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Effects of a nonplanar porphyrin rings on the spin–spin interactions in low-spin ferric porphyrin radical cations†

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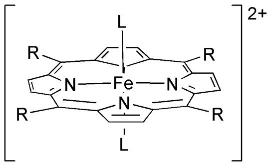
Received (in Cambridge, UK) 18th October 2002, Accepted 29th November 2002
First published as an Advance Article on the web 12th Decmber 2002

Low-spin ferric porphyrin radical cations formed by the oxidation of chloro(*meso*-tetraalkylporphyrinato)iron(III) followed by the addition of bulky 2-methylimidazole show antiferromagnetic coupling, which is interpreted in terms of the interaction between porphyrin a_{2u} and iron d_{xy} orbitals caused by the S_4 ruffling of the porphyrin core.

Porphyrin radicals have been extensively studied since they play important roles in biological oxidation catalyzed by various enzymes including cytochromes P-450.[1] Especially interesting is how the unpaired electron formed on the porphyrin ring interacts with the central iron. Although ample examples have been reported on the interactions between high-spin iron(III) or high-valent iron(IV) and porphyrin radicals,[2,3] little is known on the interactions between low-spin iron(III) and porphyrin radicals.[4] We have recently reported that porphyrin deformation induces unique orbital interactions between iron-(III) and porphyrin to give, for example, the low-spin complexes with a less common $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration or the complexes with an essentially pure intermediate-spin ($S = 3/2$) state.[5] Since recent X-ray crystallographic studies have revealed that many heme proteins have more or less nonplanar prosthetic groups,[6] it is important to reveal the spin–spin interactions of iron(III) radical cations in deformed porphyrin complexes. Here, we report on the synthesis of some low-spin iron(III) radical cations $[Fe(TRP^{\cdot})L_2]^{2+}$, where the degree of porphyrin deformation varies and discuss the spin–spin interactions on the basis of the spectroscopic results.

A series of (*meso*-tetraalkylporphyrinato)iron(III) chlorides Fe(TRP)Cl (R = Et, ^{n}Pr, ^{i}Pr) were oxidised in CD_2Cl_2 solutions by the addition of an excess amount of phenoxathiinylium hexachloroantimonate at ambient temperature.[2] Addition of 2.1 equiv of imidazole(HIm) at −78 °C to CD_2Cl_2 solutions of the high-spin radical cations $[Fe(TRP^{\cdot})Cl]^{2+}$ thus formed yielded the low-spin radical cations $[Fe(TRP^{\cdot})(HIm)_2]^{2+}$.[2] These radicals were stable at −50 °C at least for 2 h, though they rapidly decomposed at 0 °C. The ^{1}H NMR spectra of $[Fe(TEtP^{\cdot})(HIm)_2]^{2+}$ are shown in Fig. 1(a) as a typical example. The signal at an extraordinarily downfield position, +231 ppm, is assigned to the *meso*-H_α on the basis of the spectral comparison with the analogous complexes. Addition of bulky 2-methylimidazole(2-MeIm) similarly yielded the low-spin radical cations $[Fe(TRP^{\cdot})(2\text{-MeIm})_2]^{2+}$. The ^{1}H NMR spectrum of $[Fe(T^iPrP^{\cdot})(2\text{-MeIm})_2]^{2+}$ is shown in Fig. 1(b) as a typical example. Four signals in the region −20 to −23 ppm and two signals at 46.8 and 48.8 ppm are assigned to the pyrrole-H and *meso*-H_α, respectively. The splitting pattern of these signals indicates that the rotation of the 2-MeIm ligands is hindered on the ^{1}H NMR time scale and that the ligands are fixed perpendicularly along the diagonal C_{meso}–Fe–C_{meso} axes.[5a,b]



R = Et, ^{n}Pr, ^{i}Pr
L = HIm, 2-MeIm

$[Fe(TRP^{\cdot})L_2]^{2+}$

The chemical shifts of $[Fe(TRP^{\cdot})L_2]^{2+}$ are listed in Table 1 together with those of the corresponding $[Fe(TRP)L_2]^+$. We confine the discussion to the spin–spin interactions of only the Et and ^{n}Pr complexes in this section. The interactions in highly deformed ^{i}Pr complexes are discussed later. The data in Table 1 clearly indicate that the *meso*-H_α signal shows a fairly large downfield shift on going from $[Fe(TRP)L_2]^+$ to $[Fe(TRP^{\cdot})L_2]^{2+}$. The $\Delta\delta(H_\alpha)$ value, which is defined by the difference in

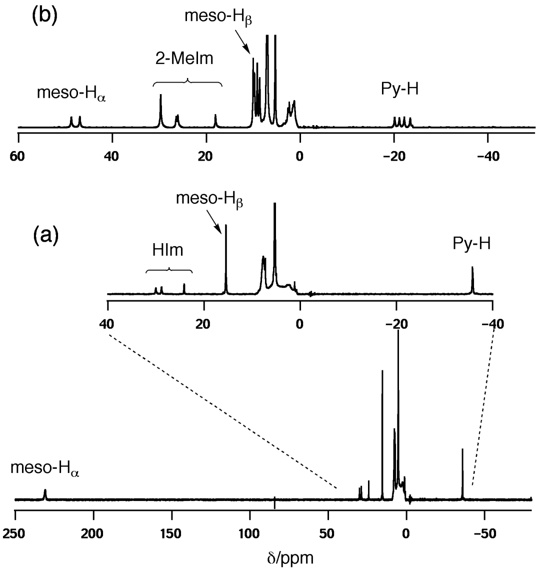


Fig. 1 ^{1}H NMR spectra of low-spin radical cations taken in CD_2Cl_2 solution at −50 °C. (a) $[Fe(TEtP^{\cdot})(HIm)_2]^{2+}$ together with the expanded spectrum; (b) $[Fe(T^iPrP^{\cdot})(2\text{-MeIm})_2]^{2+}$.

Table 1 ^{1}H NMR Chemical shifts of $[Fe(TRP)L_2]^+$ and $[Fe(TRP^{\cdot})L_2]^{2+}$ taken at −50 °C (CD_2Cl_2, δ/ppm)

Complexes	L	Py-H	H_α	H_β	$\Delta\delta(H_\alpha)$
$[Fe(TEtP)L_2]^+$	HIm	−21.2	1.3	−1.2	—
	2-MeIm	−9.4	16.7	1.1	—
$[Fe(T^nPrP)L_2]^+$	HIm	−20.9	2.4	−1.0	—
	2-MeIm	−8.8	19.8	[a]	—
$[Fe(T^iPrP)L_2]^+$	HIm	0.6	16.5	3.9	—
	2-MeIm	5.6[b]	21.2[b]	5.4[b]	—
$[Fe(TEtP^{\cdot})L_2]^{2+}$	HIm	−36.0	230.9	15.5	229.6
	2-MeIm	−33.7[b]	206.6[b]	14.4[b]	189.9
$[Fe(T^nPrP^{\cdot})L_2]^{2+}$	HIm	−34.1	232.6	−8.8	230.2
	2-MeIm	−30.9[b]	208.2[b]	*ca.* −7	188.4
$[Fe(T^iPrP^{\cdot})L_2]^{2+}$	HIm	−20.4	42.4	9.0	25.9
	2-MeIm	−21.7[b]	47.9[b]	9.4[b]	26.7

[a] Signals are not assigned due to the overlap with the other signals. [b] Averaged chemical shifts.

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of low-spin radical cations. See http://www.rsc.org/suppdata/cc/b2/b210229c/

DOI: 10.1039/b210229c

chemical shifts of the *meso*-$\mathrm{H_\alpha}$ between $[\mathrm{Fe(TRP)L_2}]^+$ and $[\mathrm{Fe(TRP^{\cdot})L_2}]^{2+}$, reaches as much as 230 ppm in $[\mathrm{Fe(TRP^{\cdot})(HIm)_2}]^{2+}$. Close examination of the data in Table 1 reveals that the $\Delta\delta$ values decrease by 40 to 45 ppm as the axial ligand changes from HIm to 2-MeIm. The results indicate that the spin densities at the *meso* carbon atoms in $[\mathrm{Fe(TRP^{\cdot})(HIm)_2}]^{2+}$ are much larger than those in $[\mathrm{Fe(TRP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$.

We have recently reported that the electron configuration of low-spin $[\mathrm{Fe(TRP)L_2}]^+$ changes from the common $(d_{xy})^2(d_{xz},d_{yz})^3$ to the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ as the *meso*-substituents and/or axial ligands become bulkier.[5a,b] This is because, the bulky *meso* substituents and/or bulky axial ligands deform the porphyrin ring in an S_4 ruffled fashion, which enables the interaction between the iron d_{xy} and porphyrin a_{2u} orbitals and places the d_{xy} orbital above the $d_\pi(d_{xz},d_{yz})$ orbitals. The a_{2u}–d_{xy} interaction induces the downfield shift of the *meso*-$\mathrm{H_\alpha}$ signals since the a_{2u} orbital has quite large spin densities on the *meso* carbon atoms.[5a,b] In fact, the *meso*-$\mathrm{H_\alpha}$ exhibits a large downfield shift in $[\mathrm{Fe(TRP)L_2}]^+$ as the axial HIm ligand is replaced by 2-MeIm; the downfield shifts reaches 17.4 ppm in $[\mathrm{Fe(T^nPrP)L_2}]^+$. As mentioned, the reverse is true for the oxidised complexes; the *meso*-$\mathrm{H_\alpha}$ signal exhibits *a large upfield shift* in $[\mathrm{Fe(TRP^{\cdot})L_2}]^{2+}$ as the axial HIm ligand is replaced by 2-MeIm; the upfield shifts are 24.4 ppm for both complexes. The result suggests that, while the $S = 1/2$ porphyrin radical ferromagnetically couples with the $S = 1/2$ iron in $[\mathrm{Fe(TRP^{\cdot})(HIm)_2}]^{2+}$, a weak antiferromagnetic coupling occurs in the case of the deformed radical cations $[\mathrm{Fe(TRP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$. In other words, the energy gap between the $S = 1$ ground state and the lower multiplicity $S = 0$ state decreases on going from $[\mathrm{Fe(TRP^{\cdot})(HIm)_2}]^{2+}$ to $[\mathrm{Fe(TRP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$. The interpretation seems to be reasonable because the iron(III) ion in relatively planar $[\mathrm{Fe(TRP^{\cdot})(HIm)_2}]^{2+}$ is expected to have the common $(d_{xy})^2(d_{xz},d_{yz})^3$ electron configuration as in the case of $[\mathrm{Fe(TRP)(HIm)_2}]^+$. Thus, the porphyrin a_{2u} orbital should be orthogonal to the iron $d_\pi(d_{xz},d_{yz})$ orbitals, leading to the ferromagnetic coupling. In contrast, the S_4 ruffled $[\mathrm{Fe(TRP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$ is expected to adopt the less common $(d_{xz},d_{yz})^4(d_{xy})^1$ electron configuration as in the case of $[\mathrm{Fe(TRP)(2\text{-}MeIm)_2}]^+$, making antiferromagnetic coupling between the $S = 1/2$ iron atom and the $S = 1/2$ porphyrin radical possible.

The theoretical calculation together with the EPR studies of (*meso*-tetrapropylporphyrinato)zinc(II) radical cation has revealed that the spin densities at the *meso* and β-pyrrole carbon atoms are 0.193 and 0.013, respectively.[7] The π spin density (ρ_π) at the *meso* carbon atom is connected with the contact shift (δ_{con}) of the *meso*-$\mathrm{H_\alpha}$ by $\delta_{\mathrm{con}} = A^{\mathrm{H}}\gamma_e/\gamma_{\mathrm{H}} S(S+1)/3kT$, where A^{H} is a hyperfine coupling constant of *meso*-$\mathrm{H_\alpha}$ and is given by $A^{\mathrm{H}}/h = B_2(\cos^2\phi)(\rho_\pi/2S)$, ϕ is a dihedral angle between $\mathrm{p_z}$–C_{meso}–$\mathrm{C_\alpha}$ and C_{meso}–$\mathrm{C_\alpha}$–H, and B_2 is a constant estimated as 140 MHz.[8] We have calculated the contact shift of the *meso*-$\mathrm{H_\alpha}$ in $[\mathrm{Fe(T^nPrP^{\cdot})(HIm)_2}]^{2+}$ to be $\delta_{\mathrm{con}} = 242$ ppm by putting $\phi = 60°$, $\rho_\pi = 0.196$, and $S = 1$ into the equation ; ϕ is a dihedral angle in analogous $[\mathrm{Fe(TEtP)(2\text{-}MeIm)_2}]^+$.[9] The value is quite close to the contact shift, 237 ppm, estimated on the basis of the observed chemical shift,[10] indicating that $[\mathrm{Fe(T^nPrP^{\cdot})(HIm)_2}]^{2+}$ has a ferromagnetically coupled ground state ($S = 1$).

The discussion given above suggests that the $S = 0$ state could be stabilised to a great extent in highly ruffled isopropyl complexes such as $[\mathrm{Fe(T^iPrP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$, since the porphyrin a_{2u} orbital is expected to interact with the iron d_{xy} orbital that possesses the unpaired electron. The data in Table 1 reveal that the $\Delta\delta$ values of the *meso*-$\mathrm{H_\alpha}$ signals are fairly small, only 26–27 ppm, for both complexes. We have calculated the contact shift of the *meso*-$\mathrm{H_\alpha}$ signal of $[\mathrm{Fe(T^iPrP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$ by assuming that $\phi = 69°$,[5b] $\rho_\pi(meso) = 0.193$ and $S = 1$; ϕ is the dihedral angle in analogous $[\mathrm{Fe(T^iPrP)(4\text{-}CNPy)_2}]^+$. The value of δ_{con} is calculated to be 124 ppm, which is *ca.* 3.5 times as much as the estimated contact shift, 35 ppm, in $[\mathrm{Fe(T^iPrP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$. The result rules out the possibility of the ferromagnetically coupled ground state ($S = 1$). Rather it supports the antiferromagnetically coupled ground state ($S = 0$) with a thermally populated $S = 1$ state. If this is the case, deviation from the Curie law behaviour should be observed in the *meso*-$\mathrm{H_\alpha}$ signals. Fig. 2 shows the Curie plots of the *meso*-$\mathrm{H_\alpha}$ signals of $[\mathrm{Fe(TEtP^{\cdot})(HIm)_2}]^{2+}$ and $[\mathrm{Fe(T^iPrP^{\cdot})(HIm)_2}]^{2+}$ together with those of $[\mathrm{Fe(TEtP)(HIm)_2}]^+$ and $[\mathrm{Fe(T^iPrP)(HIm)_2}]^+$. While the *meso*-$\mathrm{H_\alpha}$ signal of $[\mathrm{Fe(TEtP^{\cdot})(HIm)_2}]^{2+}$ linearly moves downfield as $1/T$ increases, that of $[\mathrm{Fe(T^iPrP^{\cdot})(HIm)_2}]^{2+}$ exhibits a clear non-Curie behaviour. The result strongly indicates that $[\mathrm{Fe(T^iPrP^{\cdot})(HIm)_2}]^{2+}$ has the $S = 0$ ground state with significant thermal population of the $S = 1$ state at higher temperature.

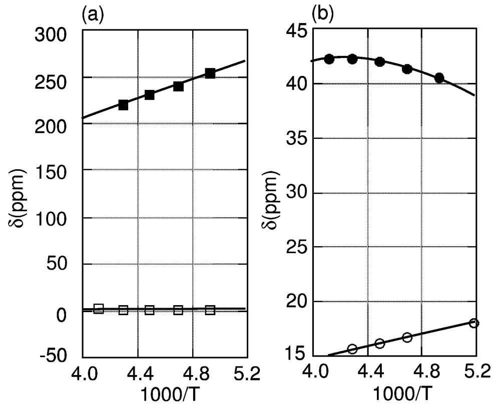

Fig. 2 Curie plots of the *meso*-$\mathrm{H_\alpha}$ signals. (a) (■) $[\mathrm{Fe(TEtP^{\cdot})(HIm)_2}]^{2+}$ and (□) $[\mathrm{Fe(TEtP)(HIm)_2}]^+$. (b) (●) $[\mathrm{Fe(T^iPrP^{\cdot})(HIm)_2}]^{2+}$ and (○) $[\mathrm{Fe(T^iPrP)(HIm)_2}]^+$.

In conclusion, we have revealed that the low-spin ferric porphyrin radical cations $[\mathrm{Fe(TRP^{\cdot})(2\text{-}MeIm)_2}]^{2+}$ exhibit an antiferromagnetic coupling in solution due to the orbital overlaps between the porphyrin a_{2u} and iron d_{xy} orbitals in highly S_4 ruffled porphyrin cores.

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