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Metal Complexes with Tetrapyrrole Ligands. 30.[1] The Manganese-Nitrogen Triple Bond. Synthesis and Molecular Stereochemistry of (5,15-Dimethyl-2,3,7,8,12,13,17,18-octaethyl-5*H*,15*H*-porphinato)nitridomanganese(V)

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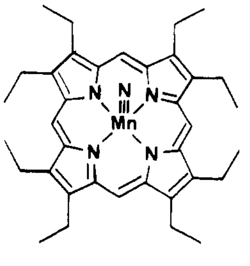
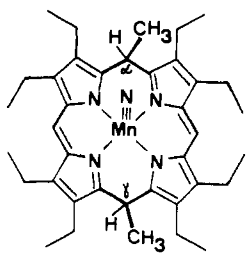
Reductive methylation of (2,3,7,8,12,13,17,18-octaethylporphinato)nitridomanganese(V) [MnN(OEP)] yields (5,15-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5*H*,15*H*-porphinato)nitridomanganese(V) [$MnN(OEPMe_2)$]. The fact that 12% of the nitridomanganese(V) species survives the strong reducing conditions (sodium anthracenide) underlines the reluctance of the $Mn\equiv N$ triple bond in MnN(OEP) to undergo reduction. Diamagnetic $MnN(OEPMe_2)$ is identified by IR, ^1H NMR, electronic absorption, and mass spectra. Its red crystals (with a green luster) are isomorphous with the previously characterized oxotitanium(IV) porphodimethene, $TiO(OEPMe_2)$. Crystal data: monoclinic, space group $C2/c$, a = 16.154 (3) Å, b = 15.934 (4) Å, c = 14.600 (3) Å, β = 114.08 (1)°, and Z = 4. The calculated and observed densities are 1.22 g/cm^3. A total of 4027 observed data were used in the structure determination. The final values of the discrepancy indices were R_1 = 0.042 and R_2 = 0.052. $MnN(OEPMe_2)$ has the 5-methyl and 15-methyl groups and the nitrido ligand occupying syn-axial positions on the rooflike folded porphodimethene core. The Mn atom is displaced by 0.43 Å from the mean plane of the four nitrogen atoms. The average equatorial Mn-N_p bond distance is 2.006 (4) Å. The axial manganese-nitrogen distance is 1.512 (2) Å—the shortest ever observed in a terminal metal-nitrogen bond. This reinforces the view of the MnN group containing a metal-nitrogen triple bond with strong covalent character.

Manganese porphyrinates in which the central metal appears in the high oxidation states +4 or +5 are of continuing interest since Calvin discussed their occurrence in the water-splitting portion of photosynthesis.[4,5] Normally, manganese appears as Mn^{III} in porphyrins.[5,6] A peroxomanganese(IV) porphyrin, $Mn(O_2)(TPP)$,[7] was thought to be the reaction product of the reversible oxygenation of Mn(TPP) at low temperatures.[8-10] The search for (oxometallo)porphyrins that could serve as catalysts for the epoxidation of olefins and the hydroxylation of aliphatic compounds further stimulated research on Mn^{IV} and Mn^V porphyrins.[11-16] The only well-defined M^{IV} compounds at present seem to be $[Mn(TPP)(N_3)]_2O$[15] and $Mn(TPP)(OMe)_2$;[16] MnO(TPP), an oxomanganese(IV) complex,[14] and MnO(TPP)Cl, a chlorooxomanganese(V) complex,[13] are only partly characterized because of their high reactivity. The Mn^{IV} and Mn^V porphyrins are obtained by oxidation of Mn^{III} porphyrins with hypochlorite or iodosylbenzene.

Efforts at Darmstadt, starting with the aim of preparing high-oxidation-state manganese porphyrins, resulted in the isolation of surprisingly stable nitridomanganese(V) porphyrins, MnN(OEP) (**1**) and MnN(TTP).[17] These compounds were obtained by hypochlorite oxidation of Mn(OMe)(OEP) in the presence of ammonia; a similar reaction later served to prepare the nitridochromium(V) porphyrins CrN(OEP) and CrN(TTP).[1] The nitridomanganese(V) porphyrins are the first manganese complexes with terminal nitrido ligands,[18a] while a nitridochromium(V) ethylenebis(salicylidenealdimine) chelate has been described quite recently.[18b]



1: MnN(OEP)



2: $MnN(OEPMe_2)$

An X-ray diffraction study of these Mn^V complexes seemed necessary to measure the length of the presumed $Mn\equiv N$ triple bond as well as to supplement the stereochemistry of manganese porphyrins previously determined at Notre Dame.[19-22] However, crystals of suitable quality for X-ray diffraction

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(7) Abbreviations used: TPP, the dianion of *meso*-tetraphenylporphyrin; OEP, the dianion of octaethylporphyrin; TTP, the dianion of *meso*-tetra-*p*-tolylporphyrin; $OEPMe_2$, the dianion of 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphodimethene; Me, methyl; N_p, nitrogen atom of a porphyrin or porphodimethene ligand; py, pyridine.

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studies have not yet been obtained. Therefore, we prepared a porphodimethene complex, namely (5,15-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5*H*,15*H*-porphinato)nitridomanganese(V), MnN(OEPMe$_2$) (**2**), because the related titanyl porphodimethene[23] TiO(OEPMe$_2$) had given excellent crystals and a diffraction analysis[24] provided accurate parameters of the titanyl (TiO^{2+}) cation.

This paper describes the reductive methylation of **1**, the identification of the product, **2**, and its crystal and molecular structure determination.

Experimental Section

Materials. (2,3,7,8,12,13,17,18-Octaethylporphinato)nitridomanganese(V), MnN(OEP) (**1**), was prepared,[17] and tetrahydrofuran (THF), sodium anthracenide, and methyl iodide (MeI) were used[25,26] as previously described. Alumina (Al$_2$O$_3$, I, neutral) was purchased from Woelm Pharmaceuticals and deactivated with water to the required grade.

Apparatus. Spectra were obtained with the following instruments: Varian MAT 311A (electron-impact mass spectrum), Perkin-Elmer 325 (IR spectrum), Unicam SP 800 B (electronic absorption spectrum), Varian EM 360 L (^{1}H NMR spectrum). The elemental analysis was performed by the Analytische Laboratorien (formerly A. Bernhard), D-5251 Elbach, West Germany, with a sample dried at 50 °C and 10^{-3} torr.

Synthesis of (5,15-Dimethyl-2,3,7,8,12,13,17,18-octaethyl-5*H*,15*H*-porphinato)nitridomanganese(V) MnN(OEPMe$_2$) (2). To a solution of 270 mg (0.45 mmol) of MnN(OEP) (**1**) in 200 mL dry deoxygenated THF was added (with stirring under Ar) a solution of sodium anthracenide in THF (from a syringe). The injection was ended when the color changes red–green–red had occurred. MeI (5 mL) was then rapidly added. The color of the solution turned orange. The solution was evaporated in vacuo, the residue extracted with cyclohexane, and the extractant was filtered. Unreacted MnN(OEP) and unidentified manganese(III) octaethylporphyrins remained in the residue. The cyclohexane phase was evaporated to dryness in vacuo and the orange solid chromatographed on neutral alumina (grade III; column 60.3 cm) with cyclohexane. Following the anthracene, an orange band of MnN(OEPMe$_2$) was eluted. The band was taken to dryness in vacuo. Recrystallization of the residue from CH$_2$Cl$_2$/MeOH yielded MnN(OEPMe$_2$) (32 mg, 11%) as prisms with a dark green luster (red in transmitted light), some of which were suitable for X-ray diffraction studies; mol wt 631.8. Anal. Calcd for C$_{38}$H$_{50}$MnN$_5$: C, 72.24; H, 7.98; N, 11.08; Mn, 8.70. Found: C, 72.09; H, 7.82; N, 10.96; Mn, 9.13 (difference). Optical spectrum (toluene): $\lambda_{\max}$ (log ϵ) 386 (4.17), 476 (4.63), 516 nm (4.55). IR (KBr): 1050 cm^{-1} (Mn≡N); 1630, 1220, 1018, 877 cm^{-1} (porphodimethene bands[23]). ^{1}H NMR [CDCl$_3$; δ values vs. internal Me$_4$Si (multiplicity, assignments)]: δ 1.14 (t, CH$_2$C*H*$_3$), 1.18 (t, CH$_2$C*H*$_3$), 2.13 (d, 5-CH$_3$, 15-CH$_3$), 2.50 (q, C*H*$_2$CH$_3$), 2.64 (q, C*H*$_2$CH$_3$), 4.39 (q, 5-CH, 15-CH), 7.00 (s, 10-CH, 20-CH). Mass spectrum [*m/e* (assignment, intensity)]: 631 (MnN(OEPMe$_2$)$^+$, 79%), 616 (MnN(OEPMe)$^+$, 100%), 601 (MnN(OEP)$^+$, 26%), 587 (Mn(OEP)$^+$, 67%), 315.5 (MnN(OEPMe$_2$)$^{2+}$, 15%), 308 (MnN(OEPMe)$^{2+}$, 11%), 300.5 (MnN(OEP)$^{2+}$, 22%), 293.5 (Mn(OEP)$^{2+}$, 19%).

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

atom	x	y	z
Mn	0	0.214721(20)	1/4
N(1)	0.13319(9)	0.18984(8)	0.29996(9)
N(2)	0.00656(9)	0.18613(8)	0.38637(9)
N(3)	0	0.30959(13)	1/4
C(a1)	0.18553(11)	0.20207(10)	0.24917(12)
C(a2)	0.19257(10)	0.16107(10)	0.39514(11)
C(a3)	0.08005(11)	0.15354(10)	0.46916(11)
C(a4)	−0.05979(11)	0.19796(10)	0.41890(12)
C(b1)	0.27783(11)	0.18075(11)	0.30774(12)
C(b2)	0.28222(11)	0.15586(10)	0.40023(12)
C(b3)	0.05517(11)	0.14315(10)	0.55152(11)
C(b4)	−0.03261(12)	0.17227(11)	0.52008(12)
C(m1)	0.14893(11)	0.23633(12)	0.14505(13)
C(1)	0.14241(14)	0.33298(14)	0.14215(16)
C(m2)	0.16545(11)	0.14377(10)	0.47118(11)
C(11)	0.35284(12)	0.18149(14)	0.27208(15)
C(12)	0.36451(17)	0.09827(19)	0.22880(22)
C(21)	0.36509(12)	0.13044(12)	0.49127(14)
C(22)	0.37827(18)	0.03759(17)	0.50553(21)
C(31)	0.11375(13)	0.10632(12)	0.65140(12)
C(32)	0.10600(22)	0.01318(16)	0.65862(18)
C(41)	−0.08980(14)	0.17690(15)	0.57939(14)
C(42)	−0.14998(18)	0.10176(20)	0.56701(19)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

Table IV. Bond Lengths (Å) in the Coordination Group and Macrocycle Skeleton[a]

Mn–N(1)	2.009 (1)	C(a4)–C(b4)	1.419 (2)
Mn–N(2)	2.003 (1)	C(a4)–C(m1)′	1.491 (2)
Mn–N(3)	1.512 (2)	C(b1)–C(b2)	1.381 (2)
N(1)–C(a1)	1.347 (2)	C(b1)–C(11)	1.501 (2)
N(1)–C(a2)	1.405 (2)	C(b2)–C(21)	1.507 (2)
N(2)–C(a3)	1.403 (2)	C(b3)–C(b4)	1.380 (2)
N(2)–C(a4)	1.351 (2)	C(b3)–C(31)	1.497 (2)
C(a1)–C(b1)	1.424 (2)	C(b4)–C(41)	1.504 (2)
C(a1)–C(m1)	1.492 (2)	C(m1)–C(1)	1.543 (3)
C(a2)–C(b2)	1.422 (2)	C(11)–C(12)	1.513 (3)
C(a2)–C(m2)	1.378 (2)	C(21)–C(22)	1.497 (3)
C(a3)–C(b3)	1.424 (2)	C(31)–C(32)	1.497 (3)
C(a2)–C(m2)	1.377 (2)	C(41)–C(42)	1.506 (3)

[a] The figures in parentheses are the estimated standard deviations in the last significant figure. Primed and unprimed symbols denote a pair of atoms related by the twofold axis.

Table V. Bond Angles (deg) in the Coordination Group and Macrocycle Skeleton[a]

N(1)MnN(1)′	157.24 (8)	N(2)C(a4)C(m1)′	122.6 (1)
N(1)MnN(2)	88.84 (5)	C(b4)C(a4)C(m1)′	125.4 (1)
N(1)MnN(2)′	86.01 (5)	C(a1)C(b1)C(b2)	106.2 (1)
N(1)MnN(3)	101.38 (4)	C(a1)C(b1)C(11)	125.8 (2)
N(2)MnN(2)′	153.70 (8)	C(b2)C(b1)C(11)	127.9 (2)
N(2)MnN(3)	103.15 (4)	C(a2)C(b2)C(b1)	106.7 (1)
C(a1)N(1)C(a2)	105.2 (1)	C(a2)C(b2)C(21)	125.5 (2)
C(a1)N(1)Mn	126.2 (1)	C(b1)C(b2)C(21)	127.8 (2)
C(a2)N(1)Mn	128.4 (1)	C(a3)C(b3)C(b4)	106.6 (1)
C(a3)N(2)C(a4)	105.2 (1)	C(a3)C(b3)C(31)	125.7 (2)
C(a3)N(2)Mn	128.6 (1)	C(b4)C(b3)C(31)	127.7 (2)
C(a4)N(2)Mn	126.2 (1)	C(a4)C(b4)C(b3)	106.4 (1)
N(1)C(a1)C(b1)	111.9 (1)	C(a4)C(b4)C(41)	125.7 (2)
N(1)C(a1)C(m1)	122.5 (1)	C(b3)C(b4)C(41)	127.9 (2)
C(b1)C(a1)C(m1)	125.6 (1)	C(a1)C(m1)C(a4)′	111.6 (1)
N(1)C(a2)C(b2)	109.9 (1)	C(a1)C(m1)C(1)	112.8 (1)
N(1)C(a2)C(m2)	123.3 (1)	C(a4)′C(m1)C(1)	110.8 (1)
C(b2)C(a2)C(m2)	126.8 (1)	C(a2)C(m2)C(a3)	127.3 (1)
N(2)C(a3)C(b3)	109.8 (1)	C(b1)C(11)C(12)	113.2 (2)
N(2)C(a3)C(m2)	123.2 (1)	C(b2)C(21)C(22)	114.4 (2)
C(b3)C(a3)C(m2)	126.4 (1)	C(b3)C(31)C(32)	114.8 (2)
N(2)C(a4)C(b4)	111.9 (1)	C(b4)C(41)C(42)	114.2 (2)

[a] The figures in parentheses are the estimated standard deviations in the last significant figure. Primed and unprimed symbols denote a pair of atoms related by the twofold axis.

Structure Determination. The molecular structure of MnN(OEPMe$_2$) was obtained by using methods and programs previously described.[24,27] The space group is *Cc* or *C*2/*c*, and the lattice constants are a = 16.154 (3) Å, b = 15.934 (4) Å, c = 14.600 (3) Å, β = 114.08 (1)°, and Z = 4. These constants gave a calculated density of 1.22 g/cm^3 (observed 1.22 g/cm^3). All independent data to 2θ = 58.7° (with Mo Kα, λ 0.71073 Å) were measured; a total of 4027 observed data were obtained and used in the structure determination.

The initial choice of *C*2/*c* requires that the molecule have C_2 symmetry; this choice of space group was fully confirmed by all

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(27) Programs used in this study included local modifications of Jacobson's ALFF and ALLS, Busing and Levy's ORFFE and ORFLS, and Johnson's ORTEP2. Atomic form factors were from: Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–323 (with real and imaginary corrections for anomalous dispersion in the form factor of the manganese atom from: Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891–1898). Scattering factors for hydrogen were from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *Ibid.* **1965**, *42*, 3175–3187.

subsequent developments during the determination of structure. The structure was refined to convergence using anisotropic temperature factors for all heavy atoms and fixed idealized coordinates for all hydrogen atom positions. The final value of R_1 was 0.042 and R_2 was 0.056.[28] The estimated standard deviation of an observation of unit weight was 1.76. A final difference Fourier was judged to be significantly free of features with no peaks greater than 0.26 e/A^3.

Atomic coordinates are listed in Table I. Anisotropic thermal factors and the fixed hydrogen atom coordinates are listed in Tables II and III, respectively, of the supplementary material. Individual bond lengths and angles are compiled in Tables IV and V, respectively. Primed and unprimed symbols, e.g., C(*i*)′ and C(*i*), denote a pair of atoms related by the twofold axis of symmetry.

Results and Discussion

Synthesis and Spectra. The reductive methylation of MnN(OEP) (**1**) formally proceeds according to eq 1 and 2,

$$\text{MnN(OEP)} + 2e^- \rightarrow [\text{MnN(OEP)}]^{2-} \quad (1)$$

$$[\text{MN(OEP)}]^{2-} + 2\text{MeI} \rightarrow \text{MnN(OEPMe}_2) + 2\text{I}^- \quad (2)$$

the electrons in eq 1 coming from the anthracenide anion radical.[23,26] The yield of crystalline MnN(OEPMe$_2$), 11%, is of the same order of magnitude as in the reductive methylation of Pt(OEP) and VO(OEP);[23] i.e., the MnN^{2+} entity in the porphyrin ligand is as reluctant to reduction by simple electron transfer as divalent platinum or tetravalent vanadium, the negative charge density in [MnN(OEP)]$^{2-}$ residing preferentially on the porphyrin ring.

MnN(OEPMe$_2$) is perfectly stable under aerobic conditions. Its red solutions show three absorption maxima 386, 476, and 516 nm with positions and intensities similar to those of TiO(OEPMe$_2$) and VO(OEPMe$_2$).[23] The latter two complexes have weak bands at about 560 nm, which are absent in MnN(OEPMe$_2$).

Further comparison of the above three square-pyramidal complexes comes from thin-layer chromatography on alumina with toluene. All complexes run as rather nonpolar species, but the R_f values decrease as follows: MnN(OEPMe$_2$), 0.9; VO(OEPMe$_2$), 0.85; TiO(OEPMe$_2$), 0.43. The small increase in polarity on replacement of MnN^{2+} by VO^{2+} could reflect the increase in the metal to axial ligand bond length or bond polarity (see below) while the much smaller R_f values of the titanyl species may be due to some specific reaction with the alumina surface reminiscent of earlier observations of basicity[29,30] or hydrate formation[31] of titanyl porphyrins, which have never been found for vanadyl porphyrins.

The proton magnetic resonance spectrum of MnN(OEPMe$_2$) (see Experimental Section) shows the typical pattern observed earlier with diamagnetic porphodimethenes.[23] The signals caused by the methine protons, 5-, 10-, 15-, and 20-H, and the protons of the peripheral ethyl groups appear at the same frequencies as in TiO(OEPMe$_2$) within ±0.03 ppm. Only the proton signals of the 5- and 15-groups (doublet at 2.13 ppm) are observed a little downfield of the corresponding signals of TiO(OEPMe$_2$) (2.05 ppm). Both of these signals have a higher chemical shift than the average of 10 porphodimethenes (1.80 ppm). The high chemical shift of TiO(OEPMe$_2$) was earlier interpreted as resulting from the syn-axial configuration of the oxo group and the 5- and 15-methyl groups,[23] which later was proven by X-ray crystallography.[24] The Ti═O group obviously has a diamagnetic anisotropy, causing downfield shifts of those protons residing close to a plane being orthogonal to the Ti–O bond and bisecting it. If a slightly larger diamagnetic anisotropy is attributed to the Mn≡N group, the ^{1}H NMR spectrum of MnN(OEPMe$_2$) can be taken as indicating practically the same configurations for this molecule and TiO(OEPMe$_2$) in solution.

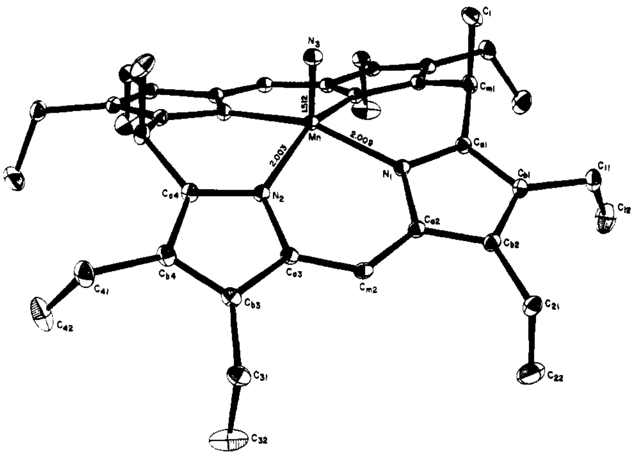

Figure 1. Computer-drawn model in perspective of the MnN(OEPMe$_2$) molecule as it exists in the crystal. The atom labels of the symmetry-unique atoms of the molecule are given as are the bond distances in the coordination group.

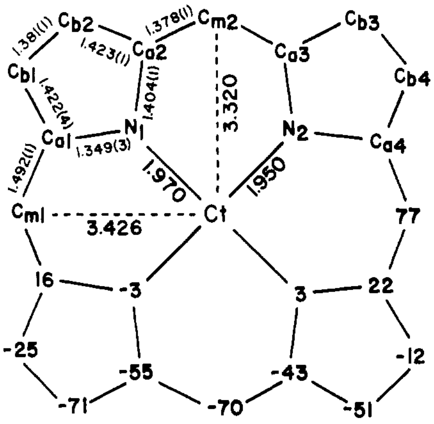

Figure 2. Formal diagram of the porphodimethene core displaying, on the upper half, the symbols identifying each atom. On the lower half of the diagram, the atom symbol is replaced by the perpendicular displacement of the atom, in units of 0.01 Å, from the mean plane of the four nitrogen atoms of the core. Displayed in the upper left of the diagram are selected bond distances, averaged in agreement with C_{2v} symmetry. Distances from the center of the four nitrogen atoms (Ct) to selected atoms are also shown.

The reductive methylation of MnN(OEPMe$_2$) thus takes the same course as in all other cases studied[23-26,32] and produces MnN(OEPMe$_2$) with the syn-axial-exo position of the Mn≡N and the 5- and 15-methyl groups. This was fully confirmed by the X-ray diffraction study.

Structural Study. The numbering system employed in the tables for the atoms in the asymmetric unit of structure are displayed in Figure 1. Figure 1 is a computer-drawn model in perspective of the MnN(OEPMe$_2$) molecule as it exists in the crystal. The crystallographically required twofold axis of symmetry passes through the manganese and nitrido nitrogen atoms (Figure 1) of the MnN^{2+} unit. Although not required of the molecule in the crystal, the core of the molecule has approximate C_{2v} symmetry. Figure 2 displays the average values of bond lengths (C_{2v} symmetry) and radii of the core.

The displacement of the skeletal carbon aroms from the mean plane of the four nitrogen atoms is given in Figure 2. In the lower half of the diagram, the symbol identifying each atom is replaced by the value of the perpendicular displacement

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(28) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

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(in units of 0.01 Å) of this atom from the mean N_4 plane. The twofold-related atoms in the upper half of the diagram have displacements of the same magnitudes and signs. Local flatness is preserved for each pyrrole ring, with the maximum deviation from exact planarity being less than 0.01 Å. The mean plane of the porphodimethene skeleton is parallel to the mean plane of the four nitrogen atoms but is displaced by 0.18 Å. Consequently, the displacement of the individual atoms from the mean plane of the core can be obtained by adding 0.18 Å to the cited displacements given in Figure 2. The manganese(V) atom is displaced 0.603 Å from the mean plane of the porphodimethene core and 0.426 Å from the N_4 plane.

As is the case for all the characterized porphodimethene derivatives, the core is folded along the line joining the two saturated meso-carbon atoms (C(m1) and C(m1)′ of Figure 2). The 41.8° angle between the pyrromethene halves (the mean plane of a pyrromethene half is defined by atom C(m2) and the two unique pyrrole rings) specifies this folding. The two pyrrole rings of a pyrromethene half are also folded by 11°. Comparable values for the other porphodimethene derivatives: Ni(II),[32] 52 and 23°; Os(CO)(py),[25] 38.1 and ~ 5.7°; Ti=O,[24] 38.2 and 4.6°. The differences in conformation of these porphodimethene derivatives are related to the size of the central hole (Ct···N) of the macrocycle. The manganese case (Ct···N = 1.960 Å) is intermediate to the nickel system (small hole size, Ct···N = 1.908 Å) and the titanyl and osmium complexes (larger hole size, Ct···N = 2.030 and 2.059 Å, respectively). The size of the central hole is related to the differing coordination requirements of the metal ion (principally the $M-N_p$ bond length). These conformational differences are also reflected in the deviation of the meso-carbon atoms from the N_4 mean plane and follow the order Ni > Mn > Os ~ Ti.

We have previously described the conformation of these macrocycles as "rooflike", with the line joining two saturated meso-carbon atoms (C(m1) and C(m1)′) defining the ridge of the roof. The methyl groups of the saturated meso-carbon atoms have the syn-axial configuration and, along with an axial ligand, occupy what could be termed the chimney positons. With use of this analogy, the conformation of the nitridomanganese(V) and titanyl derivatives can be compared in a slightly different manner. In $TiO(OEPMe_2)$, the titanium(IV) atom is almost on the "ridge", with a displacement of 0.04 Å below the ridge. In $MnN(OEPMe_2)$, however, the manganese(V) atom is displaced well below the ridge (by 0.34 Å); the difference in positions of the two metal ions from this reference line is thus 0.3 Å. Since the difference in the displacement of the metal ions from the N_4 plane[33] is only 0.15 Å, the differences in the two comparisons reflect the greater folding of the porphodimethene ligand in $MnN(OEPMe_2)$. This folding is necessary to form complexing $Mn-N_p$ bonds of 2.003 (1) and 2.009 (1) Å while allowing the significant (0.43 Å) displacement of the Mn atom from the N_4 plane.

The average $Mn-N_p$ bond distance of 2.006 (4) Å is at the low end of the range of distances observed in Mn(III) and low-spin Mn(II) porphyrins. The $Mn-N_p$ bond distance in six-coordinate $Mn^{III}(py)(Cl)(TPP)$[19] is 2.009 (9) Å and is as follows for the five-coordinate species: $Mn^{III}(Cl)(TPP)$,[34] 2.009 (15) Å; $Mn^{III}(N_3)(TPP)$,[35] 2.005 (7) Å; $Mn^{II}(NO)(TPP)$,[22] 2.004 (5) Å. The displacements of the Mn atom from the N_4 plane in these latter three species are 0.27, 0.23, and 0.34 Å, respectively. The $Mn^{IV}-N_p$ bond distance in $[Mn(TPP)(N_3)]_2O$[15] is 2.014 (19) Å.

This pattern of bond lengths is similar to that observed for the isoelectronic oxochromium(IV) species CrO(TTP).[36] The $Cr-N_p$ bond distance of 2.032 (4) Å is quite similar to those of the low-spin *Cr(II)* complexes Cr(TPP)[37] (2.033 (1) Å) and $Cr(py)_2(TPP)$[38] (2.027 (13) Å). We conclude that the increased formal charge in these highly covalent Cr(IV) and Mn(V) species has only a small effect on the complexing bond lengths to the porphyrin ligand, relative to the values observed for the same metal ion in "normal" oxidation states. Obviously, the nitrido (N^{3-}) and oxo (O^{2-}) ligands transfer so much electron density to the metal via σ and π donation that the "effective oxidation state" of the metal is much lower than the "formal oxidation number" and hence the ionic radius of the metal does not vary much. There does not appear to be any Mn(V) species to provide direct comparison of Mn^V-N bond distances. There is one additional Mn(IV) species,[39] bis(μ-oxo)tetrakis(2,2′-bipyridine)dimanganese(III,IV) perchlorate; the $Mn^{IV}-N$ bond distance in this complex is 2.022 Å.

The large (0.43 Å) displacement of the Mn atom in $MnN(OEPMe_2)$ compared to that in the manganese species cited above reflects the strong interaction of the manganese atom with the nitrido ligand. The Mn-N(nitrido) distance of 1.512 (2) Å is apparently the shortest ever observed M≡N bond.[18] It is interesting to note that the other characterized nitrido–metalloporphyrin complex, $[Fe(TPP)]_2N$,[40] also has a shorter M-N distance than other nitrido-bridged species. This very short Mn≡N distance leads to very tight N(3)···N(1) and N(3)···N(2) separations of 2.74 and 2.77 Å. N···N contacts of this magnitude were cited[22] as the major cause for the increased metal atom displacement in the series Co(NO)(TPP), Fe(NO)(TPP), and Mn(NO)(TTP). Steric factors involving the tightly bound nitrido ligand have been previously suggested as having significantly effects on the coordination geometry.[41]

Average bond distances in the core are displayed in Figure 2. The number in parentheses following each averaged value is the estimated standard deviation calculated on the assumption that all values are drawn from the same population. Differences in the values for the two symmetry-unique C(a)–N bonds and deviations of the C–C bond lengths from values found for porphyrin derivatives have been previously discussed in terms of limiting Kekulé structures for π-electron delocalization in the porphodimethene core.[32] There are no unusually short intermolecular contacts in the crystal structure of $MnN(OEPMe_2)$. The intramolecular contacts between the nitrido nitrogen atom and the methyl carbon atoms on the saturated meso-carbon atoms (N···C(1)) are 3.30 Å.

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Supplementary Material Available: Table II (anisotropic temperature factors), Table III (fixed hydrogen atom positions), and a listing of the observed and calculated structure factor amplitudes (×10) (16 pages). Ordering information is given on any current masthead page.

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