

Determination of the ^{13}C NMR chemical shifts in an a_{2u} type iron(III) porphyrin cation radical

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The ^{13}C NMR chemical shifts of all the carbons in an a_{2u} type iron(III) porphyrin radical cation, $[\text{Fe}(\text{TPP})\text{Cl}]^+$, have been determined for the first time by the titration method as well as by the chemical shift correlation; they are 2230, 1050, and -1910 ppm for the α -pyrrole, β -pyrrole, and *meso* carbon atoms, respectively.

^{13}C NMR spectroscopy is quite useful to determine the electronic structures of iron(III) porphyrin complexes.¹ Little is known, however, on the ^{13}C NMR spectra of iron(III) porphyrin radicals although their importance and usefulness in revealing the electronic structure of radical species was pointed out more than 20 years ago.² This is because some ^{13}C NMR signals in radical species are quite difficult to observe due to their extreme broadness. Since the iron porphyrin radicals are involved in various aspects of biological processes, the ^{13}C NMR chemical shifts could give useful information on their electronic structures. Thus, we have launched a project to reveal the electronic structure of iron porphyrin radicals by means of ^{13}C NMR spectroscopy. Firstly, we have tried to determine the chemical shifts of $[\text{Fe}(\text{TPP})\text{Cl}](\text{SbCl}_6)$ because the complex has been extensively studied and well-characterised as an a_{2u} type ferric porphyrin radical cation.^{3–5} Especially interesting is the chemical shift of the *meso* carbons because they have a considerable amount of spin density.

$[\text{Fe}(\text{TPP})\text{Cl}](\text{SbCl}_6)$, represented as $[\text{Fe}(\text{TPP})\text{Cl}]^+$ in the following discussion, was prepared and purified by the literature method.^{4,5} The ^1H NMR chemical shifts (CD_2Cl_2 , 298 K) are essentially the same as the previously reported ones; the *ortho*-, *meta*-, *para*- and pyrrole-H signals were observed at 40.4, -15.2 , 32.6, and 67.1 ppm, respectively. The magnitudes and signs of these chemical shifts indicate that the complex has high-spin ($S = 5/2$) iron(III) coupled with an a_{2u} type porphyrin radical in an antiferromagnetic fashion.^{4,5} The ^{13}C NMR spectrum was then taken under the same conditions. Although every signal was clearly observed in the ^1H NMR spectrum, only four signals out of seven appeared at 1054, 958, 137, and 8.7 ppm in the ^{13}C NMR spectrum. Firstly, we have tried to determine the chemical shift of the *meso* carbon. The signal was not observed, however, even by the use of *meso*- ^{13}C (99% ^{13}C) enriched $[\text{Fe}(\text{TPP})\text{Cl}]^+$. The result suggests that the *meso* signal is too broad to be detected due to the short relaxation time caused by the considerable amount of spin on these carbon atoms. We have therefore applied indirect methods to determine the *meso* carbon chemical shift; one is the titration method and the other is the chemical shift correlation method.

The *meso*- ^{13}C enriched $[\text{Fe}(\text{TPP})\text{Cl}]$ was titrated by *meso*- ^{13}C enriched $[\text{Fe}(\text{TPP})\text{Cl}]^+$ in CD_2Cl_2 solution and the resultant *meso* signal was monitored by ^{13}C NMR spectroscopy at 298 K. As Fig. 1 shows, the addition of only 0.075 equiv. of $[\text{Fe}(\text{TPP})\text{Cl}]^+$ induced a large upfield shift and a considerable broadening of the *meso* signal; the signal moved from 495 to 376 ppm while the half-height width ($W_{1/2}$) increased from 306 to 2530 Hz. When 0.23 equiv. of the radical was added, a *meso* signal with $W_{1/2} = 3890$ Hz appeared at 48.0 ppm. The signal was no longer observed when 0.3 equiv. of the radical was added. Since the electron exchange between $[\text{Fe}(\text{TPP})\text{Cl}]$ and $[\text{Fe}(\text{TPP})\text{Cl}]^+$ is fast on the ^1H NMR timescale, the observed chemical shift δ_{obs} should be expressed by eqn. (1) in the presence of t equiv. of the radical, where δ_{N} and δ_{R} are the chemical shifts of the carbon atoms in $[\text{Fe}(\text{TPP})\text{Cl}]$ and $[\text{Fe}(\text{TPP})\text{Cl}]^+$, respectively.

$$\delta_{\text{obs}} = \delta_{\text{R}} + \frac{\delta_{\text{N}} - \delta_{\text{R}}}{1 + t} \quad (1)$$

Thus, the plot of δ_{obs} against $1/(1 + t)$ should give a linear line for each carbon signal. In fact, a good linear line was obtained for the *meso* carbon signal as shown in Fig. 2. The *meso* carbon chemical

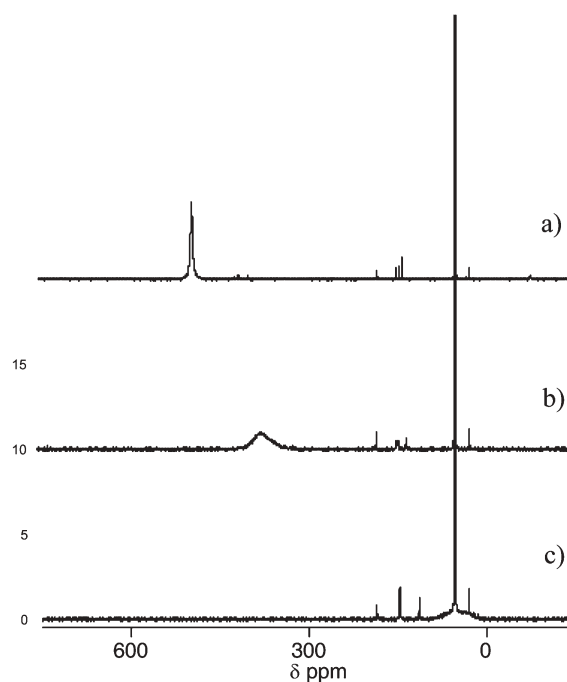


Fig. 1 Spectral change of *meso*- ^{13}C enriched $[\text{Fe}(\text{TPP})\text{Cl}]$ on addition of *meso*- ^{13}C enriched $[\text{Fe}(\text{TPP})\text{Cl}]^+$ in CD_2Cl_2 solution at 298 K: (a) 0.00, (b) 0.075, and (c) 0.23 equiv.

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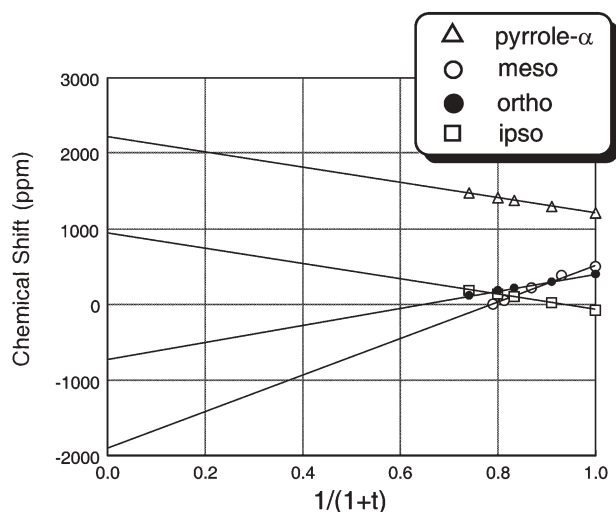


Fig. 2 Plots of chemical shifts of some ^{13}C signals in $[\text{Fe}(\text{TPP})\text{Cl}]$ against $1/(1+t)$ where t (equiv.) is the amount of $[\text{Fe}(\text{TPP})\text{Cl}]^+$ added to the CD_2Cl_2 solution of $[\text{Fe}(\text{TPP})\text{Cl}]$ at 298 K. The ^{13}C chemical shifts in $[\text{Fe}(\text{TPP})\text{Cl}]^+$ are determined from the y -intercepts.

shift of the radical was then determined to be -1910 ppm from the y -intercept. The chemical shifts of the other signals were similarly assigned. Thus, the signals observed at 1054, 958, 137, and 8.7 ppm in $[\text{Fe}(\text{TPP})\text{Cl}]^+$ were assigned to the β -pyrrole, *ipso*, *meta*, and *para* signals, respectively, since these signals correlate with the signals at 1321 (β -pyrrole), -71.7 (*ipso*), 148 and 152 (*meta*), and 143 (*para*) ppm of $[\text{Fe}(\text{TPP})\text{Cl}]$, respectively.⁶ The chemical shifts of the α -pyrrole and *ortho* signals in $[\text{Fe}(\text{TPP})\text{Cl}]^+$, though they were too broad to be detected, were determined to be 2230 and -721 ppm, respectively, from the y -intercepts of the corresponding lines shown in Fig. 2. It should be noted here that the titration method gives reliable data on the chemical shifts as is revealed from the case of the *ipso* carbon. The *ipso* chemical shift determined by the titration method is quite close to that directly obtained from the spectrum; they were 951 and 958 ppm, respectively. The chemical shifts of all the carbon signals are listed in Table 1 together with those of $[\text{Fe}(\text{TPP})\text{Cl}]$.⁷

Fig. 3 shows the correlation of the chemical shifts between *meso* and *ipso* carbons in six-coordinate *meso*-tetraarylporphyrinates $[\text{Fe}(\text{TArP})\text{L}_2]^+$. The electronic states of the complexes range from high-spin ($S = 5/2$) and admixed intermediate-spin ($S = 5/2, 3/2$), to the low-spin ($S = 1/2$) with two different electron configurations, $(d_{xy})^2(d_{xz}, d_{yz})^3$ and $(d_{xz}, d_{yz})^4(d_{xy})^1$. All these data were taken from our previous papers.¹ A linear line with a correlation coefficient of 0.979 was obtained for 31 data sets.^{8,9} The chemical shift of the *meso* carbon was then calculated to be -2040 ppm on

Table 1 ^{13}C NMR chemical shifts of $[\text{Fe}(\text{TPP})\text{Cl}]$ and $[\text{Fe}(\text{TPP})\text{Cl}]^+$ determined in CD_2Cl_2 solution at 298 K^a

Complexes	α	β	<i>meso</i>	<i>ipso</i>	<i>o</i>	<i>m</i>	<i>p</i>
$[\text{Fe}(\text{TPP})\text{Cl}]$	1204	1321	495	-71.7	400	148	143
$[\text{Fe}(\text{TPP})\text{Cl}]^+$	2230	1050	-1910	958	-721	137	8.7

^a Chemical shifts written in italics were obtained by the titration method.

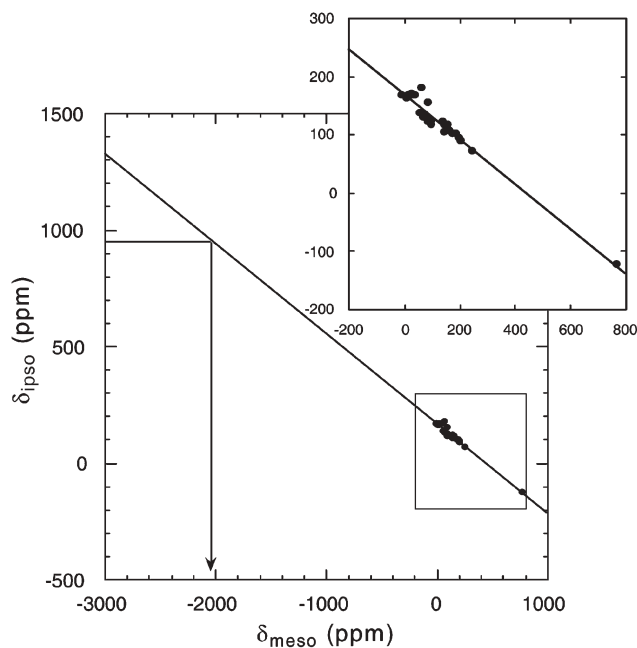


Fig. 3 Correlation of the chemical shifts between *meso* and *ipso* carbon signals. The arrow indicates the chemical shift of the *meso* carbon of the radical deduced from the *ipso* carbon chemical shift.

the basis of the *ipso* carbon chemical shift, 958 ppm. Thus, the result is consistent with that obtained by the titration method. The chemical shift correlation method can be a complement to the titration method; it could be applicable to determine the chemical shift of the carbon signals with fairly short relaxation times in the presence of trace amounts of the corresponding radical cation.

In conclusion, we have shown new methodology to determine the ^{13}C NMR chemical shifts of radical cations, which is applicable not only to this specific radical but also to a wide range of iron porphyrin radicals including ProtoIX.³

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- Abbreviations: TPP and Proto-IX are the dianions of *meso*-tetraphenylporphyrin and protoporphyrin IX, respectively.

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- 6 The titration method was used by Phillippi and Goff to assign the ^1H NMR signals of radical cationic complex, ref. 4.
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- 8 If we assume that both the metal centered dipolar shift and the delocalization of the π -spin to the phenyl ring are rather small, the isotropic shifts of the *ipso* and *meso* carbons are approximated by

- $$\delta_{ipso} = Q_{C'C}\rho_{meso}F_C \text{ and } \delta_{meso} = (S_C + 3Q_{CC'})\rho_{meso}F_C + (D\rho_{meso} + 2Q_{C'C}\rho_{\sigma\text{-py}}F_C),$$
- respectively, where S_C , $Q_{CC'}$, and $Q_{C'C}$ are the Karplus and Fraenkel constants, D is a proportionality constant for ligand centered dipolar shift, ρ_{meso} and $\rho_{\sigma\text{-py}}$ are the π -spin densities, and F_C is a constant given by $2\pi g\mu_B S(S+1)/3h\gamma_C kT$.⁹ The observed linearity indicates that the second term of δ_{meso} increases as the ρ_{meso} increases. Further discussion on the correlation between carbon shifts will be discussed elsewhere.
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