Nitrosylmetalloporphyrins. 4. Molecular Stereochemistry of Two Crystalline Forms of Nitrosyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(4-methylpiperidine)-iron(II). A Structural Correlation with ν(NO)

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Abstract: The molecular stereochemistry of two crystalline forms of nitrosyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(4-methylpiperidine)iron(II) has been determined by x-ray diffraction techniques. One form (I) crystallizes as the chloroform solvate in the orthorhombic system, space group $P2_12_12_1$. The unit cell has a = 17.638 (3), b = 25.582 (3), and c = 10.108 (1) Å, and Z = 4. The other, unsolvated, form (II) crystallizes in the triclinic system, space group $P\bar{1}$. The unit cell has a = 11.550 (2), b = 17.236 (3), and c = 10.668 (2) Å, α = 87.83 (2), β = 105.62 (2), and γ = 92.93 (2)°, and Z = 2. Measurement of diffracted intensities employed a four-circle diffractometer with Mo Kα radiation. Both forms have bent FeNO groups and an average equatorial Fe-N bond distance of 2.00 (1) Å. Significant differences in the two forms are noted for the Fe-N_b bond length to the sixth ligand, trans to NO, and in ν(NO). The Fe-N_b bond length in complex I is 2.328 (10) Å and in complex II is 2.463 (7) Å and suggest weak interaction of the iron atom with the sixth ligand. These data and the comparable data for Fe(TPP)(1-MeIm)(NO) are used to note a linear correlation between the Fe-N_b bond distance and ν(NO).

In our earlier work with nitrosyl derivatives of iron porphyrins, the preparation and structural characterization of a five-coordinate derivative, Fe(TPP)(NO),[1] and a six-coordinate derivative, Fe(TPP)(1-MeIm)(NO),[2,3] were presented. These two nitrosyl derivatives display significantly different electronic spectra[2] and NO stretching frequencies. The five-coordinate complex has an NO stretching frequency of 1670 cm^{-1}; six-coordinate Fe(TPP)(1-MeIM)(NO) has ν(NO) 1625 cm^{-1}. It was noted[2] that the spectral differences of the two nitrosyl iron porphyrins are similar to the spectral changes observed between nitrosylhemoglobin (NOHb) in the absence and presence of the allosteric effector inositol hexaphosphate (IHP).[4] These spectral changes appear to result from changes in the coordination group geometry of at least some of the heme centers. Changes in the ESR spectrum of NOHb in the absence and presence of IHP[5] also suggest changes in the coordination group geometry of some of the hemes. Maxwell and Caughey[6] have studied the changes in the NO stretching frequency of NOHb in the presence and absence of organic phosphates. They observe a single NO frequency at 1615 cm^{-1} in NOHb and two bands at 1668 and 1615 cm^{-1}, of approximately equal intensity, for NOHb in the presence of IHP. The change in the coordination group geometry of NOHb, induced by IHP, might be a cleavage of the proximal histidine to iron bond in two of the subunits. Alternatively, it was suggested[2] that the proximal histidine to iron bond was not broken, but rather that the interaction was substantially reduced by a significant stretch in the bond.

The long trans Fe-N(1-MeIm) bond of 2.180 (4) Å observed in Fe(TPP)(1-MeIm)(NO) suggests a weak interaction between the axial ligand and the iron atom. In the hope of shedding further light on the interesting question of the geometry of the hemes in the nitrosylhemoglobins we endeavored to characterize additional six-coordinate nitrosyl iron porphyrins in which the axial interaction was different than that found in Fe(TPP)(1-MeIm)(NO). An attractive class of complexes, for which such behavior might be anticipated, were derivatives in which the NO stretching frequency was increased toward the value found for the five-coordinate complex, Fe(TPP)(NO). The first derivative prepared was the 4-methylpiperidine adduct of Fe(TPP)(NO). This complex has ν(NO) 1640 cm^{-1} and a substantially longer trans Fe-N(4-MePip) bond. Unfortunate disorder involving a chloroform molecule of crystallization led us to attempt to characterize additional examples. After considerable effort, a second crystalline form of the 4-methylpiperidine adduct of Fe(TPP)(NO) was obtained. This crystalline form, which is completely ordered, differs in a significant manner from the first complex. We report herein the molecular stereochemistry of both crystalline forms. In order to distinguish the two crystalline forms of the complex, the first is denoted as Fe(TPP)(4-MePip)(NO)·$CHCl_3$ and the second as Fe(TPP)-(4-MePip)(NO).

Experimental Section

Fe(TPP)(4-MePip)(NO)·$CHCl_3$. Considerable difficulty was experienced in obtaining these six-coordinate complexes and consequently the successful procedures are described in some detail. Fe(TPP)(NO) was prepared as described previously.[1] Saturated $CHCl_3$ solutions of Fe(TPP)(NO) were prepared under an argon atmosphere. A 5-mL beaker was placed in a wide-mouthed crystallization bottle and 4 mL of $CHCl_3$, 3 mL of 4-methylpiperidine, and 0.2 mL of 1-propanol were put into the bottle (outside of the beaker). This solution was degassed by bubbling a fine stream of argon through it for 5 min. One milliliter of the saturated Fe(TPP)(NO) solution and 2 mL of 4-methylpiperidine were then placed in the beaker and degassed by bubbling argon through this solution for 5 min. NO was then bubbled through the solution in the beaker for 10 min. The sealed vessel was then set aside for 2 days. Usually, but not invariably, crystals of Fe(TPP)(4-MePip)(NO)·$CHCl_3$ were found in the beaker. On some occasions only Fe(TPP)(NO) was recovered. Attempted crystallizations from many other common solvents were unsuccessful. The infrared spectrum of the crystals so obtained was measured on a Perkin-Elmer 457 spectrometer using a KBr pellet; the strong absorption at 1640 cm^{-1} was assigned as the NO stretching frequency.

Preliminary examination of the crystals demonstrated a four-molecule orthorhombic unit cell. A summary of the crystal data for Fe(TPP)(4-MePip)(NO)·$CHCl_3$ is given in Table I. The unit cell parameters are similar to those observed for Fe(TPP)(1-MeIm)-(NO)·$CHCl_3$.[2] Lattice constants for the two crystalline compounds listed in Table I came from a least-squares refinement that utilized the setting angles of 30 reflections, each collected at ±2θ, at 20 ± 1 °C. X-ray intensity data were collected by the ω-scan technique with a crystal mounted in a thin-walled glass capillary. Data collection techniques and reduction were similar to those described previously.[2]

Table I. Summary of Crystal Data and Intensity Collection

	$Fe(TPP)(4\text{-}MePip)(NO)\cdot CHCl_3$	$Fe(TPP)(4\text{-}MePip)(NO)$
a, Å	17.638 (3)	11.550 (2)
b, Å	25.582 (3)	17.236 (3)
c, Å	10.108 (1)	10.668 (2)
α, deg	90.0	87.83 (2)
β, deg	90.0	105.62 (2)
γ, deg	90.0	92.93 (2)
Z	4	2
Calcd density, g/cm^3	1.33	1.294
Obsd density, g/cm^3	1.34	1.30
Space group	$P2_12_12_1$	$P\bar{1}$
Radiation	Graphite-monochromated Mo Kα (λ 0.71069 Å)	
μ, mm^{-1}	0.549	0.411
Scan type	ω	θ-2θ
Scan range	±0.2 from peak center	0.9° below Kα_1 to 1.1° above Kα_2
Scan speeds	0.5-6.0 deg ω/min	1.0-8.0° deg 2θ/min
Background	Stationary crystal at ±0.6° from peak center	Profile analysis
2θ limits	3.5-56.8	3.5-54.87
Criterion for observation	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
Unique obsd data	3337	3011
Crystal dimensions	0.10 × 0.27 × 0.33 mm	0.10 × 0.17 × 0.50 mm

Table II. Atomic Coordinates and Isotropic Temperature Factors in the Unit Cell ($CHCl_3$ Solvate)[a]

Atom type	Coordinates			B, Å^2 [b]
	10^4x	10^4y	10^4z	
Fe	874 (1)	1697 (1)	2283 (2)	3.1
O	393 (8)	1248 (5)	4532 (13)	9.7
N_1	933 (5)	940 (3)	1780 (9)	3.1
N_2	2011 (5)	1727 (3)	2368 (9)	3.4
N_3	835 (5)	2469 (3)	2654 (10)	3.6
N_4	−244 (5)	1702 (4)	2013 (9)	3.1
N_5	770 (6)	1516 (4)	3913 (10)	3.8
N_6	1037 (6)	1893 (4)	52 (10)	4.6
C_{a1}	314 (7)	604 (5)	1613 (12)	3.4 (3)
C_{a2}	1565 (6)	632 (4)	1829 (11)	2.8 (2)
C_{a3}	2509 (6)	1318 (4)	2217 (13)	3.5 (2)
C_{a4}	2446 (6)	2145 (4)	2651 (12)	3.2 (2)
C_{a5}	1428 (6)	2800 (4)	2911 (12)	3.2 (2)
C_{a6}	172 (7)	2766 (5)	2712 (13)	4.1 (3)
C_{a7}	−724 (6)	2109 (4)	2076 (11)	3.0 (2)
C_{a8}	−678 (7)	1261 (5)	1671 (13)	4.1 (3)
C_{b1}	586 (7)	71 (5)	1548 (13)	4.4 (3)
C_{b2}	1360 (7)	87 (5)	1696 (13)	4.0 (3)
C_{b3}	3275 (7)	1506 (5)	2358 (14)	4.5 (3)
C_{b4}	3253 (6)	2015 (4)	2618 (12)	3.6 (2)
C_{b5}	1151 (7)	3312 (5)	3173 (12)	4.3 (3)
C_{b6}	402 (7)	3297 (5)	3025 (12)	4.4 (3)
C_{b7}	−1473 (7)	1952 (5)	1761 (13)	4.5 (3)
C_{b8}	−1480 (8)	1436 (5)	1532 (14)	4.7 (3)
C_{m1}	2305 (6)	786 (4)	1970 (12)	3.3 (2)
C_{m2}	2192 (7)	2661 (4)	2914 (12)	3.6 (3)
C_{m3}	−546 (6)	2611 (4)	2444 (12)	3.5 (2)
C_{m4}	−425 (7)	737 (5)	1529 (12)	3.5 (3)
C_1	356 (8)	1769 (5)	−781 (13)	4.8
C_2	502 (11)	1872 (6)	−2216 (16)	6.6
C_3	737 (10)	2441 (6)	−2461 (15)	6.8
C_4	1462 (9)	2538 (6)	−1668 (14)	5.2
C_5	1322 (8)	2419 (5)	−176 (16)	5.1
C_6	877 (13)	2573 (8)	−3945 (17)	8.9

[a] Figures in parentheses are the estimated standard deviations. [b] Atoms for which no estimated standard deviation is given for the temperature factor were refined anisotropically.

Initial coordinates for the iron atom and atoms of the porphinato core were taken from the final coordinates of the $Fe(TPP)(1\text{-}MeIm)(NO)\cdot CHCl_3$ complex.[2] A difference Fourier then revealed the positions of the NO and 4-methylpiperidine ligands and several peaks in the region where the $CHCl_3$ solvent molecule was expected to be located. Careful examination of this Fourier map suggests two different major orientations of the $CHCl_3$ molecule and possible minor orientations as well. Full-matrix refinement[7] of the Fe(TPP)(4-MePip)(NO) molecule was commenced. The peripheral phenyl groups were refined as rigid groups, the averaged geometry of the phenyl rings found from the low-temperature refinement of the MnTPP molecule[8] was used in defining the phenyl ring rigid body parameters. Initial refinement of the coordinates of the solvent molecule, assuming two orientations, were unconstrained; the resulting coordinates departed significantly from ideal geometry. Subsequent refinements of the solvent molecule utilized the constraints of rigid body refinement; two orientations of the molecule were allowed, assuming tetrahedral geometry, a C-Cl bond distance of 1.77 Å, and an occupancy factor of 0.5 for each atom of the two orientations. The refinement[9] was then carried to convergence using anisotropic temperature factors for the iron atom, the four nitrogen atoms of the porphinato core, and all atoms of the two axial ligands, and isotropic temperature factors for the remaining atoms. Toward the end of the refinement an attempt to improve the model for the disordered solvent molecule was made; the chlorine atom coordinates derived from the rigid group were held fixed and the temperature factors were allowed to vary anisotropically. A final difference Fourier still showed a number of peaks, with densities of up to 0.7 e/Å^3, in the region of the solvent molecule; the map showed no significant features elsewhere. The final value of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.109 and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ was 0.113. The estimated standard deviation of an observation of unit weight was 2.62. The largest shift/error was 0.30 with most being less than 0.10.

Final atomic coordinates and isotropic temperature factors are given in Table II. Anisotropic temperature factors are reported in Table III.[10] Rigid group parameters and the derived atomic coordinates are reported in Tables IV and V, respectively.[10] A final listing of observed and calculated structure factors is available.

Fe(TPP)(4-MePip)(NO). In preparing crystals of the unsolvated form of Fe(TPP)(4-MePip)(NO), more satisfactory results were generally obtained when the complex was prepared directly in the crystallization vessel. Fe(TPP)(Cl) (400 mg) was dissolved in 7 mL of *trans*-dichloroethene and 7 mL of 4-methylpiperidine under argon. After the solution had been degassed by sweeping with argon, the solution was filtered under argon and stored in an Erlenmeyer flask fitted with a serum cap. Two milliliters of this solution was transferred to a 5-mL beaker that had been placed in a wide-mouthed flask filled with argon. *trans*-Dichloroethene (4 mL), 2 mL of 4-methylpiperidine, and 1 mL of 1-propanol were put into the flask (outside the beaker). Nitric oxide was bubbled through the solution in the beaker for 10 min and through the solution outside the beaker for 5 min. The sealed flask was then allowed to stand for 4 days. The desired crystals were usually then found in the beaker. The infrared spectrum of these crystals, measured in a KBr pellet, showed a strong absorption at 1653-1655 cm^{-1}. The spectrum obtained was somewhat sensitive to the conditions used to prepare the pellet (vide infra).

Preliminary x-ray examination of the crystals revealed a two-molecule triclinic unit cell. A summary of the crystal data is given in Table I. X-ray intensity data were collected by the θ-2θ scan method using a crystal mounted in a thin-walled glass capillary. Data collection and data reduction techniques have been described previously.[11] Intensity data were corrected for the effects of absorption.

The structure was solved by the usual heavy-atom method. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by all subsequent developments of structure determination. A difference Fourier synthesis, calculated after isotropic refinement, revealed electron density concentrations appropriately located for the porphyrin and ligand hydrogen atoms; these positions were idealized (C-H = 0.95 Å, B(H) = B(C) + 1.0 Å^2) and included in the refinement as fixed contributors.[9,12] Refinement was then carried to convergence using anisotropic temperature factors for the iron atom and the atoms of the two axial ligands and isotropic temperature factors for all other

Table V. Atomic Coordinates Derived from Rigid Body Refinement and Isotropic Temperature Factors ($CHCl_3$ Solvate)

Atom type	Coordinates 10^4x	10^4y	10^4z	B, Å^2
C_{11}	2919	398	1920	3.7 (3)
C_{12}	3106	165	710	5.2 (3)
C_{13}	3666	−218	640	5.3 (3)
C_{14}	4049	−373	1780	4.3 (3)
C_{15}	3867	−144	2990	4.1 (3)
C_{16}	3307	239	3059	4.5 (3)
C_{21}	2760	3063	3186	3.4 (2)
C_{22}	3062	3134	4454	4.6 (3)
C_{23}	3604	3519	4692	5.5 (3)
C_{24}	3852	3839	3665	5.5 (3)
C_{25}	3556	3772	2398	5.4 (3)
C_{26}	3014	3387	2161	5.7 (3)
C_{31}	−1158	3002	2523	3.8 (2)
C_{32}	−1454	3153	3750	4.4 (3)
C_{33}	−2033	3522	3828	6.0 (4)
C_{34}	−2326	3745	2679	6.0 (3)
C_{35}	−2036	3598	1452	5.7 (4)
C_{36}	−1457	3229	1375	4.9 (3)
C_{41}	−1007	339	1273	3.9 (3)
C_{42}	−1538	199	2240	6.6 (4)
C_{43}	−2075	−187	1992	6.8 (4)
C_{44}	−2090	−440	771	6.4 (4)
C_{45}	−1565	−304	−200	6.7 (4)
C_{46}	−1028	83	50	5.2 (3)
C_7	700	3955	9573	24.6 (43)
Cl_1	1644	4190	9642	14.5
Cl_2	372	3962	7918	13.3
Cl_3	106	4349	10574	16.1
C_8	316	4292	8760	21.4 (33)
Cl_4	1136	4670	9090	16.8
Cl_5	260	3763	9886	28.4
Cl_6	348	4052	7116	74.2 (35)

Table VI. Atomic Coordinates and Isotropic Temperature Factors in the Unit Cell (Unsolvated Form)[a]

Atom type	Coordinates 10^4x	10^4y	10^4z	B, Å$^{2\,b}$
Fe	3195 (1)	2165 (1)	1444 (1)	3.0
O	4436 (6)	1015 (4)	797 (8)	6.8
N_1	4844 (6)	2321 (4)	2617 (6)	3.2 (1)
N_2	3652 (6)	2819 (4)	56 (6)	3.0 (1)
N_3	1478 (6)	2115 (4)	343 (6)	3.1 (1)
N_4	2670 (6)	1606 (4)	2887 (6)	3.2 (1)
N_5	3639 (6)	1326 (4)	876 (7)	3.6
N_6	2745 (6)	3365 (4)	2370 (6)	3.9
C_{a1}	5265 (7)	2033 (5)	3865 (8)	3.2 (2)
C_{a2}	5797 (7)	2737 (5)	2317 (8)	3.4 (2)
C_{a3}	4769 (7)	3163 (5)	97 (8)	3.0 (2)
C_{a4}	2950 (7)	3001 (5)	−1184 (8)	3.4 (2)
C_{a5}	1073 (7)	2379 (5)	−940 (8)	3.0 (2)
C_{a6}	514 (7)	1692 (5)	628 (8)	3.4 (2)
C_{a7}	1553 (7)	1244 (5)	2819 (8)	3.4 (2)
C_{a8}	3394 (7)	1393 (5)	4107 (8)	3.6 (2)
C_{b1}	6495 (8)	2290 (5)	4373 (8)	4.1 (2)
C_{b2}	6827 (8)	2728 (5)	3458 (9)	4.2 (2)
C_{b3}	4744 (8)	3565 (5)	−1096 (9)	4.1 (2)
C_{b4}	3610 (8)	3471 (5)	−1907 (8)	4.1 (2)
C_{b5}	−177 (8)	2127 (5)	−1422 (8)	4.1 (2)
C_{b6}	−516 (8)	1723 (5)	−491 (8)	3.9 (2)
C_{b7}	1588 (8)	822 (5)	4029 (9)	4.4 (2)
C_{b8}	2700 (8)	915 (5)	4781 (8)	3.8 (2)
C_{m1}	5763 (7)	3137 (5)	1177 (8)	3.1 (2)
C_{m2}	1736 (7)	2786 (5)	−1638 (8)	3.0 (2)
C_{m3}	540 (7)	1293 (5)	1760 (7)	3.0 (2)
C_{m4}	4607 (7)	1602 (5)	4565 (8)	3.3 (2)
C_{11}	6909 (7)	3559 (5)	1095 (8)	3.3 (2)
C_{12}	7105 (9)	4318 (6)	1495 (10)	6.0 (3)
C_{13}	8178 (10)	4740 (7)	1447 (11)	7.1 (3)
C_{14}	8982 (9)	4394 (6)	999 (9)	5.4 (2)
C_{15}	8820 (9)	3669 (6)	573 (9)	5.3 (2)
C_{16}	7752 (8)	3227 (6)	597 (9)	4.9 (2)
C_{21}	1125 (7)	2996 (5)	−3029 (8)	3.4 (2)
C_{22}	1343 (8)	2565 (6)	−4021 (9)	5.1 (2)
C_{23}	807 (9)	2758 (6)	−5324 (10)	5.7 (3)
C_{24}	91 (9)	3371 (6)	−5637 (10)	5.4 (2)
C_{25}	−160 (9)	3793 (6)	−4702 (9)	5.4 (2)
C_{26}	358 (8)	3601 (6)	−3378 (9)	4.7 (2)
C_{31}	−583 (7)	854 (5)	1884 (8)	3.4 (2)
C_{32}	−742 (9)	65 (6)	1582 (9)	5.3 (2)
C_{33}	−1829 (8)	−334 (6)	1658 (9)	5.1 (2)
C_{34}	−2684 (8)	39 (5)	2000 (9)	4.3 (2)
C_{35}	−2526 (9)	799 (6)	2305 (9)	5.3 (2)
C_{36}	−1465 (8)	1214 (5)	2229 (9)	4.5 (2)
C_{41}	5224 (7)	1356 (5)	5944 (8)	3.4 (2)
C_{42}	5990 (9)	746 (6)	6188 (9)	5.3 (2)
C_{43}	6534 (9)	515 (6)	7480 (10)	5.8 (3)
C_{44}	6297 (9)	894 (6)	8470 (9)	5.3 (2)
C_{45}	5573 (9)	1496 (6)	8259 (9)	5.3 (2)
C_{46}	5005 (8)	1735 (6)	6981 (9)	4.7 (2)
C_1	3519 (9)	3501 (6)	3665 (9)	5.2
C_2	3281 (9)	4258 (6)	4265 (9)	5.6
C_3	3371 (9)	4985 (6)	3434 (10)	5.6
C_4	2564 (10)	4818 (6)	2110 (10)	6.3
C_5	2778 (9)	4051 (6)	1533 (9)	5.4
C_6	3140 (10)	5753 (6)	3986 (11)	4.9

[a] Figures in parentheses are the estimated standard deviations. [b] Atoms for which no esd is given for the temperature factor were refined anisotropically.

atoms. The final values of the discrepancy indices were $R_1 = 0.087$ and $R_2 = 0.081$. The estimated standard deviation of an observation of unit weight was 1.84. A final difference Fourier synthesis was judged to be free of significant features. The largest shift/error in the final least-squares cycle was 0.09; the final data/parameter ratio was 10.6.

Final atomic coordinates and isotropic temperature factors are listed in Table VI; anisotropic temperature factors are listed in Table VII. A final listing of observed and calculated structure factors is available.[10]

Results and Discussion

Fe(TPP)(4-MePip)(NO)·CHCl$_3$. Figure 1 is a computer-drawn model,[13] in perspective, of the Fe(TPP)(4-MePip)(NO)·$CHCl_3$ molecule as it exists in the crystal. Displayed in Figure 1 are the special symbols assigned to the atoms of the molecule. Listings of individual bond lengths and bond angles of the complex are given in Tables VIII and IX. Using C_a and C_b to denote the respective α and β carbon atoms of the pyrrole rings and C_m for methine carbon, averaged values for the chemically distinct bond lengths and angles of the porphinato core are reported in Table X.

Figure 2, a formal diagram of the porphinato core, has the same relative orientation as Figure 1. This figure displays the perpendicular displacement of each atom, in units of 0.01 Å, from the mean plane of the 24-atom core. Examination of Figure 2 shows that the displacement of the atoms in the core conforms closely to D_{2d} symmetry. A similar quasi-D_{2d} ruffling of the porphinato core was observed in crystals of Fe(TPP)(1-MeIm)(NO).[2]

The averaged length of the four complexing bonds to porphinato nitrogen is 2.004 (10) Å. This bond length is consistent with a low-spin iron(II) porphyrin and compares well with the 2.004 (3) Å value observed in bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II).[14]

The axial FeNO group is nonlinear with Fe-N_5-O = 138.5 (11)°; the Fe-N_5 bond length is 1.721 (10) Å. These parameters are comparable to values found in other nitrosyl iron porphyrins (vide infra). The iron atom is displaced by 0.09 Å

Table VII. Anisotropic Thermal Parameters (Unsolvated Form)[a]

Atom type	Anisotropic parameters,[b] Å^2					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	2.21 (5)	4.09 (6)	2.82 (5)	−0.35 (4)	−0.02 (4)	0.10 (5)
O	4.5 (4)	8.0 (5)	11.9 (6)	1.4 (4)	1.5 (4)	−4.3 (4)
N_5	2.8 (3)	4.2 (4)	4.2 (4)	0.1 (3)	0.9 (3)	−0.8 (3)
N_6	5.1 (4)	3.8 (4)	2.8 (4)	0.2 (3)	0.4 (3)	−0.3 (3)
C_1	7.4 (7)	4.3 (6)	5.0 (6)	1.0 (5)	2.1 (5)	−0.5 (5)
C_2	5.5 (6)	7.9 (7)	4.0 (5)	0.6 (5)	0.3 (5)	−1.8 (5)
C_3	4.7 (5)	6.0 (6)	5.7 (6)	0.1 (5)	0.6 (5)	−0.1 (5)
C_4	7.5 (7)	5.9 (7)	5.7 (6)	1.3 (5)	0.7 (5)	−0.6 (5)
C_5	6.7 (7)	4.9 (6)	4.7 (6)	1.3 (5)	−0.9 (5)	−0.6 (5)
C_6	7.9 (7)	3.9 (6)	9.5 (8)	1.9 (5)	1.0 (6)	−4.0 (6)

[a] Figures in parentheses are the estimated standard deviations. [b] B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$.

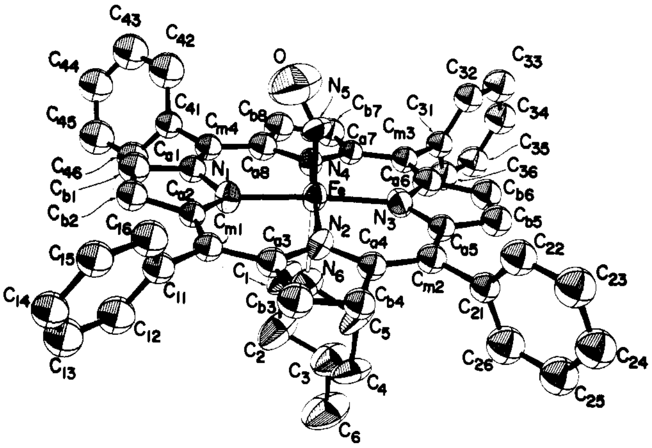

Figure 1. Computer-drawn model, in perspective, of the Fe(TPP)(4-MePip)(NO)·CHCl$_3$ molecule. The labeling scheme used for the atoms of the molecule is shown.

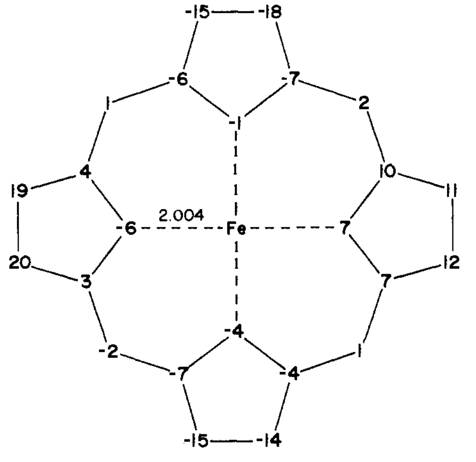

Figure 2. A formal diagram of the porphinato core in the Fe(TPP)(4-MePip)(NO)·CHCl$_3$ molecule with the same relative orientation as in Figure 1. The perpendicular displacement of each atom, in units of 0.01 Å, from the mean plane of the porphinato core is displayed.

out of the plane defined by the four porphinato nitrogen atoms and by 0.08 Å from the 24-atom mean plane. Both displacements are toward the axial NO ligand. The small displacements appear to relieve intramolecular contacts of the $N_5 \cdots N_p$ type. In contrast to the earlier derivatives studied,[1,2] the coordinated nitric oxide has only one orientation. The axial Fe-N-O group makes a dihedral angle of 38.6° with the axial plane defined by N_4, Fe, and N_5. As we have noted previously,[2,15] a value of 45° for this angle minimizes steric interactions of the $O \cdots N_p$ type. This ideal value for the orientation of the NO ligand is approached in the fourfold disordered Fe(TPP)(NO)[1] and Co(TPP)(NO)[15] derivatives. However, a single orientation of the NO ligand can arise only from intermolecular packing constraints.

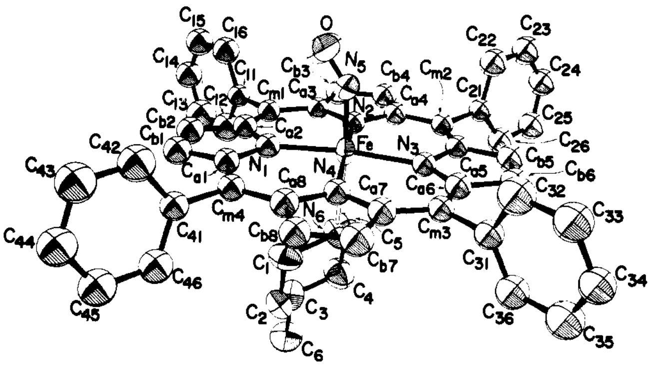

Figure 3. A computer-drawn model of the Fe(TPP)(4-MePip)(NO) molecule. The scheme used to identify the atoms is shown.

The complexing bond to the 4-methylpiperidine ligand is 2.328 (10) Å, considerably longer than the corresponding bond distance in Fe(TPP)(1-MeIm)(NO).[2] This long complexing bond distance, which will be considered further, does not appear to be attributable to steric interactions between atoms of the ligand and atoms of the porphinato core. The bond angle between the two trans ligands, N_5-Fe-N_6, is 176.7 (5)°. The dihedral angle between the plane defined by Fe, N_6, and the N_6 proton and the Fe, N_5, O plane is ~84°.

An examination of intermolecular packing contacts reveals that two atoms of the Fe(TPP)(NO)·CHCl$_3$ molecule are involved in most of the short contacts. The oxygen atom of the NO ligand has four contacts with phenyl carbon atoms of neighboring molecules of ~3.3 Å. The methyl group of the 4-methylpiperidine ligand is close (distances ≥3.4 Å) to several atoms of a pyrrole ring of the molecule translated along the *z* axis. Other intermolecular contacts range from 3.5 Å upwards; most are ≥3.8 Å.

Fe(TPP)(4-MePip)(NO. Figure 3 is a computer-drawn model of this molecule. The figure also displays the special symbols which are assigned to each atom of the molecule. Listings of the individually determined bond distances and angles of this molecule are given in Tables VIII and IX, respectively. Averaged values for the distinct bond lengths and angles are given in Table X. Figure 4 displays the perpendicular displacements of each atom from the mean plane of the porphinato core. It is seen that the core in this derivative is more nearly planar than the previously described complex. The differences in the core conformations probably reflect the differences in the crystalline environment of the two species.

The averaged iron-porphinato nitrogen bond length is 1.999

Table VIII. Bond Lengths in the Coordination Group, Porphinato Skeleton, 4-Methylpiperidine, and NO Ligand[a]

Type	Length, Å	Type	Length, Å
Fe-N_1	2.005 (8)	C_{m4}-C_{a8}	1.420 (16)
	1.989 (6)		1.387 (11)
Fe-N_2	2.010 (9)	C_{m4}-C_{a1}	1.351 (15)
	1.994 (6)		1.376 (12)
Fe-N_3	2.012 (9)	C_{m4}-C_{41}	1.468
	2.013 (6)		1.507 (11)
Fe-N_4	1.991 (8)	C_{a1}-C_{b1}	1.447 (16)
	1.998 (7)		1.430 (12)
Fe-N_5	1.721 (10)	C_{a2}-C_{b2}	1.446 (16)
	1.740 (7)		1.456 (12)
Fe-N_6	2.328 (10)	C_{a3}-C_{b3}	1.441 (15)
	2.463 (7)		1.419 (12)
N_1-C_{a1}	1.399 (14)	C_{a4}-C_{b4}	1.461 (14)
	1.372 (10)		1.428 (12)
N_1-C_{a2}	1.364 (13)	C_{a5}-C_{b5}	1.423 (15)
	1.385 (10)		1.445 (12)
N_2-C_{a3}	1.375 (13)	C_{a6}-C_{b6}	1.453 (16)
	1.383 (10)		1.442 (11)
N_2-C_{a4}	1.346 (12)	C_{a7}-C_{b7}	1.417 (15)
	1.387 (10)		1.450 (12)
N_3-C_{a5}	1.370 (13)	C_{a8}-C_{b8}	1.491 (17)
	1.390 (10)		1.428 (12)
N_3-C_{a6}	1.396 (14)	C_{b1}-C_{b2}	1.374 (16)
	1.395 (10)		1.337 (13)
N_4-C_{a7}	1.344 (12)	C_{b3}-C_{b4}	1.329 (15)
	1.389 (10)		1.366 (12)
N_4-C_{a8}	1.406 (14)	C_{b5}-C_{b6}	1.330 (15)
	1.392 (10)		1.325 (12)
C_{m1}-C_{a2}	1.371 (14)	C_{b7}-C_{b8}	1.339 (16)
	1.366 (11)		1.324 (12)
C_{m1}-C_{a3}	1.431 (15)	N_5-O	1.141 (13)
	1.392 (11)		1.112 (9)
C_{m1}-C_{11}	1.469	N_6-C_1	1.501 (15)
	1.500 (11)		1.449 (11)
C_{m2}-C_{a4}	1.420 (14)	N_6-C_5	1.455 (15)
	1.390 (11)		1.459 (12)
C_{m2}-C_{a5}	1.394 (15)	C_1-C_2	1.496 (20)
	1.359 (12)		1.544 (14)
C_{m2}-C_{21}	1.463	C_2-C_3	1.533 (20)
	1.501 (11)		1.524 (15)
C_{m3}-C_{a6}	1.354 (15)	C_3-C_4	1.530 (19)
	1.362 (11)		1.497 (14)
C_{m3}-C_{a7}	1.372 (14)	C_3-C_6	1.558 (22)
	1.394 (11)		1.533 (14)
C_{m3}-C_{31}	1.475	C_4-C_5	1.558 (19)
	1.502 (11)		1.537 (15)

[a] For each bond type, the first line gives the value for the solvated crystalline form, the second line gives the value for the unsolvated crystalline form. Figures in parentheses are the estimated standard deviations. Atoms are identified in agreement with figures.

(10) Å. The axial FeNO group is typically nonlinear with the Fe-N_5-O angle equal to 143.7 (6)°. The Fe-N_5 bond length is 1.740 (7) Å. The iron atom is displaced, toward the NO ligand, 0.11 Å from the plane defined by the four porphinato nitrogen atoms and 0.09 Å from the mean plane of the porphinato core.

The dihedral angle between the Fe-N_5-O group and the axial plane defined by N_1, Fe, and N_5 is 19.6°. This single orientation of the nitrosyl ligand is quite different from the orientation found for the other crystalline form of the complex; the orientation of the ligand in both complexes appears to be governed by intermolecular packing considerations. In Fe(TPP)(1-MeIm)(NO),[2] two orientations of the ligand with dihedral angles of 45 and 11° were found; a value of 40.6° was observed in Fe(TPP)(NO).[1] Calculations of Hoffmann et al.[16] suggest that the barrier to rotation of the nitrosyl ligand around the M-N_{NO} bond is quite low; the results for the nitrosyl iron porphyrin derivatives are quite consistent with this.

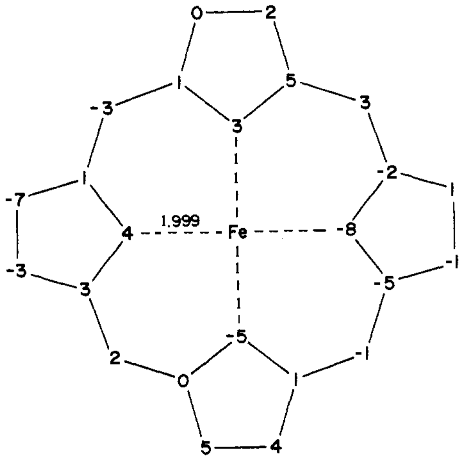

Figure 4. A formal diagram of the porphinato core in the Fe(TPP)(4-MePip)(NO) molecule. The core in the diagram has the same relative orientation as that in Figure 3. Perpendicular displacements of each atom, in units of 0.01 Å, from the mean plane of the 24-atom core are illustrated.

The bond length to the axial 4-methylpiperidine ligand is 2.463 (7) Å; this distance is longer than the corresponding distances in the other iron derivatives. The bond angle between the two axial ligands is 175.0 (3)°. The angle between the plane defined by Fe, N_6, and the N_6 proton and the Fe, N_5, O plane is ~16°.

The Fe(TPP)(4-MePip)(NO) molecules are well separated in the crystal and intermolecular packing distances are, in general, larger in this crystalline form than in Fe(TPP)(4-MePip)(NO)·$CHCl_3$.

Comparison and Summary of the Two Structures. Table XI provides a summary of the coordination group geometry of the four nitrosyl iron porphyrin derivatives of known structure. We note first the parameters involving the coordinated NO ligand. All complexes contain a strongly bent Fe-N-O group. Within the accuracy of the results, only the FeNO angle in the five-coordinate complex can be regarded as possibly differing from the other derivatives. The Fe-N(NO) bond lengths are also quite similar; the bond length in the five-coordinate complex is possibly slightly shorter than in the six-coordinate derivatives. Thus there appears to be some effect on the FeNO geometry on adding a sixth ligand, but changes in the sixth ligand do not lead to further changes in the geometry of the FeNO moiety. The iron-porphinato nitrogen bond lengths (average for the four derivatives 2.003 Å) are similar to those observed in two low-spin iron(II) porphyrin derivatives, 2.004 Å for Fe(TPP)$(Pip)_2$[14] and 1.997 Å for Fe(TPP)$(1\text{-MeIm})_2$.[18]

The displacement of the iron atom out of plane and the length of the Fe-N_b bond trans to the NO ligand are seen to be parameters of the coordination group that do change significantly. The Fe-N_b bond distances show remarkable variation from 2.180 to 2.463 Å, a difference of almost 0.3 Å. Observe that the Fe-N_b distances in the nitrosyl derivatives are considerably longer than the corresponding iron-ligand distances found in the six-coordinate iron(II) porphyrin complexes. Thus the Fe-N(1-MeIm) bond distance in Fe(TPP)(1-MeIm)(NO) is 0.17 Å longer than the corresponding distance in Fe(TPP)$(1\text{-MeIm})_2$[18] and the Fe-N(4-MePip) bond distances in the NO derivatives are respectively 0.20 and 0.33 Å longer than the Fe-N distance observed in Fe(TPP)$(Pip)_2$.[14] The Fe-N_b distance of 2.014 (4) Å[18] in Fe(TPP)$(1\text{-MeIm})_2$ is regarded as a normal axial Fe^{II}-N bond distance while the 2.127-Å value in Fe(TPP)-

Table IX. Bond Angles in the Coordination Group, Porphinato Skeleton, 4-Methylpiperidine, and NO Ligand[a]

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N_1FeN_2	89.8 (4) 90.6 (3)	$C_{m2}C_{a4}C_{b4}$	121.5 (10) 124.3 (7)	$C_{a2}C_{m1}C_{a3}$	122.0 (10) 125.2 (7)	$C_5N_6C_1$	112.5 (10) 110.0 (7)
N_1FeN_3	175.9 (5) 173.6 (3)	$N_3C_{a5}C_{m2}$	125.5 (10) 126.3 (7)	$C_{a4}C_{m2}C_{21}$	118.2 117.1 (7)	$N_6C_1C_2$	111.7 (12) 114.0 (8)
N_1FeN_4	91.3 (4) 90.0 (3)	$N_3C_{a5}C_{b5}$	110.0 (10) 108.1 (7)	$C_{a5}C_{m2}C_{21}$	118.9 117.5 (7)	$C_1C_2C_3$	111.7 (13) 113.9 (8)
N_1FeN_5	89.3 (4) 89.5 (3)	$C_{m2}C_{a5}C_{b5}$	124.5 (10) 125.6 (7)	$C_{a4}C_{m2}C_{a5}$	122.9 (10) 125.4 (7)	$C_2C_3C_4$	107.1 (13) 105.7 (8)
N_1FeN_6	87.5 (4) 85.5 (3)	$N_3C_{a6}C_{m3}$	128.0 (11) 126.0 (7)	$C_{a6}C_{m3}C_{31}$	118.3 118.6 (7)	$C_2C_3C_6$	113.8 (15) 115.9 (9)
N_2FeN_3	89.3 (4) 89.4 (3)	$N_3C_{a6}C_{b6}$	106.5 (10) 109.0 (7)	$C_{a7}C_{m3}C_{31}$	118.8 116.8 (7)	$C_4C_3C_6$	109.7 (14) 114.1 (8)
N_2FeN_4	174.0 (5) 174.2 (3)	$C_{m3}C_{a6}C_{b6}$	125.4 (11) 125.0 (8)	$C_{a6}C_{m3}C_{a7}$	122.9 (10) 124.5 (7)	$C_3C_4C_5$	110.0 (12) 115.1 (8)
N_2FeN_5	94.4 (4) 91.7 (3)	$N_4C_{a7}C_{m3}$	126.4 (10) 125.2 (7)	$C_{a8}C_{m4}C_{41}$	116.9 116.9 (7)	$C_4C_5C_6$	112.9 (12) 114.6 (8)
N_2FeN_6	84.8 (4) 88.3 (3)	$N_4C_{a7}C_{b7}$	110.8 (10) 109.8 (7)	$C_{a1}C_{m4}C_{41}$	120.8 118.4 (7)	FeN_1C_{a1}	125.6 (7) 127.1 (5)
N_3FeN_4	89.2 (4) 89.4 (3)	$C_{m3}C_{a7}C_{b7}$	122.7 (10) 124.9 (8)	$C_{a8}C_{m4}C_{a1}$	122.3 (11) 124.6 (7)	FeN_1C_{a2}	126.2 (7) 126.2 (5)
N_3FeN_5	94.7 (4) 96.9 (3)	$N_4C_{a8}C_{m4}$	127.7 (11) 124.6 (7)	$N_1C_{a1}C_{m4}$	127.3 (11) 126.2 (7)	FeN_2C_{a3}	127.1 (7) 127.3 (5)
N_3FeN_6	88.5 (4) 88.1 (2)	$N_4C_{a8}C_{b8}$	107.4 (10) 109.3 (7)	$N_1C_{a1}C_{b1}$	109.0 (10) 109.4 (7)	FeN_2C_{a4}	127.5 (7) 128.4 (5)
N_4FeN_5	91.6 (5) 94.1 (3)	$C_{m4}C_{a8}C_{b8}$	124.9 (11) 126.1 (7)	$C_{m4}C_{a1}C_{b1}$	123.6 (11) 124.3 (7)	FeN_3C_{a5}	128.0 (7) 126.1 (5)
N_4FeN_6	89.3 (4) 86.0 (3)	$C_{b2}C_{b1}C_{a1}$	107.1 (12) 108.4 (8)	$N_1C_{a2}C_{m1}$	128.0 (10) 126.2 (7)	FeN_3C_{a6}	124.8 (7) 126.6 (5)
N_5FeN_6	176.7 (5) 175.0 (3)	$C_{b1}C_{b2}C_{a2}$	106.7 (11) 106.9 (8)	$N_1C_{a2}C_{b2}$	110.4 (10) 108.5 (7)	FeN_4C_{a7}	128.5 (7) 127.2 (5)
$C_{a1}N_1C_{a2}$	106.7 (8) 106.7 (6)	$C_{b4}C_{b3}C_{a3}$	108.6 (11) 108.2 (8)	$C_{m1}C_{a2}C_{b2}$	121.6 (10) 125.1 (8)	FeN_4C_{a8}	124.6 (8) 127.0 (5)
$C_{a3}N_2C_{a4}$	105.2 (8) 104.3 (6)	$C_{b3}C_{b4}C_{a4}$	104.8 (10) 105.3 (7)	$N_2C_{a3}C_{m1}$	125.7 (10) 124.3 (7)	FeN_5O	138.5 (11) 143.7 (6)
$C_{a5}N_3C_{a6}$	107.2 (8) 106.4 (6)	$C_{b6}C_{b5}C_{a5}$	107.1 (12) 109.1 (7)	$N_2C_{a3}C_{b3}$	109.5 (10) 110.5 (7)	FeN_6C_1	113.6 (8) 112.5 (5)
$C_{a7}N_4C_{a8}$	106.9 (8) 105.1 (6)	$C_{b5}C_{b6}C_{a6}$	109.2 (12) 107.4 (8)	$C_{m1}C_{a3}C_{b3}$	124.8 (10) 125.2 (7)	FeN_6C_5	113.3 (9) 113.1 (6)
$C_{a2}C_{m1}C_{11}$	120.3 116.3 (7)	$C_{b8}C_{b7}C_{a7}$	109.2 (12) 106.6 (8)	$N_2C_{a4}C_{m2}$	126.7 (10) 123.9 (7)		
$C_{a3}C_{m1}C_{11}$	117.6 118.4 (7)	$C_{b7}C_{b8}C_{a8}$	105.7 (12) 109.2 (8)	$N_2C_{a4}C_{b4}$	111.8 (9) 111.7 (7)		

[a] For each angle type, the first line gives the value for the solvated crystalline form, the second that for the unsolvated crystalline form. The figures in parentheses are the estimated standard deviations. Atoms are identified in agreement with the figures.

Table X. Average Values for Selected Molecular Parameters of the Porphinato Core[a]

Type	Fe(TPP)(4-MePip)(NO)·$CHCl_3$	Fe(TPP)(4-MePip)(NO)
	A. Bond Lengths, Å	
Fe-N	2.004 (10)	1.999 (10)
$N-C_a$	1.38 (2)	1.39 (1)
C_m-C_a	1.39 (3)	1.38 (1)
C_a-C_b	1.45 (2)	1.44 (1)
C_b-C_b	1.34 (2)	1.34 (2)
	B. Bond Angles, deg	
C_aNC_a	106.5 (9)	105.6 (11)
NC_aC_b	109.4 (18)	109.5 (11)
NC_aC_m	126.9 (10)	125.3 (10)
$C_aC_mC_a$	122.5 (5)	124.9 (4)
$C_aC_bC_b$	107.3 (16)	107.6 (13)

[a] The numbers in parentheses are the estimated standard deviations, calculated on the assumption that the individual values are drawn from the same population.

$(Pip)_2$[14] is longer owing to the difficult steric interactions between the axial ligand atoms and atoms of the porphinato core. Similar steric interaction in the Fe(TPP)(4-MePip)(NO) derivatives might explain part of the observed difference in the Fe-N_b distance relative to Fe(TPP)(1-MeIm)(NO); however, the observed Mn-N_b distance of 2.206 (5) Å in Mn(TPP)(4-MePip)(NO)[17] does indicate how short this bond can be in the NO derivatives. Relative to a 2.01-Å value for a normal Fe^{II}-N bond, the Fe-N_b bonds in these three NO complexes are elongated by 0.17, 0.32, and 0.45 Å.

It had previously been noted[2] that the long Fe-N_b bond in Fe(TPP)(1-MeIm)(NO) was the consequence of the partial donation of the unpaired electron of NO to the d_{z^2} orbital of the iron,[19] which is an antibonding orbital with respect to the axial Fe-N_b bond and that similar structural trans effects from NO are also observed in some nitrosyl cobalt complexes.[21] These bonding considerations suggested[2] that the Fe-N_b bonds in these $\{FeNO\}^7$ complexes might be easily stretched. The results reported herein support this suggestion of an easily stretched axial bond.

The different Fe-N(4-MePip) bond lengths in the two forms of Fe(TPP)(4-MePip)(NO) appear to be real properties of

Table XI. Coordination Group Geometry for Several Nitrosylmetalloporphyrins[a]

	Distances, Å				Angles, deg		ν(NO),	
Metalloporphyrin	M-N$_p$	M-N(NO)	M···Ct[b]	M-N$_b$[c]	MNO	N$_b$MN(NO)	cm^{-1}	Ref
Fe(TPP)(1-MeIm)(NO)	2.008 (12)	1.743 (4)	0.07	2.180 (4)	142.1 (6) 138.3 (11)	176.3 (2)	1625	2
Fe(TPP)(4-MePip)-(NO)·CHCl$_3$	2.004 (10)	1.721 (10)	0.09	2.328 (10)	138.5 (11)	176.7 (5)	1640	This work
Fe(TPP)(4-MePip)(NO)	1.999 (10)	1.740 (7)	0.11	2.463 (7)	143.7 (6)	175.0 (3)	1653-1656	This work
Fe(TPP)(NO)	2.001 (3)	1.717 (7)	0.211		149.2 (6)		1670	1
Mn(TPP)(4-MePip)(NO)	2.027 (4)	1.644 (5)	0.10	2.206 (5)	176.2 (5)	177.2 (2)	1740	17

[a] Numbers in parentheses are the estimated standard deviations. [b] All metal atom displacements are toward the axial NO ligand. [c] N$_b$ is the coordinated nitrogen atom of the sixth axial ligand.

these crystalline complexes. The NO stretching frequencies appear to be sensitive to the changing Fe-N$_b$ bond distance. Figure 5 displays the correlation of ν(NO) with the value of the Fe-N$_b$ distance; the straight line relationship is remarkable. The straight line correlation of Figure 5 may in fact be accidental; additional points would be useful to confirm whether this exact relationship holds. Nonetheless, the general conclusion that an increasing ν(NO) correlates with an increased Fe-N$_b$ bond distance in the nitrosyl iron porphyrins appears sound.

An obvious and interesting question is which, if either, of the two crystalline forms of Fe(TPP)(4-MePip)(NO) represents the stereochemistry of the unconstrained complex. An unambiguous answer is not possible. However, the following, somewhat contradictory, observations can be offered. An analysis of the crystal packing suggests that packing effects in Fe(TPP)(4-MePip)(NO)·CHCl$_3$ might serve to shorten the Fe-N$_b$ bond. No such packing effects are apparent in Fe(TPP)(4-MePip)(NO). On the other hand, if it is assumed that the relationship displayed in Figure 5 is general, a solution measurement of the NO stretching frequency in Fe(TPP)-(4-MePip)(NO) is meaningful. The infrared spectrum of Fe(TPP)(NO), measured in pure 4-methylpiperidine, displays two rather broad bands. The first band occurs at 1670 cm^{-1} and is assumed to be due to the five-coordinate complex. The second band is centered at 1637 cm^{-1}; thus the infrared data suggest that crystalline Fe(TPP)(4-MePip)(NO)·CHCl$_3$ best represents the unconstrained species. The Fe(TPP)(4-MePip)(NO) crystalline complex must then be regarded as having an Fe-N$_b$ bond that is weaker and longer than the unconstrained species! A description which suggests how this is possible is to note that 4-methylpiperidine is acting partly as a ligand and partly as a simple molecule of crystallization trapped in the lattice. Indeed, the 4-methylpiperidine molecule is apparently easily lost from crystals of Fe(TPP)(4-MePip)-(NO). The infrared spectrum, in KBr pellets, is unusually sensitive to the procedures used to prepare the pellet; ordinary processing gives two bands in the NO stretching region at 1670 and 1653-1656 cm^{-1}. Prolonged grinding times ($\geq$2 min) yield a diminished 1655-cm^{-1} peak and an increased 1670-cm^{-1} peak; short ($\leq$15 s) grinding times give converse results. Further, our synthetic experiences with these nitrosyl complexes has led us to conclude that lattice stabilization effects are an important factor in permitting isolation of the six-coordinate complexes rather than the five-coordinate species.

The out-of-plane displacement of the iron atom increases with its decreasing interaction with the trans ligand to a final value of 0.21 Å for the five-coordinate complex where, of course, there is no interaction with a trans ligand. As has been noted above, displacements of the iron atom serve to diminish nonbonded contacts of the N···N(NO) type; the observed order of the displacements is wholly consistent with this.

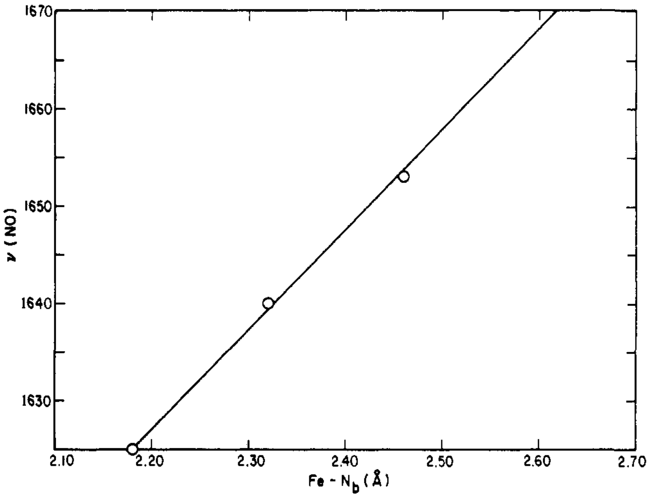

Figure 5. A diagram showing the correlation between the observed NO stretching frequency and the Fe-N$_b$ bond distance in the three six-coordinate nitrosyl iron porphyrins.

The action of inositol hexaphosphate (IHP) in switching the equilibrium of the quaternary structure of hemoglobin A from the oxy form to the deoxy form is unique to nitrosylhemoglobin.[4-6,22] The behavior of nitrosylhemoglobin in the presence of IHP is clearly anomalous compared to the behavior of other low-spin compounds of hemoglobin. The ultimate result of the action of IHP does appear to be the rupture of two iron-proximal histidine bonds;[5b] however, this process must surely be assisted by the weak and easily stretched nature of the Fe-N$_b$ bonds in the prosthetic group.

Acknowledgments. We thank the National Institutes of Health (HL-15627) for support and the Computing Center of the University of Notre Dame for an allocation of computing time. We also thank Professor J. Enemark for a helpful discussion.

Supplementary Material Available: Tables III and IV, the anisotropic thermal parameters and rigid body parameters for Fe(TPP)-(4-MePip)(NO)·CHCl$_3$ and listings of the structure factor amplitudes (×10) for both complexes (32 pages). Ordering information is given on any current masthead page.

References and Notes

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Stereoelectronic Properties of Metalloenzymes. 5. Identification and Assignment of Ligand Hyperfine Splittings in the Electron Spin Resonance Spectrum of Galactose Oxidase

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Abstract: Time-averaged electron spin resonance spectra for native galactose oxidase suggested two nitrogen-liganded atoms based on the partial resolution of superhyperfine structure in the parallel region of the spectrum. Electron spin resonance data obtained for ^{63}Cu-galactose oxidase as well as the ^{19}F$^-$-enzyme complex and imidazole-enzyme complex indicate that not only are there two nitrogen atoms present in the native protein but that these arise from liganded imidazole (histidine) nitrogen atoms. Interpretation of these spectra is dependent on the observation of superhyperfine structure in the parallel, perpendicular, and "overshoot" regions of all the spectra. A detailed discussion and an explanation for the interpretations are presented.

Galactose oxidase, a single chain copper protein, is unique because it contains a single non- or low-blue copper(II) atom.[1-4] Thus, its spectral properties exemplify those characteristic of type II copper(II) atoms[5] without interference by other prosthetic groups. As such, it offers an opportunity to gain information concerning the structure of the large class of type II sites in multi-nuclear copper proteins, especially those where detailed spectroscopic studies are made difficult by the type I or "blue" copper(II) atom(s) present.[5]

The characterization of the copper(II) coordination site in a complex ion or protein, in principle, can be achieved in large measure by the determination of the spin Hamiltonian parameters of the system. For example, for a copper(II) containing protein, the magnitudes of the principal g value and metal hyperfine coupling together have been correlated with the charge and chemical nature of the ligand atoms.[5,6] Furthermore, the overall symmetry can be suggested by the degree of anisotropy in the three g values and the exact number and chemical nature of some ligand atoms can be deduced from ligand superhyperfine structure.[5]

Blumberg et al.[1] first reported the electron spin resonance (ESR) spectrum of galactose oxidase. More recently, our laboratories[4,7] and others[8] have examined in detail this spectrum and its response to exogenous ligands.[7,9] However, to date, no hyperfine splittings due to ligand atoms have been assigned unambiguously nor has the complex "perpendicular" region of the spectrum been adequately interpreted. In this report, such assignments are made and a reasonable model for the metal coordination site in the protein is suggested.

Experimental Section

Galactose oxidase was purified from shake flask cultures of *Dactylium dendroides* as previously reported.[2] ^{63}Cu-enzyme was obtained by growing fungus in media depleted of all trace metals by passage over columns of Chelex-100 (Bio-Rad) followed by metal supplementation using reagent grade metal salts and with ^{63}CuO (Oak Ridge) as the copper source. The metal content of the medium was monitored by graphite furnace atomic absorption (Perkin-Elmer Model 360); endogenous copper was reduced to less than 10^{-9} M prior to addition of ^{63}Cu(II). The alternative method of preparing ^{63}Cu-galactose oxidase from the apoenzyme is by nature a destructive process. Preparation by growth of the isotopically pure enzyme routinely gave more well-resolved ESR spectra and was the method employed here.

Enzyme samples for spectral studies were prepared in 0.1 M sodium phosphate buffer (pH 7.0), with an enzyme concentration of ~0.5 mM. Ligand solutions were prepared in the same buffer. Imidazole was a Sigma product, twice recrystallized from benzene after initial treatment with Norite. KF was zone-refined and kindly supported by Bell Laboratories, Murray Hill, N.J. All other chemicals were reagent grade. Spectral titrations were carried out as previously described.[7] All enzyme samples regained full activity and spectral characteristics after F$^-$ or imidazole was removed by dialysis. Thus, F$^-$ and imidazole binding was completely reversible as previously seen with other anions and neutral molecules.

Electron spin resonance spectra were obtained with a Varian E-9 spectrometer operating near either 9 GHz (X-band) or 35 GHz (Q-band) microwave frequencies at 100 K. X-band spectra were calibrated employing diphenylpicrylhydrazyl (DPPH) as an internal

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