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High-Spin (*meso*-Tetraalkylporphyrinato)iron(III) Complexes As Studied by X-ray Crystallography, EPR, and Dynamic NMR Spectroscopies

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^{1}H NMR spectra of a series of high-spin (*meso*-tetraalkylporphyrinato)iron(III) chlorides, [Fe(TRP)Cl] where R = Me, Et, Pr, or ^{i}Pr, have been measured at various temperatures in CD_2Cl_2 solution. In the case of the Et, Pr, and ^{i}Pr complexes, either the methyl or the methylene signal split into two signals with equal integral intensities at low temperature. In contrast, the Me complex did not show any splitting even at −100 °C. The results have been ascribed to the hindered rotation of the *meso*-alkyl groups about $C_{meso}-C_\alpha$ bonds. The activation free energies for rotation have been determined as 8.0 (−72 °C), 8.5 (−60 °C), and 8.9 (−62 °C) $kcal \cdot mol^{-1}$ for the Et, Pr, and ^{i}Pr complexes, respectively, at coalescence temperatures given in parentheses. The small activation free energy for rotation of the isopropyl groups observed in the present system is explained in terms of the nonplanarity of the porphyrin ring, which has been verified both by the X-ray crystallographic analysis and by the EPR spectrum taken in a frozen CH_2Cl_2−toluene solution. The success in observing the hindered rotation of less bulky primary alkyl groups such as ethyl and propyl groups at an easily accessible temperature range is attributed to the large difference in chemical shifts of the mutually exchanging protons, ca. 3500 Hz in the case of the Et complex, caused by the paramagnetism of the five-coordinated ferric porphyrin complexes.

Introduction

Metal complexes of tetraalkylporphyrins have attracted much attention since their physicochemical properties greatly differ from those of well-documented tetraarylporphyrin complexes.[1−17] One of the reasons for the difference is the nonplanarity of the porphyrin ring in the former complexes. In previous papers, we have reported that the electron configuration of the low-spin ferric ions in a series of (*meso*-tetraalkylporphyrinato)iron(III) complexes, $[Fe(TRP)(CN)_2]^-$, [Fe(TRP)(2-MeIm)(CN)], and $[Fe(TRP)(2\text{-}MeIm)_2]^+$, where R is H, Me, Et, or ^{i}Pr, changes 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 bulkiness of alkyl groups increases.[11,13,18] We have ascribed the anomaly to the S_4-ruffled structure of the porphyrin ring, especially in the ^{i}Pr complex.[11,13] We are then interested in the physicochemical properties of a series of high-spin (*meso*-tetraalkylporphyrinato)iron(III) chlorides, [Fe(TRP)Cl], with various alkyl groups at the *meso* positions, since such complexes are expected to have a ruffled porphyrin ring and exhibit some novel electronic and stereodynamic properties.

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(18) Abbreviations: TRP, dianion of *meso*-tetraalkylporphyrin where R is a methyl (Me), ethyl (Et), propyl (Pr), isopropyl (^{i}Pr), or *tert*-butyl (^{t}Bu) group; TMCP, dianion of the tetramethylchiroporphyrin described in ref 17; OETPP, dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin; $TMPCl_8$, dianion of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetramesitylporphyrin; TCHP, diaion of *meso*-tetracyclohexylporphyrin; 2-MeIm, 2-methylimidazole; Py, pyridine.

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Table 1. Crystallographic Parameters for [Fe(T^{i}PrP)Cl]

empirical formula	$C_{28}H_{38}ClFeN_4$
fw	521.92
temp	293(2) K
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	
a	17.514(5) Å
b	9.666(6) Å
c	16.368(3) Å
α	90°
β	90.49(2)°
γ	90°
vol	2771(2) Å^3
Z	4
wavelength	0.710 69 Å
dens(calcd)	1.251 Mg/m^3
abs coeff	0.663 mm^{-1}
F(000)	1108
cryst size	0.5 × 0.3 × 0.2 mm
θ range for data collcn	2.33−27.48°
index range	$0 \le h \le +22$, $0 \le k \le +12$, $-21 \le l \le +21$
reflcns collctd	3167
independent reflcns	3167 [*R*(int) = 0.0000]
refinement method	full-matrix least squares on F^2
data/restraints/param	3167/0/177
goodness-of-fit on F^2	1.093
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0470$, $R_{w2} = 0.1239$
R indices (all data)	$R_1 = 0.0732$, $R_{w2} = 0.1397$
largest diff. peak and hole	0.424 and −0.322 e·Å^{-3}

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [Fe(T^{i}PrP)Cl]

	x	*y*	*z*	*U*(eq)
Fe(1)	0	2281(1)	−2500	26(1)
Cl(1)	0	4596(1)	−2500	46(1)
N(1)	864(1)	1688(2)	−3258(1)	28(1)
N(2)	−718(1)	1843(2)	−3444(1)	29(1)
C(1)	1590(2)	1219(3)	−3052(2)	32(1)
C(2)	1994(2)	937(4)	−3789(2)	41(1)
C(3)	1547(2)	1342(4)	−4423(3)	42(1)
C(4)	839(2)	1812(3)	−4098(2)	31(1)
C(5)	196(2)	2267(3)	−4551(2)	32(1)
C(6)	−537(2)	2225(3)	−4234(2)	32(1)
C(7)	−1233(2)	2339(4)	−4699(2)	45(1)
C(8)	−1811(2)	1961(4)	−4211(2)	45(1)
C(9)	−1502(2)	1660(3)	−3422(2)	33(1)
C(10)	285(2)	2755(4)	−5438(2)	39(1)
C(11)	925(2)	3784(4)	−5551(2)	58(1)
C(12)	305(3)	1564(4)	−6050(2)	59(1)
C(13)	−1909(2)	1224(3)	−2735(2)	32(1)
C(14)	−2756(2)	822(4)	−2832(2)	42(1)
C(15)	−2927(2)	−231(4)	−3497(3)	59(1)
C(16)	−3275(2)	2070(4)	−2868(2)	53(1)

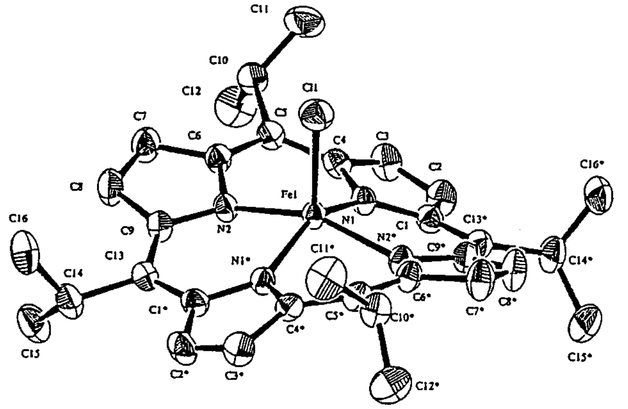

Figure 1. Molecular structure of [Fe(T^{i}PrP)Cl] together with the numbering of the atoms. Thermal ellipsoids are drawn to enclose 50% probability. Selected bond lengths (Å) and angles (deg): Fe−N1, 2.047(2); Fe−N2, 2.028(2); Fe−Cl, 2.238(2); N1−Fe−N2, 86.40(9); N1−Fe−N1*, 147.49(14); N1−Fe−N2*, 86.91(9); N2−Fe−N2*, 155.94(14).

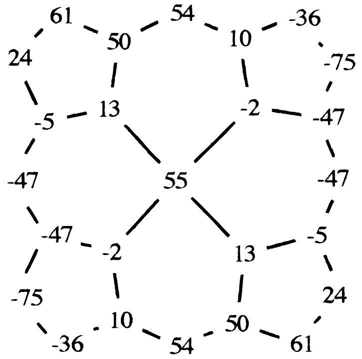

Figure 2. Formal diagram of the porphyrin core of [Fe(T^{i}PrP)Cl] showing displacements of each atom from the mean plane of the 24 atoms in units of 0.01 Å.

Herein, we report the solid and solution structure of high-spin [Fe(T^{i}PrP)Cl] as studied by X-ray crystallography, EPR, and ^{1}H NMR spectroscopies. We also report the novel examples of hindered rotation of simple primary alkyl groups such as ethyl and propyl groups in [Fe(TEtP)Cl] and [Fe(TPrP)Cl], respectively.

Results

Crystal Structure. The crystal data and experimental details are shown in Table 1. Atomic parameters for non-H atoms are given in Table 2. Figure 1 shows the molecular structure of [Fe(T^{i}PrP)Cl] together with the numbering of the atoms and selected bond lengths and angles. Thermal ellipsoids are drawn to enclose 50% probability. Figure 2 is a formal diagram of the porphyrin core showing a pattern of perpendicular displacement of the atoms from the least squares plane of the 24-atom macrocycle core. The porphyrin ring is highly ruffled; the out-of-plane displacements of the two unique *meso* carbon atoms are +0.539 and −0.469 Å. Thus, the perpendicular distance between these atoms is 1.008 Å, which is much smaller than the corresponding values of nonplanar [Zn(T^{t}BuP)(Py)] and [Fe(TMCP)Cl], 1.83 and 1.36 Å, respectively.[6,17] The ruffling dihedral angles, defined by $C_{\alpha}N-NC_{\alpha}$ for nitrogens in opposite pyrroles, are 42.8 and 33.5°. The average $Fe-N_p$ bond length is 2.038 Å, which is much shorter than the normal 2.069 Å found in other high-spin iron(III) porphyrins with anionic axial ligand[19,20] but is quite close to the lengths in highly ruffled [Fe(TMPC)Cl] and highly saddled [Fe(OETPP)Cl], 2.034 and 2.031 Å, respectively.[17,21] The iron atom is displaced toward the chlorine atom by 0.552 Å from the least squares porphyrin plane and by 0.498 Å from the least squares plane of the four nitrogen atoms. All of the isopropyl groups face the same direction and bisect the adjacent pyrrole rings.

EPR Spectroscopy. The EPR spectra of a series of [Fe(TRP)-Cl], where R = H, Me, Et, Pr, and ^{i}Pr, were taken in frozen dichloromethane−toluene (1:1) solution at 4.2 K. All of the complexes except [Fe(T^{i}PrP)Cl] showed axial type spectra typical for high-spin ferric porphyrin complexes; signals were

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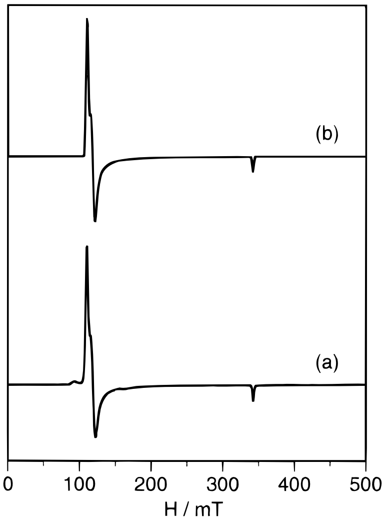

Figure 3. (a) EPR spectrum of [Fe(T^{i}PrP)Cl] taken in frozen CH_2Cl_2–toluene solution at 4.2 K. (b) Computed spectrum using $g = 6.14$, 5.17, and 1.99.

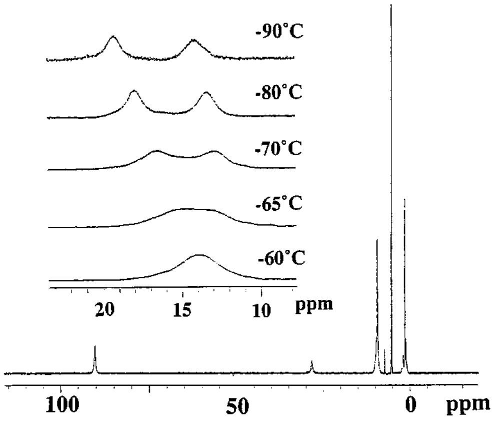

Figure 4. ^{1}H NMR spectrum of [Fe(T^{i}PrP)Cl] taken at 25 °C in a CD_2Cl_2 solution. Inset shows temperature dependence of β-methyl signals.

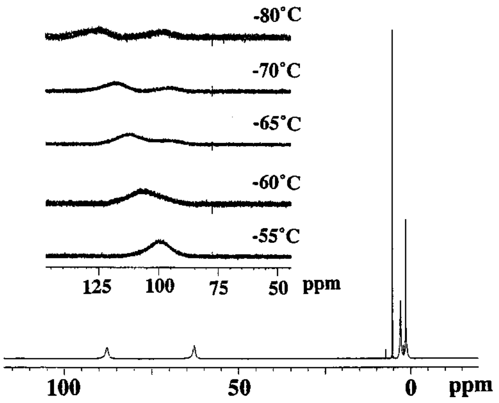

Figure 5. ^{1}H NMR spectrum of [Fe(TPrP)Cl] taken at 25 °C in a CD_2Cl_2 solution. Inset shows temperature dependence of α-methylene signals.

observed at $g = 6.0$ and 2.0.[22] In the case of [Fe(T^{i}PrP)Cl], however, the signal at 6.0 showed a splitting. The g values were determined in this case by the computer simulation of the observed spectrum. The best-fit spectrum shown in Figure 3 was obtained when three g values, 6.14, 5.17, and 1.99, were used for calculation.

^{1}H NMR Spectroscopy. The ^{1}H NMR chemical shifts of a series of [Fe(TRP)Cl] were reported in the previous paper.[11] The pyrrole signals appeared at 77.9, 87.6, 88.6, 87.7, and 90.5 ppm at 25 °C in CD_2Cl_2 solution for the R = H, Me, Et, Pr, and ^{i}Pr complexes, respectively. As the temperature was lowered, these signals moved further downfield and appeared at 113.2, 128.5, 131.5, 133.7, and 125.3 ppm at −70 °C. Figure 4 shows the ^{1}H NMR spectrum of [Fe(T^{i}PrP)Cl] taken at 25 °C as a typical example. Temperature dependent spectra of a series of [Fe(TRP)Cl] were then taken in CD_2Cl_2 solution. In the case of [Fe(T^{i}PrP)Cl], the isopropyl methyl signal splits into two signals with equal integral intensities below −62 °C, as shown in the inset of Figure 4, which indicates that a slow dynamic process takes place on the ^{1}H NMR time scale. These signals shifted to 13.4 and 17.9 ppm at −80 °C. The activation free energy for the dynamic process was calculated to be 8.9 ± 0.2 kcal·mol^{-1} at −62 °C on the basis of the spectral change of the β-methyl signals. Both the isopropyl methine and β-pyrrole signals, though broadened to some extent, did not split even at −90 °C.

Figure 5 shows the temperature dependent ^{1}H NMR spectra of [Fe(TPrP)Cl]. The α-methylene signal of the propyl group, which appeared at 62.9 ppm at 25 °C, split into two signals below −60 °C. These signals shifted to 83.9 and 99.9 ppm at −80 °C, as shown in the inset. The activation free energy was determined to be 8.5 ± 0.2 kcal·mol^{-1} at −60 °C. Although the β and γ signals, observed at 1.29 and 2.95 ppm at 25 °C, respectively, showed some broadening at lower temperature, they did not split even at −80 °C. Similar temperature dependence was observed in [Fe(TEtP)Cl]. The α-methylene signal at 61.3 ppm at 25 °C split into two signals below −70 °C. These signals moved to 85.3 and 99.9 ppm at −80 °C. In contrast to the α-methylene signal, the β-methyl signal did not show splitting even at −90 °C, though it broadened considerably. The activation free energy was calculated to be 8.0 ± 0.2 kcal·mol^{-1} at −72 °C. Contrary to the case of the Et, Pr, and ^{i}Pr complexes, the methyl signal in [Fe(TMeP)Cl] showed no splitting even at −100 °C. Thus, the dynamic NMR studies have revealed that the order of the activation free energies for the dynamic process is ^{i}Pr $\geq$ Pr $>$ Et $\gg$ Me.

Discussion

As expected, the X-ray crystallographic study of [Fe(T^{i}PrP)Cl] has revealed that the complex has a highly ruffled porphyrin ring. Figure 2 shows that the two unique *meso* carbon atoms are located out of the mean porphyrin plane by +0.539 and −0.469 Å. The perpendicular distance between these carbons, 1.008 Å, is much smaller than the corresponding value in S_4-ruffled [Fe(TMCP)Cl], 1.36 Å.[17] It should be noted, however, that the largest perpendicular distance in [Fe(T^{i}PrP)Cl] is not the distance between two adjacent *meso* carbons but the distance between C2 and C7 atoms, 1.356 Å. The result suggests that the porphyrin ring of [Fe(T^{i}PrP)Cl] is not classified as a purely ruffled structure. In order to find out the nonplanar mode of [Fe(T^{i}PrP)Cl], the perpendicular displacements of the peripheral carbon atoms from the mean porphyrin plane are plotted in Figure 6. The data from [Zn(T^{t}BuP)Py] and [Fe(OETPP)Cl] are also plotted in Figure 6 as typical examples for the S_4-ruffled and S_4-saddled conformations, respectively.[6,21] In general, the most deviated carbon atoms from planarity are *meso* carbons, C5, C10, C15, C20, in ruffled complexes, while those in saddled complexes are pyrrole β-carbons, C2, C3, C7, C8, etc. The

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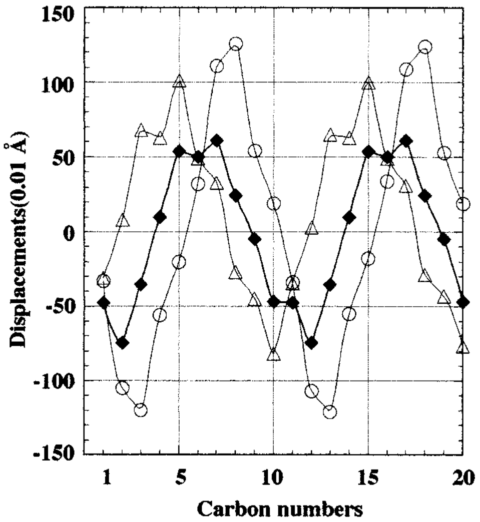

Figure 6. Displacements of the peripheral carbon atoms from the mean plane of the 24 atoms. Carbon numbers in abscissa are based on the IUPAC numbering system. ♦, [Fe(T^{i}PrP)Cl]; △, Zn(T^{t}BuP)Py]; ○, [Fe(OETPP)Cl].

curves in Figure 6 clearly indicate that the nonplanar mode of [Fe(T^{i}PrP)Cl] is quite unique because the largest deviations in this complex are found in the carbons such as C5, C6, and C7. Thus, the porphyrin ring in [Fe(T^{i}PrP)Cl] is the hybrid of a ruffled and a saddled conformation in the solid. The unique deformation mode of the porphyrin core might be ascribed to the conformation of the isopropyl groups, which will be discussed later in this section.

Evidence for the distortion of the porphyrin ring in [Fe(T^{i}PrP)Cl] was also obtained from the EPR spectrum taken in a frozen CH_2Cl_2−toluene solution. Although the R = H, Me, Et, and Pr complexes all showed axial type spectra with $g_\perp = 6.0$ and $g_\parallel = 2.0$, the ^{i}Pr complex gave three signals at $g = 6.14$, 5.17, and 1.99, as shown in Figure 3. The results can be explained as follows. The deformed porphyrin ring in a frozen CH_2Cl_2−toluene solution induces a rhombic environment around the ferric ion. In fact, the X-ray crystallographic analysis of this complex has revealed that there are two different Fe−Np distances, 2.047 and 2.028 Å, resulting in the split of the $g_\perp$ signal into a g_x and a g_y signal. A similar phenomenon was observed in highly saddled [Fe(TMPCl$_8$)Cl] and [Fe(TMPBr$_8$)Cl].[23]

As mentioned, some of the alkyl signals in the Et, Pr, and ^{i}Pr complexes split into two signals with equal integral intensities at low temperature. The activation free energies for the dynamic process are in a narrow range: 8.0, 8.5, and 8.9 kcal·mol^{-1} for the Et, Pr, and ^{i}Pr complexes, respectively. In contrast, [Fe(TMeP)Cl] did not show any splitting even at −100 °C. There are two possible mechanisms that could explain the observed temperature dependence: (i) rotation of the *meso*-alkyl groups about C_{meso}−C_α(alkyl) bonds becomes slow on the NMR time scale at low temperature while inversion of the deformed porphyrin ring is still fast, and (ii) inversion of the deformed porphyrin ring becomes slow on the NMR time scale at low temperature while rotation of the *meso*-alkyl groups is still fast. If the observed rate process is ring inversion of the deformed porphyrin ring, the activation free energies in [Fe(TEtP)Cl] and [Fe(TPrP)Cl] must be quite small compared with that of [Fe(T^{i}PrP)Cl] since the porphyrin rings of the former complexes carrying primary alkyl groups at the *meso* carbon atoms are less deformed than that of the latter as revealed from the EPR spectra. In addition, recent molecular mechanics calculation and X-ray crystallographic analysis of [Ni(TRP)] have shown that the porphyrin rings in [Ni(TEtP)] and [Ni(TPrP)] are less deformed than that in [Ni(T^{i}PrP)]; the ruffling dihedral angles for the Et and Pr complexes were calculated to be 21.0 and 20.9°, respectively, as compared with 43.7° in the ^{i}Pr complex determined by X-ray crystallography.[5,8] Thus, the observed dynamic process should be assigned to the hindered rotation of the *meso*-alkyl groups about C_{meso}−C_α(alkyl) bonds rather than the inversion of the deformed porphyrin ring; ring inversion has been observed in highly deformed dodecasubstituted porphyrin complexes.[21,24−26] The result is consistent with that of the recent paper reported by Latos-Grazynski, Marchon and coworkers on the hindered rotation of the cyclohexyl group in high-spin [Fe(TCHP)Cl].[16] The fact that [Fe(TMeP)Cl] did not show any signal splitting even at −100 °C also support the rotation process.

To understand the rotation process of the *meso*-alkyl groups, stable conformations have to be considered on the basis of the ^{1}H NMR results. As shown in Figure 4, the isopropyl methine signal of [Fe(T^{i}PrP)Cl] appeared at 28.9 ppm at 25 °C which should be compared with the chemical shifts of the *meso* α protons in [Fe(TEtP)Cl] and [Fe(TMeP)Cl], 62.1 and 127.6 ppm, respectively. The large upfield shift of the methine signal suggests that the stable conformation of the isopropyl groups is the one where the isopropyl methyl groups bisect the adjacent pyrrole ring, as is observed in the molecular structure in the solid. In such a situation the C_α−H bonds of the isopropyl groups are orientated perpendicularly to the p_z orbitals of the *meso*−carbon atoms.[16] Since the unpaired electron in a ferric ion is transferred to the porphyrin orbitals via metal to ligand charge-transfer mechanism in high-spin ferric porphyrin complexes, the perpendicular alignment between the p_z orbital and C_α−H bond results in a smaller contact shift of the *meso* α-protons.[27−30] This contrasts with the case of [Fe(TMCP)Cl] in which *meso* α-protons appeared fairly downfield, 156.3 and 198.9 ppm at 20 °C, because of the parallel orientation between the C_α−H bond and p_z orbitals.[17] Thus, the solid structure of [Fe(T^{i}PrP)Cl] shown in Figure 1 is maintained in solution in the sense that each isopropyl group bisects the adjacent pyrrole ring. It is difficult, however, to determine if the four isopropyl groups face the same direction as they are in the solid state.

In the case of [Fe(TEtP)Cl] and [Fe(TPrP)Cl] carrying primary alkyl groups at the *meso* positions, the stable conformation must be the one where the C_{meso}−C_α(alkyl)−C_β(alkyl) plane is nearly perpendicular to the porphyrin macrocycle.[26] A priori,

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there are six possible conformers in these complexes depending on the orientation of the *meso*-alkyl groups relative to the Fe−Cl bond. They are SSSS, SSSA, SSAA, SASA, SAAA, and AAAA in which S and A indicate syn and anti orientation relative to the Fe−Cl bond, respectively. It might be reasonable to assume that [Fe(TEtP)Cl] and [Fe(TPrP)Cl] exist as an SASA conformer, since the ^{1}H NMR spectrum at low temperature showed two equivalent signals for the α-methylene protons that is explainable only by this conformation; numbers for the *meso*-α-methylene signals for SSSS, SSSA, SSAA, SASA, SAAA, and AAAA conformers are 1, 4, 4, 2, 4, and 1, respectively. Recent X-ray crystallographic analysis of the Co(II) complex of tetrakis(heptafluoropropyl)porphyrin as well as the molecular mechanics calculation of [Ni(TEtP)] and [Ni(TPrP)] have shown that the SASA conformer generally prevails over others.[8,31] However, as in the case of [Fe(TCHP)Cl], there still remains a possibility that these complexes exist as a mixture of all possible conformers.[16] Two signals with equal integral intensities observed at low temperature can be explained if the methylene protons that are located in the same side of the porphyrin ring in each conformer have similar chemical shifts. Extremely broad signals at −80 °C observed for the methylene signals of [Fe(TEtP)Cl] and [Fe(TPrP)Cl] are suggestive of this case.

On the basis of the discussion described above, the dynamic process observed in the temperature dependent ^{1}H NMR spectra is ascribed to the 180° rotation of the alkyl groups around $C_{meso}-C_{\alpha}$ bonds. The apparent equivalence of the pyrrole protons in these complexes should be ascribed to the small difference in chemical shifts of these protons relative to their broad line widths. Marchon, Scheidt, and co-workers reported that the activation free energy for rotation ($\Delta G^{\neq}$) of the cyclohexyl group in [Zn(TCHP)] is 11.4 kcal·mol^{-1} (−40 °C).[4] In the present case, the $\Delta G^{\neq}$ value of the isopropyl group is 8.9 kcal·mol^{-1} (−62 °C). Thus, the decrease in $\Delta G^{\neq}$ on going from cyclohexyl to isopropyl group is 2.5 kcal·mol^{-1}. Mannschreck and co-workers reported that the $\Delta G^{\neq}$ values of the cyclohexyl and isopropyl groups bonded to mesitylene are 14.4 (−1 °C) and 12.8 (−35 °C) kcal·mol^{-1}, respectively.[32,33] The decrease in $\Delta G^{\neq}$ in this system is 1.6 kcal·mol^{-1}. Since the absolute values of activation entropy for rotation are less than 10 eu in many cases,[34] we can say that the decrease in the $\Delta G^{\neq}$ value on going from cyclohexyl to isopropyl in the porphyrin system is slightly larger than that in the mesitylene system. The result could be ascribed to the nonplanarity of the porphyrin ring in [Fe(T^{i}PrP)Cl].

In general, barriers to rotation of simple primary alkyl groups such as ethyl and propyl groups about a $C_{sp^3}-C_{sp^2}$ bond are very low, and few examples have been reported on the restricted rotation of these groups by the dynamic NMR method.[25,34−36] Some time ago, the hindered rotation of alkyl groups in a series of *N*-alkyl-4-methyl-Δ^4-thiazoline-2-thiones was reported.[37,38] The barriers to rotation of the ethyl and propyl groups about $C_{sp^3}-N_{sp^2}$ bonds were very small, 6.9 (−122 °C) and 7.1 (−119 °C) kcal·mol^{-1}, respectively, at the coalescence temperature given in parentheses. As these examples suggest, an extremely low temperature is necessary to detect the hindered rotation of ethyl and propyl groups. In the present case, we were able to observe the rotation process of the primary alkyl groups at an easily accessible temperature range; T_c's are −60 to −70 °C. The success is ascribed to the large difference in chemical shifts of the mutually exchanging protons, ca. 3500 Hz in the case of the Et complex, caused by the paramagnetism of the five-coordinated ferric porphyrin complexes.

Conclusion

We have determined the molecular structure of high-spin [Fe(T^{i}PrP)Cl] and have found that the porphyrin ring is highly deformed in a unique fashion, the hybrid of a ruffled and a saddled conformation. Corresponding to the crystal structure, the EPR spectrum of this complex has shown a split of the $g_{\perp}$ signal. Because of the deformation of the porphyrin ring, the barrier to rotation of the isopropyl groups about $C_{meso}-C_{\alpha}$ bonds showed a smaller value than those expected from the other examples. The dynamic NMR study has also shown novel examples of the hindered rotation of simple primary alkyls such as ethyl and propyl groups in [Fe(TPrP)Cl] and [Fe(TEtP)Cl]. The activation free energies for rotation are in the range of 8.0−8.9 kcal·mol^{-1}.

Experimental Section

Materials. *meso*-Tetraalkylporphyrins were prepared according to the literature.[11] Insertion of iron was carried out in refluxing methanol−chloroform (1:3) with $FeCl_2 \cdot 4H_2O$. The complexes were recrystallized from CH_2Cl_2−hexane.

Spectroscopy. ^{1}H NMR spectra were recorded in CD_2Cl_2 solution on a JEOL LA 300 spectrometer operating at 300 MHz. EPR spectra were measured at 4.2 K in frozen CH_2Cl_2−toluene solution on a Bruker EPA-300 spectrometer operating at X band and equipped with an Oxford cryostat. Computer simulation of the observed spectrum was carried out by using the standard equation.

Activation Free Energies for Rotation. The rate constant (k_c) for rotation at the coalescence temperature (T_c) was determined by the equation $k_c = \pi\Delta\nu/(2)^{1/2}$,where $\Delta\nu$ is the difference in chemical shifts when the rotation is slowed down on the NMR time scale. Since the chemical shifts are temperature dependent in paramagnetic molecules, the $\Delta\nu$ value at T_c was determined by the extrapolation from the values at lower temperatures. The activation free energy was estimated at T_c by the equation $\Delta G^{\neq} = RT_c\{22.96 + \ln(T_c/\Delta\nu)\}$.[34,35] Difficulties in determining the coalescence temperature have arisen because (i) the $\Delta\nu$ values of exchanging protons at T_c's are very large, 1000−3500 Hz and (ii) the half-height widths of mutually exchanging protons are different. Thus, the accuracy in determining the coalescence temperature is ±2 °C. Furthermore, determination of the $\Delta\nu$ value at the coalescence temperature might include ca. 20% error since the value was extrapolated from low temperature. Accordingly, the activation free energy for hindered rotation was presented with the precision of ±0.2 kcal·mol^{-1}.

X-ray Crystallography. Crystals of [Fe(^{i}PrP)Cl] for structure determination were grown by the slow diffusion of heptane into a chloroform solution of the complex. A crystal, 0.5 × 0.3 × 0.2 mm, was used for the X-ray structure analysis. Unit cell parameters were determined using 25 reflections in the range $28° < 2\theta < 30°$. Three-dimensional intensity data were collected on a Rigaku AFC5-S four-circle diffractometer using Mo Kα radiation (40 kV, 25 mA, λ = 0.710 69 Å) up to $\sin\theta/\lambda \leq 0.65$ ($0 \leq h \leq +22$, $0 \leq k \leq +12$, $-21 \leq l \leq +21$) by means of an $\omega-2\theta$ scan technique at 8° min^{-1} in ω. A total of 3167 reflections was measured, of which 2419 with $I > 2\sigma(I)$ were used for the structure determination. Absorption collection

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was applied. The structure was solved by the direct method using SIR-92 in TEXSAN[39] and refined by the full-matrix least squares technique in SHELXL-93,[40] based on F^2 and with $\omega = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 0.5782P]$, where $P = (F_o^2 + 2F_c^2)/3$. The positions of all the hydrogen atoms were calculated geometrically. Anisotropic thermal parameters were applied to non-H atoms. A total of 177 parameters was refined. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974, Vol. IV).[41] Final R and R_ω values were 0.047 and 0.123 ($I > 2\sigma(I)$), respectively; $S = 1.118$. A Crystallographic Information File (CIF) has been deposited with the Cambridge Crystallographic Data Centre (CCDC).

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Supporting Information Available: Tables of bond lengths, bond angles, torsion angles, anisotropic displacement parameters, hydrogen coordinates and figures of Curie plots of each proton in [Fe(TEtP)Cl], [Fe(TPrP)Cl], and [Fe(T^{i}PrP)Cl]. This material is available free of charge via the Internet at http://pubs.acs.org.

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