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ARTICLE TYPE

# Characterization of Saddled Nickel(III) Porphyrin Cation Radical :The NMR Explicative Model for Ferromagnetically Coupled Metalloporphyrin Radical\*\*

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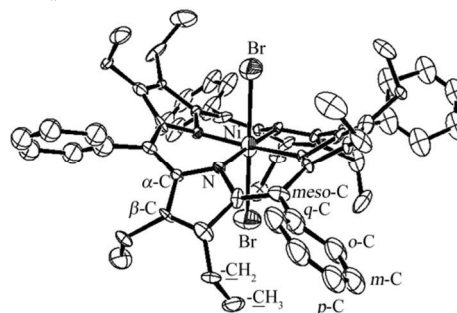
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**Ni<sup>III</sup>(OETPP·)(Br)<sub>2</sub> is the first Ni(III) porphyrin radical cation with structural, <sup>1</sup>H and <sup>13</sup>C paramagnetic NMR data for porphyrinate systems. Associating EPR, NMR analyses with DFT calculation as a new model is capable of clearly determining the dominated state from two controversial spin distributions in ring to be the Ni(III) LS coupled with an *a*<sub>1u</sub> spin-up radical.**

Nickel(III) porphyrinate derivatives have been extensively studied to understand a postulated intermediate of Factor 430 (F<sub>430</sub>), a CH<sub>3</sub>-Ni(III) tetrapyrrole as the cofactor of methyl coenzyme M reductase.<sup>1</sup> Although the redox properties of many Ni(III) porphyrinate systems are well discussed, only rare structural and magnetic spectroscopy, especially NMR, were known, and a stable Ni(III) porphyrin radical cation has not been obtainable.<sup>2</sup> Recently some essential strategies had been built up by combing <sup>13</sup>C and <sup>1</sup>H NMR data with DFT calculations to be only capable of complete characterizing the metal dominated spin system.<sup>3</sup> For those spin-coupled metalloporphyrin radical cations with considerable interests, e.g. the compound I and its model complex, oxoiron (IV) porphyrin cation radical, although quality <sup>1</sup>H NMR data had been obtained, only qualitative bonding interactions between metal *d* orbital and ring  $\pi$  orbitals of ring macrocycle are discussed, since some very down- or upfield NMR signals with regard to the structural positions which share more ring radical spin are difficult to be fully understood due to the lack of a neat manner for discriminating spin transfer from bonding or spatial induction.<sup>4</sup> Attempt to raise the comprehension in spin-coupled metalloporphyrin cation, a reliably analytic model by adopting Ni<sup>III</sup>(OETPP·)(Br)<sub>2</sub> is constructed by combing EPR zero-field splitting (D), paramagnetic <sup>1</sup>H and <sup>13</sup>C NMR data with DFT calculation in the text.

The saddled-shape OETPP (dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenyl-porphyrin), which had been noticed to be easily oxidized to form stable  $\pi$ -cation radical with antiferromagnetic coupling state, e.g. Cu<sup>II</sup>(OETPP·)ClO<sub>4</sub> with S = 0, [Fe<sup>III</sup>(OETPP·)Cl]<sup>+</sup> and Fe<sup>III</sup>(OETPP·)(ClO<sub>4</sub>)<sub>2</sub> with S = 2, is adopted in this study.<sup>3d,5</sup> Ni(III) porphyrin  $\pi$ -cation radical had only been generated and identified by electrochemical oxidation.<sup>2,6</sup> Nevertheless, Ni<sup>II</sup>(OETPP) complex can be readily one-step oxidized by two electrons via adding one equiv. of Br<sub>2</sub> in benzene solution, as evidenced by several isosbestic points in

absorption spectral changes (Figure S1). The X-ray crystal structures of Ni(OET(*p*-R)PP)(Br)<sub>2</sub> (R = H and CH<sub>3</sub>) (Figure 1 and Figure S2), all reveal six-coordinate geometries, for which orbitals coincide with *D*<sub>2d</sub> symmetry (Table S1). The detailed X-ray data and structural information are collected in Table S2-S7. The *D*<sub>2d</sub> symmetry is further evidenced by the following NMR data with high symmetric patterns.<sup>7a</sup> The variable-temperature magnetic data (Figure S3) shows that a magnetic moment of 2.63  $\mu_B$  at 300 K, referred to a S = 1 state. The 77K EPR spectrum also displays a ferromagnetically coupled signal with simulated *g*<sub>x</sub>, *g*<sub>y</sub>, *g*<sub>z</sub> values of 2.21, 2.10 and 2.13, respectively, and zfs (D) of 0.034 cm<sup>-1</sup> (Figure S4(a) and S4(b)). With S = 1 the electron configuration of Ni<sup>III</sup>(OETPP·)(Br)<sub>2</sub> can be either rationally assumed to be of Ni(III) HS state (*d*<sub>xy</sub><sup>2</sup>*d*<sub>xz,yz</sub><sup>3</sup>*d*<sub>z</sub><sup>2</sup>*d*<sub>x<sup>2</sup>-y<sup>2</sup></sub><sup>1</sup>, S = 3/2) coupled with an antiparallel *a*<sub>2u</sub> radical due to the same symmetry of *d*<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital and *a*<sub>2u</sub> orbital, or to be Ni(III) LS state (*d*<sub>xy</sub><sup>2</sup>*d*<sub>xz,yz</sub><sup>4</sup>*d*<sub>z</sub><sup>2</sup>*d*<sub>x<sup>2</sup>-y<sup>2</sup></sub><sup>0</sup>, S = 1/2) orthogonally interacted with a parallel *a*<sub>1u</sub> radical.



**Figure 1.** ORTEP representation of the structure of Ni(OETPP)(Br)<sub>2</sub> with 50% probability ellipsoids. Hydrogens are omitted for clarity.

The chemical shifts of all distinct protons are characterized by adopting *d*<sub>20</sub> phenyl-deuterated and *para*-substituted OETPPs, (Figure S5 and S6). The <sup>13</sup>C NMR spectrum also represents a broad range of shifts; especially the *meso*-C carbon signal appears at -296 ppm (Figure S7), indicating considerable negative spin density localized on the ring. Interestingly, the pattern of <sup>1</sup>H or <sup>13</sup>C NMR spectrum is analogous to that of six-coordinate Fe<sup>III</sup>(OETPP·)(ClO<sub>4</sub>)<sub>2</sub> radical cation (Table 1),<sup>8</sup> which was identified as an antiferromagnetic coupling S = 2 spin state constituted by a high-spin iron (S = 5/2) and a ring *a*<sub>2u</sub> radical (S

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts,  $\delta_{\text{obs}}$  and (isotropic shifts,  $\delta_{\text{iso}}$ ) of  $\text{Ni}^{\text{III}}(\text{OETPP})(\text{Br})_2$  and six-coordinate iron(III)OETPP complexes

chemical shifts (in ppm)	$-\text{CH}_2-$	$-\text{CH}_3$	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	<i>p</i> - $\text{CH}_3$			
$\text{Ni}^{\text{III}}(\text{OETPP})(\text{Br})_2, S = 1$	20.3, 9.8 (12.98)	3.0 (3.08)	11.6 (3.47)	6.0 (-1.58)	10.0 (2.34)	-0.65 (-3.18)			
$[\text{Fe}^{\text{III}}(\text{OETPP})(\text{THF})_2]^+, S = 3/2$ <sup>3a,b,9</sup>	38.7, 11.1 (22.85)	0.3 (0.38)	15.8 (7.70)	5.6 (-1.98)	11.5 (3.84)				
$\text{Fe}^{\text{III}}(\text{OETPP})(\text{ClO}_4)_2, S = 2$ <sup>8</sup>	91.4, 23.8 (55.53)	6.2 (6.28)	33.5 (25.4)	-7.7 (-15.36)	26.9 (19.24)				
	$C_{\text{meso}}$	$C_{\alpha}$	$C_{\beta}$	<i>q</i> -C	<i>o</i> -C	<i>m</i> -C	<i>p</i> -C	$-\text{CH}_2$	$-\text{CH}_3$
$\text{Ni}^{\text{III}}(\text{OETPP})(\text{Br})_2$	-296.3 (-416.1)	492.2 (342.0)	not identified	345.8 (206.2)	44.6 (-89.9)	131.9 (4.8)	128.3 (-6.8)	66.9 (47.8)	79.7 (63.1)
$[\text{Fe}(\text{OETPP})(\text{THF})_2]^+$	-269 (-389)	394 (244)	215 (67)	354 (214)	-74 (-210)	118 (-9)	116 (-12)	-55 (-75)	215 (198)

Diamagnetic shifts were taken from the reference complex of  $[\text{Co}^{\text{III}}(\text{OETPP})(\text{Im})_2](\text{ClO}_4)$  (Table S10).

= 1/2), and also similar to that of the six-coordinate  $[\text{Fe}(\text{OETPP})(\text{THF})_2]^+$  with  $S = 3/2$  spin state concentrated on iron center, <sup>3a,b,9</sup> whose unexpected NMR shifts have been ascribed to  $d_{xy}-a_{1u}$  orbital interaction from DFT calculations with the presumably coexistent  $d_{x^2-y^2}-a_{2u}$  interaction via spin polarization.<sup>7</sup> Nevertheless, the 15 ppm chemical shift of ethylene-protons ( $-\text{CH}_2$ ) at  $\beta$ -pyrrole of  $\text{Ni}^{\text{III}}(\text{OETPP})(\text{Br})_2$  shift as downfield as neither 58 ppm of that of  $\text{Fe}^{\text{III}}(\text{OETPP})(\text{ClO}_4)_2$ , for which this large shift was induced by  $\sigma$  bonding delocalization from a half-occupied spin in  $d_{x^2-y^2}$ , nor 25 ppm of that of  $[\text{Fe}^{\text{III}}(\text{OETPP})(\text{THF})_2]^+$ , for which less spin density is rationally held in  $d_{x^2-y^2}$  orbital. By contrast, the  $^{13}\text{C}$  NMR spectra of  $\text{Ni}^{\text{III}}(\text{OETPP})(\text{Br})_2$  and  $[\text{Fe}^{\text{III}}(\text{OETPP})(\text{THF})_2]^+$  are pretty similar in range and pattern (Figure S6). These comparisons suggest that 15 very lower spin density localized in  $d_{x^2-y^2}$  orbital.

DFT combined with paramagnetic NMR analysis has recently been shown prominent ability to interpret the detailed paramagnetic shifts for iron(III) porphyrins.<sup>3d</sup> The compositions of  $^1\text{H}$  and  $^{13}\text{C}$  paramagnetic shift terms for  $S = 1$  have been defined by the following equations, which are shown in detail in the supplementary information.<sup>3d,10</sup>

$$\delta_{\text{obs}} = \delta_{\text{dia}} + \delta_{\text{iso}}; \delta_{\text{iso}} = \delta_{\text{con}} + \delta_{\text{dip}} = \delta_{\text{con}} + \delta_{\text{dip}}^{\text{M.C.}} + \delta_{\text{dip}}^{\text{L.C.}}$$

$$\delta_{\text{con}} = \frac{2\mu_0 g_e^2 \mu_B^2}{9kT} \rho_{\alpha\beta} \quad (1)$$

$$\delta_{\text{dip}}^{\text{L.C.}} = -\frac{g_e \beta D (2\pi)}{9g_N \beta_N (kT)^2} \rho^\pi = -48.54 \left(\frac{\text{ppm}}{\text{cm}^{-1}}\right) \times D \times \rho^\pi \quad (2)$$

$$\delta_{\text{dip}}^{\text{M.C.}} = -\frac{\mu_0 g_e^2 \mu_B^2 DG}{4\pi 9(kT)^2} = -4.486 \times 10^{-3} \left(\frac{\text{ppm}}{\text{cm}^{-1}} \cdot \text{cm}^3\right) \times D \times G \quad (3)$$

where  $\delta_{\text{obs}}$  is the observed NMR chemical shift, containing the diamagnetic reference,  $\delta_{\text{dia}}$ , and the isotropic shift,  $\delta_{\text{iso}}$ . The isotropic component ( $\delta_{\text{iso}}$ ) includes Fermi-contact term and pseudo-contact dipolar terms ( $\delta_{\text{dip}}^{\text{M.C.}}$  and  $\delta_{\text{dip}}^{\text{L.C.}}$ ), which are induced by metal-porphyrin bonding, and magnetic spatial induction via spin centers, respectively. In the above equations,  $\rho_{\alpha\beta}$  refers to the unpaired spin density at zero distance from the nucleus,  $\mu_0$  is the vacuum permeability ( $4\pi \times 10^{-7} \text{ J}^{-1} \text{ T}^2 \text{ m}^3$ ),  $g_e$  is the free electron g-factor (2.0023),  $\mu_B$  is the Bohr magneton ( $9.2740 \times 10^{-24} \text{ J} \cdot \text{T}^{-1}$ ),  $D$  is zero-field splitting and  $k$  is the Boltzmann's constant, and  $T$  is the absolute temperature (298 K for this study). In the two pseudocontact terms,  $g_N$  is the nucleus g-factor ( $g_N$  for  $^{13}\text{C}$  equal to 1.4048),  $\beta_N$  is the nuclear magneton ( $5.0508 \times 10^{-27} \text{ J} \cdot \text{T}^{-1}$ ),  $2\pi$  refers to the z component of dipolar interaction for a unit unpaired spin resided in a  $2p_z$  carbon orbital (214 MHz),  $G$  is geometric factor, and  $\rho^\pi$  denotes  $\pi$  spin density at the observed

carbon.<sup>3d,10d</sup>

According to NMR equation (3) with zero-field splitting from EPR ( $D = 0.034 \text{ cm}^{-1}$ ), the slope is calculated to be  $-1.525 \times 10^{-4} (\text{ppm} \cdot \text{cm}^3)$ , which is close to zero as same as the value obtained from the conventional graph of the proton isotropic shifts at phenyl substituent as a function of their corresponding geometry factor ( $G, \text{cm}^{-3}$ ) (Figure S8). The dipolar shifts induced by  $\text{Ni}^{\text{III}}$  unpaired electron spin can be deduced as less than 0.0001 ppm for all protons and 0.001 ppm for all  $^{13}\text{C}$  nuclei in the porphyrinate ring, namely, the allowance of ignoring metal-centered dipolar factors for all NMR data (Table S8). Similarly, the ligand-centered dipolar shift, which merely exists in carbon atoms possessing  $\pi$  spin density, that is,  $\alpha$ -C,  $\beta$ -C and *meso*-C, can also be disregarded by equation (2) from which there is only ca. 1.65 ppm upfield shift for an unit unpaired  $\pi$  spin.

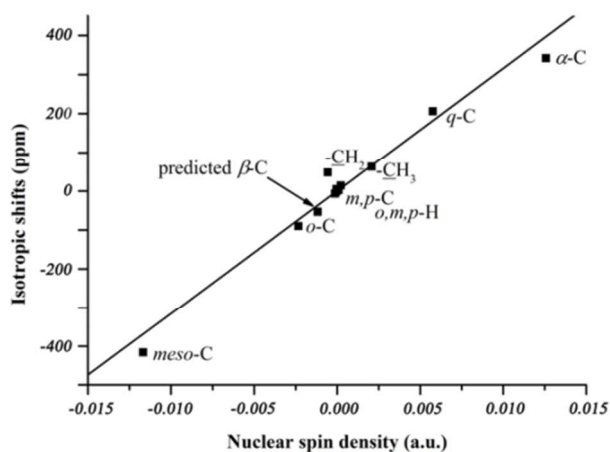
**Table 2.** Net spin populations and  $\{\pi$  spin densities  $\times 10^3\}$ , obtained from  $p_z$  orbitals which are reassigned the z axes to perpendicular to their  $sp^2$  plane in calculations and [the Fermi contact spin densities  $\rho_{\alpha\beta} \times 10^3$ ] on each symmetry-distinct atom type of  $\text{Ni}^{\text{III}}(\text{OETPP})(\text{Br})_2$  from unrestricted DFT calculations

S = 1	$\text{Ni}(\text{III})(\text{OETPP})^+(\text{LS})$	$\text{Ni}(\text{III})(\text{OETPP})^+(\text{HS})$
$\alpha$ -C	0.1619 {96.9} [12.6]	0.0126 {3.1} [1.8]
$\beta$ -C	0.0131 {7.0} [-1.4]	0.0183 {6.5} [3.2]
<i>meso</i> -C	-0.0804 {-22.7} [-11.7]	-0.0742 {-17.5} [-3.6]
<i>q</i> -C	0.0097 [5.8]	0.0062 [2.4]
$-\text{CH}_2$	-0.0013 [-0.6]	-0.0014 [-0.2]
$-\text{CH}_3$	0.0017 [2.1]	0.0015 [0.7]
<i>o</i> -C	-0.0040 [-2.3]	-0.0056 [-2.7]
<i>m</i> -C	0.0026 [0.0]	0.0018 [-0.1]
<i>p</i> -C	-0.0038 [-0.1]	-0.0055 [-0.3]
$-\text{CH}_2$	0.0007 [0.2]	0.0007 [0.4]
$-\text{CH}_3$	0.0001 [0.1]	0.0000 [0.0]
<i>o</i> -H	0.0001 [0.1]	0.0006 [0.1]
<i>m</i> -H	-0.0003 [0.0]	-0.0003 [-0.1]
<i>p</i> -H	0.0003 [0.1]	0.0003 [0.1]

Accordingly, the isotropic shifts for all positions are mainly contributed by Fermi-contact shifts for  $\text{Ni}^{\text{III}}(\text{OETPP})(\text{Br})_2$ . The negligible dipolar effects also reflect the strong probability of the low spin state on  $\text{Ni}(\text{III})$  ion rather than the high spin state. In some  $\text{Fe}(\text{III})$  porphyrinate complexes with low spin state ( $S = 1/2$ ) similar features were shown.<sup>11</sup> Density Functional Theory (DFT) calculations were employed for both LS and HS states to evaluate the critical spin populations, including total spin, localized  $\pi$  spin and Fermi contact spin densities, summarized in Table 2.

In our case, the isotropic shift ( $\delta_{\text{iso}}$ ) can be regarded as mainly contributed by Fermi-contact shift ( $\delta_{\text{con}}$ ), which is proportional to the Fermi contact spin densities ( $\rho_{\alpha\beta}$ ) for all  $^1\text{H}$  and  $^{13}\text{C}$  nuclei by equation (1). It is also noted early that the correlation graph of

DFT calculated Fermi contact spin density versus isotropic shift is able to distinguish the determined ground state from many electronic structures.<sup>10d, 12</sup> For LS state, the regression line for all atoms shows a very good fit with  $R^2 = 0.97$  and slope = 31577 au<sup>-1</sup>.ppm (Figure 2). Further estimation of isotropic shift of  $\beta$ -C from the fitted slope shows that it could be immersed in the signals containing *o*-, *m*-, *p*-carbons. However, as to the HS the corresponding graph has much worse correlation with fitted slope = 91211 au<sup>-1</sup>.ppm and  $R^2 = 0.88$  (Figure S9). The *o*- and *meso*-Cs stray away from the regression line with considerable vertical differences, 158 ppm and -88 ppm, respectively, which are regarded as dipolar contributions.<sup>3d</sup> Also, the  $\alpha$ -C is conjectured to appear 314 ppm (predicted  $\delta_{con} + \delta_{dia}$ ) in spectrum, localizing very close to *q*-C. Nevertheless, these outcomes (Table S9) are conflicting with previous experimental observations of negligible dipolar shifts, and also violate the observed <sup>13</sup>C spectrum.



**Figure 2.** Correlation between the calculated Fermi contact spin densities at each symmetry-distinct atom type and the experimental isotropic shifts of low-spin Ni<sup>III</sup>(OETPP<sup>•</sup>)(Br)<sub>2</sub> *a*<sub>1u</sub> cation radical complex with best fitted slope = 31577 au<sup>-1</sup>.ppm,  $R^2 = 0.970$ .

In summary, Ni<sup>III</sup>(OETPP<sup>•</sup>)Br<sub>2</sub> is the first example of Ni(III) porphyrin radical cation shown by X-ray structure, magnetic data, EPR spectrum and quality paramagnetic NMR spectra. These unusual NMR data has been clearly ascribed to the triplet state containing a LS Ni(III) and an *a*<sub>1u</sub> spin-up radical spin. Although the characteristic of *meso*-carbon are exactly same with very negative spin density for two plausible spin states, *a*<sub>1u</sub> with  $s = +1/2$  spin and *a*<sub>2u</sub> with  $s = -1/2$  spin, the ground state is well discriminated by qualitative comparisons with other paramagnetic cases and the neat analytic model by combining NMR spectra with DFT calculations. The case of Ni<sup>III</sup>(OETPP<sup>•</sup>)Br<sub>2</sub> has become an important prototype for exploring other ferromagnetically coupled complexes from the point of view of this explicative model.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: [syntheses, UV-Vis spectra, X-ray crystal data, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, DFT calculations]: 10.1039/b000000x/

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