cessful when applied to delocalized mixed-valence systems such as $[Fe_4S_4]^+$ clusters.[29] Other calculated quantities including the magnitudes of quadrupole splitting constants, asymmetry parameters, and isomer shifts are in good agreement with experiment. The theoretical indication that α-Fe atoms are "more reduced" than β-Fe atoms is upheld by parameter-unrestricted fits of the 4.2 K spectra of clusters **2** and **7** and by inspection of the magnetically perturbed spectra. At higher temperatures, this pattern does not always hold. The calculated energy level scheme also suggests that reduction of the Mo clusters to the $[MoFe_3S_4]^{2+}$ level will produce a $S = 2$ state, in agreement with experiment.[9,15] Irreversible reduction of the V clusters[3] has thus far prevented determination of the spin state of the $[VFe_3S_4]^+$ unit.

This research has afforded a reasonably detailed description of the electronic properties of a new set of clusters containing the $[VFe_3S_4]^{2+}$ core, as well as providing additional data for clusters with the isoelectronic $[MoFe_3S_4]^{3+}$ core. As this is a comparative study, we have tended to examine the results for differences between cluster sets **1**–**3** and **4**–**7**. However, in terms of the chemically most significant properties—spin state, existence and extent of electron delocalization, parallel vs. antiparallel spin coupling and magnetic hyperfine coupling constants, as well as geometric structures[4]—the similarities far outweigh the differences. The two core units are electronically and structurally practically interchangeable.

The interchangeability of Mo and V in these complexes takes on added significance with the recent finding of a V-nitrogenase system.[30] It will be interesting to see if the similarities that exist between Mo single cubanes and the Mo cofactor of nitrogenase—namely heterometal coordination environment and overall spin state—are also found between the V single-cubane clusters and the V-containing nitrogenase.

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Registry No. **1**, 106590-00-5; **2**, 106589-94-0; **3**, 99688-08-1; **4**, 80702-99-4; **5**, 106589-99-5; **6**, 85749-34-4; **7**, 106589-83-7.

Supplementary Material Available: Tabulated magnetic susceptibility data for compounds **1**–**3**, **5**, and **7** (6 pages). Ordering information is given on any current masthead page.

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Comparison of the Molecular and Electronic Structures of (μ-Oxo)bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)] and (μ-Oxo)bis[(7,8-dihydro-5,10,15,20-tetraphenylporphyrinato)iron(III)]

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The molecular and electronic structures of (μ-oxo)bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)], $[Fe(TPP)]_2O$, and (μ-oxo)bis[(7,8-dihydro-5,10,15,20-tetraphenylporphyrinato)iron(III)], $[Fe(TPC)]_2O$, show many similarities and one significant difference. The compound $[Fe(TPC)]_2O\cdot 4CHCl_3$ crystallizes in space group D_{2h}^6-*Pnna* ($Z = 4$) with unit cell dimensions $a = 15.467$ (4) Å, $b = 16.196$ (4) Å, $c = 32.889$ (8) Å, and $V = 8239$ (2) Å^3. The structure has been refined to an R index on F_o^2 of 0.0726 on the basis of 4741 reflections (142 K) and 472 variables. The chlorin complex has a crystallographically imposed twofold axis passing through both iron atoms and the μ-oxo bridge, requiring each chlorin macrocycle to be at least twofold disordered. The chlorin macrocycles have larger cores and are more ruffled than the porphyrin macrocycles of the literature compound $[Fe(TPP)]_2O$, but other structural features such as Fe–O–Fe angles, Fe–O distances, and Fe out-of-plane displacements are virtually the same for the two compounds. The gross magnetic behavior and Mössbauer spectra are nearly identical for the two compounds: $-2J$, δ, and ΔE_Q are 265 cm^{-1}, 0.40 mm/s, and 0.70 mm/s for $[Fe(TPC)]_2O$ and 258 cm^{-1}, 0.41 mm/s, and 0.67 mm/s for $[Fe(TPP)]_2O$, respectively. Despite all of these similarities, ^1H NMR spectra indicate that unpaired spin density may be distributed differently in the two compounds.

Introduction

Our interest in the chemical,[2-5] structural,[4,6] and magnetic[2,6-8] properties of iron hydroporphyrins[9] (chlorins and isobacteriochlorins) stems from their occurrence in a wide variety of heme proteins and enzymes.[10-12] Magnetic properties are of funda-

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(9) (a) The fully unsaturated porphyrin macrocycle contains 11 congugated double bonds. A variety of compounds are known in which the macrocycle porphyrin skeleton is retained while one or more double bonds are removed. These compounds are formally derived from porphyrins by hydrogenation and are, therefore, commonly called hydroporphyrins. Note that the generic term hydroporphyrin refers to compounds in which the substituent(s) added across the double bond(s) are hydrogen atoms, alkyl or substituted alkyl groups, alkylidene groups, or oxygen or sulfur atoms: Scheer, H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. II, pp 1–44. Scheer, H.; Inhoffen, H. H. *Ibid*, pp 45–90. (b) Chlorins, which contain 10 conjugated double bonds, are porphyrins that have interrupted conjugation at vicinal C_b atoms of a single pyrrole ring. The affected ring is called a pyrroline ring. Isobacteriochlorins, which contain nine conjugated double bonds, are porphyrins that contain two adjacent pyrroline rings.

(10) See ref 6 and references therein.

0020-1669/87/1326-0724$01.50/0

mental importance to biochemists who isolate and work with heme proteins, because data such as EPR and Mössbauer spectra, paramagnetic ^1H NMR spectra, and effective magnetic moments have been used to elucidate the molecular and electronic structures of heme active sites, usually by comparison with well-defined iron porphyrin model compounds.[13,14]

We have recently shown that the four-coordinate intermediate-spin ($S = 1$) porphyrin compounds Fe(OEP)[15] and Fe(TPP) are not competent magnetic models for their respective hydroporphyrin homologues Fe(OEC), Fe(TPC), and Fe(TPiBC).[6,7] In contrast to the axial magnetic anisotropy of the porphyrin compounds, all three hydroporphyrin derivatives exhibit large rhombic distortions:[6,7] for Fe(OEC), $-[\chi_{xx} - \chi_{yy}] \approx [\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})]$.[6,16] In addition, the two octaethyl compounds have significantly different magnetic moments and Mössbauer quadrupole coupling constants. Since there are no axial ligands in these four-coordinate complexes, these magnetic differences are unambiguously induced by the different macrocycles.

We now report a comparison of the molecular and electronic structures of $[Fe(TPP)]_2O$ and $[Fe(TPC)]_2O$, including magnetic susceptibility measurements, infrared, ^1H NMR, and Mössbauer spectra, and the crystal structure of the chlorin complex. This is only the second report of structural, magnetic, and Mössbauer data for a well-characterized iron chlorin model compound.[17] The comparison shows that the iron atoms in the two compounds are in near-identical molecular and electronic environments, in sharp contrast to the electronic differences noted above for the four-coordinate Fe(II) complexes. However, a difference in ^1H NMR spectra indicate that unpaired spin density may be distributed differently in the two compounds.

Experimental Section

Preparation of Compounds. Reagents and solvents were of the highest purity commercially available and were purified and/or dried, where appropriate, by standard techniques. The compounds Fe(TPP)[18] and Fe(TPC)[7] were prepared by treating chlorin-free $H_2(TPP)$[19a] and $H_2(TPC)$[19b] with $FeBr_2$ (Alfa) as described in the literature.[20] Brief exposure of solutions of these four-coordinate complexes to dioxygen or to $^{18}O_2$ (Cambridge, 98 atom %) produced $[Fe(TPP)]_2O$, $[Fe(TPC)]_2O$, or their oxygen-18 equivalents. The visible spectrum of $[Fe(TPC)]_2O$, in dichloromethane matches that reported by Ryan et al.[21] The chlorin macrocycles of $[Fe(TPC)]_2O$ react slowly (hours) with dioxygen in solution to produce $[Fe(TPP)]_2O$ (monitored by visible spectroscopy). The compound $[Fe(TPC)]_2O$ is air-stable indefinitely in the solid state. The compound $[Fe(TPC\text{-}7,7',8,8'\text{-}d_4)]_2O$ was prepared from $H_2(TPC\text{-}7,7',8,8'\text{-}d_4)$[22] as described above.

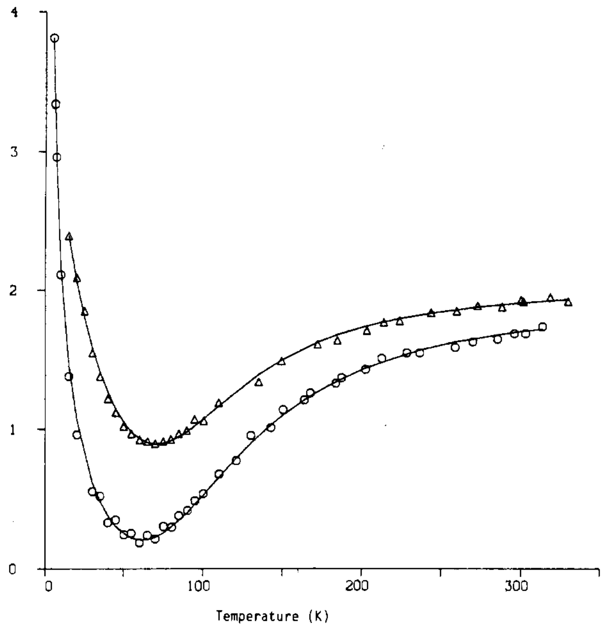

Figure 1. χ vs. T for $[Fe(TPC)]_2O$ (circles) and $[Fe(TPP)]_2O$ (triangles). The smooth curves are least-squares fits to the data as described in the Experimental Section.

The $FeBr_2$ metalation procedure occasionally produced μ-oxo complexes contaminated with several percent of Fe(TPP)Br or Fe(TPC)Br. These halide complexes can be cleanly converted to μ-oxo complexes by treating them with HgO in toluene (room temperature, several hours). For Fe(TPP)Cl or Fe(TPP)Br, this procedure works equally well with Ag_2O or Tl_2O. However, silver(I) and thallium(I) both cause oxidative dehydrogenation of $[Fe(TPC)]_2O$ to $[Fe(TPP)]_2O$.

Spectroscopy. Samples for ^1H NMR spectroscopy were dichloromethane-d_2 solutions sealed under vacuum in 5-mm NMR tubes. Spectra were recorded on a Bruker WP200SY spectrometer operating at 200.13 MHz. Samples for IR spectroscopy were Nujol mulls between KBr windows or dichloromethane solutions in 0.2 mm path length KBr cells. Spectra were recorded on a Perkin-Elmer 983 spectrometer. Mössbauer spectra of finely ground polycrystalline samples were recorded with a constant-acceleration spectrometer in connection with a 256-channel analyzer operating in the time-scale mode. The source was ^{57}Co diffused into rhodium and was kept at room temperature. Spectra were recorded in zero applied field and in horizontal transmission geometry with an applied transverse field of 0.13 T (permanent magnet). Calibrations were made by using the hyperfine splittings in the spectrum of iron metal (line widths are typically 0.30 mm/s). Isomer shifts in mm/s are relative to iron metal at room temperature.

Magnetic Susceptibility Measurements. Room-temperature solid-state magnetic susceptibilities were measured by the Faraday method with the use of a Cahn-Ventron 7600 magnetic susceptibility system with a Model RTL minibalance. $HgCo(SCN)_4$ was used as the susceptibility calibrant. Finely ground, twice recrystallized (chloroform/heptane), vacuum-dried samples of $[Fe(TPC)]_2O$ and $[Fe(TPP)]_2O$ were used. Proton NMR spectra of these samples showed no trace of chloroform after prolonged vacuum-drying. Diamagnetic corrections were taken from the literature for TPP[23] (assumed to be the same for TPC), Fe,[24] and O.[24]

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(15) Abbreviations: TPP, 5,10,15,20-tetraphenylporphyrinato dianion; TPC, 7,8-dihydro-5,10,15,20-tetraphenylporphyrinato dianion (tetraphenylchlorinato dianion); TPiBC, 2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphyrinato dianion (tetraphenylisobacteriochlorinato dianion); OEP 2,3,7,8,12,13,17,18-octaethylphorphyrinato dianion; OEC, 7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion (octaethylchlorinato dianion).

(16) We transfer the D_{4h} coordinate system of a porphyrin to hydroporphyrins, treating the loss of fourfold symmetry from the reduction of one or two pyrrole rings as a perturbation. Thus, z is perpendicular to the plane of the macrocycles and y is coincident with the in-plane C_2 axis.

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Table I. Experimental Parameters for the X-ray Diffraction Study

mol formula	$[Fe(TPC)]_2O \cdot 4CHCl_3$
mol wt	1834.5
space group	*Pnna*
unit cell dimens	
a	15.467 (4) Å
b	16.196 (4) Å
c	32.889 (8) Å
unit cell vol	8239 (2) Å^3
Z	4
calcd density	1.48 g·cm^{-3}
cryst dimens	0.44 mm (001 → 00$\bar{1}$) × 0.39 mm (010 → 0$\bar{1}$0) × 0.31 mm (100 → $\bar{1}$00)
data collecn temp	−130 (1) °C
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
abs coeff, μ	8.1 cm^{-1}
2θ range	3.5–50°
no. of unique reflcns	7978 for $-19 \leq h \leq 0$, $-20 \leq k \leq 0$, $0 \leq l \leq 40$
no. of obsd reflcns	4741 with $I > 1.5\sigma(I)$
scan type	ω (Wyckoff)
scan speed	variable (min 2.02° min^{-1}, max 29.30° min^{-1})
data/parameter ratio	10.0
R	0.0726
R_w	0.0724
GOF	1.7
g (refined)	7.4 × 10^{-4}
slope of normal probability plot	1.43

Variable-temperature susceptibilities on samples prepared the same way as above were measured with an SHE computer-controlled SQUID susceptometer as previously described.[25] The weighed samples were loaded into either Kel-F or aluminum-silicon containers in an inert-atmosphere glovebox. The data are shown in Figure 1. For each compound, the smooth curve is a least-squares fit to the data using the following equation:[26,27]

$$\chi = (Ng^2\beta^2/k)(\mathrm{NUM}/\mathrm{DEN}) + B + C/(T - \Theta)$$

where χ is the measured gram-susceptibility of the sample divided by the molecular weight of the dimer, N is Avogadro's number, $g = 2.0023$, β is the Bohr magneton, k is Boltzman's constant, $\mathrm{NUM} = 2e^{-x} + 10e^{-3x} + 28e^{-6x} + 60e^{-10x} + 110e^{-15x}$, $\mathrm{DEN} = 1 + 3e^{-x} + 5e^{-3x} + 7e^{-6x} + 9e^{-10x} + 11e^{-15x}$, $x = -2J/kT$, T is the absolute temperature, J is the antiferromagnetic coupling constant ($2J$ is the energy gap between the ground state ($S = 0$) and the first excited state ($S = 1$) for the dimers), B is the temperature-independent component of the susceptibility (diamagnetism plus any temperature-independent paramagnetism), C is the Curie constant for an impurity assumed in this model to be a simple $S = {}^5/_2$ Curie paramagnet, and Θ is the Weiss constant of the impurity. The results are, for $[Fe(TPC)]_2O$, $J = -191$ (10) K, $B = -429$ (54) × 10^{-6} cm^3/mol, $C = 3.5$ (4) × 10^{-2} cm^3·K/mol, and $\Theta = -3.4$ (1.0) K, while for $[Fe(TPP)]_2O$, $J = -186$ (10) K, $B = -562$ (102) × 10^{-6} cm^3/mol, $C = 1.2$ (1) × 10^{-2} cm^3·K/mol, and $\Theta = -25$ (1) K. The errors are expressed at the 2σ level. The validity of the model is supported by the observation that different samples gave rise to different amounts of the paramagnetic impurity (probably Fe(P)Cl or some similar species, P = TPP or TPC) but very similar values of J. Even after several recrystallizations, samples of $[Fe(TPC)]_2O$ still contained approximately 0.3% of the high-spin impurity (calculated from the results given above). Attempts to fit the data with a fixed value of B corresponding to the diamagnetic corrections mentioned above (−1432 × 10^{-6} cm^3/mol dimer) resulted in residuals that were not random. Random residuals resulted only when B was allowed to vary with the other three adjustable parameters. The difference between the calculated diamagnetic correction and the derived values of B may be due to the paramagnetic impurity since the parameters B and C are strongly correlated. Subtracting out the susceptibility due to the impurity is not possible, especially at low temperatures, since large zero-field splittings for five-coordinate $S = {}^5/_2$ Fe(III) porphyrins lead to significant departure from Curie-Weiss behavior for these compounds.[28]

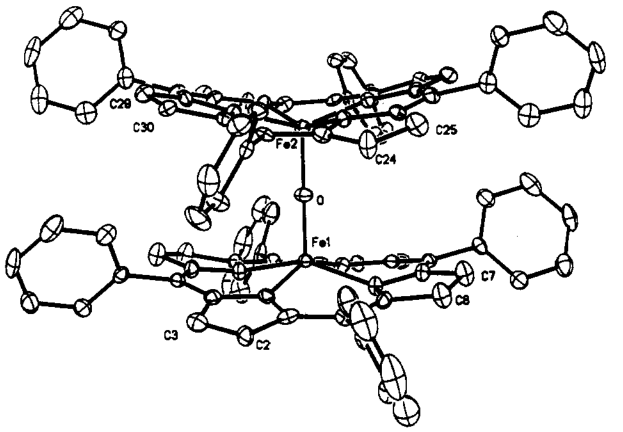

Figure 2. The $[Fe(TPC)]_2O$ molecule (50% ellipsoids shown).

Crystallographic Study. Purple crystals of $[Fe(TPC)]_2O$ were grown by slow diffusion of heptane into a chloroform solution of the compound. A parallelepiped-shaped crystal was extracted directly from the mother liquor, placed in a cold (−130 °C) nitrogen stream, and centered on a Nicolet R3m X-ray diffractometer. Exposure of the crystals to air (outside of the mother liquor) at room temperature for more than a few minutes led to loss of solvent and disintegration of the crystals. The setting angles for 25 reflections (2θ(av) = 14.6°) allowed least-squares calculation[29] of the cell constants. Relevant experimental parameters and results are listed in Table I.

The intensities of all reflections were measured by using Wyckoff ω scans, with a scan range of 1.0° below Kα_1 to 1.0° above Kα_1. The intensities of three standard reflections were measured after every 97 reflections and showed no significant trend during the course of the data collection. The data were corrected for Lorentz and polarization effects and were smoothed by using a peak profile method. The space group was determined to be *Pnnb*, which was standardized to *Pnna* by using the matrix (010/100/00$\bar{1}$) on all data points and cell constants.

The two independent iron atoms were located by Patterson methods and were found to occupy the special positions (${}^3/_4$, 0, z). Coordinates for all other non-hydrogen atoms were determined from difference electron density maps. Final least-squares refinement calculations involved anisotropic thermal parameters for all non-hydrogen atoms. The phenyl groups were refined as rigid, idealized six-membered rings; hydrogen atom coordinates for phenyl group hydrogen atoms were calculated at idealized positions 0.96 Å from carbon atoms, with isotropic thermal parameters 1.2 times the equivalent isotropic thermal parameter for the carbon atoms to which they were attached. In the final difference Fourier synthesis the maximum electron density was 1.5 e·Å^{-3} in the vicinity of a chloroform chlorine atom (Cl6).

Table II contains a list of atomic positional parameters and equivalent isotropic thermal parameters. Table III contains a list of bond distances and angles. Also available as supplementary material are lists of anisotropic thermal parameters for non-hydrogen atoms (Table S1), hydrogen atom positions and isotropic thermal parameters (Table S2), and observed and calculated structure factors (Table S3). See paragraph at end of paper regarding supplementary material.

Results and Discussion

Molecular Structure of $[Fe(TPC)]_2O \cdot 4CHCl_3$. The compound crystallized in the orthorhombic space group *Pnna*, with 4 μ-oxo complexes and 16 chloroform molecules in the unit cell. Each μ-oxo complex sits on a crystallographic twofold axis that passes through the oxygen and both iron atoms, requiring each chlorin macrocycle to be at least twofold disordered (see below). A drawing of the molecule is shown in Figure 2. Bond distances and angles for $[Fe(TPC)]_2O$ are listed in Table III. As expected, the structure is quite similar to that of $[Fe(TPP)]_2O$, first reported

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for [Fe(TPC)]$_2$O·4CHCl$_3$

atom	x	y	z	U_{iso}[b]
Fe1	7500	0	1805 (1)	13 (1)
Fe2	7500	0	737 (1)	14 (1)
O	7500	0	1274 (2)	19 (2)
N1	8573 (3)	641 (3)	1961 (1)	16 (1)
C1	9345 (4)	289 (4)	2029 (2)	20 (2)
C2	9942 (4)	963 (4)	2095 (2)	21 (2)
C3	9535 (4)	1733 (4)	2040 (2)	23 (2)
C4	8681 (4)	1526 (4)	1950 (2)	17 (2)
C5	8062 (4)	2141 (4)	1881 (2)	18 (2)
C6	7217 (4)	1962 (4)	1885 (2)	20 (2)
C7	6565 (4)	2605 (4)	1828 (2)	30 (2)
C8	5811 (4)	2169 (4)	1908 (2)	30 (2)
C9	6044 (4)	1254 (4)	1965 (2)	18 (2)
C10	5469 (4)	599 (4)	2019 (2)	21 (2)
C11	4283 (2)	1247 (3)	2401 (1)	35 (2)
C12	3444 (2)	1438 (3)	2435 (1)	49 (3)
C13	2905 (2)	1225 (3)	2120 (1)	54 (3)
C14	3205 (2)	821 (3)	1771 (1)	45 (3)
C15	4044 (2)	629 (3)	1737 (1)	35 (2)
C16	4583 (2)	842 (3)	2052 (1)	24 (2)
C17	8194 (2)	3719 (2)	2071 (1)	23 (2)
C18	8480 (2)	4550 (2)	1986 (1)	31 (2)
C19	8919 (2)	4710 (2)	1629 (1)	34 (2)
C20	9071 (2)	4038 (2)	1356 (1)	37 (2)
C21	8784 (2)	3207 (2)	1440 (1)	27 (2)
C22	8346 (2)	3047 (2)	1798 (1)	17 (2)
N2	6880 (3)	1154 (3)	1948 (1)	17 (2)
N3	6411 (3)	660 (3)	604 (1)	15 (1)
C23	5635 (4)	307 (4)	664 (2)	19 (2)
C24	5026 (4)	991 (4)	702 (2)	31 (2)
C25	5436 (4)	1772 (4)	594 (2)	27 (2)
C26	6310 (3)	1526 (4)	559 (2)	16 (2)
C27	6940 (4)	2118 (4)	470 (2)	17 (2)
C28	7788 (4)	1922 (4)	474 (2)	17 (2)
C29	8428 (4)	2535 (4)	393 (2)	20 (2)
C30	9176 (4)	2109 (4)	464 (2)	23 (2)
C31	8967 (4)	1220 (4)	570 (2)	17 (2)
C32	9544 (3)	575 (4)	646 (2)	15 (2)
N4	8124 (3)	1121 (3)	568 (1)	16 (2)
C33	10997 (2)	642 (2)	383 (1)	20 (2)
C34	11821 (2)	889 (2)	424 (1)	26 (2)
C35	12079 (2)	1339 (2)	769 (1)	32 (2)
Co6	11512 (2)	1542 (2)	1073 (1)	35 (2)
C37	10687 (2)	1295 (2)	1033 (1)	26 (2)
C38	10430 (2)	845 (2)	688 (1)	19 (2)
C39	6830 (2)	3703 (3)	631 (1)	30 (2)
C40	6566 (2)	4534 (3)	530 (1)	37 (3)
C41	6164 (2)	4681 (3)	161 (1)	39 (3)
C42	6025 (2)	3995 (3)	−106 (1)	39 (3)
C43	6288 (2)	3164 (3)	−5 (1)	30 (2)
C44	6691 (2)	3018 (3)	364 (1)	21 (2)
C45	3680 (4)	3748 (5)	1036 (2)	40 (3)
Cl1	3669 (1)	2827 (1)	1347 (1)	56 (1)
Cl2	4675 (1)	4050 (1)	902 (1)	58 (1)
Cl3	3073 (2)	3579 (2)	604 (1)	78 (1)
C46	1061 (5)	3851 (5)	1740 (2)	46 (3)
Cl4	1461 (1)	2986 (1)	2017 (1)	48 (1)
Cl5	1394 (2)	3846 (1)	1238 (1)	63 (1)
Cl6	1244 (2)	4805 (2)	1984 (1)	97 (1)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] The equivalent isotropic U is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å)[a] for [Fe(TPC)]$_2$O·4CHCl$_3$

(a) Lengths			
Fe1–O	1.747 (5)	Fe1–N1	2.066 (5)
Fe1–N2	2.101 (4)		
		Fe2–O	1.763 (5)
Fe2–N3	2.085 (4)	Fe2–N4	2.083 (4)
N1–C1	1.382 (7)	N1–C4	1.380 (7)
C1–C2	1.438 (8)		
C2–C3	1.373 (8)	C3–C4	1.451 (8)
C4–C5	1.400 (8)	C5–C6	1.396 (8)
C5–C22	1.500 (7)	C6–C7	1.463 (9)
C6–N2	1.380 (7)	C7–C8	1.419 (9)
C8–C9	1.477 (8)	C9–C10	1.388 (8)
C9–N2	1.363 (7)	C10–C16	1.487 (7)
C10–C1	1.408 (8)	N3–C23	1.384 (7)
N3–C26	1.357 (7)	C23–C24	1.452 (8)
C23–C32	1.396 (8)	C24–C25	1.423 (9)
C25–C26	1.471 (8)	C26–C27	1.402 (8)
C27–C28	1.405 (8)	C27–C44	1.491 (7)
C28–C29	1.430 (8)	C28–N4	1.389 (7)
C29–C30	1.399 (8)	C30–C31	1.459 (8)
C31–C32	1.390 (8)	C31–N4	1.373 (7)
C32–C38	1.501 (7)		
C45–C11	1.754 (8)	C45–Cl2	1.735 (7)
C45–Cl3	1.747 (7)	C46–Cl4	1.742 (8)
C46–Cl5	1.739 (8)	C46–Cl6	1.704 (8)
(b) Angles			
O–Fe1–N1	104.4 (1)	O–Fe1–N2	102.9 (1)
N1–Fe1–N2	86.5 (2)		
N1–Fe1–N1a	151.2 (3)	N2–Fe1–N1a	87.1 (2)
N2–Fe1–N2a	154.1 (3)		
O–Fe2–N3	102.1 (1)	O–Fe2–N4	105.5 (1)
N3–Fe2–N4	86.9 (2)		
N3–Fe2–N3a	155.7 (3)	N4–Fe2–N3a	86.6 (2)
N4–Fe2–N4a	149.0 (3)		
Fe1–O–Fe2	180	Fe1–N1–C1	127.8 (4)
Fe1–N1–C4	125.1 (4)	C1–N1–C4	106.3 (5)
N1–C1–C2	110.3 (5)	N1–C1–C10	125.1 (5)
C2–C1–C10	124.5 (5)	C1–C2–C3	106.6 (5)
C2–C3–C4	107.1 (5)	N1–C4–C3	109.5 (5)
N1–C4–C5	126.0 (5)	C3–C4–C5	124.4 (5)
C4–C5–C6	124.4 (5)	C4–C5–C22	116.4 (5)
C6–C5–C22	119.2 (5)	C5–C6–C7	124.8 (5)
C5–C6–N2	124.8 (5)	C7–C6–N2	110.4 (5)
C6–C7–C8	105.9 (5)	C7–C8–C9	105.0 (5)
C8–C9–C10	122.9 (5)	C8–C9–N2	111.0 (5)
C10–C9–N2	126.1 (5)	C9–C10–C16	118.3 (5)
C9–C10–C1	124.8 (5)	C16–C10–C1	116.8 (5)
C10–C16–C11	120.6 (3)	C10–C16–C15	119.4 (3)
C5–C22–C17	121.6 (2)	C5–C22–C21	118.4 (2)
Fe1–N2–C6	123.1 (4)	Fe1–N2–C9	125.4 (4)
C6–N2–C9	107.3 (4)	Fe2–N3–C23	123.0 (4)
Fe2–N3–C26	127.5 (4)	C23–N3–C26	107.2 (4)
N3–C23–C24	110.0 (5)	N3–C23–C32	124.7 (5)
C24–C23–C32	125.0 (5)	C23–C24–C25	106.2 (5)
C24–C25–C26	104.4 (5)	N3–C26–C25	111.2 (5)
N3–C26–C27	125.5 (5)	C25–C26–C27	123.2 (5)
C26–C27–C28	124.6 (5)	C26–C27–C44	117.5 (5)
C28–C27–C44	117.9 (5)	C27–C28–C29	124.3 (5)
C27–C28–N4	125.3 (5)	C29–C28–N4	110.4 (5)
C28–C29–C30	106.5 (5)	C29–C30–C31	106.4 (5)
C30–C31–C32	124.3 (5)	C30–C31–N4	109.6 (5)
C32–C31–N4	126.1 (5)	C31–C32–C38	117.4 (5)
C31–C32–C23	124.7 (5)	C38–C32–C23	117.9 (5)
Fe2–N4–C28	127.7 (4)	Fe2–N4–C31	125.1 (4)
C28–N4–C31	107.0 (4)	C32–C38–C33	120.1 (2)
C32–C38–C37	119.9 (2)	C27–C44–C39	121.2 (3)
C27–C44–C43	118.8 (3)	Cl1–C45–Cl2	112.2 (4)
Cl1–C45–Cl3	110.3 (4)	Cl2–C45–Cl3	110.9 (4)
Cl4–C46–Cl5	112.1 (4)	Cl4–C46–Cl6	110.8 (4)
Cl5–C46–Cl6	113.4 (4)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

by Hoard et al.[30] Swepston and Ibers have recently reported more accurate structural parameters for this compound;[31] only these recent results will be used in our discussion of the subtle structural differences between [Fe(TPC)]$_2$O and [Fe(TPP)]$_2$O. Figure 3 displays line drawings of the two independent chlorin macrocycles of [Fe(TPC)]$_2$O and the unique porphyrin macrocycle of [Fe(TPP)]$_2$O. These drawings show the numbering scheme used as well as relevant bond distances and deviations of the 24 atoms

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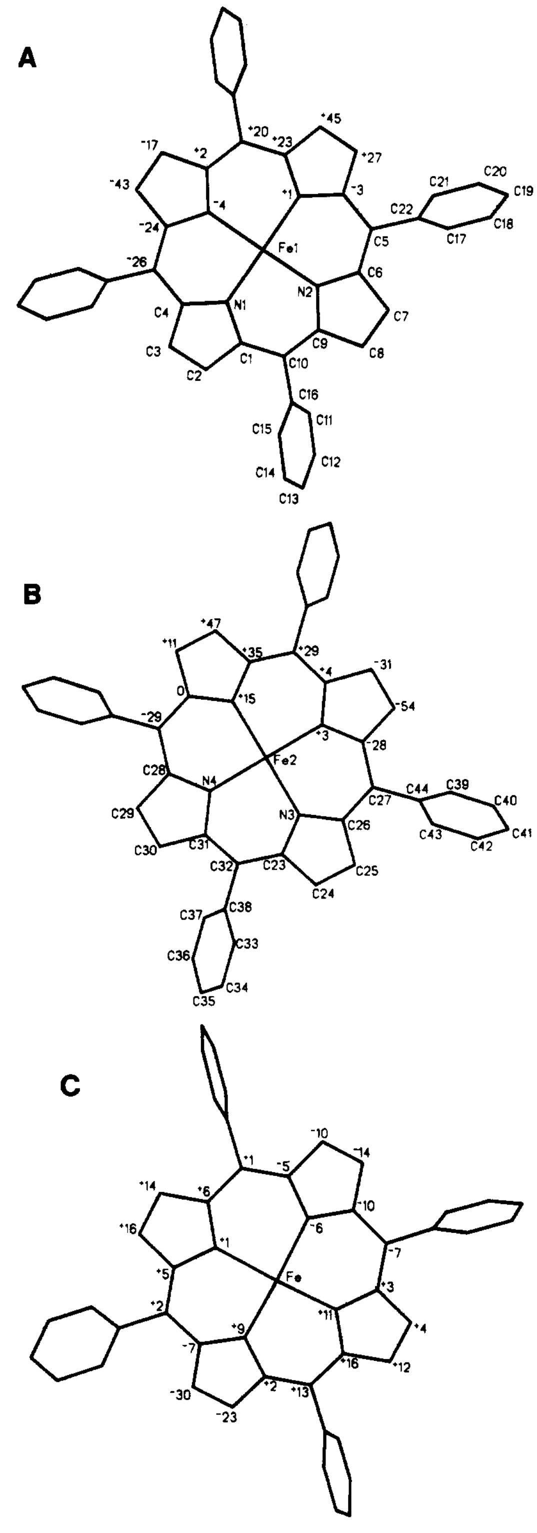

Figure 3. Numbering scheme and out-of-plane displacements (in units of 0.01 Å) for the Fe(TPC)$^+$ and Fe(TPP)$^+$ fragments of [Fe(TPC)]$_2$O (A and B) and [Fe(TPP)]$_2$O (C). The planes are defined as the best least-squares plane of the 24 atoms of each macrocycle core. The estimated standard deviation for each value is 0.01 Å.

of each macrocycle from the best least-squares plane of those atoms.

Since the pyrroline ring of a chlorin (with two sp^3 carbon atoms) is manifestly structurally different from pyrrole rings, the twofold symmetry axis of [Fe(TPC)]$_2$O requires that each independent macrocycle of this compound experience *at least* twofold rotational disorder. This can be readily seen by comparing the C_β–C_β distances in [Fe(TPC)]$_2$O and [Fe(TPP)]$_2$O. For the Fe1 chlorin macrocycle, one pair of symmetry-related C_β–C_β distances is 1.419 (9) Å and one pair is 1.373 (8) Å. This can be compared to the "true pyrrole" value of 1.352 (4) Å, the average value for [Fe(TPP)]$_2$O,[31] and the "true pyrroline" value of 1.508 (7) Å, the value for Fe(OEC).[6] Therefore, the Fe1 chlorin is approximately only twofold disordered. For the Fe2 chlorin, the pairs of C_β–C_β distances are 1.423 (9) and 1.399 (8) Å. A rotational disorder more complex than simple twofold is present here. Note that tetraphenylhydroporphyrins are quite prone to rotational disorder: while the pyrroline rings in Zn(TPC)(py)[32] (py = pyridine) and Zn(TPiBC)(py)[33] are clearly distinct from the pyrrole rings in these compounds, unusual C_β–C_β distances demonstrate some small degree of disorder. Furthermore, the compounds H$_2$(TPC)[34] and Fe(TPC)[35] sit on $\bar{4}$ symmetry axes in their respective lattices. It has become clear that detailed structural comparisons such as M–N(pyrroline) vs. M–N(pyrrole) distances will not be obtainable from metallohydroporphyrins with *meso*-phenyl groups as they are from metallohydroporphyrins with *meso*-methyl groups[36] or with β-substituents.[4,6,37-40]

Despite the disorder present in the structure of [Fe(TPC)]$_2$O, some valid structural comparisons can be made with [Fe(TPP)]$_2$O. The conformation of the chlorin and porphyrin macrocycles in these compounds is a convolution of doming and S_4 ruffling, as originally described by Hoard for [Fe(TPP)]$_2$O.[41] Doming is accomplished primarily by tilting all four pyrrole or pyrroline rings in the same direction about axes connecting their respective C_α carbon atoms.[41] S_4 ruffling twists each five-membered ring about an axis through its nitrogen atom and the midpoint of its C_β–C_β bond.[41] Opposite pyrrole or pyrroline rings twist in opposite directions. S_4 ruffling shrinks the macrocycle core, producing shorter M–N distances.[41] Figure 3 shows that both chlorins in [Fe(TPC)]$_2$O have undergone a considerably larger S_4 distortion than the porphyrins in [Fe(TPP)]$_2$O. This can be most readily seen by comparing the out-of-plane displacements for the C_m carbon atoms: these average 0.06 Å for the porphyrins and 0.23 Å for the chlorins. Despite this greater core shrinking distortion for the chlorins, the *average* Fe–N distances are the same: 2.081 (3) Å in [Fe(TPP)]$_2$O and 2.084 (7) Å in [Fe(TPC)]$_2$O. Furthermore, distances from each nitrogen atom to the centroid of its respective N$_4$ plane are 2.001 (N1), 2.048 (N2), 2.039 (N3), and 2.008 Å (N4) for [Fe(TPC)]$_2$O and range from 2.016 to 2.031 Å for [Fe(TPP)]$_2$O.[31] We have recently discussed the underlying reason for this phenomenon, the fact that hydroporphyrins have intrinsically larger cores than porphyrins.[6] The net result, which can be seen in other metallohydroporphyrin structures,[36,37] is that hydroporphyrins must undergo a *larger* S_4 distortion to achieve *the same* M–N distances as a porphyrin. Consistent with this argument is the observation that the Fe1–N2 distance in [Fe(TPC)]$_2$O is 0.03 Å longer than the Fe1–N1 distance. The N2 and N2′ nitrogen atoms belong to five-membered rings with approximately 50% pyrroline and 50% pyrrole character.

Other features of the structure of [Fe(TPC)]$_2$O are very similar to [Fe(TPP)]$_2$O. Displacements from planes defined by their four nitrogen atoms are 0.49 (1) Å for Fe1, 0.50 (1) Å for Fe2, and 0.49 (1) Å for the iron atoms in [Fe(TPP)]$_2$O.[31] Displacements from planes defined by the 24 atoms of the core macrocycles are 0.51 (1) Å for Fe1, 0.59 (1) Å for Fe2, and 0.53 (1) Å for the

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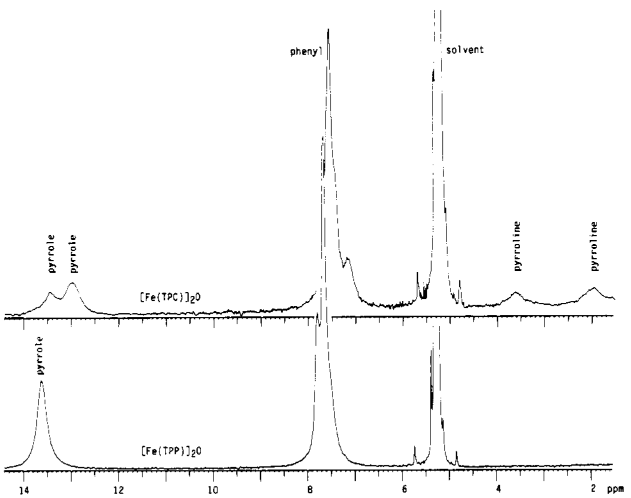

Figure 4. 200-MHz ^1H NMR spectra of $[Fe(TPC)]_2O$ and $[Fe(TPP)]_2O$ in dichloromethane-d_2 at 320 K.

iron atoms in $[Fe(TPP)]_2O$. The Fe–O distances of 1.759 (1) Å in $[Fe(TPP)]_2O$[31] can be compared with 1.747 (5) Å for Fe1–O and 1.763 (5) Å for Fe2–O (average 1.755 (8) Å). The Fe–O–Fe angles are 180° for $[Fe(TPC)]_2O$ and 176.1 (2)° for $[Fe(TPP)]_2O$. In summary, the only significant structural differences between $[Fe(TPC)]_2O$ and $[Fe(TPP)]_2O$ are the larger cores and greater S_4 ruffling of the chlorin macrocycles in the former complex.

Electronic Structure of $[Fe(TPC)]_2O$. Figure 1 shows magnetic susceptibility data for both μ-oxo complexes between 15 and 330 K. These data, combined with the molecular structural data above, leave little doubt that $[Fe(TPC)]_2O$, like its porphyrin homologue, contains two high-spin ($S = {}^5/_2$) ferric ions strongly antiferromagnetically coupled through the bridging oxygen atom.[28,42] Both μ_{eff} at 295 K (2.60 (5) μ_B for $[Fe(TPC)]_2O$ and 2.63 (5) μ_B for $[Fe(TPP)]_2O$) and $-2J$ (265 (6) cm^{-1} for $[Fe(TPC)]_2O$ and 258 (6) cm^{-1} for $[Fe(TPP)]_2O$) are indistinguishable for the two compounds. Our value of $-2J$ for $[Fe(TPP)]_2O$ is in good agreement with the 271 cm^{-1} value recently reported by Helms et al.[43] Previously reported values of $-2J$ for other Fe(III) porphyrin μ-oxo complexes range from 242 to 290 cm^{-1},[44] a range generally larger than that found for other types of Fe(III) μ-oxo complexes.[44c] The similarity in the Fe–O–Fe bridges in the two compounds is also borne out by similar values for $\nu(FeO)_{asym}$ in the solid state, 867 cm^{-1} for $[Fe(TPC)]_2O$ and 876 cm^{-1} for $[Fe(TPP)]_2O$ (827 cm^{-1} for $[Fe(TPC)]_2{}^{18}O$ and 836 cm^{-1} for $[Fe(TPP)]_2{}^{18}O$). Values for $\nu(FeO)_{asym}$ in dichloromethane solution are 869 cm^{-1} for $[Fe(TPC)]_2O$ and 875 cm^{-1} for $[Fe(TPP)]_2O$. The $\nu(FeO)_{asym}$ band is commonly found to be 870 ± 30 cm^{-1} for Fe(III) porphyrin μ-oxo complexes.[2,44b,45]

Zero-field Mössbauer spectra for the two compounds are also indistinguishable within experimental error. At 4.2 K, δ and ΔE_Q are 0.40 mm/s and 0.70 mm/s for $[Fe(TPC)]_2O$ and 0.41 mm/s and 0.67 mm/s for $[Fe(TPP)]_2O$. Our data for $[Fe(TPP)]_2O$ agree with literature values for this compound.[46,47] Furthermore, the application of a small magnetic field (1.3 kG) had no appreciable effect on the spectrum of $[Fe(TPC)]_2O$, and raising the temperature had a very minor effect on ΔE_Q for this compound (0.62 mm/s at 298 K). Both of these observations parallel the behavior of Mössbauer spectra of $[Fe(TPP)]_2O$.[47]

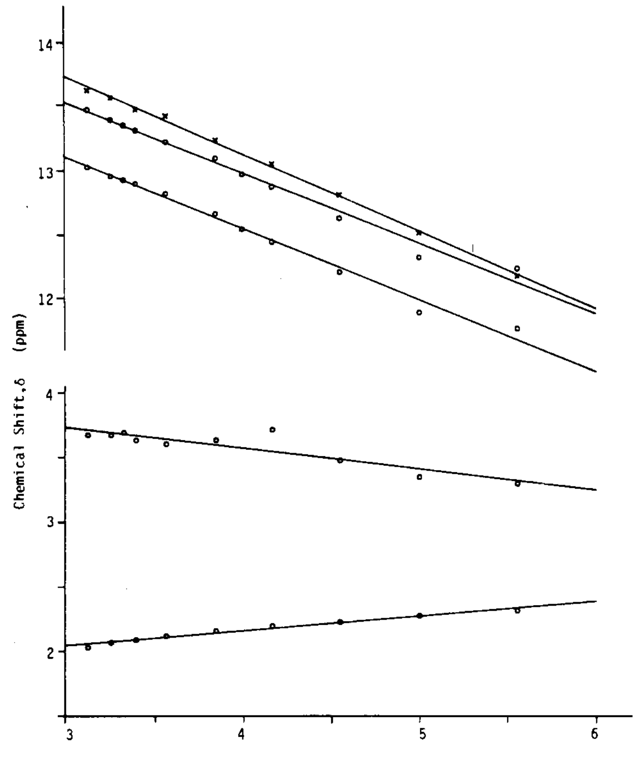

Figure 5. δ vs. $1/T$ plots for pyrrole and pyrroline protons of $[Fe(TPC)]_2O$ (circles) and $[Fe(TPP)_2O$ (crosses). The straight lines are included as a visual aid and have no special significance.

Despite all of these similarities, ^1H NMR spectra indicate that unpaired spin density may be distributed differently in the two compounds. Figure 4 shows spectra of $[Fe(TPC)]_2O$ and $[Fe(TPP)]_2O$ in dichloromethane-d_2 at 320 K. The assignment of the two pyrroline resonances is based on the spectrum of $[Fe(TPC\text{-}7,7',8,8'\text{-}d_4)]_2O$ recorded under identical conditions. Figure 5 shows the temperature dependence of the pyrrole and pyrroline proton chemical shifts. The ambiguity in pyrrole assignments for $[Fe(TPC)]_2O$ requires the use of chemical shifts instead of isotropic shifts. Proton NMR spectra of diamagnetic free-base hydroporphyrins, including $H_2(TPC)$, have been published.[48]

Variable temperature ^1H NMR spectra of monomeric, five-coordinate high-spin Fe(III) porphyrins and Fe(III) porphyrin μ-oxo complexes have been extensively studied.[49-55] The isotropic shifts for the monomeric species deviate from a simple $1/T$ dependence (Curie law). Large zero-field splittings give rise to a dipolar contribution to the shifts with a $1/T^2$ dependence.[56,57] Together with the $1/T$ dependence of the contact contribution, the temperature dependence of the isotropic shifts is very com-

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plicated.[49-55] The antiferromagnetic coupling in the μ-oxo complexes produces an even more complicated situation for these compounds. La Mar et al.[51] have pointed out that these complications prevent a meaningful calculation of $-2J$ from the temperature dependence of NMR spectra of Fe(III) porphyrin μ-oxo complexes. However, Goff et al. have recently shown that metal-based dipolar contributions to isotropic shifts must be small for compounds such as $[Fe(TPP)]_2O$ and have calculated $-2J$ = 312 cm^{-1} for this compound from variable-temperature ^{13}C NMR spectra in chloroform.[55b] This value is in agreement with earlier values derived from ^1H NMR spectra.[27,49b] The difference between solution and solid-state values of $-2J$ for $[Fe(TPP)]_2O$ cannot be explained by stronger antiferromagnetic coupling in solution; note that $\nu(FeO)_{asym}$ is virtually constant for $[Fe(TPP)]_2O$ in the solid state and in dichloromethane solution (see above).

The spin delocalization mechanism for $S = {}^5/_2$ iron porphyrins puts σ spin density at the pyrrole positions of the macrocycles.[54,55a] Thus, $[Fe(TPP)]_2O$ and Fe(TPP)Cl have pyrrole contact shifts that are downfield of their diamagnetic equivalents.[51] Figure 4 shows that the three pyrrole resonances for $[Fe(TPC)]_2O$ are downfield and the two pyrroline resonances are upfield of their respective diamagnetic values.[58] One plausible explanation for the upfield pyrroline resonances is that the pyrroline protons experience a sizable upfield π contact shift that is larger than the expected downfield σ contact shift. The occurrence of π contact shifts for meso protons in five-coordinate high-spin Fe(III) porphyrins has been documented,[54,55a] so it is possible that π spin density occurs at the pyrroline positions in $[Fe(TPC)]_2O$ via a spin delocalization mechanism similar to that in $[Fe(TPP)]_2O$ (Fe($d\pi$) $\rightarrow$ porphyrin (e_g*) π charge transfer). However, Hanson et al. have pointed out that one of the HOMO's of a chlorin (the one that has an a_{1u} counterpart in a porphyrin) has the same symmetry as, and is a good energy match with, one of the iron $d\pi$ orbitals.[59,60] Thus, it is likely that π spin delocalization for paramagnetic metallochlorins is qualitatively different from that for corresponding metalloporphyrins, since for porphyrin complexes, with effective D_{4h} symmetry, the macrocycle HOMO's (a_{1u} and a_{2u}) and the iron $d\pi$ orbitals (e_g) have different symmetries.

An alternate explanation is that any dipolar contribution to the isotropic shift has a large rhombic component, as previously shown by us for the four-coordinate $S = 1$ complexes Fe(OEC),[6] Fe(TPC),[7] and Fe(TPiBC).[7] If this were the case, however, the similarities in shifts between 13 and 14 ppm for the two compounds would require that the contact shifts for $[Fe(TPC)]_2O$ be at least quantitatively different from those for $[Fe(TPP)]_2O$, if not qualitatively different (i.e. predominantly σ vs. σ plus π). Thus, either explanation requires a different kind, or at least a different degree, of spin delocalization at the pyrrole and/or pyrroline positions.

The magnetic susceptibilities of the two compounds increase from 180 to 320 K, the limits of our NMR experiments (Figures 1 and 5). On this basis, chemical shifts for $[Fe(TPC)]_2O$ and $[Fe(TPP)]_2O$ should move in the direction of the diamagnetic reference as the temperature is lowered. A curious feature of the data presented in Figure 5 is that one, but only one, of the pyrroline resonances of $[Fe(TPC)]_2O$ exhibits the opposite behavior. We have no explanation for this observation at present, but note that this behavior (i.e. large *apparent* temperature-independent paramagnetism) was also observed for the $S = 1$ hydroporphyrin complexes mentioned above.[6,7] Our continuing study of monomeric Fe(III) hydroporphyrins may help to answer some of the questions raised by the NMR spectra of $[Fe(TPC)]_2O$.

Significance and Conclusions. The gross magnetic behavior and Mössbauer spectra of $[Fe(TPC)]_2O$ and $[Fe(TPP)]_2O$ are found to be very similar. Together with the differences reported by us for four-coordinate Fe(P) complexes,[6] it is apparent that these metal-centered properties can be quite similar or very different, depending on the spin state and/or ligation state of the complexes. However, unusual features have been observed for paramagnetic ^1H NMR spectra of both types of hydroporphyrin complexes. This is an important result since ^1H NMR spectroscopy is being used to study several paramagnetic green heme proteins.[11m-o,61] In the absence of more hydroporphyrin model compound data, comparisons of hydroporphyrin-containing proteins with porphyrin model compounds alone are tentative at best.

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Supplementary Material Available: Anisotropic thermal parameters for all non-hydrogen atoms (Table S1) and hydrogen atom positions and isotropic thermal parameters (Table S2) (3 pages); observed and calculated structure factors (Table S3) (31 pages). Ordering information is given on any current masthead page.

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(58) Our diamagnetic reference for $[Fe(TPC)]_2O$ is $H_2(TPC)$. The pyrroline chemical shift of the free-base ligand in dichloromethane-d_2 at 298 K is 4.15 ppm while the pyrrole chemical shifts are 8.17, 8.41, and 8.56 ppm. La Mar et al. have pointed out[51] that $[Sc(TPP)]_2O$ is a better diamagnetic reference for $[Fe(TPP)]_2O$ than is $H_2(TPP)$. However, the small differences in chemical shifts are only important for precise separation of contact and dipolar contributions to the isotropic shifts, which we are not attempting to do for $[Fe(TPC)]_2O$ at present.

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