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Permalink
https://escholarship.org/uc/item/6tf6h19d

Journal
Journal of the American Chemical Society, 122(19)

ISSN
0002-7863

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Publication Date
2000-05-17

DOI
10.1021/ja994478i

Peer reviewed
Reversal of H₂O and OH⁻ Ligand Field Strength on the Magnetochemical Series Relative to the Spectrochemical Series. Novel 1-equiv Water Chemistry of Iron(III) Tetrphenylporphyrin Complexes

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Received December 22, 1999. Revised Manuscript Received March 2, 2000

Abstract: Contrary to expectations based on the spectrochemical series, H₂O is found to be a significantly weaker field ligand than OH⁻ in the magnetochemical series ranking of ligand field strengths based on the spin states of iron(III) tetrphenylporphyrin complexes. The preparation and characterization of the [Fe(H₂O)₆(TPP)]⁺ ion and the spectroscopic identification of Fe(OH)(TPP) have made this assessment possible. These two species were previously thought to be unattainable because of the facile formation of the well-known μ-oxo dimer, (TPP)Fe=O=Fe(TPP). However, the special characteristics of single equivalents of water under high acidity, relevant to metalloenzyme active sites and superacidity, make them accessible in benzene solution. Their ¹H NMR β-pyrrrole chemical shifts at −43 and +82 ppm indicate admixed-intermediate S = 3/2, 5/2 and high S = 5/2 spin states for the aqua and hydroxo species, respectively. The X-ray crystal structure of the aqua complex has been determined for [Fe(H₂O)(TPP)][CB₁₁H₁₂Cl₆] and is consistent with the high degree of S = 5/2 character indicated by the NMR measurement. Mössbauer spectroscopy (∆Eₐₐ = 3.24 mm/s⁻¹), and magnetic susceptibility (μₐₐ = 4.1 μₐ) show the anhydrous precursor to these species is the “nearly bare” iron(III) porphyrin complex Fe(CB₁₁H₁₂Br₆)(TPP). Judged by its magnetic parameters (∆Eₐₐ = −62 ppm, ∆Eₐ₁ = 3.68 mm/s⁻¹, μₐₐ = 4.0 μₐ) it attains the long sought essentially “pure” S = 5/2 spin state. The magnetochemical ranking of ligand field strengths in five-coordinate high-spin and admixed-intermediate-spin iron(III) porphyrins is useful because it more closely reflects the intuitive field strengths of crystal field theory than does the usual spectrochemical ranking, which is controlled largely by π effects in octahedral low-spin d₆ complexes.

Introduction

One of the more counterintuitive orderings of ligand field strength in the spectrochemical series is OH⁻ < H₂O.¹ In the crystal field model, the anionic ligand with the shorter metal–ligand bond is expected to have a stronger effect on the d orbitals than its neutral, longer-bonded conjugate acid. In the ligand field model, the electrostatic expectations of crystal field theory are equated with σ covalent bonding and the shorter M–O bonded species is assumed to have the stronger σ bond. To rationalize the observed reversal from that anticipated from σ bonding, counteracting π bonding is invoked. Oxygen-to-metal 2pₓ−dₓ donor bonding is assumed to be sufficiently stronger with OH⁻ relative to H₂O that the σ bonding order becomes subservient to the π donor order. Indeed, it is postulated that, with few exceptions, π bonding is the dominant factor determining the ordering of ligands throughout the spectrochemical series.² It is therefore of fundamental interest to find a ligand field strength criterion that more closely reflects the σ bonding order.

We have recently developed a new method for ranking ligand field strengths, resulting in an ordering called the magnetochemical series.³ It is based on the degree of S = 3/2, 5/2 spin state admixture engendered by axial ligands X in iron(III) tetrphenylporphyrin complexes of the type FeX(TPP). Spin state-dependent properties such as the ¹H NMR β-pyrrrole shift, which ranges from −62 ppm in an S = 3/2 complex to +80 ppm in an S = 5/2 complex, are used as indicators of the degree of admixture. In its initial form, the method was applied to a variety of weak field ligands whose relative field strengths had not previously been determined: CB₁₁H₁₂⁻ < SbF₆⁻ < AsF₆⁻ < ClO₄⁻ < C(CN)₃⁻ < CF₃SO₃⁻ < BF₄⁻ < ONC(CN)₂⁻ < ReO₄⁻ < OTeF₅⁻.³ The series was expanded to include the halides, in their usual order of I⁻ < Br⁻ < Cl⁻, by considering related iron(III) phthalocyanine complexes. This magnetochemical ranking is distinguished from a spectrochemical ranking by a much greater sensitivity to experimental criterion and, most fundamentally, by its straightforward reflection of ground-state electronic structure, as opposed to small differences in the large ∆E between a ground and an excited state (of unknown structure). In a subsequent paper, the series was extended to stronger field ligands by consideration of zero field splitting and spin crossover information taken from the iron porphyrin literature.⁴ The final listing was Ag(CB₁₁H₁₂)₂⁻ < CB₁₁H₁₂⁻ < SbF₆⁻ < Co(C₅B₇H₁₂)₂⁻ < AsF₆⁻ < ClO₄⁻ < C(CN)₃⁻ <

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Reversal of $H_2O$ and $OH^-$ Ligand Field Strength

$CF_3SO_3^- < BF_3^- < ONC(CN)$_2^- < ReO_4^3^- < OTeF$_5^- < I^- < Br^- < Cl^- < NCS^- < OAc^- < N$_3^- < OPh(p-NO$_2$)$^- < OPh^- < F^- < RS^- < fluorooaryl < ary1 < alkyl < HS^- ~ trialkyltin < CO ~ NO$_2$^+.

Notably absent from this series were two classically important ligands: $OH^-$ and $H_2O$. This was not surprising because Fe-$OH$(TPP) and [Fe($H_2O$)(TPP)]$^+$ were thought to be nonexistent compounds, unstable toward dimerization to form the familiar $\mu$-oxo dimer ([TPP]Fe$-$Fe$-$O$-$TPP). The $\mu$-oxo dimer is sometimes referred to as the “thermodynamic sink” of iron(III) porphyrin chemistry. However, we have recently found conditions where both Fe-$OH$(TPP) and [Fe($H_2O$)(TPP)]$^+$ can be observed. The relative ligand field strengths of $OH^-$ and $H_2O$ can now be compared under comparable conditions to other ligands, and contrary to expectations based on the spectrochemical series, $OH^-$ is found to be the stronger field ligand. Moreover, $H_2O$ is found to be a significantly weaker field ligand than ClO$_4^-$, a ligand whose spectrochemical field strength is nearly indistinguishable from that of $H_2O$ in [Co$^{III}$(NH$_3$)$_5$X]$^+$.5

The observation of Fe-$OH$(TPP) and [Fe($H_2O$)(TPP)]$^+$ was initially made by $^1H$ NMR spectroscopy while studying the protonation of (TPP)Fe$-$O$-$Fe(TPP) to give [(TPP)Fe$-$O$-$OH$-$Fe(TPP)]$^+$. This protonation of a linear $\mu$-oxo bridge is structurally unusual in that it occurs without geometrical rehybridization at oxygen.$^6$ It became clear to us during these studies that acid/base speciation in the Fe(TPP)$^-$/H$_2$O system had a complex dependency on the nature of the counterion and the precise amount of water present. The protonation of (TPP)$-$Fe$-$O$-$Fe(TPP) is a rather delicate process, one that can only be accomplished under conditions of low solvent donority and very weakly coordinating counterions, e.g. F$_{20}$-BPh$_4^-$ or CB$_{11}$H$_6$X$_6^-$ (X = Cl, Br). Indeed, with very weakly coordinating (and weakly basic) anions in low dielectric media quite unexpected chemistry can arise from the high acidities that is generated.

Water is of particular interest at the 1 equiv level in low dielectric media. It is not widely appreciated, but in isolation, H$_2$O$^+$ is a superacid, having $>10^{12}$ higher acidity than in aqueous solution.$^3$ In the hydrophobic pocket of a metalloenzyme active site, the acidity of a single water molecule coordinated to a metal cation can be even higher than that measured in aqueous solution. In low dielectric media, [Fe-(H$_2$O)(TPP)]$^+$ can be expected to be a strong Bronsted acid, reflecting the high Lewis acidity of the bare Fe(TPP)$^+$ cation. We therefore prepared the “nearly bare” anhydrous species Fe-(TPP)(CB$_{11}$H$_6$X$_6$) for titration studies with water. With its very weakly coordinating anion, this compound is of interest in attaining the long sought pure $S = 3/2$ spin state.$^8$-12 Speciation in iron(III) porphyrin aqueous systems has also been of recent interest with respect to proton-transfer rates$^{13,14}$ and the recurring question of the true nature of species so often written loosely as Fe(TPP)$^+$.15 Strong acids are also relevant to the recent proposal that carbocations are intermediates in enzymatic reactions.$^{16}$

### Results and Discussion

The hexahalo carborane anions, CB$_{11}$H$_6$X$_6^-$ (X = Cl, Br) and the perfluorinated tetraphenylethane ion, F$_{20}$-BPh$_4^-$ were chosen for this study because of their extremely low Bronsted basicity and very weak coordinating ability.$^{17}$ This ensures that the counterions are as innocent as possible in the subsequent coordination and acid/base chemistry. There is little, if any, distinction in the chemistry of Fe(TPP)$^+$ as a function of X in the CB$_{11}$H$_6$X$_6^-$ carborane anions. The choice between them is made on the basis of practical considerations such as solubility, single-crystal formation, transparency to radiation, etc. As a result, we use the hexachloro and hexabromo carborane anions interchangeably in describing the following chemistry. The F$_{20}$-BPh$_4^-$ anion is sometimes used for solubility reasons but only in situations where the anion is noncoordinating. It can therefore be used interchangeably with the carboranes in any of the ionic formulations.

A summary of the acid/base speciation in the Fe(TPP)$^+$/H$_2$O system in benzene solution is previewed in Scheme 1.

**Scheme 1**


FeBr(TPP) + 2Ag(CB$_{11}$H$_6$X$_6$) → [(Fe(p-xylene)(TPP))[Ag(CB$_{11}$H$_6$X$_6$)$_2$]] + AgBr (1)

A clean procedure was developed by oxidizing Fe$^{III}$(TPP) with the electron-abstracting oxidant sometimes referred to as “magic

Table 1. Spin-State Parameters for Iron(III) Tetraphenylporphyrin Complexes

<table>
<thead>
<tr>
<th>compd</th>
<th>ΔE_{k} (mm·s⁻¹)</th>
<th>δ_{pyrrole} (ppm)</th>
<th>μ_{ca}\textsuperscript{25°C} (μB)</th>
<th>Fe–N_{ave} (Å)</th>
<th>Fe⋯C_{lp} (Å)</th>
<th>Fe–X_{ave} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CB_{12}H_{8}Br_{6})(TPP), 1</td>
<td>3.68 (300 K)</td>
<td>-62</td>
<td>4.0</td>
<td>1.982(14)</td>
<td>0.08</td>
<td>2.722(3)</td>
</tr>
<tr>
<td>Fe(CB_{12}H_{8})(TPP)\textsuperscript{a}</td>
<td>4.12 (77 K)</td>
<td>-59</td>
<td>4.2</td>
<td>1.961(5)</td>
<td>0.10</td>
<td>1.82(4)</td>
</tr>
<tr>
<td>Fe(PSHBr)(TPP)\textsuperscript{a}</td>
<td>4.29 (77 K)</td>
<td>-49</td>
<td>4.1</td>
<td>1.978(3)</td>
<td>0.15</td>
<td>2.105(3)</td>
</tr>
<tr>
<td>[Fe(H_{2}O)(TPP)]\textsuperscript{b, 2}</td>
<td>3.24 (300 K)</td>
<td>-43</td>
<td>4.2</td>
<td>1.979(10)</td>
<td>0.19</td>
<td>2.039(4)</td>
</tr>
<tr>
<td>Fe(OClO_{4})(TPP)\textsuperscript{b, 6}</td>
<td>2.79 (295 K)</td>
<td>-28</td>
<td>5.2</td>
<td>2.001(5)</td>
<td>0.30</td>
<td>2.029(4)</td>
</tr>
<tr>
<td>[(TPP)Fe-OFe(TPP)]\textsuperscript{c, 4}</td>
<td>1.83 (300 K)</td>
<td>+28</td>
<td>5.5</td>
<td>2.047</td>
<td>0.40</td>
<td>1.821(8)</td>
</tr>
<tr>
<td>Fe(OH)(TPP), 3</td>
<td></td>
<td>+82</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(TPP)Fe-O-Fe(TPP)</td>
<td>0.60\textsuperscript{e} (77 K)</td>
<td>+13.8</td>
<td>2.081(3)\textsuperscript{f}</td>
<td>0.54</td>
<td>1.759(1)</td>
<td></td>
</tr>
</tbody>
</table>


The full oxidizing power of the reagent (E = 0.7 V vs Fe/Fe\textsuperscript{+}) is probably not required for this oxidation, but the characteristics of the reagent under the conditions used make it synthetically convenient. To prevent overoxidation to a π-radical cation, the order of reagent addition was oxidant to Fe(TPP), both predissolved.

As expected for a tetragonal system with a very weakly bonding and very weak field axial ligand, \textsuperscript{1}H NMR shifts of essentially pure S\textsuperscript{3/2} spin state are indicators of the S\textsuperscript{3/2} spin state (3.9 μB). The quadrupole splitting in the Mössbauer spectrum (measurable only in the X = Cl compound because of γ-ray absorption by bromine atoms when X = Br) is 3.68 mm/s, among the largest reported for iron(III) porphyrins (see Table 1). The \textsuperscript{1}H NMR shift of the eight β-pyrrole protons (see Figure 1A) is -62 ppm in benzene-d\textsubscript{6}, the most upfield yet reported.\textsuperscript{3,22} These extrema indicate that 1 has attained the essentially pure S\textsuperscript{3/2} spin state. We note that the \textsuperscript{1}H NMR pyrrole resonance is sensitive to concentration and temperature, the 24 atom core (24.8 Å) is probably a reflection of the weak cation/anion binding, so comparisons to other systems must be made under comparable conditions. The X-ray structure of 1 for X = Br (see Figure 2) is also consistent with an intermediate spin state. The Fe–Br distance to the carborane anion (2.722(3) Å) is very long, ca. 0.37 Å longer than in FeBr(TPP).\textsuperscript{23} The average Fe–N distance is short (1.982(14) Å), the porphyrin core is significantly ruffled, and the out-of-plane displacement of the iron atom toward the anion is only 0.08 Å from the 24-atom core (0.13 Å from the mean 4 N plane). These dimensions are compared to closely related structures with high degrees of S\textsuperscript{3/2} character in Table 1. They reflect essentially complete depopulation of the d\textsuperscript{5} orbital and are consistent with a pure S\textsuperscript{3/2} spin state. A strict correlation of all of the parameters used as indicators of the S\textsuperscript{3/2} spin state should not be expected with solid-state data because of their sensitivity to different degrees of ruffling, weak interactions in the sixth “vacant” coordination site,\textsuperscript{24} and crystal packing effects. Indeed, it has recently been shown that the S\textsuperscript{3/2} state is favored by porphyrin-induced distortions to the coordinate geometry.\textsuperscript{25} For these reasons, we emphasize the δ\textsubscript{pyrrole} chemical shift as the preferred criterion of spin state in the present work. Derived from solution measurements in benzene, the environment is more innocent and constant than that in the solid state, so comparisons are more likely to be valid.

The particular view of 1 in Figure 2 was chosen to illustrate a rather unexpected feature of the structure, namely, the Fe–Br bond is off-normal by 23.5° relative to the mean plane of the 24 atom core (24.8° relative to the 4 N mean plane). This is probably a reflection of the weak cation/anion binding, implicit in the long Fe–Br bond length. This bond is therefore susceptible to distortion by packing forces as the crystal endeavors to achieve efficient filling of lattice space. Inspection of a packing diagram (Figure S2) also reveals a feature which must now be considered normal for five-coordinate metalloporphyrins, a laterally offset π–π interaction between the open faces.\textsuperscript{26}

Scheme 1 contains a slight but justifiable simplification concerning the nature of 1 in benzene solution. In recent studies, we have shown that 1 can be crystallized from aren solvent such as benzene, toluene, or p-xylene to give ionic materials of

\textsuperscript{(26) Scheidt, W. R.; Lee, Y. J. Struct. Bonding 1987, 64, 1–70.}
the type [Fe(arene)(TPP)][CB\textsubscript{11}H\textsubscript{6}X\textsubscript{6}].\textsuperscript{24} The arenes in these compounds are weak \(\eta^2\) ligands implying some ionization of \(^1\) even in low dielectric solvents such as benzene (eq 3).

\[
\text{Fe(TPP)(CB}_{11}\text{H}_6\text{X}_6) + \text{arene} \rightarrow [\text{Fe(arene)(TPP)}][\text{CB}_{11}\text{H}_6\text{X}_6] \quad (3)
\]

However, even though the ionic species tend to crystallize from arene solvents, the extent of this ionization in solution is probably quite small. Ionic species are expected to be considerably less soluble than their neutral precursors; they do not need to be the favored species of a labile equilibrium in order to preferentially crystallize. Indeed, \(^1\) NMR spectroscopy in benzene-\(d_6\) provides evidence for dominant anion coordination. Typically, the \(B-H\) resonances of the carborane anion are broad (ca. 1000 Hz) due to the quadrupolar effects of the boron nuclei. In \(^1\), however, the line widths are reduced to ca. 400 Hz (Figure S9A). This is presumably a paramagnetic relaxation effect arising from proximity to the \(S = \frac{5}{2}\) iron in the anion-coordinated species. Because of the labile nature of the system and the inaccessibility of a low-temperature liquid range for benzene-\(d_6\), it is not consistent with the small equilibrium constant for eq 3 and justifies the representation of \(^1\) as a neutral species in Scheme 1.

**Aqua Complex** [Fe(H\textsubscript{2}O)(TPP)][CB\textsubscript{11}H\textsubscript{6}X\textsubscript{6}], \(^2\). Titration of \(^1\) with water at the 1-equiv level displaces the coordinated carborane anion giving the monoqua complex \(^2\) (eq 4).

\[
\text{Fe(TPP)(CB}_{11}\text{H}_6\text{X}_6) + \text{H}_2\text{O} \rightarrow [\text{Fe(H}_2\text{O)(TPP)}][\text{CB}_{11}\text{H}_6\text{X}_6] \quad (4)
\]

The aqua cation is identified in benzene solution by its \(^1\) H NMR \(\beta\)-pyrrole shift at \(-43 \text{ ppm at } 25 \text{ }^\circ\text{C} \text{ (see Figure 1B). Given the range of } -62 \text{ ppm for }

Figure 2. ORTEP diagram of Fe(TPP)(CB\textsubscript{11}H\textsubscript{6}Br\textsubscript{6}). \(^1\) Thermal ellipsoids are drawn at the 30% probability level for the structure determined at 163 K.

Figure 3. Variable-temperature \(^1\)H NMR spectrum of [Fe(H\textsubscript{2}O)(TPP)][CB\textsubscript{11}H\textsubscript{6}Br\textsubscript{6}], \(^2\), in dry toluene-\(d_8\).

Figure 4. ORTEP diagram of the cation and higher-occupancy lattice water molecule in [Fe(H\textsubscript{2}O)(TPP)][CB\textsubscript{11}H\textsubscript{6}Cl\textsubscript{6}]-H\textsubscript{2}O. Thermal ellipsoids are drawn at the 30% probability level for the structure determined at 163 K.

established equilibrium on the NMR time scale. \(^1\)H NMR spectra of \(^2\) in toluene-\(d_8\) below 0 °C (Figure S10) allow discrimination of two sets of resonances for the \textit{ortho} and \textit{meta} phenyl protons, consistent with the \(C_{6v}\) symmetry of five-coordination and slow rotation of the phenyl rings. Reciprocal temperature plots of the phenyl and pyrrole chemical shifts (not shown) are similar to those reported for admixed intermediate-spin Fe(OClO\(_3\))-(TPP).\textsuperscript{22} The deuterium NMR spectrum of \(^2\) prepared with D\(_2\)O shows a resonance at 10.2 ppm attributable to coordinated water (observed by phenyl group resonances in Figure 1B).

[Fe(H\textsubscript{2}O)(TPP)][CB\textsubscript{11}H\textsubscript{6}X\textsubscript{6}] can be prepared and isolated on a preparative scale by the controlled addition of water to \(^1\). Single crystals of [Fe(H\textsubscript{2}O)(TPP)][CB\textsubscript{11}H\textsubscript{6}Cl\textsubscript{6}]-H\textsubscript{2}O suitable for X-ray crystallography were grown from benzene-\(d_6\). The molecular structure is shown in Figure 4. The average Fe–N distance of 1.979(12) Å is indistinguishable from that in \(^1\), but the out-of-plane displacement of the iron atom is slightly larger (see Table 1). The Fe–O distance is long (2.039(5) Å). These dimensions, along with the Mössbauer quadrupole splitting (3.24 mm/s) and magnetic moment (4.2 \(\mu\)\textsubscript{B}), are all in the direction expected for the admixture of a fairly small amount of \(S = \frac{5}{2}\) character into a predominantly \(S = \frac{3}{2}\) spin state. Thus, the solid-state data on isolated \(^2\) are consistent with the solution data in benzene.

Consistency does not necessarily mean identity, however. H-bonding of the coordinated water molecule to lattice solvate water is expected to perturb the ligand field strength in a measurable way, increasing the basicity of the coordinated water molecule relative to an isolated aqua ligand in a nonpolar environment. We have explored the effect of excess water by monitoring the \(-43 \text{ ppm } \beta\)-pyrrole chemical shift of \(^2\) in benzene as a function of added equivalents of water. The results are shown in Figure 5. Due to the limited solubility of water in benzene (0.0307 M at 25 °C)\textsuperscript{27} these experiments had to be

\(\textsuperscript{27}\text{Wing, J.; Johnson, W. H. } J. \text{ Am. Chem. Soc. } 1957, 79, 864–865.\)
performed at the low porphyrin concentration of 2 mM. At this concentration the initial $\beta$-pyrrole resonance is at $-57$ and not $-62$ ppm because of residual water and time-averaging of signals due to 1 and 2. Axial ligand exchange between water and anions is clearly fast on the NMR time scale. The progressive downfield shift of the high field resonance from $-43$ to $-26$ with an additional 1–4 equiv of water can be interpreted in two ways. One is in terms of a gradual increase of ligand field strength of coordinated $\text{H}_2 \text{O}$ as it becomes hydrated: consider eq 5. The other is in terms of a gradual increase of ligand field strength of coordinated $\text{H}_2 \text{O}$ as it becomes hydrated: consider eq 5. In order for this condensation to occur, $\text{H}^+$ must be lost. In other words, $\text{Fe(H}_2\text{O)}(\text{TPP})^+$ would have to be a strong enough acid to protonate either benzene or the carborane anion for eq 5 to proceed. The existence of $[\text{H(benzene)}^+][\text{CB}_{11}\text{H}_6\text{Br}_6^-]$ as an isolable superacid tells us that the anion even is more difficult to protonate than benzene. In fact, the best base in solution will be the $\mu$-oxo compound itself. The condensation reaction should therefore be written as eq 6.

$$2[\text{Fe(H}_2\text{O)}(\text{TPP})]^+ \rightarrow \text{(TPP)}\text{Fe}^+\text{O}^-\text{Fe(TPP)} + \text{H}_2\text{O}^+ + \text{H}^+ \quad (5)$$

$$2[\text{Fe(H}_2\text{O)}(\text{TPP})]^+ \rightarrow [(\text{TPP})\text{Fe}^+\text{O}^-\text{Fe(TPP)}]^+ + \text{H}_2\text{O}^+ \quad (6)$$

Even this reaction does not occur to any large extent in dry benzene. The singly hydrated proton in the $\text{H}_2\text{O}^+$ ion is too high in energy (i.e. too acidic) to be formed in benzene solution. This is consistent with the notion that an isolated $\text{H}_2\text{O}^+$ ion is superacidic. In order for eq 6 to proceed in benzene solution, additional equivalents of $\text{H}_2\text{O}$ must be available to hydrate the $\text{H}_2\text{O}^+$ ion further, lowering its acidity. This is discussed next.

**Hydroxo Complex Fe(OH)(TPP), 3.** Further inspection of Figure 5 reveals the progressive conversion of the monomeric aqua species 2 to two new products as the addition of water increases. New peaks grow in at $+34$ and $+22$ ppm. These are assigned to the $\beta$-pyrrole shifts of the $\mu$-hydroxo dimer $[\text{Fe(TPP)}\text{OH}^-\text{Fe(TPP)}]^+$, 4, and the monohydroxo complex $\text{Fe(OH)(TPP)}$, 3. Their appearance is an expression of the Bronsted acidity of 2 manifest by the addition of a base ($\text{H}_2\text{O}$). It is a logical consequence of a hydrolysis stoichiometry that can be idealized according to eq 7.

$$3[\text{Fe(H}_2\text{O)}(\text{TPP})]^+ + 7\text{H}_2\text{O} \rightarrow [\text{Fe(TPP)}\text{OH}^-\text{Fe(TPP)}]^+ + \text{Fe(OH)(TPP)} + 2\text{H}_2\text{O}_4^+ \quad (7)$$

The hydrolysis proceeds to the right-hand side only after some equivalents of water have been added because $\text{H}^+$ cannot be liberated unless it is solvated by a number of water molecules. Four water molecules in the $\text{H}_2\text{O}_4^+$ ion, the trihydrated $\text{H}_2\text{O}^+$ ion, is a reasonable proposal for the dominant formulation of an aquated proton in benzene although $\text{H}_2\text{O}_4^+$ and $\text{H}_2\text{O}_3^+$ may also be present in the early stages of the hydrolysis. $[\text{H}_2\text{O}_4^+]_\text{a}$ is an isolable discrete salt that can be recrystallized from arenne solvents. Indeed, X-ray-quality crystals of $[\text{H}_2\text{O}_4^+]_\text{a}$ were obtained from wetted Fe(TPP)–arene solutions. A more quantitative analysis of the iron porphyrin and acid speciation in this system is not possible because the least soluble species, the ionic dimer 4, precipitates from solution as the hydrolysis proceeds.

The $+82$ ppm value for a $\beta$-pyrrole shift is indicative of a species with an $S = 5/2$ high-spin state. Similar values are found for a large number of FeX(TPP) species known to be high spin ($X = \text{halide, RO}^-$, etc.). So the assignment to Fe(OH)(TPP), a neutral species in benzene solution, is very reasonable. In fact, with sterically encumbered porphyrins which inhibit dimerization (e.g. tetratetrasulfoporphyrin, pincer porphyrin, and chloroporphyrin) or with a highly fluorinated porphyrin, many monomeric hydroxoyiron(III) porphyrin complex.
plexes have been isolated. In every case, a high spin state is proven or implied by the characterization data.

One alternate formulation for the +82 ppm species could be considered, namely the diaquo species \([\text{Fe(H}_2\text{O)}(_2)\text{(TPP)}]^+\). It is unlikely on four counts. First, in acid solution, \([\text{Fe(H}_2\text{O)}(_2)\text{(TPP)}]^+\) is likely to be admixed \(S = \frac{7}{2}, \frac{5}{2}\) rather than fully high spin and have a \(\beta\)-pyrrole shift somewhat lower than 82 ppm. Indeed, for the diaqua complexes of a water-soluble methylypyridinium and \(p\)-sulfonated tetraarylporphyrins, values of 71 and 52 ppm have been reported.\(^{38,39}\) Second, carborane anion/aquo ligand exchange was shown earlier to be fast on the NMR time scale so diaqua/aqua ligand exchange is also expected to be fast. This would lead to a time-averaged signal rather than separate resonances that are observed for 2 and 3. Third, significant concentrations of a charge-exchanged ion species such as [Fe-(\(\text{H}_2\text{O)}(_2)\text{(TPP)}\)]\(^+\) are not expected to exist in a low dielectric solvent such as benzene (unless forced to as with 2 or charge-encapsulated as with 4). Fourth, the water concentration is very low and at the 2−4 equiv level is largely sequestered by protons to form aquted hydronium ions such as \(\text{H}_3\text{O}^+\).

Taken all together, it is probable that the species with the \(\beta\)-pyrrole shift at +82 ppm is Fe(OH)(TPP). From this shift value and by analogy to many known hydroxoiron(III) porphyrin complexes, we can be certain that Fe(OH)(TPP) is a high-spin species.

The identification of Fe(OH)(TPP) in slow exchange with \([\text{Fe(H}_2\text{O)}(_2)\text{(TPP)}]^+\) on the NMR time scale is consistent with the results of La and Miskelly\(^{14}\) and has important implications for proton-transfer rates. The proton carriers must be hydrated hydronium ions (e.g. \(\text{H}_3\text{O}^+\)) and their poor mobility in benzene can be understood in terms of charge in a low dielectric medium. On the other hand, water molecules mediate fast ligand exchange between 1 and 2 (and possibly \([\text{Fe(H}_2\text{O)}(_2)\text{(TPP)}]^+\)) by virtue of their charge neutrality, a property compatible with good mobility in benzene.

\(\mu\)-Hydroxo Dimer \([\text{Fe(TPP)}^+]\text{–OH–Fe(TPP)}^+\) \((Y = \text{F}_{20}^–\text{BPh}_4^–, \text{CB}_{12}\text{H}_6\text{X}_6^–)\).\(^{4}\) The synthesis and characterization of these compounds was communicated earlier.\(^6\) However, it was desirable to develop an alternative synthesis under more anhydrous conditions and carry out a more extensive solution characterization because the earlier preparation gave rise to a small amount of heme demetalation. For solubility purposes, we chose to work mostly with the \(\text{F}_{20}^–\text{BPh}_4^–\) counterion. Anhydrous acids ideally suited for protonating easily cleaved oxo bridges have recently been developed in the form of protonated aren salts.\(^{29}\) Treatment of \(\mu\)-oxo dimer \([\text{Fe–O–Fe(TPP)}^+]\text{–}[\text{H(mesitylene)}][\text{F}_{20}^–\text{BPh}_4^–]\) leads cleanly to a salt of the hydroxy-bridged cation 4 (eq 8).

\[
(\text{TPP})\text{Fe–O–Fe(TPP)} + [\text{H(mesitylene)}][\text{F}_{20}^–\text{BPh}_4^–] \rightarrow \quad \quad (\text{TPP})\text{Fe–OH–Fe(TPP)}[\text{F}_{20}^–\text{BPh}_4^–] \quad (8)
\]

The \(^1\)H NMR spectrum of the isolated product in dry dichloromethane-d_2 is shown in Figure 6. The identifying

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Br<OH~Cl<. Some variation of the OH~ field strength might be expected as a function of H-bonding, likely to be present in both Fe(OH)(tetramethylchloroporphyrin)\textsuperscript{36} and Fe(OH)(TPP).

The origin of the H\textsubscript{2}O < OH~ field strength reversal must lie in the different electronic structures of the reporter metals. The spectrochemical series is derived primarily from the electronic spectroscopy of low-spin octahedral d\textsuperscript{6} complexes. The t\textsubscript{2g}\textsuperscript{6} configuration fills the d\textsubscript{g} orbitals making their energy levels particularly sensitive to \(\pi\) effects from the ligands. On the other hand, high- and intermediate-spin complexes of iron-III have only partially filled d\textsubscript{g} orbitals. More importantly, the d\textsubscript{g} orbital, whose \(\sigma\)-antibonding lies along the axial ligand direction in FeX(TPP) complexes,\textsuperscript{32} is occupied in all high- and intermediate-spin derivatives. The consequence is long Fe–X axial bonds and a significant attenuation of \(\pi\)-bonding opportunities as a result. The ligand field effects become more a reflection of \(\sigma\) bonding and electrostatic effects. This explanation readily rationalizes the weaker ligand field of H\textsubscript{2}O (Fe–O = 2.04 Å) relative to OH~ (Fe–O estimated ~ 1.84 Å based on the X-ray structure of Fe(OCH\textsubscript{3})(mesoP)\textsuperscript{40}). That all oxygens, even perchlorate, have stronger ligand fields than H\textsubscript{2}O toward Fe(TPP)< can be rationalized in terms of charge. Indeed, the portion of the magnetocchemical series based on high- and intermediate-spin states can be viewed as a field strength ranking more closely reflecting the expectations of crystal field theory than ligand field theory. That portion is Ag(CB\textsubscript{11}H\textsubscript{12})<.

OPh<. Increasing covalency in the metal bonding appear to be rather minimal. An abbreviated reflection of increasing charge proximity to the metal and/or ordering such as SbF\textsubscript{6}< is not a much weaker field ligand than chloride; the \(\sigma\)-bonding ligands. Possibly the pentacyanoamine, (BrC\textsubscript{6}H\textsubscript{4})<, and I\textsubscript{2} might usefully accompany the introduction of crystal field theory that typically precedes ligand field theory in textbooks of inorganic chemistry.

Minor reversals of spectrochemical ligand field rankings are not uncommon in going from one metal to another. A germane example is the reversal of H\textsubscript{2}O and OH~ observed some time ago in Co(CN)<. (\(\lambda\)max = 380 nm) and Co(CN)<. (\(\lambda\)max = 375 nm).\textsuperscript{41} Unlike a typical reporter complex such as the pentamine [Co(NH\textsubscript{3})\textsubscript{8}]<, the Co(dp)[CN]X< complex has very strong \(\pi\) back-bonding ligands. Possibly the pentacyano moiety renders the sixth coordination site more sensitive \(\sigma\) bonding effects. The pentacyanocobaltate system is an interesting reporter of ligand field strengths because dichloromethane is not a much weaker field ligand than chloride; the \(\lambda\)max difference is only 13 nm.\textsuperscript{42}

It is also interesting to note that the H\textsubscript{2}O < OH~ ordering of ligand field strengths has long been implied by the magnetic data on aqua-methemoglobin. At high pH, high-spin met(H\textsubscript{2}O)-

Hb is in equilibrium with a low-spin species logically assigned the d< orbital, whose \(\sigma\)-bonding and electrostatic effects. This explanation is new eviden.
Into a mixture of (TPP)-Fe—O—Fe(TPP) (0.303 g, 0.224 mmol) and [H(mesitylene)][F$_{20}$-BPh$_4$] (0.179 g, 0.224 mmol) was added CH$_2$Cl$_2$ (ca. 10 mL). After being stirred for 30 min, the brown solution was evaporated to dryness and taken into the glovebox. The brown microcrystalline solid was washed with hexanes and collected by filtration (0.37 g, 80%). Anal. Calcd for C$_{112}$H$_{56}$BN$_4$OF$_{20}$Fe$_2$: C, 66.16; H, 2.83; N, 5.59. Found: C, 65.81; H, 3.16; N, 5.37. Mössbauer at 25°C: $\Delta_0 = 0.30$, $\delta E_q = 1.8$ mm s$^{-1}$. 

$^1$H NMR (CD$_2$Cl$_2$) at 25°C: 6.68 (8H, s, para), 7.35 (8H, t, meta, $J_{HH} = 7.3$ Hz), 7.42 (8H, s, meta), 8.73 (8H, s, ortho), 9.23 (8H, s, ortho), 10.2 (1H, br s, OH), and 28.34 (16H, s, $\beta$-pyrrole) (Figure 6). These assignments supersede those of an earlier communication where additional peaks arose from a small amount of demetalation of the iron porphyrin under prolonged exposure to aqueous acid. Treatment of solutions of 4 with 1 equiv of bis(N,N'-dimethylamino)naphthalene (Aldrich “Proton Sponge”) gave (TPP)Fe—O—Fe(TPP) ($\delta_{pyrrole} = 13.8$ ppm).

**X-ray Structure of Fe(TPP)(CB$_{11}$H$_6$Br$_2$).** Suitable crystals were obtained within 30 min of preparation of an $^1$H NMR sample in benzene-$d_6$. Data were collected on a purple single crystal in Paratone-N at $-115°C$ employing $\theta - 2\theta$ scan profiles using a Siemens R4 (Cu) four-circle diffractometer. An absorption correction was employed using data obtained from $\psi$-scans. The structure was solved using direct methods and refined using Sheldrick’s SHELXTL (Siemens) crystallographic program as previously described.

**X-ray Structure of [Fe(H$_2$O)(TPP)][CB$_{11}$H$_6$Cl$_6$]-H$_2$O.** Suitable crystals were obtained by slow evaporation of a solution of 1 containing 3 equiv of water in benzene-$d_6$. Data collection and structure determination were done in a manner identical to that for 1. There are three water molecules present in the asymmetric unit, one position fully occupied (the coordinated O1W) and two partially occupied (O2W and O3W; 78% and 22% occupancy, respectively). O1W [O...Fe distance is 2.039(4) Å] is H-bonded to O2W [O...H...O distance and angle are 2.613(8) Å and 175(5)$^\circ$, respectively]. The O1W...O3W distance is closer [2.45(2) Å], but there is no hydrogen atom is located between the two O atoms. The hydrogen bond distances and angles are given in Table S11. The highest peak in the difference electron density map is 1.28 e/Å$^3$.

**Acknowledgment.** We thank Drs. Tatiana Drovetskaya, Nathanael Fackler, Zuowei Xie, Rajeev S. Mathur, and Fook Tham and Professors Peter Boyd and Robert Bau for their contributions to this project, Professor Dennis Dougherty for access to a SQUID susceptometer, Drs. Jeffrey A. Clites and Joshua Maurer for assistance with magnetic data collection, Professor Harry Gray for helpful discussions, and the NIH (Grant GM 23851) for support.

**Supporting Information Available:** Tables of X-ray crystal data and refinement summaries, positional parameters, bond angles and bond lengths, anisotropic thermal parameters, H atom coordinates, figures of atom numbering schemes and packing diagrams and Mössbauer, magnetic susceptibility, and NMR data (PDF) and CIF files for 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

JA994478I