Electrochemical Interconversion of Mono-, Bi-, and Tetranuclear (Bipyridyl) Manganese Complexes in Buffered Aqueous Solution

Marie-Noëlle Collomb Dunand-Sauthier,*
Alain Deronzier,* and Xavier Pradon

*Laboratoire d'Electrochimie Organique et de
Photochimie Rédox, Université Joseph Fourier
UMR CNRS 5630, BP 53
38041 Grenoble Cédex 9, France*

Stéphane Ménage

*Laboratoire d'Etudes Dynamiques de la Structure
et de la Sélectivité, Université Joseph Fourier
UMR CNRS 5616, BP 53
38041 Grenoble Cédex 9, France*

Christian Philouze

*Laboratoire de Chimie Inorganique, URA CNRS 420
Institut de Chimie Moléculaire d'Orsay
Université Paris-Sud, 91405 Orsay, France*

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The photosynthetic oxidation of water at the oxygen evolving center in photosystem II is believed to occur at a tetranuclear oxomanganese cluster that can undergo sequential redox steps.[1] Much effort has been devoted over the last 10 years to designing μ-oxo-bridged manganese complexes in order to mimic the structure and the magnetic properties of this natural active center.[2] In contrast, few studies on the ability of these molecular models to act as catalysts for water oxidation have been published. Only the mixed-valence binuclear $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ (**1**) (bpy = 2,2′-bipyridine) and the analogous 1,10-phenanthroline in a solid phase have been reported to be associated with the generation of O_2 from water.[3] The assumed active species is $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$. This result, however, has not been corroborated as yet.[4] Despite this putative catalytic redox activity, knowledge about the electrochemical behavior of **1** in aqueous solution remains unclear.

In a nonaqueous medium (CH_3CN) the cyclic voltammogram of **1** exhibits a reversible 1-electron oxidation wave leading to the IV, IV species ($E_{1/2} = 1.32$ *vs* ECS) and a poorly reversible 1-electron reduction wave ($E_{1/2} = 0.36$ V), corresponding to the III, III state.[5] This latter unstable species in subsequent chemically coupled reactions affords, at least in large part, the mononuclear complex $[Mn^{II}(bpy)_3]^{2+}$ (**2**).[6] Moreover, **2** can be electrochemically converted into the binuclear mixed-valence complex **1** in this medium oxidatively, through the participation of residual water.[7]

In aqueous solution **1** is stable only in the presence of bipyridyl buffer (bpy/bpyH$^+$) in the pH range 4.3−5.4.[4,5a] The use of pure aqueous solutions or other buffers like acetate or phosphate causes very rapid decomposition of the complex. This decompositon is reflected in a deep color change, the initial green solution turning red in a few seconds. Previous electrochemical measurements in an aqueous medium have been performed only with unstabilized samples,[8] for instance in aqueous phosphate solution where partial disproportionation occurs.[9] Thus, in this paper the electrochemical behavior of **1** is studied in buffered bpy/bpyH$^+$ solution at pH 4.5. Furthermore, we report an original electrochemical method to prepare selectively high-valent polynuclear oxomanganese such as **1** and the linear tetranuclear $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ [10] (**3**) complexes from the mononuclear one (**2**) in this specific medium. We have also investigated associated back-transformations.

At a suitably polished vitreous carbon electrode,[11a] the shape of the cyclic voltammogram of **1** (2 mM) in bpy buffer[11b] is in close correspondence to that obtained in CH_3CN with a quasi-reversible oxidation wave at $E_{1/2} = 1.16$ V ($\Delta E_p = 90$ mV) and an irreversible reduction peak at $E_{pc} = 0.40$ V *vs* Ag/AgCl (Figure 1A). To characterize the respective final products issued from the oxidation and the reduction of this complex, exhaustive electrolyses have been carried out. An exhaustive oxidation of the solution at 1.25 V leads to a pronounced color change (green to red-brown), accompanied by the disappearance of the quasi-reversible system at $E_{1/2} = 1.16$ V while the irreversible peak at 0.40 V persists (Figure 1B). Unlike the electrochemical behavior of this complex in CH_3CN,[5a] the oxidized $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$ species is not stable on the time scale of the electrolysis, indicating that a chemical reaction is coupled to the electron transfer. This oxidized species has been identified as the tetranuclear cluster **3**, with a linear $[Mn_4O_6]^{4+}$ core previously prepared chemically from $Mn^{III}(bpy)Cl_3(H_2O)$ by Girerd et al.[10] In this case, formation of this tetranuclear cluster probably results from the association of two $[Mn_2^{IV,IV}O_2(bpy)_3]^{4+}$ units issued from the decoordination of one bpy ligand of the initially electrochemically formed $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$ species. The two bridging μ-oxo anions result from water deprotonation. Equation 1 summarizes the overall process.

$$2[Mn_2^{III,IV}O_2(bpy)_4]^{3+} + 2H_2O \rightleftarrows$$
$$[Mn_4^{IV}O_6(bpy)_6]^{4+} + 2bpy + 4H^+ + 2e^- \quad (1)$$
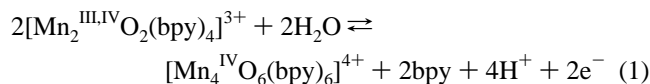
Electro- and spectrochemical characteristics of the resulting oxidized solution are identical to those of an authentic sample of **3** in the same medium. The cyclic voltammogram of **3** in

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(2) See for instance: Manchanda, R.; Brudvig, G. W.; Crabtree, R. H. *Coord. Chem. Rev.* **1995**, *114*, 1−38 and references therein.
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(10) (a) Philouze, C.; Blondin, G.; Ménage, S.; Auger, N.; Girerd, J.-J.; Vigner, D.; Lance, M.; Nierlich, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1629−1631. (b) Philouze, C.; Blondin, G.; Girerd, J.-J.; Guilhem, J.; Pascard, C.; Lexa, D. *J. Am. Chem. Soc.* **1994**, *116*, 8557−8565.
(11) (a) Working electrodes for cyclic voltammetry and exhaustive electrolysis were, respectively, a vitreous carbon disk (5 mm diameter) carefully polished with 1 μm diamond paste and rinsed with ethanol before each potential run and a carbon felt piece (10 × 10 × 4 mm; RCV 2000 from Le Carbone Lorraine). The Ag/AgCl/3 M KCl was used as the reference electrode. Potential referenced to that system can be converted to the SCE by adding 20 mV. Previous attempts to examine the cyclic voltammogram with a platinum working electrode in an aqueous bpy buffer medium failed owing to the large background current from the competing oxidation of water.[5a] (b) All electrochemical experiments were performed in buffered solutions with bpy/bpyH$^+$ mixtures; the total concentration [bpy] + [bpyH$^+$] was 0.050 M, and the pH was adjusted to 4.5 by addition of HNO$_3$. The most clearly defined cyclic voltammograms were obtained with NaBF$_4$ as additional electrolyte *vs* NaNO$_3$ or Na$_2$SO$_4$. The use of NaClO$_4$ induced the partial precipitation of **1**.
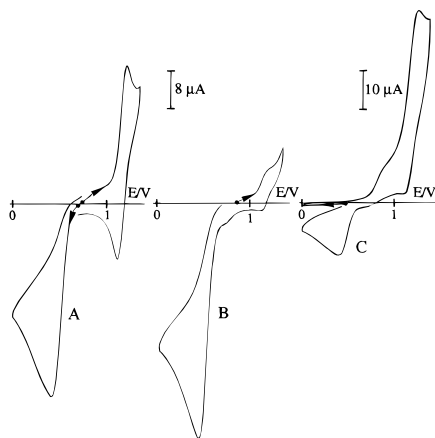
Figure 1. Cyclic voltammograms in aqueous 0.05 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M NaBF$_4$ at a carbon electrode (scan rate 20 mV s^{-1}) (A) of a 2 mM solution of [Mn$_2^{III,IV}$O$_2$(bpy)$_4$]$^{3+}$ (**1**), (B) after oxidation at 1.25 V of (A), and (C) of a 2 mM solution of [Mn(bpy)$_3$]$^{2+}$ (**2**).
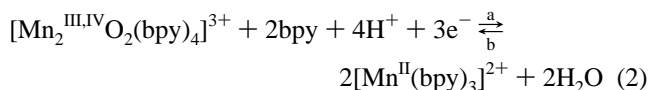
bpy buffer shows only an irreversible reduction peak at $E_{pc} = 0.40$ V.[12] The absorption spectrum, after exhaustive oxidation of a solution of **1** (2 mM), is closely surperimposable with that of **3** (1 mM) ($\lambda_{max} = 780$, 670 (sh), and 425 (sh) nm), which demonstrates that the transformation is quasi-quantitative. The oxidized solution is EPR inactive at helium temperature, according to the $S = 0$ ground spin state of **3**.[10] Moreover, this electrogenerated tetranuclear complex can be precipitated by addition of a large excess of NaBF$_4$ (2 M) to the oxidized solution. After filtration, the resulting brown powder (yield 55%) exhibits the same characteristics as a chemically prepared authentic sample of **3**.[13]

It should be noted that theoretically the oxidation involves 1 electron per molecule of binuclear complex **1**. In practice, after approximately 2–3 electrons have been consumed (depending on the experimental conditions), about 5% of the initial complex remains in solution (Figure 1B). Additional consumption of electrons does not produce the total disappearance of this complex. That the observed excess of coulometry is due to a slow, competitive oxidation of the electrolyte at this potential has been established by a separate experiment conducted in the absence of **1**.

On the other hand, exhaustive reduction of a solution of **1** at 0.20 V consumes 3 electrons per molecule of **1** and produces quantitatively the mononuclear **2,** following reaction 2a. The

$$[Mn_2^{III,IV}O_2(bpy)_4]^{3+} + 2bpy + 4H^+ + 3e^- \underset{b}{\overset{a}{\rightleftarrows}}$$

$$2[Mn^{II}(bpy)_3]^{2+} + 2H_2O \quad (2)$$

shape of the voltammogram of the resulting solution is identical to that of a solution of **2** (see below). This result is in accordance with previous studies on the chemical reduction of **1** in the same medium with reducing agents, e.g., ascorbate, hydroquinone, HSO$_3^-$, and NO$_2^-$.[4,14]

A solution of the mononuclear **2** complex in 0.05 M bpy/bpyH$^+$–0.1 M NaBF$_4$ shows an irreversible broad oxidation peak around 0.86 V on the cyclic voltammogram, corresponding to the metal oxidation process Mn(II)/Mn(III) (Figure 1C). This oxidation leads, by releasing bpy ligands, as in CH$_3$CN, to the formation of the binuclear manganese(III,IV) complex, following reaction 2b. The formation of this complex on the time scale of the cyclic voltammogram is evidenced by the presence of the quasi-reversible wave at $E_{1/2} = 1.16$ V, typical of its oxidation, and by the irreversible cathodic peak at $E_{pc} = 0.40$ V, corresponding to its reduction on the reverse scan. A careful, controlled-potential oxidation carried out at the foot of the anodic peak ($E = 0.70$ V) allows the quantitative buildup of **1**, without any formation of **3**. This is confirmed by the appearance of the typical 16-line spectrum of **1**.[15] Once again, the quantitative transformation requires an excess of coulometry (2.5 electrons per molecule of **2**). A yield of only 90% was obtained after 1.5 electrons were passed (the amount of **1** formed is evaluated by its typical visible absorption band at 688 nm ($\epsilon = 560$ L mol^{-1} cm^{-1})). A further oxidation at 1.25 V leads to the quantitative production of **3**. On the other hand, exhaustive reduction of an electrogenerated or an authentic sample solution of **3** at 0.2 V induces the restitution of **2**. The process involves the consumption of about 8 electrons per molecule of **3** in accordance with the summation of reactions 1 and 2. During this reduction some amount of **1** is formed; however, this compound cannot be generated selectively and quantitatively since reduction of **3** and **1** occurs at a similar potential ($\cong 0.4$ V).

In summary, this work presents a straighforward electrochemical method for preparing selectively Mn$_2$ and Mn$_4$ clusters from a mononuclear Mn(II) species. It also demonstrates the significant tendency of Mn(IV) species to aggregate, even in a medium containing a large excess of bpy ligands. Lastly, the above results suggest that **1** cannot act as an efficient homogeneous electrocatalyst for H$_2$O oxidation in aqueous solution, since its 1-electron-oxidized form is unstable and leads to the stable species **3**.

(12) The tetranuclear complex is stable in 0.05 M bpy/bpyH$^+$ buffer (pH 4.5) for several hours. However, **3** is slowly converted into **1** after several days despite the large excess of bpy ligand.

(13) ^{1}H NMR (CD$_3$CN) δ (ppm): 22.8 (vb), 11.4 (b), 9.0 (sh), 7.8 (s), 6.9 (s), 6.5 (s), 3.9 (b), −1.0 (s), −5.6 (s), −6.0 (b), −8.0 (vb). The spectrum differs totally from that of complex **1**, where resonances are spread out between 20 and 0 ppm. Selected IR bands (cm^{-1}) in the Mn−oxo stretching region: 728 (m), 702 (m), 662 (w), 654 (m), 644 (w), 564 (m). Philouze, C. Ph.D. Thesis, Université Paris-Sud, Orsay, 1994.

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