Formation and Solution Magnetic Behavior of Thioacetate-Ligated Iron(III) Porphyrin Complex

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Introduction

Axial thiolate ligands exist in a number of iron(III) heme protein systems.[1-3] The study of iron porphyrin complexes with sulfur donor ligands is therefore of considerable importance for understanding the biological role of the sulfur-ligated heme units.[4-7]

Only limited data are available concerning thio- or dithio-derivatives of iron porphyrins,[8] in part due to the facile oxidation-reduction reaction. Collman and Holm were the pioneers to isolate and characterize the iron(III) porphyrin thiolate complexes.[6-8] Their measurements (EPR, Mössbauer, magnetic susceptibility, and X-ray crystal analysis) indicated the presence of both low-spin (bis-ligated) and high-spin (mono-ligated) iron(III) porphyrin complexes. Hence, the goal of this work is the synthesis and characterization of iron porphyrin complexes with new sulfur ligand: (Por)Fe(III)($SC(=O)CH_3$). The bis-ligated complex can be obtained through modulation of the basicity of porphyrin ring and reaction temperature.

Many iron(III) thio-ligated complexes[2,9] have been studied due to the existence of "spin equilibria" in these complexes. However, "spin equilibria" was not observed in conventional iron(III) porphyrin complex. This report details the unexpected finding of such "spin equilibriation" phenomenon in an iron(III)(SAc) porphyrin complex. Both NMR and EPR spectroscopic techniques were utilized to monitor the formation, magnetic behavior, and spin states of the new complexe. Correlation of pyrrole ^1H chemical shifts at various temperatures with the electronic structure of the iron porphyrin was diagnostic of the "spin-equilibria" phenomenon.

Experimental

The potassium thioacetate $K^+[CH_3C(=O)S]^-$ (98%) were obtained from Aldrich and used as received. Stock solutions of the salts were prepared 1.0 M in methanol. Tetraarylporphyrins were prepared by aldehyde/pyrrole condensation, and pyrrole deuterated derivatives were prepared by pyrrole deuterium exchange prior to macrocycle condensation.[10a] Standard metal incorporation and purification methods were employed.[10b] Trifluoromethanesulfonate (triflate) complexes of iron(III) porphyrins, TPPFe(III)O_3SCF_3, were prepared by acid cleavage of the appropriate μ-oxo iron(III) porphyrin dimers.[11] Chlorinated solvents were washed successively with concentrated sulfuric acid, water, and aqueous sodium carbonate. It was dried over solid calcium chloride, and distilled from solid P_4O_{10}. Deuterated NMR solvents (Aldrich) were used as received.

Proton (360 MHz) and deuterium (55 MHz) NMR spectra of dichloromethane solutions of iron porphyrins with a concentration range of 2.0-6.0 mM were recorded on a Bruker WM-360 spectrometer. Tetramethylsilane was utilized as an internal reference, and downfield chemical shifts are given a positive sign. Temperature calibration was carried out by method of Van Geet.[12] Electron paramagnetic resonance (EPR) spectra were recorded on frozen solutions at 77 K following NMR spectroscopic examination.

Results and Discussion

The triflate iron porphyrin complex was utilized for generation of a thioacetate complex owing to the weak field ligand properties and liability of the triflate ligand. Formation of an iron porphyrin thioacetate complex was initially observed by deuterium NMR spectroscopy, in which case the signal of deuterated pyrrole at 34.2 ppm from the spin-admixed state of TPPFeO_3SCF_3[15] was converted to a unique new pyrrole signal at 72.9 ppm as shown in Figure 1. A five-coordinate, high-spin thiophenoxide iron(III) porphyrin complex is reported to have a comparable pyrrole chemical shift.[16] As shown in Figure 2, the proton NMR spectrum of the product formed from the reaction of TPPFeO_3SCF_3 with thioacetate in CH_2Cl_2 revealed a CH_3 peak of the coordinated ligand at 107.5 ppm. The experimental intensity ratio between pyrrole and coordinated thioacetate methyl is 8 : 3. The analogous methyl peak in the acetatoiron(III) porphyrin complex was paramagnetically shifted to 21.4 ppm. Hence, the bonding mode between iron(III) center and the thioacetate ligand is considered to be different from the acetate ligand, and the difference should be explained by iron-sulfur coordination. This large chemical shift difference would indicate that the spin density transmission through the sulfur atom from iron(III) to the coordinated CH_3 is much more efficient than its oxygen analogue. In the comparison between -$O(C=O)CH_3$ and -$S(C=O)CH_3$ ligands in iron porphyrin, the degree of σ-donation is similar, but the π-donation ability of the $S(C=O)CH_3$ ligand is significant. The remaining lone pairs in the 3p orbitals of the sulfur atom enhance the electron π-donation into the iron d_π orbitals. The pyrrole and phenyl resonance positions are typical for a five-

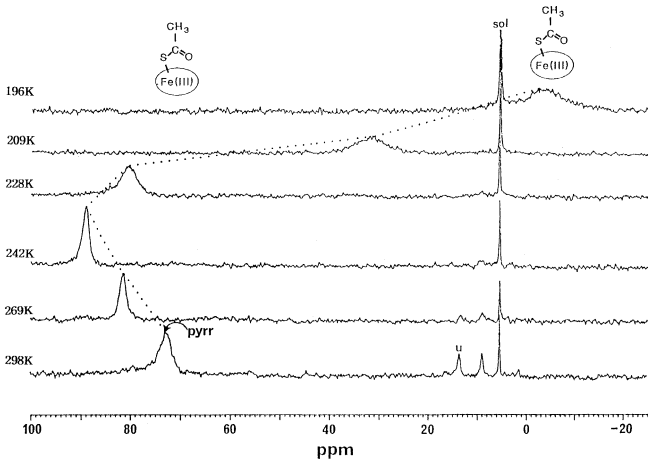


Figure 1. Deuterium NMR spectra for the reaction of 4.0 mM (d_8-TPP)Fe(III)O_3SCF_3 with 1.0 equiv. $[CH_3C(=O)S]^-K^+$/methanol in dichloromethane solution. A) 298 K, B) 269 K, C) 242 K, D) 228 K, E) 209 K, and F) 196 K. Denoted "u" indicate u-oxo dimeric species due to the contamination from the trace amount of oxygen present in solution.

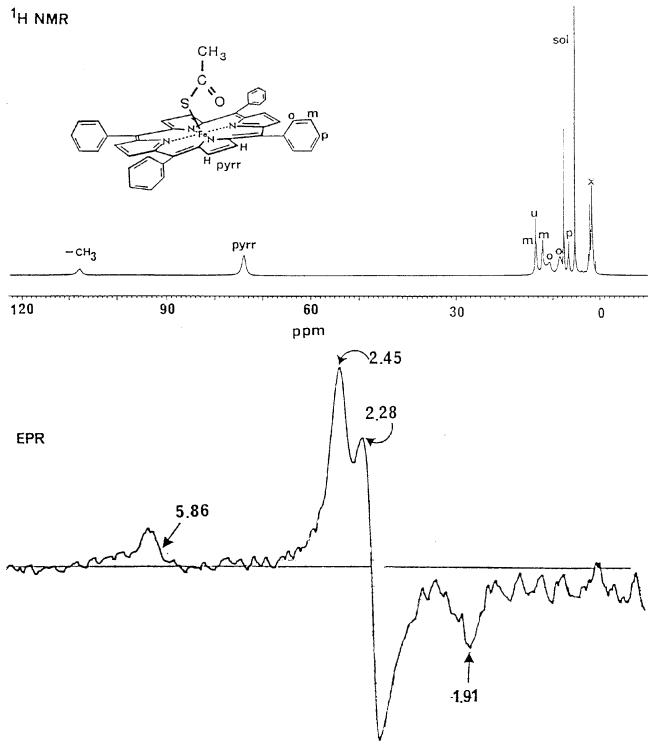
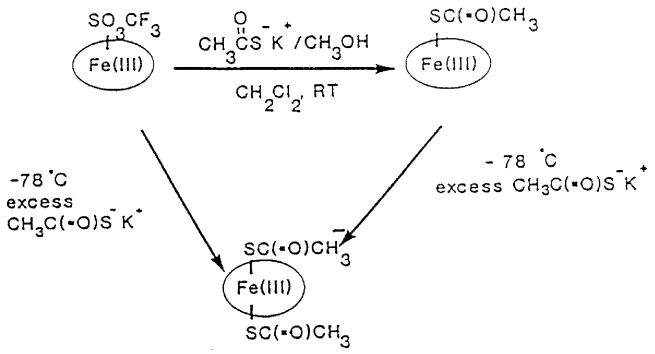


Figure 2. ^{1}H NMR (360 MHz) and EPR spectra for the reaction of (d_8-TPP)Fe(III)O_3SCF_3 with 1.0 equiv. $[CH_3C(=O)S]^-K^+$/methanol in dichloromethane solution. EPR spectrum was recorded at 77 K with 6000 G sweep, 9.19 GHz, 100 KHz modulation at 5 mwatt.

coordinate high-spin tetraphenylporphyrin complex with a pyrrole signal at 72.9 ppm and split phenyl-meta peaks at 13.2 ppm and 12.0 ppm, phenyl-ortho proton signals at 10.8 ppm and 8.2 ppm, and a phenyl-para proton signal at 7.25 ppm.

Variable-temperature measurements served to demonstrate a highly anomalous chemical shift dependence (Figure 1B-1F). Idealized Curie-law behavior would have the NMR signal in a paramagnetic complex shifted from the position for an analogous diamagnetic complex by a 1/T dependence. However, the pyrrole deuteron signal exhibits non-Curie behavior. When the temperature was lowered, the pyrrole deuteron signal is downfield-shifted direction as temperatures decreased to 253 K. However, on lowering the temperature further to 228 K, the pyrrole signal moved in an upfield direction. At the lowest temperature (196 K) the pyrrole signal was located in an upfield position at -5.4 ppm, which is common for the S=1/2 state. The 72.9 ppm pyrrole resonance was recovered by increasing the temperature back to 298 K. In the corresponding ^{1}H NMR spectra, the thioacetate ligand CH_3 signal obeyed the same behavior upon variation of temperature. In contrast, solvent effect was discussed for the iron(III) acetate porphyrin complex, since only coordinated methyl signal experienced non-Curie behavior. The formation of a low-spin iron(III) porphyrin complex is further confirmed by EPR spectroscopy with g values of 2.45, 2.28, and 1.91 at liquid N_2 temperature (Figure 2). Intensity of epr signal was relatively weaker than that of bis-ligated low-spin (TPP)Fe(III)$(SAc)_2^-$.



Scheme 1

Although the mechanism for spin-state change is not confirmed at this point, it is presumably due to "spin equilibration" between iron and axial SAc ligand at low temperature.

The formation of iron(III) bis(thioacetate) porphyrin complex is apparent from the reaction of iron(III) porphyrin triflate complex with 15 fold excess thioacetate at 200 K. This mixture gives rise to a new -16 ppm pyrrole signal in deuterium NMR spectroscopy. EPR spectrum of this complex at 77 K exhibited low-spin character with absorption bands at g = 2.43, 2.28, and 1.91. At low temperature the sixth axial position is believed to be occupied by a second molecule of thioacetate.

Conclusions

The first characterization of iron-sulfur bonded porphyrin complexes of SAc has been presented. Although the bonding configuration for the iron(III)(SAc) is not clear at present time due to its instability, the formation of monomeric iron(III)(SAc) was evident by spectroscopic results. The efficiency of spin density transmission for sulfur and oxygen bound complex can be useful to evaluate the electronic properties of the iron-sulfur bond in model compounds. This

ligand underwent a high-spin to low-spin transition upon addition of second ligand sources. While these ligands do not exist in proteins, the results could allow an assessment for the influence of sulfur ligation on the magnetic and electronic properties of bound hemes, in a relatively stable five-coordinate iron(III) complexes, and serve as a model for the thiolate ligand, which is the essential component of cytochrome P-450. The present information (high-spin and low-spin interconversion) may provide a dynamic model for the transformation associated with the substrate binding in the catalytic cycle of cytochrome P-450 enzymes in which the low-spin, six-coordinate resting form is converted to a high-spin, five-coordinate species.

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