

# Effects of porphyrin deformation on the <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts in high-spin five- and six-coordinate manganese(III) porphyrin complexes

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Dedicated to Professor Kevin M. Smith on the occasion of his 70th birthday and for his 50 years contribution to the porphyrin chemistry

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> ABSTRACT: As an extension of our study to reveal the effect of porphyrin deformation on the <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts, both five- and six-coordinate high-spin (S = 2) Mn(III) complexes such as Mn(Por)Cl and [Mn(Por)(CD<sub>3</sub>OD)<sub>2</sub>]Cl have been prepared, where Por is a porphyrin dianion such as TPP, OMTPP, and TPPP. Molecular structures of five-coordinate Mn(OMTPP)Cl and Mn(TPP)Cl have been determined by the X-ray crystallographic analysis. As expected, Mn(OMTPP)Cl and Mn(TPPP)Cl have exhibited a highly saddled and highly ruffled porphyrin core, respectively. The <sup>13</sup>C NMR spectra have revealed that these complexes generally exhibit the  $\alpha$ -pyrrole signals at the downfield positions and  $\beta$ -pyrrole and *meso* signals at the upfield positions. The results suggest that the spin polarization of Mn(III)–N<sub>P</sub>  $\sigma$  bonds, which occurs in all the high-spin Mn(III) complexes, is the major factor to determine the chemical shifts of the porphyrin carbon signals (Cheng, R.-J.; Chang, S.-H.; Hung, K.-C. *Inorg. Chem.* 2007; **46**: 1948–1950). Although the *meso* and  $\alpha$ -pyrrole signals are observed at the upfield and downfield positions, respectively, these signals are widely dispersed depending on the deformation mode of the porphyrin ring. The results have been explained in terms of the strong spin polarization of the Mn–N<sub>p</sub> bond together with the specific metal-porphyrin orbital interactions such as: (i) the  $a_{2u}-d_z^2$ interaction in five-coordinate complexes, (ii) the  $a_{2u}$ - $d_{xy}$  interaction in ruffled complexes, and (iii) the  $a_{2u}$  $d_{x}2_{y}2$  interaction in saddled complexes.

> **KEYWORDS:** nonplanar porphyrin, manganese porphyrins, electronic structure, <sup>13</sup>C NMR, <sup>1</sup>H NMR, molecular structure.

# INTRODUCTION

Elucidation of the electronic structures of iron porphyrin complexes is quite important to understand the functions and catalytic processes of naturally occurring heme proteins as well as synthetic model heme complexes [1, 2]. Among the porphyrin  $\pi$  orbitals, either the  $a_{1u}$  or  $a_{2u}$  orbital is considered to be the HOMO in the complexes with  $D_{4h}$  symmetry. Since the  $a_{1u}$  and  $a_{2u}$  orbitals are orthogonal to any of the iron 3d orbitals, there should be no interaction between the porphyrin HOMO and iron 3d orbitals. However, if the normally-planar porphyrin ring is deformed, the porphyrin HOMO can be involved in the interactions with some of the iron 3d orbitals. Table 1 lists the symmetry presentations of the metal 3d and porphyrin frontier orbitals in metal porphyrin complexes with planar  $D_{4h}$ , six-coordinate ruffled and saddled  $D_{2d}$ ,

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	$D_{4h}$	D <sub>2d</sub>	D <sub>2d</sub>	$C_{4v}$	C <sub>2v</sub>	C <sub>2v</sub>
	planar	ruffled	saddled	domed	ruffled	saddled
Metal						
d <sub>x2-y2</sub>	$b_{1g}$	$b_1$	<b>b</b> <sub>2</sub>	$b_1$	a <sub>2</sub>	$a_1$
$d_{z2}$	$a_{1g}$	a <sub>1</sub>	a <sub>1</sub>	a <sub>1</sub>	a <sub>1</sub>	$a_1$
$d_{xz}, d_{yz}$	eg	e	e	e	<b>b</b> <sub>1</sub> , <b>b</b> <sub>2</sub>	<b>b</b> <sub>1</sub> , <b>b</b> <sub>2</sub>
$d_{xy}$	$b_{2g}$	$b_2$	$b_1$	$b_2$	$a_1$	$a_2$
Porphyrin						
4eg* (LUMO)	eg	e	e	e	<b>b</b> <sub>1</sub> , <b>b</b> <sub>2</sub>	<b>b</b> <sub>1</sub> , <b>b</b> <sub>2</sub>
a <sub>1u</sub> (HOMO)	$a_{1u}$	$b_1$	$b_1$	a <sub>2</sub>	a <sub>2</sub>	$a_2$
a <sub>2u</sub> (HOMO)	$a_{2u}$	$b_2$	<b>b</b> <sub>2</sub>	$a_1$	$a_1$	$a_1$
3eg	eg	e	e	e	<b>b</b> <sub>1</sub> , <b>b</b> <sub>2</sub>	<b>b</b> <sub>1</sub> , <b>b</b> <sub>2</sub>

**Table 1.** Correlation table for the metalloporphyrin MO's [3, 4]

five-coordinate domed  $C_{4v}$ , and five-coordinate ruffled and saddled  $C_{2v}$  symmetry [3, 4].

In the case of low-spin (S = 1/2) iron(III) complexes, it is well known that the iron d<sub>xy</sub> orbital can interact with the porphyrin  $a_{2u}$  orbital in  $D_{2d}$  ruffled complex because both the iron  $d_{xy}$  and porphyrin  $a_{2u}$  orbitals are labeled as  $b_2$  [1, 2, 5]. For convenience, we will use the symmetry labels such as  $a_{1u}$  and  $a_{2u}$  in  $D_{4h}$  complexes even in the complexes with much lower symmetry such as  $D_{2d}$ ,  $C_{4v}$ , and  $C_{2v}$ . If the  $d_{xv}$  orbital is half-occupied, the  $d_{xv}$ - $a_{2u}$ interaction in ruffled complex induces sizable amount of spin densities on the meso-C and pyrrole-N atoms, which shift the *meso*-C and pyrrole- $\alpha$  signals downfield and upfield, respectively, in <sup>13</sup>C NMR spectra; note that the a<sub>2u</sub> orbital has large coefficients on the meso-C and pyrrole-N atoms [1, 2]. If the  $d_{\pi}$  orbitals are halfoccupied, the  $d_{\pi}$ -3e<sub>g</sub> interactions shift the pyrrole-H signal to the upfield position; note that the 3e<sub>g</sub> orbital has sizable coefficients on the pyrrole-C and zero coefficient on the meso-C atoms. Thus, we can determine if the lowspin Fe(III) complex adopts either the  $(d_{xz}, d_{yz})^4 (d_{xy})^1$  or  $(d_{xy})^2(d_{xz}, d_{yz})^3$  electronic ground state on the basis of the NMR chemical shifts.

We have also applied this method to determine the electronic structure of the intermediate-spin (S = 3/2) Fe(III) porphyrin complexes [6]. These complexes have three half-occupied 3d orbitals, which interact with specific porphyrin orbitals in deformed systems and affect the chemical shifts of porphyrin carbon signals such as *meso*,  $\alpha$ -pyrrole, and  $\beta$ -pyrrole signals. Furthermore, the intermediate-spin Fe(III) complexes possibly have several electronic ground states, *i.e.*  $(d_{xy})^2(d_{xz}, d_{yz})^2(d_z^2)^1$ ,  $(d_{xz}, d_{yz})^3 (d_{xy})^1 (d_z 2)^1$ , and  $(d_{xz}, d_{yz})^3 (d_z 2)^1 (d_{xy})^1$ , which makes the interpretation of the <sup>13</sup>C NMR spectra very complicated [6-10].

High-spin (S = 2) Mn(III) porphyrin complexes should be ideal to reveal the effects of metal-porphyrin orbital interactions on the NMR chemical shifts because they

always adopt the  $(d_{xy})^1(d_{yz})^1(d_{zz})^1(d_z^2)^1$  electronic ground state regardless of the deformation mode, which is in sharp contrast to the case of the low-spin and intermediatespin Fe(III) complexes mentioned above [11–14]. In order to reveal the effect of porphyrin deformation, we have used highly ruffled and highly saddled porphyrins, most of which were first prepared and developed by Smith and coworkers [15–26]. In the present study, we have measured the <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts of 14 kinds of five-coordinate Mn(Por)Cl and 17 kinds of six-coordinate [Mn(Por)(CD<sub>3</sub>OD)<sub>2</sub>]Cl, where Por are dianions of various porphyrins such as relatively planar TPP, TArP, and OEP, saddled OMTPP and OETPP, and ruffled T<sup>i</sup>PrP, TPrP, and TEtP. The purpose of this study is to report the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of various high-spin Mn(III) porphyrin complexes mentioned above and to interpret the <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts on the basis of the metal-porphyrin orbital interactions. The conclusion obtained in this study will be applicable to determine the electronic structures of metal porphyrin complexes with multi-spin systems.

### RESULTS

### X-ray crystallography

Figure 1 shows the ORTEP drawings of the molecular structures of Mn(OMTPP)Cl and Mn(T<sup>i</sup>PrP)Cl. Figure 2 shows the deviation of the peripheral carbon atoms from the least-squares plane of the 24 atoms in Mn(Por)Cl. For comparison, the corresponding data in Mn(TPP)Cl are also plotted in Fig. 2 [27]. Table 2 lists the structural parameters of these complexes together with those of the analogous Fe(III) complexes, where  $\Delta M$  is the deviation of the metal ion from the 24 atom mean plane [27–30].

As expected, Mn(OMTPP)Cl showed a highlysaddled structure. The mean deviation of the  $\beta$ -pyrrole



Fig. 1. Molecular structures of (a) [Mn(OMTPP)Cl] and (b) [Mn(TPP)Cl]. Thermal ellipsoids are drawn to enclose 50% probability



**Fig. 2.** Displacement of the peripheral carbon atoms of Mn(TPP)Cl(black) [27], Mn(OMTPP)Cl(blue) and Mn(T<sup>i</sup>PrP) Cl(red) from the mean plane of the 24-atom core. 1 pm =  $10^{-2}$  Å

carbons reached as much as 1.11 Å. The average dihedral angle between two diagonal pyrrole planes, ω, was only 122.7°. Interestingly, Mn(TPP)Cl was also saddled as shown in Fig. 2 although the average deviation of the β-pyrrole carbons was 0.38 Å and the average dihedral angle ω was 171.4° [27]. Mn(TPP)Cl showed a highly ruffled structure as revealed from the large deviation of the *meso* carbon atoms, *i.e.* 0.60 Å. The ruffling dihedral angle defined by  $C_{\alpha}N-NC_{\alpha}$  in diagonal pyrrole rings is 39.8° in average. This complex contained some saddled deformation since the C2, C7, C12, and C17 atoms were similarly deviated as shown in Fig. 2. The average Mn– N<sub>P</sub> length was quite short, 1.981 Å. In contrast, the Mn– Cl length was much longer than the corresponding bonds

 Table 2. Comparison of structural parameters of Mn(Por)Cl and Fe(Por)Cl

Complexes	M–N <sub>p</sub>	M–Cl	ΔΜ	References
Mn(TPP)Cl	2.008 (7)	2.363 (3)	0.27	27
Mn(OMTPP)Cl	2.009 (4)	2.3680 (17)	0.33	tw
Mn(T <sup>i</sup> PrP)Cl	1.981 (2)	2.4083 (15)	0.34	tw
Fe(TPP)Cl	2.070 (9)	2.211 (1)	0.57	28
Fe(OMTPP)Cl	2.034 (6)	2.24 (3)	0.51	29
Fe(T <sup>i</sup> PrP)Cl	2.038 (2)	2.238 (2)	0.55	30

in Mn(TPP)Cl and Mn(OMTPP)Cl. In spite of the short Mn–N bond, the deviation of the Mn(III) ion from the average plane is not much different from that of saddled Mn(OMTPP)Cl.

### <sup>13</sup>C NMR spectroscopy

(1) Five-coordinate Mn(Por)Cl. Figure 3 shows the <sup>13</sup>C NMR spectra of (a) Mn(TMP)Cl, (b) Mn(OMTPP) Cl, (c) Mn(OETPP)Cl, and (d) Mn(T<sup>i</sup>PrP)Cl taken in a CD<sub>2</sub>Cl<sub>2</sub> solution at 298 K. The meso-C signals of Mn(OMTPP)Cl and Mn(OETPP)Cl were too broad to detect. These signals were observed, however, in the *meso*- $^{13}$ C enriched complexes as shown in Fig. 3(b') in the case of the former complex. Table 3 lists the chemical shifts of these complexes together with those of the analogous complexes including a series of Mn(TArP)Cl [13, 31]. The meso carbon signals appeared at extremely different positions, *i.e.*  $\delta$  +216 to -406 ppm. Thus, the range in chemical shifts reached as much as 622 ppm. In contrast, the  $\alpha$ -pyrrole signals were observed in a narrower region,  $\delta$  314 to 475 ppm, though they were too broad to detect in the case of saddled Mn(OETPP)Cl. The  $\beta$ -pyrrole signals showed an upfield shift as compared



**Fig. 3.** <sup>13</sup>C NMR spectra of (a) Mn(TMP)Cl, (b) Mn(OMTPP)Cl, (c) Mn(OETPP)Cl, and (d) Mn(T<sup>i</sup>PrP)Cl taken in  $CD_2Cl_2$  solution at 298 K. <sup>13</sup>C NMR spectra of *meso*-<sup>13</sup>C enriched Mn(OMTPP)Cl and phenyl-<sup>13</sup>C enriched Mn(OETPP)Cl are shown in the insets (b') and (c'), respectively

with those of the corresponding diamagnetic complexes and appeared in a wide range,  $\delta$  +111 to -181 ppm. In the case of Mn(4-X-TPP)Cl, the chemical shifts of the *meso*,  $\alpha$ -, and  $\beta$ -pyrrole signals were not much affected by the *p*-substituents; they were observed at  $\delta$  106 to 110 ppm, 388 to 396, and -154 to -161 ppm, respectively.

(2) Six-coordinate  $[Mn(Por)(CD_3OD)_2]Cl$ . Figure 4 shows the <sup>13</sup>C NMR spectra of six-coordinate (a)

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Complexes	Porphyrin			Pyrrole <sup>a</sup>		meso <sup>b</sup>				Ref.
	meso	α-Py	β-Ρу	C(a)	C(β)	ipso	ortho	meta	para	
						$C(\alpha)$	$C(\beta)$	$C(\gamma)$		
[Mn(TPP)Cl]	110	389	-161			200	164, 163	128	128	31
[Mn(2,4,6-Et <sub>3</sub> -TPP)Cl]	122	392	-156	_	_	187	184, 172	131, 128	144	tw
[Mn(2,4,6-Me <sub>3</sub> -TPP)Cl]	118	380	-161	—	—	189	180, 165	137, 133	130	tw
[Mn(4-Me-TPP)Cl]	109	388	-159		_	200	165, 164	130	139	tw
[Mn(4-F-TPP)Cl]	107	393	-156		_	201	168, 166	117	164	tw
[Mn(4-Cl-TPP)Cl]	107	395	-155	—	—	203	167, 165	130	136	tw
[Mn(4-Br-TPP)Cl]	106	393	-155		_	204	167, 166	133	125	tw
[Mn(4-CF <sub>3</sub> -TPP)Cl]	107	396	-154		_	208	167, 163	127	132	tw
[Mn(OEP)Cl]	80	385	-75	-39	80	_	_	_	_	31
[Mn(OMTPP)Cl]	-302	314	-27	-29	_	398	84	120, 117	124	tw
[Mn(OETPP)Cl]	-406	n.d.	111, 97	0, -15	183, 174	456	-69	120, 116	114	31
[Mn(T <sup>i</sup> PrP)Cl]	216	475	-153		_	48	113	_	_	32
[Mn(TPrP)Cl]	135	386	-178	—	—	108	78	17	_	tw
[Mn(TEtP)Cl]	136	385	-181	—	—	136	104	—		tw

Table 3. <sup>13</sup>C NMR chemical shifts of [Mn(Por)Cl] taken in CD<sub>2</sub>Cl<sub>2</sub> solution at 298 K

<sup>a</sup>Substituents at the  $\beta$ -pyrrole positions. <sup>b</sup>Substituents at the *meso*-positions. Chemical shifts of the *meso*-phenyl signals are given in italic.

 $[Mn(TMP)(CD_3OD)_2]Cl, (b) [Mn(OMTPP)(CD_3OD)_2]$ Cl, (c)  $[Mn(OETPP)(CD_3OD)_2]Cl$ , and (d)  $[Mn(T^iPrP)]$  $(CD_3OD)_2$ ]Cl taken in a  $CD_2Cl_2$  solution at 298 K. The meso signals of [Mn(OMTPP)(CD<sub>3</sub>OD)<sub>2</sub>]Cl and  $[Mn(OETPP)(CD_3OD)_2]Cl$  were observed only in the *meso*- $^{13}$ C enriched complexes as shown in Fig 4(b') in the case of the former complex. Table 4 lists the chemical shifts of these complexes [31, 32]. As in the case of the five-coordinate complexes, the *meso* and the  $\beta$ -pyrrole signals dispersed in a wide range,  $\delta$  +85 to -492 ppm and +48 to -240 ppm, respectively. In contrast, the  $\alpha$ -pyrrole signals were observed in a relatively narrow range, *i.e.* 440 to 516 ppm. The para-substituent effect on the chemical shifts of the *meso*,  $\alpha$ -, and  $\beta$ -pyrrole signals in [Mn(4-X-TPP)(CD<sub>3</sub>OD)<sub>2</sub>]<sup>+</sup> were similarly small as in the case of the five-coordinated complexes Mn(TArP)Cl; they were observed at  $\delta$  -6.3 to -11 ppm, 473 to 482, and -196 to -204 ppm, respectively.

(3) *Curie plots.* Figure 5 shows the Curie plots of the *meso*-C signals in some five- and six-coordinate complexes. The Curie plots of the other <sup>13</sup>C signals of these complexes are given in Figs S1–S6 of the Supporting information (SI).

### <sup>1</sup>H NMR spectroscopy

Tables 5 and 6 list the <sup>1</sup>H NMR chemical shifts of the five- and six-coordinate complexes, respectively. As is clearly seen from these data, the pyrrole-H signals of the six-coordinate complexes appeared around -30 ppm, which are by 10 ppm more upfield than those of the corresponding five-coordinate complexes. In contrast, the pyrrole-CH( $\alpha$ ) signals of the six-coordinate complexes appeared more downfield than those of the corresponding five-coordinate complexes. The temperature dependent <sup>1</sup>H NMR spectra of Mn(OMTPP)Cl and Mn(OETPP) Cl are given in Figs S7–S9 of SI. The Curie plots of the <sup>1</sup>H NMR signals in five- and six-coordinated OMTPP, OETPP, OEP, and TPPP complexes are given in Figs S10–S13, respectively.

### UV-vis spectroscopy

The UV-vis spectra of some five- and six-coordinate complexes measured in  $CH_2Cl_2$  solution at 298 K are given in Figs S14 and S15, respectively. The absorption maxima of five- and six-coordinate complexes are listed in Tables S3 and S4.

# DISCUSSION

### Molecular structure of Mn(III) porphyrin complexes

The data in Table 2 reveal that Mn–N<sub>P</sub> bond length is much shorter than the corresponding Fe–N<sub>P</sub> bond length by 0.025–0.062 Å, which should be ascribed to the presence of the vacant  $d_x 2_y 2$  orbital in the former complexes [33]. In contrast, the Mn–Cl bond is much longer than the Fe–Cl bond in the corresponding Fe(III)



**Fig. 4.** <sup>13</sup>C NMR spectra of (a)  $[Mn(TMP)(CD_3OD)_2]Cl$ , (b)  $[Mn(OMTPP)(CD_3OD)_2]Cl$ , (c)  $[Mn(OETPP)(CD_3OD)_2]Cl$ , and (d)  $[Mn(T^{1}PrP)(CD_3OD)_2]Cl$  taken in  $CD_2Cl_2$  at 298 K. <sup>13</sup>C NMR spectra of *meso-*<sup>13</sup>C enriched  $[Mn(OMTPP)(CD_3OD)_2]Cl$ , and phenyl-<sup>13</sup>C enriched  $[Mn(OETPP)(CD_3OD)_2]Cl$  are shown in the insets (b') and (c'), respectively. Partially relaxed <sup>1</sup>H-decoupled <sup>13</sup>C NMR spectrum of  $[Mn(OETPP)(CD_3OD)_2]Cl$  with pulse interval  $\tau = 87$  ms is given in (c'')

Complexes	Porphyrin			Pyrrole <sup>a</sup>		meso <sup>b</sup>				Ref.
	meso	α-Py	β-Ρу	C(a)	C(β)	ipso	ortho	meta	para	
						$C(\alpha)$	$C(\beta)$	C(γ)		
[Mn(TPP)L <sub>2</sub> ]Cl	-8.0	473	-203		_	262	94	126	127	32
[Mn(2,4,6-Et <sub>3</sub> -TPP)L <sub>2</sub> ]Cl	-6.4	476	-208			245	120	128	145	tw
[Mn(2,4,6-Me <sub>3</sub> -TPP)L <sub>2</sub> ]Cl	-2.4	477	-209			246	112	132	139	tw
[Mn(2,6-Cl <sub>2</sub> -TPP)L <sub>2</sub> ]Cl	-1.4	488	-198			257	103	131	132	tw
[Mn(4-OMe-TPP)L <sub>2</sub> ]Cl	-7.3	482	-203			259	95	112	159	tw
[Mn(4-Me-TPP)L <sub>2</sub> ]Cl	-11	478	-204			262	94	127	137	tw
[Mn(4-F-TPP)L <sub>2</sub> ]Cl	-6.9	481	-201	_	_	262	95	114	163	tw
[Mn(4-Cl-TPP)L <sub>2</sub> ]Cl	-8.0	481	-201	_	_	264	95	127	133	tw
[Mn(4-Br-TPP)L <sub>2</sub> ]Cl	-10.5	478	-204	_	_	262	94	127	137	tw
[Mn(4-CF <sub>3</sub> -TPP)L <sub>2</sub> ]Cl	-6.9	480	-197			268	95	123	131	tw
[Mn(4-CN-TPP)L <sub>2</sub> ]Cl	-6.3	479	-196			269	95	130	112	tw
[Mn(OEP)L <sub>2</sub> ]Cl	-24	472	-108	-56	187					31
[Mn(OMTPP)L <sub>2</sub> ]Cl	-369	440	-12	-54		451	-65	120	117	tw
[Mn(OETPP)L <sub>2</sub> ]Cl	-492	n.d.	48	-32	180	520	-116	118	112	31
$[Mn(T^{i}PrP)L_{2}]Cl$	85	516	-240			99	41			31
[Mn(TPrP)L <sub>2</sub> ]Cl	9.4	463	-235	_	_	132	14	4		tw
[Mn(TEtP)L <sub>2</sub> ]Cl	8.3	463	-236		—	125	-19	—	—	tw

**Table 4.** <sup>13</sup>C NMR chemical shifts of  $[Mn(Por)L_2]Cl$  (L = CD<sub>3</sub>OD) taken in CD<sub>3</sub>OD solution at 298 K

<sup>a</sup>Substituents at the  $\beta$ -pyrrole positions. <sup>b</sup>Substituents at the *meso*-positions. Chemical shifts of the *meso*-phenyl signals are given in italic.

complex by 0.13-0.17 Å. The out-of-plane deviation of the Fe(III) ion is by 0.18-0.30 Å much larger than that of the corresponding Mn(III) ion regardless of the deformation mode of porphyrin.

As expected, [Mn(OMTPP)Cl] exhibits highly saddled distortion. The average Mn-N<sub>P</sub> bond length is shorter than the corresponding Fe(III) complex by 0.025 Å. Consequently, the saddled deformation is much larger in [Mn(OMTPP)Cl] than in [Fe(OMTPP)Cl] as is revealed from the average deviations of the  $\beta$ -pyrrole carbon atoms from the mean plane of the 24 atoms; they are 1.11 Å and 1.06 Å for [Mn(OMTPP)Cl] than in [Fe(OMTPP)Cl], respectively. As shown in Fig. S7, the saddled deformation in [Mn(OMTPP)Cl] is maintained in solution since the methyl signal has broadened as the temperature is lowered and started to split into two signals at 251 K. The process is ascribed to the ring inversion of the saddled porphyrin ring, which is commonly observed in the OMTPP and OETPP complexes [15, 16, 29, 34]. The activation parameters for ring inversion have been determined by computer simulation of the methyl signals as shown in Fig. S8. They are,  $\Delta H^{\neq} = 51.2$  kJ.mol<sup>-1</sup> and  $\Delta S^{\neq} = 34.7 \text{ J K}^{-1} \text{.mol}^{-1}$ . Thus, the activation free energies ( $\Delta G^{\neq}$ ) for ring inversion in [Mn(OMTPP)Cl] are calculated to be 42.8 and 42.2 kJ.mol<sup>-1</sup> at 243 and 258 K, respectively. These values are close to those of Fe(OMTPP)Cl; they were reported to be 42.2 kJ.mol<sup>-1</sup>

(243 K) [29] and 43.9 kJ.mol<sup>-1</sup> (258 K) [34]. As shown in Fig. S9, the barrier to inversion has increased to a great extent on going from Mn(OMTPP)Cl to Mn(OETPP)Cl. The four separated methylene signals in Mn(OETPP) Cl- $d_{20}$  at 298 K did not exhibit two signals even at 383 K. Although the molecular structure of Mn(OETPP)Cl is not available, the NMR data given above indicate that the saddled core in Mn(OETPP)Cl is much deeper than that in Mn(OMTPP)Cl.

[Mn(T<sup>'</sup>PrP)Cl] exhibits a highly ruffled structure. The average Mn–N<sub>P</sub> bond length and the average deviation of the *meso*-C atoms are 1.981(2) and 0.60 Å, respectively, which should be compared with the corresponding values in analogous [Fe(T<sup>'</sup>PrP)Cl], 2.038(2) and 0.51 Å, respectively [30]. In spite of the large difference in metal–nitrogen bond lengths, the ruffling dihedral angles, defined by  $C_{\alpha}N$ –NC<sub> $\alpha$ </sub> for nitrogen atoms in the opposite pyrrole rings, are nearly the same, *i.e.* 39.8° and 38.2° for [Mn(T<sup>'</sup>PrP)Cl] and [Fe(T<sup>'</sup>PrP)Cl], respectively.

# Orbital interactions in high-spin manganese(III) porphyrin complexes

In our previous papers on iron porphyrin complexes, we have explained the chemical shifts of the <sup>1</sup>H and <sup>13</sup>C NMR signals in terms of the orbital interactions between Fe(III) 3d and porphyrin  $\pi$  orbitals in planar, ruffled,



**Fig. 5.** Curie plots of the *meso*-C signals in five-coordinate [Mn(TPP)Cl] (filled black circle), [Mn(OMTPP)Cl] (filled blue circle), [Mn(OETPP)Cl] (filled red circle), and [Mn(T<sup>i</sup>PrP) Cl] (filled green circle) together with those in six-coordinate [Mn(TPP)(CD<sub>3</sub>OD)<sub>2</sub>]Cl (open black square), [Mn(OMTPP) (CD<sub>3</sub>OD)<sub>2</sub>]Cl (open blue square), and [Mn(T<sup>i</sup>PrP)(CD<sub>3</sub>OD)<sub>2</sub>]Cl (open green square)

and saddled complexes on the basis of the correlation tables given in Table 1 [2]. If a porphyrin MO has the same symmetry as a half-occupied iron d orbital, the interaction between metal d and porphyrin  $\pi$  orbitals occurs. The interaction increases the spin densities on the specific carbon atoms of the porphyrin ring and induces the downfield or upfield shifts of the <sup>13</sup>C and <sup>1</sup>H signals. Thus, we can determine the electronic structure of the paramagnetic metal irons on the basis of the <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts. The major interactions that should be considered in high-spin (S = 2) Mn(III) porphyrin complexes are listed below.

(1) Interactions involving the  $3e_g$  orbitals. The porphyrin  $3e_g$  orbitals in  $D_{4h}$  complexes can interact with the half-occupied  $d_{\pi}$  orbitals because they have the same symmetry. Since the  $3e_g$  orbitals have relatively large coefficients on the  $\beta$ -pyrrole-C and pyrrole-N atoms, the interactions shift the pyrrole-H signal upfield. The orbital symmetry changes depending on the deformation mode of the porphyrin ring. The  $d_{\pi}$ - $3e_g$  like interaction occurs, however, even in the deformed complexes with  $D_{2d}$ ,  $C_{4v}$ , and  $C_{2v}$  symmetry since these orbitals have the same symmetry as listed in Table 1. In addition, because the high-spin Mn(III) ion has no unpaired electron in the  $d_x^2$ -y<sup>2</sup> orbital, the pyrrole-H signals in Mn(III) porphyrin complexes always appear upfield as is clear from the data

Complexes		Pyrrole			meso <sup>b</sup>					
	Н	CH(a)	CH(β)	Н	ortho	meta	para			
					CH(a)	CH(β)	CH(γ)			
[Mn(TPP)Cl]	-21.9		_		а	8.3	7.3	31		
[Mn(2,4,6-Et <sub>3</sub> -TPP)Cl]	-19.4	_	_		(1.5, a)	8.2, 8.0	(2.9, a)	tw		
[Mn(2,4,6-Me <sub>3</sub> -TPP)Cl]	-20.3	_			а	8.1	а	tw		
[Mn(4-Me-TPP)Cl]	-21.9	—			а	8.2	( <i>3.0</i> ) <sup>c</sup>	tw		
[Mn(4-F-TPP)Cl]	-21.9	_	_		а	8.1	_	tw		
[Mn(4-Cl-TPP)Cl]	-21.7	_	_		а	8.3	_	tw		
[Mn(4-Br-TPP)Cl]	-22.0	_	_		а	8.5	_	tw		
[Mn(4-CF <sub>3</sub> -TPP)Cl]	-22.0	_	_	_	а	8.6	_	tw		
[Mn(OEP)Cl]		23.1, 0.5	2.7	52.6	_	_	_	31		
[Mn(OMTPP)Cl]		37			11.4	5.3	9.8	tw		
[Mn(OETPP)Cl]		38.4, 13.7	1.3		13.1	5.3	10.5	31		
		10.2, -2.2								
[Mn(T <sup>i</sup> PrP)Cl]	-19.4	—			9.5	3.2		31		
[Mn(TPrP)Cl]	-20.6	—	—		9.6	2.2	1.3	tw		
[Mn(TEtP)Cl]	-20.6	—	_		9.7	2.3	_	tw		

Table 5. <sup>1</sup>H NMR chemical shifts of [Mn(Por)Cl] taken in CD<sub>2</sub>Cl<sub>2</sub> solution at 298 K

<sup>a</sup>Too broad to detect. <sup>b</sup>The chemical shifts of the *meso*-phenyl signals are written in italic. <sup>c</sup>The numbers in parenthesis are the chemical shifts of the *ortho* and *para* alkyl signals.

Complexes	Pyrrole				meso <sup>b</sup>				
	Н	CH(a)	CH(β)	Н	ortho	meta	para		
					CH(a)	$CH(\beta)$	$CH(\gamma)$		
[Mn(TPP)L <sub>2</sub> ]Cl	-31.0				9.2	7.3	7.9	31	
[Mn(2,4,6-Et <sub>3</sub> -TPP)L <sub>2</sub> ]Cl	-31.6	_	—	—	$(1.2)^{c}$	6.4	(2.5) <sup>c</sup>	tw	
[Mn(2,4,6-Me <sub>3</sub> -TPP)L <sub>2</sub> ]Cl	-31.8				(1.2)	6.3	(2.1)	tw	
[Mn(4-Me-TPP)L <sub>2</sub> ]Cl	-30.9				9.1	7.1	$(2.0)^{d}$	tw	
[Mn(4-F-TPP)L <sub>2</sub> ]Cl	-30.8	_	_	_	9.3	7.2	_	tw	
[Mn(4-Cl-TPP)L <sub>2</sub> ]Cl	-31.1				9.1	7.3	_	tw	
[Mn(4-Br-TPP)L <sub>2</sub> ]Cl	-31.1				9.1	7.5	_	tw	
[Mn(4-CF <sub>3</sub> -TPP)L <sub>2</sub> ]Cl	-31.2				9.4	7.7	_	tw	
[Mn(OEP)L <sub>2</sub> ]Cl		14.5	2.3	76.4	_	_	_	31	
[Mn(OMTPP)L <sub>2</sub> ]Cl		44.2			11.8	5.1	10.0	tw	
[Mn(OETPP)L <sub>2</sub> ]Cl		30.3	1.1		13.4	4.3	11.2	31	
[Mn(T <sup>i</sup> PrP)L <sub>2</sub> ]Cl	-31.6				а	2.1	_	31	
[Mn(TPrP)L <sub>2</sub> ]Cl	-31.1	_	_	_	-3.0	2.6	1.2	tw	
[Mn(TEtP)L <sub>2</sub> ]Cl	-31.0	_			-2.4	1.1	_	tw	

**Table 6.** <sup>1</sup>H NMR chemical shifts of  $[Mn(Por)L_2]Cl$  (L = CD<sub>3</sub>OD) taken in CD<sub>3</sub>OD solution at 298 K

<sup>a</sup>Too broad to detect. <sup>b</sup>The chemical shifts of the *meso*-phenyl signals are written in italic. <sup>c</sup>The numbers in parenthesis are the chemical shifts of the *ortho* and *para* alkyl signals.

in Tables 5 and 6. As mentioned in the introduction, we will use the symmetry labels in  $D_{4h}$  complex even if the complexes deform to have lower symmetry.

(2) Interactions involving the  $a_{2u}$  orbitals. The  $a_{2u}$  orbital has large coefficients on the pyrrole-N and *meso*-C atoms. Thus, the interaction between the  $a_{2u}$  and half-occupied Mn d orbitals should induce sizable amount of spin densities on these atoms. Although the  $a_{2u}$  orbital is orthogonal to any of the metal 3d orbitals in  $D_{4h}$  complexes, it can interact with the half-occupied  $d_z 2$  orbital in all the five-coordinate complexes regardless of the deformation mode [3]. If the complex adopts either the  $D_{2d}$  or  $C_{2v}$  ruffled structure, the  $a_{2u}$  orbital can interact with the half-occupied  $d_{x2}$ -  $a_{2u}$  and  $d_{xy}$ - $a_{2u}$  interactions shift the *meso*-C signals to the downfield position.

(3) Interactions involving the  $a_{1u}$  orbitals. The  $a_{1u}$  orbital has relatively large coefficients at the  $\alpha$ - and  $\beta$ -pyrrole-C atoms. Although the  $a_{1u}$  orbital is orthogonal to any of the metal 3d orbitals in  $D_{4h}$  complexes, it can interact with the half-occupied  $d_{xy}$  orbital in the  $D_{2d}$  or  $C_{2v}$  saddled structure. The interaction should contribute to the downfield shift of the  $\alpha$ - and  $\beta$ -pyrrole-C signals [7, 37].

(4) Interaction involving the vacant  $d_x 2_y 2$  orbital. In high-spin Mn(III) complexes, the  $d_x 2_y 2$  orbital is vacant. Thus, the interaction involving this orbital should give little influence on the chemical shifts. However, it has recently been reported by Cheng and co-workers that

the donation of nitrogen lone-pair electrons to the vacant  $d_{x}2_{.y}2$  orbital in high-spin Mn(III) porphyrin complexes induces an anomalous spin polarization to the Mn–N  $\sigma$ -bond and increases positive and negative spin on the manganese and nitrogen atoms, respectively [14]. Furthermore, the negative spin on the nitrogen atoms polarizes the neighboring N–C<sub> $\alpha$ </sub>, C<sub> $\alpha$ </sub>–C<sub>meso</sub>, and C<sub> $\alpha$ </sub>–C<sub> $\beta$ </sub> bonds and induces positive spin on the  $\alpha$ -pyrrole carbon and negative spin on the *meso* and  $\beta$ -pyrrole carbon atoms [14]. Consequently, the  $\alpha$ -pyrrole signal should shift downfield while the adjacent *meso* and  $\beta$ -pyrrole carbon signal should shift upfield. This interaction occurs commonly in high-spin Mn(III) complexes regardless of the deformation modes of the porphyrin.

In addition to the spin polarization of the Mn–N  $\sigma$ -bond, the vacant  $d_x 2_{-y} 2$  orbital can interact with doublyoccupied  $a_{2u}$  orbitals in the  $D_{2d}$  or  $C_{2v}$  saddled structure [37–39]. The interaction should induce negative spin on the  $a_{2u}$  orbital and shift the *meso*-C signals upfield. Similarly, the doubly-occupied  $a_{1u}$  orbital can interact with the vacant  $d_x 2_{-y} 2$  orbital if the complex adopts either the  $D_{2d}$  or  $C_{2v}$  ruffled structure. The interaction should contribute to the upfield shift of both the  $\alpha$ - and  $\beta$ -pyrrole-C signals.

In the next section, we will discuss the <sup>13</sup>C NMR chemical shifts on the basis of the metal-porphyrin orbital interactions mentioned above and determine which interaction prevails in high-spin Mn(III) porphyrin complexes.

# Effects of metal-porphyrin orbital interactions on the NMR chemical shifts

It is well-known that both five- and six-coordinate Mn(III) porphyrin complexes adopt the high-spin (S = 2) state unless the field strength of the axial ligands is very strong;  $CN^{-}$  and HIm are known to form the low-spin (S = 1) six-coordinate complexes in nonpolar solvents such as  $CD_2Cl_2$  [13]. Since the axial ligand is either  $Cl^{-}$  or  $CD_3OD$  in the present case, all these complexes should adopt the high-spin state. [31–33].

In five-coordinate Mn(III) complexes, the relatively planar porphyrin complexes Mn(TArP)Cl exhibit the  $\alpha$ - and  $\beta$ -pyrrole signals at extremely downfield (473 to 488 ppm) and upfield (-196 to -209 ppm) positions, respectively, as revealed from the data in Table 3. In contrast, the *meso* signals appear at slightly upfield positions. The downfield shift of the  $\alpha$ -pyrrole signals together with the upfield shift of the  $\beta$ -pyrrole and *meso* signals suggest that the spin polarization of the Mn–N  $\sigma$  bonds proposed by Cheng and co-workers should be the major factor to determine the chemical shifts of the porphyrin carbon signals in high-spin five-coordinate Mn(III) complexes [14].

The data in Table 3 also indicate that the deformation of the porphyrin ring affects the chemical shifts. For example, the  $\alpha$ -pyrrole signals in Mn(TPP)Cl, Mn(OMTPP)Cl, and Mn(TPrP)Cl are observed at 396, 314, and 475 ppm, respectively. Thus, the downfield shift is the largest in ruffled complex while it is the smallest in saddled one. The difference in Mn(III)-N bond lengths should be one of the reasons. In fact, the Mn(III)-N bond length in ruffled Mn(T<sup>i</sup>PrP)Cl is 1.981(2) Å, which is shorter than Mn(TPP)Cl (2.008 Å) and Mn(OMTPP)Cl (2.009 Å) as listed in Table 2. Thus, the spin polarization of the Mn–N  $\sigma$  bond is expected to be the largest in ruffled Mn(T<sup>i</sup>PrP) Cl. However, the downfield shift of the  $\alpha$ -pyrrole signal in Mn(OMTPP)Cl is smaller than that in Mn(TPP)Cl in spite of the similar Mn-N bond length. The result should be ascribed to the less effective orbital overlap between  $d_x 2_y 2$ and nitrogen lone pair orbitals in saddled Mn(OMTPP)Cl. In fact, the average angle of the Mn–N bonds against the pyrrole plane is 154.5°, which is much smaller than 171.4° and 173.5° in Mn(TPP)Cl and Mn(TPP)Cl, respectively.

The data in Table 3 also indicate that the *meso* signal in highly saddled complexes such as Mn(OMTPP)Cl and Mn(OETPP)Cl appear extremely upfield, *i.e.* -302 and -406 ppm, respectively, as compared with 106–122 ppm in less deformed Mn(TArP)Cl. In contrast, the *meso* signal in highly ruffled Mn(TPrP)Cl is observed rather downfield, *i.e.* +216 ppm. The large upfield shift of the *meso* signal in saddled Mn(OMTPP)Cl should be ascribed to the  $d_x 2_y 2-a_{2u}$  interaction. This interaction occurs only in saddled complexes and induces the upfield shift of the *meso* signal. Much larger upfield shift observed in Mn(OETPP)Cl should be explained in terms of the stronger  $d_x 2_y 2-a_{2u}$  interaction. The downfield shift of the *meso* signal in highly ruffled Mn(T<sup>i</sup>PrP)Cl should be ascribed to the  $d_{xy}$ - $a_{2u}$  interaction. This interaction occurs only in ruffled complexes and shifts the *meso* signal downfield. Thus, the downfield shift of the *meso* signal caused by the  $d_{xy}$ - $a_{2u}$  interaction should be larger than the upfield shift of the same signal caused by the spin polarization of the Mn–N  $\sigma$  bond. As expected, the downfield shift is much smaller in the less ruffled complexes such as Mn(TPrP)Cl and Mn(TEtP)Cl due to the weaker  $d_{x^2-y^2-a_{2u}}$  interaction.

Similar tendency is observed in the six-coordinate Mn(III) complexes as revealed from the data in Table 4 although the downfield and upfield shifts are larger than those in the corresponding five-coordinate complexes. The result should be ascribed to the stronger spin polarization of the Mn–N  $\sigma$  bonds due to the more effective overlap between the vacant  $d_{x^2,y^2}$  and lone pair orbitals. Similarly, the upfield shift of the *meso* signals has increased on going from five-coordinate to six-coordinate complexes. The upfield shifts in TPP, OETPP, and T<sup>i</sup>PrP complexes are 118, 67, and 131 ppm, respectively. The large upfield shifts of the *meso* signals in six-coordinate complexes should be ascribed to the absence in  $d_z^2-a_{2u}$  interaction in six-coordinate complexes.

# EXPERIMENTAL

### **General considerations**

Pyrrole was purchased from Kanto, and was distilled and stored in a bottle under argon atmosphere at -20°C. Various aldehydes such as substituted(X) benzaldehydes (X = 4-F-, 4-Cl-, 4-Br-, 4-CF<sub>3</sub>-, 4-CN-, 4-CH<sub>3</sub>-, 4-CH<sub>3</sub>O-, 2,4,6-(CH<sub>3</sub>)<sub>3</sub>-, 2,4,6-(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-, and 2,6-Cl<sub>2</sub>-), propionaldehyde, and isobutyraldehyde together with *p*-chloranil were purchased from Tokyo Kasei Benzaldehyde and formaldehyde were purchased from Wako and Kanto, respectively. p-Toluenesulfornic acid was purchased from Aldrich. Dichloromethane, chloroform, methanol, benzene, and N,N-dimethylformamide (DMF) were purchased from Kanto. Deuterated solvents, dichloromethane- $d_2$  (CD<sub>2</sub>Cl<sub>2</sub>) and methanol- $d_4$  (CD<sub>3</sub>OD), were purchased from MercK and ISOTEC. Carbon-13 enriched benzalehyde, C<sub>6</sub>H<sub>5</sub>-<sup>13</sup>CHO and <sup>13</sup>C<sub>6</sub>H<sub>5</sub>-CHO, were purchased from ISOTEC. Computer simulation of the temperature dependent <sup>1</sup>H NMR spectra was performed with gNMR software purchased from Adept Scientific, Amor Way, Letchworth Herts SG6 1ZA, UK. For single crystal measurements, crystals with X-ray quality were grown in hexane/chloroform and cyclohexane/ chloroform for [Mn(T<sup>i</sup>PrP)Cl] and [Mn(OMTPP)Cl], respectively. X-ray crystallographic data for [Mn(T<sup>i</sup>PrP) Cl] and [Mn(OMTPP)Cl] were collected at 296 K and 200 K on a Bruker APEX II refractometer with Mo  $K_{\alpha}$ X-ray sources, respectively. The absorption correction was performed by the SADABS method. Structures were solved by the direct method and refined in the SHELXTL program [40]. The all non-atoms were refined as anisotropy and all hydrogen positions were calculated. The crystal data and structure refinement for [Mn(OMTPP)Cl] and [Mn(T<sup>i</sup>PrP)Cl] are listed in Tables S1 and S2, respectively.

### Synthesis

Free base porphyrins (Por)H<sub>2</sub>. Tetraarylporphyrins (4-X-TPP)H<sub>2</sub> where X is OMe, Me, H, F, Cl, Br, CF<sub>3</sub>, and CN were prepared by the condensation reactions between substituted benzaldehyde and pyrrole according to the Alder's methods [41]. Free base porphyrins such as  $(2,4,6-Me_3-TPP)H_2$  [42],  $(2,4,6-Et_3-TPP)H_2$  [43],  $(2,6-Cl_2-TPP)H_2$  [42],  $(TPP)H_2$  [24],  $(TEtP)H_2$  [44],  $(OETPP)H_2$  [16], and  $(OMTPP)H_2$  [16] were similarly prepared by the Lindsey's method in CHCl<sub>3</sub> solution using BF<sub>3</sub>-etherate.

[Mn(Por)Cl]. Insertion of manganese ion to free base porphyrins was performed by the slightly modified methods reported previously [32, 45]. Typical procedures are described below.

[Mn(2,4,6-Et<sub>3</sub>-TPP)Cl]. Free base porphyrin,  $(2,4,6-Et_3-TPP)H_2$  (205 mg, 0.215 mmol), was added to a 500 mL three-necked flask equipped with a pressure equalizing dropping funnel, reflux condenser, and a magnetic stirrer, and was dissolved in 100 mL DMF. Argon was bubbled into the DMF solution while it was vigorously stirred for 10 min. Solid MnCl<sub>2</sub> (110 mg, 0.874 mmol) dissolved into 20 mL DMF was added to the refluxed DMF solution in 20 min through the dropping funnel under argon atmosphere. The reaction was monitored by UV-vis spectroscopy. The DMF solution of MnCl<sub>2</sub> was repeatedly added into the reaction mixture until no appreciable free base was detected by UV-vis. Total amount of MnCl<sub>2</sub> added was 610 mg (4.85 mmol). After the solution was refluxed for 5 h, DMF was removed under reduced pressure. The remaining solid was dissolved into 100 mL CH<sub>2</sub>Cl<sub>2</sub>, and the solution was washed with 1 M HCl aqueous solution repeatedly until the aqueous layer was colorless. The organic layer was collected and rotary evaporated to dryness. Crude [Mn(2,4,6-Et<sub>3</sub>-TPP)Cl] thus obtained was purified by column chromatography on alumina. Elution with  $CH_2Cl_2$  and then with  $CH_3OH/$ CH<sub>2</sub>Cl<sub>2</sub> 1:9 gave green fractions, which were collected, washed twice with 1 M aq. HCl and then with water. The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and was then rotary evaporated to dryness. The green solid, [Mn(2,4,6-Et<sub>3</sub>-TPP)Cl], was vacuum-dried at 100 °C. Yield 92 mg (41%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm 375, 401, 481, 536, 588, 624. <sup>1</sup>H NMR (300 MHz; CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ<sub>H</sub>, ppm -19.4 (8H, Py-H), 8.2 (4H, *meta*-H), 8.0 (4H, meta-H). <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta_{C}$ , ppm 122 (meso), 392 (α-Py), -156 (β-Py), 187 (ipso), 184 (ortho), 172 (ortho), 131 (meta), 128 (meta), 144 (para), 33.3 (ortho-CH<sub>2</sub>), 28.1 (ortho-CH<sub>2</sub>), 15.1

(*ortho*-CH<sub>3</sub>), 14.8 (*ortho*-CH<sub>3</sub>), 28.1 (*para*-CH<sub>2</sub>), 14.8 (*para*-CH<sub>3</sub>).

[Mn(TEtP)Cl]. Free base porphyrin, (TEtP)H<sub>2</sub> (200 mg, 0.473 mmol), was added to a 500 mL threenecked flask equipped with a pressure equalizing dropping funnel, reflux condenser, and a magnetic stirrer, and was dissolved in 240 mL CHCl<sub>3</sub> and 60 mL CH<sub>3</sub>OH. The solution was stirred vigorously under argon atmosphere, to which the methanol solution (20 mL) of solid MnCl<sub>2</sub> (110 mg, 0.874 mmol) was added through the dropping funnel in 20 min. The reaction was monitored by UV-vis spectroscopy. The CH<sub>3</sub>OH solution of MnCl<sub>2</sub> was repeatedly added. When 799 mg (6.35 mmol) of MnCl<sub>2</sub> was added in total for 4 h, the free base porphyrin was almost disappeared in the UV-vis spectrum. The solvents were evaporated and the remaining solid was dissolved into 200 mL CH<sub>2</sub>Cl<sub>2</sub>. The solution was washed with 1 M aq. HCl repeatedly until the aqueous layer was colorless. The organic layer was collected and rotary evaporated to dryness. The crude [Mn(TEtP)Cl] thus obtained was purified by column chromatography on alumina. Elution with  $CH_2Cl_2$  and then with  $CH_3OH/CH_2Cl_2$  1:9 eluent yielded green fractions, which were washed twice with 1 M HCl aqueous solution and then washed with water. The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and was then rotary evaporated to dryness. The green solid, [Mn(TEtP)Cl] was vacuum-dried at 60 °C. Yield 68.1 mg (28%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm 376, 401, 480, 538, 597, 633. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta_{\rm H}$ , ppm -20.6 (8H, Py-H), 9.7 (8H, meso-CH<sub>2</sub>), 2.3 (12H, *meso*-CH<sub>3</sub>), 1.5 (*ortho*-CH<sub>3</sub>), 2.9 (*para*-CH<sub>3</sub>). <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ<sub>C</sub>, ppm 136 (meso), 385 (α-Py), -181 (β-Py), 136 (meso-CH<sub>2</sub>), 104 (meso-CH<sub>3</sub>).

[Mn(OMTPP)Cl]. [Mn(OMTPP)Cl] was similarly prepared from free base (OMTPP)H<sub>2</sub> (83.5 mg, 0.115 mmol) and MnCl<sub>2</sub> (32.5 mg, 0.258 mmol) in refluxed DMF. The crude [Mn(OMTPP)Cl] was purified by chromatography on alumina. Yield 20.3 mg (22%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm 377, 405, 496, 595, 635. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta_{H}$ , ppm 37 (24H, Py-CH<sub>3</sub>), 11.4 (8H, *ortho*-H), 5.3 (8H, *meta*-H), 9.8 (4H, *para*-H). <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta_{C}$ , ppm -302 (*meso*), 314 (α-Py), -27 (β-Py), -29 (β-Py-CH<sub>3</sub>), 398 (*ipso*), 84 (*ortho*), 120 (*meta*), 117 (*meta*), 124 (*para*).

#### Spectral measurement

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a JEOL LA300 spectrometer operating at 300.4 MHz for <sup>1</sup>H. Chemical shifts were referenced to the residual peaks of deuterated solvents; dichloromethane ( $\delta = 5.32$  ppm for <sup>1</sup>H and 53.8 ppm for <sup>13</sup>C) and methanol ( $\delta = 3.30$  ppm for <sup>1</sup>H and 49.0 ppm for <sup>13</sup>C). UV-vis spectra were measured on a Shimadzu MultiSpec-1500 spectrophotometer in CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>OH at ambient temperature.

# CONCLUSION

The <sup>13</sup>C NMR spectra of high-spin (S = 2) five- and six-coordinate Mn(III) complexes have revealed that the major factor that determines the chemical shifts of the  $\alpha$ -pyrrole,  $\beta$ -pyrrole, and *meso* signals is the spin polarization of the Mn(III)–N  $\sigma$  bond originally proposed by Cheng and co-workers [14]. Consequently, the  $\alpha$ -pyrrole signals appear downfield while the  $\beta$ -pyrrole and *meso* signals appear upfield. In addition to the spin polarization of the Mn(III)–N  $\sigma$ -bonds, the chemical shifts are affected by the deformation modes of the porphyrin ring. Thus, the *meso* signals are observed more upfield in saddled complexes than in planar complexes due to the  $a_{2\mu}$ - $d_x 2_{-\nu} 2$  interaction while they move downfield in ruffled complexes due to the  $a_{2u}$ -d<sub>xy</sub> interaction. The correlation between <sup>13</sup>C NMR chemical shifts and metalporphyrin orbital interactions examined in this study should be useful to determine the electronic structures of various first-row transition metal porphyrin complexes having unpaired electrons in the 3d orbitals.

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### **Supporting information**

A full list of figures, tables and CIF files (Figs S1–S15, Tables S1–S4) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under numbers CCDC-1434591 and 1434553. Copies can be obtained on request, free of charge, *via* www. ccdc.cam.ac.uk/data\_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: data\_request@ccdc.cam.ac.uk).

# ABBREVIATIONS

TPP, TPP, OMTPP are the dianions of 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetraisopropylporphyrin, and 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrin, respectively.

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