Barriers to Inversion of Nonplanar Ferric Porphyrin Radical Cations: Comparison with the Corresponding Neutral Complexes

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Received February 1, 1999

Barriers to inversion of the highly deformed porphyrin rings in two ferric porphyrin radical cations, [Fe(OMTPP)-Cl]SbCl$_6$ and [Fe(OETPP)Cl]SbCl$_6$ where OMTPP and OETPP are dianions of 2,3,7,8,12,13,17,18-octamethyl- and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, respectively, have been determined by the dynamic NMR method. Inversion barrier of [Fe(OMTPP)Cl]SbCl$_6$ is estimated to be 14.8 kcal mol^{-1} (72 °C) which is higher than that of the corresponding neutral porphyrin complex [Fe(OMTPP)Cl] by more than 4 kcal mol^{-1}. Increase in barrier to inversion has also been observed in [Fe(OETPP)Cl]SbCl$_6$, though the precise determination is hampered in this case due to the occurrence of site exchange of the ferric ion across the porphyrin ring; the latter process is verified because the activation free energies obtained from the line shape analysis of the meta and methyl signals are quite close, 18.1 (113 °C) and 17.9 (113 °C) kcal mol^{-1}, respectively. Thus, the inversion barrier in [Fe(OETPP)Cl]SbCl$_6$ is supposed to be ≫18 kcal mol^{-1}. Since the inversion barrier in the corresponding neutral porphyrin complex [Fe(OETPP)Cl] is reported to be 15.8 kcal mol^{-1}, the barrier has increased by ≫2 kcal mol^{-1}. These results are interpreted in terms of the enhanced nonplanarity of the radical cations as compared with the corresponding neutral complexes. The interaction between porphyrin a$_{2u}$ and iron d$_{x^2-y^2}$ orbitals in the radical cations, which is expected to be strengthened in the deformed structure, could be one of the reasons for the conformational change.

Introduction

Nonplanar porphyrin ring in ferric porphyrin complexes has been a current interest since it is supposed to be related with important functional roles in biological systems.[1] Typical examples of nonplanar porphyrin rings are 2,3,7,8,12,13,17,18-octa-alkyl-5,10,15,20-tetraphenylporphyrins (ORTPP)H$_2$ where R is methyl or ethyl group.[2−4] These porphyrins as well as their metal complexes are known to adopt highly S4 saddled conformation both in solution and in the crystalline state.[4,5] Because of the nonplanarity of the porphyrin ring, these compounds exhibit some pronounced properties; a large red shift in the absorption spectra,[6,7] a lowering of the oxidation potential,[7,8] and a change in the spin state of a high spin ferric ion into an admixed intermediate.[9]

The other interesting properties of these complexes are dynamic processes such as ring inversion of the deformed porphyrin ring and hindered rotation of the coordinated planar ligands.[10−12] Because of the highly deformed structure, the activation free energy for inversion in [Zn(OETPP)] was directly obtained by the dynamic NMR technique to be 16.2 kcal mol^{-1}.[4] In the course of our research on ferric porphyrin radical cations with deformed porphyrin ring,[13] we have encountered an interesting phenomenon; a large increase in barriers to ring inversion of radical species as compared with those of the starting high spin ferric porphyrin complexes. In this paper, we describe the formation and characterization of two radical cations with deformed porphyrin ring, [Fe(OMTPP)Cl]SbCl$_6$ and [Fe-(OETPP)Cl]SbCl$_6$, report the dynamic processes in these complexes such as ring inversion of porphyrin rings, hindered rotation of *meso*-phenyl groups, and site exchange of ferric ions across the porphyrin hole, and compare the activation free energies for these processes with those of the corresponding neutral porphyrin complexes, [Fe(OMTPP)Cl] and [Fe(OETPP)-Cl], reported recently.[9]

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Table 1. Chemical Shifts of Ferric Porphyrins and Their Radical Cations Taken at 25 °C in $C_2D_2Cl_4$ Solution

	pyrrole			phenyl		
complexes	H	CH_2	CH_3	o-H	m-H	p-H
[Fe(TPP)Cl]	80.1	−	−	6.2 3.8	12.6 12.0	5.8
[Fe(OMTPP)Cl][a]	−	−	51.1	11.3 8.6	12.5 12.2	7.4
[Fe(OETPP)Cl][a]	−	49.0 34.8 32.1 20.1	3.2 1.8	11.5 9.1	12.4 12.2	7.5
[Fe(TPP)Cl]$^+$ [b]	68.8	−	−	42.2	−12.3	35.0
[Fe(OMTPP)Cl]$^+$	−	−	69.9 63.0	39.7 36.9	−11.0 −12.5	31.7
[Fe(OETPP)Cl]$^+$	−	71.2 56.1 24.7 16.6	4.4 3.6	37.6 34.9	−10.1 −11.5	28.8

[a] Originally reported by Cheng and co-workers.[9] [b] Data from ref 14.

Experimental Section

Spectroscopy. ^{1}H NMR spectra were recorded at various temperature using CD_2Cl_2 and/or $CDCl_3$ as solvents on a JEOL LA 300 spectrometer operating at 300.4 MHz. For high-temperature measurement, 1,1,2,2-tetrachloro-1,2-dideuterioethane ($C_2D_2Cl_4$), bp 146.3 °C, was used. Chemical shifts were referenced to residual solvent peaks (δ 5.35 ppm for CD_2Cl_2, δ 7.25 ppm for $CDCl_3$, and δ 5.92 ppm for $C_2D_2Cl_4$).

Synthesis. Free base porphyrins, $(OMTPP)H_2$ and $(OETPP)H_2$, were prepared from benzaldehyde and the corresponding pyrroles according to the literature.[4] Insertion of iron was performed using $FeCl_2 \cdot 4H_2O$ in refluxing DMF followed by the purification of the product by the reported method.[6] [Fe(OMTPP)Cl] and [Fe(OETPP)Cl] showed the same UV−vis and ^{1}H NMR spectral properties as those reported by Cheng and co-workers for these complexes.[9]

[Fe(OMTPP)Cl]SbCl$_6$. Dichloromethane solution containing 10.0 mg (1.2×10^{-5} mol) of [Fe(OMTPP)Cl] was treated with 6.4 mg (1.2×10^{-5} mol) of phenoxathiinylium hexachloroantimonate (Phenox)-SbCl$_6$.[14] The reaction mixture was stirred for 10 min at room temperature, and hexane was slowly added for crystallization. The crystals thus formed were dried in vacuo and dissolved into $C_2D_2Cl_4$ for NMR measurement. The chemical shifts in $C_2D_2Cl_4$ at 25 °C are listed in Table 1. UV−vis (CH_2Cl_2): λ_{max}, nm (log ϵ): 396 (4.80).

[Fe(OETPP)Cl]SbCl$_6$. This complex was prepared and crystallized similarly as described above. The chemical shifts in $C_2D_2Cl_4$ at 25 °C are also listed in Table 1. UV−vis(CH_2Cl_2): λ_{max}, nm (log ϵ): 393 (4.89).

Activation Free Energies for Inversion. The rate constant (k_c) for ring inversion at the coalescence temperature (T_c) was determined by the equation, $k_c = \pi\Delta\nu/\sqrt{2}$, where $\Delta\nu$ is the difference in chemical shifts of the mutually exchanging signals in [Fe(OMTPP)Cl]SbCl$_6$ and [Fe(OETPP)Cl]SbCl$_6$ when ring inversion is slowed on the NMR time scale. Since the chemical shifts are temperature dependent in paramagnetic molecules, the $\Delta\nu$ at T_c was extrapolated from the values at low temperatures. The activation free energy was estimated at T_c by the equation, $\Delta G^{\ddagger} = RT_c\{22.96 + \ln(T_c/\Delta\nu)\}$.[15]

Results

^{1}H NMR Spectra. Figures 1 and 2 show the ^{1}H NMR spectra of radical cations, [Fe(OMTPP)Cl]SbCl$_6$ and [Fe(OETPP)Cl]-SbCl$_6$, respectively, taken at 20 °C in $C_2D_2Cl_4$. Table 1 presents the chemical shifts of these complexes at 25 °C together with
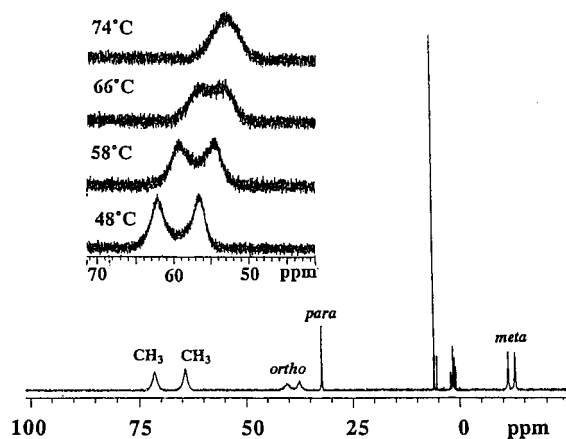
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Figure 1. ^{1}H NMR spectrum of [Fe(OMTPP)Cl]SbCl$_6$ taken in $C_2D_2Cl_4$ at 20 °C. Temperature dependence of the methyl signals is given in the inset.
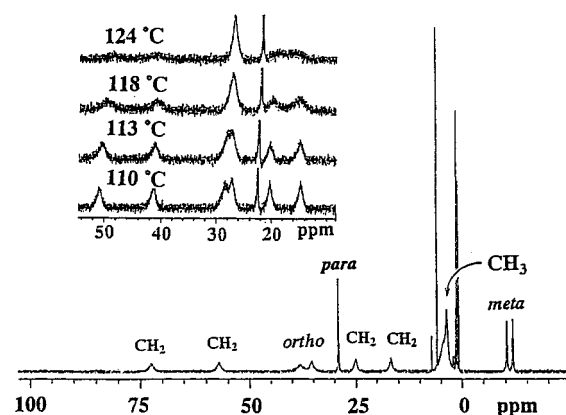

Figure 2. ^{1}H NMR spectrum of [Fe(OETPP)Cl]SbCl$_6$ taken in $C_2D_2Cl_4$ at 20 °C. Temperature dependence of the methylene and ortho signals is shown in the inset.

those of the starting ferric porphyrin complexes. Chemical shifts of [Fe(TPP)Cl] and [Fe(TPP)Cl]SbCl$_6$ are also listed for comparison.[14] While the methyl protons in [Fe(OMTPP)Cl] gave a single peak at 52.1 ppm at 20 °C, those in [Fe(OMTPP)Cl]-SbCl$_6$ showed two separate signals at 71.4 and 64.2 ppm. The data in Table 1 indicate that the phenyl signals of three radical cations showed a similar tendency in the sense that the ortho and para signals appeared downfield while the meta signals appeared upfield.

Activation Free Energies. (i) [Fe(OMTPP)Cl]$^+$. Although the methyl protons in [Fe(OMTPP)Cl]SbCl$_6$ showed two different signals at 20 °C, they broadened at higher temperature as shown in the inset of Figure 1. The coalescence temperature of the two signals was determined to be 72 °C. The activation free energy for the dynamic process was estimated as 14.8 kcal mol^{-1} at this temperature. The value was more than 4 kcal mol^{-1} higher than that of the corresponding [Fe(OMTPP)Cl].[9] Temperature dependence was also observed in the phenyl signals; the ortho and meta signals broadened and coalesced at 92 and 88 °C, respectively. The activation free energies were calculated to be 16.4 (92 °C) and 16.6 (88 °C) kcal mol^{-1}. Curie plots of the methyl, ortho, meta, and para signals are given in Figures S1−S4 of the Supporting Information, respectively.

(ii) [Fe(OETPP)Cl]$^+$. The methylene protons in [Fe(OETPP)-Cl]SbCl$_6$ gave four separate signals at 20 °C. These signals started to broaden as the temperature was raised above 100 °C as shown in the inset of Figure 2. Although the two upfield signals became close to a coalescence at 124 °C, the sample

Table 2. Activation Free Energies (kcal mol^{-1}) for the Dynamic Processes Obtained in $C_2D_2Cl_4$ Together with the Coalescence Temperatures in Parentheses

complexes	inversion	phenyl rotation	site exchange
[Fe(TPP)Cl]	−	16.1 (60 °C)[a]	≥16.1 (60 °C)[g]
[Fe(OMTPP)Cl]	10.1 (−30 °C)[b]	16.6 (96 °C)[e]	≫18 (150 °)[g]
	10.5 (−15 °C)[c]	16.6 (68 °C)[f]	
[Fe(OETPP)Cl]	15.8 (100 °C)[b]	18.9 (140 °C)[e]	≫18 (150 °C)[d]
	15.7 (70 °C)[c]	18.7 (92 °C)[f]	
	16.0 (108 °C)[d]		
[Fe(TPP)Cl]$^+$	−	∼16 (60 °C)[g]	12.4 (8 °C)[e]
			12.1 (−10 °C)[f]
[Fe(OMTPP)Cl]$^+$	14.8 (72 °C)[c]	16.4 (92 °C)[e]	∼18 (113 °C)[g]
		16.6 (88 °C)[f]	
[Fe(OETPP)Cl]$^+$	≫18 (124 °C)[g]	≥18 (113 °C)[g]	18.1 (113 °C)[c]
			>17.0 (124 °C)[d]
			17.8 (118 °C)[e]
			17.9 (113 °C)[f]

[a] Data from ref 23. [b] Data from ref 9. [c–f] Values obtained by the line shape analysis of the methyl, methylene, ortho, and meta signals, respectively. [g] See the text for the estimation.

started to decompose at this temperature. Thus, the activation free energy was estimated to be >17.0 kcal mol^{-1} at 124 °C. The methyl protons showed two unsymmetrical signals at 4.38 and 3.64 ppm at 20 °C and moved upfield as the temperature was raised. These signals coalesced at 113 °C, yielding the activation free energy of 18.1 kcal mol^{-1}. The ortho and meta signals also broadened and coalesced at 118 and 113 °C, respectively. Analysis of these signals yielded activation free energies of 17.8 (118 °C) and 17.9 (113 °C) kcal mol^{-1}, respectively. Temperature dependence of the ortho signals is also demonstrated in the inset of Figure 2. Curie plots of the methyl, methylene, ortho, meta, and para signals are given in Figures S5−S9 of the Supporting Information, respectively.

(iii) [Fe(OMTPP)Cl]. Cheng and co-workers determined the activation free energy for ring inversion to be 10.1 kcal mol^{-1} in CD_2Cl_2 at −30 °C by monitoring the methyl signals.[9] We obtained a slightly higher value: 10.5 kcal mol^{-1} in $C_2D_2Cl_4$ at −15 °C. The line shape analysis of the ortho and meta signals was also carried out. The activation free energies were 16.6 (96 °C) and 16.6 (68 °C) kcal mol^{-1}, respectively, at the coalescence temperatures given in the parentheses.

(iv) [Fe(OETPP)Cl]. The activation free energy of 15.8 (100 °C) kcal mol^{-1} was reported for ring inversion based on the line shape analysis of the methylene signals.[9] We obtained a similar value, 16.0 (108 °C) kcal mol^{-1}, from the change in line shape of the methylene signals; four methylene signals broadened, coalesced and then gave two broad signals above 110 °C. These signals gradually sharpened on further raising the temperature. The line shape analysis of the methyl signals also yielded a similar value, 15.7 (70 °C) kcal mol^{-1}. In contrast, the activation free energies obtained form the ortho and meta signals were much higher, 18.9 (140 °C) and 18.7 (92 °C) kcal mol^{-1}, respectively. Table 2 summarizes the activation free energies obtained from various protons in the radical cations and the corresponding neutral complexes.

Discussion

^{1}H NMR Spectra of Radical Cations. The data in Table 1 indicate that the three radical cations are classified as the same type: a_{2u} porphyrin π-radicals.[14,16,17] A characteristic feature in this type of radical is the large spin densities on the meso

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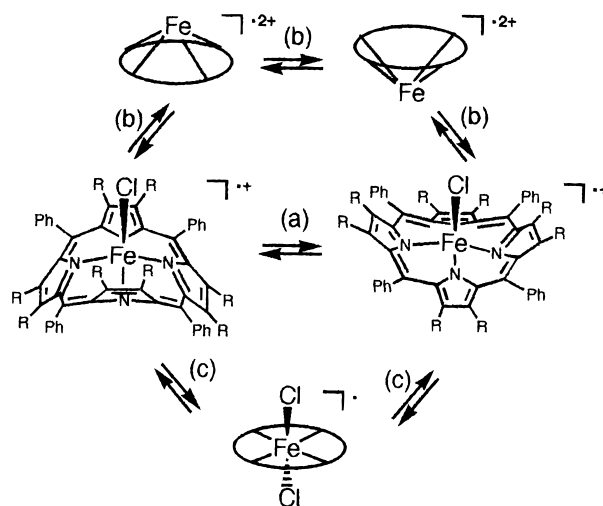

Figure 3. Possible mechanisms for the dynamic processes: inversion of the deformed porphyrin ring (a) and site exchange of a ferric ion across the porphyrin ring by the dissociative (b) and associative (c) pathways.

carbons which induce large isotropic shifts of the meso phenyl protons in the ^{1}H NMR spectrum as exemplified by the extremely downfield-shifted ortho and para signals and upfield-shifted meta signals.[14,17] Close inspection of the data in Table 1 reveals, however, that the difference in chemical shifts of the phenyl signals between neutral and radical cationic complexes decreases on going from [Fe(TPP)Cl]SbCl$_6$ to [Fe(OMTPP)-Cl]SbCl$_6$ and then to [Fe(OETPP)Cl]SbCl$_6$. For example, the downfield shift of the para signals in TPP complexes is 29.2 ppm as compared with 24.3 and 21.3 ppm in OMTPP and OETPP complexes, respectively. Similar tendency was observed for the ortho signals. The results might be ascribed to the enhanced antiferromagnetic coupling between radical and ferric ion in the deformed porphyrin complexes.[8,14] Difference in spin state of the ferric ion in the deformed system could be another reason for the smaller isotropic shifts of the phenyl protons.[9]

Mechanisms for the Dynamic Processes. (i) General Consideration. Figure 3 shows possible dynamic processes to be considered in these complexes. They are (i) inversion of the deformed porphyrin ring as shown in process (a),[4] (ii) site exchange of a ferric ion across the porphyrin ring via dissociation and association of chloride as shown in process (b),[18] and (iii) rotation of phenyl groups about $C_{meso}-C_{phenyl}$ bonds(not shown in Figure 3).[15,19] If excess chloride exists in solution, the site exchange of a ferric ion would take place by an associative mechanism given in process (c).[18] At a low temperature where all of the three processes are frozen, each of the methyl, ortho, and meta protons of [Fe(OMTPP)Cl]SbCl$_6$ should give two signals. At a high temperature where all these processes are fast on the ^{1}H NMR time scale, only one signal should be observed for each of the methyl, ortho, and meta protons. Since the activation free energies obtained from the line shape analysis of the ortho and meta signals should be the same in any case, we can obtain two kinds of activation free energies, $\Delta G^{\ddagger}$(Me) and $\Delta G^{\ddagger}$(ortho or meta). If porphyrin inversion is a process with the lowest energy barrier, then $\Delta G^{\ddagger}$(Me) < $\Delta G^{\ddagger}$(ortho or meta); inversion of the deformed porphyrin ring does not affect the line shape of the ortho and meta signals. In this case, $\Delta G^{\ddagger}$(Me) indicates the activation free energy for porphyrin inversion. If site exchange of a ferric ion shown in process (b)

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or (c) of Figure 3 has the lowest barrier, $\Delta G^{\ddagger}(Me) = \Delta G^{\ddagger}$-(ortho or meta); site exchange of a ferric ion makes not only the methyl groups but also the ortho and meta protons equivalent. In this case, we can only say that the activation free energy for porphyrin inversion is higher than $\Delta G^{\ddagger}(Me)$ or $\Delta G^{\ddagger}$-(ortho or meta). Additional pieces of evidence is necessary to determine the barrier to ring inversion. If phenyl rotation is a process with the lowest barrier, $\Delta G^{\ddagger}(Me) > \Delta G^{\ddagger}(ortho\ or\ meta)$. In this case, $\Delta G^{\ddagger}(Me)$ indicates either a barrier to porphyrin inversion or a barrier to site exchange of the ferric ion through the porphyrin hole. Again, we need some additional information to determine which process is taking place.

(ii) [Fe(OMTPP)Cl]$^+$. Coalescence behavior of the methyl signals at 72 °C in [Fe(OMTPP)Cl]SbCl$_6$ suggests that either a ring inversion or a site exchange of the ferric ion is taking place on the ^{1}H NMR time scale. As mentioned, we can differentiate ring inversion from site exchange by the line shape analysis of the phenyl signals. The activation free energy of 14.8 (72 °C) kcal mol^{-1} obtained from the methyl signals was much smaller than those obtained from the ortho and meta signals, 16.4 (92 °C) and 16.6 (88 °C) kcal mol^{-1}, respectively. Since activation entropy is considered to be a large positive or a large negative value for the dissociative or associative pathway presented in process (b) or (c) of Figure 3, respectively, one has to be very careful to conclude the existence of two different dynamic processes on the basis of the different activation free energies. We concluded, however, that the activation free energies obtained from the methyl and ortho signals (or meta signals) correspond to the different dynamic processes; even if activation entropy is +20 or −20 eu for the dissociative or associative pathway, respectively,[20,21] the difference in $\Delta G^{\ddagger}$ between 72 and 92 °C is at most ±0.4 kcal mol^{-1}. Thus, the rate process with $\Delta G^{\ddagger} = 14.8$ kcal mol^{-1} is assigned to the ring inversion of the deformed porphyrin ring. The rate process with 16.4 or 16.6 kcal mol^{-1} is then ascribed to either phenyl rotation or site exchange of the ferric ion across the porphyrin ring. We ascribed it to the phenyl rotation by the reason described later in this paper. It should be noted that the sample must be very pure since addition of 0.05 equiv of tetrabutylammonium chloride caused considerable effect on the line shape of each signal as shown in Figure S10 of the Supporting Information; two signals observed for the methyl, ortho, and meta protons at 25 °C changed to a single line due to the enhanced rate for site exchange of the ferric ion by the associative process.[18]

(iii) [Fe(OETPP)Cl]$^+$. In the case of [Fe(OETPP)Cl]SbCl$_6$, both porphyrin inversion and site exchange of the ferric ion are frozen on the ^{1}H NMR time scale at 25 °C as is clear from the four separated methylene signals. These signals should change to two signals if either porphyrin inversion or site exchange of the ferric ion becomes fast on the ^{1}H NMR time scale. As mentioned, coalescence of four signals into two was not observed even at 124 °C. Thus, the activation free energies for both porphyrin inversion and site exchange of the ferric ion were estimated to be >17.0 kcal mol^{-1} at 124 °C. Activation free energy was directly obtained, however, from the methyl signals as 18.1 kcal mol^{-1} at 113 °C. The value was quite close to those obtained form the ortho and meta signals, 17.8 (118 °C) and 17.9 (113 °C) kcal mol^{-1}, respectively. Similarity of the activation free energies obtained from the three different probes strongly suggests that the dynamic process can be assigned to site exchange rather than inversion of the deformed porphyrin ring. Since the activation free energy for site exchange of the ferric ion in [Fe(OETPP)Cl]SbCl$_6$, 18.1 kcal mol^{-1}, is expected to be quite close to that in [Fe(OMTPP)Cl]SbCl$_6$, the rate process with $\Delta G^{\ddagger} = 16.4$ to 16.6 kcal mol^{-1} obtained from the ortho and meta signals in [Fe(OMTPP)Cl]SbCl$_6$ should be ascribed to the phenyl rotation. On the basis of the discussion given above, inversion barrier in [Fe(OETPP)Cl]SbCl$_6$ is considered to be much higher than 18.1 kcal mol^{-1} at 113 °C. In principle, barrier to inversion can be obtained from the line shape analysis of the methylene signals. The four methylene signals should change into two signals due to site exchange of the ferric ion. The two signals should then coalesce to give a single line at higher temperature by ring inversion. The coalescence temperature corresponding to the latter process must be very high in [Fe(OETPP)Cl]SbCl$_6$ since four signals were still observed even at 124 °C. Thus, the activation free energy for ring inversion should be expressed as ≫18 kcal mol^{-1} at 124 °C.

(iv) Neutral Porphyrin Complexes. We obtained two different activation free energies, $\Delta G^{\ddagger}(Me)$ and $\Delta G^{\ddagger}(ortho\ or\ meta)$, for the neutral porphyrin complexes such as [Fe-(OMTPP)Cl] and [Fe(OETPP)Cl]. In each complex, $\Delta G^{\ddagger}(Me)$ is smaller than $\Delta G^{\ddagger}(ortho\ or\ meta)$, indicating that the former is the activation free energy for ring inversion as Cheng and co-workers reported.[9] The latter is then ascribed to the activation free energy for either phenyl rotation or site exchange of the ferric ion. As mentioned, these processes can be differentiated in the case of [Fe(OETPP)Cl] by the line shape analysis of the methylene signals. In fact, four methylene signals in [Fe-(OETPP)Cl] broadened, coalesced at 108 °C, and then changed into two broad signals at 120 °C due to ring inversion. These two signals gradually sharpened as the temperature was further raised; the half-height widths were 820 and 830 Hz at 130 °C, 450 and 550 Hz at 140 °C, and 300 and 380 Hz at 150 °C. If site exchange becomes fast on the NMR time scale, these two signals should broaden. Thus, the temperature dependence of these signals strongly suggests that the coalescence temperature is ≫150 °C. Correspondingly, $\Delta G^{\ddagger}$ for site exchange of the ferric ion in [Fe(OETPP)Cl] is ≫18 kcal mol^{-1} at 150 °C. Similar value is expected for [Fe(OMTPP)Cl]. Since $\Delta G^{\ddagger}$ of ≫18 kcal mol^{-1} is much larger than those obtained from the ortho and meta signals in both [Fe(OMTPP)Cl] and [Fe-(OETPP)Cl], the latter could be assigned to the $\Delta G^{\ddagger}$ for phenyl rotation. In Table 2 are given the activation free energies for inversion of porphyrin, rotation of phenyl group, and site exchange of a ferric ion.

Comparison of Barriers to Site Exchange of the Ferric Ions. From the discussion given above, barriers to site exchange of ferric ions in the neutral porphyrin complexes are higher than those in the radical cationic porphyrin complexes; $\Delta G^{\ddagger}$ for [Fe-(OETPP)Cl] is ≫18 kcal mol^{-1} at 150 °C in contrast to 18.1 kcal mol^{-1} at 113 °C in [Fe(OETPP)Cl]SbCl$_6$. A similar phenomenon was observed in TPP system; the ortho and meta phenyl protons in [Fe(TPP)Cl]SbCl$_6$ gave two signals only below 8 and −10 °C, respectively,[14,22] while they maintained two signals up to 60 °C in [Fe(TPP)Cl]. The averaging process of the meta signals in [Fe(TPP)Cl] was explained in terms of the phenyl rotation with $\Delta G^{\ddagger} = 16.1$ (60 °C) kcal mol^{-1}.[23] The

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(22) Although temperature-dependent ^{1}H NMR spectra of [Fe(TPP)Cl]SbCl$_6$ was reported, activation free energy for the dynamic process was not mentioned.[14] Line shape analysis of the ortho and meta signals have yielded activation free energies of 12.4 kcal mol^{-1} (8 °C) and 12.1 kcal mol^{-1} (−10 °C), respectively.

(23) Calculated from the rate constant given in the following reference. Walker, F. A.; La Mar, G. N. *Ann N.Y. Acad. Sci.* **1973**, *206*, 328.

averaging process of the ortho and meta signals in [Fe(TPP)-Cl]SbCl$_6$ observed at lower temperature can then be ascribed to the site exchange of the ferric ion with $\Delta G^{\ddagger} = 12.1$ (-10 °C) to 12.4 (8 °C) kcal mol^{-1}; the activation free energy for phenyl rotation in [Fe(TPP)Cl]SbCl$_6$ is expected to be similar to that in [Fe(TPP)Cl]. The large decrease in barriers to site exchange of a ferric ion on going from neutral to radical cationic complexes could be explained in terms of the decrease in basicity of porphyrin ligands in the latter complexes.[18]

Another interesting phenomenon is a large difference in activation free energies for site exchange of a ferric ion between [Fe(TPP)Cl]SbCl$_6$ and [Fe(OETPP)Cl]SbCl$_6$. While the activation free energy of the former complex was 12.4(8 °C) kcal mol^{-1}, that of the latter complex was 17.8 (118 °C) kcal mol^{-1}. It is well-known that the metal–nitrogen bond length decreases as the porphyrin ring deforms;[24,25] the average Fe–N bond length in [Fe(OETPP)Cl] is 2.031(5) Å as compared with 2.070-(9) Å in [Fe(TPP)Cl].[9,26] One electron oxidation of the complex to form radical cation does not cause a considerable change in metal–nitrogen bond lengths as is shown in the X-ray crystallographic results of [Fe(TpTP)Cl]SbCl$_6$ and [Cu(OETPP)]-ClO$_4$;[8,14] average bond lengths in [Fe(TpTP)Cl]SbCl$_6$ and [Cu(OETPP)]ClO$_4$ are 2.07(1) and 1.974(3) Å, respectively, as compared with 2.070(9) Å in [Fe(TPP)Cl] and 1.973(4) Å in [Cu(OETPP)]. Thus, the large increase in barrier to site exchange of the ferric ion observed on going from [Fe(TPP)Cl]SbCl$_6$ to [Fe(OETPP)Cl]SbCl$_6$ is ascribed to the smaller size of the cavity in the latter complex.

Comparison of Barriers to Phenyl Rotation. The data in Table 2 clearly indicate that the barrier to phenyl rotation in [Fe(TPP)Cl] is similar to those in [Fe(OMTPP)Cl] and [Fe-(OMTPP)Cl]$^+$ despite the apparent difference in steric circumstance of the phenyl groups; they are in the range of 16.1–16.6 kcal mol^{-1}. Barriers to rotation are determined by the energy difference between the ground and transition states.[27] Thus, a small difference in barriers to rotation in [Fe(TPP)Cl] and [Fe(OMTPP)Cl], and probably in [Fe(TPP)Cl]$^+$ and [Fe-(OMTPP)Cl]$^+$, could be ascribed to the nonplanarity of the porphyrin ring. Because of the saddle-shaped conformation, the *meso*-phenyl group could suffer more steric repulsion in the ground state and less steric repulsion in the transition state for rotation than it is expected to suffer in the planar porphyrin complex. Similar phenomenon was reported by Eaton and Eaton who ascribed the smaller barrier to phenyl rotation in Ti-TPP than in Ru-TPP complex to the distortion of the porphyrin ring in the former complex.[19]

Reasons for the Higher Barrier to Inversion in the Radical Cations. As mentioned, activation free energies for ring inversion greatly increased when ferric porphyrin complexes were oxidized to form radical cations; increases in activation free energies were 4.3 and ≫2 kcal mol^{-1} in [Fe(OMTPP)Cl]-SbCl$_6$ and [Fe(OETPP)Cl]SbCl$_6$, respectively. Ring inversion of highly deformed [(OETPP)H$_2$] and their metal complexes has extensively been studied.[3,10] The inversion barriers are very much different from compound to compound, ranging from 12.4

(-15 °C) kcal mol^{-1} in [Co(OETPP)OAc] to >20 (134 °C) kcal mol^{-1} in dication [(OETPP)H$_4$]$^{2+}$. The difference has been explained in terms of the nonplanarity of the porphyrin rings as well as the steric repulsion between NH protons in the case of [(OETPP)H$_4$]$^{2+}$ during the inversion process.[10] Thus, a large increase in inversion barrier observed in this study strongly suggests that the nonplanarity has increased on one electron oxidation of porphyrin ring to form porphyrin radical. There are several papers on X-ray crystallography reporting the saddle shaped structure in porphyrin radical cations.[14,28−32] Fajer and co-workers reported the increase in deformation of porphyrin core on one electron oxidation of [Cu(OETPP)] to form [Cu-(OETPP)]$^+$.[8,33] The additional distortion was attributed to the change in electronic configuration due to the oxidation and to the low-energy barriers between nonplanar conformers with different degree of nonplanarity.[8] The results obtained by the present study suggest that the increase in deformed structure caused by the oxidation is reflected on the large increase in inversion barrier in solution. Since the interaction between a$_{2u}$ and d$_{x^2−y^2}$ orbitals is expected to be stronger in the saddle-shaped porphyrin ring than in the planar one,[8,14] radical formation could deepen the S$_4$-saddled conformation in solution to achieve more favorable interactions between these orbitals. This would be one of the reasons why the difference in chemical shifts of phenyl protons between the neutral and radical cationic complexes decreases on going from [Fe(TPP)Cl]SbCl$_6$ to [Fe(OETPP)Cl]-SbCl$_6$.

Conclusion

Dynamic processes of two ferric porphyrin radical cations with a deformed porphyrin ring, [Fe(OMTPP)Cl]SbCl$_6$ and [Fe-(OETPP)Cl]SbCl$_6$, have been examined by the temperature-dependent NMR method. All of the three possible processes, i.e., inversion of the deformed porphyrin ring, site exchange of the ferric ion across the porphyrin hole, and phenyl rotation about C$_{meso}$−C$_{phenyl}$ bonds, have been observed. Line shape analysis of various protons has enabled us to estimate the activation free energies for these processes. The most striking feature is a large increase in barriers to inversion of the deformed porphyrin ring as compared with those of the corresponding neutral porphyrin complexes, [Fe(OMTPP)Cl] and [Fe(OETPP)-Cl]; the increase is estimated to be 4.3 kcal mol^{-1} in the former and ≫2 kcal mol^{-1} in the latter. Occurrence of the site exchange of the ferric ion has hampered the precise determination of the inversion barrier in [Fe(OETPP)Cl]SbCl$_6$. The large increase in barriers to inversion has been ascribed to the enhanced nonplanarity of the porphyrin ring on one electron oxidation, which is more favorable for the spin−spin interaction between iron d$_{x^2−y^2}$ and porphyrin a$_{2u}$ orbitals. It has also been observed that the barriers to site exchange of the ferric ion greatly decrease on one electron oxidation. The result is explained in terms of the weakening of porphyrin basicity in the radical cations. Highly saddled conformation of these complexes also affects the barrier to phenyl rotation. Despite the presence of octamethyl

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groups at the pyrrole β-positions, the barriers to phenyl rotation of [Fe(OMTPP)Cl] and [Fe(OMTPP)Cl]SbCl$_6$ are supposed to be similar to that of [Fe(TPP)Cl].

Supporting Information Available: Temperature dependence of the chemical shift of each signal in [Fe(OMTPP)Cl]SbCl$_6$ and [Fe-(OETPP)Cl]SbCl$_6$, and effect of chloride on the line shape of [Fe-(OMTPP)Cl]SbCl$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990139E