphyrin a_{2u} orbitals.[2] The former stabilizes d_π orbitals, and the latter destabilizes the d_{xy} orbital, resulting in the stabilization of $(d_{xz},d_{yz})^4(d_{xy})^1$ as compared with the commonly observed $(d_{xy})^2(d_{xz},d_{yz})^3$ state.

Contrary to the tetraalkylporphyrin complexes in which the porphyrin ring itself is more or less nonplanar,[13−19] tetraarylporphyrin complexes usually have planar porphyrin rings unless there is some steric repulsion between axial ligand and meso aryl groups.[20−25] This is because the half thickness of a benzene ring is 1.7 Å, which is smaller than the van der Waals radius of a methyl group, 2.0 Å.[26] Thus, the steric repulsion between the *meso*-aryl group and the pyrrole β-hydrogen can be alleviated by the rotation of the benzene ring about $C_{meso}-C_{aryl}$ bonds to maintain the porphyrin planarity. In fact, the porphyrin rings of $[Fe(TPP)(CN)_2]^-$ and $[Fe(TPP)(1\text{-}MeIm)_2]^+$ were essentially planar as revealed by the X-ray crystallographic analysis.[27,28] Accordingly, these complexes showed the ^1H NMR spectra typical for low-spin ferric porphyrin complexes; pyrrole β-signals were observed at −16.4 and −16.8 ppm at 25 °C, respectively.[29,30] The EPR spectra of these complexes are also quite typical; the former showed a large g_{max} type spectrum in which one strong signal was observed at $g = 3.70$, and the latter showed a rhombic type spectrum where three signals were observed at $g = 2.89$, 2.29, and 1.55.[10,31] Thus, the ground state electron configuration of both complexes was assigned as $(d_{xy})^2(d_{xz},d_{yz})^3$; the energy levels of the d_{xz} and d_{yz} are nearly the same in the former complex while they are different in the latter.[9]

Although the electronic ground state of $[Fe(TPP)(CN)_2]^-$ and $[Fe(TPP)(1\text{-}MeIm)_2]^+$ is presented as $(d_{xy})^2(d_{xz},d_{yz})^3$, some low-spin complexes with much weaker axial ligands have a novel $(d_{xz},d_{yz})^4(d_{xy})^1$ state.[1−4,32,33] Examples are complexes such as $[Fe(TPP)(^tBuNC)_2]^+$ and $[Fe(TPP)(4\text{-}CNPy)_2]^+$.[2,4,32] The X-ray crystallographic studies of these complexes revealed that the porphyrin core is highly S_4 ruffled in spite of the apparent absence of the steric interactions between ligands and the porphyrin core. The reason for the nonplanarity was thus ascribed to the electronic interaction. Walker, Scheidt, and coworkers pointed out the possible interactions of iron(d_π) orbitals with a low-lying ligand π^* orbital.[1−4] Simonneaux and coworkers also ascribed the novel electron configuration to the π-accepting nature of the axial ligands.[33] Because of this interaction, d_π orbitals are stabilized to a point lower than the d_{xy} orbital. The complex is further stabilized by the $a_{2u}-d_{xy}$ interaction which is possible if the porphyrin ring changes from the planar to the S_4-ruffled structure.[2] This interaction raises the energy level of the d_{xy} orbital and contributes to the increase in a $(d_{xz},d_{yz})^4(d_{xy})^1$ state. Latos-Grazynski, Marchon, and coworkers showed that the electronic ground state of some low-spin ferric complexes such as quinoxalinotetraphenylporphyrin is presented as $(d_{xz},d_{yz})^4(d_{xy})^1$ even if the axial ligands are strong σ-donors such as imidazole and cyanide.[34−36] Thus, the electron configuration of low-spin ferric ions is controlled by the steric and electronic effects of axial ligands as well as peripheral substituents.

In order to find out the general conditions for the formation of low-spin ferric porphyrin complexes with the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration, we have examined a series of low-spin (dicyano){*meso*-tetrakis(2,4,6-trialkylphenyl)porphyrinato}iron(III) complexes, $[Fe(R\text{-}TPP)(CN)_2]^-$ in which R = Me, Et, and ^{i}Pr, together with the parent $[Fe(TPP)(CN)_2]^-$, by means of ^1H NMR, ^{13}C NMR, and EPR spectroscopies. Similarly, the electron configuration of (dicyano){*meso*-tetrakis(2,6-dichlorophenyl)porphyrinato}iron(III), $[Fe(Cl\text{-}TPP)(CN)_2]^-$, has been examined to find out the effects of a bulky electronegative group at the ortho positions. We report that the ground state electronic configuration of low-spin $[Fe(R\text{-}TPP)(CN)_2]^-$ (R = Me, Et, and ^{i}Pr) is presented as $(d_{xz},d_{yz})^4(d_{xy})^1$. We also report the factors controlling the electron configuration of ferric ions in tetraarylporphyrin system.

Experimental Section

Spectral Measurement. ^1H and ^{13}C NMR spectra were recorded on a JEOL LA300 spectrometer operating at 300.4 MHz for proton. Chemical shifts were referenced to the residual peak of the deuterated solvents such as dichloromethane ($\delta = 5.32$ ppm for ^1H and 53.1 ppm for ^{13}C) and chloroform ($\delta = 7.22$ ppm for ^1H and 77.2 ppm for ^{13}C). EPR spectra were measured at 4.2 K in frozen $CH_2Cl_2-CH_3OH$ solutions with a Brucker ESP-300E spectrometer operating at X band and equipped with an Oxford helium cryostat.

Synthesis. (i) $[Fe(R\text{-}TPP)(CN)_2]^-$; R = Me, Et, or ^{i}Pr. A series of *meso*-tetrakis(2,4,6-trialkylphenyl)porphyrins, $(R\text{-}TPP)H_2$ where R = Me, Et, and ^{i}Pr, were prepared according to the Lindsey's method in $CHCl_3$ solution using BF_3•ether.[30,37] Their spectral and analytical data have already been reported in our previous paper.[30] The ^{13}C NMR chemical shifts for the free base porphyrins are listed in Table S1 of the Supporting Information. The high-spin complexes [Fe(R-TPP)Cl], prepared by refluxing a DMF solution of $(R\text{-}TPP)H_2$ with $FeCl_2$•$4H_2O$, were converted into the corresponding low-spin dicyano complexes

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$[Fe(R\text{-}TPP)(CN)_2]^-$ in an NMR sample tube by the following method. To a CD_2Cl_2 solution containing 1.5−2.0 mg of [Fe(R-TPP)]Cl was added a CD_2Cl_2 solution (4.0 molar equiv) of tetrabutylammonium cyanide ($Bu_4N^+CN^-$) to form $[Fe(R\text{-}TPP)(CN)_2]NBu_4$. The CD_2Cl_2−CD_3OD (4:1) solution was prepared by the addition of CD_3OD to a CD_2Cl_2 solution of $[Fe(R\text{-}TPP)(CN)_2]NBu_4$.

(ii) $[Fe(Cl\text{-}TPP)(CN)_2]^-$. This complex was prepared from {*meso*-tetrakis(2,6-dichlorophenyl)porphyrinato}iron(III) chloride, [Fe(Cl-TPP)]Cl,[38] and $Bu_4N^+CN^-$.

(iii) $[Fe(R\text{-}TPP)(CN)_2]^-$(pyrrole-$d_8$). A series of pyrrole-deuterated porphyrins $(R\text{-}TPP)H_2$(pyrrole-d_8) (R = Me, Et, ^{i}Pr) were prepared by the reaction of pyrrole-d_5 with the corresponding aldehydes, and they were converted to the high-spin complexes [Fe(R-TPP)Cl](pyrrole-d_8). Low-spin dicyano complexes $[Fe(R\text{-}TPP)(CN)_2]^-$(pyrrole-$d_8$) were prepared in an NMR sample tube as described above.

(iv) $[Fe(Me\text{-}TPP)(CN)_2]^-$(*meso*-^{13}C). Mesitoic acid(^{13}COOH) was prepared in 43% yield by the treatment of mesitylmagnesium bromide, obtained from 2-bromomesitylene (0.10 mol) and magnesium (0.11 mol), with 0.045 mol of $^{13}CO_2$ (99.2 atom % of ^{13}C, Isotech Inc.) in THF solution followed by the conventional workup procedure; mp 151−153 °C, ^{13}C NMR ($CDCl_3$, 25 °C) 175.5 ppm. The carboxylic acid (1.00 g, 6.1 mmol) was reduced by BH_3−THF (20 mmol) in THF solution to form 2-(hydroxymethyl)mesitylene in 92% yield;[39] mp 83−85 °C, ^{13}C NMR ($CDCl_3$, 25 °C) 59.2 ppm. The alcohol (1.0 g, 6.6 mmol) was dissolved in 50 mL of CH_2Cl_2 and was treated with 2.88 g (33 mmol) of activated MnO_2 at 25 °C.[40] Formation of mesitaldehyde-(^{13}CHO) was monitored by thin layer chromatography. The yield was 58%. ^{13}C NMR ($CDCl_3$, 25 °C): 192.4 ppm. Condensation reaction of mesitaldehyde and pyrrole gave $(Me\text{-}TPP)H_2$(*meso*-^{13}C); ^{13}C NMR ($CDCl_3$, 25 °C) 117.6 ppm. Insertion of iron was performed by the conventional method using DMF and $FeCl_2 \cdot 4H_2O$ to form high-spin [Fe(Me-TPP)Cl]; ^{13}C NMR ($CDCl_3$, 25 °C) 524 ppm. The dicyano complex $[Fe(Me\text{-}TPP)(CN)_2]^-$(*meso*-^{13}C) was prepared similarly in an NMR sample tube by the addition of $Bu_4N^+CN^-$ into a CD_2Cl_2 solution of [Fe(Me-TPP)Cl](*meso*-^{13}C); ^{13}C NMR (CD_2Cl_2, 25 °C) 125.1 ppm.

Results

(i) EPR Spectra. EPR spectra of $[Fe(TPP)(CN)_2]^-$, $[Fe(R\text{-}TPP)(CN)_2]^-$ (R = Me, Et, ^{i}Pr), and $[Fe(Cl\text{-}TPP)(CN)_2]^-$ were taken at 4.2 K in frozen CH_2Cl_2−CH_3OH (4:1) solutions as shown in Figure 1. The *g* values of these complexes are listed in Table 1.

(ii) ^{1}H NMR. Chemical shifts at −71 °C in CD_2Cl_2−CD_3OD (4:1) are listed in Table 2. The assignment of the pyrrole protons has been done by spectral comparison with the pyrrole-deuterated complexes. The Curie plots of the pyrrole and meta proton signals are given in Figure 2, panels a and b, respectively.

(iii) ^{13}C NMR Spectra. Chemical shifts of the *meso*-^{13}C signals of $[Fe(TPP)(CN)_2]^-$ and$[Fe(Me\text{-}TPP)(CN)_2]^-$ were determined over a wide temperature range by using *meso*-^{13}C enriched complexes.[41,42] In the case of $[Fe(Et\text{-}TPP)(CN)_2]^-$ and $[Fe(Cl\text{-}TPP)(CN)_2]^-$, the chemical shifts were determined by using the samples without ^{13}C enrichment. Curie plots of these signals are given in Figure 3.

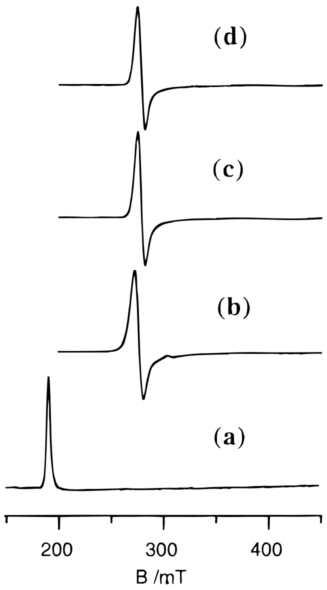

Figure 1. EPR spectra of (a) $[Fe(TPP)(CN)_2]^-$, (b) $[Fe(Me\text{-}TPP)(CN)_2]^-$, (c) $Fe(Et\text{-}TPP)(CN)_2]^-$, and (d) $[Fe(^iPr\text{-}TPP)(CN)_2]^-$ taken in frozen CH_2Cl_2−CH_3OH solution at 4.2 K.

Table 1. EPR *g* Values of $[Fe(TPP)(CN)_2]^-$ and $[Fe(R\text{-}TPP)(CN)_2]^-$ (R = Me, Et, ^{i}Pr) Taken in Frozen CH_2Cl_2−CH_3OH Solution at 4.2 K

complexes	g_x	g_y	g_z
$[Fe(TPP)(CN)_2]^-$			3.56
$[Fe(Me\text{-}TPP)(CN)_2]^-$	2.47	2.47	1.5
$[Fe(Et\text{-}TPP)(CN)_2]^-$	2.45	2.45	1.5
$[Fe(^iPr\text{-}TPP)(CN)_2]^-$	2.45	2.45	1.5

Table 2. ^{1}H NMR Chemical Shifts Measured at −71 °C in CD_2Cl_2−CD_3OD[a]

complexes	*o*	*m*	*p*	py-H
$[Fe(TPP)(CN)_2]^-$	4.01	8.72	5.46	−11.68
$[Fe(Me\text{-}TPP)(CN)_2]^-$	(2.35)	10.88	(2.79)	−5.74
$[Fe(Et\text{-}TPP)(CN)_2]^-$	(2.49^α) (0.49^β)	12.89	(3.52^α) (1.56^β)	4.39
$[Fe(^iPr\text{-}TPP)(CN)_2]^-$	(1.57^α) (1.27^β)	12.92	(3.61^α) (1.71^β)	5.97
$[Fe(Cl\text{-}TPP)(CN)_2]^-$		6.30	5.70	−27.04

[a] Numbers in parentheses are the chemical shifts of the α and *β* protons of the substituents.

Discussion

Electron Configuration of $[Fe(R\text{-}TPP)(CN)_2]^-$. (i) EPR Spectra. The electron configuration of low-spin ferric ions in porphyrin complexes can be determined by EPR spectroscopy. Three types of EPR spectra have been reported for the low-spin ferric porphyrin complexes. The first one is a rhombic spectrum where three signals appear at $g = 2.8−2.9$, 2.2−2.4, and 1.5−1.6.[9,10] This type of spectrum is generally observed in $[Fe(TPP)(L)_2]^+$ where L's are unhindered imidazoles such as imidazole and 1-methylimidazole. In these complexes two imidazole ligands align in a parallel fashion above and below the porphyrin ring. Thus, the energy level of d_{xz} differs from that of d_{yz} due to the different degree of interaction with the axially coordinated imidazole ligands, giving rhombic type spectra.[12] The second type is sometimes called a "large g_{max}" or "strong g_{max}" spectrum in which one resolved signal appears at $g > 3.3$.[11,42] This type of spectrum is observed in the complexes having two bulky imidazole ligands such as $[Fe(TPP)(2\text{-}MeIm)_2]^+$ and $[Fe(TMP)(2\text{-}MeIm)_2]^+$.[12,30] X-ray crystallographic analyses of these complexes have revealed that the imidazole ligands are perpendicularly aligned along the diagonal C_{meso}−Fe−C_{meso} axes.[21,22] In such a situation, the d_{xz} and d_{yz} orbitals are destabilized to a similar extent by the interaction

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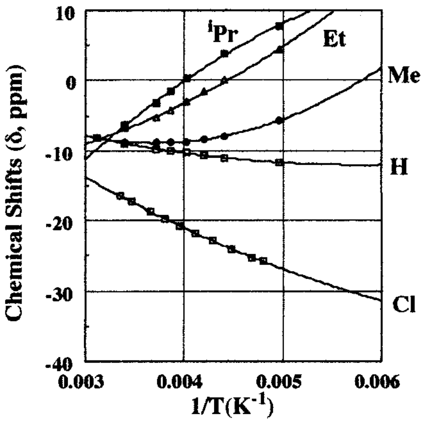
(a) pyrrole signals



(b) *meta*-signals

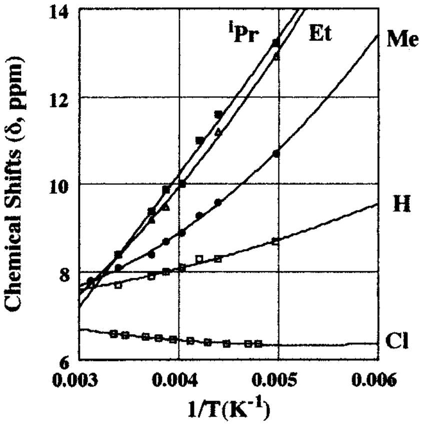


Figure 2. Curie plots of the pyrrole (a) and *meta*-proton (b) signals of $[Fe(TPP)(CN)_2]^-$, $[Fe(R\text{-}TPP)(CN)_2]^-$ (R = Me, Et, ^{i}Pr), and $[Fe(Cl\text{-}TPP)(CN)_2]^-$ taken in $CD_2Cl_2-CD_3OD$ solution.

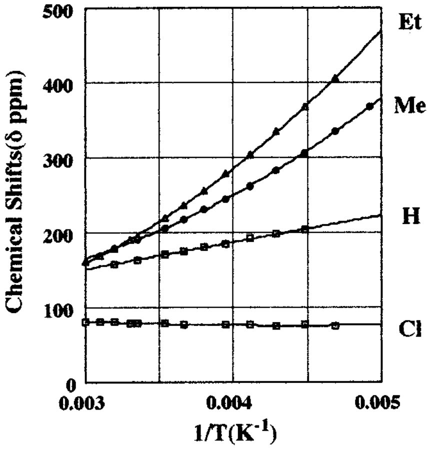


Figure 3. Curie plots of the *meso*-carbon signals of $[Fe(TPP)(CN)_2]^-$, $[Fe(R\text{-}TPP)(CN)_2]^-$ (R = Me, Et, ^{i}Pr), and $[Fe(Cl\text{-}TPP)(CN)_2]^-$ taken in $CD_2Cl_2-CD_3OD$ solution.

with the imidazole π orbitals. Thus, the orbital degeneracy is maintained, giving large g_{max} type spectra. Complexes with linear cyanide ligand such as $[Fe(TPP)(CN)_2]^-$ also exhibit large g_{max} type spectra for similar reasons.[31] Recent studies have revealed a third type of EPR spectrum, an axial spectrum, in complexes with very weak ligands such as *tert*-butyl isocyanide,[4,32] trifluoroethyl isocyanide,[43] 4-cyanopyridine,[1,2] and dimethyl phenylphosphonite.[33] The axial type spectra were also observed in the complexes with much stronger axial ligands such as cyanide, pyridines, and imidazoles, if the complexes have highly deformed porphyrin rings.[7,8,35,36,44] The axial type spectra have been ascribed to the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration as mentioned in the Introduction.

The large g_{max} type EPR spectrum of $[Fe(TPP)(CN)_2]^-$ shown in Figure 1 suggests that the electron configuration of the ferric ion of this complex is $(d_{xy})^2(d_{xz},d_{yz})^3$ in $CH_2Cl_2-CH_3OH$ solution. In contrast, the EPR spectra of the alkyl-substituted complexes all showed axial type spectra, indicating that the electron configuration is presented as $(d_{xz},d_{yz})^4(d_{xy})^1$. The differences in energy levels between d_{xy} and $d_\pi(d_{xz},d_{yz})$ orbitals in the alkyl-substituted complexes are calculated to be ca. 2.9λ.[45,46] The value is comparable in magnitude to those of $[Fe(TPP)(4\text{-}CNPy)_2]^+$ and $[Fe(Me\text{-}TPP)(4\text{-}CNPy)_2]^+$, 1.72$\lambda$ and 2.92λ, respectively,[2,3] while it is much smaller than the corresponding values of $[Fe(T^{i}PrP)(CN)_2]^-$ and $[Fe(TPP)(^{t}BuNC)_2]^+$, 4.82λ and 8.33λ, respectively.[4,7]

(ii) Pyrrole Signals in ^{1}H NMR Spectra. The electron configuration of ferric ions can also be determined by ^{1}H NMR spectroscopy. The data in Table 2 demonstrate the existence of large spin densities on the pyrrole β-carbons in $[Fe(TPP)(CN)_2]^-$; the chemical shift of the pyrrole protons of this complex is -11.68 ppm at -71 °C. The upfield shift can be explained in terms of the interaction between porphyrin($3e_g$) and iron(d_π) orbitals.[47−49] Since $3e_g$ orbitals have large electron densities on the pyrrole β-carbon atoms, the charge transfer from the porphyrin $3e_g$ to the singly occupied iron d_π orbitals induces an upfield shift of the protons directly bonded to these carbons. Thus, the large upfield shift observed in the pyrrole signal of $[Fe(TPP)(CN)_2]^-$ proves the existence of an unpaired electron in the d_{xz} or d_{yz} orbital and supports the $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration. In contrast, the pyrrole signals in $[Fe(Me\text{-}TPP)(CN)_2]^-$, $[Fe(Et\text{-}TPP)(CN)_2]^-$, and $[Fe(^{i}Pr\text{-}TPP)(CN)_2]^-$ moved downfield and appeared at -5.74, $+4.39$, and $+5.97$ ppm, respectively, at -71 °C. The result suggests that the spin densities on the pyrrole β-carbons decreased to a great extent in the alkyl-substituted complexes. The decrease can be explained if the contribution of $(d_{xz},d_{yz})^4(d_{xy})^1$ toward the electronic ground state increases in these complexes; the interaction between porphyrin($3e_g$) and singly occupied iron(d_{xy}) orbitals must be very weak because of the orthogonality of these orbitals in a planar D_{4h} porphyrin complex. Thus, the downfield pyrrole shifts in the alkyl-substituted complexes support the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration determined by the EPR spectra. However, there seem to be some discrepancies between the ^{1}H NMR and EPR results. While the chemical shifts of the pyrrole protons are still quite different among the three complexes, the EPR g values are nearly the same, $g_\perp = 2.45-2.47$ and $g_\parallel = 1.5$. The discrepancies must be ascribed to the difference in temperature where these values were obtained; even if the contribution of the $(d_{xy})^2(d_{xz},d_{yz})^3$ state is not small at 202 K where NMR spectra were taken, it could be negligibly small at 4.2 K where EPR measurements were carried out. Rather small differences in the

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pyrrole shifts among the unsubstituted and alkyl-substituted complexes at 25 °C can also be explained in terms of the increased contribution of the $(d_{xy})^2(d_{xz},d_{yz})^3$ state at higher temperature.

The difference in electron configuration can also be demonstrated by the Curie slopes of the pyrrole signals as shown in Figure 2a. While the Curie slope of $[Fe(TPP)(CN)_2]^-$ showed a small negative value, those of the Me, Et, and ^{i}Pr complexes were positive. The negative Curie slope of the pyrrole signal is commonly observed in the low-spin ferric porphyrin complexes with the $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration.[30] These results suggest that the ferric ions in the alkyl-substituted complexes are in the $(d_{xz},d_{yz})^4(d_{xy})^1$ state, while that of the unsubstituted complex is in the $(d_{xy})^2(d_{xz},d_{yz})^3$ state. A curvature observed in the Curie plots suggests that the ground state electron configuration is the admixture of $(d_{xz},d_{yz})^4(d_{xy})^1$ and $(d_{xy})^2(d_{xz},d_{yz})^3$.[50]

(iii) Meta Signals in ^{1}H NMR Spectra. A similar tendency was observed in the chemical shifts of meta signals. The data in Table 2 indicate that the meta signal moves downfield from 8.72 (R = H) to 12.92 ppm (R = ^{i}Pr). The chemical shift of the ^{i}Pr complex should be compared with those of $[Fe(Me\text{-}TPP)(4\text{-}CNPy)_2]^+$ (δ 14.59 at −80 °C) and $[Fe(TPP)(^iBuNC)_2]^+$ (δ ca. 18 ppm at −80 °C based on the Curie plots in Figure 3 of ref 32), both of which have ferric ions with the $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration.[1,32] The downfield shifts of meta signals are usually observed in high-spin ferric porphyrin complexes such as [Fe(TPP)]Cl and [Fe(Me-TPP)]Cl, which have been ascribed to the large spin densities on the *meso*-carbons; the π-spins on the *meso*-carbons delocalize to the aryl groups directly bonded to them and induce a downfield shift of the meta protons.[47−49] Thus, the ^{1}H NMR results suggest the existence of large spin densities on the *meso*-carbons especially in the ^{i}Pr complex. The result is an indication that the spin transfer from the low-spin ferric ion to the meso carbons takes place through the iron(d_{xy}) and porphyrin(a_{2u}) interaction; the a_{2u} orbital has large spin densities on the *meso*-carbons.

(iv) Meso Signals in ^{13}C NMR Spectra. The increase in spin densities on the *meso*-carbons due to the interaction between porphyrin a_{2u} and iron d_{xy} can be proved directly by the ^{13}C NMR measurement. As shown in Figure 3, the *meso*-carbon signal in $[Fe(TPP)(CN)_2]^-$ appeared at 164.2 ppm at 24 °C and shifted downfield as the temperature was lowered. Similar downfield shifts were observed in $[Fe(Me\text{-}TPP)(CN)_2]^-$ and $[Fe(Et\text{-}TPP)(CN)_2]^-$ though the slopes were much steeper. Thus, the chemical shifts of the *meso*-carbons at −50 °C are greatly different among three complexes; 204.3, 306.3, and 367.0 ppm for the R = H, Me, and Et complexes, respectively. The results clearly indicate that the spin densities on the *meso*-carbons in the R = Me and Et complexes are much larger than that of the unsubstituted complex, being consistent with the conclusion that the ferric ions of the alkyl-substituted complexes are in $(d_{xy},d_{yz})^4(d_{xy})^1$ state. Since the ^{i}Pr complex is supposed to have a ferric ion with the purest $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration among the complexes examined in this study, determination of the *meso*-^{13}C chemical shift of this complex must be quite interesting. The observation of the signal has hampered, however, due to the broadening and bad signal-to-noise ratio.

On the basis of the ^{1}H NMR, ^{13}C NMR, and EPR spectroscopic results mentioned above, it is concluded that the electron configuration of the ferric ions in $[Fe(R\text{-}TPP)(CN)_2]^-$ (R = Me, Et, ^{i}Pr) is $(d_{xz},d_{yz})^4(d_{xy})^1$, while that of $[Fe(TPP)(CN)_2]^-$ is $(d_{xy})^2(d_{xz},d_{yz})^3$. The contribution of $(d_{xz},d_{yz})^4(d_{xy})^1$ to the electronic ground state is ordered as follows: $[Fe(Me\text{-}TPP)(CN)_2]^- < [Fe(Et\text{-}TPP)(CN)_2]^- \leq [Fe(^iPr\text{-}TPP)(CN)_2]^-$.

Electron Configuration of $[Fe(Cl\text{-}TPP)(CN)_2]^-$. In order to find out the effect of bulky electronegative groups at the ortho positions, the ^{1}H NMR spectra of $[Fe(Cl\text{-}TPP)(CN)_2]^-$ have been examined. The Curie plots of the pyrrole and meta signals are given in Figure 2, panels a and b, respectively, together with those of $[Fe(TPP)(CN)_2]^-$ and $[Fe(R\text{-}TPP)(CN)_2]^-$. The Curie slope of the pyrrole signal of $[Fe(Cl\text{-}TPP)(CN)_2]^-$ showed a much larger negative value than that of $[Fe(TPP)(CN)_2]^-$ as is clear from Figure 2a. Thus, the pyrrole signal of $[Fe(Cl\text{-}TPP)(CN)_2]^-$ moved to −27.04 ppm at −71 °C as compared with −11.68 ppm in $[Fe(TPP)(CN)_2]^-$. The difference was also observed in the Curie plots of the meta signal; while the other four complexes showed positive slopes, $[Fe(Cl\text{-}TPP)(CN)_2]^-$ showed a small but negative slope. These results suggest that the contribution of the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration to the electronic ground state is much larger in $[Fe(TPP)(CN)_2]^-$ than in $[Fe(Cl\text{-}TPP)(CN)_2]^-$. This is because the existence of the electronegative chlorine atoms at the ortho positions in $[Fe(Cl\text{-}TPP)(CN)_2]^-$ weakens the coordination ability of the porphyrin toward low-spin ferric ion. In such a situation, metal to axial ligand π back-bonding is also expected to be weakened as compared with that in $[Fe(TPP)(CN)_2]^-$. As a result, the energy level of the d_π orbitals is far above that or the d_{xy} orbital in $[Fe(Cl\text{-}TPP)(CN)_2]^-$, giving a much purer $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration. The ^{13}C NMR results also support the $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration in $[Fe(Cl\text{-}TPP)(CN)_2]^-$. As shown in Figure 3, the *meso*-carbon signal appeared at 79.1 ppm at 25 °C and 76.2 ppm at −50 °C, suggesting a small spin density on *meso*-carbon atoms.

On the basis of the ^{1}H and ^{13}C NMR results of $[Fe(Cl\text{-}TPP)(CN)_2]^-$, it is concluded that the presence of the electron-withdrawing chlorine atoms at the *meso*-aryl groups stabilizes the common $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration.

Factors Controlling the Electron Configuration of Low-Spin (Tetraarylporphyrinato)iron(III) Systems. (i) Steric Effects To Induce S_4 Ruffled Porphyrin Ring. In the previous papers, we have pointed out three factors stabilizing the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration in bis(cyanide) and bis(imidazole) complexes of (*meso*-tetraalkylporphyrinato)iron(III).[7,8] They are (a) bulky meso substituents, (b) bulky axial ligands, and (c) axial ligands with a low-lying π^* orbital. Conditions a and b are steric factors necessary for the S_4-ruffled porphyrin ring. We have reported that the electron configuration of complexes such as $[Fe(T^iPrP)(CN)_2]^-$, $[Fe(T^iPrP)(1\text{-}MeIm)_2]^-$, $[Fe(T^iPrP)(2\text{-}MeIm)_2]^-$, and $[Fe(T^iPrP)(Py)_2]^+$ are presented as $(d_{xz},d_{yz})^4(d_{xy})^1$ on the basis of the NMR and EPR results.[7,8] These complexes are supposed to have highly S_4 ruffled porphyrin rings regardless of the axial ligands due to the steric repulsion between bulky *meso*-isopropyl groups and the pyrrole β-hydrogens. Similar deformation is expected in $[Fe(Me\text{-}TPP)(2\text{-}MeBzIm)_2]^+$ caused by the severe steric repulsion between bulky axial ligand and *meso*-mesityl groups. In fact, this complex showed the ^{1}H NMR, ^{13}C NMR, and EPR spectra typical for the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration.[44] Bulkiness of the axially coordinated imidazole ligands is quite important in $[Fe(Me\text{-}TPP)(L)_2]^+$ since the complex with less bulky 2-MeIm, $[Fe(Me\text{-}TPP)(2\text{-}MeIm)_2]^+$, showed a large g_{max} type signal in EPR together with the upfield-shifted pyrrole signals in ^{1}H NMR; 2-MeIm is not bulky enough to change the electron configuration of ferric ion from $(d_{xy})^2(d_{xz},d_{yz})^3$ to $(d_{xz},d_{yz})^4(d_{xy})^1$ in the tetramesitylporphyrin system.[8,30] The deformation mode of the porphyrin ring is also an important factor to determine the

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electron configuration, because our preliminary results have shown that $[Fe(OMTPP)(CN)_2]^-$, which is supposed to have a highly S_4 saddled porphyrin ring,[51−53] maintains the common $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration.[54] Thus, S_4-ruffled deformation of the porphyrin ring is necessary for the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration at least in the case of cyanide.

(ii) Electronic Effects To Strengthen Metal to Axial Ligand π Back-Donation. While conditions a and b are the steric requirements to obtain the complex with the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration, condition c is the electronic requirement to obtain it. The low-lying π^* orbital can stabilize iron d_π orbitals relative to a d_{xy} orbital.[1−4] Such ligands are *tert*-butyl isocyanide,[32] 2,2,2-trifluoroethyl isocyanide,[43] 4-cyanopyridine,[2] and dimethyl phenylphosphonite.[33] In the low-spin ferric porphyrin complexes carrying these ligands at the axial positions, the energy levels of d_π orbitals drop to a point lower than or nearly equal to that of the d_{xy} orbital. Thus, the ground state electron configuration of iron becomes an admixture of $(d_{xz},d_{yz})^4(d_{xy})^1$ and $(d_{xy})^2(d_{xz},d_{yz})^3$. The contribution of $(d_{xz},d_{yz})^4(d_{xy})^1$ could be increased by the S_4-ruffled deformation of the porphyrin ring, since the deformation of this mode enables the porphyrin(a_{2u})−iron(d_{xy}) interaction and raises the energy level of the d_{xy} orbital.[2−4] In contrast, the a_{2u}−d_{xy} interaction is impossible in complexes with an S_4-saddled deformation; the a_{2u} orbital can interact with the $d_{x^2-y^2}$ orbital in the saddle-shaped complexes.[53] The interaction causes, however, little effect on the electron configuration of the low-spin complexes because of the unoccupancy of an electron spin in this orbital. This is the reason why all of the complexes with the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration reported so far have an S_4-ruffled porphyrin ring, even if there is no appreciable steric repulsion that could deform the porphyrin ring. In other words, if the energy levels of d_{xy} and d_{yz} are close to that of d_{xy} by some electronic interactions between iron and axial ligands, or between iron and porphyrin, the porphyrin ring deforms in an S_4-ruffled mode and gains some stabilization due to the porphyrin(a_{2u})−iron(d_{xy}) interactions.

In the present system, steric reasons seem to be an unlikely explanation for the S_4-ruffled structure of the porphyrin rings. First of all, steric repulsion of the *meso*-aryl groups with pyrrole β-hydrogens or with linear cyanide ligands is expected to be negligibly small as is deduced from the crystal structures of $[Fe^{III}(TMP)(1\text{-}MeIm)_2]^+$ and $[Fe^{II}(TMP)(CN)_2]^{2-}$.[55,56] Thus, the unusual electron configuration should be ascribed to electronic reasons rather than steric ones. Although the π-accepting ability of cyanide is supposed to be much weaker than that of *tert*-butyl isocyanide and 4-cyanopyridine, it is much stronger than that of imidazoles. In fact, we have shown in our previous paper that cyanide is a much more suitable ligand than imidazoles to obtain the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration; the chemical shifts of the pyrrole protons $[Fe(T^iPrP)(1\text{-}MeIm)_2]^+$ and $[Fe(T^iPrP)(CN)_2]^-$ are 3.0 and 12.9 ppm, respectively, at −71 °C.[7,8] In addition, the results shown in this paper were obtained in the presence of methanol, which can lower the p_{π^*} orbitals of cyanide ligand by making the hydrogen bonding.[8,35,57] Thus, the iron d_π orbitals could be further stabilized by the cyanide p_{π^*} orbitals due to the metal to ligand π back-bonding.[58]

The question is left as to why the electron configuration is affected by the alkyl groups at the ortho and para positions; while the electron configuration of ferric ion in the unsubstituted complex is presented as $(d_{xy})^2(d_{xz},d_{yz})^3$, that of the alkyl-substituted complexes is proved to be $(d_{xz},d_{yz})^4(d_{xy})^1$. As mentioned, the $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration of $[Fe(Cl\text{-}TPP)(CN)_2]^-$ has been ascribed to the electron-withdrawing nature of the chlorine atoms, which weakens iron(d_π)−cyanide(p_{π^*}) interactions. Thus, the electron-donating ability of the alkyl substituents facilitates the porphyrin$(3e_g)$ to iron(d_π) charge transfer, which in turn strengthens the iron(d_π) to cyanide(p_{π^*}) back-donation, lowering the energy level of the d_π orbitals. It is not clear, however, why the contribution of the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration is larger in the ^{i}Pr and Et complexes than in the Me complex even if their electron-donating ability is almost the same. Whatever the reasons are, it is now clear that the electron configuration of ferric ions, which greatly affects the spin distribution on the peripheral carbon atoms, is controlled by a very subtle change in electronic as well as steric factors of porphyrin substituents. Further systematic work is currently in progress in this laboratory to clarify the relationship between substituents and electron configuration in low-spin (*meso*-tetraarylporphyrinato)iron(III) systems.

Conclusion

The electron configuration of a series of low-spin (dicyano){*meso*-tetrakis(2,4,6-trialkylphenyl)porphyrinato}iron(III) complexes, $[Fe(R\text{-}TPP)(CN)_2]^-$ ($R = Me, Et, {}^iPr$), together with $[Fe(Cl\text{-}TPP)(CN)_2]^-$ and $[Fe(TPP)(CN)_2]^-$, has been examined by ^{1}H NMR, ^{13}C NMR, and EPR spectroscopies. The electron configuration of the ferric ions is greatly affected by the substituents at the *meso*-phenyl groups. While the electron-withdrawing ortho chlorine atoms stabilize a common $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration, the electron-donating alkyl groups such as methyl, ethyl, and isopropyl stabilize a less common $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration. The results have been interpreted in terms of the stronger π back-donation from iron(d_π) to cyanide(p_{π^*}) in $[Fe(R\text{-}TPP)(CN)_2]^-$ than in $[Fe(Cl\text{-}TPP)(CN)_2]^-$; the d_π−p_{π^*} interaction lowers the iron $d_\pi(d_{xz},d_{yz})$ orbitals relative to the d_{xy} orbital, inducing the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration. Thus, the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ state in $[Fe(R\text{-}TPP)(CN)_2]^-$ is caused by the electronic interactions rather than the steric ones. The results are in contrast to those obtained from *meso*-tetraalkylporphyrin complexes $[Fe(TRP)(CN)_2]^-$ in which porphyrin deformation caused by the bulky *meso*-alkyl groups is the major factor to determine the electron configuration.

Acknowledgment. This work was supported by a Grant in Aid for Scientific Research (No. 10640551, to M.N.) from Ministry of Education, Science, Culture and Sports.

Supporting Information Available: ^{13}C NMR chemical shifts of a series of $(R\text{-}TPP)H_2$ taken in $CDCl_3$ at 25 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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