Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

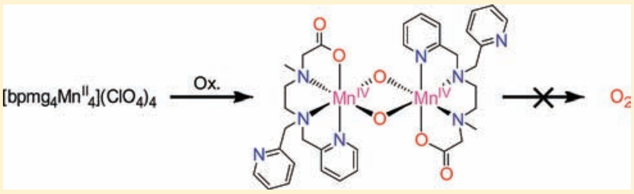
Mechanistic Studies on the Water-Oxidizing Reaction of Homogeneous Manganese-Based Catalysts: Isolation and Characterization of a Suggested Catalytic Intermediate

Gustav Berggren,[†,‡] Anders Thapper,[†] Ping Huang,[†] Lars Eriksson,[§] Stenbjörn Styring,[†] and Magnus F. Anderlund*[,†]

[†]Department of Photochemistry and Molecular Science, Uppsala University, 75120 Uppsala, Sweden
[§]Division of Structural Chemistry, Arrhenius Laboratory, Stockholm University, 10691 Stockholm, Sweden

S *Supporting Information*

ABSTRACT: The synthesis, isolation, and characterization of two high-valent manganese dimers with isomeric ligands are reported. The complexes are synthesized and crystallized from solutions of low-valent precursors exposed to *tert*-butyl hydroperoxide. The crystal structures display centrosymmetric complexes consisting of $Mn_2^{IV,IV}(\mu\text{-}O)_2$ cores, with one ligand coordinating to each manganese. The ligands coordinate with the diaminoethane backbone, the carboxylate, and one of the two pyridines, while the second pyridine is noncoordinating. The activity of these complexes, under water oxidation conditions, is discussed in light of a proposed mechanism for water oxidation, in which this type of complexes have been suggested as a key intermediate.



INTRODUCTION

The recent surge in solar energy research has led to an increased interest in photosynthesis in general and artificial photosynthesis in particular.[1,2] A key topic in this field is the oxidation of water into molecular oxygen. In nature, this reaction is carried out at low overpotential by a $CaMn_4$ cluster in photosystem II.[3] Although major effort has been invested, functional biomimetic models are scarce, and very few manganese-based homogeneous catalysts have been reported to evolve oxygen upon oxidation.[4,5] Two of these manganese complexes are as follows: a dimer based on the ligand *N*-methyl-*N*′-carboxymethyl-*N*,*N*′-bis(pyridylmethyl)ethane-1,2-diamine, $[mcbpen_2Mn_2^{II,II}(H_2O)_2](ClO_4)_2$ (**4**),[6] and a tetramer based on the isomeric ligand 2-[[2-[bis(pyridin-2-ylmethyl)amino]ethyl](methyl)amino]acetic acid, $[bpmg_4Mn_4^{II,II,II,II}](ClO_4)_4$ (**3**[7]), the ligands are depicted in Figure 1. Both **3** and **4** have been reported to evolve oxygen upon oxidation using either oxygen-atom-transferring oxidants, such as *tert*-butyl hydroperoxide (TBHP) and oxone or cerium(IV).[6−10] However, contradictory results have been reported for **4** regarding an isotope study (TBHP)[9] and an investigation of water oxidation with cerium(IV) as the terminal oxidant.[10] Because of these discrepancies and the general interest for water oxidation in the context of artificial photosynthesis, we have investigated the reactions of these compounds in more detail in an attempt to understand the mechanism behind the oxygen-evolving reaction of these complexes. During our investigation, we found that the manganese(IV) species obtained from both chemical oxidation, using $Ru(bpy)_3^{3+}$ as the oxidant, and electrochemical oxidations were stable on at least a minute time scale at room temperature.[7]

Herein we report the isolation and characterization of two high-valent $Mn_2^{IV,IV}(\mu\text{-}O)_2$ complexes, **1** and **2** (Figure 1), and their ability to evolve oxygen upon oxidation. These dimers are similar to a hypothesized structure of a high-valent manganese dimer (**2**′; Figure 1),[11] suggested to be a key intermediate in the catalytic water oxidation. In this mechanism the molecular oxygen was suggested to form through spontaneous collapse of the di-μ-oxido moiety.[6]

EXPERIMENTAL SECTION

General Procedures. Unless otherwise stated, all reagents were obtained from commercial sources and were used as received. Complexes **3**[7] and **4**[12] were prepared according to literature procedures. IR spectra were measured on a Perkin-Elmer Spectrum One with samples prepared as KBr disks. UV−vis spectra were measured on a Varian Cary Bio 50. Mass spectrometry was performed on a Finnigan LCQ deca max. The electron paramagnetic resonance (EPR) measurements were performed on a Bruker E500-ELEXSYS spectrometer with an ER 0601SHQE resonator equipped with an ESR900 cryostat and an Oxford ITC503 temperature controller. Elemental analysis (C, H, N, and Mn) was performed by Analytische Laboratorien GmbH, Industriepark Kaiserau, D-51789 Lindlar, Germany.

Caution! *Perchlorate salts are potentially explosive and should be handled accordingly!*

Preparation of $[bpmg_2Mn_2^{IV,IV}(\mu\text{-}O)_2](ClO_4)_2$ (1). Aqueous TBHP (70%, 150 μL, 1.0 mmol) was added to a stirred suspension of **3** (30 mg, 0.015 mmol) in MeCN (6 mL). The reaction was followed by UV−vis spectrometry, and once the solution had reached maximum

Received: November 22, 2010
Published: March 23, 2011

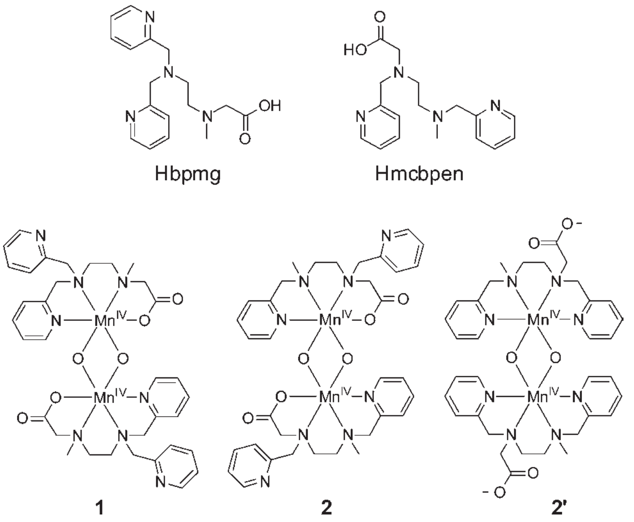


Figure 1. Ligands and complexes discussed in this study (counter ions excluded).

absorption at 650 nm, the dark-brown reaction mixture was filtered. A total of 1.5 mL of Et_2O was layered on top of the filtrate and the vial placed in an Et_2O atmosphere at −15 °C. After 4 days, **1** had precipitated as dark needlelike crystals. If the crystallization time was extended beyond 4 days, a colorless microcrystalline material appeared as well. Yield: 15 mg, 0.016 mmol, 52%. Elem anal. Calcd for $[(bpmg)_2Mn_2^{IV,IV}(\mu\text{-}O)_2](ClO_4)_2 \cdot 2H_2O$ ($C_{34}H_{46}Cl_2Mn_2N_8O_{16}$): C, 40.7; H, 4.6; N, 11.2; Mn, 10.95. Found: C, 41.0; H, 4.7; N, 11.2; Mn, 11.1. ESI-MS: m/z 866.7 ($[bpmg_2Mn_2^{IV,IV}(\mu\text{-}O)_2](ClO_4)^+$), calcd m/z 867.1.

Preparation of $[mcbpen_2Mn_2^{IV,IV}(\mu\text{-}O)_2](ClO_4)_2$ (2). Aqueous TBHP (70%, 150 μL, 1.0 mmol) was added to a stirred suspension of **4** (30 mg, 0.03 mmol) in MeCN (5 mL). The reaction was followed by UV−vis spectrometry, and once the solution had reached maximum absorption at 650 nm, the dark-brown reaction mixture was placed in an Et_2O atmosphere at −15 °C. After 4−5 days, **2** had precipitated as dark needlelike crystals. If the crystallization time was extended beyond this time, a colorless microcrystalline material appeared as well. Yield: 12 mg, 0.012 mmol, 40%. Elem anal. Calcd for $[mcbpen_2Mn_2^{IV,IV}(\mu\text{-}O)_2](ClO_4)_2 \cdot 2H_2O$ ($C_{34}H_{46}Cl_2Mn_2N_8O_{16}$): C, 40.7; H, 4.6; N, 11.2; Mn, 10.95. Found: C, 40.6; H, 4.7; N, 11.0; Mn, 10.6. ESI-MS: m/z 866.9 ($[mcbpen_2Mn_2^{IV,IV}(\mu\text{-}O)_2]$ $(ClO_4)^+$), calcd m/z 867.1.

X-ray Crystallography. The diffraction data for **1** were collected on Beamline I911-5 at the Swedish synchrotron facility MaxLab, Lund, Sweden. The data were obtained with a MARCCD using ϕ scans at 47 mm detector distance.

The diffraction data for **2** were collected with an Xcalibur-2 κ-diffractometer equipped with a Sapphire-3 CCD, from Oxford Diffraction. The data were obtained at 50 mm detector distance by several ϕ scans at different ϕ values to fill the Ewald sphere.

The structures were solved with standard structure invariant direct methods using *SHELXS97*[13] and refined with full-matrix least-squares calculations using *SHELXL97*.[13] Anomalous dispersion correction terms for the wavelength (0.9083 Å) used in **1** were obtained from *WCROMER*.[14,15]

CCDC 712178 (**1**) and CCDC 746412 (**2**) contain all of the supplementary crystallographic data and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry. Cyclic voltammetry (CV) and controlled potential bulk electrolysis were carried out by using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). Sample solutions (3 mL) were prepared from dry acetonitrile (dried over 3 Å molecular sieves) containing 0.1 M tetrabutylammonium hexaflourophosphate ($TBAPF_6$; Fluka, electrochemical grade) as the supporting electrolyte under an argon atmosphere. For CV, a 3 mm glassy carbon disk and, for potential bulk electrolysis, a 4 cm^2 cylindrical platinum net were used as working electrodes. A glassy carbon rod served as the counter electrode, and the reference electrode was a Ag/Ag^+ electrode (a silver wire immersed in 10 mM $AgNO_3$ in MeCN) with a potential of −0.07 V versus the ferrocene/ferrocenium (Fc/Fc^+) couple in dry MeCN. The counter and reference electrodes were placed in compartments separated from the bulk solution by fritted disks and were the same for all analytical and bulk electrochemical experiments. For addition of a base, 2,6-lutidine (purified by distillation, ≥99%) was diluted 1:25 in acetonitrile and 75 μL of the resulting solution was added (2.8 mg, 26 μmol) to the electrochemical cell. Lutidinium was prepared by mixing $HClO_4$ and lutidine in a 1:1 ratio.

Oxygen Detection. The polarographic signal from a standard Clark cell (Hansatech Instruments) was used for oxygen detection. Details of the operation have been described elsewhere.[10] Air-saturated deionized water at 20 °C was used for calibration of the electrode, which was performed with a standard method incorporated in the *CalMeter* software package by Calmetric.

■ RESULTS AND DISCUSSION

Synthesis. Complexes **1** and **2** were synthesized using the conditions under which **2′** was proposed to be formed by Poulsen et al.[6] Suspensions of **3** or **4** in acetonitrile were treated with an excess of TBHP, yielding **1** or **2**, respectively. Diethyl ether was added to the solutions, and they were stored at −15 °C for 4 days, during which time needlelike crystals of **1** and **2** were formed.

X-ray Crystallography. The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction (Table 1), which revealed centrosymmetric complexes with $Mn_2^{IV,IV}(\mu\text{-}O)_2$ cores, shown in Figures 2 and 3. For each manganese ion, in both **1** and **2**, the ligand backbone (diamino ethane) was coordinated trans to the di-μ-oxido bridges, forming a N_2O_2 plane. To complete the pseudooctahedral coordination of the manganese ions, the carboxylate and one of the two pyridines in the ligands were coordinated perpendicularly to the di-μ-oxido plane. The second pyridine moiety in the ligands is noncoordinating and can act as an internal base. The Mn−Mn distances of 2.670(3) and 2.6639(16) Å for **1** and **2**, respectively, were short but within the range reported for other $Mn_2(\mu\text{-}O)_2$ complexes (2.62−2.76 Å).[5] Bond-valence calculations[16,17] for manganese gave 3.82 and 3.9 respectively for **1** and **2**, which agreed with the stoichiometry found in the unit cells of the crystals and from elemental analysis.

IR Spectroscopy. The solid-state IR spectra of **1** and **2** were very similar and showed a match in the carboxylate bands centered around 1692 and 1274 cm^{-1} (Figure S1 in the Supporting Information). Furthermore, the absorbance peak at 1592 cm^{-1} confirms the presence of a noncoordinating pyridine in the complexes,[18] as seen in the crystal structures (Figure 2 and 3). This ligand coordination, with a noncoordinating pyridine, is in contrast to that proposed by McKenzie and co-workers for the intermediate obtained from oxidation of **4**; compare structures **2** (isolated) and **2′** (suggested) in Figure 1.[6,12]

Electrochemistry. The redox chemistry of **1** and **2** was studied in acetonitrile by CV (Figure 4). The CV trace of **1** revealed two quasi-reversible redox couples at $E_{1/2}^{1,1}$ = −0.44 V (ΔE = 90 mV) and $E_{1/2}^{2,1}$ = 0.29 V (ΔE = 80 mV) vs $Ag/AgNO_3$. The corresponding couples for **2** were slightly shifted: $E_{1/2}^{1,2}$ = −0.40 V (ΔE = 120 mV) and $E_{1/2}^{2,2}$ = 0.33 V (ΔE = 120 mV). Controlled potential bulk electrolysis, monitored by coulometry and EPR spectroscopy, allowed assignment of the two redox

Table 1. Crystal Data and Refinement Details for X-ray Structure Determination

	1	2
formula	$C_{34}H_{42}Mn_2N_8O_6 \cdot 2ClO_4 \cdot 2H_2O$	$C_{34}H_{42}Mn_2N_8O_6 \cdot 2ClO_4 \cdot 3.26C_2H_3N$
fw/(g mol^{-1})	1003.57	1101.02
cryst size (mm)	0.05 × 0.04 × 0.02	0.30 × 0.10 × 0.08
cryst syst	monoclinic	monoclinic
space group	$P21/c$	$P21/c$
T/K	100	293
a/Å	10.347(19)	14.8938(19)
b/Å	18.283(17)	11.0824(8)
c/Å	10.754(9)	17.612(2)
β/deg	95.91(9)	114.770(15)
V/Å^3	2024(4)	2639.6(5)
Z	2	2
ρ_{calcd}/(g cm^{-3})	1.647	1.385
μ (mm^{-1})	1.635	0.649
radiation source	synchrotron	sealed tube, Mo Kα
λ/Å	0.9083	0.71073
$2\theta_{max}$/deg	57.12	50.06
$N_{measured}$	14 658	10 256
N_{unique}	2471	4630
R_{int}	0.0644	0.1290
R1	0.0612	0.0691
wR2	0.1665	0.1717
CCDC no.	712178	746412

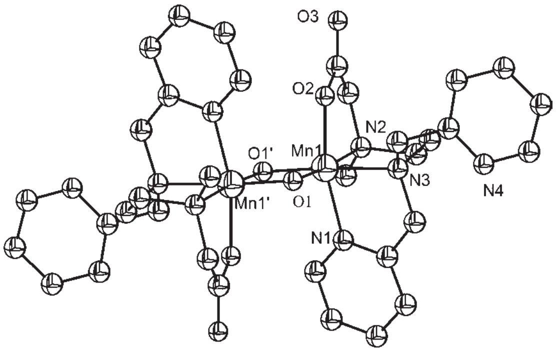


Figure 2. Crystal structure of **1**. Hydrogen atoms and counterions are omitted for clarity. Selected bond lengths [Å]: Mn1−Mn1′ 2.670(3), Mn1−O1 1.814(4), Mn1−O1′ 1.810(3).

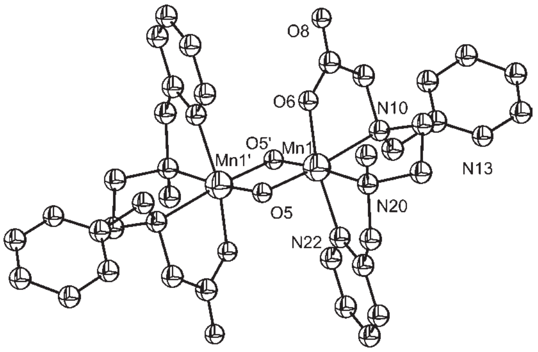


Figure 3. Crystal structure of **2**. Hydrogen atoms and counterions are omitted for clarity. Selected bond lengths [Å]: Mn1−Mn1′ 2.6639(16), Mn1−O1 1.811(4), Mn1−O1′ 1.807(4).

processes. The process at 0.29 V was assigned to a $Mn_2^{IV,IV/III,IV}$ couple based on coulometry and the appearance of a strong, 1240 G wide, 16-line EPR signal centered at $g = 2$, characteristic for a $Mn_2^{III,IV}(\mu\text{-O})_2$ species,[19] after exhaustive reduction at 0.05 V (Section S2 in the Supporting Information). The second process was assigned to the $Mn_2^{III,IV/III,III}$ couple based on coulometry (Section S2 in the Supporting Information). Further scanning up to 1.5 V, where the background current started to increase sharply, showed no more oxidation processes for **1**, while for **2**, two additional redox processes were present (Figure S3 in the Supporting Information). These were assigned to two oxidations of a $Mn_2^{III,III}(\mu\text{-O})$ species[12] with $E_{1/2} = 0.64$ V ($\Delta E =$ 100 mV) and $E_{1/2} = 1.15$ V ($\Delta E = 120$ mV). Because no catalytic current was observed within the potential range of the electrochemical oxidation of **1** or **2**, we conclude that the complexes do not act as electrochemical oxidation catalysts under the conditions used, where there is a small amount of residual water present in the solvent.

The acetonitrile solution of **1** prior to bulk electrochemistry showed a small EPR signal[20] from the $Mn_2^{III,IV}(\mu\text{-O})_2$ species. This signal was quantified to correspond to ≤10% of the Mn content of the sample (Figure S2 in the Supporting Information). The same amount of $Mn_2^{III,IV}$ was also found in the acetonitrile solution of **2**. It is not clear if this impurity is a decomposition product of the $Mn_2^{IV,IV}$ species or a byproduct formed during formation or isolation of the $Mn_2^{IV,IV}$ complexes.

To ascertain that **1** was also the product obtained when **3** was oxidized with non-oxygen-donating oxidants, **3** was subjected to exhaustive bulk electrolysis at 1.0 V, as previously reported.[7] The CV trace of the material obtained after bulk electrochemical

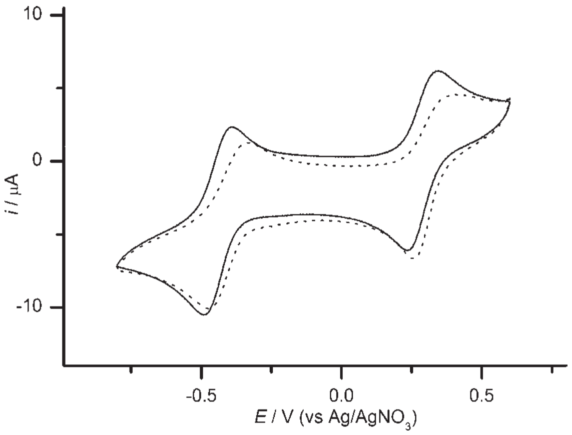


Figure 4. Cyclic voltammograms (second scans) of **1** (solid line) and **2** (dashed line), with 1 mM Mn in MeCN with 0.1 M $TBAPF_6$ as the electrolyte. Scan rate: 100 mV s^{-1}.

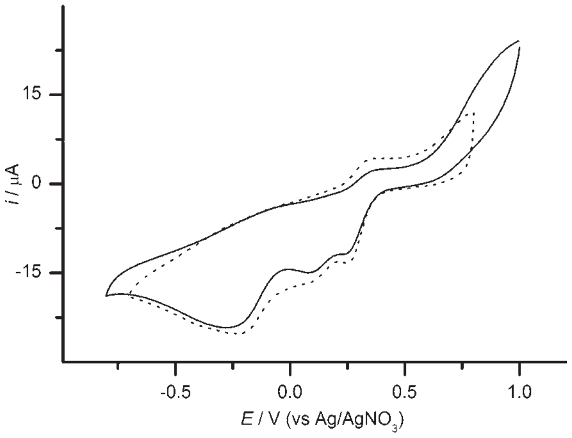


Figure 5. Cyclic voltammograms (second scans) of **3** (2 mM Mn; dashed line) with lutidine (6 mM) after bulk electrolysis at 1.0 V and **1** (1 mM Mn; solid line, current multiplied by 2) in the presence of lutidinium ions (1 mM), in MeCN with 0.1 M $TBAPF_6$ as the electrolyte. Scan rate: 100 mV s^{-1}.

oxidation looked, apart from the reductive peak at 0.25 V (Figure 5, dashed line), dramatically different from that of **1** (Figure 4, solid line). However, by the addition of lutidinium ions to the solution of **1**, the obtained CV matched the CV of **3** subjected to exhaustive bulk electrolysis (Figure 5). This behavior demonstrates that the redox properties of **1** were altered in the presence of protons, generated either from the deprotonation of water during formation of the $Mn_2^{IV,IV}(\mu\text{-}O)_2$ core upon oxidation of **3** or from the addition of lutidinium ions. Upon reduction of **1**, the expected increase in the pK_a value of the formed $Mn_2^{III,IV}(\mu\text{-}O)_2$ complex allows for protonation of the μ-oxido bridges.[18,21,22] This protonation facilitates further reduction at milder potentials and thereby suppresses the reversibility of the electrochemical processes. These results, together with the similarities in the UV−vis spectra discussed below, show that the isolated crystallized material **1** is a true representation of the $Mn_2^{IV,IV}$ species formed upon consecutive one-electron oxidation(s) of **3** in solution.

Reactivity of 1 and 2. Isolation of complexes **1** and **2** made it possible to test the speculative mechanism put forth by Poulsen et al.,[6] which states that **2** (**2′**) is a key intermediate in the catalytic water oxidation cycle. Within minutes, the complex should undergo spontaneous reductive elimination of molecular oxygen to explain the rapid oxygen evolution reported. Because the complexes showed limited stability in water (see below), the influence of water on the complex was first investigated. The UV−vis spectra of **1** and **2** in either water or acetonitrile displayed a band at ∼410 nm, a shoulder at ∼525 nm, and a broad peak at 650 nm (ε = 440; Figure S4 in the Supporting Information). The latter two features were reported by Baffert et al.[12] to originate from the proposed intermediate **2′**. This indicated that **1** and **2** were not altered when dissolved in water.

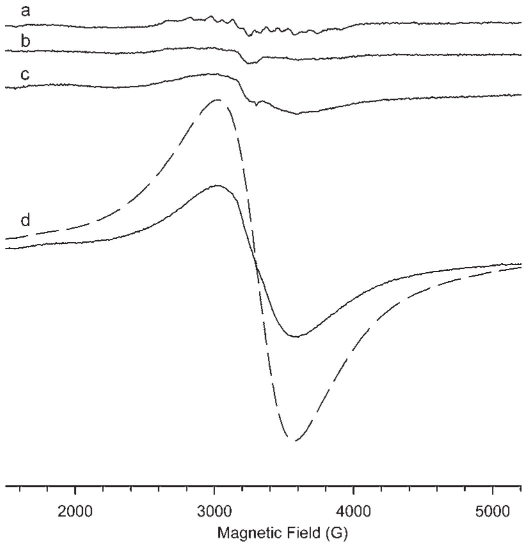


Figure 6. EPR spectra of **1** dissolved in H_2O after (a) 0 h, (b) 0.5 h, (c) 5 h, and (d) 29 h (full line). The dashed line is an EPR spectrum of **3** measured under the same conditions as those in parts a−d. EPR parameters; T, 5 K; microwave power, 125 μW; microwave frequency, 9.28 GHz.

Water solutions of **1** showed limited stability at room temperature, and the half-life was estimated as ∼15 min with UV−vis spectroscopy. When degradation of **1** was followed by EPR spectroscopy, the small $Mn_2^{III,IV}$ EPR signal disappeared within 1 h while a broad wave at g = 2 grew in during 30 h (Figure 6). This signal is identical in shape to the EPR signal of **3** and indicates that **1** was reduced all the way to Mn^{II}, and after 30 h, the signal intensity corresponded to ∼40% of the total manganese content in the sample. Analogously, Poulsen et al. reports that when **4** was oxidized with TBHP, forming a dark-brown solution of $Mn_2^{IV,IV}$ (presumably **2**), the color was bleached within 24 h upon standing, and **4** could be reisolated.[6]

To test the suggested mechanism under oxygen-evolving conditions, **2** or **1** was dissolved in water in a cell equipped with a Clark-type oxygen-sensitive electrode. The solution was deaerated with argon, and a cerium(IV) solution was added within 10 min. No oxygen evolution could be observed either before or after cerium(IV) addition, even though the concentration of **2** (and **1**) at the point of cerium(IV) addition would have produced enough oxygen to saturate the solution in the Clark electrode.[23] As a control, the experiment with **1** was repeated without the addition of cerium(IV) and no oxygen evolution could be detected over 30 min (Section S5 in the Supporting Information). This clearly shows that spontaneous collapse of the di-μ-oxido core in pure water or under oxygen-evolving conditions is not responsible for the oxygen formation either with TBHP or with cerium(IV), as hypothesized by Poulsen et al.[6]

Because no oxygen has been detected during the reductive transformation of complex **1** or **2**, there must be something else that has been oxidized. The primary candidate present in the solution is the ligand that contains carboxylate, amines, and benzyl-like positions. There are enough reducing equivalents from the ligands, even using only a small fraction of the material, to reduce the bulk of the complex back to manganese(II) species. This explanation is not unprecedented because it has been shown that $Mn_2^{IV,IV}(\mu\text{-}O)$ can oxidize hydrocarbons[24] and a $Mn_2^{III,IV}(\mu\text{-}O)_2$ complex can oxidize benzyl-like ligands.[25] Furthermore, oxidation of acetate in the presence of high-valent manganese complexes has been observed.[8]

Instead, with TBHP, the evolved oxygen could arise from the well-known radical decomposition of TBHP catalyzed by manganese.[26−28] This should not incorporate labeled oxygen from the solvent, as reported by Poulsen et al.,[6] but is in line with the observation of unlabeled oxygen reported by Styring et al.[9]

For the one-electron (non-oxygen-atom-donating) oxidant, cerium(IV), the situation is different. When **3** or **4** was exposed to the acidic nature (pH ∼ 1.3) of the cerium(IV) solution, the complexes were degraded very fast. A strong, 530 G wide, 6-line EPR signal at $g = 2$, typical for mononuclear manganese(II), dominated the EPR spectra already after a few seconds, and an additional small EPR signal at $g \sim 4$ was also observed, which can be assigned to a mononuclear manganese(IV) species (data not shown).[29−32]

The formation of di-μ-oxido cores from the dimerization of mononuclear Mn−OH species is likely to be pH-dependent and unfavored at low pH. Therefore, one hypothesis for the small observed oxygen evolution earlier reported is that this mononuclear manganese(IV) species would be oxidized all the way to a short-lived manganyl species by cerium(IV). The formed electrophilic oxygen can then undergo nucleophilic attack from water or a nucleophilic μ-oxido bond, forming a peroxy species that upon further oxidation could release the observed oxygen. A similar mechanism with external nucleophilic attack has been suggested for the $[tpy_2Mn_2^{III,IV}(\mu\text{-}O)_2(H_2O)_2]^{3+}$ complex[33] (tpy = 2,2′;6′,2″-terpyridine), a $[Mn^{III}corrole]^0$ complex,[34] and the $CaMn_4$ cluster in photosystem II.[35,36]

When solutions of **1** or **2** exposed to cerium(IV) were investigated in more detail, a small EPR signal was observed at $g \sim 4$, assigned to a mononuclear manganese(IV) species.[29−32] This EPR signal reached its maximum intensity 5 min after the addition of cerium(IV) and was present for at least 30 min (Figure S6 in the Supporting Information). Investigation of these samples with ESI-MS revealed the presence of the respective $Mn_2^{IV,IV}$ dimer in all samples. This could possibly be explained by an equilibrium between monomers and dimers, where an acid-assisted breakup of the di-μ-oxido core is responsible for formation of the mononuclear manganese(IV) species. A similar influence of acidic conditions has been suggested for the cerium(IV) oxidation of the $[tpy_2Mn_2^{III,IV}(\mu\text{-}O)_2(H_2O)_2]^{3+}$ catalyst,[37] where the low pH (1−1.4) was suggested to prevent dimerization of the catalyst. However, because this mononuclear manganese(IV) species and the $Mn_2^{IV,IV}$ dimers were observed under reported oxygen-evolving conditions, without oxygen evolution, neither of them is a catalytically active species.

CONCLUSION

We have isolated and characterized two high-valent manganese dimers, **1** and **2**. We have shown that they do not release oxygen under reported oxygen-evolving conditions or through spontaneous reductive elimination. This is in contrast to the mechanism suggested for complex **4**. In spite of this, the reported oxygen evolution from compounds **3** and **4** is interesting and warrants detailed studies of these systems in order to elucidate the elusive intermediates responsible for the observed oxygen evolution.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** IR spectra of **1** and **2**, bulk electrochemistry data, cyclic voltammograms of **1**−**3**, UV−vis spectra of **1** and **2**, oxygen measurement in the Clark cell, details of the cerium(IV) treatment of **1**, and X-ray crystallographic data for **1** and **2** in the form of CIF file data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: magnus.anderlund@fotomol.uu.se.

Present Addresses

‡Laboratoire de Chimie et Biologie des Métaux; UMR5249 CNRS-CEA-UJF, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France.

ACKNOWLEDGMENT

This work was supported by grants from the Swedish Energy Agency, Knut and Alice Wallenberg Foundation, and the EU/Energy Network project SOLAR-H2 (FP7 Contract 212508).

REFERENCES

(1) Brudvig, G. W. *Coord. Chem. Rev.* **2008**, *252*, 231.

(2) Eisenberg, R.; Gray, H. B. *Inorg. Chem.* **2008**, *47*, 1697.

(3) Dau, H.; Haumann, M. *Coord. Chem. Rev.* **2008**, *252*, 273.

(4) Cady, C. W.; Crabtree, R. H.; Brudvig, G. W. *Coord. Chem. Rev.* **2008**, *252*, 444.

(5) Mukhopadhyay, S.; Mandal, S. K.; Bhaduri, S.; Armstrong, W. H. *Chem. Rev.* **2004**, *104*, 3981.

(6) Poulsen, A. K.; Rompel, A.; McKenzie, C. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6916.

(7) Berggren, G.; Thapper, A.; Huang, P.; Kurz, P.; Eriksson, L.; Styring, S.; Anderlund, M. F. *Dalton Trans.* **2009**, *45*, 10044.

(8) Beckmann, K.; Uchtenhagen, H.; Berggren, G.; Anderlund, M. F.; Thapper, A.; Messinger, J.; Styring, S.; Kurz, P. *Energy Environ. Sci.* **2008**, *1*, 668.

(9) Styring, S.; Beckmann, K.; Berggren, G.; Uchtenhagen, H.; Anderlund, M. F.; Thapper, A.; Messinger, J.; Kurz, P. In *Photosynthesis. Energy from the sun: 14th International Congress on Photosynthesis*; Allen, J. F., Gantt, E., Golbeck, J. H., Osmond, B., Eds.; Springer: Dordrecht, The Netherlands, 2008; p 1281.

(10) Kurz, P.; Berggren, G.; Anderlund, M. F.; Styring, S. *Dalton Trans.* **2007**, 4258.

(11) The structure **2′** has been proposed by Poulsen et al.[6] although no evidence for the coordination mode of the ligand has been provided.

(12) Baffert, C.; Collomb, M. N.; Deronzier, A.; Kjaergaard-Knudsen, S.; Latour, J. M.; Lund, K. H.; McKenzie, C. J.; Mortensen, M.; Nielsen, L.; Thorup, N. *Dalton Trans.* **2003**, 1765.

(13) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, 112.

(14) Brennan, S., http://www.ccp14.ac.uk/ccp/ccp14/ftp.

(15) Kissel, L.; Pratt, R. H. *Acta Crystallogr., Sect. A* **1990**, 170.

(16) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102.

(17) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(18) Groni, S.; Hureau, C.; Guillot, R.; Blondin, G.; Blain, G.; Anxolabéhère-Mallart, E. *Inorg. Chem.* **2008**, *47*, 11783.

(19) Hureau, C.; Sabater, L.; Anxolabéhère-Mallart, E.; Nierlich, M.; Charlot, M. F.; Gonnet, F.; Rivière, E.; Blondin, G. *Chem.—Eur. J.* **2004**, *10*, 1998.

(20) A $Mn_2^{IV,IV}$ dimer is expected to be EPR inactive.

(21) Baldwin, M. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1996**, *118*, 11325.

(22) Hureau, C.; Blondin, G.; Charlot, M. F.; Philouze, C.; Nierlich, M.; Césario, M.; Anxolabéhère-Mallart, E. *Inorg. Chem.* **2005**, *44*, 3669.

(23) In the proposed mechanism, the complex is oxidized with TBHP or cerium(IV) to reach the $Mn_2^{IV,IV}$ state, but once this species is formed, the choice of oxidant should not be important.

(24) Larsen, A. S.; Wang, K.; Lockwood, M. A.; Rice, G. L.; Won, T.-J.; Lovell, S.; Sadílek, M.; Turecek, F.; Mayer, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 10112.

(25) Dubois, L.; Pécaut, J.; Charlot, M.-F.; Baffert, C.; Collomb, M.-N.; Deronzier, A.; Latour, J.-M. *Chem.—Eur. J.* **2008**, *14*, 3013.

(26) Caudle, M. T.; Riggs-Gelasco, P.; Gelasco, A. K.; Penner-Hahn, J. E.; Pecoraro, V. L. *Inorg. Chem.* **1996**, *35*, 3577.

(27) Hiatt, R. R.; Irwin, K. C.; Gould, C. W. *J. Org. Chem.* **1968**, *33*, 1430.

(28) Hiatt, R. R.; Mill, T.; Mayo, F. R. *J. Org. Chem.* **1968**, *33*, 1416.

(29) Chandra, S. K.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 760.

(30) Kessissoglou, D. P.; Li, X.; Butler, W. M.; Pecoraro, V. L. *Inorg. Chem.* **1987**, *26*, 2487.

(31) Chandra, S. K.; Basu, P.; Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 2423.

(32) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515.

(33) Limburg, J.; Vrettos, J. S.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W. *Science* **1999**, *283*, 1524.

(34) Gao, Y.; Åkermark, T.; Liu, J.; Sun, L.; Åkermark, B. *J. Am. Chem. Soc.* **2009**, *131*, 8726.

(35) McEvoy, J. P.; Gascon, J. A.; Batista, V. S.; Brudvig, G. W. *Photochem. Photobiol. Sci.* **2005**, *4*, 940.

(36) Pecoraro, V. L.; Baldwin, M. J.; Caudle, M. T.; Hsieh, W. Y.; Law, N. A. *Pure Appl. Chem.* **1998**, *70*, 925.

(37) Tagore, R.; Chen, H.; Zhang, H.; Crabtree, R. H.; Brudvig, G. W. *Inorg. Chim. Acta* **2007**, *360*, 2983.