Preparation and Characterization of Mono-Imidazole Ligated (*meso*-Tetramesitylporphyrinato)iron(III) Complexes: Model for Cytochromes *c'*

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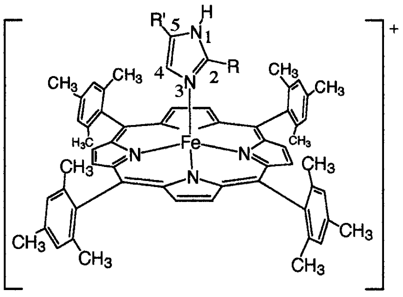
A series of mono-imidazole ligated (*meso*-tetramesitylporphyrinato)iron(III) complexes have been prepared. The spin states of these complexes are presented as the admixed intermediate (S = 3/2, 5/2) on the basis of the ^{1}H NMR, ^{13}C NMR, EPR, and magnetic moments. The S = 3/2 character has increased as the axial imidazole ligand becomes bulkier.

Cytochromes *c'* are a unique class of heme proteins found in photosynthetic, denitrifying, and nitrogen fixing bacteria. The heme iron is penta-coordinated with a histidine residue as the fifth ligand.[1] In the oxidized state, these proteins exhibit unusual EPR spectra which originate from a unique spin state; a quantum mechanical admixture of a high spin(S = 5/2) and an intermediate spin(S = 3/2) state.[2,3] The respective proportions of the S = 5/2 and S = 3/2 spin state change depending on the bacteria.[4] In most cases, S = 5/2 is predominant though the contribution of the S = 3/2 state increases in some bacteria such as *Chromatium vinosum* and *Rhodobacter capsulatus*.[4] In order to reveal the factors affecting the spin states of cytochromes *c'*, a systematic study using synthetic models is necessary. The model studies have been hampered, however, because of the instability of mono-imidazole adducts;[5] only a limited number of the studies have been reported.[6–9] In this paper, we report the formation of a series of mono-imidazole adducts shown in the Scheme and present one of the factors that affects the spin state of these complexes.



[Fe(TMP)(2-R-5-R'Im)]$^+$

R	R'
H	Me
Me	H
Et	H
^{i}Pr	H

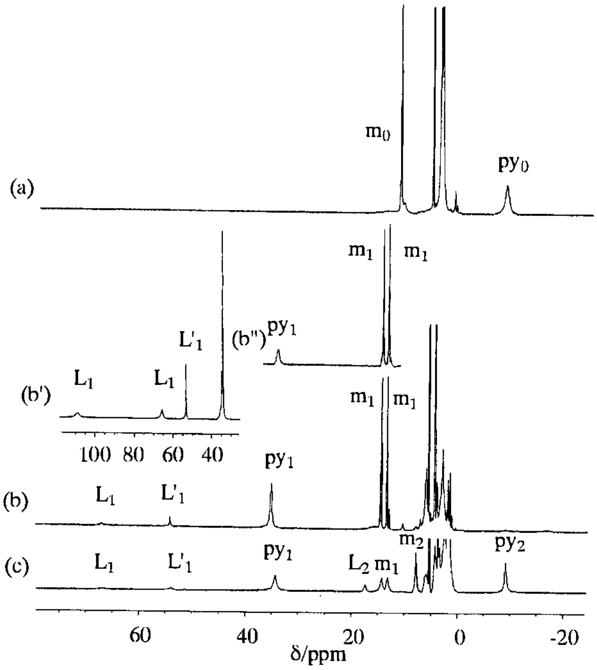


Figure 1. ^{1}H NMR spectra of [Fe(TMP)]ClO$_4$ taken in CD$_2$Cl$_2$ solution at 25 °C after the addition of (a) 0.0, (b) 1.0, and (c) 1.5 equiv of 2-MeIm. Signals labeled by (m$_0$, m$_1$, m$_2$), (py$_0$, py$_1$, py$_2$), and (L$_1$, L$_2$) are assigned to the *meta*, pyrrole, and ligand ring protons of [Fe(TMP)]ClO$_4$, [Fe(TMP)(2-MeIm)]ClO$_4$, and [Fe(TMP)(2-MeIm)$_2$]ClO$_4$, respectively. L$_1$' is the NH signal of the coordinated 2-MeIm in [Fe(TMP)(2-MeIm)]ClO$_4$. (b') Downfield region of (b). (b'') Spectrum obtained by the addition of 1.0 equiv of 2-MeIm into [Fe(TMP)]ClO$_4$(75% pyrrole deuterated).

Figure 1 shows the ^{1}H NMR spectra of [Fe(TMP)]ClO$_4$ taken at 25 °C in CD$_2$Cl$_2$ after the addition of various amounts of 2-MeIm.[10] As 2-MeIm was added, new signals appeared and increased their intensities. By the addition of 1.0 equiv of 2-MeIm, the signals for [Fe(TMP)]ClO$_4$ completely disappeared. The product showed pyrrole signal at δ 35.1 and *meta*-signals at 13.2 and 14.3 ppm, which were confirmed by the spectral comparison with the deuterated complexes. Three signals at fairly downfield, 54.0(2H), 67.0(2H), and 110.7(2H) ppm, were assigned to the ring protons of the coordinated 2-MeIm ligand. Thus, the product was identified as mono-imidazole adduct [Fe(TMP)(2-MeIm)]$^+$. Existence of the two *meta*-signals supports penta-coordination as is often found in iron(III) porphyrin complexes.[11] Large downfield shifts of the ligand signals suggest that the complex has unpaired electron in the d_{z^2} orbital, which is transferred to the ligand protons through σ bonds to induce downfield shift. Further addition of 2-MeIm decreased the signals for the mono-imidazole adduct and increased those for the well-characterized bis-imidazole adduct as is clear from the py$_2$ and m$_2$ signals at –9.13 and 7.78 ppm, respectively.[12] When 2.0 equiv of 2-MeIm was added, the mono-imidazole adduct was completely converted to the bis-imidazole adduct. Other mono-imidazole adducts were prepared similarly, whose chemical shifts are listed in Table 1.

Chemical shift of the pyrrole protons is a good probe to determine the spin state of iron(III) ions.[11] High spin complexes show pyrrole signals at fairly downfield, 80 ppm at 25 °C. In contrast, low spin complexes give pyrrole signals at much higher field, typically ca. –15 ppm. Some low spin complexes with the less common $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state exhibit the pyrrole signals at ca. 10 ppm.[13–15] Recently, Reed and coworkers reported that [Fe(TPP)(CB$_{11}$H$_6$Br$_6$)] is a pure intermediate spin complex;

Table 1. ^{1}H and ^{13}C NMR chemical shifts of $[Fe(TMP)L]^+$ at 25 °C in CD_2Cl_2.

Ligands	^{1}H NMR				^{13}C NMR		
	pyrrole		*meta*		py(α)	py(β)	*meso*
Cl^-	79.8	(125.2)	15.9	14.3	1204	1327	525
ClO_4^-	-9.3	(-61.6)	11.4		176	377	252
5-MeIm	31.0	(40.4)	13.7	12.8	774	855	322
2-MeIm	35.1	(29.3)	14.3	13.2	754	884	384
2-EtIm	32.4	(16.9)	14.1	13.1	717	862	391
2-^{i}PrIm	30.5	(4.4)	14.0	13.1	679	836	390

Data in parenthesis are the chemical shifts at –80 °C.

the pyrrole signal reached –62 ppm.[16,17] The mono-imidazole adducts examined here are neither high spin nor low spin because the pyrrole signals appeared at 30.5 to 35.1 ppm. If ligand exchange between the mono- and bis-imidazole adducts is fast on the ^{1}H NMR time scale, the pyrrole signals could appear at ca. 30 ppm. The possibility is ruled out, however, because the pyrrole signal of the bis-adduct appeared separately as shown in Figure 1c. Thus, the spin state of the mono-adducts must be the admixture of the $S = 5/2$ and $S = 3/2$. The solution magnetic moment of $[Fe(TMP)(2\text{-}MeIm)]ClO_4$ measured by the Evans method was 5.0 μ_B at 25 °C, supporting the conclusion described above. EPR spectrum of the same complex taken in frozen CH_2Cl_2 solution at 4.2 K showed signals at $g = 5.7$ and 2.0. The result indicates that the electronic ground state consists of 15% $S = 3/2$ and 85% $S = 5/2$, which is similar to that of the cytochrome c' obtained from *Rhodospirillum molischianum*.[3]

^{13}C NMR chemical shift is also a good probe to determine the ground state of iron(III) porphyrin complexes.[18,19] The chemical shifts of the carbon atoms that constitute the porphyrin core are listed in Table 1. These values are located between the corresponding values of [Fe(TMP)Cl] and $[Fe(TMP)]ClO_4$; the former is the typical high spin complex while the latter is considered to be the admixed intermediate spin complex.[20] Thus, the ^{13}C NMR chemical shifts also support that the mono-imidazole adducts examined here are in the admixed intermediate spin state. It should be noted that the contribution of the $S = 3/2$ state in the mono-imidazole adducts is much smaller than that in $[Fe(TMP)]ClO_4$.

Figure 2 shows the temperature dependence of the pyrrole proton shifts. The pyrrole signals of these complexes move upfield at lower temperature except for the 5-MeIm complex; the chemical shifts reached 40.4, 29.3, 16.9, and 4.4 ppm at –80 °C for the R = H, Me, Et, and, ^{i}Pr, respectively. The upfield shifts indicate that the $S = 3/2$ character increases as the 2-R group becomes bulkier,[16] which could be explained in terms of the steric repulsion between bulky ligand and porphyrin core. The repulsion expands the iron-ligand bond length, drops the energy level of the d_{z^2} orbital, and stabilizes the $S = 3/2$ spin state.[17] Further study on the factors affecting the spin state of the mono-imidazole adducts is now in progress.

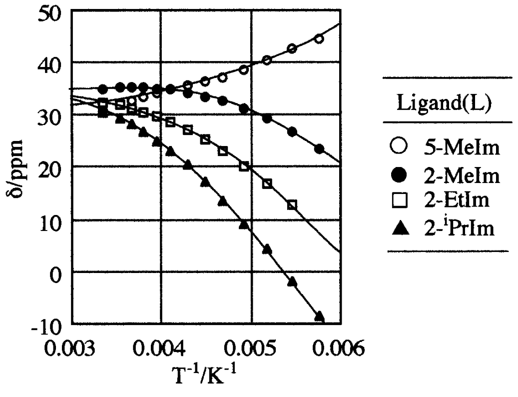


Figure 2. Temperature dependence of the chemical shift of the pyrrole protons in $[Fe(TMP)L]ClO_4$.

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10 Abbreviations: TMP, dianion of *meso*-tetramesitylporphyrin; $[Fe(TMP)]ClO_4$, (*meso*-tetramesitylporphyrinato)iron(III) perchlorate.
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