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Reversal of H_2O and OH^- Ligand Field Strength on the Magnetochemical Series Relative to the Spectrochemical Series. Novel 1-equiv Water Chemistry of Iron(III) Tetraphenylporphyrin Complexes

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Abstract: Contrary to expectations based on the spectrochemical series, H_2O 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) tetraphenylporphyrin complexes. The preparation and characterization of the $[Fe(H_2O)(TPP)]^+$ 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 ^{1}H NMR β-pyrrole 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 $[Fe(H_2O)(TPP)][CB_{11}H_6Cl_6]$ and is consistent with the high degree of $S = {}^3/_2$ character indicated by the NMR measurement, Mössbauer spectroscopy ($\Delta E_q = 3.24$ mm·s^{-1}), and magnetic susceptibility ($\mu_{eff} = 4.1\ \mu_B$). The anhydrous precursor to these species is the "nearly bare" iron(III) porphyrin complex $Fe(CB_{11}H_6Br_6)(TPP)$. Judged by its magnetic parameters ($\delta_{pyrrole} = -62$ ppm, $\Delta E_q = 3.68$ mm·s^{-1}, $\mu_{eff} = 4.0\ \mu_B$) it attains the long sought essentially "pure" $S = {}^3/_2$ 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 d_π^6 complexes.

Introduction

One of the more counterintuitive orderings of ligand field strength in the spectrochemical series is $OH^- < H_2O$.[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 $2p_\pi - d_\pi$ donor bonding is assumed to be sufficiently stronger with OH^- relative to H_2O 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) tetraphenylporphyrin complexes of the type FeX(TPP). Spin state-dependent properties such as the ^{1}H NMR β-pyrrole 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: $CB_{11}H_{12}^- < SbF_6^- < AsF_6^- < ClO_4^- < C(CN)_3^- < CF_3SO_3^- < BF_4^- < ONC(CN)_2^- < ReO_4^- < OTeF_5^-$.[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 ΔE 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 $Ag(CB_{11}H_{12})_2^- < CB_{11}H_{12}^- < SbF_6^- < Co(C_2B_9H_{11})_2^- < AsF_6^- < ClO_4^- < C(CN)_3^- <$

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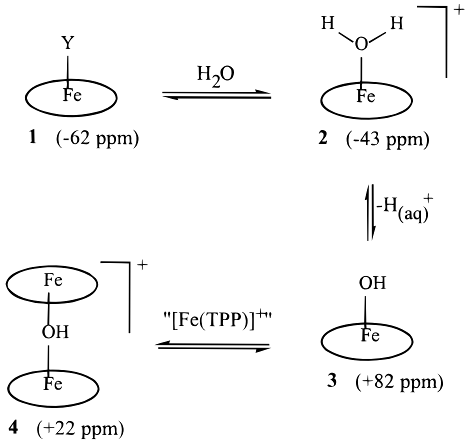
$CF_3SO_3^- < BF_4^- < ONC(CN)_2^- < ReO_4^- < OTeF_5^- < I^- < Br^- < Cl^- < NCS^- < OAc^- \sim N_3^- < OPh(p\text{-}NO_2)^- < OPh^- < F^- < RS^- <$ fluoroaryl < aryl < alkyl $\sim HS^- \sim$ trialkyltin $< CO \sim NO^+$.

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 μ-oxo dimer (TPP)Fe−O−Fe(TPP). The μ-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 $[Co^{III}(NH_3)_5X]^{n+}$.[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 $[(TPP)Fe{-}OH{-}Fe(TPP)]^+$. This protonation of a linear μ-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 $Fe(TPP)^+/H_2O$ 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 donicity and very weakly coordinating counterions, e.g. $F_{20}\text{-}BPh_4^-$ or $CB_{11}H_6X_6^-$ (X = Cl, Br). Indeed, with very weakly coordinating (and weakly basic) anions in low dielectric media quite unexpected chemistry can arise from the high acidity 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_3O^+ is a superacid, having $>10^{12}$ higher acidity than in aqueous solution.[7] In the hydrophobic pocket of a metalloenzyme active site, the acidity of a single water molecule coordinated to a metal cation can be very much higher than that measured in aqueous solution. In low dielectric media, $[Fe(H_2O)(TPP)]^+$ can be expected to be a strong Brønsted acid, reflecting the high Lewis acidity of the bare $Fe(TPP)^+$ cation. We therefore prepared the "nearly bare" anhydrous species $Fe(TPP)(CB_{11}H_6X_6)$ 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]

Scheme 1



Results and Discussion

The hexahalo carborane anions, $CB_{11}H_6X_6^-$ (X = Cl, Br) and the perfluorinated tetraphenylborate ion, $F_{20}\text{-}BPh_4^-$ were chosen for this study because of their extremely low Brønsted 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 $CB_{11}H_6X_6^-$ 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 $F_{20}\text{-}BPh_4^-$ 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 $Fe(TPP)^+/H_2O$ system in benzene solution is previewed in Scheme 1.

Its establishment required the characterization of each of the new components. We treat them in turn.

Intermediate-Spin Precursor Complex $Fe(TPP)(CB_{11}H_6X_6)$, 1. The synthesis of **1** differs from the typical silver salt metathesis procedure[8] because of the need to avoid complications from the formation of silver complex anions,[18] exemplified by eq 1.[19]

$$FeBr(TPP) + 2Ag(CB_{11}H_6X_6) \rightarrow [Fe(p\text{-xylene})(TPP)][Ag(CB_{11}H_6X_6)_2] + AgBr \quad (1)$$

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

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

compd	ΔE_q (mm·s^{-1})	$\delta_{pyrrole}$ (ppm)	$\mu_{eff}^{25\,°C}$ (μ_B)	Fe−N$_{ave}$ (Å)	Fe···Ct$_P$ (Å)	Fe−X$_{ax}$ (Å)
$Fe(CB_{11}H_6Br_6)(TPP)$, **1**	3.68 (300 K)	−62	4.0	1.982(14)	0.08	2.722(3)
$Fe(CB_{11}H_{12})(TPP)^a$	4.12 (77 K)	−59	4.2	1.961(5)	0.10	1.82(4)
$Fe(FSbF_5)(TPP)^a$	4.29 (77 K)	−49	4.1	1.978(3)	0.15	2.105(3)
$[Fe(H_2O)(TPP)]^+$, **2**	3.24 (300 K)	−43	4.2	1.979(10)	0.19	2.039(4)
$Fe(OClO_3)(TPP)^b$	2.79 (295 K)	+28	5.2	2.001(5)	0.30	2.029(4)
$[(TPP)Fe\text{-}OH\text{-}Fe(TPP)]^+$, **4**	1.8^c (300 K)	+28	5.5	2.047	0.40	1.821(8)
Fe(OH)(TPP), **3**		+82				
(TPP)Fe-O-Fe(TPP)	0.60^d (77 K)	+13.8		2.081(3)^e	0.54	1.759(1)

[a] Gupta, G. P.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022. Gupta, G. P.; Lang, G.; Reed, C. A.; Shelly, K.; Scheidt, W. R. *J. Chem. Phys.* **1987**, *86*, 5288. [b] Spartalian, K.; Lang, G.; Reed, C. A. *J Chem. Phys.* **1979**, *71*, 1832. [c] Counterion is F_{20}-BPh_4^-. [d] Simmoneaux, G.; Scholtz, W. F.; Reed, C. A.; Lang, G. *Biochim. Biophys. Acta* **1982**, *716*, 1. [e] Swepston, P. N.; Ibers, J. A. *Acta Crystallogr.* **1985**, *C41*, 671.

blue”,[20] the radical cation of tris(*p*-bromophenyl)amine ($Ar_3N^{•+}$) having a carborane counterion (eq 2).

$$\mathrm{Fe(TPP)} + [\mathrm{Ar_3N^{•+}}][\mathrm{CB_{11}H_6X_6}^-] \rightarrow \mathrm{Fe(TPP)(CB_{11}H_6X_6)} + \mathrm{Ar_3N} \quad (2)$$

The full oxidizing power of the reagent ($E = 0.7$ V vs Fc/Fc$^+$) 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 binding and very weak field axial ligand,[21] **1** has an intermediate spin state. The magnetic moment at room temperature is within experimental error of the spin-only value for a pure $S = {}^3/_2$ state (3.9 μ_B). 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 ^{1}H NMR shift of the eight β-pyrrole protons (see Figure 1A) is −62 ppm in benzene-d_6, the most upfield yet reported.[3,22] These extrema indicate that **1** has attained the essentially pure $S = {}^3/_2$ spin state. We note that the ^{1}H NMR pyrrole resonance is sensitive to concentration and temperature 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).[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 $S = {}^3/_2$ character in Table 1. They reflect essentially complete depopulation of the $d_{x^2-y^2}$ orbital and are consistent with a pure $S = {}^3/_2$ spin state. A strict correlation of all of the parameters used as indicators of the $S = {}^3/_2$ 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,[24] and crystal packing effects. Indeed, it has recently been shown that the $S = {}^3/_2$ state is favored by porphyrin-induced distortions to the coordinate geometry.[25] For these reasons, we emphasize the $\delta_{pyrrole}$ 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.

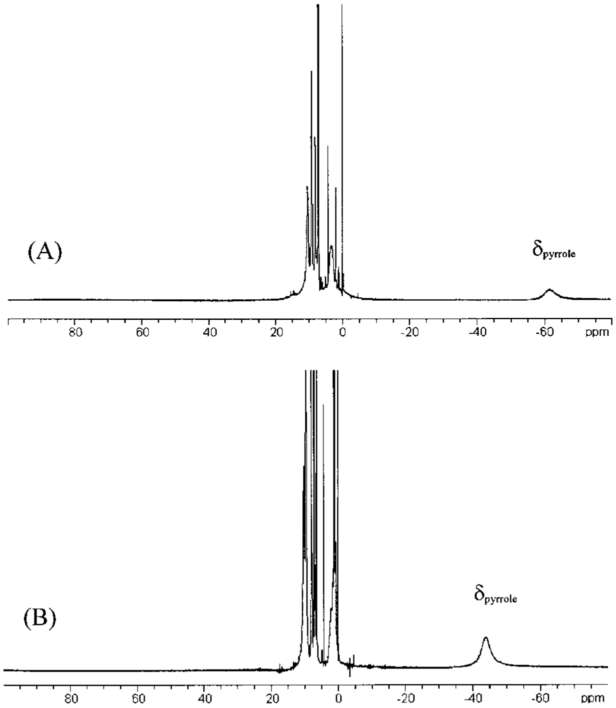

Figure 1. ^{1}H NMR spectra of (A) $Fe(TPP)(CB_{11}H_6Br_6)$, **1**, in dry benzene-d_6 at 25 °C and (B) after addition of 1 equiv of water to produce $[Fe(H_2O)(TPP)][CB_{11}H_6Br_6]$, **2**.

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 $\pi-\pi$ interaction between the open faces.[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 arene solvents such as benzene, toluene, or *p*-xylene to give ionic materials of

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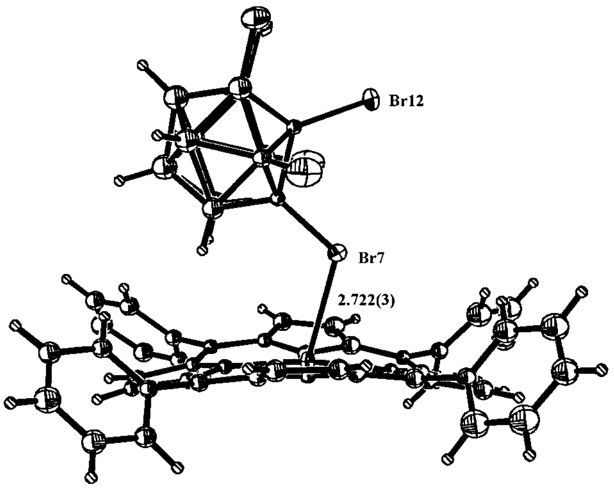

Figure 2. ORTEP diagram of $Fe(TPP)(CB_{11}H_6Br_6)$, **1**. Thermal ellipsoids are drawn at the 30% probability level for the structure determined at 163 K.

the type $[Fe(arene)(TPP)][CB_{11}H_6X_6]$.[24] The arenes in these compounds are weak η^2 ligands implying some ionization of **1** even in low dielectric solvents such as benzene (eq 3).

$$Fe(TPP)(CB_{11}H_6X_6) + arene \rightarrow [Fe(arene)(TPP)][CB_{11}H_6X_6] \quad (3)$$

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, ^1H 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 nucleii. 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 $S = {}^3/_2$ 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 (the least coordinating arene solvent used) the effect cannot be quantified. Nevertheless, it is consistent with a small equilibrium constant for eq 3 and justifies the representation of **1** as a neutral species in Scheme 1.

Aqua Complex $[Fe(H_2O)(TPP)][CB_{11}H_6X_6]$, 2. Titration of **1** with water at the 1-equiv level displaces the coordinated carborane anion giving the monoaqua complex **2** (eq 4).

$$Fe(TPP)(CB_{11}H_6X_6) + H_2O \rightarrow [Fe(H_2O)(TPP)][CB_{11}H_6X_6] \quad (4)$$

The aqua cation is identified in benzene solution by its ^1H NMR β-pyrrole shift at −43 ppm at 25 °C (see Figure 1B). Given the range of −62 ppm for intermediate-spin state **1** to +80 ppm for high-spin species, this upfield chemical shift indicates that **2** has an admixed-intermediate spin state with a fairly high degree of $S = {}^3/_2$ character. This was the first indication that H_2O is a very weak field ligand toward $Fe(TPP)^+$. The carborane B−H resonances have lost the narrowness observed in **1** and now show broadness typical of an uncoordinated anion (ca. 1000 Hz) (Figure S9B). With less than 1 equiv of water, the pyrrole resonance takes a value intermediate between −62 and −43 ppm indicating that eq 4 is a rapidly established equilibrium on the NMR time scale. ^1H NMR spectra of **2** in toluene-d_8 below 0 °C (Figure S10) allow discrimination of two sets of resonances for the *ortho* and *meta* phenyl protons, consistent with the C_{4v} 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 $Fe(OClO_3)(TPP)$.[22] The deuterium NMR spectrum of **2** prepared with D_2O shows a resonance at 10.2 ppm attributable to coordinated water (obscured by phenyl group resonances in Figure 1B).

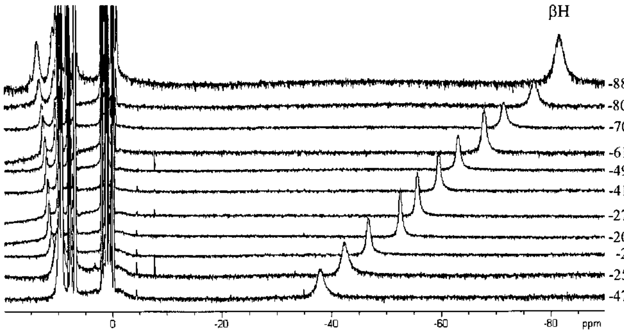

Figure 3. Variable-temperature ^1H NMR spectrum of $[Fe(H_2O)(TPP)][CB_{11}H_6Br_6]$, **2**, in dry toluene-$d_8$.

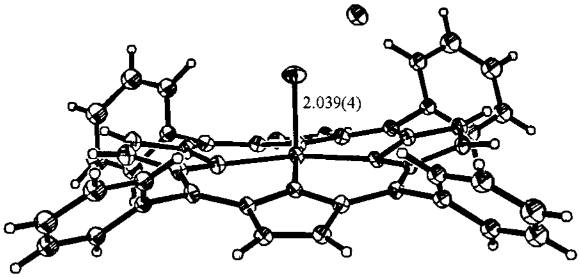

Figure 4. ORTEP diagram of the cation and higher-occupancy lattice water molecule in $[Fe(H_2O)(TPP)][CB_{11}H_6Cl_6]\cdot H_2O$. Thermal ellipsoids are drawn at the 30% probability level for the structure determined at 163 K.

$[Fe(H_2O)(TPP)][CB_{11}H_6X_6]$ can be prepared and isolated on a preparative scale by the controlled addition of water to **1**. Single crystals of $[Fe(H_2O)(TPP)][CB_{11}H_6Cl_6]\cdot H_2O$ 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 μ_B), are all in the direction expected for the admixture of a fairly small amount of $S = {}^5/_2$ character into a predominantly $S = {}^3/_2$ 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 ppm β-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)[27] these experiments had to be

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[27] Wing, J.; Johnson, W. H. *J. Am. Chem. Soc.* **1957**, *79*, 864−865.

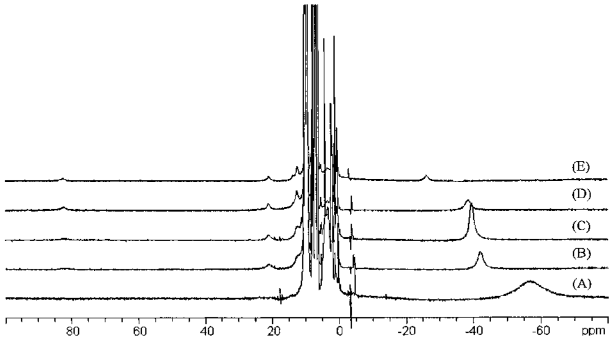

Figure 5. ^{1}H NMR spectra in benzene-d_6 at 25 °C of (A) an equilibrating mixture of **1** and **2** (mostly **1**), (B) $[Fe(H_2O)(TPP)][CB_{11}H_6Br_6]$, **2**, and (C−E) **2** as a function of an additional 1, 2, and 4 equiv of water, respectively.

performed at the low porphyrin concentration of 2 mM. At this concentration the initial β-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 H_2O as it becomes progressively H-bonded in an $(H_2O)_n$ cluster around the axial coordination site. This is observed in the crystal structure. An alternative explanation is partial coordination of the added water to the vacant (sixth) site of iron. The six-coordinate $[Fe(H_2O)_2(TPP)]^+$ is a known ion in the solid state, although its existence may be the result of H-bonding to perchlorate counterion.[28] It has a high spin state (or nearly so), and its β-pyrrole chemical shift would therefore be expected to approach +80 ppm. Under conditions of fast aqua ligand exchange, the time-averaged signal of **2** would move downfield with increasing presence of a six-coordinate bis(aqua) species. The carborane anion is much less capable of H-bonding than perchlorate so the appearance of lattice water in the vicinity of the coordinated water in the crystal structure of **2** is a better model for solution behavior. The O···O separation of the coordinated and higher occupancy lattice water molecules in the crystal structure of **2** is 2.61 Å, consistent with H-bonding. In the crystal structure, there is a partial occupancy of a water molecule H-bonded to the chloro substituents of the carborane anion. It is tempting to view this clustering of water molecules with the anion in the vicinity of the fifth coordination site as a model for ion-pairing and water solvation in benzene solution. Both lattice and coordinated water can be driven off by heating the solid under vacuum at 110 °C, producing **1**. This was inferred from infrared spectroscopy by monitoring the loss of the ν_{O-H} at 3460 cm^{-1} and from the concomitant increase in the Mössbauer quadrupole splitting.

The existence and stability of the monomeric aqua cation in **2** is unexpected given the well-known tendency of open-faced iron(III) porphyrins to form μ-oxo dimers. However, it can be understood in terms of the unusual conditions of acidity and hydration: consider eq 5.

$$2[Fe(H_2O)(TPP)]^+ \rightarrow (TPP)Fe-O-Fe(TPP) + H_3O^+ + H^+ \quad (5)$$

In order for this condensation to occur, H^+ must be lost. In other words, $Fe(H_2O)(TPP)]^+$ would have to be a strong enough acid to protonate either benzene or the carborane anion for eq 5 to proceed. The existence of $[H(benzene)^+][CB_{11}H_6X_6^-]$ as an isolable superacid[29] tells us that the anion even is more difficult to protonate than benzene. In fact, the best base in solution will be the μ-oxo compound itself. The condensation reaction should therefore be written as eq 6.

$$2[Fe(H_2O)(TPP)]^+ \rightarrow [(TPP)Fe-OH-Fe(TPP)]^+ + H_3O^+ \quad (6)$$

Even this reaction does not occur to any large extent in dry benzene. The singly hydrated proton in the H_3O^+ 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 H_3O^+ ion is superacidic.[7] In order for eq 6 to proceed in benzene solution, additional equivalents of H_2O must be available to hydrate the H_3O^+ 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 +22 and +82 ppm. These are assigned to the β-pyrrole shifts of the μ-hydroxo dimer $[Fe(TPP)-OH-Fe(TPP)]^+$, **4**, and the monohydroxo complex Fe(OH)(TPP), **3**. Their appearance is an expression of the Brønsted acidity of **2** manifest by the addition of a base (H_2O). It is a logical consequence of a hydrolysis stoichiometry that can be idealized according to eq 7.

$$3[Fe(H_2O)(TPP)]^+ + 7H_2O \rightarrow [Fe(TPP)-OH-Fe(TPP)]^+ + Fe(OH)(TPP) + 2H_9O_4^+ \quad (7)$$

The hydrolysis proceeds to the right-hand side only after some equivalents of water have been added because H^+ cannot be liberated unless it is solvated by a number of water molecules. Four water molecules in the $H_9O_4^+$ ion, the trihydrated H_3O^+ ion, is a reasonable proposal for the dominant formulation of an aquated proton in benzene although $H_5O_2^+$ and $H_7O_3^+$ may also be present in the early stages of the hydrolysis. $[H_9O_4][CB_{11}H_6Br_6]$ is an isolable discrete salt that can be recrystallized from arene solvents.[30] Indeed, X-ray-quality crystals of $[H_9O_4][CB_{11}H_6Br_6]$ 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.

A +82 ppm value for a β-pyrrole shift is indicative of a species with an $S = {}^5/_2$ high-spin state.[31] Similar values are found for a large number of FeX(TPP) species known to be high spin (X = halide, RO^-, etc.)[3,32] 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. tetramesitylporphyrin,[33,34] pincer porphyrin,[35] and chiroporphyrin[36]) or with a highly fluorinated porphyrin,[37] many monomeric hydroxoiron(III) porphyrin com-

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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 $[Fe(H_2O)_2(TPP)]^+$. It is unlikely on four counts. First, in acid solution, $[Fe(H_2O)_2(TPP)]^+$ is likely to be admixed $S = {}^5/_2, {}^3/_2$ rather than fully high spin and have a β-pyrrole shift somewhat lower than 82 ppm. Indeed, for the diaqua complexes of a water-soluble methylpyridinium 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-exposed ionic species such as $[Fe(H_2O)_2(TPP)]^+$ 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 aquated hydronium ions such as $H_9O_4^+$.

Taken all together, it is probable that the species with the β-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 $[Fe(H_2O)(TPP)]^+$ 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. $H_9O_4^+$) 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 $[Fe(H_2O)_2(TPP)]^+$) by virtue of their charge neutrality, a property compatible with good mobility in benzene.

***μ*-Hydroxo Dimer [Fe(TPP)−OH−Fe(TPP)]Y (Y = F_{20}-BPh_4^-, $CB_{11}H_6X_6^-$), 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 F_{20}-BPh_4^- counterion. Anhydrous acids ideally suited for protonating easily cleaved oxo bridges have recently been developed in the form of protonated arene salts.[29] Treatment of μ-oxo dimer (TPP)Fe−O−Fe(TPP) with [H(mesitylene)][F_{20}-BPh_4] leads cleanly to a salt of the hydroxy-bridged cation **4** (eq 8).

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

The ^1H NMR spectrum of the isolated product in dry dichloromethane-d_2 is shown in Figure 6. The identifying β-pyrrole shift appears at +28 ppm. The absence of β-pyrrole peaks at −43 or +82 ppm from monomeric aqua or hydroxo species **2** and **3**, respectively, is especially notable. The absence of water stabilizes a species heretofore unobserved in the hydrolysis chemistry of iron(III) porphyrins. The β-pyrrole resonance of **4** is +28 ppm in dry dichloromethane but appears at +22 ppm in the benzene aquation reaction studied above (Figure 5, eq 5). This may simply be a solvent effect but it also suggests that like $[Fe(H_2O)(TPP)]^+$, the hydroxo dimer may be subject to specific aquation by a few equivalents of water. This could be at the hydroxo bridge or at the vacant (sixth) coordination site. As expected, treatment of a solution of **4** with a noncoordinating base (e.g. "Proton Sponge") quantitatively reverses eq 8.

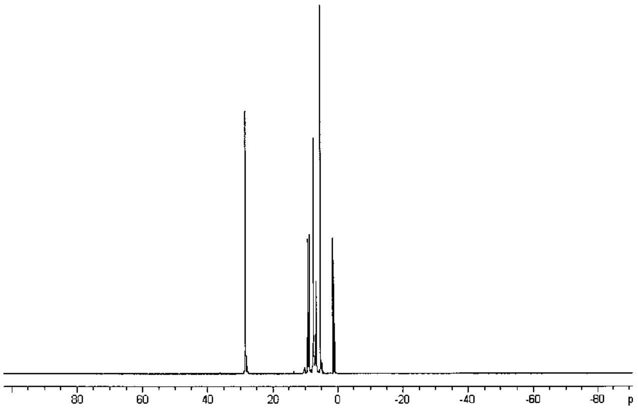

Figure 6. ^1H NMR spectrum of [(TPP)Fe−OH−Fe(TPP)][F_{20}−BPh_4], **4**, in dry CD_2Cl_2 at 25 °C.

The chemical shift value of **4** at +22 ppm reflects the $S = {}^3/_2, {}^5/_2$ admixed intermediate spin state deduced earlier from the crystal structure, Mössbauer spectrum, and magnetic susceptibility data.[6] Since antiferromagnetic coupling is believed to be very weak in the $[(TPP)Fe−OH−Fe(TPP)]^+$ cation, and therefore of little consequence in the NMR spectrum, the shift can probably be taken as a measure of the ligand field effect of a shared hydroxide ligand. Logically, it is considerably weaker than in the high-spin monomeric hydroxo complex **3**. In fact, the ligand field effect of "half" a hydroxide ligand roughly equates to that of perchlorate in $Fe(OClO_3)(TPP)$, where δ_{pyrrole} occurs at +28 ppm.

H_2O versus OH^- Ligand Field Strengths. Of the four criteria used to determine the magnetochemical ranking of ligand field strengths in iron porphyrins (μ_{eff}, $g_\perp$, ΔE_q, and δ_{pyrrole}) the ^1H NMR chemical shift of the β-pyrrole protons is the most sensitive. The value of −62 ppm in **1** is the most upfield reported to date[3] and is consistent with a pure $S = {}^3/_2$ state. At −43 ppm for **2**, H_2O is a very weak field ligand, comparable to SbF_6^- (−49 ppm) and AsF_6^- (−31 ppm). It is considerably weaker than oxyanions such as perchlorate (+28 ppm), triflate (+48 ppm), or perrhenate (+67 ppm). Compound **3** has δ_{pyrrole} at +82 ppm indicative of an $S = {}^5/_2$ state, so hydroxide is a considerably stronger field ligand than water. It is comparable to the halides. The order $H_2O < ClO_4^- < ReO_4^- < OH^- \sim Cl^-$ contrasts with that from the spectrochemical series ranking of $ReO_4^- < Cl^- \sim ClO_4^- < OH^- < H_2O$ and is most notable in the unexpectedly weak field ranking of H_2O. The near equality of OH^- and Cl^- field strengths in the magnetochemical ranking is supported by recent work with iron(III) tetramethylchiroporphyrin complexes. In the series X = Br^-, Cl^-, and OH^- in FeX(tetramethylchiroporphyrin) the averaged β-pyrrole chemical shifts are 84.6, 90.7, and 91.9 ppm, respectively.[36] This suggests the magnetochemical ordering is $H_2O < ClO_4^- < ReO_4^- <$

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$Br^- < OH^- \sim Cl^-$. Some variation of the OH^- field strength might be expected as a function of H-bonding, likely to be present in both Fe(OH)(tetramethylchiroporphyrin)[36] and Fe(OH)(TPP).

The origin of the $H_2O < OH^-$ 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^6 complexes. The $t_{2g}{}^6$ configuration fills the d_π orbitals making their energy levels particularly sensitive to π effects from the ligands. On the other hand, high- and intermediate-spin complexes of iron(III) have only partially filled d_π orbitals. More importantly, the d_{z^2} orbital, whose σ-antibonding lobe lies along the axial ligand direction in FeX(TPP) complexes,[21] is occupied in all high- and intermediate-spin derivatives. The consequence is long Fe−X axial bonds and a significant attenuation of π-bonding opportunities. As a result, the ligand field effects become more a reflection of σ bonding and electrostatic effects. This explanation readily rationalizes the weaker ligand field of H_2O (Fe−O = 2.04 Å) relative to OH^- (Fe−O estimated ~ 1.84 Å based on the X-ray structure of $Fe(OCH_3)$(mesoP)[40]). That all oxyanions, even perchlorate, have stronger ligand fields than H_2O toward $Fe(TPP)^+$ can be rationalized in terms of charge. Indeed, the portion of the magnetochemical 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 $Ag(CB_{11}H_{12})_2^- < CB_{11}H_{12}^- < SbF_6^- < Co(C_2B_9H_{11})_2^- < AsF_6^- < H_2O < ClO_4^- < C(CN)_3^- < CF_3SO_3^- < BF_4^- < ONC(CN)_2^- < ReO_4^- < OTeF_5^- < I^- < Br^- < OH^- \sim Cl^- < NCS^- < OAc^- \sim N_3^- < OPh(p\text{-}NO_2)^- < OPh^- < F^- < RS^-$. The order is largely a reflection of increasing charge proximity to the metal and/or increasing covalency in the metal−ligand σ bond. The effects of π bonding appear to be rather minimal. An abbreviated ordering such as $SbF_6^- < H_2O < ClO_4^- < CF_3SO_3^- < BF_4^- < ReO_4^- < I^- < Br^- < OH^- \sim Cl^- < OAc^- < OPh(p\text{-}NO_2)^- < OPh^- < F^- < RS^-$ 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_2O and OH^- observed some time ago in $Co(CN)_5(H_2O)^{2-}$ (λ_{max} = 380 nm) and $Co(CN)_5(OH)^{3-}$ (λ_{max} = 375 nm).[41] Unlike a typical reporter complex such as the pentammine $[Co(NH_3)_5X]^{n+}$, the $Co^{III}(CN)_5X^{n-}$ complex has very strong π back-bonding ligands. Possibly the pentacyano moiety renders the sixth coordination site more sensitive σ 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 λ_{max} difference is only 13 nm.[42]

It is also interesting to note that the $H_2O < OH^-$ ordering of ligand field strengths has long been implied by the magnetic data on aqua-methemoglobin. At high pH, high-spin met(H_2O)-Hb is in equilibrium with a low-spin species logically assigned to met(OH)Hb.[43] Yet, to our knowledge, this inconsistency with the spectrochemical series has never been discussed in the chemical literature. Its explanation is now evident.

More generally, the prevalence of σ-bonding ligands and high-spin states in metalloenzymes and metallobiomolecules means that the magnetochemical series may become preferred over the spectrochemical series for correlating ligand field strengths throughout bioinorganic chemistry.

Experimental Section

All manipulations of air-sensitive materials were carried out in a Vacuum Atmospheres drybox (O_2, H_2O < 1 ppm) or on a dual manifold vacuum line using Schlenk techniques and flame-dried glassware. Arene solvents and hexanes were dried by distillation from Na/benzophenone outside the drybox and again from Na/K alloy inside the drybox immediately prior to use. NMR solvents were dried over molecular sieves. NMR spectra were recorded on Bruker Aspect (200 and 360 MHz) or Bruker AMX (500 MHz) systems. ^1H NMR spectra were referenced internally to TMS or to residual *proto*-solvent. ^{11}B NMR spectra were referenced externally to 1.0 M BBr_3 in hexanes (40 ppm) and ^{19}F to external C_6F_6 (−162 ppm) both as inserts in a tube containing acetone-d_6. Mössbauer spectra were recorded using instrumentation assembled by Tom Kent of Web Research. Samples (10−50 mg) were embedded in melted paraffin wax and referenced to iron foil at room temperature. SQUID magnetic susceptibility data were recorded at 2 and 10 kG on ground, packed samples on Quantum Design instrumentation at the California Institute of Technology. Diamagnetic corrections were applied using values of -600×10^{-6} cgs units for TPP, and Pascal constants, for the remainder of the atoms. Fe(TPP)[44] and [H(mesitylene)][F_{20}−BPh_4][29] were prepared using published procedures. Water titrations were done using microsyringe techniques in the drybox.

Fe(TPP)($CB_{11}H_6X_6$), 1. $AgCB_{11}H_6Br_6$ (0.4221 g, 0.583 mmol) was added to a Schlenk flask, **A**, equipped with a stir bar and placed on a double-manifold vacuum line where it was thoroughly dried by evacuation/ argon refill cycling. A separate Schlenk flask, **B**, equipped with a stir bar was charged with vacuum-dried tris-*p*-bromophenylamine, $(BrC_6H_4)_3N$ (0.2827 g; 0.587 mmol), and iodine (0.0783 g; 0.3085 mmol). The flask was flushed with argon, cooled to liquid-N_2 temperature, evacuated to 100 mTorr, removed from the N_2-bath, and back-filled with argon. This was repeated five times, taking care to prevent loss of iodine. Dichloromethane (ca. 25 mL) was vacuum transferred into this flask and stirred until dissolution of the solids was achieved. The contents of **B** were then transferred to **A** using a Schlenk transfer tube, and the resultant solution in flask **A** was stirred vigorously for 15 min. Flask **A** was then transferred to the drybox where the AgI precipitate was removed by filtration through both medium- and fine-porosity frits. The solvent was removed under reduced pressure. The navy blue microcrystalline material was repeatedly washed with hexanes to remove excess iodine to give $[(BrC_6H_4)_3N][CB_{11}H_6Br_6]$ (0.429 g, 67%). The corresponding hexachlorocarborane compound was made in a simliar manner. Fe(TPP) (0.1 g, 0.149 mmol) was dissolved in benzene (25 mL) at gentle reflux, and $[(BrC_6H_4)_3N][CB_{11}H_6X_6]$ (25 mL of a 6 mM solution in *o*-dichlorobenzene) was added gradually. After 30 min of gentle reflux, the solvent volume was reduced by half and hexanes (150 mL) were added. The brown microcrystalline product was collected on a fine frit, washed with hexanes, and dried under vacuum (138 mg, 91%). Anal. Calcd (X = Cl) for $C_{45}H_{34}B_{11}N_4Cl_6Fe$: C, 53.08; H, 3.37; N, 5.50. Found: C, 52.36; H, 3.31; N, 5.15. Mössbauer (X = Cl) at 25 °C: $\delta = 0.33$, $\Delta E_q = 3.68$ mm/s (Figure S5). μ_{eff} (X = Cl) = 4.0 μ_B at 25°C (Figure S6). ^1H NMR (X = Br) 20 mM in benzene-d_6 at 25 °C: −62 (8H, β-pyrrole, s, br), 2.1 (1H, carborane, s, br), 3.4 (5H, carborane, s, br), 8.1 (4H, para, s, br), 9.1 (8H, *meta*, s, br), and 10.4 (8H, ortho, s, br) (Figures 1A, S9A).

[Fe(H_2O)(TPP)][$CB_{11}H_6X_6$], 2. A 1-equiv amount of water was added to a refluxing solution of **1** in benzene. After 30 min, a 10-fold addition of hexanes was used to precipitate the brown microcrystalline product, which was collected on a fine frit and allowed to dry (85%). Anal. Calcd (X = Cl) for $C_{45}H_{36}B_{11}N_4OCl_6Fe$: C, 52.16; H, 3.50; N, 5.41. Found: C, 50.96; H, 3.47; N, 4.98. IR (X = Br): 3427 w (ν_{O-H}) cm^{-1}. Mössbauer (X = Cl) at 25 °C: $\delta = 0.30$, $\Delta E_q = 3.24$ mm·s^{-1} (Figure S7). μ_{eff} (X = Cl) = 4.2 μ_B at 25 °C (Figure S8). ^1H NMR (X = Br) 20 mM in benzene-d_6 at 25 °C: −43 (8H, β-pyrrole, s, br), 7.9 (4H, *para*, s, br), 9.5 (8H, *meta*, s, br), and 10.2 (8H, *ortho*, s, br) (Figures 1B, S9B, S10).

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[(TPP)Fe−OH−Fe(TPP)][F_{20}-BPh_4], 4. 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_2Cl_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 $C_{112}H_{56}BN_4OF_{20}Fe_2$: C, 66.16; H, 2.83; N, 5.59. Found: C, 65.81; H, 3.16; N, 5.37. Mössbauer at 25 °C: $\delta = 0.30$, $\Delta E_q = 1.8$ mm·s^{-1}. ^{1}H NMR (CD_2Cl_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, β-pyrrole) (Figure 6). These assignments supersede those of an earlier communication[19] 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)($CB_{11}H_6Br_6$). 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 ψ-scans. The structure was solved using direct methods and refined using Sheldrick's SHELXTL (Siemens) crystallographic program as previously described.[6]

X-ray Structure of [Fe(H_2O)(TPP)][$CB_{11}H_6Cl_6$]·H_2O. 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)°, 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.

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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.

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