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Magnetic Properties of Iron(III) Porphyrin Dimers in Aqueous Solution

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Received May 5, 1976

AIC603246

Existence of μ-oxo-bridged iron(III) porphyrin dimers in the solid state has been demonstrated by a variety of physical techniques.[1] A limited amount of evidence in the form of diminished magnetic moments (characteristic of antiferromagnetic coupling through an oxo bridge) also exists for μ-oxo-bridged iron(III) protoporphyrin (FeProt)[2,3] and iron(III) *meso*-tetrakis(4-sulfonatophenyl)porphine (FeTPPS4)[4] dimers in aqueous solution.[5] However, a high magnetic moment found for the hemin *c* dimer[6] suggests that iron(III) porphyrins do not necessarily dimerize by formation of oxo bridges. To test this hypothesis magnetic mesurements have been carried out on aqueous solutions of several water-soluble iron(III) prophyrins.

Iron(III) protoporphyrin chloride was purchased from Sigma Chemical Co. Hemin *c*,[6] iron(III) deuteroporphyrin chloride (FeDeut),[7] iron(III) deuteroporphyrin 2,4-disulfonic acid (FeDDS),[7,8] FeTPPS4,[4] and iron(III) *meso*-tetrakis(*N*-methyl-4-pyridyl)porphine pentaperchlorate (FeTMpyP)[9-11] were prepared by the cited literature methods. FeTMpyP was converted from the perchlorate salt to the more water-soluble chloride salt by passage through Dowex 1X-1 anion-exchange resin. Iron(III) *meso*-tetrakis(4-carboxyphenyl)porphine (FeTCPP) was prepared by reaction of ferrous acetate with TCPP[9] in glacial acetic acid employing the procedure devised for hemin *c*.[6] Magnetic moment calculations are based on the iron content of iron(III) porphyrins as determined by Drabkin's *o*-phenanthroline method.[12] Magnetic measurements were made by Evans' (NMR) method[13] using a coaxial capillary (Wilmad Co.) for the reference material. Experiments carried out to check the validity of this technique for iron(III) porphyrins have been described previously.[6] Magnetic moments reported here were calculated from the molar paramagnetic susceptibility per iron atom using the spin-only formula.

Results of magnetic measurements at a variety of pH and ionic strength conditions are shown in Table I. The low magnetic moments of the meso-substituted iron(III) porphyrins (FeTPPS4, FeTCPP, and FeTMpyP) at neutral pH are consistent with the presence of μ-oxo bridges. Additional data for the pH dependence of FeTPPS4 and FeTMpyP paramagnetic susceptibilities are shown in Figure 1. The curves correspond to the dimerization equilbrium

$$2H_2OFe(Por) \overset{Q_D}{\rightleftharpoons} (Por)Fe\text{-}O\text{-}Fe(Por) + 2H^+$$

where $Q_D = 4 \times 10^{-7}$ M for FeTPPS4 and $Q_D = 1.4 \times 10^{-8}$ M for FeTMpyP at 35 °C at the solution conditions listed in Figure 1. The magnetic acid–base titrations were reversible for both compounds. A dimerization equilibrium quotient of 2×10^{-8} M was previously obtained for FeTPPS4 under different concentration conditions.[4] Dimerization of FeTMpyP is highly ionic strength dependent (see the magnetic moments at pH 7.2 in Table I) as might be expected for interactions of highly charged species. Prior spectrophotometric titrations of FeTMpyP may be interpreted in terms of the dimerization equilibrium shown above with $Q_D = 9 \times 10^{-9}$ M.[14] An anomalous magnetic moment was obtained for FeTMpyP in very basic media (see Table I), perhaps due to the formation of dihydroxo monomeric species. Dimerization work has not been reported for FeTCPP, and low solubility precluded magnetic measurements at acid pH. Additional data supporting formation of oxo-bridged FeTPPS4, FeTCPP, and FeTMpyP dimers are found in the temperature dependence of magnetic moments given in Table II. Antiferromagnetic coupling is expected to decrease the magnetic moment with a decrease in temperature,[1] and this effect is qualitatively

Table I. Magnetic Moments of Iron(III) Porphyrins

Iron(III) porphyrin	Magnetic moments, μ_B [a] pH 2.5[b]	pH 5.1[c]	pH 7.2[d]	pH 9.2[e]	pH 12.0[f]	pH 14.0[g]
$FeTPPS_4$	6.0	3.2	2.8	2.7	2.8	2.6
FeTCPP	*h*	*h*	3.2	3.2	3.1	2.9
FeTMpyP	6.1[i]	4.3[j]	4.4, 2.8[j]	2.9[k]	3.0	4.7
FeDeut	*h*	*h*	5.5	5.4	5.5, 3.9[l]	3.6
FeDDS	*h*	5.7	5.7	5.8	5.7	5.8
Hemin *c*[m]	*h*	*h*	5.5	5.5	5.3, 5.3[l]	5.4

[a] At 308 K and 14.2 kG, per iron atom; iron(III) porphyrin concentration 5×10^{-3} to 1×10^{-2} M; uncertainties 0.05–0.10 μ_B. [b] 0.05 M phosphate buffer, $I = 0.10$ with $NaClO_4$. [c] 0.05 M acetate buffer, $I = 0.10$ with $NaClO_4$. [d] 0.05 M phosphate buffer, $I = 0.10$. [e] 0.05 M borate buffer, $I = 0.10$ with $NaClO_4$. [f] 0.05 M phosphate buffer, $I = 0.18$. [g] 1.0 M NaOH. [h] Solubility limitations precluded measurements. [i] 0.05 M phosphate buffer only. [j] 0.25 M M NaCl only. [k] 0.05 M borate buffer, $I = 0.25$ with NaCl. [l] 0.05 M phosphate buffer, $I = 1.0$ with $NaClO_4$. [m] Data from ref 6.

Table II. Temperature Dependence of Magnetic Moments

Iron(III) porphyrin	Magnetic moments, μ_B [a] 276 K	308 K	363 K
$FeTPPS_4$	2.17	2.76	3.2
FeTCPP	2.68	3.1	3.5
FeTMpyP	2.76	3.0	4.0
FeDeut	5.4	5.5	5.2
FeDDS	5.6	5.7	5.4
FeProt	3.3	3.5	3.7
Hemin *c*[b]	5.4[c]	5.5	4.9[d]

[a] 5×10^{-3} to 1×10^{-2} M iron(III) porphyrin; 0.05 M sodium phosphate buffer; pH 12.0; 2% *tert*-butyl alcohol; at 14.2 kG; μ_{eff} per iron atom; uncertainties in μ_{eff} 0.05–0.10 μ_B; iron(III) porphyrin concentration corrected for solvent volume changes. [b] From ref 6 at pH 8.0. [c] 278 K. [d] 348 K.

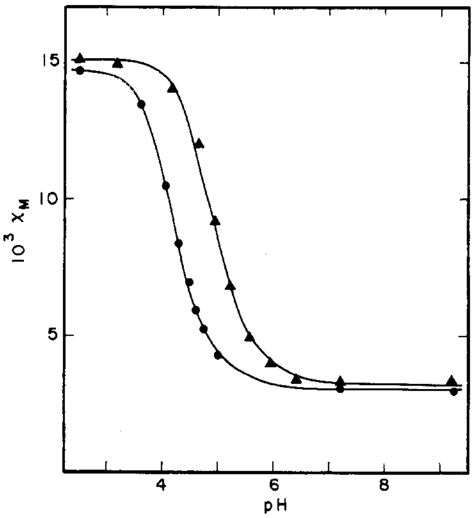

Figure 1. pH dependence of $FeTPPS_4$ and FeTMpyP paramagnetic susceptibilities: ●, 0.01 M $FeTPPS_4$ in 0.05 M acetate buffer, 0.075 M $NaClO_4$, 2% *tert*-butyl alcohol from pH 3.6 to pH 5.0; ▲ 0.01 M FeTMpyP in 0.25 M NaCl, 2% *tert*-butyl alcohol from pH 3.2 to pH 7.2. For solution composition at other pH values see Table I.

observed for the meso-substituted iron(III) porphyrin dimers.

At near neutral pH the pyrrole-substituted derivatives of natural iron(III) porphyrins (hemin *c*, FeDeut, and FeDDS) exhibit magnetic moments only slightly diminished from the expected high-spin value of 5.9 μ_B. However, spectrophotometric[6,8,15] and kinetic[16] studies are consistent with essentially complete dimerization of these compounds under the concentration conditions examined here. FeProt also showed a high magnetic moment[3] under conditions where the spectrophotometric study[15] revealed the compound was dimeric. Although μ-oxo-bridge formation in these pyrrole-substituted iron(III) porphyrin dimers was postulated from the pH dependence of dimer formation,[8,15,16] the nearly high-spin magnetic moments suggest other types of interactions. As was previously discussed for hemin *c*,[6] it appears that pyrrole-substituted iron(III) porphyrins dimerize by formation of a dihydroxo bridge in which antiferromagnetic coupling is not so important[17] or by π-donor–acceptor interactions which require iron(III) hydrolysis to diminish charge and solvation at the iron center to allow porphyrin stacking. However, in high ionic media both FeProt[2,3] and FeDeut (Table I) show diminished magnetic moments consistent with μ-oxo-bridge formation. Apparently changes in the ionic atmosphere can convert these nonantiferromagnetic coupled dimers to μ-oxo-bridged species. FeProt is much more sensitive in this respect than FeDeut. Temperature dependence of hemin *c*, FeDeut, and FeDDS magnetic moments also suggests that at higher temperatures some of the μ-oxo-bridged species may be formed.

Other evidence in the literature supports differences in the type of dimers formed by meso-substituted and pyrrole-substituted iron(III) porphyrins. Rate constants for the dissociation of FeDDS,[8] FeDeut,[16] and metal-free porphyrin dimers[18–20] are approximately three orders of magnitude greater than corresponding rate constants for the FeTPPS$_4$ dimer[4,21] and other known oxo-bridged iron(III) complexes.[1] Increased dimer dissociation rates for pyrrole-substituted iron(III) porphyrins suggest the presence of the expectedly more labile dihydroxo bridges[22] or π-donor–acceptor complexes. Dimerization equilibria for FeTPPS$_4$[4,21] and pyrrole-substituted iron(III) porphyrins[6,8,15,23] also differ in that no predimerization hydrolysis step leading to a hydroxo species is observed for FeTPPS$_4$. Visible–uv spectra may distinguish two types of iron(III) porphyrin dimers since dimerization of hemin *c*[6], FeDeut,[15] and FeProt[15] results in a shift of the near-uv Soret absorption band to shorter wavelengths, whereas dimerization of FeTPPS$_4$[4] and FeTMpyP[14] results in a shift to longer wavelengths. Furthermore, FeTPPS$_4$ dimers were not split by aqueous detergents which are effective for pyrrole-substituted iron(III) porphyrins.[24]

The different solution properties of meso-substituted and pyrrole-substituted iron(III) porphyrins cannot be fully explained at this time. Steric differences must be important, and perhaps meso-substituted porphyrins can be staggered such that aromatic meso groups of interacting porphyrins are parallel, allowing closer approach of porphyrin planes and formation of oxo bridges. It may be that for steric reasons only the edges of pyrrole-substituted porphyrins or selected pyrroles overlap and the iron centers are not properly aligned for bridging. The possible importance of both steric constraints and charge in pyrrole-substituted iron(III) porphyrins is illustrated by the greatly decreased tendency of hemin *c* (with bulky cysteine side chains) and FeDDS (with two negatively charged sulfonate groups) to form oxo bridges in high ionic strength media compared to FeDeut and FeProt.

Registry No. FeTPPS$_4^{3-}$, 60489-11-4; FeTCPP^{3-}, 60489-12-5; FeTMpyP^{5+}, 60489-13-6; FeDeut$^-$, 60489-14-7; FeDDS^{3-}, 60489-98-7; FeProt$^-$, 60489-15-8.

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Spontaneous Demethylation of *N*-Methyltetraphenylporphinatocopper(II) Chloride in Chloroform Producing Methyl Chloride and Tetraphenylporphinatocopper(II)

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Received June 9, 1976

AIC604254

While the initial impetus for the study of metal complexes of N-substituted porphyrins was to provide information relative to the corresponding metalloporphyrins,[1] it is now evident that metallo-N-substituted porphyrins have unique properties themselves. Thus rhodium(I)[2] and cobalt(I)[3] *N*-methylporphyrins undergo oxidative addition forming CH_3–Rh^{III} and CH_3–Co^{III} adducts, and homoporphyrins, having a two-carbon meso bridge,[4] are among the products of Ni^{II}-*N*-CH_2CO_2EtP (P = porphyrin) reactions. We earlier demonstrated[5] that ZnP is the product of the demethylation of Zn-*N*-MeP in refluxing pyridine and that porphyrin demethylations are promoted by coordinated metal ions. Lavallee[6] has found that *N*-methyltetraphenylporphinatocopper(II) (Cu-*N*-MeTPP$^+$) in the presence of added nucleophiles such as pyridine (or di-*n*-butylamine) produces CuTPP and the methylpyridinium ion (or di-*n*-butylmethylamine). We report another demethylation pathway for Cu-*N*-MeTPP$^+$Cl$^-$, in which the nucleophilic agent is the associated anion itself.