Published in final edited form as:

Inorganica Chim Acta. 2007 June 10; 360(9): 2983–2989.

Homogenous Water Oxidation by a Di- μ -Oxo Dimanganese Complex in the Presence of Ce^{4+}

Ranitendranath Tagore, Hongyu Chen, Hong Zhang, Robert H. Crabtree, and Gary W. Brudvig
Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut, 06520-8107.

Abstract

O_2 evolution was observed upon mixing aqueous $[(\text{terpy})(\text{H}_2\text{O})\text{Mn}(\text{O})_2\text{Mn}(\text{H}_2\text{O})(\text{terpy})](\text{NO}_3)_3$ (**1**, terpy = 2,2':6',6''-terpyridine) with aqueous solutions of Ce^{4+} . However, when the solution of **1** was incubated at pH = 1 (by dissolving in dilute HNO_3) before mixing with Ce^{4+} , very small amounts of O_2 were observed. This observation of acid-induced deactivation suggests an explanation, both for the previously reported lack of O_2 evolution from aqueous solutions of **1** with Ce^{4+} as oxidant, and the present observation of low amounts of O_2 production with the very acidic Ce^{4+} reagent. Evidence is provided for water being the source of evolved O_2 , and for the requirement of a high valent multinuclear Mn species for O_2 evolution. We test the possibility of complications in the use of cerium ammonium nitrate (CAN) in oxidation chemistry due to the presence of the oxidizable NH_4^+ ion.

Introduction

The mechanism of oxygen evolution by the oxygen evolving complex (OEC) of photosystem II (PS II) has been the subject of extensive research.^{1,2} Considerable advances have recently been made in the X-ray crystallography of PS II.^{3–7} On the basis of their recent crystallographic data, Ferreira et al. have modeled the OEC as a cuboidal Mn_3CaO_4 tetramer with a fourth ‘dangling’ manganese attached by a mono- μ -O bridge.⁶ Inorganic model chemistry has provided insights into the structural and spectroscopic properties of the OEC.^{8–11} However, the only structurally relevant inorganic Mn complexes that have been claimed so far as functional models for the OEC are the complex $[(\text{terpy})_2\text{Mn}_2\text{O}_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$ (**1**, where terpy = 2,2':6',2''-terpyridine),¹² the complex $[\text{Mn}^{\text{II}}_2\text{L}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**2**, where L = *N*-methyl-*N'*-glycyl-*N*, *N'*-bis(2-pyridylmethyl)ethane-1,2-diamine), which is proposed to form higher valent oxo-bridged complexes *in situ*,¹³ and the Mn-O cubane complex $\text{L}_6\text{Mn}_4\text{O}_4$ (**3**, where L = bis(tolyl)phosphinate).¹⁴ While **3** undergoes structural rearrangement to produce only stoichiometric amounts of O_2 from its bridging oxo groups, **1** and **2** have been found to be multiple-turnover water oxidation catalysts. In the studies of catalytic water oxidation by **1**, the oxo-transfer reagents ClO^- and HSO_5^- were used as the source of oxidizing equivalents.¹⁵ Turnover numbers greater than 50 were found, but isotope labeling studies were necessary to show that water was indeed the source of oxygen atoms in the evolved O_2 . The

Email: gary.brudvig@yale.edu and robert.crabtree@yale.edu.

Synopsis Text

The title compound (**1**) is shown to oxidize water in the presence of Ce^{4+} as the primary electron acceptor. Evidence is provided for higher oxidation states of **1** as the water-oxidizing species, and low-valent mononuclear manganese species formed from **1** under acidic conditions are shown to be inactive. The potential for catalytic water oxidation by **1** in the presence of electron acceptor oxidants is discussed.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

same is true for **2**, where the use of *tert*-butylhydroperoxide was necessary for catalytic activity, and the use of Ce^{4+} yielded less than one molecule of O_2 per molecule of **2**. Baffert et al. have suggested that the use of oxo-transfer primary oxidants is a necessary condition for water oxidation catalyzed by **1**.¹⁶ If that were the case, the relevance of **1** to the chemistry of the OEC would not be so strong, since electron transfer is the source of oxidizing equivalents in PS II. We, therefore, examined the reaction of **1** with Ce^{4+} .

Ce^{4+} , widely recognized as a pure electron transfer oxidant, unlike the oxo-transfer oxidants we have previously employed for water oxidation, has a standard reduction potential of more than 1.4 V versus NHE. It has been used as the primary oxidant in the oxidation of water to dioxygen catalyzed by Ru complexes.^{17–21} Yagi et al. have demonstrated its use in the catalysis of water oxidation with **1** adsorbed on clay.²² However, they did not detect any oxygen evolution in homogenous aqueous solutions of **1** with Ce^{4+} as primary oxidant.

We now show that it is possible to extend the use of Ce^{4+} as primary oxidant in homogenous oxygen evolution by **1**, avoiding the use of oxo-transfer reagents. Our data suggest that **1** could catalyze homogenous water oxidation with purely electron-transfer primary oxidants if an oxidant with a high enough reduction potential at a suitable pH range could be found. We attribute the previously reported absence of oxygen evolution from aqueous solutions containing Ce^{4+} and **1** to a difference in the conditions used in those experiments, notably the incubation of **1** at low pH, leading to its deactivation. Our results emphasize the importance of pH in maintaining the active structure of **1**.

Experimental Section

Materials

Solutions used in the Stable Isotope Ratio Mass Spectrometry (SIR-MS) experiments were prepared using HPLC grade water, and all other solutions were prepared using doubly deionized water. Exetainer[®] vials used for SIR-MS experiments were purchased from Labco Inc. and were incubated in pH = 1 HNO_3 solution for two days, rinsed and dried in an oven. Commercially available reagents were used as received. Solid cerium ammonium nitrate (CAN), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and 2,2':6',2''-terpyridine were purchased from Sigma Aldrich. Nitric acid was purchased from J. T. Baker. HPLC grade acetonitrile was obtained from Fisher Scientific. **1**¹² and $[(\text{phen})_4\text{Mn}_2^{\text{III/IV}}(\mu\text{-O})_2](\text{ClO}_4)_3$ (**4**, where phen = 1,10-phenanthroline)²³ were synthesized according to literature procedures. *Safety note: While we have not experienced any problems, perchlorate salts are potentially explosive, and should be handled with appropriate care.*

¹⁸O labeling/Stable Isotope Ratio Mass Spectrometry

Analyses were performed using a Thermo-Finnigan GasBench II connected to a Thermo-Finnigan Delta^{plus} XP stable isotope ratio mass spectrometer operating in continuous flow mode. Both the GasBench and Delta^{plus} XP were controlled by Isodat software (ver. 1.5). Using the GasBench II, the headspace of a vial was sampled via a double-layered transfer needle, where He (set to 16 psi) flowed into the vial through the upper aperture (close to the septum) in the needle and the resultant mixture flowed back through the lower aperture of the same needle. The gas mixture was then directed into a Nafion[®] (trade mark of DuPont) drying tube, and out through a 100 μl sampling loop in a Valco switching valve. Once the sampling loop was flushed with headspace gas, it was switched to inject the sample in the loop onto an integral gas chromatograph (GC) with a Varian CP7551 PLOT fused silica 25 m $\times$ 0.32 mm column (coating: Poraplot Q) at 32 $^\circ\text{C}$ to separate the O_2 from CO_2 . The separated gases were then carried through a second drying tube to an open split where a glass capillary would continuously draw in helium and sample gases to the mass spectrometer for analysis. The dilution factor of

the open split can be adjusted to decrease signal intensity, if necessary. In the mass spectrometer, the samples were ionized (electron ionization) and analyzed in three cups set to O₂ peaks with masses 32, 33 and 34. The relative nominal amplification for the three cups is 1, 100 and 300.

Under the conditions used, the sample vials were only slightly pressurized, as the sampling gas mixture from the vial was either directly vented (with the Valco-valve set to “inject” mode) or was vented after going through the sampling loop (with the Valco-valve set to “load” mode).

O₂ assay

Oxygen evolution from aqueous solutions of **1** in the presence of Ce⁴⁺ was measured at 298 K by an oxygen probe (Clark electrode) connected to a YSI 5300A oxygen monitor with digital readout, interfaced to a computer for data logging. The sample chamber was maintained at 25 °C with a circulating water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water kept stirred in the air-tight sample chamber under the Clark electrode. After ensuring a constant baseline reading, the water was taken out, and 5 mL of an aqueous solution of CAN was introduced into the sample chamber. After allowing time for equilibration (~5–10 min), 1 mL of an aqueous solution of manganese complex was injected into the CAN solution. In control experiments, 1 mL of blank solvent was added to 5 mL of the CAN solution. The control readings were subtracted from the sample readings to get the final oxygen-evolution data. The subtraction of controls typically produced less than a 2 % change in the oxygen-evolution data.

UV-visible and EPR spectroscopy

UV-visible spectra were recorded at room temperature on a Cary-50 UV-visible spectrophotometer, using a 1 cm path length quartz cuvette. EPR spectra were collected on an X-band Bruker E-500 spectrometer equipped with a SHQ cavity and an Oxford ESR-900 liquid helium cryostat. All EPR spectra were collected at 10 K on frozen samples with the following settings: modulation amplitude = 20 G, modulation frequency = 100 kHz, and microwave power = 1 mW.

Results and Discussion

Activity assay

When a 30 mM CAN solution was mixed with an aqueous solution of **1**, O₂ evolution was observed by the gas-phase SIR-MS instrument (Figure 1). However, when the solution of **1** was prepared in dilute nitric acid at pH = 1, there was very little oxygen evolution. In both cases, however, a significant amount of CO₂ evolution was observed. This indicates oxidation of the terpy ligand, since terpy is the only carbon source in solution.

For convenient quantification of the evolved oxygen, the reaction between **1** and Ce⁴⁺ was carried out in the Clark electrode cell (Figure 2). Solutions of **1** in water showed significant O₂ production upon reaction with Ce⁴⁺ solutions at pH 1 and 1.5. Solutions of **1** adjusted to pH 1.5 before mixing with Ce⁴⁺ showed considerably lower O₂ yield, in agreement with the SIR-MS experiments. A solution of [(phen)₄Mn₂^{III/IV}(μ-O)₂](ClO₄)₃ (**4**, where phen = 1,10-phenanthroline) showed very little O₂ evolution, and a solution of 1:1 Mn(ClO₄)₂:terpy showed none.

Dependence of catalytic efficiency on catalyst concentration

The oxygen yield per mole of **1** was found to be inversely dependent on [**1**]. At the concentration used in the SIR-MS experiment ([**1**] = 590 μM), 0.37 mol O₂ were produced per mole of **1**. This number increased to 0.43 and 0.54 at [**1**] = 250 μM and 67 μM, respectively (Figure 3).

Measurements at lower [1] were not feasible due to low signal:noise ratio. Lower turnover numbers at higher [1] suggest bimolecular degradative pathways that would be more pronounced at higher concentrations.

Effect of pH

The deleterious effect of low pH incubation, as seen in the SIR-MS experiment was also verified by the Clark electrode measurements, where the activity of a solution of **1** was found to be much lower when the solution was made in dilute HNO₃ than when it was made in water (Figure 2). Surprisingly, however, adjusting the pH of a 30 mM CAN solution to a pH lower than its native pH (~1.4) did not affect the activity (Figure 2). Measurements at pH values higher than the native pH of CAN in water were restricted by the insolubility of Ce⁴⁺ at pH greater than 2, together with the effect of pH on its redox potential.²⁴

The complex **1** is known to disproportionate into Mn²⁺ and Mn₂^{IV/IV} dimers at low pH.⁹ The pK_a associated with this disproportionation is ~2.5, so that in the pH range of our assays (pH 1 – 1.5), the disproportionation is expected to be complete. The Mn²⁺ thus formed cannot be re-oxidized to **1** by Ce⁴⁺ as verified by monitoring the reaction between Ce⁴⁺ and Mn²⁺ by UV-visible spectroscopy, which do not show the characteristic visible absorbances of **1** or the corresponding Mn₂^{IV/IV} dimer or Mn₄^{IV/IV/IV/IV} tetramer. This is in contrast to the oxidation of 1:1 Mn²⁺:terpy solutions by 0.75 molar equivalents HSO₅⁻ to yield the Mn₂^{III/IV} dimer.^{12,25} While the addition of 1:1 Mn²⁺:terpy solution to excess HSO₅⁻ gives oxygen evolution via the production of the corresponding high-valent Mn dimers *in situ*,²⁵ addition of 1:1 Mn²⁺:terpy to a CAN solution does not lead to oxygen evolution (Figure 2). This further shows that CAN is unable to generate Mn species active in oxygen evolution from mononuclear Mn²⁺ precursors.

EPR experiments (Figure 4, left panel) showed no new signals accompanying the disappearance of the g = 2 signal from Mn²⁺ upon the addition of Ce⁴⁺ to a 1:1 Mn²⁺:terpy solution. This again confirms the absence of Mn₂^{III/IV} dimers as well as Mn^{IV} monomers, which would give characteristic EPR signals. Oxo-bridged species with manganese in oxidation states lower than Mn^{IV} are unstable in the low pH conditions associated with Ce⁴⁺ due to the protonation and opening of the oxo-bridges. Since a mononuclear Mn species at an oxidation state of V or VI is extremely unlikely in this system, and since the UV-visible spectrum did not show MnO₄⁻ formation, we conclude that a mononuclear Mn^{III} species (expected to be EPR silent under these conditions) is most likely the product of the reaction between Mn^{II} and Ce⁴⁺. This is supported by the ~1:1 end point of the titration (by UV-visible spectroscopy) between Ce⁴⁺ and 1:1 Mn²⁺:terpy (Figure 4, right panel).

A higher pH range than those used for the present experiments is necessary to prevent the deactivation of **1** by disproportionation. However, the accessible pH range is restricted by the effect of pH on the solubility and redox potential of Ce⁴⁺,²⁴ which necessitates the use of low pH. Thus, in effect, a very narrow pH range is available, and the conditions cannot be optimized for **1** and Ce⁴⁺ simultaneously.

UV-visible spectroscopy

The time course of the UV-visible spectra of solutions containing 30 mM CAN and 67 μM **1** are shown in Figure 5. The insets show the time course of the absorbance at 440 nm. Fifty microliters of 8 mM **1** in water (left panel), or in dilute HNO₃ (pH 1, right panel), was injected into 6 mL of 30 mM CAN. In the left panel, the first spectrum (one minute after mixing) does not show the characteristic absorption peak at 550 nm due to **1**. This is expected, since the Mn₂^{III/IV} oxidation state is quickly depleted by the oxidation of Mn₂^{III/IV} to Mn₂^{IV/IV} by Ce⁴⁺, and by the acid induced disproportionation of Mn₂^{III/IV} to Mn₂^{IV/IV} and Mn^{II}.⁹ The EPR

spectrum of the solution after 30 sec shows no signals at $g = 2$, and confirms the absence of significant amounts of **1** or Mn^{2+} (Figure 4, left panel). The high UV-vis absorbances between 400 and 500 nm are consistent with the presence of high-valent Mn species.⁹ In the subsequent scans, the absorbance between 400 and 500 nm decreases, indicating the decay of multinuclear species. In the right panel, the absorbances between 400 and 500 nm are lower at one minute compared to the left panel. This becomes clearer upon a comparison of the insets in the left and right panels, where the absorbance at 440 nm starts out considerably higher in the left panel than in the right panel, and becomes very similar from 30 min onwards.

Water oxidation and deactivation pathways

Based on the data presented above, we can construct a scheme of reactions occurring in an acidic solution containing **1** and Ce^{4+} (Scheme 1). The water oxidation pathway consists of Reactions 1 – 3. The electrochemical oxidation of **1** has been shown to occur in aqueous solution at ~ 1.2 V versus NHE.¹⁶ The redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple (~ 1.4 V versus NHE at pH 1.5)²⁴ is sufficiently high to oxidize $\text{Mn}_2^{\text{III/IV}}$ to $\text{Mn}_2^{\text{IV/IV}}$ (Reaction 1). The formation of $\text{Mn}_2^{\text{IV/IV}}$ is in line with our UV-visible and EPR data. To account for oxygen evolution, we need to invoke a Mn species at a higher oxidation level than Mn(IV), since both $[(\text{terpy})_2\text{Mn}_2^{\text{IV/IV}}\text{O}_2(\text{SO}_4)_2]$ (**5**) and $[(\text{terpy})_4\text{Mn}_4^{\text{IV/IV/IV/IV}}\text{O}_5(\text{H}_2\text{O})_2](\text{ClO}_4)_6$ (**6**) are stable in acidic aqueous solution in the absence of added oxidants. Although Baffert et al. do not observe signals from the electrochemical oxidation of **5** or **6** up to a potential of ~ 1.3 V versus NHE,¹⁶ this does not rule out such an oxidation occurring in the presence of Ce^{4+} , which has a higher reduction potential than the 1.3 V achieved in the electrochemical experiments. Moreover, the electrochemical experiments were done at pH 3 – 4, whereas ours are done in the presence of Ce^{4+} at pH 1 – 1.4. The difference in conditions clearly leads to different pathways as shown by the absence of any features due to $\text{Mn}_4^{\text{IV/IV/IV/IV}}$ species in our UV-visible data, whereas this was the dominant species after electrochemical oxidation. The effect of acid treatment is also seen in a comparison of the left and right panels of Figure 5, where acid pre-incubation of **1** gives rise to permanganate formation, shown by distinct absorption features centered around 550 nm in the left panel. Thus, we introduce the Mn species **Q**, formed by oxidation of $\text{Mn}_2^{\text{IV/IV}}$ by Ce^{4+} (Reaction 2). Upon oxidation of water, **Q** is reduced to a four-electron reduced state, **Q'** (Reaction 3). Alternatively, the source of evolved oxygen could be the coupling and oxidation of oxo-bridges between the manganese. This possibility is rendered unlikely by the much lower oxygen evolution by **4** as compared to **1** (Figure 2). An important distinction between **1** and **4** is the presence of terminal water coordination sites on **1**, a feature that has been shown to enable efficient water oxidation by **1** in comparison to analogous coordinatively saturated complexes.^{12,26,27} On the other hand, **1** and **4** have similar redox potentials^{16,28} and pK_a values for the protonation of the oxo-bridges,^{9,29} and are, therefore, expected to show similar reactivities with respect to protonation and oxidation of the oxo-bridges.

When the solution of **1** is incubated in acidified water (pH 1.5) prior to mixing with Ce^{4+} , an O_2 yield of less than 50 %, as compared to a solution of **1** in pure water, is obtained. We note that under low pH conditions, 25 % of the manganese is deactivated towards O_2 evolution by disproportionation to Mn^{II} (Reaction 4).⁹ The remaining 75 % of the manganese in $\text{Mn}_2^{\text{IV/IV}}$ form is expected to participate in water oxidation according to Reactions 1 – 3. However, in the previous study of low pH disproportionation of **1**, it was found that the disproportionation became irreversible at pH lower than ~ 2.5 , suggesting that there is a difference in the reactions taking place above and below pH 2.5. Thus, in order to explain the low oxygen yields from the acid-incubated solution of **1**, we propose the conversion of the majority of **1** to a form inactive in water oxidation upon incubation at pH 1.5. This deactivation occurs only upon incubation at low pH in the absence of Ce^{4+} , since a solution of **1** in distilled water retains O_2 -evolving activity upon addition to CAN solutions of pH 1 – 1.4.

Catalytic water oxidation is prevented due to competing processes as shown in Reactions 5 – 7. In order to achieve catalytic cycling, the reduced species Q' needs to be re-oxidized to the starting $Mn_2^{III/IV}$ form. Since Q' is a four-electron reduced product of Q , it is at the oxidation level of a $Mn_2^{II/III}$ dimer. Oxo-bridges on a $Mn_2^{II/III}$ complex will have a pK_a much higher than the pK_a of the oxo bridges in **1** (estimated to be ~ 2.5).⁹ Therefore, at the pH of our oxygen evolution experiments, Q' is proposed to decompose to monomeric Mn^{II} and Mn^{III} by protonation of oxo bridges (Reaction 5). If decomposition to monomers (Reaction 5) takes place before re-oxidation by Ce^{4+} to a high-valent state, then there will be no catalytic cycling. Ce^{4+} is unable to oxidize the Mn^{II} formed in Reactions 4 and 5 to high-valent multinuclear manganese species, and instead produces monomeric Mn^{III} (Reaction 6) according to our UV-visible titration (Figure 5, right panel), and EPR results (Figure 4) shown above. The inability of Ce^{4+} to oxidize monomeric Mn^{III} further to form high-valent multinuclear manganese species precludes catalytic turnover. We have observed the rapid formation of mixed ligand complexes of **1** when derivatized terpy ligands are added to a solution of **1**, showing that the terpy ligands in **1** are labile. This lability is expected to be more pronounced under acidic conditions. Dissociated terpy ligands could be easy targets for oxidation by high-valent manganese species such as Q , accounting for the CO_2 evolution observed in the SIR-MS experiments (Reaction 7). Since the concentrations of both Q and free terpy ligand are expected to be proportional to the concentration of **1**, Reaction 7 may be expected to show a second order dependence on [**1**], explaining the observed inverse dependence of oxygen yield per mole of **1** on [**1**] (Figure 3). The conversion of high-valent manganese dimers to monomeric Mn^{II} and Mn^{III} explains the decrease of the 440 nm absorbance over time (Figure 5).

Comparisons with earlier work

Yagi and Narita²² found catalytic O_2 evolution from **1** adsorbed on Kaolin clay, suspended in a Ce^{4+} solution, with 13.5 mol O_2 produced per mole of **1** over 7 days. They saw an inverse relation between MnO_4^- formation and O_2 evolution, and concluded that MnO_4^- formation was the major pathway competing with O_2 evolution. However, these authors did not observe O_2 evolution from aqueous solutions of **1** and Ce^{4+} , whereas we see a significant amount of O_2 evolution. Upon careful comparison of experimental conditions in our work with that used in the previous work, we find differences in the procedures used for making solutions of **1**. Yagi and Narita report, as supporting information, the adjustment of a 5 mM aqueous solution of **1** to pH 4 by the addition of HNO_3 . In contrast, we find the native pH of aqueous solutions of **1** to be acidic, with higher concentrations giving more acidic solutions. At a concentration of 0.5 mM, the pH is found to be ~ 3.6 . We find that addition of HNO_3 to solutions of **1** causes loss of oxygen-evolving activity (as discussed above). The previous authors also report the absence of O_2 evolution from an aqueous solution containing 0.42 mM **1**, and 50 mM Ce^{4+} at pH = 3. Although **1** is considerably more stable at pH 3, the redox potential of Ce^{4+} at this pH may be unsuitable for oxidizing **1** to the state required for water oxidation.²⁴ Moreover, the negative effect of adding HNO_3 to the dimer solution would still be operative in this experiment. The adsorption of **1** onto a solid clay surface and the conditions used in the study of Yagi and Narita²² lead to increased robustness of adsorbed **1**, and may provide a means of studying the water oxidation mechanism in the absence of undesired decomposition pathways.

A note on the use of Ce^{4+}

$(NH_4)_2Ce(NO_3)_6$ (CAN) is a commonly used commercial form of Ce^{4+} that is crystalline, and has high solubility in water. However, the NH_4^+ cation may not be innocent in all applications. We have found that addition of NH_4NO_3 to the present catalytic system gave lower turnover numbers. We also observed a greater extent of MnO_4^- formation in the catalytic solutions containing NH_4NO_3 as compared to the ones without. The use of $Ce(NO_3)_4$, available as a 1 N solution from Alfa Aesar, was tried as an alternative to CAN. This increased the rate of the reaction by about 2-fold without, however, improving the total turnover number. The solution

of $\text{Ce}(\text{NO}_3)_4$ is prone to reduction on standing (as seen by the fading of the color characteristic of Ce^{4+}). This made CAN preferable over $\text{Ce}(\text{NO}_3)_4$ in our experiments. However, the present case demonstrates that researchers need to be aware of the possible deleterious effect of NH_4^+ , a potential reductant, when using CAN as an oxidizing agent.

Conclusions

We have shown oxygen evolution from homogenous aqueous solutions of **1** in the presence of the sacrificial electron-acceptor oxidant, Ce^{4+} . Our data support water oxidation as the means of oxygen evolution, and the requirement of high-valent multinuclear manganese species for oxygen evolution. Thus, while the low pH conditions necessary for the use of Ce^{4+} prevent catalytic turnover due to the predominance of decomposition pathways, our study suggests that **1** can, in principle, act as a water oxidation catalyst in the presence of purely electron-transfer oxidants. This justifies our proposal that **1** is a functional model for the OEC of PSII. We provide data to explain the previous report in the literature of the absence of oxygen evolution by **1** in solution in the presence of Ce^{4+} . We suggest that a key disadvantage of the use of Ce^{4+} as primary oxidant, is its inability to re-oxidize low-valent manganese species, generated due to oxygen evolution and low pH decomposition, to high-valent oxo-bridged species. This is in contrast to previously used oxidants such as HSO_5^- and NaOCl , and accounts for the lack of catalytic turnover when Ce^{4+} is used as the primary oxidant. These results justify the investigation of the mechanism of the efficient O_2 evolution by **1** in the presence of the O-donor oxidant HSO_5^- , which is amenable to use under pH conditions where **1** is stable in solution.²⁷

Acknowledgements

This work has been supported by the National Institutes of Health (GM 32715). The National Science Foundation (CHE-0215926) enabled the purchase of the Bruker ELEXSYS EPR spectrometer used in this work. We thank Dr. Gerard Olack (Department of Geology and Geophysics, Yale University) for help with the SIR-MS work.

References

1. McEvoy JP, Brudvig GW. Chem Rev 2006;106:4455–4483. [PubMed: 17091926]
2. Renger G. Photosynthesis Research 2003;76:269–288. [PubMed: 16228587]
3. Zouni A, Witt HT, Kern J, Fromme P, Krauss N, Saenger W, Orth P. Nature (London) 2001;409:739–743. [PubMed: 11217865]
4. Kamiya N, Shen JR. Proc Natl Acad Sci (U S A) 2003;100:98–103. [PubMed: 12518057]
5. Biesiadka J, Loll B, Kern J, Irrgang KD, Zouni A. Phys Chem Chem Phys 2004;6:4733–4736.
6. Ferreira KN, Iverson TM, Maghlaoui K, Barber J, Iwata S. Science 2004;303:1831–1838. [PubMed: 14764885]
7. Loll B, Kern J, Saenger W, Zouni A, Biesiadka J. Nature (London) 2005;438:1040–1044. [PubMed: 16355230]
8. Manchanda R, Brudvig GW, Crabtree RH. Coord Chem Rev 1995;144:1–38.
9. Chen H, Faller JW, Crabtree RH, Brudvig GW. J Am Chem Soc 2004;126:7345–7349. [PubMed: 15186173]
10. Mukhopadhyay S, Mandal SK, Bhaduri S, Armstrong WH. Chem Rev 2004;104:3981–4026. [PubMed: 15352784]
11. Mishra A, Wernsdorfer W, Abboud KA, Christou G. Chem Commun 2005;1:54–56.
12. Limburg J, Vrettos JS, Liable-Sands LM, Rheingold AL, Crabtree RH, Brudvig GW. Science 1999;283:1524–1527. [PubMed: 10066173]
13. Poulsen AK, Rompel A, McKenzie CJ. Angew Chem Int Ed 2005;44:6916–6920.
14. Yagi M, Wolf KV, Baesjou PJ, Bernasek SL, Dismukes GC. Angew Chem Int Ed 2001;40:2925–2928.

15. Limburg J, Vrettos JS, Chen H, de Paula JC, Crabtree RH, Brudvig GW. *J Am Chem Soc* 2001;123:423–430. [PubMed: 11456544]
16. Baffert C, Romain S, Richardot A, Lepretre J-CLB, Deronzier A, Collomb M-N. *J Am Chem Soc* 2005;127:13694–13704. [PubMed: 16190735]
17. Gersten SW, Samuels GJ, Meyer TJ. *J Am Chem Soc* 1982;104:4029–4030.
18. Ramaraj R, Kira A, Kaneko M. *J Chem Soc, Chem Commun* 1986;23:707–709.
19. Rotzinger FP, Munavalli S, Comte P, Hurst JK, Gratzel M, Pern FJ, Frank AJ. *J Am Chem Soc* 1987;109:6619–6626.
20. Sens C, Romero I, Rodriguez M, Llobet A, Parella T, Benet-Buchholz J. *J Am Chem Soc* 2004;126:7798–7799. [PubMed: 15212526]
21. Zong R, Thummel RP. *J Am Chem Soc* 2005;127:12802–12803. [PubMed: 16159265]
22. Yagi M, Narita K. *J Am Chem Soc* 2004;126:8084–8085. [PubMed: 15225027]
23. Manchanda R, Brudvig GW, de Gala S, Crabtree RH. *Inorg Chem* 1994;33:5157–5160.
24. Bondareva TN, Stromberg AG. *Zhurnal Obshchei Khimii* 1955;25:666–671.
25. Chen H, Tagore R, Das S, Incarvito C, Faller JW, Crabtree RH, Brudvig GW. *Inorg Chem* 2005;44:7661–7670. [PubMed: 16212393]
26. Limburg J, Brudvig GW, Crabtree RH. *J Am Chem Soc* 1997;119:2761–2762.
27. Chen H, Tagore R, Olack G, Vrettos JS, Weng TC, Penner-Hahn JE, Crabtree RH, Brudvig GW. *Inorg Chem* 2007;46:34–43. [PubMed: 17198410]
28. Cooper SR, Calvin M. *J Am Chem Soc* 1977;99:6623–6630.
29. Manchanda R, Brudvig GW, Crabtree RH. *New J Chem* 1994;18:561–568.

Figure 1.

Oxygen evolution, as measured by SIR-MS: (a) upon mixing 3 mL of a 1.08 mM solution of **1** in water with 3 mL of a 60 mM solution of CAN (b) upon mixing 3 mL of a 1.08 mM solution of **1** in dilute nitric acid (pH = 1) with 3 mL of a 60 mM solution of CAN.

Figure 2.

Time dependence of O_2 evolution from solutions of Mn complexes and Ce^{4+} , as measured by a Clark Electrode. (●): 250 μM **1** + 30 mM CAN. (○): 250 μM **1** + 30 mM CAN, repeat run. (▲): 250 μM **1** + 30 mM CAN (CAN adjusted to pH 1 before mixing). (▪): 250 μM **4** + 30 mM CAN. (△): 250 μM **1** (**1** adjusted to pH 1.5 before mixing) + 30 mM CAN. (□): 250 μM 1:1 $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$:terpy + 30 mM CAN.

Figure 3. Variation of oxygen yield per mole of **1** with initial [**1**]. [**1**] = 67 μM (●), 250 μM (■), and 590 μM (◆).

Figure 4.

Left Panel: EPR spectra of (a) 1:1 terpy:Mn(ClO₄)₂·6H₂O; (b) Solution (a) + 10 molar equivalents of CAN frozen ~15 sec after mixing; (c) Solution (b) warmed back up to room temperature, and re-frozen after ~1 minute; (d) 67 μM **1** + 30 mM CAN, 30 sec after mixing. Right panel: Titration of a 200 μM CAN solution (adjusted to pH 1 with nitric acid) by added 1:1 terpy:Mn(ClO₄)₂·6H₂O. The titration was followed by UV-visible absorption changes, and showed a break at 1:1 Mn:Ce⁴⁺. The changes at 450 nm are shown in this graph. Both the Ce⁴⁺ and Mn²⁺ solutions had negligible absorbance at 450 nm. The rise in absorbance with Mn²⁺ is, therefore, due to formation of Mn³⁺ product, and the constancy of the absorbance beyond a 1:1 ratio of Mn²⁺: Ce⁴⁺ is due to added Mn²⁺ remaining unreacted.

Figure 5.

Time course of UV-visible absorbance changes in a pH 1.4 solution of 67 μM **1** + 30 mM CAN. Arrows show the direction of absorbance change with time. Left panel: 50 μL of an 8 mM solution of **1** in water was injected into 6 mL of 30 mM aqueous CAN solution. Right panel: 50 μL of an 8 mM solution of **1** in pH 1 HNO_3 was injected into 6 mL of 30 mM aqueous CAN solution. The initial spectra were taken one minute after mixing. Subsequent spectra are shown at 30 minute intervals. Insets show the time course of the absorbance at 440 nm. Representative error bars indicate the deviation about the average of two runs.

Water-oxidation **Disproportionation** **Decomposition / Deactivation** **Scheme 1.**

Reactions proposed in an acidic solution of **1** + Ce^{4+} .