Bis(tetrahydrofuran)(2,7,12,17-tetrapropylporphycenato)iron(III) Perchlorate: A Pure Intermediate Spin Complex

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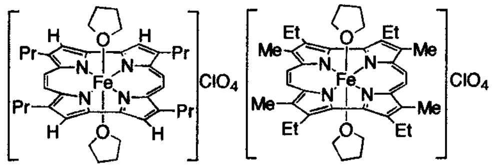
Introduction

Iron(III) porphyrin complexes with very weak axial ligands, such as $[Fe(TPP)(THF)_2]ClO_4$ and $[Fe(OEP)(THF)_2]ClO_4$, show a quantum mechanically spin-admixed S = 5/2, 3/2 state.[1,2] In the course of our studies on the relationship between heme properties and deformed porphyrin ring,[3] we have found that the bis(THF)(porphyrinato)iron(III) complexes with highly ruffled and sadddled porphyrin cores, $[Fe(T^iPrP)(THF)_2]ClO_4$ and $[Fe(OETPP)(THF)_2]ClO_4$, respectively, exhibit quite pure intermediate spin (S = 3/2) characters.[4] The results are explained in terms of the smaller cavities to accommodate the iron(III) ions in these nonplanar complexes, as compared with the planar ones.[5,6] This finding has lead us to investigate the spin states of the iron(III) complexes of porphyrin analogues, such as porphycene, corrphycene, and corrole, since they have unique cavity sizes and cavity shapes different from those of porphyrins.[7] Studies on these complexes must be quite important not only for the deeper understanding of the biologically important porphyrin complexes but for the elucidation of the novel physicochemical properties expected for these complexes.[7−9]

Scheme 1



$[Fe(TPrPc)(THF)_2]ClO_4$ (**1**) $[Fe(EtioPc)(THF)_2]ClO_4$(**2**)

In this paper, we report that bis(THF)(2,7,12,17-tetrapropylporphycenato)iron(III) perchlorate, $[Fe(TPrPc)(THF)_2]ClO_4$ (**1**), is a quite pure intermediate spin complex on the basis of the ^{1}H NMR, EPR, and Mössbauer spectroscopy, as well as SQUID magnetometry (Scheme 1).

Experimental Section

Synthesis. The chloro−iron(III) complex, [Fe(TPrPc)Cl], was prepared by the Vogel's method.[8] [Fe(TPrPc)Cl] was converted to **1** by reaction with 1.0 equiv of $AgClO_4$ in THF solution. The purple solid obtained after the workup procedure was recrystallized from THF−heptane. ^{1}H NMR(CD_2Cl_2, 25 °C): δ 47.9 (8H, α-CH_2), 1.64 (8H, β-CH_2), 2.54 (12H, CH_3), −76.2 (4H, pyrrole), 0.2 (4H, meso), 11.2 (8H, THF), 17.9 (8H, THF).

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL LA300 spectrometer, operating at 300.4 MHz for proton. EPR spectra were recorded on a Bruker E500 spectrometer operating at X band and equipped with an Oxford helium cryostat. To determine the g values, the observed EPR spectrum was simulated by Bruker WIN-EPR Sim Fonia program using Gaussian line function. The solid-state magnetic susceptibilities were measured between 2 and 300 K under a magnetic field of 0.5 T with a SQUID magnetometer (Quantum Design MPMS-7). The measured data were corrected for diamagnetic contributions. Iron-57 Mössbauer spectra were measured on a Wissel Möessbauer spectrometer system. The samples were kept in a gas-flow cryostat, and the ^{57}Co(Rh) source was kept at room temperature. Isomer shifts (δ) are given relative to the α-iron foil at room temperature.

Results and Discussion

Figure 1a shows the ^{1}H NMR spectrum taken at 298 K. The $CH_2(\alpha)$, $CH_2(\beta)$, and $CH_3(\gamma)$ signals were observed at δ 47.9, 1.64, and 2.54 ppm, respectively. Two broad signals observed at −76.2 and ca. 0 ppm were assigned to the pyrrole and meso protons, respectively, by spectral comparison with $[Fe(EtioPc)(THF)_2]ClO_4$(**2**); a broad meso signal was observed at 0.15 ppm in **2,** as shown in the inset of Figure 1a. Two signals at 11.2 and 17.9 ppm, each corresponding to 8H, were unambiguously assigned to the coordinated THF protons by spectral comparison with $[Fe(TPrPc)(THF\text{-}d_8)_2]ClO_4$, as shown in Figure 1b. Extremely upfield shifted pyrrole and downfield shifted α-methylene signals suggest that the iron has unpaired electrons in both

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(2) Abbreviations: TPP, OEP, TMCP, T^iPrP, OETPP: dianions of 5,-10,15,20-tetraphenylporophyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, tetramethylchiroporphyrin, 5,10,15,20-tetraisopropylporphyrin, and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, respectively. TPrPc, EtioPc: diaions of 2,7,12,17-tetrapropylporphycene and 3,6,13,16-tetraethyl-2,7,12,17-tetramethylporphycene, respectively.

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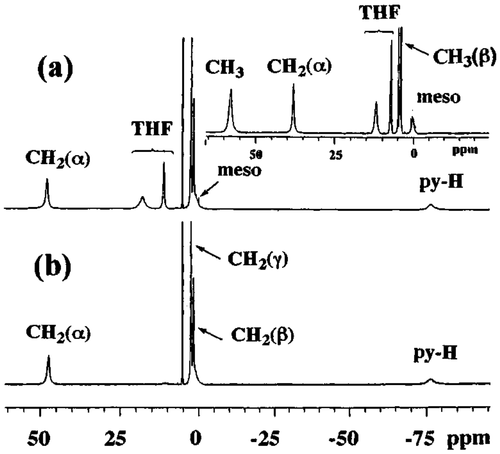

Figure 1. ^{1}H NMR spectra taken in CD_2Cl_2 solution at 298 K. (a) [Fe(TPrPc)(THF)$_2$]ClO_4 (**1**); (b) Fe(TPrPc)(THF-d_8)$_2$]ClO_4; Inset of (a) [Fe(EtioPc)(THF)$_2$]ClO_4 (**2**).

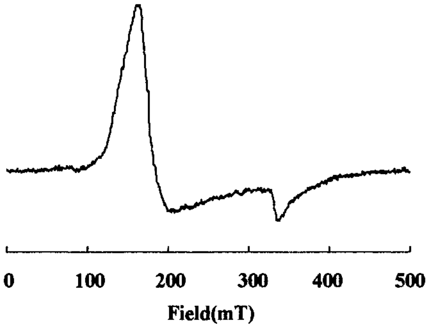

Figure 2. EPR spectrum of **1** taken in frozen CH_2Cl_2 solution at 4.2 K.

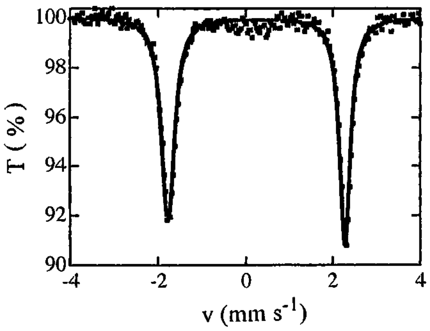

Figure 3. Mössbauer spectrum of **1** measured on a microcrystalline sample at 77 K.

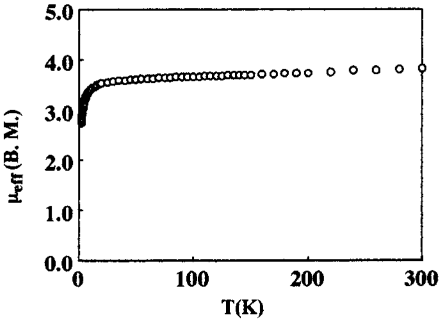

Figure 4. Temperature dependence of the effective magnetic moments for a microcrystalline sample of **1** in the range of 2−300 K.

the d_{xz} and d_{yz} orbitals; the unpaired electrons in these orbitals are delocalized to the porphycene ring via the d_π(iron)−p_π(porphycene) interaction and are distributed at the pyrrole β-carbon atoms. As a result, large contact shifts are induced to these signals.[10] The chemical shift of the pyrrole protons, −76.2 ppm at 298 K, is comparable in magnitude with that of the pure $S = 3/2$ porphyrin complex [Fe(TPP)]($CB_{11}H_6Br_6$) reported by Reed et al.[11] Existence of the downfield shifted THF signals suggests that the d_{z^2} orbital is occupied by an unpaired electron. All the ^{1}H NMR results support that **1** is an intermediate spin complex with the $(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^1$ electron configuration.

Figure 2 shows the EPR spectrum of **1** taken in a frozen CH_2Cl_2 solution at 4.2 K. Computer simulation of the slightly rhombic spectrum yielded the *g* values; $g_x = 4.15$, $g_y = 3.85$, and $g_z = 2.04$. The result strongly indicates that **1** is a quite pure intermediate spin complex, since the $(g_x + g_y)/2$ value of 4.0 is diagnostic of a quartet state.[12] Figure 3 shows the Mössbauer spectrum measured on a microcrystalline sample at 77 K. The isomer shift (IS; relative to α-iron foil) and quadrupole splitting (QS) were 0.27 and 4.03 mm s^{-1}, respectively. The large QS values are usually observed in the intermediate or admixed intermediate spin complexes.[13] In fact, iron(III) N_4-macrocycles characterized as quite pure intermediate spin complexes all showed large QS values.[4,11,14,15] Figure 4 shows the temperature dependence of the magnetic moments, obtained by SQUID magnetometry, in the solid over the temperature range 2−300 K. The effective magnetic moment (μ_{eff}) is almost constant at 50−300 K, which is quite close to the spin only value, $\mu_{eff} = 3.87\ \mu_B$, expected for the $S = 3/2$ spin state. Taken together, it is concluded that complex **1** has attained the essentially pure intermediate spin ($S = 3/2$) state.

In iron(III) porphyrins, the pure intermediate spin complexes commonly have either or both of the following two characteristics; i) very weak anionic axial ligands such as $(CB_{11}H_6Br_6)^-$,[11] and ii) highly nonplanar porphyrin cores such as TMCP,[14] OETPP,[4] and T^{i}PrP.[4] In the former case, even the planar TPP ligand can produce the intermediate spin complex as exemplified by [Fe(TPP)]($CB_{11}H_6Br_6$).[11] In the latter case, even the axial ligand, such as EtOH or THF, can form the pure $S = 3/2$ complex, as shown in [Fe(TMCP)(EtOH)$_2$]ClO_4, [Fe(T^{i}PrP)(THF)$_2$]ClO_4, and [Fe(OETPP)(THF)$_2$]ClO_4;[4,14] THF and EtOH are supposed to be much stronger ligands than $CB_{11}H_6Br_6^-$.[12] Although the crystal structure of **1** is not available at present, porphycenes and metalloporphycens are reported to have smaller cavity sizes than the corresponding porphyrins and metalloporphyrins.[8,9,16,17] Thus, porphycene cavities resemble those of

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nonplanar porphyrins in size, resulting in the formation of the pure intermediate spin complex; the average Fe−N bond lengths in highly ruffled [Fe(T^{i}PrP)]Cl and [Fe(T^{i}PrP)(THF)$_2$]ClO$_4$ are 2.038(2) and 1.967(12) Å, resepctively.[6,18] To our knowledge, this is the first example showing the pure intermediate spin state in iron(III) complexes of porphyrin isomers.

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