Solution Characterization of a New Iron(III) Porphyrin Hydrolyzed Complex

ARDEN D. BOERSMA and HAROLD M. GOFF*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, U.S.A.

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Iron porphyrins are known to form a large variety of dimeric structures. Well characterized species include those with the following bridging ligands: oxo [1], nitrido [2], carbido [3], sulfato [4], peroxo [5], imidazolato [6], pyrazine [7], and hydroquinone [8]. Evidence for aqueous equilibria involving hydroxo-bridged iron(III) porphyrin complexes has also been presented [9]. The μ-oxo dimeric iron(III) porphyrin is generally accepted as the sole product resulting from alkaline hydrolysis of iron(III) porphyrin complexes contained in non-coordinating organic solvents. This appears to be the case for iron(III) tetraarylporphyrin derivatives other than those that are excessively sterically hindered. However, during preparation of μ-oxoiron(III) pyrrole-alkyl-substituted porphyrin compounds we have noted formation of variable amounts of a component which exhibits a previously unidentified proton NMR spectrum. *In situ* generation and spectroscopic characterization of the species is described in this report.

Experimental

Trifluoromethanesulfonate and perchlorate complexes of iron(III) porphyrins were prepared by acid cleavage of the appropriate μ-oxo dimer [10]. The new hydrolyzed complexes were generated *in situ* in NMR tubes by hydrolysis of the very weak field complexes. Either $CF_3SO_3^-$ or ClO_4^- complexes in CD_2Cl_2 or $CDCl_3$ solvents may be utilized. Equilibration with D_2O, dilute NaOD–D_2O solution, or phosphate–D_2O buffer solutions served to generate the species of interest. The following method gave optimum yields. To a 5 mm NMR tube containing 2.0 mg of the trifluoromethanesulfonate complex is added 0.5 ml of CD_2Cl_2. After complete dissolution, 10 μl of pH 8.2, 0.05 M potassium phosphate buffer is added. The capped tube is vigorously agitated for 5 min by a vortex mixer. The water droplets adhere to the wall of the tube and NMR measurements are made directly on this mixture.

Proton NMR spectra were recorded at 90 MHz and 360 MHz on respective JEOL FX-90Q and Bruker WM-360 pulsed FT spectrometers. The Evans NMR method (at 360 MHz) [11, 12] was used to obtain solution magnetic susceptibilities. Tetramethylsilane (1%) was employed as a reference substance in solutions 5 mM in iron porphyrin. Optical spectra were obtained in 0.01 cm quartz cells using solutions which had been examined by proton NMR spectroscopy. Electron paramagnetic resonance spectra were also recorded on such solutions at 1.2 mM using an X-band Varian E-104A instrument with the temperature set at −180 °C.

Results and Discussion

The proton NMR spectrum of an iron(III) etioporphyrin I (ETIOFe(III)) solution treated as described above is shown in Fig. 1. Signals are identified for HDO present as droplets and dissolved in CD_2Cl_2. Significant μ-oxo dimer is generated and peak assignments for this species are made on the basis of those reported for natural-derivative porphyrins [13]. Assignment of the far downfield, far upfield, and 3.0 ppm signals was confirmed by examination of the iron(III) octaethylporphyrin (OEPFe(III)) analogue. These signals at 26.44, 26.23, 20.57, 19.72, 3.07 and −6.90 ppm do not match those for any known ETIOFe(III) complex. For example, the ring methyl signal of $ETIOFeSO_3CF_3$ appears at 64.0 ppm and that for ETIOFeCl is found at 52.4 ppm. Splitting of diastereotopic ring methylene signals as is observed here is apparent for all iron(III) porphyrin complexes in which the iron center is drawn out of the porphyrin plane toward the axial ligand(s). Splitting of the ring methyl signal is not observed at 90 MHz, but the peak is non-Lorentzian at this frequency. The doublet character of the ring methyl signal at 360 MHz is consistent with formulation as a μ-dihydroxo dimer in which case the symmetry is reduced from four-fold to two-fold. Treatment of the μ-oxo dimer, $(ETIOFe)_2O$, with alkaline buffer as described above also produced detectable amounts of the new species. Reaction of the iron(III) tetraphenylporphyrin trifluoromethanesulfonate complex by the same method yielded predominantly μ-oxo dimer and no new iron porphyrin complex was detectable by proton NMR spectroscopy.

A methylene chloride solution containing largely the presumed dihydroxo dimer of ETIOFe(III) exhibits an optical spectrum with a Soret band at 369 nm and non-distinct shoulders at 504, 536, and

*Author to whom correspondence should be addressed.

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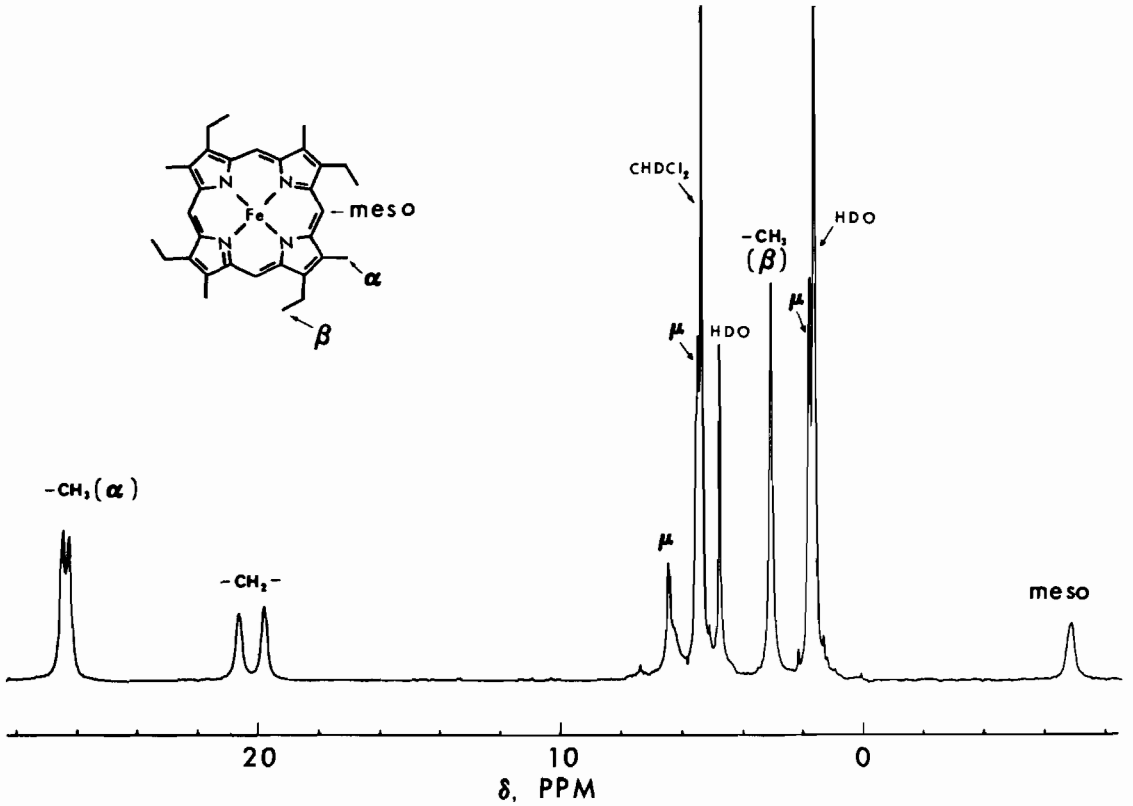


Fig. 1. Proton NMR spectrum (360 MHz) of hydrolyzed ETIOFe(SO_3CF_3) complex, 25 °C, 5 mM total iron porphyrin concentration, CD_2Cl_2 solvent, saturated with aqueous 0.05 M phosphate pH 8.2 buffer, signals referenced to $(CH_3)_4Si$.

632 nm. The spectrum of the corresponding μ-oxo dimer prepared by passage of the solution through a column of basic alumina [13] exhibits bands at 389, 562, and 589 nm. These spectra are sufficiently different to clearly indicate formation of a new species.

A frozen solution of the new dihydroxo complex was examined by EPR spectroscopy at −180 °C. Weak g ≈ 6 and g = 2 signals were observed, but the amplitude of these signals was considerably lower than those observed for a solution of ETIOFeCl at the same concentration. The weak signals presumably result from a minor monomeric high-spin iron(III) component and the dihydroxo dimer appears to be EPR silent at −180 °C. This finding is totally reasonable for a dimeric complex by virtue of the fact that metal ions in close proximity would induce efficient spin–spin relaxation.

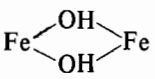
Determination of the solution magnetic moment of the dihydroxo dimer required accounting for the μ-oxo dimer present. This was accomplished by integration of appropriate μ-oxo and dihydroxo iron(III) porphyrin signals at the same time the NMR susceptibility measurements were made. At 34 °C a magnetic moment of 3.7 ± 0.3 B.M. was calculated on a per iron basis for the presumed dihydroxo dimer. It is perhaps fortuitous that a value of 3.7 B.M. has also been estimated for what is presumed to be the dihydroxo dimer of aquo iron(III), $(H_2O)_4Fe(OH)_2Fe(H_2O)_4^{4+}$ [14]. On the other hand the well-characterized dihydroxo dimer of a dipicolinatoiron(III) complex exhibits a magnetic moment of 4.86 B.M. at 27 °C [15].

The magnetic moment for $(EtIOFeOH)_2$ is temperature dependent, and at −52 °C the value had dropped to 3.1 ± 0.3 B.M. The reduced, temperature-dependent magnetic moment, as well as attenuated hyperfine NMR shifts are consistent with an antiferromagnetic coupling mechanism. Variable temperature magnetic measurements in general can be fit to an appropriate function to extract the superexchange coupling constant, J, as defined by the Hamiltonian $H = -2JS_1S_2$. However, large uncertainties in the 'corrected' magnetic moments measured here do not warrant an attempt to fit the data. It is pertinent to note that two antiferromagnetically coupled $S = 5/2$ centers with a coupling constant of $J = -57$ cm^{-1} would yield a $\mu = 3.7$ B.M. value at ambient temperature [16].

An attempt was also made to calculate J from variable temperature proton NMR measurements, as signals for the dihydroxo species clearly do not

follow Curie law behavior. For example, the (average) ring methyl signal of $(ETIOFeOH)_2$ is located at 26.3 ppm at 25 °C and moves to only 27.3 ppm at −60 °C. It was assumed that Curie law deviation for the ring methyl signal results from antiferromagnetic coupling of two iron(III) centers. As such, the variable temperature chemical shift values were fit by non-linear least-squares analysis to a contact shift function [17–19] assuming that only $S = 0$, $S = 1$, $S = 2$, and $S = 3$ states are significantly populated near ambient temperature. An antiferromagnetic coupling constant of $J = -122$ cm^{-1} was obtained. (This is to be compared with a value of $J = -143$ cm^{-1} for $(OEPFe)_2O$ obtained by fitting of variable temperature carbon-13 NMR data [20].) The $J = -122$ value is considerably different than the value of $J = -57$ cm^{-1} required to produce the observed magnetic moment for $(ETIOFeOH)_2$. We have reason to believe that the fit to NMR data is unreliable as a consequence of perturbations in additional chemical equilibria at low temperatures. In particular, hysteresis is apparent in chemical shift values as the solution is cycled from ambient to low temperatures. A reasonable explanation would involve hydrogen bonding between OH^- bridges and H_2O dissolved in CD_2Cl_2. Removal of H_2O at low temperatures through ice formation could thus affect porphyrin chemical shift values, and these perturbations would not be distinguished from antiferromagnetic contributions in the multiple parameter fitting routine.

Natural-derivative iron(III) porphyrin dimethyl ester species may also be converted to the presumed μ-dihydroxo dimer. Attenuated ring methyl proton chemical shift values similar to those for $(ETIOFeOH)_2$ provide for characterization of the species. Ring methyl signals at 26.10, 26.00 and 24.50 (2 methyls) ppm were observed for the dihydroxo iron(III) mesoporphyrin IX dimethyl ester dimer. Lack of symmetry in this porphyrin could in principle yield a large number of isomer types defined by the orientation of the plane



Absence of additional ring splitting of the type observed for $(ETIOFeOH)_2$ suggests that one preferred isomer is formed for this particular porphyrin. A broad manifold of ring methyl signals centered at 24.7 ppm (with a smaller signal at 23.7 ppm) for the protoporphyrin IX dimethyl ester analogue suggests more than one isomer type is present. This type of complexity and possible additional hydrophobic aggregation have precluded observation of well-resolved proton NMR spectra of high-spin iron(III) porphyrin complexes in alkaline aqueous solution.

In summary, the controlled hydrolysis of pyrrole-substituted iron(III) porphyrins bearing a very weak-field anionic ligand yields a new species which has distinctive proton NMR and optical spectra. Assignment as a monomeric hydroxo complex is unreasonable on the basis of attenuated NMR hyperfine shifts, reduced magnetic moments, and absence of an EPR spectrum at −180 °C. Simple coordination of water in a position *trans* to a μ-oxo dimer linkage would not serve to explain the unusual ring methyl splitting of the ETIOFe(III) complex. We therefore suggest a dihydroxo linkage as the most reasonable structural unit. Efforts to grow quality crystals of the material have been unsuccessful, as the resulting solid product contains predominantly μ-oxo dimer.

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