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*-¹³C 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 ¹³C NMR spectra.¹ In this paper, we report that the chemical shift of *meso*-¹³C 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 $(\mathbf{a}-\mathbf{c})$ to the CD₂Cl₂ solutions of [Fe(TPP)]ClO₄ 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-CH₃ in 1b is +81.2 ppm. The results suggest that a considerable amount of spin in the iron $d_{\pi}(d_{xz}$ 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 CH₂Cl₂ 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} Α 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 ¹³C NMR spectra of high-spin 6-coordinate complexes because no ¹³C NMR spectra have ever been reported for these complexes. Fig. 2 shows the ¹³C NMR spectra of meso-13C 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]ClO₄ (δ -82.5 ppm).⁶ Therefore, the ¹³C 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 highspin or the low-spin state. In the previous papers, we have reported that the *meso*-¹³C 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





NMR spectra, Curie plots and EPR spectra of **1** and **2**. See http: //www.rsc.org/suppdata/cc/b3/b303785a/



Fig. 1 ¹H NMR spectra of (a) 1a, (b) 1b, and (c) 1c taken in CD_2Cl_2 solutions at $-50^{\circ}C$.

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Fig. 2 ¹³C NMR spectra of *meso*-¹³C enriched complexes taken in CD₂Cl₂ at 25°C. The *meso*-¹³C signals are signified by the arrow. (a) [Fe(TPP)Cl], (b) [Fe(OETPP)Cl], (c) [Fe(TPP)(PyNO)₂]ClO₄ (**1a**), (d) [Fe(OETPP)(Py-NO)₂]ClO₄ (**2a**), (e) [Fe(OETPP)(THF)₂]ClO₄. Curie plots of the *meso*-carbons are given in the inset: \triangle , [Fe(TPP)Cl]; \times , [Fe(OETPP)Cl]; \bigtriangledown , [Fe(TPP)F₂]Bu₄N; $\textcircled{\bullet}$, [Fe(TPP)(PyNO)₂]ClO₄; \square , [Fe(TPP)(DMSO)₂]-ClO₄; \clubsuit , [Fe(TPP)(DMF)₂]ClO₄; \bigcirc , [Fe(OETPP)(PyNO)₂]ClO₄; +, [Fe(OETPP)(THF)₂]ClO₄; \bigcirc , [Fe(OETPP)(THF)₂]ClO₄; \frown]

present study further reveals that the *meso*-¹³C 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*-¹³C. 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*-¹³C appear in the range -20 to 15 ppm and 50 to 800 ppm,



Fig. 3 Relation of chemical shifts between pyrrole-H and *meso*⁻¹³C nuclei at 25°C: \bigcirc , 33 low spin complexes of the types [Fe(TArP)L₂][±] and [Fe(TRP)L₂][±]; \square , 9 high-spin five-coordinate complexes of the types [Fe(TPP)X] and [Fe(TRP)X]; \bullet , 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.

respectively. Both the pyrrole-H and the meso-13C 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-13C 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-13C chemical shift could be a better probe to determine the coordination structure of high-spin ferric heme proteins if we utilize enzymes reconstituted with ¹³C labeled heme; ¹³C labeled protoheme IX can be biosynthesized using ¹³C labeled δ -aminolevulinic acid.¹¹

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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, 2,3,7,8,12,13,17,18octaethylporphyrin, and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, respectively.
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