Direct Observation of Conformers Caused by the Difference in Ligand Orientation in Low Spin Iron(III) Porphyrin Complex

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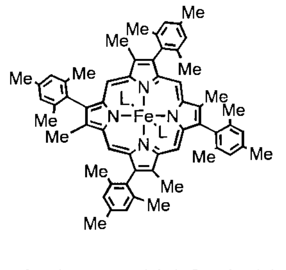
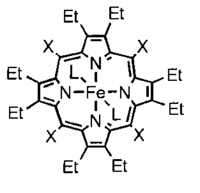
EPR spectrum of low spin bis(dimethylaminopyridine)(3,8,13,18-tetramesityl-2,7,12,17-tetramethylporphyrinato)iron(III) perchlorate taken in frozen CH_2Cl_2 solution at 4.2 K showed both large g_{max} and rhombic type signals. The result has been explained in terms of the presence of two conformers where the dihedral angles between two ligands are different.

Physicochemical properties of low spin iron(III) porphyrin complexes as well as naturally occurring heme proteins are controlled by various factors. In the complexes carrying one or two imidazole ligands at the axial positions, orientation of the ligands relative to the heme plane is considered to be one of the factors.[1,2] Although imidazole ligands are fixed in the cavities of heme proteins, they are rapidly rotating in the synthetic iron(III) porphyrin complexes. Thus, the observed properties could be the average of the several conformers where the ligand orientation is different. However, there is no report on the observation of conformers in solution. Some time ago, we reported the first example of the complex in which the axially coordinated 2-methylimidazole ligands are fixed on the ^1H NMR time scale.[3] Even in such a case, the complex existed as a conformationally pure species.[4,5] In this paper, we report the first example of the direct observation of two conformers in frozen solution.

The complex in question is bis(dimethylaminopyridine)(3,8,13,18-tetramesityl-2,7,12,17-tetramethylporphyrinato)iron(III) perchlorate, $[Fe(TMTMP)(DMAP)_2]ClO_4$ (**1**).[6-8] **1** was prepared by the addition of 4.0 equiv of DMAP into the CD_2Cl_2 solution of $[Fe(TMTMP)]ClO_4$ in an NMR sample tube.



$[Fe(TMTMP)(L)_2]ClO_4$ (**1**)
(L = DMAP)



$[Fe(OEP)(L)_2]ClO_4$ (**2**)
(X = H; L = DMAP)

$[Fe(OETPP)(L)_2]ClO_4$ (**3**)
(X = Ph; L = DMAP)

Formation of **1** was confirmed by the ^1H NMR spectrum at -20 °C as shown in Figure 1. The downfield shifted pyrrole methyl signal, δ 14.7 ppm, and the upfield shifted *meso* signal, δ -2.7 ppm, strongly suggest that the complex adopts the common $(d_{xy})^2(d_{zx}, d_{yz})^3$ ground state.[9-11] The $(d_{xy})^2(d_{zx}, d_{yz})^3$ ground state was further supported by the ^{13}C NMR spectra; **1** showed the α-pyrrole signals at 35.9 and 41.0 ppm, β-pyrrole signals at 135.7 and 144.3 ppm, and *meso* signal at 23.6 ppm at 25 °C, which are quite close to the corresponding signal positions of $[Fe(OEP)(1\text{-}MeIm)_2]Cl$.[12]

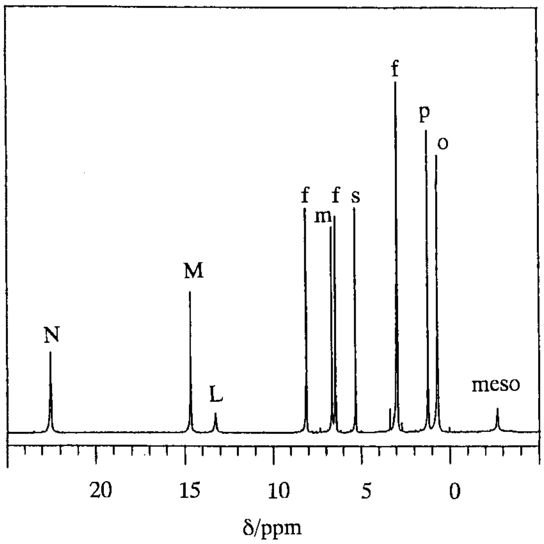


Figure 1. ^1H NMR spectra of $[Fe(TMTMP)(DMAP)_2]ClO_4$ taken in CD_2Cl_2 at -20 °C. Signal assignment: o, m, and p; ortho-, meta- and para-protons. M; pyrrole methyl protons. L and N; ring and N-methyl protons of the coordinated DMAP ligand. f; free DMAP. s; dichloromethane.

In order to determine the orientation of the axially coordinated DMAP ligands, the EPR spectrum of **1** was taken in frozen CH_2Cl_2 solution at 4.2 K.[13] Figure 2(a) clearly exhibited both large g_{max} and rhombic type spectra. The rhombic component has $g_z = 2.86$, $g_y = 2.28$, and $g_x = 1.62$, while the large g_{max} component has a signal at $g_z = 3.58$. For the comparison, the EPR spectra of the analogous $[Fe(OEP)(DMAP)_2]ClO_4$(**2**) and $[Fe(OETPP)(DMAP)_2]ClO_4$(**3**) were examined; **3** was prepared by the addition of 4.0 equiv of DMAP into the CH_2Cl_2 solution of $[Fe(OETPP)]ClO_4$.[14-16] Figures 2(b) and 2(c) show the EPR spectra of **2** and **3**, respectively, taken in frozen CH_2Cl_2 solution at 4.2 K. The former exhibited the rhombic spectrum with $g_z = 2.81$, $g_y = 2.28$, and $g_x = 1.64$,[17] while the latter showed the large g_{max} type spectrum with $g_z = 3.24$.

Walker, Schidt and coworkers have established that the large g_{max} and rhombic type spectra are originated from the perpendicular and parallel alignment of the ligands, respectively.[17,18] In fact, **2** has two parallelly oriented planar ligands as revealed from the crystallographic result.[17] On the contrary, **3** is expected to have perpendicularly aligned ligands because the OETPP ring is highly S_4-saddled and creates cavities along the diagonal N-Fe-N axes.[15] Since the planar axial ligands are placed along the cavities, the stereoisomer with perpendicularly aligned axial ligands could be formed as in the case of the analogous cobalt(III) complexes.[19] The present result strongly sug-

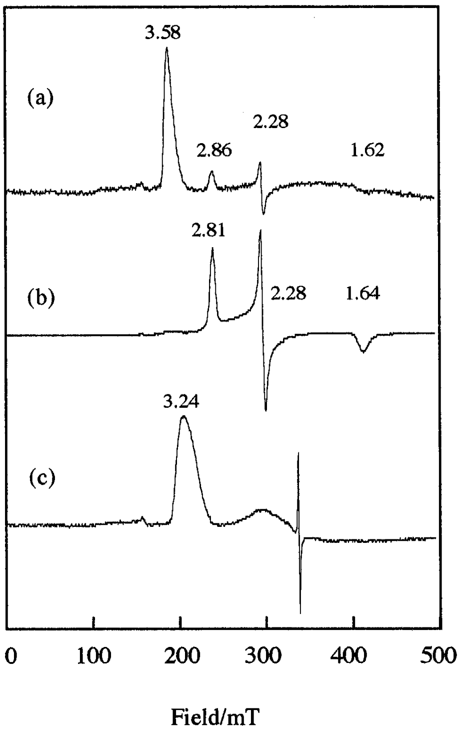


Figure 2. EPR spectra of (a) $[Fe(TMTMP)(DMAP)_2]ClO_4$, (b) $[Fe(OEP)(DMAP)_2]ClO_4$, and (c) $[Fe(OETPP)(DMAP)_2]ClO_4$, taken in frozen CH_2Cl_2 solution at 4.2 K. The g value of each signal is also given. Experimantal conditions: Microwave power 1.02 mW, sweep width 500 mT, sweep time 168 s, modulation frequency 100 KHz, modulation amplitude 7.58 G.

gests that **1** has two conformers in which the dihedral angles between two axial ligands are different.[20] Observation of the two types of EPR signals in a single complex is not unprecedented.[18,21,22] For example, $[Fe(TPP)(HIm)_2]Cl$ shows two overlapping rhombic spectra,[21] and $[Fe(T2,6Cl_2PP)(1\text{-}VinIm)_2]ClO_4$ displays both large g_{max} and rhombic spectra.[18] In these cases, however, the EPR spectra were taken in the solid state. In the frozen solution where the solid-state packing effects are absent, both complexes exhibit a single rhombic spectrum. To our knowledge, **1** is the first example showing the presence of conformers in frozen solution. If we assume that the equilibrium constant between two isomers is ca. 10 in favor of the perpendicular isomer, the ΔG° is calculated to be 80 J/mol at 4.2 K. Thus, this phenomenon is observable when the difference in thermodynamic stability of the isomers is fairly small.

The results presented here indicate the importance of EPR spectroscopy to elucidate the presence of conformers and their relative ratios. EPR measurement at various temperatures could yield the thermodynamic parameters, ΔH° and ΔS°, which would help understand the properties of these biologically relevant complexes.

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6 Abbreviations: TMTMP, OEP, OETPP, TPP, $T2,6Cl_2PP$: diaions of 3,8,13,18-tetramesityl-2,7,12,17-tetramethylporphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, *meso*-tetraphenylporphyrin, and *meso*-tetrakis(2,6-dichloro-phenyl)porphyrin, respectively. DMAP: 4-dimethylaminopyridine. 1-VinIm: 1-vinylimidzaole. HIm: imidazole. 1-MeIm: 1-methylimidazole.

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12 $[Fe(OEP)(1\text{-}MeIm)_2]Cl$: ^{13}C NMR ($CDCl_3$, 26 °C, δ ppm) α-pyrrole, 45.4; β-pyrrole, 146.7; *meso*, 23.6 ppm. H. M. Goff, *J. Am. Chem. Soc.*, **103**, 3714 (1981).

13 ^1H NMR spectra of **1** were taken at low temperature. No broadening due to the hindered rotation of the axial ligand was observed even at -100 °C.

14 $[Fe(OETPP]ClO_4$ was prepared by the addition of 1.0 equiv of $AgClO_4$ into the THF solution of [Fe(OETPP)Cl].[15] The crude product was recrystallized from THF-hexane. ^1H NMR (CD_2Cl_2, 25 °C, δ ppm): 14.2 (8H, CH_2); 43.2 (8H, CH_2); 0.7 (24H, CH_2); 13.0 (8H, *o*-H); 6.5 (8H, *m*-H); 9.7 (4H, *p*-H).

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16 $[Fe(OETPP)(DMAP)_2]ClO_4$: ^1H NMR (CD_2Cl_2, -50 °C, δ ppm): 3.4 (8H, CH_2); 12.5 (8H, CH_2); 1.3 (24H, CH_3); 2.7 (8H, *o*-H); 4.8 (8H, *m*-H); 6.0 (4H, *p*-H); 15.8 (4H, ligand); -2.7 (4H, ligand); 18.0 (12H, NCH_3). ^{13}C NMR (CD_2Cl_2, -50 °C, δ ppm): 132 (Py-α); 164 (Py-β); -28 (*meso*); 159 (*ipso*); 102 (*o*); 122 (*m*); 123 (*p*); -40 (CH_2); 102 (CH_3).

17 The g values of **2** taken in frozen CH_2Cl_2 solution at 25 K were reported to be 2.818, 2.278, and 1.642. M. K. Safo, G. P. Gupta, F. A. Walker, and W. R. Scheidt, *J. Am.Chem. Soc.*, **113**, 5497 (1991).

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20 In the case of **2**, the two DMAP ligands are coplanar. The orientation of the axial ligands with the closest Fe-N vector is 36°.[17] Introduction of the bulky mesityl groups at 3,8,13, and 18 positions would destabilizes this conformation. As a result, the energy difference between the parallel and perpendicular conformers is supposed to be much smaller, making the observation of both conformers possible.

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