Water Oxidation

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Cerium(IV)-Driven Water Oxidation Catalyzed by a Manganese(V)–Nitrido Complex[**]

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Abstract: *The study of manganese complexes as water-oxidation catalysts (WOCs) is of great interest because they can serve as models for the oxygen-evolving complex of photosystem II. In most of the reported Mn-based WOCs, manganese exists in the oxidation states III or IV, and the catalysts generally give low turnovers, especially with one-electron oxidants such as* Ce^{IV}*. Now, a different class of Mn-based catalysts, namely manganese(V)–nitrido complexes, were explored. The complex* $[Mn^V(N)(CN)_4]^{2-}$ *turned out to be an active homogeneous WOC using* $(NH_4)_2[Ce(NO_3)_6]$ *as the terminal oxidant, with a turnover number of higher than 180 and a maximum turnover frequency of 6 min*$^{-1}$*. The study suggests that active WOCs may be constructed based on the* $Mn^V(N)$ *platform.*

The search for efficient catalysts for the oxidation of water has been an important challenge for chemists in recent years.[1–3] Among the various transition-metal-based water-oxidation catalysts (WOCs), those based on manganese have received special attention because they can function as models for the catalytic Mn_4CaO_5 center in the oxygen-evolving complex (OEC) of photosystem II (PSII).[4–6] A variety of dimanganese and tetramanganese complexes were designed as models of the OEC in recent years.[7,8] However, few manganese complexes are efficient WOCs, especially with one-electron oxidants such as $[Ru(bpy)_3]^{3+}$ or Ce^{IV}.[9–13] So far, in most of the reported Mn-based WOCs, the Mn center exists in oxidation states III or IV. In search for more active catalysts, we explored a different class of Mn catalysts, namely manganese(V)–nitrido complexes. We report herein that the manganese(V)–nitrido compounds $[N(CH_3)_4]_2Na[Mn(N)(CN)_5]$ (**1**) and $(PPh_4)_2[Mn(N)(CN)_4]$ (**2**) are highly active homogeneous WOCs when $(NH_4)_2[Ce(NO_3)_6]$ (CAN) is used as the terminal oxidant, with a turnover number (TON) of higher than 180.

The six-coordinate complex **1** and the square-pyramidal complex **2** used in this work were prepared by Wieghardt and co-workers.[14] We recently reported that **2** is a highly efficient catalyst for the oxidation of alkanes, alkenes, and alcohols using H_2O_2 or CAN as the oxidant.[15,16] Based on experimental results and DFT calculations we proposed that the active intermediate is a Mn^{VII} nitrido oxo species, $[Mn^{VII}(N)(O)(CN)_4]^{2-}$, which is generated through O-atom transfer from H_2O_2 to Mn^V, or by proton-coupled electron transfer between Mn^V and Ce^{IV} ($Mn^V\text{-}OH_2 + 2\,Ce^{IV} \rightarrow Mn^{VII}{=}O + 2\,Ce^{III} + 2\,H^+$).[16] However, when **2** was dissolved in H_2O/CH_3CN without any organic substrate, O_2 evolution was readily observed upon the addition of CAN. Most water-oxidation experiments were carried out using the water-soluble complex **1** as the catalyst, which is predominantly present as the 5-coordinate $[Mn(N)(CN)_4]^{2-}$ ion in water (Supporting Information), and it gave a TON that was around 20% higher than that of **2** (Table 1, entries 6 and 8).

Table 1: Water oxidation by $Mn^V(N)$/CAN under various conditions.[a]

Entry	Cat./Conc.	O_2 [μmol]	TON[b]
1[c]	**1**/20 μM	0.96	6
2[d]	**1**/20 μM	0.96	6
3	**1**/10 μM	0.56	7
4	**1**/5 μM	0.48	12
5	**1**/1 μM	0.34	42
6	**1**/0.5 μM	0.52	130
7[e]	**1**/0.5 μM	0.73	183
8	**2**/0.5 μM	0.42	105
9[f]	**2**/0.5 μM	0.44	110

[a] Reaction conditions: [CAN] = 125 mM, $T = 25\,°C$, $t = 30$ min. For **1**, solvent was 8 mL 0.1 M HNO_3. For **2**, the catalyst was dissolved in 0.02 mL CH_3CN and added to 7.98 mL 0.1 M HNO_3. [b] TON = (mol of O_2 after subtracting the blank)/(mol of catalyst). 0.04 μmol of O_2 was produced in the absence of catalyst. O_2 was determined by GC-TCD. Each value is the average of at least three replicates. Error ±5%. [c] 93% of CAN (116 mM) remained after the catalysis, as determined by iodometric titration. [d] Pure water was used as solvent. [e] The catalyst was slowly added by syringe pump over 40 min. [f] 250 mM of CAN was used.

Table 1 shows the TONs for the oxidation of water by catalyst **1** and **2** under various conditions.[17] The evolved oxygen was detected by GC-TCD (TCD = thermal conductivity detector). A TON of 6 was observed when **1** and CAN were used in concentrations of 20 μM and 125 mM, respectively. The TON increased upon lowering the concentration of the catalyst, and a TON of 130 could be achieved using 0.5 μM of **1**, with a maximum turnover frequency (TOF) of 6 min^{-1} (Figure S1b). The TON further increased to 183 when a solution of **1** in 0.1M HNO_3 was slowly added to CAN using a syringe pump. The amount of O_2 that evolved also increased with the concentration of CAN (Figure S1a). When

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the reaction was carried out in $H_2{}^{18}O$ (98% ^{18}O-labeled), the evolved oxygen was 97% ^{18}O-labeled, as monitored by GC-MS.

The oxygen evolution from the **1**/CAN system was also continuously monitored by using a Clark-type electrode (Figure 1). The amount of O_2 increased with [**1**] and the initial rates depended linearly on [**1**], with a first-order rate constant of $(1.18 \pm 0.04) \times 10^{-2}\,s^{-1}$.

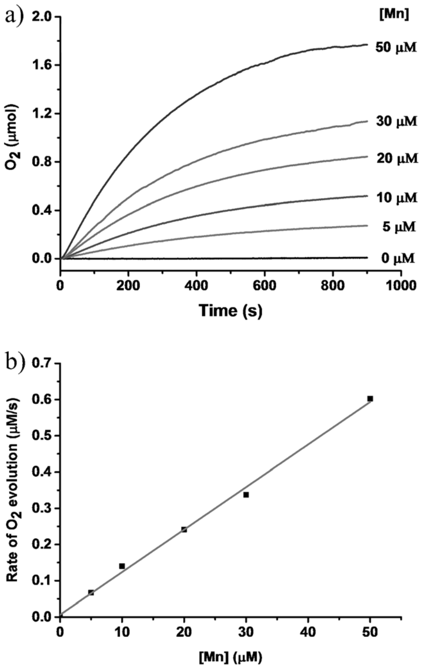


Figure 1. a) Plots of O_2 evolution versus time for water oxidation catalyzed by **1** at various concentrations using 125 mM Ce^{IV} as oxidant in 0.1 M HNO_3. b) Plot of initial rate of O_2 evolution versus the concentration of Mn ([Mn]).

In the catalytic oxidation of water, metal complexes may function only as precatalysts that are converted to metal oxides as the real catalysts.[18] In order to determine whether the catalytic oxidation by $[Mn(N)(CN)_4]^{2-}$ is homogeneous or heterogeneous, dynamic light scattering (DLS) experiments were performed to detect any particles formed during the oxidation of water. As shown in Figure S2 (Supporting Information), no particles were detected after 30 min upon adding **1** (30 or 100 µM in 0.1M HNO_3) to CAN (125 mM) in 0.1M HNO_3, which suggests that the catalysis is homogeneous. The DLS instrument we used can detect MnO_2 particles down to a concentration of 0.1 µM (Figure S2d). Hence for 100 µM of **1**, we would be able to detect particles even if only 0.1% of **1** has decomposed to MnO_x. Moreover, although MnO_x in various forms are known to be WOCs,[19] TONs (mol of O_2/mol of Mn) are in general smaller than 1 per hour at room temperature, whereas **1** can reach a TON of 180 within 30 min. Based on these results, we conclude that **1** functions as homogeneous, molecular catalyst for the oxidation of water by CAN.

The cyclic voltammogram of **1** in 0.1M HNO_3 showed a reversible electron transfer at 1.18 V versus SCE ($\Delta E =$ 60 mV), which we assigned to the $Mn^{VI/V}$ couple. This couple is independent of the pH value in the range of 1 to 7 (Figure 2, and Figures S3–S8 in the Supporting Information). On further scanning to a more positive potential, a catalytic current is observed, which is consistent with further oxidation to a Mn^{VII} species that oxidizes water on the CV time scale.

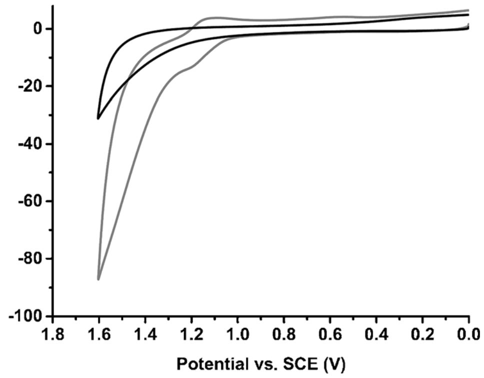


Figure 2. Cyclic voltammogram of **1** in 0.1 M HNO_3. Scan rate = 50 mV s^{-1}. SCE = saturated calomel electrode.

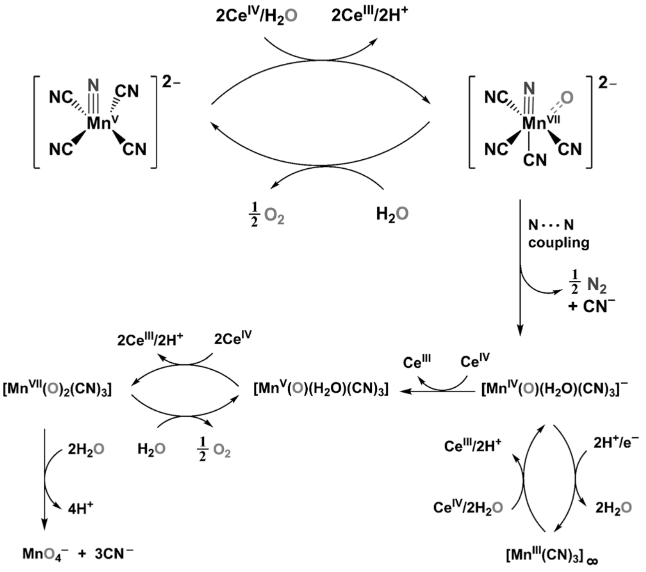
Although attempts to detect an active Mn^{VII} intermediate from **1**/CAN in water by ESI/MS were unsuccessful, we have previously been able to observe $[Mn^{VII}(N)(O)(CN)_4]^{2-}$ from the reaction of **2** with H_2O_2 in CF_3CH_2OH by ESI/MS.[16]

We also monitored the reaction of **1** with CAN by UV-Vis spectrophotometry. The reaction of **1** with 1 equiv of CAN immediately generated a species with λ_{max} at 435 nm, which gradually decayed with $t_{1/2}$ of approximately 30 s at 25°C (Figure S9a). This species was assigned as $[Mn^{VI}(N)(CN)_4]^-$ (or $[Mn^{VI}(N)(CN)_4(OH_2)]^-$). On the other hand, when 2 equiv of CAN were added, a species with λ_{max} at 409 nm was immediately observed (Figure S9b), which may be $[Mn^{VII}(N)(O)(CN)_4]^{2-}$. This species also decayed with a $t_{1/2}$ of around 30 s.

The observed increase in the TON with a decreasing concentration of the catalyst (Table 1) suggests that the Mn catalyst is deactivated through a bimolecular pathway. Nitrido complexes such as those of ruthenium[20] and osmium[21] are known to undergo an N···N coupling reaction, that is, $2\,M^{n}{\equiv}N \rightarrow 2\,M^{n-3} + N_2$. In order to detect any stoichiometric production of N_2, we used a relatively high concentration of **1** (2.5 mM) and treated it with 125 mM of CAN in 0.1M HNO_3 (8 mL). Under these conditions, we could detect N_2 in 85% yield (8.5 µmol), together with O_2 (23.4 µmol) using GC-TCD. When we used ^{15}N-labelled **2**, the N_2 that evolved was exclusively ^{15}N labeled (Figure S13), thus confirming the N···N coupling of a Mn(N) species formed between **1** and CAN, presumably *cis*-$[Mn^{VII}(N)(O)(CN)_4]^{2-}$. The product of this coupling reaction could be isolated as a pale orange precipitate upon addition of 2 equiv of CAN to an aqueous solution of **1**. The solid is insoluble in water and common organic solvents. Elemental analysis is consistent with the formula $Mn(CN)_3{\cdot}2H_2O$ (**3**). The IR spectroscopic analysis showed a single ν(CN) band at 2183 cm^{-1}. The observed magnetic moment of $\mu_{eff} = 4.91$ BM (Gouy method) is consistent with high-spin Mn^{III} ($S = 2$). These results suggest that compound **3** is probably a 3D cyano-bridged Mn^{III} coordination polymer.

Compound **3** readily redissolved upon adding CAN in 0.1 M HNO_3, and oxygen evolved, which was monitored by a Clark electrode (Figure S14). However, it is a much less efficient catalyst than **1**, with a maximum TON of 2.4.

Based on our experimental results, Scheme 1 shows the proposed water oxidation and catalyst deactivation reactions that occur upon adding **1** to CAN.[22] $[Mn^{V}(N)(CN)_4]^{2-}$ (which is probably better formulated as $[Mn^{V}(N)(CN)_4(OH_2)]^{2-}$ when dissolved in water) is oxidized by Ce^{IV} to *cis*-$[Mn^{VII}(N)(O)(CN)_4]^{2-}$, which then oxidizes H_2O to give O_2. The Mn^{VII} species also undergoes parallel N···N coupling to give a $Mn^{IV}(O)$ species and N_2. In the presence of excess Ce^{IV}, $Mn^{IV}(O)$ is presumably oxidized to a Mn^{VII} dioxo species, which can also oxidize water, but will decompose to give MnO_4^- after two to three turnovers. Monitoring the catalysis by UV-Vis spectrophotometry shows the gradual appearance of signals that are characteristic for MnO_4^- (Figure S15). In the absence of excess Ce^{IV}, the $Mn^{IV}(O)$ species may decompose to a $[Mn^{III}(CN)_3]_n$ polymer. According to this proposed scheme, the main catalyst deactivation pathway should be the N···N coupling of the active $Mn^{VII}(N)(O)$ species, and the coupling product eventually decomposes to MnO_4^-. As the coupling is a bimolecular process, the use of a lower catalyst concentration together with the slow addition of the catalyst to CAN would slow down the coupling process and result in a higher TON for the water oxidation. Such a phenomenon is also fully consistent with molecular catalysis; if the complex is just a precatalyst that decomposes to give MnO_x or a cyano-bridged oligomer as the real catalyst, then the amount of oxygen produced should not increase when the catalyst concentration is decreased.



Scheme 1. Proposed mechanisms for water oxidation and catalyst deactivation.

In conclusion, we have demonstrated that $[Mn^{V}(N)(CN)_4]^{2-}$ is an active molecular water-oxidation catalyst using CAN as the terminal oxidant, with a TON of higher than 180, which is more than 10 times higher than reported $Mn^{II/III}$ catalysts and various forms of MnO_x. We anticipate that a new class of robust Mn-based catalysts for the oxidation of water may be constructed based on $Mn^{V}(N)$ platform, for example by using bulky multidentate ancillary ligands to prevent N···N coupling and ligand dissociation, and/or by entrapping the $Mn^{V}(N)$ catalyst into a metal–organic framework.[12]

Keywords: cerium · homogeneous catalysis · manganese complexes · nitrides · oxidation

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[17] Catalysts **1** and **2** are unstable at low pH values and will eventually precipitate out from solution as a purple solid. Stock solutions of **1** were prepared in pure water and **2** in CH_3CN, and they are stable for days in these solutions. The stock solutions were added to CAN in 0.1 M HNO_3 to start the catalysis, and as the catalytic water oxidation is usually complete within 20 min,

the decomposition of the catalyst in acidic solution is a minor pathway.

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[22] The exact number of cyanide ligands in the proposed Mn intermediates is uncertain. As water oxidation is carried out in an acidic medium, protonation and loss of a cyanide ligand as HCN can be facile. Cyanide may also be oxidized to cyanate. Cyanide loss and oxidation may also contribute to catalyst deactivation.

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