Solution Nuclear Magnetic Resonance Spectral Characterization of Iron(II) Porphyrin Complexes of Weakly Coordinating Anions

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Weakly coordinating anions show little affinity for binding to unfunctionalized iron(II) porphyrins. The electron-deficient 5, 10, 15, 20-tetrakis(pentafluorophenyl)porphinatoiron(II) compound is utilized in this study to demonstrate solution coordination by chloride, bromide and acetate ions. The binding strength of anions to the iron(II) porphyrin is reflected by a systematic change in pyrrole proton chemical shift in ^{1}H NMR spectra; the pyrrole resonance moves downfield when the σ-donor ability of anions is decreased.

Keywords : Anion binding, Iron porphyrin.

Introduction

Iron in the +2 oxidation state is of great importance in hemoprotein chemistry for oxygen binding and activation. Iron(II) porphyrins can exist in the high (S=2), low (S=0), or intermediate (S=1) spin state. The high-spin iron(II) porphyrins are generally five-coordinate with one axial ligand of moderate or weak-field strength. Strong ligands such as cyanide or nitrite ion give the low-spin complex.[1,2]

A number of studies demonstrate anion coordination to iron(II) porphyrins in the solid state and in non-aqueous solutions.[2-17] Anionic ligands that give a five-coordinate, high-spin iron(II) porphyrin complex include acetate, bromide, chloride, fluoride, hydroxide, imidazolate, mercaptide, methoxide, perchlorate, and phenoxide. Kadish and Rhodes reported the first evidence for transient halide ion binding to simple iron(II) porphyrins in conjunction with electrochemical reduction of the iron(III) complexes.[8] In this instance, chloride ion rapidly dissociated as the chloroiron(III) was reduced to iron(II). The X-ray crystal structure of a chloroiron(II) "picket fence" porphyrin anionic complex was obtained from the unexpected product of an attempted synthesis of a five-coordinate (thiolato)iron(II) "picket fence" porphyrin complex.[3,6] The analogous acetoiron(II) anionic complex has been structually characterized.[13] The weakly coordinating anions are stabilized as iron(II) ligands through polarity effects of "picket" amide groups. The "picket fence" porphyrin thus presents a facilitated coordination environment, and the question is addressed here as to the more general nature of anion binding to iron(II) porphyrins.

Substitution of electron-withdrawing chlorine or fluorine groups at phenyl positions of tetraarylporphyrins produces a relatively electron-deficient environment at the metal and porphyrin ring atoms. This results in increase of oxidation potentials and increase of affinity toward axial ligation by Lewis bases. This report describes the binding of relatively weak anions to the electron-deficient tetrakis(pentafluorophenyl)porphinatoiron(II), (F$_{20}$-TPP)Fe(II), in non-aqueous media, as monitored by magnetic resonance spectroscopy.

Experimental Section

The tetrabutylammonium salts of BH$_4^-$, Cl$^-$, CH$_3$CO$_2^-$, Br$^-$, F$^-$, OH$^-$, and I$^-$ were purchased from Aldrich, recrystallized from ethylacetate/pentane and stored in a desiccator prior to use. Solutions of these reagents (1.0 M in dichloromethane) were prepared for use in the ligand addition reactions. Porphyrins were synthesized by an established aldehyde/pyrrole condensation method[18] and iron was incorporated to give the chloroiron(III) porphyrin complex.[19] The chloroiron(III) pentafluorophenylporphyrin, (F$_{20}$-TPP)Fe-(III)Cl, was obtained from Aldrich. Iron(II) tetraphenylporphyrin, TPPFe(II), and (F$_{20}$-TPP)Fe(II) were prepared in a nitrogen-filled dry box by reduction of the chloroiron(III) complex by mercury-activated zinc powder in either benzene or toluene solution.[7]

Proton (360 MHz, tetramethylsilane as an internal reference) and fluorine-19 (282 MHz, CFCl$_3$ as an internal reference) NMR spectra were recorded on Bruker WM-360 and Bruker AC-300 spectrometers, respectively. Deuteratrd solvents were used for ^{1}H-NMR spectroscopy. Temperature calibration was carried out by the method of Van Geet.[20,21] Iron porphyrin concentrations ranged from 2.0 mM to 6.0 mM in toluene or benzene solution. Electronic spectra were recorded on an HP 8452A diode array spectrometer in toluene solution with typically 10^{-5} M iron porphyrin concentration.

Results and Discussion

Chloride ion addition to square-planar (F$_{20}$-TPP)Fe(II) was monitored by proton NMR spectroscopy. Titration of 4 mM (F$_{20}$-TPP)Fe(II) in d$_8$-toluene solution with 1.0 M Bu$_4$NCl/CH$_2$Cl$_2$ resulted in conversion of the parent 4.6 ppm pyrrole proton signal to a new, unique signal at 40.7 ppm. The proton NMR spectrum for the 1 : 1 mixture is shown in Figure 1A. Addition of up to five equivalents of chloride ion caused no further change in the pyrrole proton signal, thus suggesting no high affinity association of a second chloride
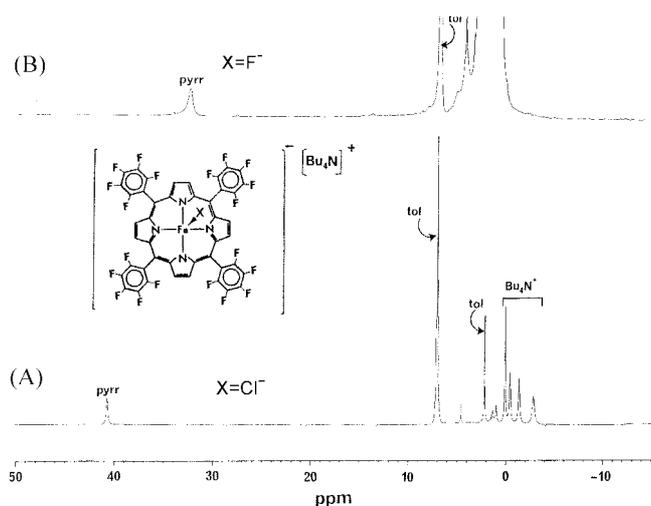
Figure 1. ^{1}H NMR spectra (360 MHz) for the reaction of 4.0 mM (F_{20}-TPP)Fe(II) with, (A) 1.0 equiv. Bu_4NCl, (B) 5.0 equiv. Bu_4NF to solution A), in d_8-toluene solution at 25 °C; TMS reference.

ion. Upfield-shifted proton NMR signals are also observed for the Bu_4N^+ counter ion of [(F_{20}-TPP)Fe(II)(Cl)$^-$][Bu_4N^+]. Presumably this reflects both dipolar and ring-current shift contributions for a tightly ion-paired Bu_4N^+ ion. The Bu_4N^+ signals were not shifted in acetonitrile or tetrahydrofuran (THF) solution as these more polar solvents may solvate and separate the anion-cation pair. The pyrrole chemical shift value is quite solvent dependent (Table 1).

The pyrrole proton signal for (F_{20}-TPP)Fe(II)Cl$^-$ is in the region seen for other high-spin iron(II) tetraarylporphyrin complexes (values in the range of 30 to 60 ppm). The electronic spectrum of (F_{20}-TPP)Fe(II)Cl$^-$ in toluene with bands at 434 (Soret) and 564 nm resembles that for the analogous F- complex.[5,15] The liquid nitrogen temperature EPR scan for a frozen toluene solution of (F_{20}-TPP)Fe(II)Cl$^-$ gave no signal as expected for the even-spin iron(II) complex. Variable temperature NMR spectroscopy revealed that the pyrrole proton signal belonged to a single species and was not a product of dynamical averaging. Hence, a shift difference of 16.3 ppm was seen on variation of temperature from 218 K to 338 K. The plot of isotropic (paramagnetic) shift *vs.* 1/T was linear, with a slope of 10,498 ± 339 ppm/K and an intercept of 2.5 ± 0.6 ppm. This Curie law behavior indicates (F_{20}-TPP)Fe(II)Cl$^-$ is a chemi-

cally and magnetically simple species over the temperature range indicated.

Fluorine-19 NMR spectroscopy of (F_{20}-TPP)Fe(II)Cl$^-$ in toluene solution showed splittings of phenyl ortho- and meta-fluorine signals. The phenyl ortho- and meta-fluorine signal splitting is well beyond usual fluorine-fluorine coupling constants, and is best explained by inequivalence of phenyl fluorine atoms with respect to the axial ligand of the iron center. Only phenyl ortho-fluorines are split for CD_3CN solution and no splitting is evident in THF solution. A logical explanation would involve progressively stronger association of acetonitrile and THF at the sixth coordination site. A sixth ligand would demand that the ferrous atom lie nearly in the porphyrin plane, and asymmetry of the phenyl fluorine atoms could be unresolved.

Analogous titrations with Bu_4NBr and $Bu_4N(CH_3CO_2)$ yield unique pyrrole proton signals at 45.3 ppm and 35.1 ppm, respectively. Addition of up to 50 equivalents of Bu_4NI to a 4 mM toluene solution of (F_{20}-TPP)Fe(II) showed no pyrrole signal in this region. Hence, iodide coordination is much less favorable as compared with the other halide ions.

A ligand competition study of (F_{20}-TPP)Fe(II)X$^-$ (X$^-$ = Br$^-$, Cl$^-$, $CH_3CO_2^-$) was carried out by addition of fluoride ion (F$^-$) and hydroxide ion (OH$^-$) which are regarded as stronger σ-donor ligands than X$^-$. Figure 1B shows that the chloride axial ligand of (F_{20}-TPP)Fe(II)Cl$^-$ with a pyrrole resonance at 40.7 ppm in toluene solution was readily displaced by excess F$^-$ (2 to 5 equiv.) to give (F_{20}-TPP)Fe-(II)F$^-$ with a pyrrole proton signal at 32.6 ppm. Hydroxide ion addition gave the same pattern with comparable concentrations.

Iron(III) porphyrin ligand-field strength increases in the order I$^-$ < Br$^-$ < Cl$^-$ < $CH_3CO_2^-$ < F$^-$.[22] This ligand-field order may well apply for the iron(II) porphyrin, on the basis of an empirical observation of pyrrole proton chemical shift values. Pyrrole proton chemical shift values for toluene solutions of (F_{20}-TPP)Fe(II)X$^-$ are: Br$^-$, 45.3 ppm; Cl$^-$, 40.7 ppm; $CH_3CO_2^-$, 35.1 ppm; OH$^-$, 33.6 ppm; and F$^-$, 32.6 ppm. Only complexes of OH$^-$ and F$^-$ are detectable for (TPP)Fe(II). The electron-deficient iron(II) in (F_{20}-TPP)-Fe(II) shows remarkably increased affinity for additional donor anions, and thus will form *in situ* stable (F_{20}-TPP)-Fe(II)X$^-$.

When dry oxygen was added to the dichloromethane solution of (F_{20}-TPP)Fe(II)Cl$^-$ the pyrrole resonance shifted to 82 ppm. This value matches that of the corresponding iron(III) porphyrin complex. No signal is seen for the (F_{20}-TPP)Fe(III)-(-O)-Fe(III)(F_{20}-TPP) species as the fluorinated porphyrin is resistant to aggregation.

Figure 2 depicts the spectrum of (F_{20}-TPP)Fe(II)(O$_2$CCH$_3$)$^-$. A very broad resonance (610 Hz line width) due to the methyl substituent of the coordinated ligand was observable in the upfield region at -7.1 ppm. The iron(III) porphyrin analogue showed the coordinated CH$_3$ peak at 32.1 ppm in CH_2Cl_2 solution.[23] Proton NMR chemical shift values for the pyrrole signal of the iron(II) acetate porphyrin complex in toluene solution follow Curie law behavior with an intercept

Table 1. Proton and fluorine-19 NMR spectra of (F_{20}-TPP)Fe(II)Cl$^-$ in three solvents, 25 °C

Solvent	^{1}H NMR pyrrole resonance (ppm)[a]	^{19}F NMR phenyl fluorine resonance[a]		
		ortho	meta	para(ppm)
d_8-toluene	40.7	-131.0	-165.1	-157.9
		-132.2	-166.0	
d_3-acetonitrile	37.9	-126.0	-160.3	-154.2
		-127.7		
d_8-THF[b]	45.0	-142.5	-174.1	-163.4

[a][1]H spectra referenced to TMS; ^{19}F spectra referenced to CFCl$_3$. [b]the pyrrole resonance of (F_{20}-TPP)Fe(II)(thf)$_2$ was seen at 59 ppm.

Anion Binding in Iron Porphyrin Complexes

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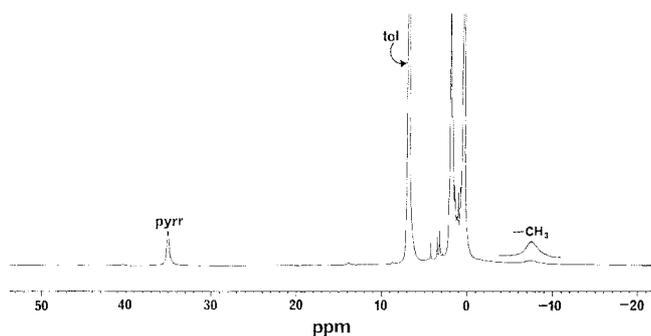
Figure 2. ^{1}H NMR spectrum (360 MHz) for 4.0 mM (F_{20}-TPP)Fe(II)(O_2CCH_3)$^-$ in d_8-toluene solution. The pyrr, and -CH_3 labels correspond to the pyrrole and ligand CH_3 signals at 25 °C; TMS reference.

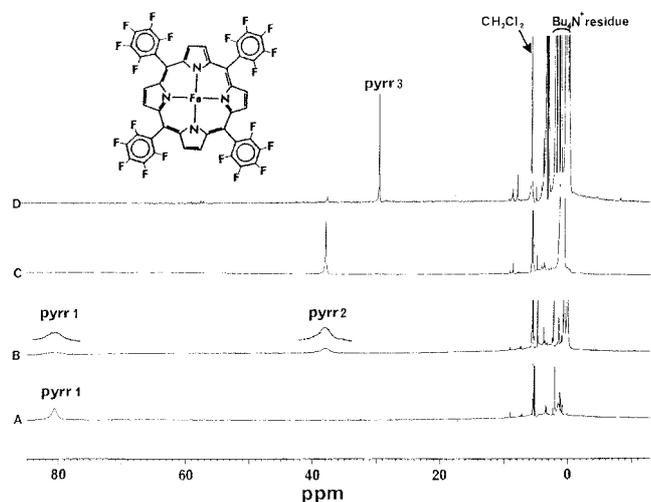**Figure 3**. ^{1}H NMR (360 MHz) spectra for titration of 4.0 mM (F_{20}-TPP)Fe(III)Cl with Bu_4NBH_4 in CD_2Cl_2 solution at 25 °C, TMS reference. A) 0.0 equiv. Bu_4NBH_4, B) 1.0 equiv., C) 2.0 equiv., D) 50.0 equiv. The pyrr1, pyrr 2, and pyrr 3 labels correspond to pyrrole resonances of iron(III)-Cl, iron(II)-Cl$^-$, and iron(I)$^-$ porphyrin complexes.

of 2.5 ± 0.2 ppm and a slope of 9718 ± 136 ppm (K). The methyl signal also exhibits Curie behavior. This indicates that the acetate ligand is not in rapid exchange on the NMR time scale, and the monodentate/bidentate behavior proposed for the iron(III) complex is not evident in the iron(II) case. This near upfield chemical shift value is of relevance to assignment of coordinated carboxylate proton NMR signals in ferrous proteins.[23]

An attempt to synthesize an as yet unreported hydrido-iron(III) porphyrin complex by titration of (F_{20}-TPP)Fe(III)-Cl with BH$_4^-$ also gave the (F_{20}-TPP)Fe(II)Cl$^-$ complex. Addition of 1.0 equiv. of BH$_4^-$ ion to (F_{20}-TPP)Fe(III)Cl solution in dichloromethane caused the appearence of a new pyrrole proton signal at 37.6 ppm in the ^{1}H NMR spectrum, and the pyrrole proton signal for the parent (F_{20}-TPP)-Fe(III)Cl species was entirely disappeared after addition of 2.0 equiv of BH$_4^-$ ion, as shown in Figure 3. The (F_{20}-TPP)Fe(I)$^-$ complex, with a pyrrole signal at 29.1 ppm, was
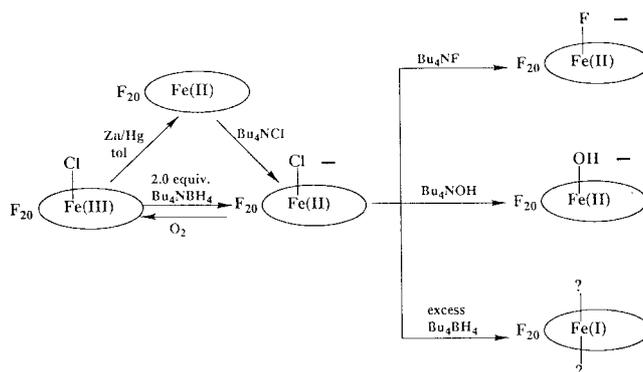
Scheme 1

ultimately produced by addition of a large excess of Bu_4NBH_4. The initial reduction product with a pyrrole proton signal at 37.6 ppm is the chloroiron(II) anion complex.

The reaction sequence included an observable iron(III) intermediate when toluene was utilized as solvent. Addition of 1.0 equiv. Bu_4NBH_4 to (F_{20}-TPP)Fe(III)Cl in toluene solvent caused the appearance of a new, very broad pyrrole proton resonance located at 71 ppm. This unique signal presumably corresponds to a species that contains a coordinated BH$_4^-$ ion. Further addition of Bu_4NBH_4 resulted in loss of the pyrrole signal at 71 ppm and appearance of the signal at 40.7 ppm corresponding to (F_{20}-TPP)Fe(II)Cl$^-$. Borohydride reduction of (F_{20}-TPP)Fe(III)Cl and the various competition and oxidation reactions are summarized in Scheme 1.

In summary, this study provides the first solution investigation of weak anion coordination to iron(II) porphyrins. Previous investigations have been restricted to solid state structural determinations in which the unique high dielectric "picket-fence" environment was utilized to facilitate anion binding. The electron-deficient iron(II) porphyrins form complexes with weak donor anions to generate stable anionic five-coordinate iron(II) porphyrin complexes. Hence, numerous new coordination modes are possible through use of the electron-deficient metalloporphyrins.

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