

Formation of pure intermediate spin complexes in highly nonplanar iron(III) porphyrins

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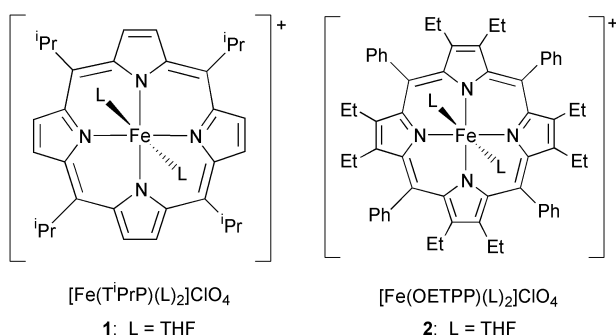
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Bis(thf)(porphyrinato)iron(III) complexes with highly S_4 -ruffled and S_4 -saddled porphyrin cores are determined to be very pure intermediate spin complexes on the basis of NMR, EPR, Mössbauer, and magnetic data.

Iron(III) porphyrins with an intermediate spin state ($S = 3/2$) have attracted much attention since Maltempo pointed out the important contribution of this spin state in certain bacterial heme proteins known as cytochromes c' .¹ Among various attempts to prepare complexes with the intermediate spin state, the use of anionic ligands with a very weak ligand field, such as ClO_4^- , has brought about successful results.^{2–5} In general, iron(III) ions of these complexes are in the admixed intermediate spin state represented as $S = 5/2, 3/2$.⁶ Thus, Reed and Guiset ranked the relative field strengths of weak axial ligands on the basis of the characteristics of the admixed spin state and called the hierarchy a magnetochemical series.⁷ Cheng and coworkers reported that highly saddle shaped $[\text{Fe}(\text{OETPP})\text{Cl}]$ is in the admixed $S = 5/2, 3/2$ spin state in spite of the presence of the much stronger chloride ligand at the axial position.^{8,9} Weiss and coworkers quite recently reported, however, that the $S = 3/2$ character in these complexes is much smaller than originally reported.¹⁰ We have been interested in the effects of nonplanar porphyrin rings on the physicochemical properties of iron(III) porphyrin complexes.^{11–13} We have anticipated that the iron(III) complexes of highly nonplanar porphyrins such as $[\text{Fe}(\text{T}^i\text{PrP})(\text{THF})_2]\text{ClO}_4$ (**1**) and $[\text{Fe}(\text{OETPP})(\text{THF})_2]\text{ClO}_4$ (**2**)



could show a very pure intermediate spin state as compared with well characterized $[\text{Fe}(\text{TPP})(\text{THF})_2]\text{ClO}_4$, since the $d_{x^2-y^2}$ orbitals in the deformed porphyrin complexes are destabilized by the short Fe–N bond lengths.^{8,13} In this paper, we report that strongly S_4 -ruffled **1** and S_4 -saddled **2** actually show very pure intermediate spin states.

1 was prepared from AgClO_4 and $[\text{Fe}(\text{T}^i\text{PrP})\text{Cl}]$ in THF solution. The purple crystals were recrystallized from THF/heptane. The ^1H NMR spectrum taken at 233 K showed the pyrrole signal at -52.1 ppm and the CH and CH_3 signals at 9.8 and 4.8 ppm, respectively. Two signals at 14.4 and 20.5 ppm,

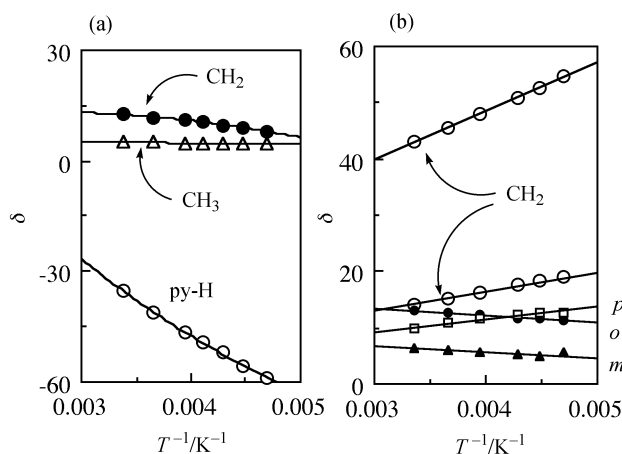


Fig. 1 Temperature dependence of the ^1H NMR chemical shifts of some protons in (a) **1** and (b) **2** taken in CD_2Cl_2 solution.

each corresponding to 8H, were assigned to the methylene protons of the coordinated THF ligands; these signals disappeared when the sample recrystallized from THF-d_8 /heptane was used. Fig. 1a shows the temperature dependence of the chemical shifts of some protons. The existence of the extremely upfield shifted pyrrole signal indicates that **1** is in the admixed intermediate ($S = 3/2, 5/2$) spin state where the $S = 3/2$ state is the main contributor.⁷ The downfield shift of the THF signals can be explained in terms of the occupancy of an unpaired electron in the d_{z^2} orbital; the unpaired electron in this orbital is transferred to the axial ligand *via* σ bonding to induce downfield shifts of the ligand signals. Fig. 2a shows the EPR spectrum taken in frozen CH_2Cl_2 solution at 4.2 K. The g values were

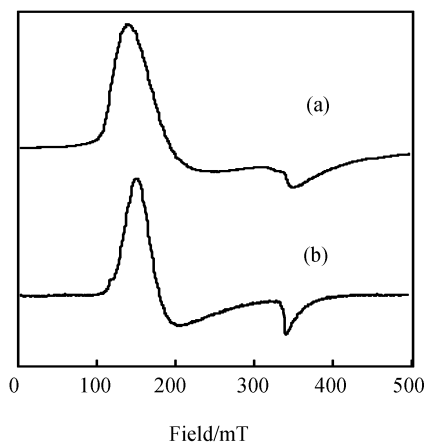


Fig. 2 EPR spectra of (a) **1** and (b) **2** taken in frozen CH_2Cl_2 solution at 4.2 K.

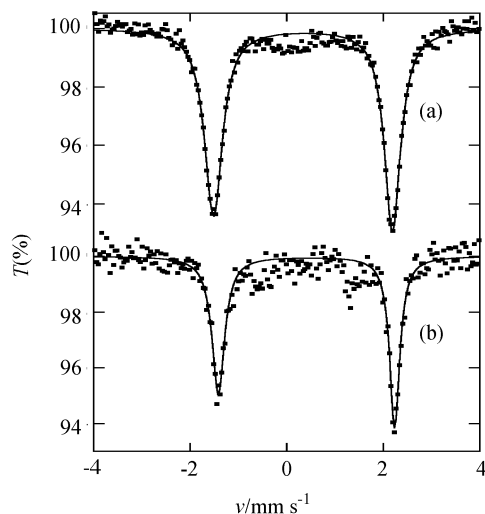


Fig. 3 Mössbauer spectra of (a) **1** taken at 76 K and (b) **2** taken at 290 K.

estimated to be 3.99 and 1.97, suggesting that the spin state of **1** should be regarded as $S = 3/2$ at 4.2 K. Magnetic moments taken for the solid sample by SQUID showed almost constant values, $3.90 \pm 0.10 \mu_B$ at 50–300 K, which are quite close to the spin only value $\mu = 3.87 \mu_B$ expected for $S = 3/2$ complexes. Fig. 3a shows the Mössbauer spectrum measured on a microcrystalline sample at 76 K. The isomer shift (δ ; relative to α -iron foil) and quadrupole splitting (ΔE_q) were determined to be 0.34 and 3.71 mm s^{-1} , respectively. Large ΔE_q values are usually observed for complexes with $S = 3/2$ or $S = 3/2, 5/2$.¹⁴ Taken together, it is concluded that **1** is a highly pure intermediate spin complex.

2 was similarly prepared from $[\text{Fe}(\text{OETPP})\text{Cl}]$ and AgClO_4 in THF solution. The coordination of the THF ligands was confirmed by ^1H NMR analysis. Fig. 1b shows the temperature dependence of the chemical shifts of some protons. Fairly large downfield shifts of the methylene signals, 51.0 and 17.5 ppm at 233 K, clearly indicate that the β -pyrrole carbons have a considerable amount of π -spin density. Fig. 2b shows the EPR spectrum taken in frozen CH_2Cl_2 solution at 4.2 K. The g values were 4.01 and 2.00, suggesting that the spin state of **2** should also be represented as $S = 3/2$ at 4.2 K. The spin state was further confirmed by the magnetic moments determined by the Evans method in CH_2Cl_2 solution as well as by SQUID magnetometry in the solid; the former showed the magnetic moment to be $4.0 \pm 0.1 \mu_B$ at 193–303 K, and the latter gave values $3.85 \pm 0.05 \mu_B$ at 20–300 K. Fig. 3b shows the Mössbauer spectrum measured on a microcrystalline sample at 290 K. The δ and ΔE_q values were determined to be 0.50 and 3.50 mm s^{-1} , respectively. Taken together, it is concluded that **2** is also a very pure intermediate spin complex.

Formation of the very pure intermediate spin complexes, **1** and **2**, indicates that the $S = 3/2$ state is stabilized in both ruffled and saddled porphyrin complexes. The major reason must be the short Fe–N(porphyrin) bond lengths commonly observed in

highly deformed porphyrin complexes.^{8,15} We have recently determined the crystal structure of **1**.¹⁶ As expected, **1** has a strongly S_4 -ruffled porphyrin core with the *meso*-carbons deviating above and below the average porphyrin plane by *ca.* 0.68 Å. The Fe–N(porphyrin) bond distances of **1**, *av.* 1.967(12) Å, are significantly shorter than those of other bis(THF) complexes such as $[\text{Fe}(\text{OEP})(\text{THF})_2]\text{ClO}_4$ (*av.* 1.994 Å),⁴ $[\text{Fe}(\text{TEtP})(\text{THF})_2]\text{ClO}_4$ (*av.* 2.006 Å)¹⁷ and $[\text{Fe}(\text{TPP})(\text{THF})_2]\text{ClO}_4$ (*av.* 2.016 Å).¹⁸

In conclusion, we have shown that highly S_4 -ruffled **1** and S_4 -saddled **2** are highly pure intermediate spin complexes on the basis of the NMR, EPR, Mössbauer, and magnetic data.

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- Abbreviations: OETPP, TPrP, TEtP, and OEP are the dianions of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetraisopropylporphyrin, 5,10,15,20-tetraethylporphyrin, and 2,3,7,8,12,13,17,18-octaethylporphyrin, respectively.
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