

Ligand Substituent Effects in Manganese Pyridinophane Complexes: Implications for Oxygen-Evolving Catalysis

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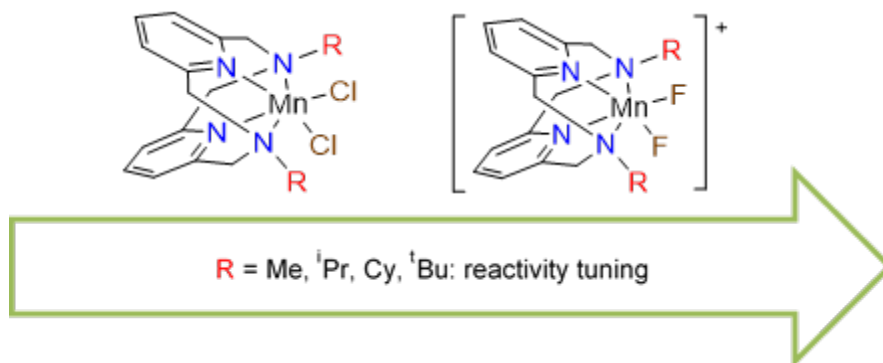
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Dedicated to Professor Dr. Karl Wieghardt on the occasion of his 75th birthday anniversary

Abstract:

A series of Mn(II) complexes of differently substituted pyridinophane ligands, $(\text{Py}_2\text{NR}_2)\text{MnCl}_2$ ($\text{R} = \text{}^i\text{Pr}$, Cy) and $[(\text{Py}_2\text{NR}_2)\text{MnF}_2](\text{PF}_6)$ ($\text{R} = \text{}^i\text{Pr}$, Cy, ${}^t\text{Bu}$) are synthesized and characterized. The electrochemical properties of these complexes are investigated by cyclic voltammetry, along with those of previously reported $(\text{Py}_2\text{N}^t\text{Bu}_2)\text{MnCl}_2$ and the Mn(III) complex $[(\text{Py}_2\text{NMe}_2)\text{MnF}_2](\text{PF}_6)$. The electronic structure of this and other Mn(III) complexes is probed experimentally and theoretically, respectively by high-frequency and -field electron paramagnetic resonance (HF-EPR) spectroscopy and by *ab initio* quantum chemical theory (QCT). These studies showed the complexes to contain relatively typical six-coordinate Mn(III). The catalytic activity of these complexes towards both H_2O_2 disproportionation and H_2O oxidation has also been investigated. The rate of H_2O_2 disproportionation decreases with increasing substituent size. Some of these complexes are active for electrocatalytic H_2O oxidation, however this activity cannot be rationalized in terms of simple electronic or steric effects.



Introduction:

An attractive strategy for meeting the dramatically increasing demand of clean and renewable energy is to use hydrogen gas as the energy source, which can be obtained from splitting of H₂O to H₂ and O₂.¹⁻³ H₂O is split by Nature under mild conditions using natural oxygenic photosynthesis, which is achieved by the Oxygen Evolving Center (OEC) of Photosystem II. The active site of OEC has been characterized as a Mn₄Ca cluster through spectroscopic, X-ray diffraction (XRD), and computational studies.⁴⁻⁷ Mechanistic investigations suggest that the product O-O bond is formed at higher manganese oxidation states, which are accessed via a series of proton coupled electron transfer steps, but detailed information on/about the structure and electron configuration of the transient state in which O-O coupling occurs is still lacking.⁵

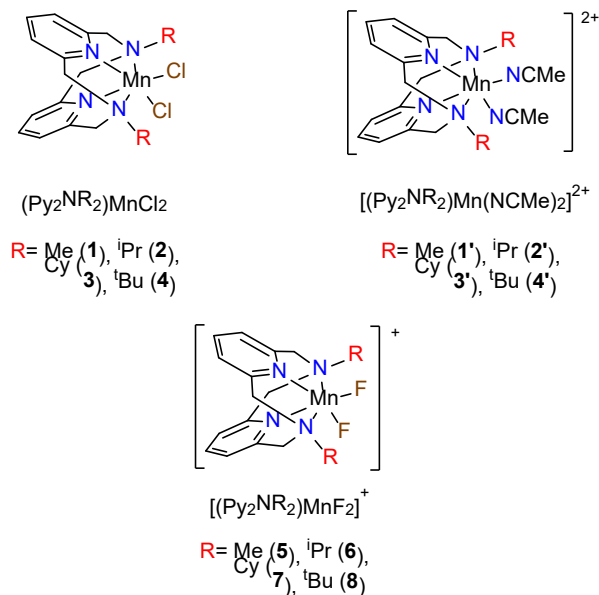
To better understand this natural H₂O splitting process, numerous functional and structural model complexes have been synthesized and investigated.^{1, 8} Due to Mn being at the active site of the OEC, Mn-based water oxidizing complexes are of particular interest.⁵ While a number of biomimetic/bio-inspired di- and multi-nuclear Mn water oxidation catalysts have been reported, mononuclear manganese catalysts for water oxidation catalyst are rare.⁸ As well as being more synthetically accessible, mononuclear complexes have the potential for relatively straightforward delineation of structure/activity relationships on water oxidation reactivity. Previously our group reported one such complex, (Py₂N^tBu)₂MnBr₂ (Py₂N^tBu₂ is the *N,N'*-di-*tert*-butyl-2,11-diaza[3,3](2,6)-pyridinophane ligand), which catalyzes H₂O oxidation to O₂ at *ca.* -1.5 V vs NHE. Since control experiments did not find evidence for the formation of nanoparticulate or heterogeneous catalysts, water oxidation catalysis is likely homogeneous in nature.⁹ Interestingly, replacing the *tert*-butyl ligand substituent in (Py₂N^tBu)₂MnBr₂ with hydrogen or

methyl groups, respectively to give $(\text{Py}_2\text{NH}_2)\text{MnBr}_2$ and $(\text{Py}_2\text{NMe}_2)\text{MnBr}_2$, results in loss of water oxidation activity; however these complexes were found to catalyze H_2O_2 disproportionation to H_2O and O_2 .⁹⁻¹⁰ The latter complexes are thus functional models of the nonheme type II, Mn-containing catalases (Mn-CAT), which perform this reaction in a broad range of microorganisms.¹¹

In addition to H_2O oxidation and H_2O_2 disproportionation, the Py_2NR_2 ligand framework has been shown to support metal complexes that catalyze a variety of other reactions. For example, Koch showed early on that $\text{Fe}^{\text{III}}/\text{Py}_2\text{NMe}_2$ catalyzes the oxidative degradation of catechols by O_2 .¹²⁻¹³ More recently, Mirica reported carbon-carbon and carbon-heteroatom bonds formation catalyzed by $\text{Ni}^{\text{III}}/\text{Py}_2\text{N}^t\text{Bu}_2$.¹⁴ In addition to catalysis, spin crossover was also observed for a $\text{Fe}^{\text{II}}/\text{Py}_2\text{N}^t\text{Bu}_2$ complex.¹⁵ The ability to modify the R groups of Py_2NR_2 ligands allows the catalytic behavior of their metal complexes to be tuned. For example, Cho reported that aldehyde deformylation catalyzed by $\text{Ni}^{\text{III}}/\text{Py}_2\text{NR}_2$ can be significantly accelerated when switching from R = *tert*-butyl to cyclohexyl, which they attribute to a reduction in bulkiness.¹⁶ Since we previously demonstrated that the catalytic reactivity of $\text{Mn}/\text{Py}_2\text{NR}_2$ towards O_2 evolution is influenced by the pyridinophane ligand substituent, we became interested in systematically delineating the relationship between the pyridinophane ligand substituents and the reactivity of their manganese complexes.

We report here the synthesis and structural characterization of $(\text{Py}_2\text{NR}_2)\text{MnCl}_2$ (R = *i*Pr **2**, Cy **3**) and $[(\text{Py}_2\text{NR}_2)\text{MnF}_2](\text{PF}_6)$ (R = *i*Pr **6**, Cy **7**, *t*Bu **8**) complexes (Scheme 1). Along with structural, electrochemical and catalytic properties of previously reported $(\text{Py}_2\text{NMe}_2)\text{MnCl}_2$ **1**, $[(\text{Py}_2\text{NMe}_2)\text{MnF}_2]^+$ **5** complexes,¹⁷ we have investigated the effect of the *N*-substituents on their catalytic reactivity of these complexes towards H_2O_2 disproportionation and H_2O oxidation.

Scheme 1. $(\text{Py}_2\text{NR}_2)\text{MnCl}_2$, $[(\text{Py}_2\text{NR}_2)\text{Mn}(\text{NCMe})_2]^{2+}$ and $[(\text{Py}_2\text{NR}_2)\text{MnCl}_2]^+$ complexes in this work.



We have also elucidated the electronic structure of these complexes through a combination of experiment and theory, primarily high-frequency and -field electron paramagnetic resonance (HF-EPR) spectroscopy and quantum chemical theory (QCT) calculations. While density functional theory (DFT) calculations on $[(\text{Py}_2\text{NMe}_2)\text{MnF}_2](\text{PF}_6)$ (**5**) were reported by Albela *et al.*,¹⁷ herein a multi-configurational treatment allows for a more accurate assessment of the electronic structure description and zero-field splitting (ZFS).¹⁸⁻¹⁹ Therefore, we used the complete active space self-consistent field (CASSCF) method^{18, 20-22} (treating spin-orbit coupling (SOC) effects perturbatively²³) to investigate the electronic structure of $[(\text{Py}_2\text{NR}_2)\text{MnX}_2]^+$ ($X = \text{F}^-, \text{Cl}^-$), including *n*-electron valence (electron) second-order perturbation theory (NEVPT2)²⁴⁻²⁶ to account for dynamic electron correlation effects and multi-reference configuration interaction (MRCI)^{18, 20, 27} to assess the spin-spin contribution, as well as DFT level for completeness. These results provide an experimental calibration for a similar computational investigation of the

hydroxido complex, $[(\text{Py}_2\text{N}^t\text{Bu}_2)\text{Mn}(\text{OH})_2]^+$ which has been proposed as an intermediate in electrocatalytic water oxidation by a Mn pyridinophane complex.²⁸⁻²⁹

Results and Discussion

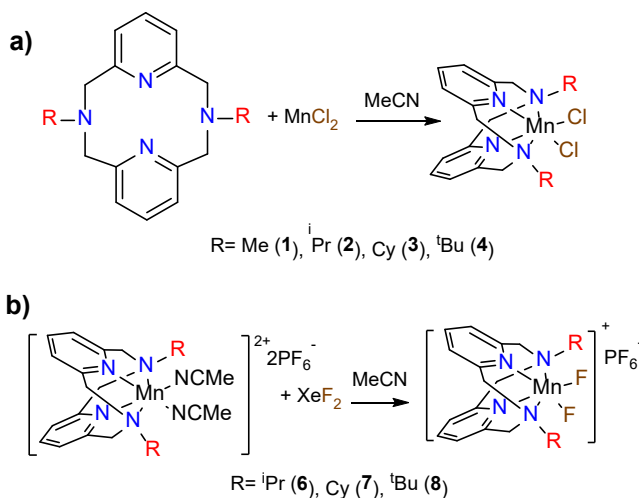
Preparation and Characterization of $(\text{Py}_2\text{NR}_2)\text{MnCl}_2$ and $[(\text{Py}_2\text{NR}_2)\text{MnF}_2]^+$ (R = Me, ⁱPr, Cy, ^tBu)

Similarly to the previously reported bromide analogues, $(\text{Py}_2\text{NR}_2)\text{MnBr}_2$ (R = H, Me, ^tBu),⁹⁻¹⁰ complexes **1** – **4** were prepared by treating the appropriate Py_2NR_2 ligand with anhydrous MnCl_2 in acetonitrile solution (Scheme 2a). The pale yellow $(\text{Py}_2\text{NR}_2)\text{MnCl}_2$ products were characterized by single crystal X-ray diffraction and high resolution mass spectrometry. Complex **2** can be converted to the acetonitrile-solvated complex, **2'**, by treating **2** with 2 equiv of TIPF_6 in acetonitrile solution, as previously reported for **1'** and **4'**.⁹⁻¹⁰ Complex **2'** has also been characterized by single crystal X-ray diffraction.

The Mn(III) difluoride complex **6** can be prepared in an analogous manner to the synthesis of **5**,¹⁷ wherein a mixture of $\text{Py}_2\text{N}^i\text{Pr}_2$ and MnF_3 is gently heated in MeOH. Unfortunately, this protocol does not work for the synthesis of complexes **7** and **8**, presumably due to the poor methanol solubility of the ligands, with their bulky aliphatic substituents. However, these complexes can be obtained by the fluorination of **3'** and **4'** with XeF_2 in MeCN, similarly to the preparation of other organometallic fluoride complexes.³⁰⁻³¹ Complex **6** can also be prepared by this method. Complexes **6**, **7**, and **8** were isolated as dark orange crystals and characterized by single crystal X-ray diffraction and high resolution mass spectrometry. It is worth noting that XeF_2 is typically a two-electron oxidant that transfers two fluorine atoms to the metal,³¹ however only the one-electron oxidized products, **6**, **7**, and **8** were obtained from these fluorination

reactions (Scheme 2b). We therefore propose that the Mn(III) complexes (**6**, **7**, **8**) are generated through comproportionation of the two-electron oxidized Mn(IV) complexes $[(\text{Py}_2\text{NR}_2)\text{MnF}_2]^{2+}$ (formed by two-electron oxidation by XeF_2) and the Mn(II) reagents, $[(\text{Py}_2\text{NR}_2)\text{Mn}(\text{NCMe})_2]^{2+}$.

Scheme 2. Synthesis of the (a) $\text{Py}_2\text{NR}_2\text{MnCl}_2$ and (b) $[(\text{Py}_2\text{NR}_2)\text{MnF}_2](\text{PF}_6)$ complexes



The UV-vis spectra of complex **6** – **8** each show a band around 500 nm that has a low extinction coefficient (Figures S4 – S6) similarly to observations for **5**.¹⁷ The high spin state of Mn(III) ($3d^4$, $S = 2$) is confirmed by the magnetic susceptibility of **8** ($\mu_{\text{eff}} = 5.20 \mu_{\text{B}}$ determined by Evans' method), which consistent with the theoretical value calculated for $S = 2$ ($\mu_{\text{eff}} = 4.90 \mu_{\text{B}}$).

Molecular structures of $[(\text{Py}_2\text{NR}_2)\text{Mn}(\text{NCMe})_2]^{2+}$ and $[(\text{Py}_2\text{NR}_2)\text{MnF}_2]^+$ (R = Me, ⁱPr, Cy, ^tBu)

X-ray quality crystals of **1'**, **2'**, **4'**, **3**, **6**, **7**, and **8** were obtained by slow diffusion of diethyl ether into concentrated acetonitrile solution at ambient temperature. Representations of the molecular structures are shown in Figures 1 and 2, with selected bond distances and angles given

in Tables 1 and 2. We were unable to isolate crystals of **3'** suitable for X-ray diffraction studies, although its chloride analogue, **3** was successfully characterized by single crystal X-ray diffraction, providing data for comparison with the acetonitrile complexes (**1'**, **2'**, and **4'**).

According to structural data summarized in Table 1, the structures of the Mn(II) complexes, **1'**, **2'**, and **4'** are generally similar to the previous reported analogues, **1** and the bromido series $(\text{Py}_2\text{NR}_2)\text{MnBr}_2$ ($\text{R} = \text{Me}, \text{}^t\text{Bu}$).^{9-10, 17} Specifically, these mononuclear complexes all exhibit pseudo-octahedral geometries with an equatorial plane consisting of two acetonitrile ligands and two pyridine donors, with the amines occupying the axial positions. The geometry of the pyridinophane ligand ensures that the acetonitrile (or other ancillary) ligands are *cis* with respect to other with the two pyridines *trans* to the acetonitrile ligands. Complex **3** has a similar structure to **1'**, **2'**, **4'**, although the N(amine)-Mn-N(amine) and N(pyridine)-Mn-N(pyridine) bond angles are significantly smaller for **3**, likely a consequence of the larger chlorido ligands. This response to the change in ancillary ligands suggests the pyridinophane ligand has flexibility in its binding mode. It is worth noting that similar bond angles involving the pyridinophane ligand are observed for **1**, which has been reported previously.¹⁷

The data in Table 1 suggests that the pyridinophane substituents have a significant effect on the Mn-amine distances in the $[(\text{Py}_2\text{NR}_2)\text{Mn}(\text{NCMe})_2]^{2+}$ complexes. For example, the Mn-N(amine) distance in **4'** is 0.103 Å longer than the corresponding distance in **1'**. By contrast, the complexes show no significant difference in Mn-N(pyridine) and Mn-N(acetonitrile) distances. Assuming that the chloride ligands in **3** do not significantly perturb the other bond lengths, the combined data suggests that the Mn-N(amine) distance increases with increasing bulkiness of the pyridinophane substituent.

The Mn(III) complexes **6** - **8** are generally similar in structure to those of the Mn(II) complexes discussed above. Thus, the Mn ions are also coordinated by the tetradentate macrocycle and two fluoride ligands that are *cis* with respect to other (Table 2). However, the Mn(III) complexes generally have shorter bond lengths, which is attributed to the smaller size of the Mn(III) ion. Similarly to **5**,¹⁷ **6** - **8** also show characteristic Jahn-Teller elongations along the axis containing the amine donors, as revealed by Mn-N(amine) bond lengths that are significantly longer (*ca.* 0.3 Å) than the Mn-N(pyridine) distances. Interestingly, the Mn-N(amine) distances for **5** are significantly shorter than for **6** - **8**, which are similar in magnitude, suggesting that this distance is not strongly dependent on the size of the substituent, in contrast to the Mn(II) complexes.

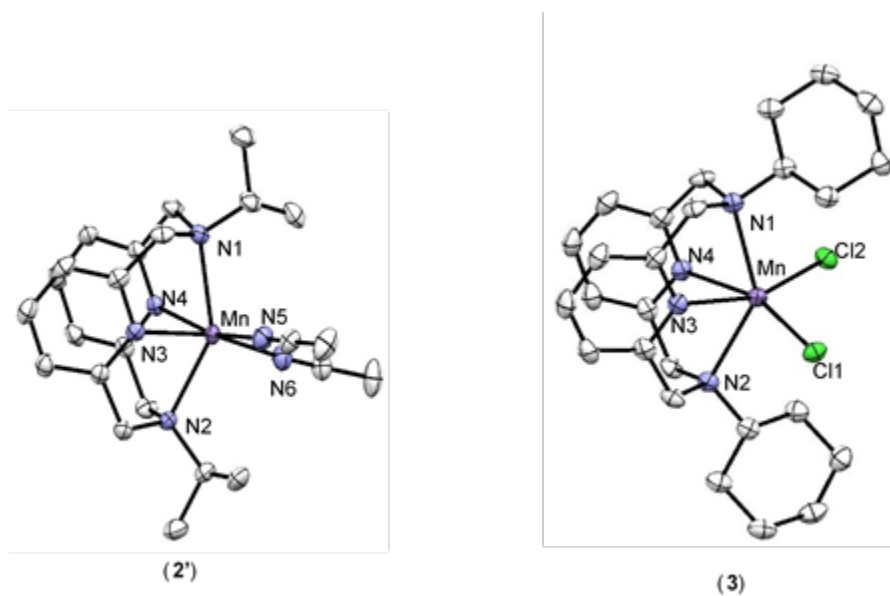


Figure 1. ORTEPs of complexes **2'** and **3** (50% ellipsoids, hydrogen atoms and PF₆ anions are omitted for clarity). Selected bond lengths (Å) and angles (°) for **3**: Mn-N1 2.444(2); Mn-N2 2.444(2); Mn-N3 2.273(2); Mn-N4 2.273(2); Mn-Cl1 2.4350(8); Mn-Cl2 2.4350(8); N1-Mn-N2 138.42(2); N3-Mn-N4 72.84(13); Cl1-Mn-Cl2 104.54.

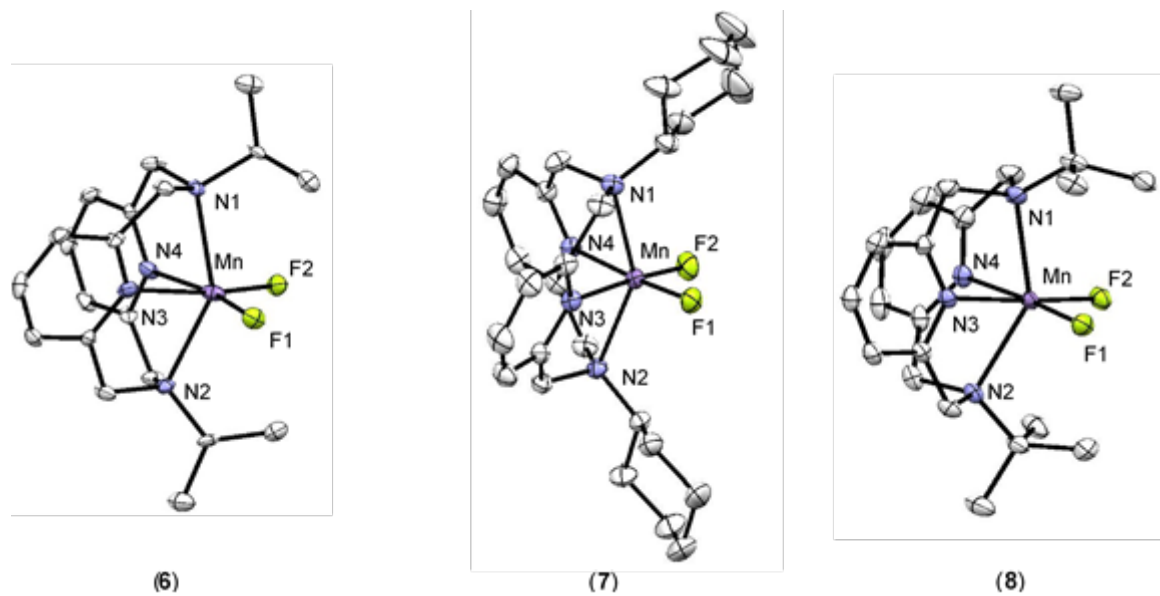


Figure 2. ORTEPs of complexes **6**, **7**, and **8** (50% ellipsoids, hydrogen atoms and PF_6 anions are omitted for clarity).

Table 1. Selected bond lengths (Å) and angles (°) of **1'**, **2'**, and **4'**.

	[Py ₂ NR ₂ Mn ^{II} (NCMe) ₂] ²⁺		
	Me (1') ¹⁷	ⁱ Pr (2')	^t Bu (4') ⁹
Mn-N1	2.327(2)	2.357(1)	2.455(2)
Mn-N2	2.328(2)	2.365(2)	2.415(2)
Mn-N3	2.198(2)	2.198(1)	2.236(2)
Mn-N4	2.213(2)	2.216(1)	2.165(2)
Mn-N5	2.174(2)	2.191(1)	2.152(2)
Mn-N6	2.184(2)	2.208(2)	2.210(2)
N1-Mn-N2	143.44(6)	143.52(5)	143.41(6)
N3-Mn-N4	77.61(6)	77.58(4)	75.10(7)
N5-Mn-N6	94.54(7)	90.74(5)	96.91(8)

Table 2. Selected bond lengths (Å) and angles (°) of **5**, **6**, **7**, and **8**.

	[Py ₂ NR ₂ Mn ^{III} F ₂] ⁺			
	Me (5) ¹⁷	ⁱ Pr (6)	Cy (7)	^t Bu (8)
Mn-N1	2.274(2)	2.328(4)	2.314(2)	2.337(1)
Mn-N2	2.278(2)	2.328(4)	2.310(2)	2.332(2)
Mn-N3	2.024(2)	2.089(3)	2.002(2)	2.018(2)
Mn-N4	2.020(2)	2.089(3)	2.009(2)	2.008(1)
Mn-F1	1.805(2)	1.754(3)	1.806(2)	1.805(1)
Mn-F2	1.801(2)	1.754(3)	1.811(1)	1.810(1)
N1-Mn-N2	147.03(8)	145.3(2)	145.14(8)	145.37(5)
N3-Mn-N4	77.07(8)	79.61(8)	86.76(8)	85.72(6)
F1-Mn-F2	94.89(8)	100.58(7)	92.94(7)	95.77(5)

High-Frequency and -Field EPR

Given that Mn(III) complexes in general are highly amenable to study by HFEPR,³²⁻³⁵ and the pyridinophane complex [(Py₂NMe₂)MnF₂](PF₆) (here, **5**) in particular had been previously investigated experimentally by HFEPR, as well as computationally, by Albela et al.,¹⁷ we decided to confirm and extend those studies. HFEPR investigation of **6** was most successful and clearly showed the $S = 2$ ground state, with a negative D value, as seen in the HFEPR spectrum and simulations shown in Figure 3. HFEPR spectra of **5** gave spin Hamiltonian parameters in agreement with those previously reported and was thus not extensively studied here. In the case of **6**, a complete set of multi-frequency spectra was recorded. Analysis of this 2-D field-frequency dependence,³⁶ shown in Figure 4, gave the full set of spin Hamiltonian parameters, which were similar, but not identical to those of **5**, showing the sensitivity of ZFS parameters to small structural/electronic changes. Full details are given in the Supporting Information.

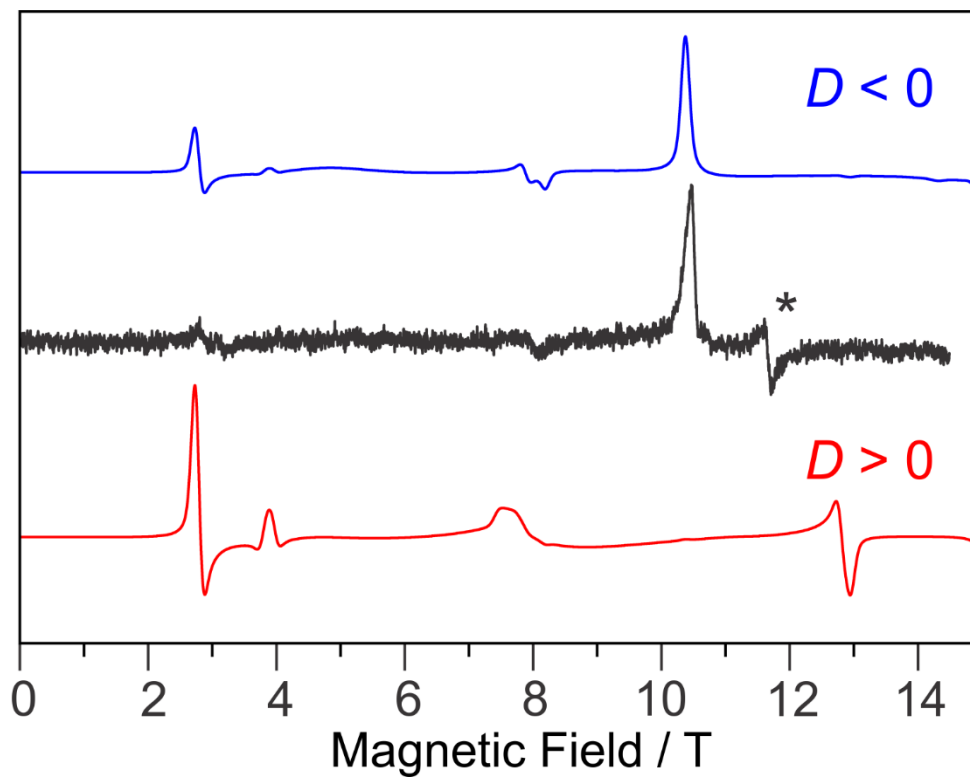


Figure 3. A 633.6 GHz, 5 K HF-EPR spectrum of **6** as a pellet (black trace) with two simulations, using the following spin Hamiltonian parameters: $|D| = 3.78 \text{ cm}^{-1}$; $|E| = 0.064 \text{ cm}^{-1}$ ($E/D = 0.02$); $\mathbf{g} = [2.00, 2.01, 2.02]$. Blue trace: $D < 0$; red trace: $D > 0$. The resonance at 11.7 T marked with the asterisk could not be attributed to the $S = 2$ spin system under study, and is thus not simulated.

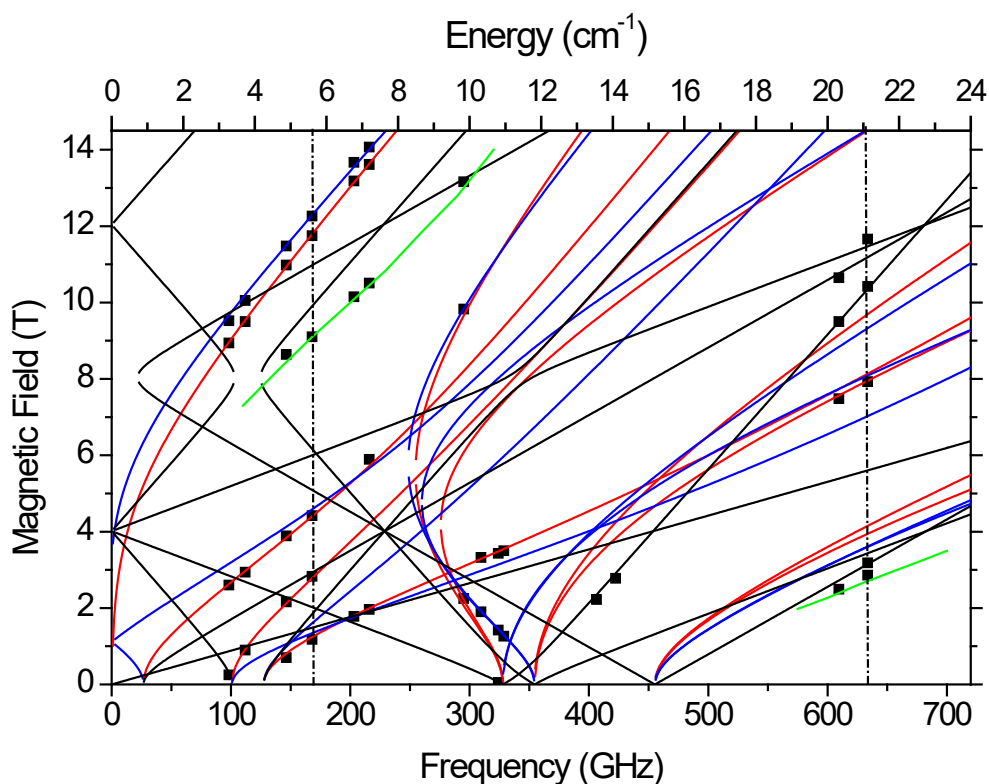


Figure 4. A 2-D map of turning points in the powder spectra of **6** as a function of frequency. The squares are experimental points while the curves are simulations: Red curves: magnetic field B_0 parallel to the x axis of the ZFS tensor, blue curves: $B_0 \parallel y$; black curves $B_0 \parallel z$; green curves: off-axis turning points. The simulation parameters were: $|D| = 3.79 \text{ cm}^{-1}$; $|E| = 0.15 \text{ cm}^{-1}$ ($E/D = 0.04$); $g = [1.94, 2.08, 2.02]$. The dashed vertical lines represent the frequencies at which spectra shown in Figs. S14 (lower frequency) and 3 (higher frequency) were recorded.

A LFT analysis of the electronic absorption spectra of **5** agreed with Albela *et al.*, but also provided both crystal-field (as defined by Ballhausen) and AOM parameters quantifying the bonding of the pyridinophane ligand. Full details are given in the SI. QCT investigation of several complex cations of general formula $[(\text{Py}_2(\text{NR})_2)\text{MnX}_2]^+$ ($\text{R} = \text{Me}, \text{Cy}$; $\text{X} = \text{F}, \text{Cl}, \text{OH}$) clearly show the spin quintet ground state with the "hole" in d_{xy} in agreement with the earlier,

DFT calculations on **5** (Figure 5).¹⁷ The reported sa-CASSCF(4,5) based calculations lead to D values ranging from -3.8 cm^{-1} to -4.0 cm^{-1} when taking into account the spin-spin coupling (SSC) interaction (using MRCI) and NEVPT2 dynamic electron correlation effects, where the SSC contribution is about 5 times larger (-0.5 cm^{-1}) than dynamic electron correlation effects (-0.1 cm^{-1}) in the case of the optimized geometries, see Tables S5 and S6 (Supporting Information).³⁷ The BLYP DFT method underestimates the D parameter by ca. 1 cm^{-1} , and B3LYP results are even less satisfactory, see Tables S5 and S6 (Supporting Information). Full details of the QCT studies are given in Supporting Information, which also provides frontier B3LYP MO diagrams of complexes of interest (Figure S19). Importantly, the calculations show that $[(\text{Py}_2(\text{NR})_2)\text{Mn}(\text{OH})_2]^+$, which is proposed as an intermediate in water oxidation,²⁸ has the same electronic structure as $[(\text{Py}_2(\text{NR})_2)\text{MnX}_2]^+$ ($X = \text{F}, \text{Cl}$). Thus, the properties of the latter complexes are expected to provide a good model for those of $[(\text{Py}_2(\text{NR})_2)\text{Mn}(\text{OH})_2]^+$, which has so far eluded experimental isolation.

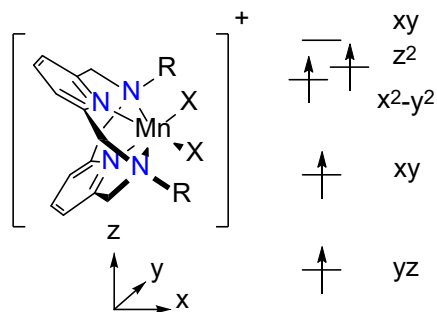


Figure 5. Qualitative d-orbital manifold for $[(\text{Py}_2(\text{NR})_2)\text{MnX}_2]^+$ complexes.

Electrochemical Studies

The electrochemical properties of **1** – **4** were investigated in $\text{NBu}_4\text{PF}_6/\text{MeCN}$, with all potentials referenced to Fc/Fc^+ (Table 3). As illustrated by the cyclic voltammogram of **4** (Figure 6), all complexes show one quasi-reversible reductive and one reversible oxidative process, with

complexes **1** and **4** showing an additional quasi-reversible oxidative process at higher potential. This second oxidative process is irreversible for **2** and **3** (Figures S8 – S10).

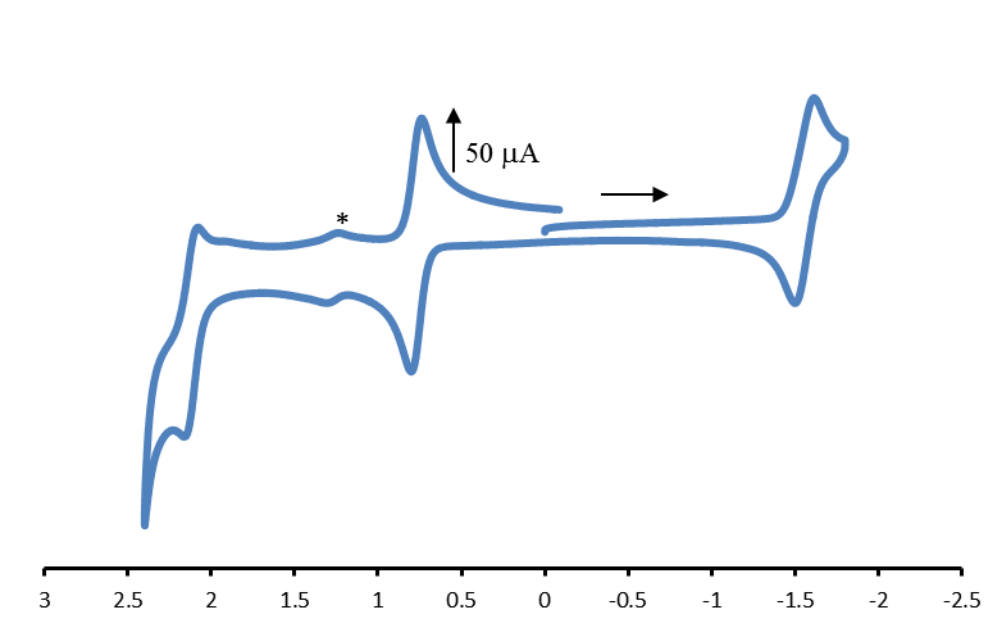


Figure 6. Cyclic voltammogram of **4** recorded at room temperature in MeCN solution. GC electrode, 0.1 M NBu₄PF₆ as electrolyte (scan rate=100 mV/s). * -impurity.

Since the Zn analogue, [(Py₂N^tBu₂)Zn(OTf)(NCMe)]⁺, shows a reduction event at *ca.* -2 V vs Fc/Fc⁺ that has been assigned as a ligand-based reduction,³⁸ we have likewise assigned the quasi-reversible reductive processes to ligand-based reduction. The first oxidative wave is assigned to the Mn^{III}/Mn^{II} couple, which is confirmed through independent synthesis (see below) and the second quasi-reversible oxidation wave is tentatively assigned to the Mn^{IV}/Mn^{III} couple. The electrochemical data clearly shows the superior ability of Py₂N^tBu₂ to stabilize Mn(III) (Table 3). Notably, the Mn^{III}/Mn^{II} and Mn^{IV}/Mn^{III} potentials of these complexes are at a significantly higher potential than for analogous manganese complexes of dimethyl substituted cross-bridged tetraazamacrocyclic ((BCA)MnCl₂ and (BCE)MnCl₂, Figure S12): where $E_{1/2}$ (Mn^{III}/Mn^{II}) is -0.055 V for (BCA)MnCl₂ and -0.174 V for (BCE)MnCl₂; $E_{1/2}$ (Mn^{IV}/Mn^{III}) is +0.703 V for (BCA)MnCl₂ and +0.592 V for (BCE)MnCl₂.³⁹ The difference in potentials is likely due to the

different donor strengths of these macrocycles, all of which create a *cis*-divacant coordination environment.

Table 3. Redox potentials ($E_{1/2}$) for **1** – **4** (vs Fc/Fc⁺).

	Py/Py•	Mn ^{III} /Mn ^{II}	Mn ^{IV} /Mn ^{III}
1	-2.37	0.16	1.24
2	-2.37	0.20	1.38 ^a
3	-2.32	0.21	1.29 ^a
4	-2.28	0.04	1.40

^a Irreversible waves, E_{pa} values are shown.

The reversibility of the first oxidative process observed in the CV of **4** has been confirmed by chemical oxidation. Treating **4** with the thianthrenyl cation (Th•BF₄, $E_{1/2} = 0.86$ V vs Fc/Fc⁺)⁴⁰ results in an immediate color change from pale yellow to dark orange (Scheme 3). The oxidized product is characterized as [(Py₂N^tBu)MnCl₂]BF₄ (**9**) by ESI-MS and single crystal X-ray diffraction, with the structure shown in Figure 7. The UV-vis spectrum of **9** shows a band around 500 nm, similarly to the spectroscopically characterized complex [(Py₂NMe)MnCl₂]⁺ (Figure S7).¹⁷ The magnetic susceptibility of **9**, as measured by Evans' method ($\mu_{eff} = 5.05$ μ_B), is consistent with high spin ($S = 2$) Mn(III).

Scheme 3. Formation of [(Py₂N^tBu₂)Mn^{III}Cl₂]⁺ (**9**) by chemical oxidation of **4**.

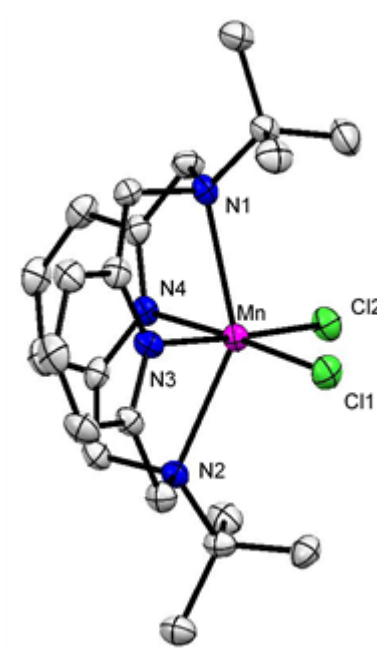
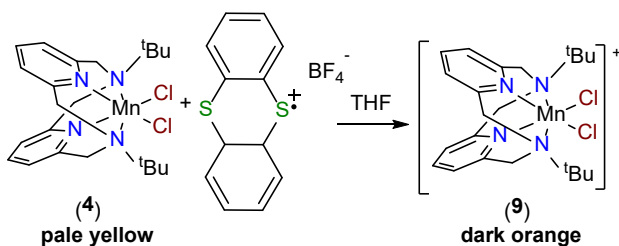


Figure 7. ORTEP diagram of **9** (50% ellipsoids, hydrogen atoms and PF_6^- anions are omitted for clarity). Selected bond lengths (\AA) and angles ($^\circ$): Mn-N1 2.392(3); Mn-N2 2.396(3); Mn-N3 2.028(3); Mn-N4 2.014(4); Mn-Cl1 2.242(1); Mn-Cl2: 2.236(1); N1-Mn-N2 142.8(1); N3-Mn-N4 85.4(1); Cl1-Mn-Cl2 93.94(4).

In order to delineate the effect of the pyridinophane ligand substituents on the stability of higher oxidation states, we analyzed the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ electrochemical data in terms of steric and electronic parameters. While $E_{1/2}$ does not correlate well with the steric parameter of the ligand substituent, as measured by the A value (Figure S13),⁴¹⁻⁴² there is a good linear relationship with the Hammett parameter, σ_p (Figure 8).⁴³⁻⁴⁴ This suggests that the donor strength of the

pyridinophane ligand is the key factor that affecting the stability of the Mn(III) oxidation state, despite the significant effect of substituent sterics on the molecular structures (Tables 1 and 2).

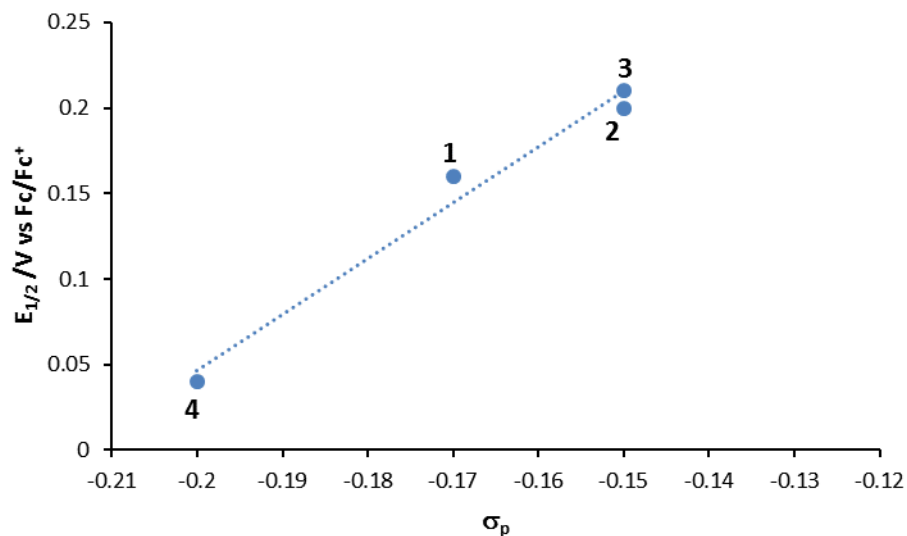


Figure 8. $E_{1/2}(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}})$ for **1 - 4** vs Hammett values (σ_p) of the amine substituents. Plot fits to equation: $y = 3.2687x + 0.7$, $R^2 = 0.9793$.

Catalytic activity in O₂ evolution.

We have previously demonstrated that complex **1** is catalytically active towards H₂O₂ disproportionation whereas (Py₂N^tBu₂)MnCl₂ is not.¹⁰ On the other hand, complex **4** is active in electrocatalytic oxidation of H₂O to O₂ whereas **1** is not.⁹ To better delineate the effect of pyridinophane ligand substitution on these catalytic reactions, we investigated reactivity of **2** and **3** towards both H₂O₂ disproportionation and H₂O oxidation.

The catalytic reactivity towards H₂O₂ disproportionation of complexes **1 - 3** along with (Py₂NH₂)MnCl₂⁹ shows that the rate of O₂ formation has a clear dependence on the pyridinophane substituent (Figure 9): bulkier substituents significantly slow the rate of reaction,

with **4**, which has the bulkiest substituents, being inactive. The linear relationship between $\log(k)$ and the steric parameter (A value)⁴¹ confirms that the ligand bulkiness plays in controlling the rate of catalysis (Figure 8, inset).

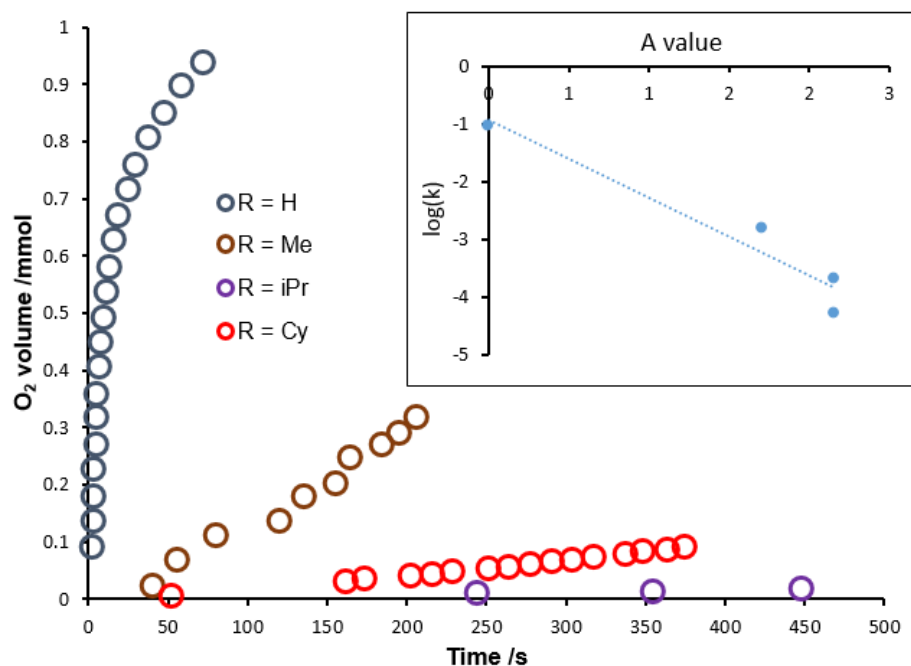


Figure 9. Oxygen formation by H₂O₂ disproportionation catalyzed by Py₂NH₂MnCl₂ and complexes **1** - **3**. Initial conditions: [(Py₂NR₂)MnCl₂] = 0.4 mM, [H₂O₂] = 3.1 M, pH = 7.0, 298 K. Inset: plot of $\log(k)$ vs A value (k : initial rate of O₂ formation). Plot fits to equation: $y = -1.3497x - 0.937$, $R^2 = 0.9335$.

We have used cyclic voltammetry to investigate the ability of complexes **1**⁹ – **4** towards electrocatalytic H₂O oxidation (Figure 10). The cyclic voltammogram of **2** and **3** toward H₂O oxidation exhibits either a large oxidation wave (complex **2**) or enhanced current (complex **3**), suggesting both are active toward H₂O oxidation at similar overpotential to **4**.⁴⁵ Similarly to H₂O₂ disproportionation, the activity of (Py₂NR₂)MnCl₂ toward electrochemical H₂O oxidation also depends on the size of the pyridinophane ligand, however there is no simple relationship

between the substituent size and any electrochemical parameter (e.g., onset potential or peak current).

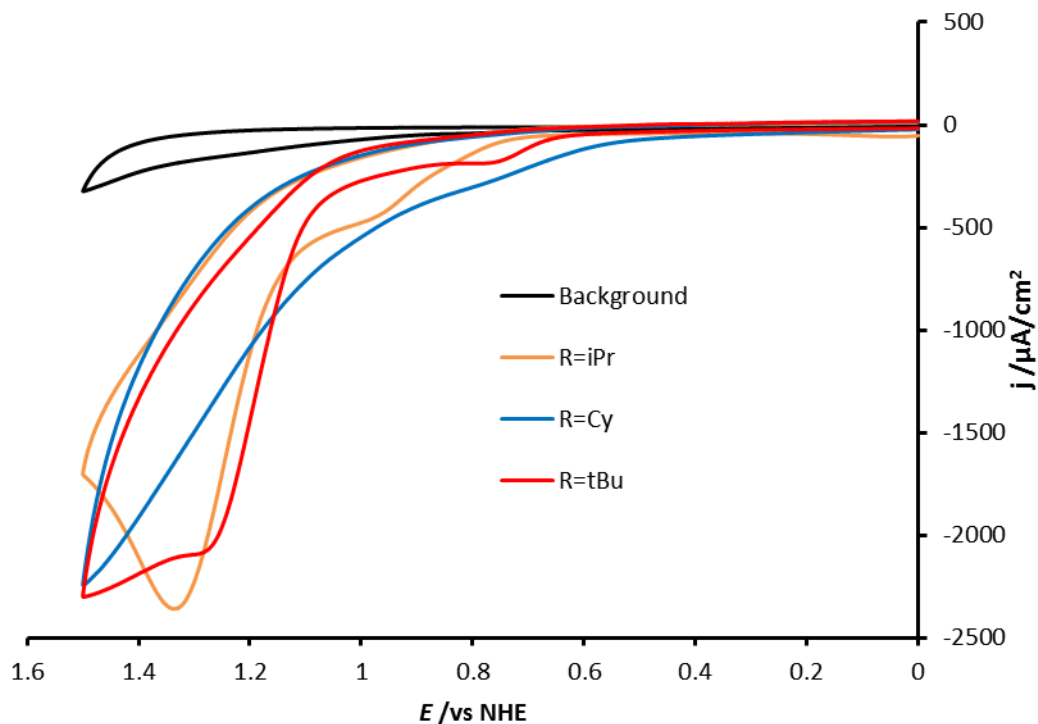


Figure 10. Cyclic voltammogram of solution without $(\text{Py}_2\text{NR}_2)\text{MnCl}_2$ complex (black), and with $\text{Mn}(\text{II})$ complexes at 0.5 mM: $\text{R} = \text{iPr}_2$ (**2**) (orange), $\text{R} = \text{Cy}$ (**3**) (blue), $\text{R} = \text{tBu}$ (**4**) (red), all at $\text{pH} = 12.2$, GC electrode, 50 mM KOTf, scan rate = 100 mV/s.

Previous computational investigations into the mechanism of catalytic H_2O oxidation by **4** implicate the formation of high valent Mn-oxo/oxyl species as precursors to O-O coupling and consequent O_2 generation.²⁸⁻²⁹ Since the overpotential for water oxidation depends on the accessibility of these species, the pyridinophane substituents may be expected to play an important role in the energetics of catalysis. Using the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ couple as an indicator for the accessibility of higher oxidation states, it is notable that there is no relationship between the onset of catalytic activity and $E_{1/2}(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}})$, and consequently the donor strength of the ligand

(c.f. Figure 8). For example, despite complex **4** having the lowest $E_{1/2}(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}})$ (by over 0.1 V), the onset of catalysis is similar to that observed for complexes **2** and **3**. Moreover, although $E_{1/2}(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}})$ for **1** is at a lower potential than for **2** or **3**, this complex shows no evidence for H₂O oxidation catalysis.⁹ Thus, the activity of these complexes for electrocatalytic water oxidation cannot be related to simple electronic effects.

Despite the apparent lack of electronic effect of ligand donor strength on water oxidation catalysis, it is evident that only the complexes with smaller pyridinophane ligand substituents, i.e. (Py₂NH₂)MnCl₂ and **1**, are not catalytically active. However, there is no simple trend that relates catalytic activity to the size of the pyridinophane ligand. Thus, although there appears to be a steric threshold for achieving water oxidation electrocatalysis, the catalytic activity of (Py₂NR₂)MnCl₂ complexes cannot be related to simple steric or electronic factors.

Summary and Conclusions

A series of Mn(II) and Mn(III) complexes bearing pyridinophane ligands with different substituents have been prepared and characterized. While a relationship between the size of the pyridinophane amine substituent and the metrical parameters of the Mn(II) complexes (**1** – **4**) was observed, no such trend was observed for the structures of the Jahn-Teller distorted Mn(III) complexes (**5** – **8**). HFEP spectroscopy of **6** was characteristic for six-coordinate high-spin Mn(III), in terms of having a negative D value of modest magnitude: $D = -3.79 \text{ cm}^{-1}$, with slight rhombicity $|E/D| = 0.04$. Computational investigation at an *ab initio* level of theory are fully consistent with experiment, providing calculated D values in the range from -3.8 to -4.0 cm^{-1} . The cyclic voltammograms of the Mn(II) complexes reveal reversible Mn^{III}/Mn^{II} redox couples, which has been synthetically confirmed through the synthesis and characterization of

$[(\text{Py}_2\text{N}^t\text{Bu}_2)\text{MnCl}_2]\text{BF}_4$ (**9**). The stability of the Mn(III) state was found to be directly related to the donor strength of pyridinophane ligand substituents.

The donor strength of the ligand is critical for accessing higher Mn oxidation states, and thus suggests that the pyridinophane ligand platform is in general terms well suited for $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ activation catalysis. What is also apparent, however, is that rather than further tuning the donor properties of this platform, the size of the ligand is also critical, as seen in comparing the catalytic activity of **1** – **4**. In the case of H_2O_2 disproportionation, the rate of reaction decreases as the size of the R group increases, while electrocatalytic water oxidation was observed for complexes only having bulky ligand substituents. The relative insensitivity to electronic effects bodes well for similarly converting other H_2O_2 disproportionation catalysts to water oxidation catalysts through increase in ligand bulk, similar to the tuning achieved of the organic substituents in widely used ligands such as phosphines, pyrazolyl borates, and N-heterocyclic carbenes.

Experimental

General Considerations

All anaerobic manipulations, including non-aqueous electrochemical measurements, were performed under nitrogen atmosphere by using standard Schlenk techniques or in an M. Braun Labmaster glovebox. Glassware was dried at 150 °C overnight. Organic solvents were purified by the Glass Contour solvent system. Deionized water was used for all aqueous experiments or measurements. ¹H NMR data were recorded on a Varian Unity 400 spectrometer (400 MHz) at 22 °C. UV-visible spectra were recorded with an Agilent Cary 60 UV-visible spectrometer. High resolution mass spectra were recorded using positive electrospray ionization on a Thermo Electron Corp MAT-95XP spectrometer. Trifluoroacetic acid (CF₃COOH) was used as protonation agent for neutral complexes. Solution magnetic susceptibilities were determined by Evans' method.⁴⁶ Electrochemical measurements were recorded on a CHI 600D electrochemical analyzer (CH Instruments). Working electrode: glassy carbon (GC) electrode (3×3 mm², CH Instruments). Auxiliary electrode: platinum wire (Alfa Aesar, 99.99%). Pseudo-reference electrode: Ag wire (Alfa Aesar, 99.99%). The final redox potentials were calculated by comparing the measured potentials with $E_{1/2}$ of Fc/Fc⁺ in the same solution. The reproducibility of all cyclic voltammetry experiments are verified by several repeat scans.

Synthesis of compounds

The compounds of 2,6-bis(bromomethyl)pyridine,⁴⁷ *N, N'*-di-methyl-2,11-diaza[3,3](2,6)-pyridinophane (Py₂NMe₂), 2,11-diaza[3,3](2,6)-pyridinophane (Py₂NH₂),⁴⁸ **1** and **5**,¹⁷ *N, N'*-di-isopropyl-2,11-diaza[3,3](2,6)-pyridinophane (Py₂NⁱPr₂)³⁸, **1'**,¹⁰ **4'**,⁹ and thianthrenyl cation (Th^{•+}BF₄⁻)⁴⁹ were prepared according to literature procedures. All other compounds were obtained from commercial suppliers and used as received.

Preparation of Py₂N^tBu₂ ligand. The synthesis of *N, N'*-di-*tert*-butyl-2, 11-diaza[3,3](2,6)-pyridinophane (Py₂N^tBu₂) was adapted from reported literature procedures.⁵⁰ *tert*-Butylamine (7.61 mL, 71 mmol, 9 eq) was added to a solution of 2, 6-dibromomethyl pyridine (2.1 g, 7.92 mmol) in benzene (200 mL) and water (500 mL) at ambient temperature. The resulting solution of mixture was heated at 80 °C overnight then cooled to room temperature. After spontaneous separation, the organic phase was washed with water (2 × 100 mL) and dried over sodium sulfate. The solvent were then removed by vacuum evaporation to yield a sticky solid. After washing with hexane, the solid was chromatographed (column, SiO₂) by eluting with dichloromethane containing increasing concentrations of triethylamine (0-5%) to yield Py₂N^tBu₂ as a white solid (150 mg, 11 %). The spectral properties are identical to those reported in the literature.⁵⁰ ¹H NMR (CDCl₃, 400 MHz): δ 1.37 (18H, s, CH₃); 3.97 (8H, s, PyCH₂); 6.68-6.76 (4H, d, 3, 5-Py H) and 6.91-7.27 (2H, m, 4-Py H).

Preparation of Py₂NCy₂ ligand. Py₂NCy₂ is prepared according to a modified procedure modified from the literature.¹⁶ A 125 mL RB flask was charged with Py₂NH₂ (0.048 g, 0.50 mmol), cyclohexylbromide (3 mL, 50 mmol, 100 eq), anhydrous K₂CO₃ (1.38 g, 10 mmol, 20 eq) and dry MeCN (50 mL). The reaction was heated at reflux under a nitrogen atmosphere for 7 days. The solution was then cooled to RT and the solvent was removed under reduced pressure. The residue was suspended in CH₂Cl₂ (50 mL) and then washed with 1 M NaOH (2 × 50 mL) solution and water (2 × 50 mL). The CH₂Cl₂ layer was isolated, dried over anhydrous MgSO₄, evaporated, and further dried under vacuum to give an off-white powder (0.56 g, 69%). The spectra properties are identical to those reported in the literature.¹⁶

Preparation of (Py₂NR₂)MnCl₂ complexes. Complexes **2**, **3**, **4** were prepared by adding MnCl₂ to a stirred solution of Py₂NR₂ ligand in MeCN. After stirring overnight at room

temperature, (Py₂NR₂)MnCl₂ was obtained as pale yellow solid after removing the solvent under vacuum. Crystals suitable for single crystal X-ray diffraction were directly obtained by slow diffusion of diethyl ether into MeCN solutions of the complexes. Yields for **2**: 70 %, **3**: 66 %, **4**: 58 %. The complexes were characterized in MeCN solution by HRMS (ESI): calcd for (Py₂NR₂)MnCl₂ complexes: **2**: (C₂₀H₂₈ClMnN₄) m/z: 414.1383 ([M-Cl]⁺); found: 414.1366; **3**: (C₂₆H₃₆MnN₄CF₃COO) m/z: 572.2171 ([M-CF₃COO]⁺); found: 572.2167; **4**: C₂₂H₃₂MnN₄CF₃COO m/z: 520.1858 ([M-CF₃COO]⁺); found: 520.1860.

Preparation of 2'. Complex **2'** was synthesized by treating **2** (23 mg, 0.05 mmol) with TIPF₆ (35 mg, 0.1 mmol) in acetonitrile (10 mL). After stirring at room temperature overnight, the reaction mixture was filtered and the solvent was removed under reduced pressure to yield an off-white powder (44 mg, 60%).

Preparation of 6, 7, 8: Under anaerobic conditions, **2'**, **3'**, **4'** (0.045 mmol, 1 eq) were mixed with XeF₂ (0.048 mmol, 1.05 eq) in acetonitrile (10 mL). The mixtures were stirred overnight to yield red-brown solutions which were concentrated under reduced pressure to *ca.* 5 mL. Red-orange crystals of **6**, **8** suitable for single crystal X-ray diffraction were obtained by slow diffusion of diethyl ether into these solutions. Yields for **6**: 40%, **7**: 30%, **8**: 45%. Complexes were characterized in MeCN solution by HRMS (ESI): calcd for [(Py₂NR₂)MnF₂]⁺ complexes: **6**: (C₂₀H₂₈MnN₄F₂) m/z: 417.1663 ([M]⁺); found: 417.1665; **7**: (C₂₆H₃₆MnN₄F₂) m/z: 497.2289 ([M]⁺); found: 497.2282; **8**: C₂₂H₃₂MnN₄F₂ m/z: 445.1975 ([M]⁺); found: 445.1979. UV-vis (CH₃CN): λ_{max} (ε/L.mol⁻¹.cm⁻¹) = 468 (92), 489 (89) nm for **2**; 468 (133), 494 (130) nm for **3**; 465 (134), 501 (189) nm for **4**.

Synthesis of 6 from MnF₃. The Py₂NⁱPr₂ ligand (20 mg, 0.05 mmol) was added to a slurry of MnF₃ (5.6 mg, 0.05 mmol) in MeOH (15 mL). The mixture was then warmed at 50 °C until the

yellow-cloudy solution became clear brown (ca. 4 h). Aqueous NaPF₆ (5 mL, 16.8 mg, 0.1 mmol) was then added to the solution, which was dried under reduced pressure to give a brown residue. The product was extracted into 10 mL dichloromethane and the solvent was removed under reduced pressure to give **6** as a brown powder (10 mg, 30%). An orange crystal for single crystal X-ray diffraction was obtained through slow diffusion of pentane into a concentrated dichloromethane solution at ambient temperature. The spectra properties are identical to the characterizations of **6** prepared through XeF₂ fluorination described above.

Preparation of 9. Under anaerobic conditions, Th^{•+}BF₄⁻ (19 mg, 0.06 mmol) was added to a solution of (Py₂N^tBu₂)MnCl₂ (25 mg, 0.05 mmol) in THF (15 mL). The reaction was further stirred at room temperature overnight until the yellow slurry change to red, filtered through Celite and washed with THF (5 mL) to afford a dark orange solid. Dark orange crystals of **9** suitable for single crystal X-ray diffraction were obtained by slow diffusion of diethyl ether into its acetonitrile solution. Yield: 11 mg, 40 %. Complexes **9** was characterized in MeCN solution by HRMS (ESI): calcd for C₂₂H₃₂Cl₂MnN₄ m/z: 477.1385 ([M]⁺); found: 477.1381. UV-vis (CH₃CN): λ_{max} (ε/L.mol⁻¹.cm⁻¹) = 494 (255), 518 (335) nm.

HFEPR spectroscopy. HFEPR measurements were made using a spectrometer described elsewhere.⁵¹ The samples were investigated both as loose microcrystalline powders and compressed into pellets. HFEPR spectra were simulated with the program SPIN, from A. Ozarowski,⁵² using a standard spin Hamiltonian for $S = 2$,⁵³ with only second order ZFS terms.

Ligand-Field Theory. The programs Ligfield, from J. Bendix,⁵⁴ and DDN and DDNFIT,⁵⁵ from J. Telsler, were used for LFT analysis of the Mn(III) complexes as described in Supporting Information.

Quantum Chemical Theory. Gaussian09⁵⁶ software was used for B3LYP⁵⁷⁻⁶⁰/6-311G*⁶¹⁻⁶³ geometry optimizations of Mn(III) complexes and production of particular MOs shown in Supporting Information. The ORCA program package by F. Neese and co-workers (version 3.0.0)⁶⁴⁻⁶⁵ was used for calculation of spin Hamiltonian parameters, specifically employing CASSCF,^{18, 20-23} NEVPT2,²⁴⁻²⁶ and MRCI^{18, 20, 27} methods. Further details are given in Supporting Information.

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