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Reversible O−O Bond Cleavage and Formation between Mn(IV)-Peroxo and Mn(V)-Oxo Corroles

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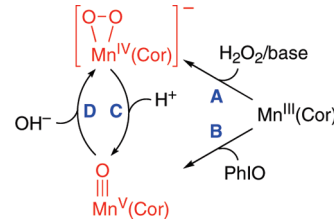
Abstract: Mn(IV)-peroxo and Mn(V)-oxo corroles were synthesized and characterized with various spectroscopic techniques. The intermediates were directly used in O−O bond cleavage and formation reactions. Upon addition of proton to the Mn(IV)-peroxo corrole, the formation of the Mn(V)-oxo corrole was observed. Interestingly, addition of base to the Mn(V)-oxo corrole afforded the formation of the Mn(IV)-peroxo corrole. Thus, we were able to report the first example of reversible O−O bond cleavage and formation reactions using in situ generated Mn(IV)-peroxo and Mn(V)-oxo corroles.

Dioxygen O−O bond-cleaving and bond-forming reactions occur at transition metal centers in a number of metalloenzymes. For example, heme and nonheme iron monooxygenases bind and activate O_2 to generate high-valent iron-oxo intermediates via O−O bond cleavage of iron(III)-peroxo precursors, $[Fe(III)\text{-}O_2]^+$.[1] The O−O bond activation of iron−O_2 adducts has for that reason been intensively investigated using synthetic iron porphyrins to elucidate mechanisms of the iron-oxo intermediate formation over the past several decades (e.g., heterolysis vs homolysis).[2]

In the case of the O−O bond formation, the photosynthetic conversion of water into dioxygen occurs at the oxygen-evolving complex (OEC) in photosystem II (PS II); a manganese(V)-oxo intermediate has been implicated as an active species for the O−O bond formation.[3] Very recently, Gao et al. reported an elegant result that the reaction of a Mn(V)-oxo corrole and hydroxide affords O_2 evolution; the O−O bond formation in the reaction was proposed to occur via nucleophilic attack of hydroxide ion on a Mn(V)-oxo moiety.[4] Thus, O−O bond cleavage and O−O bond formation reactions in metalloenzymes have been successfully mimicked by biomimetic model studies. However, reversible O−O bond cleavage and formation between metal-O_2 and metal-oxo species has not been successfully modeled.[5] Herein we report the first example of a reversible conversion between manganese-peroxo and -oxo corrole complexes via O−O bond cleavage and formation processes (see Scheme 1).

Addition of 1.2 equiv of H_2O_2 to a solution containing a manganese(III) corrole, Mn(TFMPC) (**1**, 3×10^{-2} mM) (TFMPC = 5,10,15-tris(3,5-trifluoromethylphenyl)corrolato trianion) (see structure in Supporting Information (SI), Figure S1), and tetramethylammonium hydroxide (TMAH, 20 equiv) in CH_3CN at 10 °C afforded the formation of a new intermediate, **2**, with absorption bands at 435 and 590 nm within 1 min (Scheme 1, reaction A; Figure 1 and SI, Figure S2 for UV−vis spectral changes). The intermediate was stable enough to be characterized by various spectroscopic methods (∼10 min at 10 °C). The electrospray ionization mass spectrum (ESI MS) of **2** exhibited a prominent ion peak at a mass-to-charge ratio (*m*/*z*) of 1090.8, which corresponds to the mass and isotope distribution pattern of $[Mn(TFMPC)(O_2)(CH_3CN)(CH_3OH)]^-$ (calculated *m*/*z* 1091.1; Figure 2a). The ESI MS of **2**, prepared with D_2O_2 in D_2O, showed the identical mass peak (SI, Figure S3), whereas **2**, prepared with $H_2{}^{18}O_2$ in $H_2{}^{16}O$, showed a mass peak at *m*/*z* 1094.8, which corresponds to $[Mn(TFMPC)(^{18}O_2)(CH_3CN)(CH_3OH)]^-$ (Figure 2a, inset). The 4 mass unit increase upon the substitution of ^{16}O with ^{18}O indicates that **2** contains an O_2 unit derived from H_2O_2. The X-band EPR spectrum of **2** exhibited a broad signal at $g \approx 4$ (Figure 2b and SI, Figure S4 for EPR spectra taken during reactions), which we assign to a high-spin $S = 3/2$ Mn(IV) with a strong zero-field splitting.[6] Taken together, the spectroscopic data provide strong evidence that **2**, generated in the reaction of **1** and H_2O_2 in the presence of base, is a high-spin Mn(IV) complex bearing an O_2 ligand, $[Mn(IV)(TFMPC)(O_2)]^-$.[7]

Scheme 1



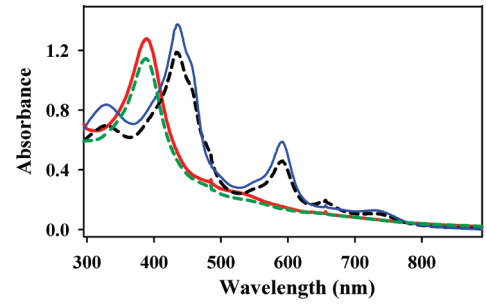


Figure 1. UV−vis spectra of **2** (solid blue line), **3** (solid red line), after addition of acid (20 equiv of $HClO_4$) to **2** (dashed green line), and after addition of base (20 equiv of TMAH) to **3** (dashed black line).

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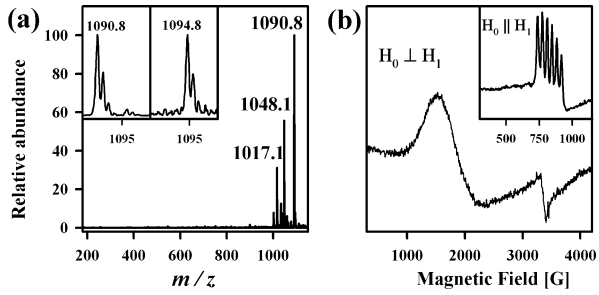


Figure 2. (a) ESI MS spectrum of **2**. Inset shows isotope distribution patterns for **2**-^{16}O (left) and **2**-^{18}O (right). The mass peaks at *m*/*z* 1017.1 and 1048.1 correspond to $[Mn(TFMPC)(CH_3O)]^-$ and $[Mn(TFMPC)(CH_3O)_2]^-$, respectively. (b) EPR spectrum of **2**. Inset shows a parallel mode X-Band CW-EPR spectrum of the starting Mn^{III}(TFMPC) complex. Also, see SI, Figure S4.

We then synthesized a Mn(V)-oxo corrole complex, **3**, by reacting **1** with 2.0 equiv of iodosylbenzene (PhIO) in CH_3CN at 10 °C (Scheme 1, reaction B; Figure 1 and SI, Figure S5 for UV−vis spectral changes).[8] The ESI MS of **3** exhibited a prominent ion peak at *m*/*z* 1002.1, whose mass and isotope distribution pattern corresponds to Mn(TFMPC)(O) (calculated *m*/*z* 1002.1; Figure 3a). When **3** was prepared with isotopically labeled PhI^{18}O in the presence of $H_2{}^{18}O$, a mass peak corresponding to Mn(TFMPC)(^{18}O) appeared at *m*/*z* 1004.2 (calculated *m*/*z* 1004.1; Figure 3a, inset). **3** is EPR silent (SI, Figure S4), suggesting a diamagnetic d^2 ($S = 0$) species as has been reported for other Mn(V)-oxo corrole and corrolazine complexes.[8,9] The resonance Raman spectrum of **3**, measured in CH_3CN at −40 °C with 442-nm laser excitation, displays an isotope sensitive band at 957 cm^{-1}, which shifts to 920 cm^{-1} upon introduction of ^{18}O (Figure 3b). The observed isotopic shift of −37 cm^{-1} with ^{18}O substitution is in close agreement with the value calculated for a Mn−O diatomic oscillator (−42 cm^{-1}). The calculated force constant for the 957 cm^{-1} mode by a simple Hook's law is 6.7 mdyne/Å, which is consistent with triply bonded Mn−O bonds in Mn(V)-oxo complexes.[8c,9,10] Taken together, the spectroscopic data demonstrate that **3** is a Mn(V)-oxo corrole with a Mn−O triple bond, Mn^V(O)(TFMPC).

Remarkably, a reversible conversion between the Mn(IV)-peroxo and Mn(V)-oxo corroles was observed upon addition of acid and base (Scheme 1, reactions C and D); this reversible cycle could be repeated several times without showing a significant decrease of the absorption bands corresponding to the products. First, the Mn(IV)-peroxo complex, **2**, was converted to the Mn(V)-oxo complex, **3**, upon addition of $HClO_4$ (Scheme 1, reaction C); the full formation of **3** was confirmed by the UV−vis and EPR spectra of the resulting solution (Figure 1 and SI, Figure S4). In addition,

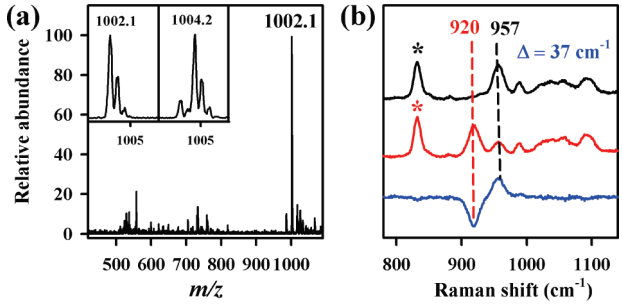
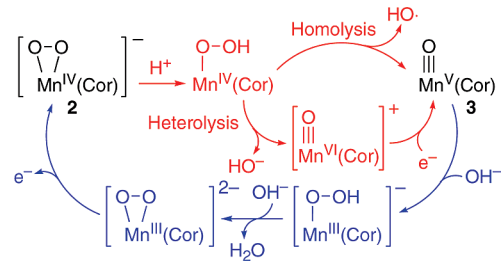


Figure 3. (a) ESI MS spectrum of the complex **3**. Inset shows isotope distribution patterns prepared with PhI^{16}O (left) and PhI^{18}O (right). (b) Resonance Raman spectra of **3** prepared with PhI^{16}O (black line) and PhI^{18}O (red line), and the difference spectrum of **3**-^{16}O−**3**-^{18}O (blue line). The peaks marked with * are from solvent.

2 was converted to **3** by addition of benzoyl chloride (data not shown). It has been well-documented that the reactions of metal-peroxo species, including Mn(III)-peroxo porphyrins, with benzoyl chloride lead to formation of their corresponding high-valent metal-oxo species.[11] However, the O−O bond cleavage mechanism of the putative Mn(IV)−OOH intermediate is not yet clear at this moment (see Scheme 2 for O−O bond homolysis vs heterolysis). Nevertheless, to our knowledge, this is the first demonstration of the analogous conversion of a Mn-peroxo corrole to a Mn-oxo corrole upon protonation.

Scheme 2. Proposed Mechanisms of O−O Bond Cleavage and Formation between Mn-Peroxo and -Oxo Corroles



In the O−O bond formation reaction, addition of base to the Mn(V)-oxo complex, **3**, produced the Mn(IV)-peroxo complex, **2**, quantitatively (Scheme 1, reaction D; Figure 1). The formation of **2** was further confirmed by taking EPR and ESI MS of the resulting solution; a broad signal at $g \approx 4$ was observed in the EPR spectrum (SI, Figure S4). In ESI MS experiments, **2** prepared in the reaction of Mn(V)^{16}O and $^{16}OH^-$ contained an $^{16}O^{16}O$ group (SI, Figure S6). Similarly, **2** prepared in the reaction of Mn(V)^{18}O and $^{16}OH^-$ contained an $^{18}O^{16}O$ group (SI, Figure S6). These results demonstrate that the peroxo ligand in **2** was generated by the O−O bond formation between the Mn-oxo moiety in **3** and the hydroxide ion, followed by a deprotonation of a hydroperoxo ligand by another hydroxide ion (Scheme 2).[4,12] However, there is an electron missing in the proposed mechanism, and this is probably due to a greater stability of a Mn(IV)-peroxo corrole species under the reaction conditions.

In conclusion, we have synthesized and characterized new Mn(IV)-peroxo and Mn(V)-oxo corroles and used them in O−O bond cleavage and formation reactions. We have also shown the first example of reversible O−O bond cleavage and formation between high-valent metal-oxo and metal-peroxo species. Future studies will be focused on understanding mechanistic aspects involved in the O−O bond cleavage and formation processes.

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Supporting Information Available: Experimental details and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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