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Photocatalysis

Photosensitized Water Oxidation by Use of a Bioinspired Manganese Catalyst**

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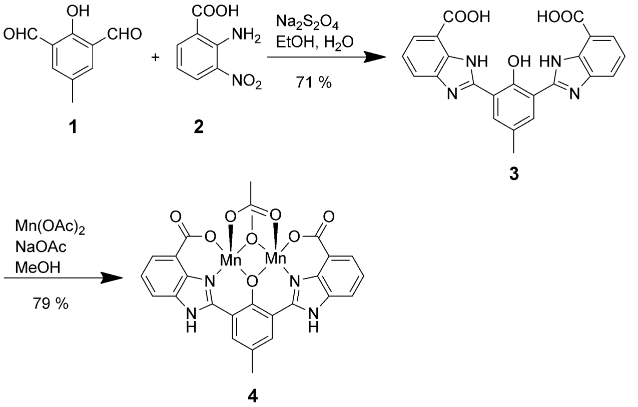
The search for renewable and clean energy sources is one of the most important challenges of the 21st century.[1–3] The utilization of sunlight is an environmentally friendly alternative, and together with nuclear fusion, it is the only sustainable and carbon-free energy source with sufficient potential to replace fossil fuels and satisfy future energy demands. A promising approach is to mimic nature and develop a system for artificial photosynthesis that converts water into oxygen and hydrogen gas. The key determinant for a breakthrough is the development of an efficient catalyst for water oxidation. Although a series of catalysts based on ruthenium have been developed,[4–15] catalysts based on earth-abundant metals are rare. However, a few catalysts based on cobalt[16,17] and iron[18] have been reported.

Homogeneous manganese-containing complexes have been widely studied as models of the oxygen-evolving center (OEC) in photosystem II, but only a few of these complexes have been reported to evolve oxygen gas, mainly by using oxygen atom donors such as HSO_5^-, NaOCl, and *t*BuOOH.[19–26] However, none of these complexes has been shown to oxidize water catalytically when using single-electron oxidants under homogeneous conditions. Herein we describe complex **4** (Scheme 1), which is the first manganese complex capable of oxidizing water to oxygen in homogeneous solution when using a single-electron oxidant, $[Ru(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine). Complex **4** also catalyzes the photochemical oxidation of water when using a $[Ru(bpy)_3]^{2+}$-type photosensitizer and $Na_2S_2O_8$ as electron acceptor.



Scheme 1. Synthesis of ligand **3** and complex **4**.

We have previously prepared a dinuclear manganese complex that is capable of delivering three electrons to a photochemically generated electron acceptor.[27] In this process, the complex was oxidized from $Mn_2^{II,II}$ to $Mn_2^{III,IV}$. A fourth electron transfer probably takes place, just as in the OEC, but leads to oxidative decomposition of the catalyst rather than water oxidation. A probable decomposition pathway could start with oxidation of the benzylic amines in the ligand.

We have therefore prepared complex **4**, which is based on a new ligand, **3**, that contains imidazole groups in place of the benzylic amines present in many previously reported manganese complexes (Scheme 1).[21,27,29] The ligand also contains negatively charged carboxylate groups, shown to dramatically reduce the redox potentials of the metal center,[14,15,28,29] which is required for use in a catalytic system with $[Ru(bpy)_3]^{2+}$-type photosensitizers. It is interesting to note that both imidazole and carboxylate groups act as ligands in the OEC.[30,31] Ligand **3** was prepared from commercially available starting materials (dialdehyde **1** and amine **2**) by combined condensation and reductive cyclization. Complexation with manganese(II) acetate afforded complex **4** in an overall yield of 56 % (Scheme 1). Complex **4** was characterized by ESI-MS (Figure S12 in the Supporting Information) and elemental analysis.

Crystals suitable for X-ray structure determination were obtained by heating complex **4** to reflux in methanol followed by crystallization at room temperature, which resulted in loss of the bridging acetate ion and formation of an S_2-symmetric dimer, **5** (Figure 1). Interestingly, this structure has four proximate Mn atoms that are bridged by oxygen atoms, reminiscent of the Mn_4Ca cluster in the OEC. Based on bond

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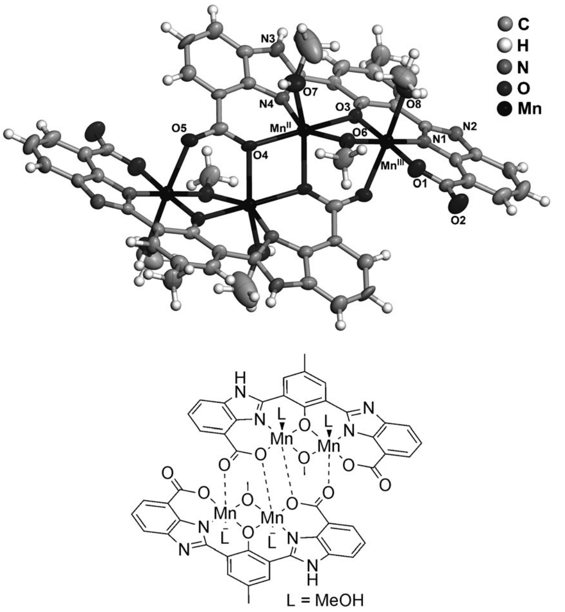

Figure 1. X-ray crystal structure of dimer **5** at 50% probability level (upper) and structural formula of **5** (lower).

valence calculations (Table S1), the oxidation states of the two unique Mn atoms were determined to be Mn^{II} and Mn^{III}. In the same way, O3 and O6, which are coordinated to both Mn atoms, were determined to be deprotonated, while O7 and O8 are protonated. Considering hydrogen bonds in the crystal structure (Table S2), one proton was added to N3 to form a hydrogen bond with O2 while there is no proton on N2 since it acts as acceptor for the hydrogen bonds with O7 and O8. Since no additional ions were found in the crystal structure, dimer **5** was considered to be neutral, which also is in accordance with the above-mentioned oxidation and protonation states.

The catalytic activity of complex **4** was investigated by addition of a 480-fold excess of the single-electron oxidant $[Ru(bpy)_3](PF_6)_3$ in phosphate buffer (0.1 M, pH 7.2). The reaction was performed in an evacuated reaction vessel connected to a mass spectrometer (see the Supporting information). Oxygen evolution was detected with an initial turnover frequency (TOF = amount of O_2/(amount of **4** × time)) of approximately $0.027\,s^{-1}$, which lasted for about 1 hour, thus giving a turnover number (TON = amount of O_2/amount of **4**) of approximately 25 (Figure 2). A control experiment using manganese(II) acetate in the absence of ligand **3** gave only substoichiometric amounts of oxygen (Figure S9). In another control experiment, buffer solution was added to $[Ru(bpy)_3](PF_6)_3$, which resulted in decomposition of the oxidant without any detectable oxygen production. However, a small amount of carbon dioxide was produced.

In principle, decomposition of the oxidant could generate a ruthenium species that could react with ligand **3** to give an active catalyst. When a solution of ligand **3** in phosphate buffer was added to $[Ru(bpy)_3](PF_6)_3$, no oxygen evolution was observed, thus confirming that manganese complex **4** is necessary for the catalytic activity. Furthermore, the absence of an induction period when catalyst **4** was used could be an indication that the active catalyst is present from the beginning of the reaction, and is thus not produced by decomposition. Finally, to demonstrate that the produced dioxygen indeed originates from water, the experiment was repeated with ^{18}O-labeled water (Figure S10). With a relative ^{18}O concentration of 5.8%, the ratio $^{16,18}O_2/^{16,16}O_2$ was found to be 0.10, which is close to the theoretical value 0.12 $(=2(1-0.058)\,0.058/(1-0.058)^2)$, when both oxygen atoms are derived from water.

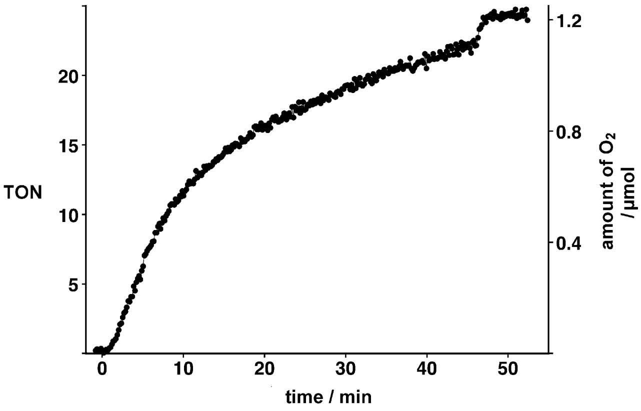

Figure 2. Oxygen evolution using $[Ru(bpy)_3]^{3+}$ as stoichiometric oxidant. A solution of complex **4** (0.5 mL, 84 µM) in phosphate buffer (0.1 M, pH 7.2) was added to $[Ru(bpy)_3](PF_6)_3$ (20 mg, 20 µmol) at $t=0$. The jump at $t=45$ min is due to bursting of gas bubbles.

Light-induced oxygen formation was also studied. In these experiments, $[Ru(bpy)_3](PF_6)_2$ was initially used as photosensitizer, and give a TON of approximately 1. However, when using $[Ru(bpy)_2(deeb)](PF_6)_2$ (deeb = 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine) as photosensitizer, and thereby increasing the Ru$^{III/II}$ redox potential from +1.26[14] to +1.40 V[32] versus the normal hydrogen electrode (NHE), oxygen evolution occurred with a TON of approximately 4 (Figure 3). Several control experiments were performed.

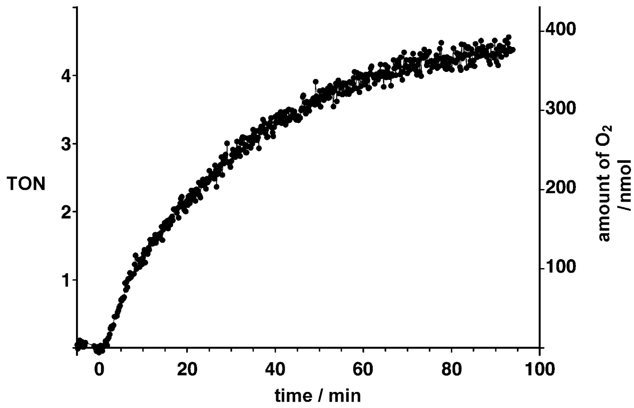

Figure 3. Light-driven oxygen evolution catalyzed by complex **4**. A solution of complex **4** (1.0 mL, 84 µM) in phosphate buffer (0.1 M, pH 7.2) was added to $Na_2S_2O_8$ (4.7 mg, 20 µmol) and $[Ru(bpy)_2(deeb)](PF_6)_2$ in acetonitrile (50 µL, 10 mM). The light was switched on at $t=0$.

Under identical conditions, no oxygen was produced in the absence of catalyst **4**. Omitting the photosensitizer resulted in no oxygen evolution, and switching off the light terminated oxygen evolution, thus confirming that complex **4** and the photosensitizer are essential for the light-induced water oxidation.

The properties of complex **4** in solution were studied in the presence of K_3PO_4 by ^1H NMR spectroscopy and X-band EPR spectroscopy in D_2O and H_2O, respectively (Figures S1–S8). The relatively narrow chemical shift range in combination with the absence of any EPR signal at 77 K indicate the presence of an antiferromagnetically coupled $Mn_2^{III,III}$ complex with a singlet ground state, that is, the $Mn_2^{II,III}$ complex **4** was oxidized to $Mn_2^{III,III}$ by atmospheric oxygen because the redox potential is lowered as the pH value is increased. The broadening of the NMR signals could be attributed to the population of excited spin states at ambient temperature. During the course of the water oxidation, the complex is expected to cycle between the initial $Mn_2^{III,III}$ oxidation state and $Mn_2^{V,V}$. In contrast with the EPR experiments in aqueous solution, where the complex had been oxidized to $Mn_2^{III,III}$, the spectrum recorded in dimethyl sulfoxide (DMSO) at 77 K shows a broad (100 mT) signal at $g = 2.0$ (Figure S11), which is indicative of a $Mn_2^{II,III}$ complex.[33] This signal is overlapped by a sharp six-line signal from trace amounts of free Mn^{2+} ions in solution. A similar broad signal from $Mn_2^{II,III}$ was also observed upon reduction of the $Mn_2^{III,III}$ complex in aqueous solution by addition of ascorbic acid (Figure S11). In this spectrum, the six-line signal from free Mn^{2+} ions is absent, thus indicating that the ligand backbone of complex **4** is intact in solution under conditions similar to those used in the water oxidation experiments.

The NMR spectra recorded at 25 °C and low concentrations (1.4–2.8 mM**)** of complex **4** show three broad signals with chemical shifts of 7.52, 7.31, and 6.69 ppm, which correspond to the aromatic protons of the ligand (Figures S1 and S2). The sharp signals at 3.34, and 1.90 ppm correspond to methanol and acetate ions, respectively, which are released into solution upon dissolution of complex **4** in D_2O in the presence of K_3PO_4. The chemical shifts of the aromatic protons were shown to be essentially independent of the concentration of complex **4** (Figures S1–S4), which again indicates that the backbone of complex **4** is intact in solution, that is, there is no rapid equilibrium between the complex and the uncoordinated ligand. However, at higher concentrations (5.6–8.5 mM), a set of three new, very broad signals was observed (Figures S3 and S4). This feature could be attributed to an equilibrium between the monomeric and dimeric forms in solution. At low concentrations, the monomer should be favored, thus giving rise to the initial set of three signals, while at higher concentrations a mixture of monomer and dimer could be observed. In addition, NMR spectra recorded at different temperatures (5, 25, 50, and 80 °C) indicate that the dimerization is favored at higher temperatures (Figures S5–S8), possibly because of entropic effects as coordinated solvent molecules are released into solution. The changes with temperature are reversible and on cooling to 25 °C, the spectrum at 80 °C (Figure S8) reverts to the spectrum at 25 °C (Figure S6).

In conclusion, we have reported a homogeneous manganese-based catalyst **4**, which is capable of catalyzing oxidation of water to molecular oxygen in the presence of a single-electron oxidant $[Ru(bpy)_3]^{3+}$. More importantly, **4** also catalyzes photochemical water oxidation when using either $[Ru(bpy)_3]^{2+}$ or the related $[Ru(bpy)_2(deeb)]^{2+}$ complex as photosensitizer. A major difference between catalyst **4** and a series of related catalysts developed by us and other research groups is that the benzylic amine function has been replaced by imidazole, thus making the ligand more resistant towards oxidation. Furthermore, it may be even more important that imidazole, as in many natural systems, can promote proton-transfer reactions as the oxidation states of the manganese atoms change.

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