

**S38-007**

## **High-valent Ruthenium-Manganese Complexes for Solar Energy**

### **Production.**

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*Keywords:* biomimetics, manganese, ruthenium, Photosystem II

### **Introduction.**

In oxygenic photosynthesis, Photosystem II (PSII), extracts electrons from water, that are necessary to reduce CO<sub>2</sub> to carbohydrates. Water oxidation is catalyzed by the water oxidizing complex (WOC), which involves a redox active tyrosine, Tyr<sub>Z</sub>, and a cluster of four Mn ions functioning as a charge storing device for oxidizing equivalents. The manganese cycles through five oxidation states, and in the highest state the cluster is believed to have three Mn<sup>IV</sup> and one Mn<sup>III</sup>. Tyrosine<sub>Z</sub> participates possibly by abstracting protons and/or hydrogen atoms from metal-bound water molecules. To mimic the properties of the WOC, we have coupled a Ru<sup>II</sup> *tris*-bipyridine (Ru<sup>II</sup>(bpy)<sub>3</sub>) photosensitizer to a redox active moiety, containing one manganese ion, in a series of compounds (Sun et al. 1997). In all these compounds, we have observed light induced electron transfer from the Mn ion to the photooxidized Ru moiety in the presence of external electron acceptors.

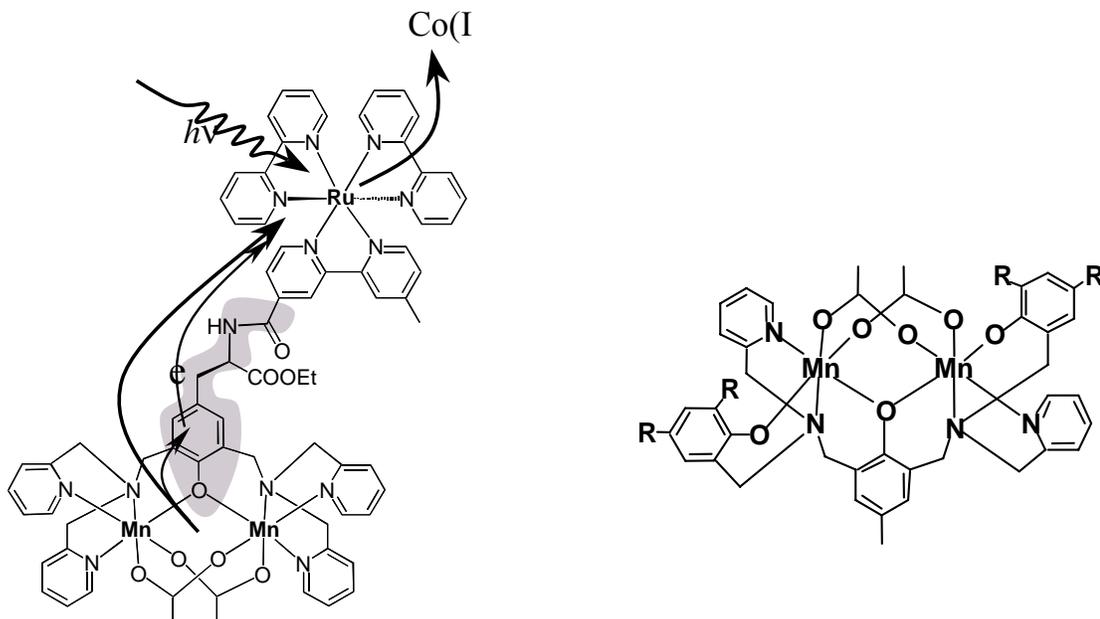
In the present paper, we describe the structure and properties of two new, Mn containing compounds. In the first compound, we have coupled a dimeric Mn complex, the Mn<sub>2</sub><sup>II,II</sup>-bpmp (bpmp = 2,6-bis[[*N*, *N*-di(2-pyridylmethyl)amino]methyl]-4-methylphenol) dimer, to a Ru<sup>II</sup>(bpy)<sub>3</sub> center via a modified L-tyrosine, to form compound **1** (Figure 1). In a functional artificial system, as in nature, we believe that the manganese complex must reach high oxidation states. We therefore investigated this capability in **1** by flash photolysis in the presence of electron acceptors.

To take the biomimicking properties further, and increase the number of oxygen ligands for the metal, we then constructed phenolate-containing Mn ligands. The increased oxygen-to-nitrogen ratio provides more negative charges at the Mn ions, than the bpmp ligand, and would be better at stabilizing higher oxidations of the manganese. For this purpose, the Mn ligand in **1** was modified by introducing a phenol group into the dpa arm, forming compound **2** (Figure 2). The ligand in **2** also coordinates two manganese ions, forming a Mn<sup>III,III</sup> dimer. Introduction of the anionic phenolate into the ligand is expected to increase the possibility of storing more oxidizing equivalents in the Mn complex, and thus also increase the possibility of forming the intermediates necessary for water oxidation.

In the present work we describe the characterization of the spectroscopic and chemical properties of **1** and **2**, by cyclic voltammetry and EPR.

## General methods.

Synthesis and basic characterization of **1** was described in Sun et al. 2000. The synthesis of **2** will be described elsewhere. **1** and **2** were analyzed with ESI-MS, elementary analysis, cyclic voltammetry, spectroelectrochemistry and EPR spectroscopy. All EPR spectra were recorded at liquid He temperatures with a Bruker E500 spectrometer equipped with a rectangular dual-mode resonator and an Oxford ESR900 cryostat. Samples were dissolved in neat acetonitrile or in a mixture of acetonitrile and buffered water at pH 7.0. Flash photolysis experiments were performed with a Spectra-Physics Nd/YAG laser operating at a frequency of 5Hz.



**Figure 1.** The trinuclear complex **1**, containing a  $\text{Mn}^{\text{II,II}}$  dimer linked to  $\text{Ru}(\text{bpy})_3$ . Under illumination, an electron is transferred from Ru to the acceptor, and the Ru is re-reduced by the Mn complex. The direction of electron transfer is indicated by arrows.

**Figure 2.** The dinuclear complex **2**, a di- $\mu$ -carboxylato bridged  $\text{Mn}^{\text{III,III}}$  dimer, similar to the Mn-moiety in **1**, but with three phenolic Mn ligands instead of one.

## Results and Discussion.

### i) Complex 1.

Under illumination, the excited  $\text{Ru}^{\text{II}*}(\text{bpy})_3$  in **1** can reduce an external electron acceptor (Sun et al 2000). The  $\text{Ru}^{\text{III}}$  then retrieves an electron via intramolecular electron transfer ( $k_{\text{ET}} > 1 \times 10^7 \text{ s}^{-1}$ , see also Figure 1). In this study, we performed flash photolysis experiments in a solvent mixture of acetonitrile and buffered water. Flash photolysis was first performed on a  $\text{Mn}_2^{\text{II,II}}$ -bpmp dimer, identical to that in complex **1**, with a simple  $\text{Ru}(\text{bpy})_3$  as photosensitizer and  $\text{Co}^{\text{III}}$ -pentaamine as external electron acceptor. The sample was analysed with EPR after photolysis. The spectrum in the dark was dominated by signals from the magnetically coupled  $\text{Mn}^{\text{II}}$  ions in the dimer. After successive flashes, more electrons were transferred from the Ru moiety to the acceptor, which then displayed an EPR signal. At the same time, the Mn dimer

became stepwise more and more oxidized. The  $\text{Mn}^{\text{II,II}}$  dimer EPR spectrum was replaced by a 1300 Gauss wide signal, with 16 hyperfine lines, typical for the  $\text{Mn}_2^{\text{III,IV}}$  state. A similar experiment was repeated with the trinuclear complex **1**. The results were very similar, with the  $\text{Mn}^{\text{III,IV}}$  EPR spectrum growing in after successive flashing.

Cyclic voltammetry measurements showed that the  $\text{Mn}^{\text{II,II}}$  dimer could reach the  $\text{Mn}_2^{\text{II,III}}$  and  $\text{Mn}_2^{\text{III,III}}$  oxidation states in dry organic solvents. The Mn dimer displayed a 2300 Gauss “multiline” EPR signal, typical for a strongly coupled  $\text{Mn}^{\text{II,III}}$  dimer, after the first oxidative voltammetry wave, which was completely reversible. However, in order to go beyond the  $\text{Mn}^{\text{III,III}}$  and reach the  $\text{Mn}_2^{\text{III,IV}}$  state, it was necessary to include water in the reaction mixture or electrolyte. Only then did the voltammogram display a third wave at a potential of ca +1.0 V. The ligand molecule itself, without metal, was not oxidized at this potential. It is clear that the presence of water is essential to reach the higher oxidation state in **1**. Since di- $\mu$ -carboxylato bridged Mn dimers such as these often undergo ligand exchange reactions (Boelrijk et al. 2000), it is likely that exchange of the bridging acetate groups for water, followed by formation of  $\mu$ -oxo bridges, is an essential step in the formation of the  $\text{Mn}_2^{\text{III,IV}}$  state.

When **1** was electrochemically or chemically oxidized to form  $\text{Mn}_2^{\text{II,III}}$  and  $\text{Mn}_2^{\text{III,III}}$ , we did not observe any formation of  $\text{Mn}^{\text{III,IV}}$  from disproportionation. Therefore, the photochemical generation of  $\text{Mn}_2^{\text{III,IV}}$  in **1** is a direct result of light-induced intramolecular electron transfer to the Ru moiety from the Mn dimer.

#### ii) Complex 2.

In complex **2**, cyclic voltammetry was first performed in dry acetonitrile, then repeated in a water/acetonitrile mix. The starting compound was found by elemental analysis to be in the  $\text{Mn}^{\text{III,III}}$  state, and from it the  $\text{Mn}^{\text{II,II}}$  and  $\text{Mn}^{\text{II,III}}$  states could be afforded by reductive electrolysis at -0.3 V and 0.06 V respectively. The EPR as well as optical spectra confirmed the nature of the reduction products. In the other direction, the  $\text{Mn}^{\text{III,IV}}$  state could be reversibly formed, by electrolysis at a potential of +0.92 V. At a closeby potential, ca +1.25V, an additional oxidation took place. This reaction resulted in the formation of magnetically uncoupled  $\text{Mn}^{\text{IV}}$ , observed both by EPR and supported by optical spectroscopy. Thus, both Mn ions in compound **2** reached the  $\text{Mn}^{\text{IV}}$  state at the higher potential, but also larger structural rearrangements seemed to take place, since the Mn ions were magnetically uncoupled from each other in this oxidation state.

Flash photolysis was performed for **2** in an aqueous medium, similar to that for **1**.  $\text{Ru}(\text{bpy})_3$  was used as photosensitizer, and  $\text{Co}^{\text{III}}$ -pentaamine chloride was used as electron acceptor. Very similar to the results with cyclic voltammetry, the  $\text{Mn}^{\text{III,IV}}$  state was reached by light-induced electron transfer, and after subsequent flashing the uncoupled  $\text{Mn}^{\text{IV}}$  state was observed. In addition to this, the EPR signal from an organic radical could be observed around  $g=2$ , under the same circumstances as the monomeric  $\text{Mn}^{\text{IV}}$  species. The radical possibly originates from the ligand molecule. Since the ligand contains three phenolates, it is tempting to suggest that the observed radical originates from the phenol.

### Conclusion.

The trinuclear compound **1** undergoes several intramolecular electron transfer reactions when illuminated, which results in stepwise oxidation of the Mn dimer. The highest oxidation state we have observed is the  $\text{Mn}^{\text{III,IV}}$  state, which is reached at a potential close to +1 V.

Compound **2**, which so far is not covalently connected to the Ru-moiety, can also reach several oxidation states, the highest seemingly being a magnetically uncoupled  $\text{Mn}^{\text{IV}}$  – containing complex. Then, an additional “oxidation state” could be observed, in which an

organic radical, possibly a phenolic radical, was formed. This is highly interesting from a biomimicking point of view, since a tyrosine radical is essential for the natural water oxidation process. In PSII, the tyrosine radical is decidedly formed in the higher (“late”) oxidation states of the catalytic cycle, where the  $\text{Tyr}_Z^\bullet/\text{S}_2'$  state is in equilibrium with the  $\text{S}_3$  state (Geijer et al., see also Bernát et al., these proceedings). If a similar equilibrium can be formed in **2**, we are perhaps closer than ever in creating a compound which truly mimicks the water oxidizing center in PSII.

### Acknowledgements.

This project was financed by grants from the Knut and Alice Wallenberg Foundation, The Swedish National Energy Administration, the Delegation for Energy Supply in South Sweden (DESS), the Swedish Natural Science Research Council (NFR), the Swedish Research Council for Engineering Sciences (TFR), the European TMR Programme (TMR network CT96-0031) and the Nordic Energy Research Programme.

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