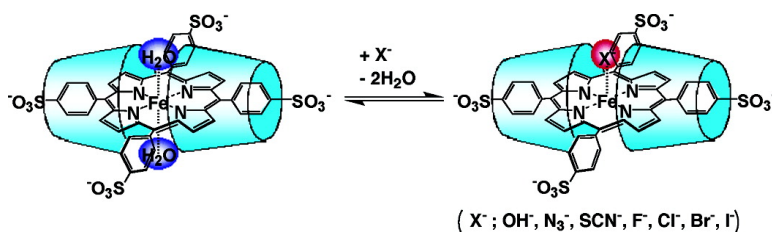Article

Anion Binding to a Ferric Porphyrin Complexed with Per-*O*-methylated β-Cyclodextrin in Aqueous Solution

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(X⁻ ; OH⁻, N₃⁻, SCN⁻, F⁻, Cl⁻, Br⁻, I⁻)

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Anion Binding to a Ferric Porphyrin Complexed with Per-*O*-methylated *β*-Cyclodextrin in Aqueous Solution

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Abstract: 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphinato iron(III) (Fe(III)TPPS) forms a very stable 1:2 complex with heptakis(2,3,6-tri-*O*-methyl)-*β*-cyclodextrin (TMe-*β*-CD), whose iron(III) center is located at a hydrophobic cleft formed by two face-to-face TMe-*β*-CD molecules. Various inorganic anions (X$^-$) such as F$^-$, Cl$^-$, Br$^-$, I$^-$, N$_3^-$, and SCN$^-$ coordinate to Fe(III)TPPS(TMe-*β*-CD)$_2$ to form five-coordinate high-spin Fe(III)TPPS(X)(TMe-*β*-CD)$_2$, while no coordination occurs with ClO$_4^-$, H$_2$PO$_4^-$, NO$_3^-$, and HSO$_4^-$. Except for F$^-$, none of the anions investigated coordinate to Fe(III)TPPS in the absence of TMe-*β*-CD due to extensive hydration to the anions as well as to Fe(III)TPPS. The present system shows a high selectivity toward the N$_3^-$ anion. The thermodynamics suggests that Lewis basicity, hydrophilicity, and shape of an X$^-$ anion are the main factors to determine the stability of the Fe(III)TPPS(X)(TMe-*β*-CD)$_2$ complex.

The microenvironments presented by proteins are essential factors that determine the selective formation of enzyme–substrate complexes. The X-ray structures of myoglobin (Mb)[1] and hemoglobin (Hb)[2] indicate that the dioxygen (O$_2$) binding sites of these hemoproteins are located near the surfaces of the proteins. Such structures are important to capture O$_2$ by the iron(II) porphyrin (Fe(II)Por) and to protect the *μ*-oxo dimer formation. Mimicking the functions of proteins by employing completely artificial systems has been a challenging task in the area of biomimetic chemistry. Collman and co-workers utilized the picket-fence porphyrins as models of hemoproteins.[3] The steric hindrance resulting from the picket fences attached to the peripheral phenyl groups facilitates the formation of five-coordinate Fe(II)Por-2MIm (2MIm = 2-methylimidazolyl) and protection of the *μ*-oxo-dimer. This type of sophisticated model has been regarded as the simplest Mb model, although the fact that the syntheses of picket-fence porphyrins are far from straightforward. The concept demonstrated by Collman et al. for the Mb model has been succeeded by capped Pors, cross-strapped Pors, hybrid Pors, and basket Pors.[4,5] For synthetic reasons as well as for avoiding acid- or base-induced autoxi-dation of Fe(II)Por, most models work only in organic solvents. Preparation of functional models for aqueous system is a

challenging subject. To achieve such an aim, we have to place an iron center at a hydrophobic environment formed in aqueous solution. We have been interested in cyclodextrins (CDs) as simple, water-soluble functional models of proteins. CD provides an asymmetric cavity that can enantioselectively include various guests.[6] In addition, CD provides a microscopically hydrophobic environment from which water molecules are excluded.[7] We assumed that the Por-CD composite systems might act as promising models of hemoproteins. Several groups have studied Por-CD systems as metal–protein models.[8–14] Lawrence et al. found the formation of stable 1:2 complexes of water-soluble Pors and heptakis(2,6-di-*O*-methyl)-*β*-CD (2,6-DMe-*β*-CD).[15] Two 2,6-DMe-*β*-CD molecules include peripheral aryl groups

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at the 5- and 15-positions of water-soluble meso-tetraarylpor-phyrins to form trans-type 1:2 complexes, which are significantly more stable than the 1:2 complexes of Pors and native β-CD.[16] Metalloporphyrins were also shown to form 1:2 inclusion complexes of 2,6-DMe-β-CD[15c], as well as of native β-CD.[17] These studies, however, have not paid attention to the hydrophobic environments around the centers of metalloporphyrins.

It has been found that heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TMe-β-CD) forms the extremely stable 1:2 inclusion complexes with various water-soluble Pors (Por/TMe-β-CD = 1:2) in aqueous solution.[7,18,19] On the basis of the pK_a values of the complexed tetrakis(4-sulfonatophenyl)porphyrin (TPPS) free base, the stability of the 1:2 complex of TPPS and TMe-β-CD was expected to be much larger than that of the TPPS–2,6-DMe-β-CD complex.[7] In aqueous solution, it was impossible to determine the binding constants for the formation of 1:1 (K_{11}) and 1:2 complexes (K_{12}) of TPPS and TMe-β-CD because of too large K values. A stoichiometric solution of TPPS (1 × 10^{-6} M) and TMe-β-CD (2 × 10^{-6} M) yields the 1:2 complex quantitatively. The results indicate that the K_{11} value is > 10^6 M^{-1}. Even in 1:3 H$_2$O–ethylene glycol solution, the K_{11} and K_{12} values are 2.0 × 10^4 and 5.8 × 10^4 M^{-1}, respectively.[18] This strong tendency of TMe-β-CD to form inclusion complexes with water-soluble tetraarylporphyrins was utilized to construct supramolecular heteroporphyrin arrays in aqueous solution.[20] The center of the porphyrin capped by two TMe-β-CD molecules is placed in a nonpolar environment from which most water molecules are excluded.[7] This type of environment is similar to the microenvironments around the iron centers of Mb and Hb.

In the present study, we used the striking nature of TMe-β-CD to construct a hydrophobic environment around a center of Fe(III)TPPS to which various inorganic anions coordinate in aqueous solution. Most anions in aqueous solution are unable to coordinate to Fe(III)Por at any pH due to extensive hydration and/or hydroxylation of the anions and the iron center, although many anions can coordinate to Fe(III)Por in organic solvents.[21] Furthermore, in homogeneous aqueous media, it was demonstrated that various anions (X$^-$) such as SCN$^-$, F$^-$, OCN$^-$, N$_3$$^-$, and CN$^-$ are able to bind to the dioxygen complex of Mb ((O$_2$)-Mb) to accelerate autoxidation of Mb yielding metMb(X) and the superoxide anion.[22] These anions accelerate the autoxidation of (O$_2$)Mb through an S$_N$2 mechanism.[23] Although many papers dealing with anion binding to hemoproteins have been published,[23,24] no detailed mechanism on anion binding to Fe(III)-Por has been studied. It might be very important to prepare the suitable model systems of Mb, Hb, and their oxidized forms.

Meanwhile, investigations concerning the selective sensing of inorganic anions are receiving a great deal of interest in the area of supramolecular chemistry. Although many anion receptors have been developed so far,[25] most receptors have been designed to work in organic solvents to make use of the binding forces such as hydrogen bonding, Coulomb interactions, and/or coordination to a metal ion, all of which are weaker in aqueous solution. To realize anion sensing in aqueous media, serious considerations should be given to the design a receptor that is preorganized.[26] In this study, we found that TMe-β-CD includes Fe(III)TPPS whose center is placed in a very hydrophobic environment yielding selective anion coordination to the Fe(III)Por in aqueous solution. The present system might be regarded as a simple metMb model.

Results and Discussion

Complexation of Fe(III)TPPS with TMe-β-CD. The pH-dependent equilibria of Fe(III)TPPS has been reported elsewhere.[27] The UV–vis absorption spectral changes of Fe(III)-TPPS (1 × 10^{-5} M) in aqueous solution containing 100 equiv amounts of TMe-β-CD and 0.1 M NaClO$_4$ were measured upon lowering the pH using HClO$_4$ (Figure 1a). Although Fe(III)-TPPS forms the μ-oxo dimer (λ_{max} = 408 nm) at higher pH (pK_{app} = 6.6) in the absence of TMe-β-CD, the species formed in the presence of TMe-β-CD (λ_{max} = 415 nm) at a higher pH range was not the μ-oxo-dimer but was identified as the monohydroxo complex (Fe(III)TPPS(OH)).[27d,28] Interaction with TMe-β-CD completely prevents the formation of the μ-oxo dimer. A similar effect was observed with β-CD which significantly depresses, but not completely, the formation of the μ-oxo-dimer of Fe(III)TPPS.[17a,29] No formation of the dihydroxo complex (Fe(III)TPPS(OH)$_2$) was observed even in a strong alkaline solution of TMe-β-CD. Lowering the pH to below 6 resulted in marked spectral changes and gave a pK_a value of 4.3. This pK_a corresponds to the equilibrium constant between Fe(III)TPPS(OH) and Fe(III)TPPS(H$_2$O)$_2$ and is much lower than the pK_a value (6.4) reported for the μ-oxo-dimer-Fe(III)-TPPS(H$_2$O)$_2$ equilibrium in the absence of CD.[17a] Since the pK_a value for the Fe(III)TPPS(H$_2$O)$_2$-μ-oxo dimer equilibrium in the absence of TMe-β-CD corresponds to that for the

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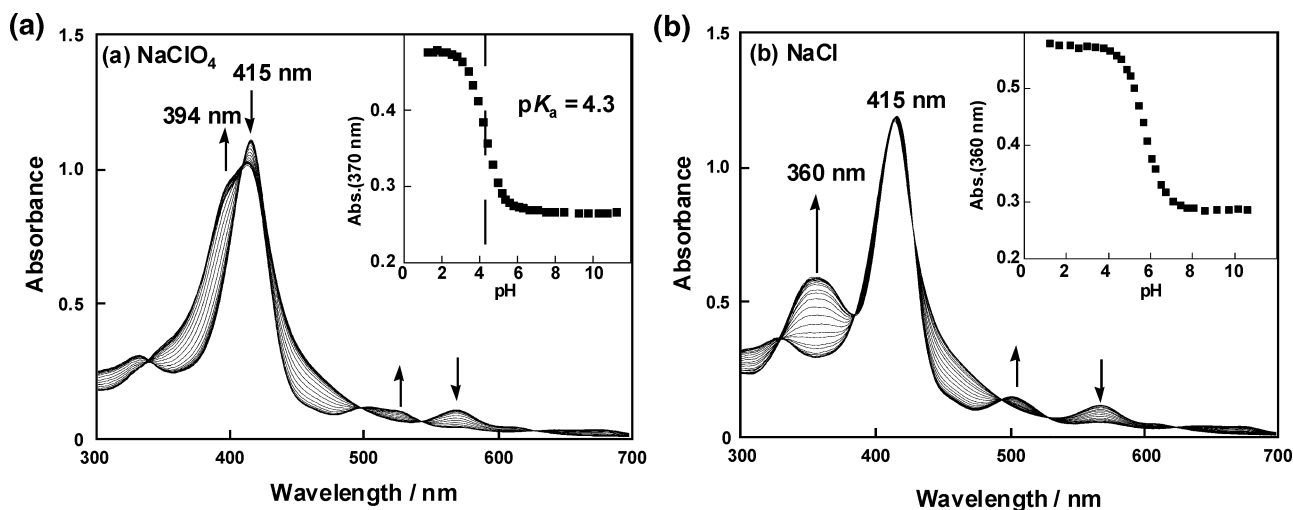(29) Sur, S. K.; Bryant, R. G. *J. Phys. Chem.* **1995**, *99*, 7172–7179.

Figure 1. UV−vis absorption spectral changes of Fe(III)TPPS (1×10^{-5} M) in aqueous TMe-β-CD (1×10^{-3} M) solutions in the presence of 0.1 M NaClO$_4$ (a) and 0.1 M NaCl (b) as a function of pH. The pH of the solutions was initially adjusted to 11.3 by NaOH and then gradually decreased upon addition of HClO$_4$ (a) and HCl (b).

Fe(III)TPPS(H$_2$O)$_2$−Fe(III)TPPS(OH) one in the presence of TMe-β-CD because Fe(III)TPPS(OH) immediately yields μ-oxo dimer without protection of TMe-β-CD, it can be concluded that TMe-β-CD markedly enhances the dissociation of Fe(III)-TPPS(H$_2$O)$_2$.

When NaCl (0.1 M) was used as an inorganic salt to adjust the ionic strength, the pH-dependent spectral changes of Fe(III)-TPPS (Figure 1b) differed from those of the system where NaClO$_4$ was used. Upon the pH being lowered, the absorbance at 360 nm increased until pH 4 and then reached a plateau. The absorption spectrum having $\lambda_{\max}$ at 360 nm corresponds to that of Cl$^-$-coordinated Fe(III)TPPS (Fe(III)TPPS(Cl)) formed in organic solvent.[30] It should be emphasized that no Fe(III)TPPS-(Cl) was formed in aqueous NaCl solution in the absence of TMe-β-CD.

The stoichiometries of the complexes of Fe(III)TPPS and TMe-β-CD were determined in aqueous solutions with and without NaCl at pH 5 and 1.5 by the continuous variations method for the absorption spectral changes (Supporting Information).[31] The Job's plots clearly indicated that the 1:2 and 1:1 complexes of Fe(III)TPPS and TMe-β-CD were formed in 0.1 M aqueous NaClO$_4$ solutions at pH 5.0 and 1.5, respectively. The formation of the trans-type 1:2 complexes of the TPPS free base and TMe-β-CD has been well established.[7,18] It is easy to understand that Fe(III)TPPS(OH) possessing no charge on the center of the metalloporphyrin forms the trans-type 1:2 inclusion complex of TMe-β-CD (Fe(III)TPPS(OH)(TMe-β-CD)$_2$). At lower pH, however, the center of Fe(III)TPPS(H$_2$O)$_2$ possesses one positive charge. The environment of this polar center of the guest porphyrin should be unfavorable for being covered by two TMe-β-CD molecules. This assumption was supported by the stoichiometry of the Fe(III)TPPS(Cl)−TMe-β-CD complex at pH 1.5. The Job's plot for the complexation of Fe(III)-TPPS with TMe-β-CD in 0.1 M aqueous NaCl solution at pH 1.5 indicated the formation of the 1:2 complex, Fe(III)TPPS-

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Table 1. Binding Constants for Complexation of Fe(III)TPPS with TMe-β-CD in Aqueous Solutions at Various pH's and 298 K[a]

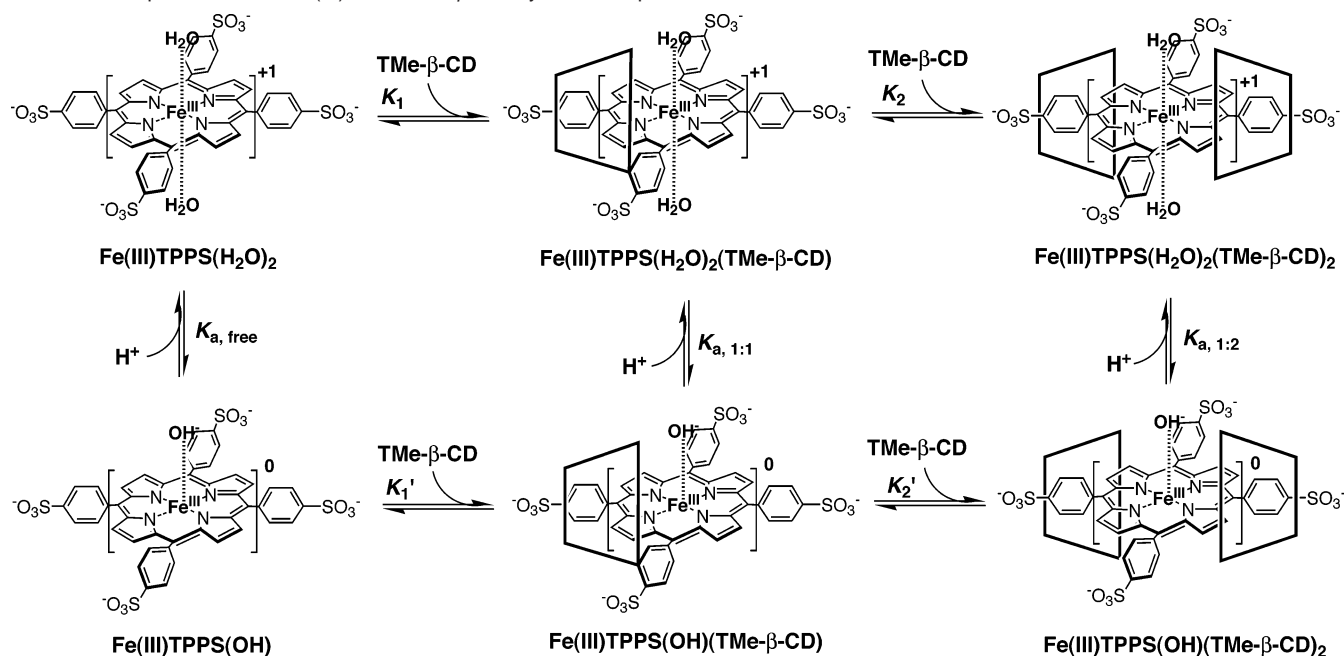| pH	$10^{-5}K_{11}$/M^{-1}	$10^{-4}K_{12}$/M^{-1}
1.5	3.06 ± 0.17	0.56 ± 0.06
3.75	3.13 ± 0.31	1.11 ± 0.05
4.0	2.84 ± 0.34	1.36 ± 0.06
4.25	2.64 ± 0.30	1.91 ± 0.06
4.5	3.47 ± 0.49	2.87 ± 0.07
4.75	2.75 ± 0.46	4.22 ± 0.13
5.0	2.85 ± 0.53	6.96 ± 0.23

[a] The 0.01 M succinic acid buffers containing 0.1 M NaClO$_4$ were used except for the solution at pH 1.5. For the sample at pH 1.5, HClO$_4$ was used to adjust the pH, and the measurement was carried out in the presence of 0.1 M NaClO$_4$.

(Cl)(TMe-β-CD)$_2$. Neutralization of the positive charge at the center of the Fe(III)Por due to coordination of Cl$^-$ facilitates the formation of the 1:2 inclusion complex even in acidic solution.

Binding Constants and Kinetics. The apparent binding constants for the formation of the 1:1 (K_{11}) and 1:2 complexes (K_{12}) of Fe(III)TPPS and TMe-β-CD in 0.1 M aqueous NaClO$_4$ solutions were determined at various pHs. The pH of the solutions was adjusted by HClO$_4$ to 1.5, while 0.01 M succinic acid buffers were used for pH 3.75−5.0. The absorption spectral changes of Fe(III)TPPS as a function of [TMe-β-CD] were measured at various pHs, and the titration curves obtained were analyzed by the nonlinear least-squares method as previously described.[18] The results are listed in Table 1. The K_{11} values are almost constant over the pH range of 1.5 and 5.0. At pH 1.5, the K_{11} value is ca. 54-times larger than the K_{12} value, which corresponds to the fact that the 1:1 complex, Fe(III)TPPS(H$_2$O)$_2$-(TMe-β-CD), is predominantly formed under the conditions used for measuring the Job's plot. The K_{12} value gradually increases with increasing the pH, indicating that formation of the 1:2 inclusion complex is easy to occur at higher pH. This can be ascribed to neutralization of the positive charge at the Fe(III)-TPPS center by ligation of OH$^-$ to iron(III). The pH-dependent equilibria of Fe(III)TPPS in aqueous NaClO$_4$ solution containing TMe-β-CD is shown in Scheme 1. The apparent binding

Scheme 1. Equilibria for the Fe(III)TPPS-TMe-β-CD System in Aqueous Solution

constant for the formation of the 1:2 complex (K_{12}) is represented by

$$K_{12} = \{[\text{Fe(III)TPPS(H}_2\text{O)}_2(\text{TMe-}\beta\text{-CD)}_2] +$$
$$[\text{Fe(III)TPPS(OH)(TMe-}\beta\text{-CD)}_2]\} \Big/$$
$$\{\{[\text{Fe(III)TPPS(H}_2\text{O)}_2(\text{TMe-}\beta\text{-CD)}] +$$
$$[\text{Fe(III)TPPS(OH)(TMe-}\beta\text{-CD)}]\} [\text{TMe-}\beta\text{-CD}]\}$$

$$= \frac{K_2\left\{1 + \dfrac{K_{a,1:2}}{[\text{H}^+]}\right\}}{\left\{1 + \dfrac{K_{a,1:1}}{[\text{H}^+]}\right\}} \qquad (1)$$
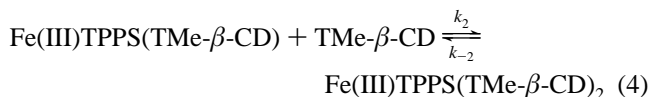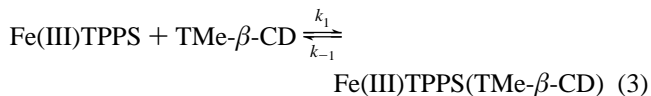
where K_2 is defined as

$$K_2 = \frac{[\text{Fe(III)TPPS(H}_2\text{O)}_2(\text{TMe-}\beta\text{-CD)}_2]}{[\text{Fe(III)TPPS(H}_2\text{O)}_2(\text{TMe-}\beta\text{-CD)}][\text{TMe-}\beta\text{-CD}]} \qquad (2)$$

Equation 1 indicates that K_{12} is dependent on pH. K_2, $K_{a,1:1}$, and $K_{a,1:2}$ evaluated by analyzing the plot of K_{12} vs [H$^+$] using the nonlinear least-squares method (Supporting Information) were determined to be 7540 ± 702 M^{-1}, (4.6 ± 6.1) × 10^{-7} and (8.6 ± 1.3) × 10^{-5} M, respectively. It is expected that the calculated K_2 value would be almost the same as the experimentally determined K_{12} value in acidic solution. Indeed, the calculated K_2 value (7540 M^{-1}) agrees well with the measured K_{12} value at pH 1.5 (5600 M^{-1}). The p$K_{a,1:2}$ value is calculated to be 4.1, which fairly agrees with the pK_a value (4.3) for the equilibrium between Fe(III)TPPS(H$_2$O)$_2$(TMe-β-CD)$_2$ and Fe(III)-TPPS(OH)(TMe-β-CD)$_2$ determined from the pH titration of Fe(III)TPPS in the presence of 100 equiv amounts of TMe-β-CD (vide supra). The p$K_{a,1:1}$ is calculated to be ca. 6.3, which is very close to the apparent pK_a value (6.6) for the equilibrium between the μ-oxo dimer and Fe(III)TPPS(H$_2$O)$_2$ in aqueous solution without TMe-β-CD. Since half of the porphyrin center of the 1:1 inclusion complex is opened in a direction toward the aqueous bulk phase, the apparent pK_a value for the

dissociation of Fe(III)TPPS(H$_2$O)$_2$(TMe-β-CD) to Fe(III)-TPPS(OH)(TMe-β-CD) seems to be almost the same as the pK_a for the μ-oxo dimer.

Complexation of Fe(III)TPPS with TMe-β-CD was also studied kinetically. The forward (k_1, k_2) and backward reaction rate constants (k_{-1}, k_{-2}) were determined from the analysis of the time courses of the
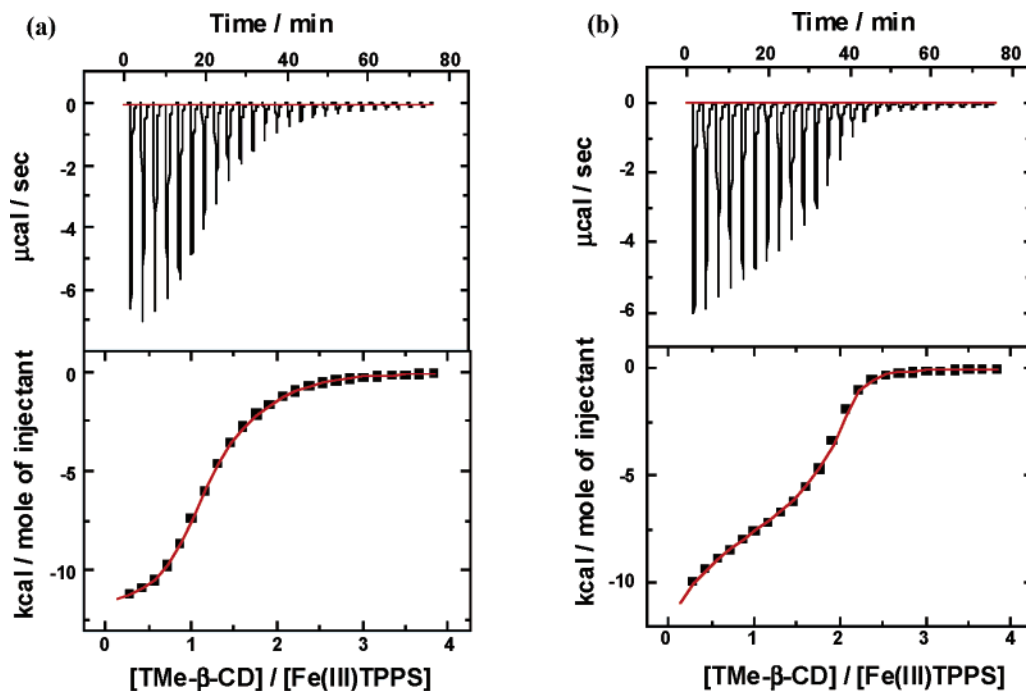
$$\text{Fe(III)TPPS} + \text{TMe-}\beta\text{-CD} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$\text{Fe(III)TPPS(TMe-}\beta\text{-CD)} \quad (3)$$

$$\text{Fe(III)TPPS(TMe-}\beta\text{-CD)} + \text{TMe-}\beta\text{-CD} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$
$$\text{Fe(III)TPPS(TMe-}\beta\text{-CD)}_2 \quad (4)$$

optical density changes (ΔA) of the Fe(III)TPPS after mixing with various amounts of TMe-β-CD (Supporting Information). The detailed method for determining the rate constants has been reported elsewhere.[18] The results are shown in Table 2. The k_1 and k_{-1} values for the first step of complexation are independent of pH, while the k_2 value increases and the k_{-2} value decreases with increasing pH. The pH dependency of k_2 suggests the contribution of the inclusion process via the Fe(III)TPPS(OH)-(TMe-β-CD) to form Fe(III)TPPS(OH)(TMe-β-CD)$_2$ at higher pH. The decrease in the k_{-2} value at higher pH is reasonable because Fe(III)TPPS(OH)(TMe-β-CD)$_2$ is more stable than Fe(III)TPPS(H$_2$O)$_2$(TMe-β-CD)$_2$. The K_{11} (k_1/k_{-1}) and K_{12} values (k_2/k_{-2}) calculated from the reaction rate constants are in agreement with those obtained from spectroscopic titrations.

Thermodynamic Parameters for Complexation of Fe(III)-TPPS with TMe-β-CD. Isothermal titration calorimetry (ITC) was employed to determine the thermodynamic parameters for complexation of Fe(III)TPPS with TMe-β-CD in 0.1 M succinic acid buffer at pH 4.0 in the absence and the presence of 0.05 M NaCl. Measurement at lower pH range could not be carried out because of the corrosive problem for the cell of the apparatus. The isothermal calorimetric titration curves obtained

Table 2. Rate Constants for Formation and Dissociation of 1:1 and 1:2 Complexes of Fe(III)TPPS with TMe-β-CD at 25 °C[a]

pH[b]	$10^{-6}k_1$/M^{-1} s^{-1}	k_{-1}/s^{-1}	$10^{-6}k_2$/M^{-1} s^{-1}	k_{-2}/s^{-1}	$10^{-5}K_{11}$[c]/M^{-1}	$10^{-4}K_{12}$[c]/M^{-1}
1.5	3.9 ± 0.2	14.7 ± 1.6	nd[d]	nd[d]	2.7	nd[d]
4.0	3.8 ± 0.2	11.5 ± 1.7	0.52 ± 0.99	37.8 ± 1.4	3.3	1.4
4.5	4.4 ± 0.3	7.3 ± 2.0	0.78 ± 0.02	21.5 ± 0.3	5.9	3.6
5.0	3.9 ± 0.9	11.1 ± 0.9	1.01 ± 0.02	11.7 ± 0.2	3.5	8.7

[a] Reaction rates were measured by following the absorbance at 425.2 nm of Fe(III)TPPS (1×10^{-5} M) after mixing TMe-β-CD (($1, 2, 3, 4, 5) \times 10^{-5}$ M) by a stopped-flow apparatus. [b] The 0.01 M succinic acid buffers were used except for the case of pH 1.5. The pH was adjusted to 1.5 by adding HClO$_4$ into the aqueous solution containing 0.1 M NaClO$_4$. [c] K_{11} (k_1/k_{-1}) and K_{12} (k_2/k_{-2}) were calculated from the rate constants. [d] nd = not determined.

Figure 2. Calorimetric titrations of Fe(III)TPPS (5×10^{-4} M) with 25 aliquots (10 μL each) of TMe-β-CD (2×10^{-3} M) in the absence (a) and presence of 0.05 M NaCl (b) in 0.1 M succinate buffer at pH 4.0 and 298.15 K. The solid line represents the best fit of the experimental data to the 1:2 sequential binding sites model in the ORIGIN software.

Table 3. Effects of NaCl and Na$_2$SO$_4$ on Thermodynamic Parameters for Complexation of Fe(III)TPPS with TMe-β-CD in 0.1 M Succinic Acid Buffer at pH 4.0 and 298.15 K

salt	$10^{-6}K_{11}$ M^{-1}	ΔH_{11} kJ mol^{-1}	ΔS_{11} J mol^{-1} K^{-1}	$10^{-5}K_{12}$ M^{-1}	ΔH_{12} kJ mol^{-1}	ΔS_{12} J mol^{-1} K^{-1}
none	1.26 ± 0.09	-48.7 ± 0.2	-46.6 ± 1.3	0.63 ± 0.04	-11.7 ± 0.2	52.6 ± 1.2
0.05 M NaCl	1.15 ± 0.42	-48.6 ± 2.1	-47.7 ± 11.3	5.70 ± 0.88	-14.0 ± 2.0	63.2 ± 8.1
0.05 M Na$_2$SO$_4$	1.51 ± 0.11	-47.3 ± 0.2	-40.4 ± 1.3	0.87 ± 0.05	-11.6 ± 0.2	55.6 ± 1.1

by the addition of TMe-β-CD to the Fe(III)TPPS solutions in the absence and the presence of NaCl are shown in Figure 2. The titration curves were analyzed by using the equation for the simultaneous formation of the 1:1 and 1:2 complexes (sequential binding sites model),[32] and the results are summarized in Table 3. Both K_{11} and K_{12} values determined from the calorimetric method for the complexation in water in the absence of inorganic salt were ca. 4.5 times larger than the corresponding values derived from absorption spectroscopy. This might be due to the effects of NaClO$_4$. In the case of analysis by absorption spectroscopy, 0.1 M NaClO$_4$ was added to adjust the ionic strength, while no inorganic salt was used for the ITC analysis. Although no evidence was obtained for interaction between ClO$_4^-$ and Fe(III)TPPS(TMe-β-CD)$_2$, it might be possible that this anion interferes with the interaction between

(32) *ITC Data Analysis in Origin − Tutorial Guide*; MicroCal: Northampton, MA, 1998; pp 76−78.

Fe(III)TPPS and TMe-β-CD due to weak ligation of ClO$_4^-$ to iron(III). The formation of the 1:1 complex of Fe(III)TPPS and TMe-β-CD is promoted by the large and negative enthalpy change (ΔH_1) and is unfavorable in the entropy term. Complexation of Fe(III)TPPS with TMe-β-CD results in significant restriction of free rotation of the peripheral sulfonatophenyl groups, thus leading to a large and negative entropy change (ΔS_1). Meanwhile, the second step leading to the formation of the 1:2 complex is an entropically driven process. This can be ascribed to extensive dehydration from the host TMe-β-CD molecules and the central iron(III) of the porphyrin. At pH 4.0, Fe(III)TPPS(H$_2$O)$_2$ and Fe(III)TPPS(OH) coexist in the system. The axial ligands of these species (H$_2$O and OH$^-$) strongly interact with bulk water molecules through hydrogen bonding. These water molecules seem to be excluded upon complexation of Fe(III)TPPS(TMe-β-CD) with an additional TMe-β-CD

molecule to form the 1:2 complex. This process generates a positive ΔS_2.

The K_{11} value for the system in the presence of 0.05 M NaCl is almost the same as that in the absence of NaCl. This is reasonable since no effect of Cl^- is anticipated for the complexation of Fe(III)TPPS(H$_2$O)$_2$ or Fe(III)TPPS(OH) with TMe-β-CD to form Fe(III)TPPS(H$_2$O)$_2$(TMe-β-CD) or Fe(III)-TPPS(OH)(TMe-β-CD). In contrast, the K_{12} value in the presence of NaCl is 9-times larger than that in the absence of NaCl, supporting the assumption that neutralization of the positive charge at the Fe(III)TPPS center by coordination of Cl^- facilitates the inclusion of the second TMe-β-CD molecule. The second complexation to form the 1:2 complex in the presence of NaCl is enthalpically and entropically more favorable than that in the absence of NaCl. No marked difference in thermodynamic parameters was observed between the solutions in the absence and the presence of Na$_2$SO$_4$, suggesting that the HSO$_4^-$ anion does not interact with Fe(III)TPPS even in the presence of TMe-β-CD.

Magnetic Resonances. Reed and co-workers developed an NMR spectroscopic method to determine the spin states of Fe(III)Pors.[33] It has been known that the iron(III) of a halogen-coordinated Fe(III)Por(X) in organic solvent is in a high-spin state ($S = {}^5/_2$) where the pyrrole β-protons show their chemical shift at around 80 ppm. Meanwhile, Fe(III)Por coordinated by ClO$_4^-$ or CB$_{11}$H$_{12}^-$ (carborane anion) takes an admixed intermediate spin state ($S = {}^5/_2, {}^3/_2$) whose pyrrole β-protons appear in the range between 80 and -62 ppm.

As shown in Figure 3, the pyrrole β-protons of Fe(III)TPPS (0.01 M) in D$_2$O containing 0.1 M NaCl at pD 1.5 (DCl) in the absence of TMe-β-CD were observed at 53 ppm as a sharp singlet (Figure 3a). Such a chemical shift agrees well with that reported for Fe(III)TPPS(H$_2$O)$_2$[34] possessing an admixed intermediate spin state. Upon addition of TMe-β-CD (0.03 M) to this solution, the signal due to the pyrrole β-protons shifted to 83 ppm (apparently a triplet signal, Figure 3g), indicating that a change of spin state from the admixed intermediate to high spin had occurred upon coordination of Cl^- to form the five-coordinate Fe(III)TPPS(Cl)(TMe-β-CD)$_2$ complex. These results clearly show that inclusion of the aryl groups of Fe(III)TPPS by TMe-β-CD is essential to bind Cl^- with Fe(III)TPPS in aqueous solution. When NaClO$_4$ was added to the system in place of NaCl, the pyrrole β-protons were observed at 66 and 67 ppm (two singlet signals, Figure 3b). The fact that the absorption spectrum of Fe(III)TPPS in aqueous TMe-β-CD solution is not affected by NaClO$_4$ indicates that the ClO$_4^-$ anion does not coordinate strongly to Fe(III)TPPS at any pH. In organic solvent, however, the ClO$_4^-$ anion coordinates to Fe(III)Por to form Fe(III)Por(ClO$_4$), whose pyrrole β-proton signal appears at 13 ppm.[35] It is clear, therefore, that the downfield shift of the signal upon addition of TMe-β-CD is ascribed to the inclusion of Fe(III)TPPS(H$_2$O)$_2$ by TMe-β-CD, not coordination of ClO$_4^-$.

Further verification of the formation of the five-coordinate high-spin Fe(III)TPPS(Cl)(TMe-β-CD)$_2$ complex was achieved by means of ESR spectroscopy. Fe(III)TPPS(H$_2$O)$_2$ in acidic solution at pH 1.5 in the absence of TMe-β-CD showed a very

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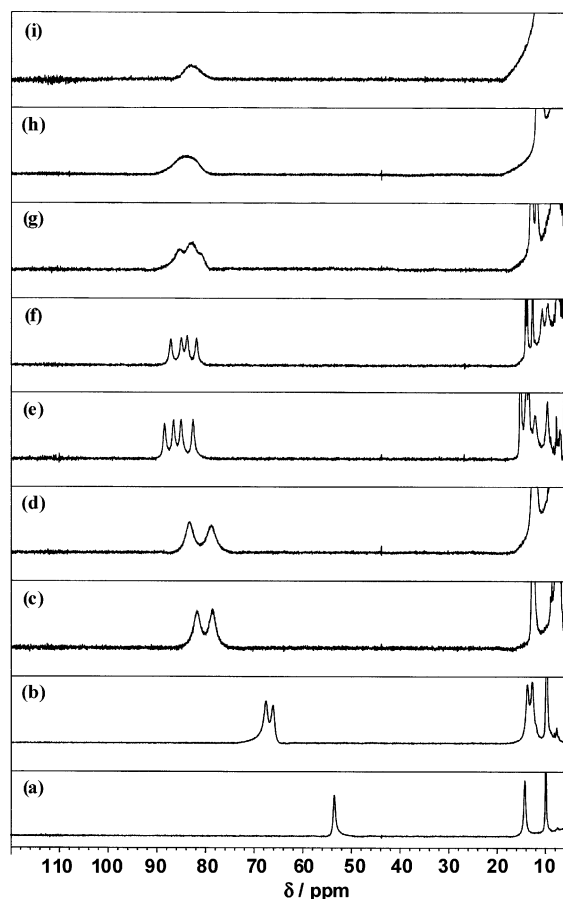(35) Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 581−586.

Figure 3. ^{1}H NMR spectra of Fe(III)TPPS (0.01 M) in D$_2$O in the absence (a) and presence of TMe-β-CD (0.03 M) (b−i) containing inorganic salts or NaOD: (a) 0.1 M NaCl at pD 1.5 (DCl); (b) 0.1 M NaClO$_4$ at pD 1.5; (c) 0.1 M NaSCN at pD 1.5 (D$_2$SO$_4$); (d) 0.1 M NaN$_3$ at pD 3.5 (D$_2$SO$_4$); (e) 0.1 M NaI at pD 1.5 (D$_2$SO$_4$); (f) 0.1 M NaBr at pD 1.5 (HBr); (g) 0.1 M NaCl at pD 1.5 (DCl); (h) 0.1 M NaF at pD 3.5 (D$_2$SO$_4$); (i) NaOD at pD 12.0.

broad and weak singlet signal with $g \approx 5.9$, which corresponds to the admixed intermediate spin state of Fe(III)TPPS(H$_2$O)$_2$ (Supporting Information). Meanwhile, a sharp singlet ($g = 5.9$) was observed with the Fe(III)TPPS (1×10^{-3} M) solution at pH 1.5 containing TMe-β-CD (3×10^{-3} M) and NaCl (0.1 M). The ESR spectrum indicates the formation of the five-coordinate high-spin iron(III) complex, Fe(III)TPPS(Cl)(TMe-β-CD)$_2$.

The ^{1}H NMR spectra of Fe(III)TPPS in the absence and the presence of TMe-β-CD were also measured at pD 12 (NaOD) (Figure 3i and Supporting Information). In the absence of TMe-β-CD, the signal due to the pyrrole β-protons was observed at 13 ppm, indicating formation of the μ-oxo dimer.[34] Addition of TMe-β-CD resulted in a marked downfield shift, the signal being detected at 80 ppm as a broad singlet. Such a result indicates that five-coordinate high-spin Fe(III)TPPS(OH)(TMe-β-CD)$_2$ is formed even in a strong alkaline solution.

Anion Selectivity. The anion selectivity of the present system was then investigated. The absorption spectral changes of Fe(III)TPPS in 0.05 M succinic acid buffer at pH 4.0 containing a large excess amount of TMe-β-CD (100 equivalent) were measured upon the addition of various kinds of inorganic salts (NaX) (Supporting Information). The new absorption band at 360 nm, which is characteristic of five-coordinate Fe(III)TPPS-(X)(TMe-β-CD)$_2$, appeared when F^-, Cl^-, Br^-, I^-, SCN^-, or N$_3^-$ was added as X^-. The ^{1}H NMR spectra of Fe(III)TPPS(X)-

Table 4. Apparent Binding Constants ($K_{X,app}$) for Coordination of Inorganic Anions to Fe(III)TPPS (5×10^{-6} M) Complexed with TMe-β-CD (5×10^{-4} M)

anion	$K_{X,app}$/M^{-1}			
	pH 1.5	pH 3.5	pH 4.0	pH 4.5
F$^-$	nd^a	953 ± 10	851 ± 7	564 ± 6
Cl$^-$	583 ± 9	288 ± 2	183 ± 2	122 ± 4
Br$^-$	165 ± 1	77 ± 1	55 ± 1	28 ± 1
I$^-$	81 ± 1	nd^a	nd^a	nd^a
N$_3^-$	nd^a	11 621 ± 164	19 160 ± 607	20 295 ± 670
SCN$^-$	515 ± 4	303 ± 13	158 ± 3	87 ± 1

^{a} Not determined.

Table 5. Corrected Binding Constants (K_X) for Coordination of Inorganic Anions to Fe(III)TPPS (5×10^{-6} M) Complexed with TMe-β-CD (5×10^{-4} M)^a

anion	K_X/M^{-1}		
	pH 3.5	pH 4.0	pH 4.5
F$^-$	$(1.70 \pm 0.03) \times 10^3$	$(1.42 \pm 0.03) \times 10^3$	$(1.34 \pm 0.02) \times 10^3$
Cl$^-$	339 ± 1	290 ± 2	269 ± 1
Br$^-$	90 ± 1	80 ± 1	73 ± 2
N$_3^-$	$(2.37 \pm 0.03) \times 10^5$	$(1.94 \pm 0.02) \times 10^5$	$(1.43 \pm 0.02) \times 10^5$
SCN$^-$	273 ± 2	225 ± 2	198 ± 2

^{a} The corrected K_X values were evaluated from the analysis of the data using eq 8.

(TMe-β-CD)$_2$ are shown in Figure 3, which clearly indicates the formation of five-coordinate high-spin Fe(III)TPPS(X) for these anions. Except for F$^-$, no Fe(III)TPPS(X) was formed in the absence of TMe-β-CD. Meanwhile, no absorption spectral change was detected with HSO$_4^-$, ClO$_4^-$, NO$_3^-$, or H$_2$PO$_4^-$, even in highly concentrated inorganic salt solutions. In the case of CN$^-$, the formation of six-coordinate low-spin Fe(III)TPPS-(CN)$_2$(TMe-β-CD)$_2$ was measured by means of ^{1}H NMR spectroscopy, the pyrrole β-protons being observed at -14.34, -16.24, -18.74, and -20.97 ppm as four singlets. From this qualitative analysis, it can be concluded that Fe(III)TPPS(TMe-β-CD)$_2$ recognizes the shape of the anion. Namely, both spherical and linear anions can coordinate to Fe(III)TPPS(TMe-β-CD)$_2$, but the anions having trigonal planar and tetrahedral shapes are unable to coordinate.

In the case of linear-shaped anions such as SCN$^-$ and N$_3^-$, the ^{1}H NMR signals due to the pyrrole β-protons were detected as two singlets. As can be recognized from Scheme 1, Fe(III)-TPPS(X)(TMe-β-CD)$_2$ has two different types of pyrrole β-protons. Meanwhile, four singlet signals were observed with the spherical and large anions such as I$^-$ and Br$^-$. In the case of these anions, two TMe-β-CD molecules must be placed asymmetrically in the Fe(III)TPPS(X)(TMe-β-CD)$_2$ complex due to large steric hindrance. Details of ^{1}H NMR spectra of halogen-coordinated Fe(III)TPPS(X)(TMe-β-CD)$_2$ are now under investigation.

To discuss the anion selectivity quantitatively, the binding constants for the coordination of X$^-$ were determined. The absorption spectral changes upon addition of NaX provided the titration curves, and plots of the absorbances at a certain wavelength vs [NaX] were analyzed by the nonlinear least-squares method.[18] The apparent K values ($K_{X,app}$) thus obtained are summarized in Table 4. Sulfuric acid was used to adjust the pH to be 1.5, while 0.05 M succinic acid buffers were used for other pH values. At pH 1.5, the $K_{X,app}$ values for the F$^-$ and N$_3^-$ anions could not be determined, since these anions exist as their conjugate acids, HF (pK_a 3.2) and HN$_3$ (4.7). Among the halogen ions, the Cl$^-$ anion shows the largest $K_{X,app}$ value, and the $K_{X,app}$ value decreases with increasing atomic number. Several factors seem to participate in such order. Namely Lewis basicity, size, and hydrophilicity of X$^-$ should be taken into consideration. The $K_{X,app}$ value for each halogen ion decreases with increasing pH, suggesting that the formation of Fe(III)-TPPS(OH)(TMe-β-CD)$_2$ inhibits the coordination of X$^-$. In contrast, the $K_{X,app}$ value for N$_3^-$ increases with increasing pH. Such a phenomenon can be interpreted in terms of the increase in the concentration of N$_3^-$ at higher pH. Measurements of the $K_{X,app}$ values for the coordination of I$^-$ were impossible at a
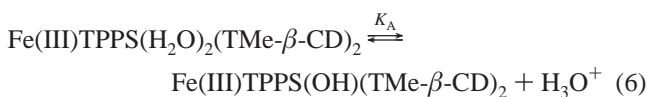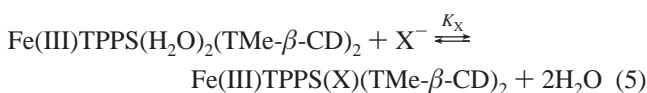
higher pH region because the values were too small. The present system shows the high selectivity toward N$_3^-$.

The pK_a value of 4.3 for the equilibrium between Fe(III)-TPPS(H$_2$O)$_2$(TMe-β-CD)$_2$ and Fe(III)TPPS(OH)(TMe-β-CD)$_2$ indicates that the K value for the complexation of a strong Lewis base OH$^-$ with Fe(III)TPPS(H$_2$O)$_2$(TMe-β-CD)$_2$ giving Fe(III)-TPPS(OH)(TMe-β-CD)$_2$ is 5×10^9 M^{-1}, which is much larger than those for other anions. The $K_{X,app}$ values listed in Table 4 represent apparent values, since inhibition due to the formation of Fe(III)TPPS(OH)(TMe-β-CD)$_2$ was not taken into consideration when determining the $K_{X,app}$ values. Assuming that Fe(III)TPPS(H$_2$O)$_2$(TMe-β-CD)$_2$ is the sole active species that forms Fe(III)TPPS(X)(TMe-β-CD)$_2$ in the presence of a large excess amount of TMe-β-CD, the pH-independent binding constants (K_X) for the ligation of X$^-$ to Fe(III)TPPS(H$_2$O)$_2$-(TMe-β-CD)$_2$ can be determined by considering the following equilibria:

$$\text{Fe(III)TPPS(H}_2\text{O)}_2\text{(TMe-}\beta\text{-CD)}_2 + \text{X}^- \overset{K_X}{\rightleftharpoons}$$
$$\text{Fe(III)TPPS(X)(TMe-}\beta\text{-CD)}_2 + 2\text{H}_2\text{O} \quad (5)$$

$$\text{Fe(III)TPPS(H}_2\text{O)}_2\text{(TMe-}\beta\text{-CD)}_2 \overset{K_A}{\rightleftharpoons}$$
$$\text{Fe(III)TPPS(OH)(TMe-}\beta\text{-CD)}_2 + \text{H}_3\text{O}^+ \quad (6)$$

$$\text{HX} \overset{K_B}{\rightleftharpoons} \text{H}^+ + \text{X}^- \quad (7)$$

For such equilibria, the absorbance (Abs) of Fe(III)TPPS at a certain wavelength can be represented as[28b]

$$\text{Abs} = [\text{Fe}]_t \frac{[\text{H}^+]\left\{\epsilon_{\text{H}_2\text{O}} + \dfrac{\epsilon_{\text{OH}}K_A}{[\text{H}^+]} + \dfrac{\epsilon_X K_X K_B [\text{X}]_t}{[\text{H}^+] + K_B}\right\}}{[\text{H}^+] + K_A + \dfrac{[\text{H}^+] K_X K_B [\text{X}]_t}{[\text{H}^+] + K_B}} \quad (8)$$

where [Fe]$_t$ represents the total concentration of Fe(III)TPPS and $\epsilon_{\text{H}_2\text{O}}$, ϵ_{OH}, and ϵ_X are the extinction coefficients of Fe(III)-TPPS(H$_2$O)$_2$(TMe-β-CD)$_2$, Fe(III)TPPS(OH)(TMe-β-CD)$_2$, and Fe(III)TPPS(X)(TMe-β-CD)$_2$, respectively. The absorption spectral changes of Fe(III)TPPS upon the addition of NaX were analyzed by eq 8 giving pH-independent K_X. In the analysis, the experimentally obtained K_A (pK_a for the diaqua-monohydroxo equilibrium in the presence of a large excess amount of TMe-β-CD is 4.3) was used. Under the present conditions, over 97% of Fe(III)TPPS exists as a 1:2 complex of Fe(III)TPPS and TMe-β-CD. The K_X values obtained at various pH's are listed in Table 5. At pH 3.5–4.5, the K_X value for each anion

is essentially independent of pH, although the K_X value for each anion decreases slightly with increasing pH. Although no evidence was obtained for the coordination of the succinate anion to Fe(III)TPPS, a weak interaction between these two species might possibly lower the K_X value at higher pH. Indeed, increasing the concentration of the succinate buffer resulted in a decrease in the K_X value for each anion (the data are not shown herein). The highly selective binding of N_3^- to Fe(III)TPPS-$(H_2O)_2(TMe-\beta-CD)_2$ is shown in Tables 4 and 5. The strong binding of F^- and N_3^- to Fe(III)TPPS$(H_2O)_2(TMe-\beta-CD)_2$ is very similar to anion selective binding to metMb.[22,36]

Since anions play an important role in biological systems, many studies on abiotic anion receptors have been carried out.[25] Limiting the story to cyclic oligo-pyrroles, Sessler et al. demonstrated that expanded porphyrins (sapphyrins) and calix-[n]pyrroles act as highly selective anion receptors.[37] Diprotonated sapphyrins selectively interact with F^- and phosphate anions in organic solvents through electrostatic and hydrogen bonding interactions.[37a,c] Phosphate anions in water ($K \approx 10^2$ M^{-1}) are bound to sapphyrins 2 orders of magnitude weaker than in methanol ($K \approx 10^4$ M^{-1}).[38] The calix[4]pyrroles also show the selectivity for F^- in CD_2Cl_2.[39] Reinhoudt and co-workers prepared a self-assembled bifunctional receptor composed of a zinc tetraphenylporphyrin and a calix[4]arene, which associate each other through complementary hydrogen bonding between the sidearms attached to the porphyrin and the calix[4]arene in organic solvents.[40] This type of receptor captures NaSCN by incorporating Na^+ into the calix[4]arene portion and SCN^- into the ZnPor portion ($K = 2.5 \times 10^4$ M^{-1} in toluene). In organic solvent, hydrogen bonding between anions and the urea moieties introduced into the sidearms of tetraphenylporphyrin can be utilized for the selective capture of Cl^-.[41] A F^- selective allosteric receptor was constructed using a doubly strapped porphyrin that operated in DMSO.[42] Compared with previous anion receptors, our present system has the following characteristics:

(1) The anion receptor is easily prepared by mixing Fe(III)-TPPS and TMe-β-CD in aqueous solution.

(2) The receptor works in aqueous solution, while previous receptors work most effectively in organic solvents.

(3) The receptor is much more sensitive to N_3^- than the halogen anions.

(4) The present system resembles biological metMb in terms of anion binding.

Thermodynamic Parameters for Anion Binding. Thermodynamic parameters can provide important information concerning coordination of inorganic anions to Fe(III)Por. ITC was

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Table 6. Thermodynamic Parameters for Coordination of Inorganic Anions to Fe(III)TPPS (2×10^{-3} M) Complexed with TMe-β-CD (2×10^{-2} M) in 0.1 M Succinic Acid Buffer at pH 4.0 and 298.15 K[a]

anion[b]	$K_{X,app}$/M^{-1}	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J mol^{-1}K^{-1}
Cl$^-$	237 ± 2	−13.5 ± 0.1	−2.2 ± 0.1	37.9 ± 0.7
N$_3^-$	(1.28 ± 0.03) × 10^4	−23.4 ± 0.1	−13.9 ± 0.1	31.9 ± 0.7
Br$^-$	54 ± 1	−9.9 ± 0.1	−1.2 ± 0.1	29.2 ± 0.7
SCN$^-$	130 ± 2	−12.1 ± 0.1	−15.1 ± 0.1	−10.1 ± 0.7

[a] The thermodynamic parameters were determined by microcalorimetric titrations. [b] The anions are listed in the order of Hofmeister series.

employed to determine the thermodynamic parameters of a system whereby NaX solution was added to the Fe(III)TPPS solution containing 10 equiv amounts of TMe-β-CD. Succinic acid buffer (0.1 M) at pH 4.0 was used. The titration curve obtained for each NaX was analyzed using the equation relating to 1:1 complex formation. The results are summarized in Table 6. Because of the lack of reproducibility concerning the heat of dilution, the parameters for F^- could not be determined. The apparent K value for each anion agrees well with the value obtained from the absorption spectroscopic titration (see Table 4). The ΔS value increases in the order $SCN^- < Br^- < N_3^- < Cl^-$, which corresponds to the order of hydrophilicity in the Hofmeister series.[25d,43] Coordination of the most hydrophobic SCN^- anion to Fe(III)TPPS shows a negative ΔS, while large and positive ΔS values were determined for the more hydrophilic Cl^-, N_3^-, and Br^- ions. These results strongly suggest the occurrence of extensive dehydration of the hydrophilic anion X^- during penetration of X^- into the cleft between two face-to-face TMe-β-CD molecules to coordinate to Fe(III). Entropically driven complexation due to dehydration of the host and/or the guest has commonly been observed in the cyclodextrin system.[44] The ΔH value seems to be dependent on the shape and the size of the anion. Linear anions such as N_3^- and SCN^- show the negative and large ΔHs, while spherical and large anions such as Cl^- and Br^- show negative but small ΔHs.

In general, ΔH is dependent upon temperature:

$$\Delta H(T_2) = \Delta H(T_1) + (T_2 - T_1)\Delta C_p \qquad (9)$$

where $\Delta H(T_2)$ and $\Delta H(T_1)$ represent the enthalpy changes for complexation at higher temperature (T_2) and lower temperature (T_1), respectively, and ΔC_p represents the heat capacity change. If we accept the first approximation that the enthalpy of Fe(III)-TPPS$(X)(TMe-\beta-CD)_2$ at lower temperature is almost the same as that at higher temperature, temperature dependency of ΔH depends on the enthalpies of both host and guest before complexation. The X^- anion is more extensively hydrated at lower temperature than at higher temperature. Therefore, ΔH at higher temperature should be smaller than that at lower temperature. For such a case, ΔH would decrease with increasing temperature. The ΔC_p values for the coordination of Cl^- and Br^- to Fe(III)TPPS$(TMe-\beta-CD)_2$ at pH 4.0 were determined from the linear relationships between ΔH and temperature (Supporting Information). The ΔC_p values thus determined were -320 ± 30 and -345 ± 31 J mol^{-1} K^{-1} for Cl^- and Br^-, respectively. The ΔC_p values obtained in this study also support

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dehydration that occurs in the course of coordination of the halogen anions to Fe(III)TPPS(TMe-β-CD)$_2$.

Conclusions

The present study demonstrates that some inorganic anions can coordinate to Fe(III)Por in water by the aid of per-O-methylated β-CD. The coordination of hydrophilic anions is the entropically driven process, where dehydration from the anion occurs. This study reveals that high selectivity of the present system toward N_3^- is caused by several factors. Namely, the natures of this anion such as a higher Lewis basicity, a linear shape leading to a negative and large ΔH (van der Waals interaction), and a higher hydrophilicity leading to a positive and large ΔS might participate in the highly selective binding of the N_3^- to Fe(III)TPPS(TMe-β-CD)$_2$. The present system is a primary model of metMb. Extension of the present system might make it possible to prepare the simple Mb model that works in aqueous solution.[45]

Experimental Section

Materials. Fe(III)TPPS was prepared and purified according to the procedures described in the literatures.[27a,46] The purity was checked by elemental analysis. Anal. Calcd for C$_{44}$H$_{28}$N$_4$S$_4$O$_{12}$Na$_3$Fe4H$_2$O: C, 46.77; H, 3.21; N, 4.96. Found: C, 47.24, H, 3.43; N, 4.87. UV (water at pH 3.0 adjusted using HClO$_4$ in the presence of 0.1 M NaClO$_4$) λ_{max} 394 nm (ϵ 150 000), 528 (13 000), 680 (2600). TMe-β-CD (Nacalai) was purchased and used as received.

Measurements. Absorption spectra were taken using a Shimadzu UV-2100 spectrophotometer with a thermostatic cell holder. ^{1}H NMR spectra were recorded on a JEOL JNM-A400 spectrometer (400 MHz) in D$_2$O (CEA, 99.9%) using sodium 3-trimethylsilyl[2,2,3,3-^{2}H$_4$]-propionate (TSP, Aldrich) as an external standard. ESR spectra were taken on a JEOL IES-TE200 spectrometer at X-band with a frequency

of 9.115 42 GHz, power of 1.08 mW, field of 120 ± 50 mT, sweep time of 0.5 min, modulation of 0.1 mT, and time constant of 0.03 s. Microcalorimetric measurements were carried out with a MicroCal Isothermal Titration Calorimeter VP-ITC, and the data were subsequently analyzed using the ORIGIN software program. Determination of the binding constants from the absorption spectral titrations and determination of the reaction rate constants for complexation of Fe(III)-TPPS with TMe-β-CD was performed according to a previous method.[18]

Supporting Information Available: Job's plots for complexation of Fe(III)TPPS with TMe-β-CD in aqueous solutions at pH 1.5 in the absence and the presence of NaCl, absorption spectral changes of Fe(III)TPPS in succinic acid buffer at pH 4.0 upon addition of TMe-β-CD and the results of curve fitting to determine K_{11} and K_{12}, derivation of eq 1, the plot of K_{12} vs [H$^+$], the time courses of complexation of Fe(III)TPPS with TMe-β-CD, ESR spectra (X-band) of Fe(III)TPPS in aqueous TMe-β-CD solutions with and without NaCl at pH 1.5 and 77 K, ^{1}H NMR spectra of Fe(III)TPPS in D$_2$O with and without TMe-β-CD at pD 12, absorption spectral changes of Fe(III)-TPPS complexed with TMe-β-CD in succinic acid buffer at pH 4.0 upon addition of various kinds of inorganic salts, ITC data for ligation of various anions to Fe(III)TPPS complexed with TMe-β-CD, plots of ΔHs for ligation of Cl$^-$ and Br$^-$ to Fe(III)-TPPS complexed with TMe-β-CD vs temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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