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A Monomeric Mn^{III}−Peroxo Complex Derived Directly from Dioxygen

Ryan L. Shook,[†] William A. Gunderson,[‡] John Greaves,[†] Joseph W. Ziller,[†] Michael P. Hendrich,[‡] and A. S. Borovik*,[†]

Department of Chemistry, University of California—Irvine, 1102 Natural Sciences II, Irvine, California 92697-2025, and Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Received April 15, 2008; E-mail: aborovik@uci.edu

The binding and activation of dioxygen is an essential process in synthetic and biological chemistry.[1] The activation processes are often proposed to involve formation of peroxometal complexes, as exemplified by bleomycin and the mono-oxygenases cytochromes P450.[2] It is generally agreed that the initial steps in the O_2 binding/activation process in these enzymes involve a superoxoiron(III) intermediate that converts to a hydroperoxoiron(III) species through addition of an electron and proton. In this report, we demonstrate that a similar O_2 to peroxo conversion is operable in a synthetic manganese system.

The observation of synthetic monomeric peroxometal complexes is frequently difficult because of their inherent reactivity. This is especially true for peroxomanganese complexes, where the $Mn^{IV}_2(\mu$-1,2-peroxo) complex of Wieghardt is the only O_2-derived system that has been structurally characterized.[3,4] Others have found that treating Mn^{II} or Mn^{III} complexes with superoxides[5] or peroxides[6] produce systems with monomeric peroxomanganese centers—this approach has yielded a handful of complexes at low temperatures that were stable enough to be characterized. We have been investigating the interactions of dioxygen with manganese complexes containing intramolecular hydrogen bonding (H-bond) networks.[7] Our systems utilize urea-based tripodal ligands that provide H-bond donors to coordinated O-atom species. The Mn^{II} complexes of these ligands bind and activate dioxygen producing monomeric oxomanganese complexes.[7,8] We have developed a hybrid ligand (H_5bupa) that combines two urea arms with one carboxyamidopyridyl moiety[9]—the Mn^{II} complex of this ligand binds O_2 to produce a detectable peroxomanganese(III) species.

Preparation of the precursor **1** is outlined in Figure 1.[10] Treating H_5bupa with 3 equiv of KH in dimethylacetamide (DMA) followed by 1 equiv of $Mn(OAc)_2$ afforded K[**1**] and 2 equiv of KOAc.

The molecular structure of **1** determined by X-ray diffraction shows a five-coordinate Mn^{II} complex, having a distorted trigonal bipyramidal geometry.[10] The trigonal plane is defined by the deprotonated urea and pyridyl nitrogen atoms of $[H_2bupa]^{3-}$; the apical N1 atom and carbonyl oxygen O1 from the deprotonated carboxamide occupy the axial positions. The remaining portions of the urea groups form the scaffolding of a cavity, in which NH groups are positioned inward toward atom O1. However, the N6(N7)···O1 distances are greater than 3.2 Å, distances that are too long for intramolecular H-bonds.

A new green species (**2**) is formed in approximately 50% yield[11] when $[Mn^{II}H_2bupa]^-$ reacts with O_2 at room temperature. In DMA, the reaction is relatively slow (~30 min), yet the formation of **2** can be completed in approximately 10 min when 0.5 equiv of diphenylhydrazine (DPH) is added to the reaction mixture (Figure 1). The yield of **2** also increases to nearly 80% when using DPH,

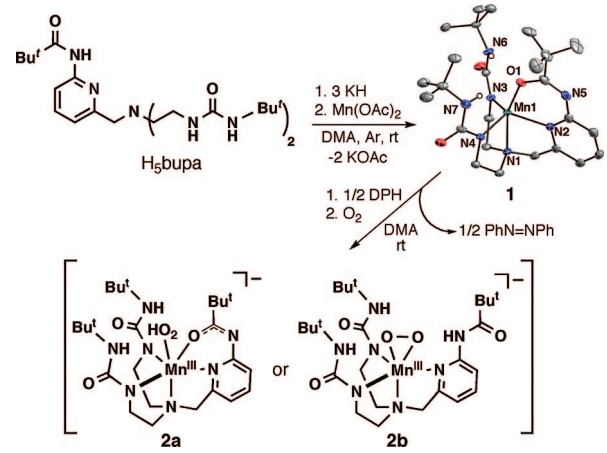

Figure 1. Preparative routes for **1** and **2**, showing two possible tautomers for **2**. The thermal ellipsoid plot of $[Mn^{II}H_2bupa]^-$ is drawn at the 50% probability level, and non-urea hydrogen atoms are omitted for clarity. Selected distances (Å): Mn1−N1, 2.275(3); Mn1−N2, 2.214(3); Mn1−N3, 2.100(3); Mn1−N4, 2.125(3); Mn1−O1, 2.070(2).

which is converted to azobenzene (>95% yield). Monitoring the reactions with optical spectroscopy shows that **2** has a visible absorbance band at $\lambda_{max} \approx 660$ nm and a shoulder at 490 nm (Figure S1).[12] Similar spectra have been reported for Mn^{III} complexes containing a coordinated peroxo ligand.[5d,6b]

The oxygenation of **1** was followed by electron paramagnetic resonance (EPR) spectroscopy (Figure S2). Perpendicular-mode X-band EPR spectra of $[Mn^{II}H_2bupa]^-$ reveal the complex as a nearly axial $S = 5/2$ spin system with a large zero-field splitting constant of $D \sim 0.3$ cm^{-1}. After exposure to O_2, the $S = 5/2$ signal decreases as a new parallel-mode EPR signal associated with **2** appears at a g value of 8.2 (Figure 2A). A quantitative simulation of the signal (Figure 2B) indicates an $S = 2$ ground state with a six-line ($I = 5/2$) hyperfine splitting of $a = 57$ G. Variable temperature studies determined that the signal is from the ground doublet with $D = -2.0(5)$ cm^{-1}. The spin state, zero-field splitting, and hyperfine constant are in agreement with other known monomeric Mn^{III} species.[5d,13] Moreover, the negative sign for the axial zero-field splitting constant is consistent with tetragonally elongated octahedral coordination geometry. The simulations also indicate that **2** accounts for 80(10)% of the Mn in the sample. In perpendicular-mode, this sample also showed the signal of the initial Mn(II) complex (6%) and a mixed valent species at $g = 2$ (4%). The parallel-mode signal vanishes after prolonged incubation (6 h) at room temperature—the identity of the resultant species are under investigation.

Isotopic labeling studies support the presence of a peroxo ligand coordinated to the Mn^{III} center in **2**. Solution FTIR spectra recorded at room temperature contained a peak at 885 cm^{-1} for **2** prepared

[†] University of California—Irvine.
[‡] Carnegie Mellon University.

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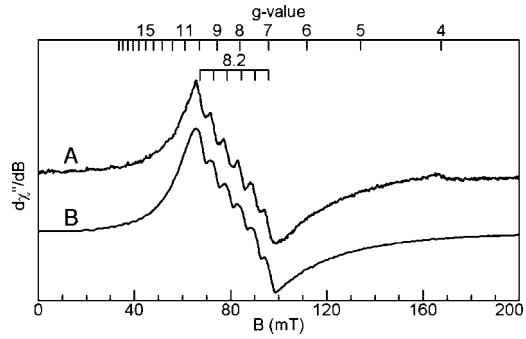


Figure 2. Parallel-mode EPR spectrum (A) and simulation (B) of **2** (10 mM in DMF) recorded at 11 K. Microwave frequency and power, 9.379 GHz, 0.2 mW; modulation, 10 G. Simulation parameters: $S = 2$, $g = 2.0$, $D = -2$ cm^{-1}, $E/D = 0.13(3)$, $A = 160$ MHz.

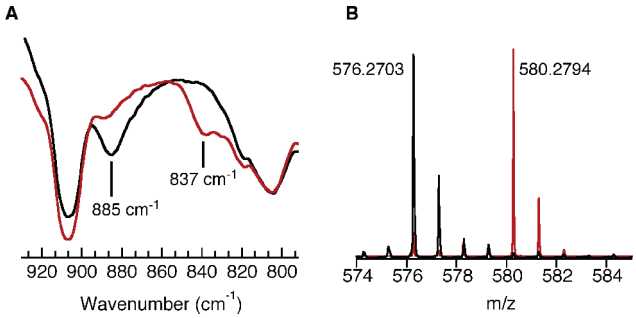
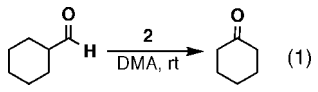


Figure 3. FTIR (A) and negative-mode ESI-MS (B) spectra of **2** after exposure to $^{16}O_2$ (black) and $^{18}O_2$ (red) collected from DMA solutions at room temperature.

under a $^{16}O_2$ atmosphere (Figure 3A). The ^{18}O-isotopomer can be prepared from $^{18}O_2$, causing a shift in the peak to 837 cm^{-1}. The observed vibrational change between the two isotopomers is as expected based on a harmonic O−O oscillator ($\nu(^{16}O_2)/\nu(^{18}O_2) = 1.06$; calcd = 1.07).[14] These vibrational values are in the range normally observed for other metal-based peroxo systems. For instance, the η^2-peroxoMn^{III}(Tp)[15] complexes of Kitajima, formed using H_2O_2, have FTIR-active peaks at 892 cm^{-1} that were assigned to $\nu(O_2)$.[6a] The electrospray ionization mass spectrum (ESI-MS) of **2** prepared with $^{16}O_2$ exhibits a strong ion with a mass-to-charge ratio (m/z) of 576.2703 (Figure 3B), a shift of 33 mass units from the peak associated with **1** (Figure S3). The mass and calculated isotopic distribution corresponds to the addition of a hydroperoxo ligand to **1** (calcd, 576.2706; Figure S4A). Furthermore, when **2** was prepared from $^{18}O_2$, the molecular ion peak shifts by 4 mass units (Figure 3B) to a m/z of 580.2794 (calcd, 580.2792; Figure S4B).

Preliminary reactivity studies indicate that **2** leads to the oxidative deformylation of aldehydes. For instance, treating **2** with cyclohexanecarboxaldehyde afforded cyclohexanone as the only GC−MS detectable product in an unoptimized yield of 40% (eq 1). Note that deformylation reactions are known for iron(III)[16] and manganese(III)[6b] peroxo complexes.



(1)

The spectroscopic, mass spectrometry, and reactivity results are consistent with **2** being a monomeric peroxomanganese(III) complex. A possible mechanism for its formation would involve a superoxomanganese(III) intermediate that reacts with solvent or external substrates, such as DPH, via a H-atom abstraction process to initially produce a η^1-hydroperoxoMn(III) complex (Figure 1, **2a**). The reduction and protonation of the superoxo ligand mirrors steps proposed during turnover in cytochrome P450. The tautomeric η^2-peroxomanganese(III) species (Figure 1, **2b**) could be formed from **2a** by intramolecular proton transfer from the hydroperoxo to the carboxamido component of the tripodal ligand. In this pathway, the pivaloylamide moiety is re-formed to provide an additional H-bond donor within the cavity. At present, we cannot distinguish between these two structural possibilities. Nevertheless, our findings establish that a mononuclear peroxoMn(III) can be produced from O_2 at room temperature.

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

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(11) Yields are obtained from EPR simulations using SpinCount developed by one of the authors (M.P.H.).
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