Bis(1-methylimidazole) Complex of Iron(III) Oxypyriporphyrin Adopting an Intermediate-spin State

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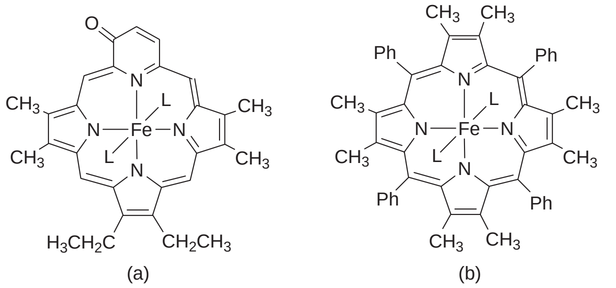
Bis(1-methylimidazole) complex of iron(III) oxypyriporphyrin adopts an essentially pure intermediate-spin ($S = 3/2$) state at 298 K, which is the first example of the iron(III) porphyrinoid adopting the $S = 3/2$ in spite of the bis-coordination of imidazole ligand.

Recent studies have revealed that iron(III) complexes with core-modified porphyrins exhibit unique electronic structures that have rarely been observed in the corresponding porphyrin complexes. For example, bis(^{t}BuNC) complex of iron(III) diazaporphyrin exhibits the $(d_{xy})^2(d_{xz},d_{yz})^3$ ground state,[1] while bis(HIm) complex of iron(III) oxophlorin shows the $(d_{xz},d_{yz})^4(d_{xy})^1$ ground state;[2] bis(^{t}BuNC) and bis(HIm) complexes of iron(III) porphyrins almost always adopt the $(d_{xz},d_{yz})^4(d_{xy})^1$ and $(d_{xy})^2(d_{xz},d_{yz})^3$ ground state, respectively.[3–7] In any cases, however, bis(imidazole) complexes of iron(III) porphyrins including core-modified porphyrins exhibit the low-spin state. In this study, we report that iron(III) oxypyriporphyrin(OxyPyP) serves the first example showing an intermediate-spin state at 298 K in spite of the bis-imidazole coordination.

A series of six-coordinate $[Fe(OxyPyP)L_2]^{\pm}$ (**1**–**4**) were prepared by the addition of 6 to 12 equiv of bases to the CH_2Cl_2 solutions of Fe(OxyPyP)Cl or $[Fe(OxyPyP)(THF)_2]ClO_4$,[8] where L is CN^- (**1**), DMAP (**2**), HIm (**3**), or 1-MeIm (**4**). Figure 1 shows the ^1H NMR spectra of **1**–**4** taken in CD_2Cl_2 solutions at 263 K. Formation of the six-coordinate complex was verified by the two sharp signals ascribed to the CH_2 protons; five-coordinate complexes obtained by the addition of small amount of bases showed four signals. The integral intensities of the CH_3 signals of the coordinating DMAP and 1-MeIm ligands in **2** and **4**, respectively, further confirmed the bis-coordination. In every complex examined, the four pyr-CH_3 signals appeared at the most downfield positions. However, the chemical shifts were very much different among complexes as listed in Table 1. While **1** showed the four pyr-CH_3 signals at 21 to 23 ppm, **4** showed them at 58 to 71 ppm. It is quite unusual that the chemical shifts of the pyr-CH_3 signals are different between bis(CN^-) and bis(1-MeIm) complexes. The results suggest that the spin state of **1** is different from that in **4**. Since the chemical shifts of the pyr-CH_3 signals in low-spin $[Fe(OMTPP)(CN)_2]^-$ (**5**) and $[Fe(OMTPP)(HIm)_2]^+$ (**6**) are quite close to those of **1**,[9] it is reasonable to assume that **1** is in the low-spin state. Similarly, **4** must adopt an intermediate-spin state since the average chemical shift of the pyr-CH_3 signals is close to that in intermediate-spin $[Fe(OMTPP)(THF)_2]^+$ (**7**); the chemical shifts of the pyr-



Scheme 1. (a) $[Fe(OxyPyP)L_2]^{\pm}$ examined in this study, where L is CN^- (**1**), DMAP (**2**), HIm (**3**), and 1-MeIm (**4**). (b) $[Fe(OMTPP)L_2]^{\pm}$ where L = CN^- (**5**), HIm (**6**), and THF (**7**).

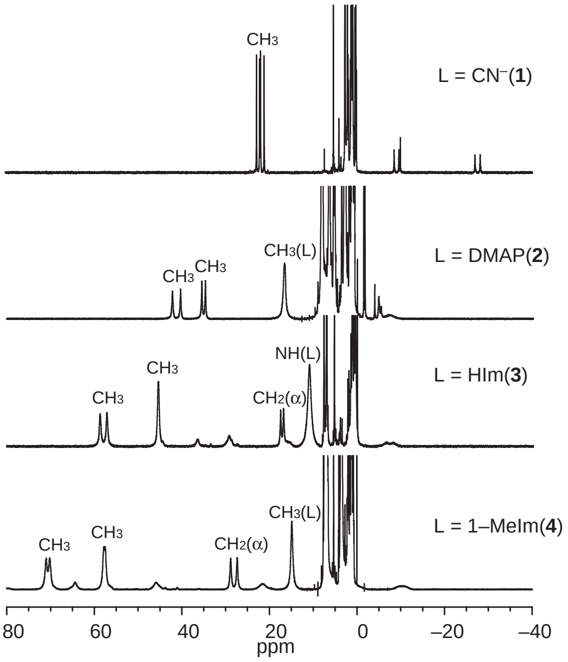


Figure 1. ^1H NMR spectra of **1**–**4** taken in CD_2Cl_2 at 263 K.

Table 1. ^1H NMR chemical shifts (CD_2Cl_2 at 263 K)

Complexes	pyr-CH_3[a]					pyr-$CH_2(\alpha)$		$CH_3(\beta)$	
1(CN^-)	22.8	22.1	21.9	21.1	(22.0)	2.00	1.85	0.38	0.19
2(DMAP)	42.2	40.4	35.5	34.7	(38.2)	0.91[b]	0.41[b]	−1.45	−1.72
3(HIm)	58.7	57.2	45.4	45.4	(51.7)	17.6	16.9	0.66	0.47
4(1-MeIm)	71.3	70.5	58.2	57.8	(64.5)	29.2	27.7	1.78	1.78

[a]Data in the parenthesis are average chemical shifts. [b]Extrapolated from low temperature.

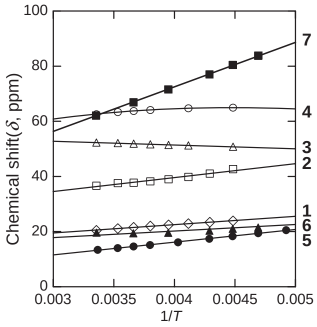


Figure 2. Curie plots of the average chemical shifts of the pyr-CH_3 signals in $[Fe(OxyPyP)L_2]^{\pm}$ (**1**–**4**), $[Fe(OMTPP)(CN)_2]^-$ (**5**), $[Fe(OMTPP)(HIm)_2]^+$ (**6**), and $[Fe(OMTPP)(THF)_2]^+$ (**7**).

CH_3 signals in **5**, **6**, and **7** were reported to be 15.4, 18.9, and 69.3 ppm, respectively, at 263 K.[9]

Figure 2 shows the Curie plots of the average chemical shifts of the pyr-CH_3 signals in **1**–**4** together with those in **5**–**7**. The Curie plots of **1**, **5**, and **6** are almost overlapping; they exhibit good linearity with positive slopes. Thus, it is clear that **1** adopts the low-spin state at the temperature range examined. In contrast, the Curie plots of **4** and **7** are quite different though the average chemical shift of the pyr-CH_3 signals of **4** is quite close to that of **7** at 298 K; **7** showed a good linearity with a positive slope while **4** exhibited a slight curvature with very small temperature dependence. Thus, the difference in chemical shifts, $\delta(\mathbf{7})$–$\delta(\mathbf{4})$, increased from −3.6 ppm at 298 K to +15.4 ppm at 223 K. The result suggests that the spin state of **4** varies from the $S = 3/2$ to the $S = 1/2$ as the temperature is lowered.[4,9,10] Complexes **2** and **3** showed a similar tendency.

We have then measured the effective magnetic moments, $\mu_{\rm eff}$, of these complexes by the Evans methods in CH_2Cl_2 solution by assuming that **1** maintains a pure low-spin state with $\mu_{\rm eff} = 1.73\ \mu_{\rm B}$ throughout the temperatures examined.[11] At 283 K, the $\mu_{\rm eff}$ values for **2**, **3**, and **4** were determined to be 2.2, 3.9, and 4.1 $\mu_{\rm B}$, respectively. These values decreased to 1.8, 3.3, and 3.5 $\mu_{\rm B}$ at 243 K and further decreased to 1.7, 2.8, and 3.2 $\mu_{\rm B}$ at 203 K. Thus, the temperature dependence of the $\mu_{\rm eff}$ values of **2**–**4** is consistent with the Curie plots shown in Figure 2 though the values for **2** are somehow much smaller than expected.

Figure 3 shows the EPR spectra of **1**–**4** taken in frozen CH_2Cl_2 solutions at 4.2 K. The g values are also given in Figure 3. All of these complexes showed rhombic spectra with g_1, g_2, and g_3 values ranging from 2.75–2.98, 2.21–2.48, and 1.57–1.68, respectively. The results suggest that they adopt the low-spin state at 4.2 K. It should be noted that even **1** showed the rhombic type spectra because of the unsymmetrical core structure; bis(CN^-) complexes usually exhibit large $g_{\rm max}$ type spectra in planar D_{4h}, ruffled D_{2d}, and saddled D_{2d} complexes.[4] The fact that the g_1 values are 2.75–2.98 indicates that these complexes adopt the $S = 1/2$ with the $(d_{xy})^2(d_{xz},d_{yz})^3$ ground state.[3] Thus, the EPR results are consistent with the NMR results since the latter showed a spin transition from the $S = 3/2$ to the $S = 1/2$ as the temperature is lowered.

In summary, we have found that $[Fe(OxyPyP)(1\text{-}MeIm)_2]^+$ adopts the $S = 3/2$ at 298 K, and converts it to the $S = 1/2$ at lower temperature. To our knowledge, this is the first example of the iron(III) porphyrinoid showing the $S = 3/2$ in spite of the bis-coordination of imidazole ligands; all the bis(1-MeIm) and bis(HIm) complexes of porphyrins and porphyrinoids reported previously adopt the low-spin state. The weak equatorial field strength caused by the wide N4 cavity with a large pyridine unit and the presence of the electron-withdrawing carbonyl group should stabilize the $S = 3/2$. The structural and theoretical studies are now in progress in this laboratory to elucidate the anomaly.

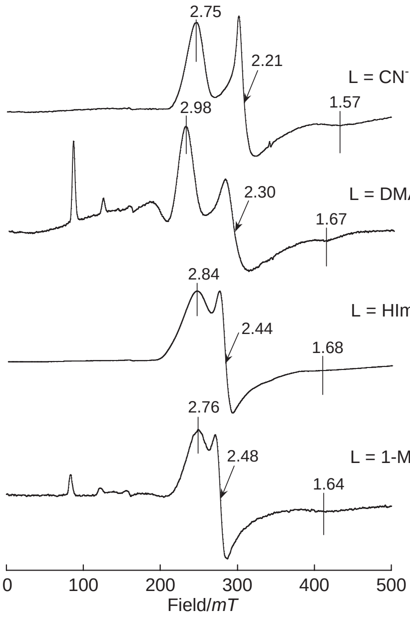


Figure 3. EPR spectra of **1**–**4** taken in frozen CH_2Cl_2 solutions at 4.2 K.

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References and Notes

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