Formation and ^{1}H NMR Spectra of Low Spin Ferric Porphyrin Radical Cations with Orientationally Fixed Imidazole Ligands

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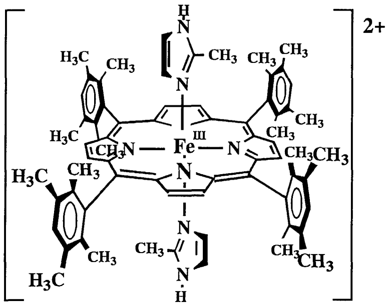
Chemical oxidation of tetradurylporphyrinatoiron(III) chloride followed by the addition of 2-methylimidazole at -78 °C gave the first example of the low spin ferric porphyrin radical cation with orientationally fixed imidazole ligands, [Fe(TDP$^{\bullet}$)(2-MeIm)$_2$]$^{2+}$. The degree of asymmetric spin distribution on the pyrrole β carbons in the radical cation was estimated to be close to that in the starting low spin complex, [Fe(TDP)(2-MeIm)$_2$]$^+$, which was ascribed to the orthogonality of porphyrin a_{2u} with imidazole π orbitals.

Porphyrin radicals have been extensively studied since they are playing important roles in biological oxidations catalyzed by peroxidase, catalase, and cytochrome P450.[1] Furthermore, recent studies using model complexes have suggested the involvement of porphyrin radicals in heme catabolism.[2] In most of the heme proteins, central iron is coordinated by either one or two histidyl imidazoles which are orientationally fixed relative to the porphyrin plane. Thus, molecular orbitals of the porphyrin could be perturbed through electronic and steric interactions with the orientationally fixed imidazole ligands.[3,4] Such interactions are expected to induce asymmetric spin distribution on the porphyrin ring; unpaired electron resides on some specific carbon and nitrogen atoms of the heme. In order to elucidate if this is the case, ferric porphyrin radical cations with orientationally fixed imidazole ligands are necessary. In this paper, we would like to report the first example of such complexes together with their peculiar ^{1}H NMR spectra.

Tetradurylporphyrinatoiron(III) chloride [Fe(TDP)]Cl was chemically oxidized in a CD_2Cl_2 solution by the addition of excess phenoxathiinylium hexachloroantimonate.[5-7] The oxidized porphyrin complex, which was stable at least for 3 hrs at room temperature, gave a ^{1}H NMR spectrum shown in Figure 1a. The complex was assigned to the high spin iron(III) radical cation, [Fe(TDP$^{\bullet}$)](SbCl$_6$)(Cl), based on the characteristic pyrrole and aryl signals.[7,8] To the high spin radical cation was added a CD_2Cl_2 solution of 2-MeIm at -78 °C. The ^{1}H NMR spectrum, taken at -56 °C after the addition of 4.0 equiv of the ligand, exhibited well resolved signals as shown in Figure 1b. The four separate signals at δ -45.6, -45.9, -51.7 and -54.7 ppm, assigned to the pyrrole protons of the low spin radical cation [Fe(TDP$^{\bullet}$)(2-MeIm)$_2$](SbCl$_6$)(Cl) based on the spectral comparison with the analogous complex,[9] clearly indicate that the rotation of the coordinated imidazole ligands is hindered on the NMR time scale.[10] Since the sample still contained ca. 20% of the starting high spin radical cation as revealed by the *para*-H signal at δ 16.6 ppm, another two equiv of 2-MeIm was added. The resultant spectrum showed complete conversion to the low spin radical cation, although each signal at a paramagnetic region broadened considerably. Integral intensities of the six signals at δ 25 to 50 ppm suggested that three of them correspond to 6H, and the other three to 2H. To assign these signals, perdeuterated 2-MeIm was added to the high spin complex.[11] Only three signals were observed in this region as shown in Figure 1c. Thus, the signal at the lowest magnetic field δ 49.5 ppm (6H) was assigned to the methyl of the coordinated 2-MeIm and the signals at δ 42.4 and 34.0 ppm were assigned to the *ortho*-methyls. Other methyl signals appeared in less paramagnetically shifted positions as shown in Figure 1f: *ortho*-methyls, δ 8.0 and 6.7; *meta*-methyls, δ 4.7, 3.7, -0.6, and -0.7 ppm.[12] Two signals at δ -1.0 and -2.1 ppm, each corresponding to 2H, were assigned to the *para*-H of the duryl ring based on the spectral comparison with the *para*-D complex. The signal assignment thus determined is given in Figure 1b and Figure 1f. The fact that four signals were observed for the pyrrole and *ortho*-methyl protons and two signals for the *para*-H at -56 °C indicates that the frozen conformation of this complex is the one where two ligands are placed perpendicularly in the deformed porphyrin cavities developed along the *Cmeso*-Fe-*Cmeso* axes as observed in [Fe(TMP)(1,2-Me$_2$Im)$_2$]ClO$_4$ and [Fe(TMP)(2-MeIm)$_2$]Cl in the solid and in solution, respectively.[13-15] The low spin radical cation was stable at -56 °C for at least 3 hrs. It was quickly reduced, however, to the low spin [Fe(TDP)(2-MeIm)$_2$]$^+$ on standing the sample at room temperature for 10 seconds. The reduced low spin complex gave four pyrrole signals at lower magnetic field, δ -10.1, -13.9, -16.1, and -18.7 ppm, at -56 °C as shown in Figure 1d.



[Fe(TDP$^{\bullet}$)(2-MeIm)$_2$]$^{2+}$

In order to compare the spectral properties of [Fe(TDP$^{\bullet}$)(2-MeIm)$_2$]$^{2+}$ with those of the complex carrying rapidly rotating imidazole ligands, the corresponding bis(imidazole) complex [Fe(TDP$^{\bullet}$)(HIm)$_2$]$^{2+}$ was prepared. In Figure 1e is given the ^{1}H NMR spectrum taken at -56 °C in CD_2Cl_2. As expected, the pyrrole signal appeared at δ -49.1 ppm as a single line, indicating that the ligand is rapidly rotating on the NMR time scale. The *ortho*-methyl, *meta*-methyl, and *para*-H also gave single lines at 19.0, 2.2, and -1.8 ppm, respectively. It is noteworthy that these signals are quite close to the average values of the split signals in [Fe(TDP$^{\bullet}$)(2-MeIm)$_2$]$^{2+}$; -49.5 for the pyrrole protons and 22.8, 1.8 and -1.6 ppm for the *ortho*-, *meta*-, and *para*-protons, respectively. Three signals at δ 36.9, 34.6, and 29.3 ppm were assigned to the ring protons of the coordinated imidazole ligands based on their integral intensities.

The large paramagnetic shifts of the aryl protons are indicative of the formation of a_{2u} type radical where large spin density is on

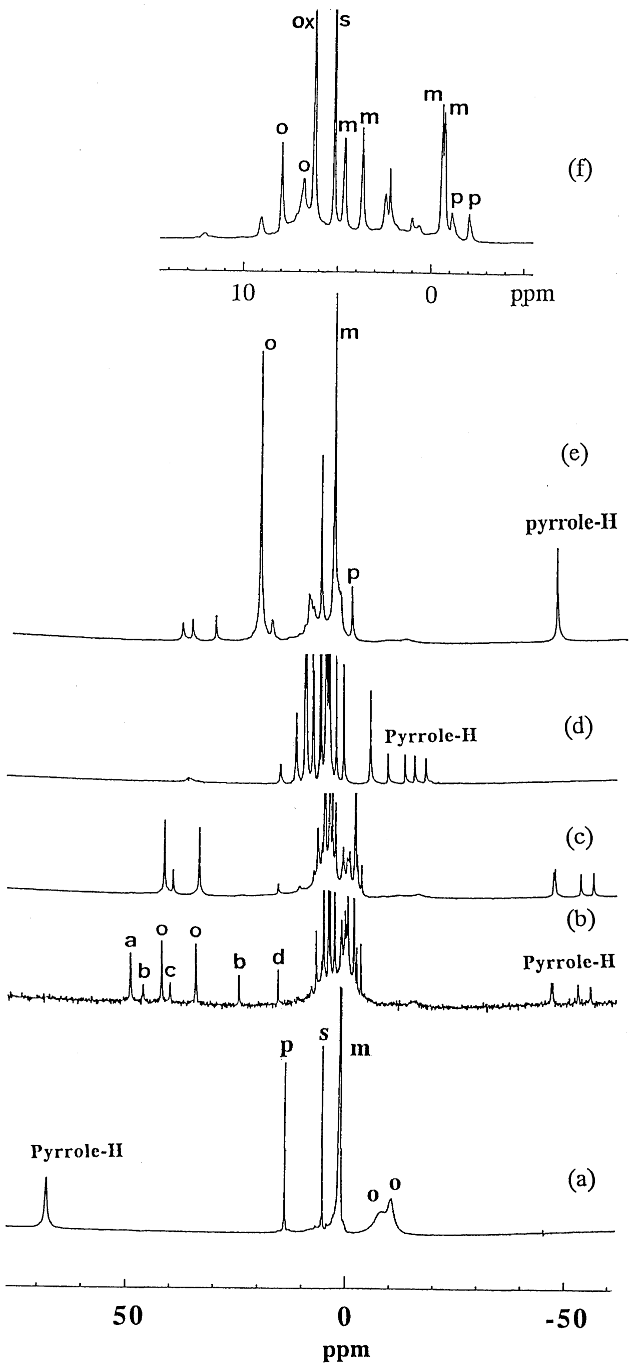


Figure 1. ^{1}H NMR spectra taken in CD_2Cl_2 solution at -56 °C: (a) high spin $[Fe(TDP^{\cdot})]^{2+}$, (b) low spin $[Fe(TDP^{\cdot})(2\text{-MeIm})_2]^{2+}$ obtained by the addition of 4.0 equiv of 2-MeIm into $[Fe(TDP^{\cdot})]^{2+}$, (c) low spin $[Fe(TDP^{\cdot})(2\text{-MeIm})_2]^{2+}$ where all the protons of 2-MeIm except N-H are deuterated, (d) low spin $[Fe(TDP)(2\text{-MeIm})_2]^+$ obtained after standing $[Fe(TDP^{\cdot})(2\text{-MeIm})_2]^{2+}$ at room temperature for 10 seconds, (e) low spin $[Fe(TDP^{\cdot})(HIm)_2]^{2+}$ obtained by the addition of 1.5 equiv of HIm into $[Fe(TDP^{\cdot})]^{2+}$, and (f) expansion of -5 to 15 ppm region of $[Fe(TDP^{\cdot})(2\text{-MeIm})_2]^{2+}$ obtained by the addition of 6.0 equiv of 2-MeIm. Signal assignment: o, m, and p; *ortho-*, *meta* and *para*-protons; a, imidazole methyl; b, imidazole C-H; c, imidazole N-H; d, *para*-H of $[Fe(TDP^{\cdot})]^{2+}$; s, solvent; ox, reduced oxidant.

the *meso* carbons and pyrrole nitrogens.[16] The ^{1}H NMR spectrum in Figure 1b has revealed that the dispersion of the four pyrrole signals, defined by the chemical shift difference between the highest and lowest pyrrole signals, is 9.1 ppm in the low spin radical cation at -56 °C. This value is quite close to that of the corresponding low spin complex $[Fe(TDP)(2\text{-MeIm})_2]^+$, 8.6 ppm at the same temperature as shown in Figure 1d. These results suggest that the degree of asymmetric spin distribution on the pyrrole β carbons in $[Fe(TDP^{\cdot})(2\text{-MeIm})_2]^{2+}$ is close to that in the low spin $[Fe(TDP)(2\text{-MeIm})_2]^+$. A large upfield shift of the pyrrole protons, observed on going from $[Fe(TDP)(2\text{-MeIm})_2]^+$ to $[Fe(TDP^{\cdot})(2\text{-MeIm})_2]^{2+}$, indicates that the spin density on the pyrrole β carbons increases upon oxidation. Thus, the similar dispersion of the pyrrole protons in $[Fe(TDP^{\cdot})(2\text{-MeIm})_2]^{2+}$ and $[Fe(TDP)(2\text{-MeIm})_2]^+$ strongly suggests that the orthogonality of a_{2u} with imidazole π orbitals is maintained in this highly deformed porphyrin complex.

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5 Abbreviations: TDP, TMP, and TPP are dianions of 5,10,15,20tetra duryl-, 5,10,15,20-tetramesityl-, and 5,10,15,20-tetraphenyl-porphyrins, respectively. 2-MeIm and HIm are 2-methylimidazole and imidazole, respectively.

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12 These signals were assigned based on the integral intensities and the spectral comparison with the corresponding $[Fe(TMP^{\cdot})(2\text{-MeIm})_2]^{2+}$.

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