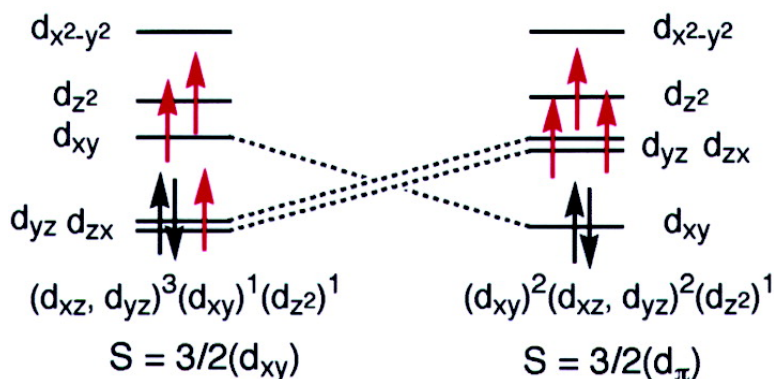Communication

Formation of the Intermediate-Spin Iron(III) Porphyrin Complexes with (d, d)(d)(d) Electron Configuration

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Formation of the Intermediate-Spin Iron(III) Porphyrin Complexes with $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1$ Electron Configuration

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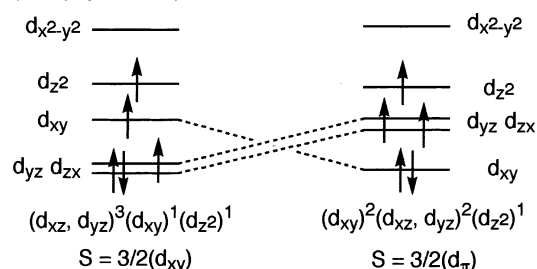
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Recent studies have revealed that the ruffled porphyrin ring affects the electron configuration of low-spin $(S = \frac{1}{2})$ iron(III) porphyrins and increases the contribution of $(d_{xz}, d_{yz})^4(d_{xy})^1$ relative to that of $(d_{xy})^2(d_{xz}, d_{yz})^3$.[1] Thus, highly ruffled [Fe(T^iPrP)(4-CNPy)$_2$]$^+$ exhibits a quite pure $(d_{xz}, d_{yz})^4(d_{xy})^1$.[1,2] In contrast, the saddled deformation of the porphyrin ring stabilizes a ground state of $(d_{xy})^2(d_{xz}, d_{yz})^3$.[3] Since the energy levels of the d_{xy} and d_π (d_{yz}, and d_{zx}) orbitals are affected differently due to the deformation mode of the porphyrin ring, it would be quite natural to expect the existence of the two types of intermediate-spin $(S = \frac{3}{2})$ complexes with different electron configurations, namely $(d_{xz}, d_{yz})^3(d_{xy})^1(d_{z^2})^1$ and $(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^1$ as shown in Scheme 1; the spin states with these electron configurations are tentatively called as $S = \frac{3}{2}(d_{xy})$ and $S = \frac{3}{2}(d_\pi)$, respectively. It should be noted that the electron configuration of the $S = \frac{3}{2}$ complexes reported previously is considered to be $S = \frac{3}{2}(d_\pi)$.[4,5] In this communication, we report that highly ruffled [Fe(TEtPrP)(THF)$_2$]$^+$ (**1a**) and [Fe(TEtPrP)ClO$_4$] (**1b**) exhibit the novel $S = \frac{3}{2}(d_{xy})$, while highly saddled [Fe(OETPP)(THF)$_2$]$^+$ (**2a**) and [Fe(OETPP)ClO$_4$]$^+$ (**2b**) adopt the conventional $S = \frac{3}{2}(d_\pi)$ (Scheme 2).[6]
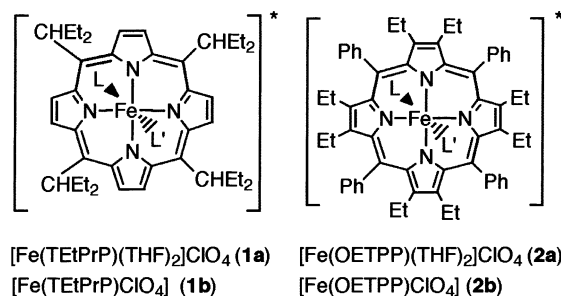
1a was prepared according to the literature,[7] which was converted to **1b** by the removal of the axial THF ligand under reduced pressure at 60 °C for 5 h.[8] The ${}^1H$ NMR spectra (CD$_2$Cl$_2$, 298 K) of **1a** and **1b** were quite similar; the pyrrole and *meso*-CH appeared at −35.6 and 8.4 ppm in **1a**, and −32.8 and 10.8 ppm in **1b**, respectively. **1a** showed the THF signals at 5.8 and 10.0 ppm.[9] The large upfield and downfield shifts of the pyrrole and THF signals, respectively, suggest that both **1a** and **1b** are $S = \frac{3}{2}$, or admixed $S = \frac{3}{2}, \frac{5}{2}$ with the major contribution of the $S = \frac{3}{2}$.[6a,10,11] The conclusion was further verified by the EPR spectra taken in frozen CH$_2$Cl$_2$ at 4.2 K; the $g_\perp$ and $g_{\parallel}$ values were 4.15 and 2.00 for **1a** and 4.09 and 1.98 for **1b**. The Mössbauer spectra also indicated that **1a** adopts the $S = \frac{3}{2}$ spin state in a wide range of temperatures; the IS and QS values were 0.24 and 3.80 mm s^{-1} at 290 K and 0.31 and 3.84 mm s^{-1} at 77 K, respectively.[6,10,11] Furthermore, the effective magnetic moment of **1a** determined by SQUID was 3.8−4.0 μ_B in 200−300 K. Although the Mössbauer and SQUID data of **1b** were unable to be obtained at present, these results clearly indicate that both **1a** and **1b** are essentially pure $S = \frac{3}{2}$ complexes.

We have then measured the ${}^{13}C$ NMR spectra since the *meso*-${}^{13}C$ chemical shift is known to be a powerful probe to determine the electronic state of the iron(III) porphyrins.[1b,3,10,12] In the case of low-spin complexes, for example, the *meso*-${}^{13}C$ signal moves downfield from 55 ppm in [Fe(TPP)(HIm)$_2$]$^+$ to 707 ppm in [Fe-(T^iPrP)(4-CNPy)$_2$]$^+$ as the $(d_{xz}, d_{yz})^4(d_{xy})^1$ contribution increases.

Scheme 1. Possible Electron Configurations of the $S = \frac{3}{2}$ Iron(III) Porphyrin Complexes

Scheme 2. Complexes Examined in This Study

[Fe(TEtPrP)(THF)$_2$]ClO$_4$ (**1a**)
[Fe(TEtPrP)ClO$_4$] (**1b**)

[Fe(OETPP)(THF)$_2$]ClO$_4$ (**2a**)
[Fe(OETPP)ClO$_4$] (**2b**)

In other words, the downfield shift of the *meso*-${}^{13}C$ signal is proportional to the population of the unpaired electron in the d_{xy} orbital.[1b] We have exploited this tendency to determine the electron configurations of the $S = \frac{3}{2}$ complexes. For the unambiguous assignment, the *meso*-${}^{13}C$-enriched (99% ${}^{13}C$) **1a** and **1b** were prepared, starting from the condensation reaction between pyrrole and 2-ethylbutanal (1-${}^{13}C$).[13] Figure 1 shows the ${}^{13}C$ NMR spectrum of **1b** taken at 298 K. The signal at 342 ppm was assigned to the *meso* carbon by the spectral comparison with the *meso*-${}^{13}C$-enriched **1b** shown in the inset (a). This signal moved upfield in a hyperbolic fashion by the addition of THF as shown in the inset (b) and approached to 104 ppm.[14] Thus, the *meso*-${}^{13}C$ chemical shift of the bis(THF) complex (**1a**) was estimated to be 104 ppm. Similar upfield shift was observed in **2b** by the addition of THF as shown in the inset (b). The *meso*-${}^{13}C$ chemical shifts of **2a** and **2b** were determined to be −244 and −47 ppm, respectively, at 298 K. The downfield shifts of the *meso*-${}^{13}C$ signals in five-coordinate **1b** and **2b** relative to those in the six-coordinate **1a** and **2a** should be ascribed to the $d_{z^2}−a_{2u}$ interaction in the former complexes as reported recently by Cheng et al.[15] As mentioned, the ruffled **1a** and **1b** exhibited the *meso*-${}^{13}C$ signals fairly downfield as compared with the saddled **2a** and **2b**. The difference in chemical shifts between **1a** and **2a** is 348 ppm, and that for **1b** and **2b** is 389 ppm at 298 K. The large difference in chemical shifts can be interpreted in terms of the presence or absence of the unpaired electron in the

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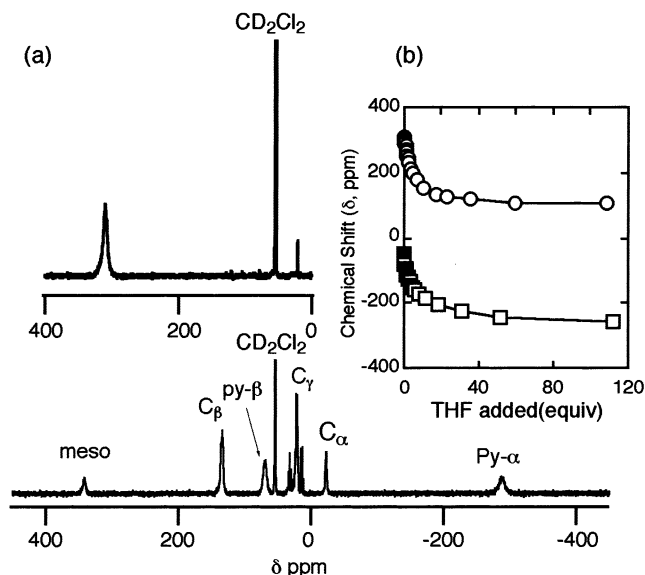¶ Department of Chemistry, Faculty of Science.

Figure 1. ^{13}C NMR spectrum of **1b** taken in CD$_2$Cl$_2$ solution at 298 K. Inset: (a) ^{13}C NMR spectrum of *meso*-^{13}C enriched **1b**. (b) Change in chemical shifts of the *meso*-^{13}C signal as observed by the addition of THF into the CD$_2$Cl$_2$ solutions of **1b** (○) and **2b** (□).

d_{xy} orbital; the unpaired electron in this orbital is transferred to the *meso*-positions by the d_{xy}–a_{2u} interaction and induces the downfield shift of the *meso*-^{13}C signals.[1b,3] Therefore, the results strongly indicate that the ruffled **1a** and **1b** adopt the novel $S = ^3/_2(d_{xy})$. The upfield shift of the *meso*-^{13}C signals in the saddled complexes is then ascribed to the conventional $S = ^3/_2(d_\pi)$, which enables the unpaired electrons in the d_π orbitals disperse to the pyrrole ring by the d_π–$3e_g$ interactions. Since the $3e_g$ orbitals have nodes at the *meso* positions, the interactions cause the upfield shift of the *meso*-^{13}C signals due to the spin polarization.[10]

Reed and Guiset reported that [Fe(TPP)(Br$_6$CB$_{11}$H$_6$)] adopts an essentially pure $S = ^3/_2$ spin state and that the complex shows the pyrrole signal at an extremely upfield position, −62 ppm.[16,17] In contrast, [Fe(TEtPrP)ClO$_4$] (**1b**) exhibits the pyrrole signal more downfield, −33 ppm. The large difference in pyrrole shifts, 29 ppm, between these two $S = ^3/_2$ complexes serves another line of evidence supporting that **1b** actually adopts a novel $S = ^3/_2(d_{xy})$. This is because, the $S = ^3/_2(d_{xy})$ complexes have only one unpaired electron in the d_π orbitals, while the $S = ^3/_2(d_\pi)$ complexes have two; the unpaired electron in the d_π orbitals is the major factor for the upfield shift of the pyrrole signals.[5] The electron configuration mentioned above is further supported by the fact that the difference in pyrrole shifts between low-spin [Fe(T^{i}PrP)(4-CNPy)$_2$]$^+$ and [Fe(TPP)(HIm)$_2$]$^+$ is also quite large, ca. 30 ppm.[1b] The large difference should again be explained in terms of the number of the unpaired electrons in the d_π orbitals. While [Fe(T^{i}PrP)(4-CNPy)$_2$]$^+$ has no unpaired electron, [Fe(TPP)(HIm)$_2$]$^+$ has one; the electron configurations of these complexes are expressed as $(d_{xz}, d_{yz})^4(d_{xy})^1$ and $(d_{xy})^2(d_{xz}, d_{yz})^3$, respectively.[1b]

Determination of the spin states and electron configurations for all the oxidation states of heme irons, iron(II)–iron(V), is quite important to elucidate the biological processes where heme proteins are involved. Rivera et al. pointed out that the $(d_{xz}, d_{yz})^4(d_{xy})^1$-type

low-spin complex, possibly formed in the heme degradation process, could play a crucial role in the reaction.[18] Shaik et al. proposed that the diverse reactions catalyzed by cytochromes P450 could be explained in terms of the difference in reactivity between the high-spin and low-spin states of the compound I, i.e., oxo–iron(IV) porphyrin radical cation.[19] Thus, characterization of the complexes with a novel $S = ^3/_2(d_{xy})$ can contribute to the better understanding of the heme-containing biological processes.

Supporting Information Available: EPR spectra of **1a** and **1b**, temperature dependence of the *meso*-^{13}C chemical shifts of **1a**, **1b**, **2a**, and **2b**, Mössbauer spectra of **1a**, and effective magnetic moments of **1a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) Abbreviations. TPP, T^{i}PrP, OETPP, and T(EtPr)P are dianions of 5,10,-15,20-tetra-phenylporphyrin, 5,10,15,20-tetraisopropylporphyrin, 2,3,7,8,-12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, and 5,10,15,20-tetrakis(1-ethylpropyl)porphyrin, respectively. 4-CNPy: 4-cyanopyridine; HIm: imidazole.
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