Anomalous ^{13}C NMR Chemical Shifts of High-spin Saddle Shaped Manganese(III) Octaethyltetraphenylporphyrin Complexes

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NMR spectra of highly saddled Mn(III) porphyrinates such as Mn(OETPP)$(CD_3OD)_2{}^+$ have been measured. The extraordinarily upfield shifted *meso*-^{13}C signals, which reach as much as -492 ppm at 298 K, are ascribed to the $d_{x^2-y^2}$–a_{2u}, d_{xy}–a_{1u}, and d_π–$3e_g$ interactions, the former two of which occur only when the porphyrin ring is saddled.

Electronic structures of metal porphyrinates are controlled not only by the number and nature of the axial ligands but also by the nonplanarity of porphyrin ring.[1] This is because some metal–porphyrin interactions, which are symmetry forbidden in planar complexes, become possible by the ring deformation.[2–4] In the process of studying the physicochemical properties of deformed Mn(III) porphyrinates, we found that highly saddled Mn(OETPP)Cl (**1a**) and Mn(OETPP)$(CD_3OD)_2{}^+$ (**1b**) exhibit quite unusual ^{13}C NMR spectra. In this paper, we report the anomalous ^{13}C NMR chemical shifts of **1** and explain the reasons for the anomaly.

Five-coordinate **1a** was prepared from (OETPP)H_2 and $MnCl_2$ in refluxed DMF solution,[5,6] which was converted to six-coordinate **1b** in CD_3OD solution.[7] These complexes are high-spin ($S = 2$) with $(d_{xy})^1(d_{yz})^1(d_{xz})^1(d_{z^2})^1$ in solution as revealed by the effective magnetic moments, 5.1 μ_B for both complexes, determined by the Evans method.[8] The ^{1}H and ^{13}C NMR chemical shifts of the analogous OEP (**2**), TPP (**3**), T^{i}PrP (**4**), and T^{t}BuP (**5**) were also examined for comparison (Scheme 1).[9–12]

Figures 1 and 2 show the ^{1}H, ^{2}H, and ^{13}C NMR spectra. Table 1 lists the chemical shifts at 298 K. The four and two methylene signals in **1a** and **1b**, respectively, suggest that the saddled structure is maintained in solution. Several spectroscopic characteristics are clearly seen in the data of Table 1 which can be explained in terms of the Mn(III)–porphyrin orbital interactions. In the high-spin five-coordinate complexes (**1a**–**5a**), the unpaired electrons delocalize through the d_π–$3e_g$ and d_{z^2}–a_{2u} interactions regardless of the porphyrin structures.[2,13] The former induces the upfield shift of the Py–H and the downfield shifts of the CH_2 signals while the latter causes the downfield shift of the *meso*-C and *m*-H signals; note that the $3e_g$ orbital has relatively large coefficient at the β-C while the a_{2u} orbital has large coefficient at the *meso*-C as shown in Scheme 2. In the six-coordinate complexes (**1b**–**4b**), the Mn(III) ion is in the center of the N4 plane. Thus, the d_π–$3e_g$ interaction is strengthened while the d_{z^2}–a_{2u} interaction is weakened; note that the a_{2u} and d_{z^2} orbitals are orthogonal in the complexes with D_{2d} symmetry. As a result, both the Py–H and the *meso*-C signals exhibit a large upfield shift by ca. 10 and 100 ppm, respectively.

The data in Table 1 also suggest that the chemical shifts of **1** are quite different from those of **2**–**5**. The major differences are i) the upfield shift of the *meta*-H, ii) the downfield shifts of the *o*- and *p*-H, and iii) the presence of an extremely upfield shifted *meso*-C signal. These NMR characteristics, which suggest the presence of a large negative spin at the *meso*-carbon atoms,[14–16]

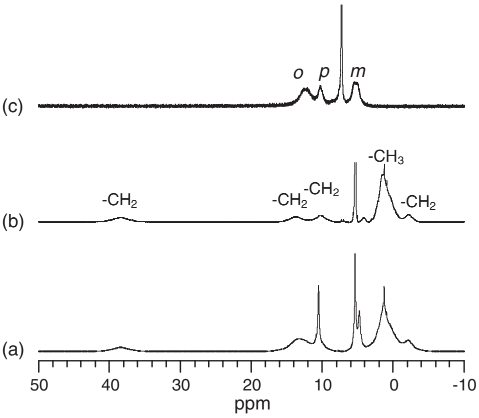
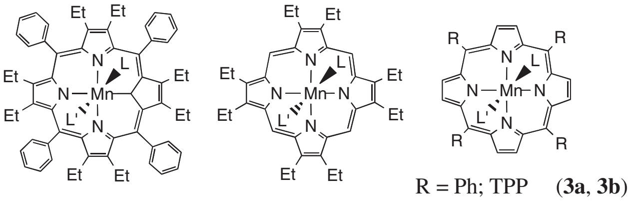


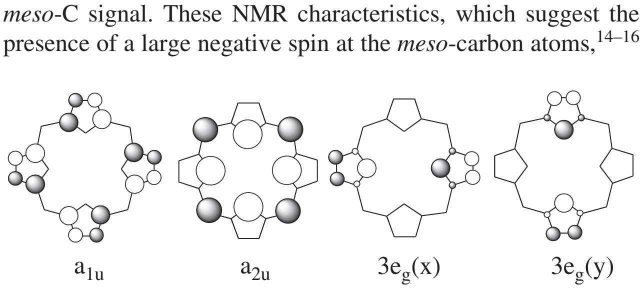
Figure 1. ^{1}H NMR spectra of (a) **1a** and (b) phenyl-deuterated **1a**-d_{20} taken in CD_2Cl_2 at 298 K. (c) ^{2}H NMR spectrum of **1a**-d_{20} determined in $CHCl_3$ at 298 K.



OETPP (**1a**, **1b**) OEP (**2a**, **2b**)

R = Ph; TPP (**3a**, **3b**)
R = ^{i}Pr; T^{i}PrP (**4a**, **4b**)
R = ^{t}Bu; T^{t}BuP (**5a**)

Scheme 1. Mn(III) porphyrinates examined in this study. **1a**–**5a** are five-coordinate complexes where axial ligand is Cl^- (**1a**–**4a**) or $CH_3CO_2{}^-$ (**5a**). **1b**–**4b** are six-coordinate complexes where axial ligand is CD_3OD.



Scheme 2. Frontier orbitals of porphyrin.

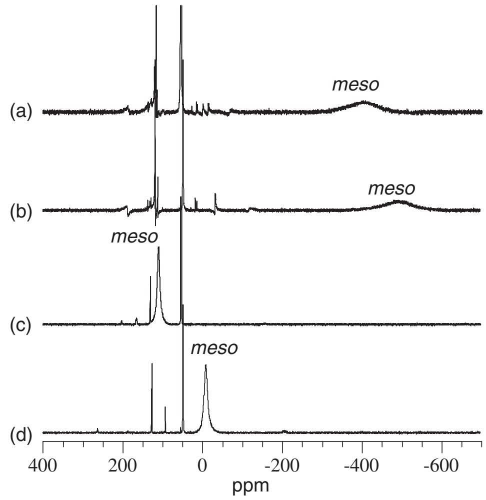


Figure 2. ^{13}C NMR spectra of *meso*-^{13}C enriched (a) **1a**, (b) **1b**, (c) **3a**, and (d) **3b** taken at 298 K.

Table 1. ^{1}H and ^{13}C NMR chemical shifts[a] (298 K, δ ppm)

Complexes	^{1}H NMR								^{13}C NMR
	Py-H	CH_2		CH_3	*meso*	*o* (CH_α)	*m* (CH_β)	*p*	*meso*
1a	—	38.4 10.2	13.7 −2.2	1.3	—	13.1 12.3	5.3 4.7	10.5	−406
1b	—	30.3	3.3	1.1	—	13.4	4.3	11.2	−492
2a	—	23.1	0.5	2.7	52.6	—	—	—	80
2b	—	14.5		2.3	76.4	—	—	—	−24
3a[b]	−21.9	—		—	—	—[d]	8.3	7.3	110
3b[b]	−30.8	—		—	—	9.2	7.3	7.9	−8
4a[b]	−19.4	—		—	—	(9.5)	(3.2)	—	216
4b[b]	−31.6	—		—	—	—[d]	(2.1)	—	87
5a[c]	−2.9, −28.3	—		—	—	(—)	(3.2)	—	—[d]

[a] **1a**–**5a** were taken in CD_2Cl_2 while **1b**–**4b** were taken in CD_3OD. [b] ref 11. [c] $L = CH_3CO_2^-$, Ref. 12. The pyrrole protons give two signals due to the slow inversion rate of the ruffled porphyrin ring on the ^{1}H NMR timescale. [d] Signals were too broad.

should be ascribed to the specific orbital interactions such as the $d_{x^2-y^2}$–a_{2u} and d_{xy}–a_{1u} that can occur only when the planar porphyrin ring is saddled.[2–4] Cheng and co-workers recently proposed on the basis of the DFT calculation that the interaction between the empty $d_{x^2-y^2}$ orbital and the nitrogen lone pairs in high-spin Mn(III) porphyrinate causes anomalous spin polarization along the bonding skeleton, inducing the negative and positive spin at the pyrrole nitrogen and α carbon atoms, respectively.[17] Thus, it is possible that the interaction between the empty $d_{x^2-y^2}$ and the doubly occupied a_{2u} orbital in saddled complexes induces a large negative spin at the *meso*-carbon and shifts the meso signal upfield with a considerable broadening. In addition, the d_{xy}–a_{1u} and d_π–$3e_g$ interactions could further contribute to the upfield shift since both the a_{1u} and $3e_g$ orbitals have zero coefficient at the *meso*-carbon atoms.[18] We have reported that the structurally analogous intermediate-spin Fe(III) complexes such as Fe(OETPP)(4-CNPy)$_2^+$ and Fe(OETPP)(THF)$_2^+$ also exhibit the meso signals rather upfield.[16,19,20] Thus, the upfield shift of the meso signal must be the phenomenon commonly observed in highly saddled $S = 2$ Mn(III) and $S = 3/2$ Fe(III) complexes.

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