Iodo(etiohemiporphycenato)iron(III). Unexpected Difference in Magnetic Behavior in Solution and Solid

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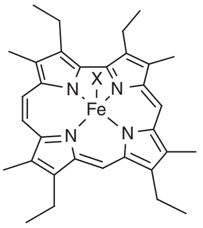
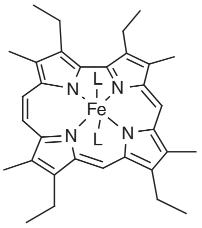
Although iodo(etiohemiporphycenato)iron(III) showed an admixed intermediate-spin state ($S = 3/2$, $5/2$) with a major contribution of $S = 3/2$ in solution, the same complex exhibited the high-spin state ($S = 5/2$) in the solid phase. Importance of the crystal packing has been pointed out for the formation of the high-spin complex in the solid.

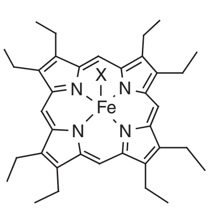
Porphyrin isomers such as porphycene (Pc), corrphycene (Cn), and hemiporphycene (Hpc) have attracted much attention because of their characteristic molecular structures.[1] The central cavities surrounded by the four nitrogen atoms are quite different among Pc, Cn, and HPc; they are rectangular, trapezoidal, and quadrilateral, respectively. Thus, each macrocycle serves a unique ligand field to the central metal ion, which could in turn give unique physicochemical properties to the metal complexes different from those of the corresponding porphyrin (P) complexes.[2,3] Among the porphyrin isomers, Hpc is quite peculiar because the macrocycle possesses four nonequivalent nitrogen atoms. Thus, the d-orbitals of Hpc complexes could split differently to form the complexes with unique electronic structure. Although several groups have reported the synthesis and characterization of Hpc and its metal complexes,[4–8] little is known on the physicochemical properties of the iron complexes. Here, we report the spin states of 5- and 6-coordinated (etiohemiporphycenato)iron(III) complexes, **1**–**5**, both in solution and in the solid.[9] We also report the X-ray molecular structures of **4** and the analogous porphyrin complex(**6**).



[Fe(EtioHPc)X]
X = F(**1**), Cl(**2**), Br(**3**), I(**4**)



[Fe(EtioHPc)L$_2$]ClO$_4$
L = THF(**5**)



[Fe(OEP)X]
X = I(**6**)

(EtioHpc)H$_2$ was synthesized from 3,3′-diethyl-5′-formyl-4,4′-dimethyl-2,2′-dipyrrylmethane and 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyl-2,2′-bipyrrole.[5,10] Insertion of iron followed by the HCl treatment afforded **2**, which was further converted to the corresponding μ-oxo-dimer. Complexes **1**, **3**, and **4** were prepared by the cleavage of the μ-oxo-dimer with HClO$_4$ in the presence of the corresponding potassium halides. **5** was prepared by addition of AgClO$_4$ to a THF solution of **2** followed by the recrystallization from CH$_2$Cl$_2$/THF solution.

Figure 1 shows the molecular structures of **4** and **6** determined by X-ray crystallographic analysis.[11,12] Because **4** is a chiral complex, the crystals are racemic; both the enantiomers are placed as a pair around the center of symmetry. Table 1 lists the selected structural data of **4** and **6** together with those of some relevant complexes.[3,12] In the previous paper, we have pointed out that the essentially pure intermediate-spin ($S = 3/2$) complexes are characterized by the narrower cavity and smaller iron displacement, ΔFe, than the high-spin ($S = 5/2$) complexes.[3] The data in Table 1 indicate that the cavity size and ΔFe value are the smallest in the $S = 3/2$ complex, Fe(EtioPc)I, and increase in the following order:

[Fe(EtioPc)I] $<$ [Fe(EtioCn)I] $\leq$ [Fe(EtioHpc)I] (**4**) $<$
[Fe(EtioP)I], [Fe(TPP)I], [Fe(OEP)I] (**6**).[3]

Since [Fe(EtioCn)I] has been characterized as a high-spin complex, it is reasonable to consider that **4** is also a high-spin complex from the X-ray crystallographic point of view. To further examine the spin states of **4** and **6** in the solid, we have measured the effective magnetic moments(μ_{eff}) by SQUID magnetometry over 2–300 K. Complexes **4** and **6** are high-spin be-

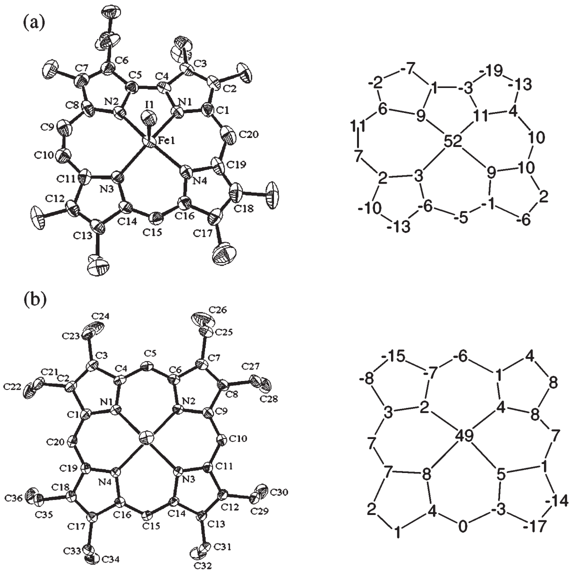


Figure 1. Molecular structures of (a) **4** and (b) **6**. Left: ORTEP drawings, right: perpendicular displacements of each atom from the least-squares plane of peripheral 24 atoms.

Table 1. Some structural data

Complexes	Fe–N_p /Å	Fe–X /Å	Cavity area /Å^2	ΔFe /Å	Spin state^a	Ref
Fe(TPP)I	2.07	2.55	8.123	0.459	5/2(5/2)	12
Fe(EtioP)I	2.061(7)	2.617(1)	8.094	0.454(4)	5/2(5/2)	3
Fe(EtioCn)I	2.034(2) 2.056(2)	2.615(1)	7.897	0.387(1)	5/2(5/2)	3
Fe(EtioPc)I	1.956(3)	2.664(1)	7.355	0.343(2)	3/2(3/2)	3
Fe(EtioHpc)I(**4**)	2.042(4) 2.039(5) 2.051(4) 2.050(5)	2.618(1)	7.882	0.438(2)	5/2(3/2)	b
Fe(OEP)I(**6**)	2.068(2)	2.610(1)	8.151	0.466(1)	5/2(5/2)	b

^{a} Spin state in the solid. Spin state in solution is given in the parenthesis.
^{b} This work.

cause the μ_{eff} values are 5.5–5.9 μ_B above 30 K. The Mössbauer spectra have also suggested that these complexes are high spin at 77 K; the *IS* and *QS* values are 0.39 and 1.34 mm s^{-1} for **4** and 0.43 and 1.10 mm s^{-1} for **6**, respectively. It should be noted that the Mössbauer spectra of **4** contain ca. 20% of **2**; the *IS* and *QS* values of **2** are 0.36 and 0.58 mm s^{-1}, respectively, at 77 K.

The spin states of **1**–**6** have then been examined in solution. The ^{1}H NMR spectra of **1**–**4** were fairly complicated because these complexes have four nonequivalent methyl and ethyl groups. The μ_{eff} values determined by the Evans method in CH_2Cl_2 solution at 298 K were 5.4, 4.5, 4.1, and 5.3 μ_B for **2**, **4**, **5**, and **6**, respectively. The results suggest that, while **2** and **6** are in the $S = 5/2$ state with minor contribution of $S = 3/2$, **4** and **5** are in the $S = 3/2$ state with minor contribution of $S = 5/2$. The slightly larger μ_{eff} value of **4**, 4.5 μ_B, could be the result of contamination of high-spin **2** as is revealed from the Mössbauer result. We have then examined the EPR spectra in frozen CH_2Cl_2–toluene solution at 4.2 K. The EPR spectra of **1**, **3**, and **4** exhibited the hyperfine coupling with the axial ligands, indicating explicitly that F^-, Br^-, and I^- actually bind to the iron. The *g* values are as follows; **1**: $g_x = g_y = 5.86$, $g_z = 2.03$; **2**: $g_x = g_y = 5.80$, $g_z = 2.00$; **3**: $g_x = 6.09$, $g_y = 5.80$, $g_z = 2.00$; **4**: $g_x = g_y = 4.24$, $g_z = 2.00$; **5**: $g_x = 4.92$, $g_y = 3.84$, $g_z = 1.97$; **6**: $g_x = g_y = 5.80$, $g_z = 1.96$. Consistent with the Mössbauer result, the EPR spectrum of **4** showed contamination of **2**. Nevertheless, the EPR *g* values clearly indicate that **4** and **5** adopt mainly the $S = 3/2$ state while **1**, **2**, **3**, and **6** exhibit $S = 5/2$.

The question arises as to why the spin state of **4** in solution is different from that in the solid. One possible reason for this anomaly is an extraordinarily labile nature of the iodide ligand in **4**. In fact, we found that **4** was completely converted to **2** by addition of 1.0 equiv. of $Bu_4N^+Cl^-$. By contrast, only 40% of **6** was converted to [(OEP)FeCl] under the same condition. The results suggest that the coordination of iodide ion to the iron in **4** must be much weaker than that in **6**. As a result, the iron is dragged toward the N4 cavity and, consequently, the complex adopts the intermediate-spin state in solution.[13–15] In the crystal lattice, however, the packing force could contract the labile Fe–I bond. Therefore, the iron is lifted toward the iodide ion, resulting in the formation of a typical high-spin 5-coordinated structure. The hypothesis mentioned above is supported by the fact that the Fe–I bond length in **4** is shorter by 0.046 Å while the ΔFe is longer by 0.095 Å than the corresponding values in [Fe(EtioPc)I]. On the basis of these results, we have concluded that the crystal packing is one of the important factors for the formation of the high-spin complex in the solid.

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9 Abbreviations: EtioPc, TPrPc, EtioHpc, OEP, TPP; dianions of 3,6,13,16-tetraethyl-2,7,12,17-tetramethylporphycene, 2,7,12,17-tetrapropylporphycene, 3,6,13,17-tetraethyl-2,7,12,18-tetramethylhemiporphycene, 2,3,7,8,12,13,17,18-octaethylporphyrin, and 5,10,15,20-tetraphenylporphyrin, respectively.

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11 *Crystallographic details:* Pure crystals of **4** and **6** were obtained from the $CHCl_3$ solutions. *Crystal data* for **4** ($FeC_{33}H_{37}Cl_3N_4I$, $M = 778.77$) were collected on Rigaku RAXIS-RAPID Imaging plate diffractometer at 298 K with MoKα radiation (λ = 0.71069 Å). Crystal system, triclinic; Space group, *P*-1(#2); $a = 9.430(1)$, $b = 13.089(1)$, $c = 14.392(1)$ Å, $\alpha = 115.73(1)$, $\beta = 106.72(1)$, $\gamma = 90.69(1)°$, $V = 1513.2(2)$ Å^3, $Z = 2$. A total 13614 reflections were collected and of 6591 unique reflections 4679 ($I > 2\sigma(I)$) were used. Final R factors were $R1 = 0.070$(observed data) and $wR2 = 0.209$ (all data); CCDC reference number 200304. *Crystal data* for **6** ($FeC_{37}H_{45}Cl_3N_4I$, $M = 834.87$) were collected similarly as in the case of **4**. Crystal system, triclinic; Space group, *P*-1(#2); $a = 10.342(2)$, $b = 13.846(2)$, $c = 14.815(3)$ Å, $\alpha = 71.12(1)$, $\beta = 83.80(1)$, $\gamma = 76.42(1)°$, $V = 1950.0(6)$ Å^3, $Z = 2$. A total 15664 reflections are collected and of 8691 unique reflections 7061 ($I > 2\sigma(I)$) were used. Final *R* factors were $R1 = 0.070$ and $wR2 = 0.209$ (all data). CCDC reference number 200305.

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