



Exploring Mn-O Bonding in the Context of an Electronically Flexible Secondary Coordination Sphere: Synthesis of a Mn(III)-Oxo

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COMMUNICATION

Exploring Mn–O Bonding in the Context of an Electronically Flexible Secondary Coordination Sphere: Synthesis of a Mn(III)-Oxo.

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Complexes containing manganese-oxygen bonds have been implicated in a variety of biological and synthetic processes. Herein, we describe the synthesis of a family of stable, high-spin trigonal bipyramidal manganese complexes of the electronically flexible ligand tris(5-cyclohexylimino-pyrrol-2-ylmethyl)amine [$\text{H}_3\text{N}(\text{pi}^{\text{Cy}})_3$] featuring apical water, hydroxyl, and oxo ligands. Terminal $\text{Mn}^{\text{III}}\text{-O}$ complexes are rare and the formation of this species was achieved from a variety of reagents including O_2 , PhIO and NO_2^- . Described herein is the preparation, structural and electronic properties of these manganese complexes.

Long touted for their role in biological processes, manganese-oxo complexes are proposed as key intermediates in a variety of biological systems, including the oxygen evolving complex (OEC) of photosystem II,¹ peroxidases,² catalases³ and manganese oxidizing bacteria.⁴ In all examples, the manganese centre traverses through multiple oxidation states, with Mn–O bonding interactions ranging from dative to multiple. The OEC, consisting of a Mn_4Ca cluster, is supported by both bridging hydroxos or oxos, and aspartic acid and histidine side chains from the protein, with the manganese metal centres ranging in oxidation state from three to five.^{3b, 5} Key intermediates in water oxidation include, manganese aqua, hydroxyl and oxo species.^{3, 5d, 5g} Hydrogen-bonding also plays a significant role in influencing the structure-function relationship of metalloenzymes.⁶ In the case of the OEC, hydrogen-bonds are influential in water oxidation, as they mediate proton transfer and stabilize the cubane structure. Additionally, several amino acids (tyrosine, histidine, tryptophan and cysteine) have been shown to facilitate electron transfer, alleviating the electronic burden often placed on the metal centre.^{6b}

Complexes featuring Mn–O bonds have played a key role in chemical catalysis, whereby the key intermediate in these oxidation processes is formation of the metal oxo species.⁷ Several reports have illustrated the generation of Mn–O bonds from a variety of substrates.^{8–11} However, prior to the work by Borovik,^{11a, 12} reports of low-valent manganese-oxo complexes were limited to bridging oxo moieties.^{3a, 13} Stabilization of the low valent terminal $\text{Mn}^{\text{III}}\text{-O}$

was realized in 2000, when a ligand architecture that featured a hydrogen-bonding cavity was used.^{11a} This remains the only example of a terminal $\text{Mn}(\text{III})\text{-O}$ complex. Recently, our research group reported the synthesis and characterization of a family of iron complexes supported by the electronically flexible ligand platform, tris(5-cyclohexylimino-pyrrol-2-ylmethyl)amine [$\text{H}_3\text{N}(\text{pi}^{\text{Cy}})_3$], (Scheme 1).¹⁴ Interested in examining the relationship between the tautomeric states accessible for the ligand platform and their role in the stabilization of metal-oxygen bonds, we postulated that this ligand platform would be ideal for the development of a model system for the OEC. Herein we describe the facile generation of key intermediates found in water oxidation including a Mn–OH, Mn–OH₂, and Mn–O supported by a ligand capable of tautomerizing to be either hydrogen-bond donating (tris(5-cyclohexylamino-azafulvene-2-methyl)amine, $\text{H}_3\text{N}(\text{afa}^{\text{Cy}})_3$) or accepting ($\text{H}_3\text{N}(\text{pi}^{\text{Cy}})_3$). The facile generation of a Mn(III)-oxo from a variety of reagents, including O-atoms transfer reagents, O_2 , and NO_2^- , is described, whereby the latter reaction represents the first example of facile nitrite reduction to afford a Mn(III)-oxo complex.

Scheme 1. Synthesis of complexes 1–3

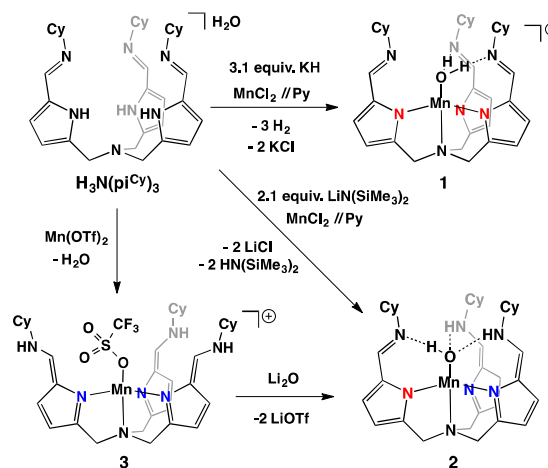


Figure 1. Molecular structure of complexes **1** - **4** shown with 30% probability ellipsoids. Selected hydrogen atoms, solvent molecules and counter ions have been removed for clarity.

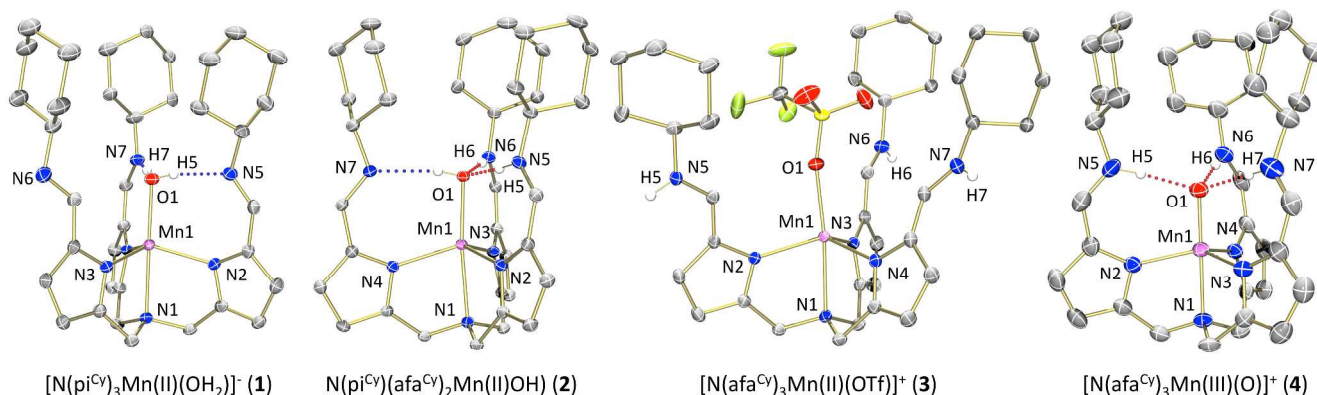


Table 1. Selected structural parameters of complexes **1-4**.

Bond	1 (Å)	2 (Å)	3 (Å)	4 (Å)
Mn1-N1	2.347(2)	2.3295(15)	2.3398(17)	2.114(5)
Mn1-N(pyr)	2.126(2) – 2.165(2)	2.1427(15) – 2.1784(15)	2.1201(17) – 2.1480(18)	2.056(5) – 2.067(5)
Mn1-O1	2.096(2)	2.0524(12)	2.1450(16)	1.789(4)
O1-H5	0.74(4)	1.75(2)	--	-- ^b
O1-H6	--	1.66(2)	--	-- ^b
O1-H7	0.89(5)	0.78(2)	--	-- ^b
C=N stretch	1617 cm ⁻¹	1645 cm ⁻¹	1641 cm ⁻¹	1659 cm ⁻¹
Magnetic Moment	6.15(15) μ _B	-- ^a	5.88(7) μ _B	5.22(16) μ _B

^aA reliable magnetic moment could not be obtained for complex **2** due to its insolubility. ^bH atoms were calculated in this structure, therefore hydrogen-bonding distances are not pertinent. O1-NX (X = 5, 6, 7) distances ranging from 2.673(7) – 2.747(16) Å support hydrogen-bonding interactions.

Synthesis of the desired manganese complexes, $[N(\pi^{Cy})_3Mn(OH_2)]^-$ (**1**), $N(\pi^{Cy})(afa^{Cy})_2Mn(OH)$ (**2**) and $[N(afa^{Cy})_3Mn(OTf)]^+$ (**3**) was accomplished following the previously reported synthetic procedures for the iron derivatives in comparable yields (Scheme 1). As complexes **1-3** are ¹H NMR silent, characterization of these species was performed by X-ray crystallography and IR spectroscopy (Figure 1, Table 1). As expected, distorted trigonal bipyramidal structures, analogous to those reported for the family of iron complexes, were observed. Most notably, ligand tautomerizations determined by intraligand bond distances, confirmed the desired electronic configuration of the ligand platform upon metallation (Chart S1).¹⁴⁻¹⁵ The solid-state infrared spectra (FTIR-ATR) of complexes **1-3** feature bands corresponding to the C=N stretches of the ligand platform similar to those reported for iron (**1-Fe**: 1603 cm⁻¹; **2-Fe**: 1624, 1655 cm⁻¹; **3-Fe**: 1637 cm⁻¹) and supported analogous coordination modes of the ligand between the different metal centres.

Following the synthesis of complexes **1-3**, oxidation experiments were explored to evaluate the propensity of these complexes to reduce small molecules. Exposure of complex **1** to an atmosphere of oxygen quickly afforded decomposition, indicated by free ligand noted in the ¹H NMR spectrum. In contrast, complex **2** was completely inert to oxygen. We propose this is a result of the hydrogen-bonding observed in the structure of **2**, protecting the metal centre from external substrates. Furthermore, the presence of H-bonding likely disfavours ligand dissociation which is required for the reactivity of O₂ to occur.

Oxidation of **3** was attempted via exposure to O₂, resulting in a gradual colour change from yellow to green over the course of 24 hours (Scheme 2). The green solid was obtained in 75% yield following workup. Characterization by ¹H NMR spectroscopy

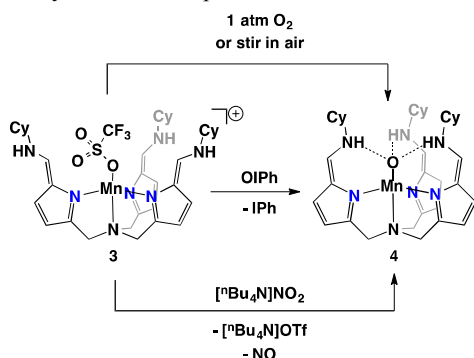
revealed 5 paramagnetically broadened and shifted features, ranging from -16.39 to 13.06 ppm (Figure S1). The solution magnetic moment of the product in dimethylformamide (μ_{eff} = 5.22(16) μ_B), as determined by the Evans' method, corresponds to high-spin Mn(III).^{11a, 16} ESI MS revealed the parent ion of **4** ($[N(afa^{Cy})_3Mn(O)]^+$, m/z = 652.35, Figure S2), which matches the predicted isotope pattern for the product and is consistent with the proposed molecular formula. Furthermore addition of 90% isotopically enriched PhIO¹⁸ showed the parent ion for the O¹⁸ isotopologue of **4** (m/z = 654.35) with 60% incorporation of O¹⁸. We believe the depreciation in O¹⁸ incorporation is due to rather fast exchange with water, which has previously been observed.¹⁷ The infrared spectrum of **4** does not indicate any O-H or N-H stretches consistent with this fast water exchange. The solution X-Band EPR spectrum of crystalline **4** in a 1:1 DCM/Toluene mixture (5 mM), collected in perpendicular mode displays a weak and broad transition centred at g = 8 (Figure S3). In parallel mode, the spectrum displays a forbidden, ±2 transition with a six-line hyperfine splitting centred at g_{eff} = 7.9 and simulated with the following: g_z = 1.95; E/D = 0.09; A_z = 262 MHz (Figure S3).

To confirm the formation of the proposed Mn(III)-oxo species, independent synthesis was attempted via oxygen-atom transfer reagents. Exposure of **3** to an equivalent of pyridine-N-oxide resulted in recovery of starting materials despite prolonged reaction periods. Heating the mixture gave rise to decomposition of complex **3**, as identified by the presence of free ligand in the ¹H NMR spectrum. However, addition of an equivalent of iodosylbenzene (PhIO) to an acetonitrile solution of **3** resulted in a gradual colour change from yellow to green-brown (Scheme 2). Trituration with THF resulted in the isolation of a green solid, confirmed as **4** by ¹H

NMR spectroscopy and mass spectrometry, albeit in depreciated yields (41%).

Refinement of structural data obtained from green crystals of **4** revealed a pseudo trigonal bipyramidal manganese centre with three datively coordinated azafulvene rings composing the equatorial plane, and a terminal oxygen bound *trans* to the apical nitrogen of the ligand platform (Figure 1, Table 1). As in the structure of the previously reported Fe(III)oxo, $[\text{N}(\text{afa}^{\text{Cy}})_3\text{Fe}(\text{O})]^+$,¹⁸ all three arms of the ligand platform are rotated inwards, with the amino hydrogen atoms composing a secondary coordination sphere and engaging in hydrogen-bonding interactions with the oxygen atom $[\text{O}1 \cdots \text{NX} = 2.673(7) \text{ \AA} (X=5), 2.747(16) \text{ \AA} (X=6), 2.706(7) \text{ \AA} (X=7)]$ (Note: Due to the quality of the crystal structure, H-atoms could not be located in the difference map, thus evidence for hydrogen-bonding comes from the O–N distances consistent with that of $[\text{N}(\text{afa}^{\text{Cy}})\text{Fe}(\text{O})]^+$.¹⁸ The Mn1–O1 distance of 1.789(4) Å is statistically identical to that of Borovik's Mn(III)-oxo (1.771(5) Å).^{12a} Furthermore, the Mn–O distance of **4** is significantly shorter than that of reported Mn(III)–OH bond distances which range from

Scheme 2. Synthesis of complex **4**.



1.806(13) – 1.8540(8) Å),^{8, 16} consistent with our assignment of the product as the Mn(III) terminal-oxo species.

To investigate the electronic changes upon oxidation of **3**, electronic absorption spectroscopy was employed (Figure S4). In the case of complex **3**, a single band centred at 327 nm ($\epsilon = 84386 \text{ M}^{-1}\text{cm}^{-1}$), attributed to the $\pi \rightarrow \pi^*$ transition of the ligand platform, is detected in the UV region of the spectrum. Upon oxidation to **4**, this $\pi \rightarrow \pi^*$ transition is slightly red-shifted, as a result of the reduction of electron density at the metal centre [$\lambda_{\text{max}} (\epsilon_{\text{m}}) = 335 \text{ nm} (33620 \text{ M}^{-1}\text{cm}^{-1})$]. Additionally, the spectrum of **4** resembles that previously reported for $[\text{Mn}(\text{III})\text{H}_3\text{buea}(\text{O})]^{2-}$ [$\lambda_{\text{max}} (\epsilon_{\text{m}}) = 498 \text{ nm} (490 \text{ M}^{-1}\text{cm}^{-1}), 725 \text{ nm} (240 \text{ M}^{-1}\text{cm}^{-1})$], with notable bands blue-shifted, located at 458 nm ($\epsilon = 507 \text{ M}^{-1}\text{cm}^{-1}$) and 621 nm ($\epsilon = 477 \text{ M}^{-1}\text{cm}^{-1}$).¹⁹ These energy differences are proposed to arise from the dative versus anionic coordination, respectively, of the ligand platforms.

In an effort to explore alternative synthetic routes to access complex **4**, the reactivity of the Mn(II) azafulvene complex (**3**) towards the reduction of nitrite was investigated (Scheme 2). Previously, our research group has reported the facile reduction of NO_2^- by an iron(II) non-heme species, $[\text{N}(\text{afa}^{\text{Cy}})_3\text{Fe}(\text{OTf})(\text{OTf})]$, resulting in the isolation of a terminal Fe(III)oxo complex, $[\text{N}(\text{afa}^{\text{Cy}})_3\text{Fe}(\text{O})](\text{OTf})$.¹⁸ Due to the similarities in structures of the iron and manganese starting materials, the ability of the manganese system to perform the analogous anion reduction was explored. Upon exposure of **3** to an equivalent of $[(^n\text{Bu})_4\text{N}](\text{NO}_2)$, formation of complex **4** was noted over a period of 24 hours at elevated temperatures (61%). This extended reaction time is in contrast to the immediate reduction noted by iron. Reduction of nitrite by a

manganese centre is exceedingly rare, with the sole example reported for a Mn-porphyrin system induced by irradiation of the Mn-nitrito precursor.²⁰

Structural characterization of Mn(III)-oxo complexes is exceedingly rare. To the best of our knowledge, the only synthesized complex preceding the example reported here is derived from the urea functionalized tris(2-aminoethyl)amine ligand platform studied by Borovik.^{11a} The ability to access these low valent metal oxo species is attributed to the presence of three amino moieties composing a hydrogen-bonding secondary coordination sphere.^{6a, 21} Additionally, as structural parameters of the starting material depict three amino moieties pointing away from the pocket of the complex, engaging in hydrogen-bonding interactions with the outer sphere triflate anion. Simple rotation about the C=C bond of the azafulvene moiety is not possible without tautomerization, suggesting dissociation of the arm of the ligand prior to appropriate positioning of the secondary coordination sphere. The amino groups of the ligand platform reposition themselves for the stabilization of the Mn(III)-oxo species. Similar to the dynamic flexibility in metalloenzymes, the dative coordination of the ligand platform, in concert with the electronic flexibility of the pyrrole-2-imine arms, negotiates this transformation.

Conclusions

Having a ligand scaffold that is capable of each arm tautomerizing independently, as reflected in the intraligand bond lengths of complex **2**, may adequately mimic the electronic nuances of the amino acids found within the protein superstructure of metalloenzymes. Capable of participating in bond cleavage events, dioxygen activation and subsequent formation of the Mn(III)-oxo species may be assisted by the hydrogen-bonding network found in the secondary coordination sphere of our ligand. Furthermore, the various synthetic protocols established to access the Mn-oxo complex (summarized in Scheme 2) illustrate the propensity of this system to cleave E–O multiple bonds (where E = N, O and I). Ongoing studies in the laboratory include accessing higher valent Mn–O moieties as well as studying the microscopic reverse of water oxidation; the catalytic conversion of O_2 to H_2O .

Notes and references

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