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PAPER

One-electron oxidized product of diffuoroiron(III) porphyrin: is it iron(IV) porphyrin or iron(III) porphyrin π -cation radical?[†]

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The electronic structure of [Fe(TMP)F₂], which is formally a one-electron oxidation equivalent above [Fe^{III}(TMP)F₂]⁻, has been examined in solution by ¹H NMR, UV-Vis, and Mössbauer spectroscopy. In CD₂Cl₂–CD₃OD solution at 193 K, the pyrrole-H and *m*-H signals appeared at 128.2 and 116.7 ppm, respectively. The UV-Vis spectrum showed broad absorption bands at 560–680 nm. The Mössbauer spectrum taken in frozen toluene–methanol solution exhibited a very broad single line from which the IS and QS values were determined by computer simulation to be 0.50 and 0.14 mm s⁻¹, respectively. On the basis of these results, it was concluded that the one-electron oxidized product of [Fe(TMP)F₂]⁻ should be formulated as the iron(III) radical cation [Fe^{III}(TMP[•])F₂], not as iron(IV) porphyrin [Fe^{IV}(TMP)F₂] as previously suggested.

Introduction

High-valent iron porphyrin complexes are key reactive intermediates in heme enzymes such as Cytochrome P450 and peroxidase.¹⁻³ Revealing the nature of the reactive intermediates has been an issue of great interest. Thus, extensive studies have been done on the formation and characterization of various one- and twoelectron oxidized products of iron(III) porphyrins.^{4,5} In principle, one-electron oxidation of iron(III) porphyrin produces either iron(IV) porphyrin or the iron(III) porphyrin radical cation.⁶⁻¹² Actually however, iron(IV) porphyrins are rarely obtained except for the complexes having an Fe^{IV}=O unit.^{11,12} A unique example is [Fe^{IV}(TMP)(OMe)₂] reported by Groves et al. in 1985.^{13,14} The factors affecting the iron(IV) states have been discussed theoretically by Ghosh et al.^{15,16} Finding another example of an iron(IV) complex is quite important to reveal the general conditions that stabilize the iron(IV) porphyrin relative to the iron(III) porphyrin radical cation.¹⁷⁻¹⁹ Among various axial ligands, fluoride should be the most plausible candidate because it is classified as a strong field ligand as methoxide.20 In fact, the oxidation potential of $[Fe^{III}(TPP)F_2]^-$ is quite unusual because the first oxidation wave is observed at +0.68 V, which is ca. 0.4 V less anodic than that of a large number of high-spin five-coordinate [Fe^{III}(TPP)X] compounds.²¹ However, the isolation of the oneelectron oxidized species was unsuccessful due to the instability of the product.^{21,22} Density functional studies also predicted the formation of $[Fe^{IV}(TPP)F_2]$ rather than $[Fe^{III}(TPP)F_2]$.²³ Recently, Ghosh and Taylor reported the opposite result on the basis of the more accurate and sophisticated CASPT2 calculations; $[Fe^{III}(TPP)F_2]$ is 0.31 eV more stable than $[Fe^{IV}(TPP)F_2]$.²⁴ More recently, Panchmatia *et al.* reached the same conclusion by using DFT+U and UB3LYP techniques.²⁵ In this paper, we will describe the electronic structure of $[Fe(Por)F_2]$, which corresponds to the one-electron oxidized product of $[Fe^{III}(Por)F_2]^-$, not only to answer the controversial issue but also to seek for the general conditions to obtain iron(IV) porphyrin complexes.

Results and discussion

¹H NMR spectroscopy

To obtain the complex that is the one-electron oxidation equivalent above $[Fe^{III}(TMP)F_2]^-$, the methanol-d₄ (CD₃OD) solution of tetrabutylammonium fluoride(Bu₄NF) was added at 193 K to the CD₂Cl₂ solution of $[Fe(TMP^{\bullet})(ClO_4)_2]$ in an NMR sample tube as shown in Scheme 1. The starting complex, $[Fe^{III}(TMP^{\bullet})(ClO_4)_2]$,



 $\label{eq:scheme1} \begin{array}{l} \mbox{Formation of the complex that is the one-electron oxidation} \\ \mbox{equivalent above } [Fe^{III}(TMP)F_2]^{-}. \end{array}$

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should be partially converted to $[Fe^{III}(TMP^{\bullet})(CD_3OD)_2](CIO_4)_2$ and/or $[Fe^{III}(TMP^{\bullet})(CIO_4)(CD_3OD)](CIO_4)$ in $CD_2Cl_2-CD_3OD$ solution. In fact, the pyrrole-H signal appeared at *ca*. 100 ppm at 195 K, which clearly indicates that the complex adopts the S = 5/2spin state; $[Fe^{III}(TMP^{\bullet})(CIO_4)_2]$ shows the pyrrole-H signal at -22.5ppm since the complex adopts the mixed S = 3/2, 5/2 spin state.^{6,13} The *o*-CH₃, *m*-H, and *p*-CH₃ signals were observed extremely downfield at 41, 121, and 27 ppm, respectively, in $CD_2Cl_2-CD_3OD$ solution, suggesting that the porphyrin has a half-occupied a_{2u} orbital.¹³

Fig. 1 shows the ¹H NMR spectra taken after the addition of (a) 1.0, (b) 1.5, and (c) 2.0 equiv of Bu₄NF. When 1.0 equiv of Bu₄NF was added, the starting complex was completely converted to the new complex signified as **A** as shown in Fig. 1(a). The signal at 112.8 ppm was assigned to the pyrrole-H of **A** by the spectral comparison with the pyrrole-d₈ complex shown in Fig. 1(a-1). The presence of the downfield shifted pyrrole-H signal indicates that **A** adopts the high-spin (S = 5/2) state. The mesityl signals shifted upfield but they still appeared at extremely downfield positions; the *o*-CH₃, *m*-H, and *p*-CH₃ signals were observed at 31.4 (average), 89.3 (average), and 18.7 ppm, respectively. Thus, the radical cationic state is maintained even after the addition of 1.0 equiv of Bu₄NF. Close inspection of the spectrum revealed that the *o*-CH₃ gave two very broad signals as shown in Fig. 1(a-



Fig. 1 ¹H NMR spectral changes of $[Fe^{III}(TMP^{*})(ClO_{4})_{2}]$ observed when (a) 1.0, (b) 1.5, and (c) 2.0 equiv. of $(Bu_{4}N)F$ was added at 193 K. (a-1) and (c-1) are the downfield region of the pyrrole-d₈ complex. Symbols o¹, m¹, p¹, and py¹ correspond to the *o*-CH₃, *m*-H, *p*-CH₃, and pyrrole-H signals of mono-F complex (A). Similarly, the symbols o², m², *etc.* correspond to those of bis-F complex (B).

2). The results suggest that **A** is the mono-F complex formulated either by five-coordinate [Fe^{III}(TMP[•])F]ClO₄ or by six-coordinate [Fe^{III}(TMP[•])F(CH₃OH)]ClO₄ and/or [Fe^{III}(TMP[•])F(ClO₄)]. By the further addition of Bu₄NF, the signals of **A** were gradually replaced by those of the new complex signified as **B** as shown in Fig. 1(b). When 2.0 equiv of Bu₄NF was added, the signals of **A** were almost completely replaced by those of **B** as shown in Fig. 1(c). The broad signal at 129.0 ppm was assigned to the pyrrole-H on the basis of the spectral comparison with the pyrrole-d₈ complex as shown in Fig. 1(c-1). Thus, the high-spin state of the iron(III) ion is maintained during the addition of Bu₄NF. The large downfield shifts of the *o*-CH₃ and *m*-H indicate that **B** should be best formulated as high-spin (S = 5/2) six-coordinate [Fe^{III}(TMP[•])F₂] where the radical spin is in the porphyrin a_{2n} orbital.

The same reaction was carried out in CD₂Cl₂ solution containing no CD₃OD. By the addition of 1.0 equiv of Bu₄NF, the ¹H NMR spectrum completely changed to show the formation of a new complex signified as A' as given in Fig. S1(a) of the ESI.[†] Although the pyrrole signal of A' was observed at a downfield position, *i.e.* 114.6 ppm, as in the case of A formed in CD₂Cl₂-CD₃OD solution, all the other signals appeared in the opposite direction. For example, the o-CH₃ signals were observed at -8.6 and -11.7 ppm, m-H signals at -34.9, -37.8 ppm, and the p-CH₃ signal at -5.7 ppm. Thus, the ¹H NMR spectrum of A' resembles that of five-coordinate [Fe^{III}(TPP)Cl]SbCl₆,⁷ and should be expressed as [Fe^{III}(TMP[•])F]ClO₄. The large upfield shift of the *m*-H signals can then be explained in terms of the antiferromagnetic coupling between the unpaired electrons in the $a_{2\mu}$ and dz² orbitals;^{7,26,27} this interaction is symmetry allowed in fivecoordinate complexes where the iron(III) ion is placed out of the porphyrin plane.^{28,29} The result, in turn, indicates that the mono-F complex A formed in CD₂Cl₂-CD₃OD solution should be formulated as high-spin six-coordinate [Fe^{III}(TMP[•])F(CD₃OD)]ClO₄ and/or $[Fe^{III}(TMP')F(ClO_4)]$ rather than $[Fe(TMP')F]ClO_4$.

When 2.0 equiv of Bu_4NF was added, [Fe(TMP')F]ClO₄ was completely converted to the new complex signified as **B'**. Since the ¹H NMR spectrum of **B'** shown in Fig. S1(b)† is essentially the same as that of **B** formed in CD₂Cl₂–CD₃OD solution, **B'** should be formulated as [Fe^{III}(TMP')F₂]. We have noticed that **B** is much more stable than **B'**. That is, while the reduction of **B'** took place during the ¹H NMR measurement at 223 K, no reduction was observed in the case of **B** even at 298 K. The result suggests that methanol is playing an important role in stabilizing [Fe^{III}(TMP')F₂]. Presumably, the hydrogen bonding with methanol weakens the field strength of fluoride, which in turn weakens the reducing ability of the coordinating fluoride ions. Table 1 lists the chemical shifts of these complexes together with those of analogous oxidized complexes.

In order to confirm if **B** is really the one-electron oxidation equivalent above $[Fe^{III}(TMP)F_2]^-$, the titration experiment was carried out using Bu₄NI as a reducing agent. As shown in Fig. 2(a) and (b), the addition of 0.5 equiv of Bu₄NI converted 50% of **B** to high-spin $[Fe^{III}(TMP)F]$. Complete conversion to $[Fe^{III}(TMP)F]$ was achieved by the addition of 1.1 equiv of Bu₄NI as shown in Fig. 2(c). Thus, the titration result clearly indicates that **B** is one-electron oxidation equivalent above the iron(III) porphyrin. It should be noted that the one-electron reduction of $[Fe^{III}(TMP)F_2](B)$ produces $[Fe^{III}(TMP)F]$ rather than

 Table 1
 ¹H NMR chemical shifts of one-electron oxidized complexes

Complexes ^a	T/K	Solv ^b	Ру	o-CH ₃	т	<i>p</i> -CH ₃	ES ^g	Ref.
$\overline{[Fe(TMP)F(CH_{3}OH)]X(A)}$	193	i	112.8	32.0 30.8	89.5 89.1	18.7	$Fe^{III} (S = 5/2)$, Por	This work
[Fe(TMP)F]X(A')	193	ii	116.6	-8.6 -11.7	-34.9 -37.8	-5.7	$\operatorname{Fe^{III}}(S = 5/2), \operatorname{Por}, \operatorname{AF}$	This work
$[Fe(TMP)F_2](B)$	193	i	128.2	40.2	116.7	23.2	Fe^{III} (S = 5/2), Por [•]	This work
$[Fe(TMP')F_2](B')$	193	ii	123.3	40.7	112.2	21.2	Fe^{III} (S = 5/2), Por [•]	This work
$[Fe(TMP')(BuNC)_2]X_2$	193	ii	4.71	2.51	6.63	2.15	Fe^{III} (S = 1/2, d_{xy}), Por, AF	9
$[Fe(TMP')(HIm)_2]X_2$	193	ii	-61.2	23.0	58.2	7.1	Fe^{III} (S = 1/2, d _π), Por	9
[Fe(TMP')(ClO ₄) ₂]	195	ii	-22.5	32.2	90.9	19.7	Fe ^{III} $(S = 5/2, 3/2)$, Por	13
[Fe(TMP')(CH ₃ OH) ₂]X ₂	193	iii	100.3	38.1	113.2	24.2	Fe^{III} (S = 5/2), Por	This work
[Fe(TPP•)Cl]X	299	ii	66.1	37.6° 34.4°	-12.3	29.5 ^r	Fe^{III} (S = 5/2), Por [•] , AF	7
$[Fe(T^{i}PrP^{\bullet})X_{2}]$	298	ii	-64.1	109.7^{d}	23.8 ^e		Fe ^{III} ($S = 3/2$), Por [•]	10
[Fe(TMP)(OCH ₃) ₂]	195	i	-37.5	2.4	7.72	2.86	Fe^{IV} (S = 1)	13

^{*a*} X = ClO₄^{-, *b*} Solvents: (i) CD₂Cl₂–CD₃OD, (ii) CD₂Cl₂, (iii) CD₃OD. ^{*c*} *o*-H. ^{*d*} *meso*-CH(α). ^{*e*} *meso*-CH₃. ^{*f*} *p*-H. ^{*g*} ES: Electronic structure, Por⁺: porphyrin radical cation, AF: antiferromagnetic coupling between iron(III) and porphyrin radical.



Fig. 2 ¹H NMR spectral changes of **B** after the addition of (a) 0.0, (b) 0.5, and (c) 1.1 equiv of iodide at 193 K. The symbols o^2 , m^2 , p^2 , and py^2 indicate the *o*, *m*, *p*, and pyrrole signals of [Fe^{III}(TMP')F₂] (**B**), while the symbols m^0 and py^0 are *m* and pyrrole signals of [Fe^{III}(TMP)F].

 $[Fe^{III}(TMP)F_2]^-$. This is understandable because $[Fe^{III}(TMP)F]$ is converted to $[Fe^{III}(TMP)F_2]^-$ only in the presence of a large excess of fluoride.³⁰ This is in sharp contrast to the case of the corresponding iron(III) radical cation $[Fe^{III}(TMP^{\bullet})(CIO_4)_2]$. In the latter case, 2.1 equiv of fluoride is sufficient to convert $[Fe^{III}(TMP^{\bullet})(CD_3OD)_2]$ to $[Fe^{III}(TMP^{\bullet})F_2]$ (**B**).

Fig. 3 shows the temperature dependence of the ¹H NMR signals of **B**. Plots of the chemical shifts against 1/T showed an adequately good straight line within the range 298 to 173 K (1/T: 0.00336



Fig. 3 Temperature dependence of the ¹H NMR chemical shifts of **B** taken in CD_2Cl_2 - CD_3OD solution.

to 0.00578); both pyrrole-H and *m*-H show a slight curvature at higher temperature. Most of the lines exhibit sizable deviation from the diamagnetic position at 1/T = 0 which is observed in other iron(III) porphyrin radical cations.⁷

UV-vis spectroscopy

UV-vis spectroscopy is a useful method to determine the oxidation site in the complex.²⁶ Fig. 4 shows the UV-vis spectral changes observed when Bu_4NF was added to the $CH_2Cl_2-CH_3OH$ solution of [Fe^{III}(TMP[•])(ClO₄)₂]. The black, green, and red lines represent the spectra measured at 193 K after the addition of 0.0, 1.0. and 3.0 equiv of Bu_4NF , respectively. The spectra drawn by the green and red lines, therefore, correspond to the complexes **A** and **B**, respectively. It should be noted that both **A** and **B** exhibit the broad absorption bands at 560–680 nm characteristic to the porphyrin radical. In contrast, the absorption maxima of the six-coordinate iron(IV) complex [Fe^{IV}(TMP)(OCH₃)₂] were reported to be 425.5, 546, and 575 nm. Thus, the UV-Vis spectra clearly indicate that both **A** and **B** have a radical cationic porphyrin ring.

Mössbauer spectroscopy

Mössbauer spectroscopy is also a powerful method to elucidate the oxidation and spin states of iron porphyrin complexes.^{31,32} Fig.



Fig. 4 UV-vis spectral changes observed after the addition of 0.0 (black), 1.0 (green), and 3.0 (red) equiv of Bu_4NF to the $CH_2Cl_2-CH_3OH$ solution of $[Fe^{III}(TMP)(ClO_4)_2]$ at 195 K.

5 shows the Mössbauer spectra taken at 77 K after the addition of (a) 0.0, (b) 1.0, and (c) 2.0 equiv of Bu_4NF to the toluene– methanol solution of ⁵⁷Fe-enriched [Fe^{III}(TMP[•])(ClO₄)₂] (95.5% ⁵⁷Fe). Fig. 5(a) shows a broad unsymmetrical doublet, which can be explained in terms of the presence of several complexes with different axial ligands. As mentioned, they are supposed to be [Fe^{III}(TMP[•])(ClO₄)₂], [Fe^{III}(TMP[•])(ClO₄)(CH₃OH)]⁺, and [Fe^{III}(TMP[•])(CH₃OH)₂]²⁺. In fact, the observed Mössbauer spectrum shown by the yellow line was reproduced by considering the presence of the three kinds of complexes. The complex **P1** drawn by the red line has the largest population, *i.e.* 53%, and its IS and QS values were 0.54 and 1.06 mm s⁻¹, respectively. In contrast, the complex **P2** drawn by the green line accounts for only 12%. The IS and QS values were 0.20 and 0.60 mm s⁻¹, respectively. The small QS values suggest that both **P1** and



Fig. 5 Mössbauer spectra observed after the addition of (a) 0.0, (b) 1.0, and (c) 2.0 equiv of Bu_4NF to the toluene–methanol solution of $[Fe^{III}(TMP)(CIO_4)_2]$ (95.5% ⁵⁷Fe) at 77 K.

P2 adopt the S = 5/2 state. Thus, they were assigned to either [Fe^{III}(TMP[•])(ClO₄)(CH₃OH)]⁺ or [Fe^{III}(TMP[•])(CH₃OH)₂]²⁺. The complex **P3** given by the blue line accounts for 33% and consists of a very broad doublet with a line width of 0.87 mm s⁻¹. The IS and QS values were determined to be 0.58 and 2.14 mm s⁻¹, respectively, though these values should contain a sizable amount of error due to the signal broadness. The relatively large QS value suggests that **P3** is assigned to [Fe^{III}(TMP[•])(ClO₄)₂], which adopts the mixed S = 5/2, 3/2 spin state as revealed by the ¹H NMR spectrum. The presence of the S = 3/2 isomer should expand the QS value, assuming that the exchange rate between the S = 5/2 and S = 3/2 spin isomers is fast on the Mössbauer timescale at 77 K; the QS values of the S = 3/2 complexes are in general larger than 3.0 mm s⁻¹.^{33,34,35}

Fig. 5(b) shows the Mössbauer spectrum obtained by the addition of 1.0 equiv of Bu₄NF. Obviously, two species are present in the frozen solution. The minor species was assigned to the unreacted [Fe^{III}(TMP[•])(ClO₄)₂], since the IS and QS values, 0.60 and 2.21 mm s⁻¹, respectively, are similar to those of **P3** in Fig. 5(a). The major component shows a typical paramagnetically relaxed spectrum, which was analyzed using a Blume–Tjon model.³⁶ The obtained Mössbauer parameters were IS = 0.51, e^2qQ (quadrupole coupling constant) = 0.99 mm s⁻¹, H_{int} (internal magnetic field) = 8.0 T, τ (relaxation time) = 8.8 ns with fixed η (asymmetric parameter) = 0. The positive value of e^2qQ leads the QS value to be 0.50 mm s⁻¹. This species was assigned to the mono-F complex (A), [Fe^{III}(TMP[•])F(ClO₄)] or [Fe^{III}(TMP[•])F(CH₃OH)]⁺, as mentioned in the ¹H NMR section.

In contrast to Fig. 5(a) and (b), Fig. 5(c) shows only one iron site suggesting the formation of $[Fe^{III}(TMP^{\bullet})F_2]$ (B). This is understandable because the solution contains 2.0 equiv of F- which has much stronger field-strength than ClO₄⁻ and CH₃OH. The spectrum again showed a paramagnetically relaxed spectrum and was analyzed using the same model. The Mössbauer parameters were estimated to be IS = 0.50, $e^2 qQ = 0.29 \text{ mm s}^{-1}$, $H_{int} = 8.0 \text{ T}$, $\tau =$ 9.9 ns. The estimated QS value was thus 0.14 mm s⁻¹. The small QS value confirms that the complex also adopts the high-spin state. Table 2 lists the Mössbauer parameters of all the complexes observed during the titration processes together with the possible structural formulae. It should be noted that the QS value decreased from 1.06 (P1) to 0.50 (A) and then to 0.14 mm s⁻¹ (B) as the weak axial ligands such as perchlorate and/or methanol were replaced by much stronger fluoride in a stepwise fashion. The result is understandable because the increase in the σ -donor strength of the axial ligand should decrease the electric field gradient V_{zz} . Interestingly the estimated QS value for A is close to the average of those for P1 and B, suggesting that the V_{zz} value is varied by the axial ligands additively.

Conclusion and perspective

The ¹H NMR, UV-vis, and Mössbauer spectroscopy have been used to elucidate the electronic structure of the complex which is formally the one-electron oxidation equivalent above $[Fe^{III}(TMP)F_2]^-$. The electronic structure of $[Fe(TMP)F_2]$ turns out to be quite different from that of $[Fe(TMP)(OCH_3)_2]$ although the field strength of F^- is similar to that of OCH_3^- . As shown in Fig. 6, the stable structure of the former complex is formulated as the iron(III) porphyrin radical cation $[Fe^{III}(TMP^*)F_2]$ while the latter is

 Table 2
 Mössbauer parameters in frozen toluene-methanol solution at 77 K

F- added	Complex ^a	IS	QS	Area (%)	Structural formula
0.0 equiv	P1	0.54	1.06	55	$\left([\text{Fe}^{\text{III}}(\text{TMP})(\text{CIO}_4)(\text{CH}_3\text{OH})]^+ \text{ or } \right)^b$
	P2	0.20	0.60	12	$[Fe^{III}(TMP^{\bullet})(CH_{3}OH)_{2}]^{2+}$
	P3	0.58	2.14	33	$[Fe^{III}(TMP^{\bullet})(ClO_4)_2]$
1.0 equiv	Α	0.51	0.50	major	$\left([Fe^{III}(TMP)F(ClO_4)] \text{ or } \right)^{b}$
					$\left(\left[\text{Fe}^{\text{III}}(\text{TMP})F(\text{CH}_{3}\text{OH}) \right]^{+} \right)$
	P3	0.60	2.21	minor	$[Fe^{III}(TMP^{\bullet})(ClO_4)_2]$
2.0 equiv	В	0.50	0.14	100	$[Fe^{III}(TMP)F_2]$

^{*a*} P1, P2, P3 are the iron sites in the starting complexes. A and B are the mono-F and di-F complexes, respectively. See the text. ^{*b*} Structures are not specified.



Fig. 6 Electronic structures of the complexes that are one-electron oxidation equivalents above (a) $[Fe^{III}(TMP)F_2]^-$ and (b) $[Fe^{III}(TMP)(OMe)_2]^-$.

expressed as the iron(IV) porphyrin [Fe^{IV}(TMP)(OCH₃)₂]. It should be pointed out here that the formation of [Fe^{III}(TMP')F₂] does not necessarily indicate that [Fe^{III}(TMP')F₂] is the initial product upon oxidation of [Fe^{III}(TMP)F₂]⁻. It could be possible that the initially formed iron(IV) complex is immediately converted to the thermodynamically more stable iron(III) radical cation.³⁷ One possible way to prepare iron(IV) porphyrin is to use much stronger anionic bases such as metal amides. However, such a strong base should easily reduce the iron(IV) ion as we have experienced the reduction of [Fe(TMP')F₂] to [Fe(TMP)F] by the coordinating F⁻ ion in CH₂Cl₂ solution. Thus, a fine tuning of the field-strength of anionic ligands by using suitable solvent is quite important for the synthesis of rare six-coordinate iron(IV) porphyrins without an Fe^{IV}=O unit. Such a study is now in progress in this laboratory.

Experimental

Spectral measurements

UV-Vis spectra were recorded for the CH₂Cl₂–CH₃OH solutions at 195 K on a Shimadzu MultiSpec-1500 spectrophotometer equipped with a UNISOKU liquid nitrogen cryostat, CoolSpec UV USP-203-A. ¹H NMR spectra were recorded for the CD₂Cl₂ solution in the presence and absence of CD₃OD on a JEOL LA300 spectrometer operating at 300.4 MHz for ¹H. Chemical shifts were referenced to the residual peak of dichloromethane ($\delta = 5.32$ ppm). Iron-57 Mössbauer spectra were measured on a Wissel Mössbauer spectrometer system (MR-260S, MA-260A, DFG-500, and CMCA-550). The samples were kept in a Heli-Tran LT-3 gas-flow cryostat from Advanced Research System Inc. equipped with a 9620 digital temperature controller from Scientific Instruments Inc., and the ⁵⁷Co(Rh) source was kept at room temperature. The data were analyzed on a Möss Winn 3.0i XP Program. The isomer shift is given relative to R-iron foil at room temperature.

Sample preparation

[Fe^{III}(TMP)(ClO₄)] was prepared by the addition of AgClO₄ to the CH₂Cl₂ solution of [Fe^{III}(TMP)Cl] by the method reported by Reed *et al.*²⁶ Oxidation of [Fe^{III}(TMP)(ClO₄)] was performed using Fe(ClO₄)₃ as the oxidant according to the procedure reported by Groves *et al.*^{13 57}Fe-enriched [Fe^{III}(TMP)Cl] (95.5% ⁵⁷Fe) was prepared by metallating (TMP)H₂ with 0.8 equiv ⁵⁷FeCl₂ in refluxed DMF solution.

Titration experiment

The ¹H NMR sample tube containing a CD_2Cl_2 solution of $[Fe^{III}(TMP)(ClO_4)_2]$ was placed in a liquid nitrogen bath, to which a CD_3OD solution of Bu_4NF was added. The sample tube was then immersed in a dry-ice–acetone bath and shaken for several minutes. The ¹H NMR spectra were recorded at each time after the addition of a certain amount of Bu_4NF .

A Mössbauer sample was similarly prepared. A flask containing the toluene solution of $[Fe^{III}(TMP)(ClO_4)_2]$ was placed in a liquid nitrogen bath, to which a CH₃OH solution of Bu₄NF was added. The flask was then placed in the dry-ice–acetone bath and shaken for several minutes to prepare the fluoride complexes. The solution containing the fluoride complexes was transferred to a Mössbauer cell placed in a liquid nitrogen bath with a syringe already cooled by dry ice.

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- 14 Abbreviations: TPP, Por, TMP, and TⁱPrP: dianions of *meso*-tetraphenylporphyrin, porphyrin, *meso*-tetramesitylporphyrin, and *meso*-tetraisopropylporphyrin, respectively.
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