

Quantum-Chemical Calculations for Paramagnetic ^{13}C NMR Chemical Shifts of Iron-Bound Cyanide Ions of Iron Porphyrins in Ground and Low-Lying Excited States Containing Ferric $(d_{xy})^2(d_{xz},yz)^3$ and $(d_{xy})^1(d_{xz},yz)^4$ Configurations

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The ^{13}C NMR chemical shift of iron-bound ^{13}CN in the bis-cyanide Fe(III) porphyrin complex was observed far upfield at -2516 ppm from TMS.¹ As is well known, the paramagnetic NMR shift mainly contributes to this large upfield shift. Recently, the ^{13}C NMR signal of iron-bound ^{13}CN in the cyanide-imidazole Fe(III) porphyrin complex, which is a model for cyanide complexes in heme proteins, was observed more upfield at -3926 ppm.² This fact indicates that the paramagnetic shift increases significantly by replacing the proximal trans-ligand from CN^- with neutral imidazole. This was explained by the change of the Fermi-contact term as a result of the trans-ligand effect, which enhances the spin polarization in the $\sigma(\text{CN})$ orbital induced by the d-electron spin density.² This idea was further confirmed by the following fact; by replacing neutral imidazole ligand with anionic imidazolate, the chemical shift decreased significantly to -3507 ppm.^{2,3}

On the other hand, electronic configurations of Fe ions in Fe(III) porphyrin complexes have been intensively discussed.³⁻⁵ The iron electron configuration in Fe(III) porphyrin complexes is typically $(d_{xy})^2(d_{xz},yz)^3$, while those in *meso*-substituted complexes, which have a ruffled porphyrin ring, have the unusual $(d_{xy})^1(d_{xz},yz)^4$ configuration, suggesting that the $(d_{xy})^1(d_{xz},yz)^4$ configuration is stabilized by the ruffling of the porphyrin ring.⁵

The ^{13}C chemical shifts are also affected by the difference of the $(d_{xy})^2(d_{xz},yz)^3$ and $(d_{xy})^1(d_{xz},yz)^4$ configurations. Therefore, it is difficult to present a unified view involving electronic configurations and ^{13}C chemical shifts.

The objectives of this Communication are as follows: (i) Using an accurate quantum-chemical method, SAC/SAC-CI,^{6,7} we present accurate energy levels for ferric $(d_{xy})^2(d_{xz},yz)^3$ and $(d_{xy})^1(d_{xz},yz)^4$ in bis(cyanide)porphyrinato iron(III) [FeP(CN)₂], bis(cyanide)*meso*-tetraethylporphyrinato iron(III) [FeTEP(CN)₂], and (cyanide)(imidazole)porphyrinato iron(III) [FeP(CN-Im)].⁸ (ii) We calculate the paramagnetic ^{13}C NMR chemical shifts of iron-bound ^{13}CN of the above three complexes, both in the ground and in the low-lying excited states, including the ferric $(d_{xy})^2(d_{xz},yz)^3$ and $(d_{xy})^1(d_{xz},yz)^4$ configurations. We then show the relations between the calculated ^{13}C chemical shifts, the electronic configurations, and the ruffling of the porphyrin rings.

All of the calculated energy levels up to 1.0 eV are summarized in Table 1 (right-hand side). The energy values are relative to the ground state of each molecule. The ground state of FeP(CN)₂ is 1^2E_g , which has the usual ferric $(d_{xy})^2(d_{xz},yz)^3$ configuration, and this result agrees with experiment. As expected from experimental evidence,⁵ the alternative ferric $(d_{xy})^1(d_{xz},yz)^4$ configuration shown by 1^2B_{2g} is located at 0.57 eV relative to the ground state. The 1^2A_{2u} state at 0.09 eV has a ferrous $(d_{xy})^2(d_{xz},yz)^4$ configuration and has a diffuse open-shell orbital around the CN ligand. The energy level of this state, therefore, may be sensitive to the surrounding environment. In FeP(CN-Im), the $1^2\text{A}'$ state contains the ferrous $(d_{xy})^2(d_{xz},yz)^4$ configuration and has a diffuse open-shell orbital such

Table 1. Excitation Energies of Three Cyanide Fe(III) Porphyrins and Their ^{13}C NMR Chemical Shifts of Iron-Bound ^{13}CN from TMS

term	energy (eV)	main configuration	chemical shift (ppm)
(1) Bis(cyanide)porphyrinato Iron(III) [FeP(CN) ₂]			
1^2E_g	0.00	$(d_{xy})^2(d_{xz},yz)^3$	-2789 (-2516)
1^2A_{2u}	0.09	$(d)^6[\sigma(\text{CN})-\pi(\text{por})_{\text{HOMO}}]^1$	16 557
1^2B_{2g}	0.57	$(d_{xy})^1(d_{xz},yz)^4$	-3502
1^2A_{1u}	0.74	$(d)^6[\sigma(\text{CN})-\pi(\text{por})]^1$	-242
(2) (Cyanide)(imidazole)porphyrinato Iron(III) [FeP(CN-Im)]			
$1^2\text{A}'$	0.00	$(d)^6[\sigma^*(\text{CN})-4p(\text{Fe})]^1$	10 870
$2^2\text{A}'$	0.13	$(d_{xy})^2(d_{xz},yz)^3$	-3312 (-3926)
$1^2\text{A}''$	0.19	$(d_{xy})^1(d_{xz},yz)^4$	-3003
$2^2\text{A}''$	0.46	$(d_{xy})^2(d_{xz},yz)^4$	-4026
$3^2\text{A}''$	0.49	$(d)^6[\pi(\text{por})]^1$	-932
(3) Bis(cyanide) <i>meso</i> -tetraethylporphyrinato Iron(III) [FeTEP(CN) ₂]			
1^2B_2	0.00	$(d_{xy})^1(d_{xz},yz)^4$	4039 (-3507)
1^2E	0.04	$(d_{xy})^2(d_{xz},yz)^3$	-3121
2^2B_2	0.37	$(d)^6[\sigma(\text{CN})-\pi(\text{por})_{\text{HOMO}}]^1$	10 061
1^2B_1	1.00	$(d)^6[\pi(\text{por})]^1$	99

as 1^2A_{2u} of FeP(CN)₂. Although this result shows that the $1^2\text{A}'$ state is the ground state of FeP(CN-Im) in the gas phase, the experimental evidence indicates that this state is not appropriate as the ground state in solution or in proteins. The $2^2\text{A}'$ and $1^2\text{A}''$ states, both of which contain the ferric $(d_{xy})^2(d_{xz},yz)^3$, are degenerate to within 0.06 eV. One of these states is the ground state in solution or in proteins. The alternative configuration $(d_{xy})^1(d_{xz},yz)^4$ exists in the $2^2\text{A}''$ state, located 0.13 eV higher than the $2^2\text{A}'$ state. The energy separation between $(d_{xy})^2(d_{xz},yz)^3$ and $(d_{xy})^1(d_{xz},yz)^4$ is smaller in FeP(CN-Im) than in FeP(CN)₂. This is understandable because imidazole is weakly bound to Fe in comparison with anionic cyanide.

The ground state of FeTEP(CN)₂ is 1^2B_2 , which has the unusual $(d_{xy})^1(d_{xz},yz)^4$ configuration as experimentally suggested, while the lowest excited state 1^2E is $(d_{xy})^2(d_{xz},yz)^3$. The 1^2B_2 and 1^2E states are degenerate to within 0.04 eV. The diffuse state 2^2B_2 becomes unstable in comparison with FeP(CN)₂. This unstabilization may be due to the effect of the ruffling of the porphyrin ring or the ethyl groups on the porphyrin ring. To understand the difference between FeP(CN)₂ and FeTEP(CN)₂, the following points need to be considered. When the molecular symmetry decreases from D_{2h} [FeP(CN)₂] to S_4 [FeTEP(CN)₂], the A_{2u} and B_{2g} states in D_{2h} are mixed with each other and one state is stabilized and the other is destabilized in S_4 , while the E_g state is not mixed with the other states.

The calculated and observed ^{13}C NMR chemical shifts of iron-bound ^{13}CN from TMS are also summarized in Table 1. In the case of FeP(CN)₂, the calculated chemical shift in the ground state 1^2E_g (-2789 ppm) agrees reasonably well with the observed shift (-2516 ppm). The calculated shift in the excited 1^2A_{2u} state is largely downfield, and that in 1^2B_{2g} is again upfield. This trend

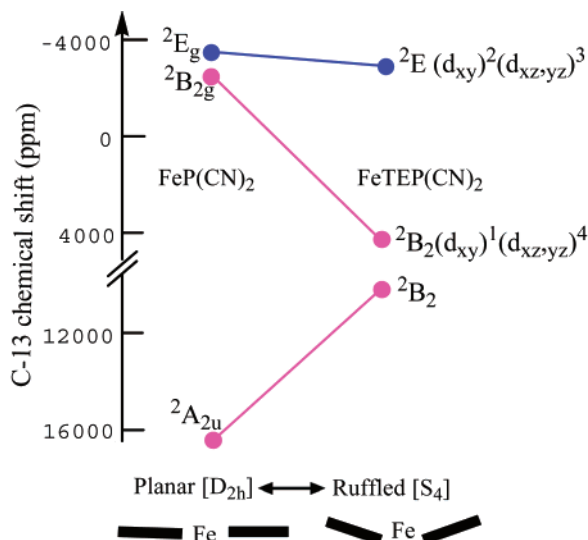
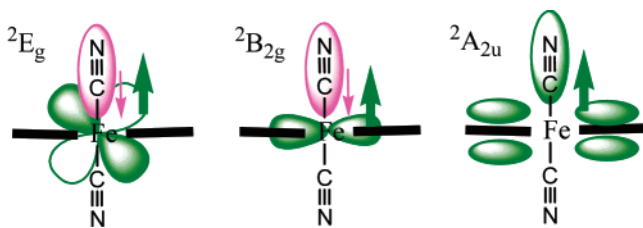


Figure 1. Correlation of electronic states and ^{13}C chemical shifts of iron-bound ^{13}C N between bis(cyanide)porphyrinato iron(III) (left-hand side) and bis(cyanide)(*meso*-tetraethyl)porphyrinato iron(III) (right-hand side) in three low-lying electronic states.

agrees qualitatively with a simple picture by the $d(\text{Fe}) \rightarrow \sigma(\text{CN})$ spin-polarization mechanism.



In the case of $\text{FeP}(\text{CN}-\text{Im})$, the calculated shift increases up to -3312 ppm. The observed trend of replacing CN with imidazole is reproduced, and detailed component analysis shows that this increase in chemical shift is essentially due to the Fermi-contact term. This result supports the idea of enhancement of the spin polarization by the *trans*-ligand effect.²

In the case of $\text{FeTEP}(\text{CN})_2$, the observed ^{13}C chemical shift decreases up to about -1800 ppm, while the calculated shift decreases to $+4039$ ppm which is too far downfield. This result is apparently questionable. Figure 1 shows the correlation of the calculated ^{13}C chemical shifts between $\text{FeP}(\text{CN})_2$ and $\text{FeTEP}(\text{CN})_2$. Because the direct effect of the four ethyl groups in $\text{FeTEP}(\text{CN})_2$ on the chemical shifts is quite small, this figure shows the effects of the ruffling of the porphyrin ring. The ^{13}C chemical shifts in ${}^2\text{B}_{2g}$ and ${}^2\text{A}_{2u}$ are extremely sensitive to the ruffling of the porphyrin ring, while that in ${}^2\text{E}_g$ is not. The amount of increase in ${}^2\text{A}_{2u}$ and decrease in ${}^2\text{B}_{2g}$ is almost equivalent, suggesting that this change occurs by the spin-density mixing between the ${}^2\text{B}_{2g}$ and ${}^2\text{A}_{2u}$ states due to symmetry lowering. To discuss and explain the observed ^{13}C chemical shifts in ruffled Fe(III) porphyrins using theoretical methods, consideration of vibration in the ruffling mode and/or thermal distribution between the ${}^2\text{B}_2$ and ${}^2\text{E}$ states is necessary.

In the final paragraph, we explain the computational details. Geometrical parameters of three complexes were optimized at the B3LYP/6-311G level. $\text{FeP}(\text{CN})_2$ has a highly symmetric D_{4h} structure, while the porphyrin ring of $\text{FeTEP}(\text{CN})_2$ is ruffled and in S_4 symmetry as experimentally observed. The porphyrin ring of $\text{FeP}(\text{CN}-\text{Im})$ is almost planar. Next, the SAC and SAC-CI

methods,^{6,7} which are newly implemented in Gaussian 03,⁹ were used to calculate the ground and excited electronic states, respectively, using more extended basis functions.¹⁰ The nuclear magnetic shielding tensor was calculated using Ramsey's equation,¹¹ and the Fermi-contact term was included as a temperature-dependent (paramagnetic) term.^{12,13} In the doublet spin multiplicity, the Fermi-contact term at nucleus N is expressed in the form,

$$\sigma_{N,\text{Fermi-contact}} = 4\pi g^2 \beta^2 \langle \Psi | \hat{S} \delta_N | \Psi \rangle / 3k_B T \quad (1)$$

where Ψ is the wave function of the total system, \hat{S} is the spin-operator, and δ_N is a delta-function at nucleus N . The other temperature-dependent term called the spin-dipolar term is neglected, because it is much smaller than the Fermi-contact term in the present molecules.

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