Evidence for catalytic water oxidation by a dimanganese tetrakis-Schiff base macrocycle

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A dimanganese tetrakis-Schiff base complex \([\text{Mn}^{II}_2\text{L}]^{2+}\), where \(\text{L}\) provides a \(\text{N}_x\text{O}_y\) coordination environment, has been synthesized and characterized via electrochemical and spectroscopic studies. Cyclic voltamograms (CV) of \([\text{Mn}^{II}_2\text{L}]^{2+}\) in propylene carbonate, to which water has been added as a limiting reagent, show an increase in current starting at +1.3 V versus \(\text{Fc}^{+}/\text{Fc}\). The current shows a first order dependence on \(\text{H}_2\text{O}\) and \([\text{Mn}^{II}_2\text{L}]^{2+}\), indicative of electrocatalytic water oxidation. Controlled potential electrolysis produced \(\text{O}_2\) in 39–45% Faradaic efficiency. Blocking the axial coordination site to the manganese centers by a \(\mu\)-carboxylato axial ligand in an analogous Schiff base complex \([\text{Mn}^{II}_2\text{L}\text{Ac}]^{2-}\) lowers the catalytic activity, suggesting the importance of an open coordination site to the central manganese atoms for water oxidation. Photosensitization of \([\text{Mn}^{II}_2\text{L}]^{2+}\) with \([\text{Ru}^\text{II}(\text{bpy})_3]^3+\) and \(\text{K}_2\text{S}_2\text{O}_8\) in acetonitrile–water mixtures produced \(\text{O}_2\) as measured by a Clark electrode, with the rate of \(\text{O}_2\) evolution proportional to \([\text{Mn}^{II}_2\text{L}]^{2+}\).

1. Introduction

The development of an artificial photosynthetic device to convert and store solar energy as chemical fuels is a promising source of renewable energy [1]. The development of molecular components (organic and inorganic) for artificial photosynthetic devices offers the ability to control the photo- and electrochemical properties of the building blocks through synthetic modification, but stability, efficiency, and device integration remain primary concerns [2–4]. These are especially true for the oxidative catalysts where the potential required to drive water oxidation leads to high energy intermediates that are often capable of ligand degradation. Nevertheless, numerous transition metal coordination complexes have been developed as homogeneous catalytic water oxidation catalysts. Of these, the complexes based on ruthenium and iridium have been the most successful.

In an effort to utilize an earth abundant transition metal source, many manganese oxo complexes have been synthesized to mimic the structure of the Oxygen Evolving Complex (OEC), a \(\text{Mn}_4\text{O}_5\text{Ca}\) cluster, found in Photosystem II of green plants and cyanobacteria [5,6]. While these complexes have been valuable in understanding the spectroscopic properties of the OEC, very few have shown homogenous water oxidation activity. The majority of these Mn-based systems rely on chemical oxidants that are capable of oxygen–atom transfer reactions to drive water oxidation [7–12]. Considerably fewer examples exist that display water oxidation activity using single electron, outer-sphere chemical oxidants such as photochemically generated \([\text{Ru}^\text{II}(\text{bpy})_3]^3+\) [13], or that can be driven electrochemically [14–16]. This potentially limits their incorporation into an artificial photosynthetic device.

We have recently become interested in dinuclear tetrakis-Schiff base macrocycles as potential mimics for the OEC due to their synthetic tunability and potential to coordinate two low-valent, redox-active transition metals in relatively close proximity. In 1970, Robson showed that a wide range of these complexes could be self-assembled from 2,6-diformyl-4-methylphenol and diaminoalkanes using various first row transition metal dications, including \(\text{Mn}^\text{II}\) [17]. These macrocycles provided a planar \(\text{N}_2\text{O}_2\) coordination environment for two metal centers located approximately 3.2 Å apart. Following this general procedure, Nagata and co-workers synthesized a series of carboxylate-bridged dimanganese tetrakis-Schiff base macrocycles with a \(2,2\)-diamino-N-methylidylylamine backbone which generate a \(\text{N}_2\text{O}_2\) coordination environment for the two \(\text{Mn}^\text{II}\) centers [18–21]. These di-manganese complexes have shown promising catalase activity towards \(\text{H}_2\text{O}_2\) disproportionation [18,19], but to the best of our knowledge, no subsequent studies were reported on water oxidation activity. Given the reported catalase activity of these complexes and lack of subsequent catalytic studies, we were intrigued by their ability to act as water oxidation catalysts. We have previously reported the structural, electrochemical, and spectroscopic investigation of...
[MnII(LAc)]+ and its higher oxidation states in anhydrous organic solvents [22]. Herein we report evidence for electrocatalytic water oxidation by a related dimanganese tetrakis-Schiff base complex, [MnII(L)]2+, in a nonaqueous solvent with water added as a limiting reagent at neutral pH. Water oxidation was also observed in aqueous solution via photochemical generation of [Ru(bpy)3]3+ with persulfate as an electron acceptor.

2. Experimental

2.1. General methods

MALDI-TOF MS were obtained on a Bruker Ultraflex III. Elemental analysis were obtained from Atlantic Microlabs, Inc., Norcross, GA. Electronic absorption spectra were taken on a Perkin-Elmer Lambda 950 or Agilent 8453A spectrophotometer at 1°C with a 1.0 cm quartz cell under a nitrogen atmosphere. Infrared absorption spectra were acquired using a Biorad Excalibur FTS-3000MX equipped with a liquid N2 cooled MCT detector. Manipulations of air-sensitive samples of [MnII(L)]2+ were performed in a nitrogen-filled MBraun MB-150-M glovebox.

2.2. Materials

4-tert-butyl-2,6-diformylphenol was purchased from Sigma-Aldrich and was purified by column chromatography on silica gel with methylene chloride. All other chemicals and solvents used were of the highest purity available from Aldrich and Fluka. Anhydrous acetonitrile (ACN) and dichloromethane (DCM) were purified by circulating the nitrogen-purged solvent through a solid-state column purification system (Vacuum Atmospheres Company, Hawthorne, CA) prior to use [23]. Propylene carbonate (PC) was obtained from Sigma–Aldrich and dried over molecular sieves. Tetrahydrofuran (THF) was purchased from Acros and recrystallized twice from hot ethyl acetate before use in electrochemical experiments. [MnII(LAc)](ClO4)2 was synthesized as reported elsewhere [22].

2.3. Synthesis of [MnII(L)](ClO4)2

[MnII(L)]2+ was synthesized following a method to [MnIII(LAc)]+ as shown in Scheme S1 [22]. Mn(ClO4)2·6H2O (200 mg, 0.55 mmol), 4-tert-butyl-2,6-diformylphenol (100 mg, 0.48 mmol) were dissolved in 10 mL methanol and purged with nitrogen. To this solution was added N-methyl-2,2’-diaminodiethyldiamine (62 µL, 0.48 mmol) dissolved in 1 mL of methanol drop-wise while stirring. The mixture was refluxed for 2 h under nitrogen, then cooled and the volume of the solvent reduced under reduced pressure to about ¼ initial volume which yielded yellow-green powder product. The solid was filtered and washed with cold methanol followed by anhydrous diethyl ether. Recrystallization from DCM and ether gave [MnII(L)](ClO4)2 (mass 152 mg, 63% yield). (Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and handled behind suitable protective shield.) Anal. Calc. for MnII(C29H36N6O2)(ClO4)2·(H2O): C, 44.50; H, 5.71; Cl, 7.73; N, 9.16; O, 20.92; Mn, 11.97; Found: C, 44.25; H, 5.84; N, 9.39%. MALDI LR-MS: Calcd for [MnII(L)(ClO4)]+ 781.20, found 781.06 m/z.

2.4. Magnetic susceptibility

The magnetic susceptibility of a solid powder sample of [MnIII(L)]2+ and [MnIII(MnIII)L]3+ were measured on a Johnson Matthey (Mark1) magnetic susceptibility meter at room temperature (298 K) and corrected for diamagnetic contributions using Pascal’s constants.

2.5. Electrochemistry

All cyclic voltammetric experiments were performed and analyzed using a CHI440A (CH Instruments, Austin, TX) potentiostat. Electrolyte solutions (0.1 M TBAPF6) were prepared with anhydrous solvents and deoxygenated with nitrogen prior to use. A Pt wire was used as the counter electrode and a glassy carbon macro disk electrode was used as the working electrode. A silver wire was used as a pseudo-reference electrode with ferrocene (purified by sublimation) added as an internal reference at the end of each experiment. All experiments were run under a nitrogen atmosphere. Differential pulse voltammograms (DPV) scans utilized a 4 mV step potential, 50 mV amplitude, 100 ms pulse width, and pulse period 300 ms.

Rotating Ring-Disc Electrode (RRDE) studies were performed with a Pine Instruments WaveDriver 20 potentiostat and rotator. The disc electrode was a polished glassy carbon (Pine model AF6D050P040GC) and ring electrode was platinum (Pine model AFE6R1PT). The counter electrode was a platinum wire coil isolated in a glass tube with fine frit (Pine model AFCTR5). A silver wire was used as a pseudo-reference electrode with ferrocene (purified by sublimation) added as an internal reference at the end of each experiment. Electrolyte solutions (0.1 M TBAPF6) were prepared with anhydrous propylene carbonate and deoxygenated with nitrogen prior to use. The empirical collection efficiency with this electrode geometry was calculated to be 25.2% for a 10 mM K3[Fe(CN)6] aqueous solution with 1 M KNO3 and 20.8% for 3 mM [MnII(LAc)](ClO4)2 in PC with 0.1 M TBAPF6 at 300 rpm.

Controlled potential electrolysis (CPE) was carried out in a 150 ml 2-neck round bottom flask, using a Ag wire reference electrode, Pt foil counter electrode, and a 4 cm × 2 cm carbon paper (Fuel Cell Earth, part # MGL280) as the working electrode. Electrolyte solutions were 0.1 M TBAPF6 in PC. The flask and electrolyte were purged with He for ca. 30 min before conducting the CPE. The headspace was sampled with a gas-tight syringe and analyzed with a Gow-Mac Series 350 gas chromatograph equipped with a molecular sieve 13X column for separation of N2 and O2, a Porapak Q 80/100 column for separation of CO2, a thermal conductivity detector, and He as the carrier gas. The background N2 and O2 peaks were due to the transfer of the sample via the syringe and were consistent among repeated background scans.
2.6. Photosensitized catalysis

The oxygen evolution was recorded with a Clark-type oxygen electrode (Hansatech Instruments, Oxygraph OXYG1 and DW1/AD unit). Before each experiment a fresh Teflon membrane was installed over the probe tip and the probe was calibrated in oxygen-free (N₂ purge) and oxygen saturated (O₂ purge) water. A 100 µl degassed 35% acetonitrile and 65% water solution of varying concentrations of [Mn₂L²⁺] was injected using a syringe through a septum into pH 7 phosphate buffered 35% acetonitrile and 65% water solution, containing 0.66 mM [Ru(bpy)₃Cl₂]PF₆ and 22 mM K₂S₂O₇. The setup was then purged with N₂ to obtain a steady O₂ free baseline. A strip of 7 modules of 4 blue LEDs (λ = 470 ± 10 nm) each was wrapped around the water jacketed reaction setup containing the reaction vessel and adjusted to 20 °C. The generated O₂ was measured and recorded versus time by a Clark type electrode under illumination by the LEDs. LEDs were obtained from OPEK Technology, part number OVM18FB487.

3. Results and discussion

3.1. Synthesis and characterization of [Mn₂L]²⁺ and [Mn₃LAc]⁺

The syntheses of [Mn₂L]²⁺ and [Mn₃LAc]⁺, where L is the tetra-kis-Schiff base ligand, were based on a Mn(II) templated [2+2] macrocyclic condensation reaction between 4-tert-butyl-2,6-diformylphenol and N-methyl-2,2’-diaminodihydroxymethane following Robson’s method (Scheme S1) [17,21,24]. Completion of the [2+2] condensation was verified by MALDI–MS (Fig. S1), infrared spectroscopy (IR), and elemental analysis. FTIR spectra (Fig. S2) show bands for the C=O stretches in the range of 1660–1630 cm⁻¹, phenyl breathing modes at 1537 cm⁻¹, and phenolic C–O stretch at 1360 cm⁻¹ [25]. Additionally, the lack of peaks at 1577 and 1440 cm⁻¹ confirms the absence of a coordinating acetate ligand.

Whereas [Mn₃LAc]⁺ could be easily isolated, we observed oxidation of [Mn₂L]²⁺ to [Mn₃L]³⁺ if the reaction solution was exposed to air prior to work up. This phenomenon is supported by UV–Vis spectroscopy (Fig. S5) that shows the same absorption spectra as that of [Mn₃L]³⁺ oxidized with NOPF₆. Molar magnetic susceptibility (χ_M) values of 5.94 and 6.60 µB were measured for [Mn₂L]²⁺ and [Mn₃LAc]⁺ respectively at room temperature. The values are intermediate between that expected for the ferromagnetic high-spin and low-spin states suggesting weak antiferromagnetic coupling between the manganese centers. Similar magnetic interactions were predicted by density functional theory calculations of [Mn₃LAc]²⁺ and [Mn₃L]³⁺, and measured for analogous dimanganese tetrakis-Schiff base macrocycles [20,22,26].

Unfortunately, we were unable to obtain single crystals of [Mn₂L]³⁺ (n = 2, 3) suitable for X-ray crystallographic analysis. We have previously reported the structure of [Mn₃LAc]⁺ where the Mn₃O₂ type macrocycle provides a pentadentate chelating environment for each of the two Mn centers held 3.26 Å apart from each other and bridged by an acetate ligand [22]. All other known dimanganese tetrakis-Schiff base complexes with Mn₃O₂ coordination environments have comparable twisted butterfly-like ligand structures, but show a range of metal–metal distances (3.09 Å for a μ₂-Cl) [18], 3.23–3.28 Å for carboxylate bridged [19,21,22,27], and 3.32–3.59 Å for a non-bridging ligand [20,26,28]). We surmise that the lack of a bridging ligand in [Mn₂L]³⁺ (n = 2, 3) would afford two adjacent coordination sites for potential water binding.

3.2. Electrochemistry of [Mn₂L]²⁺ and [Mn₃LAc]⁺

We have previously reported the electrochemistry of [Mn₃LAc]⁺ in anhydrous acetonitrile (ACN) which revealed two chemically reversible oxidation waves for [Mn₃LAc]⁺ to [Mn₃Mn₃LAc]²⁺ to [Mn₃L₃]³⁺, followed by irreversible oxidations of the phenolate moieties (Fig. 1a). We concluded that the bridging acetate ligand limits the valence state of each Mn³⁺ by not providing higher charge compensation, thus leading to phenolate oxidations [22]. Fig. 1 shows cyclic voltammograms (CV) and differential pulse voltammograms (DPV) of [Mn₂L]²⁺ in ACN with 0.25% H₂O (v/v) at a glassy carbon working electrode. Two quasi-reversible waves are observed for the metal-centered oxidations of [Mn₂L]²⁺ to [Mn₇-Mn₃L]⁺ to [Mn₃L]³⁺ at +0.3 and 0.4 V versus FeCl₃. An additional anodic wave is observed at +0.8 V prior to phenolate oxidations that can be tentatively assigned as [Mn₃Mn₅L]⁴⁺. (We have labeled the valence states of Mn in [Mn₃L]³⁺ for oxidation states where spectroscopic and electrochemical comparison to [Mn₃LAc]⁺ show a clear correlation.)

CVs of [Mn₂L]²⁺ taken in anhydrous ACN, propylene carbonate (PC), and dichloromethane (DCM) are similar to those in Fig. 1, but the first two oxidation appear closer together (Figs. S3 and S4). The peak current for these redox processes showed a linear dependence on n⁰/² indicating a diffusion controlled species (Fig. S4) [29]. An additional oxidation in ACN at potentials >+1.4 V may be attributed to phenolate oxidation similar to [Mn₃LAc]⁺.

The redox transitions observed in CV measurements of [Mn₂L]²⁺ were correlated to UV–Vis and IR spectroscopic changes through spectrophotometric titrations. Oxidation of [Mn₂L]²⁺ with NOPF₆, in anhydrous ACN at 0 °C revealed four distinct redox transitions corresponding to the single electron oxidations of [Mn₂L]²⁺ to [Mn₃LAc]⁺ (Fig. S5). The spectral changes followed the electrochemical results and were closely related to those previously observed for [Mn₃LAc]⁺, allowing for the straightforward characterization of the intermediate oxidation states [22]. The ligand

![Fig. 1. (a) CVs of [Mn₃LAc]⁺ at a scan rate v = 100 mV/s in ACN (data adapted from previous study [22]). (b) CVs (scan rate v = 100 mV/s) and (d) DPV scans of [Mn₃LAc]⁺ in ACN with 0.25% H₂O added. All electrochemical scans were performed at 298 K with 0.1 TBPF₆ supporting electrolyte at a glassy carbon (GC) working electrode. Arrows indicate initial direction of scan.](image-url)
centered π−π* transition showed a red-shift for the [Mn^II]²⁺ to [Mn^III]⁰ oxidation. This is consistent with the involvement of the π orbitals from the azomethine groups for this transition and the increasing positive charge of the metal center [30]. Further oxidation to [Mn^IV]⁰ and [Mn^VI]⁰ shows additional red-shift of the lowest energy π−π* transition and a new peak in the UV, consistent with phenolate oxidation, as observed for [Mn^II]²⁺. FTIR spectra of intermediate oxidation states showed no additional vibrational bands for Mn−NO type complexes (Fig. S6) [31,32]. The redox changes of the Mn centers influence the C–O stretching frequencies of the tetrakis-Schiff base macrocycles. The first three oxidations of [Mn^II]²⁺ are accompanied by a shift of the C=N stretch at 1631 to 1660 cm⁻¹, consistent with the stronger binding environment and decrease in d-orbital backbonding of the Mn^II III ions. Oxidation to [Mn^IV]⁰ and [Mn^VI]⁰ shows a sharp increase in intensity of the phenolic C–O stretch at ν = 1305 cm⁻¹ consistent with phenolate to phenoxyl oxidation of the ligand.

The electrochemistry of [Mn^II]²⁺ was further analyzed over a pH range of 4–11 in a H₂O − trifluoroethanol (TFE) mixture to characterize the PCET steps. A selection of anodic DPV scans at various pHs is shown in Fig. S7 and the resulting plot of Eox vs pH is shown in Fig. 2. The first anodic wave shows a 65 mV/pH dependence over the range of 6–10 pH (green triangles). The slope of this trend is close to 59 mV/pH and is consistent with a 1 e−/1 H+ proton-coupled electron transfer (PCET) process. Assuming the starting complex is [Mn^II(H₂O)²⁺]²⁺ (region I), this oxidation would lead to [Mn^III]⁰(H₂O)[OH]²⁺ (region II). The second oxidation shows a 50 mV/pH dependence over the same range (6–11) and is also consistent with a 1 e−/1 H+ PCET process (navy blue squares) likely leading to the formation of [Mn^IV]⁰(OH)²⁺. A third oxidation shows no dependence on pH over the range of 6–9 (pink squares) which would suggest an oxidation to [Mn^V]⁰[OH][OH]²⁺ (region IV). A fourth oxidation shows a 65 mV/pH dependence over the range of 5–9 pH, suggesting a 1 e−/1 H+ PCET process (cyan diamond), generating [Mn^VI]⁰(O)[OH][OH]²⁺ (region VI). The final oxidation is consistent with an electrocatalytic process and shows a 49 mV/pH dependence from 4 to 9 (green diamonds), and remains constant to 11 (red triangles).

To examine the ability of [Mn^II]²⁺ to catalyze water oxidation, we investigated its electrochemical response in PC with the addition of H₂O (Fig. 3). PC is stable over a wide potential window, coordinates weakly when competing with water, and has considerable miscibility with water, which makes it a suitable solvent for electrocatalytic studies [33]. We observed all the previously described redox processes in the absence of water with an additional strong catalytic wave starting at +1.3 V upon addition of 1% H₂O. The onset of this electrocatalytic wave was preceded by two oxidations at approximately +1.1 and +1.3 V observed in DPV scans (Fig. S8) prior to phenolate oxidation. Assuming these oxidations to be metal centered, one electron processes, they can be attributed to Mn^II[OH]³⁻ and Mn^IV[OH]⁵⁻ enabled by H₂O coordination-deprotonation. The CVs of [Mn^II]²⁺ with subsequent addition of up to 7.5% H₂O by volume as substrate (Fig. 3) show an increase in catalytic current (i_cat). The background subtracted i_cat for water oxidation at 1.6 V varies linearly with [H₂O]³⁻ and linearly with concentration of [Mn^II]²⁺ (Fig. S9). In addition, the scan rate normalized catalytic current (i_cat/v^½) at +1.6 V decreases as scan rate increases (Fig. S10) suggesting a rate-limiting chemical step prior to electron transfer to the electrode [33,34]. In order to characterize the product of electrocatalysis, controlled potential electrolysis (CPE) of 1 mM [Mn^II]²⁺ was carried out at +1.6 V in presence of 6% H₂O in PC with stirring in a sealed flask sparged with He using carbon paper as the working electrode (Fig. 4). The head space above the electrolyte solution was examined by gas chromatography (GC) at various time points throughout the CPE and O2 was detected in 39 – 45% Faradaic efficiency. In addition to O2, we also examined the headspace for CO₂ and found no detectable amount as a result of CPE with the catalyst as compared to background scans.

Fig. 3. CVs at a GC electrode of 0.1 M TRAPF₆ in PC with addition of water as indicated by the percentages in the figure. (a) Background CVs without catalyst. (b) CVs of 1 mM [Mn^II]²⁺. All cyclic voltammetry is performed at 298 K, v = 100 mV/s. Arrows indicate initial direction of scan.
Encouraged by the fact that NOPF₆⁻ was able to act as an outer-sphere oxidant towards [MnII][L]²⁺ and [MnII][LAc]²⁺, we investigated [Ru(bpy)₃]³⁺ as a potential oxidant. Starting with [Mn̄⁸⁺MnI⁴⁺L]³⁺, spectrophotometric titrations were performed using [Ru(bpy)₃]³⁺ generated via charge-transfer quenching of the [Ru(bpy)₃]²⁺ excited state with K₂S₂O₈ in a mixture of H₂O and acetonitrile [36–40]. UV–Vis absorbance spectra taken of [Mn⁸⁺MnI⁴⁺L]³⁺ with addition of stoichiometric equivalents [Ru(bpy)₃]³⁺ yielded three sequential oxidations and were accompanied by a red-shift in the lowest energy π→π⁺ transition absorbance maxima (Fig. S14). These transitions were nearly identical to those observed with NOPF₆⁻, but also include the overlapping absorption spectra of [Ru(bpy)₃]²⁺. To examine the ability of [Ru(bpy)₃]³⁺ to drive water oxidation with [MnII][L]²⁺, we performed a photosensitization experiment. [MnII][L]²⁺ was injected into a 35% acetonitrile and 65% H₂O solution of 0.66 mM [Ru(bpy)₃]²⁺ and 22 mM K₂S₂O₈ in a pH 7 phosphate buffer solution. The solution was degassed thoroughly until the dissolved O₂ concentration, measured with a Clark electrode, had stabilized. The solution was then irradiated by an assembly of blue LEDs (λ = 470 ± 10 nm) [36] and the consequent O₂ evolution was monitored. O₂ evolution was observed after an initial delay time of ~2 min of irradiation (Fig. 5a). The induction period is due in

![Image](54x536 to 282x726)

3.3. Photochemical water oxidation with [MnII][L]²⁺

To test the possibility of catalytic current arising from heterogeneous species deposited on the electrode surface during the CVs, several control experiments were performed. First, the GC electrode was scanned with [MnII][L]²⁺ in the presence of 5% H₂O to generate the catalytic wave, then removed and the uncleaned electrode immediately placed in fresh electrolyte containing 5% H₂O. The resulting CVs of the uncleaned electrode show current levels similar to background signals without catalyst (Fig. S11). Second, we explored the electrochemical response of Mn(ClO₄)₂ as a potential Mn(II) source for heterogeneous MnOₓ species in the same electrode solutions. The current densities at +1.6 V were similar to background scans over the range of [H₂O] studies (Fig. S9). Finally, Rotating Ring-Disk Electrochemistry (RRDE) was performed, following the method outline by Brudvig and co-workers [35], to show the oxidized species remain in solution under the same conditions as those in Fig. 3. The potential of the GC disk of the RRDE was scanned while the outer Pt ring was held at −1.5 V, a sufficiently low potential to reduce H₂O₂, O₂, and any partially oxidized [MnII][L]²⁺ species. Upon scanning anodically to +1.4 V for both [MnII][L]²⁺ alone and in the presence of 5% H₂O, a large cathodic signal is observed at the ring. When correcting for the collection efficiency of the RRDE, the cathodic current observed at the ring is roughly equivalent to the anodic generated at the GC disk, suggesting all products generated at the disk make it to the ring (Fig. S12).

Electrocatalytic studies were also performed on [MnII][LAc]²⁺ to investigate the effect of acetate coordination on the rate of H₂O oxidation. CVs of [MnII][LAc]²⁺ in anhydrous PC resembled those taken in ACN (Figs. 1 and S13). Upon addition of at least 1.5% H₂O by volume, the CVs start to change and begin to resemble [MnII][L]²⁺. This suggests in-situ generation of a H₂O coordinated dimanganese species from [MnII][LAc]²⁺, which is facilitated with increasing concentration of H₂O. Such a phenomenon was also observed by Nagata et al. for related acetate bridge dimanganese tetrakis-Schiff base macrocycles in catalase activity [19]. In addition, an electrocatalytic wave is observed starting at +1.3–1.4 V and increases with increasing addition of H₂O, similar to [MnII][L]²⁺. The magnitude of iₗₐₜ for [MnII][LAc]²⁺ as compared to that of [MnII][L]²⁺ under identical experimental conditions is slightly lower, suggesting that acetate displacement affects the electrocatalytic rate.

![Image](325x106 to 550x465)

Fig. 4. Left: Current–time controlled potential electrolysis (CPE) plot for [MnII][L]²⁺ (1 mM) in propylene carbonate/6% H₂O v/v at +1.6 V vs Fe⁺/⁻ (carbon paper). Right: Gas chromatograms of the headspace from the CPE experiment in the presence (red line) and absence (black dashed line) of [MnII][L]²⁺.

Fig. 5. (a) O₂ evolution (colored symbols) upon blue light irradiation of various concentrations of [MnII][L]²⁺ with [Ru(bpy)₃]²⁺ and K₂S₂O₈. Control experiments (open grey symbols) lacking [Ru(bpy)₃]²⁺, replacing [MnII][L]²⁺ with [Mn(ClO₄)₂], and without [MnII][L]²⁺. (b) Initial rate of O₂ production (red circles) vs [MnII][L]²⁺ concentration (determined between t = 500 and 1000 s) and TON determined after 30 min (blue diamonds). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
part to the low light intensity of the LEDs in this setup and the small driving force of [Ru(bpy)3]3+ toward the higher oxidation states of [MnII]2+ required for water oxidation [36,41]. O2 evolution from the system was observed for several concentration ranges of [MnII]2+ and proceeded over 30 min. A series of control experiments confirmed all four components (i.e., catalyst, photosensitizer, electron acceptor, and appropriate light source) were necessary for photocatalytic O2 evolution. Each of these experiments displayed O2 evolution rates that were the same as background signals (Fig. 5a). Also, when Mn(ClO4)2 was used as a precursor to form MnO (a known water oxidation catalyst) instead of [MnII]2+, the rate of O2 evolution was the same as other control experiments. The stability of [MnII]2+ during the photocatalytic experiment was validated by monitoring the UV–Vis absorbance at the end of each experiment and indicated some degree of decomposition/loss of [MnII]2+.

The dependence of oxygen evolution on catalyst concentration was also examined. Fig. 5b shows the initial oxygen evolution rate (red circles), which was calculated between t = 500 and 1000 s, increased linearly with [MnII]2+ concentration up to 20 µM, suggesting the rate law for formation of O2 is first order in [MnII]2+. At 40 µM [MnII]2+, the rate from 400 to 800 s is moderately higher than 20 µM, but begins to level off. At concentrations higher than 40 µM, the initial rates of oxygen evolution are higher, but decreased significantly and were accompanied by some precipitation that was not active towards water oxidation. This suggests that a catalyst deactivation pathway involving catalyst-catalyst self-reaction may be contributing to the decrease in turnover numbers (TON) at higher concentrations. A similar phenomenon was observed by others using a photosensitized homogeneous water oxidation catalysts [40]. This phenomena is consistent with calculated TON after 30 min of irradiation with light as shown in Fig. 5b. The highest TON, 11.2, was observed at 5 µM [MnII]2+, while the values generally decreased at higher concentrations to 2.7 at 40 µM [MnII]2+. Diffusion controlled oxidation of the catalyst and lack of a substantial driving force of [Ru(bpy)3]3+ to quickly generate the higher oxidation intermediates of [MnII]2+ could also be a factor for such a low TON.

4. Conclusions

The preliminary results shown here describe a new class of bio-inspired dimanganese complexes, based on tetrakis-Schiff base macrocycles, which display evidence of catalytic water oxidation activity to molecular oxygen. These water oxidation catalysts provide a rare example of Mn-based coordination complex that can be driven electrochemically and with non-oxo atom transfer oxidants [13]. This is a particularly important aspect of Mn-based complexes for incorporation into a photosynthesis mimicking system for solar driven fuel production. Further studies are ongoing to elucidating mechanistic steps, identify and fully characterize the intermediate oxidation states, and immobilize the catalyst on electrode surfaces.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jica.2014.08.007.

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