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Spin–spin interactions in iron(III) porphyrin radical cations with ruffled and saddled structure

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ABSTRACT

Oxidation of essentially pure intermediate-spin iron(III) porphyrinates such as ruffled Fe(T^{i}PrP)ClO$_4$ and saddled Fe(OETPP)ClO$_4$ produces the corresponding six-coordinate iron(III) porphyrin(por) radical cations [Fe(Por•)(ClO$_4$)$_2$], where T^{i}PrP and OETPP are dianions of 5,10,15,20-tetraisopropylporphyrin and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, respectively.

Spin–spin interactions in these complexes are very much different; while ruffled [Fe(T^{i}PrP•)(ClO$_4$)$_2$] exhibits no antiferromagnetic coupling, saddled [Fe(OETPP•)(ClO$_4$)$_2$] does exhibit it. The difference in magnetic behaviors has been explained in terms of the deformation mode and electron configuration of these complexes.

1. Introduction

It is well known that iron(III) porphyrin complexes usually adopt either high-spin ($S=5/2$) or low-spin ($S=1/2$) state depending on the nature and number of the axial ligands [1,2]. If field strength of axial ligand is extremely weak, they adopt even intermediate-spin ($S=3/2$) state [3]. One electron oxidation of iron(III) porphyrins produces either iron(IV) poprphyrins or iron(III) porphyrin radical cations depending mainly on the nature of axial ligands [4]. Oxo ligand stabilizes the iron(IV) state as is revealed from a number of examples having Fe^{IV} O bond [5–7]. On the other hand, the iron(IV) complexes without Fe^{IV} O bond are quite limited. To our knowledge, the bis-methoxo complex, [Fe^{IV}(TMP)(OMe)$_2$], is the only example that is well characterized [8]. As for the iron(III) porphyrin radical cations, there are ample examples where the iron(III) ions adopt high-spin ($S=5/2$), low-spin ($S=1/2$), or mixed high- and intermediate-spin ($S=3/2$, $5/2$) states [9–13]. However, there is no example of the iron(III) radical cation where the iron(III) ion adopts a pure intermediate-spin state. We and others have reported that the deformation of porphyrin ring stabilizes the intermediate-spin state [14–20]. In fact, ruffled or saddled complexes carrying weak axial ligands such as Fe(T^{i}PrP)ClO$_4$ and Fe(OETPP)ClO$_4$ exhibit an essentially pure intermediate-spin state [21,22]. It should then be possible to obtain iron(III) radical cation with a pure intermediate-spin state by the oxidation of the deformed complexes mentioned above. In this paper, we will report the ^{1}H NMR study on the spin–spin interactions of one-electron oxidized products shown in Scheme 1, *i.e.* six-coordinate Fe^{III}(Por•)(ClO$_4$)$_2$ and five-coordinate [Fe^{III}(Por•)Cl]SbCl$_6$ where Por indicates the dianion of either ruffled T^{i}PrP or saddled OETPP, and discuss the effect of deformation mode on the electronic structure.

2. Experimental

Free base porphyrins, (T^{i}PrP)H$_2$ and (OETPP)H$_2$, were prepared according to the literature[23,24]. Insertion of iron was performed using FeCl$_2$·4H$_2$O in refluxing CHCl$_3$ – CH$_3$OH or DMF followed by the purification of the products by the reported method [19,25]. Fe(T^{i}PrP)Cl and Fe(OETPP)Cl thus formed showed the same ^{1}H NMR and UV–visible (UV–Vis) data as those reported previously [26,27]. One-electron oxidized products of iron(III) chloride such as [Fe(T^{i}PrP•)Cl](SbCl$_6$) and [Fe(OETPP•)Cl](SbCl$_6$) were prepared by the addition of phenoxathiinylium hexachloroantimonate to the CH$_2$Cl$_2$ solutions of Fe(T^{i}PrP)Cl and Fe(OETPP)Cl [28,29]. The radical cations thus formed were purified by the recrystallization from CH$_2$Cl$_2$-hexane. One-electron oxidized Fe (T^{i}PrP•)(ClO$_4$)$_2$ was prepared by the addition of thianthrene radical cation perchlorate to the CH$_2$Cl$_2$ solution of Fe(T^{i}PrP)(ClO$_4$) [11], while the one electron oxidized [Fe(OETPP•)(ClO$_4$)$_2$] was prepared by the addition of 4 equiv. of AgClO$_4$ to the CH$_2$Cl$_2$ solution of Fe(OETPP)Cl. The

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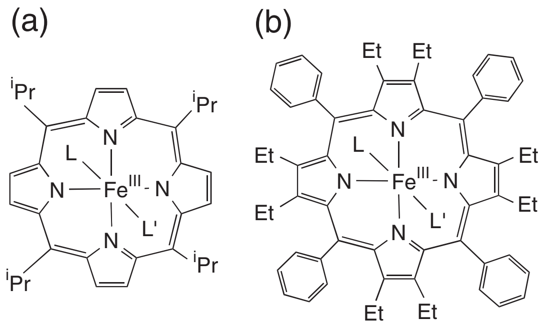

$[Fe(T^iPrP^{\cdot})Cl]SbCl_6$
$L = Cl^-$; $L' = SbCl_6^-$
$Fe(T^iPrP^{\cdot})(ClO_4)_2$
$L = L' = ClO_4^-$

$[Fe(OETPP^{\cdot})Cl]SbCl_6$
$L = Cl^-$; $L' = SbCl_6^-$
$Fe(OETPP^{\cdot})(ClO_4)_2$
$L = L' = ClO_4^-$

Scheme 1. Iron(III) porphyrin radical cations examined in this study.

^1H NMR spectra were recorded using CD_2Cl_2 as solvent on a JEOL LA 300 spectrometer operating at 300.4 MHz. Chemical shifts were referenced to residual solvent peaks (δ 5.32 ppm).

3. Results and discussion

Fig. 1 shows the ^1H NMR spectra of $[Fe(T^iPrP\bullet)Cl](SbCl_6)$ and $Fe(T^iPrP\bullet)(ClO_4)_2$ taken in a CD_2Cl_2 solution at 298 K. It is clear from these spectra that electron is removed from the porphyrin a_{2u} orbital because the meso-CH signals showed extremely large upfield or downfield shift; they appeared at −38.1 and 109.7 ppm in $[Fe(T^iPrP\bullet)Cl](SbCl_6)$ and $Fe(T^iPrP\bullet)(ClO_4)_2$, respectively. Table 1 lists the ^1H NMR chemical shifts of $[Fe(T^iPrP\bullet)Cl](SbCl_6)$ and $Fe(T^iPrP\bullet)(ClO_4)_2$ together with those of analogous $[Fe(TPP\bullet)Cl](SbCl_6)$ and $Fe(TPP\bullet)(ClO_4)_2$ reported previously [10,11]. For comparison, the chemical shifts of the parent complexes such as $Fe(T^iPrP)X$ and $Fe(TPP)X$ (X is Cl^- or ClO_4^-) are also listed [19,26,28,30,31].

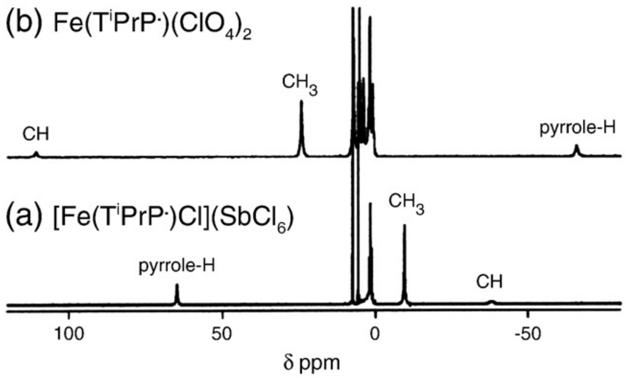

Fig. 1. ^1H NMR spectra of (a) $[Fe(T^iPrP\bullet)Cl](SbCl_6)$ and (b) $Fe(T^iPrP\bullet)(ClO_4)_2$ taken in a CD_2Cl_2 solution at 298 K.

Table 1
^1H NMR chemical shifts of some cation radicals (in ppm) and their parent complexes taken in a CD_2Cl_2 solution at 298 K.

Complexes	Pyrrole			Meso			Ref.
	H	CH_2	CH_3	CH (ortho)	CH_3 (meta)	(para)	
T^iPrP							
$[Fe(T^iPrP^\bullet)Cl](SbI_6)$	64.6	–	–	−38.1	−9.6		This work
$Fe(T^iPrP^\bullet)(ClO_4)_2$	−64.1	–	–	109.7	23.8		This work
$Fe(T^iPrP)Cl$	90.4	–	–	28.3	9.5		[19]
$Fe(T^iPrP)(ClO_4)$	−31.2	–	–	13.8	5.3		[19]
TPP							
$[Fe(TPP^\bullet)Cl](SbI_6)$	66.1	–	–	(37.6, 34.4)	(−12.4)	(29.5)	[10]
$Fe(TPP^\bullet)(ClO_4)_2$	31.4	–	–	(−19.3)	(34.7)	(−12.9)	[31]
$[Fe(TPP)Cl]$	80.1	–	–	(6.2, 3.8)	(12.6, 12.0)	(5.8)	[28]
$Fe(TPP)(ClO_4)$	13.0	–	–	(9.2)	(11.9)	(7.7)	[31]
OETPP							
$[Fe(OETPP^\bullet)Cl](SbF_6)$	–	71.2, 56.1 24.7, 16.6 (42.2)	4.4, 3.6 (4.0)	(37.6, 34.9)	(−10.1, −11.5)	(28.8)	[28]
$Fe(OETPP^\bullet)(ClO_4)_2$	–	91.4, 23.8 (57.6)	6.2	(33.5)	(−7.7)	(26.9)	This work
$Fe(OETPP)Cl$	–	49.0 34.8 32.1 20.1 (34.0)	1.8 3.2 (2.5)	(11.5, 9.1)	(12.4, 12.2)	(7.5)	[27,28]
$Fe(OETPP)(ClO_4)$	–	13.0 42.7 (27.9)	0.7	(13.4)	(7.1)	(9.8)	[16]

The pyrrole-H chemical shifts are known to be a good probe to determine the spin state of the iron porphyrin complexes [21,22]. For example, the pyrrole-H signals of $Fe(T^iPrP)Cl$ and $Fe(T^iPrP)(ClO_4)$ appear at 90.4 and −31.2 ppm, respectively, which indicate that these complexes adopt the high-spin and intermediate-spin states, respectively [19]. Thus, the pyrrole-H signals of radical cations, $[Fe(T^iPrP\bullet)Cl](SbCl_6)$ and $Fe(T^iPrP\bullet)(ClO_4)_2$, observed at +64.6 and −64.1 ppm, respectively, suggest that the iron(III) ions of these complexes maintain the spin states of the starting complexes. The reversal of the sign in the *meso*-CH chemical shifts between $[Fe(T^iPrP\bullet)Cl](SbCl_6)$ and $Fe(T^iPrP\bullet)(ClO_4)_2$ should be ascribed to the presence of antiferromagnetic coupling between the S = 5/2 iron(III) ion and the S = 1/2 porphyrin radical in the former complex. The same antiferromagnetic coupling was reported in $[Fe(TPP\bullet)Cl](SbCl_6)$; the signs of the *ortho*, *meta*, and *para*-H chemical shifts of this complex are just opposite to those of $Fe(TPP\bullet)(ClO_4)_2$ [11]. Thus, the antiferromagnetic coupling occurs only in five-coordinate complexes such as $[Fe(TPP\bullet)Cl](SbCl_6)$ and $[Fe(T^iPrP\bullet)Cl](SbCl_6)$. This is because the half-occupied a_{2u} orbital of porphyrin can interact with the half-occupied iron d_z2 orbital in the five-coordinate high-spin complexes; these orbitals are signified as a_1 in C_{4v} domed complexes [32].

The question then arises as to why there is no antiferromagnetic coupling in ruffled six-coordinate $Fe(T^iPrP\bullet)(ClO_4)_2$ in spite of the well known fact that the half-occupied iron d_{xy} orbital can interact with the doubly occupied porphyrin a_{2u} orbital in low-spin iron(III) complexes with ruffled porphyrin framework [21,22,33,34]; both d_{xy} and a_{2u} orbitals in planar D_{4h} complex are signified as b_2 in ruffled D_{2d} complex [35,36]. A possible explanation is that radical cationic $Fe(T^iPrP\bullet)(ClO_4)_2$ posseses no unpaired electron in the d_{xy} orbital. In other words, the complex adopts the $(d_{xy})^2(d_{xz}, d_{yz})^2(d_z2)^1(a_{2u})^1$ electronic ground state rather than $(d_{xz}, d_{yz})^3(d_z2)^1(d_{xy}, a_{2u})^2$ [37]. Thus, the a_{2u} radical maintains the positive spin in $Fe(T^iPrP\bullet)(ClO_4)_2$.

We have once reported that essentially pure intermediate-spin iron(III) complexes such as $Fe(T^iPrP)(ClO_4)$ and $[Fe(T^iPrP)(THF)_2](ClO_4)$ adopt the $(d_{xz}, d_{yz})^3(d_{xy})^1(d_z2)^1$ ground state rather than $(d_{xy})^2(d_{xz}, d_{yz})^2(d_z2)^1$ [15]. However, the DFT calculations have suggested different electronic ground states for the latter complex [38,39]. We have later corrected that $[Fe(T^iPrP)(THF)_2](ClO_4)$ adopts