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Preparation and Properties of a Monomeric $Mn^{IV}-Oxo$ Complex

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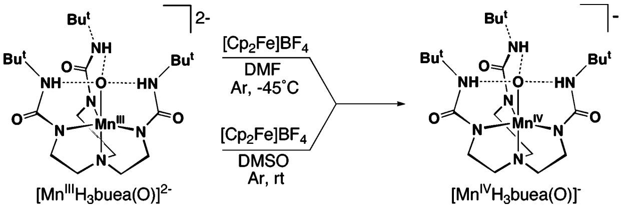
Described herein is the preparation and properties of a Mn^{IV} complex containing a terminal oxo ligand—its formation was accomplished using a $Mn^{III}-O$ complex whose oxo ligand is derived from O_2. The Mn^{IV}−oxo complex converts some phosphines to phosphine oxides via an O-atom transfer process.

Manganese−oxo complexes have long been investigated because of their proposed roles in biological and chemical catalysis.[1] For instance, the reactive species in various synthetic oxidation processes catalyzed by Mn are postulated to be monomeric oxomanganese species that are generated with O-atom transfer agents, such as PhIO, peroxy acids, or bleach.[2] The stabilization of Mn^{V}−oxo complexes has been achieved using anionic tetradentate ligands, which has led to the development of some structure−function correlations.[3] In contrast, Mn^{IV} complexes with terminal oxo ligands are rare,[4] thus limiting our knowledge of their physical properties and chemical reactivity. These transient oxomanganese species are important because they are implicated as key intermediates in the oxidation of substrates. Monomeric oxomanganese(IV) porphyrins are the most thoroughly characterized systems, which are often prepared under basic conditions utilizing an oxidizing agent, such as *m*-chloroperoxybenzoic acid.[4,5]

The preparation of our oxomanganese(IV) complex began with $[Mn^{III}H_3buea(O)]^{2-}$ ($[H_3buea]^{3-}$, tris[(*N*′-*tert*-butylureaylato)-*N*-ethylene]aminato), a monomeric $Mn^{III}-O$ complex in which the oxo ligand arises from cleavage of dioxygen or deprotonation of water (Scheme 1).[6] The $[H_3buea]^{3-}$ ligand regulates the secondary coordination sphere by providing a sterically constrained hydrogen bond (H-bond) network around the $Mn^{III}-O$ unit, thus minimizing formation of $Mn-(O)_n-Mn$ species that are usually observed for nonprotected systems.[7] Cyclic voltammetric studies showed that $[Mn^{III}H_3buea(O)]^{2-}$ has a one-electron redox process at −0.076 mV versus Cp_2Fe^+/Cp_2Fe, which was assigned to the $Mn^{IV}(O)/Mn^{III}(O)$ couple.[6] In DMSO, this is an electrochemically reversible process at 50 $V \cdot s^{-1}$; however, slower scan velocities produced voltammograms indicative of EC processes.

Scheme 1. Synthetic Routes for the Preparation of $[Mn^{IV}H_3buea(O)]^-$



On the basis of the above findings, we reasoned that the Mn^{IV}−oxo complex could be formed at lower temperatures using relatively mild oxidants. This was realized by treating the purple $[Mn^{III}H_3buea(O)]^{2-}$ with $[Cp_2Fe]BF_4$ at −45 °C in DMF (Scheme 1) to produce a new green species that is stable for several hours. The formation of this new species was monitored optically as shown in Figure 1A; the distinctive features of the $Mn^{III}-O$ complex at $\lambda_{max}(\epsilon_M) = 498$ (490) and 725 (240) nm are replaced with a single, more intense band at $\lambda_{max} = 635$ nm after oxidation.

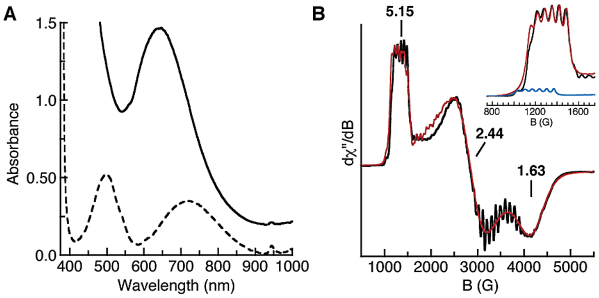


Figure 1. (A) Absorbance spectra of $[Mn^{III}H_3buea(O)]^{2-}$ (- - -) and $[Mn^{IV}H_3buea(O)]^-$ (—) recorded in DMF at −45 °C. (B) X-band EPR spectrum (black line) of $[Mn^{IV}H_3buea(O)]^-$ measured at 3.6 K and spectral simulation (red line). Inset: Enlargement of the $g = 5$ region (black line), showing the contributions from the $m_s = 1/2$ (red line) and $m_s = 3/2$ (blue line) doublets.

Electron paramagnetic resonance (EPR) measurements indicate that the green species is a monomeric Mn^{IV} complex. The X-band EPR spectrum of the green species in DMF collected at 4 K has g values of 5.15, 2.44, and 1.63, which correspond to a species having an $S = {}^3/_2$ state with an $E/D = 0.26$. Using the conventional spin Hamiltonian with zero-field splitting terms D and E/D, the simulation of the spectrum shows that the peak at $g = 5.15$ has contributions from both the ground (±1/2) and excited (±3/2) doublets. The temperature dependence and simulation of the signals indicate a value of $D = 3.0\ cm^{-1}$, which is comparable to that of other Mn^{IV} complexes.[4g,8] Spin quantification finds that the EPR signal corresponds to 70(10)% of the total manganese content in the sample, indicating that the green species is the major product of oxidation.[9] The six-line hyperfine pattern indicates a hyperfine constant of $a = 66$ G ($A = 190$ MHz). This value is consistent with a Mn^{IV} species, but is lower than that typically observed for other Mn^{IV} complexes ($a > 70$ G). The lower value is possibly attributed to the increased covalency of the Mn−O bond, which lowers the electronic spin density at the Mn nucleus. The multiline hyperfine signal near $g = 2$ is attributed to a minor impurity (<10%) from a mixed valent dinuclear Mn species.

We have also found that this Mn^{IV} complex can be prepared at room temperature in DMSO (Scheme 1). The complex has relatively low stability with a half-life of ca. 5 h. Nonetheless, we have been able to prepare the ^{16}O- and ^{18}O-isotopomers of the green complex from the corresponding O_2 isotopes to confirm the presence of a Mn^{IV}−oxo unit. Solution FTIR spectra collected at room temper-

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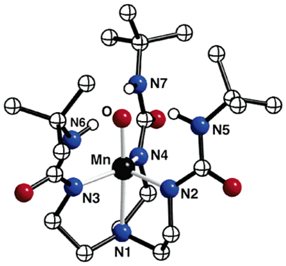
10.1021/ja062332v CCC: $33.50 © 2006 American Chemical Society



Selected Metrical Values

N2-Mn-N3	107.8°
N2-Mn-N4	111.6°
N3-Mn-N4	134.3°
Mn-O	1.706 Å
Mn-N1	2.219 Å
Mn-N2	1.922 Å
Mn-N3	1.954 Å
Mn-N4	1.978 Å

Figure 2. Molecular structure of $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ obtained from geometry-optimized DFT (B3LYP/6-311G) calculations. Only urea hydrogen atoms are shown for clarity.

ature in DMSO for the green species generated from $^{16}O_2$ contain a new peak at 737 cm^{-1} (Figure S1), which shifts to 709 cm^{-1} in the ^{18}O-isotopomer ($\nu(\mathrm{Mn^{16}O})/\nu(\mathrm{Mn^{18}O}) = 1.04$; calcd 1.05).[10] This value is comparable to the $\nu(\mathrm{MnO}) = 754\ cm^{-1}$ reported for $[\mathrm{Mn^{IV}}$-TMP(O)] (TMP, tetramesitylporphyrin), but is significantly smaller than the $\nu(\mathrm{MnO})$ of 979 cm^{-1} found by Collins for his monomeric $\mathrm{Mn^{V}}$−oxo complex. Note that the starting $\mathrm{Mn^{III}}$−oxo complex, $[\mathrm{Mn^{III}H_3buea(O)}]^{2-}$, has a $\nu(\mathrm{MnO}) = 700\ cm^{-1}$.

The spectroscopic data are consistent with the green species being a $\mathrm{Mn^{IV}}$ complex with a terminal oxo ligand (i.e., $[\mathrm{Mn^{IV}H_3buea(O)}]^-$). Results from the DFT calculations further support this assignment.[11] The geometry-optimized molecular structure for $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ (Figure 2) reveals a monomeric five-coordinate complex with three intramolecular H-bonds involving the oxo ligand (avg. N···O distance is 2.743 Å). A Mn−O bond of 1.706 Å was calculated, which is shorter than that found in $[\mathrm{Mn^{III}H_3buea(O)}]^{2-}$ (by 0.065 (exptl) and 0.054 Å (calcd)).[6b,c] There are large differences in bond distances and angles within the basal plane; for instance, the N3−Mn−N4 angle is 134.3°, while the N2−Mn−N3 is 107.8° (Figure 2). These deviations are attributed to a Jahn−Teller distortion around the high-spin $\mathrm{Mn^{IV}}$ center that would alter the molecular structure of $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ from trigonal symmetry. Additional support for this calculated molecular geometry comes from the highly rhombic EPR spectrum obtained for $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ (Figure 1B), which would arise from a structure like the one predicted from the DFT calculations.

$[\mathrm{Mn^{IV}H_3buea(O)}]^-$ does not react with PPh_3 or PCy_3 in DMSO at room temperature or at −45 °C in DMF. However, treating $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ with $PMePh_2$ under either reaction conditions produces $O{=}PMePh_2$ in 50−70% yields (average of three independent experiments for each reaction condition). Moreover, $^{18}O{=}PMe_2Ph$ (∼50% yield) was produced when the reaction was carried out with $[\mathrm{Mn^{IV}H_3buea(^{18}O)}]^-$. Similarly, O-atom transfer was observed to form $O{=}PMe_2Ph$ when PMe_2Ph was employed as the substrate. Oxygen-atom transfer is normally a two-electron process and would yield phosphine oxide and the corresponding $\mathrm{Mn^{II}}$ complex, presumably $[\mathrm{Mn^{II}H_3buea}]^-$. Evidence for the production of this complex comes from EPR studies. X-band EPR spectra (Figure S4) of reaction mixtures after O-atom transfer contain signals for a species having a ground system spin state of $S = {}^5/_2$, as would be expected for a high spin $\mathrm{Mn^{II}}$ complex, such as $[\mathrm{Mn^{II}H_3buea}]^-$. $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ also reacts with X−H bonds (X = C, N) as illustrated by its reactivity with 1,2-diphenylhydrazine, which produces azobenzene (greater than 95% yield) and $[\mathrm{Mn^{III}H_3buea(OH)}]^-$.

A summary of the reactivity of the Mn complexes is outlined in Scheme 2. Dioxygen activation by $[\mathrm{Mn^{II}H_2buea}]^{2-}$ affords $[\mathrm{Mn^{III}H_3buea(O)}]^{2-}$, which is capable of cleaving X−H bond with bond dissociation energies of less than 80 kcal/mol.[6b] Similarly, its redox partner, $[\mathrm{Mn^{IV}H_3buea(O)}]^-$, reacts via "one-electron" pathways to cleave X−H bonds. In addition, $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ is capable of O-atom transfer to some phosphines; however, similar reactivity is not observed in the $\mathrm{Mn^{III}}$−O complex. The factors controlling formation of monomeric oxomanganese complexes and their subsequent reactivity are still unknown, especially those where the source of the oxo ligand is dioxygen—preparation of $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ and $[\mathrm{Mn^{IV}H_3buea(O)}]^-$ enables us to address the roles of the primary and secondary coordination spheres on the fundamental reactivity of Mn−O complexes.

Scheme 2. Reactivity Summary for the Manganese Complexes

$$\begin{tikzcd}
{[\mathrm{Mn^{II}H_2buea}]^{2-}} \arrow[r, "O_2"] & {[\mathrm{Mn^{III}H_3buea(O)}]^{2-}} \arrow[r, "X{-}H"] \arrow[d, "{[oxidant]}"] & {[\mathrm{Mn^{II}H_3buea(OH)}]^{2-}} \\
{[\mathrm{Mn^{II}H_3buea}]^{-}} & {[\mathrm{Mn^{IV}H_3buea(O)}]^{-}} \arrow[l, "SO\quad S_{red}"'] \arrow[r, "X{-}H"] & {[\mathrm{Mn^{III}H_3buea(OH)}]^{-}}
\end{tikzcd}$$

X = C,N

Acknowledgment. The NIH (GM50781 to A.S.B.; GM77387 to M.P.H.) is acknowledged for financial support of this work. We thank Dr. M. Miller for initial work on this project.

Supporting Information Available: Experimental details for all chemical reactions and calculations, figures for all spectra, and complete citation for ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA062332V