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Thermodynamics of Proton and Electron Transfer in Tetranuclear Clusters with Mn–OH₂/OH Motifs Relevant to H₂O Activation by the Oxygen Evolving Complex in Photosystem II

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Abstract

We report the synthesis of site-differentiated heterometallic clusters with three Fe centers and a single Mn site that binds water and hydroxide in multiple cluster oxidation states. Deprotonation of Fe^{III/II}₃Mn^{II}–OH₂ clusters leads to internal reorganization resulting in formal oxidation at Mn to generate Fe^{III/II}₃Mn^{III}–OH. ⁵⁷Fe Mössbauer spectroscopy reveals that oxidation state changes (three for Fe^{III/II}₃Mn–OH₂ and four for Fe^{III/II}₃Mn–OH clusters) occur exclusively at the Fe centers; the Mn center is formally Mn^{II} when water is bound and Mn^{III} when hydroxide is bound. Experimentally determined p*K*_a (17.4) of the [Fe^{III}₂Fe^{II}Mn^{II}–OH₂] cluster and the reduction potentials of the [Fe₃Mn–OH₂] and [Fe₃Mn–OH] clusters were used to analyze the O–H bond dissociation enthalpies (BDE_{O–H}) for multiple cluster oxidation states. BDE_{O–H} increases from 69, to 78, and 85 kcal/mol for the [Fe^{III}Fe^{II}₂Mn^{II}–OH₂], [Fe^{III}₂Fe^{II}Mn^{II}–OH₂], and [Fe^{III}₃Mn^{II}–OH₂] clusters, respectively. Further insight of the proton and electron transfer thermodynamics of the [Fe₃Mn–OH_x] system was obtained by constructing a potential–p*K*_a diagram; the shift in reduction potentials of the [Fe₃Mn–OH_x] clusters in the presence of different bases supports the BDE_{O–H} values reported for the [Fe₃Mn–OH₂] clusters. A lower limit of the p*K*_a for the hydroxide ligand of the [Fe₃Mn–OH] clusters was estimated for two oxidation states. These data suggest BDE_{O–H} values for the [Fe^{III}₂Fe^{II}Mn^{III}–OH] and [Fe^{III}₃Mn^{III}–OH] clusters are greater than 93 and 103 kcal/mol, which hints to the high reactivity expected of the resulting [Fe₃Mn=O] in this and related multinuclear systems.

Graphical Abstract

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Supplementary Data (PDF)

Crystallographic data files (CIFs)

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INTRODUCTION

During photosynthesis, water oxidation is catalyzed at the active site of Photosystem II (PSII) by a CaMn_4O_5 cluster known as the Oxygen Evolving Complex (OEC).¹ The catalytic mechanism is outlined by the Kok cycle, with the cluster transitioning through five distinct so-called S-states (S_0 , S_1 , ..., S_4).² Four sequential oxidations of the cluster occur ($\text{S}_0 \rightarrow \text{S}_4$), followed by the O–O bond forming step, with concomitant loss of O_2 and binding of H_2O to complete the cycle ($\text{S}_4 \rightarrow \text{S}_0$). Protons are sequentially released from the active site during the S-state cycle; deprotonation of bound H_2O in this stepwise manner prevents the buildup of significant charge at the active site, facilitating the further oxidation of the CaMn_4O_5 cluster.³ PSII utilizes a nearby tyrosine radical (Y_{Z}) as a mediator to transfer electrons/protons away from the OEC during turnover; because of the nature of the tyrosine radical, proton-coupled electron transfer (PCET) of the H_2O -derived ligands bound to the OEC is considered to play an important role in the Kok cycle.^{3–4} Due to the wealth of information available in X-ray crystallographic^{1b–d, 5}, EPR⁶, and X-ray absorption^{2b, 6d, 7} spectroscopic techniques, much is known about the Mn oxidation states and electronic environment of the OEC in the S_0 through S_3 states of the Kok cycle. More challenging has been understanding the precise protonation state of H_2O ligands and relevant neighboring amino acid residues of any S-state; computational studies of the OEC have considered a variety of possible protonation states.^{4c, 8} Experimentally, time-resolved IR spectroscopy has been helpful in gaining insight to the dynamics of protons at the active site during turnover.^{6j, 9} Furthermore, multiple computational models of the OEC mechanism invoke a terminal Mn-oxo as a crucial part of the O–O bond forming S_4 intermediate^{2c, 10}. Therefore, there is significant interest in understanding the chemistry of a Mn– OH_2 species undergoing multiple proton and electron transfers to reach a reactive terminal Mn-oxo.

The chemistry of synthetic Mn-aquo, -hydroxo, and -oxo motifs has been a subject of interest for inorganic chemists, particularly within the context of gaining insight into the thermodynamic basis of Mn– OH_x PCET reactivity and how it relates to the mechanism of the OEC.^{11, 12, 13} Reported mononuclear systems have been able to probe the roles of Mn oxidation state^{12c, 12d, 12i}, ligand field^{11a, 11f, 13b}, and oxygen ligand protonation state^{11j, 12j} on PCET reactions and the intrinsic O–H bond dissociation enthalpies (BDE) of Mn– OH_x moieties. There are fewer examples of such studies with multinuclear Mn complexes, with most of the reports examining the PCET chemistry of bridging oxo moieties¹⁴, as opposed to terminally bound OH_x ligands.¹⁵ Most of these reports are limited to binuclear Mn complexes or systems where only a single redox couple could be examined. The PCET

reactivity of a synthetic $\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}\text{O}_3(\text{OH})$ cubane cluster has been examined, where the $\text{BDE}_{\text{O-H}}$ of the $\mu_3\text{-OH}$ could be estimated to be >94 kcal/mol; however, precise determination of the thermodynamic bond strength was complicated by subsequent decomposition of the protonated cubane.^{14d} A report of proton and electron transfer at a terminal Mn-OH_x moiety with an adjacent Mn center over three oxidation states (Mn^{III}_2 , $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$, and Mn^{IV}_2) represents a very rare example of thermodynamic studies of a terminal Mn-OH_x in a multinuclear system.^{15a} Access to a suitable synthetic platform to interrogate the effects of *multiple* neighboring redox-active metal centers on the chemistry of a terminal Mn-OH_x motif may facilitate a more complete picture of the dynamics of proton and electron transfer of the OEC leading up to its reactive S_4 state, and more generally lead to a better understanding of the behavior of metal clusters in reactions involving water, dioxygen, and multi-electron transformations.

Our group has demonstrated the utility of rationally-designed, well-defined molecular clusters for probing structure-function relationships in multinuclear first-row transition metal complexes, acting as models of complex active sites found in biology.^{16, 17} Recently, we have studied a family of tetranuclear Fe and Mn complexes composed of three coordinatively-saturated metal ions bridged to a fourth (apical) metal center through substituted pyrazolate (or phenyl-imidazolate) ligands and a μ_4 -single atom ligand.¹⁸ The apical metal has a coordination site available for exogenous ligands, allowing for the study of substrate binding and reactivity by a molecular cluster. With bulky and nonpolar phenyl substituents in the 3 position of the pyrazolate ligands coordination of bulk-ier ligands remains inhibited, and intramolecular ligand activation had been encountered.^{18d-f} In contrast, we have established that amino-phenylpyrazolate ligands, which are more open and facilitate hydrogen bonding interactions, support oxo-bridged tetramanganese clusters bearing a $\text{Mn}^{\text{III}}\text{-OH}$ moiety and are competent for catalyzing electro-chemical water oxidation, demonstrating O-O bond formation function relevant to the OEC.¹⁹ Here, clusters with unsubstituted bridging pyrazolate ligands (Pz^-) were synthesized to further promote intermolecular reactivity between apical Mn-OH_x groups and external acids, bases, or hydrogen atom donors/acceptors. A heterometallic cluster composition, in this case Fe_3Mn , was targeted to provide a spectroscopic handle of metal oxidation states within the cluster, via ^{57}Fe Mössbauer spectroscopy. The thermodynamic aspects of the PCET reactivity of these $\text{LFe}_3\text{O}(\text{Pz})_3\text{Mn}(\text{OH}_x)^{n+}$ clusters were investigated through examination of the discrete electron and proton transfers taking place over multiple redox states. The results herein establish the significant influence redox changes at distal metal sites in a cluster have on a Mn-OH_x motif and, conversely, how this motif's protonation state can modulate the electron distribution between metals in the cluster.

RESULTS AND DISCUSSION

Synthesis and Characterization of Pyrazolate Bridged $[\text{Fe}_3\text{Mn}]$ Clusters.

The $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{Mn}^{\text{II}}]$ cluster (**2-OTf**) can be prepared via one-pot synthesis, starting from previously reported $[\text{LFe}_3(\text{OAc})(\text{OTf})][\text{OTf}]$ complex.^{18a} Sequential addition of $\text{Ca}(\text{OTf})_2$ (which serves to sequester the equivalent of acetate in the starting material, to avoid mixtures of counterions), potassium pyrazolate, iodosobenzene (PhIO), and manganese (II)

trifluoromethanesulfonate bis-acetonitrile solvate ($\text{Mn}(\text{OTf})_2 \cdot 2 \text{ MeCN}$) allows for isolation of the desired complex (Figure 1C; see Experimental Section in Supporting Information for complete synthetic details). ^1H NMR and Mössbauer spectra of **2-[OTf]** are similar to our previously reported $[\text{LFe}_3\text{O}(\text{PhPz})_3\text{Mn}][\text{OTf}]_2$ cluster which was synthesized using sodium phenyl pyrazolate, supporting the assignment that the apical metal is Mn (Figures S3 and S48).^{18e} The structure of **2-[OTf]** was confirmed by single crystal X-ray diffraction (Figure S62; see Figure 1A for isostructural **1-[OTf]**); the cluster geometry is analogous to the substituted pyrazolate and imidizolate tetranuclear clusters, with a single μ_4 -interstitial ligand and pyrazolates bridging each Fe center of the tri-nuclear core to the apical Mn.¹⁸ In the case of the previously reported clusters, the apical metal typically adopts a four-coordinate, trigonal pyramidal geometry since the sterics of the substituted pyrazolate ligands disfavor binding of one of the triflate counterions to the apical metal. Here, the apical Mn is ligated by one triflate counterion with a trigonal bipyramidal geometry, indicative of the increased steric accessibility of the apical metal with the unsubstituted pyrazolates.

Cyclic voltammetry (CV) data of **2-[OTf]** in MeCN show a quasi-reversible oxidation at -0.11 V , a quasi-reversible reduction wave at -0.84 V , and an irreversible reductive process below -1.50 V (Figure S25; all potentials vs Fc/Fc^+). The one electron reduced (**1-[OTf]**), and one electron oxidized (**3-[OTf]**) clusters were prepared via chemical reduction/oxidation of **2-[OTf]** with cobaltocene (CoCp_2) and silver trifluoromethanesulfonate (AgOTf), respectively. The X-ray crystal structures of these three compounds all have identical coordination modes for the metal centers (Figure 1A, Figures S61–S63). Bond distances between the metals and the μ_4 -oxo are consistent with the redox processes taking place at the Fe centers, with the apical Mn maintaining a +2 oxidation state across the series **1-[OTf]** – **3-[OTf]** (Table 1). Mössbauer data corroborate these oxidation state assignments, and are similar to our previously characterized clusters (Figures S46–S49).^{18a–e}

Preparation of Mn–OH₂ and Mn–OH Clusters.

Binding of water to these clusters was investigated; however, the coordination of triflate to the apical Mn complicates direct access to the Mn–OH₂ moiety for all oxidation states of the cluster. The triflate ligand in **2-[OTf]** is sufficiently labile to allow for isolation of the Mn–OH₂ cluster as single crystals by slow diffusion of Et_2O into a MeCN/5% H_2O solution of the cluster, and its structure was confirmed via X-ray crystallography (**2-[OTf] (H₂O)**; Figure 2B). Attempts to obtain crystals of the analogous reduced Mn–OH₂ cluster (**1-[OTf] (H₂O)**) were unsuccessful; we postulate that the difficulty lies in poor crystallinity of the complex, as opposed to an inability to coordinate H_2O over triflate. Crystallization attempts of **3-[OTf]** in MeCN/5% H_2O solutions produced crystals of triflate coordinated clusters (Figure S63), demonstrating the complication of preparing Mn–OH₂ clusters across these oxidation states with the triflate counterions. The structure of **2-[OTf] (H₂O)** displays H_2O coordinated to the apical Mn, with a long Mn–O distance of $2.163(6) \text{ \AA}$, consistent with a $\text{Mn}^{\text{II}}\text{--OH}_2$ assignment^{13e, 20}; furthermore, both triflate counterions are hydrogen bonding to each proton of the Mn–OH₂ moiety through one of the sulfonate oxygens ($\text{O}_{\text{aquo}}\text{--OOTf}$ distances of 2.787 and $2.695 \text{ \AA}$; Figure S63).

To ensure that H₂O remained coordinated to the cluster in solution, experiments were performed in THF, a less coordinating solvent than MeCN, and triflate counterions were replaced with the non-coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ([BAr^F₄]) anion. This was accomplished by reducing the dicationic cluster, **2**-[OTf], with Na/Hg amalgam in THF to obtain the neutral all M^{II} cluster, **4**, as a blue solid (Figure 1C). Similar to the related neutral phenyl pyrazolate clusters,^{18a} **4** is either insoluble or unstable in most organic solvents, so its chemistry towards H₂O was not pursued. Oxidation of **4** with 1 and 2 equivalents of Ag[BAr^F₄] • 2 MeCN affords **1**-[BAr^F₄] and **2**-[BAr^F₄], respectively (Figure 1C). The [Fe^{III}₃Mn^{II}] cluster, **3**-[BAr^F₄], was prepared by oxidation of **2**-[BAr^F₄] with acetyl-ferrocenium ([^{Ac}Fc][BAr^F₄]). All these clusters are highly soluble in THF and bind H₂O under conditions where it is present in ~100 molar equivalents (Figures S7 - S9). Significant decomposition is observed when H₂O concentrations above ~1000 equivalents were used; therefore, all the studies described herein were performed on ca. 2 mM of a cluster with [BAr^F₄][−] counterions in THF solution with 250 mM H₂O, as these conditions displayed ¹H NMR spectra consistent with complete or near complete binding of H₂O to the apical Mn.

Deprotonation of the Mn–OH₂ moiety in the [Fe^{III}₂Fe^{II}Mn^{II}] cluster, **2**-[BAr^F₄], was accomplished by addition of 1 equivalent of a relatively strong organic base, 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU; p*K*_a(THF) = 19.1)²¹, or by stirring a THF solution of **2**-[BAr^F₄] over solid KOH for 30 minutes. Both reactions lead to the same species based on the ¹H NMR and UV-Vis absorbance features, assigned to the Mn–OH cluster, **6**-[BAr^F₄]. Structural confirmation of this species was obtained by performing analogous reactions on **2**-[OTf] to prepare the triflate salt, **6**-[OTf], which displays the same ¹H NMR features (Figure S11). This species could be crystallized from MeCN solution by slow diffusion of Et₂O, and was characterized via X-ray diffraction (Figure 2C). The structure of **6**-[OTf] is similar to **2**-[OTf] (H₂O), displaying Mn binding to the hydroxide ligand with a trigonal bipyramidal geometry. Notably, the Mn–O distance to the hydroxide ligand is contracted by approximately 0.3 Å relative to **2**-[OTf] (H₂O) (1.843(9) vs 2.163(6) Å). Furthermore, the distance of the apical Mn to the interstitial μ₄-O in the cluster is also shortened significantly (1.838(8) vs 2.064(5) Å in **2**-[OTf] (H₂O); Table 1); both of these observations are consistent with a Mn^{III}–OH assignment.²² The Mn–OH and Mn–μ₄-O distances of ~1.8 Å are similar to the bond metrics observed in our previously reported hydroxide-bound tetramanganese cluster in the [Mn^{III}₂Mn^{II}₂] oxidation state.¹⁹ There, the Mn–OH bond is slightly longer (1.872(2) Å) due to hydrogen bonding to the pendant *tert*-butyl-phenyl-aminopyrazolate ligands. The structural data for **6**-[OTf] are consistent to an oxidation state assignment of [Fe^{II}₂Fe^{III}Mn^{III}] for the cluster; corroborated by the Mössbauer spectrum of **6**-[BAr^F₄] (Figure S58). Deprotonation of the Mn^{II}–OH₂ in **2** to form **6** leads to rearrangement of the redox states of the metals in the cluster to produce a Mn^{III}–OH site. Similar ‘valence tautomerizations’ have been observed in Mn^V(O)-corrole systems, where protonation or binding a Lewis acid to the oxo moiety leads to reversible formation of a Mn^{IV}(O–X)-(corrole-radical cation) complexes.²³

Electrochemistry.

The electrochemistry of the $[\text{Fe}_3\text{OMn-OH}_2]$ and $[\text{Fe}_3\text{OMn-OH}]$ clusters was investigated by cyclic voltammetry of **2**-[**BAR**^F₄] and **6**-[**BAR**^F₄]. Two quasi-reversible redox events were observed in **2**-[**BAR**^F₄]: an oxidation at -0.02 V and a reduction at -0.90 V (all potentials vs Fc/Fc^+ ; Figure 3, red trace). These redox events were assigned to the $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{Mn}^{\text{II}}] \rightarrow [\text{Fe}^{\text{III}}_3\text{Mn}^{\text{II}}]$ and $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_2\text{Mn}^{\text{II}}] \rightarrow [\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{Mn}^{\text{II}}]$ couples. Mössbauer spectra collected on **1**-[**BAR**^F₄] – **3**-[**BAR**^F₄] in THF with 250 mM H_2O show that both oxidation state changes occur at the Fe centers (Figures S50 – S54), leading to the conclusion that the apical Mn remains divalent when bound to H_2O across all the oxidation states observed in the CV experiment, and only the distal Fe centers change oxidation states. The hydroxide-bound cluster, **6**-[**BAR**^F₄], displays two oxidations: a quasi-reversible couple at -0.49 V ($[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_2\text{Mn}^{\text{III}}] \rightarrow [\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{Mn}^{\text{III}}]$), and an irreversible event at +0.26 V ($[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{Mn}^{\text{III}}] \rightarrow [\text{Fe}^{\text{III}}_3\text{Mn}^{\text{III}}]$). A quasi-reversible reduction for the $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_2\text{Mn}^{\text{III}}] \rightarrow [\text{Fe}^{\text{II}}_3\text{Mn}^{\text{III}}]$ couple is also observed at -1.34 V. The Mössbauer spectra of **5** – **7**-[**BAR**^F₄] (Figures S56 – S60) are again consistent with redox changes occurring exclusively at Fe. Notably, no catalytic oxidation wave is observed at high potentials for **6**-[**BAR**^F₄], in contrast to our previously reported tetramanganese cluster bridged with ter-butyl-phenylaminopyrazolates.¹⁹ Reasons for this difference may be the ~100 mV negative shift in reduction potentials for the $[\text{Fe}_3\text{Mn-OH}]$ clusters, along with the lower concentration of H_2O . The lack of electrocatalytic oxidation by **6**-[**BAR**^F₄] could also suggest the importance of pendant basic groups near the $\text{Mn}^{\text{III}}\text{-OH}$ moiety for water oxidation catalysis.

Determination of $\text{p}K_a$ of H_2O Ligand in $[\text{Fe}_3\text{Mn}^{\text{II}}\text{-OH}_2]$ Clusters.

The $\text{p}K_a$ of the aquo-ligand bound to **2**-[**BAR**^F₄] was measured by mixing this cluster with various concentrations of 1,1,3,3-tetramethyl-2-phenylguanidine (PhTMG; $\text{p}K_a(\text{THF}) = 16.5$).²¹ The ratio of **2**-[**BAR**^F₄] and **6**-[**BAR**^F₄] was examined by UV-Vis absorbance spectroscopy as a function of PhTMG concentration, and a $\text{p}K_a$ value of 17.5 for **2**-[**BAR**^F₄] was obtained (Figure S24). Analogous experiments were attempted on the oxidized aquo-cluster, **3**-[**BAR**^F₄]; however, the changes in UV-Vis spectral features upon deprotonation are minor (Figures S21 and S23). The $\text{p}K_a$ of **3**-[**BAR**^F₄] could be obtained by examining its ¹H NMR resonances in the presence of a suitable exogenous base, 2,6-Me₂-pyridine (Figure S13; $\text{p}K_a(\text{THF}) = 9.5$).²¹ As expected, the acidity of the $[\text{Fe}_3\text{Mn-OH}_2]$ cluster increases upon oxidation; a $\text{p}K_a$ value of 9.2 was obtained for **3**-[**BAR**^F₄]. While a titration on the reduced $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_2\text{Mn}^{\text{II}}]$ cluster, **1**-[**BAR**^F₄], was not conducted, we determined that its $\text{p}K_a$ is significantly higher than the other clusters investigated, since it does not react with excess DBU (Figure S7; $\text{p}K_a(\text{THF}) = 19.1$).²¹

$\text{BDE}_{\text{O-H}}$ and PCET Reactivity of the Different Redox States.

The homolytic bond dissociation enthalpy of the aquo O-H ($\text{BDE}_{\text{O-H}}$) were determined for the three cluster oxidation states observed (**1**-[**BAR**^F₄] – **3**-[**BAR**^F₄]) by analyzing the $\text{p}K_a$ and reduction potentials of the aquo- and hydroxide-bound clusters (Figure 4). This calculation combines the energies of the discrete proton and electron transfers involved, along with the energy of formation of the hydrogen atom in THF (C ; 66 kcal/mol²⁴).²⁵

$$\text{BDE}_{\text{O-H}}(\text{kcal/mol}) = 1.37\text{p}K_a + 23.06E^\circ + C \quad (1)$$

Therefore, summing the energy of the oxidation of **1**-[BAr^F₄] (−0.90 V; −20.6 kcal/mol) and the energy of deprotonation of **2**-[BAr^F₄] (17.5; 24.0 kcal/mol) with *C* establishes an energy of 69 kcal/mol for the formal H-atom transfer from **1**-[BAr^F₄] to **6**-[BAr^F₄]. Likewise, the oxidation of **2**-[BAr^F₄] (−0.02 V; −0.5 kcal/mol) followed by the deprotonation of **3**-[BAr^F₄] (9.2; 12.6 kcal/mol) leads to a BDE_{O-H} of 78 kcal/mol for the aquo-ligand of **2**-[BAr^F₄] (formal HAT to form **7**-[BAr^F₄]). An alternate way to determine the BDE_{O-H} of **2**-[BAr^F₄] is from the p*K*_a of **2**-[BAr^F₄] and the reduction potential of **6**-[BAr^F₄], leading to a similar bond enthalpy of 78.7 kcal/mol. The same square scheme analysis can be done to obtain a BDE_{O-H} of 85 kcal/mol for **3**-[BAr^F₄]. With these measured values, the p*K*_a of **1**-[BAr^F₄] could be estimated; a BDE_{O-H} of 69 kcal/mol for **1**-[BAr^F₄] means the enthalpy of deprotonation for this cluster is expected to be ~34 kcal/mol (p*K*_a = 24.9), by combining this energy with the oxidation of **5** (−1.34 V; −30.9 kcal/mol).

The BDE_{O-H} values of these clusters were evaluated by investigating their proton-coupled electron transfer (PCET) reactivity towards different organic radicals. The PCET reagents employed were (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO; BDE_{O-H} = 70 kcal/mol) and 2,4,6-tri-*tert*-butylphenoxy radical (2,4,6-TBPR; BDE_{O-H} = 82 kcal/mol).^{25c} Formal hydrogen atom transfer from **1**-[BAr^F₄] to form **6**-[BAr^F₄] could be accomplished using either one equivalent of TEMPO or 2,4,6-TBPR, consistent with a BDE_{O-H} less than 70 kcal/mol (Scheme 1; Figure S14). **2**-[BAr^F₄] reacts with 1 equivalent 2,4,6-TBPR to form **7**-[BAr^F₄], but no reaction is observed between this cluster and TEMPO, indicative of a BDE_{O-H} that is between 70 and 82 kcal/mol (Figure S15). **3**-[BAr^F₄] does not react with either PCET reagent, which supports the assignment of a BDE_{O-H} greater than 82 kcal/mol (Figure S16).

Potential–p*K*_a Diagram of [Fe₃Mn–OH_x] Clusters.

Further insight into the basis of PCET reactivity of these clusters was obtained by investigating the effect of external bases on the reduction potentials of the aquo- and hydroxide-bound clusters. Typically, this type of analysis is conducted under aqueous conditions, where the reduction potentials can be measured as a function of solution pH; data are presented as a potential–pH plot, known as a Pourbaix diagram.²⁶ Aqueous Pourbaix diagrams have been helpful in understanding the speciation of a number of molecular Ru/Mn water oxidation catalysts and related complexes.^{15b, 27} Recently, Pourbaix theory has been applied to nonaqueous solvents, where the reduction potential of PCET will depend on the p*K*_a of an external acid/base (and the concentration of this acid/base relative to its conjugate base/acid at Nernstian equilibrium).²⁸ For the system reported here, a potential–p*K*_a plot was constructed as a means of providing experimental support for the aquo-ligand p*K*_a and BDE_{O-H} values of **1**-[BAr^F₄] - **3**-[BAr^F₄] and to gain information about the thermochemistry of PCET with the Mn–OH clusters to form a terminal Mn-oxo moiety.

Measuring the CV of **2**-[BAr^F₄] with one equivalent of various organic bases, with p*K*_a values of their conjugate acids in THF ranging from 7.5 to 28.1, produced the potential–p*K*_a plot depicted in Figure 5 (blue points; see Table S3 and Figures S31 – S42 for individual CVs). For relatively weak bases (p*K*_a < 10), the reduction potentials of **2**-[BAr^F₄] do not significantly deviate from their potentials in the absence of any base. As the strength of the base increases, the reduction potential for the oxidation of **2**-[BAr^F₄] is lowered as a function of the conjugate acid p*K*_a, consistent with PCET occurring between the p*K*_a range 10–17. The data points in this p*K*_a range follow the diagonal line calculated for the **2**-[BAr^F₄]→**7**-[BAr^F₄] PCET process, based on the reduction potentials of **2**-[BAr^F₄] and **6**-[BAr^F₄] and the p*K*_a values of **2**-[BAr^F₄] and **3**-[BAr^F₄]. Observing the predicted linear decrease in reduction potential for **3**-[BAr^F₄] in the p*K*_a range 10 – 17 supports the p*K*_a values reported for **2**-[BAr^F₄] and **3**-[BAr^F₄] in Figure 4. Similar support is given to the p*K*_a of **1**-[BAr^F₄] (24.9) when using strong bases (p*K*_a > 17.5). Evidence for the **1**-[BAr^F₄]→**6**-[BAr^F₄] PCET process was observed under these conditions, again with the data roughly matching the diagonal line with an intercept at –1.34 V and a p*K*_a of 24.9. Furthermore, when a base was employed with a p*K*_a > 24.9, the reduction potentials observed were nearly identical to the potentials reported for **6**-[BAr^F₄] in the absence of any acid or base.

As expected, deviations of the data from the calculated diagonal line occur as the base p*K*_a approaches the p*K*_a of the cluster (see **2**-[BAr^F₄]→**7**-[BAr^F₄] around p*K*_a of 10, for example), based on predicted potential–p*K*_a relationships for ET-PT or PT-ET reaction mechanisms.²⁸ Further deviations from the predicted solid lines in Figure 5 could be due to incompatibility of the chosen base with this system (too coordinating, electrochemically unstable, etc.). Ultimately, inconsistencies between the potential–p*K*_a data of **2**-[BAr^F₄] and the BDE_{O–H} values reported in Figure 4 only amount to a difference of ~3 kcal/mol, which is a reasonable uncertainty for these bond energy determinations.^{25c} Based on the PCET reactivity of these complexes towards TEMPO and TBPR (vide supra), it is unlikely that these BDE_{O–H} values could deviate more than a few kcal/mol.

Potential–p*K*_a data were also obtained for **6**-[BAr^F₄] in the presence of relatively strong organic bases in attempts to observe a PCET process accessing Mn=O clusters, since this technique has been previously useful for gaining insight into the proton and electron transfer thermodynamics for unstable species.²⁸ Based on the potential–p*K*_a plot constructed in Figure 5, PCET to form a Mn-oxo cluster could be possible at high potentials with a strong base (top right area of the diagram). The CV of **6**-[BAr^F₄] with one equivalent tert-butylimino-tri(pyrrolidino)phosphorene (*t*-BuP₁(pyrr); p*K*_a(THF) = 22.8)²¹ shows no shift in the Mn–OH cluster reduction potentials. Similarly, no change is observed with the **5**→**6**-[BAr^F₄] and **6**-[BAr^F₄]→**7**-[BAr^F₄] reduction potentials with 1-ethyl-2,2,4,4,4-pentakis(dimethylamino)2-λ⁵,4λ⁵-catenadi(phosphazene) (EtP₂(dma); p*K*_a(THF) = 28.1).^{21, 29} These experimental observations provide a lower limit to the p*K*_a values of **8**-[BAr^F₄] and **7**-[BAr^F₄], respectively. With these values, the BDE_{O–H} of **7**-[BAr^F₄] and **8**-[BAr^F₄] are predicted to be greater than 93 and 103 kcal/mol, respectively (Figure 6).³⁰ These BDE_{O–H} estimates are higher than Mn complexes, where these bond strengths have been reported.^{11c, 12d, 12i, 12k} The large BDE_{O–H} values for these hydroxide clusters suggest that if these terminal oxo moieties could be accessed, they would be highly reactive. Indeed,

previous attempts to generate a terminal oxo species on related phenyl-pyrazolate bridged multimetallic clusters results in activation of strong bonds, although the identity of the reactive intermediate in these reactions could not be established (terminal metal-oxo or iodosylbenzene adduct).^{18d-f}

CONCLUSIONS

We have reported the synthesis of tetranuclear $[\text{Fe}_3\text{Mn}-\text{OH}_x]$ clusters bearing bridging unsubstituted pyrazolate ligands, leading to a sterically open coordination environment around the apical Mn center. These clusters were used to investigate the implications of distal metal redox changes on the activation of water by Mn in terms of the aquo-cluster pK_a , reduction potential, and homolytic O–H bond strength. Increasing the oxidation state of a distal Fe center by one increases the acidity of the aquo ligand by ~ 7 pKa units (in THF), while raising the $\text{BDE}_{\text{O-H}}$ 8 kcal/mol, on average. By only changing the redox states of the distal Fe centers, a wide range of $\text{BDE}_{\text{O-H}}$ values could be measured for the $\text{Mn}-\text{OH}_2$ moiety (69 – 85 kcal/mol), which nearly spans the range of the reported $\text{BDE}_{\text{O-H}}$ measured in reported in mononuclear $\text{Mn}-\text{OH}_2$ complexes.^{11c, 12e, 12f, 12i} The three different oxidation states of the aquo-cluster (**1**- $[\text{BAr}^{\text{F}}_4]$ – **3**- $[\text{BAr}^{\text{F}}_4]$) underwent PCET reactions with TEMPO and 2,4,6-TBPR consistent with their measured $\text{BDE}_{\text{O-H}}$ values. The increase in $\text{BDE}_{\text{O-H}}$ of ~ 8 kcal/mol by increasing distal Fe oxidation state is similar to the increases that have been observed in mononuclear Mn systems where $\text{BDE}_{\text{O-H}}$ studies could be accomplished over multiple Mn oxidation states.^{12d, 12i} This is in contrast to the previous example of a binuclear Mn system, where $\text{Mn}-\text{OH}_2$ $\text{BDE}_{\text{O-H}}$ values could be measured over three oxidation states, where small changes in the bond strength of ~ 4 kcal/mol for the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}-\text{OH}_2$ complex versus $\text{Mn}^{\text{III}}_2-\text{OH}_2$ were observed.^{15a}

Importantly, the large effect of the remote metals on the $\text{BDE}_{\text{O-H}}$ demonstrates that the cluster as a whole has a significant impact in the activation of substrate water molecules. The range of $\text{BDE}_{\text{O-H}}$ reported here is achieved without change in the redox state of Mn; therefore, consideration of the effect of metal centers not directly supporting the substrate must be taken into account for multimetallic biological active sites as well as synthetic clusters. Additionally, the present findings demonstrate that, in comparison to monometallic complexes, transition metal clusters not only provide the possibility of increased storage of redox equivalents, but also can serve to dynamically tune reactivity through remote oxidation state changes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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29. The redox couple that would be assigned to the 7-[BArF4] to 8-[BArF4] reduction potential unexpectedly increases, inconsistent with PCET to a Mn-oxo and may suggest an undesirable side reaction takes place at these potentials with the base employed.
30. Attempts to obtain supporting data via stoichiometric deprotonation of 7-[BArF4] with various bases led to decomposition via reduction, with no evidence of forming a transient Mn-oxo moiety (Figures S16 and S17). Investigations into the characterization and reactivity of these putative Mn-oxo species (M = Fe, Mn) in these and related clusters is ongoing.

Figure 1.

(A) Crystal structure of tetranuclear Fe₃Mn cluster 1-[OTf] with ellipsoids shown at the 50% probability level. Solvent molecules, outer-sphere counterions, and H atoms are omitted for clarity. (B) 1,3,5-triarylbenzene ligand platform (L³⁻). (C) Synthetic scheme of Fe₃Mn clusters with triflate and [BARF₄] counterions. Conditions: (i) One-pot synthesis in THF with (1) Ca(OTf)₂ (1 equiv., 60 min), (2) potassium pyrazolate (3.1 equiv., 20 min), (3) PhIO (1 equiv., 90 min), and (4) Mn(OTf)₂ • 2 MeCN (1.3 equiv., 18 hr); (ii) CoCp₂ (1 equiv.), THF, 60 min; (iii) Na/Hg (2.6 equiv. Na), THF, 4 hr; (iv) AgOTf (1 equiv.), THF, 30 min; (v) Ag[BARF₄] • 2 MeCN (2 equiv.), Et₂O, 15 min; (vi) [AcFc][BARF₄] (1 equiv.), THF, 10 min; (vii) Ag[BARF₄] • 2 MeCN (1 equiv.), Et₂O, 15 min.

Figure 2.

Truncated crystal structures of (A) **1**-[OTf], (B) **2**-[OTf] (H_2O), and (C) **6**-[OTf]. Ellipsoids are shown at the 50% probability level with solvent molecules, outersphere counterions, and hydrogen atoms (except for hydrogen atoms on O2) are omitted for clarity.

Figure 3.

Cyclic voltammograms of **2**-[BAr^F₄] (red trace) and **6**-[BAr^F₄] (green trace); 2 mM compound in THF with 250 mM H₂O and 100 mM [nPr₄N][BAr^F₄] at a scan rate of 50 mV/s with glassy carbon, Pt-wire, and Ag-wire as working, counter, and reference electrodes, respectively. The open circuit potentials were -0.2 V for **2**-[BAr^F₄] and -1.0 V for **6**-[BAr^F₄].

Figure 4.

Thermodynamic cycles to evaluate the $\text{BDE}_{\text{O-H}}$ of Mn-OH₂ clusters **1**-[BAr^F₄] - **3**-[BAr^F₄]. Reduction potentials (horizontal lines) are referenced to Fc/Fc⁺. $\text{p}K_a$ values (vertical lines) are based on relative $\text{p}K_a$ values of acids in THF. Diagonal lines are the $\text{BDE}_{\text{O-H}}$ values calculated from the reduction potential and $\text{p}K_a$ according to the Bordwell equation (equation 1). Approximate values (~) are extrapolated from the Bordwell equation.

Figure 5.

Potential– pK_a diagram of **2**-[BArF₄] (blue squares) and **6**-[BArF₄] (green squares). Data points are the observed reduction potentials of the compounds (y-axis) in the presence of one equivalent base with various pK_a values in THF (x-axis). The horizontal lines correspond to the measured reduction potentials of **2**-[BArF₄] and **6**-[BArF₄] in the absence of any external base. Vertical lines correspond to the pK_a values of Mn–OH₂ clusters **1**-[BArF₄] - **3**-[BArF₄]. The horizontal line for the **7**-[BArF₄]→**8**-[BArF₄] redox couple is dashed at high pK_a values due to the possibility of PCET from the Mn–OH with a strong enough base.

Figure 6.

Estimated $\text{BDE}_{\text{O-H}}$ values for $\text{Mn}^{\text{III}}\text{-OH}$ clusters **6**-[BAR^{F}_4] and **7**-[BAR^{F}_4] based on their oxidation potentials and lower bound of their $\text{p}K_a$ (where no PCET occurs in their CV with an external base). The reduction potentials of the Mn-OH clusters were unchanged in the presence of *tert*-butylimino-tri(pyrrolidino)phosphorene ($\text{p}K_a(\text{THF}) = 22.8$), consistent with $\text{p}K_a$ values of **6**-[BAR^{F}_4] and **7**-[BAR^{F}_4] greater than 22.8. Furthermore, the **6**-[BAR^{F}_4] $\rightarrow$ **7**-[BAR^{F}_4] potential is unchanged with 1-ethyl-2,2,4,4,4-pentakis(dimethylamino)-2- $\lambda^5,4\lambda^5$ -catenadi(phosphazene) ($\text{p}K_a(\text{THF}) = 28.1$), consistent with a $\text{p}K_a$ of **6**-[BAR^{F}_4] greater than 28.1. According to the Bordwell equation, this is consistent with $\text{BDE}_{\text{O-H}}$ values greater than 93 and 103 kcal/mol for **6**-[BAR^{F}_4] and **7**-[BAR^{F}_4], respectively. The metal oxidation states of the resulting putative Mn-oxo clusters are left ambiguous since multiple oxidation state distributions are possible.

Scheme 1

. Proton Coupled Electron Transfer (PCET) Reactions of Mn–OH₂ clusters, 1-[BArF₄] - 3-[BArF₄].

Table 1.

Selected Bond Distances, ^{57}Fe Mössbauer Parameters, and Oxidation State Assignments for Structurally Characterized Compounds

Metal Center	M- μ_4 -O1; (Mn1-O2) distance (Å)	δ (mm/s)	$ E_q $ (mm/s)	Assignment
1-[OTf]				
Fe1	1.912(2)	0.56	1.32	<i>h.s.</i> Fe ^{III}
Fe2, Fe3	2.054(2), 2.112(2)	1.14, 1.13	3.51, 3.02	<i>h.s.</i> Fe ^{II}
Mn1	1.997(2); (2.249(2))			Mn ^{II}
2-[OTf]				
Fe1, Fe2	1.951(2), 1.966(2)	0.47, 0.42	0.58, 0.91	<i>h.s.</i> Fe ^{III}
Fe3	2.097(2)	1.12	2.93	<i>h.s.</i> Fe ^{II}
Mn1	2.053(2); (2.167(3))			Mn ^{II}
2-[OTf] (H₂O)				
Fe1, Fe2	1.923(5), 1.984(5)			<i>h.s.</i> Fe ^{III}
Fe3	2.092(5)			<i>h.s.</i> Fe ^{II}
Mn1	2.064(5); (2.163(6))			Mn ^{II}
3-[OTf]				
Fe1,	1.980(4),	0.44	0.80	<i>h.s.</i> Fe ^{III}
Fe2, Fe3	1.982(4), 1.989(4)			
Mn1	2.107(4); (2.162(5))			Mn ^{II}
6-[OTf]				
Fe1	2.003(7)	0.53	0.76	<i>h.s.</i> Fe ^{III}
Fe2, Fe3	2.126(7), 2.051(7)	1.09, 1.08	3.09, 2.58	<i>h.s.</i> Fe ^{II}
Mn1	1.838(8); (1.843(9))			Mn ^{III}