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New Chemical and Electrochemical Synthesis of the $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ Cluster. Electrochemical Interconversion with Corresponding Bi- and Mononuclear Complexes

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Abstract: A new chemical and electrochemical synthesis of the linear tetranuclear manganese complex, $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ (bpy = 2,2′-bipyridine) (**4**) is described. This complex can be synthesized by a two-electron oxidation of an aqueous solution of the mononuclear $[Mn^{II}(bpy)_3]^{2+}$ (**1**) one. The aqueous solutions were buffered at pH 4.5 with acetate for the chemical synthesis and bpy for the electrochemical one to stabilize the intermediate binuclear $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ (**2**) formed. In the case of chemical synthesis, $KMnO_4$ is used as oxidizing agent. Electrochemical behavior of these complexes, including the trinuclear $[Mn_3^{IV}O_4(bpy)_4(H_2O)_2]^{4+}$ derivative (**3**), have been investigated in organic (CH_3CN) and bpy/bpyH$^+$ buffer (pH 4.5). Carefully controlled potential oxidations of a solution of the mononuclear Mn(II) **1** in this latter medium lead to the successive formation of the high-valent oxo binuclear Mn_2(III,IV) (**2**) and tetranuclear Mn_4(IV) (**4**) complexes. These two dimerization reactions are quantitative. They result from the decoordination of bpy ligands and interaction with water of the unstable $[Mn^{III}(bpy)_3]^{3+}$ and $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$ electrochemically generated species. In CH_3CN, the higher stability of $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$ avoids the second dimerization process. All transformations are chemically reversible by reduction processes, although in aqueous buffered medium, the two steps are not clearly separated. Indeed, **2** cannot be generated quantitatively and selectively by reduction of **4** without any formation of **1**, since the reduction potentials of **2** and **4** are too close. The electrochemical behavior of the trinuclear **3** complex in aqueous buffered solution follows the same process as that of **4** although its reduction is slightly easier than **2** and **4**. Pertinent aspects of the electrochemistry of these oxo manganese complexes toward the modeling of the Mn_4 active site of PSII are also discussed.

Introduction

Over the last two decades, the inorganic modeling of the structure and function of active sites of metalloproteins has seen an increased interest. In particular much effort has been focused on the oxomanganese tetranuclear (Mn_4) cluster contained in the oxygen-evolving center in photosystem II.[1] Indeed, this cluster catalyzes the photosynthetic oxidation of water to dioxygen which is a crucial photochemical reaction in the nature. The mechanism of production of O_2, involving a four electrons and four protons process (eq 1) is still not yet entirely elucidated.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

In the proposed model of Kok et al.,[2a] based on the works of Joliot et al.,[2b] the Mn_4 cluster cycles through five distinct oxidation levels designated S_0 to S_4, involving Mn oxidation states in the range II−IV.[1] The most oxidized one, S_4 is unstable and relaxes back to S_0 with releasing of O_2. According to EXAFS experiments by Klein et al.,[3] the structure of this natural site would composed by two di-μ-oxo $Mn_2(\mu\text{-}O)_2$ units linked by a μ-oxo-bis-μ-carboxylate bridge.

Much effort has been devoted over the last 10 years to designing di- and multinuclear μ-oxo-bridged manganese complexes in order to mimic the structure and the magnetic and spectral properties of this natural active center.[1,4] In contrast, few studies concerning the reactivities of such molecular models toward water oxidation have been published.

Up to now, it was shown that only the mixed-valence binuclear complex $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ (**2**) (bpy = 2,2′-bipyridine) and the related 1,10-phenanthroline (phen) are associated with the generation of O_2 from water.[5] Moreover such complexes seem to be catalytically active only when used in heteregeneous electrochemical (modified electrodes)[5a] and chemical[5b] systems. In this latter case, Ce(IV) is used as external oxidant. The assumed active species is $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$. This result, however has not been corroborated as yet.[6]

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A recent work by Brudrig et al.[7] shows that only di-μ-oxo Mn_2(III, IV) binuclear complexes with planar tridentate ligands (terpyridine or dipicolinate) are convenient for O_2 evolution in homogeneous catalysis (acetate buffer). The external oxidant used in this system is HSO_5^-, a highly oxidizing oxygen atom transfer reagent. In the same experimental conditions, bidentate ligands (bpy, phen, and picolinate) also forms di-μ-oxo Mn_2 (III, IV) binuclear complexes which appear poorly efficient toward O_2 evolution. Despite these results in these specific conditions, it is important to know the electrochemical behavior of this kind of complex in aqueous solution to try to understanding mechanistic aspects which can prevent the oxidation of water. We have focused our interest toward the bpy complex **2** and we have, in a preliminary work,[8] reported the first study of its electrochemical behavior in a convenient aqueous solution stabilizing this complex: a bipyridyl buffer (bpy/bpyH$^+$) at pH 4.5. Furthermore, we reported an original electrochemical method to prepare selectively high-valent polynuclear oxomanganese complexes such as **2** and the linear tetranuclear $[Mn_4^{IV}O_6(bpy)_6]^{4+}$ (**4**) from the mononuclear $[Mn^{II}(bpy)_3]^{2+}$ (**1**) one in this specific medium.

We present here the detailed study of the electrochemical behavior of these complexes including the trinuclear $[Mn_3^{IV}O_4(bpy)_4(H_2O)_2]^{4+}$ parent complex (**3**) in aqueous bpy/bpyH$^+$ buffered and organic (CH_3CN) media. We also report a new and easy chemical synthesis of $[Mn_4^{IV}O_6(bpy)_6][BF_4]_4$ on the basis of our previous electrochemical investigations.[8]

Experimental Section

Electrochemistry. Electrochemical measurements were carried out using an EG&G PAR model 173 potentiostat equipped with a 179 digital coulometer and a model 175 programmer with out put recorded on a Sefram TGM 164 X−Y recorder.

In organic medium, electrochemical experiments were run under an argon atmosphere in a glovebox, using a standard three-electrode electrochemical cell. The electrolytes were a 0.1 M solution of tetra-*n*-butylammonium perchlorate (TBAP) or tetra-*n*-butylammonium tetrafluoroborate (TBATF) in CH_3CN (Rathburn, HPLC grade S). Potentials are referred to an Ag/10 mM Ag$^+$ reference electrode in CH_3CN + 0.1 M TBAP electrolyte. The working electrode was a platinum disk (0.2 cm^2) polished with 1 μm diamond paste. Exhaustive electrolyses were carried out with a 5 cm^2 platinum cylinder or a 10 × 10 × 4 mm^3 carbon felt electrode (RVC 2000, 65 mg cm^{-3}, from Le Carbone Lorraine).

In aqueous medium, electrochemical experiments were performed in buffered solutions with bpy/bpyH$^+$ mixtures, the total concentration [bpy] + [bpyH$^+$] was 0.02 or 0.05 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_2SO_4. The use of $NaClO_4$ induced the partial precipitation of complexes **1**−**4**.

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. Working electrodes for cyclic voltammetry and exhaustive electrolysis were, respectively, a vitreous carbon disk (0.2 cm^2) carefully polished with 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). Previous attempts to examine the cyclic voltammogram with a platinum working electrode in this medium failed, owing to the large background current from the competing oxidation of water.[9]

Synthesis. The ligand 2,2′-bipyridine (bpy) was purchased from Aldrich. The complexes $[Mn_2^{III,IV}O_2(bpy)_4][BF_4]_3$ (**2**), $[Mn_2^{III,IV}O_2(bpy)_4][NO_3]_3$ (**2′**), $[Mn_4^{IV}O_6(bpy)_6][ClO_4]_4$ (**4′**), $[Mn^{II}(bpy)_3][BF_4]_2$ (**1**), and $[Mn_3^{IV}O_4(bpy)_4(H_2O)_2][ClO_4]_4$ (**3**) were prepared according to the literature.[9−12] In this work, for **2** and **1**, BF_4^- and NO_3^- were employed as counterion instead of ClO_4^-.

^{1}H NMR (CD_3CN) d(ppm) for **2**: 19 (b); 13.8 (b); 10.4 (s); 6.7 (s); 4.0 (s).

Chemical Synthesis of $[Mn_4^{IV}O_6(bpy)_6][BF_4]_4$ (4). A solution of 0.49 g of $Mn(OOCCH_3)_2 \cdot 4H_2O$ (2 mmol) in 7 mL of H_2O was added to 0.79 g of bpy (5 mmol) in 4 mL of acetone. The resulting yellow solution was stirred for 15 min and then filtered. Acetate buffer (1 mL, 1M, pH 4.5) was added to the yellow solution, and the pH adjusted to 4.5 with glacial acetic acid. The solution was then cooled to 0 °C in an ice bath, and a solution of 0.21 g of $KMnO_4$ (1.34 mmol) in 6 mL of H_2O was added dropwise with stirring. During the addition of the oxidant, the color of the solution changed from yellow to green and finally red brown. The resulting solution was stirred for 15 min at 0 °C after the addition was complete before it was filtered. A H_2O solution of 0.85 g (10 mmol) of sodium tetrafluoroborate was then added to the solution. Several fractions of product as brown powder could be collected from the continuing precipitation which proceeds slowly when the solution is maintained at 0 °C (total yield 80%). In the first fractions, collected after several hours, **4** is contaminated by small amount of **2**. A pure crystalline material could be isolated after 1 day (yield 25%). The purity of **4** is checked by EPR and IR measurements.

^{1}H NMR (CD_3CN) δ (ppm): 22.9 (b); 11.5 (b); 9.0 (s); 7.8 (s); 7.1 (s); 6.4 (s); 4.0 (b); −1.0 (s); −5.4 (s); −6.0 (vb); −8.2 (b).

Selected IR bands (KBr pellet) (cm^{-1}) in the Mn−oxo stretching region: 728 (m); 702 (m); 662 (w); 654 (m); 644 (w); 564 (m). In the 4000−900 cm^{-1} region, the IR bands are identical to those of **2**.[9]

Electrochemical Synthesis of 4. Exhaustive oxidation of 8.2 mg of **2** at 1.25 V vs Ag/AgCl in aqueous 0.02 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M $NaBF_4$ as electrolyte on a carbon felt leads to the formation of the **4** complex. This electrogenerated complex is precipitated by addition of a large excess of $NaBF_4$ (4 g) to the oxidized solution. After filtration, the resulting brown powder (yield 55%) exhibits the same characteristics as a chemically prepared sample of **4**.

Spectroscopies. Electronic absorption spectra were recorded on a Cary 1 Varian spectrometer equipped with an Epson PC AX2e computer for the experiments conducted in aqueous medium. In CH_3CN medium, electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer equipped with a Compaq 286 computer and a Citizen 120D printer. Initial and electrolyzed solutions were transferred to a conventional cuvette cell in the glovebox. The cell was inserted into an optical translator connected to the spectrophotometer through a fiber optic system (Photonetics Spectrofip System). The optical fibers pass through the wall of the drybox via seals.

EPR spectra were recorded at 100 K on a Brucker EPS 300E spectrometer operating at 9.4 GHz (X band). IR spectra were recorded on a Magna-IR TM 550 Nicolet spectrometer. NMR spectra were obtained on a Bruker AC 200 MHz FT-NMR spectrometer using CD_3CN as solvent. Chemical shift δ in ppm were referenced to the residual protic solvent peak.

Results and Discussion

New Synthesis of $[Mn_4^{IV}O_6(bpy)_6][BF_4]_4$ (2). In 1992, Girerd et al.[10] reported the original synthesis of $[Mn_4^{IV}O_6(bpy)_6][ClO_4]_4 \cdot H_2O$ (**4′**) which represents a type of Mn_4 cluster with a linear $[Mn_4O_6]^{4+}$ core. As yet, to our knowledge, no other complexes with this particular geometry have been isolated. This

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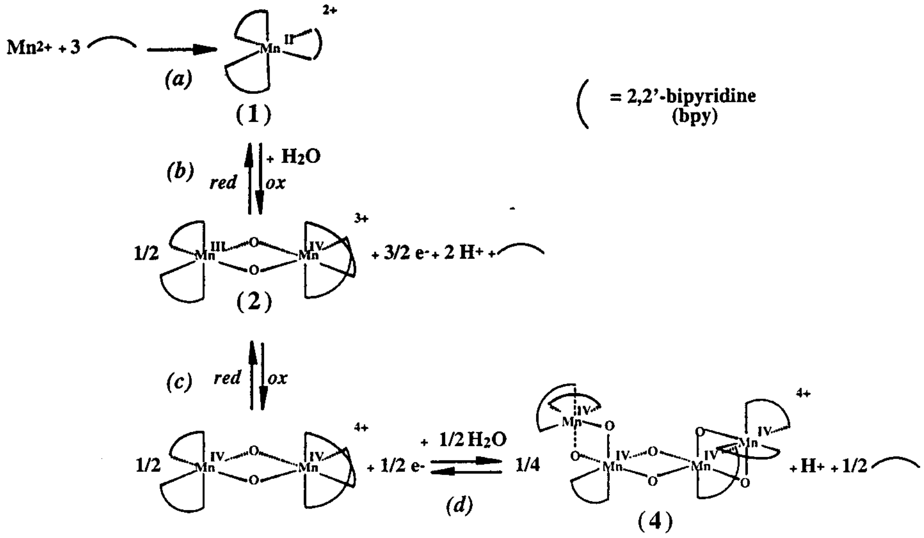
Scheme 1. Redox Interconversion for Mono-, Bi-, and Tetranuclear Manganese Complexes in Aqueous Buffered Solutions at pH 4.5 (Acetate or bpy/bpyH$^+$ Buffers, See the Text)



cluster was obtained by disproportionation of the mononuclear $[Mn^{III}(bpy)Cl_3(H_2O)]$ in an aqueous nitric acid solution at pH 2.

The formation of this species is conditioned by the pH value of the solution. Indeed, the condensation of $[Mn(bpy)Cl_3(H_2O)]$ in aqueous solution leads to the binuclear cluster **2** at a moderate pH value (pH = 4.5) and to the trinuclear cluster **3** at a more acidic pH value (pH = 0.4). The trinuclear cluster can also be obtained by acidification of a solution of **2** in water.[13]

By another way, Dave et al.[14] have also trapped the tetranuclear complex by addition of K_2CrO_7 to a solution of the binuclear (III, IV) **2**. However, this complex crystallized with two $Cr_2O_7^{2-}$ as counterions and is insoluble in usual solvents.

Our alternative synthesis of the tetranuclear complex is drawn by the method of Cooper et al.[9] used for the synthesis of binuclear (III, IV) ones containing bidentate ligands (L = bpy, phen). These complexes are obtained by permanganate ($KMnO_4$) oxidation of $[Mn^{II}(L)_3]^{2+}$ generated in situ by complexation of Mn^{2+} cations with L (Sheme 1a) in acetate buffer at pH 4.5. $KMnO_4$ is employed both as an oxidizing agent and a Mn source. In this procedure, the amount of $KMnO_4$ added corresponds exactly to that needed to ensure the 1.5 electrons oxidation of all Mn^{2+} cations (Scheme 1b), taking into account that the reduction of MnO_4^- is a five-electron process (eq 2):

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad (2)$$

On the other hand, in accord with our previous results concerning the electrochemical oxidation of **2** in aqueous medium,[8] **4** is obtained by a one-electron oxidation of **2**. Indeed, in bpy/bpyH$^+$ buffer (pH 4.5) the initially formed $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$ species is unstable and dimerizes into **4** by decoordination of bpy ligand (Scheme 1c,d). This result has been transposed to a chemical way, by adjusting the amount of $KMnO_4$ to obtain a two-electron oxidation of Mn^{2+} cations. The ratio bpy/Mn used is equal to 1.5 in accord with the reaction stochiometry. (See Experimental Section.) Furthermore the utilization of the acetate buffer (pH 4.5) allows avoidance of the competitive formation of the trinuclear complex **3**. In the case of the method use by Dave et al.,[14] $Cr_2O_7^{2-}$ probably plays the both role of the oxidation and counterions.

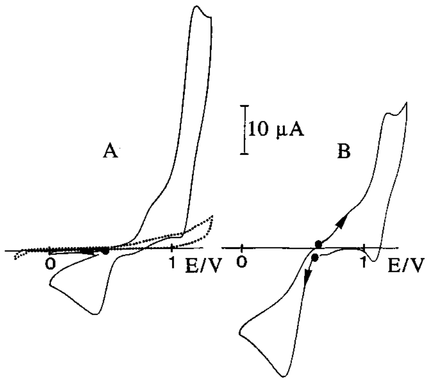


Figure 1. Cyclic voltammograms in aqueous 0.05 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M $NaBF_4$ at a carbon working electrode and an Ag/AgCl reference electrode (scan rate 20 mV s^{-1}): (A) (···) electrolyte and (—) of a 2mM solution of **1**; and (B) after oxidation at 0.7 V of A.

Electrochemistry. Electrochemical Behavior of $[Mn^{II}(bpy)_3]^{2+}$ (1) in Aqueous bpy/bpyH$^+$-Buffered Medium (pH 4.5). In a preliminary work,[8] we have shown that the Mn_2(III,IV) **2** complex can be quantitatively generated by the electrochemical oxidation of the mononuclear **1** one in aqueous bpy/bpyH$^+$ buffered medium at pH 4.5. Previously, this transformation had only been clearly evidenced in organic CH_3CN medium (Scheme 1b).[11]

At a vitreous carbon electrode, the electroactivity of the aqueous 0.05 M bpy/bpyH$^+$−0.1 M $NaBF_4$ electrolyte is in the range −0.5 to 1.3 V vs Ag/AgCl (Figure 1A). The mononuclear **1** complex can be formed in situ by the addition of Mn^{2+} cations to the solution (Scheme 1a). The visible absorption spectrum of the yellow pale solution obtained (shoulder at 350 nm), as well as its cyclic voltammogram, is identical to a solution of a synthetic sample of **1** in the same electrolyte (Figure 2, spectrum a). This result indicates that the added Mn^{2+} are, in situ in a large part coordinated by the bpy ligands of the electrolyte. Figure 1A shows the cyclic voltammogram of **1** which exhibits

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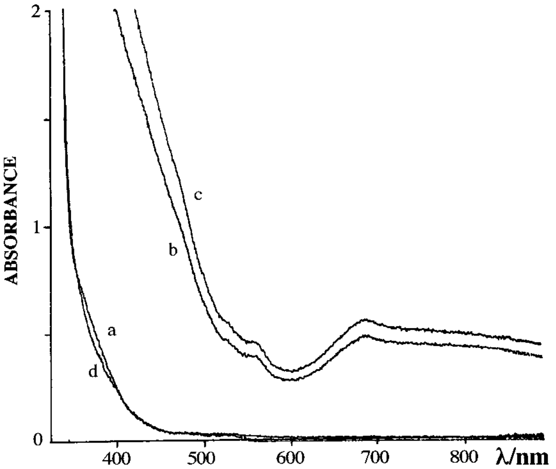

Figure 2. Spectral changes during electrolyses in aqueous 0.05 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M NaBF$_4$ of a 2 mM solution of **1**: (a) initial solution; (b) after oxidation at 0.7 V, $Q = 1.5$ electrons per molecule; (c) $Q = 2.5$; and (d) after exhaustive reduction at 0.2 V of c; $l = 1$ cm.

an irreversible broad oxidation peak around 0.86 V, corresponding to the metal oxidation process Mn(II)/Mn(III).

As in CH$_3$CN, the electrogenerated Mn(III) species, [Mn(bpy)$_3$]$^{3+}$ is unstable and leads, via a disproportionation reaction, bpy ligands releasing and interaction with water, to the Mn$_2$(III,IV) complex, following reaction 3a:

$$\underset{(\mathbf{1})}{2[\mathrm{Mn^{II}(bpy)_3}]^{2+}} + 2\mathrm{H_2O} \underset{b}{\overset{a}{\rightleftarrows}} \underset{(\mathbf{2})}{[\mathrm{Mn_2^{III,IV}O_2(bpy)_4}]^{3+}} + 2\mathrm{bpy} + 4\mathrm{H^+} + 3e^- \quad (3)$$

The formation of this complex on the time scale of the cyclic voltammogram is evidenced by the presence of a quasi-reversible wave at $E_{1/2} = 1.16$ V, typical of its oxidation and by an irreversible cathodic peak at $E_{\mathrm{p_c}} = 0.40$ V vs Ag/AgCl, corresponding to its reduction on the reverse scan (Figure 1A). A careful, controlled-potential oxidation carried out at the foot of the anodic peak ($E = 0.70$ V) allows the quantitative build up of **2**, without any formation of **1** (see next section). This is confirmed by EPR study on the resulting green solution showing that the initial six-line spectrum characteristic of Mn(II) species changed to a 16-line spectrum typical of **2**. Moreover as we will see in the next section, the cyclic voltammogram obtained (Figure 1B), as well as its visible absorption spectrum are characteristic of a solution of **2** (Figure 2, spectrum c).

However, the quantitative transformation requires an excess of coulometry (2.5 electrons per molecule of **1**). This is illustrated in Figure 2 which shows the visible spectra of the solution as a function of the extent of electrolysis. A yield of only 90% was obtained after the theorical 1.5 electrons were passed (the amount of **2** formed is evaluated by its visible absorption band at 688 nm using the ϵ value of 560 l mol^{-1} cm^{-1} (Figure 2, spectrum b). The observed excess of coulometry is probably due to a slow, competitive oxidation of the electrolyte which has been established by a separate experiment conducted in the absence of **1**. As will be discussed in detail in the next section, the tetranuclear **4** complex can be quantitatively produced by a further oxidation at 1.25 V of this resulting solution of **2**.

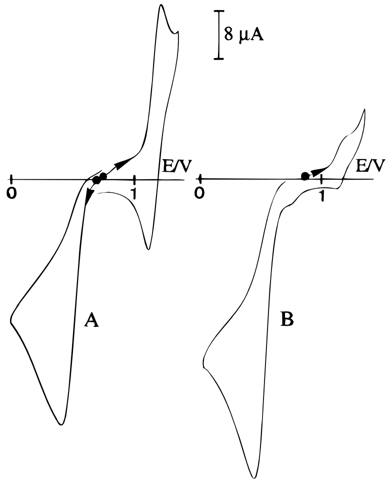

Figure 3. Cyclic voltammograms in aqueous 0.05 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M NaBF$_4$ at a carbon working electrode and an Ag/AgCl reference electrode (scan rate 20 mV s^{-1}) (A) of a 2 mM solution of **2** and (B) after exhaustive oxidation at 1.25 V of A.

On the other hand, as in CH$_3$CN,[15] the dimerization reaction 3 is an overall reversible process. Indeed, a subsequent controlled reduction at 0.20 V of the electrochemically generated solution of **2** restores entirely the initial amount of **1** after the consumption of three electrons per molecule of **2** (Figure 2, spectrum d).

Electrochemical Behavior of [Mn$_2$$^{\mathrm{III,IV}}O_2(bpy)_4$]$^{3+}$ (2) in Aqueous bpy/bpyH$^+$-Buffered Medium (pH 4.5). In a nonaqueous medium (CH$_3$CN) the cyclic voltammogram of **2** exhibits a reversible one-electron oxidation wave leading to the (IV,IV) binuclear species ($E_{1/2} = 0.99$ V vs Ag/Ag$^+$ 10 mM) and a poorly reversible one-electron reduction wave ($E_{\mathrm{p_c}} = 0.03$ V), corresponding to the (III,III) state.[9] This latter unstable species in a subsequent disproportionation reaction affords the mononuclear complex **1**.[15]

In aqueous solution **2** is stable only in the presence of bipyridyl buffer (bpy/bpyH$^+$) in the pH range 4.3–5.4.[6,9] The use of pure aqueous solutions or other buffers such as acetate or phosphate causes disproportionation of the complex as reflected in a deep color change, the initial green solution turning red in a few seconds.

At a suitably vitreous carbon electrode (see Experimental Section), the shape of the cyclic voltammogram of **2** in bpy buffer is in close correspondence to that obtained in CH$_3$CN with a quasi-reversible oxidation wave at $E_{1/2} = 1.16$ V ($\Delta E_\mathrm{p} = 90$ mV) and an irreversible reduction peak at $E_{\mathrm{p_c}} = 0.4$ V vs Ag/AgCl (Figure 3A). To characterize the respective final products issued from the oxidation and the reduction of this complex, exhaustive electrolyses have been carried out. As expected, an exhaustive reduction of the solution at 0.20 V consumes three electrons per molecule of **2** and produces quantitatively the mononuclear complex **1** (Scheme 1b), following reaction 3b. The quantitative generation of **1** is due to the presence of an excess of free bpy ligands in this specific aqueous medium. In CH$_3$CN, we have observed that the reduction of **2** as its analogous dimethyl-substituted bipyridine[15] furnishes only one stochiometric amount of **1** and consumes only one electron per binuclear complex. These results show that the initially formed [Mn$_2$$^{\mathrm{III,III}}O_2(bpy)_4$]$^{2+}$ species is unstable both in aqueous buffered and organic media. In this latter medium, the lack of free bpy ligand probably induces the

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(15) Collomb Dunand-Sauthier, M.-N.; Deronzier, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1997**, *428*, 65–71.

disproportionation of $[\mathrm{Mn_2}^{\mathrm{III,III}}\mathrm{O_2(bpy)_4}]^{2+}$ into **1** and an undefined Mn(IV) oxide species[15] attested by the presence of a brown side-product in the reduced solution. Reaction 4a summarized the overall process:

$$\underset{(\mathbf{2})}{[\mathrm{Mn_2}^{\mathrm{III,IV}}\mathrm{O_2(bpy)_4}]^{3+}} + \mathrm{e}^- \underset{b}{\overset{a}{\rightleftarrows}} \underset{(\mathbf{1})}{[\mathrm{Mn^{II}(bpy)_3}]^{2+}} + \text{“}\mathrm{Mn^{IV}O_2}\text{”} + 2\mathrm{bpy} \tag{4}$$

In the both media (reactions 3 and 4) the overall chemical process is reversible as demonstrated by a subsequent oxidation of reduced solutions. In $\mathrm{CH_3CN}$, the oxidation involves the disappearance of the Mn(IV) oxide precipitate and restores almost entirely the initial amount of **2**.

On the other hand, an exhaustive oxidation at 1.25 V of a solution of **2** in aqueous buffered medium 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 3B). Unlike the electrochemical behavior of this complex in $\mathrm{CH_3CN}$,[16] the oxidized $[\mathrm{Mn_2}^{\mathrm{IV,IV}}\mathrm{O_2(bpy)_4}]^{4+}$ species is not stable on the time scale of the electrolysis (Scheme 1c), indicating that a chemical reaction is coupled to the electron transfer. The final oxidized species has been identified as the tetranuclear cluster **4**, with a linear $[\mathrm{Mn_4O_6}]^{4+}$ core[8] (Scheme 1d). A reasonable reaction mechanism for the formation of **4** involves the association of two $[\mathrm{Mn_2}^{\mathrm{IV,IV}}\mathrm{O_2(bpy)_3}]^{4+}$ units issued from the decoordination of one bpy ligand of the initially electrochemically formed $[\mathrm{Mn_2}^{\mathrm{IV,IV}}\mathrm{O_2(bpy)_4}]^{4+}$ species. The two bridging μ-oxo anions results from water deprotonation. Equation 5a summarizes the overall process:

$$2\underset{(\mathbf{2})}{[\mathrm{Mn_2}^{\mathrm{III,IV}}\mathrm{O_2(bpy)_4}]^{3+}} + 2\mathrm{H_2O} \underset{b}{\overset{a}{\rightleftarrows}} \underset{(\mathbf{4})}{[\mathrm{Mn_4}^{\mathrm{IV}}\mathrm{O_6(bpy)_6}]^{4+}} + 2\mathrm{bpy} + 4\mathrm{H}^+ + 2\mathrm{e}^- \tag{5}$$

Electro- and spectrochemical characteristics of the resulting oxidized solution are identical to those of an authentic sample of **4** in the same medium**.**

Between 0 and 1.3 V, the cyclic voltammogram of **4** in bpy buffer[17] shows only an irreversible reduction peak close to that of **2** ($E_{\mathrm{p_c}} = 0.40$ V), leading to the formation of the mononuclear **1** complex as final product (Figure 4). Indeed, on the second positive scan in this potential region, the irreversible oxidation peak of **1** located at 0.9 V appears followed by the quasi-reversible peak system of **2** at $E_{1/2} = 1.16$ V (Figure 4). These observations have been confirmed by an exhaustive reduction of the solution at 0.20 V. The process involves the consumption of about eight electrons per molecule of **4** in accord with the summation of reactions 3b and 5b. However, during the reduction, some amount of **2** is formed. As judged by the electro- and spectrochemical analysis of the solution, a maximum yield of about 35% (reaction 4b) is obtained after the consumption of four electrons per molecule of **4**. This compound cannot be generated selectively and quantitatively since the reduction of **4** and **2** occurs at a similar potential (~0.4 V).

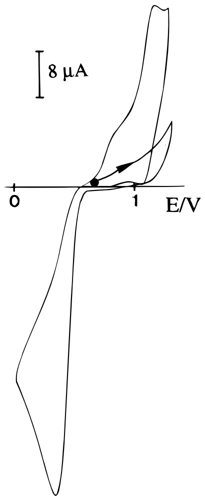

Figure 4. Cyclic voltammograms in aqueous 0.05 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M $\mathrm{NaBF_4}$ at a carbon working electrode and an Ag/AgCl reference electrode (scan rate 20 mV s^{-1}) of a 1 mM solution of **4′**.

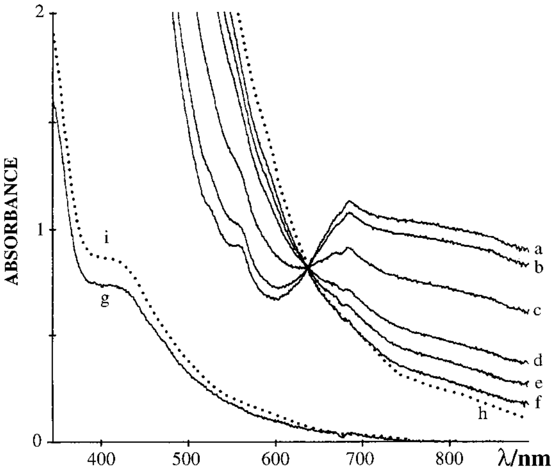

Figure 5. Spectral changes during electrolysis in aqueous 0.05 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M $\mathrm{NaBF_4}$ of a 2 mM solution of **2**: (a) initial solution; (b) after oxidation at 1.25 V, $Q = 0.5$ electrons per molecule; (c) $Q = 1$; (d) $Q = 2$; (e) $Q = 4$; (f) $Q = 6$; $l = 1$ cm; and (g) solution f with $l = 0.1$ cm. Spectra of a 1 mM solution of **4**: (h) $l = 1$ cm; (i) $l = 0.1$ cm.

Figure 5 illustrates the spectral changes during the oxidation of a solution of **2** (2 mM). The successive visible spectra pass through an isosbestic point at 636 nm which attests to the formation of a single species. Moreover, the absorption spectrum of the solution at the end of the oxidation, is closely superimposable with that of **4** (1 mM) ($\lambda = 780$ (sh), 670 (sh), and 425 (sh) nm), which demonstrates that the transformation is quasi-quantitative (Figure 5).

The oxidized solution is EPR inactive at helium temperature, according to the $S = 0$ ground spin state of **4**.[10]

Moreover, this electrogenerated tetranuclear complex can be precipitated by addition of a large excess of $\mathrm{NaBF_4}$ to the oxidized solution. (See Experimental Section.) After filtration, the resulting brown powder exhibits the same characteristics as a chemically prepared sample of **4**.

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[16] Morrison, M. M.; Sawyer, D. T. *J. Am. Chem. Soc.* **1976**, *2*, 257−258. In $\mathrm{CH_3CN}$, as observed by these authors, the oxidation of **2** causes some decomposition and yields a reddish brown solution containing 60% of $[\mathrm{Mn_2}^{\mathrm{IV,IV}}\mathrm{O_2(bpy)_4}]^{4+}$. If they have no hypothesis concerning the nature of the secondary oxidation products, we can supposed that they correspond to polynuclear complexes (nuclearity > 2) of manganese (IV) indicated by the presence on the cyclic voltammogram of the produced solution of an additional reduction peak at $E_{\mathrm{p_c}} = 0.12$ V closed to that of **2** ($E_{\mathrm{p_c}} = 0.03$ V).

[17] The tetranuclear **4** complex is stable in 0.05 M bpy/bpyH$^+$ buffer (pH 4.5) for several hours. However, **4** is slowly converted to **2** after several days despite the large excess of bpy ligand.

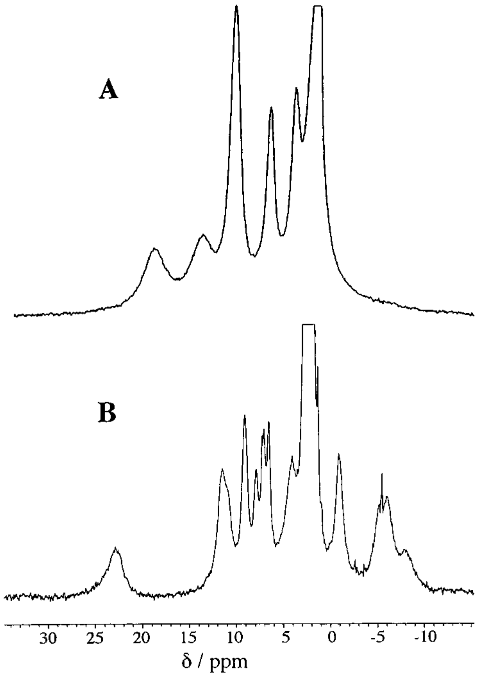

Figure 6. ^{1}H NMR spectra (250 MHz) in CD_3CN (A) of a 10 mM solution of **2** and (B) of a 10 mM solution of **4**.

The ^{1}H NMR spectrum of **4** (Figure 6B) displays resonances of the bipyridine protons between 25 and −10 ppm. The observed chemical shifts range shows that the manganese ions are strongly antiferromagnetically coupled. It has to be noted that this spectrum differs totally from that of complex **2** (Figure 6A), where resonances are spread out between 22 and 0 ppm. With reference to the observation of upfield resonances, they may be attributed to those of the protons of the central metal ions on the basis of their integration values. Their positions are probably related to the sign of the local spin of the central metal ions. Although such proton resonances cannot be unambiguously assigned due to the absence of analogue complexes, we tentatively assigned them on the basis of the resonances integrals and shape. The ortho protons, the closest protons to a paramagnetic center, are attributed to the broadest and more deshielded peaks at 22.9, − 8.2, − 6.0, and − 5.4 ppm. The meta protons, further from the metal ions are attributed to the resonances at 11.5, 9.0, 4.0, and − 1.0 ppm. The para protons, less affected by the magnetic field of the Mn ions, are observed at 7.8, 7.1, and 6.4 ppm. Such a behavior has been also observed in linear μ-oxo polynuclear iron(III) complexes.[18]

Distinction between **4** and **2** can be also easily accomplished by infrared spectroscopy experiments since spectra of these compounds exhibit strong difference in the 750−500 cm^{-1} region (Figure 7). The IR bands for these two compounds are identical in the 4000−900 cm^{-1} region. As for all compounds containing the $\{Mn_2O_2\}$ core, the 689 cm^{-1} band of **2** is assigned to a stretching mode of the di-μ-oxo bridge (Figure 7c).[9] For compound **2**, a similar band is observed with a shift of 12 cm^{-1}. This band (located at 702 cm^{-1}) can be unambiguously attributed to the stretching mode of the three di-μ-oxo bridges of **4** (Figure 7a,b). The 728 cm^{-1} band present in the IR spectrum of the two compounds is associated with the stretching mode of the Mn−O bands.[19]

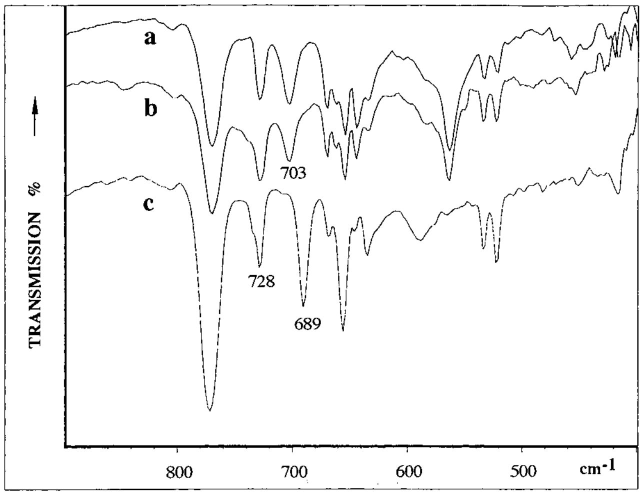

Figure 7. Infrared spectra (KBr pellet) of a chemical (a) and electrochemical (b) samples of **4** and (c) of **2**.

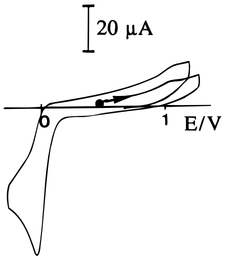

Figure 8. Cyclic voltammogram in CH_3CN containing 0.1 M TBATF at a platinum working electrode and an Ag/Ag$^+$ 10^{-2} M reference electrode (scan rate 100 mV s^{-1}) of a 1 mM solution of **4′**.

In CH_3CN, 0.1 M TBATF[20] the cyclic voltammogram of **4** exhibits only a well-defined irreversible reduction peak at $E_{p_c} = -0.05$ V vs Ag/Ag$^+$ 10 mM lying at a more cathodic potential than that of **2** ($E_{p_c} = 0.03$ V) (Figure 8). On the reverse scan a small anodic peak is detected at $E_{p_a} = 1.0$ V showing the formation of the mononuclear complex **1**. This is confirmed by an exhaustive reduction of the solution carried out at −0.2 V which consumes two electrons per molecule of **1** and yields a brown solution, indicating the accompanying formation of manganese oxide. Equation 6 summarizes the overall reaction:

$$\underset{\textbf{(4)}}{[Mn_4^{IV}O_6(bpy)_6]^{4+}} + 2e^- \rightarrow \underset{\textbf{(3)}}{[Mn^{II}(bpy)_3]^{2+}} + 3Mn^{IV}O_2 + 3\ bpy \quad (6)$$

An important point to be noted is since **2** is more reducible than **4**, **2** cannot be electrogenerated from reduction of **4**.

Electrochemical Behavior of $[Mn_3^{IV}O_4(bpy)_4(H_2O)_2][ClO_4]_4$ (4) in Aqueous bpy/bpyH$^+$-Buffered Medium (pH 4.5). In

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[18] (18) Vincent, J.-M.; Ménage, S.; Latour, J.-M.; Bousseksou, A.; Tuchagues, A. D.; Fontecave, M. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 205−207.

[19] (19) (a) Nakamoto, N. *Infrared spectra of inorganic and coordination compounds*; J. Wiley: New York, **1970**. (b) Boucher, L. J.; Coe, C. G. *Inorg. Chem.* **1975**, *14*, 1289.

[20] (20) The use of TBAP as supporting electrolyte induces the partial precipitation of the complex. The electrochemical properties of **4′** have been briefly studied by Girerd et al.,[10b] in propylene carbonate (PC) and in aqueous nitric acid solution (pH = 2). In PC, the electrochemistry of this complex is characterized by several successive irreversible peaks ill-defined around 0.2 V vs SCE. A preparative electrolysis conducted in aqueous acidic medium involves an eight-electron reduction of the complex leading to Mn(II):

$$[Mn_4^{IV}O_6(bpy)_6]^{4+} + 8e^- + 12H^+ \rightarrow 4Mn^{II} + 6bpy + 6H_2O$$

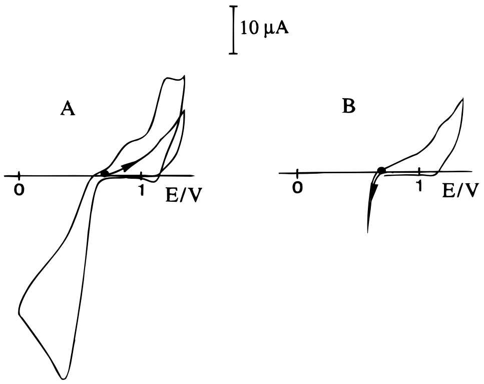

Figure 9. Cyclic voltammograms in aqueous 0.05 M bpy/bpyH$^+$ buffer at pH 4.5 containing 0.1 M NaBF$_4$ at a carbon working electrode and an Ag/AgCl reference electrode (scan rate 20 mV s^{-1}) of a 2 mM solution of **3**: (A) potential range between 0 and 1.30 V and (B) between 0.58 and 1.30 V.

aqueous buffered medium,[21] the electrochemical behavior of the trinuclear **3** complex is close to that of **4**. The only difference consists of the fact that **3** is slightly more easely reducible than **4** and **2** complexes in this medium. This is evidenced, on the cyclic voltammogram of a solution of **3** by the presence of a shoulder preceding the irreversible reduction peak of **2** at $E_{\mathrm{p_c}} = 0.40$ V vs Ag/AgCl (Figure 9A). This shoulder corresponds to the formation of **2** following reaction 7:

$$\underset{(\mathbf{3})}{2[\mathrm{Mn_3}^{\mathrm{IV}}\mathrm{O_4(bpy)_4(H_2O)_2}]^{4+}} + 4\mathrm{bpy} + 4\mathrm{H}^+ + 3\mathrm{e}^- \rightarrow \underset{(\mathbf{2})}{3[\mathrm{Mn_2}^{\mathrm{III,IV}}\mathrm{O_2(bpy)_4}]^{3+}} + 6\mathrm{H_2O} \quad (7)$$

Indeed, if the potential range is restricted at the foot of the shoulder (0.58 V), only the quasi-reversible oxidation wave of **2** at $E_{1/2} = 1.16$ V is then detected on the reverse scan (Figure 9B). The irreversible reduction peak at $E_{\mathrm{p_c}} = 0.40$ V obviously corresponds to the reduction of **2** formed since on the reverse scan the irreversible oxidation of its reduced species **1** is also observed (Figure 9B) (Reaction 3b). However, **2** cannot be generated selectively and quantitatively without any formation of **1**, even by an electrolysis of the solution carried out at the foot of the shoulder ($E = 0.60$ V). In these conditions, **2** is obtained with a maximum yield of 40% following reaction 7 after the consumption of 1.5 electrons per molecule of **3**. The continuation of the electrolysis at this potential increases the amount of **1** formed. The completion of the electrolysis at 0.2 V induces the total consumption of about six electrons per molecule of **3** and yields quantitatively **1** according to reaction 8:

$$\underset{(\mathbf{3})}{[\mathrm{Mn_3}^{\mathrm{IV}}\mathrm{O_4(bpy)_4(H_2O)_2}]^{4+}} + 5\mathrm{bpy} + 8\mathrm{H}^+ + 6\mathrm{e}^- \rightarrow \underset{(\mathbf{1})}{3[\mathrm{Mn}^{\mathrm{II}}\mathrm{(bpy)_3}]^{2+}} + 6\mathrm{H_2O} \quad (8)$$

In CH$_3$CN 0.1 M TBAP, the cyclic voltammogram of **3** exhibits only a well-defined irreversible peak at $E_{\mathrm{p_{c1}}} = 0.37$ V vs Ag/Ag$^+$ 10 mM between 0.2 and 1.3 V which indicates that, in this solvent, as in buffered aqueous medium, **3** is more easily reducible than **4** and **2** ($E_{\mathrm{p_c}} = -0.05$ and 0.03 V respectively, Figure 10A, (—)). This irreversible reduction leads to the formation of **2**, as previously shown by Sarneski et al.[13a] The formation of this complex is evidenced by the appearance of its reversible oxidation system at $E_{1/2} = 0.99$ V (Figure 10A, (—)) during a second scan through this potential domain. If the cathodic potential is extended to -0.20 V, its irreversible reduction peak is then detected at $E_{\mathrm{p_{c2}}} = 0.03$ V (Figure 10A, (•••)) and on the reverse scan the irreversible oxidation peak of **1** issued from the reduction of **2** is observed. As expected, an exhaustive reduction of the solution at 0.35 V consumes one electron per molecule of **3** and yields a green solution which presents electrochemical (Figure 10B) and spectrochemical characteristics of **2**. A brown side product partially soluble of manganese oxide is also formed in solution, as for the reduction of **2** into **1** in the same medium. Equation 9 summarizes the proposed overall process:

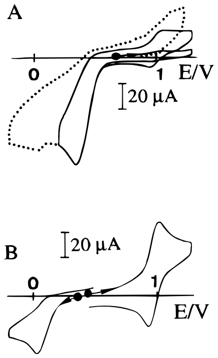

Figure 10. Cyclic voltammograms in CH$_3$CN containing 0.1 M TBAP at a platinum working electrode and an Ag/Ag$^+$ 10^{-2} M reference electrode (scan rate 100 mV s^{-1}) of a 2 mM solution of **3**: (A) initial solution and (B) after exhaustive reduction at 0.3 V of A.

$$\underset{(\mathbf{3})}{[\mathrm{Mn_3}^{\mathrm{IV}}\mathrm{O_4(bpy)_4(H_2O)_2}]^{4+}} + \mathrm{e}^- \rightarrow \underset{(\mathbf{2})}{[\mathrm{Mn_2}^{\mathrm{III,IV}}\mathrm{O_2(bpy)_4}]^{3+}} + \mathrm{Mn^{IV}O_2} + 2\mathrm{H_2O} \quad (9)$$

This reaction is not quantitative, since only a 55% yield of **4** is obtained in comparaison with the theorical quantity expected following reaction 9. A further reduction at 0 V involves the consumption of an additional electron and yields, as expected, **1** in accordance with the summation of reactions 9 and 4a.

Conclusion

This work presents a straighforward chemical and electrochemical method for selectively preparing by oxidative processes the binuclear Mn$_2$(III,IV) **2** and the linear tetranuclear Mn$_4$(IV) **4** bipyridyl complexes from the mononuclear Mn(II) **1** one in aqueous solutions (Scheme 1). To stabilize the intermediate binuclear **2** species, the solutions were respectively buffered at pH 4.5 with acetate and bpy. The formation of these high-valent polynuclear oxomanganese complexes is due to the significant tendency of Mn(IV) species to aggregate by decoordination of bpy ligands and interaction with water, even in a medium containing a large excess of bpy ligands. The electrochemistry measurements in aqueous buffered solutions show that if all transformations are chemically reversible by reduction processes (Scheme 1), the steps c, d, and b are not clearly separated. Indeed, **2** cannot be generated selectively by

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[21] Reddy, K. R.; Rajasekharan, M. V.; Arulsamy, N.; Hodgson, D. J. *Inorg. Chem.* **1996**, *35*, 2283−2286. These authors have reported that the analogous trinuclear complex [$\mathrm{Mn_3}^{\mathrm{IV}}\mathrm{O_4(phen)_4(H_2O)_2}$]$^{4+}$ is slowly reduced into the binuclear [$\mathrm{Mn_2}^{\mathrm{III,IV}}\mathrm{O_2(phen)_4}$]$^{3+}$ one in phen/phenH$^+$ buffer at pH 4.5 after several days. We have observed a similar evolution for **3** in bpy/bpyH$^+$ buffer but this complex is stable enough in this medium (several hours) to be electrochemically studied.

reduction of **4** without any formation of **1**, since the reduction potential of **2** and **4** are very close. The reduction of the trinuclear **3** complex in aqueous buffered solution follows the same process as that of **4** although its reduction is slightly easier than **2** and **4**. In contrast, **3** cannot be regenerated by oxidation of **1** or **2** in buffered water bpy/bpyH$^+$ since this complex is preferentially formed at low pH. Moreover, **4** and **3** results from two different modes of association.

Last, the above results suggest that **2** cannot act as an efficient homogeneous electrocatalyst for H_2O oxidation in aqueous bpy/bpyH$^+$-buffered solution, since its one-electron oxidized form $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$ is unstable, leading to a stable tetranuclear species **4** in aqueous media. This indicates that **4** cannot be involved in O_2 evolution in aqueous bpy/bpyH$^+$ buffer.

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