Synthesis and structure of a Mn^{III}(OH) complex generated from dioxygen

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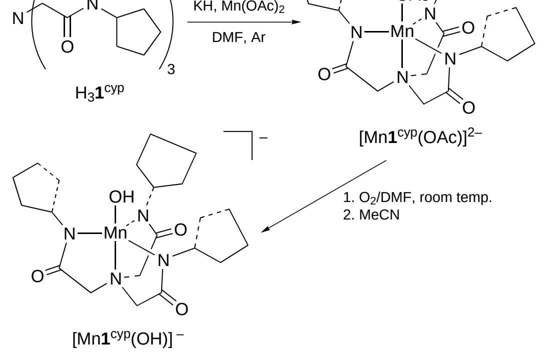
Dioxygen activation at room temperature by a new Mn^{II} complex having a cavity motif yields a monomeric Mn^{III} complex with a terminally bonded hydroxo ligand whose oxygen atom is derived from O_2.

The interactions of manganese ions with dioxygen are involved in a number of biological and synthetic processes.[1] In synthetic manganese complexes, dioxygen activation often leads to the isolation of multinuclear μ-oxo (hydroxo) bridged species having Mn–Mn separation of < 3.5 Å.[2,3] We recently developed a new class of tripodal ligands based on tris(*N*-alkylcarbamoylmethyl)amine that, when coordinated to a metal ion, create cavities that can regulate subsequent ligand binding.[4] Modeling studies (CPK) suggested that appending cyclopentyl groups from the amidate nitrogen (H_3**1**^{cyp})[5] would afford a cavity that has space for binding only one exogenous donor to the metal, in addition to preventing the formation of multinuclear metal complexes with metal–metal distances of < 3.5 Å. Thus, while the binding and activation of dioxygen by Mn^{II} complexes of [**1**^{cyp}]$^{3-}$ is possible, the formation of oxo(hydroxo)-bridge manganese complexes should be hindered, allowing us to study the formation of a new manganese complex derived from dioxygen.[6] Here, we report the room-temperature O_2 activation by a Mn^{II} complex of [**1**^{cyp}]$^{3-}$ that produces a monomeric Mn^{III} complex with a terminally bonded hydroxo ligand whose oxygen atom is derived from dioxygen. Preliminary mechanistic studies suggest a reaction pathway that involves C–H bond cleavage from solvent to form the hydroxo ligand.[7]

Treating an anhydrous dmf solution of K_2[Mn**1**^{cyp}(OAc)]† with 1 equiv. of dry O_2 at room temp. results in the formation of blue K[Mn**1**^{cyp}(OH)]‡ in 63% yield after washing with MeCN (Scheme 1). K[Mn**1**^{cyp}(OH)]18-crown-6 can be isolated in 90% yield when the reaction is carried out at room temp. in anhydrous MeCN. Initial assignment of the product as a monomeric Mn^{III}(OH) species is based on its room-temp. solid-state magnetic moment of 4.96 μ_B which is typical of a high-spin Mn^{III} ion,[8] and its FTIR spectrum containing a sharp peak at 3643 cm^{-1}, within the range found for known M–OH complexes.[9]



Scheme 1

The presence of a monomeric Mn^{III}(OH) moiety in K[Mn**1**^{cyp}-(OH)] was confirmed by an X-ray diffraction study.¶ The solid-state molecular structure of [Mn**1**^{cyp}(OH)]$^{-}$ shows the Mn ion having a trigonal-bipyramidal coordination geometry (Fig. 1). The three amidate nitrogens of [**1**^{cyp}]$^{3-}$ bind in the trigonal plane with an average Mn–N_{amide} distance of 2.069(2) Å and N_{amide}–Mn–N_{amide} angle of 117.07(7)°. These Mn–N_{amide} distances are significantly longer than those observed in the only other structurally characterized Mn^{III} amidate complex where the amidate nitrogens coordinate in a square-planar arrangement [av. M–N_{amide} 1.913(3) Å].[3] The Mn ion sits 0.355 Å out of the trigonal plane toward the hydroxo ligand. The hydroxo oxygen O(4) is positioned nearly *trans* to the apical nitrogen N(1) [N(1)–Mn–(O4) 177.7(2)°] with Mn–N(1) and Mn–O(4) distances of 2.036(2) and 1.816(4) Å. The Mn–O(4) distance observed in [Mn**1**^{cyp}(OH)]$^{-}$ is comparable to that reported for the only other known monomeric Mn^{III}(OH) complex {[Mn**1**(OH)];[5] Mn–O, 1.827(3) Å}.[10] The OH^{-} is located in a cavity formed by the three cyclopentyl substituents which are oriented such that the methine hydrogens on each ring are positioned outside the cavity toward the amide carbonyl groups. This conformation of cyclopentyl groups leads to a cavity structure that enshrouds the Mn^{III}(OH) motif, preventing the OH ligand from binding to another Mn complex.

Complexes containing Mn(OH) moieties are rare: only four other structurally characterized synthetic complexes have been reported.[10,11] Of these four, only one contains a monomeric Mn^{III}(OH) unit which is obtained by treating [Mn**1**Cl] with NaOH to yield the six-coordinate complex [Mn**1**(OH)].[10] The structure most closely associated with that found in [Mn**1**^{cyp}-(OH)]$^{-}$ is the active site of the manganese superoxide dismutase (MnSOD) isolated from *Thermus thermophilus*; this site contains a trigonal-bipyramidal geometry around a Mn^{III} center with an axially coordinated hydroxo ligand.[12] The hydroxo ligand in MnSOD, like those found in synthetic Mn(OH) complexes, is derived from a source other than dioxygen (*e.g.*, OH^{-} or H_2O). Although Mn^{III}(OH) complexes have been proposed as either intermediates or products in several reactions involving O_2 and Mn ions there are no examples,[1,13] to our knowledge, where structural proof verifies the identity of these species.

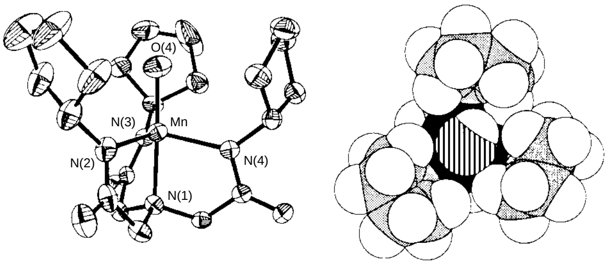


Fig. 1 Thermal ellipsoid diagram of [Mn**1**^{cyp}(OH)]$^{-}$ and a space-filling representation of the complex. The ellipsoids are drawn at the 50% probability level and hydrogens are removed for clarity. Selected bond distances (Å) and angles (°): Mn–N(1) 2.036(3), Mn–N(2) 2.061(3), Mn–N(3) 2.053(3), Mn–N(4) 2.094(3), Mn–O(4) 1.816(4), N(2)–Mn–N(3) 125.43(1), N(2)–Mn–N(4) 113.5(1), N(3)–Mn–N(4) 112.3(1), N(1)–Mn–O(4) 177.7(2).

In $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OH})]^-$ the oxygen atom of the hydroxo group originates from O_2: this was confirmed by treating $K_2[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OAc})]$ with $^{18}O_2$ in MeCN to afford $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(^{18}\mathrm{OH})]^-$ [FTIR; $\nu(^{18}\mathrm{OH})$ 3630 cm^{-1}, $\nu(^{16}\mathrm{OH})/\nu(^{18}\mathrm{OH}) = 1.004$; calc. 1.003]. In addition, the stoichiometry of the O_2 reaction, as determined by manometry, gives Mn complex : O_2 = 2 : 1. In the presence of PPh_3P (1 equiv.), the oxidation of $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OAc})]^{2-}$ with O_2 produces $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OH})]^-$ and Ph_3PO which is observed in 33% yield. Moreover, when the reaction is carried in CD_3CN (99.5% D) the product is exclusively $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OD})]^-$ [FTIR; ν(OD) 2687 cm^{-1}, $\nu(\mathrm{OH})/\nu(\mathrm{OD}) = 1.356$; calc. 1.374], demonstrating that solvent can serve as the source of the hydrogen (or deuterium) in the $\mathrm{Mn^{III}[OH(D)]}$ moiety. Similar results were obtained when the oxidation reaction was performed in $[^2H_8]$thf.

These observations are consistent with the formation of a dinuclear peroxo-bridge species during the reaction. A 1,2-μ-peroxo bridge species is postulated because the steric constraints of the cyclopentyl cavity prevents other modes of peroxide coordination.[14] Homolysis of the O–O bond can produce a Mn oxo intermediate whose oxo moiety is sufficiently buried inside the cavity that it is unable to react with other hindered Mn centers to form oxo-bridged clusters. With this pathway eliminated, the Mn oxo species is competent to react with solvent to form $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}\{\mathrm{OH(D)}\}]^-$, a process that most likely occurs *via* a H atom abstraction. Support for an oxo intermediate comes from the observed oxygenation of PPh_3 to Ph_3PO: such oxo-transfer reactions have been proposed to be promoted by high-valent oxo species.[15] Further studies into the mechanism and oxo-transfer properties of this system are in progress.[16]

The O_2 reactivity exhibited by $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OAc})]^{2-}$ is the first Mn complex of which we are aware that mediates the formation of a terminally bonded hydroxo ligand directly from O_2. In fact, this type of reactivity is rare for transition-metal complexes[17] and usually only occurs for reactions done at low temperatures (*e.g.*, $\mathrm{Fe^{II}}$ porphyrins).[6a] The room-temperature activation process observed for $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OAc})]^{2-}$ is controlled, in part, by the cavity motif provided by $[\mathbf{1}^{\mathrm{cyp}}]^{3-}$ that surrounds the O_2 binding site. This result contrasts with that reported by Floriani and coworkers for the room-temp. O_2 reactivity of a non-cavity containing $\mathrm{Mn^{II}}$ Schiff-base complex.[18] In that system, a μ-OH bridged $\mathrm{Mn^{III}}$ polymer is formed after O_2 activation with concomitant oxidation of the Schiff-base ligand where an imino group is converted to an amidato. We have not detected[19] any products that indicate modification of $[\mathbf{1}^{\mathrm{cyp}}]^{3-}$ during O_2 activation. A possible explanation for the lack of ligand oxidation in our system is the positioning of the methine C–H bonds of the cyclopentyl groups outside the cavity, away from the metal centers,[20] which protects these reactive sites from interacting with the activated (di)oxygen–Mn center(s).

Finally, $\mathrm{Mn^{III}(OH)}$ moieties have been recently proposed as key intermediates in the pathway for O_2 production from the oxygen evolving complex of photosynthesis.[21] Now that $[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OH})]^-$ is well characterized, reactivity studies will allow us to further evaluate the feasibility of this model,[22] efforts for which are underway.

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Footnotes and References

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† *Selected data* for $K_2[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OAc})]$: $\mu_{\mathrm{eff}} = 6.02\ \mu_B$ (solid, 298 K). FTIR (Nujol, cm^{-1}), ν(CO) 1661 (dmf, s); 1558 (amide, s); 1581 and 1343 (acetate, s, $\Delta\nu = 238$ cm^{-1}); and ν(CN) 2150 (MeCN, m); $\Delta\nu$ observed for the two acetate bands in $K_2[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OAc})]$ is consistent with monodentate acetato coordination.[9]

‡ *Selected data* for $K[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OH})]$: $\mu_{\mathrm{eff}} = 4.96\ \mu_B$ (solid, 298 K). FTIR (Nujol, cm^{-1}), ν(OH) 3643, ν(CO) 1606 and 1584; λ_{max}/nm (dmf) 433 (285 dm^3 mol^{-1}), 673 (460); $E_{\mathrm{pa}} = 0.48$ V *vs.* SCE; $E_{\mathrm{pc}} = -1.29$ V *vs.* SCE.

§ $E_{\mathrm{pa}} = 0.48$ V *vs.* SCE; $E_{\mathrm{pc}} = -1.29$ V *vs.* SCE.

¶ *Crystal data* for $K[\mathrm{Mn}\mathbf{1}^{\mathrm{cyp}}(\mathrm{OH})]C_3H_7NO$: triclinic, space group $P\bar{1}$, $a = 9.1855(5)$, $b = 10.3085(5)$, $c = 15.9444(8)$ Å, $\alpha = 90.182(1)$, $\beta = 94.849(1)$, $\gamma = 112.600(1)°$; $V = 1397.79(12)$ Å^3, $Z = 2$. Of 7341 reflections collected [Mo-Kα, $1.28 \leqslant \theta \leqslant 25.05°$; 173(2) K] 4752 were unique data ($R_{\mathrm{int}} = 0.0399$) and 3962 with $F_o^2 > \sigma F_o^2$; $R_1 = 0.0540$ and $wR_2 = 0.12137$ with a GOF (F^2) = 1.083. CCDC 182/593.

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