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Chemical shift of *meso*-carbon: a powerful probe to determine the coordination structure and electron configuration of ferric porphyrin complexes†

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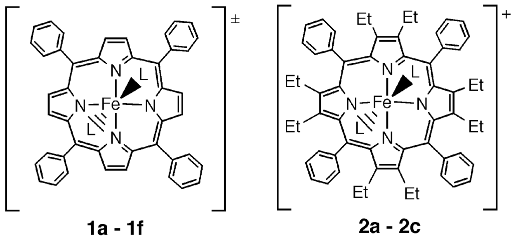
The *meso*-^{13}C chemical shifts have been revealed to serve a powerful probe to determine the coordination structure and electron configuration of ferric porphyrin complexes.

In the course of our research to produce high-valent iron–oxo species by the reactions of pyridine *N*-oxide with ferric porphyrin complexes such as [Fe(TPP)]ClO$_4$ and [Fe(OETPP)]ClO$_4$, we have found that the bis(pyridine *N*-oxide) complexes, [Fe(TPP)L$_2$]ClO$_4$(**1a–1c**, Scheme 1) and [Fe(OETPP)L$_2$]ClO$_4$(**2a–2c**), showed unprecedented ^{13}C NMR spectra.[1] In this paper, we report that the chemical shift of *meso*-^{13}C can be a powerful probe to determine not only the electron configuration,[2] but also the coordination structure of ferric porphyrin complexes.

Fig. 1 shows the ^{1}H NMR spectra of **1a–1c** formed by the addition of 4.0 equiv. of pyridine *N*-oxides (**a–c**) to the CD$_2$Cl$_2$ solutions of [Fe(TPP)]ClO$_4$ at −50 °C. Bis-coordination of the ligand is unambiguously verified from the integral intensities of the coordinated ligand signals. The downfield shifts of the pyrrole signals in **1a–1c**, *ca.* 100 ppm at −50 °C, clearly indicate that these complexes are high-spin (S = 5/2).[3] The ligand signals were observed at extremely far upfield and downfield positions. Furthermore, the sign of the isotropic shift was reversed by the methyl substitution; the chemical shift of the 4-H in **1a** is −75.5 ppm while that of the 4-CH$_3$ in **1b** is +81.2 ppm. The results suggest that a considerable amount of spin in the iron d_π(d_{xz} and d_{yz}) orbitals is delocalized to the axial ligands through d_π–p_π interactions.[4] Similar π electron delocalization was observed in **2**. The ^{1}H NMR spectra, chemical shifts and Curie plots of these complexes are given in the ESI.† To determine the spin states of **2**, EPR spectra were taken in frozen CH$_2$Cl$_2$ solution at 4.2 K. The $g_\perp$ and $g_\parallel$ values of **2a** were 5.05 and 2.00, while those of **1a** were 5.95 and 2.00, respectively. Thus, **2a** is in an admixed intermediate-spin state (S = 5/2, 3/2) with *ca.* 50% of the S = 3/2 contribution.[5] The observed and simulated spectra of **1a** and **2a** are given as ESI.† The result is in accordance with our recent observation that the saddle deformation stabilizes the S = 3/2 spin state.[6]

Most of the synthetic high-spin ferric porphyrins are 5-coordinate. There are, however, a limited number of examples showing 6-coordination.[3,4,7] A typical example is [Fe(OEP)(DMSO)$_2$]$^+$, whose *meso*-H signals appear fairly downfield, at δ 40.1 ppm. Interestingly, the *meso*-H signals of 5-coordinate high-spin [Fe(OEP)Cl] are observed in the opposite direction, δ −55.6 ppm.[4b,8] We are very much interested in the ^{13}C NMR spectra of high-spin 6-coordinate complexes because no ^{13}C NMR spectra have ever been reported for these complexes. Fig. 2 shows the ^{13}C NMR spectra of *meso*-^{13}C enriched **1a** and **2a** together with those of some relevant complexes. The high-spin **1a** showed the *meso* signal at 27.8 ppm at 25 °C, which differs from that of typical high-spin 5-coordinate [Fe(TPP)Cl] by 460 ppm.[9] Similarly, high-spin **1b–1f** exhibited the *meso* signals at 25.5, 29.1, 10.0, 5.2, and 56.7 ppm, respectively. By contrast, the *meso* signal of **2a** was observed at δ −55.1 ppm, which is between the *meso* signals of high-spin **1a** (δ 27.8 ppm) and intermediate-spin [Fe(OETPP)(THF)$_2$]ClO$_4$ (δ −82.5 ppm).[6] Therefore, the ^{13}C NMR results are consistent with the EPR results in the sense that **2a** is an admixed intermediate-spin complex.

The ferric ions in synthetic porphyrin complexes and naturally occurring heme proteins usually show either the high-spin or the low-spin state. In the previous papers, we have reported that the *meso*-^{13}C chemical shift is a good probe to determine the electron configuration of low-spin complexes; the ferric ions with $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ electron configuration show the *meso* signals at 50 to 100 ppm at 25 °C, while those with $(d_{xz}, d_{yz})^4$ $(d_{xy})^1$ exhibit them at much lower magnetic field.[2] The



1a - 1f **2a - 2c**

Axial Ligand (L)	
Pyridine N-oxide(**a**)	Dimethylsulfoxide(**d**)
4-Methylpyridine N-oxide(**b**)	Dimethylformamide(**e**)
3,5-Dimethylpyridine N-oxide(**c**)	Fluoride(**f**)

Scheme 1

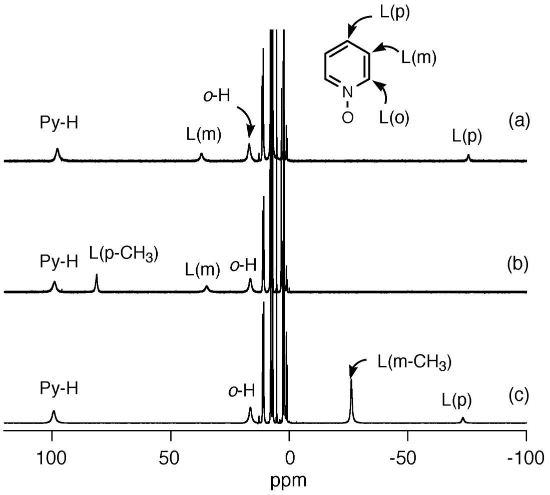


Fig. 1 ^{1}H NMR spectra of (a) **1a**, (b) **1b**, and (c) **1c** taken in CD$_2$Cl$_2$ solutions at −50°C.

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† Electronic supplementary information (ESI) available:chemical shifts, ^{1}H NMR spectra, Curie plots and EPR spectra of **1** and **2**. See http://www.rsc.org/suppdata/cc/b3/b303785a/

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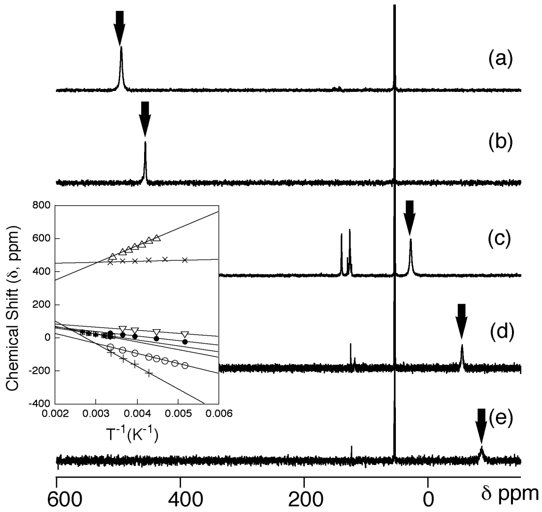

Fig. 2 ^{13}C NMR spectra of *meso*-^{13}C enriched complexes taken in CD_2Cl_2 at 25°C. The *meso*-^{13}C signals are signified by the arrow. (a) [Fe(TPP)Cl], (b) [Fe(OETPP)Cl], (c) [Fe(TPP)(PyNO)$_2$]ClO$_4$ (**1a**), (d) [Fe(OETPP)(PyNO)$_2$]ClO$_4$ (**2a**), (e) [Fe(OETPP)(THF)$_2$]ClO$_4$. Curie plots of the *meso*-carbons are given in the inset: △, [Fe(TPP)Cl]; ×, [Fe(OETPP)Cl]; ▽, [Fe(TPP)F$_2$]Bu$_4$N; ●, [Fe(TPP)(PyNO)$_2$]ClO$_4$; □, [Fe(TPP)(DMSO)$_2$]ClO$_4$; ◆, [Fe(TPP)(DMF)$_2$]ClO$_4$; ○, [Fe(OETPP)(PyNO)$_2$]ClO$_4$; +, [Fe(OETPP)(THF)$_2$]ClO$_4$.

present study further reveals that the *meso*-^{13}C chemical shift can indicate the coordination structure of high-spin complexes. This is most explicitly demonstrated in Fig. 3, which shows the correlation of chemical shifts between pyrrole-H and *meso*-^{13}C. Three types of ferric complexes, *i.e.* 6-coordinate low spin, 5-coordinate high-spin, and 6-coordinate high-spin, are clearly classified. In the low spin complexes, the pyrrole-H and *meso*-^{13}C appear in the range -20 to 15 ppm and 50 to 800 ppm, respectively. Both the pyrrole-H and the *meso*-^{13}C signals move downfield as the $(d_{xz}, d_{yz})^4 (d_{xy})^1$ character increases, giving a semi-parabolic curve with a positive slope. In the high-spin complexes, the plots for the 5-coordinate complexes are located far above those for the 6-coordinate ones. Therefore, both the coordination structure and electron configuration can be determined by the *meso*-^{13}C signals. La Mar and coworkers pointed out the importance of the *meso*-H chemical shifts to determine the coordination structure of high-spin ferric heme proteins,[10] though the observation of the *meso*-H signals is sometimes hampered because of their extreme breadth. In this regard, the *meso*-^{13}C chemical shift could be a better probe to determine the coordination structure of high-spin ferric heme proteins if we utilize enzymes reconstituted with ^{13}C labeled heme; ^{13}C labeled protoheme IX can be biosynthesized using ^{13}C labeled δ-aminolevulinic acid.[11]

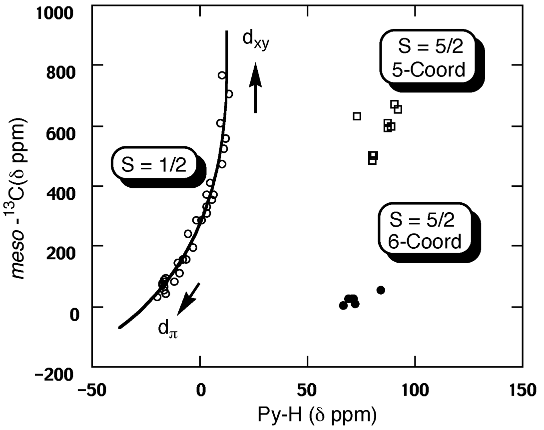

Fig. 3 Relation of chemical shifts between pyrrole-H and *meso*-^{13}C nuclei at 25°C: ○, 33 low spin complexes of the types [Fe(TArP)L$_2$]$^\pm$ and [Fe(TRP)L$_2$]$^\pm$; □, 9 high-spin five-coordinate complexes of the types [Fe(TPP)X] and [Fe(TRP)X]; ●, 6 high-spin six-coordinate complexes, **1a–1f**, determined in this study. The d_{xy} and d_π indicate the $(d_{xz}, d_{yz})^4(d_{xy})^1$ and $(d_{xy})^2(d_{xz}, d_{yz})^3$ electron configuration, respectively.

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Notes and references

1 Abbreviations: TPP, TRP, OEP, OETPP, dianions of 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetraalkylporphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, respectively.

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