Novel spin transition between $S = 5/2$ and $S = 3/2$ in highly saddled iron(III) porphyrin complexes at extremely low temperatures†

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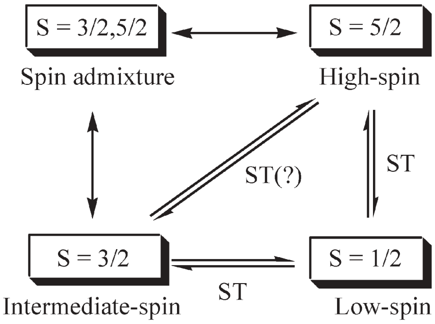
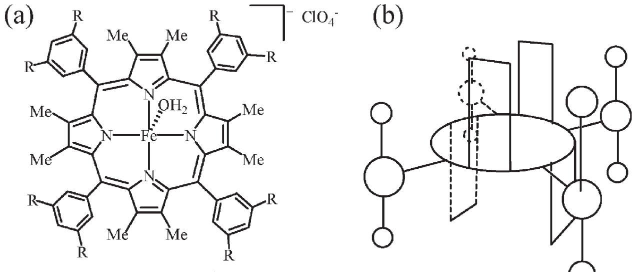
A novel spin transition between $S = 5/2$ and $S = 3/2$ has been observed for the first time in five-coordinate, highly saddled iron(III) porphyrinates by EPR and SQUID measurements at extremely low temperatures.

A wide variety of research has been carried out on the spin transition in naturally occurring heme proteins because of their relevance to the important functional tuning process.[1] For example, the ferrihemes in cytochrome P450 adopt the low-spin ($S = 1/2$) in the resting state. However, the spin transition to the high-spin state ($S = 5/2$) occurs on binding the organic substrate, which triggers the one-electron reduction to proceed the catalytic oxidation reaction.[2] The spin transition between $S = 5/2$ and $S = 1/2$ has also been studied in model complexes such as $[Fe(OEP)(3\text{-}ClPy)_2]^+$.[3,4] In contrast to high-spin and low-spin states, the intermediate-spin state ($S = 3/2$) is quite rare.[5] Reed and Guiset reported that [Fe(TPP)]X is in an essentially pure intermediate-spin state if the axial anionic ligand X is extremely weak, $[Ag(Br_6CB_{11}H_6)_2]^-$.[6] Ourselves and others have also reported that highly saddled porphyrins such as $[Fe(OETPP)L_2]ClO_4$, and core-contracted porphycenes and corroles such as $[Fe(TPrPc)L_2]ClO_4$ and $[Fe(TPFC)L_2]$ adopt a quite pure intermediate-spin state if the field strengths of the axial ligands are fairly weak.[7] Furthermore, the saddled complex with a much stronger pyridine (Py) ligand, $[Fe(OETPP)(Py)_2]^+$, exhibits a novel spin transition between $S = 3/2$ and $S = 1/2$.[8] Occurrence of a similar spin transition has recently been reported by Rivera and Caignan in the heme metabolism process mediated by human heme oxygenase.[9] While the spin transitions between $S = 5/2$ and $S = 1/2$, and between $S = 3/2$ and $S = 1/2$ have been observed both in heme proteins and model heme complexes, the spin transition between $S = 5/2$ and $S = 3/2$ has never been observed before. In fact, the mixed $S = 5/2$ and $S = 3/2$ spin state is considered to be a quantum mechanical spin admixture caused by the spin–orbit coupling between $S = 3/2$ and $S = 5/2$ states (Scheme 1).[10] In the course of our studies on the spin transition in highly saddled complexes, we found that structurally similar complexes $[Fe(OMTArP)(H_2O)]ClO_4$ (**1** and **2**), shown in Scheme 2, serve an unprecedented example showing the spin transition between $S = 3/2$ and $S = 5/2$ spin states.



Scheme 1 Possible spin transitions (ST) in iron(III) porphyrinates.



1: R = Me, **2**: R = ^{t}Bu
$[Fe(OMTArP)(H_2O)]ClO_4$

Scheme 2 (a) Complexes **1** and **2** examined in this study, and (b) a schematic drawing of them.

Complexes **1** and **2** were prepared by the condensation reactions between 3,4-dimethylpyrrole and 3,5-dimethylbenzaldehyde/3,5-di-*tert*-butylbenzaldehyde, followed by the insertion of iron using $FeCl_2 \cdot 4H_2O$ in DMF, and then by the addition of a benzene solution of $AgClO_4$.[11] ^1H NMR (CD_2Cl_2, 298 K): **1** $\delta = 60.1$ (pyrrole-CH_3), 3.78 (*meta*-CH_3), 11.7 (*ortho*-H) and 9.17 (*para*-H); **2** $\delta = 60.4$ (pyrrole-CH_3), 11.7 (*ortho*-H) and 9.12 (*para*-H). The large downfield shift of the pyrrole-CH_3, as well as of the *ortho*- and *para*-H signals, suggests that these complexes are in the intermediate-spin state at ambient temperature.[12]

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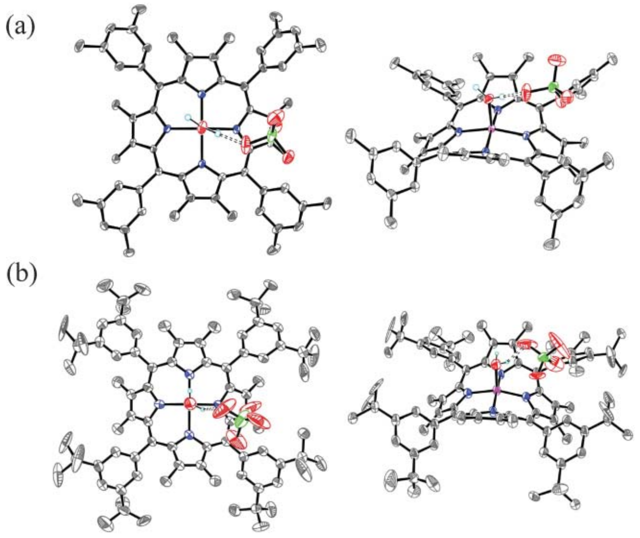

Fig. 1 Molecular structures of (a) **1** and (b) **2**. Ellipsoids are colored in grey (carbon), blue (nitrogen), red (oxygen), green (chlorine), cyan (hydrogen) and magenta (iron). Hydrogen bonds are shown as dotted lines.

Table 1 Comparison of various geometric parameters in five-coordinated saddle-shaped iron(III) porphyrin complexes

Complex	$Fe–N_p$/ Å^a	$Fe–X_{ax}$/ Å^b	ΔFe/ Å^c	N4 area/ Å^{2d}	S^e	Ref.
1	1.946(4)	2.084(4)	0.285(2)	7.45	$3/2$	This work
2	1.960(2)	2.056(2)	0.232(1)	7.59	$3/2$	This work
Fe(OMTPP)Cl	2.034	2.247	0.464	7.87	$5/2$	15
Fe(OETPP)Cl	2.030	2.242	0.467	7.83	$5/2$	15
$Fe(OETPP)ClO_4$	1.963	2.059	0.262	7.59	$3/2$	7*b*

[a] Bond length between the iron and the pyrrole nitrogen. [b] Bond length between the iron and the axial ligand. [c] Out-of-plane deviation of the iron(III) ion from the N_4 plane. [d] The area of the plane consisting of the four nitrogen atoms of the pyrrole rings. [e] Spin state at ambient temperature.

At first, we expected that the complexes obtained should be $[Fe(OMTArP)]ClO_4$. However, the X-ray crystallographic analysis shown in Fig. 1 has revealed that both **1** and **2** are highly saddled five-coordinated mono(aqua) complexes.[13,14] Fig. 2 shows the perpendicular displacement of the peripheral carbon atoms. The maximum deviations from the least-squares plane are 1.32–1.35 Å, which are seen in the pyrrole β-carbons for both complexes. Thus, these complexes can be classified into the group of those that have a severely saddled porphyrin ring.[16] Table 1 lists some geometric parameters of **1** and **2**, together with those of some analogous complexes.

Temperature dependent EPR spectra of **1** and **2** have been acquired both in frozen CH_2Cl_2 solution and in the solid state. Parts of them are given in Fig. 3. Each complex shows a similar spectral change in both solution and the solid state. The EPR spectra at 4 K exhibit two types of signals characteristic of high-spin and intermediate-spin species.[17] The g values, determined by computer simulations of the observed spectra, are as follows: **1**, 6.10, 5.90, 2.00 ($S = 5/2$), and 4.20, 3.80, 2.10 ($S = 3/2$); **2**, 6.10, 5.90, 2.00 ($S = 5/2$), and 4.37, 3.77, 1.99 ($S = 3/2$). To our great surprise, the signal intensities for the intermediate-spin species increased while those for the high-spin species decreased as the temperature was raised. Thus, both **1** and **2** exist exclusively as the intermediate-spin species above 70 K. This process turns out to be reversible because the original spectra were observed when the temperature was lowered back to 4 K. The temperature dependence of the EPR spectra could best be explained in terms of the spin transition between $S = 5/2$ and $S = 3/2$. It should be noted that, while **2** shows an almost complete spin transition between $S = 3/2$ and $S = 5/2$, **1** exists mainly as the intermediate-spin species throughout the temperature range examined. The population of each species has been determined by computer simulation of the observed spectra. The van't Hoff plots yield ΔH° and ΔS° values, corresponding to the equilibrium given in (eqn. 1), of 60 J mol^{-1} and 48 J mol^{-1} K^{-1} for **1**, and 100 J mol^{-1} and 19 J mol^{-1} K^{-1} for **2**, respectively.

$$\text{high-spin} \xrightleftharpoons{K} \text{intermediate-spin} \qquad (1)$$

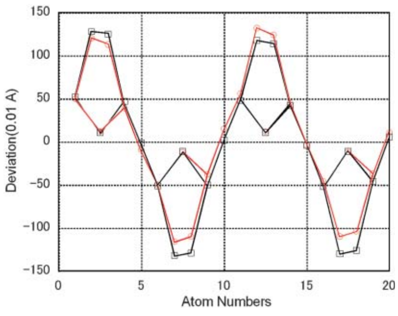

Fig. 2 Perpendicular displacement of 24 peripheral atoms from the N4 mean plane: ○(red), **1**; □(black), **2**.

Fig. 4 shows the correlation of magnetic susceptibility (χ) with $1/T$.

The curved line of **1** almost coincides with that of intermediate-spin Fe(EtioPc)I at higher temperature when $1/T$ is less than 0.05 (or T is higher than 20 K).[18] As $1/T$ becomes larger than 0.05 (or T is lower than 20 K), it starts to deviate from the curved line of Fe(EtioPc)I and approaches that of high-spin Fe(OEP)I. Complex **2** exhibits a similar behavior. These results suggest that the spin transition takes place from the $S = 3/2$ to the $S = 5/2$ state as the temperature is lowered below 20 K.

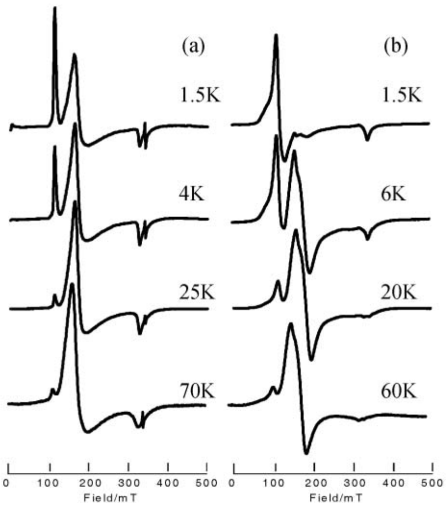

Fig. 3 EPR spectra of (a) **1** taken in frozen CH_2Cl_2 solution and (b) **2** taken in the solid state at various temperatures.

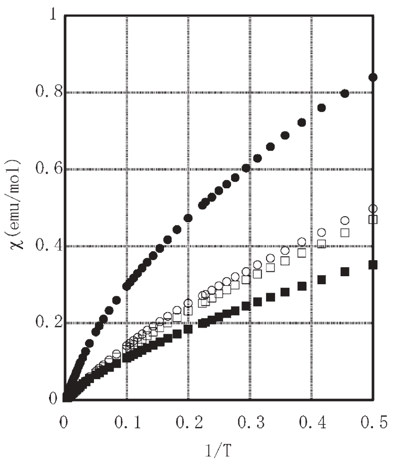

Fig. 4 Correlations between magnetic susceptibility (χ) and inverse temperature ($1/T$). ○, **1**; □, **2**; ●, Fe(OEP)I; ■, Fe(EtioPc)I.

The novel spin transition described above should be ascribable to the unique molecular and crystal structures of **1** and **2**. The data in Table 1 indicate that the out-of-plane deviations of the iron(III) ion, which are signified as ΔFe, are quite different from other saddle-shaped complexes. While the ΔFe values of high-spin complexes are 0.46–0.47 Å, they are only 0.23–0.29 Å in the intermediate-spin complexes. As the temperature is lowered, the unit cell volume is expected to shrink.[19] As **1** and **2** have highly saddled structures with bulky substituents at the porphyrin periphery, as illustrated in Scheme 2, the shrinkage of the unit cell could directly affect each molecule from the lateral side. As a result, the narrow N4 cavities of **1** and **2** could further decrease at extremely low temperature, which could extrude the iron(III) ion away from the N4 plane. The large out-of-plane displacement of the iron(III) ion could stabilize the $d_{x^2-y^2}$ orbital and induce spin transition from the $S = 3/2$ to the $S = 5/2$ state. Needless to say, the X-ray analysis of these complexes at extremely low temperature is clearly necessary to prove the above hypothesis. This now in progress in our laboratory.

In summary, we have found a spin transition between high-spin and intermediate-spin states by EPR spectroscopy and SQUID magnetometry for the first time.

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3 Abbreviations: OEP, TPP, OETPP, TPrPc, TPFC and EtioPc: dianions of 2,3,7,8,12,13,17,18-octaethylporphyrin, 5,10,15,20-tetraphenylporphyrin, 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, 2,7,12,17-tetrapropylporphycene, 5,10,15-tris(pentafluorophenyl)corrole and 3,6,13,16-tetraethyl-2,7,12,17-tetramethylporphycene, respectively. 3-ClPy: 3-chloropyridine.

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12 (*a*) T. Ikeue, Y. Ohgo, O. Ongayi, M. G. H. Vicente and M. Nakamura, *Inorg. Chem.*, 2003, **42**, 5560; (*b*) SQUID magnetometry has revealed that the effective magnetic moments for **1** and **2** at 300 K are 3.71 μ_B and 3.82 μ_B, respectively.

13 Crystal and molecular structural data for **1**: $C_{60}H_{62}ClFeN_4O_5$, M = 1010.44, orthorhombic, a = 14.4113(3), b = 16.9296(4), c = 21.1176(5) Å, V =5152.2(2) Å^3, T = 110 K, space group $P2_12_12_1$ (no. 19), Z = 4, μ(Mo-K$_\alpha$) = 0.324 mm^{-1}, 53820 reflections measured, 18104 unique ($R_{\rm int}$ = 0.0787) which were used in all calculations. $R(F)$ = 0.0631 ($I > 2\sigma(I)$), 0.0891(all data), $wR(F^2)$ = 0.156 ($I > 2\sigma(I)$), 0.166 (all data), goodness of fit S = 0.941. CCDC 297040. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601412g. Diffraction data were collected on a Rigaku MERCURY CCD system installed on the NW2 beam line of the Advanced Ring (AR), the Photon Factory (PF) of the High Energy Accelerator Research Organization (KEK) using a 18.00 keV (λ = 0.68878 Å) monochromatized X-ray beam.

14 Crystal and molecular structural data for **2**: $C_{85}H_{112}Cl_3FeN_4O_5$, M = 1415.94, triclinic, a =15.160(4), b = 15.846(4), c = 18.698(5) Å, α = 68.533(7), β = 79.192(9), γ = 83.227(9)°, V = 4100(2) Å^3, T = 298 K, space group P-1 (no. 2), Z = 2, μ(Mo-K$_\alpha$) = 0.331 mm^{-1}, 58762 reflections measured, 17675 unique ($R_{\rm int}$ = 0.16) which were used in all calculations. $R(F)$ = 0.131 ($I > 2\sigma(I)$), 0.22 (all data), $wR(F^2)$ = 0.33 ($I > 2\sigma(I)$), 0.38 (all data), goodness of fit S = 1.039. CCDC 297041. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601412g.

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