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Nitrosoarene Complexes of Manganese Porphyrins

Shelia J. (Schultze) Fox, Li Chen,
Masood A. Khan, and George B. Richter-Addo*

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Norman, Oklahoma 73019

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Introduction

Nitrosoalkanes and nitrosoarenes (*C*-nitroso compounds) are known to bind to heme-containing biomolecules such as hemoglobin, myoglobin, cytochrome P450, and guanylyl cyclase.[1−3] We and others have shown (by single-crystal X-ray crystallography) that *C*-nitroso ligands bind to d^6 metalloporphyrin complexes of Fe[4,5] and Os[6] via the *N*-atom of the nitroso group. James has also shown by IR and NMR spectroscopies that nitrosobenzene binds via its *N*-atom to d^6 ruthenium porphyrins.[7]

Prior to 1996, *O*-binding of *C*-nitroso compounds to monometallic complexes had been established by X-ray crystallography in only two metal complexes, namely $ZnCl_2(p\text{-}ONC_6H_4NMe_2)_2$ and $SnCl_2Me_2(p\text{-}ONC_6H_4NMe_2)_2$, where both metals have a formal d^{10} configuration.[8] On the basis of the data available, it was assumed that such *O*-binding was indeed restricted to d^{10} metals.[9] We recently reported the then unprecedented *O*-binding of a *C*-nitroso compound to a non-d^{10} metalloporphyrin complex of Fe in which the metal center is formally d^5.[4] To complement our studies on iron porphyrins, we were interested in determining whether, indeed, such *O*-binding could be expanded to include metals whose configurations were those other than d^{10} or d^5.

Nitric oxide is known to bind to manganese-substituted porphyrins,[10−13] phthalocyanine,[14] hemoglobin and myoglobin,[15] and cytochrome P450,[16] however, not much is known about related adduct formation between *C*-nitroso compounds and manganese-substituted heme models. This is somewhat surprising, given that *C*-nitroso compounds are known to bind to many transition metals.[9] Furthermore, although (porphyrin)MnCl compounds are catalysts for nitroarene ($ArNO_2$) generation from the oxidation of the corresponding ArNO compounds,[17] to the best of our knowledge no isolable *C*-nitroso compounds of manganese porphyrins have been reported. In this note, we report the synthesis and characterization of the first ArNO complexes of manganese porphyrins. We also show that the ArNO ligand is coordinated in a rare *O*-bound fashion to the formally d^4 Mn^{III} center in a representative complex.

Experimental Section

The syntheses of the air- and moisture-sensitive nitrosoarene derivatives were performed under inert atmosphere (prepurified N_2) using standard Schlenk techniques or an Innovative Technology Labmaster 100 dry box. Solvents were distilled from the appropriate drying agents under nitrogen just prior to use: CH_2Cl_2 (CaH_2), THF (Na/benzophenone), and hexane (Na/benzophenone/tetraglyme). *N,N*-dimethyl-4-nitrosoaniline (97%), *N,N*-diethyl-4-nitrosoaniline (97%), $AgClO_4\cdot H_2O$, and $AgSbF_6$ (98%) were obtained from Aldrich and used as received. The (porphyrin)MnCl compounds were synthesized by published procedures.[18]

Infrared spectra were recorded on a Bio-Rad FT-155 FT IR spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Mass spectra were obtained on a VG-ZAB-E instrument.

Preparation of [(Porphyrin)Mn(THF)$_2$]X (X = SbF_6, ClO_4).[19] The following is representative of the synthetic method followed: (T(p-CH_3)PP)MnCl (0.200 g, 0.264 mmol) and $AgSbF_6$ (0.090 g, 0.26 mmol) were dissolved in THF (30 mL). The solution flask was heated to boiling for 30 min. A white precipitate formed. The solution was filtered, and the volume of the filtrate was reduced to ca. 10 mL. Hexane (20 mL) was carefully added to form a layer on top of the filtrate, and the mixture was cooled at −20 °C overnight, resulting in the precipitation of green-black crystals of $[(T(p\text{-}CH_3)PP)Mn(THF)_2]SbF_6\cdot THF$ which were isolated and dried under vacuum (38% yield). Anal. Calcd for $C_{60}H_{60}O_3N_4MnSbF_6$: C, 61.29; H, 5.14; N, 4.76. Found: C, 61.59; H, 4.89; N, 5.05. IR (KBr, cm^{-1}): ν_{SbF_6} 657 (vs); also 1685 (w), 1495 (m), 1457 (w), 1340 (m), 1205 (m), 1184 (m), 1110 (w), 1077 (w), 1035 (m), 1010 (vs), 874 (w), 849 (w), 802 (s), 721 (w), 524 (m). The other bis-solvated complexes were prepared similarly in 28−68% isolated yields.

Preparation of [(Porphyrin)Mn(ONC$_6$H$_4$NR$_2$)$_2$]X (R = Me, Et; X = SbF_6, ClO_4). The following is representative of the synthetic method followed: To a stirred CH_2Cl_2 (12 mL) solution of $[(TPP)Mn(THF)_2]SbF_6$ (0.109 g, 0.104 mmol) was added *N,N*-dimethyl-4-nitrosoaniline (0.064 g, 0.43 mmol). The solution was stirred for 1 h, and then the volume was reduced to ca. 4 mL. Hexane (12 mL) was carefully added to form a layer on top of the reaction mixture. The resulting mixture was cooled at −20 °C overnight. Small dark green (needle-shaped) crystals formed, which were collected by filtration and washed several times with hexane to remove unreacted ligand. The dark green crystals were dried under vacuum to give [(TPP)Mn-

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$(ONC_6H_4NMe_2)_2]SbF_6$ in 54% yield. Anal. Calcd for $C_{60}H_{48}O_2N_8MnSbF_6$: C, 59.87; H, 4.02; N, 9.31. Found: C, 60.58; H, 4.22; N, 9.13. IR (KBr, cm^{-1}): ν_{SbF_6} 658 (vs); also 1604 (s), 1558 (w), 1487 (w), 1441 (w), 1396 (w), 1364 (m), 1339 (m), 1303 (w), 1241 (m br), 1142 (s), 1119 (s), 1072 (w), 1012 (s), 933 (w), 830 (m), 803 (m), 757 (m), 726 (m), 704 (m), 632 (m), 604 (w). Low-resolution mass spectrum (FAB): *m/z* 683 ([(TPP)Mn(O)]$^+$, 7), 667 ([(TPP)Mn]$^+$, 100), 151 ([$ONC_6H_4NMe_2$ + H]$^+$, 60).

[(T(*m*-CH$_3$)PP)Mn(ONC$_6$H$_4$NMe$_2$)$_2$]SbF$_6$: 74% yield. Anal. Calcd for $C_{64}H_{56}O_2N_8MnSbF_6$: C, 61.01; H, 4.48; N, 8.89. Found: C, 60.74; H, 4.63; N, 8.65. IR (KBr, cm^{-1}): ν_{SbF_6} 659 (vs); also 1604 (s br), 1552 (m), 1483 (w), 1443 (w), 1395 (m), 1365 (m), 1340 (m), 1303 (w), 1244 (m br), 1206 (w sh), 1136 (m br), 1120 (m br), 1078 (sh), 1040 (w), 1010 (m), 928 (m), 913 (w), 891 (w), 831 (s), 806 (s), 782 (s), 727 (s), 706 (m), 632 (s), 606 (m), 582 (w), 506 (w), 445 (m). Low-resolution mass spectrum (70 eV EI): *m/z* 150 ([$ONC_6H_4NMe_2$]$^+$, 100).

[(TPP)Mn(ONC$_6$H$_4$NEt$_2$)$_2$]SbF$_6$: 54% yield. Anal. Calcd for $C_{64}H_{56}O_2N_8MnSbF_6$: C, 61.01; H, 4.48; N, 8.89. Found: C, 61.22; H, 4.58; N, 8.88. IR (KBr, cm^{-1}): ν_{SbF_6} 657 (vs); also 1601 (s br), 1539 (m), 1486 (m), 1442 (w), 1420 (m), 1380 (m), 1342 (m), 1301 (m), 1239 (s br), 1141 (s br), 1072 (m), 1012 (s), 833 (m), 800 (s), 756 (s), 705 (s), 630 (s), 604 (m). Low-resolution mass spectrum (FAB): *m/z* 683 ([(TPP)Mn(O)]$^+$, 7), 667 ([(TPP)Mn]$^+$, 97), 179 ([$ONC_6H_4NEt_2$ + H]$^+$, 100).

[(T(*p*-CH$_3$)PP)Mn(ONC$_6$H$_4$NEt$_2$)$_2$]ClO$_4$: 69% yield. Anal. Calcd for $C_{68}H_{64}O_6N_8MnCl\cdot0.4CH_2Cl_2$: C, 67.69; H, 5.38; N, 9.23; Cl, 5.26. Found: C, 67.84; H, 5.49; N, 9.37; Cl, 5.28. IR (KBr, cm^{-1}): ν_{ClO_4} 1086 (s), 626 (s); also 1602 (s br), 1539 (m), 1490 (w), 1446 (w), 1418 (m), 1340 (m), 1293 (s), 1228 (s), 1184 (w), 1144 (s), 1008 (s), 836 (m), 823 (w), 804 (s), 708 (s), 607 (m). Low-resolution mass spectrum (FAB): *m/z* 739 ([(T(*p*-CH$_3$)PP)Mn(O)]$^+$, 8), 723 ([(T(*p*-CH$_3$)PP)Mn]$^+$, 100), 179 ([$ONC_6H_4NEt_2$ + H]$^+$, 47).

[(T(*m*-CH$_3$)PP)Mn(ONC$_6$H$_4$NEt$_2$)$_2$]SbF$_6$: 74% yield. Anal. Calcd for $C_{68}H_{64}O_2N_8MnSbF_6\cdot0.3CH_2Cl_2$: C, 61.15; H, 4.85; N, 8.35; Cl, 1.59. Found: C, 60.71; H, 4.84; N, 8.30; Cl, 1.79. IR (KBr, cm^{-1}): ν_{SbF_6} 658 (vs); also 1601 (s br), 1540 (m), 1482 (w), 1455 (w), 1417 (m), 1381 (m), 1342 (m), 1301 (w), 1229 (s br), 1208 (sh), 1136 (s br), 1075 (m), 1040 (w), 1008 (s), 926 (w), 891 (w), 835 (m), 806 (s), 783 (s), 736 (w), 706 (s), 630 (m), 605 (m). Low-resolution mass spectrum (FAB): *m/z* 739 ([(T(*m*-CH$_3$)PP)Mn(O)]$^+$, 8), 723 ([(T(*m*-CH$_3$)PP)Mn]$^+$, 100), 179 ([$ONC_6H_4NEt_2$ + H]$^+$, 24).

X-ray Structural Determination. Crystals were grown from a CH_2Cl_2/hexane solution at −20 °C. The data were collected on a Siemens P4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å). The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans was applied. The structure was solved by direct methods using the SHELXTL (Siemens) system and refined by full-matrix least-squares on F^2 using all reflections. The asymmetric unit contains only one-half of the cation, one-half of the SbF_6 anion, and a molecule of dichloromethane solvent. The Mn atom of the cation is located at the center of symmetry, and the Sb atom is located along the 2-fold axis. The (O)NC_6H_4 fragment of the nitrosoarene ligand is disordered at two sites, with one component labeled as (N3Y, C1Y−C6Y) and the other component labeled as (N3Z, C1Z−C6Z). Refinement of the occupancy factor suggested 44% and 56% occupancy, respectively, for these atoms. The fluorine atoms of the SbF_6 anion are also disordered, as indicated by their high thermal motion. Crystal data are given in Table 1.

Results and Discussion

p-Amino-substituted nitrosoarenes react with the [(por)Mn(THF)$_2$]$^+$ cations in CH_2Cl_2 to generate the bis-nitrosoarene complexes [(por)Mn($ONC_6H_4NR_2$)$_2$]$^+$ in 54−74% isolated yields. Unlike their iron analogs previously reported by us,[4] the d^4 [(por)Mn^{III}($ONC_6H_4NR_2$)$_2$]$^+$ complexes are air-sensitive both in solution and in the solid state. Their IR spectra (as KBr pellets) reveal the presence of the nitrosoarene groups. In particular, bands at *ca.* 1364 and 1339 cm^{-1} in the IR spectra of the [(por)Mn($ONC_6H_4NMe_2$)$_2$]$^+$ complexes are assigned to the O−N and N−C stretching frequencies, respectively, of the coordinated nitrosoarene.[20] However, IR data is ambiguous with regard to $ONC_6H_4NR_2$ coordination.[21] The IR spectra also contains strong bands at *ca.* 658 cm^{-1} for the uncoordinated SbF_6 anion[22] or at 1086 and 626 cm^{-1} for the perchlorate anion.[23]

Table 1. Crystal Data for [(TPP)Mn($ONC_6H_4NEt_2$)$_2$]$SbF_6\cdot(CH_2Cl_2)_2$

formula	$C_{66}H_{60}Mn_1N_8O_2SbF_6Cl_4$
fw	1429.71
T (K)	188(2)
space group	*C*2/*c*
a (Å)	19.633(3)
b (Å)	15.3709(14)
c (Å)	22.998(4)
β (deg)	109.810(14)
V (Å^3)	6530(2)
Z	4
D_{calcd} (g cm^{-3})	1.454
no. of data/restraints/param	5747/173/464
final *R* [$I > 2\sigma(I)$]^{a,b}	R1 = 0.0641, wR2 = 0.1594
R (all data)^{a,b}	R1 = 0.1026, wR2 = 0.1930

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

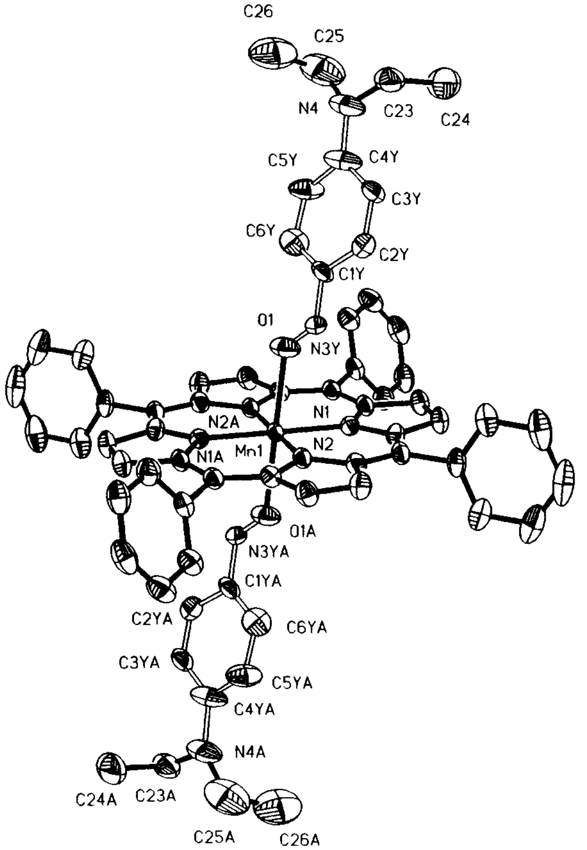

Figure 1. View of the [(TPP)Mn($ONC_6H_4NEt_2$)$_2$]$^+$ cation with 40% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Only one of the two disordered positions of the nitrosoarene phenyl ring and the N3 atom are shown. Selected bond distances (Å) and angles (deg): Mn1−N1 = 2.017(3), Mn1−N2 = 2.015(4), Mn1−O1 = 2.211(4), O1−N3Y = 1.057(10), N3Y−C1Y = 1.36(2), C4Y−N4 = 1.391(14); N3Y−O1−Mn1 = 133.4(7), O1−N3Y−C1Y = 121.9(12), C4Y−N4−C23 = 108.6(10), C4Y−N4−C25 = 134.5(10), C23−N4−C25 = 116.7(6).

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(21) For example, the proposed *N*-bound and *O*-bound formulations have very similar IR spectral patterns.[20]

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Although the manganese nitrosoarene products are very difficult to crystallize into single crystals, we were finally (after *ca.* 2 years) able to obtain a single crystal suitable for X-ray diffraction studies. The structure of the cation of [(TPP)Mn($ONC_6H_4NEt_2$)$_2$]SbF_6 is shown in Figure 1. The (O)NC_6H_4 fragment of the nitrosoarene ligand is disordered over two positions. The nitroso O−N bond length (average 1.08 Å) is unusually short for a coordinated *C*-nitroso compound and is significantly shorter than the reported value of 1.27(1) Å for the free ligand (which was also disordered)[24] or the reported values for the related d^{10} complexes of the *dimethyl* derivative (1.218(4) Å for $SnCl_2Me_2$(*p*-$ONC_6H_4NMe_2$)$_2$; 1.305 Å for $ZnCl_2$(*p*-$ONC_6H_4NMe_2$)$_2$)[8] and is shorter than that for the analogous Fe^{III} complex reported by us (average 1.11 Å).[4] The origin of this unusual shortening is unclear, and we are hesitant to over-interpret the accuracy of the bond lengths and angles in this highly disordered nitroso fragment. The (O)N−C bond length of 1.36 Å is, however, comparable to the reported value of 1.38(1) Å reported for the free ligand or the d^{10} complexes containing the *dimethyl* derivative (1.398(6) Å for $SnCl_2Me_2$(*p*-$ONC_6H_4NMe_2$)$_2$; 1.342 Å for $ZnCl_2$(*p*-$ONC_6H_4NMe_2$)$_2$).

The axial Mn−O distance of 2.211(4) Å is long and may be compared with the axial Mn−O distances in related Mn^{III} complexes of the form [(TPP)Mn(L)$_2$]ClO_4 (L = DMF (2.217(4) Å), MeOH (2.252(2) and 2.270(2) Å), 2,6-lutidine-*N*-oxide (2.263(4) and 2.264(4) Å)).[19ab,25] The average Mn−N(por) bond length of 2.016 Å is within the range normally expected for six-coordinate Mn^{III} porphyrins.[10b,19,25] The long axial Mn−O bond lengths relative to Mn−N(por) for [(TPP)Mn($ONC_6H_4NEt_2$)$_2$]SbF_6 are consistent with the tetragonal elongation expected for a singly occupied antibonding d_{z^2} orbital in the Mn^{III} center.[10b,19,25,26] The disordered nitroso groups are essentially staggered or eclipsed with respect to the porphyrin nitrogen atoms, with the N3−O1−Mn1−N1 torsion angles being 47° (for N3Y) and 98° (for N3Z). The axial nitrosoarene ligands are also labile in solution, being readily displaced quantitatively by THF or by chloride ion.

Our observation of *O*-binding of ArNO to the formally d^4 Mn^{III} center is interesting. This *O*-binding of ArNO to a d^4 metal center is, thus, only the second example of such a binding to non-d^{10} metal centers[4] and suggests that this binding mode may indeed be more accessible than was previously thought.

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Supporting Information Available: ORTEP diagrams and tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles, and least-squares planes (19 pages). Ordering information is given on any current masthead page.

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(26) Indeed, the UV−vis spectrum of [(TPP)Mn($ONC_6H_4NEt_2$)$_2$]SbF_6 (1.0×10^{-5} M in toluene, ϵ in units of $mM^{-1}\ cm^{-1}$) shows peaks at 392 (126), 413 (106, sh), 480 (56), 570 (15), and 603 (11) nm. The spectrum is almost identical to the spectrum of [(TPP)Mn(DMF)$_2$]ClO_4[19a] which has been fully characterized as a d^4 high-spin system.