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Intramolecular C–H and C–F Bond Oxygenation by Site-Differentiated Tetranuclear Manganese Models of the OEC

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Abstract

The dangler manganese center in the oxygen-evolving complex (OEC) of photosystem II plays an important role in the oxidation of water to dioxygen. Inspired by the structure of the OEC, we synthesized a series of site-differentiated tetra-manganese clusters $[\text{LMn}_3(\text{PhPz})_3\text{OMn}][\text{OTf}]_x$ (**2**: $x = 2$; **3**: $x = 1$) that features an apical manganese ion – distinct from the others – which is appended through an μ_4 -oxygen atom bridge to a trinuclear manganese core. This cluster design was targeted to facilitate studies of high-valent Mn-oxo formation, which is a proposed step in the mechanism for water oxidation by the OEC. Terminal Mn-oxo species – supported by multinuclear motif – were targeted by treating **2** and **3** with iodosobenzene. Akin to our previously reported iron complexes, intramolecular arene hydroxylation was observed to yield the C–H bond oxygenated complexes $[\text{LMn}_3(\text{PhPz})_2(\text{OArPz})\text{OMn}][\text{OTf}]_x$ (**5**: $x = 2$; **6**: $x = 1$). The fluorinated series $[\text{LMn}_3(\text{F2ArPz})_3\text{OMn}][\text{OTf}]_x$ (**8**: $x = 2$; **9**: $x = 1$) was also synthesized in order to mitigate the observed intramolecular hydroxylation. Interestingly, treating **8** and **9** with iodosobenzene results in intramolecular arene C–F bond oxygenation as judged by electrospray ionization mass spectrometry (ESI-MS). The observed aromatic C–H and C–F hydroxylation is suggestive of a putative high-valent terminal metal-oxo species and it is one of the very few examples capable of oxygenating C–F bonds.

TOC Synopsis

This study describes novel manganese clusters that model structural aspects of the OEC. Upon treatment with an O-atom transfer reagent, iodosobenzene, these complexes oxygenate aromatic C–H and C–F bonds, as evidenced by ^1H NMR spectroscopy, mass spectrometry, and independent synthesis of the resulting oxygenated products. The observed reactivity suggests the formation of a high-valent Mn-oxo species.

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ASSOCIATED CONTENT

For additional synthetic procedure, Figures S1–S34, Tables S1 and S2, and crystallographic information files. The Supporting Information is available free of charge on the ACS Publications website at DOI:

Introduction

Biological water oxidation to O_2 occurs at the oxygen evolving complex (OEC) in photosystem II (PSII).¹ The active site consists of a multinuclear cluster of manganese and calcium ions that are bridged by oxide moieties displaying a cubane motif $[\text{Mn}_3\text{CaO}_4]$.² Appended to this cubane, via a μ_4 -oxo bridge, is a fourth manganese center ("dangler"), proposed to coordinate at least one substrate water molecule.² Multiple oxidations and deprotonations convert this water molecule to either a terminal or bridging oxo moiety, which ultimately forms the O–O bond.³ Despite our current understanding, several aspects of water oxidation by the OEC remain unknown.^{1b} Nonetheless, understanding the structure-function relationships within the OEC is important, as this knowledge can contribute towards developing new technologies relying on water oxidation.⁴

Towards this end, structurally related synthetic model complexes can provide valuable information by allowing structure-functions, without the added complexity of the native enzyme.⁵ For instance, the $[\text{Mn}_3\text{CaO}_4]$ cubane motif in the OEC has been successfully reproduced in a few synthetic model complexes,⁶ some of them even incorporating an additional fifth "dangling" metal ion.^{6a–c} However, none of these complexes have been reported to support terminal high-valent Mn-oxo motifs.

The formation of such a terminal Mn-oxo species is an important step in some of the proposed mechanisms for water oxidation by the OEC.^{1b} Several synthetic complexes featuring high-valent Mn(IV) or Mn(V)-oxo species have been reported, and are supported with ligands that include porphyrins,⁷ corroles,⁸ corrolazines,⁹ or other types of macrocyclic ligands.¹⁰ Furthermore, a series of Mn(III)-,¹¹ Mn(IV)-,¹² and Mn(V)-oxo¹³ complexes supported by tetradentate tripodal ligands have been reported, where the Mn(V)-oxo models the manganese dangler in its highest oxidation state.^{13–14} The electronic description of this Mn(V)-oxo is of particular importance, and highly relevant for mechanistic proposals involving O–O bond formation.^{14–15} Other Mn-oxo complexes with similar coordination environments have also been reported.¹⁶ Despite the prevalence of high-valent terminal metal-oxo motifs on monometallic complexes, such motifs on multimetallic scaffolds are scarce and have only been observed or proposed in bimetallic complexes,¹⁷ discrete tetra or penta-nuclear clusters,¹⁸ or polyoxometallates.¹⁹ Notwithstanding, the synthesis and characterization of well-defined multimetallic clusters containing terminal Mn-oxo moieties will provide valuable information regarding its electronic structure and reactivity, data highly relevant for the OEC in PSII.

Recently, we reported the synthesis of a series of well-defined tetranuclear clusters containing a triiron core and a fourth apical Fe or Mn metal center.^{18b, 20a} These clusters are capable of intramolecular C(sp²)-H and C(sp²)-F bond oxygenation, most likely facilitated by a putative high-valent terminal metal oxo moiety.^{18b, 20a}

Modeling the structural features of the OEC including the dangler (Figure 1), we describe herein a series of tetranuclear manganese clusters and their reactivity with oxygen atom transfer (OAT) reagents. Related Mn₄ clusters displaying hydrogen bonding interactions have been shown very recently to support electrochemical water oxidation to H₂O₂.^{20b} The clusters [LMn₃(PhPz)₃OMn][OTf]_x (**2**: x = 2; **3**: x = 1) contain three six-coordinate manganese ions related by pseudo-C₃ axis and a fourth (site-differentiated) lower coordinate manganese center, which is appended to the other three metal centers through a μ₄-oxygen atom and three phenyl pyrazolate ligands (Figure 1). Treating these clusters with OAT reagents resulted in intramolecular C(sp²)-H oxygenation of the bridging phenyl pyrazole ligand. This type of reactivity is consistent with the formation of a reactive Mn-oxo. Although this reactivity has been observed for analogous multimetallic iron complexes,^{18b} the oxygenation of C(sp²)-H bonds by multimetallic manganese complexes is rare.²¹ To mitigate intramolecular oxidation, the analogous clusters [LMn₃(F₂ArPz)₃OMn][OTf]_x (**7**: x = 2; **8**: x = 1) were synthesized. The structure and reactivity of these complexes with OATs are discussed as well.

Results and discussion

The envisioned complexes [LMn₃(PhPz)₃OMn][OTf]_x (**2**: x = 2, **3**: x = 1) were synthesized according to a previously reported procedure for [LFe₃(PhPz)₃OFe][OTf]_x (x = 1–3).²² Starting from LMm(OAc)(OTf)₂, addition of sodium 3-phenyl-pyrazolate (NaPhPz; 3.2 equiv.) followed by oxidation with iodosobenzene (PhIO; 1.1 equiv.) yielded a purple-brown powder with ¹H-NMR spectrum distinct from LMn₃(OAc)(OTf)₂ (Figure S1 and S2). This intermediate was tentatively assigned as [LMn₃(PhPz)₃ONa][OTf] (**1**) based on its ESI-MS spectrum (Figure S18; m/z = 1488.3). Complex **1** was crystallized before salt metathesis with Mn(OTf)₂·2MeCN (2.0 equiv.) to yield the tetra-nuclear manganese complex [LMn₃(PhPz)₃OMn][OTf]₂ (**2**) in ca. 45% yield (Scheme 1).

Single crystals suitable for X-ray diffraction (XRD) were obtained by vapor diffusion of diethyl ether into a concentrated solution of **2** in acetonitrile. Complex **2** displays a [Mn₄-O] cluster, with three manganese ions supported by bridging alkoxides and nitrogen donors from ligand L, while the distinct fourth Mn is bridged by pyrazolates (Figure 2A). The metals bound to ligand L, described as the basal trinuclear core, are all six-coordinate. The apical metal, modeling the dangler Mn, is five-coordinate with three pyrazolate ligands, a μ₄-O donor, and one acetonitrile in the coordination sphere. Two outer sphere triflate counter ions are present. Based on charge balance, complex **2** displays two Mn(III) and two Mn(II) metal centers. The three basal pseudo-octahedral manganese centers (Mn1–Mn3) are connected via a μ₄-oxo bridge. Based on the Mn1–O1 (2.240(3) Å), Mn2–O1 (1.886(3) Å), and Mn3–O1 (1.891(3) Å) bond distances, the oxidation state of the trimanganese core is assigned as Mn^{III}₂Mn^{II}. The observed bond metrics in **2**, are comparable to other complexes featuring similar [Mn₄(μ₄-O)] core geometries,²³ supporting the discrete oxidation state

assignments of the individual manganese metal centers. The relatively long Mn1–N13 bond distance of 2.159(4) Å – compared to the Mn2–N23 (2.011(3) Å) and Mn3–N33 (1.998(3) Å) bond distances – corroborates this assignment (Table 1). The apical manganese metal center (Mn4) is trigonal bipyramidal ($\tau_5 = 0.79$)²⁴ and connected to the trimanganese core through a μ_4 -oxo bridge (O1). The apical manganese ion is assigned as Mn(II) based on charge balance and the long Mn4–O1 bond distance of 2.108(3) Å.^{23d23e} The overall oxidation state of **2** is thus assigned as [LMn^{II}Mn^{III}₂(PhPz)₃OMn^{II}][OTf]₂, analogous to our previously reported iron complexes.^{18b22}

The cyclic voltammogram (CV) of **2** shows two distinct quasireversible redox events at –1.67 V ([Mn^{II}₄]⁰/[Mn^{II}₃Mn^{III}]¹⁺) and at –0.60 V ([Mn^{II}₃Mn^{III}]¹⁺/[Mn^{II}₂Mn^{III}₂]²⁺) vs. Fc/Fc⁺ (Figure 3). An additional irreversible redox event, corresponding to the [Mn^{II}₂Mn^{III}₂]²⁺/[Mn^{II}Mn^{III}₃]³⁺ redox-couple, was found at more positive potentials (*ca.* 0.21 V). The deviation from reversible electrochemical behavior is attributed to large structural rearrangements upon oxidizing Mn(II) to Mn(III). In particular, the population of the d_{z^2} σ -antibonding orbital results in bond elongation along the z-axis. Irreversible or quasireversible behavior has been observed for other multimetallic manganese complexes.^{5f, 25} Such structural distortions are absent in the analogous iron-manganese complex [LFe₃(PhPz)₃OMn][OTf]₂, where three reversible one electron oxidation processes are observed.^{18b} Indeed, for compound **2**, large distortions are observed in the Mn–O(alkoxide) distances (Mn–O = 0.34 Å), while for corresponding iron complexes, these distortions are significantly lower (Fe–O = 0.15 Å).^{18b, 22}

The electrochemical studies indicate that the reduced or oxidized complexes [LMn₃(PhPz)₃OMn][OTf]_x (x = 1 or 3) might be accessed through chemical oxidation/reduction. While the addition of silver triflate (AgOTf; 1.1 equiv.) resulted in the formation of an intractable mixture, addition of cobaltocene (CoCp₂; 1.1 equiv.) to a solution of **2** in CH₂Cl₂, resulted in a markedly different ¹H NMR spectrum, attributed to a new paramagnetic species **3** (Figure S4).

This new paramagnetic species was assigned as [LMn₃(PhPz)₃OMn][OTf]₁ based on single crystal XRD (Figure 2B). The coordination environment around the apical manganese metal center (Mn4) is trigonal pyramidal. The distance between the centroid defined by the Mn1|Mn2|Mn3 trigonal plane (Mn_{core}) and O1, elongates from 0.913 Å to 0.962 Å upon reduction from **2** to **3**. The elongation is proposed to result from decrease in Lewis acidity of the Mn_{core}, weakening the interaction with O1. Other notable differences are observed in the Mn_{core}–O1 distances. Consistent with the reduction of a Mn(III) metal center, the Mn2–O1 bond distance elongates from 1.886(3) Å in **2** to 2.189(2) Å in **3**, supporting an overall Mn^{III}Mn^{II}₂ oxidation state assignment of the trimanganese core.²³

With isostructural complexes **2** and **3** in hand, we investigated their abilities to access high-valent terminal metal-oxo species. The differences in oxidation state of the trimanganese core (Mn^{III}₂Mn^{II} vs. Mn^{III}Mn^{II}₂) could influence the electronic structure or reactivity of the terminal metal-oxo moiety (i.e. nucleophilic vs. electrophilic).²⁶ Addition of iodosobenzene (PhIO; 1.1 equiv.) to complexes **2** and **3** afforded brown-black species with a highly complicated ¹H-NMR spectrum (Figures S7 and S11). The ¹H NMR spectra are

difficult to interpret due to paramagnetic broadening by manganese. This is contrast to the ^1H NMR spectra previously reported for iron complexes, for which sharper NMR resonances could be observed.²² However, ESI-MS analysis of the reaction mixtures showed single peaks corresponding to $[\text{LMn}_3(\text{PhPz})_2(\text{OArPz})\text{OMn}]^{2+}$ (**5**; $m/z = 767.8$) and $[\text{LMn}_3(\text{PhPz})_2(\text{OArPz})\text{OMn}]^{1+}$ (**6**; $m/z = 1534.8$), consistent with an overall process corresponding to intramolecular $\text{C}(\text{sp}^2)$ –bond oxygenation of the surrounding ligand scaffold (Figure S21 and S23). Unfortunately, repeated crystallization from the reaction mixture did not result in X-ray quality crystals of the tentatively assigned complexes $[\text{LMn}_3(\text{PhPz})_2(\text{OArPz})\text{OMn}][\text{OTf}]_2$ (**5**) and $[\text{LMn}_3(\text{PhPz})_2(\text{OArPz})\text{OMn}][\text{OTf}]_1$ (**6**).

To verify arene hydroxylation, complexes **5** and **6** were synthesized independently (Figure 4). Addition of sodium 2 (pyrazol-3-yl)phenolate (NaOArPzH ; 1.1 equiv.) to complex **2** resulted in the formation of **6** (Figure S9). One electron oxidation with AgOTf (1.0 equiv.) resulted in the formation of **5** (Figure S6). Both independently synthesized complexes show nearly identical ESI-MS and ^1H NMR spectra when compared to the crude reaction mixtures of **2** and **3** respectively, confirming that intramolecular C–H bond oxygenation is the most probable reaction pathway (Figure S8, S12, S22, and S24)

Previous studies have indicated that intramolecular $\text{C}(\text{sp}^2)$ –H bond oxygenation is preceded by rate-limiting oxygen atom transfer from an iodosobenzene-adduct, most likely generating a high-valent terminal $\text{Mn}^{\text{IV}}\text{-oxo}$.^{18b} Given the similar reactivity of **1** and previously reported $[\text{LFe}_3(\text{PhPz})_3\text{OMn}][\text{OTf}]_2$, a high-valent terminal Mn-oxo might be involved in the intramolecular $\text{C}(\text{sp}^2)$ -H bond oxygenation. This is notable as an example of a Mn_4 cluster structurally reminiscent of the OEC that supports reactive terminal Mn-oxo CH oxygenation.

Definite structural evidence for C–H bond oxygenation was provided by X-ray crystallography (Figure 2C). Single crystals of the phenoxide-coordinated cluster $([\text{LMn}_3(\text{PhPz})_2(\text{OArPz})\text{OMn}][\text{OTf}]_1, \textbf{6})$ could be obtained only after substituting of the outer sphere anion with tetraphenylborate (**6'**; see the supporting information for experimental details). Complex **6'** shows the oxygenated phenylpyrazole ligand, where O2 is coordinated to the apical manganese center (Mn_4). The $\text{Mn}_{\text{core}}\text{-O1}$ bond distances of 2.179(3) Å (Mn1-O1), 2.274(3) Å (Mn2-O1), and 1.904(3) Å (Mn3-O1), resemble those of **3** (Table 1) and indicate no changes in the Mn_{core} oxidation states ($\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}$). The contraction of Mn4-O1 bond distance from 2.108(3) Å to 1.851(3) Å suggests oxidation of the apical manganese metal center from Mn^{II} to Mn^{III} .²³ Similar to related iron-based systems, oxidation exclusively occurs at the site-differentiated metal center.^{18b, 20a} These results indicate that formed oxidizing species – postulated to be a high-valent $\text{Mn}(\text{IV})=\text{O}$ motif – are competent for hydroxylation of strong C–H bonds. High valent Mn-oxo motifs have similarly been invoked as key intermediates in olefin epoxidation,²⁷ C–H bond hydroxylation,²⁸ hydride transfer,²⁹ and hydrogen peroxide disproportionation.³⁰

In order to avoid the observed intramolecular oxygenation, 3-(2,6-difluorophenyl)pyrazole was selected as bridging ligand to eliminate C–H bonds that are sterically accessible to the proposed metal-oxo moiety. Furthermore, the oxygenation of C–F bonds by metal oxo species is very rare.^{20, 31} Consequently ligand fluorination might prevent the oxygenation reaction, allowing potential characterization of a transient terminal $\text{Mn}(\text{IV})\text{-oxo}$

intermediate. Complexes of the general formula $[\text{LMn}_3(\text{F}_2\text{ArPz})\text{OMn}][\text{OTf}]_x$ (**8**: $x = 2$; **9**: $x = 1$; $\text{F}_2\text{ArPz} = 3$ (2,6-difluorophenyl)pyrazolate) were synthesized according to the procedure outlined in Scheme 1. Complexes **8** and **9** were characterized by single crystal X-ray diffraction. The solid-state structure of **9** (Figure 5) is quite different than that of **2**. An interaction between the manganese metal center (Mn^{IV}) and one of the *ortho* fluorine substituent (F_4) is observed. The $\text{Mn}^{\text{IV}}-\text{F}_4$ distance of 2.469(1) is significantly shorter than the sum of the corresponding van der Waals radii (3.55 Å).³² Additionally, this interaction is evident from the inward orientation of one of phenyl rings of the pyrazolate ligands (Figure 5). Such an interaction is absent in **8**, where acetonitrile is coordinated to the apical metal center (Figure S33). The bond metrics are similar to those of **3**. For example, the $\text{Mn}^{\text{IV}}-\text{O}1$ (2.127(1) Å), $\text{Mn}^{\text{IV}}-\text{O}1$ (2.192(2) Å) and $\text{Mn}^{\text{IV}}-\text{O}1$ (1.801(1) Å) suggest an overall $[\text{Mn}^{\text{IV}}_2\text{Mn}^{\text{III}}]$ oxidation state for the trimanganese core, as in **3**. Compared to **8**, the $\text{Mn}^{\text{IV}}-\text{O}1$ bond distance has elongated from 1.914(3) (**8**) to 2.192(2) (**9**) indicative of reduction from Mn^{III} to Mn^{IV} (Table 1). Based on charge balance, the manganese oxidation states **9** are assigned as $[\text{LMn}^{\text{IV}}_2\text{Mn}^{\text{III}}(\text{F}_2\text{ArPz})_3\text{OMn}^{\text{IV}}][\text{OTf}]_2$.

Continuing our efforts to target a high-valent terminal $\text{Mn}^{\text{(IV)}}\text{-oxo}$, complexes **8** and **9** were treated with PhIO (1.1 equiv.). The ESI-MS spectrum – taken from the crude reaction mixtures – showed peaks corresponding to $[\text{LMn}_3(\text{F}_2\text{ArPz})_2(\text{OFArPz})\text{OMn}]^{2+}$ (**10**; $m/z = 812.7$) and $[\text{LMn}_3(\text{F}_2\text{ArPz})_3\text{OMnF}]^{2+}$ (**11**; $m/z = 823.7$) for the reaction of PhIO with complex **8**, or peaks corresponding to $[\text{LMn}_3(\text{F}_2\text{ArPz})_2(\text{OFArPz})\text{OMn}]^+$ (**12**; $m/z = 1624.9$) and $[\text{LMn}_3(\text{F}_2\text{ArPz})_3\text{OMnF}]^{2+}$ (**13**; $m/z = 1646.8$) for the reaction of PhIO with complex **9** (Figures S28 and S29). As described for the Fe analogs, these reactions correspond to C–F bond oxygenation coupled to fluoride and electron transfer to starting cluster **8** (or **9**). Unfortunately, the tentatively assigned complexes **10–13** could not be isolated in analytically clean form by repeated crystallization of the reaction mixtures. Independent synthesis was also problematic for a variety of reasons, including selectivity of metallations and solubility differences. Sufficient characterization data for complexes **10–13** was not obtained to undoubtedly assign them as the $\text{C}(\text{sp}^2)\text{-F}$ bond oxygenation products. Moreover, the highly complicated ^1H NMR spectrum of the crude reaction mixture – containing at least two different species given the nature of the reaction – precluded us from making meaningful comparison based on ^1H NMR alone (Figures S16 and S17). Notwithstanding, the ESI-MS data does reveal that complexes **8** and **9** are capable of intramolecular $\text{C}(\text{sp}^2)\text{-F}$ bond oxygenation, which has rarely been observed with Mn,³³ and is exceedingly rare with other metal complexes.^{20, 31a–f}

For general C–H bond oxygenation, three general mechanisms are envisioned: (i) direct C–H activation by an iodosobenzene adduct, (ii) H-atom abstraction from the proximal C–H with subsequent radical rebound, or (iii) electrophilic activation via the π system of the arene (Figure 6). Mechanism (i) proceeds through concerted C–H insertion and elimination of iodosobenzene, avoiding the formation of a high-valent terminal Mn-oxo. Direct substrate oxygenation from manganese-oxidant adducts has been reported.^{7a, 34} Mechanisms (ii) and (iii) invoke the formation of a transient high-valent terminal Mn-oxo species. Computational studies have suggested that mechanism (iii) is the preferred reaction pathway for arene hydroxylation in cytochrome P450.³⁵ Such a mechanism might also be operating in the

present study. Recently, we observed and crystallographically characterized an unusual iodosobenzene adduct on a heterobimetallic cluster featuring a similar site-differentiated manganese metal center.^{18b} These studies suggested that a Mn-oxo species, rather than an intermediate iodosobenzene adduct, is most likely responsible for the observed arene activation. In line with the proposed mechanism for benzene hydroxylation by P450,³⁵ a putative Mn(IV)-oxo species generated at the apical metal and is expected to perform initial electrophilic attack on the π -system of the arene ring at the closest accessible position. In the present system, the corresponding phenoxide is generated, with the overall loss of an H-atom.^{18b,20,36}

Related mechanisms have been proposed for haloarene hydroxylation with iron-oxo species.^{31b,37} Computational studies of a mononuclear iron complex competent for C–F bond oxygenation support a mechanism involving electrophilic arene attack by an observable high-valent Fe(IV)-oxo species.^{31b} Similarly, for the clusters reported here, an intermediate terminal Mn(IV)-oxo species could undergo electrophilic attack on the arene π -system, followed by rearomatization by expelling a fluorine anion. Additionally, for multinuclear systems, intramolecular electron transfer between manganese metal centers is possible. One-electron reduction of a high-valent Mn(IV)-oxo by a basal Mn(II) center to form a basal Mn(III) site and a Mn(III)-oxide that undergoes nucleophilic aromatic substitution cannot be ruled out based on the current results. Overall, such nucleophilic aromatic substitution results in the same overall transformation as by an electrophilic mechanism. Noting that the crystal structure of **9** shows an interaction between the arene F substituent and the manganese center (Figure 5), C–F bond cleavage may be facilitated by metal coordination to the fluorine moiety. However, displacement of the aryl-fluoride ligand by acetonitrile in **8** suggests that upon coordination of an additional ligand, such as the oxygen atom transfer reagent, fluoride binding is disfavored.

Summary

Inspired by the site-differentiation of the oxygen-evolving complex of photosystem II (Scheme 1), two series of tetra-manganese clusters with general formulae $[\text{LMn}_3(\text{PhPz})_3\text{OMn}][\text{OTf}]_x$ (**2**: $x = 2$; **3**: $x = 1$) and $[\text{LMn}_3(\text{F}_2\text{ArPz})_3\text{OMn}][\text{OTf}]_x$ (**8**: $x = 2$; **9**: $x = 1$) were synthesized. Addition of iodosobenzene (PhIO) to **2** and **3** resulted in C–H bond oxygenation of the bridging phenyl pyrazolate, while addition of PhIO to **8** and **9** resulted in highly unusual arene C–F bond oxygenation. These studies suggest that the formation of putative high-valent terminal Mn-oxo motifs on multimetallic scaffolds is possible. These reactive species are of interest in the context of modeling the function of the OEC. Current efforts are focused on addressing the effect of cluster structure and composition on reactivity.

EXPERIMENTAL SECTION

General Considerations

All reactions were performed at room temperature in an N₂-filled M. Braun Glovebox or by using standard Schlenk techniques unless otherwise specified. Glassware was oven dried at 140 °C for at least 2 h prior to use, and allowed to cool under vacuum. All reagents were

used as received unless otherwise stated. Sodium 5-phenylpyrazolate (NaPhPz),^{20a} sodium 5-(2,6-difluoro)phenylpyrazolate (NaF2ArPz),^{20a} sodium 2-(1*H*-pyrazol-5-yl)phenolate (NaOArPzH),^{20a} sodium 3-fluoro-2-(1*H*-pyrazol-5-yl)phenolate (NaOFArPzH),^{20a} iodosobenzene (PhIO),³⁸ silver tetraphenylborate (AgBPh₄),³⁹ and Mn(OTf)₂(MeCN)₂⁴⁰ were prepared according to literature procedures. Caution! *PhIO is a potential explosive and should therefore be synthesized and stored in minimal quantities.* MeOTf, Na(N(SiMe₃)), and AgOTf were purchased from Sigma Aldrich and Strem Chemicals. Cobaltocene (Cp₂Co) and decamethylcobaltocene (Cp*₂Co) were purchased from Strem Chemicals and sublimed before use. Anhydrous tetrahydrofuran (THF) was purchased from Aldrich in 18 L Pure-Pac™ containers. Anhydrous CH₂Cl₂, diethyl ether, hexane and THF were purified by sparging with nitrogen for 15 minutes and then passing under nitrogen pressure through a column of activated A2 alumina. Anhydrous 1,2-dimethoxyethane (DME) was dried over sodium/benzophenone and vacuum-transferred onto molecular sieves. The ¹H and ¹⁹F NMR spectra were recorded at 300.13 and 282.36 MHz, respectively, on a Varian 300 MHz spectrometer. All chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hz. The ¹H NMR spectra were referenced using residual solvent peaks in the deuterated solvent. The ¹⁹F chemical shifts are reported relative to the internal lock signal. Deuterated solvents (CD₂Cl₂ and CD₃CN) were purchased from Cambridge Isotope Laboratories, dried over calcium hydride, degassed by three freeze-pump-thaw cycles and vacuum transferred prior to use. The UV-vis spectra were recorded on a Varian Cary Bio 50 spectrophotometer. Fast atom bombardment-mass spectrometry (FAB-MS) analysis was performed with a JEOL JMS-600H high-resolution mass spectrometer. Elemental analyses were performed at Caltech.

Electrochemical measurements

CVs were recorded with a Pine Instrument Company AFCBP1 bipotentiostat using the AfterMath software package. All measurements were performed in a three-electrode cell configuration that consisted of (1) a glassy-carbon ($\phi = 3.0$ mm) working electrode, (2) a Pt wire as the counter electrode, and (3) an Ag wire as the reference electrode. All electrochemical measurements were performed at RT in an M. Braun N₂-filled glovebox. Dry dichloromethane or acetonitrile that contained 0.1 M Bu₄NPF₆ was used as the electrolyte solution. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an internal standard for all measurements.

X-ray crystallography

For compounds **2**, **3**, **6'**, and **9**, low temperature (100 K) diffraction data (ϕ - and ω -scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Mo K α radiation ($\lambda = 0.71073$ Å) or with Cu K α ($\lambda = 1.54178$ Å). For compound **8**, low-temperature (100 K) diffraction data (ϕ - and ω -scans) was collected on a Bruker AXS KAPPA APEX II diffractometer coupled to an APEX II CCD detector with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.⁴¹ Absorption corrections were applied using SADABS.⁴² Structures were solved by direct methods using SHELXS⁴³ and refined against *F*² on all data by full-matrix least squares with SHELXL-2016⁴⁴ using established

refinement techniques.⁴⁵ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity or distance restraints on the 1,2- and 1,3-distances and displacement parameters as well as enhanced rigid bond restraints for anisotropic displacement parameters. Due to the size of compounds most crystals included solvent accessible voids containing co-crystallized disordered solvent molecules. In most cases, this disorder could be modeled satisfactorily but the solution was not always ideal. These disordered solvent molecules were largely responsible for the alerts generated by the checkCIF protocol.

LMn₃(OAc)(OTf)₂

In the glovebox, to a yellow slurry of LMn₃(OAc)₃ (480.0 mg, 0.401 mmol) in CH₂Cl₂ (10 mL) was added dropwise methyl triflate (MeOTf; 0.132 mL, 1.203 mmol). During the course of ten minutes, the mixture became an opaque off-white suspension. After stirring for thirty minutes, all volatiles were removed under reduced pressure to yield an off-white powder. The solid was triturated in diethyl ether (10 mL), collected on a medium porosity glass frit, and washed with additional diethyl ether (3 × 10 mL). The solid was dried under vacuum to yield LMn₃(OAc)(OTf)₂ as an off-white powder. Yield 540 mg (98 %). ¹H NMR (300 MHz, CD₃CN): δ 63.9 (br), δ 43.7 (br), δ 11.01 (br), δ -10.8 (br). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -76.9 (br). UV-Vis (CH₃CN) [ε (M⁻¹ cm⁻¹): 254 nm (6.4 × 10⁴). Anal Calcd. for C₆₁H₄₂F₆Mn₃N₆O₁₁S₂: C 53.17, H 3.07, N 6.10. Found: C 52.93, H 3.28, N 6.36.

[LMn₃(PhPz)₃OMn][OTf]₂ (2)

In the glovebox, to thawing suspension of LMn₃(OAc)(OTf)₂ (550.0 mg, 0.401 mmol) in CH₂Cl₂ (5 mL) was added a thawing solution of NaPhPz (220.0 mg, 1.323 mmol) in THF (7 mL). The resulting suspension became homogeneous yellow-orange over the course of thirty minutes. After two hours, iodosobenzene (PhIO; 93.0 mg, 0.421 mmol) was added as a suspension in CH₂Cl₂ (2 mL), resulting in the formation of a purple slurry. After sixteen hours, the solvent was removed under reduced pressure, and the solids were triturated in diethyl ether (10 mL). The suspension was filtered over a Celite pad on top a coarse porosity glass frit, and subsequently washed with toluene (3 × 5 mL), and diethyl ether (10 mL). The remaining purple brown solid was collected using a minimal volume of CH₂Cl₂. Purple needles (500 mg) of the putative [LMn₃(F₂ArPz)₃ONa] [OTf] (**1**) were obtained by vapor diffusion of diethyl ether into a concentrated solution of **1** in CH₂Cl₂. The crystals were slurried in minimal THF (5 mL) and Mn(OTf)₂(MeCN)₂ (338.7 mg, 0.856 mmol) was added. During the course of one hour, the mixture turned brown-purple and was stirred for another sixteen hours. Next, the brown purple solids were collected on a Celite pad on top a coarse porosity glass, and washed with dimethoxyethane (DME; ca. 15 mL) until the purple filtrate became near-colorless. The remaining solid was collected with acetonitrile and dried under reduced pressure, yielding [LMn₃(PhPz)₃OMn][OTf]₂ as a brown-purple solid. Yield 512.0 mg (45 %). X-ray quality crystals of **2** were obtained by vapor diffusion of diethyl ether into a concentrated solution of **2** in acetonitrile. ¹H NMR (300 MHz, CD₂Cl₂): δ 50.0 (br), δ 35.2 (br), δ 31.2 (br), δ 13.3 (br), δ 10.61 (br), δ -12.4 (br), δ -19.0 (br). ¹⁹F NMR

(282 MHz, CD₂Cl₂): δ -78.6 (s). UV-Vis (CH₂Cl₂) [ϵ (M⁻¹ cm⁻¹): 253 nm (8.9×10^4). Anal Calcd. for C₈₆H₆₀F₆Mn₄N₁₂O₁₀S₂: C 56.78, H 3.32, N 9.24. Found: C 56.37, H 3.37, N 9.54.

[LMn₃(PhPz)₃OMn][OTf]₁ (**3**)

In the glovebox, to a stirring solution of **2** (100.0 mg, 55.0 μ mol) in CH₂Cl₂ (4 mL) was added cobaltocene (CoCp₂, 10.9 mg, 58.0 μ mol). The color changed from brown-purple to red-purple, and after two hours the solvent was removed under reduced pressure. The solid was stirred as a purple suspension in DME (8 mL) and filtered over a Celite pad on top of a coarse porosity glass frit to remove cobaltocenium triflate. The remaining purple solid was eluted with CH₂Cl₂ (2 mL) and the solvent was removed under reduced pressure to yield [LMn₃(PhPz)₃OMn][OTf]₁ as a faint red purple solid. Yield 74.0 mg (81 %). X-ray quality crystals of **3** were obtained by vapor diffusion of diethyl ether into a solution of **3** in acetonitrile. ¹H NMR (300 MHz, CD₂Cl₂): δ 39.9 (br), δ 36.6 (br), δ 31.1 (br), δ 11.7 (br), δ -7.5 (br), δ -8.9 (br). ¹⁹F NMR (282 MHz, CD₂Cl₂): - δ 78.8 (s). UV-Vis (CH₂Cl₂) [ϵ (M^{δ1} cm^{δ1}): 256 nm (9.9×10^4), 371 nm (2.8×10^3). Anal Calcd. for C₈₅H₆₀F₃Mn₄N₁₂O₇S: C 61.12, H 3.62, N 10.06. Found: C 61.36, H 3.76, N 9.87.

[LMn₃(PhPz)₂(OArPz)OMn][OTf]₂ (**5**)

Procedure A—In the glovebox, to a stirring solution of **2** (320.0 mg, 0.18 mmol) in CH₂Cl₂ (10 mL) was added PhIO (40.3 mg, 0.18 mmol) as a suspension in CH₂Cl₂ (2 mL). During the course of one hour, the color changed to black, and the mixture turned homogeneous. The reaction was allowed to stir for sixteen hours, where after the solvent was removed under reduced pressure to yield an intense dark black/brown powder. The powder was triturated in toluene (*ca.* 6 mL), and the solid was collected on top of a coarse glass frit. The solid was washed with additional toluene (*ca.* 6 mL), and finally eluted with CH₂Cl₂ (4 mL). The solvent was removed under reduced pressure to yield [LMn₃(PhPz)₂(OArPz)OMn][OTf]₂ as a dark brown solid. Yield 310 mg (96 %). The ¹H NMR spectrum of **5** is identical to that from *Procedure B*.

Procedure B—In the glovebox, to a stirring solution of **6** (40.0 mg, 23.7 μ mol) in CH₂Cl₂ (2 mL) was added silver triflate (AgOTf; 6.4 mg, 24.9 μ mol) as a suspension in CH₂Cl₂ (2 mL). The solution darkened to off-black over the course of ten minutes. After two hours, the solution was filtered over a glass frit to remove metallic silver. The solvent was removed under reduced pressure to yield **5** as an off-black powder (39.8 mg, 90 %). ¹H NMR (300 MHz, CD₂Cl₂): δ 82.0 (br), δ 77.6 (br), δ 73.1 (br), δ 70.5 (br), δ 68.0 (br), δ 64.5 (br), δ 58.7 (br), δ 55.7 (br), δ 51.4 (br), δ 48.7 (br), δ 46.9 (br), δ 41.8 (br), δ 38.6 (br), δ 36.1 (br), δ 33.8 (br), δ 24.9 (br), δ 16.6 (br), δ 14.9 (br), δ 13.8 (br), δ 13.1 (br), δ 10.66 (br), δ -2.1 (br), δ -3.5 (br), δ -4.5 (br), δ -10.1 (br), δ -11.0 (br), δ -12.8 (br), δ -14.4 (br), δ -17.2 (br), δ -19.4 (br), δ -20.7 (br), δ -21.9 (br), δ -24.3 (br), δ -29.3 (br), δ -30.2 (br). ¹⁹F NMR (282 MHz, CD₂Cl₂): - δ 78.8 (s). UV-Vis (CH₂Cl₂) [ϵ (M⁻¹ cm⁻¹): 245 nm (1.29×10^5), 371 nm (1.7×10^4). Anal Calcd. for C₈₆H₅₉F₆Mn₄N₁₂O₁₁S₂ • 2CH₂Cl₂: C 53.16, H 3.24, N 8.45. Found: C 52.98, H 3.02, N 8.66.

[LMn₃(PhPz)₂(OArPz)OMn][OTf]₁ (6)

Procedure A—In the glovebox, to a stirring solution of **3** (40.0 mg, 23.9 μ mol) in CH₂Cl₂ (2 mL) was added PhIO (5.5 mg, 25.1 μ mol) as a suspension in CH₂Cl₂ (2 mL). Over the course of one hour, the red-purple slurry became homogeneous and changed color to dark brown. After sixteen hours the solvent was removed under reduced pressure to yield a dark brown solid. The solid was triturated in benzene (3 mL) and filtered over a glass frit. The remaining solid was dissolved in CH₂Cl₂ (2 mL) and dried under reduced pressure to yield [LMn₃(PhPz)₂(OArPz)OMn][OTf]₁ as a dark brown solid. Yield 36.5 mg (92 %). The ¹H NMR spectrum of **6** was identical to that of Procedure B.

Procedure B—In the glovebox, to a solution of **2** (40.0 mg, 22.0 μ mol) in CH₂Cl₂ (2 mL) was added NaOArPzH (4.4 mg, 24.2 μ mol) in CH₂Cl₂ (2 mL). After thirty minutes, the reaction mixture darkened to black. After forty-eight hours, the solvent was removed under reduced pressure to give a brown black solid. The solid was triturated with benzene and collected on a glass frit. The remaining solid was washed with benzene (10 mL) and diethyl ether (5 mL), and finally eluted with CH₂Cl₂ (5 mL). The solvent was removed under reduced pressure to yield **6** as a brown/black solid. Yield 23.7 mg (85 %). ¹H NMR (300 MHz, CD₂Cl₂): δ 56.6 (br), δ 55.2 (br), δ 52.5 (br), δ 49.4 (br), δ 47.0 (br), δ 42.9 (br), δ 38.1 (br), δ 36.2 (br), δ 34.5 (br), δ 30.0 (br), δ 27.8 (br), δ 22.8 (br), δ 13.5 (br), δ 13.2 (br), δ 12.3 (br), δ 10.55 (br), δ -1.11 (br), δ -1.79 (br), δ -2.63 (br), δ -4.0 (br), δ -10.7 (br), δ -12.8 (br), δ -13.8 (br), δ -15.6 (br), δ -16.9 (br), δ -17.9 (br), δ -26.7 (br). ¹⁹F NMR (282 MHz, CD₂Cl₂): - δ 78.8 (s). UV-Vis (CH₂Cl₂) [ϵ (M⁻¹ cm⁻¹): 251 nm (1.43 $\times$ 10⁵), 355 nm (1.00 $\times$ 10⁴), 513 nm (2.01 $\times$ 10³). Anal Calcd. for C₈₅H₅₉F₃Mn₄N₁₂O₈S: C 60.58, H 3.53, N 9.97. Found: C 60.42, H 3.74, N 10.04.

[LMn₃(F₂ArPz)₃OMn][OTf]₂ (8)

In the glovebox, to a thawing suspension of LMn₃(OAc)(OTf)₂ (100.0 mg, 0.073 mmol) in CH₂Cl₂ (5 mL) was added a thawing solution of NaF₂ArPz (220.0 mg, 1.323 mmol) in THF (7 mL). During the course of thirty minutes, the resulting suspension became homogeneous and changed color to yellow-orange. After two hours, PhIO (16.8 mg, 0.076 mmol) was added as a suspension in CH₂Cl₂ (2 mL) resulting in the formation of a purple-brown slurry. After sixteen hours the solvent was removed under reduced pressure, and the solids were triturated with diethyl ether (15 mL). The suspension was filtered over a Celite pad on top a coarse porosity glass frit, and subsequently washed with benzene (20 mL), and diethyl ether (10 mL). The remaining purple-brown solid was collected using a minimal volume of CH₂Cl₂. Purple needles of the proposed [LMn₃(F₂ArPz)₃ONa][OTf] (**7**) were obtained by vapor diffusion of diethyl ether into a concentrated solution of **7** in CH₂Cl₂. The crystals (50 mg) were slurried in minimal THF (5 mL) and Mn(OTf)₂(MeCN)₂ (60 mg, 0.057 mmol) was added. During the course of one hour, the mixture turned brown-violet and was stirred for another sixteen hours. The solvent was removed under reduced pressure to yield [LMn₃(F₂ArPz)₃OMn][OTf]₂ as a brown-violet solid. Yield 60 mg (45 %). X-ray quality crystals of **8** were obtained by vapor diffusion of diethyl ether into a concentrated solution of **8** in acetonitrile. ¹H NMR (300 MHz, CD₂Cl₂): δ 51.1 (br), δ 35.1 (br), δ 31.2 (br), δ 14.1 (br), δ 10.7 (br), δ 8.4 (br), δ -11.9 (br), δ -19.6 (br). ¹⁹F NMR (282 MHz, CD₂Cl₂): - δ 78.8 (s). UV-Vis (CH₂Cl₂) [ϵ (M⁻¹ cm⁻¹): 249 nm (9.9 $\times$ 10⁴), 324 nm (4.5 $\times$ 10³). Anal

Calcd. for $C_{86}H_{54}F_{12}Mn_4N_{12}O_{10}S_2$: C 53.60, H 2.82, N 8.72. Found: C 53.90, H 2.04, N 8.57.

[LMn₃(F₂ArPz)₃OMn] [OTf] (9)

In the glovebox, to a stirring solution of **8** (55.0 mg, 28 μ mol) in THF (3 mL) was added CoCp₂ (5.7 mg, 30 μ mol). The color changed from brown-violet to red-purple and after two hours the solvent was removed under reduced pressure. The solid was stirred as a violet suspension in DME (3 mL) and was subsequently filtered over a Celite pad on top a coarse porosity glass frit to remove cobaltocenium triflate. The remaining purple solid was collected in CH₂Cl₂ (2 mL) and dried under reduced pressure to yield [LMn₃(F₂ArPz)₃OMn] [OTf]₁ as a faint red-purple solid. Yield 30 mg (60 %). X-ray quality crystals of **9** were obtained by vapor diffusion of diethyl ether into a solution of **9** in CH₂Cl₂. ¹H NMR (300 MHz, CD₂Cl₂): δ 40.1 (br), δ 37.0 (br), δ 31.1 (br), δ 11.66 (br), δ 9.9 (br), δ -8.8 (br). ¹⁹F NMR (282 MHz, CD₂Cl₂): - δ 78.8 (s). UV-Vis (CH₂Cl₂) [ϵ (M⁻¹ cm⁻¹): 249 nm (9.9×10^4), 324 nm (4.5×10^3). UV-Vis (CH₂Cl₂) [ϵ (M⁻¹ cm⁻¹): 253 nm (7.6×10^4), 380 nm (2.9×10^3). Anal Calcd. for $C_{86}H_{54}F_9Mn_4N_{12}O_7S$: C 57.41, H 3.06, N 9.45. Found: C 57.66, H 3.43, N 8.89.

Addition of PhIO to LMn₃(F₂ArPz)₃OMn][OTf]₂ (8)

In the glovebox, to a stirring solution of **8** (25.0 mg, 13.0 μ mol) in CH₂Cl₂ (2 mL) was added PhIO (3.0 mg, 14.0 μ mol) as a suspension in CH₂Cl₂ (1 mL). During the course of one hour, the color changed to black, and the mixture turned homogeneous. The reaction was allowed to stir for sixteen hours where after the solvent was removed under reduced pressure to yield a brown black powder. The powder was triturated in toluene (ca. 2 mL), collected on top a glass frit, and subsequently washed with additional toluene (ca. 2 mL). The remaining solid was dissolved in CH₂Cl₂, filtered, and the solvent was removed under reduced pressure to yield a brown-black powder. ESI-MS analysis is consistent with the formation of [LMn₃(F₂PhPz)₂(OFArPz)OMn][OTf]₂ (**10**) and [LMn₃(F₂PhPz)₃OMn(F)][OTf]₂ (**11**).

Addition of PhIO to [LMn₃(F₂ArPz)₃OMn][OTf]₁ (9)

In the glovebox, to a stirring solution of **9** (20.0 mg, 11.0 μ mol) in CH₂Cl₂ (2 mL) was added PhIO (2.5 mg, 11.0 μ mol) as a suspension in CH₂Cl₂ (2 mL). During the course of one hour, the color changes to brown/black and the mixture turned homogeneous. The mixture was stirred for another sixteen hours, where after the solvent was removed under reduced pressure to yield a brown/black powder. The powder was triturated in toluene (ca. 2 mL), collected on top a glass frit, and subsequently washed with additional toluene (ca. 2 mL). The remaining solid was dissolved in CH₂Cl₂, filtered, and the solvent was removed under reduced pressure to yield a brown-black powder. ESI-MS analysis is consistent with the formation of [LMn₃(F₂PhPz)₂(OFArPz)OMn][OTf]₁ (**12**) and [LMn₃(F₂PhPz)₃OMn(F)][OTf]₁ (**13**).

Supplementary Material

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Figure 1.

Structural similarity of tetranuclear manganese clusters $[LMn_3(PhPz)_3OMn(O)]^{n+}$ ($n = 1$ or 2 ; top right) reported here to the oxygen evolving complex (OEC) in photosystem II (top left). The metal centers are supported by pyrazolates (inset) and a 1,3,5-triarylbenzene-based ligand (L).

Figure 2.

Solid-state structure of (A) $[\text{LMn}_3(\text{PhPz})_3\text{OMn}][\text{OTf}]_2$ (**2**), (B) $[\text{LMn}_3(\text{PhPz})_3\text{OMn}][\text{OTf}]_1$ (**3**), and (C) $[\text{LMn}_3(\text{PhPz})_2(\text{OArPz})\text{OMn}][\text{BPh}_4]_1$ (**6'**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, outer sphere counter ions, and co-crystallized solvent molecules are omitted for clarity. See Table 1 for selected bond angles and distances.

Figure 3. Cyclic voltammogram of $[\text{LMn}_3(\text{PhPz})_3\text{OMn}] [\text{OTf}]_2$ (**2**) recorded at 100 mV s^{-1} in dichloromethane at a 2 mM concentration. The recorded potentials are referenced against the Fc/Fc^+ redox couple.

Figure 4.
Reactivity of complex **2** with PhIO, and independent syntheses of complexes **5** and **6**.

Figure 5.

Solid-state structure of [LMn₃(F₂ArPz)₃OMn] [OTf]₁ (9), showing a weak interaction between Mn4 and the *ortho* fluorine (F4) of the pyrazolate ligand. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, outer sphere counter ions, and co-crystallized solvent molecules are omitted for clarity

Figure 6.

Proposed mechanisms for arene hydroxylation observed with complex 2 via: (a) direct C–H insertion by an iodosobenzene adduct, (b) a high-valent Mn-oxo. Both paths require the loss of a hydrogen atom to access the final observed product.

Scheme 1.
Synthesis of complexes **1–3** and **7–9**.

Table 1Select bond distances and angles for Complexes **2**, **3**, **6'**, **8**, and **9**.

Bond Distances (Å)	Complex				
	2	3	6'	8	9
Mn1–O1	2.240(3)	2.116(2)	2.179(3)	2.216(3)	2.127(1)
Mn2–O1	1.886(3)	2.189(2)	2.247(3)	1.914(3)	2.192(2)
Mn3–O1	1.891(3)	1.816(1)	1.094(3)	1.892(3)	1.801(1)
Mn4–O1	2.108(3)	1.987(1)	1.851(3)	2.098(3)	2.012(1)
Mn4–O2	–	–	1.842(4)	–	–
Mn1–N11	2.202(3)	2.210(2)	2.201(4)	2.331(5)	2.234(2)
Mn1–N12	2.361(3)	2.346(2)	2.382(4)	2.171(4)	2.349(2)
Mn1–N13	2.159(4)	2.255(2)	2.220(4)	2.164(2)	2.247(2)
Mn2–N21	2.076(4)	2.234(2)	2.214(4)	2.216(4)	2.220(2)
Mn2–N22	2.318(3)	2.373(2)	2.341(4)	2.103(5)	2.239(2)
Mn2–N23	2.011(3)	2.197(2)	2.154(4)	2.007(5)	2.189(2)
Mn3–N31	2.108(3)	2.072(2)	2.092(4)	2.304(4)	2.072(2)
Mn3–N32	2.195(3)	2.377(2)	2.338(4)	2.089(4)	2.332(2)
Mn3–N33	1.998(3)	2.099(2)	2.033(4)	2.024(5)	2.097(2)
Mn4–N14	2.194(4)	2.122(2)	2.042(4)	2.138(4)	2.143(2)
Mn4–N24	2.170(3)	2.109(2)	2.013(4)	2.194(5)	2.134(2)
Mn4–N34	2.202(3)	2.131(2)	2.106(4)	2.187(5)	2.149(2)
N13–N14	1.381(6)	1.379(3)	1.380(6)	1.383(6)	1.369(3)
N23–N24	1.382(5)	1.380(2)	1.369(6)	1.375(7)	1.372(3)
N33–N34	1.384(6)	1.379(2)	1.375(6)	1.378(6)	1.376(3)
Bond Angles (°)					
N14–Mn4–N24	111.9(1)	118.19(7)	129.8(2)	116.0(2)	111.86(7)
N24–Mn4–N34	124.9(1)	120.44(7)	109.8(2)	126.5(2)	123.37(7)
N34–Mn4–N14	119.9(1)	120.63(7)	120.3(2)	114.8(2)	124.72(7)
Torsion Angles (°)					

Bond Distances (Å)	Complex				
	2	3	6'	8	9
Mn1–N13–N14–Mn4	30.4(4)	3.5(2)	26.9(4)	–10.5(5)	1.7(2)
Mn2–N23–N24–Mn4	31.2(3)	–5.1(2)	–5.5(5)	–3.6(5)	20.8(2)
Mn3–N33–N34–Mn4	5.3(4)	2.7(2)	21.4(4)	–22.6(5)	–0.6(2)
Centroid Distances (Å)					
Mn1 Mn2 Mn3–N14 N24 N34	2.772	2.925	2.860	2.801	2.945
Mn1 Mn2 Mn3–O11 O21 O31	1.150	1.127	1.096	1.162	1.111
N14 N24 N34–O11 O21 O31	3.921	4.046	3.948	3.959	4.055
Mn1 Mn2 Mn3–O1	0.913	0.962	1.049	0.924	0.958