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Highly saddle shaped (porphyrinato)iron(III) iodide with a pure intermediate spin state

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Combined analyses using NMR, EPR and Mössbauer spectroscopy as well as SQUID magnetometry have revealed that highly saddle shaped Fe(OETPP)I adopts an essentially pure intermediate spin state in spite of the coordination of an iodide ligand.

Spin states of five-coordinated iron(III) porphyrin complexes are controlled by the ligand field strength of axial ligands.[1] While most of the anionic ligands such as halides and hydroxide lead to the formation of the complexes with high-spin (S = 5/2) state, extremely weak ligands such as ClO_4^- and SbF_6^- give the complexes with admixed (S = 3/2, 5/2) spin state.[2] We have recently reported that six-coordinated iron(III) porphyrin complexes such as $[Fe(OETPP)(4\text{-}CNPy)_2]ClO_4$ and $[Fe(OETPP)(THF)_2]ClO_4$ are in an essentially pure intermediate-spin (S = 3/2) state at ambient temperature because of the presence of highly saddle shaped porphyrin rings.[3–5] Fajer and coworkers have also reported that five-coordinated $Fe(OETPP)ClO_4$ is an essentially pure S = 3/2 complex on the basis of the EPR and crystallographic studies.[6] We thus expected that even five-coordinated iron(III) halides such as Fe(OETPP)I could show the S = 3/2 spin state though the analogous Fe(OETPP)Cl is reported to be in the S = 5/2 spin state with only a small amount of the S = 3/2 spin admixture.[7] Here, we report the spin states of a series of saddle shaped complexes, **1**–**4**, on the basis of the spectroscopic and magnetic results. We also report that Fe(OETPP)I is the first example of the five-coordinated (porphyrinato)iron(III) halide that has an essentially pure intermediate spin state.

Complex **2** was prepared according to the literature,[8,9] and was converted to [Fe(OETPP)(OH)] by treatment with aqueous KOH. **1**, **3** and **4** were prepared by the addition of perchloric acid to the CH_2Cl_2 solutions of [Fe(OETPP)(OH)] in the presence of KF, KBr and KI, respectively. ^1H NMR chemical shifts of these complexes exhibit some differences depending on the axial halides as listed in Table 1; the *ortho* and *para* signals move downfield while the *meta* signals shift upfield on going from **1** to **4**. Because the pure intermediate spin complexes such as $[Fe(OETPP)(4\text{-}CNPy)_2]ClO_4$ and $[Fe(OETPP)(THF)_2]ClO_4$ are characterized by downfield shifted *ortho* and *para* signals together with a slightly upfield shifted *meta* signal, the ^1H NMR results are indicative of the change in spin state from S = 5/2 to S = 3/2 as the axially coordinated F^- is replaced by Cl^-, Br^- and then by I^-. To obtain much conclusive evidence for the spin state, the EPR spectra were measured in frozen CH_2Cl_2 solution at 4.2 K as shown in Fig. 1. The g values listed in Table 1 are determined by the computer simulation of the observed spectra.[10] In the case of **4**, hyperfine coupling with axially coordinated iodide, 49 G, is clearly observed for the signal at g = 2. The contributions of the S = 3/2 spin state in the admixed S = 3/2, 5/2 system can be estimated as $(6 - g_\perp)/2$,[11] which are calculated to be 5.0, 4.3, 89 and 94% for **1**, **2**, **3** and **4**, respectively. Thus, the EPR results clearly indicate that, while **1** and **2** are in the S = 5/2 with a small amount of the S = 3/2 spin admixture, **3** and **4** have S = 3/2 with a small amount of the S = 5/2 spin admixture.

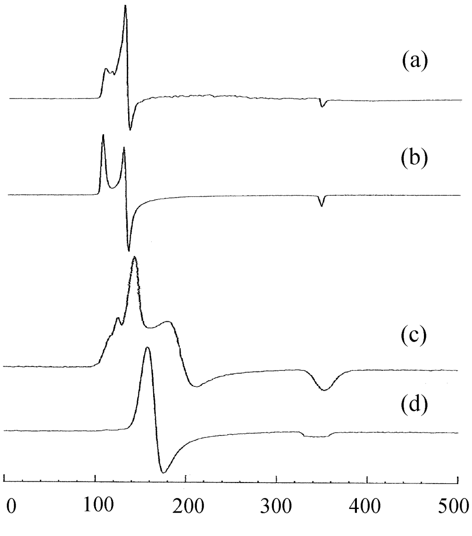

Fig. 1 EPR spectra of (a) **1**, (b) **2**, (c) **3** and (d) **4** taken in frozen CH_2Cl_2 solutions at 4.2 K.

Table 1 ^1H NMR chemical shifts and EPR g values

	^1H NMR (CD_2Cl_2, 298 K)					EPR (CH_2Cl_2, 4.2 K)		
Complexes	CH_2	CH_3	*o*	*m*	*p*	*g* values		
[Fe(TPP)Cl][a]	—	—	3.8, 6.2	12.0, 12.6	5.8	6.0	6.0	2.0
[Fe(OETPP)F] (**1**)	24.1, 35.4, 38.4, 45.0	1.6, 3.7	8.1, 10.6	12.9, 13.1	7.0	6.50	5.30	2.00
[Fe(OETPP)Cl] (**2**)[a]	20.1, 32.1, 34.8, 49.0	1.8, 3.2	9.1, 11.5	12.2, 12.4	7.5	6.56	5.27	1.97
[Fe(OETPP)Br] (**3**)	18.1, 32.6, 34.3, 45.8	1.0, 2.3	10.4, 13.5	11.7, 12.2	8.4	4.95	3.50	1.95
[Fe(OETPP)I] (**4**)	11.9, 29.3, 32.1, 47.3	0.4, 0.9	12.6, 15.8	10.3, 10.8	9.6	4.14	4.14	2.00
$[Fe(OETPP)(L^1)_2]^+$ [b]	16.2, 42.6	−0.7	14.0	5.31	2.0	4.28	3.80	2.08
$[Fe(OETPP)(L^2)_2]^+$ [c]	14.2, 43.1	0.7	13.0	6.5	9.7	4.01	4.01	2.00

[a] NMR data cited from ref. 19. [b] L^1 = 4-CNPy; ref. 4. [c] L^2 = THF; ref. 5.

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Fig. 2 shows the Mössbauer spectrum of **4** taken for a microcrystalline sample at 77 K. The IS and QS values are 0.42 and 3.05 mm s^{-1}, respectively. The large QS value indicates that the complex is either in the pure S = 3/2 or in the admixed S = 3/2, 5/2 spin state;[12] the IS and QS values for the pure S = 3/2 complex [Fe(OETPP)(THF)$_2$]ClO$_4$ are 0.50 and 3.50 mm s^{-1}, respectively, at 80 K.[5] To further confirm the spin state of **4**, the effective magnetic moments (μ_{eff}) were measured in the temperature range 2–300 K by SQUID magnetometry. As shown in Fig. 3, the μ_{eff} values are 3.8–3.9 μ_{B} in a wide range of temperature, which are quite close to the spin-only value, 3.87 μ_{B}, expected for the S = 3/2 state. On the basis of the spectroscopic and magnetic results, we have concluded that **4** is an essentially pure intermediate spin complex.

Formation of the very pure intermediate spin complex **4** could be explained in terms of the short Fe–N$_{\text{p}}$ bond lengths expected for the strongly S$_4$ saddled OETPP core.[4–9,13] The short Fe–N$_{\text{p}}$ bond length is the general condition for the iron(III) ions in porphyrins and porphyrin isomers to have an intermediate spin state. In fact, we have reported that both [Fe(T$^{\text{i}}$PrP)(THF)$_2$]$^+$ and [Fe(TPrPc)(THF)$_2$]$^+$ have an essentially pure S = 3/2 spin state;[5,14] the former has short Fe–N$_{\text{p}}$ bonds due to the strongly S$_4$ ruffled porphyrin ring,[15,16] and the latter is supposed to have short Fe–N$_{\text{p}}$ bonds because of the intrinsic nature of the porphycene core. Thus, even five-coordinated Fe(etioPc)Cl is in the admixed S = 3/2, 5/2 spin state as is revealed from the magnetic and structural measurements.[17] The results are consistent with the proposal given by Reed and Guiset that the increased tetragonality of the macrocycle shift high spin complexes into the admixed intermediate spin regime.[2] In addition to the short Fe–N$_{\text{p}}$ bonds, the S$_4$ saddling of the core could further raise the energy levels of the d$_\pi$ orbitals due to the strong iron (d$_\pi$)–porphyrin (p$_\pi$) interactions caused by the effective overlap of these orbitals.[18] Thus, the energy gap between the d$_{z^2}$ and d$_\pi$ orbitals decreases as the porphyrin core deforms. Under this situation, if the axially coordinated halide ligand changes from F$^-$ and Cl$^-$ to Br$^-$, and then to I$^-$, the energy level of the d$_{z^2}$ orbital continues to drop to form the pure S = 3/2 spin state in the iodide complex. In conclusion, we have shown that even five-coordinated (porphyrinato)iron(III) complexes carrying an iodide ligand can be in an essentially pure intermediate spin state if the porphyrin cores are strongly S$_4$ saddled.

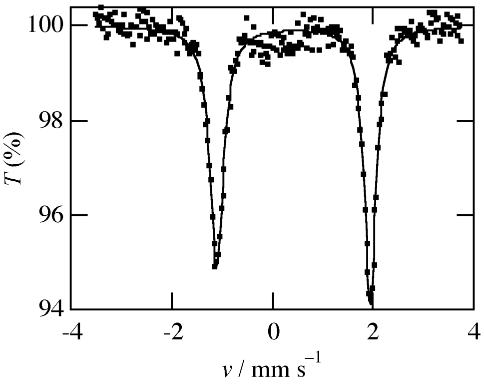

Fig. 2 Mössbauer spectrum of **4** taken at 77 K.

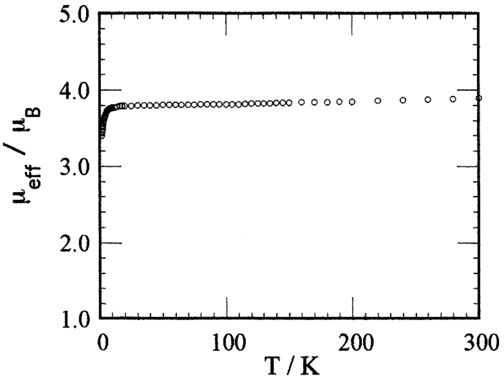

Fig. 3 Temperature dependence of the effective magnetic moments of **4**.

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3 Abbreviations: OETPP, TPrPc, and etioPc; dianions of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, 2,7,12,17-tetrapropylporphycene, and 3,6,13,16,-tetraethyl-2,7,12,17-tetramethylporphycene, respectively. 4-CNPy; 4-cyanopyridine.
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