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Nitrosylmetalloporphyrins. III. Synthesis and Molecular Stereochemistry of Nitrosyl-α,β,γ,δ-tetraphenylporphinato(1-methylimidazole)iron(II)[1,2]

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Abstract: The preparation and molecular structure of nitrosyl-α,β,γ,δ-tetraphenylporphinato(1-methylimidazole)iron(II) are described. The title compound crystallizes, as the chloroform solvate, in the orthorhombic space group $P2_12_12_1$ with a = 17.733 (13), b = 25.339 (22), and c = 9.752 (10) Å. Calculated and experimental densities are 1.35 and 1.36 g/cm^3, respectively, at 20 °C. Measurement of diffracted intensities employed ω scanning with Mo Kα radiation on a four-circle diffractometer; the 4148 reflections retained as observed were used for the determination and refinement of structure. Final discrepancy indices are $R_1 = 0.052$ and $R_2 = 0.074$. Equatorial bond distances in the FeN_6 coordination group average to 2.008 Å; Fe–N$_{NO}$ is 1.743 (4) Å. The Fe–N–O bond angle is ~140°. The Fe–N$_{Im}$ bond trans to the nitric oxide is quite long at 2.180 (4) Å. The importance of these results in understanding some properties of nitrosylhemoglobin is discussed.

Complexes of metalloporphyrins with diatomic molecules have been intensively investigated, primarily as model heme protein systems.[3-6] We have been investigating the reactions and stereochemistry of nitrosylmetalloporphyrins and report herein the preparation and molecular stereochemistry of nitrosyl-α,β,γ,δ-tetraphenylporphinato(1-methylimidazole)iron(II), to be written as Fe(TPP)(NO)(1-MeIm). With nitric oxide and 1-methylimidazole as the axial ligands, Fe(TPP)(NO)(1-MeIm) is a particularly cogent model system for the coordination group geometry of nitrosyl heme protein derivatives. We compare the stereochemistry and spectral properties of Fe(TPP)(NO)(1-MeIm) with the closely related five-coordinate derivative nitrosyl-α,β,γ,δ-tetraphenylporphinatoiron(II).[1] The results are discussed in terms of some observations recently made on nitrosylhemoglobin.

Experimental Section

Preparation and Characterization of ON(1-MeIm)FeTPP. All reactions were carried out under argon using Schlenk glassware. ClFeTPP was prepared as previously described.[7] A solution of 0.20 g of ClFeTPP in 50 ml of dry chloroform and 8 ml of 1-methylimidazole was carefully degassed. Nitric oxide, purified by passing through a KOH column, was bubbled into the solution for 15–20 min. Excess NO was then removed by bubbling argon through the solution and dry methanol slowly added until crystals of Fe(TPP)(NO)(1-MeIm) appeared. Filtration, under argon, yielded the crystalline complex. These bulk preparations were frequently contaminated with varying amounts of the five-coordinate complex ONFeTPP, as judged from ir spectra. Pure six-coordinate complexes could always be prepared by very slow crystallizations as described below.

The infrared spectrum of Fe(TPP)(NO)(1-MeIm) was recorded on a Perkin-Elmer 457 spectrometer using a KBr pellet; the strong absorption at 1625 cm^{-1} was assigned as the NO stretching frequency. The absorption spectrum of Fe(TPP)(NO)(1-MeIm) shows peaks at 4150, 4600, 5450, 5800 (shoulder), and 6425 Å with extinction coefficients of 181 × 10^3, 18.1 × 10^3, 9.72 × 10^3 6.0 × 10^3, and 1.12 × 10^3 M^{-1} cm^{-1}, respectively. The magnetic susceptibility is 2.2–2.3 μ_B. Anal. ($FeC_{48}H_{34}N_7O \cdot CHCl_3$) calcd, C, 65.38; H, 3.92; N, 10.89; Fe, 6.2. ($FeC_{48}H_{34}N_7O \cdot \frac{1}{2}CHCl_3$) calcd, C, 69.31; H, 4.14; N, 11.67; Fe, 6.6; found, C, 67.04; H, 3.95; N, 11.53; Fe, 5.9.

Crystallographic and X-Ray Data. Crystals of Fe(TPP)(NO)(1-MeIm) suitable for x-ray study were grown by vapor diffusion of anhydrous methanol into a chloroform solution of the complex, prepared in situ, under an argon–nitric oxide atmosphere. Lattice constants, a = 17.733 (13) Å, b = 25.339 (22) Å, and c = 9.752 (10) Å (λ 0.71069) came from a least-squares refinement that utilized the setting angles of 30 reflections, each collected at ±2θ, at 20 ± 1°. The calculated density for a cell content of 4[$FeON_7C_{48}H_{34} \cdot CHCl_3$] is 1.35 g/cm^3; the experimental density is 1.36 g/cm^3.

X-ray intensity data were collected using graphite-monochromated Mo Kα radiation on a Syntex P$\bar{1}$ diffractometer. A freshly prepared crystal with approximate dimensions of 0.8 × 0.5 × 0.3 mm was mounted in a thin-walled glass capillary filled with argon. All independent reflections in the range $3 < 2\theta < 55°$ ($\sin\theta/\lambda < 0.65$ Å^{-1}) were measured by the ω-scan technique.[8] The ω scan was performed in 0.027° increments of ω and extended ±0.15° from the calculated peak position. When the observed peak position did not coincide with the calculated peak position, one or two additional steps were taken to assure centering of the scan. Background counts were taken at ±0.5° ω displacement from the peak center for a duration of one-half the time required for the scan. Four standard reflections that were well distributed in reciprocal space were used for periodic checking (every 50 reflections) on the alignment and possible deterioration of the crystal; only random variations in intensity were noted during the course of measurements. With a linear absorption coefficient of 0.56 mm^{-1} for Mo Kα radiation, the maximum error in any structure amplitude resulting from the neglect of absorption corrections was seen to be <3.5%. Consequently, intensity data were reduced and standard deviations calculated as described previously.[9] Data was retained as objectively observed if $F_o > 3\sigma(F_o)$; 4148 data were retained, some 81% of the total number possible in the range of 2θ examined.

The structure was solved by the usual heavy-atom method.[10] During the latter stages of structure development, it became apparent that the chloroform molecule of crystallization was disordered. The disorder appeared to be rotational disorder, and was approximated by assigning four positions for the three chlorine atoms. Subsequent unconstrained refinement of the occupancy factors for these atoms gave 2.82 for the sum, to be compared to the theoretical value of 3.00.

Table I. Atomic Coordinates in the Unit Cell[a]

Atom type	Coordinates $10^4 x$	$10^4 y$	$10^4 z$
Fe[b]	934 (0)	1676 (0)	2249 (1)
O_1	504 (5)	1516 (6)	4890 (8)
O_2	1183 (15)	1690 (8)	4987 (15)
N_1	975 (2)	900 (1)	1770 (4)
N_2	2067 (2)	1712 (1)	2186 (4)
N_3	896 (2)	2453 (1)	2632 (4)
N_4	−187 (2)	1653 (1)	2118 (4)
N_5	903 (3)	1543 (1)	4001 (4)
N_6	911 (2)	1877 (2)	75 (4)
N_7	1150 (3)	2235 (2)	−1940 (5)
C_{a_1}	378 (3)	561 (2)	1653 (5)
C_{a_2}	1615 (3)	597 (2)	1743 (5)
C_{a_3}	2559 (3)	1303 (2)	1975 (5)
C_{a_4}	2511 (3)	2153 (2)	2372 (5)
C_{a_5}	1495 (3)	2786 (2)	2885 (6)
C_{a_6}	265 (3)	2750 (2)	2846 (6)
C_{a_7}	−676 (2)	2076 (2)	2250 (6)
C_{a_8}	−629 (3)	1226 (2)	1833 (5)
C_{b_1}	646 (3)	27 (2)	1577 (6)
C_{b_2}	1407 (3)	41 (2)	1615 (6)
C_{b_3}	3318 (3)	1483 (2)	1990 (6)
C_{b_4}	3297 (3)	2007 (2)	2230 (6)
C_{b_5}	1222 (3)	3296 (2)	3272 (7)
C_{b_6}	463 (3)	3283 (2)	3261 (7)
C_{b_7}	−1437 (3)	1909 (2)	1993 (6)
C_{b_8}	−1412 (3)	1385 (2)	1721 (6)
C_{m_1}	2359 (3)	767 (2)	1803 (5)
C_{m_2}	2259 (3)	2654 (2)	2729 (6)
C_{m_3}	−480 (3)	2588 (2)	2621 (6)
C_{m_4}	−377 (3)	701 (2)	1642 (5)
C_1	326 (4)	1781 (3)	−838 (7)
C_2	470 (4)	1997 (4)	−2045 (7)
C_3	1379 (3)	2156 (2)	−659 (6)
C_4	1553 (5)	2538 (4)	−3036 (8)
C_5	2973 (3)	361 (2)	1723 (5)
C_6	3178 (3)	139 (2)	473 (6)
C_7	3708 (4)	−257 (3)	432 (7)
C_8	4040 (3)	−442 (2)	1621 (7)
C_9	3855 (3)	−210 (3)	2847 (7)
C_{10}	3311 (3)	190 (2)	2914 (6)
C_{11}	2825 (3)	3078 (2)	2938 (6)
C_{12}	3178 (3)	3148 (2)	4206 (7)
C_{13}	3708 (3)	3538 (3)	4411 (8)
C_{14}	3898 (3)	3862 (2)	3344 (8)
C_{15}	3543 (4)	3807 (2)	2092 (8)
C_{16}	3014 (3)	3409 (2)	1876 (6)
C_{17}	−1099 (2)	2984 (2)	2800 (6)
C_{18}	−1331 (3)	3143 (2)	4100 (6)
C_{19}	−1936 (4)	3501 (2)	4218 (7)
C_{20}	−2281 (3)	3703 (2)	3090 (7)
C_{21}	−2040 (4)	3558 (2)	1808 (7)
C_{22}	−1465 (4)	3196 (2)	1653 (6)
C_{23}	−966 (3)	289 (2)	1394 (6)
C_{24}	−1496 (3)	169 (2)	2368 (9)
C_{25}	−2057 (4)	−199 (3)	2121 (11)
C_{26}	−2093 (4)	−441 (2)	902 (11)
C_{27}	−1544 (4)	−343 (2)	−139 (9)
C_{28}	−977 (4)	26 (2)	148 (6)
C_{29}	726 (10)	3961 (6)	59 (14)
Cl_1	116 (3)	4369 (2)	10 (10)
Cl_2	1579 (3)	4241 (4)	−795 (7)
Cl_3	558 (5)	3396 (2)	−576 (8)
Cl_4	356 (7)	3911 (9)	7497 (31)

[a] Figures in parentheses are the estimated standard deviations.
[b] For Fe $10^5 x = 9,340$ (4), $10^5 y = 16,762$ (2), $10^5 z = 22,486$ (6).

After preliminary refinement by full matrix least squares,[11] a difference Fourier synthesis suggested that the coordinated nitrosyl ligand had a second orientation, related to the first by a rotation of ~124° around the Fe–N_{NO} bond. Accordingly, coordinates for two oxygen atoms were specified; the final refined values for the occupancy factors of the oxygen atoms, 0.67 (3) for O_1 and 0.32 (2) for O_2, suggest that these two orientations completely define the nitrosyl ligand. Further refinement was followed by difference Fourier syntheses which showed electron densities appropriately located for all hydrogen atom positions. Hydrogen atoms were then fixed at their theoretically calculated positions (C–H 1.0 Å) and included as fixed contributors ($B_H = B_C + 1.0$) in all subsequent refinement cycles. Final refinement utilized anisotropic temperature factors for all heavy atoms; this refinement was carried out in three blocks owing to computer storage limitations. The final value[12] of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.052, that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$ was 0.074; the estimated standard deviation of an observation of unit weight was 0.73. Further refinement, using coordinates of the mirror image of the enantiomorph previously assumed, led to $R_1 = 0.058$ and $R_2 = 0.084$. The first choice is clearly the correct one and its coordinates are reported herein. A final difference Fourier synthesis had no peak greater than 0.6 e/Å^3; most of the largest peaks were in the region of the disordered chloroform molecule.

The final atomic coordinates and the associated anisotropic thermal parameters for the asymmetric unit of structure are listed in Tables I and II, respectively. The numbering of atoms given in Figures 1 and 2 is maintained in all tables.

Results and Discussion

Figure 1 is a computer-drawn model,[13] in perspective, of the Fe(TPP)(NO)(1-MeIm) molecule as it exists in the crystal. Figure 2 illustrates the two distinct orientations of the nitrosyl ligand with respect to the porphinato core and the other axial ligand (1-MeIm). Displayed in Figure 1 are the special symbols assigned to the atoms of the axial ligands and the peripheral phenyl group atoms and in Figure 2 those assigned to the atoms of the porphinato core. Tables III and IV are listings of the bond lengths and bond angles, respectively, in the coordination group, porphinato skeleton, and axial ligands of the Fe(TPP)(NO)(1-MeIm) molecule.

Bond lengths and angles in the porphinato core conform rather well to a pattern of fourfold symmetry and we report averaged values of each chemical type. 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 lengths are N–C_a, 1.372 (6, 6); C_a–C_m, 1.399 (11, 7); C_a–C_b, 1.442 (11, 7); C_b–C_b, 1.350 (3, 8) Å, wherein the first figure in parentheses is the mean deviation (in units of 0.001 Å) from the average and the second is the estimated standard deviation for an independently determined distance. Averaged bond angles are C_aNC_a, 105.9 (4, 4); NC_aC_b, 110.1 (5, 4); NC_aC_m, 126.1 (4, 4); $C_aC_mC_a$, 123.2 (3, 4); and $C_aC_bC_b$, 106.9 (6, 4)°.

The averaged value for the internal angles in the peripheral phenyl rings is 120.0° and the averaged value for the 24 individually determined C–C bonds is 1.384 Å with a mean deviation from the average of 0.014 Å. Individual values of distances and angles are tabulated in Table V (microfilm edition).

The averaged length of the four complexing bonds to porphinato nitrogen is 2.008 (9, 4) 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)-*meso*-tetraphenylporphinatoiron(II).[14] The averaged distance is comparable to the 2.001 (3) Å Fe–N bond observed in five-coordinate ONFeTPP.[1] Other pertinent Fe–N bond distances to be compared are 1.989 (4) Å in low-spin bis(imidazole)-*meso*-tetraphenylporphinatoiron(III)[15] and 1.990 (5) Å in the bis(imidazole)iron(III) derivative of protoporphyrin-IX.[16] As expected, the Fe–N distance is substantially shorter than the 2.086 Å observed in high-spin (2-methylimidazole)-*meso*-tetraphenylporphinatoiron(II)[17] and the 2.07 Å appropriate for high-spin iron(III) porphyrins.[18]

The formal diagram of the porphyrin core in Figure 3, which has the same orientation as in Figure 2, displays the perpendicular displacement of each atom from the mean

Table II. Thermal Parameters for the Atoms in the Unit Cell[a]

Atom type	Anisotropic parameters,[b] Å²					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	3.23 (2)	3.21 (2)	3.44 (2)	0.02 (2)	0.07 (2)	−0.16 (2)
O_1	6.4 (6)	26.2 (17)	5.0 (4)	2.9 (7)	1.6 (4)	3.5 (6)
O_2	16.9 (31)	9.7 (12)	3.9 (7)	−3.3 (14)	−2.1 (10)	−2.8 (7)
N_1	3.6 (1)	3.3 (1)	4.0 (1)	0.2 (1)	−0.1 (2)	−0.2 (1)
N_2	3.5 (1)	3.6 (1)	3.9 (1)	−0.1 (1)	−0.3 (1)	−0.2 (2)
N_3	4.0 (1)	3.6 (1)	4.0 (1)	−0.2 (1)	−0.1 (2)	−0.3 (1)
N_4	3.5 (1)	3.5 (1)	3.9 (2)	0.0 (1)	0.0 (1)	−0.3 (2)
N_5	5.1 (2)	3.8 (2)	3.6 (2)	0.5 (2)	0.1 (2)	−0.2 (1)
N_6	4.0 (2)	4.2 (2)	4.0 (2)	−0.2 (2)	−0.1 (2)	−0.1 (1)
N_7	5.0 (2)	6.1 (2)	4.6 (2)	−0.4 (2)	−0.4 (2)	−0.0 (2)
C_{a1}	4.2 (2)	3.3 (2)	4.0 (2)	−0.0 (2)	0.4 (2)	−0.2 (2)
C_{a2}	3.4 (2)	4.0 (2)	3.7 (2)	0.7 (2)	−0.1 (2)	0.1 (2)
C_{a3}	3.7 (2)	3.8 (2)	4.0 (2)	0.2 (1)	−0.1 (2)	−0.3 (2)
C_{a4}	4.1 (2)	4.2 (2)	3.8 (2)	−0.3 (2)	−0.1 (2)	−0.1 (2)
C_{a5}	4.6 (2)	3.6 (2)	4.7 (2)	−0.4 (2)	−0.2 (2)	−0.3 (2)
C_{a6}	4.1 (2)	4.0 (2)	4.3 (2)	−0.1 (2)	−0.3 (2)	−0.8 (2)
C_{a7}	3.4 (2)	3.7 (2)	4.4 (2)	0.1 (1)	0.4 (2)	−0.3 (2)
C_{a8}	3.4 (2)	3.4 (2)	4.1 (2)	−0.4 (1)	0.2 (2)	−0.1 (2)
C_{b1}	4.5 (2)	3.3 (2)	5.2 (2)	0.0 (2)	0.2 (2)	−0.0 (2)
C_{b2}	4.2 (2)	3.7 (2)	4.6 (2)	0.1 (2)	0.1 (2)	0.3 (2)
C_{b3}	3.6 (2)	5.1 (2)	4.7 (3)	0.1 (2)	0.0 (2)	−0.1 (2)
C_{b4}	3.9 (2)	5.0 (2)	4.9 (2)	−0.4 (2)	−0.4 (2)	−0.3 (2)
C_{b5}	4.6 (2)	3.9 (2)	6.6 (3)	−0.6 (2)	−0.2 (2)	−1.0 (2)
C_{b6}	4.4 (2)	3.9 (2)	7.3 (3)	0.2 (2)	0.4 (2)	−1.0 (2)
C_{b7}	3.6 (2)	4.1 (2)	6.0 (3)	0.2 (2)	−0.2 (2)	−0.6 (2)
C_{b8}	3.6 (2)	4.1 (2)	5.6 (3)	−0.3 (2)	−0.4 (2)	−0.0 (2)
C_{m1}	3.5 (2)	3.9 (2)	3.8 (2)	0.4 (1)	−0.1 (2)	−0.1 (2)
C_{m2}	3.9 (2)	3.8 (2)	4.2 (2)	−0.5 (2)	−0.6 (2)	−0.1 (2)
C_{m3}	4.2 (2)	3.5 (2)	4.4 (2)	0.6 (1)	0.0 (2)	−0.4 (2)
C_{m4}	3.8 (2)	3.6 (2)	4.3 (2)	−0.2 (2)	0.1 (2)	0.0 (2)
C_1	5.7 (3)	9.0 (4)	4.9 (3)	−3.0 (3)	−0.5 (2)	0.4 (3)
C_2	6.7 (4)	10.8 (5)	4.6 (3)	−2.6 (4)	−1.5 (3)	0.6 (3)
C_3	4.4 (2)	5.9 (3)	5.0 (2)	−0.9 (2)	0.1 (2)	1.0 (2)
C_4	8.0 (4)	10.0 (5)	5.5 (4)	−2.3 (4)	0.5 (3)	2.3 (4)
C_5	3.5 (2)	4.4 (2)	4.1 (2)	0.3 (2)	−0.1 (2)	−0.2 (2)
C_6	5.0 (2)	5.1 (2)	5.1 (2)	0.8 (2)	0.4 (2)	−0.1 (2)
C_7	5.3 (3)	6.0 (3)	5.6 (3)	1.1 (2)	0.9 (2)	−0.5 (2)
C_8	4.2 (2)	6.3 (3)	7.0 (3)	1.0 (2)	−0.2 (3)	−0.5 (3)
C_9	4.7 (2)	6.5 (3)	6.0 (3)	1.4 (2)	−1.0 (2)	0.1 (3)
C_{10}	5.3 (2)	6.0 (3)	4.4 (2)	1.4 (2)	−0.2 (2)	−0.1 (2)
C_{11}	3.8 (2)	3.7 (2)	5.1 (2)	−0.2 (2)	0.3 (2)	−0.0 (2)
C_{12}	5.2 (2)	5.1 (2)	5.6 (3)	−0.7 (2)	−0.9 (2)	0.2 (2)
C_{13}	4.8 (2)	5.7 (3)	7.1 (3)	−0.6 (2)	−1.5 (2)	−0.8 (3)
C_{14}	3.6 (2)	5.3 (3)	8.7 (4)	−0.6 (2)	0.4 (2)	−0.9 (3)
C_{15}	5.2 (3)	5.3 (3)	8.1 (4)	−0.9 (2)	1.3 (3)	0.9 (3)
C_{16}	5.4 (2)	5.3 (3)	5.3 (3)	−0.8 (2)	0.3 (2)	0.3 (2)
C_{17}	4.0 (2)	3.3 (2)	4.5 (2)	0.3 (1)	0.3 (2)	0.0 (2)
C_{18}	5.2 (2)	4.6 (2)	4.3 (2)	1.1 (2)	−0.1 (2)	0.0 (2)
C_{19}	5.8 (3)	5.6 (3)	5.4 (3)	1.2 (2)	1.2 (2)	−0.7 (2)
C_{20}	5.2 (2)	4.0 (2)	7.0 (4)	0.5 (2)	0.1 (2)	−0.2 (2)
C_{21}	6.7 (3)	5.2 (3)	5.7 (3)	1.2 (2)	−1.0 (3)	0.7 (2)
C_{22}	5.8 (3)	5.0 (2)	4.5 (2)	0.6 (2)	0.4 (2)	0.0 (2)
C_{23}	4.1 (2)	3.3 (2)	6.0 (2)	0.2 (2)	−0.5 (2)	0.5 (2)
C_{24}	4.4 (2)	4.8 (2)	9.0 (4)	−0.5 (2)	0.7 (3)	0.4 (3)
C_{25}	5.2 (3)	4.8 (2)	11.8 (6)	−0.9 (2)	0.4 (4)	0.4 (4)
C_{26}	5.4 (3)	4.2 (3)	13.2 (7)	−1.1 (2)	−1.7 (4)	0.7 (4)
C_{27}	7.7 (4)	4.0 (2)	9.6 (5)	−0.2 (3)	−3.3 (4)	−0.2 (3)
C_{28}	5.8 (3)	3.8 (2)	6.6 (3)	−0.1 (2)	−1.3 (3)	−0.2 (2)
C_{29}	19.1 (13)	15.6 (11)	11.1 (8)	8.8 (10)	0.9 (9)	1.5 (8)
Cl_1	10.4 (3)	15.7 (4)	31.1 (9)	5.0 (3)	−2.5 (4)	−5.0 (5)
Cl_2	11.2 (3)	41.2 (12)	14.9 (4)	−5.1 (5)	3.5 (3)	−1.6 (6)
Cl_3	31.1 (10)	11.5 (4)	17.4 (6)	5.1 (4)	5.8 (6)	0.2 (3)
Cl_4	11.6 (7)	38.4 (28)	43.2 (33)	−3.4 (11)	4.0 (14)	3.6 (26)

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

plane of the core in units of 0.01 Å. Characteristically, the individual pyrrole subunits retain local flatness (to within 0.01 Å). Examination of Figure 3 reveals that the displacement of atoms in core conforms closely to D_{2d} symmetry. The quasi-D_{2d} ruffling of the porphinato core in the Fe(TPP)(NO)(1-MeIm) molecule differs from the quasi-D_{2d} ruffling observed in FeTPP,[19] CoTPP,[20] NiTPP,[21] and CuTPP.[22] In Fe(TPP)(NO)(1-MeIm), the methine carbon atoms lie on the dihedral twofold axes and the Fe-N bonds in the diagonal mirror planes, whereas in the MTPP series the dihedral twofold axes are along the M-N bonds and the methine carbon atoms lie in the diagonal mirror planes. The MTPP type of D_{2d} ruffling has been shown[23] to be geometrically conducive to a significant shortening of the com-

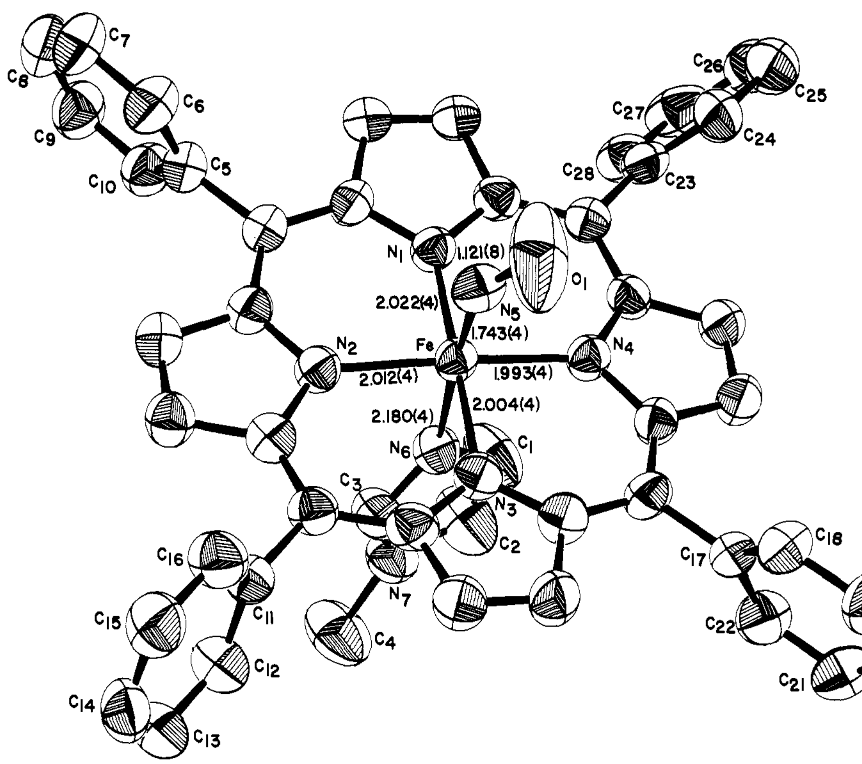

Figure 1. Computer-drawn model, in perspective, of the Fe(TPP)(NO)(1-MeIm) molecule. Also shown are the bond distances in the coordination group and the numbering scheme employed for atoms in the phenyl groups and the axial ligands.

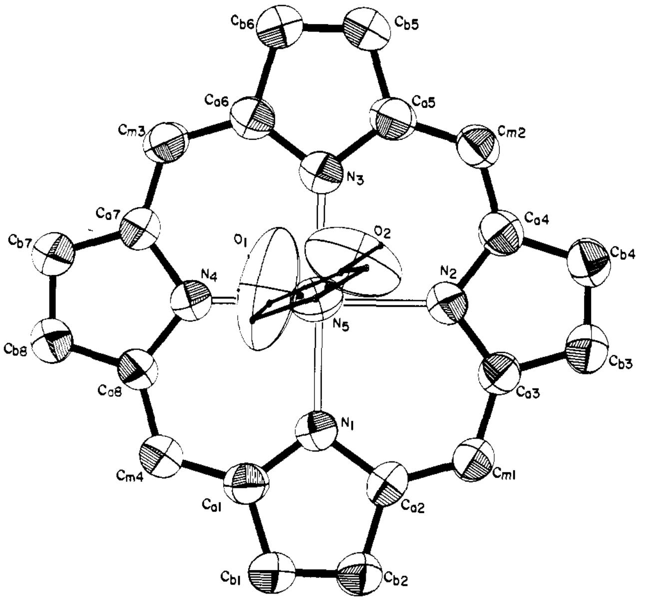

Figure 2. Computer-drawn model of the porphinato core in Fe(TPP)(NO)(1-MeIm) displaying the numbering scheme used for atoms of the core. The relative orientations of the axial ligands are displayed; O_1 represents the major orientation of the nitrosyl ligand and O_2 the minor orientation.

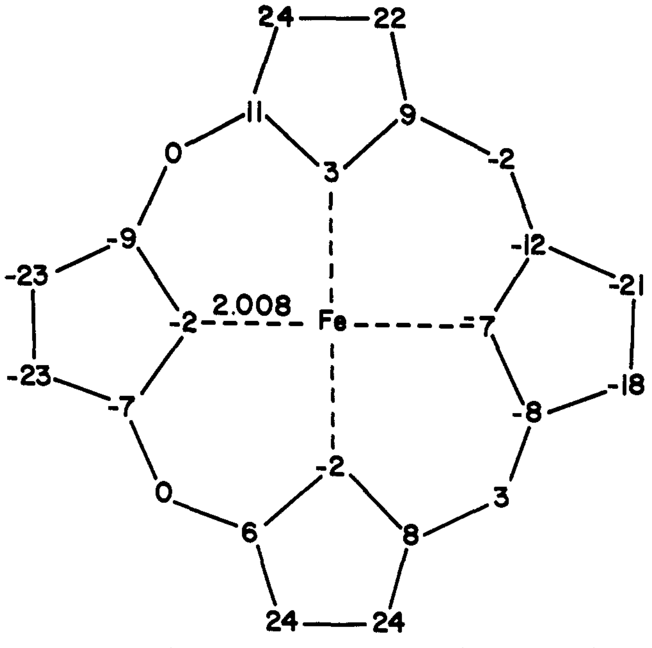

Figure 3. Formal diagram of the porphinato core with the same relative orientation as Figure 2. Each atom symbol has been replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core.

plexing bonds relative to a planar core. On the other hand, the type of D_{2d} ruffling observed for Fe(TPP)(NO)(1-MeIm) should not lead to shortened complexing bonds; indeed it may well lead to a slight increase in the bond length. Of immediate interest is the observation that the $[Im_2\text{-}FeTPP]^+$ cation[15] with an MTPP type of D_{2d} ruffled core also has Fe-N 1.989 (4) Å, or 0.02 Å shorter than found in Fe(TPP)(NO)(1-MeIm).

We now consider the geometry of the coordinated nitric oxide ligand. We first note that model calculations of Hoffmann et al.[26] suggest that the barrier to rotation of the nitrosyl ligand about the $M\text{-}N_{NO}$ bond is quite low. Thus, for an unconstrained Fe(TPP)(NO)(1-MeIm) molecule, four equivalent orientations of the nitrosyl ligand would be expected from considerations of steric interactions of the intramolecular $O \cdots N_p$ type. This type of interaction is minimized by orienting the plane of the axial Fe-N-O group so that it makes a dihedral angle of 45° with an axial plane defined by N_p, Fe, and N_5. Orientations of the nitrosyl ligand approach this ideal dihedral angle in ONCoTPP[27] (39.7°)

Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, 1-Methylimidazole, and NO Ligand[a]

Type	Length, Å	Type	Length, Å	Type	Length, Å
$\mathrm{Fe{-}N_1}$	2.022 (4)	$\mathrm{C_{m1}{-}C_5}$	1.500 (6)	$\mathrm{C_{a6}{-}C_{b6}}$	1.452 (7)
$\mathrm{Fe{-}N_2}$	2.012 (4)	$\mathrm{C_{m2}{-}C_{a4}}$	1.389 (7)	$\mathrm{C_{a7}{-}C_{b7}}$	1.436 (7)
$\mathrm{Fe{-}N_3}$	2.004 (4)	$\mathrm{C_{m2}{-}C_{a5}}$	1.404 (7)	$\mathrm{C_{a8}{-}C_{b8}}$	1.449 (7)
$\mathrm{Fe{-}N_4}$	1.993 (4)	$\mathrm{C_{m2}{-}C_{11}}$	1.485 (7)	$\mathrm{C_{b1}{-}C_{b2}}$	1.350 (7)
$\mathrm{Fe{-}N_5}$	1.743 (4)	$\mathrm{C_{m3}{-}C_{a6}}$	1.402 (7)	$\mathrm{C_{b3}{-}C_{b4}}$	1.349 (8)
$\mathrm{Fe{-}N_6}$	2.180 (4)	$\mathrm{C_{m3}{-}C_{a7}}$	1.392 (7)	$\mathrm{C_{b5}{-}C_{b6}}$	1.346 (8)
$\mathrm{N_1{-}C_{a1}}$	1.368 (6)	$\mathrm{C_{m3}{-}C_{17}}$	1.497 (6)	$\mathrm{C_{b7}{-}C_{b8}}$	1.356 (7)
$\mathrm{N_1{-}C_{a2}}$	1.370 (6)	$\mathrm{C_{m4}{-}C_{a8}}$	1.415 (6)	$\mathrm{N_5{-}O_1}$	1.121 (8)
$\mathrm{N_2{-}C_{a3}}$	1.370 (6)	$\mathrm{C_{m4}{-}C_{a1}}$	1.386 (7)	$\mathrm{N_5{-}O_2}$	1.144 (14)
$\mathrm{N_2{-}C_{a4}}$	1.377 (6)	$\mathrm{C_{m4}{-}C_{23}}$	1.496 (7)	$\mathrm{N_6{-}C_1}$	1.389 (7)
$\mathrm{N_3{-}C_{a5}}$	1.379 (6)	$\mathrm{C_{a1}{-}C_{b1}}$	1.437 (7)	$\mathrm{N_6{-}C_3}$	1.304 (6)
$\mathrm{N_3{-}C_{a6}}$	1.365 (6)	$\mathrm{C_{a2}{-}C_{b2}}$	1.461 (7)	$\mathrm{C_1{-}C_2}$	1.324 (9)
$\mathrm{N_4{-}C_{a7}}$	1.385 (6)	$\mathrm{C_{a3}{-}C_{b3}}$	1.421 (7)	$\mathrm{C_2{-}N_7}$	1.352 (8)
$\mathrm{N_4{-}C_{a8}}$	1.365 (6)	$\mathrm{C_{a4}{-}C_{b4}}$	1.449 (7)	$\mathrm{N_7{-}C_3}$	1.328 (8)
$\mathrm{C_{m1}{-}C_{a2}}$	1.389 (7)	$\mathrm{C_{a5}{-}C_{b5}}$	1.430 (7)	$\mathrm{N_7{-}C_4}$	1.498 (8)
$\mathrm{C_{m1}{-}C_{a3}}$	1.415 (7)				

[a] Figures in parentheses are the estimated standard deviations. Atoms are identified in agreement with figures.

Table IV. Bond Angles in the Coordination Group, Porphinato Skeleton, 1-Methylimidazole Ring, and Nitric Oxide[a]

Angle	Value, deg	Angle	Value, deg
$\mathrm{N_1FeN_2}$	90.1 (2)	$\mathrm{N_2C_{a4}C_{b4}}$	109.3 (4)
$\mathrm{N_1FeN_3}$	177.4 (2)	$\mathrm{C_{m2}C_{a4}C_{b4}}$	124.4 (4)
$\mathrm{N_1FeN_4}$	89.6 (2)	$\mathrm{N_3C_{a5}C_{m2}}$	125.3 (4)
$\mathrm{N_1FeN_5}$	92.2 (2)	$\mathrm{N_3C_{a5}C_{b5}}$	109.8 (4)
$\mathrm{N_1FeN_6}$	90.2 (2)	$\mathrm{C_{m2}C_{a5}C_{b5}}$	124.8 (4)
$\mathrm{N_2FeN_3}$	89.7 (2)	$\mathrm{N_3C_{a6}C_{m3}}$	125.9 (4)
$\mathrm{N_2FeN_4}$	174.5 (2)	$\mathrm{N_3C_{a6}C_{b6}}$	111.0 (4)
$\mathrm{N_2FeN_5}$	94.0 (2)	$\mathrm{C_{m3}C_{a6}C_{b6}}$	122.9 (4)
$\mathrm{N_2FeN_6}$	88.8 (2)	$\mathrm{N_4C_{a7}C_{m3}}$	126.1 (4)
$\mathrm{N_3FeN_4}$	90.4 (2)	$\mathrm{N_4C_{a7}C_{b7}}$	110.2 (4)
$\mathrm{N_3FeN_5}$	90.4 (2)	$\mathrm{C_{m3}C_{a7}C_{b7}}$	123.7 (4)
$\mathrm{N_3FeN_6}$	87.2 (2)	$\mathrm{N_4C_{a8}C_{m4}}$	126.2 (4)
$\mathrm{N_4FeN_5}$	91.5 (2)	$\mathrm{N_4C_{a8}C_{b8}}$	110.2 (4)
$\mathrm{N_4FeN_6}$	85.8 (2)	$\mathrm{C_{m4}C_{a8}C_{b8}}$	123.6 (4)
$\mathrm{N_5FeN_6}$	176.3 (2)	$\mathrm{C_{b2}C_{b1}C_{a1}}$	107.6 (4)
$\mathrm{C_{a1}N_1C_{a2}}$	106.7 (3)	$\mathrm{C_{b1}C_{b2}C_{a2}}$	106.3 (4)
$\mathrm{C_{a3}N_2C_{a4}}$	105.6 (4)	$\mathrm{C_{b4}C_{b3}C_{a3}}$	106.9 (4)
$\mathrm{C_{a5}N_3C_{a6}}$	105.4 (4)	$\mathrm{C_{b3}C_{b4}C_{a4}}$	107.1 (4)
$\mathrm{C_{a7}N_4C_{a8}}$	105.8 (3)	$\mathrm{C_{b6}C_{b5}C_{a5}}$	108.4 (5)
$\mathrm{C_{a2}C_{m1}C_5}$	118.4 (4)	$\mathrm{C_{b5}C_{b6}C_{a6}}$	105.4 (5)
$\mathrm{C_{a3}C_{m1}C_5}$	118.9 (4)	$\mathrm{C_{b8}C_{b7}C_{a7}}$	106.9 (4)
$\mathrm{C_{a2}C_{m1}C_{a3}}$	122.7 (4)	$\mathrm{C_{b7}C_{b8}C_{a8}}$	106.8 (4)
$\mathrm{C_{a4}C_{m2}C_{11}}$	118.7 (4)	$\mathrm{C_3N_6C_1}$	102.6 (5)
$\mathrm{C_{a5}C_{m2}C_{11}}$	117.6 (4)	$\mathrm{N_6C_1C_2}$	110.7 (5)
$\mathrm{C_{a4}C_{m2}C_{a5}}$	123.7 (4)	$\mathrm{C_1C_2N_7}$	106.7 (5)
$\mathrm{C_{a6}C_{m3}C_{17}}$	118.5 (4)	$\mathrm{C_2N_7C_3}$	106.1 (5)
$\mathrm{C_{a7}C_{m3}C_{17}}$	118.2 (4)	$\mathrm{C_2N_7C_4}$	126.8 (5)
$\mathrm{C_{a6}C_{m3}C_{a7}}$	123.3 (4)	$\mathrm{C_3N_7C_4}$	127.0 (5)
$\mathrm{C_{a8}C_{m4}C_{23}}$	117.2 (4)	$\mathrm{N_7C_3N_6}$	113.8 (5)
$\mathrm{C_{a1}C_{m4}C_{23}}$	119.8 (4)	$\mathrm{FeN_1C_{a1}}$	127.0 (3)
$\mathrm{C_{a8}C_{m4}C_{a1}}$	123.0 (4)	$\mathrm{FeN_1C_{a2}}$	125.4 (3)
$\mathrm{N_1C_{a1}C_{m4}}$	126.0 (4)	$\mathrm{FeN_2C_{a3}}$	127.3 (3)
$\mathrm{N_1C_{a1}C_{b1}}$	109.9 (4)	$\mathrm{FeN_2C_{a4}}$	127.1 (3)
$\mathrm{C_{m4}C_{a1}C_{b1}}$	124.1 (4)	$\mathrm{FeN_3C_{a5}}$	126.8 (3)
$\mathrm{N_1C_{a2}C_{m1}}$	127.7 (4)	$\mathrm{FeN_3C_{a6}}$	127.5 (3)
$\mathrm{N_1C_{a2}C_{b2}}$	109.4 (4)	$\mathrm{FeN_4C_{a7}}$	126.6 (3)
$\mathrm{C_{m1}C_{a2}C_{b2}}$	122.8 (4)	$\mathrm{FeN_4C_{a8}}$	127.5 (3)
$\mathrm{N_2C_{a3}C_{m1}}$	125.8 (4)	$\mathrm{FeN_5O_1}$	142.1 (6)
$\mathrm{N_2C_{a3}C_{b3}}$	111.1 (4)	$\mathrm{FeN_5O_2}$	138.3 (11)
$\mathrm{C_{m1}C_{a3}C_{b3}}$	123.1 (4)	$\mathrm{FeN_6C_1}$	126.6 (4)
$\mathrm{N_2C_{a4}C_{m2}}$	126.1 (4)	$\mathrm{FeN_6C_3}$	130.4 (4)

[a] Figures in parentheses are the estimated standard deviations. Atoms are identified in agreement with figures.

and ONFeTPP[1] (40.6°). However, most bent nitrosyl ligands eclipse a metal-ligand bond in the basal plane. Electronic effects resulting from coordination of the axial 1-methylimidazole ligand could favor particular orientations of the nitric oxide; this could possibly reduce the range of geometries possible to two equivalent orientations. Hence, a single orientation of the nitrosyl ligand could only arise from *intermolecular* packing constraints. The two observed orientations of the nitrosyl appear to reflect the best compromise between the minimization of intermolecular and intramolecular steric interactions. The minor orientation of the nitric oxide, in which the $\mathrm{FeN_5O_2}$ plane makes ideal dihedral angles of ~45° with the axial planes defined by $\mathrm{N_2}$, Fe, and $\mathrm{N_5}$ and $\mathrm{N_3}$, Fe, and $\mathrm{N_5}$ (Figure 2), has a close intermolecular contact $\mathrm{C_{Im}{\cdots}O_2} \approx 3.0$ Å. The major orientation, wherein the $\mathrm{FeN_5O_1}$ plane has a dihedral angle of only 11° with the $\mathrm{N_4FeN_5}$ axial plane corresponding to a $\mathrm{N_4{\cdots}O_1}$ separation of 2.99 Å, has less severe *intermolecular* contacts than the minor orientation. Model calculations for an $\mathrm{FeN_5O}$ plane oriented to minimize intramolecular contacts between oxygen and $\mathrm{N_1}$ and $\mathrm{N_2}$ or $\mathrm{N_1}$ and $\mathrm{N_4}$ (Figure 2) reveal that these orientations are apparently precluded by intermolecular interactions.

The axial bond system of the FeNO group is decidedly nonlinear with $\mathrm{Fe{-}N_5{-}O_1} = 142.1\ (6)°$ and $\mathrm{Fe{-}N_5{-}O_2} = 138.3\ (11)°$. The exact values of the FeNO angles depend on the position of the nitrosyl nitrogen atom, which may be slightly different for the two NO orientations; least-squares refinement leads to an $\mathrm{N_5}$ position that is the weighted average of the two NO orientations. An off axis displacement of the nitrosyl nitrogen atom is frequently observed for bent nitrosyls.[27,28] Examination of the thermal parameters of $\mathrm{N_5}$ and the $\mathrm{N_5{-}O_1}$ and $\mathrm{N_5{-}O_2}$ bond lengths [1.121 (8) and 1.144 (14) Å, respectively] suggest that any unresolved disorder in the position of $\mathrm{N_5}$ is small and consequently the maximum change in the apparent FeNO bond angles will be <2°. By comparison to these results and consideration of *intramolecular* contacts, the estimate[29] of 110° for the FeNO bond angle in nitrosylhemoglobin appears too small.

The axial $\mathrm{Fe{-}N_5}$ distance of 1.743 (4) Å is slightly longer than the 1.717 (7) Å distance in five-coordinate ONFeTPP.[1] The 0.03 Å increase in the $\mathrm{Fe{-}N_{NO}}$ length and the ~8-10° decrease in the Fe-N-O bond angle in Fe(TPP)(NO)(1-MeIm) compared to ONFeTPP suggest decreased π bonding between iron and NO, the presumed consequence of the *trans*-1-methylimidazole ligand. An interesting question, as yet unanswered, is whether the FeNO axial bond parameters are particularly sensitive to changes in the trans ligand. The iron atom is displaced 0.07 Å from the mean plane of the four porphinato nitrogen atoms and 0.05 Å from the mean porphinato plane toward the coordinated nitric oxide and bespeaks a strong $\mathrm{Fe{-}N_{NO}}$ interaction. The small displacement out-of-plane does, however, relieve intramolecular contacts of the $\mathrm{N_5{\cdots}N_p}$ type. A 0.21 Å displacement out-of-plane was observed in ONFeTPP.[1]

Comparison of the axial bond parameters of Fe(TPP)(NO)(1-MeIm) with the nitrosyl derivatives of Mn(II) and Co(II) porphyrins yields detailed descriptions of alterations in the stereochemistry of the axial M-N-O group concomitant with the stepwise removal or addition of a 3d electron. The $\mathrm{Mn{-}N_{NO}}$ bond distance is 1.644 (5) Å in low-spin Mn(TPP)(NO)(4-MePip)[2,30] (4-MePip = 4-methylpiperidine) and $\mathrm{Co{-}N_{NO}} = 1.833\ (52)$ Å in low-spin ONCoTPP.[27] The Mn-N-O bond angle is 176.2 (5)°; Co-N-O ≤128.5°. The order of bond distances is thus $\mathrm{Co{-}N_{NO}} > \mathrm{Fe{-}N_{NO}} > \mathrm{Mn{-}N_{NO}}$; the M-N-O bond angles display the reverse trend with Co-N-O < Fe-N-O < Mn-N-O. The trends in both bond distance and bond angles are suggestive of the increasing importance of π interactions with the removal of d electrons within the series.[31]

The complexing bond to the 1-methylimidazole ligand in Fe(TPP)(NO)(1-MeIm) is quite long with $\mathrm{Fe{-}N_6} = 2.180$

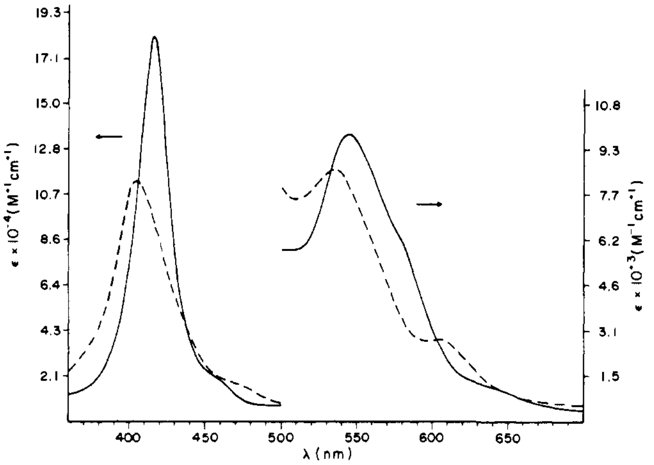

Figure 4. Electronic spectra for ONFeTPP (- - -) (chloroform solution) and Fe(TPP)(NO)(1-MeIm) (—) (chloroform–20% 1-methylimidazole solution).

(4) Å. This long bond is not attributable to steric interaction between atoms of the ligand and atoms of the core; bond stretching from such steric effects has been observed in five-coordinate (1,2-DiMeIm)CoTPP.[32] Although the Fe–N_{Im} bond distance for a low-spin bis(imidazole)iron(II) porphyrin is not known, a value of ~2.0 Å appears to be a reasonable estimate and consistent with the following known porphyrin and porphyrin model structures. The Fe–N_{Im} distances in the bis(imidazole)iron(III) derivatives of *meso*-tetraphenylporphyrin[15] and protoporphyrin-IX[16] are 1.974 and 1.977 Å, respectively; a slightly longer bond for an iron(II) derivative should result from the decrease in nuclear charge. The Fe–N_{Im} bond distance in bis(dimethylglyoximato)diimidazoleiron(II)[33] is 1.985 Å. The long Fe–N_6 bond length is thus the result of a structural trans effect from the nitric oxide of ~0.20 Å in magnitude. This electronic effect on the trans bond appears to be of some importance with respect to the detailed behavior of nitrosyl derivatives of hemoglobin (vide infra). Similar structural trans effects are observed in *trans*-chloronitrosylbis(ethylenediamine)cobalt(III) perchlorate[28a] (0.33 Å) and nitrosylpentaamminecobalt(III)[28b] (0.24 Å). The magnitude of the structural trans effect in a six-coordinate nitrosylcobalt(II) porphyrin is an interesting question; comparison of the iron(II) and cobalt(II) results would afford evaluation of the effect concomitant with the addition of one 3d electron.

The dihedral angle between the imidazole plane and the mean plane of the porphinato skeleton is 82.4°. This tilting of the imidazole plane from the normal to the mean porphinato plane has been observed in the five-coordinate imidazolecobalt(II) porphyrins and in a high-spin six-coordinate bis(imidazole)nickel(II) porphyrin.[34] It is not characteristic of the bis(imidazole)iron(III) porphyrin derivatives.[15,16] The angle, ϕ, between the normal to the imidazole plane and the normal to the coordinate plane defined by N_2FeN_6 or N_4FeN_6 is 25.4 and 25.0°, respectively; a value of 45° represents the best orientation for minimizing steric interactions between the ligand and the core. Values of $\phi \leq 20°$ (at 0° the axial ligand plane is along a M–N_p bond) have been observed in five-coordinate cobalt(II) porphyrins[8,32,35] and six-coordinate iron(III) porphyrins.[15,16] It is not clear whether intramolecular or intermolecular packing forces or other factors predominate in determining the value of the orientation parameter ϕ for imidazole ligands. The dihedral angle between the imidazole plane and the axial plane FeN_5O_1 is 36.1° and that between the imidazole plane and FeN_5O_2 is 21.0°.

The long Fe–N_b bond to the axial 1-methylimidazole ligand is the consequence of the partial donation of the unpaired electron of NO to the d_{z^2} orbital of the iron, which is an antibonding orbital with respect to the axial Fe–N_b bond. Electron spin resonance studies[3a,36] of six-coordinate nitrosyliron(II) porphyrins (including the present model compound) indicate substantial d_{z^2} population; the spectrum shows nine lines resulting from hyperfine coupling of the two ^{14}N nuclei along the *z* axis. The generally accepted qualitative relationship between bond length and bond strength and the substantial population of the $3d_{z^2}$ orbital suggests that the already quite long Fe–N_b bond in six-coordinate nitrosyliron(II) porphyrins is also easily stretched. Indeed, some of the properties of nitrosylhemoglobin derivatives, which appear anomalous by comparison to other ligated hemoglobin derivatives, are quite explicable upon allowance of a readily stretched Fe–N_ϵ bond. (N_ϵ represents the coordinated nitrogen atom of the proximal histidine). The limit of a stretched bond is no bond at all, adequately represented for nitrosyliron(II) porphyrins by ONFeTPP.[1] It does not follow that properties of nitrosyliron(II) porphyrins that are dependent on the Fe–N_b bond distance will vary smoothly as a function of this distance.

It has been found[37] that significant visible and ultraviolet spectral changes occur when inositol hexaphosphate (IHP) is added to nitrosylhemoglobin (NO-Hb); very much smaller changes are found for the oxy or carbonmonoxy derivatives under the same conditions. Organic polyphosphates, of which IHP is the most notable example,[38] cause a shift in the allosteric equilibrium between the two quaternary structures of certain ferrihemoglobin derivatives with the deoxyhemoglobin quaternary structure (type T) being favored over the oxyhemoglobin structure (type R). The allosteric equilibrium between the two alternate quaternary structures is thought to be governed by the distance of N_ϵ of the proximal histidine from the plane of the porphyrin, longer distances favoring the T structure.[39] The spectral changes observed[37] between NO-Hb and NO-Hb upon addition of IHP are similar to the spectral differences between Fe(TPP)(NO)(1-MeIm) and ONFeTPP, with similar decreases in the intensity of the Soret band. The magnitude of the blue shift is about 1.5 nm in NO-Hb and 10 nm in the nitrosyliron(II) tetraphenylporphyrins. The similarity of the spectra of the model heme complexes and NO-Hb provides strong evidence for stretching of the Fe–N_ϵ bond in NO-Hb upon addition of IHP; a complete Fe–N_ϵ bond rupture in NO-Hb is probably unlikely. Equivalent changes in the coordination group geometry of all subunits of NO-Hb, upon addition of IHP, are not required and indeed differences are suggested by ESR experiments (vide infra).[45]

Two sets of ESR experiments suggest Fe–N_ϵ bond stretching in NO-Hb. ESR spectra of NO-Hb show enhanced hyperfine splitting from ^{14}NO upon addition of IHP,[40] indicating greater delocalization of the unpaired electron on NO (and less on N_ϵ of the proximal histidine) consistent with the suggested structure changes induced by IHP. ESR experiments employing hybrid hemoglobins are also indicative of changing coordination group geometry as a function of Hb quaternary structure. The ESR spectrum of hybrids,[41] wherein the α chains are nitrosylated and the ligation state of the β chains is varied, show a nine-line spectrum when the β chains are in the low-spin state (R quaternary structure) and a three-line spectrum when the β chains are in the high-spin state. The nine-line spectrum indicates that the unpaired spin interacts strongly with two nitrogen nuclei (NO and proximal histidine) whereas the three-line spectrum must be a consequence of decreased interaction with the proximal histidine. However, when the β chains are nitrosylated the ESR spectrum does not depend on the spin state of the α chains. These results suggest that the coordination group geometry of the hemes of the α chains can show more variation than the hemes of the β chains. It does not seem necessary to assume that a deprotonation reaction of the heme-bound proximal histidine is responsible for the ESR changes as had been suggested.[42]

The heterogenity in reactions of nitrosylhemoglobin in the presence of IHP[43] and the pH dependence of the ESR spectrum of nitrosyl trout hemoglobin[44] are likely experimental manifestations of the relative ease of coordination group changes of the heme. Clearly, detailed study of spectral changes, ESR parameters, and other physical properties of the six-coordinate nitrosyliron(II) porphyrins as a function of steric requirements of the axial base (which should mimic bond stretching in the protein) are of interest. These are currently in progress.

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Supplementary Material Available: A listing of structure factor amplitudes (×10) (22 pages). Ordering information is given on any current masthead page.

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