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Isolation of Monomeric $Mn^{III/II}-OH$ and $Mn^{III}-O$ Complexes from Water: Evaluation of O−H Bond Dissociation Energies

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We report the synthesis and properties of monomeric $Mn^{III/II}-OH$ and $Mn^{III}-O$ complexes derived from water. Furthermore, we have been able to estimate the $Mn^{III/II}O-H$ bond dissociation energies (BDE_{OH}), which are important to understand the function of Mn−O(H) units in metalloproteins.

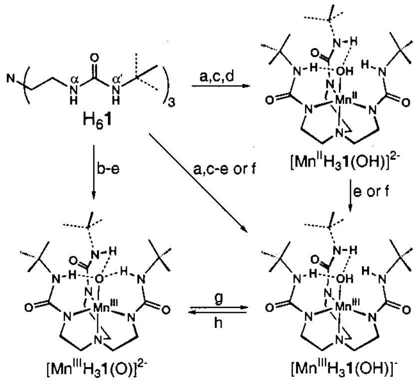
Non-heme manganese complexes with terminal hydroxo and oxo ligands are proposed intermediates in a variety of metalloproteins.[1] This includes the tetramanganese cluster of the oxygen evolving complex (OEC) in photosystem II (PSII).[2] Current theories on the mechanism of water oxidation in OEC have suggested that water or hydroxo ligands are terminally coordinated to at least one of the Mn centers in the cluster.[3] Stepwise conversion to a MnO species is accomplished via the net transfer of hydrogen atom(s). This conversion is mediated by a tyrosyl radical ($Y_ZO^\bullet$), located ~4.5 Å from the manganese cluster,[4] which acts to abstract the hydrogen atom.[3a,4] The theories predict that the MnO unit(s) is ultimately involved in O−O coupling to form O_2.[2a−4]

There is still substantial debate on the details of these mechanisms, yet for them to be thermodynamically viable, the energy for cleaving the MnO−H bonds must be similar to the energy produced upon forming the Y_ZO-H bond. Tyrosine has a BDE_{OH} of 86 kcal/mol,[5a] which is significantly smaller than that found for water ($BDE_{OH} = 119$ kcal/mol).[5b] However, water coordinated to a manganese center alters the thermodynamic properties for hydrogen-atom abstraction from that of free water. For example, BDE_{OH} values range from 82 to 94 kcal/mol for the terminal water ligands in a series of $Mn^{III}_2L_2OH_2$ and $Mn^{IV}_2L_2OH_2$ complexes (L = 1,3-bis(salicylideneamino)propane).[6a] In addition, BDE_{OH} values of ~77 kcal/mol have been reported for bridging hydroxo ligands in $Mn^{III}Mn^{IV}$ complexes.[6b,7]

Less is known about the reactivity and thermodynamic properties of manganese complexes[8] with terminal hydroxo ligands. This type of complex is difficult to isolate synthetically because OH^- ligands tend to bridge between manganese centers. We recently introduced the tripodal ligand tris[(*N′*-*tert*-butylureayl)-*N*-ethyl)]amine (H_6**1**),[9] which assists in isolating monomeric, five-coordinate metal complexes. The tetradentate metal ion chelate ($[H_3\mathbf{1}]^{3-}$) is formed by deprotonating αN−H groups on each urea arm (Scheme 1). Upon metal-ion binding, $[H_3\mathbf{1}]^{3-}$ generates a rigid H-bond cavity around vacant coordinate sites on the metal. This ligand has been used to synthesize terminal oxo and hydroxo complexes of Fe^{III} and Mn^{III} ions by activation of O_2.[9b,c]

During the course of these studies, we found that deprotonating the α′ nitrogens yields metal complexes with basic sites within the cavity.[9c,d] These sites act to scavenge protons produced upon coordination of external ligands with concomitant formation of α′N−H groups within the cavity. This approach has permitted the synthesis of $Mn^{III/II}-OH$ and $Mn^{III}-O$ complexes *directly from water*, which have been used to probe the physical properties and reactivity of complexes with Mn−O(H) units.

Scheme 1 [a]



[a] Conditions: (a) 4 equiv KH, DMA, Ar, RT; (b) 5 equiv KH, DMA, Ar, RT; (c) $Mn(OAc)_2$, Ar, RT; (d) 1 equiv H_2O, Ar, RT; (e) 0.5 equiv O_2 or I_2, Ar, RT; (f) 1 equiv Fc^+, Ar, RT (g) 1 equiv HA, DMA, Ar, RT; (h) 1 equiv $KOCH_3$, DMA, Ar, RT.

Scheme 1 outlines the syntheses of the $[Mn^{III/II}H_3\mathbf{1}(OH)]^{-/2-}$ and $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ complexes.[10,11] $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ is formed in 72% yield by treating H_6**1** with 4 equivalents (equiv) of KH prior to metalation and water addition. This amount of KH deprotonates one α′ and all α nitrogens in H_6**1**. $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ can be oxidized to $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ using either I_2, ferrocenium (Fc^+), or O_2, with isolated yields for $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ of 46%. The $Mn^{III}-O$ complex, $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ is obtained in 60% isolated yield, when *5 equiv* of KH are employed. Dioxygen or I_2 were used as oxidants to form the $Mn^{III}-O$ complex. All of the manganese complexes are high-spin, with either $S = {}^5/_2$ or 2 ground states.

Water was confirmed as the source of oxygen in the hydroxo and oxo ligands of $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ and $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ by isotopic labeling studies. The syntheses of $[Mn^{III}H_3\mathbf{1}(^{18}O)]^{2-}$ and $[Mn^{III}H_3\mathbf{1}(^{18}OH)]^{-}$ were accomplished by the routes in Scheme 1, using I_2 or Fc^+ as oxidants and $H_2{}^{18}O$. For $[Mn^{III}H_3\mathbf{1}(^{16}O)]^{2-}$, the $\nu(Mn^{16}O)$ band is at 700 cm^{-1},[12] which shifts to 672 cm^{-1} in $[Mn^{III}H_3\mathbf{1}(^{18}O)]^{2-}$ (FTIR: $\nu(Mn^{16}O)/\nu(Mn^{18}O) = 1.04$; calcd 1.05). $[Mn^{III}H_3\mathbf{1}(^{16}OH)]^{-}$ exhibits a $\nu(^{16}OH) = 3616$ cm^{-1}, while in $[Mn^{III}H_3\mathbf{1}(^{18}OH)]^{-}$ it is at 3605 cm^{-1} (FTIR: $\nu(^{16}OH)/\nu(^{18}OH) = 1.003$; calcd 1.003). Each complex incorporated >90% of the ^{18}O label.

X-ray diffraction studies add further support that the complexes are monomeric.[10] All complexes in this series have trigonal bipyramidal coordination geometry, as depicted in Figure 1 for $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ and $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$. The trigonal plane around the manganese ions is formed by α-urea nitrogens of $[H_3\mathbf{1}]^{3-}$. N1, the apical nitrogen of $[H_3\mathbf{1}]^{3-}$, and O1 of the oxo or hydroxo ligands complete the primary coordination sphere and are positioned nearly trans to each other (O1−Mn1−N1 ~177°). An average Mn1−O1 distance

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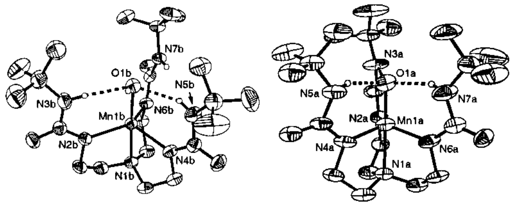

Figure 1. Thermal ellipsoid diagrams of $[Mn^{II}H_3\mathbf{1b}(OH)]^{2-}$ (left), $[Mn^{III}H_3\mathbf{1a}(O)]^{2-}$ (right) derived from water. Ellipsoids drawn at 50% probability level, and only urea and hydroxide hydrogens shown. Selected bond lengths (Å) and angles (deg) for $[Mn^{III}H_3\mathbf{1a}(O)]^{2-}$ $\{[Mn^{II}H_3\mathbf{1b}(OH)]^{2-}\}$:Mn1−O1, 1.780(5){2.059(2)}; Mn1−N1, 2.141(5) {2.317(2)}; Mn1−N2, 2.047(5){2.135(2)}; Mn1−N4, 2.102(5){2.163(2)}; Mn1−N6, 2.062(5){2.182(2)}; O1−Mn1−N1, 178.1(2){176.73(7)}, N2−Mn1−N4, 120.1(2){123.61(8)}; N2−Mn1−N6, 124.7(2){118.78(7)}; N4−Mn1−N6, 108.2(2){104.42(8)}.

of 1.771(4) Å is observed in $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$,[12,13] which is significantly shorter than those found in $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ (2.059(2) Å) and $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ (1.872(2) Å).[9b] The α′N−H groups of $[H_3\mathbf{1}]^{3-}$ are directed toward the Mn−O(H) units, with O1⋯α′N distances < 2.95 Å. These distances are indicative of intramolecular H-bonds.

Cyclic voltammetry (CV) in DMSO reveals that the $[Mn^{III/II}H_3\mathbf{1}(OH)]^{-/2-}$ complexes have a redox couple ($E_{1/2} = -1.51$ V vs $Fc^{+/0}$). This potential is consistent with synthetic results, which showed that mild oxidants, such as I_2 ($E_{1/2} = -0.14$ V vs $Fc^{+/0}$ in acetonitrile),[14] can convert $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ to $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ (vide infra). $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ has two redox processes at $E_{1/2} = -0.59$ and -0.076[15] V vs $Fc^{+/0}$, which are assigned to the $Mn^{III/II}$−O and $Mn^{IV/III}$−O couples, respectively. Treating $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ with various weak acids in DMSO affords $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ in isolated yields of >90%. A pK_a of 28.3(1) was determined for $[Mn^{III}H_3\mathbf{1}(OH)]^{-} \rightleftarrows [Mn^{III}H_3\mathbf{1}(O)]^{2-} + H^{+}$, in DMSO.[10,16]

The BDE_{OH} for $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ can be obtained from the $E_{1/2}$ and pK_a values, using the thermodynamic approach introduced by Bordwell and adapted by Mayer for $[HOMnO_3]^{-}$.[8,10,17,18] A BDE_{OH} value of 77(4) kcal/mol for $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ in DMSO was determined by this method. To corroborate this calculated value, the reactivity of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ was investigated with RH_2 substrates of known C−H bond strengths (eq 1). Treating $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$

$$2\,[Mn^{III}H_3\mathbf{1}(O)]^{2-} + RH_2 \rightarrow 2\,[Mn^{II}H_3\mathbf{1}(OH)]^{2-} + R \tag{1}$$

with 1,4-cyclohexadiene (CHD, $BDE_{CH} = 73$ kcal/mol)[18a] produced $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ (95% yield) and benzene (82% yield). Similarly, $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ reacts with 9,10-dihydroanthracene (DHA, $BDE_{CH} = 78$ kcal/mol) to afford anthracene and $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ in >90% isolated yields. However, no reaction was observed when $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ was treated with hydrocarbons having $BDE_{CH} \geq 80$ kcal/mol. These substrates include, 2,3-dimethyl-2-butene (DMB), diphenylmethane, and ethylbenzene.[8c,18a] In contrast, treating $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ with 4-methoxyphenol and 2,4,6-tri-*tert*-butylphenol affords only $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ in yields of >95%. Note that $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ does not react with either CHD, DHA, or DMB.

By a similar thermodynamic method, a BDE_{OH} value of 110(4) kcal/mol was calculated for $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$. The 33 kcal/mol difference in BDE_{OH} between $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ and $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ most likely reflects the higher affinity of the Mn^{IV}−oxo complex, $[Mn^{IV}H_3\mathbf{1}(O)]^{-}$, for a hydrogen atom compared to that of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$. The large BDE_{OH} value for $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ agrees with recent findings from density functional theory on a monomeric Mn^{III}O−H complex.[19] A BDE_{OH} value of 103 kcal/mol has been reported for the conversion of Mn^{III}O−H to Mn^{IV}═O in a neutral complex by formal transfer of a hydrogen atom.

To our knowledge, this is the first instance in which a series of monomeric manganese complexes with terminal hydroxo and oxo ligands were prepared with the use of water. Structural and physical studies demonstrate that $[Mn^{III/II}H_3\mathbf{1}(OH)]^{-/2-}$ and $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ have similar primary and secondary coordination spheres. $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ cleaves weak C−H bonds, as was shown by its reactivity with CHD and DHA. These results indicate that Mn^{II}O−H bond strength in $[Mn^{II}H_3\mathbf{1}(OH)]^{2-}$ is ~13 kcal/mol less than that for phenol in DMSO (BDE_{OH}(phenol) = 90(3) kcal/mol).[18a] However, the calculated BDE_{OH} for $[Mn^{III}H_3\mathbf{1}(OH)]^{-}$ is ~20 kcal/mol greater than that for phenol. This value supports theoretical predictions that homolytic cleavage of a Mn^{III}O−H bond is thermodynamically difficult and may not occur by reaction with a tyrosyl radical.[19,20]

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Supporting Information Available: Full synthetic details of all new complexes, data for isotopic labeling studies, $E_{1/2}$ and pK_a values, and descriptions of BDE_{OH} calculations (PDF). CIF format for X-ray analyses of $K_2[Mn^{II}H_3\mathbf{1}(OH)]\cdot 4DMA$ and $K_2[Mn^{III}H_3\mathbf{1}(O)]\cdot 4DMA$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) See Supporting Information for details.

(11) For other $M^{III/II}$−OH complexes with $[H_3\mathbf{1}]^{3-}$ see ref 9d.

(12) In a previous account on the properties of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ derived from O_2, a $\nu(Mn^{16}O) = 617\ cm^{-1}$ and a Mn−O1 distance of 1.801(4) Å were reported.[9b] The solid-state structure of the dipotassium salt of that complex has a potassium−oxo interaction (K^{+}- - -O1 = 2.837(3) Å), which is absent in the dipotassium salt of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ derived from H_2O. This difference between the crystal structures results from solvent packing. The ν(MnO) and Mn−O1 bond length differences are attributed to the absence of the K^{+}- - -O1 in the salt reported here.

(13) These complexes crystallized with two independent, but nearly identical, anions in the asymmetric unit.[10]

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(15) Obtained at a scan rate of 50 V/s using a 50 μm Pt electrode.

(16) Measured spectrophotometrically with 4-aminopyridine.

(17) The O−H bond strength was calculated from the equation $BDE_{OH} = 23.06E_{1/2} + 1.37pK_a + 73.3$ (kcal/mol).[8c,18]

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