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

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Abstract

The binding and activation of dioxygen by transition metal complexes is a fundamentally and practically important process in chemistry. Often the initial steps involve formation of peroxometal species that is difficult to observe because of their inherent reactivity. The interaction of dioxygen with a manganese(II) complex (**1**) of bis[*N'*-*tert*-butylurealy]-*N*-ethyl]-6-pivalamido-2-pyridylmethyl)amine was investigated, leading to the detection of a new intermediate that is a peroxomanganese(III) complex (**2**). This complex is high-spin ($S = 2$) with a g -value of 8.2 and $D = -2.0(5)$ as determined by parallel-mode electron paramagnetic resonance spectroscopy. The coordination of a peroxo ligand was established using Fourier transform infrared spectroscopy that reveals a new signal at 885 cm^{-1} for **2** when formed from $^{16}\text{O}_2$ —this band shifts to 837 cm^{-1} when $^{18}\text{O}_2$ is used in the preparation. Moreover, electrospray ionization mass spectra contain a strong ion at an m/z of 576.2703 for the ^{16}O -isotopomer that shifts to 580.2794 in the ^{18}O -isotopomer. Complex **2** also is capable of oxidatively deformylating aldehydes, which is a known reaction of peroxometal complexes. The similarities of **2** to the peroxo intermediates in cytochrome P450 are noted.

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 $\text{Mn}^{\text{IV}}_2(\mu\text{-}1,2\text{-peroxo})$ 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

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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>.

superoxides⁵ or peroxides⁶ 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 (H₅bupa) that combines two urea arms with one carboxyamidopyridyl moiety⁹—the Mn^{II} complex of this ligand binds O₂ to produce a detectable peroxomanganese(III) species.

Preparation of the precursor **1** is outlined in Figure 1.¹⁰ Treating H₅bupa with 3 equivalents (equiv) of KH in dimethylacetamide (DMA) followed by one 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 [H₂bupa]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% yield¹¹ when [Mn^{II}H₂bupa]⁻ reacts with O₂ 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, which is converted to azobenzene (>95% yield). Monitoring the reactions with optical spectroscopy shows that **2** has a visible absorbance band at λ_{max} ≈ 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}H₂bupa]⁻ reveal the complex as a nearly axial *S* = 5/2 spin system with a large zero-field constant of *D* ~ 0.3 cm⁻¹. After exposure to O₂, 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 6-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.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 presences 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 under a ¹⁶O₂ atmosphere (Figure 3A). The ¹⁸O-isotopomer can be prepared from ¹⁸O₂, 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 (*v*(¹⁶O₂)/*v*(¹⁸O₂) = 1.06; calc'd = 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 H₂O₂, have FTIR-active peaks at 892 cm⁻¹ that were assigned to $\nu(\text{O}_2)$.^{6a} The electrospray ionization mass spectrum (ESI-MS) of **2** prepared with ¹⁶O₂ 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** (calc'd, 576.2706; Figure S4A). Furthermore, when **2** was prepared from ¹⁸O₂ the molecular ion peak shifts by 4 mass-units (Figure 3B) to a m/z of 580.2794 (calc'd, 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 un-optimized 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 an 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 reformed 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 O₂ at room temperature.

Supplemental Materials

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Figure 1.

Preparative routes for **1** and **2**, showing two possible tautomers for **2**. The thermal ellipsoid plot of [Mn^{II}H₂bupa]⁻ 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).

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: $S = 2$, $g = 2.0$, $D = -2 \text{ cm}^{-1}$, $E/D = 0.13(3)$, $A = 160 \text{ MHz}$.

Figure 3. FTIR (A) and negative-mode ESI-MS (B) spectra of **2** after exposure to ¹⁶O₂ (—) and ¹⁸O₂ (—) collected from DMA solutions at room temperature.