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The characterization of the saddle shaped nickel(III) porphyrin radical cation: an explicative NMR model for a ferromagnetically coupled metallo-porphyrin radical†

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Ni(III)(OETPP[•])(Br)₂ is the first Ni(III) porphyrin radical cation with structural and ¹H and ¹³C paramagnetic NMR data for porphyrinate systems. Associating EPR and NMR analyses with DFT calculations as a new model is capable of clearly determining the dominant state from two controversial spin distributions in the ring to be the Ni(III) LS coupled with an a_{1u} spin-up radical.

Nickel(III) porphyrinate derivatives have been extensively studied to understand a postulated intermediate of Factor 430 (F₄₃₀) and a CH₃-Ni(III) tetrapyrrole as the cofactor of methyl coenzyme M reductase.¹ Although the redox properties of many Ni(III) porphyrinate systems are well discussed, structural and magnetic spectroscopy data, especially NMR, are scarce and a stable Ni(III) porphyrin radical cation has not been obtained.² Recently some essential strategies have been developed by combining ¹³C and ¹H NMR data with DFT calculations, which are capable of completely characterizing the metal dominated spin system.³ For the spin-coupled metalloporphyrin radical cations of considerable interest, *e.g.* compound I and its model complex, oxoiron(IV) porphyrin radical cations, although quality ¹H NMR data have been obtained, only qualitative bonding interactions between metal d orbitals and ring π orbitals of the macrocyclic ring 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 fully understand due to the lack of a neat method for discriminating spin transfer from bonding or spatial induction.⁴ To gain the knowledge of spin-coupled metalloporphyrin cations, a reliable analytical model by adopting Ni(III)(OETPP[•])(Br)₂ is constructed by combining EPR zero-field splitting (*D*), paramagnetic ¹H and ¹³C NMR data with DFT calculations.

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The saddle-shaped OETPP (the dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenyl-porphyrin), which has been noted to be easily oxidized to form a stable π-cation radical with the antiferromagnetic coupling state, *e.g.* Cu^{II}(OETPP[•])-ClO₄ with *S* = 0, [Fe(III)(OETPP[•])Cl]⁺ and Fe(III)(OETPP[•])(ClO₄)₂ with *S* = 2, is adopted in this study.^{3d,5} Ni(III) porphyrin π-cation radicals have only been generated and identified by electrochemical oxidation.^{2,6} Nevertheless, the Ni(II)(OETPP) complex can be readily one-step oxidized by two electrons *via* adding one equiv. of Br₂ in benzene solution, as evidenced by several isosbestic points in absorption spectral changes (Fig. S1, ESI†). The X-ray crystal structures of Ni(OET(*p*-R)PP)(Br)₂ (R = H and CH₃) (Fig. 1 and Fig. S2, ESI†) all reveal six-coordinate geometries, for which orbitals coincide with D_{2d} symmetry (Table S1, ESI†). The detailed X-ray data and structural information are collected in Tables S2–S7 (ESI†). The D_{2d} symmetry is further shown by the following NMR data with high symmetric patterns.^{7a} The variable-temperature magnetic data (Fig. S3, ESI†) show a magnetic moment of 2.63 μ_B at 300 K, referred to as the *S* = 1 state. The 77 K EPR spectrum also displays a ferromagnetically coupled signal with simulated *g_x*, *g_y*, and *g_z* values of 2.21, 2.10 and 2.13, respectively, and a ZFS (*D*) of 0.034 cm⁻¹ (Fig. S4(a) and (b), ESI†). With *S* = 1 the electronic configuration of Ni(III)(OETPP[•])(Br)₂ can be either rationally assumed to be of

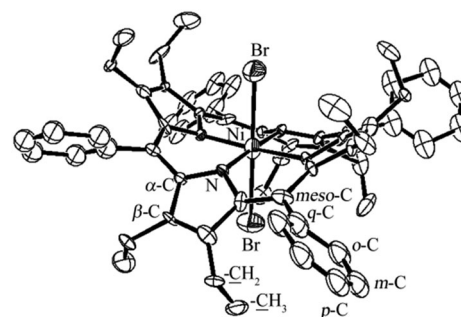


Fig. 1 ORTEP representation of the structure of Ni(OETPP)(Br)₂ with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1 ^1H and ^{13}C NMR chemical shifts, δ_{obs} and (isotropic shifts, δ_{iso}) of Ni(III)(OETPP*)(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> -CH $_3$
Ni(III)(OETPP*)(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)
[Fe(III)(OETPP*)(THF) $_2$] $^+$, $S = 3/2^{3a,b,9}$	38.7, 11.1 (22.85)	0.3 (0.38)	15.8 (7.70)	5.6 (−1.98)	11.5 (3.84)	
Fe(III)(OETPP*)(ClO $_4$) $_2$, $S = 2^8$	91.4, 23.8 (55.53)	6.2 (6.28)	33.5 (25.4)	−7.7 (−15.36)	26.9 (19.24)	

	C_{meso}	C_α	C_β	q-C	<i>o</i> -C	<i>m</i> -C	<i>p</i> -C	$-\text{CH}_2$	$-\text{CH}_3$
Ni(III)(OETPP*)(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)
[Fe(OETPP*)(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 [Co(III)(OETPP*)(Im) $_2$](ClO $_4$) (Table S10, ESI).

the Ni(III) HS state ($d_{xy}^2 d_{xz} d_{yz}^3 d_{z^2}^1 d_{x^2-y^2}^1$, $S = 3/2$) coupled with an antiparallel a_{2u} radical due to the same symmetry of the $d_{x^2-y^2}$ orbital and the a_{2u} orbital, or to be of the Ni(III) LS state ($d_{xy}^2 d_{xz} d_{yz}^4 d_{z^2}^1 d_{x^2-y^2}^0$, $S = 1/2$) orthogonally interacting with a parallel a_{1u} radical.

The chemical shifts of all distinct protons are characterized by adopting d_{20} phenyl-deuterated and *para*-substituted OETPPs (Fig. S5 and S6, ESI †). The ^{13}C NMR spectrum also represents a broad range of shifts; especially the *meso*-C carbon signal appears at -296 ppm (Fig. S7, ESI †), indicating a considerable negative spin density localized on the ring. Interestingly, the pattern of the ^1H or the ^{13}C NMR spectrum is analogous to that of the six-coordinate Fe(III)(OETPP*)(ClO $_4$) $_2$ radical cation (Table 1), 8 which was identified as an antiferromagnetic coupling $S = 2$ spin state constituted by a high-spin iron ($S = 5/2$) and a ring a_{2u} radical ($S = 1/2$), and also similar to that of the six-coordinate [Fe(OETPP*)(THF) $_2$] $^+$ with the $S = 3/2$ spin state concentrated on the iron center, 3a,b,9 whose unexpected NMR shifts have been ascribed to $d_{xy}-a_{1u}$ orbital interactions from DFT calculations with the presumably co-existing $d_{x^2-y^2}-a_{2u}$ interactions *via* spin polarization. 7 Nevertheless, the ethylene protons ($-\text{CH}_2$) at the β -pyrrole of Ni(III)(OETPP*)(Br) $_2$ shift downfield by 15 ppm compared to the 58 ppm shift of the protons of Fe(III)(OETPP*)(ClO $_4$) $_2$, for which this large shift was induced by σ bonding delocalization from a half-occupied spin in $d_{x^2-y^2}$, and the 25 ppm shift of the protons of [Fe(III)(OETPP*)(THF) $_2$] $^+$, for which low spin density is rationally held in the $d_{x^2-y^2}$ orbital. By contrast, the ^{13}C NMR spectra of Ni(III)(OETPP*)(Br) $_2$ and [Fe(III)(OETPP*)(THF) $_2$] $^+$ are pretty similar in range and pattern (Fig. S6, ESI †). These comparisons suggest a very low spin density localized on the $d_{x^2-y^2}$ orbital.

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

$$\delta_{\text{obs}} = \delta_{\text{dia}} + \delta_{\text{iso}}; \delta_{\text{iso}} = \delta_{\text{con}} + \delta_{\text{dip}} = \delta_{\text{con}} + \delta_{\text{dip}}^{\text{M.C.}} + \delta_{\text{dip}}^{\text{L.C.}} \quad (1)$$

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

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

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

$$G = \left[\frac{(3 \cos^2 \theta - 1)}{r^3} \right] / (10^{21}) \text{cm}^{-3} \quad (3)$$

where δ_{obs} is the observed NMR chemical shift, containing the diamagnetic reference, δ_{dia} , and the isotropic shift, δ_{iso} . The isotropic component (δ_{iso}) includes the 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, μ_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), μ_B is the Bohr magneton ($9.2740 \times 10^{-24} \text{J T}^{-1}$), D is the zero-field splitting and k is 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}C equal to 1.4048), β_N is the nuclear magneton ($5.0508 \times 10^{-27} \text{J T}^{-1}$), 2Π refers to the z component of dipolar interaction for a unit unpaired spin residing in a $2p_z$ carbon orbital (214 MHz), G is the geometric factor, and ρ^π denotes π spin density at the observed carbon. 3d,10d

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

Accordingly, the isotropic shifts for all positions are mainly contributed by Fermi-contact shifts for Ni(III)(OETPP*)(Br) $_2$. The negligible dipolar effects also reflect the strong probability of

Table 2 Net spin populations and (π spin densities $\times 10^3$), obtained from p_z orbitals which are reassigned to the z axes 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 Ni(III)(OETPP[•])(Br)₂ from unrestricted DFT calculations

$S = 1$	Ni(III) (OETPP [•]) ⁺ (LS)	Ni(III) (OETPP [•]) ⁺ (HS)
α -C	0.1619{96.9} [12.6]	0.0126{3.1} [1.8]
β -C	0.0131{7.0} [-1.4]	0.0183{6.5} [3.2]
meso-C	-0.0804{-22.7} [-11.7]	-0.0742{-17.5} [-3.6]
q-C	0.0097 [5.8]	0.0062 [2.4]
-CH ₂	-0.0013 [-0.6]	-0.0014 [-0.2]
-CH ₃	0.0017 [2.1]	0.0015 [0.7]
o-C	-0.0040 [-2.3]	-0.0056 [-2.7]
m-C	0.0026 [0.0]	0.0018 [-0.1]
p-C	-0.0038 [-0.1]	-0.0055 [-0.3]
-CH ₂	0.0007 [0.2]	0.0007 [0.4]
-CH ₃	0.0001 [0.1]	0.0000 [0.0]
o-H	0.0001 [0.1]	0.0006 [0.1]
m-H	-0.0003 [0.0]	-0.0003 [-0.1]
p-H	0.0003 [0.1]	0.0003 [0.1]

the low spin state of Ni(III) ions rather than the high spin state. In some Fe(III) porphyrinate complexes with a low spin state ($S = 1/2$) similar features were observed.¹¹ Density Functional Theory (DFT) calculations were employed for both LS and HS states to evaluate the critical spin populations, including total spin, localized π spin and Fermi contact spin densities, summarized in Table 2.

In our case, the isotropic shift (δ_{iso}) can be regarded as being mainly contributed by Fermi-contact shift (δ_{con}), which is proportional to the Fermi contact spin densities ($\rho_{\alpha\beta}$) of all ¹H and ¹³C nuclei by eqn (1). It was also noted earlier 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.^{10d,12} For the LS state, the regression line for all atoms shows a very good fit with $R^2 = 0.97$ and slope = 31577 au⁻¹ ppm (Fig. 2). Further estimation of the isotropic shift of β -C that forms the fitted

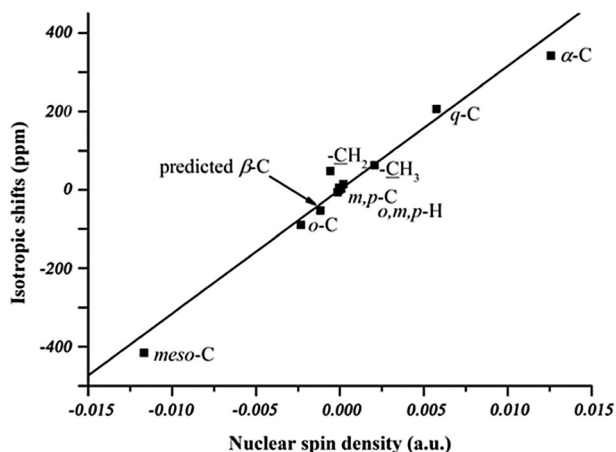


Fig. 2 Correlation between the calculated Fermi contact spin densities at each symmetry-distinct atom type and the experimental isotropic shifts of the low-spin Ni(III)(OETPP[•])(Br)₂ a_{1u} cation radical complex with best fitted slope = 31577 au⁻¹ ppm, $R^2 = 0.970$.

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 the fitted slope = 91211 au⁻¹ ppm and $R^2 = 0.88$ (Fig. S9, ESI[†]). 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.^{3d} Also, the α -C is conjectured to appear at 314 ppm (predicted $\delta_{con} + \delta_{dia}$) in the spectrum, localizing very close to q-C. Nevertheless, these outcomes (Table S9, ESI[†]) are conflicting with previous experimental observations of negligible dipolar shifts, and also violate the observed ¹³C spectrum.

In summary, Ni(III)(OETPP[•])Br₂ is the first example of Ni(III) porphyrin radical cations shown by the X-ray structure, magnetic data, the EPR spectrum and quality paramagnetic NMR spectra. These unusual NMR data have been clearly ascribed to the triplet state containing a LS Ni(III) and an a_{1u} spin-up radical spin. Although the characteristics of $meso$ -carbon are exactly the same with very negative spin density for two plausible spin states, a_{1u} with $s = +1/2$ spin and a_{2u} with $s = -1/2$ spin, the ground state is well discriminated by qualitative comparisons with other paramagnetic cases and the neat analytical model by combining NMR spectra with DFT calculations. The case of Ni(III)(OETPP[•])Br₂ has become an important prototype for exploring other ferromagnetically coupled complexes from the point of view of this explicative model.

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