

plicable as well to ordered ones and the conclusions drawn from such an analysis are not dependent on the potential chosen, as long as a reasonable function is employed.

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Six Coordination in High-Spin Ferric Porphyrins. A New Structural Type and Models for Aquomethemoglobin

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Abstract: The synthesis and definitive characterization of the first examples of six-coordinate high-spin ferric porphyrin complexes are reported. Perchlorato(tetraphenylporphyrinato)iron(III) reacts with various weak field ligands L (sulfoxides, dimethylformamide, triphenylphosphine oxide, pyridine *N*-oxide) to give isolable crystalline derivatives [FeL₂(tetraphenylporphyrin)]ClO₄. Magnetic, Mössbauer, ESR, and structural data support a high-spin state assignment and certain properties parallel those of aquomethemoglobin. The crystal structure of bis(tetramethylene sulfoxide)(tetraphenylporphyrinato)iron(III) perchlorate, FeN₄C₅₂H₄₄S₂O₆Cl, has been determined: space group *P* $\bar{1}$; *Z* = 2; *a* = 14.003 (5), *b* = 15.246 (5), *c* = 12.108 (3) Å; α = 113.20 (2), β = 89.24 (2), γ = 76.67 (4)°; 7586 reflections, *Mo K* α ; *R*₁ = 0.076, *R*₂ = 0.089 with final data/parameter ratio of 13.2. In contrast to all other known high-spin ferric porphyrins the iron atom is precisely located in the plane of an expanded porphyrin core with mean Fe-N 2.045 (5) Å. The axial tetramethylene sulfoxide ligands are O-bound with Fe-O 2.069 (3) and 2.087 (3) Å, respectively, in the two independent half-molecules of the unit cell.

A curious feature of heme chemistry is that while *six* coordination is known in high-spin ferric hemoproteins it has been frequently ignored, largely because decades of ferric porphyrin isolation has yielded only *five*-coordinate high-spin derivatives.⁴ Illustrative of this point is the contrast of six coordination in aquo- and fluoromethemoglobin with five coordination in complexes such as μ -oxo derivatives, hemin fluoride, FeCl(TPP),⁵ and numerous others.⁶⁻⁸ The five-coordinate derivatives invariably have considerable iron atom displacements from the mean plane of the porphyrin⁷ and this has led to the converse belief that high-spin states imply five coordination. While this remains a reasonable belief for *ferrous* porphyrins (and ferrous hemoproteins) the first experimental evidence that this might not be true for *ferric* porphyrins came with the very recently reported structure of [Fe(H₂O)₂(TPP)]ClO₄.⁹ Also, metal ion size effects have been questioned in theoretical studies^{10,11} which, with a certain degree of simplification, stress the importance of nonbonding repulsions of the axial ligands with the porphyrin core rather than the

mismatch of large metal ions with the restricted porphyrin hole size. We report herein the first definitively characterized examples of six-coordinate high-spin ferric porphyrins. Although rather abiological in the identity of their axial ligands, certain properties of these complexes model high-spin methemoglobin derivatives. The X-ray crystal structure of one complex, [Fe(TMSO)₂(TPP)]ClO₄, reveals an in-plane iron atom and emphasizes that considerable caution must be exercised in assigning the stereochemistry of ferric porphyrin complexes and ferric hemoproteins from magnetic properties. Concurrent with our synthetic and structural work NMR studies have shown that six coordination exists in dimethyl sulfoxide solutions of high-spin ferric porphyrins.¹² Prior to the aforementioned [Fe(H₂O)₂(TPP)]ClO₄ all characterized six-coordinate ferric porphyrins have been *low* spin having axial ligands of moderate to high field strength (e.g., imidazole,¹³ 2-methylimidazole,¹⁴ cyanide,¹⁵ thiolates,⁸ thiol,¹⁶ halides, pseudo-halides, thioethers,¹⁷ and some combinations thereof).

The characterization of six-coordinate synthetic models for

the high-spin methemoglobins is of interest on several counts and it comes as a surprise to many to be reminded that much of what we know about the structure of oxyhemoglobins has been inferred from the X-ray structures of the isomorphous aquomethemoglobins. The displacement of the iron atom from the heme plane is of particular interest since those of aquomethemoglobin (0.07 ± 0.06 and 0.21 ± 0.06 Å in the α and β chains of horse hemoglobin¹⁸) differ significantly from aquometmyoglobin (0.40 Å in sperm whale myoglobin¹⁹). This is one of the few pieces of evidence for tension in hemoprotein ligation and it has been suggested that this may be a compression consequence of the constraint mechanism of cooperativity in hemoglobin.²⁰ The significance of protein influences on heme stereochemistry can be better appreciated when the possibilities in definitively characterized model complexes provide a reference point for discussion. Our studies attempt to answer several questions. Can a high-spin ferric atom be accommodated within the plane of the porphyrin? Can the out of plane displacement of a high-spin iron(III) atom vary according to the axial ligand combination and is there a large energy difference between in-plane and out of plane positions? Do the spin-state/stereochemistry relationships²¹ which are obeyed without exception in ferrous hemes²⁰ still apply to ferric hemes? Does a six-coordinate ferric heme have a greatly expanded porphyrin core and can model complexes shed light on the problem of core expansion vs. doming in interpreting the resonance Raman frequencies of hemoproteins?²²⁻²⁴ Is a high-spin state the natural consequence of a weak plus moderate field axial ligand combination (H_2O and histidine in aquomethemoglobin) and which other combinations dictate a high-spin state? Is the common assumption that a high-spin state implies five coordination rigorously valid in ferric hemoproteins other than the methemoglobins? In cytochrome P₄₅₀ enzymes the evidence is convincingly affirmative⁸ but in the cytochromes *c'* and peroxidases the situation is quite unclear.²⁵ Can comparative studies on five- and six-coordinate high-spin ferric porphyrins lead to a set of criteria for unambiguous assignment of axial ligation in hemoproteins and which physical probes are the most sensitive? The definitive identification of axial ligation modes remains a challenge in a large number of hemoproteins and with certain limitations the characterization of possible combinations in model complexes can provide considerable progress in this endeavor.

The lack of precise knowledge about the existence of six coordination in high-spin ferric porphyrins has led previously to some uncertainty²⁶ and to conclusions which must now be reinterpreted.²⁷ The clarification of the behavior of ferric porphyrins in dimethyl sulfoxide solution is particularly important since Me_2SO has been a popular choice of solvent for NMR and electrochemical studies with otherwise poorly soluble hemin derivatives.²⁸

Experimental Section

Synthesis. As a precaution against formation of the μ -oxo dimer $[Fe(TPP)]_2O$ all reactions were carried out in dried solvents either in Schlenk tubes or in a Vacuum Atmospheres drybox under a He or N₂ atmosphere. Tetrahydrofuran was distilled from sodium/benzophenone, heptane from CaH₂, and other solvents were dried over molecular sieves. $FeCl(TPP)$ was prepared by an adaptation of a literature method²⁹ and all other chemicals were of reagent grade. Magnetic susceptibilities were measured in air on a Cahn 7600 Faraday system and are corrected for diamagnetism. Quantitative solvate and ligand analyses were done on a Hewlett-Packard 5710A GLC and are accurate to about 90% certainty. ESR spectra were run as solids or in dilute frozen 2-methyltetrahydrofuran solution at 10 K on a Varian E12 spectrometer equipped with an Air Products Heli-Tran cryostat with a temperature controller.

$Fe(OCIO_3)(TPP) \cdot 0.5C_7H_8$. A mixture of $FeCl(TPP)$ (2.00 g, 2.84 mmol), $AgClO_4$ (0.58 g, 2.84 mmol), and THF (120 mL) was boiled gently for several minutes and then filtered through a coarse frit. Heptane (180 mL) was added gradually with continuous swirling and

set aside overnight for crystallization. Fine purple crystals of the product were collected by filtration and washed with heptane. Recrystallization was achieved by dissolving the product in a minimum of hot toluene (40–50 mL), filtering through a medium frit, and adding heptane (100 mL). The yield of 0.5 toluene solvate was 2.03 g (88%). IR (KBr) ν_{ClO_4} 1170, 1150, 1120, 840, 610 cm^{-1} . $\mu_{eff} = 5.19 \mu_B$ at 25 °C. Anal. Calcd for $C_{47.5}H_{32}O_4N_4ClFe$: C, 70.08; H, 3.96; N, 6.88. Found: C, 70.51; H, 4.41; N, 6.97. λ_{max} (THF) 400, 526, 658 nm. $g_{\perp} = 4.75$, $g_{\parallel} = 2.03$ (solid).

$[Fe(Me_2SO)_2(TPP)]ClO_4$. To a solution of $Fe(OCIO_3)(TPP) \cdot 0.5C_7H_8$ (326 mg, 0.40 mmol) in THF (25 mL) was added dimethyl sulfoxide (0.1 mL, 1.2 mmol) followed by heptane (25–30 mL) slowly with swirling over a 10-min period. After a few hours purple needles were collected on a frit, washed with heptane, and dried by suction (350 mg, 95%). IR (KBr) ν_{SO} 950; ν_{ClO_4} 1100, 620 cm^{-1} . $\mu_{eff} = 6.00 \mu_B$ at 27 °C. Anal. Calcd for $C_{48}H_{40}O_6N_4S_2ClFe$: C, 62.37; H, 4.36; N, 6.06. Found: C, 62.70; H, 4.57; N, 6.08. Quantitative GLC analysis for Me_2SO : calcd 16.9; found 14.0. λ_{max} (THF) 400, 527, 660 nm. $g_{\perp} = 6.09$, $g_{\parallel} = 2.00$ (2-MeTHF).

$[Fe(TMSO)_2(TPP)]ClO_4$. To a solution of $Fe(OCIO_3)(TPP) \cdot 0.5C_7H_8$ (326 mg, 0.40 mmol) in THF (25 mL) was added tetramethylene sulfoxide (0.1 mL, 0.11 mmol). Upon standing overnight, fine purple prisms were collected (370 mg, 95%). IR (KBr) ν_{ClO_4} 1090, 1075, 620; ν_{SO} 935 cm^{-1} . $\mu_{eff} = 6.05 \mu_B$ at 25 °C. Anal. Calcd for $C_{52}H_{44}O_6N_4S_2ClFe$: C, 63.97; H, 4.54; N, 5.74. Found: C, 63.90; H, 4.74; N, 5.69. Quantitative GLC analysis for TMSO: calcd 21.3; found 21.0. λ_{max} (THF) 400, 527, 660 nm. $g_{\perp} = 6.06$, $g_{\parallel} = 1.98$ (solid).

$[Fe(Me_2SO)_2(TPP)]BPh_4$. $[Bu_4N][BPh_4]$ and $Ag[BPh_4]$ were prepared as follows. To a solution of $Na[BPh_4]$ (1.03 g, 3 mmol) in THF (40 mL) was added $[Bu_4N]Cl$ (0.83 g, 3 mmol) in small portions and the reaction mixture stirred for 10 min. After filtration heptane (60 mL) was added and after 2 h fine, colorless needles of $[Bu_4N][BPh_4]$ were collected (1.65 g, 98%); ¹H NMR (acetone-*d*₆, Me₄Si) δ 7.3–7.0 (m, ortho BPh₄, 8 H), 7.0–6.5 (m, meta, para BPh₄, 12 H), 3.4–3.0 (m, α -methylene Bu₄N, 8 H), 2.1–0.8 (m, β , γ -methylene Bu₄N, methyl Bu₄N, 28 H). $AgClO_4$ (0.21 g, 1 mmol) was dissolved in THF (30 mL) and $[Bu_4N][BPh_4]$ (0.56 g, 1 mmol) was added in small portions with stirring. After stirring overnight the product, $Ag[BPh_4]$, was filtered off and washed with THF (0.41 g, 96%) IR (KBr) 3040, 2980, 1570, 1475, 1420, 740, 720, 610 cm^{-1} .

A mixture of $FeCl(TPP)$ (141 mg, 0.20 mmol) and $Ag[BPh_4]$ (90 mg, 0.21 mmol) in dimethyl sulfoxide (2 mL) was stirred for 24 h and then THF (10 mL) was added. The precipitate was removed by filtration through a medium frit and the red-brown filtrate concentrated to a thick oil (ca. 0.5 mL) under vacuum. THF (5–10 mL) was added followed by heptane (30–40 mL) in small portions with swirling. Purple crystals of product were collected by filtration and recrystallized from THF–heptane (190 mg, 90%). IR (KBr) ν_{SO} 945 cm^{-1} . $\mu_{eff} = 5.82 \mu_B$ at 26 °C. Anal. Calcd for $C_{72}H_{60}O_2N_4S_2BFe$: C, 7.59; H, 5.29; N, 4.90. Found: C, 75.36; H, 5.55; N, 4.62. Quantitative GLC analysis for Me_2SO : calcd 13.7; found 14.7. λ_{max} (THF) 400, 528, 660 nm. $g_{\perp} = 5.96$, $g_{\parallel} = 1.99$ (solid).

$[Fe(pyO)_2(TPP)]ClO_4$. To a solution of $Fe(OCIO_3)(TPP) \cdot 0.5C_7H_8$ (163 mg, 0.2 mmol) in THF (50 mL) was added a solution of pyridine *N*-oxide (48 mg, 0.5 mmol) in THF (10 mL). After 2 h fine, purple plates were collected by filtration and washed with heptane (190 mg, 99%). IR (KBr) ν_{ClO_4} 1105, 1090, 1075, 1070, 620; ν_{NO} obscured by TPP but possibly 1175 or 1205 cm^{-1} . $\mu_{eff} = 5.99 \mu_B$ at 26 °C. Anal. Calcd for $C_{54}H_{38}O_6N_6ClFe$: C, 67.69; H, 4.00; N, 8.77. Found: C, 67.41; H, 4.16; N, 8.57. Quantitative GLC analysis for pyO: calcd 19.8; found 20.9. λ_{max} (THF) 399, 528, 686 nm. $g_{\perp} = 5.88$, $g_{\parallel} \sim 2$ (solid); $g = 5.98$, 4.40, 1.99 (2-MeTHF).

$[Fe(Ph_3PO)_2(TPP)]ClO_4 \cdot C_7H_8$. To a solution of $Fe(OCIO_3)(TPP) \cdot 0.5C_7H_8$ (163 mg, 0.2 mmol) in toluene (35 mL) was added triphenylphosphine oxide (278 mg, 1.0 mmol) in toluene (10 mL). Immediate precipitation of a reddish powder occurred. This product was filtered on a medium frit, washed with toluene, and dried under vacuum (280 mg, 99%). IR (KBr) ν_{PO} 1150; ν_{ClO_4} 1120, 1090, 620 cm^{-1} . $\mu_{eff} = 5.96 \mu_B$ at 22 °C. Anal. Calcd for $C_{87}H_{66}O_6N_4P_2ClFe$: C, 73.76; H, 4.70; N, 3.95. Found: C, 72.81; H, 4.60; N, 4.01. Quantitative GLC solvate for toluene: calcd 6.5; found 6.2. λ_{max} 400, 528, 685 nm. $g_{\perp} = 5.67$, $g_{\parallel} = 1.99$ (solid); $g_{\perp} = 5.75$, $g_{\parallel} = 1.99$ (2-MeTHF).

$[Fe(DMF)_2(TPP)]ClO_4$. $Fe(OCIO_3)(TPP) \cdot 0.5C_7H_8$ (163 mg, 0.2 mmol) was dissolved in dimethylformamide (2 mL) and toluene (40

Table I. Atomic Coordinates in the Unit Cell of $[\text{Fe}(\text{TMSO})_2(\text{TPP})]\text{ClO}_4$

atom type	coordinates ^a		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
Fe ₁	0	0	0
Fe ₂	1/2	1/2	0
S ₁	262 (1)	1950 (1)	2270 (1)
S ₂	4313 (1)	3808 (1)	1336 (1)
N ₁	491 (2)	-623 (2)	1180 (2)
N ₂	-1394 (2)	-129 (2)	277 (3)
N ₃	3693 (2)	5803 (2)	1067 (3)
N ₄	5737 (2)	5343 (2)	1496 (3)
C _{a1}	-101 (2)	-842 (2)	1906 (3)
C _{a2}	1409 (3)	-739 (3)	1566 (3)
C _{a3}	-1708 (3)	-434 (3)	1118 (3)
C _{a4}	-2202 (3)	147 (3)	-244 (3)
C _{a5}	2771 (3)	5882 (3)	687 (3)
C _{a6}	3559 (3)	6219 (3)	2310 (3)
C _{a7}	6734 (3)	5047 (3)	1529 (4)
C _{a8}	5320 (3)	5846 (3)	2690 (3)
C _{b1}	475 (3)	-1116 (3)	2737 (4)
C _{b2}	1390 (3)	-1057 (3)	2532 (4)
C _{b3}	-2744 (3)	-348 (3)	1111 (4)
C _{b4}	-3049 (3)	-003 (3)	277 (3)
C _{b5}	2042 (3)	6382 (3)	1741 (4)
C _{b6}	2528 (3)	6582 (3)	2715 (4)
C _{b7}	6947 (3)	5384 (4)	2759 (4)
C _{b8}	6073 (3)	5874 (3)	3460 (4)
C _{m1}	2219 (3)	-514 (3)	1138 (3)
C _{m2}	-1118 (3)	-761 (3)	1872 (3)
C _{m3}	4303 (3)	6255 (3)	3066 (3)
C _{m4}	7448 (3)	4494 (3)	509 (4)
C ₁	3148 (3)	-621 (3)	1717 (3)
C ₂	3504 (3)	201 (3)	2309 (4)
C ₃	4363 (4)	119 (4)	2856 (4)
C ₄	4862 (3)	-779 (5)	2854 (5)
C ₅	4511 (3)	-1600 (4)	2273 (4)
C ₆	3666 (3)	-1531 (3)	1701 (4)
C ₇	-1621 (3)	-1022 (3)	2762 (4)
C ₈	-2014 (5)	-333 (4)	3882 (4)
C ₉	-2490 (5)	-569 (5)	4683 (5)
C ₁₀	-2604 (4)	-1454 (4)	4398 (5)
C ₁₁	-2233 (7)	-2156 (5)	3286 (7)
C ₁₂	-1726 (6)	-1934 (4)	2479 (6)
C ₁₃	8508 (3)	4336 (3)	721 (4)
C ₁₄	9128 (4)	3396 (4)	367 (4)
C ₁₅	10 107 (4)	3271 (4)	564 (5)
C ₁₆	10 466 (4)	4074 (5)	1134 (5)
C ₁₇	9863 (4)	5003 (5)	1496 (5)
C ₁₈	8897 (4)	5139 (5)	1284 (5)
C ₁₉	3981 (3)	6721 (3)	4399 (3)
C ₂₀	3723 (4)	6183 (4)	4968 (4)
C ₂₁	3352 (5)	6640 (5)	6182 (5)
C ₂₂	3262 (5)	7608 (5)	6821 (4)
C ₂₃	3531 (6)	8142 (5)	6262 (5)
C ₂₄	3889 (5)	7700 (4)	5055 (5)
C ₂₅	-557 (4)	3148 (4)	3168 (4)
C ₂₆	-720 (5)	3263 (5)	4440 (5)
C ₂₇	-453 (6)	2317 (6)	4484 (6)
C ₂₈	383 (5)	1662 (4)	3562 (5)
C ₂₉	4882 (5)	2532 (6)	1316 (6)
C ₃₀	4212 (5)	1947 (4)	623 (6)
C ₃₁	3429 (5)	2615 (8)	268 (8)
C ₃₂	3288 (7)	3644 (5)	1030 (7)
C ₁	2321 (1)	3466 (1)	3923 (1)
O ₁	1899 (5)	3054 (6)	2919 (5)
O ₂	1778 (5)	3666 (7)	4994 (6)
O ₃	3234 (5)	2763 (5)	3860 (6)
O ₄	2664 (6)	4229 (5)	4011 (7)
O ₅	-410 (2)	1357 (2)	1492 (2)
O ₆	4830 (2)	3755 (2)	197 (3)

^a The numbers in parentheses are the estimated standard deviations in the last significant figure.

mL) was added. Heptane (10 mL) was added dropwise with swirling and after 30 min fine, purple needles were collected and washed thoroughly with heptane (180 mg, 98%). IR (KBr): ν_{CO} 1640; ν_{ClO_4} 1090, 620 cm^{-1} . $\mu_{\text{eff}} = 5.87 \mu_{\text{B}}$ at 22 °C. Anal. Calcd for $\text{C}_{50}\text{H}_{42}\text{O}_6\text{N}_6\text{ClFe}$: C, 65.69; H, 4.63; N, 9.19. Found: C, 65.71; H, 4.80; N, 9.15. Quantitative GLC analysis for DMF: calcd 16.0; found 16.8. λ_{max} (THF) 400, 527, 662 nm. $g_{\perp} = 5.58$, $g_{\parallel} = 1.99$ (solid); $g_{\perp} = 6.04$, $g_{\parallel} = 1.99$ (2-MeTHF).

Mössbauer Studies. The Mössbauer spectra of powdered samples of the unenriched material were recorded in horizontal transmission geometry using a constant acceleration spectrometer operated in connection with a 256 channel analyzer in the time scale mode. The source was kept at room temperature and consisted of 35 mCi of ^{57}Co diffused in rhodium foil. The spectrometer was calibrated against a metallic iron foil and zero velocity was taken as the centroid of its room temperature Mössbauer spectrum. In these calibration spectra line widths of about 0.23 mm/s were normally observed. The duration of a typical high-field run was 24 h. High fields were attained with a split-coil superconducting magnet (American Magnetics) capable of reaching a maximum of 6 T. The field was transverse to the γ -ray beam. The sample was cooled to 4.2 K by immersion in liquid helium.

X-ray Structure Determination. A crystal of $[\text{Fe}(\text{TMSO})_2(\text{TPP})]\text{ClO}_4$ with approximate dimensions of $0.8 \times 0.4 \times 0.3$ mm was mounted in a thin-walled glass capillary. Preliminary examination of the crystal on a Syntex PT automated diffractometer established a two-molecule triclinic unit cell, space group $P\bar{1}$. Least-squares refinement of the setting angles of 56 reflections, collected at 2θ , led to the following cell constants (λ 0.710 69 Å): $a = 14.003$ (5) Å, $b = 15.246$ (5) Å, $c = 12.108$ (3) Å, $\alpha = 113.20$ (2)°, $\beta = 89.24$ (2)°, and $\gamma = 76.67$ (4)°. For a unit cell content of $2[\text{Fe}(\text{N}_4\text{C}_{44}\text{H}_{28})(\text{C}_8\text{H}_{16}\text{O}_2)\text{ClO}_4]$, the calculated density is 1.412 g/cm^3 . The experimental density, measured by flotation, is 1.42 g/cm^3 at 20 ± 1 °C.

Intensity data were measured on the Syntex diffractometer using graphite-monochromated Mo $K\alpha$ radiation and θ - 2θ scanning. Variable 2θ scan rates (2–12°/min) with scans of 0.5° below $K\alpha_1$ and 0.7° above $K\alpha_2$ and backgrounds collected at the extremes of the scan for 0.5 times the time required for the scan were employed. Four standard reflections were measured every 50 reflections during data collection to monitor the long-term stability; no significant deviations were noted. Intensity data were reduced and standard deviations calculated as described previously.³⁰ A total of 7586 reflections having $(\sin \theta) \lambda \leq 0.648 \text{ \AA}^{-1}$ and $F_o > 3\sigma(F_o)$ were retained as observed (72% of the theoretical number possible) and used in the solution and refinement of the structure.

The structure was solved by the heavy-atom method³¹ and refined by block-diagonal least-squares techniques.³² A Patterson calculation did not reveal an Fe-Fe vector in the expected general position but rather Fe-Fe vectors consistent only with iron atom positions of 0, 0, 0 and $1/2, 1/2, 0$. Thus, with the choice of $P\bar{1}$ as the space group, the iron atoms are located at centers of symmetry and the crystallographically unique atoms are the two half $[\text{Fe}(\text{TMSO})_2(\text{TPP})]$ ions and the perchlorate anion. All subsequent developments of structure solution and refinement were consistent with the choice of $P\bar{1}$ as the space group. After several refinement cycles, a difference Fourier synthesis showed the position of all hydrogen atoms of the porphyrinato ligand and some for the axial ligands. The hydrogen atom positions were idealized ($\text{C}-\text{H} = 0.95 \text{ \AA}$ for porphyrin and 1.0 \AA for the axial ligand, $B(\text{H}) = C(\text{H}) + 1.0 \text{ \AA}^2$) and included in subsequent refinement cycles as fixed contributors. The refinement was carried to convergence using anisotropic temperature factors for all heavy atoms. The final values of the discrepancy indexes were $R = \Sigma[|F_o| - |F_c|] / \Sigma|F_o| = 0.076$ and $R = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o^2)]^{1/2} = 0.089$, and a final data/parameter ratio of 13.2. A final difference Fourier synthesis showed a peak of 1.5 $\text{e}/\text{\AA}^3$ near the disordered tetramethylene sulfide ligand associated with Fe₂. Other peaks in the map were $\pm 0.5 \text{ e}/\text{\AA}^3$.

A listing of the final observed and calculated structure amplitudes is available (see paragraph at end of paper regarding supplementary material). Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are given in Tables I and II.

Results and Discussion

The synthesis of $[\text{Fe}(\text{sulfoxide})_2(\text{TPP})]^+$ salts and related

Table II. Thermal Parameters in $[\text{Fe}(\text{TMSO})_2(\text{TPP})]\text{ClO}_4$

atom type	anisotropic parameters ^a						B_i^b Å ²
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
Fe ₁	3.06 (3)	3.28 (4)	2.57 (3)	-1.22 (3)	-0.26 (3)	1.45 (3)	2.7
Fe ₂	3.02 (3)	2.79 (3)	2.33 (3)	-0.48 (3)	0.16 (3)	0.69 (3)	2.8
S ₁	4.31 (6)	4.35 (6)	3.47 (5)	-1.42 (4)	-0.26 (4)	0.65 (4)	4.2
S ₂	11.2 (1)	3.90 (6)	5.12 (7)	-1.84 (7)	2.76 (7)	1.35 (5)	5.7
N ₁	3.3 (1)	3.1 (1)	2.7 (1)	-1.2 (1)	-0.2 (1)	1.4 (1)	2.8
N ₂	3.2 (1)	3.2 (1)	2.5 (1)	-1.1 (1)	-0.2 (1)	1.4 (1)	2.8
N ₃	3.1 (1)	3.0 (1)	2.4 (1)	-0.4 (1)	0.2 (1)	0.8 (1)	2.9
N ₄	3.2 (1)	3.2 (1)	2.4 (1)	-0.5 (1)	0.2 (1)	0.6 (1)	3.1
C _{a1}	3.7 (2)	3.1 (2)	2.8 (2)	-1.4 (1)	-0.3 (1)	1.4 (1)	2.9
C _{a2}	3.4 (2)	3.1 (2)	2.8 (2)	-1.0 (1)	-0.5 (1)	1.4 (1)	3.0
C _{a3}	3.1 (2)	3.1 (2)	2.7 (2)	-1.0 (1)	-0.3 (1)	0.9 (1)	2.9
C _{a4}	3.0 (2)	3.0 (2)	2.8 (2)	-1.0 (1)	-0.1 (1)	1.0 (1)	2.9
C _{a5}	3.2 (2)	3.0 (2)	3.0 (2)	-0.2 (1)	0.2 (1)	1.1 (1)	3.1
C _{a6}	3.7 (2)	2.8 (2)	2.6 (2)	-0.5 (1)	0.4 (1)	0.8 (1)	3.1
C _{a7}	3.4 (2)	3.3 (2)	3.2 (2)	-0.7 (1)	-0.1 (1)	1.1 (1)	3.3
C _{a8}	3.8 (2)	3.3 (2)	2.7 (2)	-0.8 (1)	0.1 (1)	0.8 (1)	3.3
C _{b1}	4.0 (2)	4.4 (2)	3.8 (2)	-1.4 (2)	-0.2 (2)	2.4 (2)	3.6
C _{b2}	3.7 (2)	4.1 (2)	3.5 (2)	-0.9 (2)	-0.6 (1)	2.2 (2)	4.1
C _{b3}	3.4 (2)	3.2 (2)	3.0 (2)	-1.2 (1)	0.2 (1)	0.9 (1)	3.2
C _{b4}	3.2 (2)	3.4 (2)	2.9 (2)	-1.1 (1)	-0.0 (1)	1.0 (1)	3.2
C _{b5}	3.2 (2)	4.4 (2)	3.5 (2)	-0.1 (1)	0.5 (1)	1.3 (2)	3.8
C _{b6}	3.5 (2)	4.3 (2)	3.0 (2)	-0.2 (2)	0.5 (1)	1.2 (2)	3.7
C _{b7}	3.5 (2)	5.0 (2)	3.1 (2)	-1.0 (2)	-0.6 (2)	1.4 (2)	3.8
C _{b8}	4.2 (2)	4.6 (2)	2.5 (2)	-1.2 (2)	-0.3 (1)	0.9 (2)	3.8
C _{m1}	3.0 (2)	2.9 (2)	2.9 (2)	-0.9 (1)	-0.3 (1)	1.2 (1)	2.9
C _{m2}	3.7 (2)	3.2 (2)	3.7 (2)	-1.1 (1)	0.2 (1)	1.4 (1)	2.9
C _{m3}	3.7 (2)	3.2 (2)	2.4 (2)	-0.8 (1)	0.3 (1)	0.7 (1)	3.1
C _{m4}	3.3 (2)	3.1 (2)	3.2 (2)	-0.4 (1)	-0.1 (1)	1.2 (1)	3.2
C ₁	3.0 (2)	4.1 (2)	2.7 (2)	-1.0 (1)	-0.1 (1)	1.6 (1)	3.1
C ₂	3.8 (2)	4.6 (2)	3.0 (2)	-1.2 (2)	-0.0 (2)	1.5 (2)	3.7
C ₃	4.1 (2)	7.0 (3)	3.6 (2)	-2.5 (2)	-0.5 (2)	1.8 (2)	4.5
C ₄	2.9 (2)	8.6 (4)	4.6 (2)	-0.7 (2)	-0.5 (2)	3.1 (2)	4.8
C ₅	3.6 (2)	5.7 (3)	5.1 (2)	-0.0 (2)	-0.0 (2)	3.0 (2)	4.5
C ₆	3.8 (2)	4.2 (2)	4.0 (2)	-0.6 (2)	0.2 (2)	1.8 (2)	4.0
C ₇	3.3 (2)	3.7 (2)	3.4 (2)	-0.9 (1)	0.1 (1)	2.0 (2)	3.2
C ₈	8.8 (4)	6.0 (3)	3.3 (2)	-4.2 (3)	1.2 (2)	0.8 (2)	5.0
C ₉	8.1 (4)	8.0 (4)	3.3 (2)	-3.3 (3)	1.8 (2)	1.2 (2)	5.4
C ₁₀	6.3 (3)	6.7 (3)	4.9 (3)	-1.2 (2)	1.3 (2)	3.6 (2)	4.9
C ₁₁	17.8 (7)	4.5 (3)	8.9 (4)	-3.0 (4)	6.9 (5)	1.9 (3)	7.0
C ₁₂	16.2 (6)	4.0 (3)	6.3 (3)	-2.9 (3)	6.9 (4)	0.3 (2)	5.8
C ₁₃	3.2 (2)	4.4 (2)	3.1 (2)	-0.4 (2)	0.1 (1)	1.4 (2)	3.6
C ₁₄	4.5 (2)	4.8 (2)	3.5 (2)	-0.1 (2)	-0.1 (2)	1.7 (2)	4.3
C ₁₅	3.6 (2)	7.9 (3)	4.7 (2)	1.3 (2)	0.6 (2)	3.1 (2)	4.9
C ₁₆	3.3 (2)	11.0 (5)	5.7 (3)	-1.0 (3)	-0.3 (2)	4.1 (3)	5.7
C ₁₇	4.4 (3)	9.6 (4)	6.5 (3)	-3.3 (3)	-0.9 (2)	3.0 (3)	6.0
C ₁₈	4.0 (2)	5.1 (3)	5.3 (3)	-1.3 (2)	0.1 (2)	1.7 (2)	4.8
C ₁₉	3.5 (2)	4.0 (2)	2.5 (2)	-0.6 (2)	0.1 (1)	0.6 (1)	3.4
C ₂₀	7.5 (3)	4.6 (3)	3.5 (2)	-1.8 (2)	0.7 (2)	1.1 (2)	4.9
C ₂₁	8.3 (4)	8.9 (4)	4.2 (3)	-2.7 (3)	1.0 (2)	3.0 (3)	6.1
C ₂₂	7.7 (4)	8.0 (4)	2.8 (2)	-1.5 (3)	1.3 (2)	0.2 (2)	5.7
C ₂₃	13.9 (6)	5.5 (3)	3.6 (3)	-2.3 (3)	1.5 (3)	-0.9 (2)	6.7
C ₂₄	10.0 (4)	4.9 (3)	3.5 (2)	-2.2 (3)	1.6 (2)	0.0 (2)	5.7
C ₂₅	6.4 (3)	3.6 (2)	4.1 (2)	-1.4 (2)	-0.1 (2)	0.7 (2)	4.7
C ₂₆	8.6 (4)	7.5 (3)	4.0 (3)	0.4 (3)	1.5 (3)	1.2 (3)	6.6
C ₂₇	13.1 (6)	8.3 (4)	5.4 (3)	0.8 (4)	3.0 (4)	3.4 (3)	7.8
C ₂₈	8.1 (4)	5.1 (3)	4.2 (2)	-0.7 (2)	-1.9 (2)	1.2 (2)	5.6
C ₂₉	9.0 (4)	10.0 (5)	6.9 (4)	-4.6 (4)	-0.6 (3)	4.5 (4)	7.3
C ₃₀	7.9 (4)	4.3 (3)	7.5 (3)	-2.7 (3)	0.5 (3)	1.6 (2)	6.0
C ₃₁	7.4 (4)	6.0 (4)	12.0 (5)	-2.4 (3)	1.5 (4)	2.4 (4)	7.9
C ₃₂	14.2 (6)	5.6 (4)	8.0 (4)	0.4 (4)	-0.2 (4)	2.9 (3)	8.7
C ₁	8.0 (9)	9.5 (1)	5.7 (7)	-5.5 (8)	-2.5 (7)	3.7 (7)	6.2
O ₁	16.4 (5)	27.8 (8)	9.4 (4)	-15.5 (6)	-7.7 (4)	8.5 (5)	11.2
O ₂	12.7 (5)	29.0 (9)	8.7 (4)	-10.0 (5)	-1.4 (3)	7.6 (5)	13.1
O ₃	16.2 (6)	12.9 (5)	11.1 (4)	-1.1 (4)	-4.0 (4)	4.2 (4)	13.3
O ₄	22.4 (7)	12.2 (5)	17.6 (6)	-11.5 (5)	-2.5 (5)	6.8 (5)	13.1
O ₅	4.0 (1)	3.4 (1)	3.2 (1)	-1.0 (1)	-0.3 (1)	0.8 (1)	3.6
O ₆	5.4 (2)	3.4 (1)	3.6 (1)	-1.2 (1)	0.8 (1)	1.2 (1)	3.9

^a The numbers in parentheses are the estimated standard deviations. The B_{ij} 's are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}a_i^*a_j^*$.

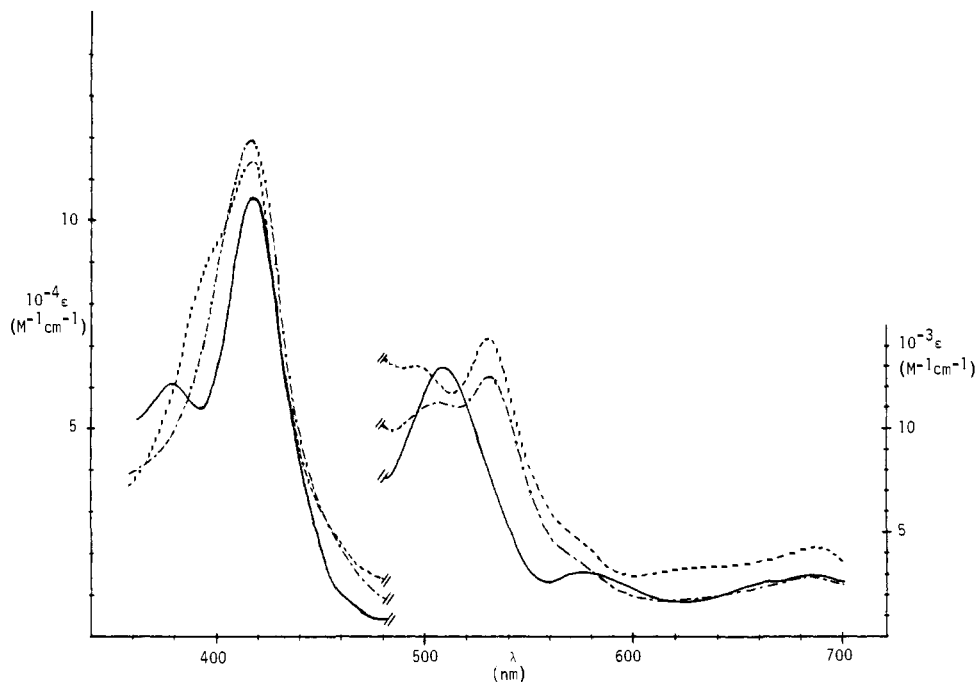


Figure 1. Comparison of visible spectra: 0.2 mM FeCl(TPP) in CHCl₃ (—), 0.2 mM [Fe(Me₂SO)₂(TPP)]BPh₄ in Me₂SO (---), and 0.2 mM [Fe(DMF)₂(TPP)]ClO₄ in DMF (-·-·-).

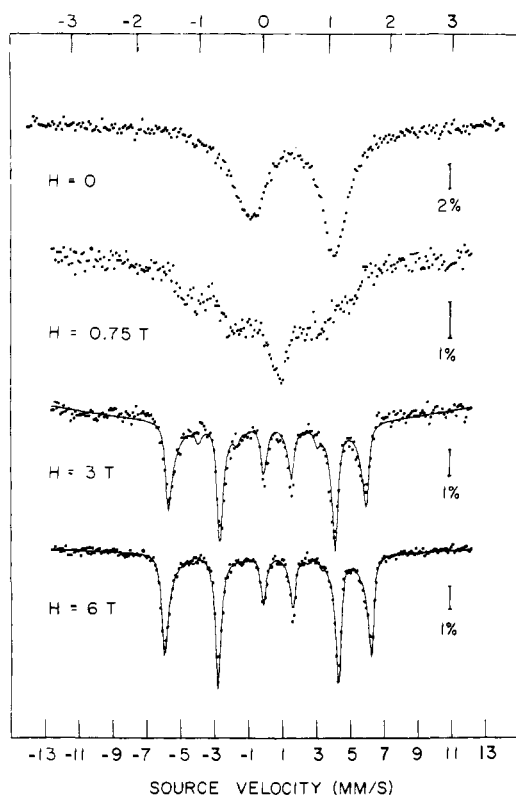


Figure 2. Mössbauer spectra of [Fe(Me₂SO)₂(TPP)]ClO₄ at 4.2 K in various applied fields as shown. The solid lines are the results of spin-Hamiltonian calculations as described in the text. The top velocity scale refers to the zero-field spectrum only.

complexes is best achieved by displacement of coordinated perchlorate from Fe(OCIO₃)(TPP) according to the equation



(L = Me₂SO, tetramethylene sulfoxide, pyridine *N*-oxide,

triphenylphosphine oxide, DMF). Isolated as nicely crystalline, purple solids, their room temperature magnetic moments (5.8–6.0 μ_B) are indicative of high-spin d⁵ (*S* = 5/2) systems. The coordination of sulfoxide ligands was suspected from the infrared observation of ν_{SO} some 110 cm⁻¹ lower than in the free ligand and is confirmed by a single-crystal X-ray structure determination for the tetramethylene sulfoxide derivative. Steric effects and hard metal/hard ligand preference considerations led us to the prediction that O-bound rather than S-bound sulfoxides would be found and it is clear from the numerous short Fe–O bond distances in a variety of iron(III) complexes that oxygen donor atoms are highly suited as ligands for ferric ions. In fact, the single crystals of [Fe(TMSO)₂(TPP)]ClO₄ used in the structural study discussed below arose from an initially unsuccessful attempt to coordinate tetramethylene sulfide (tetrahydrothiophene) to Fe(OCIO₃)(TPP). Presumably the preference of the ferric center for oxygen ligands favored the binding of the commonly occurring trace amounts of sulfoxide in the sulfide. It seems safe to assume that coordination through oxygen occurs in all of the present complexes. A strong, broad band centered near 1090 cm⁻¹ and a strong, sharp band at 620 cm⁻¹ are diagnostic of uncoordinated perchlorate and for the Me₂SO derivative a metathesis reaction to yield the tetraphenylborate salt was done to establish their salt character.

In solution all new complexes have a distinctive red-brown color and their visible spectra are essentially identical. They differ diagnostically from the more common, brown, five-coordinate high-spin complexes such as FeCl(TPP), as illustrated in Figure 1. The ESR spectra of all of the [FeL₂(TPP)]ClO₄ derivatives in 2-methyltetrahydrofuran solution are very similar and have the familiar tetragonal features (*g*_⊥ ≈ 6, *g*_∥ ≈ 2) of high-spin ferric porphyrins.

The Mössbauer spectra of polycrystalline [Fe(Me₂SO)₂(TPP)]ClO₄ corroborate the high-spin assignment. Figure 2 shows these spectra at 4.2 K in various external magnetic fields. In zero field the spectrum consists of two broad, asymmetric absorption lines that develop into a well-defined, six-line pattern as the field is raised to 6 T. The spectra at 3 and 6 T were least-squares fitted by computer using as model the usual spin

Table III. Spin Hamiltonian and Shift Parameters of Some High-Spin Ferric Heme Derivatives Measured by the Mössbauer Effect^a

material	H_{sat} , kG	D , cm^{-1}	$\Delta E q$, mm s^{-1}	δ , $^{\circ} \text{mm s}^{-1}$	ref
fluoromet Hb	529 (20)	7.0 (15)	0.70 (2)	0.40	33
fluoromet Mb	525 (3)	6.3 (5)	0.8 (1)	0.40	33
aquomet Mb (proto)	498 (4)	10.0 (10)	1.3 (1)	0.40	33
aquomet Mb (meso)	493 (4)	10.0 (10)	1.3 (1)	0.40	33
cyt <i>c'</i> (pH 7.0) ^d	461 (10)	15 (2)	1.35 (15)	0.37	34
cyt <i>c</i> peroxidase	490 (11)	15 (3)	1.2 (1)		33
[Fe(Me ₂ SO) ₂ (TPP)]ClO ₄	543 (4)	12.5 (10)	1.22 (4) ^b	0.45 (5)	this work
Fe(PPIXDME)(OC ₂ H ₅)	522 (8)	5.3 (2)	0.46 (5)	0.32 (3)	8

^a Numbers in parentheses are estimated errors in the last significant digits. ^b The asymmetry parameter η is zero; $\Delta E q = QV_{zz}/2$. ^c Relative to metallic iron. ^d Major component.

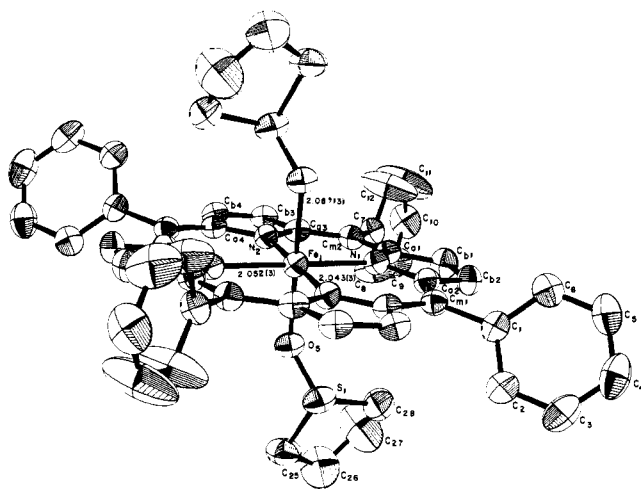


Figure 3. Computer-drawn model of [Fe(TMSO)₂(TPP)]⁺ (molecule 1). The label assigned to each crystallographically unique atom is displayed. Also shown are the unique bond distances of the coordination group. The thermal ellipsoids are contoured at the 50% probability level.

Hamiltonian:

$$\mathcal{H} = D[S_z^2 - \frac{1}{3}S(S+1)] + A \mathbf{I} \cdot \mathbf{S} + \frac{QV_{zz}}{4} [I_z^2 - \frac{1}{3}I(I+1)] + 2\beta_e \mathbf{H} \cdot \mathbf{S} - g_n \beta_n \mathbf{H} \cdot \mathbf{I}$$

with effective spin $S = 5/2$. The first term describes the zero-field splittings of the S ground state and is a parametrization of higher orbital-state admixtures via spin-orbit coupling, the second term describes the magnetic hyperfine (Fermi contact) interaction, the third term describes the quadrupole interaction, and the last two terms describe the interaction of the electronic and nuclear spins, respectively, with the applied magnetic field.

This spin Hamiltonian, as written above in its axially symmetric form, was sufficient to yield good fits (Figure 2, solid lines) to the data at 3 and 6 T. The values of the parameters found from the fits were $D = 12.5 \text{ cm}^{-1}$, $QV_{zz}/4 = 0.61 \text{ mm s}^{-1}$, and $A = 1.46 \text{ mm s}^{-1}$ (excited state). The isomer shift is 0.45 mm/s with respect to metallic iron and the quadrupole splitting $\Delta E q$ is 1.22 mm s^{-1} . Values are in the range of ones obtained from other heme proteins measured by the Mössbauer effect and are compared in Table III. In [Fe(Me₂SO)₂(TPP)]ClO₄ the relatively high saturation value of the internal magnetic field indicates reduced covalency with respect to all high-spin hemoproteins in keeping with replacement of a histidine ligand by a sulfoxide. It is possible that high values of $\Delta E q$ may distinguish six coordination from five but it is clear that considerably more data must be accumulated on a variety of complexes before Mössbauer spectroscopy can be considered a good diagnostic probe of axial ligation number and type in high-spin ferric hemoproteins.

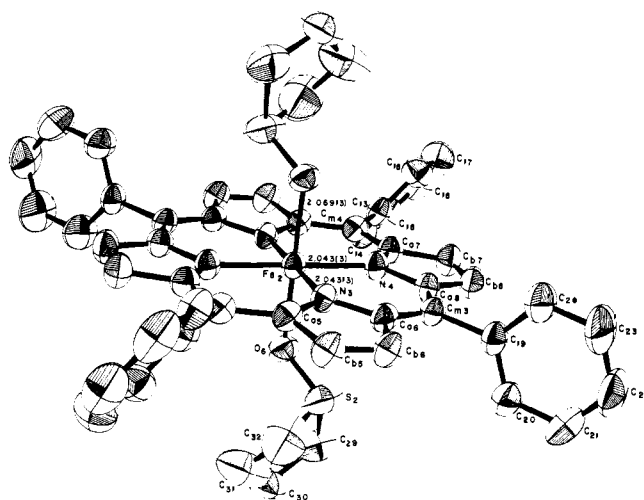


Figure 4. Computer-drawn model of the second molecule.

Note that in an applied field of 0.75 T the magnetic hyperfine pattern of [Fe(Me₂SO)₂(TPP)]ClO₄ is undeveloped in contrast to the high-spin proteins whose magnetic hyperfine spectra are usually sharp and fully split in fields as low as 0.05 T. This is so because in the polycrystalline sample the iron atoms are probably not magnetically isolated; coupling via spin-spin interaction prevails at low external fields and the spectra are characteristic of intermediate or fast electronic spin relaxation rates. As the external field increases, however, the coupling of the spins is broken and one observes spectra characteristic of the slow relaxation regime. In heme proteins the polypeptide usually ensures magnetic dilution so that with appreciable separation between neighboring iron atoms no spin-spin relaxation can arise.

Figures 3 and 4 are computer-drawn³⁵ models of the crystallographically unique [Fe(TMSO)₂(TPP)]ClO₄ molecules. Also displayed in the figures are the bond distances in the coordination groups and the symbols used to identify the crystallographically unique atoms. Individual bond lengths and important radii in the two porphyrinato cores are given in Figures 5 and 6. Bond lengths of the axial ligands and perchlorate anion are given in Table IV and individual bond angles for the molecule in Table V.

The requirement of C_{2v} symmetry for the two independent [Fe(TMSO)₂(TPP)]⁺ ions leads to rigorous centering of the iron(III) atoms in the porphyrinato plane. In order to accommodate the high spin iron(III) atom, the porphyrinato cores undergo a significant radial expansion. The average Fe-N bond distance (which is congruent with the hole size, $\text{Ct} \cdots \text{N}$) of $2.045 (5) \text{ \AA}$ is substantially increased from the 1.990 \AA value appropriate for low-spin six-coordinate iron(III) porphyrins.³⁶ A similar Fe-N distance of $2.041 (8) \text{ \AA}$ is found for the high-spin [Fe(H₂O)₂(TPP)]⁺ ion.⁹ These Fe-N distances can be compared with the Ni-N bond distance of 2.038 \AA in

Table V. Bond Angles in [Fe(TMSO)₂(TPP)]ClO₄^{a,b}

type	value, deg	type	value, deg	type	value, deg
N ₁ Fe ₁ N ₂	91.1 (1)	N ₃ Fe ₂ N ₄	90.0 (1)	C _{a1} C _{b1} C _{b2}	107.7 (3)
N ₁ Fe ₁ O ₅	87.4 (1)	N ₃ Fe ₂ O ₆	90.1 (1)	C _{a2} C _{b2} C _{b1}	107.7 (4)
N ₂ Fe ₁ O ₅	86.9 (1)	N ₄ Fe ₂ O ₆	89.7 (1)	C _{a3} C _{b3} C _{b4}	107.7 (3)
Fe ₁ O ₅ S ₁	128.1 (2)	Fe ₂ O ₆ S ₂	122.4 (2)	C _{a4} C _{b4} C _{b3}	107.5 (4)
Fe ₁ N ₁ C _{a1}	125.3 (3)	Fe ₂ N ₃ C _{a5}	126.1 (2)	C _{a5} C _{b5} C _{b6}	107.5 (4)
Fe ₁ N ₁ C _{a2}	127.6 (2)	Fe ₂ N ₃ C _{a6}	126.2 (3)	C _{a6} C _{b6} C _{b5}	107.9 (4)
Fe ₁ N ₂ C _{a3}	125.4 (3)	Fe ₂ N ₄ C _{a7}	126.6 (3)	C _{a7} C _{b7} C _{b8}	106.9 (4)
Fe ₁ N ₂ C _{a4}	127.1 (2)	Fe ₂ N ₄ C _{a8}	126.7 (3)	C _{a8} C _{b8} C _{b7}	108.0 (4)
O ₅ S ₁ C ₂₅	104.4 (2)	O ₆ S ₂ C ₂₉	102.8 (2)	C _{a2} C _{m1} C _{a4}	124.6 (4)
O ₅ S ₁ C ₂₈	107.1 (2)	O ₆ S ₂ C ₃₂	106.1 (3)	C _{a2} C _{m1} C ₁	118.1 (3)
C ₂₅ S ₁ C ₂₈	91.2 (2)	C ₂₉ S ₂ C ₃₂	96.7 (3)	C _{a4} C _{m1} C ₁	117.2 (3)
C ₂₅ C ₂₆ C ₂₇	109.6 (5)	C ₂₉ C ₃₀ C ₃₁	108.1 (5)	C _{a1} C _{m2} C _{a3}	126.2 (3)
C ₂₆ C ₂₇ C ₂₈	110.2 (6)	C ₃₀ C ₃₁ C ₃₂	113.4 (7)	C _{a1} C _{m2} C ₇	116.5 (3)
S ₁ C ₂₅ C ₂₆	109.7 (4)	S ₂ C ₂₉ C ₃₀	102.2 (5)	C _{a3} C _{m2} C ₇	117.3 (3)
S ₁ C ₂₈ C ₂₇	108.3 (4)	S ₂ C ₃₂ C ₃₁	107.2 (6)	C _{a6} C _{m3} C _{a8}	125.9 (3)
C _{a1} N ₁ C _{a2}	106.2 (3)	C _{a5} N ₃ C _{a6}	106.9 (3)	C _{a6} C _{m3} C ₁₃	116.7 (4)
C _{a3} N ₂ C _{a4}	107.2 (3)	C _{a7} N ₄ C _{a8}	106.5 (3)	C _{a8} C _{m3} C ₁₃	117.3 (4)
N ₁ C _{a1} C _{b1}	109.1 (3)	N ₃ C _{a5} C _{b5}	108.5 (3)	C _{a5} C _{m4} C _{a7}	124.3 (4)
N ₁ C _{a1} C _{m2}	125.4 (3)	N ₃ C _{a5} C _{m4'}	126.7 (3)	C _{a5} C _{m4} C ₁₉	117.9 (3)
C _{m2} C _{a1} C _{b1}	125.3 (3)	C _{m4} C _{a5} C _{b5}	124.8 (4)	C _{a7} C _{m4} C ₁₉	117.8 (4)
N ₁ C _{a2} C _{b2}	109.2 (3)	N ₃ C _{a6} C _{b6}	109.2 (4)	O ₁ ClO ₂	114.8 (4)
N ₁ C _{a2} C _{m1}	125.0 (3)	N ₃ C _{a6} C _m	126.0 (4)	O ₁ ClO ₃	107.3 (5)
C _{m1} C _{a2} C _{b2}	125.6 (4)	C _m C _{a6} C _{b6}	124.8 (4)	O ₁ ClO ₄	116.5 (5)
N ₂ C _{a3} C _{b3}	108.8 (3)	N ₄ C _{a7} C _{b7}	109.2 (3)	O ₂ ClO ₃	105.8 (5)
N ₂ C _{a3} C _{m2}	126.0 (3)	N ₄ C _{a7} C _{m4}	126.1 (4)	O ₂ ClO ₄	110.6 (5)
C _{m2} C _{a3} C _{b3}	125.1 (3)	C _{m4} C _{a7} C _{b7}	124.7 (4)	O ₃ ClO ₄	100.1 (5)
N ₂ C _{a4} C _{b4}	108.8 (3)	N ₄ C _{a8} C _{b8}	109.5 (4)		
N ₂ C _{a4} C _{m1'}	126.3 (3)	N ₄ C _{a8} C _{m3}	124.8 (4)		
C _{m1'} C _{a4} C _{b4}	124.9 (4)	C _{m3} C _{a8} C _{b8}	125.7 (4)		

^a The numbers in parentheses are the estimated standard deviations in the last significant figure. ^b c_i and c_{i'} denote atoms related by the center of inversion.

heme stereochemistry. Also, a decrease in the out of plane displacement may bring the iron atom closer to its low-spin crossover point. We are currently attempting to structurally characterize unconstrained synthetic analogues with mixed axial ligands by employing porphyrins with appended ligand "tails" and by other methods. It is interesting to note how much structure-related information has been assumed about "tail" porphyrins when none have been fully structurally characterized.⁴⁸ The possible complication of dimers has recently been suggested.⁴⁹

To investigate five vs. six coordination in high-spin ferric hemoproteins it is apparent that one should be very cautious in the use of magnetic probes. Rather, a structure-sensitive probe such as resonance Raman spectroscopy may better be able to exploit the differences in the porphyrin core which model complexes suggest will exist in hemoproteins. A typical five-coordinate ferric porphyrin has a small amount of doming and the core bond angles and bond distances are close to their optimum unconstrained values;⁷ the metal ion is ~0.45 Å out of the mean plane of the porphyrin toward the axial ligand. On the other hand, the prototypical six-coordinate high-spin ferric heme has an essentially flat porphyrin core with no doming; the core angles and distances show significant radial expansion and the metal atom is in plane. While the high-spin methemoglobins may have structures intermediate between these two extremes, the present six-coordinate species should be tested as likely better models than the five-coordinate FeX(porphyrin) species. Such experiments are in progress⁵⁰ and may help to clarify the importance of core expansion^{23,24} vs. doming²² in the interpretation of the structure-sensitive resonance Raman frequencies.

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Supplementary Material Available: Listings of structure factor amplitudes (×10) (34 pages). Ordering information is given on any current masthead page.

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Small Ring Metallo-cycles. 4.¹ Synthesis and Chemical Reactivity of *cyclo*-Metalladisiloxanes, $\overline{\text{MSiR}_2\text{OSiR}_2}$, and *cyclo*-Metalladisilabutanes, $\overline{\text{MSiR}_2\text{CH}_2\text{SiR}_2}$

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Abstract: The new metallo-cycles, $\text{L}_2\text{Pd}(\text{Si}_2\text{Me}_4\text{O})$, $\text{L}_2(\text{CO})(\text{H})\text{Ir}(\text{Si}_2\text{Me}_4\text{O})$, $\text{L}_2(\text{CO})(\text{H})\text{Ir}(\text{Si}_2\text{Me}_4\text{CH}_2)$, $\text{L}_2\text{Pt}(\text{Si}_2\text{Me}_4\text{CH}_2)$, and $\text{L}_2\text{Pd}(\text{Si}_2\text{Me}_4\text{CH}_2)$ ($\text{L} = \text{Ph}_3\text{P}$), have been prepared and characterized. The metallo-cycles contain the four-membered ring, $\overline{\text{MSiXSi}}$ ($\text{X} = \text{O}, \text{CH}_2$). Wilkinson's catalyst, L_3RhCl , also reacts with tetramethyldisiloxane to give an unstable metallo-cycle which is postulated to be dinuclear. These new complexes have been shown to act as catalysts for the disproportionation of tetramethyldisiloxane into dimethylsilane and linear polysiloxanes at room temperature. The rhodium metallo-cycle gives, in addition, cyclic polysiloxanes. This disproportionation involves the breaking and re-forming of strong Si-O bonds. A mechanism is proposed in which the four-membered ring cleaves to form an intermediate with coordinated silylene and silaketone. It is postulated that relief of angle strain in the four-membered ring is the driving force for the cleavage of the Si-O bond, and hence is responsible for the catalytic activity observed for the metallo-cycles. The scission of the four-membered metallo-cycle is similar to that postulated for metallo-cyclobutanes in the catalysis of the olefin metathesis reaction.

Introduction

Small-ring metallo-cycles have been implicated as intermediates in a large number of reactions catalyzed by transition metal complexes. Thus, metallo-cyclobutanes are postulated to play a key role in the catalysis of the olefin metathesis reaction.²⁻⁸ Metallo-cycles are also implicated in various ring openings and rearrangements,⁹⁻¹¹ cyclooligomerizations of olefins,¹²⁻¹⁵ the polymerization of silacyclobutanes,^{16,17} and the addition of acetylenes to strained Si-Si bonds.¹⁸⁻¹⁹ In many instances, the metallo-cycles may be isolated.^{17,20}

In spite of their apparent ubiquity in many important reactions, very little is known about the chemistry of small-ring metallo-cycles. A metallo-cyclobutane, for example, could react by reductive elimination of cyclopropane, β -elimination to give propene, scission to give coordinated carbene and olefin, or

insertion of other small molecules into the metal-carbon bond. The oxidation state, coordination number, and electron configuration of the metal and the nature of the ancillary ligands could all affect the reactivity of the metallo-cycle and change the course of its reactions. Indeed, some platinacyclobutanes may be caused to give propene or cyclopropane, depending on the nature of added ligands.²¹ We have begun a program to study the synthesis and chemistry of small-ring metallo-cycles so that the nature of their reactivity may be better understood. A better understanding of metallo-cycle reactivity should allow a more rational design of catalysts for transformations involving metallo-cycles.

In this paper, we report some of our initial studies on *cyclo*-metalladisiloxanes and disilametallacyclobutanes, metallo-cycles which could show some interesting reactivity as