bridging carbonyl ligands is observed. This aspect is being investigated further.

It is anticipated that the study of "A-frame" complexes and their chemistries with small unsaturated molecules will, in addition to yielding a great deal of interesting and varied chemistry, be of tremendous value in furthering the understanding of catalytic processes involving multicentered metal catalysts.

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Registry No. $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$, 67235-83-0.

Supplementary Material Available: Tables VII and VIII, showing the idealized hydrogen parameters and the root-mean-square amplitudes of vibration of the individual atoms, respectively, and a listing of the observed and calculated structure amplitudes (39 pages). Ordering information is given on any current masthead page.

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Nitrosylmetalloporphyrins. 5. Molecular Stereochemistry of Nitrosyl(5,10,15,20-tetratolylporphinato)manganese(II) and Nitrosyl(4-methylpiperidine)(5,10,15,20-tetraphenylporphinato)manganese(II)

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The molecular stereochemistries of five-coordinate nitrosyl(5,10,15,20-tetratolylporphinato)manganese(II) (I) and six-coordinate nitrosyl(4-methylpiperidine)(5,10,15,20-tetraphenylporphinato)manganese(II) (II) have been determined by X-ray diffraction methods. I crystallizes as the benzene solvate in the monoclinic system, space group $P2_1/a$. The unit cell has a = 15.755 (6) Å, b = 16.979 (4) Å, c = 17.389 (3) Å, β = 112.43 (2)°, and Z = 4. II crystallizes as a chloroform solvate in the orthorhombic system, space group $P2_12_12_1$. The unit cell constants are a = 17.561 (6) Å, b = 25.580 (13) Å, and c = 10.175 (6) Å for Z = 4. Both complexes have essentially linear Mn–N–O groups. The Mn–N(NO) bond distances [1.641 (2) Å (I) and 1.644 (5) Å (II)] are not affected by the increase in coordination number, but the Mn–N(porphinato) bond distances [2.004 (5) Å (I) and 2.027 (3) Å (II)] are affected. The data for I along with the results for Fe(TPP)(NO) and Co(TPP)(NO) permit an assessment of the effects of nonbonded repulsion between the axial ligand and porphinato ligand on the displacements of the respective metal atoms.

The interaction of diatomic ligands with metalloporphyrins has been intensively investigated in recent years.[2-14] Much of our work in this area has dealt with the interaction of nitric oxide with metalloporphyrins. Our earlier reports of the preparations and stereochemistry of nitrosylmetalloporphyrins emphasized the iron[11-13] and cobalt[14] derivatives. Herein we report the characterization of two $\{MnNO\}^6$ derivatives:[15] five-coordinate nitrosyl(5,10,15,20-tetra-*p*-tolylporphinato)-manganese(II), written as Mn(TTP)(NO), and six-coordinate nitrosyl(4-methylpiperidine)(5,10,15,20-tetraphenylporphi-

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nato)manganese(II) written as Mn(TPP)(4-MePip)(NO). A preliminary account of the latter structure has appeared.[16] These two structures allow comparison of the stereochemical changes attending the addition of a sixth ligand and, together with the analogous iron derivatives, the changes in stereochemistry caused by the removal of one d electron. The five-coordinate Mn(TTP)(NO) derivative, along with the previously reported Fe(TPP)(NO)[13] and Co(TPP)NO)[14] structures, also permits an assessment of the effects of nonbonded repulsion between the axial ligand and porphinato ligand on the displacements of the respective metal atoms.

Experimental Section

Mn(TTP)(NO). A variety of difficulties were encountered in our attempts to prepare adequate crystals of Mn(TPP)(NO). Accordingly, we utilized derivatives of 5,10,15,20-tetra-*p*-tolylporphyrin, H_2TTP, in subsequent experiments. "Mn(TTP)(OH)" was prepared by reaction of H_2TTP with $Mn(OAc)_2$ in DMF, precipitation with $NaOH/H_2O$, and recrystallization from CH_3OH/H_2O.[17] The compound was reduced to Mn(TTP) with $NaBH_4$ under an Ar atmosphere. The Mn(TTP) was dissolved in benzene, and the benzene solution was dried over sodium metal. The solution was reacted with NO, and crystals of Mn(TTP)(NO) were prepared by allowing nonane to diffuse into the benzene solution. The product is very air sensitive even in crystalline form.

Preliminary examination of a crystal mounted in a thin-walled glass capillary on a Syntex $P\bar{1}$ automated diffractometer established a four-molecule monoclinic unit cell. The systematic absences were consistent with the space group $P2_1/a$. Least-squares refinement of the setting angles of 60 reflections collected at $\pm 2\theta$ gave the following cell constants: ($\bar{\lambda}$ 0.71069 Å) $a = 15.755$ (6) Å, $b = 16.979$ (4) Å, $c = 17.389$ (3) Å, and $\beta = 112.43$ (2)°. For a cell content of $4[MnON_5C_{48}H_{36}{\cdot}C_6H_6]$, the calculated density is 1.293 g/cm^3, which is a reasonable value for this class of compounds. A measured density was hampered by the air sensitivity of the compound; a rough value of 1.28 g/cm^3 was obtained.

Intensity data were collected with graphite-monochromated Mo Kα radiation and θ–2θ scanning. Variable 2θ scan rates (2–10°/min in 2θ) with scans of 2.1° at $2\theta = 0°$ and background counts collected at the extremes of the scan were used. The measurement of four standard reflections (every 50 data points) showed insignificant variation with time. Intensity data were processed as described previously.[18] A total of 6555 unique reflections having $F_o > 3\sigma(F_o)$ were retained as observed (67% of the theoretical number possible) to a 2θ limit of 55°.

The structure was solved by the usual heavy-atom method and refined by block-diagonal least-squares methods.[19] After isotropic refinement, a difference Fourier synthesis revealed approximate hydrogen atom positions for all hydrogen atoms of the porphinato ligand. These positions were idealized and included in subsequent refinement cycles as fixed contributors. The refinement was then carried to convergence using anisotropic temperature factors for all heavy atoms. Final values of the discrepancy indices are $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.053$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2} = 0.061$ and the estimated standard deviation of observation of unit weight is 1.86. A final difference Fourier synthesis showed no significant features with peaks of less than 0.4 e/Å^3. A final listing of observed and calculated structure amplitudes is available as supplementary material.

The atomic coordinates and the associated anisotropic thermal parameters for the asymmetric unit of structure are listed in Tables I and II, respectively.

Mn(TPP)(4-MePip)(NO). The synthesis of Mn(TPP)(4-MePip)(NO) has been described previously.[20] Crystals suitable for diffraction study were prepared by vapor diffusion of anhydrous methanol into a chloroform solution of the complex, prepared in situ, under an argon–nitric oxide atmosphere. All crystals were mounted in thin-walled glass capillaries filled with argon.

Preliminary examination of a crystal on a Syntex $P\bar{1}$ automated diffractometer established a four-molecule orthorhombic unit cell. The systematic absences are uniquely consistent with the choice of $P2_12_12_1$ as the space group. Least-squares refinement of the setting angles of 46 reflections, each having $2\theta > 25°$, gave the following cell constants ($\bar{\lambda}$ 0.71069 Å): $a = 17.561$ (6) Å, $b = 25.580$ (13) Å, and $c = 10.175$ (6) Å. The calculated density for a cell content of $4[MnON_6C_{50}H_{38}{\cdot}CHCl_3]$ is 1.33 g/cm^3; the experimental density was 1.29 g/cm^3. All measurements were preformed at the ambient laboratory temperature of 20 ± 1 °C.

Table I. Atomic Coordinates of Mn(TTP)(NO) in the Unit Cell[a]

atom type	coordinates		
	10^4x	10^4y	10^4z
Mn[b]	3786 (0)	1129 (0)	1993 (0)
O	3757 (2)	−519 (1)	1931 (1)
N_1	5144 (1)	1318 (1)	2555 (1)
N_2	3883 (1)	1410 (1)	913 (1)
N_3	2424 (1)	1269 (1)	1442 (1)
N_4	3677 (1)	1324 (1)	3088 (1)
N_5	3786 (1)	163 (1)	1966 (1)
C_{a1}	5663 (2)	1330 (1)	3398 (1)
C_{a2}	5777 (2)	1265 (1)	2183 (1)
C_{a3}	4680 (2)	1438 (1)	755 (1)
C_{a4}	3177 (2)	1555 (1)	148 (1)
C_{a5}	1901 (2)	1310 (2)	598 (1)
C_{a6}	1796 (2)	1157 (2)	1810 (2)
C_{a7}	2879 (2)	1341 (1)	3246 (1)
C_{a8}	4379 (2)	1431 (2)	3858 (1)
C_{b1}	6621 (2)	1273 (2)	3550 (2)
C_{b2}	6690 (2)	1219 (2)	2807 (2)
C_{b3}	4458 (2)	1645 (2)	−105 (2)
C_{b4}	3547 (2)	1717 (2)	−466 (1)
C_{b5}	954 (2)	1198 (2)	443 (2)
C_{b6}	887 (2)	1086 (2)	1186 (2)
C_{b7}	3089 (2)	1512 (2)	4098 (2)
C_{b8}	4006 (2)	1565 (2)	4477 (2)
C_{m1}	5568 (2)	1309 (1)	1332 (1)
C_{m2}	2247 (2)	1486 (2)	−11 (1)
C_{m3}	1998 (2)	1199 (1)	2659 (1)
C_{m4}	5313 (2)	1398 (2)	4017 (1)
C_1	6320 (2)	1224 (1)	1016 (1)
C_2	6295 (2)	622 (2)	471 (2)
C_3	6960 (2)	547 (2)	141 (2)
C_4	7682 (2)	1072 (2)	349 (2)
C_5	7722 (2)	1662 (2)	908 (2)
C_6	7054 (2)	1747 (2)	1234 (2)
C_7	1579 (2)	1603 (2)	−887 (1)
C_8	1354 (2)	2343 (2)	−1218 (2)
C_9	762 (2)	2450 (2)	−2042 (2)
C_{10}	370 (2)	1818 (2)	−2544 (2)
C_{11}	571 (2)	1086 (2)	−2209 (2)
C_{12}	1175 (2)	974 (2)	−1392 (2)
C_{13}	1236 (2)	1144 (2)	2976 (1)
C_{14}	547 (2)	1707 (2)	2764 (2)
C_{15}	−107 (2)	1690 (2)	3114 (2)
C_{16}	−99 (2)	1118 (2)	3679 (2)
C_{17}	569 (2)	546 (2)	3860 (2)
C_{18}	1230 (2)	556 (2)	3519 (2)
C_{19}	5977 (2)	1446 (2)	4909 (1)
C_{20}	6479 (2)	2114 (6)	5221 (2)
C_{21}	7084 (2)	2144 (2)	6044 (2)
C_{22}	7195 (2)	1517 (2)	6576 (2)
C_{23}	6693 (2)	853 (2)	6255 (2)
C_{24}	6089 (2)	817 (2)	5436 (2)
C_{25}	3962 (3)	766 (3)	6864 (3)
C_{26}	3770 (4)	805 (3)	7547 (3)
C_{27}	2898 (4)	773 (3)	7482 (3)
C_{28}	2205 (3)	741 (3)	6732 (3)
C_{29}	2399 (3)	706 (2)	6027 (2)
C_{30}	3280 (3)	713 (2)	6095 (3)
C_{31}	8387 (2)	1009 (2)	−51 (2)
C_{32}	−254 (3)	1948 (3)	−3448 (2)
C_{33}	−777 (2)	1142 (2)	4101 (2)
C_{34}	7856 (3)	1554 (3)	7480 (2)

[a] Numbers in parentheses are the estimated standard deviations. [b] For Mn $10^5x = 37856$ (2), $10^5y = 11287$ (2), and $10^5z = 19930$ (2).

X-ray intensity data were collected with graphite-monochromated Mo Kα radiation using a crystal with approximate dimensions of 0.25 × 0.25 × 0.30 mm. All independent reflections in the range $3° < 2\theta < 53°$ were measured by means of the "wandering" ω-scan technique using experimental conditions described previously.[12] Intensity data were reduced[18] and a reflection was retained as observed

Table II. Thermal Parameters[a] for the Atoms of Mn(TTP)(NO) in the Unit Cell

atom type	anisotropic parameters, Å^2					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	2.82 (1)	3.63 (2)	2.55 (1)	0.03 (1)	0.73 (1)	−0.05 (1)
O	9.6 (2)	4.3 (1)	7.1 (1)	−0.7 (1)	2.0 (1)	−0.2 (1)
N_1	3.0 (1)	3.7 (1)	2.8 (1)	−0.1 (1)	0.9 (1)	−0.1 (1)
N_2	3.0 (1)	3.9 (1)	2.7 (1)	0.2 (1)	0.8 (1)	−0.0 (1)
N_3	3.0 (1)	4.2 (1)	2.7 (1)	0.3 (1)	0.8 (1)	0.0 (1)
N_4	2.9 (1)	4.0 (1)	2.7 (1)	−0.2 (1)	0.9 (1)	−0.1 (1)
N_5	3.9 (1)	3.9 (1)	3.4 (1)	−0.1 (1)	1.0 (1)	−0.1 (1)
C_{a1}	3.3 (1)	4.1 (1)	2.9 (1)	−0.3 (1)	0.8 (1)	0.0 (1)
C_{a2}	3.0 (1)	3.7 (1)	3.3 (1)	0.0 (1)	0.9 (1)	−0.1 (1)
C_{a3}	3.6 (1)	3.7 (1)	3.1 (1)	−0.2 (1)	1.3 (1)	−0.2 (1)
C_{a4}	3.5 (1)	3.9 (1)	2.9 (1)	0.3 (1)	0.9 (1)	−0.1 (1)
C_{a5}	3.0 (1)	5.0 (1)	3.0 (1)	0.5 (1)	0.6 (1)	−0.1 (1)
C_{a6}	2.9 (1)	4.5 (1)	3.6 (1)	0.2 (1)	0.9 (1)	0.1 (1)
C_{a7}	3.3 (1)	4.1 (1)	3.0 (1)	−0.1 (1)	1.2 (1)	0.1 (1)
C_{a8}	3.6 (1)	4.0 (1)	2.7 (1)	−0.6 (1)	1.0 (1)	−0.1 (1)
C_{b1}	3.0 (1)	5.7 (2)	3.5 (1)	−0.0 (1)	0.7 (1)	0.2 (1)
C_{b2}	2.9 (1)	5.3 (1)	3.7 (1)	0.1 (1)	1.0 (1)	0.1 (1)
C_{b3}	4.1 (1)	5.2 (1)	3.2 (1)	0.2 (1)	1.5 (1)	0.3 (1)
C_{b4}	4.3 (1)	5.2 (1)	2.7 (1)	0.5 (1)	1.0 (1)	0.5 (1)
C_{b5}	3.2 (1)	7.6 (2)	3.4 (1)	0.2 (1)	0.5 (1)	−0.4 (1)
C_{b6}	2.9 (1)	8.1 (2)	3.7 (1)	−0.3 (1)	0.9 (1)	−0.1 (1)
C_{b7}	4.0 (1)	5.7 (2)	3.4 (1)	−0.2 (1)	1.9 (1)	−0.3 (1)
C_{b8}	3.9 (1)	5.7 (2)	2.9 (1)	−0.7 (1)	1.2 (1)	−0.5 (1)
C_{m1}	3.1 (1)	3.6 (1)	3.3 (1)	−0.2 (1)	1.3 (1)	−0.2 (1)
C_{m2}	3.6 (1)	4.5 (1)	2.7 (1)	0.5 (1)	0.7 (1)	−0.2 (1)
C_{m3}	3.1 (1)	3.9 (1)	3.4 (1)	0.1 (1)	1.3 (1)	0.1 (1)
C_{m4}	3.3 (1)	4.2 (1)	2.5 (1)	−0.5 (1)	0.7 (1)	−0.1 (1)
C_1	3.2 (1)	3.8 (1)	3.3 (1)	0.0 (1)	1.1 (1)	0.1 (1)
C_2	3.8 (1)	4.1 (1)	4.1 (1)	−0.7 (1)	1.4 (1)	−0.5 (1)
C_3	4.0 (1)	4.7 (1)	4.0 (1)	0.5 (1)	1.5 (1)	−0.6 (1)
C_4	3.2 (1)	5.2 (1)	3.9 (1)	0.4 (1)	1.4 (1)	0.8 (1)
C_5	3.7 (1)	5.1 (1)	4.4 (1)	−1.0 (1)	1.4 (1)	0.5 (1)
C_6	4.6 (1)	4.0 (1)	3.6 (1)	−0.7 (1)	1.6 (1)	−0.3 (1)
C_7	3.3 (1)	5.3 (1)	2.8 (1)	0.5 (1)	0.8 (1)	0.1 (1)
C_8	6.1 (2)	5.4 (2)	4.4 (1)	0.6 (1)	−0.4 (1)	−0.2 (1)
C_9	6.7 (2)	6.0 (2)	4.7 (2)	1.0 (2)	−0.4 (1)	1.0 (1)
C_{10}	4.0 (1)	7.4 (2)	3.5 (1)	0.6 (1)	0.3 (1)	0.5 (1)
C_{11}	5.7 (2)	6.6 (2)	3.7 (1)	−0.4 (1)	0.3 (1)	−0.8 (1)
C_{12}	5.3 (2)	5.5 (2)	3.8 (1)	−0.1 (1)	0.4 (1)	0.2 (1)
C_{13}	3.1 (1)	4.4 (1)	3.3 (1)	−0.3 (1)	1.1 (1)	−0.1 (1)
C_{14}	4.1 (1)	4.6 (1)	4.7 (1)	0.2 (1)	2.0 (1)	0.6 (1)
C_{15}	3.8 (1)	5.2 (2)	5.4 (2)	0.4 (1)	1.9 (1)	−0.4 (1)
C_{16}	3.8 (1)	6.1 (2)	4.0 (1)	−1.1 (1)	1.7 (1)	−0.7 (1)
C_{17}	4.5 (1)	6.1 (2)	4.4 (1)	−0.8 (1)	1.8 (1)	0.9 (1)
C_{18}	3.6 (1)	4.9 (1)	4.7 (1)	0.1 (1)	1.5 (1)	0.8 (1)
C_{19}	3.3 (1)	4.7 (1)	2.9 (1)	−0.1 (1)	1.0 (1)	−0.3 (1)
C_{20}	5.1 (1)	5.5 (2)	3.9 (1)	−1.2 (1)	0.3 (1)	0.1 (1)
C_{21}	5.5 (2)	6.3 (2)	4.8 (2)	−1.7 (1)	0.2 (1)	−0.9 (1)
C_{22}	3.9 (1)	7.4 (2)	3.4 (1)	0.2 (1)	0.5 (1)	−0.6 (1)
C_{23}	5.5 (2)	6.4 (2)	3.7 (1)	0.5 (1)	1.2 (1)	1.1 (1)
C_{24}	4.9 (1)	5.3 (2)	3.4 (1)	−0.8 (1)	0.8 (1)	0.2 (1)
C_{25}	7.5 (2)	7.6 (2)	11.2 (3)	−1.0 (2)	2.8 (2)	1.2 (2)
C_{26}	13.3 (4)	9.0 (3)	6.0 (2)	−3.0 (3)	0.7 (2)	−0.5 (2)
C_{27}	16.6 (4)	8.9 (3)	8.4 (3)	−2.8 (3)	6.6 (3)	−3.2 (2)
C_{28}	9.6 (3)	7.8 (3)	12.4 (3)	0.0 (2)	4.9 (3)	−2.3 (2)
C_{29}	10.4 (3)	6.6 (2)	6.2 (2)	−0.1 (2)	0.2 (2)	0.2 (2)
C_{30}	11.1 (3)	7.0 (2)	7.7 (2)	−0.5 (2)	4.9 (2)	1.5 (2)
C_{31}	4.5 (1)	8.4 (2)	6.3 (2)	0.5 (1)	3.0 (1)	0.9 (2)
C_{32}	7.2 (2)	11.7 (3)	3.8 (2)	1.4 (2)	0.4 (1)	1.0 (2)
C_{33}	5.1 (2)	9.9 (3)	6.7 (2)	−1.2 (2)	3.6 (2)	−0.4 (2)
C_{34}	6.2 (2)	12.1 (3)	3.5 (1)	−0.7 (2)	−0.1 (1)	−0.3 (2)

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

if $F_o > 3\sigma(F_o)$; 3440 data were retained as observed, some 73% of the total number possible in the 2θ range examined.

The structure was solved by using the atomic coordinates of the metal atom and the porphinato core of Fe(TPP)(1-MeIm)(NO)[12] as trial coordinates. The coordinates of the remaining heavy atoms were found from a difference Fourier synthesis.[19] It was quickly apparent that the chloroform molecule of crystallization was disordered. This disorder appeared to allow two different orientations of the chloroform molecule. The occupancy factors of the resulting six chlorine atoms and two carbon atoms were allowed to vary. The final values were adjusted so that all chlorine atoms of one orientation of the molecule had the same occupancy. The sum of the occupancy factors for the six chlorine atoms was 2.39; for complete occupancy by one chloroform molecule this sum should equal 3.0. Thus the presence of 3.2 chloroform molecules/unit cell was indicated. This value leads to a calculated density of 1.29 g/cm^3, in excellent agreement with the observed value. Full-matrix least-squares 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 =

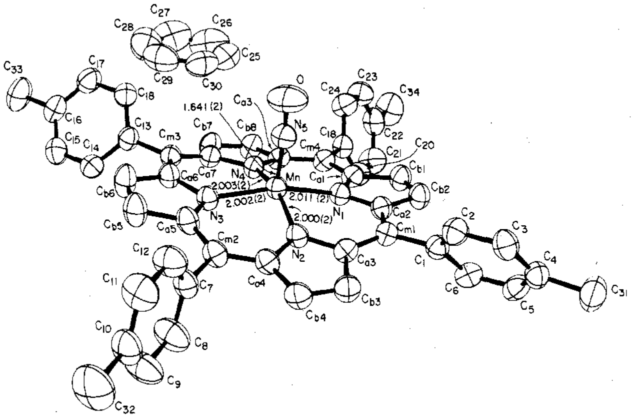

Figure 1. Computer-drawn model, in perspective, of the Mn(TTP)(NO) molecule. The labeling scheme used for the atoms of the molecule is shown. Also displayed are the bond distances in the coordination group.

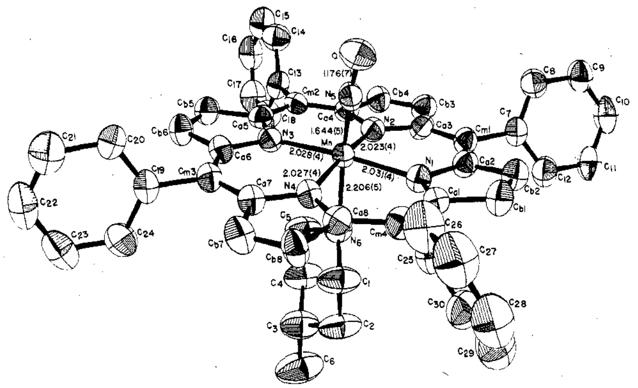

Figure 2. Computer-drawn model, in perspective, of the Mn(TPP)(4-MePip)(NO) molecule. The figure also displays the bond distances in the coordination group and the labeling scheme used for the atoms.

1.0 Å) and included as fixed contributors ($B(H) = B(\mathrm{C}) + 1.0$ Å^2) in all subsequent refinement cycles. Final refinement was accomplished by block-diagonal least squares with anisotropic temperature factors for all heavy atoms. The final value of R_1 was 0.053 and that of R_2 was 0.078, and the estimated standard deviation of an observation of unit weight was 1.214. Further refinement, using coordinates of the mirror image of the enantiomorph previously assumed, led to $R_1 = 0.059$ and $R_2 = 0.086$. The first choice of enantiomorph was clearly the correct choice and its coordinates are reported herein. A final difference Fourier synthesis had no peaks greater than 0.46 e/Å^3; the largest peaks were in the region of the disordered chloroform molecule.

The final atomic coordinates and the associated anisotropic temperature factors for the asymmetric unit of structure are listed in Tables III and IV, respectively.

Sundry Physical Data. Infrared spectra of both complexes were obtained as KBr pellets on a Perkin-Elmer 457 spectrometer: Mn(TTP)(NO) has a strong nitrosyl stretch at 1735 cm^{-1}; the corresponding peak in Mn(TPP)(4-MePip)(NO) is found at 1740 cm^{-1}. Both complexes were found to be diamagnetic species; the Evans method was utilized.[21]

Results and Discussion

Figure 1 provides an overall perspective of the five-coordinate Mn(TTP)(NO) molecule. Also displayed in Figure 1 are the special symbols assigned to the atoms in the molecule. Figure 2 provides the equivalent information for the six-coordinate derivative Mn(TPP)(4-MePip)(NO). Tables V and VI furnish listings of the bond lengths and bond angles, respectively, in the coordination group, porphinato skeleton, and axial ligand of the Mn(TTP)(NO) molecule. Tables VII and VIII provide the corresponding information for the six-coordinate Mn(TPP)(4-MePip)(NO) molecule. Average values for each chemical type of bond length and angle of the porphinato core in each molecule are given in Table IX. C_a and C_b are used to denote the respective α- and β-carbon atoms

Table III. Atomic Coordinates in the Unit Cell of Mn(TPP)(4-MePip)(NO)

	coordinates^a		
atom type	10^4x	10^4y	10^4z
Mn^b	865 (0)	1706 (0)	2272 (1)
O	698 (4)	1364 (2)	4890 (5)
N_1	924 (3)	947 (2)	1697 (5)
N_2	2016 (2)	1736 (2)	2343 (4)
N_3	817 (2)	2481 (2)	2685 (4)
N_4	−276 (2)	1698 (2)	1974 (4)
N_5	776 (3)	1522 (2)	3813 (5)
N_6	992 (3)	1913 (2)	178 (5)
C_{a1}	315 (3)	616 (2)	1544 (6)
C_{a2}	1556 (3)	638 (2)	1728 (6)
C_{a3}	2508 (3)	1327 (2)	2157 (6)
C_{a4}	2456 (3)	2161 (2)	2636 (6)
C_{a5}	1416 (3)	2802 (2)	2982 (5)
C_{a6}	169 (3)	2783 (2)	2760 (6)
C_{a7}	−762 (3)	2116 (2)	2090 (6)
C_{a8}	−712 (3)	1274 (2)	1657 (6)
C_{b1}	580 (4)	80 (2)	1484 (7)
C_{b2}	1342 (3)	93 (2)	1581 (6)
C_{b3}	3289 (3)	1510 (2)	2315 (7)
C_{b4}	3258 (3)	2027 (2)	2581 (7)
C_{b5}	1142 (4)	3324 (2)	3263 (6)
C_{b6}	383 (3)	3305 (2)	3131 (6)
C_{b7}	−1519 (4)	1948 (2)	1786 (8)
C_{b8}	−1504 (3)	1430 (2)	1519 (7)
C_{m1}	2309 (3)	809 (2)	1904 (6)
C_{m2}	2196 (3)	2662 (2)	2956 (5)
C_{m3}	−563 (3)	2620 (2)	2469 (6)
C_{m4}	−442 (4)	754 (2)	1478 (6)
C_1	378 (5)	1757 (3)	−714 (8)
C_2	519 (5)	1874 (3)	−2122 (7)
C_3	770 (5)	2425 (3)	−2407 (7)
C_4	1409 (4)	2562 (3)	−1528 (7)
C_5	1295 (4)	2430 (3)	−102 (7)
C_6	892 (8)	2554 (4)	−3833 (9)
C_7	2938 (3)	404 (2)	1826 (6)
C_8	3114 (4)	163 (2)	648 (7)
C_9	3677 (4)	−217 (3)	585 (8)
C_{10}	4046 (3)	−364 (2)	1729 (8)
C_{11}	3890 (4)	−126 (3)	2906 (8)
C_{12}	3308 (4)	253 (2)	2952 (7)
C_{13}	2767 (3)	3080 (2)	3241 (7)
C_{14}	3071 (4)	3140 (3)	4488 (7)
C_{15}	3629 (4)	3504 (3)	4741 (8)
C_{16}	3877 (4)	3825 (3)	3753 (10)
C_{17}	3584 (4)	3773 (3)	2494 (10)
C_{18}	3032 (4)	3393 (3)	2235 (8)
C_{19}	−1192 (3)	3019 (2)	2572 (6)
C_{20}	−1485 (4)	3166 (3)	3793 (7)
C_{21}	−2062 (5)	3525 (3)	3884 (9)
C_{22}	−2351 (4)	3759 (3)	2773 (10)
C_{23}	−2072 (4)	3616 (3)	1579 (9)
C_{24}	−1503 (4)	3245 (3)	1464 (7)
C_{25}	−1025 (4)	340 (2)	1218 (7)
C_{26}	−1560 (4)	202 (3)	2182 (9)
C_{27}	−2090 (4)	−188 (3)	1928 (12)
C_{28}	−2095 (4)	−432 (3)	724 (11)
C_{29}	−1575 (5)	−308 (3)	−243 (11)
C_{30}	−1037 (4)	87 (2)	12 (8)
C_{31}	399 (14)	4290 (9)	8720 (37)
C_{32}	754 (17)	4134 (19)	9933 (34)
Cl_1	400 (5)	3915 (3)	7501 (12)
Cl_2	280 (8)	3887 (4)	10183 (10)
Cl_3	1084 (6)	4717 (4)	9010 (12)
Cl_4	168 (6)	4472 (6)	10763 (12)
Cl_5	275 (6)	3904 (7)	8517 (23)
Cl_6	1594 (5)	4227 (7)	9727 (15)

[a] The numbers in parentheses are the estimated standard deviations. [b] For Mn $10^5x = 8654$ (4), $10^5y = 17060$ (3), and $10^5z = 22719$ (8).

Table IV. Thermal Parameters of Mn(TPP)(4-MePip)(NO)[a]

	anisotropic parameters, Å^2					
atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	3.00 (2)	2.73 (2)	3.35 (3)	0.19 (3)	−0.03 (3)	−0.04 (3)
O	11.8 (4)	6.1 (2)	3.8 (2)	1.1 (3)	0.7 (3)	1.7 (2)
$\mathrm{N_1}$	3.4 (2)	3.3 (2)	4.0 (2)	−0.0 (2)	−0.0 (2)	−0.3 (2)
$\mathrm{N_2}$	3.5 (2)	3.6 (2)	3.6 (2)	0.2 (2)	−0.3 (2)	−0.2 (2)
$\mathrm{N_3}$	3.3 (2)	3.4 (2)	3.8 (2)	0.0 (2)	−0.4 (2)	−0.1 (2)
$\mathrm{N_4}$	3.3 (2)	3.3 (2)	4.2 (2)	0.2 (2)	0.0 (2)	−0.1 (2)
$\mathrm{N_5}$	4.2 (2)	3.0 (2)	4.1 (2)	0.6 (2)	−0.0 (2)	−0.1 (2)
$\mathrm{N_6}$	4.2 (2)	3.8 (2)	3.8 (2)	−0.7 (2)	−0.3 (2)	0.2 (2)
$\mathrm{C_{a1}}$	4.0 (2)	3.4 (2)	3.8 (3)	0.4 (2)	−0.4 (2)	−0.1 (2)
$\mathrm{C_{a2}}$	3.9 (2)	3.4 (2)	4.5 (3)	−0.1 (2)	−0.2 (2)	−0.2 (2)
$\mathrm{C_{a3}}$	3.6 (2)	4.0 (2)	3.7 (2)	0.3 (2)	−0.1 (2)	−0.6 (2)
$\mathrm{C_{a4}}$	3.6 (2)	3.7 (2)	3.3 (2)	0.1 (2)	−0.0 (2)	−0.3 (2)
$\mathrm{C_{a5}}$	4.4 (2)	3.5 (2)	3.3 (2)	0.0 (2)	0.0 (2)	0.0 (2)
$\mathrm{C_{a6}}$	3.9 (2)	3.0 (2)	4.2 (2)	0.4 (2)	0.2 (2)	0.6 (2)
$\mathrm{C_{a7}}$	3.7 (2)	3.5 (2)	4.2 (2)	0.2 (2)	0.1 (2)	−0.1 (2)
$\mathrm{C_{a8}}$	3.7 (2)	4.1 (2)	3.7 (2)	−0.2 (2)	0.4 (2)	0.2 (2)
$\mathrm{C_{b1}}$	4.2 (2)	3.3 (2)	6.0 (3)	−0.5 (2)	0.3 (2)	−0.5 (2)
$\mathrm{C_{b2}}$	4.1 (2)	3.4 (2)	5.1 (3)	0.1 (2)	0.0 (2)	−0.2 (2)
$\mathrm{C_{b3}}$	3.4 (2)	4.9 (2)	5.1 (3)	0.3 (2)	−0.3 (2)	−0.4 (2)
$\mathrm{C_{b4}}$	4.1 (2)	4.3 (2)	5.1 (3)	0.5 (2)	−0.4 (2)	−0.4 (2)
$\mathrm{C_{b5}}$	4.6 (2)	3.2 (2)	5.0 (3)	−0.0 (2)	0.0 (2)	−0.2 (2)
$\mathrm{C_{b6}}$	4.2 (2)	2.9 (2)	5.7 (3)	0.5 (2)	0.1 (2)	−0.1 (2)
$\mathrm{C_{b7}}$	4.1 (3)	4.0 (2)	6.6 (4)	0.6 (2)	0.0 (3)	0.2 (3)
$\mathrm{C_{b8}}$	2.8 (2)	3.6 (2)	7.1 (4)	0.0 (2)	−0.7 (2)	0.2 (2)
$\mathrm{C_{m1}}$	3.9 (2)	3.3 (2)	3.8 (2)	0.5 (2)	0.3 (2)	−0.4 (2)
$\mathrm{C_{m2}}$	3.6 (2)	3.6 (2)	3.6 (2)	0.1 (2)	−0.5 (2)	−0.1 (2)
$\mathrm{C_{m3}}$	3.4 (2)	3.5 (2)	4.5 (3)	0.5 (2)	0.2 (2)	−0.1 (2)
$\mathrm{C_{m4}}$	4.4 (3)	3.5 (2)	4.8 (3)	−0.4 (2)	0.5 (2)	0.3 (2)
$\mathrm{C_1}$	6.8 (4)	6.9 (4)	5.2 (4)	−3.5 (4)	−1.3 (3)	0.7 (3)
$\mathrm{C_2}$	7.4 (4)	8.2 (4)	4.0 (3)	−3.3 (4)	−1.2 (3)	0.2 (3)
$\mathrm{C_3}$	7.5 (4)	7.1 (4)	4.2 (3)	−1.9 (4)	0.1 (3)	0.9 (3)
$\mathrm{C_4}$	6.2 (4)	6.0 (3)	4.7 (3)	−2.4 (3)	−0.0 (3)	0.5 (3)
$\mathrm{C_5}$	6.7 (4)	5.7 (3)	4.4 (3)	−1.9 (3)	−0.7 (3)	0.6 (3)
$\mathrm{C_6}$	16.1 (9)	8.9 (6)	4.9 (4)	−5.6 (7)	−1.2 (6)	1.8 (4)
$\mathrm{C_7}$	3.8 (2)	3.4 (2)	4.9 (3)	0.3 (2)	−0.2 (2)	−0.4 (2)
$\mathrm{C_8}$	5.4 (3)	3.8 (2)	5.1 (3)	0.5 (2)	−0.2 (3)	−0.0 (2)
$\mathrm{C_9}$	5.4 (3)	4.2 (3)	6.3 (4)	0.9 (3)	1.2 (3)	−0.9 (3)
$\mathrm{C_{10}}$	3.3 (2)	4.1 (3)	8.6 (4)	0.8 (2)	0.7 (3)	0.2 (3)
$\mathrm{C_{11}}$	3.8 (2)	4.8 (3)	6.6 (4)	1.1 (2)	−0.5 (3)	0.1 (3)
$\mathrm{C_{12}}$	4.5 (3)	4.1 (3)	5.4 (3)	0.6 (2)	−0.2 (3)	−0.4 (2)
$\mathrm{C_{13}}$	3.1 (2)	3.5 (2)	5.7 (3)	−0.3 (2)	−0.1 (2)	−0.7 (2)
$\mathrm{C_{14}}$	4.8 (3)	5.0 (3)	5.2 (3)	−0.4 (2)	−0.7 (3)	0.0 (2)
$\mathrm{C_{15}}$	5.2 (3)	5.1 (3)	7.1 (4)	−0.3 (3)	−1.2 (3)	−1.1 (3)
$\mathrm{C_{16}}$	3.8 (3)	4.7 (3)	10.8 (6)	−0.4 (2)	0.3 (3)	−1.4 (4)
$\mathrm{C_{17}}$	5.5 (3)	4.7 (3)	8.6 (5)	−1.2 (3)	1.5 (4)	0.4 (3)
$\mathrm{C_{18}}$	5.3 (3)	5.3 (3)	5.6 (3)	−0.7 (3)	−0.0 (3)	0.5 (3)
$\mathrm{C_{19}}$	3.9 (2)	3.2 (2)	5.0 (3)	0.4 (2)	0.2 (2)	0.1 (2)
$\mathrm{C_{20}}$	5.1 (3)	5.1 (3)	5.4 (3)	1.6 (2)	0.2 (3)	−0.7 (2)
$\mathrm{C_{21}}$	5.7 (4)	5.8 (4)	7.9 (5)	0.8 (3)	1.1 (4)	−1.4 (4)
$\mathrm{C_{22}}$	5.1 (3)	4.5 (3)	9.8 (6)	1.8 (3)	−0.6 (4)	−0.7 (4)
$\mathrm{C_{23}}$	5.8 (3)	4.5 (3)	8.4 (5)	0.5 (3)	−2.0 (4)	0.9 (3)
$\mathrm{C_{24}}$	6.0 (3)	4.8 (3)	4.9 (3)	−0.2 (3)	−0.1 (3)	0.8 (3)
$\mathrm{C_{25}}$	4.7 (3)	3.1 (2)	6.0 (3)	0.1 (2)	−0.1 (3)	−0.1 (2)
$\mathrm{C_{26}}$	5.1 (3)	5.1 (3)	8.5 (5)	−1.1 (3)	1.5 (4)	0.5 (3)
$\mathrm{C_{27}}$	4.9 (3)	6.1 (4)	12.5 (7)	−1.5 (3)	1.1 (4)	1.4 (4)
$\mathrm{C_{28}}$	4.2 (3)	4.5 (3)	12.4 (7)	−1.5 (3)	−1.6 (4)	0.4 (4)
$\mathrm{C_{29}}$	6.5 (4)	4.7 (3)	10.5 (6)	−1.1 (3)	−2.5 (4)	−0.2 (4)
$\mathrm{C_{30}}$	5.4 (3)	4.0 (3)	7.0 (4)	−0.5 (2)	−0.7 (3)	−0.1 (3)
$\mathrm{C_{31}}$	5.8 (12)	6.0 (10)	18.8 (27)	1.8 (9)	−1.2 (15)	5.2 (14)
$\mathrm{C_{32}}$	4.6 (14)	16.2 (35)	7.7 (17)	1.6 (19)	1.6 (14)	1.9 (22)
$\mathrm{Cl_1}$	9.8 (4)	9.0 (4)	18.8 (8)	−1.0 (4)	4.7 (6)	0.4 (5)
$\mathrm{Cl_2}$	27.4 (12)	10.4 (5)	11.5 (6)	−0.7 (7)	5.4 (7)	4.4 (4)
$\mathrm{Cl_3}$	14.4 (7)	10.5 (5)	13.8 (7)	−7.1 (5)	−0.2 (6)	1.5 (5)
$\mathrm{Cl_4}$	12.5 (7)	21.7 (11)	12.9 (7)	9.0 (7)	2.9 (6)	2.9 (7)
$\mathrm{Cl_5}$	8.3 (5)	22.2 (12)	41.4 (26)	0.3 (7)	−5.5 (9)	−17.5 (16)
$\mathrm{Cl_6}$	5.9 (4)	32.0 (17)	22.2 (13)	−2.9 (6)	3.0 (6)	−13.8 (13)

[a] The number in parentheses following each datum is the estimated standard deviation in the least significant figure. B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$.

of the pyrrole rings and $\mathrm{C_m}$ denotes the methine carbon atoms.

The nitrosyl ligand is coordinated in a linear fashion with Mn–N–O angles of 177.8 (3) and 176.2 (5)°, an expected feature of $\{\mathrm{MnNO}\}^6$ systems.[15,22] The geometry of the coordinated nitrosyl groups agrees quite well with that observed[23] for $\mathrm{K_3Mn(CN)_5(NO)}$ where the Mn–N(NO) bond distance was 1.66 (1) Å. The Mn–N(NO) bond lengths, 1.641 (2) Å in Mn(TTP)(NO) and 1.644 (5) Å in Mn(TPP)(4-Me-

Table V. Bond Lengths in the Coordination Group, Porphinato Skeleton, and NO Ligand of Mn(TTP)(NO)

type	length, Å	type	length, Å
$\mathrm{Mn{-}N_1}$	2.011 (2)	$\mathrm{C_{a7}{-}C_{b7}}$	1.420 (3)
$\mathrm{Mn{-}N_2}$	2.000 (2)	$\mathrm{C_{a8}{-}C_{b8}}$	1.428 (4)
$\mathrm{Mn{-}N_3}$	2.002 (2)	$\mathrm{C_{a1}{-}C_{m4}}$	1.388 (3)
$\mathrm{Mn{-}N_4}$	2.003 (2)	$\mathrm{C_{a2}{-}C_{m1}}$	1.391 (3)
$\mathrm{Mn{-}N_5}$	1.641 (2)	$\mathrm{C_{a3}{-}C_{m1}}$	1.393 (3)
$\mathrm{N_1{-}C_{a1}}$	1.379 (3)	$\mathrm{C_{a4}{-}C_{m2}}$	1.388 (4)
$\mathrm{N_1{-}C_{a2}}$	1.384 (3)	$\mathrm{C_{a5}{-}C_{m2}}$	1.396 (4)
$\mathrm{N_2{-}C_{a3}}$	1.385 (3)	$\mathrm{C_{a6}{-}C_{m3}}$	1.389 (3)
$\mathrm{N_2{-}C_{a4}}$	1.392 (3)	$\mathrm{C_{a7}{-}C_{m3}}$	1.395 (3)
$\mathrm{N_3{-}C_{a5}}$	1.384 (3)	$\mathrm{C_{a8}{-}C_{m4}}$	1.391 (4)
$\mathrm{N_3{-}C_{a6}}$	1.381 (3)	$\mathrm{C_{b1}{-}C_{b2}}$	1.340 (4)
$\mathrm{N_4{-}C_{a7}}$	1.386 (3)	$\mathrm{C_{b3}{-}C_{b4}}$	1.335 (4)
$\mathrm{N_4{-}C_{a8}}$	1.385 (3)	$\mathrm{C_{b5}{-}C_{b6}}$	1.349 (4)
$\mathrm{C_{a1}{-}C_{b1}}$	1.434 (4)	$\mathrm{C_{b7}{-}C_{b8}}$	1.342 (4)
$\mathrm{C_{a2}{-}C_{b2}}$	1.435 (3)	$\mathrm{C_{m1}{-}C_1}$	1.491 (3)
$\mathrm{C_{a3}{-}C_{b3}}$	1.443 (3)	$\mathrm{C_{m2}{-}C_7}$	1.498 (3)
$\mathrm{C_{a4}{-}C_{b4}}$	1.425 (4)	$\mathrm{C_{m3}{-}C_{13}}$	1.502 (3)
$\mathrm{C_{a5}{-}C_{b5}}$	1.423 (4)	$\mathrm{C_{m4}{-}C_{19}}$	1.507 (3)
$\mathrm{C_{a6}{-}C_{b6}}$	1.434 (4)	$\mathrm{N_5{-}O}$	1.160 (3)

Table VI. Bond Angles in the Coordination Group, Porphinato Skeleton, and Nitric Oxide of Mn(TTP)(NO)

angle	value, deg	angle	value, deg
$\mathrm{N_1{-}Mn{-}N_2}$	88.3 (1)	$\mathrm{C_{a1}{-}C_{b1}{-}C_{b2}}$	107.1 (2)
$\mathrm{N_2{-}Mn{-}N_3}$	88.5 (1)	$\mathrm{C_{a2}{-}C_{b2}{-}C_{b1}}$	107.4 (2)
$\mathrm{N_3{-}Mn{-}N_4}$	88.3 (1)	$\mathrm{C_{a3}{-}C_{b3}{-}C_{b4}}$	107.5 (2)
$\mathrm{N_4{-}Mn{-}N_1}$	88.4 (1)	$\mathrm{C_{a4}{-}C_{b4}{-}C_{b3}}$	107.7 (2)
$\mathrm{N_1{-}Mn{-}N_3}$	156.7 (1)	$\mathrm{C_{a5}{-}C_{b5}{-}C_{b6}}$	107.2 (2)
$\mathrm{N_2{-}Mn{-}N_4}$	163.9 (1)	$\mathrm{C_{a6}{-}C_{b6}{-}C_{b5}}$	107.0 (2)
$\mathrm{N_1{-}Mn{-}N_5}$	99.3 (1)	$\mathrm{C_{a7}{-}C_{b7}{-}C_{b8}}$	107.7 (2)
$\mathrm{N_2{-}Mn{-}N_5}$	102.1 (1)	$\mathrm{C_{a8}{-}C_{b8}{-}C_{b7}}$	107.1 (2)
$\mathrm{N_3{-}Mn{-}N_5}$	96.8 (1)	$\mathrm{N_1{-}C_{a1}{-}C_{m4}}$	125.1 (2)
$\mathrm{N_4{-}Mn{-}N_5}$	101.2 (1)	$\mathrm{N_1{-}C_{a2}{-}C_{m1}}$	125.0 (2)
$\mathrm{Mn{-}N_5{-}O}$	177.8 (3)	$\mathrm{N_2{-}C_{a3}{-}C_{m1}}$	126.1 (2)
$\mathrm{Mn{-}N_1{-}C_{a1}}$	127.5 (2)	$\mathrm{N_2{-}C_{a4}{-}C_{m2}}$	125.0 (2)
$\mathrm{Mn{-}N_1{-}C_{a2}}$	125.8 (2)	$\mathrm{N_3{-}C_{a5}{-}C_{m2}}$	124.6 (2)
$\mathrm{Mn{-}N_2{-}C_{a3}}$	126.5 (2)	$\mathrm{N_3{-}C_{a6}{-}C_{m3}}$	124.9 (2)
$\mathrm{Mn{-}N_2{-}C_{a4}}$	128.3 (2)	$\mathrm{N_4{-}C_{a7}{-}C_{m3}}$	125.2 (2)
$\mathrm{Mn{-}N_3{-}C_{a5}}$	127.6 (2)	$\mathrm{N_4{-}C_{a8}{-}C_{m4}}$	125.5 (2)
$\mathrm{Mn{-}N_3{-}C_{a6}}$	126.0 (2)	$\mathrm{C_{b1}{-}C_{a1}{-}C_{m4}}$	124.4 (2)
$\mathrm{Mn{-}N_4{-}C_{a7}}$	127.2 (2)	$\mathrm{C_{b2}{-}C_{a2}{-}C_{m1}}$	124.7 (2)
$\mathrm{Mn{-}N_4{-}C_{a8}}$	127.9 (2)	$\mathrm{C_{b3}{-}C_{a3}{-}C_{m1}}$	124.4 (2)
$\mathrm{C_{a1}{-}N_1{-}C_{a2}}$	104.9 (2)	$\mathrm{C_{b4}{-}C_{a4}{-}C_{m2}}$	124.7 (2)
$\mathrm{C_{a3}{-}N_2{-}C_{a4}}$	105.0 (2)	$\mathrm{C_{b5}{-}C_{a5}{-}C_{m2}}$	124.7 (2)
$\mathrm{C_{a5}{-}N_3{-}C_{a6}}$	104.8 (2)	$\mathrm{C_{b6}{-}C_{a6}{-}C_{m3}}$	124.4 (2)
$\mathrm{C_{a7}{-}N_4{-}C_{a8}}$	104.8 (2)	$\mathrm{C_{b7}{-}C_{a7}{-}C_{m3}}$	124.7 (2)
$\mathrm{N_1{-}C_{a1}{-}C_{b1}}$	110.5 (2)	$\mathrm{C_{b8}{-}C_{a8}{-}C_{m4}}$	124.4 (2)
$\mathrm{N_1{-}C_{a2}{-}C_{b2}}$	110.1 (2)	$\mathrm{C_{a2}{-}C_{m1}{-}C_{a3}}$	122.7 (2)
$\mathrm{N_2{-}C_{a3}{-}C_{b3}}$	109.5 (2)	$\mathrm{C_{a4}{-}C_{m2}{-}C_{a5}}$	123.7 (2)
$\mathrm{N_2{-}C_{a4}{-}C_{b4}}$	110.1 (2)	$\mathrm{C_{a6}{-}C_{m3}{-}C_{a7}}$	123.1 (2)
$\mathrm{N_3{-}C_{a5}{-}C_{b5}}$	110.6 (2)	$\mathrm{C_{a8}{-}C_{m4}{-}C_{a1}}$	123.5 (2)
$\mathrm{N_3{-}C_{a6}{-}C_{b6}}$	110.3 (2)		
$\mathrm{N_4{-}C_{a7}{-}C_{b7}}$	110.1 (2)		
$\mathrm{N_4{-}C_{a8}{-}C_{b8}}$	110.1 (2)		

Table VII. Bond Lengths in the Coordination Group, Porphinato Skeleton, and 4-Methylpiperidine Ligand of Mn(TPP)(4-MePip)(NO)[a]

type	length, Å	type	length, Å	type	length, Å
$\mathrm{Mn{-}N_1}$	2.031 (4)	$\mathrm{C_{m1}{-}C_7}$	1.517 (8)	$\mathrm{C_{a6}{-}C_{b6}}$	1.438 (8)
$\mathrm{Mn{-}N_2}$	2.023 (4)	$\mathrm{C_{m2}{-}C_{a4}}$	1.399 (8)	$\mathrm{C_{a7}{-}C_{b7}}$	1.430 (9)
$\mathrm{Mn{-}N_3}$	2.028 (4)	$\mathrm{C_{m2}{-}C_{a5}}$	1.415 (8)	$\mathrm{C_{a8}{-}C_{b8}}$	1.454 (8)
$\mathrm{Mn{-}N_4}$	2.027 (4)	$\mathrm{C_{m2}{-}C_{13}}$	1.496 (8)	$\mathrm{C_{b1}{-}C_{b2}}$	1.344 (9)
$\mathrm{Mn{-}N_5}$	1.644 (5)	$\mathrm{C_{m3}{-}C_{a6}}$	1.384 (8)	$\mathrm{C_{b3}{-}C_{b4}}$	1.351 (9)
$\mathrm{Mn{-}N_6}$	2.206 (5)	$\mathrm{C_{m3}{-}C_{a7}}$	1.390 (8)	$\mathrm{C_{b5}{-}C_{b6}}$	1.342 (9)
$\mathrm{N_1{-}C_{a1}}$	1.373 (8)	$\mathrm{C_{m3}{-}C_{19}}$	1.505 (8)	$\mathrm{C_{b7}{-}C_{b8}}$	1.352 (9)
$\mathrm{N_1{-}C_{a2}}$	1.363 (8)	$\mathrm{C_{m4}{-}C_{a8}}$	1.423 (8)	$\mathrm{N_5{-}O}$	1.176 (7)
$\mathrm{N_2{-}C_{a3}}$	1.371 (7)	$\mathrm{C_{m4}{-}C_{a1}}$	1.378 (9)	$\mathrm{N_6{-}C_1}$	1.465 (9)
$\mathrm{N_2{-}C_{a4}}$	1.367 (7)	$\mathrm{C_{m4}{-}C_{25}}$	1.497 (9)	$\mathrm{N_6{-}C_5}$	1.455 (9)
$\mathrm{N_3{-}C_{a5}}$	1.368 (7)	$\mathrm{C_{a1}{-}C_{b1}}$	1.449 (8)	$\mathrm{C_1{-}C_2}$	1.483 (11)
$\mathrm{N_3{-}C_{a6}}$	1.377 (7)	$\mathrm{C_{a2}{-}C_{b2}}$	1.451 (8)	$\mathrm{C_2{-}C_3}$	1.506 (11)
$\mathrm{N_4{-}C_{a7}}$	1.376 (7)	$\mathrm{C_{a3}{-}C_{b3}}$	1.457 (8)	$\mathrm{C_3{-}C_4}$	1.477 (11)
$\mathrm{N_4{-}C_{a8}}$	1.365 (7)	$\mathrm{C_{a4}{-}C_{b4}}$	1.450 (8)	$\mathrm{C_4{-}C_5}$	1.502 (10)
$\mathrm{C_{m1}{-}C_{a2}}$	1.404 (8)	$\mathrm{C_{a5}{-}C_{b5}}$	1.447 (8)	$\mathrm{C_3{-}C_6}$	1.503 (12)
$\mathrm{C_{m1}{-}C_{a3}}$	1.395 (8)				

[a] The numbers in parentheses are the estimated standard deviations.

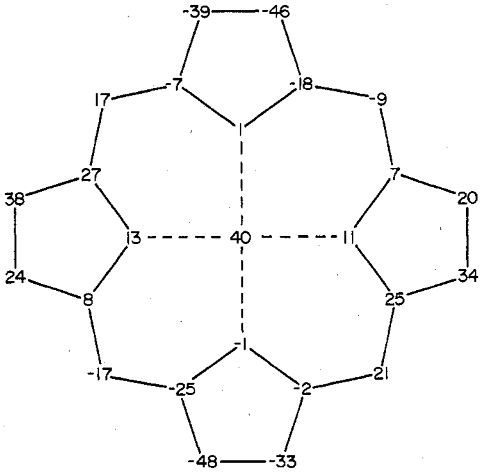

Figure 3. Formal diagram of the porphinato core in the Mn(TTP)(NO) molecule with the same relative orientation as in Figure 1. The perpendicular displacement of each atom, in units of 0.01 Å, from the mean plane of the porphinato core is displayed.

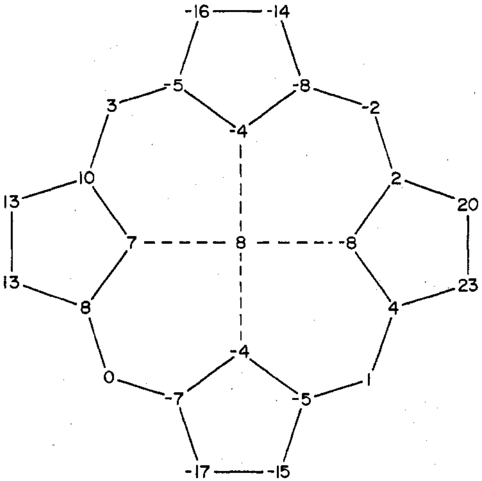

Figure 4. Formal diagram of the porphinato core in the Mn(TPP)(4-MePip)(NO) molecule with the same relative orientation as in Figure 2. The perpendicular displacement of each atom, in units of 0.01 Å, from the mean plane of the porphinato core is displayed.

Pip)(NO), appear not to be affected by the addition of the sixth ligand. Unlike the iron systems,[11,12] the addition of a sixth ligand does not significantly change the NO stretching frequency.

The addition of the sixth ligand does appear to influence the value of the Mn–N(porphinato) bond distance. In Mn(TTP)(NO), Mn–N is 2.004 (5) Å; the Mn–N distance in the six-coordinate complex is increased to 2.027 (3) Å. It is possible that the modest core expansion in the six-coordinate complex slightly alleviates the tight contacts between the axial nitrosyl nitrogen atom and the nitrogen atoms of the porphinato core (vide infra). It should be noted that the differences in the average porphinato bond parameters (Table IX) are in the direction expected for a core expansion.[24] The Mn–N(porphinato) bond distances in both nitrosyl derivatives are considerably shorter than the Mn–N bond distances observed in high-spin four-coordinate Mn(TPP) (>2.082 Å)[25] and in high-spin five-coordinate Mn(TPP)(1-MeIm) (2.128 (7) Å).[26] The observed Mn–N bond distances in both nitrosyl

Table VIII. Bond Angles in the Coordination Group, Porphinato Skeleton and 4-Methylpiperidine Ligand of Mn(TPP)(4-MePip)(NO)[a]

angle	value, deg	angle	value, deg
N_1-Mn-N_2	89.8 (2)	N_2-C_{a4}-C_{b4}	110.6 (5)
N_1-Mn-N_3	175.2 (2)	C_{m2}-C_{a4}-C_{b4}	123.0 (5)
N_1-Mn-N_4	89.8 (2)	N_3-C_{a5}-C_{m2}	126.0 (5)
N_1-Mn-N_5	90.3 (2)	N_3-C_{a5}-C_{b5}	110.0 (5)
N_1-Mn-N_6	86.9 (2)	C_{m2}-C_{a5}-C_{b5}	123.9 (5)
N_2-Mn-N_3	89.8 (2)	N_3-C_{a6}-C_{m3}	126.0 (5)
N_2-Mn-N_4	173.3 (2)	N_3-C_{a6}-C_{b6}	108.7 (5)
N_2-Mn-N_5	94.1 (2)	C_{m3}-C_{a6}-C_{b6}	125.3 (5)
N_2-Mn-N_6	85.7 (2)	N_4-C_{a7}-C_{m3}	126.1 (5)
N_3-Mn-N_4	90.0 (2)	N_4-C_{a7}-C_{b7}	108.9 (5)
N_3-Mn-N_5	94.4 (2)	C_{m3}-C_{a7}-C_{b7}	124.9 (5)
N_3-Mn-N_6	88.3 (2)	N_4-C_{a8}-C_{m4}	125.8 (5)
N_4-Mn-N_5	92.6 (2)	N_4-C_{a8}-C_{b8}	110.0 (5)
N_4-Mn-N_6	87.6 (2)	C_{m4}-C_{a8}-C_{b8}	124.2 (5)
N_5-Mn-N_6	177.2 (2)	C_{b2}-C_{b1}-C_{a1}	107.1 (5)
C_{a1}-N_1-C_{a2}	106.2 (4)	C_{b1}-C_{b2}-C_{a2}	106.8 (5)
C_{a3}-N_2-C_{a4}	106.3 (4)	C_{b4}-C_{b3}-C_{a3}	107.3 (5)
C_{a5}-N_3-C_{a6}	106.6 (4)	C_{b3}-C_{b4}-C_{a4}	106.2 (5)
C_{a7}-N_4-C_{a8}	106.8 (4)	C_{b6}-C_{b5}-C_{a5}	106.1 (5)
C_{a2}-C_{m1}-C_7	117.8 (5)	C_{b5}-C_{b6}-C_{a6}	108.6 (5)
C_{a3}-C_{m1}-C_7	118.4 (5)	C_{b8}-C_{b7}-C_{a7}	108.7 (5)
C_{a2}-C_{m1}-C_{a3}	123.8 (5)	C_{b7}-C_{b8}-C_{a8}	105.6 (5)
C_{a4}-C_{m2}-C_{13}	118.7 (5)	C_5-N_6-C_1	113.2 (5)
C_{a5}-C_{m2}-C_{13}	117.7 (5)	N_6-C_1-C_2	115.0 (6)
C_{a4}-C_{m2}-C_{a5}	123.5 (5)	C_1-C_2-C_3	115.0 (7)
C_{a6}-C_{m3}-C_{19}	117.6 (5)	C_2-C_3-C_4	109.2 (6)
C_{a7}-C_{m3}-C_{19}	117.6 (5)	C_2-C_3-C_6	115.7 (7)
C_{a6}-C_{m3}-C_{a7}	124.8 (5)	C_4-C_3-C_6	115.1 (7)
C_{a8}-C_{m4}-C_{25}	117.2 (5)	C_3-C_4-C_5	115.5 (6)
C_{a1}-C_{m4}-C_{25}	119.1 (5)	C_4-C_5-N_6	116.3 (6)
C_{a8}-C_{m4}-C_{a1}	123.7 (5)	Mn-N_1-C_{a1}	125.6 (4)
N_1-C_{a1}-C_{m4}	126.8 (5)	Mn-N_1-C_{a2}	126.1 (4)
N_1-C_{a1}-C_{b1}	109.8 (5)	Mn-N_2-C_{a3}	126.6 (4)
C_{m4}-C_{a1}-C_{b1}	123.4 (5)	Mn-N_2-C_{a4}	127.1 (4)
N_1-C_{a2}-C_{m1}	126.0 (5)	Mn-N_3-C_{a5}	126.9 (4)
N_1-C_{a2}-C_{b2}	110.2 (5)	Mn-N_3-C_{a6}	126.4 (4)
C_{m1}-C_{a2}-C_{b2}	123.8 (5)	Mn-N_4-C_{a7}	126.4 (4)
N_2-C_{a3}-C_{m1}	126.3 (5)	Mn-N_4-C_{a8}	126.4 (4)
N_2-C_{a3}-C_{b3}	109.5 (5)	Mn-N_5-O	176.2 (5)
C_{m1}-C_{a3}-C_{b3}	124.1 (5)	Mn-N_6-C_1	117.4 (4)
N_2-C_{a4}-C_{m2}	126.4 (5)	Mn-N_6-C_5	116.4 (4)

[a] The numbers in parentheses are the estimated standard deviations.

Table IX. Average Bond Lengths and Angles[a]

type	value in Mn(TPP)(4-MePip)(NO)	value in Mn(TTP)(NO)
	A. Bond Lengths, Å	
Mn-N	2.027 (3)	2.004 (5)
N-C_a	1.370 (5)	1.384 (4)
C_a-C_m	1.398 (15)	1.391 (3)
C_a-C_b	1.447 (9)	1.430 (8)
C_b-C_b	1.347 (5)	1.342 (6)
Ct···C_m[b]	3.441	3.426
Ct···N[b]	2.025	1.975
	B. Bond Angles, Deg	
C_a-N-C_a	106.5 (3)	104.9 (1)
N-C_a-C_b	109.7 (6)	110.2 (3)
N-C_a-C_m	126.2 (3)	125.2 (2)
C_a-C_m-C_a	124.0 (6)	123.2 (4)
C_a-C_b-C_b	107.0 (11)	107.3 (3)

[a] The number in parentheses is the estimated standard deviation calculated on the assumption that all values are drawn from the same population. [b] Ct is the symbol used for the center of the porphinato ligand.

derivatives are thus seen to be consistent with the assignment of a low-spin ground state.

Figures 3 and 4 are formal diagrams of the porphinato core displaying the perpendicular displacement of each atom from the mean plane of the core in units of 0.01 Å for Mn(TTP)(NO) and Mn(TPP)(4-MePip)(NO), respectively. It is seen that the cores in both derivatives display quasi-D_{2d} ruffling with significantly larger displacements observed in the five-coordinate complex. In Mn(TTP)(NO), the manganese atom is displaced, toward the nitrosyl ligand, 0.40 Å from the mean plane of the core and 0.34 Å from the mean plane of the four porphinato nitrogen atoms. Of course, the addition of the sixth ligand leads to a substantially smaller displacement of the manganese atom in Mn(TPP)(4-MePip)(NO): 0.08 Å from the mean plane of the core and 0.10 Å from the mean plane of the four porphinato nitrogen atoms. The relatively short Mn-N(NO) bond distance and the concomitant tight N···N(NO) contacts apparently preclude centering of the metal atom in the porphinato plane. The observed N···N contacts in Mn(TPP)(4-MePip)(NO) are 2.674 Å; these would decrease to an extremely tight 2.610 Å for an in-plane manganese atom. The modest expansion of the porphinato core, relative to that of the five-coordinate complex, also serves to increase these N···N nonbonded contacts. It appears that this displacement of the manganese atom is responsible for the relatively long axial Mn-N(4-MePip) bond of 2.206 (5) Å. The Ct···N(4-MePip) distance of 2.10 Å engenders difficult steric interactions between the axial ligand and atoms of the porphinato core.[27]

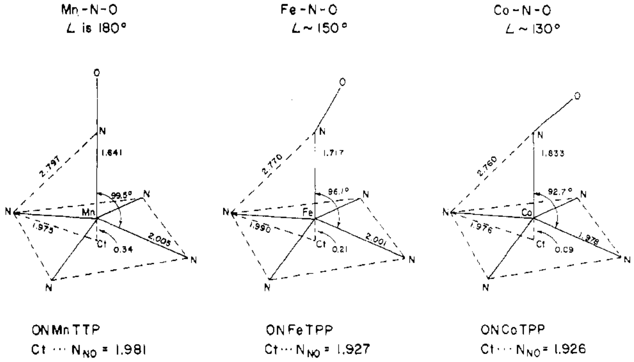

Figure 5. Diagrams of the five-coordination group around each metal atom in the nitrosylmetalloporphyrins of manganese, iron, and cobalt. When more than one value for a given type of parameter is available, the averaged (C_{4v}) value is shown.

Figure 5 provides a comparison of the coordination group geometry of the five-coordinate nitrosylmetalloporphyrins of cobalt,[14] iron,[13] and manganese. The parameters of the coordinated nitrosyl and porphyrin are typical of these low-spin derivatives. The M–N(NO) distances and M–N–O angles suggest the ordering Mn > Fe > Co for π interaction in the axial NO bonding system.

The expected (and observed) inequivalence of the M–N(NO) bond distances provides a set of complexes for examining the effects of the nonbonded repulsion between the fifth ligand and the porphinato core on the magnitudes of the displacement of the metal atom out of the porphinato plane. The low-spin state of each metal atom could allow[28] the metal atom to be centered in the porphinato plane. Thus, to a first approximation, the structures of these three nitrosyl derivatives would be square pyramidal with the metal atom centered in the hole of the porphinato ligand, essentially equal M–N(porphinato) and unequal M–N(NO) bond distances. This would lead to the three complexes having different nonbonded interactions between the nitrosyl nitrogen atom and the nitrogen atoms of the porphinato core. Diminution of the nonbonded repulsion in this series can be achieved only by stretching the M–N(NO) bond or by displacing the metal atom out of plane. Hence, any displacement of the metal atom can be considered as an observation of the effects of nonbonded repulsions and the expected order of the metal atom displacements would be Mn

> Fe > Co. As is seen in Figure 5, the metal atom displacements do follow this order. Moreover, the essentially constant Ct···N(NO) (1.93–1.98 Å) and particularly the N···N(NO) nonbonded distances (2.76–2.79 Å) provide confirmation that the nitrosyl nitrogen atom position (and by implication the metal atom position as well) is governed by minimizing the axial nonbonded interactions. We conclude that the minimum N···N nonbonded separation for an axial ligand in five-coordinate metalloporphyrins is ~2.80 Å; thus, structural adjustments must occur to prevent N···N separations significantly less than 2.80 Å.

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Supplementary Material Available: Listings of the structure factor amplitudes (×10) for both complexes (46 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of (1,8-Bis(2-pyridyl)-3,6-dithiaoctane)copper(I) Hexafluorophosphate and Perchlorato(1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(II) Perchlorate: Stereodynamics of the Copper(II)–Copper(I) Couple

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The crystal and molecular structures of the title compounds have been determined by single-crystal X-ray diffraction using counter data to *R* values of 0.061 for the copper(I) complex (**1**) and 0.068 for the copper(II) complex (**2**). The unit cell constants for **1** are $a = 8.219\ (1)$ Å, $b = 22.543\ (3)$ Å, and $c = 11.044\ (1)$ Å; the space group is *Pbcn*, and $Z = 4$. For **2**, $a = 8.902\ (1)$ Å, $b = 21.343\ (2)$ Å, $c = 11.879\ (1)$ Å, $\beta = 108.03\ (1)°$, the space group is $P2_1/c$, and $Z = 4$. Coordination about **1** is tetrahedral and about **2** is square pyramidal.

We have chosen to approach a description of the copper site of blue proteins via the characterization of reversible copper(II)–copper(I) redox systems. The accumulated evidence suggests that the stereochemistry of the oxidized and reduced species,[1,2] the presence of sulfur,[3,4] or the presence of heterocyclic nitrogen donor atoms govern the reversibility and redox potential of the couple. Accordingly, we have reexamined the copper(II) and copper(I) complexes with 1,8-bis(pyridyl)-3,6-dithiaoctane (pdto), first described by Goodwin and Lions about 20 years ago.[5]

Experimental Section

Syntheses. 1,8-Bis(2-pyridyl)-3,6-dithiaoctane, (1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(II) perchlorate, and (1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(I) hexafluorophosphate were prepared by the methods of Goodwin and Lions.[5]

Electrochemical Methods. Electrochemical measurements were performed on a PAR Model 174A polarographic analyzer equipped with a PAR Model 175 function generator. Hanging mercury drop, platinum, carbon paste, or gold thin-cell test electrodes were used, as appropriate. A Chemtrix double-junction Ag/AgCl reference electrode was used in all cases, as was 0.1 N KNO_3 supporting electrolyte. Coulometric measurements were made with an Alpha Research Model 701 precision digital current intergrating coulometer.

X-ray Methods. A crystal of the Cu(I) complex was mounted with the [130] axis coincident with the ϕ axis of a Picker FACS-I diffractometer. Examination of the reciprocal lattice showed *mmm* symmetry and systematic extinctions characteristic of the space group *Pbcn*. Lattice constants were determined by carefully measuring the $\pm 2\theta$ copper radiation doublet from 16 reflections with $2\theta > 60°$, peak fitting the profiles, and then determining the cell constants by least-squares analysis. The resultant constants are $a = 8.219\ (1)$, $b = 22.543\ (3)$, and $c = 11.044\ (1)$ Å. The calculated density of 1.665 g cm^{-3} for $CuC_{16}H_{20}F_6N_2PS_2$ agrees with the experimental density 1.66 g cm^{-3} (flotation in CBr_4 and CCl_4) for $Z = 4$.

Three-dimensional intensity data were collected using Ni-filtered Cu Kα radiation on a modified computer-controlled Picker FACS-I diffractometer. A fixed scan rate (2° min^{-1}), variable scan width (2.4° + 0.72 tan θ) θ–2θ scan with 10-s background measurements at the