

Synthesis and Reactivity of a Mononuclear Manganese(II) Complex Having Pseudo-Seven Coordination Environment

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Utilizing a planar five coordinating N3S2 ligand, 2,6-bis(2-methylthiophenyliminomethyl)pyridine, a pseudo 7-coordinated manganese(II) complex with two labile triflate anions in the axial positions was synthesized. The reaction of the manganese(II) complex with an oxidant, iodosylbenzene, produced a metastable high-valent manganese(IV)-oxo species at 0°C. The high-valent Mn(IV)-oxo intermediate was characterized with a UV-vis spectrophotometer and an electrospray ionization mass spectroscopy. Reactivity studies of the Mn(IV)=O species revealed that the intermediate is capable of oxygenating PPh₃ and *N*-dealkylating *N,N*-dimethyl-toludine.

Key Words: Bioinorganic chemistry, Seven coordination, High-valent manganese-oxo, Oxygenation, *N*-Dealkylation

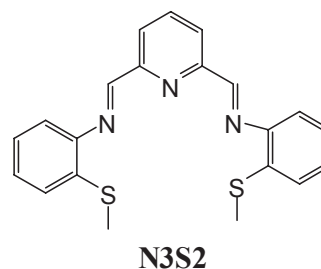
Introduction

Together with iron, manganese occupies a central place in chemistry and biology owing to its rich catalytic redox reactivity.¹⁻⁴ The active site located in the oxygen evolving center (OEC) at photosystem II^{1,2} and oxidation catalysts^{3,4} are examples of well-known place containing manganese ions at their active sites. Interestingly, high-valent manganese-oxo intermediates are claimed as a key species both in the OEC and catalytic transformations.¹⁻⁴ The importance of high-valent Mn-oxo intermediates has stimulated interests in creating synthetic analogues to probe aspects of their bonding and reactivity as well as expanding this chemistry to new applications, such as development of new catalysts which can generate O₂ from water molecules: The two Mn(V)=O species, resulted from two consecutive oxidations of the Mn(III)-OH₂ motif, can couple to generate Mn(IV)-O-O-Mn(IV) intermediates, which release O₂ leaving two Mn(III) sites.⁵

Recently, manganese(V)-oxo porphyrin intermediates have been generated and characterized in aqueous solution and their stability and reactivities, depending on the pH of the reaction solutions, were reported.⁶ It is noteworthy that manganese(V)-oxo complexes bearing non-porphyrinic macrocycles, such as corrole and corrolazine, have been reported to be very stable at room temperature.^{7,8} Much insight into the chemical properties of the high-valent manganese-oxo intermediates has been obtained by recent researches on manganese(V)-oxo complexes of porphyrin and non-porphyrin ligands. However, the detailed understanding of the relationship between the structure and the function of manganese complexes has not been achieved yet, which requires more modeling complexes synthesized to address each corresponding factor.

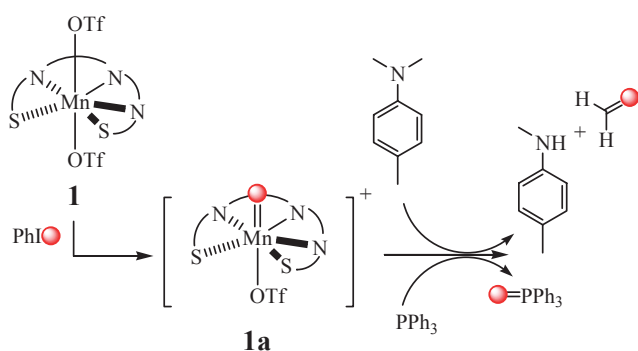
In this regard, we have initiated a program aimed at creating a new model system that can readily generate high-valent Mn-oxo intermediates. Exploring other geometries, different

from previous attempts, may allow access to high-valent manganese centers with new and potentially interesting electronic, magnetic, and reactivity properties. The first deliberate efforts to position metal site in high or low coordination environment in model complexes are described here. We now report a manganese(II) complex with a new pseudo-seven coordination environment and its ability to form a high-valent Mn(IV)-oxo intermediate as an oxygen atom transfer reagent in oxidation reactions.



Experimental

General Considerations. 2,6-Bis(2-methylthiophenyliminomethyl)pyridine, ligand **N3S2**, was synthesized as previously described.⁹ 4-Methoxystyrene, *N,N*-dimethyl-toludine, triphenylphosphine, and solvents with high purity were obtained from commercial suppliers and used as received unless otherwise noted. PhIO¹⁰ and Mn(OTf)₂·2CH₃CN¹¹ were synthesized according to the reported procedures. PhI¹⁸O (0.6 mM), prepared by treating PhI¹⁶O with H₂¹⁸O (5 mM, 95% ¹⁸O enriched) in CH₃OH. H₂¹⁸O (95% ¹⁸O-enriched) was purchased from ICON Services Inc. (Summit, NJ, USA). All syntheses and air-sensitive manipulations were carried out under nitrogen in a glovebox. FT-IR spectra were recorded in KBr disks with a Varian FTS-800 FT-IR spectrophotometer (USA). UV-Vis spectra of solutions were recorded on a



Scheme 1. Proposed Reaction Pathway for Oxygenation of **1** with the Substrates.

Hewlett Packard 8453 spectrophotometer equipped with USP-203-A variable-temperature liquid-nitrogen cryostat (UNISOKU). The reaction products of oxidations were determined and analyzed by Agilent Technologies 6890N gas chromatograph (GC), equipped with a HP-1 capillary column (phenyl methyl siloxane, 25 m \times 0.32 mm \times 0.52 μ m) and flame-ionization detector. Electron spray ionization mass spectra (ESI-MS) were collected using on Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. The spray voltage was set at 3.7 kV and the capillary temperature at 220 $^{\circ}$ C. MeOH was used as the solvent with and without TFA (CF₃COOH, 0.006% in MeCN) added, and mass spectra were measured in positive mode and in the range m/z = 581.0 (cal. 581.0). Elemental Analysis was performed by the Thermo Finnigan Italia SpA (Flash EA[®] 1112) CHN analyzer. 2,5-Bis(5'-*tert*-butyl-2-benzoxazol-2-yl)thiophene (BBOT) was used as a reference standard.

[Mn(N3S2)(OTf)₂] (1). To a rapidly stirred CH₃CN (2 mL) solution of Mn(OTf)₂·2CH₃CN (100 mg, 0.23 mmol) was added the CH₃CN solution (2 mL) of N3S2 ligand (75 mg, 0.20 mmol) under the nitrogen condition. The resulting solution was stirred for 5 min. Crystals of **1** suitable for X-ray crystallography were obtained by layering diethylether over the solution (yield 88%). Anal. Calcd. for C₂₃H₁₉F₆MnN₃O₆S₄: C, 37.95; H, 2.84; N, 5.76 %. Found: C, 37.81; H, 2.62; N, 5.75 %. FT-IR (KBr, cm⁻¹) 3030 (w), 1710 (s), 1430 (s), 1220 (s), 1090 (w), 900 (w).

X-ray Crystallographic Studies. Intensity data were collected on a APEX CCD with a graphite-monochromatized Mo-K α radiation, controlled by a PC running the SMART software package. A single crystal was mounted at room temperature on the tips of quartz fibers and cooled to 173 K under a stream of cold nitrogen. The structure was solved by the direct method and refined on F^2 using the SHELXTL software package.¹² All non-hydrogen atoms were refined anisotropically and hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to 1.5 times the thermal parameter of the carbon atom to which they were attached. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (CCDC-717108). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/peril/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK;

Table 1. Summary of X-ray Crystallographic Information for [Mn(N3S2)(OTf)₂]

Empirical formula	MnC ₂₃ H ₁₉ F ₆ N ₃ O ₆ S ₄
Formula weight	735.59
Space group	Fdd2
<i>a</i> , Å	12.139(2)
<i>b</i> , Å	38.735(8)
<i>c</i> , Å	12.004(2)
<i>V</i> , Å ³	5645(2)
<i>Z</i>	8
Temperature, K	293(3)
Absorption coefficient, mm ⁻¹	0.849
Reflections collected	8555
Independent reflections	3296 [R(int)=0.0671]
<i>P</i> _{calcd} , g/cm ³	1.19
R1 (%) ^a	4.24
wR2 (%) ^b	10.32
Largest diff. peak and hole (e.Å ⁻³)	0.573 and -0.254

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

Table 2. Selected inter-atomic distances (Å) for [Mn(N3S2)(OTf)₂] (**1**).

Mn1–O1	2.130(2)
Mn1–N1	2.226(4)
Mn1–N2	2.430(3)
Mn1...S1	2.7504(12)

fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Detailed crystallographic information is provided in Table 1 and selected interatomic distances are listed in Table 2.

Results

Synthesis and Structural Characterization of [Mn(N3S2)(OTf)₂] (1**).** Addition of 1.5 equiv. of [Mn(OTf)₂] to N3S2 ligand in CH₃CN afforded the mononuclear manganese(II) complex, **1**, in good yield. The structure of the complex is

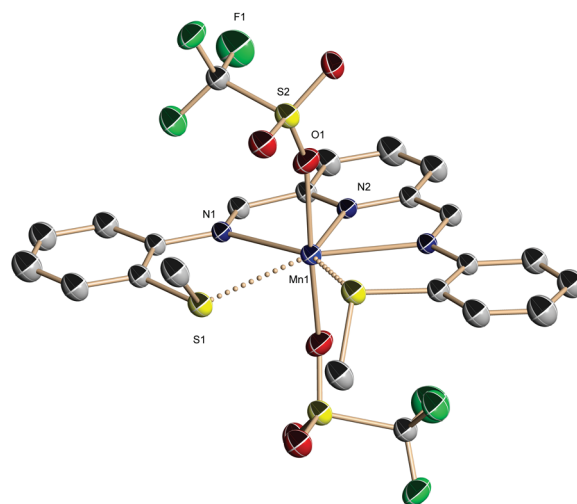


Figure 1. The ORTEP diagram of [Mn(N3S2)(OTf)₂] (**1**) showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

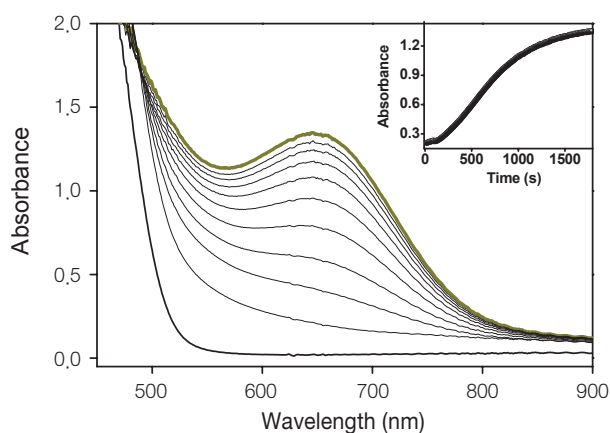


Figure 2. UV-vis spectral changes that occur during reaction of **1** (1 mM) with 3 equiv. of PhIO in acetone at 0 °C. Inset shows absorbance traces monitored at 650 nm.

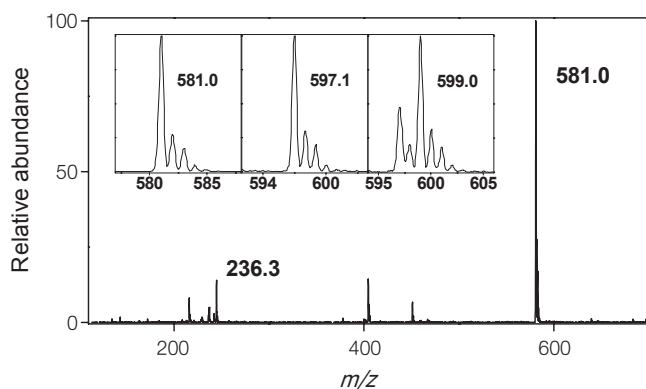


Figure 3. Electrospray ionization mass spectrum of **1** in a solvent of acetone. Insets show the observed isotope distribution patterns for (far left) **1**, (middle) **1** and PhI¹⁶O, and (far-right) **1** and PhI¹⁸O.

depicted in Figure 1, and Table 2 lists selected interatomic distances. The manganese center has pseudo 7-coordinated geometry bound to two triflate anion, each in monodentate fashion with Fe-O distances of 2.130(3) Å. The other coordination sites are occupied by two S donors with the Mn...S1 distances of (2.7504(12) Å) and by three N atoms with the Mn...N distances of 2.226(4) and 2.430(3) Å. The comparatively long Fe-to-N1 distances are consequence from the strain of two five-membered rings, composed by the Mn atom and the N3S2 ligand.⁹ Though it is seven-coordinated species in the solid state, we can envision that the two axial triflate anions may be in dissociation equilibrium in solution, generating pseudo-six coordinated species with one open coordination site in axial position.

Reaction of [Mn(N3S2)(OTf)₂] with PhIO. Addition of PhIO to a solution of **1** in acetone solvent at 0 °C resulted in the gradual generation of a strong band at 650 nm over 30 min (Figure 2). The intermediate, possibly [(N3S2)(OTf)Mn^{IV}=O]⁺ (**1a**), persisted over 1 hrs at 0 °C. The formation of **1a** was also observed when **1** was treated with another oxidant, peracetic acid, with triethylamine. The generation process of the manganese(IV)-oxo intermediate, **1a**, was further understood by electrospray ionization mass spectroscopy (ESI-MS). First, ESI-MS of **1** exhibited a prominent ion at a mass-

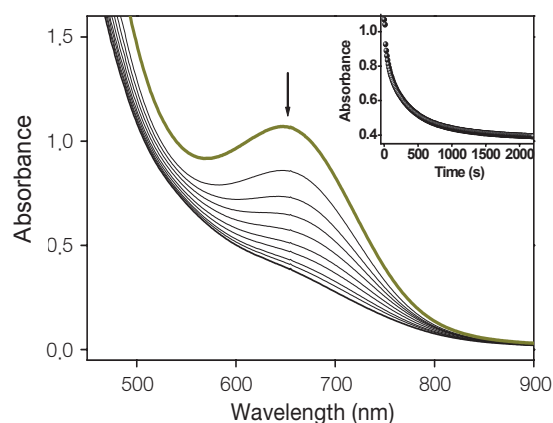


Figure 4. UV-vis spectral changes of **1a** (1 mM) with 100 equiv. of 4-methoxystyrene at -10 °C. Inset shows absorbance traces monitored at 650 nm.

to-charge ratio (m/z) of 581.0 (calculated m/z of 581.0), whose mass and isotope distribution pattern correspond to [Mn(II)-(N3S2)(OTf)]⁺ (Figure 3). Interestingly, the ESI-MS peak at 597.1 developed upon the treatment of 3 equiv. PhIO into the solution of **1** and corresponds to [Mn(IV)(¹⁶O)(N3S2)(OTf)]⁺ (calculated m/z of 597.0). The mass peak at m/z of 599.0 (calculated m/z of 599.0) attributed to the 2-mass unit shift, accordingly upon introduction of ¹⁸O when ¹⁸O-labeled PhIO was used instead of PhI¹⁶O. These results clearly demonstrate that a mononuclear Mn(IV)=O intermediate was generated in the reaction of **1** and PhIO oxidant.

Reactivity of the Intermediate [(N3S2)(OTf)Mn^{IV}=O]⁺ with Substrates. The metastable manganese(IV)=O species, **1a**, with a potential substrate (25 equiv. 4-methoxy styrene) decays slowly with a rate of $1.2 \times 10^{-3} \text{ s}^{-1}$ at 0 °C (Figure 4). To understand the reaction product of **1a** with organic substrates, **1** (1 mM) was dissolved in a solvent (2 mL) of acetone under Ar atmosphere and then mixed with 3 equiv. PhIO in methanol, followed by the addition of 10 equiv. of substrate, *N,N*-dimethyl-*p*-toluidine, at 0 °C. After no color change was observed, solution of the reaction product was analyzed, resulting in the formation of *N*-methyl-*p*-toluidine with 77 % yield. This result indicates that the oxidative *N*-dealkylation occurs upon reaction with the high-valent manganese(IV) oxo intermediate and the substrate. In the case of using triphenylphosphine (PPh₃) as a substrate, triphenylphosphine oxide (O=PPh₃) was analyzed as a reaction product with the yield of 80%.

Summary

The d^5 compound **1** with the N3O2S2 coordination environment exhibits low spin ($S = 1/2$) signals in ESR at 4K (data are not shown). However, as seen in the ESI-MS peak of **1**, one triflate anion in the axial position can displace, resulting in the [Mn(II)(N3S2)(OTf)]⁺ species. This cationic species may react with the excess of the oxidant, PhIO, resulted in the formation of a high-valent Mn(IV)=O intermediate, **1a**, instead of Mn(V)=O species (Scheme 1).¹³ In general, the redox potential of the metal center determines the ease with which the complex goes from one oxidation state to another. This means

how easily the formation of the high-valent metal-oxo intermediates takes place in the reaction process. The redox property of manganese center depends on the nature of ligand bound to it.¹⁴ Thus, the N3S2 ligand motif may predetermine which oxidation state of manganese intermediates be generated. Upon reaction with substrates, the generated high-valent Mn=O intermediate transfers the oxygen atom. The more complete understanding of the electrochemical effects of N3S2 ligand is clearly desirable. Although we now have clear evidence that compound **1** generates a high-valent Mn(IV)=O species, its exact structural information and how to generate Mn(V)=O species by moderate changes of the N3S2 ligand framework remains to be elucidated.

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