Proton Nuclear Magnetic Resonance Contact Shifts of Binuclear Oxo-Bridged Iron(III) Porphyrins[1]

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Abstract: The proton nmr spectra of some binuclear oxo-bridged iron(III) complexes containing the porphyrin ligands tetraphenylporphine, protoporphyrin IX dimethyl ester, and deuteroporphyrin IX dimethyl ester have been assigned and attributed solely to a contact interaction. The dipolar term resulting from a *g*-tensor anisotropy or a zero-field splitting is shown to be negligible. Assuming a model in which strong antiferromagnetic exchange coupling occurs, the contact shifts are quantitatively accounted for by considering the thermal population of the paramagnetic $S = 1$ and $S = 2$ states. Possible spin delocalization mechanisms for these complexes are discussed. It is also shown that imidazole does not axially coordinate to these binuclear complexes, so it is expected that binuclear oxo-bridged hemeproteins are not naturally occurring.

In recent years much attention has been given to a group of oxo-bridged, binuclear, high-spin iron(III) complexes generally represented as $(FeL_n)_2O$, where ligands such as 1,10-phenanthroline,[2] porphines,[3-5] ethylenediaminetetraacetate,[6] and tetradentate Schiff bases[7] are coordinated to iron(III). Principally from Mossbauer[8] and magnetic susceptibility studies[2,7,8] it is generally accepted that all such oxo-bridged iron-(III) complexes contain high-spin ($S = 5/2$) iron(III) ions which are antiferromagnetically coupled. In those cases where magnetic susceptibility studies have been done,[2,6b,7,8] J, the exchange coupling constant resulting from $H = -2JS_1 \cdot S_2$, has been found to vary from -85 to $-110 \, \mathrm{cm}^{-1}$.

In this laboratory, we have been interested in the proton nmr spectra of these binuclear complexes and have briefly reported on the nmr spectra of the complexes $[Fe_2(phen)_4O]Cl_4$[9] and $[Fe_2(bipy)_4O]Cl_4$[10] (phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine) and some of their methyl-substituted derivatives. The proton nmr spectra were most notable in that the line widths were relatively small due to the exchange coupling, whereas mononuclear high-spin iron(III) complexes are generally not easily amenable to proton nmr study because of excessive line broadening. Thus *via* these strongly coupled binuclear complexes, iron(III)–ligand bonding interactions can hopefully be studied through their nmr isotropic shifts.

This work is concerned with the proton nmr spectra of the binuclear oxo-bridged iron(III) porphyrin complexes containing the following porphyrins: *meso*-tetraphenylporphine[4,5] (TPP), deuteroporphyrin IX dimethyl ester[3,5] (DTP), and protoporphyrin IX dimethyl ester[11] (PTP). The latter two ligands are shown in Figure 1. These porphyrin complexes are potentially important in that they would serve as a biochemical model system for any naturally occurring binuclear oxo-bridged hemeproteins (which are as yet unknown).

Experimental Section

Preparation of Compounds. Of the three porphyrins used, *meso*-tetraphenylporphine was prepared by the method of Adler,[12] while protoporphyrin IX dimethyl ester and deuteroporphyrin IX dimethyl ester were purchased from Sigma Chemical Co. and Koch-Light Laboratories, respectively. The porphyrin ligands were then reacted with ferrous chloride to prepare the ferric chloride intermediates[13] from which the binuclear oxo-bridged dimers could be synthesized.

The binuclear complex $[Fe(TPP)]_2O$ was prepared by the method of Fleischer and Srivastava[4] in which Fe(TPP)Cl in chloroform solution is reacted with aqueous KOH. The chloroform layer was condensed to small volume and was chromatographed on a column packed with alumina. The first band which contained unreacted ligand was discarded and the second band containing the dimer was retained. This latter chloroform solution was condensed and rechromatographed on alumina a second time in order to minimize the possibility of paramagnetic impurities. The final chloroform solution was evaporated to near dryness, and the product was recrystallized from a petroleum ether–chloroform mixture. Both $[Fe(PTP)]_2O$ and $[Fe(DTP)]_2O$ could be prepared from their respective hemin chloride either by the previous method or by the procedure of Caughey, *et al.*[3a]

Anal. Calcd for $C_{88}H_{56}N_8Fe_2O$ ($[Fe(TPP)]_2O$): C, 78.12; H, 4.14. Found: C, 78.03; H, 4.24. Calcd for $C_{72}H_{72}O_9N_8Fe_2$ ($[Fe(PTP)]_2O$): C, 66.26; H, 5.56; N, 8.59. Found: C, 65.91; H, 5.65; N, 8.42. Calcd for $C_{64}H_{64}O_9N_8Fe_2$ ($[Fe(DTP)]_2O$): C, 64.00; H, 5.37; N, 9.33. Found: C, 64.18; H, 5.68; N, 9.23.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Spectral Measurements. Proton magnetic resonance spectra were obtained with both a Varian T-60 and Varian HA-100 spectrometer. Variable temperature studies were done on the latter instrument equipped with a Varian-4341 variable temperature accessory precalibrated with methanol. Electronic spectra were measured using a Cary 14 spectrophotometer.

(1) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(2) A. V. Khedekar, J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc., A*, 1561 (1967).

(3) (a) N. Sadasivan, H. Eberspaecher, W. Fuchsman, and W. S. Caughey, *Biochemistry*, 8, 534 (1969); (b) J. O. Alben, W. H. Fuchsman, C. A. Beaudreau, and W. S. Caughey, *ibid.*, 7, 624 (1968); (c) W. S. Caughey, J. L. Davies, W. H. Fuchsman, and S. McCoy in "Structure and Function of Cytochromes," K. Okunuki, M. D. Kamen, and I. Sekuzu, Ed., University of Tokyo Press, Tokyo, 1968.

(4) E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, 91, 2403 (1969).

(5) I. Cohen, *ibid.*, 91, 1980 (1969).

(6) (a) H. Schugar, C. Wallings, R. B. Jones, and H. B. Gray, *ibid.*, 89, 3713 (1967); (b) H. J. Schugar, G. R. Rossman, and H. B. Gray, *ibid.*, 91, 4564 (1969).

(7) J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 1014 (1967).

(8) W. M. Reiff, G. J. Long, and W. A. Baker, Jr., *J. Amer. Chem. Soc.*, 90, 6347 (1968).

(9) M. Wicholas, *ibid.*, 92, 4141 (1970).

(10) M. Wicholas and D. Jayne, *Inorg. Nucl. Chem. Lett.*, 7, 443 (1971).

(11) S. B. Brown, P. Jones, and I. R. Lantzke, *Nature (London)*, 223, 960 (1969).

(12) A. Adler, *et al.*, *J. Org. Chem.*, 32, 476 (1967).

(13) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, 32, 2443 (1970).

Table I. Proton Nmr Contact Shifts (ppm) of Binuclear Oxo-Bridged Iron(III) Porphyrins

Compound		Meso-H	Pyrrole-H	–CH₂CH₂	–CH₂CH₂	–OCH₃	–CH₃	Vinyl
[Fe(DTP)]₂O	ν	−1.31	−13.50	−6.24	−2.82	−3.54	−5.26	
	Δν	+8.44	−4.62	−1.99	+0.36	+0.07	−1.75	
[Fe(PTP)]₂O	ν	−1.31		−6.10	−2.72	−3.55	−5.13	−9.46 CH ∼−6.0 CH₂
	Δν	+8.28		−1.92	+0.38	+0.08	−1.78	∼−1.6 CH ∼+0.2 CH₂

Results and Discussion

Nmr Spectral Assignments. The proton nmr spectrum of [Fe(TPP)]₂O in CDCl₃ at 35° consists of two peaks centered at −13.7 and −7.7 ppm downfield from TMS.
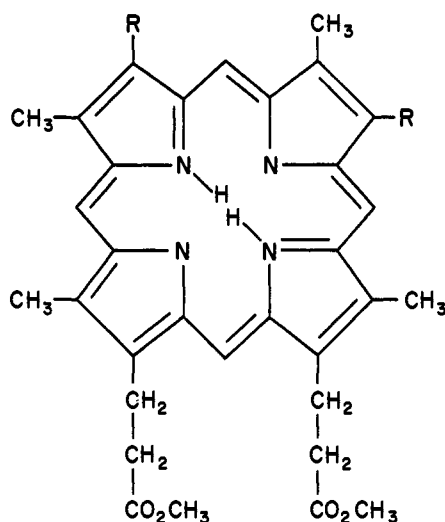

Figure 1. Structural representation of porphyrins. R = CH=CH₂, protoporphyrin IX dimethyl ester; R = H, deuteroporphyrin IX dimethyl ester.

These are assigned as being due to the pyrrole and phenyl protons, respectively, on the basis of their relative signal areas (1:5 ratio). Quite notably the phenyl proton resonance remains unsplit and is in the region expected for aromatic protons. These phenyl protons effectively experience no isotropic shift, whereas the pyrrole resonance is shifted downfield approximately 4 ppm. The spectra of [Fe(PTP)]₂O and [Fe(DTP)]₂O, shown in Figure 2, are more complex but can quite easily be assigned on the basis of relative areas and line widths. This assignment is consistent with the partial assignment for [Fe(PTP)]₂O given by Caughey.[14] The chemical shifts and isotropic shifts for [Fe(PTP)]₂O and [Fe(DTP)]₂O are listed in Table I. In lieu of the analogous diamagnetic cobalt(III) oxo-bridged dimers, the chemical shifts of the diamagnetic porphyrin ligands in CDCl₃ are used as the diamagnetic references[15] for these binuclear complexes. Because the isotropic shifts are small and the diamagnetic references inappropriate, it is best to assume that the β-methylene, β-vinyl, and the methyl ester proton resonances, of which all are very close to their diamagnetic position, are essentially unshifted. The pyrrole methyl, α-methylene,

α-vinyl, and pyrrole proton resonances show a significant downfield shift whereas only the meso protons are shifted upfield.
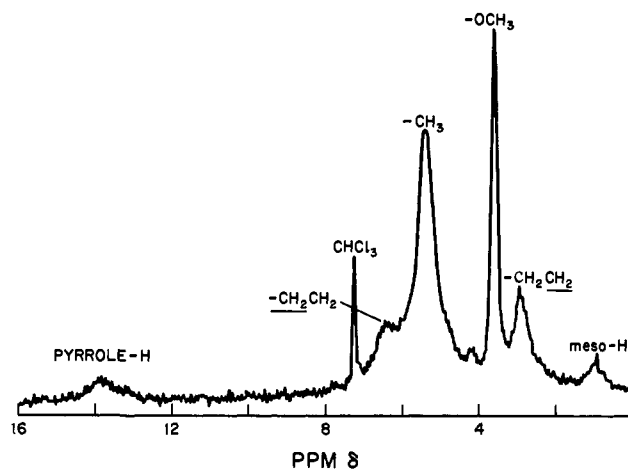

Figure 2. Proton nmr spectrum of [Fe(DTP)]₂O in CDCl₃ at 60 MHz and 35°.

Model for Isotropic Shifts. As a result of the antiferromagnetic exchange coupling between the two $S = \frac{5}{2}$ iron(III) ions, a manifold of six spin states results with spin $S = 0, 1, \ldots, 5$.[16] Of these the ground state is diamagnetic $(S = 0)$, and the isotropic shifts are then a consequence of the thermal population of the paramagnetic excited states. Averaging the isotropic shifts over all thermally populated states,[17] the isotropic shift, $\Delta \nu = \nu - \nu_r$, for a proton in these binuclear complexes is given as

$$\nu - \nu_r = \sum_i (N_i/N_t)\Delta \nu_i \tag{1}$$

For the proton of concern, ν is the chemical shift and ν_r is the chemical shift of the appropriate diamagnetic reference, both relative in this case to TMS. $\Delta \nu_i$ is the isotropic shift in each of the excited states, and N_i/N_t is the Boltzmann population of each state which in turn is dependent on J. From magnetic susceptibility measurements, J is approximately −190 cm⁻¹ in [Fe(PTP)]₂O.[18] The fact that J is larger for [Fe(PTP)]₂O than for other nonporphyrin binuclear complexes is not surprising. In [Fe(TPP)]₂O, for example, the Fe–O–Fe bond angle is 168°,[4] whereas in a nonporphyrin binuclear complex such as [Fe(salen)]₂O, the angle is 142° and $J = -87$ cm⁻¹.[19] A more linear

(14) W. S. Caughey, *Advan. Chem. Ser.*, No. 100, 248 (1971).
(15) (a) W. S. Caughey and W. S. Koski, *Biochemistry*, 1, 923 (1962); (b) S. Sano, T. S. Hingu, J. M. French, and E. Thonger, *Biochem. J.*, 97, 250 (1965).

(16) A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, London, 1968, Chapter 5.
(17) J. P. Jesson, *J. Chem. Phys.*, 47, 579 (1967); B. R. McGarvey, *ibid.*, 53, 86 (1970).
(18) W. S. Caughey and T. H. Moss, private communication.
(19) P. Coggon, A. T. McPhail, F. E. Mabbs, and V. N. McLachlan, *J. Chem. Soc. A*, 1014 (1971).

angle in these binuclear complexes is conducive to more effective π bonding and superexchange and greater values of J. Using $J = -190$ cm^{-1} for these binuclear complexes, the Boltzmann population of each state along with their relative energies is tabulated in Table II. Considering the relative populations, it is clear

Table II. Energy Levels and Boltzmann Populations for [Fe–O–Fe–]$^{4+}$

Energy states	Multiplicity, $2S + 1$	Energy, $J [S(S + 1)]$, J	Boltzmann population % (293°K, $J = -190$ cm^{-1})
5	11	−30	
4	9	−20	
3	7	−12	6.5×10^{-3}
2	5	−6	1.25
1	3	−2	31.3
0	1	0	67.5

that the isotropic shifts result principally from occupation of the $S = 1$ and $S = 2$ excited states, and for this discussion the contribution from the other paramagnetic states can be ignored.

The first task in interpreting the proton nmr isotropic shifts for the three binuclear complexes is to determine the relative contributions of both contact and dipolar shifts. The dipolar term will be considered first. For a "spin-only" complex, the dipolar term is dependent on both the magnetic anisotropy and zero-field splitting as recently shown by Kurland and McGarvey.[20] For example, the dipolar shift of a proton in the $S = 1$ excited state of these binuclear complexes is given in eq 2. D

$$(\Delta\nu/\nu)\text{dipolar} = \frac{-2\beta^2(g_\parallel{}^2 - g_\perp{}^2)(3\cos^2\theta - 1)}{9kTR^3} \times \left[1 - \frac{(g_\parallel{}^2 + \frac{1}{2}g_\perp{}^2)}{3(g_\parallel{}^2 - g_\perp{}^2)} \cdot \frac{D}{kT}\right] \quad (2)$$

is the zero-field splitting parameter and $(3 \cos^2\theta - 1)/R^3$ is the geometric factor for which R is the distance from the proton of concern to the metal ion and θ is the angle between R and the principle magnetic axis assuming axial symmetry. Clearly, if $g_\parallel = g_\perp$, the first term in the dipolar shift equation is zero and if $D = 0$, then the second term is zero. For these binuclear complexes, there is good evidence that $g_\parallel = g_\perp$. For a related oxo-bridged binuclear complex, [Fe(salen)]$_2$O, where salen is the tetradentate ligand N,N'-ethylenebis(salicylideneiminate), Mabbs, et al.,[19] have shown by single-crystal magnetic susceptibility measurements that the susceptibility is isotropic with a g value of 2. There is no reason not to expect similar magnetic behavior for any of the binuclear oxo-bridged high-spin iron(III) complexes. Also the isotropic shifts for these oxo-bridged porphyrin dimers are very similar in pattern to those reported for the paramagnetic adducts of nickel(II) porphyrins[21] where dipolar shifts are not expected since octahedral nickel(II) complexes are magnetically isotropic. Caughey, et al.,[3a] have also reported that no zero-field splitting for [Fe(DTP)]$_2$O could be detected in the range $0 < D < 28$ cm^{-1}; hence we do not anticipate any dipolar contribution to the isotropic shifts.[22]

(20) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, 2, 286 (1970).
(21) R. J. Abraham and P. F. Swinton, *J. Chem. Soc. B*, 903 (1969); B. D. McLees and W. S. Caughey, *Biochemistry*, 7, 642 (1968).

Assuming then that the observed shifts are contact shifts, eq 1 yields upon substitution of the Boltzmann expression and McConnell's contact shift equation[23]

$$\nu = -K/T\sum_i a_i x_i + \nu_r \quad (3)$$

where

$$K = g\beta\gamma_e/3k\gamma_H\nu_0, \quad x_i = \frac{S_i(S_i + 1)n_i e^{+\epsilon_i/kT}}{\sum_i n_i e^{+\epsilon_i/kT}}$$

In the above equation a_i (in gauss) is the electron spin-nuclear spin hyperfine coupling constant in each of the paramagnetic excited states, and n_i and ϵ_i are respectively the degeneracy and energy of each state. The above equation is a linear nonhomogeneous equation that can be solved by least-squares analysis to yield both ν_r[24] and the coupling constants a_1 and a_2 for any proton in these binuclear complexes, given a set of temperature-dependent contact shifts. Knowledge of these coupling constants also allows one to determine the relative contribution of the $S = 1$ and $S = 2$ excited states to the observed contact shifts. A least-squares analysis has been done for the pyrrole proton nmr resonance data of [Fe(TPP)]$_2$O in CDCl$_3$ using eq 3 with $g = 2.0$ and allowing J to vary from -85 to -200 cm^{-1} in increments of 5 cm^{-1}. The best least-squares fit was obtained for $J = -155$ cm^{-1} and the results are as follows: $a_1 = 0.0456 \pm 0.0076$ G, $a_2 = 0.0434 \pm 0.0018$ G, and $\nu_r = -9.04 \pm 0.57$ ppm.[25] The value of ν_r is very credible for a pyrrole proton in a diamagnetic TPP species since for TPP in CDCl$_3$ we find the pyrrole proton resonance at -8.90 ppm. The excellent agreement between the observed and calculated pyrrole proton resonances for [Fe(TPP)]$_2$O is shown in Table III and affords further evidence for the correct-

Table III. Comparison of the Experimental and Calculated Chemical Shifts for the Pyrrole Proton in [Fe(TPP)]$_2$O Using $a_1 = 0.0456$ G, $a_2 = 0.0434$ G, and $J = -155$ cm^{-1}

Temp, °K	Chemical shift, ν (ppm) Exptl	Calcd
218	−12.73	−12.74
227	−12.84	−12.85
236	−12.96	−12.94
246	−13.03	−13.04
256	−13.12	−13.12
268	−13.19	−13.21
280	−13.29	−13.29
293	−13.37	−13.37

(22) For the pyrrole proton which is about 5.25 Å from the center of the porphyrin ring, we would expect a dipolar shift of approximately 0.015 ppm if $D = 1.0$ cm^{-1}, the highest possible value, considering both the $S = 1$ and $S = 2$ states. This is of negligible magnitude.
(23) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 27, 1361 (1958).
(24) Since the value of ν_r is uncertain we prefer to use ν as a parameter in eq 3 rather than $\Delta\nu$. The least-squares fit will give ν_r as the intercept, and the calculated value of ν_r can be used as a further guide as to the correctness of the fit.
(25) After completion of this work, a similar temperature-dependent study was reported in the literature for [Fe(TPP)]$_2$O by P. D. W. Boyd and T. D. Smith, *Inorg. Chem.*, 10, 2041 (1971). These authors incorrectly assumed one coupling constant, A, for all the paramagnetic states[17] and also used $\Delta\nu$ as a parameter rather than the more accurately known ν; however, their results are similar in that their coupling constant, A, was reported to be 0.0460 G (which is almost identical with a_1), and J was -155 cm^{-1}.

ness of the derived parameters a_1, a_2, and ν_r. We do not find it disconcerting that J for $[Fe(PTP)]_2O$ in the solid state is higher by 40 cm^{-1} than J for $[Fe(TPP)]_2O$. First, J for $[Fe(TPP)]_2O$ is derived from a solution measurement; hence the values of J need not agree. Secondly, the porphyrin ligands are different and could substantially influence the value of J. Both of these could explain the above disparity in J for $[Fe(PTP)]_2O$ and $[Fe(TPP)]_2O$.

Using the above values of a_1, a_2, and ν_r, a contact shift of -4.34 ppm at 293°K is expected, of which -3.54 ppm is due to molecules in the $S = 1$ state and -0.80 ppm to the $S = 2$ state. This shows the importance of the contribution of the $S = 2$ state molecules to the pyrrole proton contact shift even though the population of the $S = 2$ state is only 3.0% at 293°K.[26] Clearly, however, this need not be true for other protons in $[Fe(PTP)]_2O$ and $[Fe(DTP)]_2O$ where J may be different. The relative importance of the states $S = 1$ and $S = 2$ for a given proton contact shift can only be ascertained by a similar least-squares analysis from which the a_i can be derived.

Mechanism of Spin Delocalization. The problem of spin delocalization in these binuclear porphyrin complexes is quite complex in that one must propose mechanisms for both the $S = 1$ and $S = 2$ states in order to account for the observed contact shifts. Since the nmr contact shifts for $[Fe(TPP)]_2O$ can yield no information as to the mechanism of spin delocalization in these binuclear porphyrin complexes, it is useful to look at the protoporphyrin IX dimethyl ester and deuteroporphyrin IX dimethyl ester analogs in which there are many chemically distinct protons. From the contact shifts of $[Fe(PTP)]_2O$ and $[Fe(DTP)]_2O$ two observations can be made. First, whether a methyl group or hydrogen is attached to the pyrrole ring, the contact shifts for both types of protons are negative and not opposite in sign as would be expected for π-spin delocalization in porphyrins.[27] Secondly, although the meso proton contact shifts are positive, this may not necessarily be construed as evidence of π delocalization, which is the putative conclusion. For example, Horrocks and Johnston[28] have shown from INDO molecular orbital calculations of substituted pyridine ligands that positive contact shifts in these ligands can result from σ delocalization; however, without accurate molecular orbital calculations of σ-spin densities for a porphyrin ligand, it is impossible to predict the effect of σ-spin delocalization on the meso-proton contact shifts, and this thwarts any effort to conclusively identify the origin of the contact shifts here. At best we can conclude that π delocalization is not dominant and that possibly the shifts are entirely due to σ delocalization.

The above conclusion that π-spin delocalization is not important can also be arrived at by inspection of the visible electronic spectra of these binuclear complexes. The visible spectra of metal porphyrins have been used as a rough guide[29] in gauging the extent of

metal–ligand π interaction in porphyrin complexes. In metalloporphyrins for which a "normal" visible spectrum (Soret band at approximately 23–25 kk and α,β transition in the 16–20 kk region) is found, little or no π bonding is expected. The binuclear oxo-bridged iron(III) porphyrins also have "normal" visible spectra. For example, the visible spectra of $[Fe(PTP)]_2O$ and $[Fe(TPP)]_2O$ in CHCl$_3$ are, respectively, 24.88 (139 $\times$ 10^3), 17.27 (16 $\times$ 10^3), 16.5 (8 $\times$ 10^3), and 24.54 (162 $\times$ 10^3), 17.53 (17 $\times$ 10^3), 16.37 kk (8 $\times$ 10^3).

Of great interest is the fact that the same pattern of contact shifts observed in $[Fe(PTP)]_2O$ and $[Fe(DTP)]_2O$ is also found in substituted porphyrins of nickel(II)[21] and of mononuclear, high-spin iron(III).[30] This naturally implies that a common delocalization mechanism is occurring in these complexes.[31] This is quite unexpected since each has different d-electron configurations. In nickel(II) porphyrins only σ delocalization is expected, whereas in high-spin iron(III)[32] porphyrins an admixture of σ and π delocalization is expected. If this is to be explained, accurate porphyrin σ-spin densities will be needed as a first step.

Possibility of Naturally Occurring Binuclear Oxo-Bridged Hemeproteins. There is increasing evidence that certain naturally occurring iron proteins exhibit reduced magnetic susceptibilities indicative of antiferromagnetic exchange coupling between iron(III) pairs.[34] To test whether binuclear oxo-bridged hemeproteins could exist in natural systems, we have studied the interaction of $[Fe(PTP)]_2O$ and imidazole both by visible and proton nmr spectroscopy. In this case $[Fe(PTP)]_2O$ would represent the binuclear heme and imidazole would represent the proximal histidine ring of the protein. In no case could we find any evidence for interaction of imidazole and iron(III); i.e., the electronic spectrum of $[Fe(PTP)]_2O$ in CHCl$_3$ was unchanged upon addition of 2 equiv of imidazole, and the nmr chemical shifts of the imidazole protons in CDCl$_3$ were unchanged in the presence of 0.5 equiv of $[Fe(PTP)]_2O$. No evidence could also be found for interaction between imidazole and $[Fe(TPP)]_2O$. Obviously the imidazole nitrogen lone pair is not sufficiently basic to coordinate trans to the oxo ligand. This is probably because of the large donation of charge by the oxo ligand into the d_{z^2} orbital together with the fact that the iron(III) ion is displaced by about 0.5 Å out of the porphyrin plane and toward the oxo ligand.[4] On this basis the occurrence of binuclear oxo-bridged heme-

(26) For $J = -155$ cm^{-1}, the Boltzmann populations of the $S = 0, 1,$ 2, and 3 states at 293°K are, respectively, 58.6, 38.3, 3.04, and 0.04%.

(27) R. G. Schulman, S. H. Glarum, and M. Karplus, *J. Mol. Biol.*, **57**, 93 (1971).

(28) W. D. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1835 (1971).

(29) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966).

(30) W. S. Caughey and L. F. Johnson, *Chem. Commun.*, 1362 (1969).

(31) A notable exception are the low spin cyanide adducts of iron(III) porphyrins in which the contact shifts have been explained by π delocalization involving the highest filled porphyrin π orbitals.[27] Their calculated contact shifts, after allowance for a sizable dipolar interaction, are entirely unlike those of the binuclear iron(III) complexes.

(32) Using the molecular orbital scheme[7,33] for binuclear oxo-bridged complexes of D_{4h} symmetry, we would predict that σ delocalization would occur in the $S = 1$ state, and σ and π delocalization in the $S = 2$ state. The ground state would have the following configuration: $(a_{1g})^2(e_u)^4(a_{2u})^2(e_g)^4(b_{2g})^2(b_{1u})^2(a_{1g})^2(b_{1g})^0(b_{2u})^0(a_{2u})^0(e_u)^0$. The e_u, e_g, b_{2g}, and b_{1u} orbitals are of π symmetry and the remainder are of σ symmetry. In this scheme the 3d orbitals of Fe(III) and the 3s and 3p orbitals of O^{2-} have been used.

(33) H. H. Schmidtke, *Theor. Chim. Acta*, **20**, 92 (1971).

(34) See, for example, the magnetic susceptibility data for hemerythrin: T. H. Moss, C. Moleski, and J. L. York, *Biochemistry*, **10**, 840 (1971).

proteins is not probable unless the protein were attached to a pyrrole ring rather than being coordinated to iron(III).

Characterization of a d^7 Iron System. Tetraphenylporphineiron(I) Anion

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Abstract: The reduction of μ-oxo-bis(tetraphenylporphineiron(III)) by Na·Hg in THF has been found to sequentially produce several products. The first reduction product has been examined by esr, visible spectroscopy and magnetic measurements and found to contain the [TPPFe(I)]⁻ anion. The Fe(I) appears to be an $S = \frac{1}{2}$ system in frozen THF (77°K) and an $S = \frac{3}{2}$ system in THF solution (200–300°K). These results are interpreted as due to a structural difference for the ion between the solid and solution phases. This appears to be the first reported study of an Fe(I) porphyrin.

Compounds containing d^7 metal ions, predominantly Co(II), have been the subject of extensive chemical and spectroscopic study. The motivation for much of that work has been the great synthetic utility of Co(II) compounds such as $K_3Co(CN)_5$ and [(dimethylglyoxime)$_2$Co]. The Fe(I) complexes studied, however, have been quite restricted in the ligands with which they are found—generally nitrosyl, carbonyl, or sulfur donors. There has been little synthetic work dealing with Fe(I); most of the effort has consisted of spectroscopic studies and has been primarily concerned with establishing the metal oxidation state.[1] Not surprisingly, porphyrins are a class of ligands for which an Fe(I) complex has never been isolated. However, Taube, et al., have performed extensive studies on the reduction products of iron phthalocyanine.[2–6] They were able to isolate Li[Fe(phthalocyanine)]·4.5THF but interpret their Mössbauer data as indicative of a d^6 rather than a d^7 iron, hypothesizing that the additional electron is taken up by the ligand.

Our own interests include iron porphyrins with unusual axial ligands. In order to facilitate the synthesis of such compounds, we sought an anionic, low-valent iron porphyrin, possibly of the d^7 type. It was hoped that this compound would undergo reactions similar to those of $NaMn(CO)_5$, $Na_2Fe(CO)_4$, or $K_3Co(CN)_5$. We, therefore, examined the reduction product of an iron(III) porphyrin. This paper reports the characterization of that product, Na[tetraphenylporphineiron(I)].

Experimental Section

Materials. The hematin,[7] (TPPFe)$_2$O, was prepared as previously described.[8] Tetrahydrofuran was refluxed over LiAlH$_4$ overnight, distilled in air, vacuum degassed four times, and used within 1 hr. Na·Hg (1%) was freshly prepared and decanted from any solids present.

Electron spin resonance spectra were recorded on a Varian V-4500-10A spectrometer at 77°K. The frequency was measured using DPPH and the field sweep was calibrated with an nmr probe. The cell consisted of a reaction compartment containing a magnetic stirring bar and a neck with a constriction leading to a joint for attachment to the vacuum line. Two side arms were attached to the reaction compartment. One contained a 10-mm coarse glass frit and was connected *via* a Pyrex to quartz graded seal to a quartz esr cell. The other, smaller side arm was charged with the sodium amalgam (*ca.* 10–20-fold excess). A CH$_2$Cl$_2$ solution of (TPPFe)$_2$O (*ca.* 25 mg) was placed in the reaction chamber and the solvent removed *in vacuo*. The pressure was reduced to below 10⁻³ mm and THF (*ca.* 5 ml) was distilled into the liquid nitrogen-cooled reaction compartment. The cell was sealed while evacuated. After the THF returned to room temperature and the solid was dissolved, the Na·Hg was mixed with the hematin solution by tipping the cell. The contents were strongly agitated with the magnetic stirrer for the required time (see Results). The product solution was removed from contact with the Na·Hg by tipping the cell so that it passed through the filter into the esr tube. The spectrum was then recorded and the solution allowed to return to the reaction compartment for additional reduction when necessary.

Optical spectra in the visible region were recorded on a Cary 14 spectrophotometer. The cell consisted of a 1-cm square Pyrex cuvette attached to one side of a medium fritted glass disk (50 mm diameter). The other side of the filter was attached to a constricted neck and a joint for attachment to the vacuum line. A CH$_2$Cl$_2$ solution of hematin was poured through the filter disk into the cell and the CH$_2$Cl$_2$ was removed *in vacuo*. The Na·Hg was placed on top of the filter disk and the cell evacuated. THF was distilled *in vacuo* and condensed on the solid at 77°K and the cell was then sealed at the constriction. When the THF returned to room temperature, the reaction was initiated by inverting the cell, thus allowing the THF solution to mix with the Na·Hg. The mixture was shaken for the required time (see Results) and the cell replaced in an upright position. After the solution returned to the cuvette the

(1) For a review of esr studies of Fe(I) compounds, see B. A. Goodman and J. B. Raynor, *Advan. Inorg. Chem. Radiochem.*, **13**, 135 (1970).

(2) E. Fluck and R. Taube in "Developments in Applied Spectroscopy," Vol. 8, E. L. Grove, Ed., Plenum Press, New York, N. Y., 1970, p 244.

(3) R. Taube, H. Drevs, E. Fluck, P. Kuhn, and K. F. Brauch, *Z. Anorg. Allg. Chem.*, **364**, 297 (1969).

(4) R. Taube, H. Drevs, and T. Duc-Hiep, *Z. Chem.*, **9**, 115 (1969).

(5) R. Taube and H. Drevs, *Angew. Chem., Int. Ed. Engl.*, **6**, 358 (1967); *Angew. Chem.*, **79**, 313 (1967).

(6) R. Taube, *Chem. Zvesti*, **19**, 215 (1965).

(7) TPP = the dianion of tetraphenylporphine.

(8) I. A. Cohen, *J. Amer. Chem. Soc.*, **91**, 1980 (1969).