Control of electronic structure of a six-coordinate iron(III) porphyrin radical by means of axial ligands

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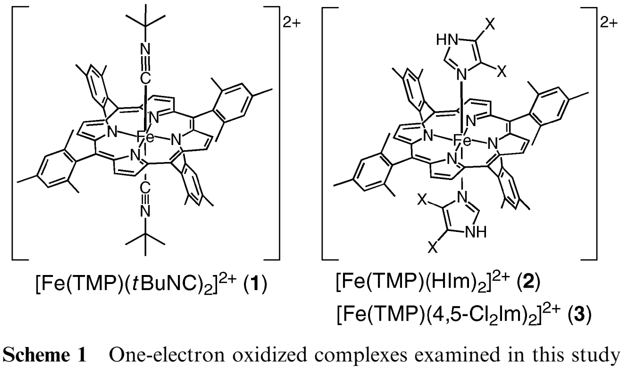
Received (in Cambridge, UK) 14th January 2008, Accepted 11th February 2008
First published as an Advance Article on the web 13th March 2008
DOI: 10.1039/b800674a

Addition of *tert*-butylisocyanide (^{t}BuNC) to a CD_2Cl_2 solution of the bis(perchlorato)(*meso*-tetramesitylporphyrinato) iron(III) cation radical leads to the formation of the corresponding bis(adduct), $[Fe(TMP)(^tBuNC)_2]^{2+}$, whose electronic structure is in sharp contrast to that of the corresponding imidazole(HIm) complex, $[Fe(TMP)(HIm)_2]^{2+}$; the former adopts the $S = 0$ while the latter exhibits the $S = 1$ electronic ground state.

High-valent iron porphyrin complexes have been extensively studied both experimentally and theoretically since they play important roles in the catalytic cycles of a number of heme and nonheme enzymes.[1–3] As is well known, one-electron oxidation of iron(III) porphyrins usually forms iron(III) porphyrin radical cations, where the iron(III) ion adopts either $S = 5/2$ or $S = 1/2$ state depending on the nature and numbers of axial ligands.[4,5] Radical spin on the porphyrin ring cannot be independent of the iron center. For five-coordinate iron(III) porphyrin radical $[Fe(TPP^{\bullet})Cl](SbCl_6)$, a strong antiferromagnetic coupling occurs between the $S = 5/2$ iron(III) ion and the $S = 1/2$ porphyrin radical to form an overall $S = 2$ spin state.[5,6] We can then expect that a strong antiferromagnetic coupling of the $S = 1/2$ iron(III) ion with the $S = 1/2$ porphyrin radical cation could give a diamagnetic complex though no examples have ever been found.[7] Recent studies on the heme electronic structures have revealed that $S = 1/2$ $[Fe(Por)(^tBuNC)_2]^+$ usually have a ruffled porphyrin core, and adopt the less common $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state.[8,9] In these complexes, the half-filled iron d_{xy} orbital strongly interacts with the filled a_{2u}-like porphyrin orbital to induce large spin delocalization from the metal to the porphyrin. It is then expected that $[Fe(TMP)(tBuNC)_2]^{2+}$(**1**) behaves as a diamagnetic complex, where the half-filled iron d_{xy} orbital antiferromagnetically couples with the half-filled porphyrin a_{2u}-like orbital. In this paper, we will report that **1** is actually the first example that shows mostly diamagnetic characters (Scheme 1).

1 was prepared by the addition of 20 equiv of *t*BuNC to a frozen CD_2Cl_2 solution of $Fe(TMP^{\bullet})(ClO_4)_2$ at 195 K.[10–12] ^{1}H NMR spectrum of **1** showed sharp signals in a narrow frequency region, 1–7 ppm as shown in Fig. 1a. Three intense signals at 2.03, 2.43, and 2.83 ppm shown in the inset (i) were assigned to the *p*-, *o*-, and ligand-CH_3 protons, respectively, on the basis of the relative integral intensities. Two signals at 6.52 and 4.73 ppm were assigned to the *meta* and pyrrole protons, respectively, by the spectral comparison with the pyrrole-d_8 complex as shown in the inset (ii). **1** was reduced quantitatively to $S = 1/2$ $[Fe(TMP)(tBuNC)_2]^+$ by the addition of 1.0 equiv of $(C_4H_9)_4N^+I^-$. Curie plot of each ^{1}H signal of **1** is shown in Fig. 2a. Although all the signals of **1** appeared in a so-called diamagnetic region, $\delta = 0$–10 ppm, the *meta* and pyrrole signals appeared more upfield than the corresponding signals of diamagnetic $[Co(TMP)(tBuNC)_2]^+$ by 0.82 and 4.23 ppm, respectively. Similarly, **1** showed the *meso*-^{13}C signal at 160 ppm at 173 K, which is 42 ppm more downfield than that of $[Co(TMP)(tBuNC)_2]^+$. Curie plots of the *meso*-^{13}C signal shown in Fig. 2b exhibited a slight curvature. The effective magnetic moment (μ_{eff}) of **1** determined by the Evans method in CH_2Cl_2 solution was as small as 0.45 μ_B at 173 K and slightly increased to 0.57 μ_B at 223 K.[13] The fairly small paramagnetic character of **1** at 173 K as revealed by ^{1}H NMR, ^{13}C NMR, and μ_{eff} values can best be explained in terms of the antiferromagnetic coupling between the half-filled iron d_{xy} and half-filled a_{2u}-like orbital of the ruffled porphyrin to form an overall $S = 0$ ground state; the a_{2u} orbital can interact with the d_{xy} orbital if the porphyrin ring is ruffled.[9] Thus, the origin of the fairly small paramagentic character of **1** should be compared with that of saddled $[Cu(OETPP^{\bullet})]^+$ reported by Fajer and co-workers, where the half-filled $d_{x^2-y^2}$ orbital of Cu(II) antiferromagnetically couples with the half-filled a_{2u}-like orbital of porphyrin to form a diamagnetic species.[14] An equivalent expression on the electron configuration of **1** should be $S = 0$ $(d_{xz}, d_{yz})^4(d_{xy}, a_{2u})^2$ (signified as **A**) as proposed by Ghosh *et al.*[15]



$[Fe(TMP)(tBuNC)_2]^{2+}$ (**1**) $[Fe(TMP)(HIm)_2]^{2+}$ (**2**)
$[Fe(TMP)(4,5\text{-}Cl_2Im)_2]^{2+}$ (**3**)

Scheme 1 One-electron oxidized complexes examined in this study.

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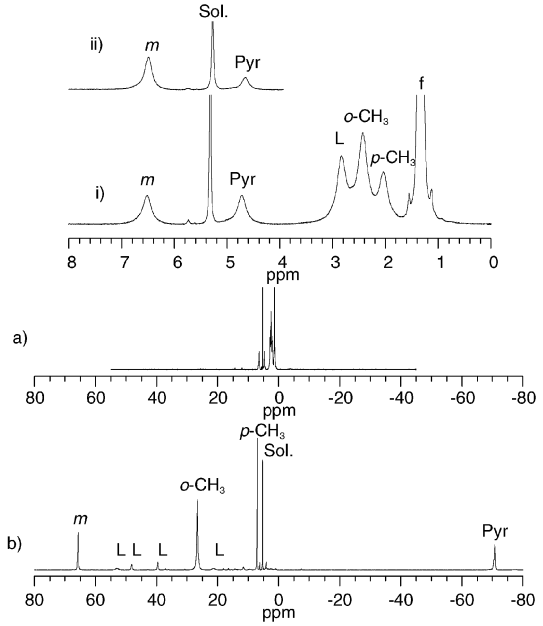

Fig. 1 (a) ^{1}H NMR spectra of **1** taken in CD$_2$Cl$_2$ solution at 173 K. Inset (i) shows the 0–8 ppm region, and inset (ii) shows the spectrum obtained from the pyrrole-d$_8$ complex. (b) ^{1}H NMR spectrum of **2** taken in CD$_2$Cl$_2$ solution at 173 K. Signals labeled by Pyr, *m*, L, F, and Sol are ascribed to the pyrrole, *meta*, coordinating ligand, free ligand, and solvent protons, respectively.

Deviations of the *meso*-^{13}C signal of **1** to the downfield direction at higher temperatures can be explained in terms of the increase in population of the thermally accessible S = 1 excited state, where the a$_{2u}$ orbital has some spin population. Increase in the radical cationic nature of **1** at higher temperature is, however, most explicitly observed in the half-height widths of the *meso*-^{13}C signal shown in Fig. 2b; the half-height width increased from 84 Hz(173 K) to 452 Hz(223 K). The result can be explained in terms of the large decrease in relaxation time of the *meso*-^{13}C nuclei caused by the presence of a slight amount of the radical at higher temperature.[16]

Fig. 3 shows the UV-vis spectra of **1** and its precursor Fe(TMP$^\bullet$)(ClO$_4$)$_2$ taken in CH$_2$Cl$_2$ solution at 193 K. The UV-vis spectrum of Fe(TMP$^\bullet$)(ClO$_4$)$_2$ is exactly the same as the one reported previously.[10] A very broad band observed at 550–700 nm is characteristic to the porphyrin radical. By the careful addition of ^{t}BuNC to Fe(TMP$^\bullet$)(ClO$_4$)$_2$ at 193 K, the Soret band at 395 nm shifted to 416 nm. The Q band also shifted from 507 to 540 nm. The spectral change clearly indicates that Fe(TMP$^\bullet$)(ClO$_4$)$_2$ is completely converted to **1**. It should be noted that **1** still has a very broad band at 600–700 nm, suggesting that **1** maintains a radical cationic nature.

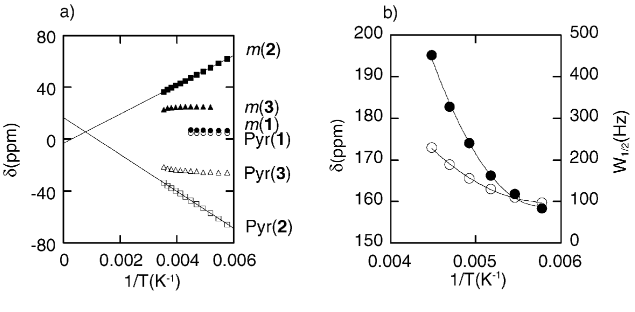

Fig. 2 (a) Curie plots of the *meta* and pyrrole-H chemical shifts of **1**, **2**, and **3**. (b) Curie plots (○) and temperature dependence of the half-height width (●) of the *meso*-C signal of **1**.

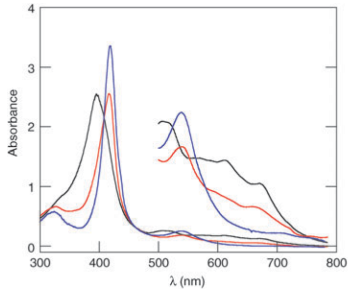

Fig. 3 UV-Vis spectra of Fe(TMP$^\bullet$)(ClO$_4$)$_2$ (black) and **1** (red) taken in CH$_2$Cl$_2$ solution at 193 K. UV-Vis spectrum of [Fe(TMP)-(tBuNC)$_2$]ClO$_4$.

In order to further characterize the electronic structure of **1**, we have prepared analogous one-electron oxidized complexes such as [Fe(TMP)(HIm)$_2$]$^{2+}$(**2**) and [Fe(TMP)(4,5-Cl$_2$Im)$_2$]$^{2+}$(**3**). ^{1}H NMR spectrum of **2** taken at 173 K is given in Fig. 1b, which is completely different from that of **1**. The large downfield and upfield shifts of the *meta* and pyr-H signals, respectively, clearly indicate that **2** is a radical cation as in the case of the analogous complexes reported previously.[4,17] ^{1}H NMR spectra of **3** taken at various temperatures are given in Fig. 4. Although the pyr-H, *meta*-H, and *o*-CH$_3$ gave single lines at 253 K, they broadened and split into several lines at lower temperature. The phenomenon can be explained in terms of the hindered rotation of the coordinating 4,5-Cl$_2$Im around the Fe–N bonds.[7,17] Table 1 summarizes the ^{1}H NMR chemical shifts of **1–3** determined at 173 and 213 K.

Curie plots of the *meta* and pyrrole signals of **2** and **3** are also given in Fig. 2a. These data clearly indicate that the radical cationic nature decreases on going from **2** to **3**, and then to **1**. The result can be explained in terms of the energy gap between the d$_{xy}$ and d$_\pi$(d$_{xz}$, d$_{yz}$) orbitals. We have reported that S = 1/2 iron(III) porphyrin complexes have two isomers with different electronic ground states.[18] One is a planar complex with the (d$_{xy}$)^2(d$_{xz}$, d$_{yz}$)^3 ground state and the other is a ruffled complex

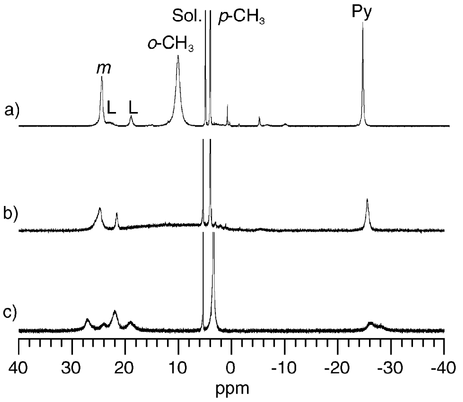

Fig. 4 ^{1}H NMR spectra of **3** taken in CD$_2$Cl$_2$ solution at (a) 253 K, (b) 213 K, and (c) 173 K.

Table 1 ^{1}H NMR Chemical shifts of one-electron oxidized complexes

Complex	T/K	Pyr	m	o-CH_3	p-CH_3	Ligand	Electronic structure[a]	Ref.
1[d]	173	4.73	6.52	2.43	2.03	2.83	A	This work
	213	4.64	6.78	2.66	2.24	2.64[b]		
2[d]	173	−70.8	65.7	26.6	7.1	53.1, 48.2 39.6, 21.3	B	This work
	213	−53.2	52.1	20.1	7.0	39.5, 36.9 29.5, 14.4		
3[d]	173	[c]	[c]	[c]	3.4	24.8, 21.6	A, B	This work
	213	−25.6	24.8	[c]	4.0			
4[e]	195	−37.5	2.4	7.72	2.86	—	C	10
5[f]	203	8.4	6.4, 6.0	3.3, —	2.6	—	C	20

[a] See the text. [b] Extrapolated from low temperatures. [c] Each signal split into several signals due to the show rotation about Fe–N_{axial} bond. [d] CD_2Cl_2. [e] CD_2Cl_2–CD_3OD(5%). [f] Toluene-d_8.

with the $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state. In the case of **2**, because of the σ and π donating ability of HIm, the iron d_π orbitals are located above the d_{xy} orbital. Thus, **2** should adopt the $S = 1$ $(d_{xy})^2(d_{xz}, d_{yz})^3(a_{2u})^1$ (signified as **B**) ground state. As a result, **2** has shown a radical cationic nature. Replacement of HIm by 4,5-Cl_2Im stabilizes **A** relative to **B** due to the weaker σ-donating and stronger π-accepting ability of the ligand. The steric interaction between bulky 4,5-Cl_2Im and porphyrin core should deepen the ruffled deformation and further stabilize **A**.[19] As a result, the radical cationic nature of **3** decreases.

The third extreme case in the electronic structure of one-electron oxidized complexes should be Fe(TMP)$(OCH_3)_2$(**4**) reported by Groves *et al.*[10] This complex adopts the S = 1 $(d_{xy})^2(d_{xz}, d_{yz})^2(a_{2u})^2$ (signified as **C**) ground state,[10] because the axial CH_3O^- ligand has strong σ- and π-donating ability and thus lifts the iron d_π orbitals far above the d_{xy} orbital. Thus, the electron is removed mainly from the metal. Fairly large upfield shift observed for the pyrrole-H signal, −37.5 ppm at 195 K, is then ascribed to the presence of two unpaired electrons in the d_π orbitals as in the case of the $S = 3/2$ iron(III) porphyrin complexes; the unpaired electrons in the d_π orbitals delocalize to the porphyrin ring especially on the β-carbon atoms due to the d_π–$3e_g$ interactions and induce large upfield shifts of the β-pyrrole resonance.[19]

Electronic ground state of $Fe^{IV} = O$ complexes such as Fe(TMP)O (**5**) has also been represented as $S = 1$ $(d_{xy})^2(d_{xz}, d_{yz})^2(a_{2u})^2$ (**C**).[20,21] However, the ^{1}H NMR chemical shifts of **5** listed in Table 1 are quite different from those of **4** in spite of the similarity of the electronic structure; the pyrrole-H chemical shift of **4** is −37.5 ppm(195 K) while that of **5** is 8.4 ppm (203 K). This is because the unpaired electrons in **5** are localized on the central Fe=O unit and do not delocalize to the porphyrin ring, which is supported by the theoretical studies.[22] As a result, **5** shows every signal in a diamagnetic region as in the case of **1** though the electronic ground states of **1** and **5** are completely different.

As mentioned, we have shown for the first time the mostly diamagnetic complex $[Fe(TMP)(tBuNC)_2]^{2+}$(**1**) at 173 K. Thus, all of the three kinds of low-spin one-electron oxidized complexes of iron(III) porphyrinates have now been defined. They are complex **1** with the $S = 0$ $(d_{xz}, d_{yz})^4(d_{xy}, a_{2u})^2$ ground state (type **A**), complex **2** with the $S = 1$ $(d_{xy})^2(d_{xz}, d_{yz})^3(a_{2u})^1$ (type **B**) ground state, and complexes **4** and **5** with the $S = 1$ $(d_{xy})^2(d_{xz}, d_{yz})^2(a_{2u})^2$ ground state (type **C**). One can argue that the type **A** electronic ground state should rather be represented as $S = 0$ $(d_{xz}, d_{yz})^4(d_{xy})^0(a_{2u})^2$ where the unpaired electron in the iron d_{xy} orbital is completely transferred to the porphyrin a_{2u} orbital to form Fe(IV) porphyrin as in the case of **4**. Although it is difficult to totally rule out this possibility, we think that the possibility is rather small because the UV-vis spectrum exhibited a radical cationic nature as shown in Fig. 2, and also because the coordination of *t*BuNC makes the iron electron poor due to the metal to ligand π back donation.

In summary, we have revealed that the electronic structure of biologically important one-electron oxidized products of iron(III) porphyrinates can be drastically changed by the nature of the axial ligands.

This work was supported by the Grant-in-Aid for Scientific Research (No. 16550061 and 18750155) from Ministry of Education, Culture, Sports, Science and Technology, Japan. A. I. thanks The Sumitomo Foundation (No. 060296) for financial support.

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